Substance Name: 2-Benzotriazol-2-yl-4,6-di-tert-butylphenol (UV-320)

EC Number: 223-346-6

CAS Number: 3846-71-7

MEMBER STATE COMMITTEE

SUPPORT DOCUMENT FOR IDENTIFICATION OF

2-BENZOTRIAZOL-2-YL-4,6-DI-TERT-BUTYLPHENOL (UV-320)

AS A SUBSTANCE OF VERY HIGH CONCERN BECAUSE OF ITS PBT/vPvB[1] PROPERTIES

Adopted on 27 November 2014

[1] PBT means persistent, bioaccumulative and toxic; vPvB means very persistent and very bioaccumulative

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TABLES

Substance Name(s): 2-benzotriazol-2-yl-4,6-di-tert-butylphenol (UV-320)

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The substance is identified as PBT according to Article 57 (d) and as vPvB according to Article 57(e).

Summary of how the substance meets the criteria set out in Article 57 of the REACH Regulation

Persistence

The persistence of UV-320 has been assessed by using a weight of evidence approach.

Conclusions of the weight of evidence approach:

- ready biodegradation tests of UV-320 suggest the substance is not subject to biological degradation (0% after 28 days);

- There are no simulation tests on UV-320 for water and sediment. The degradation of the substance EC 407-000-3 (Reaction mass of branched and linear C7-C9-alkyl-3-[3-(2-H-benzotriazol-2-yl)-5-(1,1-dimethyl)-4-hydroxyphenyl]-propionates) was studied in several simulation tests. In these studies, a major degradation product M1 was analyzed. This metabolite is structurally very similar to UV-320 only with a minor different substitution group in position 4 of the phenolic ring and was therefore used in a read-across assessment for UV-320. M1 was formed in the water phase, and dissipated rapidly in a few days to the sediment compartment. In the sediment, M1 is persistent with calculated disappearance half-lives up to 238 and 248 days depending on the sediment type. As the disappearance in this case has to be faster than the degradation of M1, $DegT_{50}$-values in turn have to be higher than the DT50-values. The differing side chain of M1 will be faster degraded than that of UV-320. Therefore, and assuming that the fate properties of UV-320 and M1 are very similar in a degradation simulation test, the results on M1 may be expected to be a best case representative on the disappearance and degradation of UV-320;

- In a recent field study dissipation in soil using the structural very similar substance UV-328 was tested. Using the results of this test, a DT_{50} of up to 223 days was calculated. As the disappearance has to be shorter or as long as the degradation, the respective $DegT_{50}$-values will have to exceed the numerical vP-criterion of 180 days for the soil compartment as defined in Annex XIII as well. These results were taken as a read-across on UV-320;

- For the very similar substances UV-327 and UV-328 available monitoring studies indicate presence of the substances in sediments decades after environmental releases had stopped. Model calculations indicate that these findings can only be explained if the half life for degradation is exceeding the Annex XIII trigger of 180 days. These results on UV-327 and UV-328 were taken as a read-across on UV-320;

- Thus, applying the weight of evidence approach, UV 320 clearly fulfils the P- and vP-criteria of REACH Annex XIII as defined under Sections 1.1.1. and 1.2.1.

Bioaccumulation

In a BCF study on fish according to the OECD Guideline 305 C lipid normalized BCF values of 5905 and 12041 were found in two of the three test concentrations Therefore UV-320 fulfils the B (BCF >2000) and vB criterion (BCF >5000) of REACH Annex XIII as defined under Sections 1.1.2. and 1.2.2.

Toxicity (only relevant for PBT substances)

There is evidence based on the RAC opinion[2] on UV-320 that indicates that the substance meets the criteria for classification as STOT RE 2 as defined in the CLP Regulation (EC) 1272/2008. As a consequence, the toxicity criterion of REACH Annex XIII is fulfilled.

Conclusion

In conclusion, UV-320 meets the criteria for a PBT/vPvB substance according to Art. 57(d) and (e) of REACH.

Registration dossiers submitted for the substance: No

[2] http://echa.europa.eu/documents/10162/13641/rac_opinion_uv-320-328_en.pdf

Justification

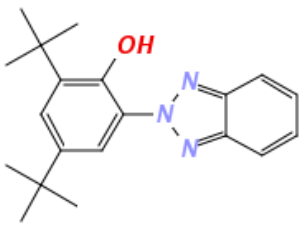
1. Identity of the substance and physical and chemical properties

1.1. Name and other identifiers of the substance

Table 1: Substance identity

EC number:	223-346-6
EC name:	2-Benzotriazol-2-yl-4,6-di-tert-butylphenol
CAS number (in the EC inventory):	3846-71-7
CAS number:	3846-71-7
Deleted CAS numbers:	3135-21-5, 29820-26-6, 104817-17-6, 131242-54-1, 134512-21-3, 189377-88-6, 208761-49-3, 420135-91-7, 474264-63-6, 796971-92-1
CAS name:	Phenol, 2-(2H-benzotriazol-2-yl)-4,6-bis(1,1-dimethylethyl)-
IUPAC name:	2-(2H-benzotriazol-2-yl)-4,6-di-tert-butylphenol
Index number in Annex VI of the CLP Regulation	-
Molecular formula:	$C_{20}H_{25}N_3O$
Molecular weight range:	323.432 g/mol
Synonyms:	UV 320 2-(2'-Hydroxy-3',5'-di-t-butylphenyl)benzotriazole 2-(2'-Hydroxy-3',5'-di-tert-butylphenyl)benzotriazole 2-(2'-Hydroxy-3'5-di-tert-butylphenyl) benzotriazole 2-(2-Benzotriazolyl)-4,6-di-tert-butylphenol 2-(2-Hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole 2-(2-Hydroxy-3,5-di-tert-butylphenyl)benzotriazole 2-(3',5'-Di-tert-butyl-2'-hydroxyphenyl)benzotriazole

Structural formula:



1.2. Composition of the substance

Name: 2-benzotriazol-2-yl-4,6-di-tert-butylphenol

Description: Organic substance

Substance type: mono-constituent (degree of purity ≥ 80 – 100 % (w/w))

1.3. Identity and composition of structurally related substances (used in a grouping or read-across approach)

Table 2: Structurally related substance identity of UV-328

EC number:	247-384-8
EC name:	2-(2H-Benzotriazol-2-yl)-4,6-ditertpentylphenol
SMILES:	Oc(c(cc(c1)C(CC)(C)C)C(CC)(C)C)c1n(nc(c2ccc3)c3)n2
CAS number (in the EC inventory):	25973-55-1
CAS number:	25973-55-1
CAS name:	Phenol, 2-(2H-benzotriazol-2-yl)-4,6-bis(1,1-dimethylpropyl)-
IUPAC name:	2-(2H-benzotriazol-2-yl)-4,6-bis(2-methylbutan-2-yl)phenol
Index number in Annex VI of the CLP Regulation	-
Molecular formula:	C22H29N3O
Molecular weight range:	351.50 g/mol
Synonyms:	UV 328

Substance type: mono-constituent (degree of purity ≥ 80 – 100 % (w/w))

Structurally related substance(s) formula:

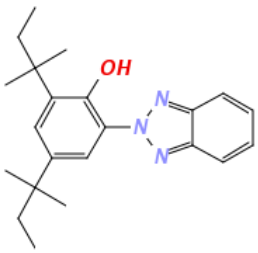


Table 3: Structurally related substance identity of UV-327

EC number:	223-383-8
EC name:	2,4-di-tert-butyl-6-(5-chlorobenzotriazol-2-yl)phenol
SMILES:	Oc(c(cc(c1)C(C)(C)C)C(C)(C)C)c1n(nc(c2cc(c3)Cl)c3)n2
CAS number (in the EC inventory):	3864-99-1
CAS number:	3864-99-1
CAS name:	Phenol,2-(5-chloro-2H-benzotriazol-2-yl)-4,6-bis(1,1-dimethylethyl)-
IUPAC name:	2,4-Di-tert-butyl-6-(5-chloro-2H-benzotriazol-2-yl)phenol
Index number in Annex VI of the CLP Regulation	-
Molecular formula:	$C_{20}H_{24}ClN_3O$
Molecular weight range:	357.8771 g/mol
Synonyms:	Phenol, 2,4-di-tert-butyl-6-(5-chloro-2H-benzotriazol-2-yl)-; 2,4-Di-tert-butyl-6-(5-chloro-2H-benzotriazol-2-yl)phenol; 2,4-di-tert-butyl-6-(5-chlorobenzotriazol-2-yl)phenol; 2-(2-Hydroxy-3,5-di-tert-butylphenyl)-5-chloro-2H-benzotriazole; 2-(2-Hydroxy-3,5-di-tert-butylphenyl)-5-chlorobenzotriazole; 2-(2'-Hydroxy-3',5'-di-tert-butylphenyl)-5-chlorobenzotriazole; 2-(3,5-Di-tert-butyl-2-hydroxyphenyl)-5-chloro-2H-benzotriazole; 2-(3,5-Di-tert-butyl-2-hydroxyphenyl)-5-chlorobenzotriazole; 2-(3',5'-Di-tert-butyl-2'-hydroxyphenyl)-5-chlorobenzotriazole; 5-Chloro-2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole; 5-Chloro-2-(2-hydroxy-3,5-di-tert-butylphenyl)benzotriazole; 5-Chloro-2-(3,5-di-tert-butyl-2-hydroxyphenyl)-2H-benzotriazole; 5-Chloro-2-(3,5-di-tert-butyl-2-hydroxyphenyl)benzotriazole; 5-Chloro-2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)benzotriazole; ADK Stab LA 34; Antioxidant 327; Cyasorb UV 5357; Eversorb 75; Hisorb 327;

	Hisorp 327; Kemisorb 72; LA 34; Lowilite 27; Mark LA 34; Seesorb 702; TNV 327; Tinuvin 327; UV 2; UV 2 (UV stabiliser); UV-327; UV-Chek AM 607; Viosorb 580

Substance type: mono-constituent (degree of purity ≥ 80 – 100 % (w/w))

Structurally related substance formula:

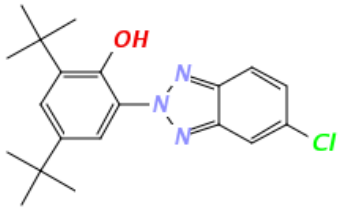
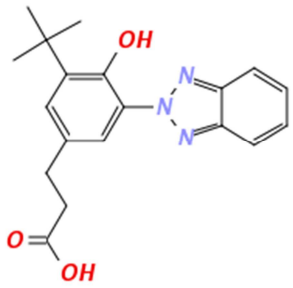


Table 4: Structurally related substance identity of 3-[3-(2H-Benzotriazol-2-yl)-5-tert-butyl-4-hydroxyphenyl]propionic acid (M1)

EC number:	-
EC name:	-
SMILES:	CC(C)(C)c1cc(cc(c1O)n2nc3ccccc3n2)CCC(=O)O
CAS number (in the EC inventory):	-
CAS number:	84268-36-0
CAS name:	Benzenepropanoic acid,3-(2H-benzotriazol-2-yl)-5-(1,1-dimethylethyl)-4-hydroxy-
IUPAC name:	3-[3-(2H-Benzotriazol-2-yl)-5-tert-butyl-4-hydroxyphenyl]propionic acid
Index number in Annex VI of the CLP Regulation	-
Molecular formula:	$C_{19}H_{21}N_3O_3$
Molecular weight range:	339.39 g/mol
Synonyms:	3-(2H-benzotriazol-2-yl)-5-(1,1-dimethylethyl)-4-hydroxy-benzenepropanoic acid

Substance type: mono-constituent (degree of purity ≥ 80 – 100 % (w/w))

Structurally related substance formula:



1.4. Physicochemical properties

Table 5: Overview of physicochemical properties

Property	Description of key information	Value	Reference/source of information
Physical state at 20°C and 101.3 kPa	-	-	-
Melting/freezing point	-	191 °C	result from MPBPWIN-module in EPISUITE v4.10; US EPA 2011
Boiling point	-	444.0 ± 55.0°C	calculated properties using Advanced Chemistry Development (ACD/Labs) Software V11.02 (©1994-2010 ACD/Labs)
Vapour pressure	-	1.70*10-8 Torr, 25 °C	calculated properties using Advanced Chemistry Development (ACD/Labs) Software V11.02 (©1994-2010 ACD/Labs)
Density	-	-	-
Water solubility	-	0.1503 mg/l at 25°C	QSAR estimation from log Kow with the EPISuite module WSkowWIN v1.42; US EPA 2011, log Kow used for calculation: 6.27
Partition coefficient n-octanol/water (log value)	-	6.853 ± 1.254, Temperature = 25 °C 6.27 7.39	calculated properties using Advanced Chemistry Development (ACD/Labs) Software V11.02 (©1994-2010 ACD/Labs) EPISuite v.4.10 COSMOtherm v. C30_1201
Dissociation constant	-	-	-

2. Harmonised classification and labelling

None

3. Environmental fate properties

3.1. Degradation

3.1.1. Abiotic degradation

3.1.1.1. Hydrolysis

There are no studies on hydrolysis available.

The chemical bond between the benzotriazole group and the aromatic ring is very strong and able to resist hydrolytical degradation. In addition, the aliphatic groups in the side chains of the phenol ring are functional groups that are expected to be also resistant to hydrolysis. Due to the high log K_{OW} and the high adsorption potential to organic carbon the substance will adsorb to sewage sludge and suspended organic matter when it is released to the sewage treatment system or to the aquatic environment.

Therefore, hydrolysis is not expected to be a relevant degradation pathway of UV-320.

3.1.1.2. Oxidation

There are no studies on oxidation of UV-320 available.

AOPWIN (v1.92) predicts the generic structure alert "Reaction with Nitrate radicals may be important" based on the fact that there is a phenolic group in the molecule. But to our knowledge there are no experimental studies in the literature available showing a reaction of UV-320 and atmospheric Nitrate radicals.

As phenolic benzotriazoles are mainly used as UV absorbers they are designed to be robust. Given their chemical structure and the lack of other information oxidation has to be assumed to be a rather negligible degradation pathway.

3.1.1.3. Phototransformation/photolysis

There are no studies on phototransformation/photolysis available.

Phenolic benzotriazoles are mainly used as UV absorbers. At the molecular level UV-radiation excites the phenolic benzotriazole from its ground state. In the excited state, a proton from the OH-group is transferred to a nitrogen atom. From this structure, a radiationless deactivation coupled with another proton transfer from the nitrogen back to the OH-group will bring the molecule back to its ground state. The UV-protection properties are based on this fully reversible and non-destructive process. Therefore, degradation through photolysis can be regarded as negligible.

3.1.1.4. Summary on abiotic degradation

In conclusion, abiotic degradation is not relevant for UV-320.

3.1.2. Biodegradation

3.1.2.1. Biodegradation in water

3.1.2.1.1. Estimated data

Not relevant for the SVHC identification of the substance according to Article 57 (d) and (e).

3.1.2.1.2. Screening tests

In a 28 day ready biodegradability test (performed according to the conditions of the test guidelines MITI I, OECD 301C; reliability rated Klimisch 2) using 100 mg of the substance /l and 30 mg suspended solids of sludge /l the degradation rate was 0 percent (measured parameter: BOD) (NITE, 2012). Hence, the substance is not readily biodegradable and fulfils the screening persistence criterion.

3.1.2.1.3. Simulation tests (water and sediments)

No simulation tests of the phenolic benzotriazole UV-320 itself are available for water and sediment. However, data on the dissipation of the substance EC 407-000-3 (Reaction mass of branched and linear C7-C9 alkyl 3-[3-(2-H-benzotriazol-2-yl)-5-(1,1-dimethyl)-4-hydroxyphenyl]propionates) in two water-sediment studies according to OECD 308 are available (dossier on 407-000-3). In these studies, the first metabolite of EC 407-000-3 is 3-(2H-benzotriazol-2-yl)-5-(1,1-dimethylethyl)-4-hydroxy-benzenepropanoic acid (CAS 84268-36-0), further on called M1. As will be shown in the rationale for read-across assessment, M1 has the common structure and degradation behaviour of all phenolic benzotriazoles. Thus, the studies are used for a read-across on the persistence of the phenolic benzotriazoles and conclusions for M1 will be used in a read-across to UV 320.

Rationale for read-across assessment:

Please note that the rationale presented here is valid for UV-320, UV-328, M1 and UV-327. The latter one is not important for the assessment of the simulation study but is used later in this chapter.

According to REACH regulation Annex XI 1.5 (Grouping of substances and read-across approach) the aim of a read-across is to avoid testing of every substance for every endpoint by using data known for one substance for other, similar substances. Substance similarity may be based on three criteria:

(1) a common functional group (cf. Figure 1);

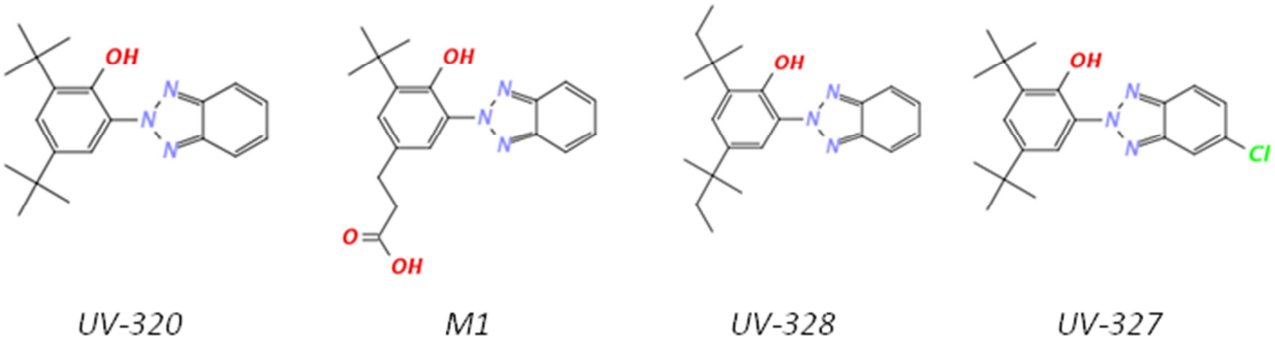


Figure 1: Chemical structure of UV-320, UV-328, M1 and UV-327

As can be seen in Figure 1 UV-320, UV-328, and M1 are structurally very similar and differ only slightly in the substitution groups in position 4 (and 6) of the phenolic ring. UV-327 differs from UV-320 only by the substitution of one hydrogen atom for a chlorine atom in the benzotriazole moiety. Based on this structural relationship they should have similar physicochemical properties. Unfortunately, only few experimental data are available on UV-328 and UV-327 and none on the other two substances, therefore it is not possible to prove this definitely by a comparison of physico-chemical properties. Nevertheless, the missing experimental data were simulated with the QSAR-methods provided by EPISuite and

COSMOtherm to at least give an estimate of the region they lie in. The comparison shows that the substances are all lipophilic with a strong tendence for binding to organic carbon. M1 is more water soluble and thus less lipophilic than the other substances and is likely therefore to distribute slightly differently in the environment. However, more watersoluble substances can be assumed to be degraded faster in the environment since they are more bioavailable. If there is a certain effect on the degradation times it should therefore in the direction of shorter DT50-values. The comparison is shown in Table 6.

Table 6: Overview of available physico-chemical data for UV-320, UV-328, M1 and UV-327

	UV-320			UV-328			M1			UV-327		
EC-Nr	223-346-6			247-384-8			-			223-383-8		
CAS-Nr	3846-71-7			25973-55-1			-			3864-99-1		
SMILES	Oc(c(cc(c1)C(C)(C)C)C(C)(C)C)c1n(nc(c2ccc3)c3)n2			Oc(c(cc(c1)C(CC)(C)C)C(CC)(C)C)c1n(nc(c2ccc3)c3)n2			CC(C)(C)c3cc(CCC(=O)O)cc(n2nc1ccccc1n2)c3O			Oc(c(cc(c1)C(C)(C)C)C(C)(C)C)c1n(nc(c2cc(c3)Cl)c3)n2		
Mol. Weight [g/mol]	323.4			351.5			339.4			357.9		
	Exp.	EPISuite	COSMO therm	Exp.	EPISuite	COSMO therm	Exp.	EPISuite	COSMO therm	Exp.	EPISuite	COSMO therm
Log K_{OW}	n.a	6.3	7.4	>6.5[3]	7.3	7.9	n.a	3.3	3.0[4]	n.a	6.9	7.9
Log K_{OC}	n.a.	5.1/4.6	5.2	n.a.	5.7/5.2	5.5	n.a.	3.8/2.2	3.96	n.a.	5.3/5.0	5.7
Water solubility [mg/L]	n.a.	0.2/4.6	9.0E-4	0.015[5] < 0,001 (at 20°C)**Error! Bookmark not defined.**	1.0E-2/ 0.4	3.0E-4	n.a.	102/213	1.29[4]	0.022	3E-2/1	2.0E-4
Vapor pressure [Pa]	n.a.	8.2E-6	5.4E-5	0,000005 (at 20°C)**Error! Bookmark not defined.**	2.6E-6	2.4E-5	n.a.	6.9E-10	1.0E-7	n.a.	3.6E-8	1.1E-5

n.a.: not available

[3] according to the registration dossier
[4] Using a pKA of 4.65 as calculated by ACDLabs
[5] according to Lopez-Avila, Hites (1980)

(2) common precursors and/or the likelihood of common breakdown products via physical and biological processes, which result in structurally similar chemicals (see Figure 2);

According to the simulation of the biodegradation pathway with the Biocatalysis/Biodegradation Prediction System PPS[6], the breakdown products are similar. Three generalized degradation pathways are possible:

a) The first one starts at the benzene ring of the benzotriazole moiety. While this is degraded, this degradation pathway always ends when a triazole group is left (Figure 2a).

b) The second pathway starts with the degradation at the side chain in position four (para-position) to the hydroxyl group. This degradation pathway ends when the side chain is completely degraded (Figure 2b).

c) For the complete degradation of the phenolic benzotriazoles the third degradation pathway is the most relevant, as this one results in the degradation of the bond between the phenol ring and the benzotriazole moiety which is never directly cleaved (Figure 2c).

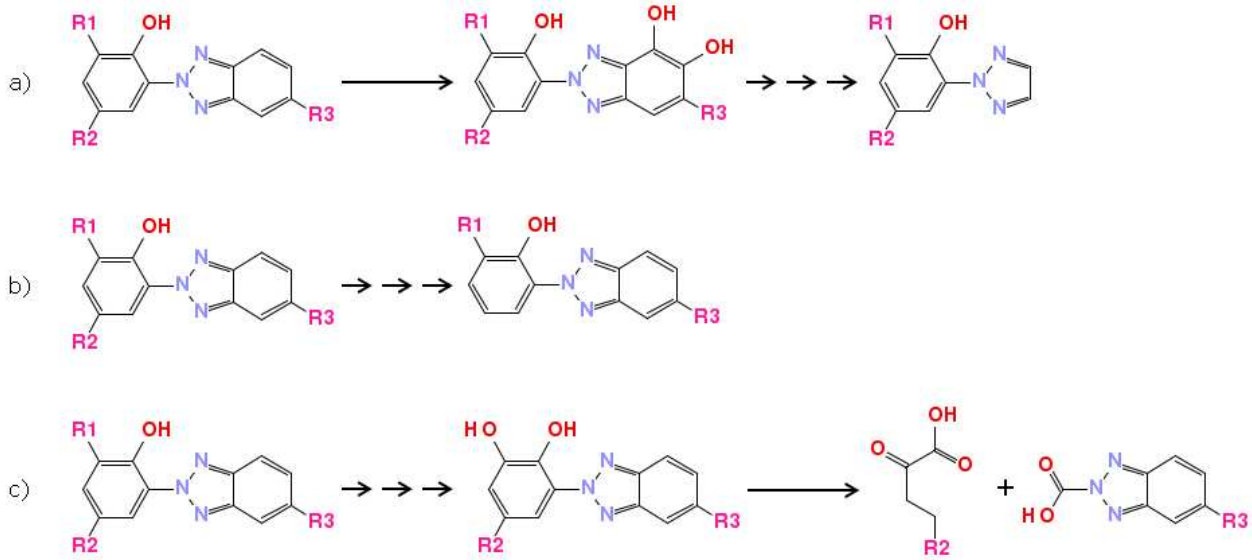


Figure 2: Simulated simplified mechanisms for the degradation of the phenolic benzotriazoles. a) Degradation of the benzotriazole moiety; b) Degradation of side chain R2; c) Degradation of side chain R1 leading to the ring cleavage of the phenolic ring R1, R2: alkyl; R3: H or Cl. Side reactions are for the sake of simplicity not considered here.

Please note that it is not possible to predict rate constants with this system.and that the rules of the PPS were not explicitly derived for cleavage of phenolic rings bound to benzotriazole and therefore it is uncertain if the mechanism proposed by PPS is relevant in the environment."

(3) a constant pattern in the changing of the potency of the properties across the category.

A qualitative estimation of the expected degradation times shows a constant pattern. The estimation considers chemical composition and complexity of the substitution groups of the two phenolic benzotriazoles and M1.

The following conclusion is drawn: $DegT_{50}(M1) < DegT_{50}(UV\text{-}320) \approx DegT_{50}(UV\text{-}328)$

Degradation of the side-chains R1 and R2 will be crucial for the difference in the degradation of the substances. As a basic rule it can be stated that the longer the aliphatic chain, the longer

[6] http://eawag-bbd.ethz.ch/predict/ (accessed 12.06.2012)

degradation takes. Furthermore the degree of substitution of the carbon atoms is important (quaternary, tertiary, secondary or primary) while R1 is essentially the same in all three molecules and thus will have a minor influence on degradation. R2 of M1 is different to R2 of UV-320 and UV-328. R2 of M1 is a linear n-propionic acid, which will be more easily degraded than R2 of both other substances. As the degradation of M1 should be faster than for the two phenolic benzotriazoles, the results of M1 can be regarded as a best case-scenario for the degradation half-lives of UV-320 or UV-328. This can also be verified by looking at the incremental values of the respective side chains in common QSAR-models. For example, BIOWIN3 which predicts the ultimate degradation half life, predicts for a tert-benzyl group (UV-320) a value of 3.14 (meaning a degradation in weeks), for a tert-pentyl group (UV-328) a value of 3.11 (also meaning weeks) and for a n-propionic acid side chain (M1) a value of 3.40 (meaning a degradation in days to weeks). Please note that in BIOWIN3 higher values indicate shorter degradation times.

In conclusion, the general rules for applying a read-across approach under REACH seem to be met as far as can be evaluated without reference to reliable physico-chemical data relevant for biodegradation. Thus, the degradation pattern of M1 in the simulation studies of EC 407-000-3 can be used for the assessment of the phenolic benzotriazoles and a comparison of degradation behavior of UV-320, UV-328 and UV-327 is appropriate.

General remarks on the results of the two simulation studies on EC 407-000-3:

Both simulation tests according to OECD 308 under aerobic or anaerobic conditions give valuable information on emergence and dissipation of M1 in a more environmentally relevant system than the screening test. In describing test conditions and assessment of test data it is important to differentiate between the underlying removal processes and to present them by use of appropriate terms for half-life. These are

> DT_{50}: Disappearance half-life time; all processes which contribute to the disappearance of a substance are subsumed in this term, i.e. shift to other compartments through, e.g. adsorption or volatilisation as well as degradation processes. It usually remains unknown which processes contribute to the half-life.
>
> $DegT_{50}$: Degradation half-life time; used to express that the half-life was caused by degradation processes. In most cases a $DegT_{50}$ value is higher than a DT_{50} value, because $DegT_{50}$ comprises mere degradation processes, only, whereas DT_{50} takes into account additional dissipation mechanisms.

Both simulation tests allow for calculation of $DT_{50,}$ but not of $DegT_{50}$. The $DegT_{50}$ is decisive for a direct comparison with the trigger values as defined in Annex XIII of REACH. Nevertheless, if a DT_{50} reaches the trigger value, the respective $DegT_{50}$ is exceeding the trigger, too. The exception to this general rule is when the parent continuously forms the metabolite. Thus, the FOCUS Guidance on Estimating Persitence and Degradation Kinetics (2006) states: "The overall decline in concentrations of metabolites in soil and water-sediment systems is often slower than degradation due to the continuous formation of the metabolite from the parent compound". In this specific example, this is not the case as there is no unlimited reservoir of EC 407-000-3 and from monitoring the concentration of the parent, we know that the decline of it is fast and already after 14 days most EC 407-000-3 has reacted and is very small in comparsion to the concentration of M1. Nevertheless, it should be kept in mind that the calculated DT50 –values may be either over- or underestimates.

Assessment of a water-sediment study according to OECD 308 on EC 407-000-3 (aerobic conditions)

Description of test system

Test conditions are generally well described and the test was performed according to GLP. However, the reported validity descriptors either remain unknown or even question the reliability of the study, i.e. Chi^2 is not reported and many graphs do not sufficiently match the corresponding values. The report is reliable with restrictions (2 according to Klimisch).

Two systems of different organic carbon level were used. A river system with low level and a pond system with high level of organic carbon. Sampling locations of water and sediment were a pond and the river Rhine. For both systems it could be assumed that sampling locations have not been pre-exposed to the test substance or structurally similar substances. The pond did not receive effluent discharge and this was assumed for the river Rhine, too. However as no exact sampling location was given, some uncertainty remains. The test substance was radiolabeled in the benzene ring of the triazole moiety. Test systems were allowed to acclimatise for two weeks after filling. Water sediment ratio was 3.3:1. A stock solution which consisted of test substance in acetone was diluted stepwise to give a final concentration of the test substance of 3 µg/L. This concentration is below the water solubility of EC 407-000-3 (18 µg/L). The test substance was applied dropwise onto the water surface. Samples were taken and water and sediment were separately analysed on six occasions. Two traps were employed for volatile substances. Further information on test conditions is given in Table 7.

Table 7: Detailed test conditions

System	org. C in %	Temperature in °C	substance concentration in µg/L	Test duration in days	Recovery rate in %	Analysis methods
Pond	5.04	20 ± 2	3	100	99.9 % (97.6-101.9 %)	TLC HPLC LSC
River	0.95				98.7 % (96.2-101.2 %)	

M1 was detected as the main metabolite in quantities exceeding 10 % of the applied radioactivity.M1 was analyzed in the water as well as in the sediment phase. Twelve other metabolites were detected, but not identified. Volatile metabolites did not emerge. Three metabolites reached amounts of 5 to 8 % each in the total system at day 100 (Overall sum of other metabolites than M1 at day 100: aerobic river 27.2%, aerobic pond 16.2%). The other metabolites were detected only in very small amounts and defined as negligible. Data were given for M1 to M8, only. Thus, only these can be considered in the assessment.

Please note that the focus of the following evaluation is on the metabolite M1 and not on the original test substance EC 407-000-3.

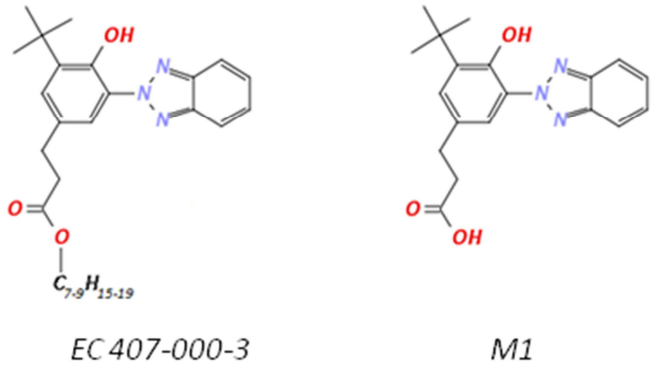


Figure 3: Molecular structure of EC 407-000-3 and M1 in comparison.

Results:
There are two studies which were assessed (Dossier on 407-000-3): A first study examined dissipation of the parent EC 407-000-3 and M1 in a river system and in a pond system under

aerobic conditions. A second study examined dissipation of the parent EC 407-000-3 and M1 merely in a pond system under anaerobic conditions.
DT_{50} was modelled using data as reported in the study following the specifications as given in the FOCUS Guidance on Estimating Persitence and Degradation Kinetics (FOCUS, 2006) using the software KinGUI. This means also that the calculated DT50-values refer to a test-temperature of 20±2°C. Calculations considered the model Double First Order in Parallel mode (DFOP) for EC 407-000-3 in the whole system, Single First Order kinetics (SFO) for M1 in the water and the sediment phase separately and SFO for NER. For further details see Annex 1.
Figure 4 and Figure 5 give a subsumption of data observed in and trends modelled for the river and the pond system under aerobic conditions. Data and trends are consecutively discussed separately for the water and the sediment phase. This is done first for the aerobic study and then for the anaerobic study.

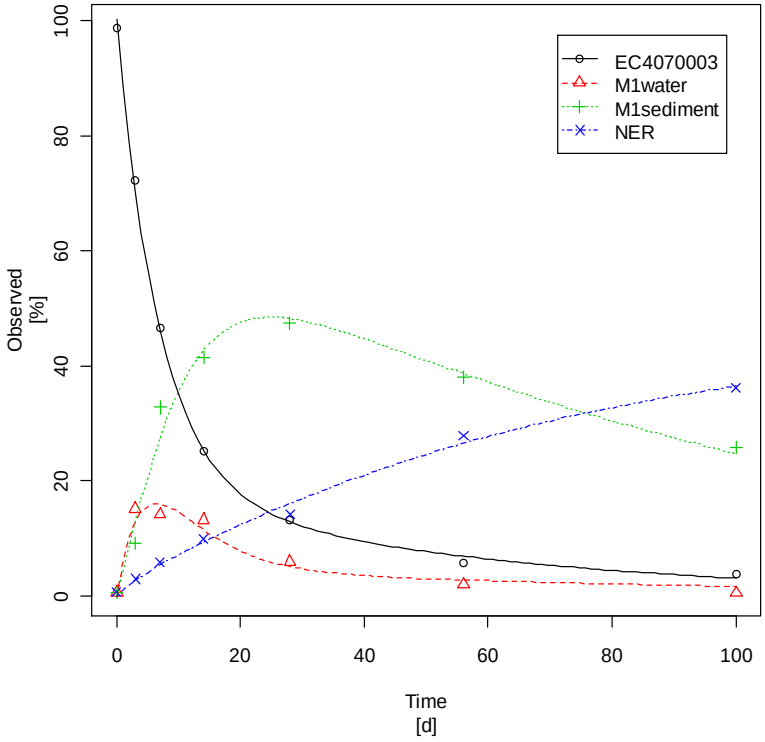


Figure 4: Measured and predicted (kinetic model) residues vs. time for the river system under aerobic conditions.

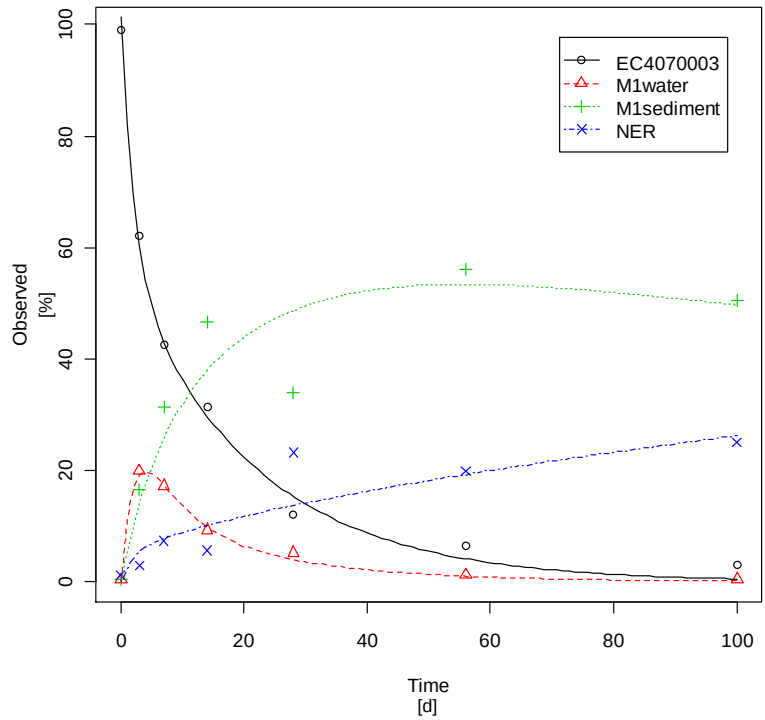


Figure 5: Measured and predicted (kinetic model) residues vs. time for the pond system under aerobic conditions.

M1 in the water phase under aerobic conditions

In the aerobic river system M1 reached the maximum concentration of 15 % in water at day 3 and declined to 0.6 % at test end.

M1 concentration in water is well described by a single first order kinetic (SFO) and results in a DT_{50} of 3.4 days. Visual fit (see Figure 6) and chi^2 of 15 show that the model used describes data well. This reflects the dissipation of M1 from water to sediment starting after a maximum has been reached at day 3.

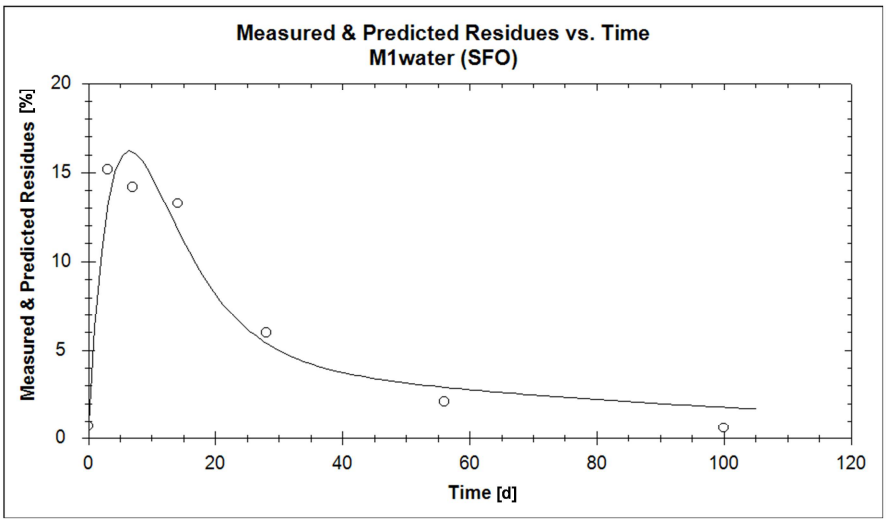


Figure 6: Measured and predicted (SFO model) residues of M1 vs. time in the water phase of the river system under aerobic conditions.

For further details please refer to section 2.2.2.3. and Table 23 to Table 25 in Annex 1.

River system, aerobic conditions: M1 in water phase DT_{50} 3.4 days

In the aerobic pond system M1 reached the maximum concentration of 19.9 % in water at day 3 and declined to 0.5 % at test end (see Figure 6).
M1 concentration in water is well described by a single first order kinetic (SFO) and results in a DT_{50} of 3.9 days. Visual fit (see Figure 7) and chi^2 of 5.2 show that the used model describes data well.

As in the river system M1 dissipates again from water to sediment.

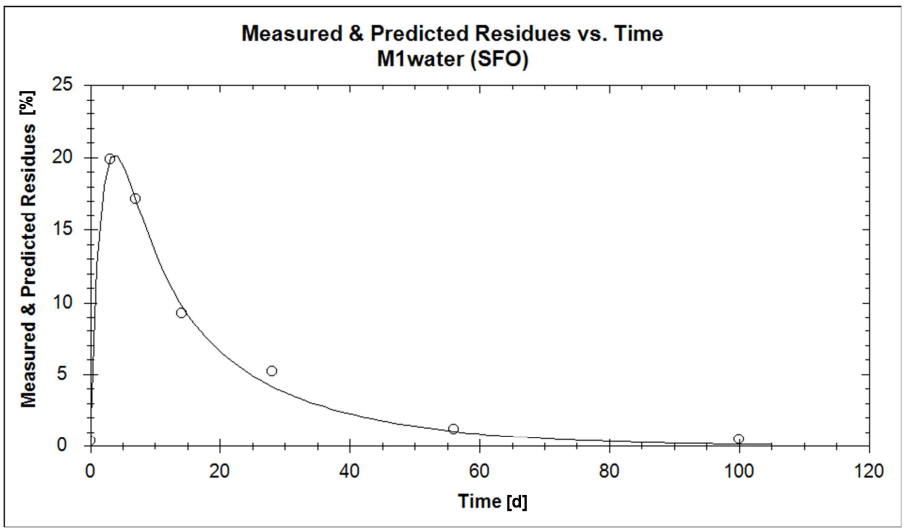


Figure 7: Measured and predicted (SFO model) residues of M1 vs. time in the water phase of the pond system under aerobic conditions.

For further details, please refer to section 2.4.2.3 and Table 29 to Table 31 in Annex 1.

Pond system, aerobic conditions: M1 in water phase DT_{50} 3.9 days

M1 in the sediment phase under aerobic conditions

Please note that the recovery rates in the sediment phase of the river and of the pond system constantly dropped as more non-extractable residues (NER) were formed.

In the aerobic river system M1 reached a maximum sediment concentration of approximately 47 % at day 28 which decreased to 26 % at test end. Model calculation results in a SFO DT_{50} of 31.6 days. Visual fit (see Figure 8) and chi^2 of 8.3 show that the used model describes data well.

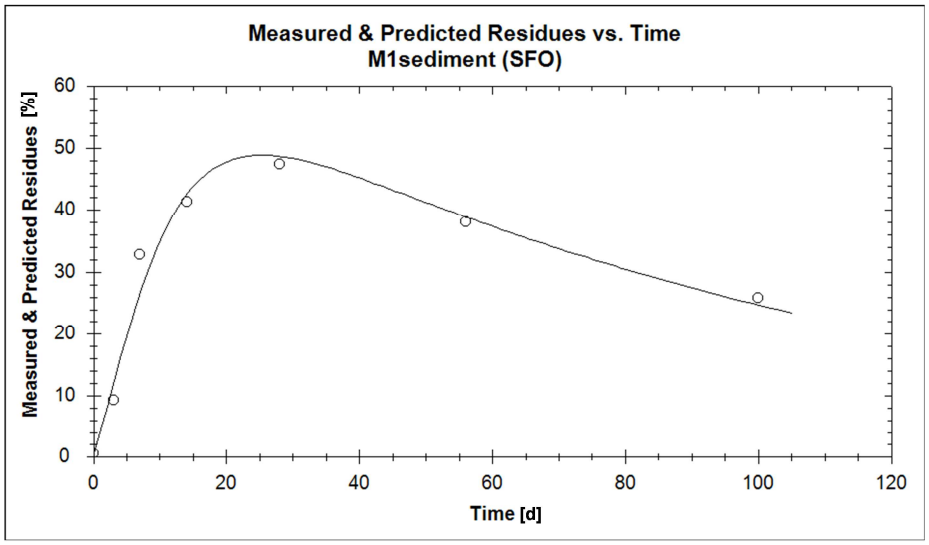


Figure 8: Measured and predicted (SFO model) residues of M1 vs. time in the sediment phase of the river system under aerobic conditions.

For further details, please refer to section 2.2.2.4. and Table 23 to Table 25 in Annex 1.

River system, aerobic conditions: M1 in sediment phase DT_{50} 31.6 days

In the aerobic pond system M1 concentration in sediment of M1 steeply increased to 46.7 % at day 14. It was interrupted by an interim decrease followed by an increase. The 28 days value may be an error of measurement but this remains speculation. M1 reached a maximum concentration of 56 % at day 56 which only slightly decreased to 50.4 % at test end. Model calculation results in a SFO DT_{50} of 248.2 days. Visual fit (see Figure 9) shows that the used model describes data sufficiently well although chi^2 is elevated with 19.2. The reason for this is that it is unclear whether M1 in sediment has reached a plateau or it is slowly degraded. Due to this, the absolute DT_{50}-value has to be taken with care.

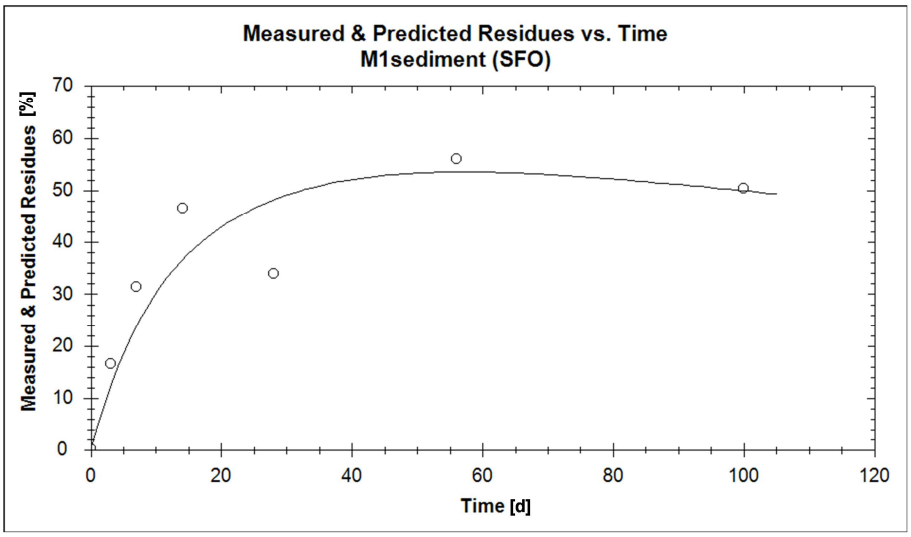


Figure 9: Measured and predicted (SFO model) residues of M1 vs. time in the sediment phase of the pond sediment under aerobic conditions.

For further details, please refer to section 2.4.2.4 and Table 29 to Table 31 in Annex 1.

Pond system, aerobic conditions: M1 in sediment phase DT_{50} 248.2 days

Assessment of a water-sediment study according to OECD 308 on EC 407-000-3 (anaerobic conditions)

Description of test system

A further test according to OECD 308 on degradation of EC 407-000-3 in water and sediment under anaerobic conditions was reported in the dossier on EC 407-000-3. The test was done according to the same procedure and under the same conditions described above for aerobic conditions. Sediment was taken from an organic rich pond, only. No river system was tested. Apart from M1 eight further metabolites (M2-9) were detected (Overall sum of other metabolites than M1 at day 100: 2.6%). M2 was the metabolite which was detected second-most but it only once slightly exceeded 1 %.

Results:

DT_{50} was modelled using data as reported in the study following the specifications as given in the FOCUS guidance (FOCUS, 2006) using KinGUI. Calculations considered DFOP for EC 407-000-3 in the whole system, SFO for M1 in the water and the sediment phase separately and

SFO for NER. For further details please see Annex 1.
Figure 10 gives a subsumption of data observed in and trends modelled for the river and the pond system under anaerobic conditions. Data and trends are consecutively discussed separately for the water and the sediment phase.

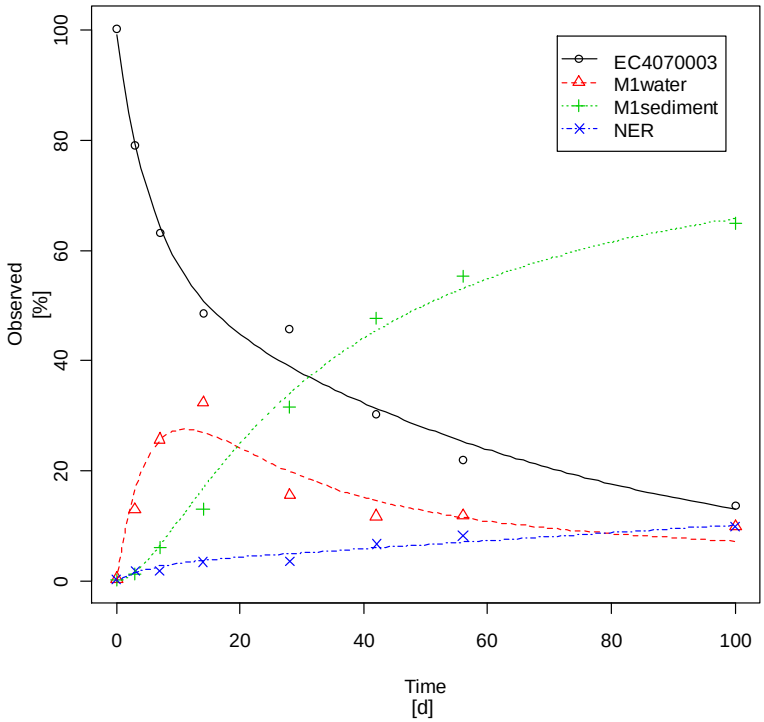


Figure 10: Measured and predicted (kinetic model) residues vs. time in the pond system under anaerobic conditions.

<u>M1 in the water phase under anaerobic conditions</u>

M1 reached a maximum of 32.4 % in water at day 14 and declined to 15.5 % at day 28. Thereafter the decline markedly slowed down with M1 reaching 9.9 % at test end. Model calculation results in a SFO DT_{50} of 12.2 days. Visual fit (see Figure 10) and chi^2 of 16.8 show that the used model describes data well though chi^2 is slightly elevated.

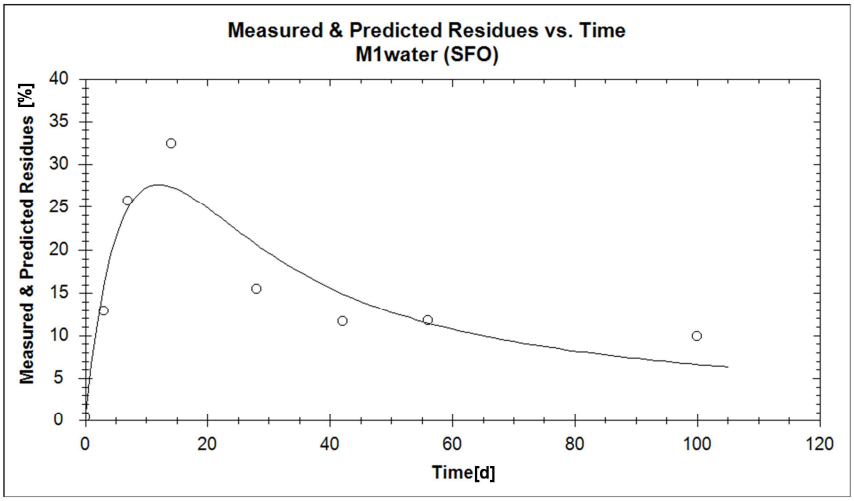


Figure 11: Measured and predicted (SFO model) residues of M1 vs. time in the water phase of the pond system under anaerobic conditions.

For further details please refer to section 3.2.2.3. and Table 35 to Table 37 in Annex 1.

Pond system, anaerobic conditions: M1 in water phase DT_{50} 12.2 days

M1 in the sediment phase under anaerobic conditions

M1 concentration in sediment rose steadily up to day 42 (see Figure 12). Thereafter the rise got less pronounced but stayed steady up to the test end. M2-9 which represent the next degradation steps did not exceed 2.2 %. This was reached at day 56 and did not change afterwards. Non-extractable residues (NER) slowly but steadily increased up to 9.8 % at test end. There was no degradation, but a constant build-up of M1 in the sediment phase. No plateau of M1 was observed. Model calculation results in a SFO DT_{50} of 237.7days. Visual fit (see Figure 12) and chi^2 of 5.4 show that the used model describes data well, the t-test concludes that the degradation constant for M1 in sediment is essentially zero as can be seen from the partial curve modelled. Therefore, the absolute value calculated for DT_{50} has to be taken with care,

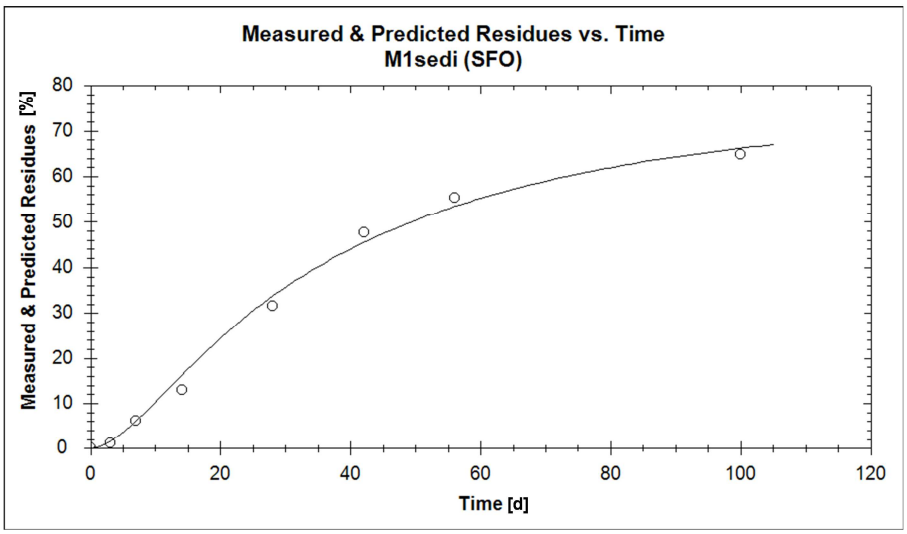


Figure 12: Measured and predicted (SFO model) residues of M1 vs. time in the sediment phase of the pond system under anaerobic conditions.

For further details please refer to section 3.2.2.4. and Table 35 to Table 37 in Annex 1.

Pond system, anaerobic conditions: M1 in sediment phase DT_{50} 237.7 days

3.1.2.2. Biodegradation in soil

3.1.2.2.1. Simulation tests

Assessment of a simulation field study

Very recently a study by Lai et al (Lai et al., 2014) was published. In this study the authors examined the dissipation behaviour of Benzotriazole and Tolytriazole as well as several phenolic benzotriazoles (UV-326, UV-327, UV-328, UV-329 and UV-P) in order to assess whether the application of biosolids as fertilizers in agricultural land might be a relevant pathway for environmental contamination.

Description:

In the study dewatered sludge from a WWTP in Beijing was applied onto agricultural land in Shandong, China. All reported information on the field trial sites like soil types or average temperatures are given in Table 8. The sludge was not further amended with reference substances or benzotriazoles meaning that all benzotriazoles were incorporated in it. In the first experiment (Treatment T1) this was done only once in May 2007 while in the second experiment (Treatment T2) application was repeated every year in October until 2010. Each treatment consisted of application of the same dewatered sludge at a concentration of 6 kg/m^2 on four replicates (3m x 2m each). Also, there was a control site where no treatments were conducted.

In order to incorporate the sludge the trial fields were ploughed to a depth of 20 cm. On the fields wheat and maize were cultivated. Information on the field trail sites and the treatments is summarized in Table 8.

Table 8: Detailed information on the field trial sites and treatments according to Lai (2014)

Treat-ment	Crops	Annual average temp. [°C]	Annual total rainfall [mm]	Soil type/ texture	Soil moisture [%]	pH	TOC [%]	Clay (<0.002 mm) [%]	Biosolid application [kg/m^2]
Control	Wheat and maize	12.9[7]	522	Fluvo-aquic soil /clay loam	23	7.6±0.2	0.6±0.0	21.7±4.2	0
T1	Wheat and maize	12.9	522	Fluvo-aquic soil /clay loam	23	7.6±0.1	1.0±0.1	21.9±1.5	6, once
T2	Wheat and maize	12.9	522	Fluvo-aquic soil /clay loam	23	7.6±0.1	1.4±0.3	26.0±0.8	6, four times

Starting from October 2010 until October 2011 soil samples were taken monthly in a depth between 0 and 20 cm. Each sampling of the four replicates consisted of five subsamples that were mixed. Due to experimental problems this practice was stopped in winter and resumed in March 2011. The soil samples were extracted with methanol/dichloromethane (50:50, v/v) at 120°C for 5 minutes in two cycles. Concentrations of the benzotriazoles were detected via GC-MS. The recovery rate was depending on the substance between 75 and 117% (80% for UV-328). For UV-328 the limit of detection was 1.13 ng/g and the limit of quantification 3.76 ng/g. For UV-327 the limit were considerably higher (limit of detection 2.77 and limit of quantification 9.23).

Results:

At the beginning of the measurements (October 2010 to March 2011) considerable variations (i.e. a rise) of the concentrations were reported by Lai et al. (2014). The authors attribute them to problems with obtaining a homogenous sample during the frost period or the degradation processes in samples during storage until extraction. No information is given if these were the reasons for the occurring variations and how this problem was finally solved. Beginning with March 2011 the problem stopped. Therefore the authors only fitted the data starting from March 2011 to October 2011. This was also done by the dossier submitters.

In all the control samples only trace concentrations at the limit of quantification of Benzotriazole, Tolyltriazole and UV-327 were detected, other phenolic benzotriazoles were not found. The reported concentrations for UV-328 are shown in Figure 13 and Figure 14.

[7] According to Wikipedia (checked 08.07.2014) the temperature in Shandong ranges between -5 to 1°C in January and 24 to 28°C in July.

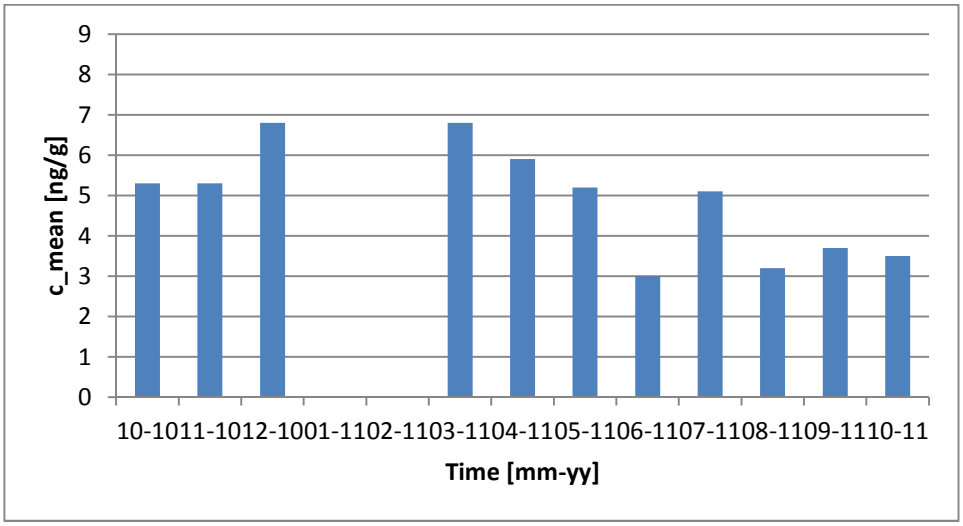


Figure 13: Reported concentrations of UV-328 during the one-year monitoring of Treatment 1 (one time application of sludge in October 2007), standard errors where calculated and lie between 0.1 and 1.7%. As the errors are so small they are not shown in the figure.

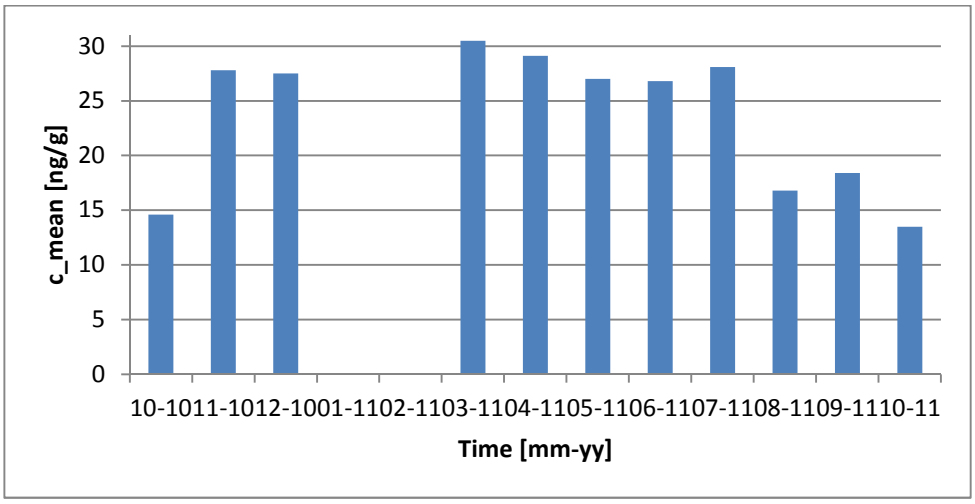


Figure 14: Reported concentrations of UV-328 during the one-year monitoring of Treatment 2 (yearly application of sludge from October 2007 to October 2010). standard errors where calculated and lie between 2 and 10.4%. As the errors are so small they are not shown in the figure.

Due to the problem described above the authors performed a dynamic curve-fitting only between March 2011 and October 2011. They report the following times for field dissipation:

Table 9: Overview of reported DT_{50}-values by Lai et al. (2014)

Substance	**UV-326**		**UV-327**		**UV-328**		**UV-329**		**UV-P**	
	T1	**T2**	**T1**	**T2**	**T1**	**T2**	**T1**	**T2**	**T1**	**T2**
DT_{50} [d]	104	141	151	192	179	218	129	98	113	75
Error [d]	10	17	19	28	27	42	28	16	35	14

As the authors employed SFO-kinetics there should be essentially no difference in DT50-values between T1 and T2 as this kinetic model is independent of concentration. As can already be seen in Table 9 in some cases T1 is larger and in some T2 but when also taking into account the reported errors there is an overlap of the band of T1- and T2-values for all substances with the exception of UV-326.

The results of this study have to be regarded as best cases for the disappearance in the environment as

- they only reflect the warmer period of the year;
- three years lie between (first) application and measurements, therefore potentially allowing microorganisms to adapt;
- only dissipation was monitored;
- NER were not considered at all.

In order to do an assessment comparable to the one done in case of the water sediment studies assessed above, the dossier submitters employed the same scheme for kinetic modelling on the results for UV-328 in this study, i.e. they used the approach of the FOCUS group and employed kinGUI. Details of the simulation can be found in Annex 1. As Lai et al. did, only the data from March 2011 to October 2011 was considered. The initial concentrations in March 2011 for UV-328 were 6.8 (±1.1%) ng/g after the single application in 2007 (experiment T1) and 30.5 (±2.8%) ng/g for the repeated applications (experiment T2). Please note that the fact that there is still non-marginal concentrations are found in T1 is already some evidence that the substances are persistent in the environment. A SFO DT_{50} of 197.0 days for Treatment 1 and a SFO DT_{50} of 222.8 days for Treatment 2 was calculated. The visual fits and chi^2-values (Treatment 1: 12.9, Treatment 2: 9.6) show that the used model describes the data well. The simulated curves are shown in Figure 15 and Figure 16. More details are provided in Annex 1. The estimations are comparable to those of the original paper. As the authors did, the dossier submitters do not expect different DT_{50}-values for T1 and T2 therefore the different values give an indication of the broad range for the DT_{50}.

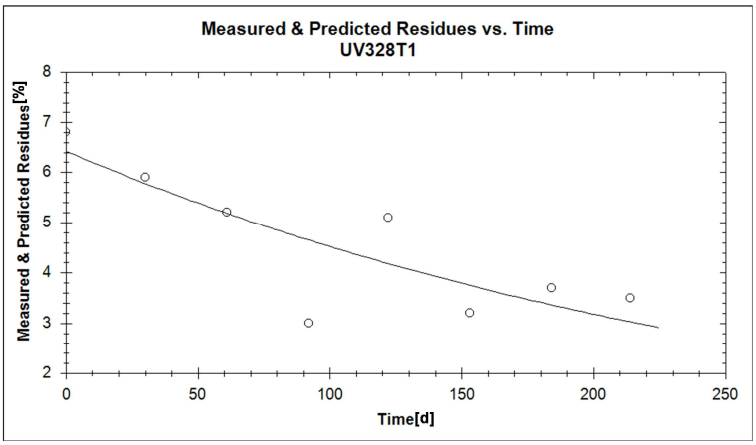


Figure 15: Measured and predicted (SFO model) residues of UV-328 in Treatment 1 vs. time.

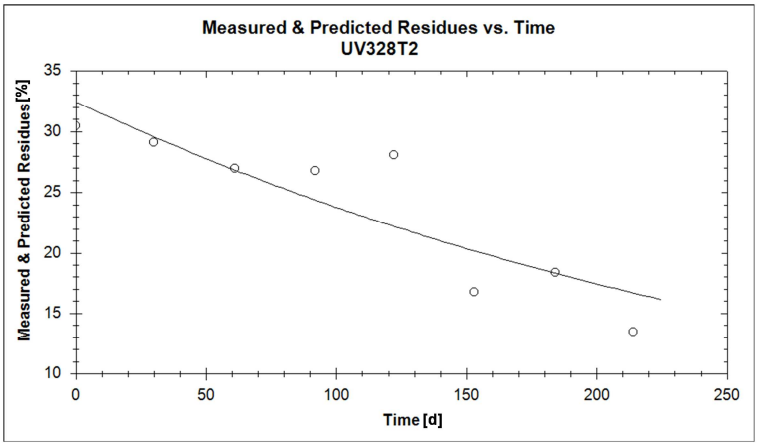


Figure 16: Measured and predicted (SFO model) residues of UV-328 in treatment 2 vs. time.

Field dissipation study, treatment 1 (one time application): UV-328 in soil DT_{50} 197.0 days

Field dissipation study, treatment 2 (repeated application): UV-328 in soil DT_{50} 222.8 days

3.1.2.3. Summary and discussion on biodegradation

Screening Tests:

In a study according to OECD Guideline 301 C the degradation of UV 320 was 0%, therefore the substance is not readily biodegradable according to the OECD definition.

Simulation Tests Water/Sediment:

Two simulation tests for the substance EC 407-000-3 and its main metabolite M1 were evaluated. The results for M1 were used for read-across of the data to UV-320. These tests were conducted according to OECD 308. One test was done under aerobic conditions for a river system and a pond system, the other test was conducted under anaerobic conditions for a pond system. It was not possible to derive $DegT_{50}$ values for comparison with the trigger values as given in Annex XIII of REACH, but DT_{50} values. The absolute values for the pond systemhave to be taken with care as only part of the degradation curves of M1 was monitored.

Depending on the test system the observed dissipation half-lives for M1 varied (see Table 10).

Table 10: Summary of dissipation half-lives of M1 for water and sediment under different conditions

		Water DT_{50}	Sediment DT_{50}
Aerobic conditions	River system (low org. C)	3.4 days	31.6 days
	Pond system (high org. C)	3.9 days	248.2 days
Anaerobic conditions	Pond system (high org. C)	12.2 days	237.7 days

Field Dissipation Study on degradation of phenolic benzotriazoles in soil:

Dissipation of several phenolic benzotriazoles (UV-326, UV-327, UV-328, UV-329, UV-P) in sludge-amended soils was monitored over a year and DT_{50}-values were calculated (Lai, 2014).

UV-327 and UV-328 can be used for read-across as they are similar to UV-320 in being 4,6-substituted phenolic benzotriazoles where the side chains are complex (see rationale for read-across in 3.1.2.1.3. For UV-327 a DT_{50}-value up to 192 days and for UV-328 a DT_{50}-value up to 218 days were calculated. Both substances are very similar to UV-320 (see Read-Across argumentation in section 3.1.2.1.3). Kinetic simulation of the data for UV-328 using the same approach as for the water/sediment study results in slightly higher DT_{50}-values of 197 or 223 days, depending whether the results were calculated for a experiment where UV-328-contaminated sludge was applied only once or repeatedly. The results have to be assessed as best case estimations for degradation in the environment as only dissipation was monitored, preadaptation of microorganisms was possible, only the warmer period of the year was simulated and NER were not considered at all. These results show that UV-320 will be very persistent in soils.

Overall assessment of results:

In summary, it is concluded that UV-320, which has also a tert-butyl group as side chain in ortho-position, is at least as hard to degrade as the both molecules in the simulation tests (M1 and UV-328). Accordingly the degradation half-life is assumed to be at least as long (see also rationale for read-across assessment). This is supported by the simulated degradation pathway.

3.1.3. Field data

For UV-327 and UV-328 several studies are available investigating their distribution in sediments in a highly contaminated area (Narragansett Bay, Rhode Island, USA). Considering the justification for read across presented in Chapter 3.1.2.1.3, the results of these studies can also be applied to UV-320. Taken together, this information can be used as an indication for the degradation potential in environmental sediments of UV-320.

UV-327 and UV-328 were historically produced in an industrial plant at the Pawtuxet River which flows into the brackish Providence River and consequently the Narragansett Bay (Reddy et al. 2000, Jungclaus et al. 1980, Lopez-Avila and Hites 1980, Hites et al., 1979). Production of UV-327 was reported between 1963 and 1972, while UV-328 was produced from 1970 to 1985 (Hartmann et al. 2005, Lopez-Avila and Hites, 1980). According to Pruell and Quinn (Pruell and Quinn, 1984) the chemical plant was the unique source of phenolic benzotriazoles in the Pawtuxet River. This is confirmed by C. Reddy (personal communication 1/2014) and by analysis of phenolic benzotriazoles in river water and sediments upstream and downstream from the chemical plant (Jungclaus et al., 1978, Hites et al. 1979, White et al., 2008). Although the plant produced a wide range of compounds including pharmaceuticals, herbicides, antioxidants, thermal stabilisers, UV absorbers, optical brighteners and surfactants, UV-327 and UV-328 were generally the most abundant compounds in the water and sediment samples.

There was and still is a municipal wastewater treatment plant situated a certain distance upstream of the (former) chemical plant (Oviatt et al., 1987), http://www.dem.ri.gov/programs/benviron/water/permits/wtf/potwops.htm). Oviatt et al. found UV-327 (7.88 ± 6.49 µg/g dw) and UV-328 (180 ± 103 µg/g dw) in the sewage sludge of this WWTP. However, White et al. (White et al. 2008) did not find both substances in sediment samples taken upstream of the chemical plant, which means that potential emissions of the WWTP do not result in measurable concentrations of the compounds in the sediments.

Three studies provide information on the environmental concentrations during production of UV-328 and few years after the production phase out of UV-327:

Jungclaus et al. (Jungclaus et al., 1978) analysed industrial WWTP effluent, receiving waters and sediments from the chemicals manufacturing plant. 16 River water samples and 19 sediment samples were collected in Providence River and its tributary Pawtuxet River in 1975

and 1976. UV-328 was detected in industrial WWTP effluent (0.55 – 4.7 µg/g), in river water (0.007 – 0.085 µg/g) and in sediments (1-100 µg/g). UV-327 was produced until 3-4 years before sampling and detected only in sediment, with concentrations of 2 – 300 ppm.

Lopez-Avila and Hites investigated the same chemicals manufacturing plant. Eight sediment cores were taken in 1977/78 at three locations in the Pawtuxet River. The sites were selected for an abundance of fine-grained material. Further sediment cores were taken at four locations in the Pawtuxet Cove and 13 locations in the Providence River and Narragansett Bay. The core concentrations of the compounds in the sediment were condensed into a single number. However, the authors think that the values given are representative of the sediment concentrations. Concentrations decrease both with depth in the sediment and with increase in distance from the discharge (Lopez-Avila and Hites, 1980).

Table 11: Concentrations of phenolic benzotriazoles in sediment cores (in µg/g) according to Lopez-Avila and Hites (1980).

	Pawtuxet River			**Pawtuxet Cove**	**Providence River**		
	near plant	**mid river**	**near dam**		**near to the plant**	**Far from the plant**	**bay**
UV-327	300	400	20	80	20	2	0.5
UV-328	300	300	70	100	10	5	0.6

With regard to the study discussed in the following, the dossier submitters were asked to include information on phthalates. Only DEHP concentrations are given in the study. It should be borne in mind that DEHP is persistent under anaerobic conditions according to a screening test (http://esis.jrc.ec.europa.eu/doc/risk_assessment/REPORT/dehpreport042.pdf, DEHP Risk Assessment Report 2008).

Pruell and Quinn (1985) investigated phenolic benzotriazoles, total hydrocarbons, PAH and DEHP. Sediment concentrations of all compounds were highest in the Providence River and decreased with distance downbay. The observed decreases were approximately exponential for all compounds; however, the distances at which the concentrations decreased to one-half of their initial concentrations (half-distance, log2/slope) were different:

organic carbon	12.5 km
total PAHs	7.18 km
total hydrocarbons	6.40 km
DEHP	4.70 km
UV 327	3.91 km
UV 328	3.81 km

Factors that may influence the half-distance are: physical properties of the compound (water solubility, log K_{ow} etc.), composition of the sediment (grain size, organic carbon content etc.), characteristics of the depositional environment (water depth, particle load, currents etc.), environmental stability of the compound (photochemical and biological reactivity etc.), interaction between chemicals. Pruell et al. come to the conclusion, that in the Pawtuxet case "the uniqueness of the inputs to the northern portion of the bay appears to primarily determine the rate at which the concentrations decrease with distance from the head to the mouth of Narragansett Bay". Total hydrocarbons and total PAH enter the bay via urban runoff all along the bay as well as from direct atmospheric deposition. The major inputs of DEHP are industrial effluents and sewage treatment plants, primarily in the Providence River. The unique source of the phenolic benzotriazoles is the Pawtuxet River, which flows into the Providence River. Because of the different input conditions the dossier submitter believe that no conclusions can be drawn from a comparison of the concentrations of the different substance groups in the sediment transect.

Pruell and Quinn (1985) also investigated depth distribution of the different

substances/substance groups including DEHP, UV-327 and UV-328 in three sediment cores taken in 1979/80 along a transect from the head (Providence River) to the mouth of Narragansett Bay. About 1 cm was scraped from the outside of the cores to prevent contamination from the plastic core liner. The core collected near the head of the bay showed a well defined historical record of phenolic benzotriazole input to the bay: UV-328 concentration was highest in the surface (ca. 7.5 µg/g dw) followed by decrease with depth, while UV-327 displayed a subsurface concentration maximum (ca. 6 µg/g dw) in the 10-15 cm horizon and then decreased with depth. Both compounds could not be detected below 20 cm in the core. DEHP concentration was highest in the surface (ca. 3.8 µg/g dw) followed by decrease with depth. A sharp decrease between 18 and 22 cm was observed (from ca. 3.0 to ca. 0.1 µg/g dw). At 28 cm and deeper no DEHP was detected. At a mid-bay location the record was smeared because of extensive bioturbation. A sediment core collected near the mouth of the bay showed a subsurface increase of the compounds. It is suggested that this horizon may have been influenced by dredge spoil material.

Two other studies provide some evidence on the concentrations of the phenolic benzotriazole compounds several years after their production ceased:

Reddy et al. (Reddy et al., 2000) examined the free and bound fractions of different substituted benzotriazoles in two sediment cores from the Pawtuxet River and Narragansett Bay. The Pawtuxet River sediment core was collected in 1989 and sectioned at 2-3 cm intervals. Eleven sections from 0-2 cm to 50-52 cm were analysed. The redox potential discontinuity, determined visually, was in the top 2 cm of the core. The Narragansett Bay core was collected in 1997. Six sections from the top 13 cm of the core were analysed. The sediments in this area become anoxic within a few millimetres of the surface. The method detection limit was ca. 20 ng/g for each (free and bound) fraction. In the Pawtuxet River core no bound benzotriazoles were detected. UV-327 was most abundant: the highest concentration was ca. 5000 µg/g dw and the substance was observed down to 50-52 cm. Concentrations vary in the first 20 cm and continuously decrease with depth starting at 20-22 cm. Taking into account a sedimentation rate of 2-3 cm/year for this site, a depth of 20 cm means that sediments of this layer were deposited ca. 1979 - 1982. Assuming that releases were constant during the years of production, the decrease in the UV-327 concentration between 20 and 50 cm depth should reflect the degradation rate of UV-327. As a very rough estimate concentration decrease in depth can be compared to a decrease calculated with a $DegT_{50}$ of 180 days (see Table 12, assumption according to the literature: 2.5 cm depth reflects 1 year).

Table 12: Concentration profile of UV-327 based on a graphical evaluation from Reddy et al. (2000) and expected concentration based on a $DegT_{50}$ of 180 d at the different depths

Depth [cm]	measured concentration [µg/g dw]	expected concentration assuming a $DegT_{50}$ of 180 d [µg/g dw]
20	100	100
25	4	6.3
30	0.6	0.4
40	0.3	$1.5*10^{-3}$
52	0.1	$2.0*10^{-6}$

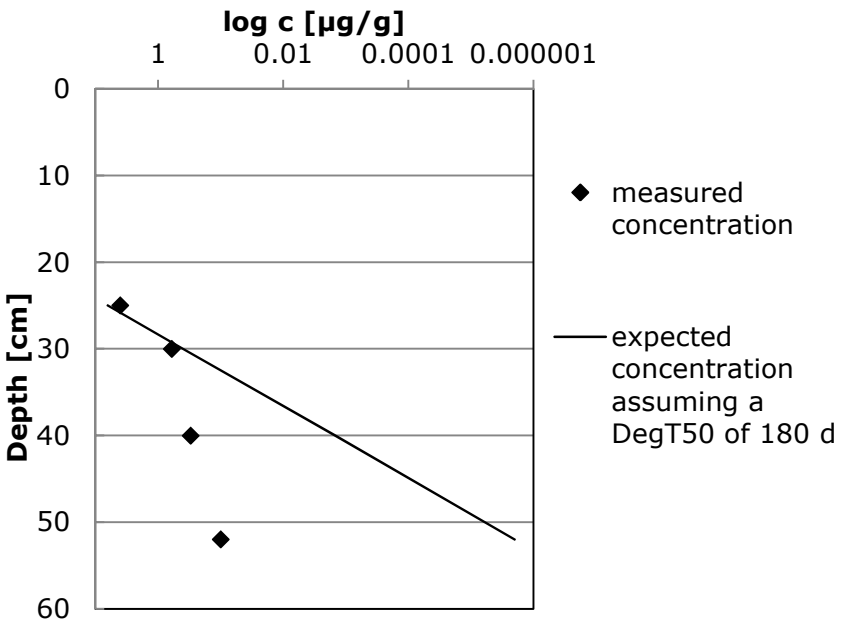


Figure 17: Graphical plot of the measured concentrations in different depths. Also included is a comparison with the concentrations that would be measured, if UV-327 had a $DegT_{50}$ of 180 days. Please note that the concentration scale is logarithmic.

Although this is a very rough estimation for which uncertainties need to be taken into account, it supports a very slow degradation of UV-327, considerably longer than 180 days.

In addition, the study, as well as a second study by Hartmann et al (2005) can be used to compare actual concentrations with historical data which also may provide some information on the degradation time. Hartmann et al. (2005) took sediment cores at three locations in Narragansett Bay in 1997 (Apponaug Cove, Seekonk River, Quonset Point). The cores were analysed for several contaminants including UV-327 and UV-328. Two of the cores were split into 2 cm sections, and the third core (Quonset Point) was split into 10 cm sections.

The concentrations of UV-327 and UV-328 at the different depths are summarised inTable 13.

Table 13: Concentrations of phenolic benzotriazoles in sediment cores from Narragansett Bay (concentrations taken from a graph)

Quonset Point core			**Apponaug Cove core**			**Seekonk River core**	
depth [cm]	**UV-327 [µg/g dw]**	**UV-328 [µg/g dw]**	**depth [cm]**	**UV-327 [µg/g dw]**	**UV-328 [µg/g dw]**	**UV-327 [µg/g dw]**	**UV-328 [µg/g dw]**
0 – 2	ca. 0.04	ca. 0.16	0 - 2	ca. 0.13	ca. 0.27	ca. 0.03	ca. 0.12
0 – 10	ca. 0.06	ca. 0.26	2 - 4	ca. 0.03	ca. 0.08	ca. 0.02	ca. 0.07
10 - 20	ca. 0.08	ca. 0.36	6 - 8	ca. 0.05	ca. 0.14	ca. 0.03	ca. 0.14
20 - 30	ca. 0.1	ca. 0.84	10 – 12	ca. 0.07	ca. 0.12	-	-
30 - 40	ca. 0.13	ca. 1.1	12 - 14	-	-	ca. 0.005	ca. 0.02
40 – 50	ca. 0.69	ca. 1.18	20 – 22	n.d.	n.d.	n.d.	n.d.
50 - 60	ca. 0.48	ca. 0.040	30 – 32	n.d.	n.d.	-	-
60 - 70	n.d.	n.d.	38 – 40	-	-	n.d.	n.d.
80 - 90	n.d.	n.d.	40 – 42	n.d.	n.d.	-	-
100 - 110	n.d.	n.d.	48 - 50	-	-	n.d.	n.d.
119 - 129	n.d.	n.d.					

n.d. = not detected
- = not measured

Taking into account the specific sedimentation rate at each site, it is possible to identify the layer which probably represents the time of active production of UV-327 and UV-328. This might be used – as a very rough estimate - to compare concentrations with historical concentrations during production in order to get an idea about whether or not degradation occurred. Unfortunately, historical data are not available for the three sampling sites and thus the comparison is highly uncertain. The results of this comparison are summarized in Table 14.

The comparison shows that the concentrations measured 12 to 25 years after production stop are of the same or only slightly lower magnitude than during production. If the DegT50 would be 180 days already after 4 years only $1/2^8$ (0.4%) of the original concentration should be present. Therefore, this approach provides further support for the assumption that degradation of UV-327 and UV-328 in sediments is expected to be very slow. In a read-across assessment, it is plausible that the $DegT_{50}$ of UV-320 will be of comparable length.

Table 14: Comparison of concentrations from literature after and during the respective production periods

Study	Detection limit [µg/g]	Site	Year of collection	Sedimentation rate [cm]	Layer assumed to reflect production period [cm]	c at that layer [ppm]	c (historical, but probably not at the exact same spot) [µg/g]
UV-327 (production period 1963 -1972)							
Reddy et al., 2000	0.02	Pawtuxet River	1989	2-3	34 -69	0.1 (at 52 cm)	20 – 300 (Jungclaus et al, Pawtuxet River)
Hartmann et al., 2005	0.01	Quonset Point (Narragansett Bay)	1997	2	54 – 68	0.5 (at 50 – 60 cm)	0.5 (Lopez-Avila and Hites, 1980, Narragansett Bay)
Hartmann et al., 2005	0.01	Apponaug Cove (Narragansett Bay)	1997	0.5 – 0.85	14 – 29	0.07 (at 10 -12 cm)	0.5 (Lopez-Avila and Hites, 1980, Narragansett Bay)
UV-328 (production period 1970 – 1985)							
Hartmann et al., 2005	0.01	Quonset Point	1997	2	24 – 54	0.04 (at 50 – 60 cm)	0.6 (Lopez-Avila and Hites, 1980, Narragansett Bay)
Hartmann et al., 2005	0.01	Apponaug Cove	1997	0.5 – 0.85	6 - 23	0.13 (at 10 -12 cm)	0.6 (Lopez-Avila and Hites, 1980, Narragansett Bay)

3.1.4. Summary and discussion of degradation

Summary on findings

Biodegradation is expected to be the most relevant pathway for degradation of UV-320, if degradation might occur.

The overall evidence presented in chapter 3.1.2 and 3.1.3 indicates in a weight of evidence approach that UV-320 will persist in the environment. This is based on the following findings:

The ready biodegradation test on UV-320 indicates a very low potential for mineralisation (0% after 28 days).

From the simulation studies on radiolabeled EC 407-000-3, the first metabolite of the substance (M1), which is its carboxylic acid, is used for a read-across-assessment. This is considered as best case example, because according to the read-across assessment M1 is similar to UV-320, but probably easier degradable. Relevant for the assessment of the persistence of M1 is especially the sediment DT_{50}-value in the aerobic pond system which was calculated to be 248 days and in the anaerobic pond system which is 238 days.

In addition a field dissipation study on soil treated with sludge contaminated with several phenolic benzotriazoles (UV-326, UV-327, UV-328, UV-329, UV-P) is available. Especially the results for UV-328 (and UV-327) can be used for a read-across assessment for the dissipation behaviour of UV-320 in soil as these substances are also 4,6-substituted phenolic benzotriazoles with complex side chains.. Depending on the treatment and the substance DT_{50}-values between 151 days (UV-327, single treatment) and 218 days (UV-328, repeated treatment) were reported. The dossier submitter's kinetic modelling on UV-328 supports these findings.

The monitoring studies on UV-327 and UV-328 from Rhode Island show persistence of the phenolic benzotriazoles in the environment. In these studies the concentrations found during or few years after production of the two substances are given as well as concentrations found up to 25 years later. It is not possible to derive reliable $DegT_{50}$ from these studies. Also caution is needed when comparing the data, as for each study different sampling sites and methods were employed. In addition, an exact description of the samples is missing (e.g. oxygen content, etc.). We also have no detailed information on microbial viability. Given the history and state of pollution there might not be many microorganisms in the sediment. On the other hand the studies show that other contaminents are at least partially degraded. Overall, it is nevertheless possible with the available data to semi-quantitatively model the concentration curve assuming slow degradation. According to this the $DegT_{50}$ of UV-327 would be larger than 180 days. Furthermore, the concentration levels found up to 25 years after the production for the substances ceased were of comparable level or only an order of magnitude smaller. In a read-across assessment it is plausible that the degradation behaviour of UV-320 will be comparable.

Summary on remaining uncertainty

While the results of the tests on ready biodegradability are concordant, they are not suited for comparison with the numerical criteria on persistence of Annex XIII as the test systems are artificial and their duration is too short.

According to Annex XIII, the ultimate decision on the persistence of a substance is due to half lives determined in experimental studies. The example of the test on EC 407-000-3 shows some shortcomings associated with the evaluation of the test system for very lipophilic substances in general: The water solubility of EC 407-000-3 is very low. The substance strongly tends to bind to organic carbon. This leads to an experimental complexity which

renders the subsequent assessment difficult. In relation to the phenolic benzotriazole assessed M1 is more water soluble due to its carboxylic acid group. This will probably lead in this case to a slightly different behavior in the environment compared to the target molecules. However, with regard to DT50-values more water soluble substances can be assumed to be more bioavailable and therefore faster degraded, therefore the DT50-values calculated might be lower for M1 than could be expected for UV-320. The highest uncertainty in this particular experiment is associated with the very high fraction of non extractable residues. While this is already high for M1, it would probably be even higher for the target substance, which has a higher lipophilicity. Since only the first metabolite of EC 407-000-3 was identified, no degradation half-lives can be calculated for complete mineralization and only estimations of apparent disappearance half-lives (including degradation as well as dissipation) are possible. All three test systems of the study show very different graphs. Unfortunately, only very few data points are available especially at the end of the testing period (there is one point at 56 days and the next one already at 100 days). Also information on standard errors for the measured concentrations is missing. These limits the explanatory power of the quantitative DT50-values tremendously. Nevertheless, the results and associated uncertainties can be explained:

The difference of the DT50-values between the aerobic river system and the aerobic pond systems can be understood when looking at the concentration of the different metabolites and the NER at day 100: The amount of other metabolites than M1 was in all cases not large (river 27.2%, aerobic pond 16.2%, anaerobic pond 2.6%), but the formation of NER was considerable especially in case of the river system (river 36.2%, aerobic pond 25.1%, anaerobic pond 9.8%). This means while certainly more metabolites where formed in the river system even more important is the amount of NER. For some reason obviously more M1 was bound in the NER in the river system although this system contains significantly lower organic carbon than the pond system. Thus M1 disappears more rapidly (into NER) and the DT_{50} value is considerably lower than for the other two systems. The more polar metabolite M1 might adsorb also via ionic interaction in addition to adsorption to organic carbon. For example it is known that some cationic clay fractions interact with anions. In this case adsorption of M1 should have been more pronounced in the sediment of the pond system which contained 33 % clay as compared to the river system. As discussed the NER trend does not confirm higher adsorption. However, the trend of extractable M1 in sediment was more pronounced in the pond system which may reflect ionic interaction. In this case degradation should have been easier to accomplish because a bigger portion of M1 should have been bioavailable. However, the sum of all other metabolites is even lower than in the river system.

The DT50-result for the aerobic pond is certainly influenced by the fact that the last two data points of the concentration of M1 in sediment seem to indicate that either a plateau is reached or a very slow decline is beginning. If the associated errors of the concentration values would be known or if there were more data points at the end of the experiment, it would be possible to do a sensitivity analysis on the resulting DT_{50}-values depending on these points. As it is, the absolute value has to be handled with caution as it might be lower or higher than simulated, but it is unknown by how much.

Finally, in case of the anaerobic pond, only a small part of the degradation curve of M1 was observed. Up to day 100 M1 is still formed and the maximum was not reached yet. Therefore, it is unknown how the actual disappearance curve will look like. If it follows the same trend as the aerobic pond, the resulting DT_{50}-value would be higher than the one calculated and maybe even longer than for the aerobic pond (as from a biological and chemical point of view it should be).

Nevertheless, the overall level of the values for the aerobic and anaerobic pond is very high and they are a best case estimation. The real degradation half-lives of the phenolic benzotriazoles are expected to be higher than the estimated disappearance half-lives for the proxy substance, but it is uncertain to which extent. It should also be noted that in cases

where conflicting results from similar tests are available, which is the case here for the simulation degradation study, the principle specified in Section 3.1.5 of Annex I to REACH can be applied. It requires to use the results giving rise to the highest concern to draw the conclusion. This is application of precautionary principle under REACH.

The field study of Lai et al. (2014) has some practical shortcomings: The concentrations of the different benzotriazoles in the sludge is missing and also no initial concentration values for the different field trails after the first (and in case of T2 the subsequent) applications of the biosolid are given. Also, the limits of detection and quantification are quite high at least compared to the concentrations found in T1. To assess the overall method it would have been also helpful to determine the level of NERs. Furthermore, the concentration values during the sampling time varied: For unknown reasons there was a rise in concentration levels during the winter months. This was solved by not considering them in the kinetic simulation, which in turn lowers the number of data points for fitting. Finally, it would have been helpful to employ a substance with known DT_{50} value as a point of reference. A shortcoming for the use in this dossier is that it gives only information on primary disappearance as none of the metabolites were determined.

The case study of degradation of phenolic benzotriazoles in the Pawtuxet River and the Narragansett Bay comprises four different studies by different authors, drawing overall conclusions is associated with some uncertainty. The four studies had different purposes and used different methods, the sampling sites are different and the samples are sometimes not well described. As the number of sampling sites is limited, it is uncertain whether the findings can be generalized, as there might have been events that disturbed the sediment layers, e.g. storms, floods, bioturbation, etc. Finally, the sediment layer samples all seem to be anaerobic, while usually aerobic sediments are used for degradation assessment. Therefore, it is merely possible to state generally that the contaminant levels during production and 12 to 25 years after production are of the same level or only slightly different. Assuming that the sediment layers were not disturbed in these years, the degradation was very slow.

Overall assessment of uncertainties and findings:

Each of the different information sources shows by itself limitations, deficiencies or uncertainties. Considering each information source on its own would make it impossible to conclude with ample confidence that phenolic benzotriazoles are persistent in the environment according to the requirement defined by REACH. However, as all pieces of information presented are independent of each other, it is possible to combine the information pieces into a broader picture disregarding individual shortcomings. In this picture, the overall level of uncertainty becomes much lower: All individual results point to a considerable potential for high persistence in the environment. There is no confounding data at all, only uncertainty regarding comparison with the numerical criteria set down in Annex XIII.

In conclusion, the available data indicate that the substance is highly persistent in the environment.

3.2. Environmental distribution

3.2.1. Adsorption/desorption

As there is no registration dossier available QSAR-based calculations were performed to estimate the adsorption behaviour to soil or suspended organic matter for this substance. Details of the prediction can be found in Annex 2. The default input parameters were used.

Table 15: Results adsorption behaviour predictions of UV-320

Model	QSAR result	Overall model performance	QPREF
EPISuite 4.1 KOW-method	K_{OC} (L/kg): 4.30 10^4 Log K_{OC}: 4.63	Reliable with Restrictions (Klimisch 2)	Annex 2.4
EPISuite 4.1 MCI-method	K_{OC} (L/kg): 1.17 10^5 Log K_{OC}: 5.07	Reliable with Restrictions (Klimisch 2)	Annex 2.4
COSMOtherm	K_{OC} (L/kg): 1.48 10^5 Log K_{OC}: 5.17	Reliable with Restrictions (Klimisch 2)	Annex 2.4

The results of the estimation of the adsorption behaviour lead to the conclusion that UV-320 will strongly adsorb to soil and suspended organic matter.

3.2.2. Volatilisation

The tendency for volatilisation from the water phase was estimated by calculation of the Henry constant. Due to the absence of measured data on some physical-chemical properties an estimated melting point of 191 °C (result from MPBPWIN-module in EPISUITE v4.10; US EPA 2011) and an estimated water solubility of 0.1503 mg/l (result from WSkowWIN v1.42; US EPA 2011) were used for calculation of the Henry's law constant[8]. It was determined to be $4.884*10^{-3}$ $Pa*m^3*Mol^{-1}$ indicating only little tendency for volatilisation. The air-water partitioning coefficient ($K_{air-water}$) may be derived from the Henry's law constant and is calculated to be $2.061*10^{-6}$ m^3/m^3. As $K_{air-water}$ and Henry's law constant are manually calculated from QSAR-based physical-chemical substance properties the reliability of the values is rated Klimisch 2.

The $K_{air-water}$ and Henry's law constant are very low suggesting that volatilisation is unlikely to be a significant removal mechanism for UV-320 from aquatic systems and it is unlikely that the substance will be transported very far in the atmosphere (due to its atmospheric half-life estimated to be 9.534 hours).

3.2.3. Distribution modelling

Fugacity Level III distribution modelling

When released to the environment UV-320 will be distributed to the environmental compartments in different amounts. The table below shows the result of Fugacity Level III distribution modelling (Multiple Level III output) using EPI Suite v4.10 with the substance properties calculated within EPI Suite. The reliability of the result from the EPI Suite calculation is rated Klimisch 2.

[8] according to equation R.16-4 from ECHA Guidance on Information requirements and Chemical Safety Assessment – Part R.16 (May 2010)

Table 16: Distribution according to Mackay Level III Fugacity Model (estimation with standard parameters as provided by EPI Suite v4.10)

compartment	mass amount (percent)
air	$2.37*10^{-5}$
water	4.37
soil	63.3
sediment	32.3

The results of the distribution modelling and physical-chemical substance properties lead to the conclusion that the overall amount of the substance will adsorb to the soil (63.3%) and the sediment (32.3%).

Distribution in waste water treatment plants

One major route of exposure for UV-320 is expected to be wastewater which is treated in sewage treatment plants. Therefore, calculations based on physical-chemical data retrieved from QSAR have been used to estimate the distribution of the substance in sewage treatment plants with the help of SimpleTreat. The calculation was done assuming that the substance is not biodegradable (k=0/h) and the reliability was rated Klimisch 2.

Table 17: Distribution in sewage treatment plants (acc. to SimpleTreat 3.0, debugged version; 7 Feb 1997)

Summary of distribution	percent
to air	0.0
to water	9.5
via primary sludge	65.6
via surplus sludge	25.0
Degraded	0.0
Total	*100*

The results of the calculation lead to the following conclusion: When UV-320 is released into waste water, it will predominantly be concentrated in the sewage sludge. This is in agreement with experimental findings (see Part 2 and Annex 4). It has to be kept in mind that the use of sludge from municipal sewage treatment plants for agricultural purposes is a common practice in many regions. In this way of exposure the substance might be released into agricultural soil.

3.2.4. Field data

See Annex 4.

3.2.5. Summary and discussion of environmental distribution

The available data indicates that UV-320 will predominately distribute to soil and suspended organic matter.

3.3. Data indicating potential for long-range transport

None

3.4. Bioaccumulation

To the dossier submitter's knowledge there are no experimental log K_{OW}-values for UV-320. Therefore, the value was calculated with the QSAR model KOWWIN of EPISuite 4.10 and with COSMOtherm. Details on these calculations can be found in Annex 3.

Table 18: QSAR-Results for log K_{OW}-predictions of UV-320

Model	QSAR result	Overall model performance	QPREF
EPISuite 4.1 KOWWIN	Log K_{OW}: 6.27	Reliable	Annex 3.3
COSMOtherm	Log K_{OW}: 7.39	Reliable	Annex 3.3

The estimated log K_{OW}-values are larger than 4.5, thus, it is expected that UV-320 has a high potential to bioaccumulate.

3.4.1. Bioaccumulation in aquatic organisms (pelagic and sediment organisms)

A test on UV-320 using fish according to MITI guideline (OECD 305 C) was re-evaluated based on excerpts of the original test protocol which was made available by NITE (NITE, 2012).

Test duration was 14 weeks except for the test with a concentration of 0.1 µg/L where it was only 10 weeks. As dispersant HCO-20 and olive oil was used. Not all test conditions can be reported because only the summary of the study is available.

In general, the data of the three test concentrations 10.0, 1.0 and 0.1 µg/L show similar trends although maximum BCF values are less than or above 2000 for the highest test concentration and well above 2000 for the other two test concentrations (*cf.* Table 19).

Table 19: Compilation of BCF maxima and BCF values at test end (values refer to whole body wet weight basis unless no other information is provided) (data based on re-evaluation of NITE, 2012)

Test concentration in µg/L	Maximum BCF measured	Maximum BCF normalised to 5% lipid content	average BCF measured at test end	average BCF at test end normalised to 5% lipid content
10	(2250[1 3])	(3040[3])	(1440[3])	(1945[3])
1	7785[1]	10520	4370	5905
0.1	9265[2]	12868	8670	12041

[1] Lipid content of test fish 3.7 %

[2] Lipid content of test fish 3.6 %

[3] Data not reliable (reasons see below)

Data of all test concentrations show a quite steady increase of BCF reaching a maximum after 10-12 weeks. Some variability is observed in each data row (two parallel samples per sampling time point for each concentration) but it does not necessarily mean that this renders the data not reliable. It rather reflects difficulties in accurate determination of the BCF which are observed in many cases with substances of low water solubility. For example it might be that the actual water solubility was overestimated and the test concentrations were therefore above it.

A BCF of 2250 was measured in one data row of the highest test concentration in week 10, but dropped to 703 in week 12 and raised again to 1540 in week 14. As there is no explanation for this unusual trend these data should be treated as not reliable.

Neither of the data rows of the medium or the low test concentration reaches steady state. BCF data for the medium concentration reach a maximum at week 10 or 12 and drop again at week 14. BCF data for the lowest test concentration reach a maximum at week 8 or 10 at which time the test ended.

A comparison of BCF data from the three test concentrations shows a trend of higher BCF values with lower test concentrations. Such trends are common in cases in which the test concentration in water is overestimated. Considering the calculated water solubility of 0.15 mg/L this is not believed to have had an influence in the test, though.

It is concluded that the test is reliable though no steady state was reached with the above mentioned one exception. Thus for the assessment the maximum BCF values and the values at the test end should be considered. Maximum BCF values represent the worst case and the BCF at test end represent a best case for the high and medium concentration.

3.4.2. Field data

UV-320 is expected to accumulate in top predators because accumulation through the food chain was shown for the structurally similar substances UV-327 and UV-328[9]. Several biomonitoring studies suggest that as well (see Annex 4).

3.4.3. Summary and discussion of bioaccumulation

For two of three test concentrations BCF are exceeding 10000. There is a trend of higher BCF values with lower test concentrations.

Also, data for structurally similar substances support the assumption. For UV-327 a lipid-normalised BCF of 8817 was shown. Biomonitoring studies suggest a strong dependency of the bioaccumulation potential of phenolic benzotriazoles on the species considered. In addition ,enrichment in top predators is at least in some cases suggested (see Annex 4).

In conclusion, the data presented in the assessed studies demonstrate the very high bioaccumulation potential of UV-320.

4. Human health hazard assessment

4.1. Repeated dose toxicity

RAC adopted the following opinion based on a ECHA request according to Article 77(3) of REACH on 10 June 2013:

"The RAC has formulated its opinion on:

a) whether the information provided in the Annex XV SVHC dossiers is sufficient to develop an opinion of a similar robustness to a CLH opinion,

b) whether the information provided shows that the substance meets the criteria for classification for specific target organ toxicity after repeated exposure (STOT RE category 1 or

[9] For more details please refer to the Annex XV report on UV-328 (EC 247-384-8)

2) under CLP.

After examination of the information provided in the SVHC Annex XV dossiers and the comments related to specific target organ toxicity following repeated exposure raised during the public consultation, the RAC agreed that this information shows that the substances UV-320 and UV-328 both meet the criteria for classification as STOT RE 2 as defined in the CLP Regulation (EC) 1272/2008."[10]

5. Environmental hazard assessment

No data relevant for assessing the T-criterion can be reported.

6. Conclusions on the SVHC Properties

6.1. PBT and vPvB assessment

6.1.1. Assessment of PBT/vPvB properties

6.1.1.1. Persistence

The persistence of UV-320 has been assessed by using a weight of evidence approach.

Conclusions of the weight of evidence approach:

- ready biodegradation tests of UV-320 suggest the substance is not subject to biological degradation (0% after 28 days);

- The degradation of the substance EC 407-000-3 (Reaction mass of branched and linear C7-C9-alkyl-3-[3-(2-H-benzotriazol-2-yl)-5-(1,1-dimethyl)-4-hydroxyphenyl]-propionates) was studied in several simulation tests. In these studies, a major degradation product M1 was analyzed. This metabolite is structurally very similar to UV-320 only with a minor different substitution group in position 4 of the phenolic ring and was therefore used in a read-across assessment for UV-320. M1 was formed in the water phase, and dissipated rapidly in a few days to the sediment compartment. In the sediment, M1 is persistent with calculated disappearance half-lives up to 238 and 248 days depending on the sediment type. As the disappearance in this case has to be faster than the degradation of M1, $DegT_{50}$-values in turn have to be higher than the DT50-values. The differing side chain of M1 will be faster degraded than that of UV-320. Therefore, and assuming that the fate properties of UV-320 and M1 are very similar in a degradation simulation test, the results on M1 may be expected to be a best case representative on the disappearance and degradation of UV-320;

- In a recent field study dissipation in soil using the structural very similar substance UV-328 was tested. Using the results of this test, a DT_{50} of up to 223 days was calculated. As the disappearance has to be shorter or as long as the degradation, the respective $DegT_{50}$-values will have to exceed the numerical vP-criterion of 180 days for the soil compartment as defined in Annex XIII as well. These results were taken as a read-across on UV-320;

[10] http://echa.europa.eu/documents/10162/13641/rac_opinion_uv-320-328_en.pdf

- For the very similar substances UV-327 and UV-328 available monitoring studies indicate presence of the substances in sediments decades after environmental releases had stopped. Model calculations indicate that these findings can only be explained if the half life for degradation is exceeding the Annex XIII trigger of 180 days. These results on UV-327 and UV-328 were taken as a read-across on UV-320;

- Thus, applying the weight of evidence approach, UV 320 clearly fulfils the P- and vP-criteria of REACH Annex XIII as defined under Sections 1.1.1. and 1.2.1.

6.1.1.2. Bioaccumulation

In a BCF study on fish according to the OECD Guideline 305 C lipid normalized BCF values of 5905 and 12041 were found in two of the three test concentrations. Therefore UV-320 fulfils the B (BCF >2000) and vB criterion (BCF >5000) of REACH Annex XIII as defined under Sections 1.1.2. and 1.2.2.

6.1.1.3. Toxicity

There is evidence based on the RAC opinion[11] on UV-320 that indicates that the substance meets the criteria for classification as STOT RE 2 as defined in the CLP Regulation (EC) 1272/2008. As a consequence, the toxicity criterion of REACH Annex XIII is fulfilled.

6.1.2. Summary and overall conclusions on the PBT and vPvB properties

In conclusion, UV-320 meets the criteria for a PBT/vPvB substance according to Art. 57(d) and (e) of REACH.

[11] http://echa.europa.eu/documents/10162/13641/rac_opinion_uv-320-328_en.pdf

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Annex 1: Degradation kinetic modelling of two simulation studies and a field study

1. Remarks on procedure

For modelling and fitting of the degradation kinetics the software KinGUI Version 2.0 was used and the stepwise procedure and kinetic models described in FOCUS Guidance on Estimating Persitence and Degradation Kinetics (FOCUS, 2006) was followed. Data were taken from the dossier on 407-000-3. The final degradation kinetic modelling considered parent EC 407-000-3 for the whole system, main metabolite M1 seperately for water and sediment phase, and NER. For a better understanding more details on the stepwise procedure are given in each chapter under the heading "Preliminary notes on modelling" (2.2.2.1., 2.4.2.1. and 3.2.2.1.) at the beginning of the particular test system evaluation.

As the parent supplies the system with its metabolite M1 a pre-condition for accurately modelling M1 decline is the use of a fitting model for the parent. Thus, for each particular test system it was first evaluated which model is able to represent the parent's trend best.

Please note that not in all cases the DT_{50} was reached within the experimental period. Extrapolation of data is always insecure and thus respective DT_{50} should be interpreted with care. Nevertheless, it is possible to conclude on reaching certain trigger values although it is impossible to define exact values.

The three kinetic models to be considered are:

Single First-order kinetics (SFO):

Integrated Formula:	$M = M_0 * e^{(-k*t)}$
Half time:	$DT_{50} = \ln(2)/k$
Parameters to be determined:	M_0 (amount of chemical at t=0), k (rate constant)
Description:	Simple exponential decay. The concentration of the chemical is assumed to be low in comparison to the enzymes or number of water molecules in case of hydrolysis.

Gustafson and Holden model (First-order multi-compartment model, FOMC):

Integrated Formula:	$M = M_0/(t/beta+1)^{alpha}$
Half time:	$DT_{50} = beta*(2^{1/alpha} -1)$
Parameters to be determined:	M_0 (amount of chemical at t=0), alpha (shape parameter determined by coefficient of variation of k-values), beta (location parameter)
Description:	Exponential decay in a large number of sub-compartments.

Bi-exponential model (Double First order in Parallel mode, DFOP):

Integrated Formula:	$M = M_0*[g*e\text{^}^{-k1*t} + (1-g)*e^{-k2*t}]$
Half time:	DT_x can only be found with an iterative procedure as an analytical solution does not exist
Parameters to be determined:	M_0 (amount of chemical at t=0), g (fraction of M_0 applied to compartment 1), k1 (rate constant in compartment 1), k2 (rate constant in compartment

	2)
Description:	Exponential decay in two parallel existing compartments. The concentration of the chemical is assumed to be low in comparison to the enzymes or number of water molecules in case of hydrolysis.

To assess goodness of fit and to compare the kinetic models the recommendations of the FOCUS Guidance (FOCUS, 2006) were followed. For all simulations first a visual assessment of the goodness of the fit was done. This includes the analysis of the residuals of measured vs. predicted results for systematic deviations. Second, the Chi2-errors were calculated and compared. This test indicates whether the model is probably not appropriate, i.e. demonstrating that the differences between calculated and measured values are unlikely due to chance. For this test the calculated values are compared to tabulated values that are dependent on the number of degrees of freedom and the probability to obtain this or higher Chi2 by chance. FOCUS recommends using a probability of 5%, which we have also done. Generally, the smaller the Chi2-value is, the better the fit is as well. At last, the t-test was observed for each parameter of the fitted kinetic model. If the probability (p-value) is smaller than 0.05 then the parameter is considered significantly different from zero. In general, this was was the case and consequently our fitting created robust results and endpoints. However, in some cases, the parameter does not differ significantly from zero and the endpoints derived from the parameter are uncertain and should be interpreted with caution. In consequence, in this case this means that the actual DT50 derived may even be longer.

2. Kinetic modelling of data from a water-sediment study according to OECD 308 on EC 407-000-3 under aerobic conditions

2.1 River system: EC 407-000-3 dissipation in whole system

2.1.1. Limitations to modelling of EC 407-000-3 dissipation

A quick dissipation of the parent EC 407-000-3 from water to sediment was observed after the substance had been added to the water surface. In all test systems high concentrations of EC 407-000-3 in sediment were already found at day 0 (see Figure 18 and Figure 19).

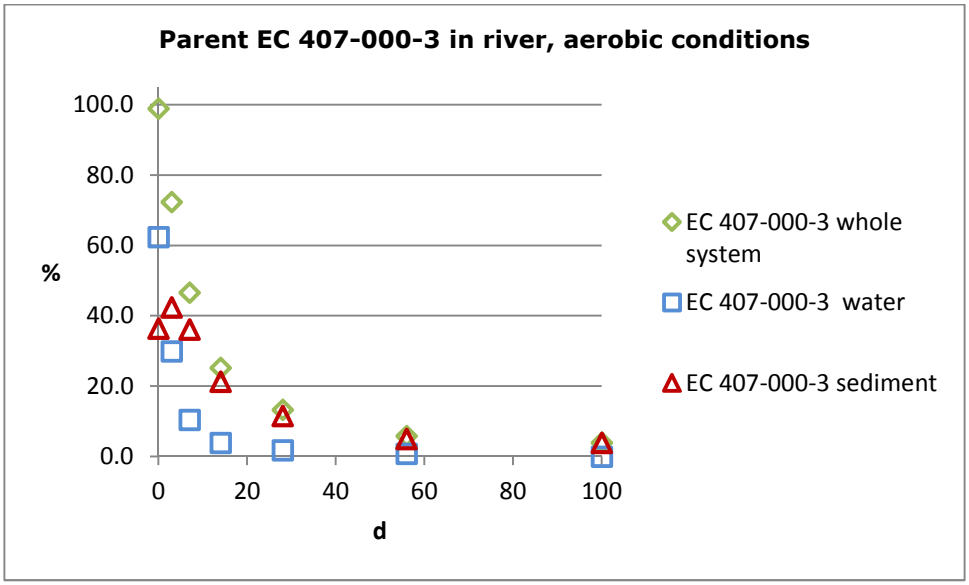


Figure 18: Distribution of EC 407-000-3 in a river system under aerobic conditions

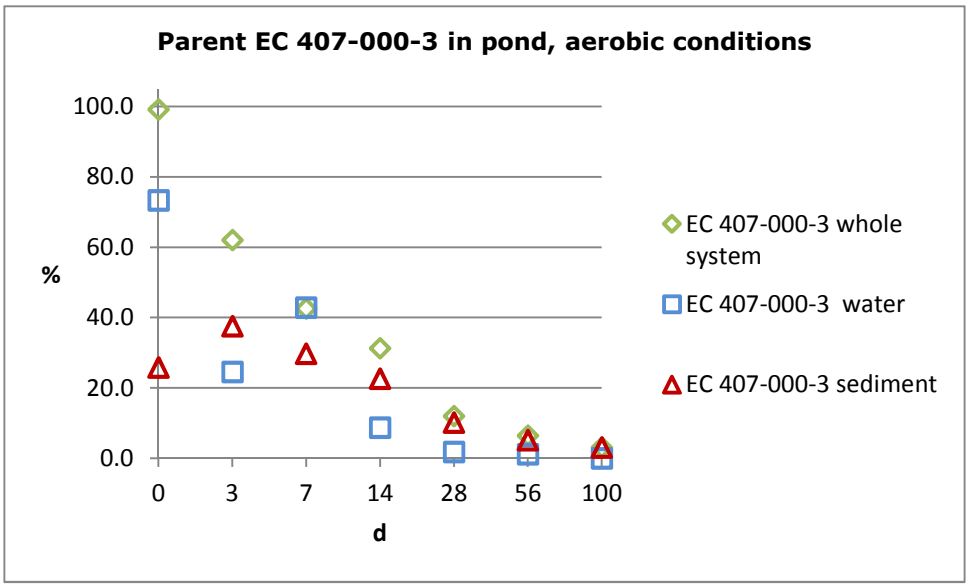


Figure 19: Distribution of EC 407-000-3 in a pond system under aerobic conditions

Unfortunately, test protocols do not give information how much time passed between onset of the substance and the first measurement. With the exact time of the first measurement missing, it is impossible to correct the time for the first data point in order to do an accurate calculation. Without this information it is impossible to model parent concentration for the water phase or the sediment phase independently. Moreover, the concentration of EC 407-000-3 in the sediment has two maxima. Such a curve progression cannot be modelled by degradation kinetics. Fortunately, both problems can be circumvented if the concentration of the parent is modelled only for the whole system, which was done in all following calculations.

2.1.2. Kinetic modelling of EC 407-000-3 in whole system

The model setup used in all kinetic modelling of parent substance EC 407-000-3 is shown in Figure 20. It is simple and considers one sink only, without differentiating it further.

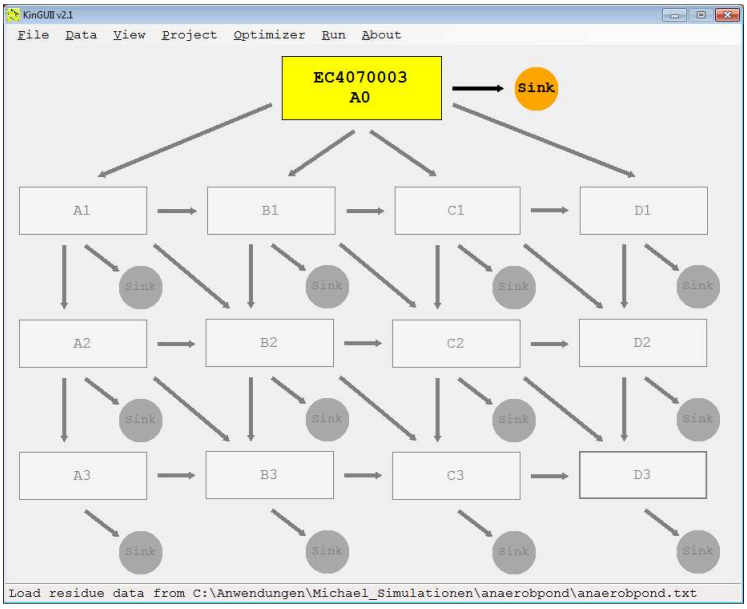


Figure 20: Model setup for dissipation modelling of EC 407-000-3 in river system under aerobic conditions.

2.1.3. EC 407-000-3 SFO

The data shown in Figure 21 are adequately described by SFO up to day 14. Concentration at day 0 is underestimated, concentrations for day 3 to 14 are overestimated. Concentrations measured at later dates are markedly underestimated by SFO kinetics (see Figure 22). The residual plot shows systematic deviations from day 28 on. Chi^2-error is acceptable.

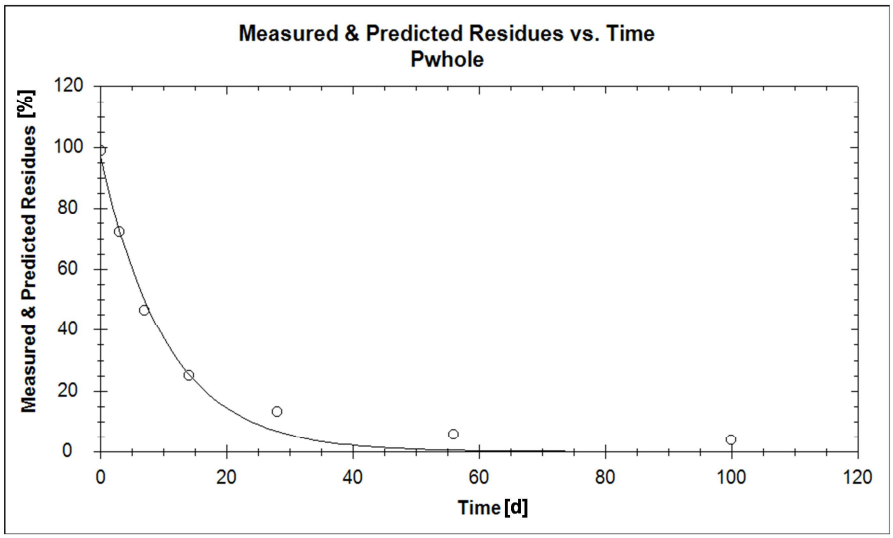


Figure 21: Measured and predicted residues of EC 407-000-3 vs. time in the whole system of an aerobic river – SFO.

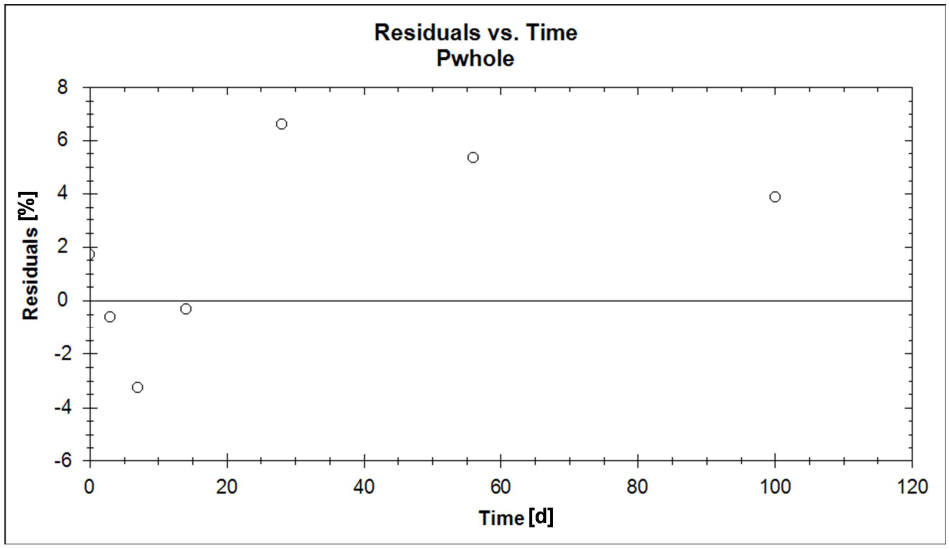


Figure 22: Residuals of EC 407-000-3 vs. time in the whole system of an aerobic river – SFO.

Table 20: Chi^2 and dissipation times of EC 407-000-3 using SFO kinetic

Parameter	EC 407-000-3	All	Kinetic model
Chi2Err%	7.9640	7.9640	SFO
DT50 in d	7.2613		
DT90 in d	24.1220		

2.1.4. EC 407-000-3 FOMC

Data are well described by FOMC kinetic. The curve fits closely to the measured data. The residual plot shows that data initially scatter around the zero line. The last three data points show a systematic deviation from the measured values. Chi^2-error is acceptable.

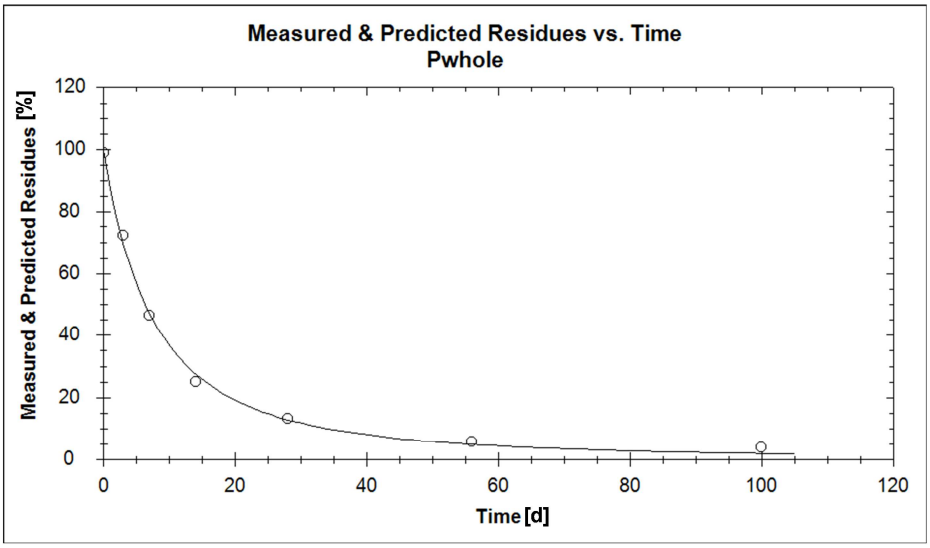


Figure 23: Measured and predicted residues of EC 407-000-3 vs. time in the whole system of an aerobic river – FOMC.

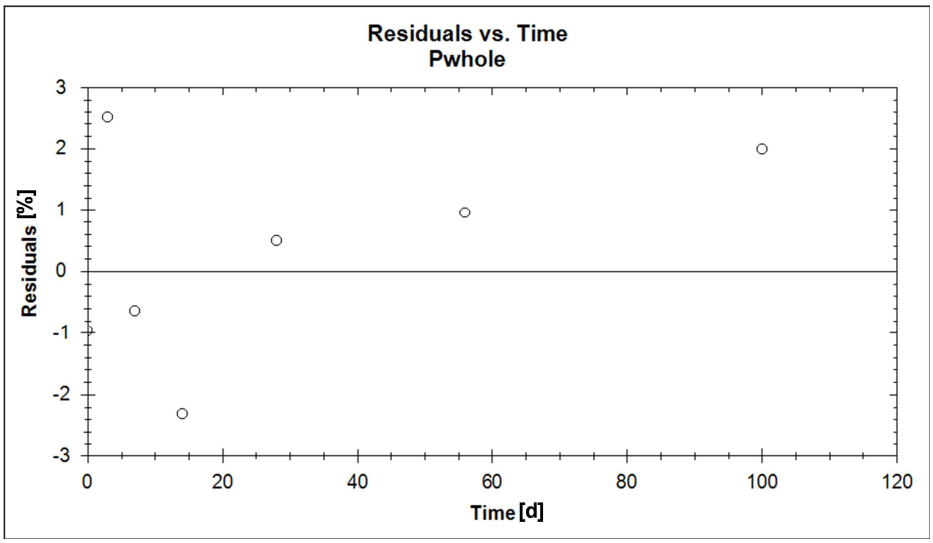


Figure 24: Residuals of EC 407-000-3 vs. time in the whole system of an aerobic river – FOMC.

Table 21: Chi^2 and dissipation times of EC 407-000-3 using FOMC kinetic

Parameter	EC 407-000-3	All	Kinetic model
Chi2Err%	3.6450	3.6450	FOMC
DT50 in d	6.3731		
DT90 in d	33.8950		

2.1.5. EC 407-000-3 DFOP

Data are well described by DFOP kinetic and the curve fits closely to the measured data. The calculated curve matches the observed behaviour well. The residuals are small and except day 7 and 14 they are randomly scattered around the zero line. Chi^2-error is acceptable.

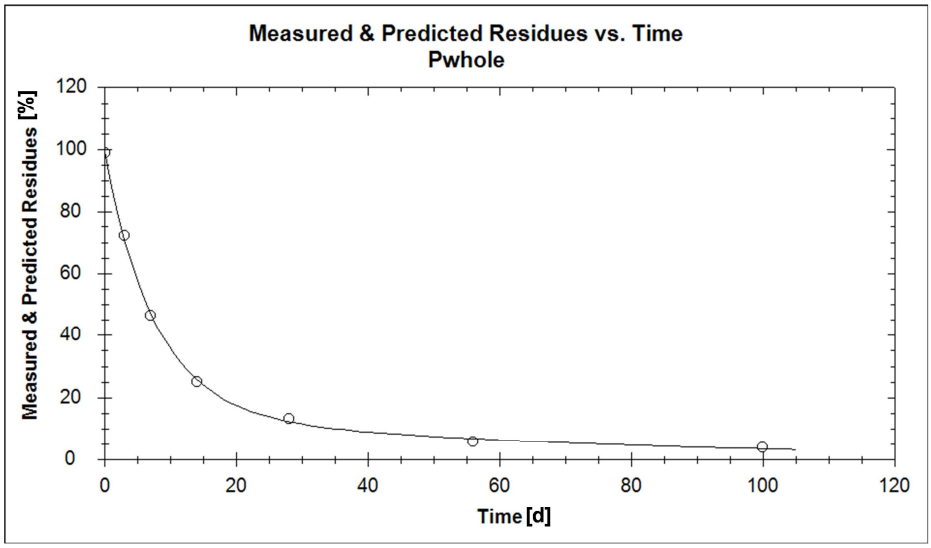


Figure 25: Measured and predicted residues of EC 407-000-3 vs. time in the whole system of an aerobic river – DFOP.

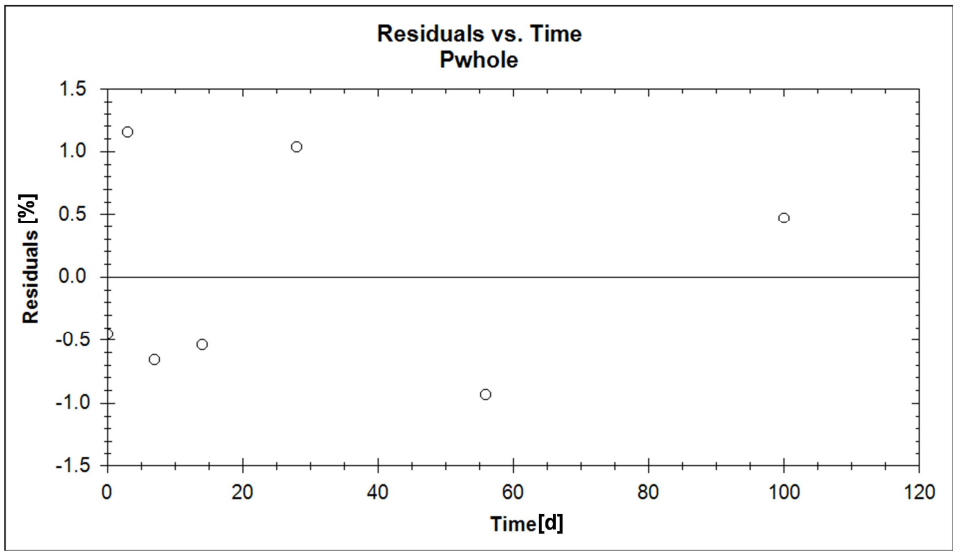


Figure 26: Residuals of EC 407-000-3 vs. time in the whole system of an aerobic river – DFOP.

Table 22: Chi^2 and dissipation times of EC 407-000-3 using DFOP kinetic.

Parameter	EC 407-000-3	All	Kinetic model
Chi2Err%	1.978	1.978	DFOP
DT50 in d	6.480		
DT90 in d	35.296		

2.1.6. Conclusion on dissipation of EC 407-000-3

SFO is not suitable to model the measured data as deviation of the residuals is systematic. FOMC and DFOP both fit well. However, FOMC shows systematic deviation in the last three measurements. DFOP is the slightly better choice because only two residuals show a systematic deviation. Apart from these all data are randomly scattered around the zero line.

Thus, DFOP has been used for modelling EC 407-000-3 in all subsequent calculations of M1 dissipation.

2.2. River System: Model fitting of M1 dissipation in water and sediment phase

2.2.1. Limitations to modelling the dissipation of EC 407-000-3

As discussed in section 2.1.1. it is impossible to calculate the dissipation of EC 407-000-3 in water or sediment phase separately. Therefore, dissipation of it is considered as DFOP in the following modelling of M1.

2.2.2 M1 SFO for water and sediment

2.2.2.1. Preliminary notes on modelling

M1 is the first metabolite of the parent EC 407-000-3. FOCUS Guidance advises to use a first order kinetic to model dissipation (FOCUS 2006). The dossier submitters followed its advice and used SFO for modelling of M1 dissipation (level M-I calculation).

Figure 27 shows the adjustments used in modelling. In addition to the sink for water or sediment phase Non Extractable Residues are considered because a distinct NER formation of 36 or 25% had been observed for river or pond system. From a mathematical point of view this means that the resulting DT_{50} values are shorter than if NER were not considered. Please note that for technical reasons a rateconstant for NER has to be calculated (k_{NER}). It has no physical meaning and has to be zero, nevertheless information on it is given as well. The chosen set is no worst case but it reflects the actual conditions met in the test. Thus, this model setup is considered justified. All metabolites and CO_2 evolution are subsumed in the sink.

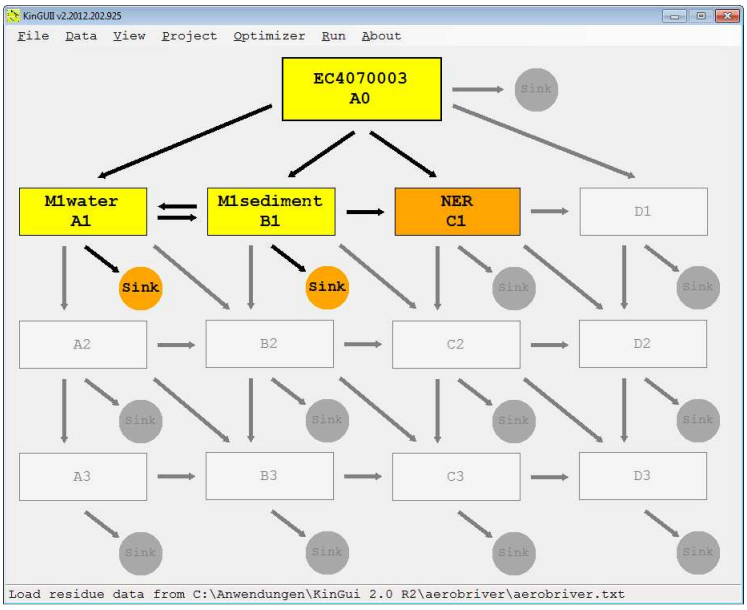


Figure 27: Considered compartments and sinks in river system under aerobic conditions.

2.2.2.2. EC 407-000-3 in whole system

Data of EC 407-000-3 are well described by DFOP kinetic. The curve fits closely to the measured data and matches the observed behaviour well (see Figure 28). The residuals are

small and randomly scattered around the zero line (see Figure 29). Chi^2-error is acceptable (see Table 23).

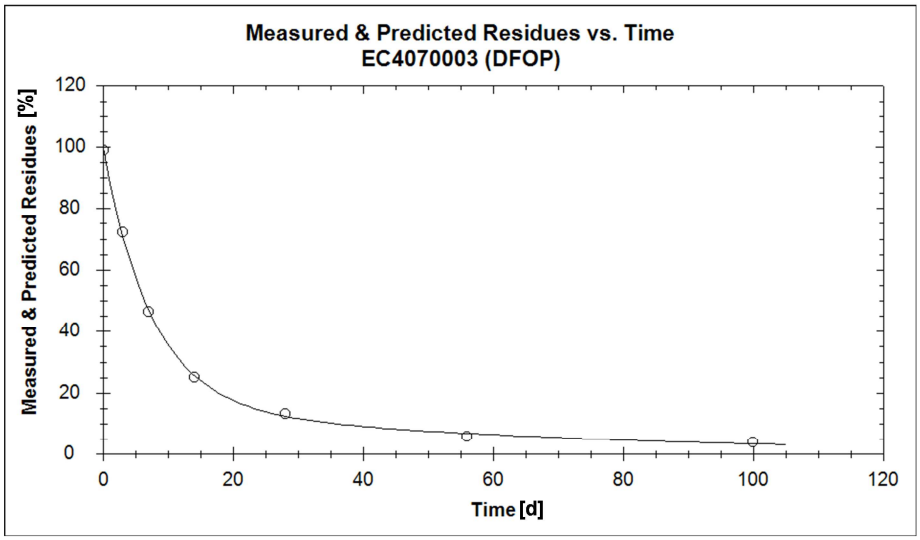


Figure 28: Residuals of EC 407-000-3 vs. time in the whole system of an aerobic river – DFOP.

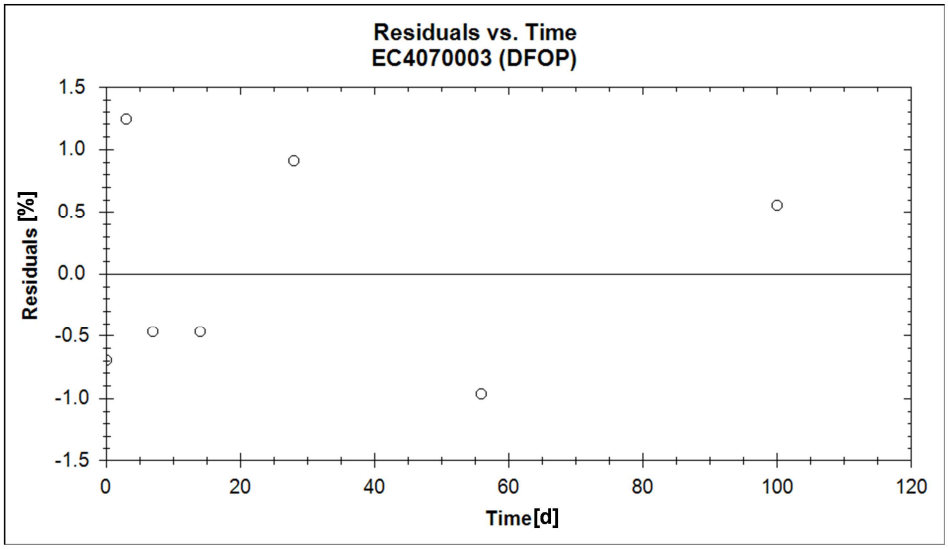


Figure 29: Measured and predicted residues of EC 407-000-3 vs. time in the whole system of an aerobic river – DFOP.

2.2.2.3. M1 in water

Data of M1 in the water phase are well described by SFO kinetic (see Figure 30). The curve fits well to the measured data. The residuals are small and there is no systematic deviation (see Figure 31). However, fit is not well at the two latest data points which are clearly overestimated. This is unusual because normally SFO kinetic tends to underestimate those late data points. Nevertheless, visual fit and the acceptable Chi^2-value show that the fit is acceptable (see Table 23).

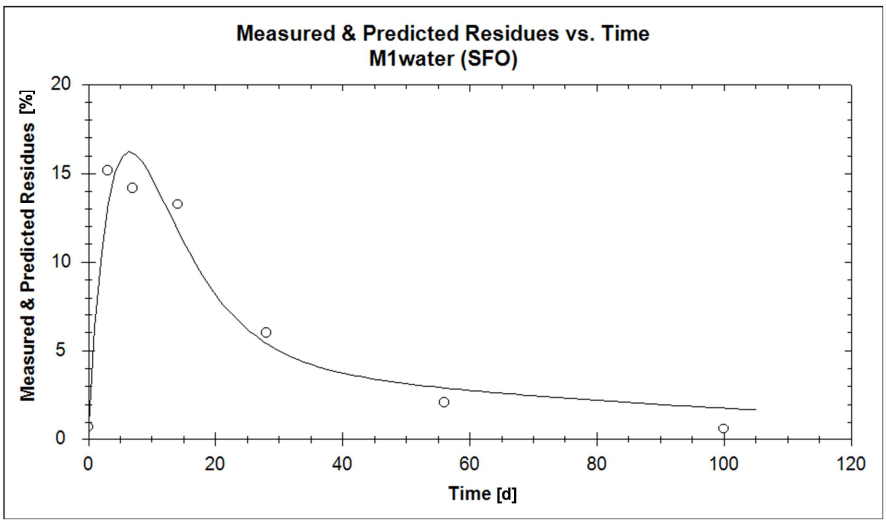


Figure 30: Measured and predicted residues of M1 vs. time in the water phase of an aerobic river – SFO.

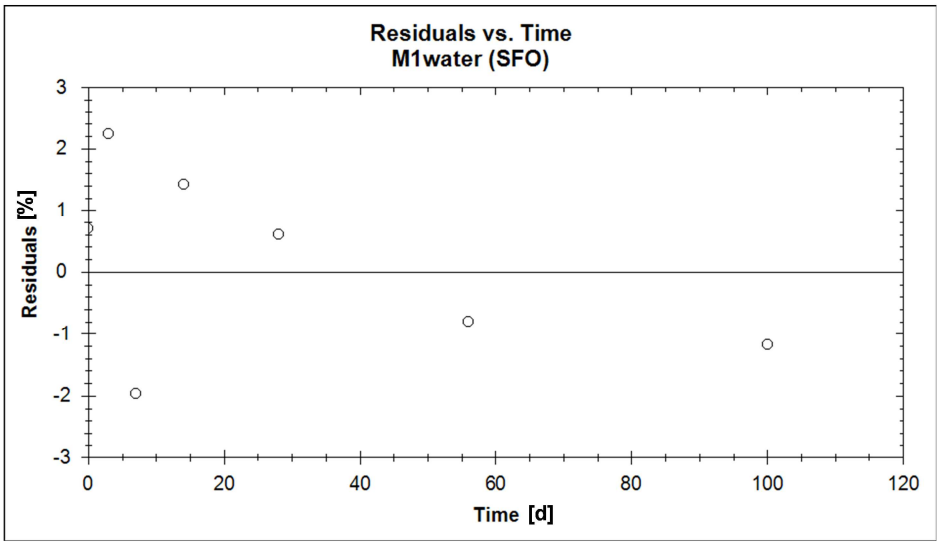


Figure 31: Residuals of M1 vs. time in the water phase of an aerobic river – SFO.

2.2.2.4. M1 in sediment

Data of M1 in the sediment phase are well described by SFO kinetic (see Figure 32). The curve fits to the measured data. Residuals show a small but systematic overestimation for day 14 to 56 (see Figure 33). Nevertheless, the last two data points are well represented by model although SFO kinetic frequently tends to underestimate the last data points. Thus the visual fit is still adequate. Chi^2 is acceptable (see Table 23). It is concluded that the fit is acceptable.

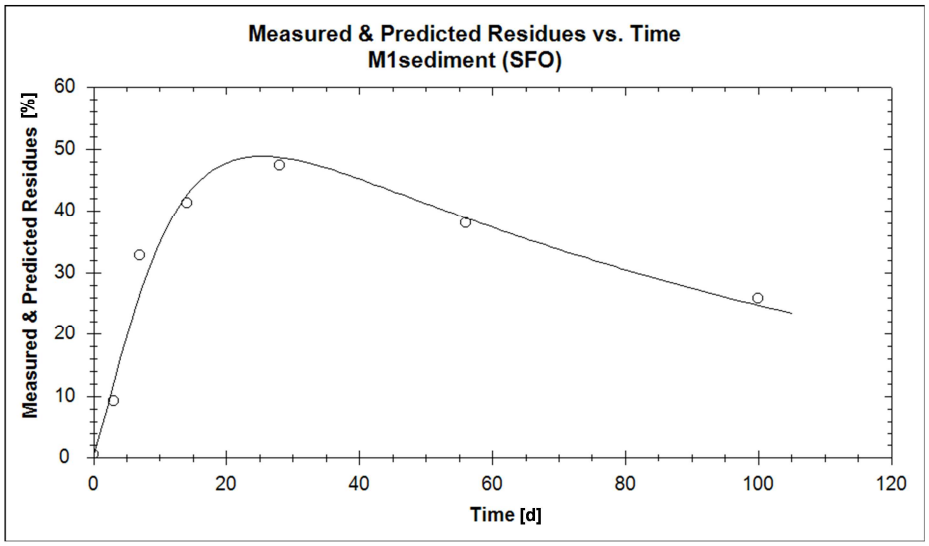


Figure 32: Measured and predicted residues of M1 vs. time in the sediment phase of an aerobic river – SFO.

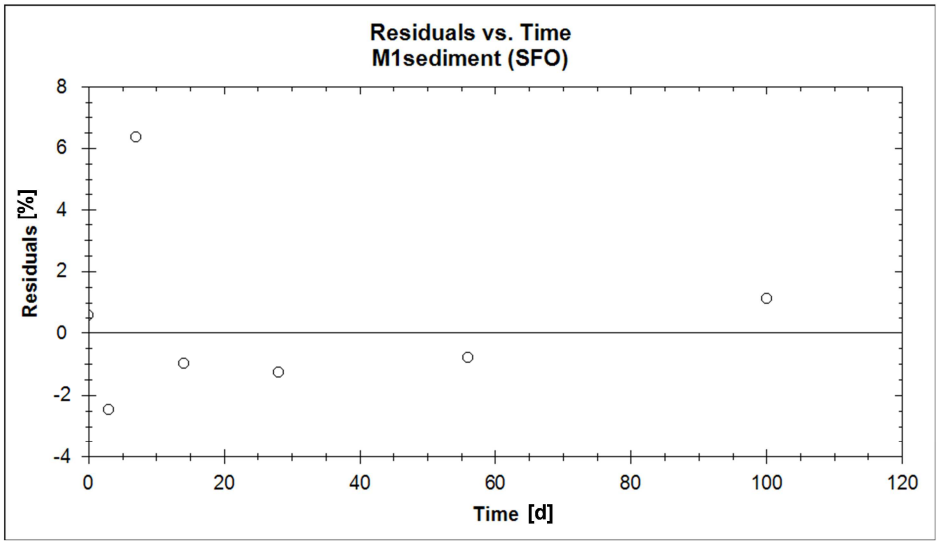


Figure 33: Residuals of M1 vs. time in the sediment phase of an aerobic river – SFO.

2.2.2.5. NER in whole system

Data of NER are well described by SFO kinetic (see Figure 34). Residuals are small but there is a systematic underestimation from day 0 to 14. Chi^2 is acceptable (see Table 23). Nevertheless, the visual fit shows that the fit is adequate.

Please note that the kinetic constant for NER is in this case very low and essentially zero. This can be understood when looking at the experimental results and the way the kinetic model is composed: Up to the end of the experiment NER is constantly formed.

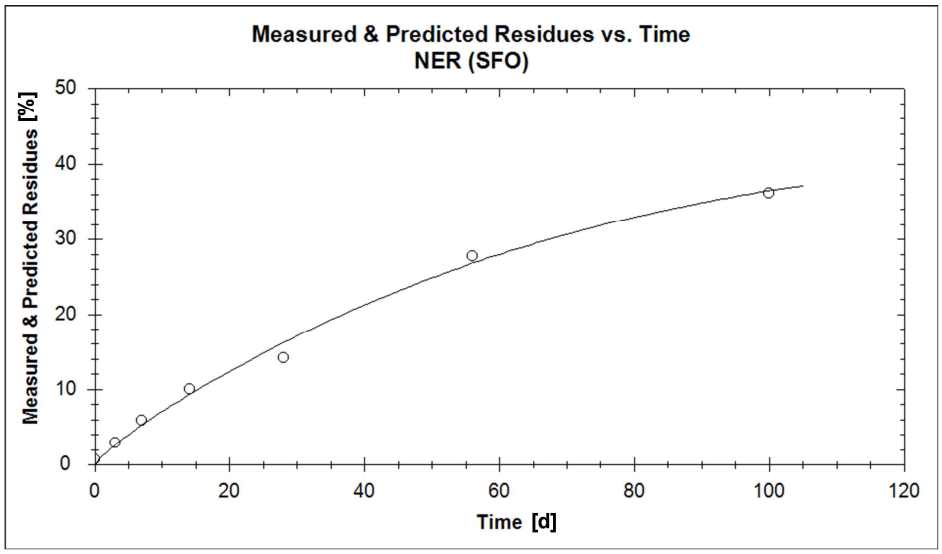


Figure 34: Measured and predicted residues of NER vs. time in the whole system of an aerobic river – SFO.

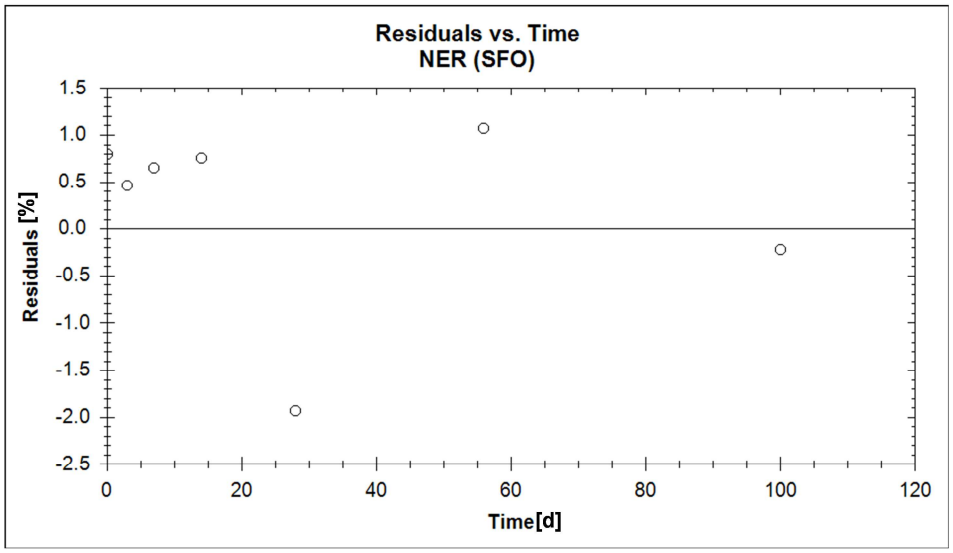


Figure 35: Residuals of NER vs. time in the whole system of an aerobic river – SFO.

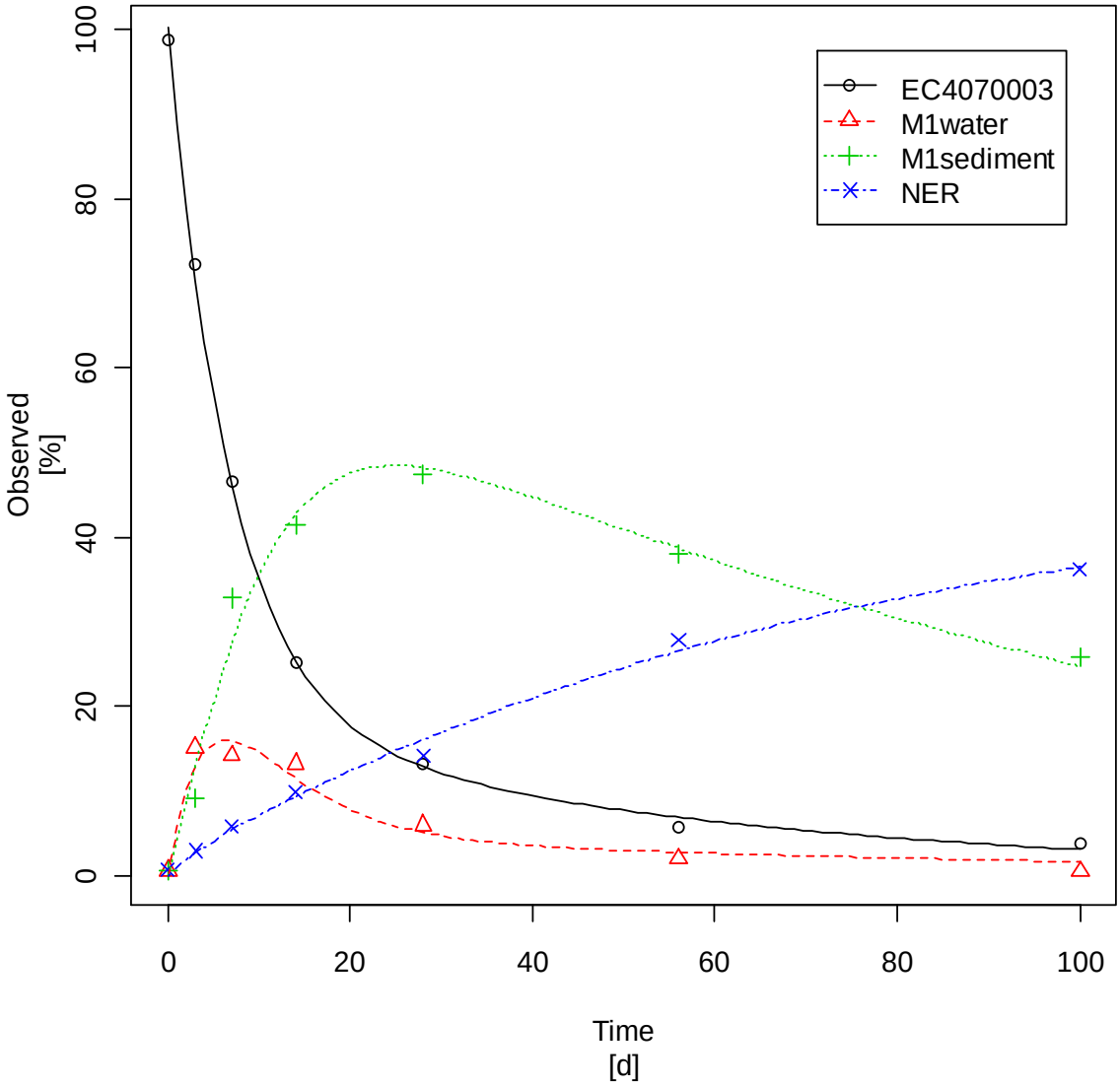


Figure 36 gives an overview of the measured and predicted data of EC 407-000-3, M1 and NER.

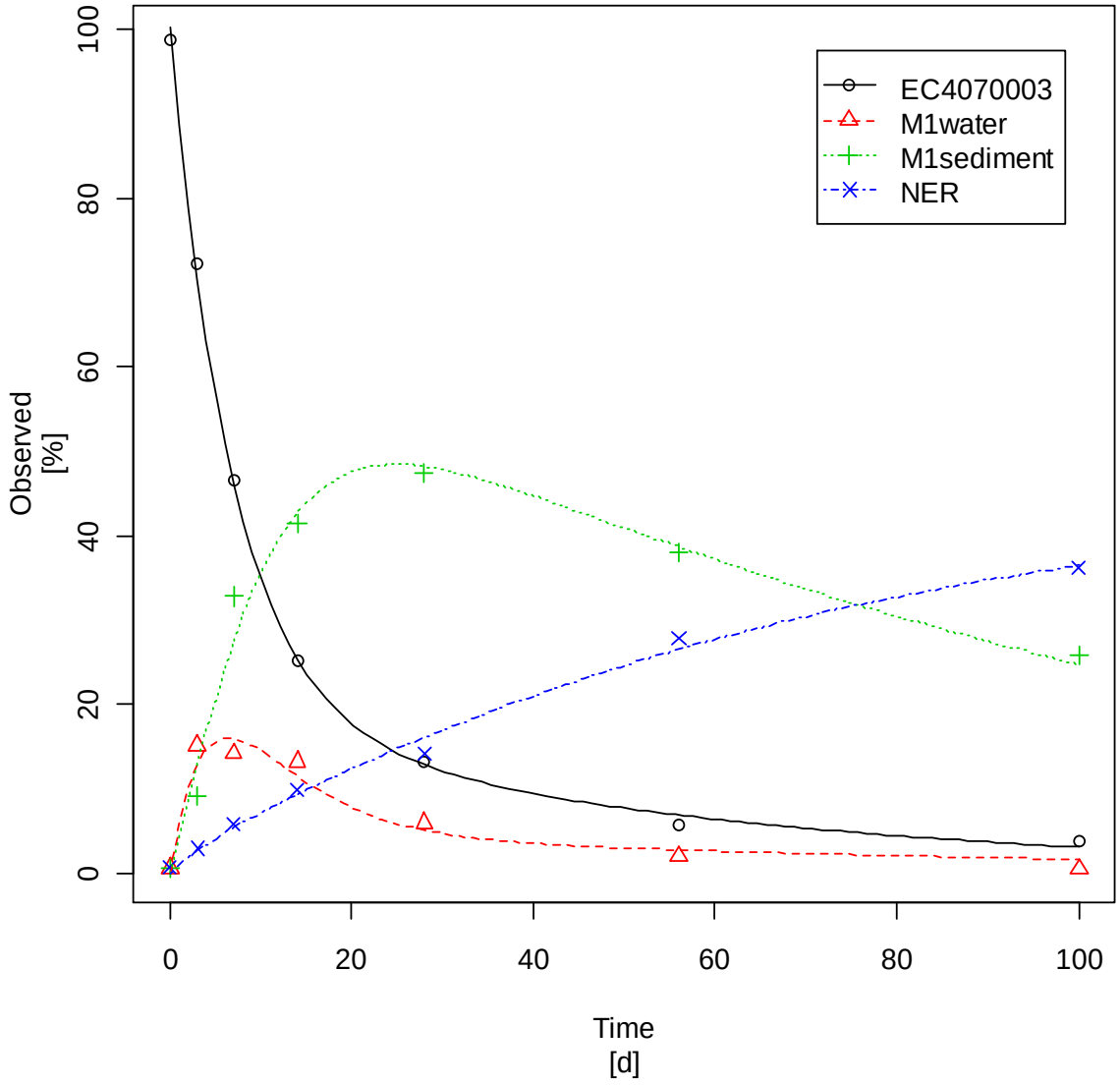


Figure 36: Combined diagram of measured data and respective trends in a river system under aerobic conditions.

Table 23: Chi^2-error and dissipation times of EC 407-000-3, M1 and NER in an aerobic river system

	EC4070003	M1water	M1sediment	NER	All
Chi2Err%	2.862	15.003	8.344	5.256	7.818
DT50 in d	6.4174	3.4002	31.635	275.53	
DT90 in d	35.730	11.295	105.09	915.30	
Kinetic model	DFOP	SFO	SFO	SFO	

Table 24: Parameter estimation (Degrees of Freedom: 16)

Parameter	Estimate	Lower 95% CI	Upper 95% CI	St.Dev	Result t-test
M0 EC4070003	9.95E+01	9.76E+01	101.434	9.87E-01	$< 2.0*10^{-16}$
k1 EC4070003	1.59E-02	6.70E-03	0.025	4.69E-03	$1.9*10^{-3}$

k2 EC4070003	1.35E-01	1.18E-01	0.152	8.56E-03	$1.8*10^{-11}$
g EC4070003	1.65E-01	9.03E-02	0.239	3.79E-02	$2.5*10^{-4}$
k M1water	2.04E-01	2.56E-02	0.382	9.09E-02	$2.0*10^{-2}$
k M1sediment	2.19E-02	-5.25E-05	0.044	1.12E-02	$3.4*10^{-2}$
k NER[12]	2.52E-03	-3.82E-03	0.009	3.23E-03	**$2.2*10^{-1}$**

Table 25: Measured vs. predicted values

Time [d]	variable	Observed [%]	err-std [%]	Predicted [%]	Residual [%]
0	EC4070003	98.8	0.8052	99.4996	-0.6996
3	EC4070003	72.3	0.8052	71.0621	1.2379
7	EC4070003	46.5	0.8052	46.9697	-0.4697
14	EC4070003	25.2	0.8052	25.6737	-0.4737
28	EC4070003	13.3	0.8052	12.3931	0.9069
56	EC4070003	5.8	0.8052	6.7691	-0.9691
100	EC4070003	3.9	0.8052	3.3434	0.5566
0	M1water	0.7	1.4043	0	0.7
3	M1water	15.2	1.4043	12.9502	2.2498
7	M1water	14.2	1.4043	16.1672	-1.9672
14	M1water	13.3	1.4043	11.8834	1.4166
28	M1water	6	1.4043	5.3898	0.6102
56	M1water	2.1	1.4043	2.8992	-0.7992
100	M1water	0.6	1.4043	1.7684	-1.1684
0	M1sediment	0.6	2.7101	0	0.6
3	M1sediment	9.2	2.7101	11.6783	-2.4783
7	M1sediment	32.8	2.7101	26.4364	6.3636
14	M1sediment	41.4	2.7101	42.39	-0.99
28	M1sediment	47.4	2.7101	48.6527	-1.2527
56	M1sediment	38.1	2.7101	38.8784	-0.7784
100	M1sediment	25.8	2.7101	24.6751	1.1249
0	NER	0.8	0.986	0	0.8
3	NER	3	0.986	2.5377	0.4623
7	NER	5.9	0.986	5.2476	0.6524
14	NER	10	0.986	9.2439	0.7561
28	NER	14.2	0.986	16.139	-1.939
56	NER	27.8	0.986	26.7304	1.0696
100	NER	36.2	0.986	36.424	-0.224

[12] According to the t-test the value is essentially zeromeaning that there is no degradation in the NER.

2.3. Pond System: Dissipation of EC 407-000-3 in whole system

2.3.1 Limitations to modelling the dissipation of EC 407-000-3

As discussed in section 2.1.1. it is impossible to calculate the dissipation of EC 407-000-3 in water or sediment phase separately. Therefore, modelling the whole system has to be considered.

2.3.2. Kinetic modelling of EC 407-000-3 in whole system

The model setup used in all kinetic modelling of the parent substance EC 407-000-3 is shown in Figure 37. It is simple and considers one sink only, without differentiating it further.

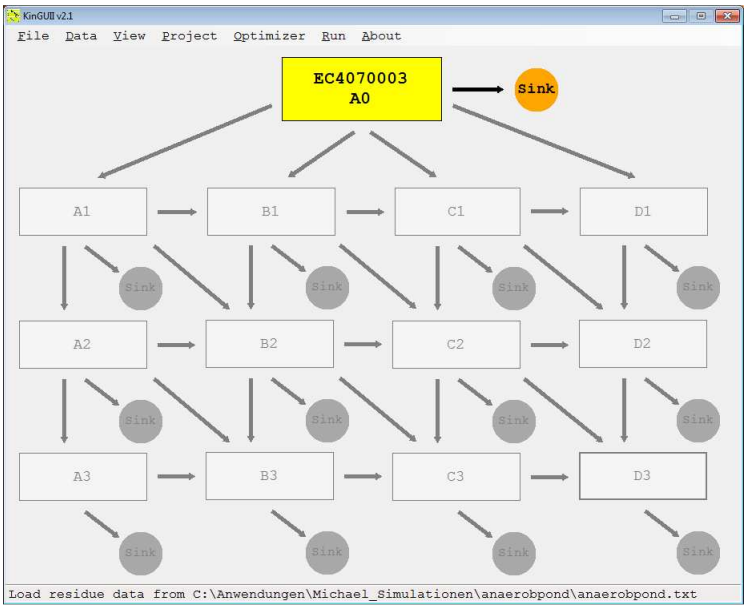


Figure 37: Model setup for modelling dissipation of EC-407-000-3 in pond system under aerobic conditions

2.3.3. EC 407-000-3 SFO

The data shown in Figure 38 are adequately described by SFO up to day 7. Concentrations measured at later dates are underestimated by SFO kinetics and the residual plot shows systematic deviations (see Figure 39). From day 14 on all residuals remain positive. Chi^2-error is acceptable (see Table 26).

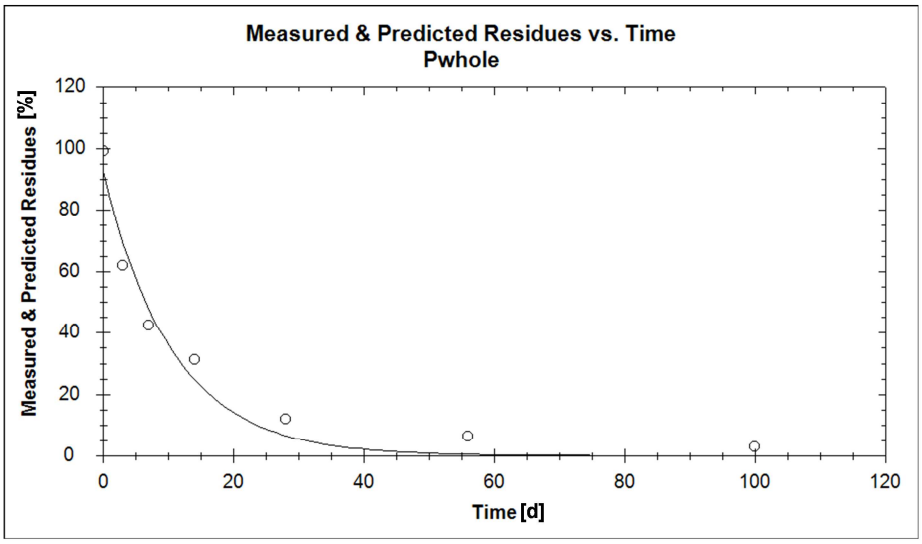


Figure 38: Measured and predicted residues of EC 407-000-3 vs. time in the whole system of an aerobic pond – SFO.

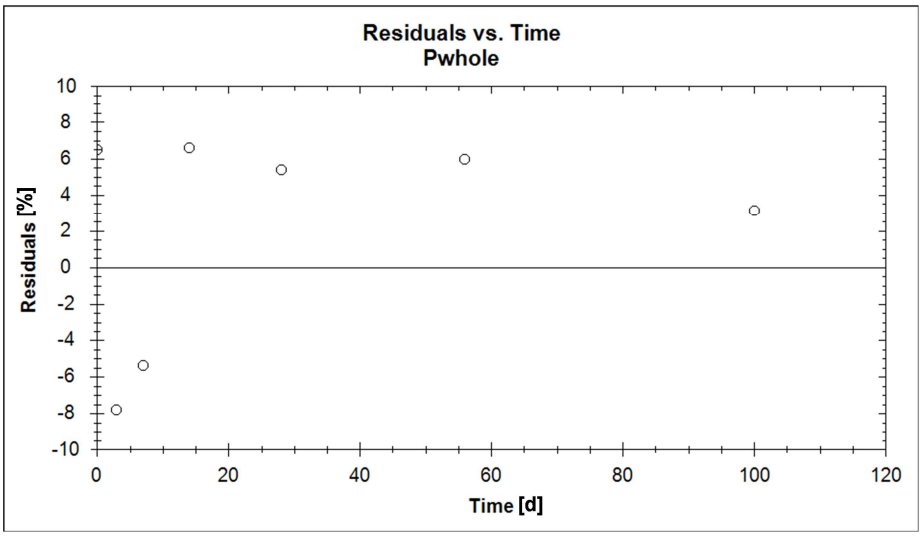


Figure 39: Residuals of EC 407-000-3 vs. time in the whole system of an aerobic pond – SFO.

Table 26: Chi^2 and dissipation times of EC 407-000-3 using SFO kinetic

Parameter	EC 407-000-3	All	Kinetic model
Chi2Err%	12.9300	12.9300	SFO
DT50 in d	7.3499		
DT90 in d	24.4160		

2.3.4. EC 407-000-3 FOMC

Data are well described by FOMC kinetic. The curve fits closely to the measured data. The residual plot shows that data initially scatter around the zero line which is an indication that there is no systematic deviation from the measured values. Nevertheless, it is obvious that there is a systematic overestimation from day 28 on. Chi^2-error is small and acceptable.

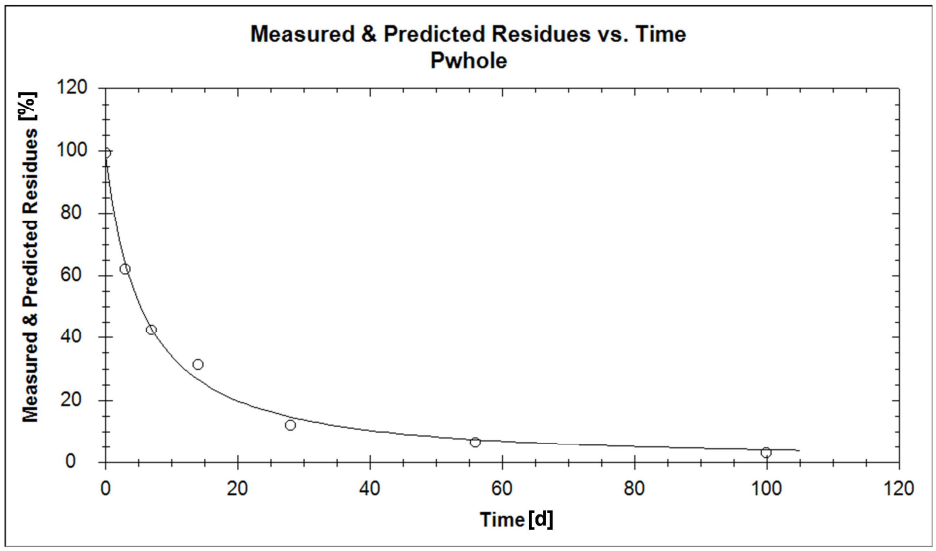


Figure 40: Measured and predicted residues of EC 407-000-3 vs. time in the whole system of an anaerobic pond – FOMC.

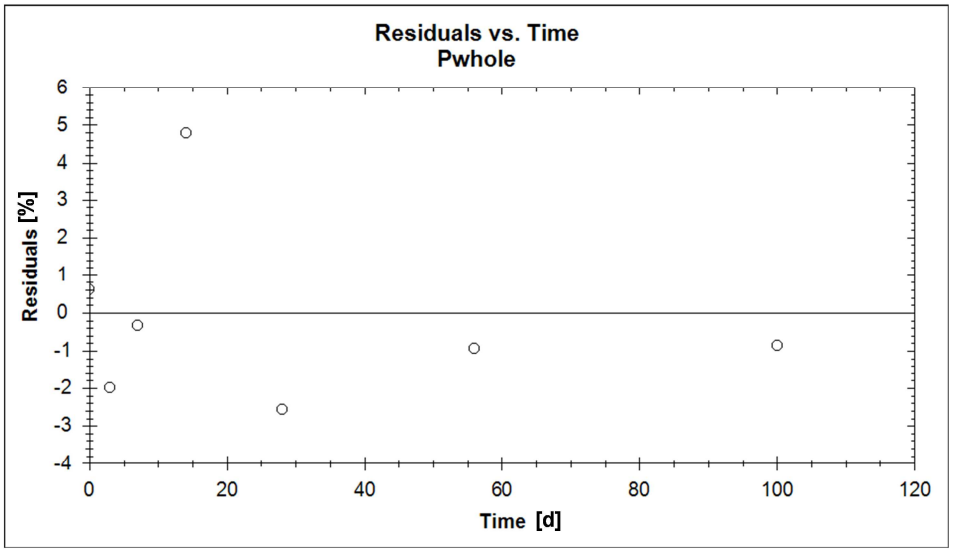


Figure 41: Residuals of EC 407-000-3 vs. time in the whole system of an anaerobic pond – FOMC.

Table 27: Chi^2 and dissipation times of EC 407-000-3 using FOMC kinetic

Parameter	EC 407-000-3	All	Kinetic model
Chi2Err%	5.2810	5.2810	FOMC
DT50 in d	5.4485		
DT90 in d	41.9500		

2.3.5. EC 407-000-3 DFOP

Data are well described by DFOP kinetic. The curve fits closely to the measured data. The calculated curve matches the observed behaviour well. The residuals are small and randomly scattered around the zero line. Chi^2-error is acceptable and with 4.994 smaller than Chi^2-error of 5.281 of FOMC, i.e. overall deviations are smaller and DFOP describes data better than FOMC.

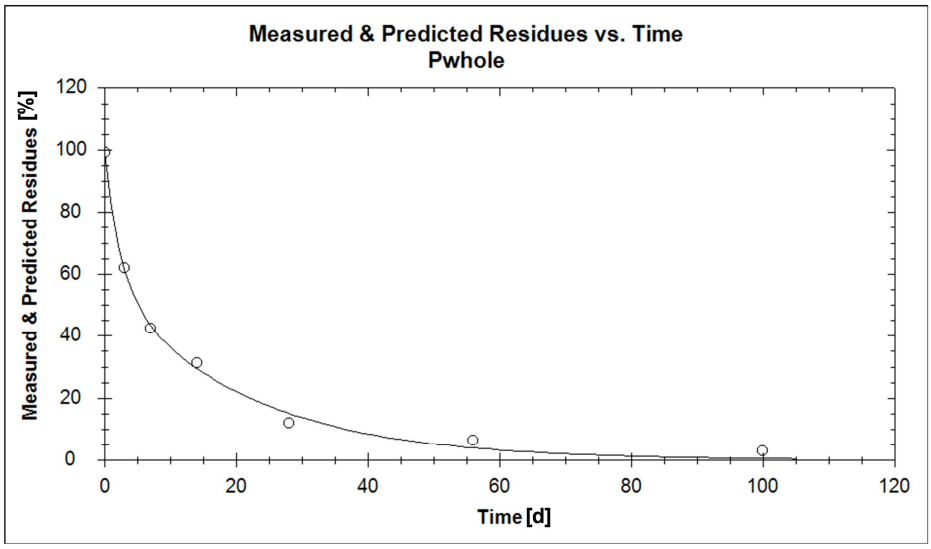


Figure 42: Measured and predicted residues of EC 407-000-3 vs. time in the whole system of an anaerobic pond – DFOP.

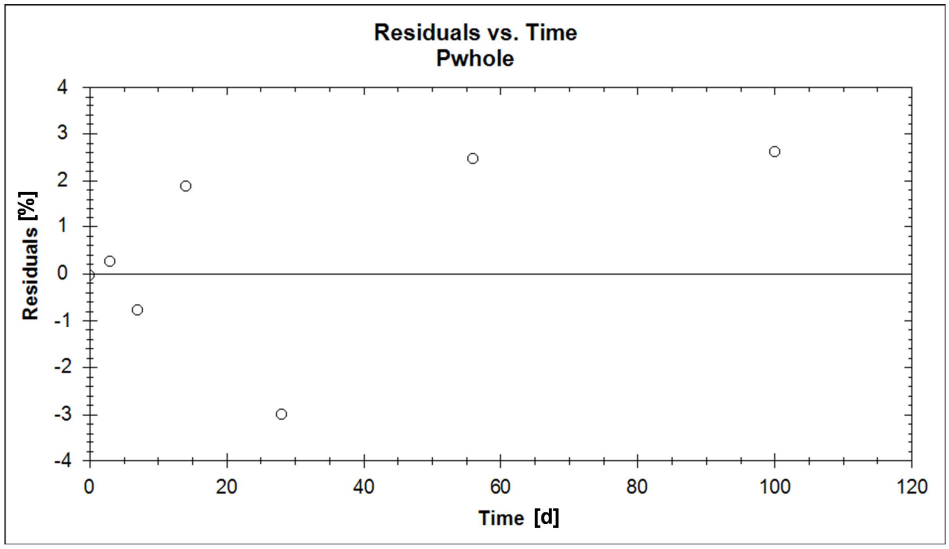


Figure 43: Residuals of EC 407-000-3 vs. time in the whole system of an anaerobic pond – DFOP.

Table 28: Chi^2 and dissipation times of EC 407-000-3 using DFOP kinetic

Parameter	EC 407-000-3	All	Kinetic model
Chi2Err%	4.9940	4.9940	DFOP
DT50 in d	5.1916		
DT90 in d	36.6510		

2.3.6. Conclusion on dissipation of EC 407-000-3

SFO is not suitable to model the measured data as deviation of the residuals is systematic. FOMC and DFOP both fit well but residuals show that DFOP is the better choice because data are randomly scattered around the zero line.

Visual Fit (see Figure 39) shows that Single First Order Kinetic (SFO) cannot be accepted

although Chi^2 is acceptable. A comparison of the two biphasic kinetics Double First Order in Parallel (DFOP) with First Order Multi-Compartment (FOMC) shows DFOP to be the best fit. Thus, DFOP has been used for modelling EC 407-000-3 in all subsequent calculations of M1 dissipation**.**

2.4. Pond system: Model fitting of M1 dissipation in water and sediment phase

2.4.1 Limitations to modelling the dissipation of EC 407-000-3

As discussed in 2.3.1. it is impossible to calculate the dissipation of EC 407-000-3 in water or sediment phase. Dissipation of EC 407-000-3 is considered as DFOP in the following modelling of M1.

2.4.2. M1 SFO for water and sediment

2.4.2.1. Preliminary notes on modelling

M1 is the first metabolite of the parent EC 407-000-3. FOCUS Guidance advises to use a first order kinetic to model dissipation (FOCUS 2006). The dossier submitters followed its advice and used SFO for modelling of M1 dissipation (level M-I calculation).

Figure 44 shows the adjustments used in modelling. In addition to the sink for water or sediment phase Non Extractable Residues are considered because a distinct NER formation of 36 or 25% had been observed for river or pond system. From a mathematical point of view this also means that the resulting DT_{50} values are shorter than if NER were not considered. Please note that for technical reasons a rateconstant for NER has to be calculated (k_{NER}). It has no physical meaning and has to be zero, nevertheless information on it is given as well. The chosen set is no worst case but it reflects the actual conditions met in the test. Thus, the model setup is considered justified. All metabolites and CO_2 evolution are subsumed in the sink.

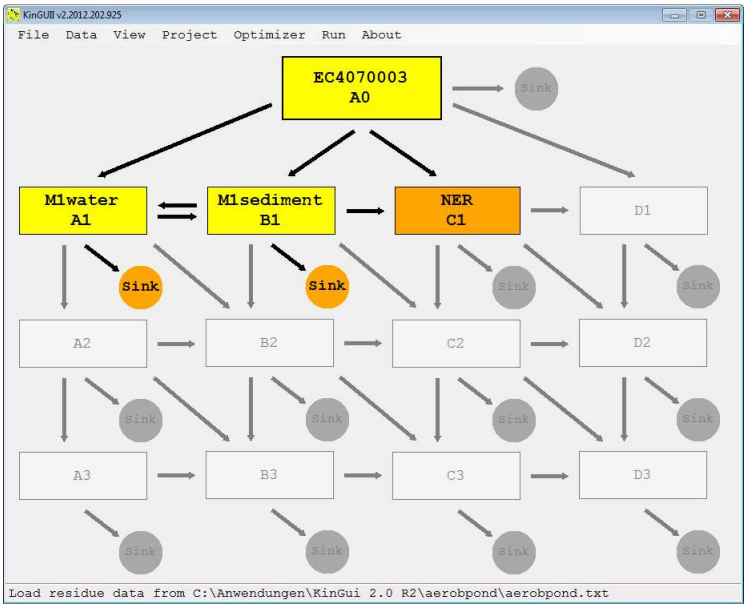


Figure 44: Considered compartments and sinks in pond system under aerobic conditions

2.4.2.2. EC 407-000-3 in whole system

Data of EC 407-000-3 are well described by DFOP kinetic. The curve fits closely to the

measured data and matches the observed behaviour well (see Figure 45). The residuals are small and randomly scattered around the zero line except day 56 and 100, which both are underestimated (see Figure 46). Chi^2-error is acceptable (see Table 29).

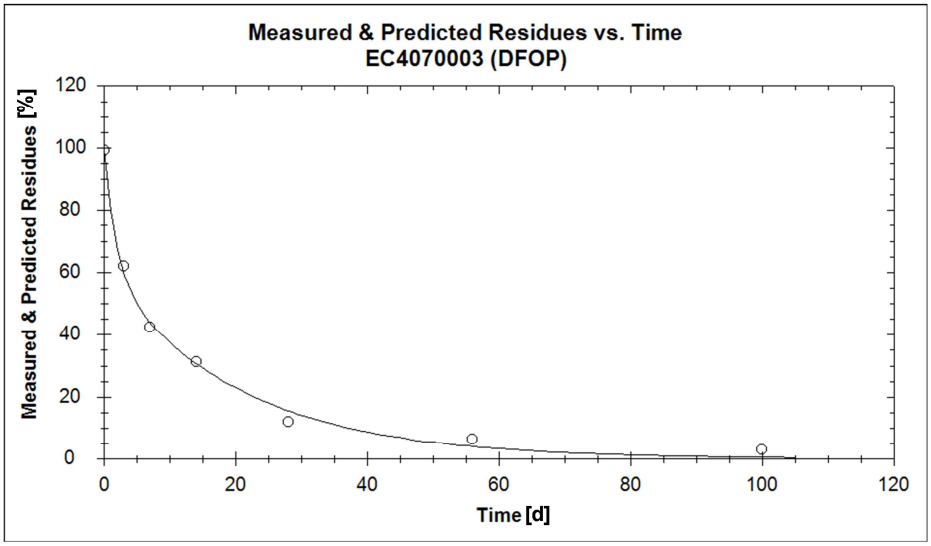


Figure 45: Measured and predicted residues of EC 407-000-3 vs. time in the whole system of an aerobic pond – DFOP.

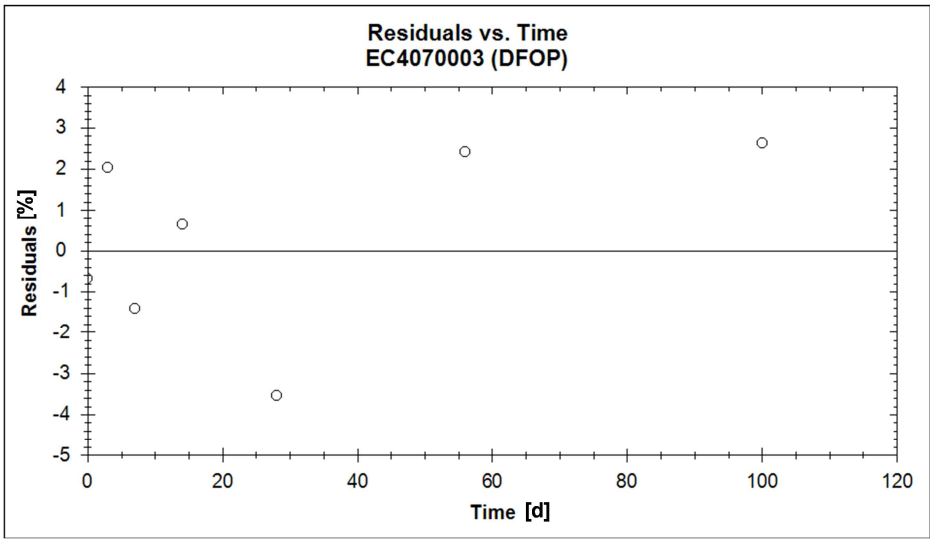
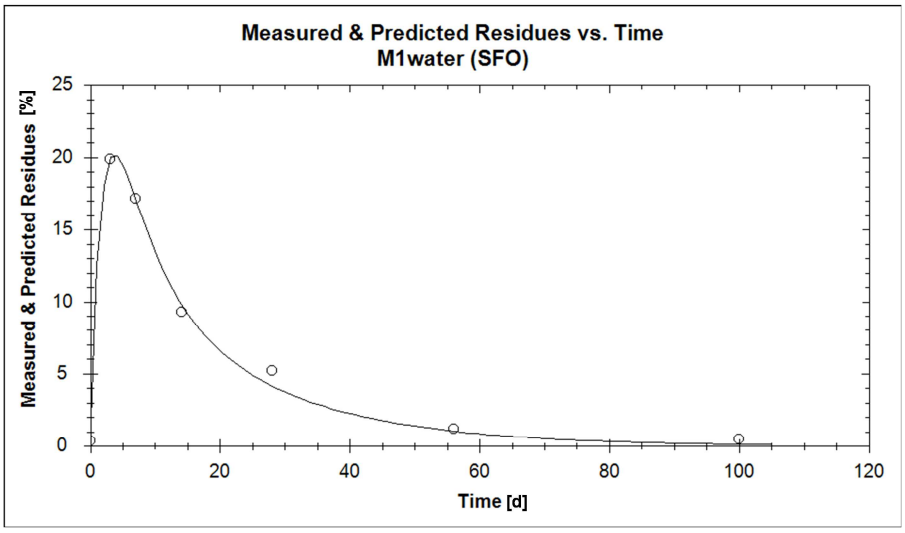


Figure 46: Residuals of EC 407-000-3 vs. time in the whole system of an aerobic pond – DFOP.

2.4.2.3. M1 in water



Data of M1 in the water phase are well described by SFO kinetic (see

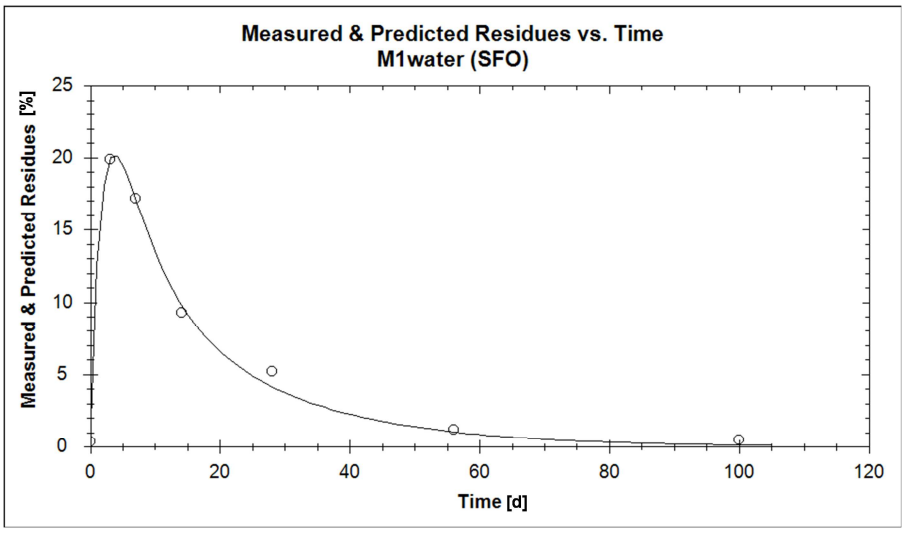


Figure 47). The curve fits to the measured data. The residuals are small but there is a constant underestimation except on day 14 (see Figure 48). This underestimation is very small at day 3 and 7. Therefore it is concluded that data up to day 7 are insufficient as proof of a systematic deviation. However, data from day 28 to day 100 clearly show a systematic deviation and measured data are underestimated. The reason is that a SFO kinetic has to half concentration in a certain time period. This results frequently in a curve which underestimates the last measured data. It is concluded that the fit is acceptable.

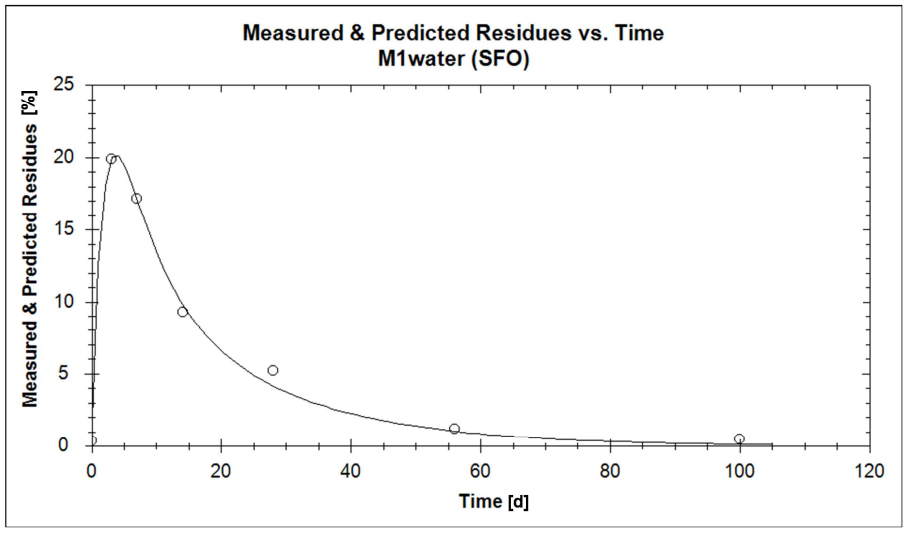


Figure 47: Measured and predicted M1 concentrations in pond water under aerobic conditions

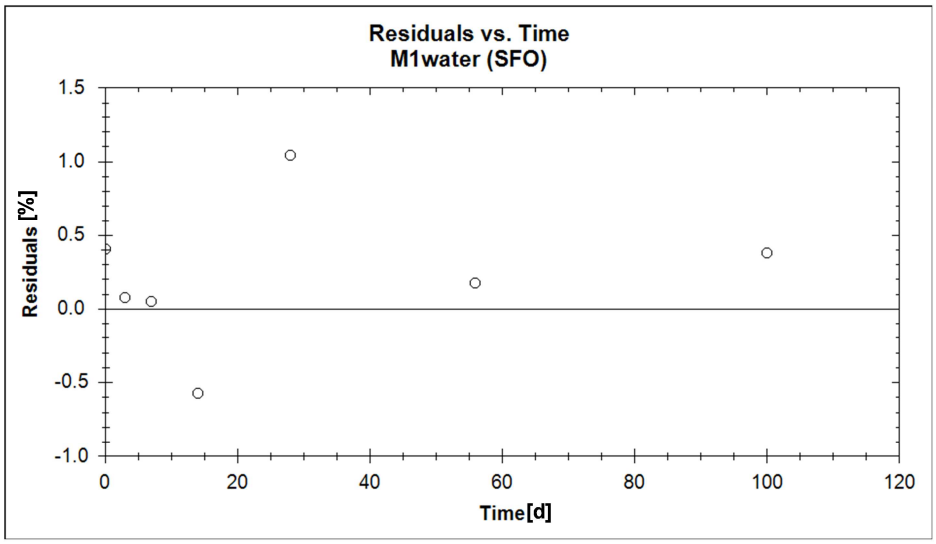


Figure 48: Residuals of M1 concentrations in pond water under aerobic conditions

2.4.2.4. M1 in sediment

Data of M1 in the sediment phase are well described by SFO kinetic (see Figure 49). The curve fits to the measured data. The visual fit is still adequate though it is impaired by the day 28 value which causes a constant underestimation of the other values (see Figure 50). The last two data points are well represented by model although SFO kinetic frequently tends to underestimate the last data points. Chi^2 is only slightly elevated (see Table 29). A t-test is not done by the software but would probably indicate a value being essentially zero. Giving the circumstances and the data points, the dossier submitter nevertheless concludes that the fit is acceptable.

Please note that the kinetic Parameter for M1 in sediment is very small and near zero (the results for the t-test are therefore missing). This can be understood when looking at the curve progression of M1 in sediment: The last two data points could either indicate reaching a plateau or the beginning of a slight decline. To decide about the fate of M1 in sediment either more datapoints or a longer experiment would have been necessary. As it is, this means that

the absolute DT_{50}-value has to be taken with care.

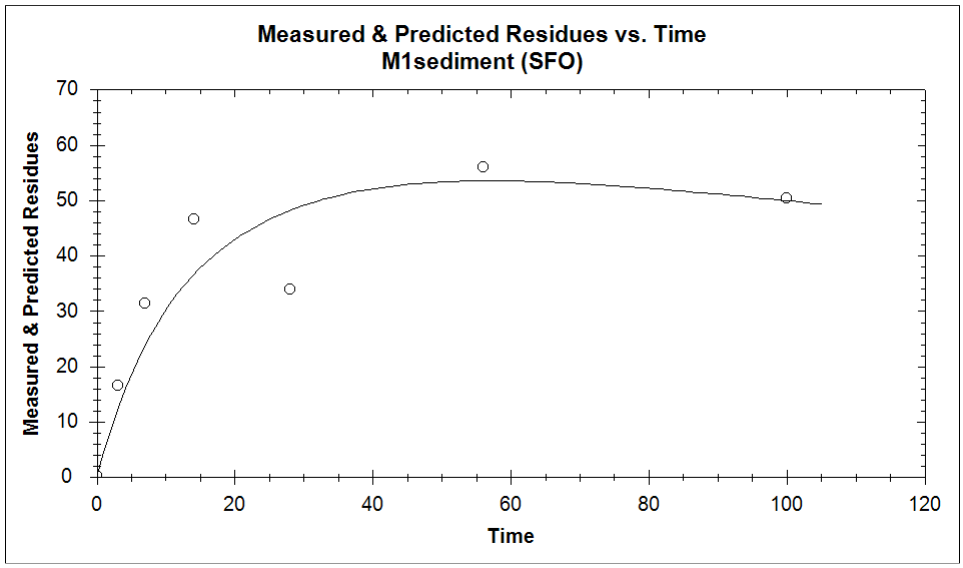


Figure 49: Measured and predicted M1 concentrations in pond sediment under aerobic conditions

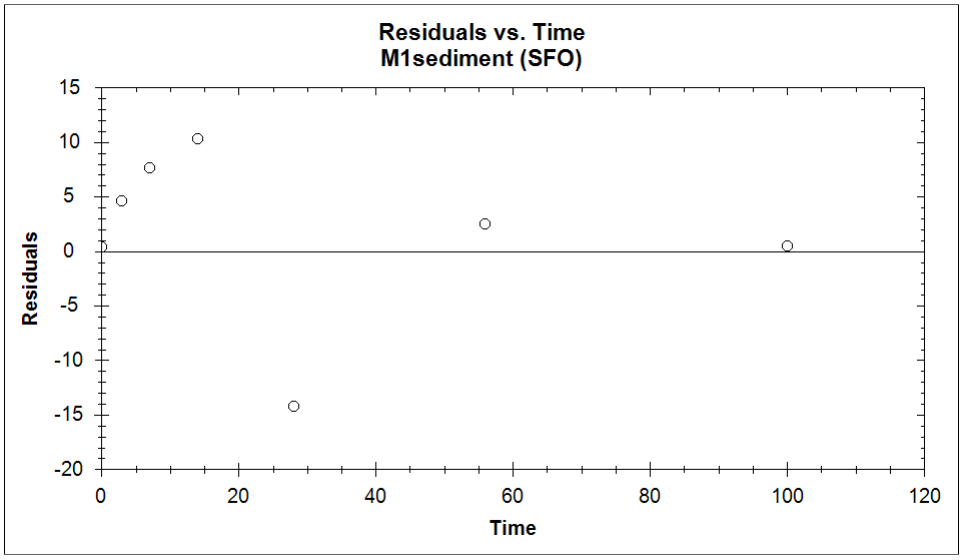


Figure 50: Residuals of M1 concentrations in pond sediment under aerobic conditions

2.4.2.5. NER in whole system

Data of NER are sufficiently well described by SFO kinetic (see Figure 51). Most residuals are small (see Figure 52). The data points of day 3, 7 and 14 are overestimated but the day 7 value only marginally deviates from the zero line. Thus these overestimated data points are not interpreted as systematic deviation. Chi^2-error is elevated, i.e. above 15, especially for M1 in sediment and the NER (see Table 29). Nevertheless, the visual fit shows that the fit is still adequate. The reason for the problems in fitting these two parameters is independent from the model due to the data points of M1 in sediment and NER at day 28. These might be considered outliers but there was no explanation given for this in the original study. Therefore, the data points were kept in the modelling.

Please note that the kinetic constant for NER is in this case very low and essentially zero. This can be understood when looking at the experimental results and the way the kinetic model is composed: Up to the end of the experiment NER is constantly formed.

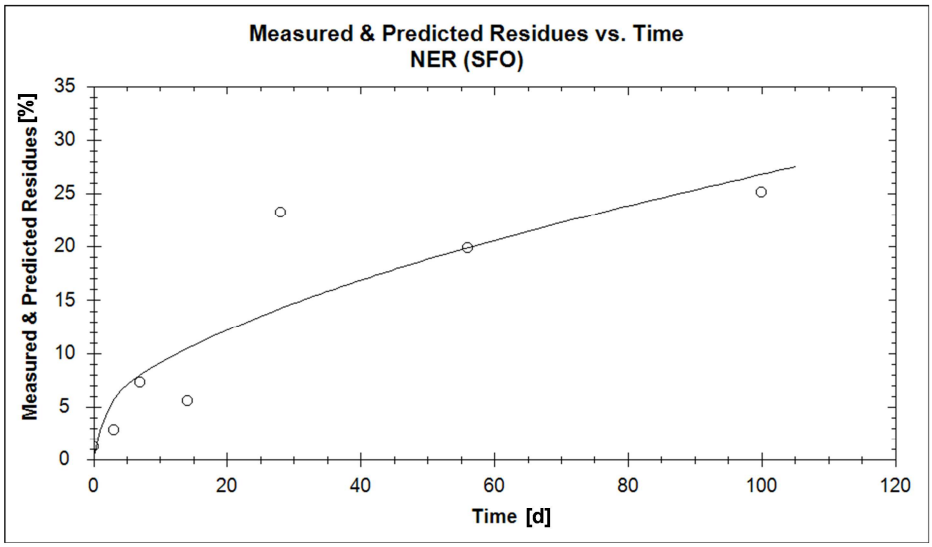


Figure 51: Measured and predicted NER concentrations in pond sediment under aerobic conditions

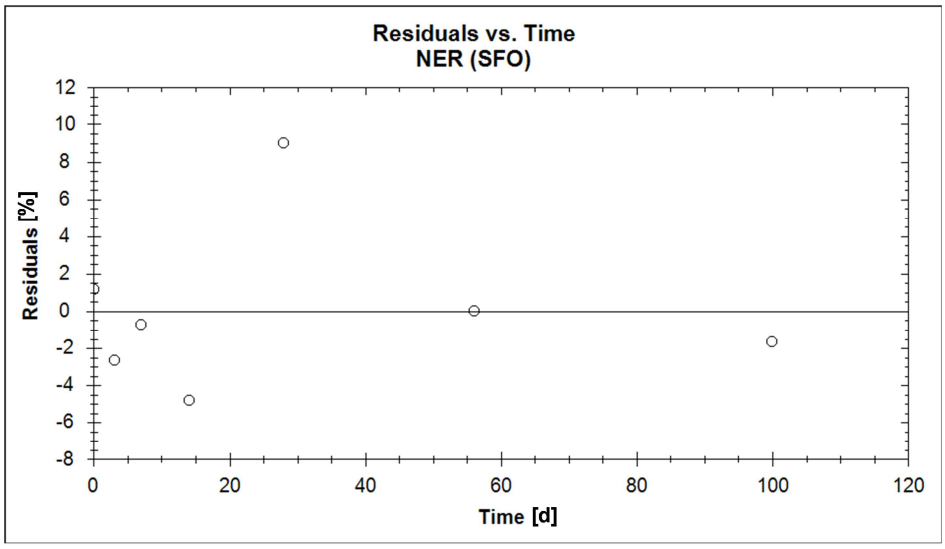


Figure 52: Residuals of NER concentrations in pond sediment under aerobic conditions

Figure 53 gives an overview of the measured and predicted data of EC 407-000-3, M1 and NER.

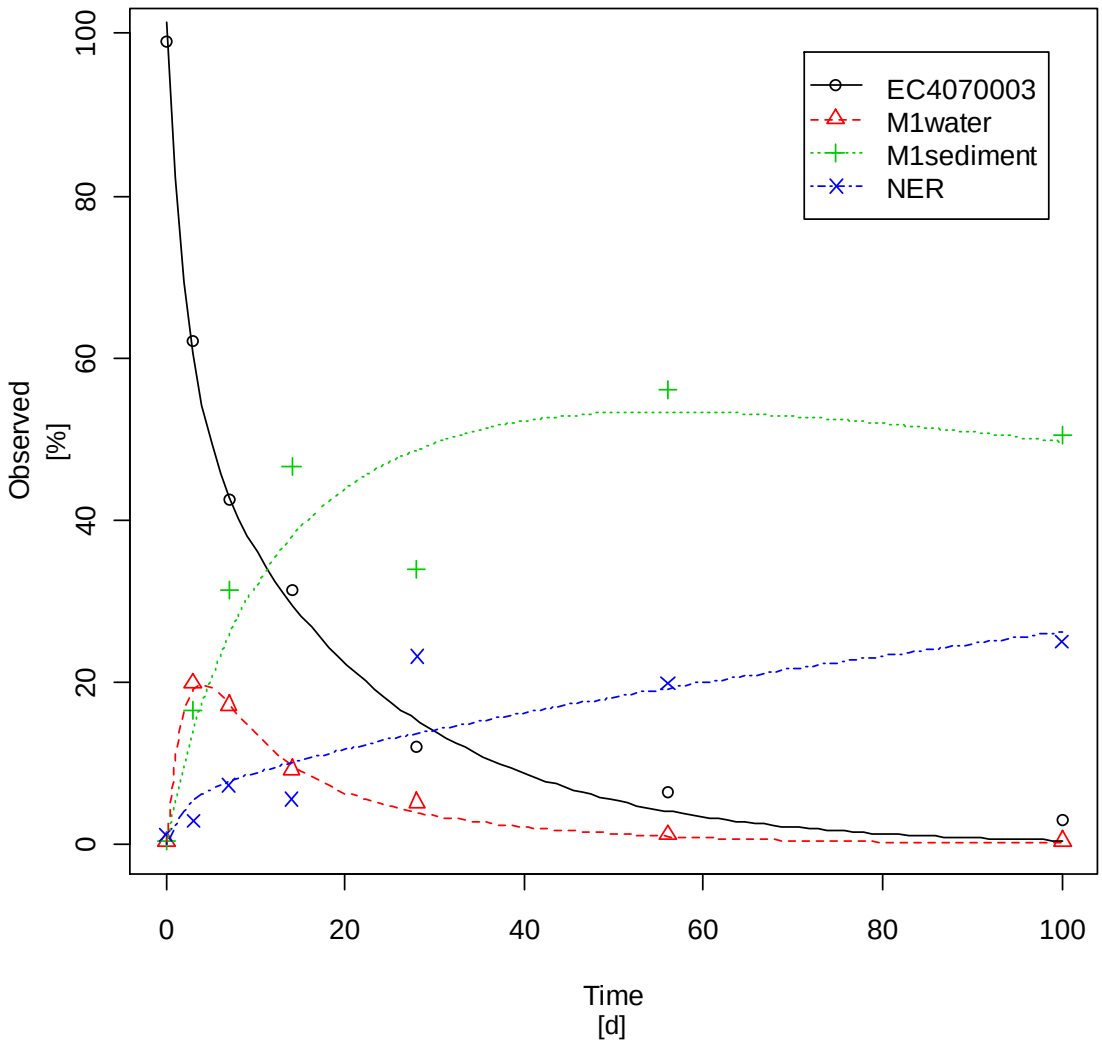


Figure 53: Combined diagram of measured data and respective trends in a pond system under aerobic conditions

Table 29: Chi^2-error and dissipation times of EC 407-000-3, M1 and NER in an aerobic pond system

	EC4070003	M1water	M1sediment	NER	All
Chi2Err%	7.908	5.186	19.170	24.924	20.195
DT50 in d	5.0379	3.9189	248.190	1.0678E+10	
DT90 in d	37.123	13.018	824.480	3.547E+10	
Kinetic model	DFOP	SFO	SFO	SFO	

Table 30: Parameter estimation (Degrees of Freedom: 16)

Parameter	Estimate	Lower 95% CI	Upper 95% CI	St.Dev	Result t-test
M0 EC4070003	9.98E+01	9.44E+01	105.115	2.72E+00	< $2.0*10^{-16}$

k1 EC4070003	4.85E-02	3.58E-02	0.061	6.51E-03	$6.8*10^{-7}$
K2 EC4070003	5.44E-01	3.34E-01	0.753	1.07E-01	$5.5*10^{-5}$
g EC4070003	6.06E-01	5.06E-01	0.706	5.09E-02	$1.2*10^{-9}$
k M1water	1.77E-01	1.34E-01	0.22	2.18E-02	$2.3*10^{-7}$
k M1sediment	2.79E-03	NA	NA	NA	NA
k NER	6.49E-11[13]	NA	NA	NA	NA

Table 31: Measured and predicted values

Time [d]	variable	Observed [%]	err-std [%]	Predicted [%]	Residual [%]
0	EC4070003	99.1	2.1418	99.7752	-0.6752
3	EC4070003	62.0	2.1418	59.9622	2.0378
7	EC4070003	42.5	2.1418	43.9209	-1.4209
14	EC4070003	31.3	2.1418	30.6674	0.6326
28	EC4070003	12.0	2.1418	15.5352	-3.5352
56	EC4070003	6.4	2.1418	3.9916	2.4084
100	EC4070003	3.1	2.1418	0.4718	2.6282
0	M1water	0.4	0.5011	0	0.4000
3	M1water	19.9	0.5011	19.8262	0.0738
7	M1water	17.2	0.5011	17.1484	0.0516
14	M1water	9.3	0.5011	9.8737	-0.5737
28	M1water	5.2	0.5011	4.1602	1.0398
56	M1water	1.2	0.5011	1.0265	0.1735
100	M1water	0.5	0.5011	0.1212	0.3788
0	M1sediment	0.4	7.5090	0	0.4000
3	M1sediment	16.6	7.5090	12.0129	4.5871
7	M1sediment	31.4	7.5090	23.7722	7.6278
14	M1sediment	46.7	7.5090	36.4263	10.2737
28	M1sediment	33.9	7.5090	48.1433	-14.2433
56	M1sediment	56.0	7.5090	53.4966	2.5034
100	M1sediment	50.4	7.5090	49.9258	0.4742
0	NER	1.2	4.0678	0	1.2000
3	NER	2.9	4.0678	5.5627	-2.6627
7	NER	7.3	4.0678	7.9869	-0.6869
14	NER	5.6	4.0678	10.4219	-4.8219
28	NER	23.2	4.0678	14.2069	8.9931
56	NER	19.9	4.0678	19.8637	0.0363
100	NER	25.1	4.0678	26.7581	-1.6581

[13] This value is essentially zero.

3. Kinetic modelling of data from a water-sediment study according to OECD 308 on EC 407-000-3 under anaerobic conditions

3.1. Pond System: Dissipation of EC 407-000-3 in whole system

3.1.1. Limitations to modelling of the dissipation of EC 407-000-3

Substance behaviour under anaerobic conditions basically resembled behaviour under aerobic conditions. A quick dissipation of EC 407-000-3 from water to sediment was observed. High concentrations of EC 407-000-3 in sediment were already found at day 0.

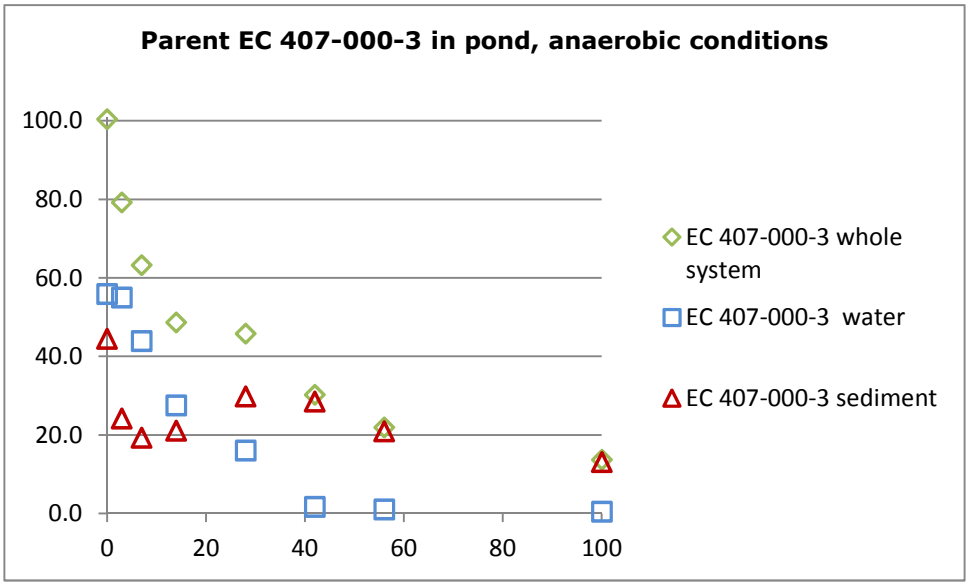


Figure 54: Distribution of EC 407-000-3 in a pond system under anaerobic conditions

As discussed earlier it is impossible to model the concentration of EC 407-000-3 for the water phase or the sediment phase separately due to missing information in the report on the exact time of the first measuring. Additionally, the concentration in the sediment shows two peaks. This curve progression cannot be modelled. Thus, EC 407-000-3 was modelled for the whole system, only.

3.1.2. Kinetic modelling of EC 407-000-3 in whole system

The model setup used in all kinetic modelling of EC 407-000-3 is shown in Figure 55. It is simple and considers one sink, only, without differentiating it further.

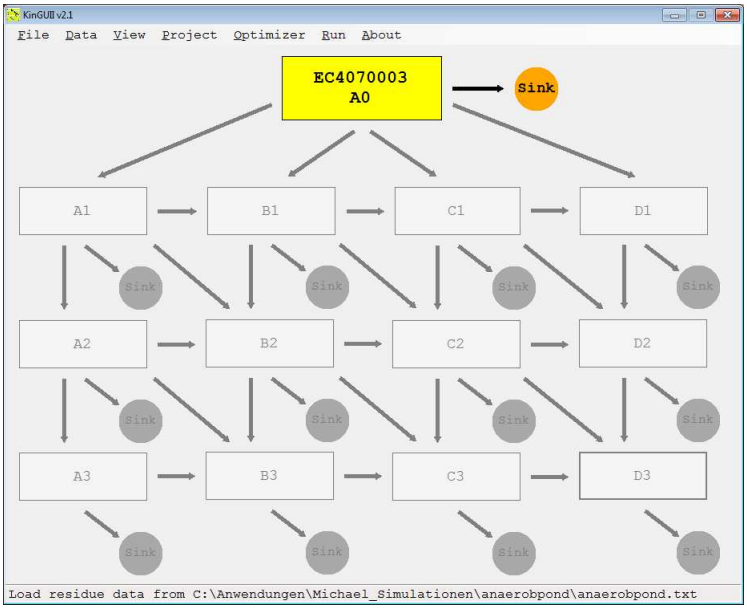


Figure 55: Model setup for modelling of EC 407-000-3 in pond system under anaerobic conditions

3.1.3. EC 407-000-3 SFO

The data shown in

Figure 56 are adequately described by SFO but residuals show systematic underestimation from day 28 to 100 (see Figure 57). Chi^2-error is acceptable (see Table 32).

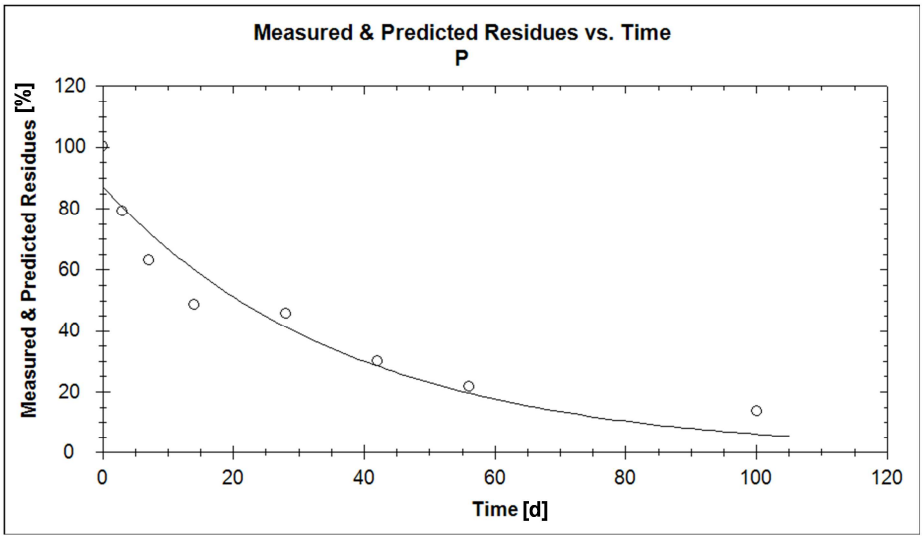


Figure 56: Measured and predicted residues of EC 407-000-3 vs. time in the whole system of an anaerobic pond – SFO.

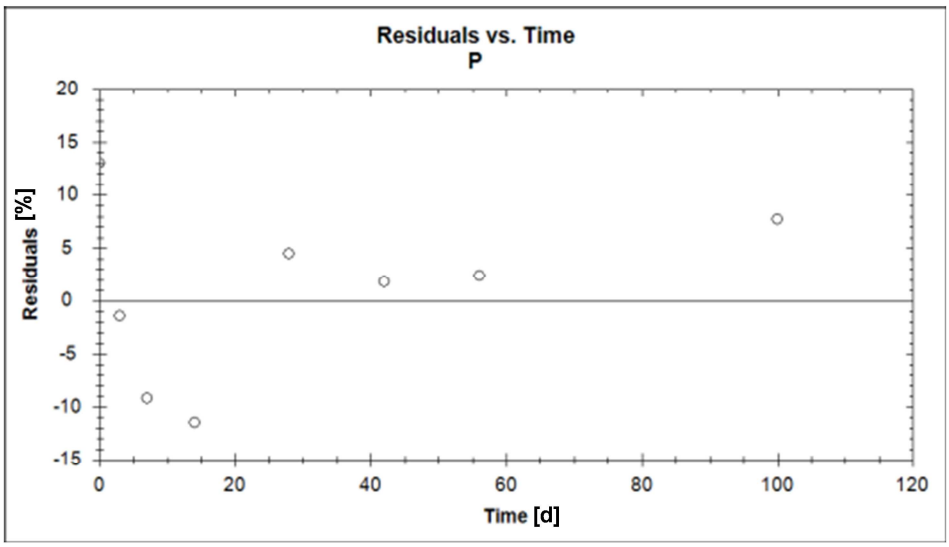


Figure 57: Residuals of EC 407-000-3 vs. time in the whole system of an anaerobic pond – SFO.

Table 32: Chi^2 and dissipation times of EC 407-000-3 using SFO kinetic

Parameter	EC 407-000-3	All	Model
Chi2Err%	12.220	12.220	SFO
DT50 in d	25.884		
DT90 in d	85.986		

3.1.4. EC 407-000-3 FOMC

Data are well described by FOMC kinetic and the curve fits closely to the measured data (see Figure 58). Residuals show a systematic overestimation for day 3 to 14 (see Figure 59). Chi^2 is small and acceptable (see Table 33).

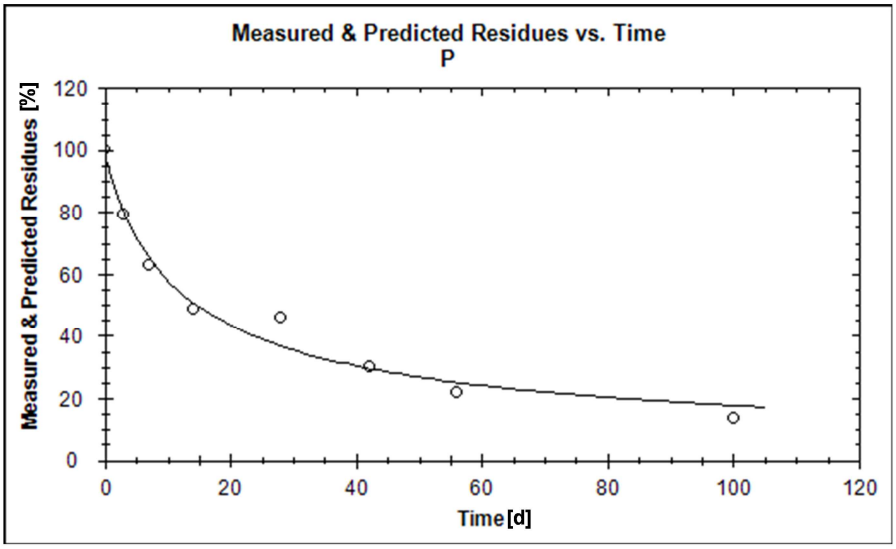


Figure 58: Measured and predicted residues of EC 407-000-3 vs. time in the whole system of an anaerobic pond – FOMC.

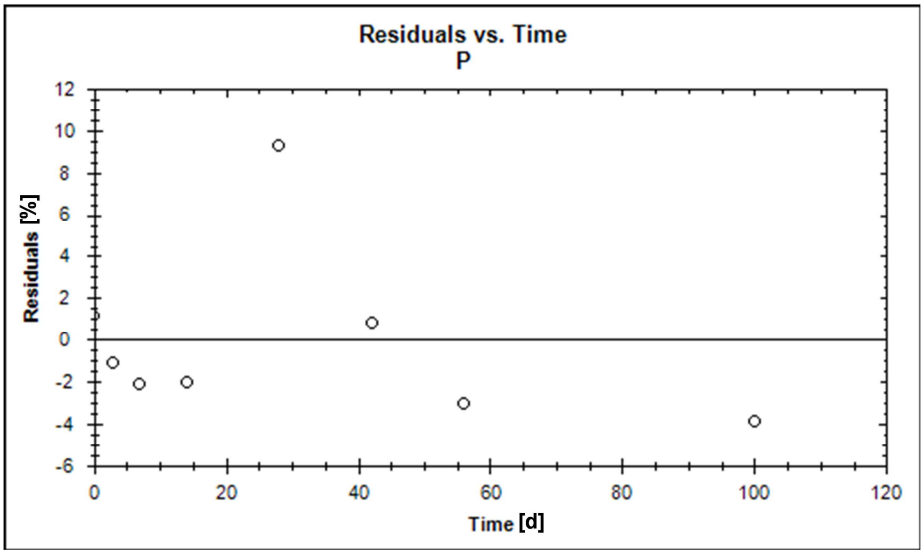


Figure 59: Residuals of EC 407-000-3 vs. time in the whole system of an anaerobic pond – FOMC.

Table 33: Chi^2 and dissipation times of EC 407-000-3 using FOMC kinetic

Parameter	EC 407-000-3	All	Model
Chi2Err%	6.604	6.604	FOMC
DT50 in d	14.677		
DT90 in d	247.830		

3.1.5. EC 407-000-3 DFOP

Data are well described by DFOP kinetic. The curve fits closely to the measured data and matches the observed behaviour well (see Figure 60). The residuals are small and randomly scattered around the zero line (see Figure 61). Chi^2-error is small and acceptable and with 4.937 (see Table 34) smaller than Chi^2-error of 6.604 of FOMC.

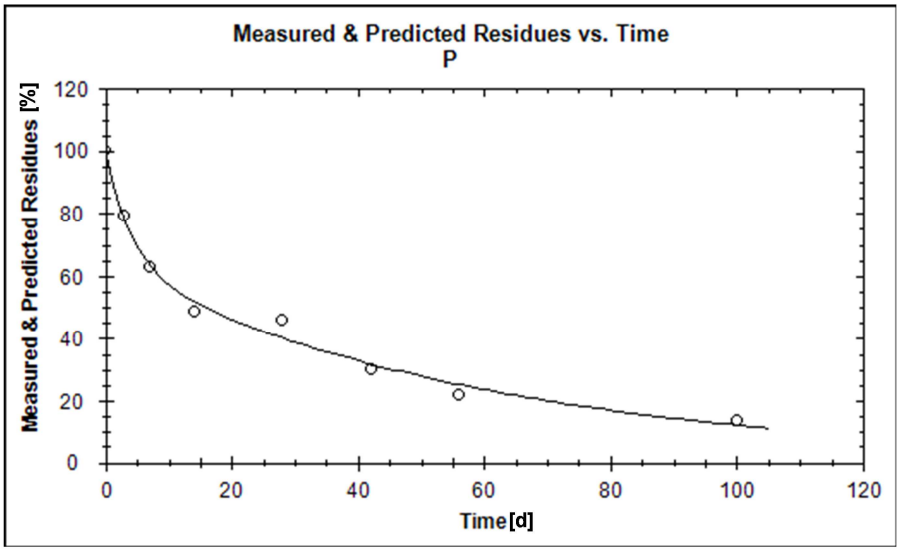


Figure 60: Residuals of EC 407-000-3 vs. time in the whole system of an anaerobic pond – DFOP

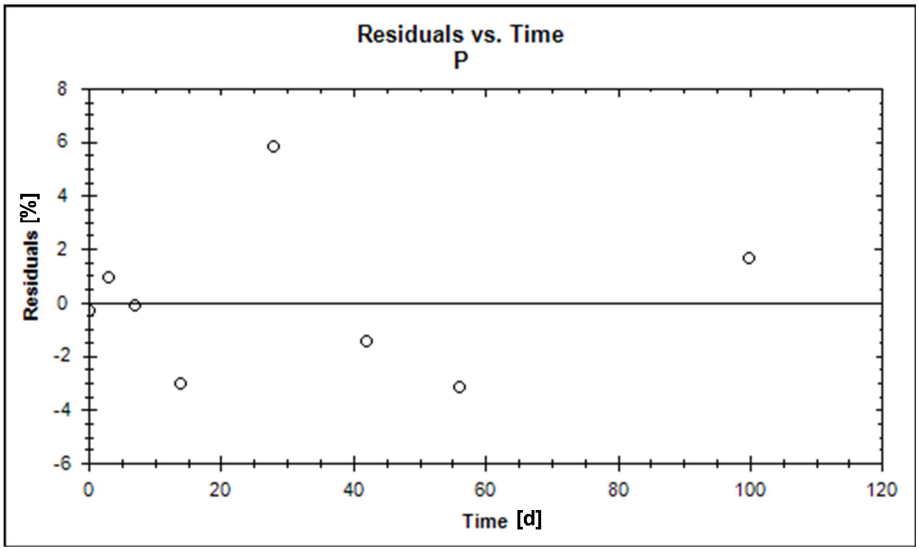


Figure 61: Measured and predicted residues of EC 407-000-3 vs. time in the whole system of an anaerobic pond – DFOP

Table 34: Chi^2 and dissipation times of EC 407-000-3 using DFOP kinetic

Parameter	EC 407-000-3	All	Kinetic model
Chi2Err%	4.937	4.937	DFOP
DT_{50} in d	15.179		
DT90 in d	110.830		

3.1.6. Conclusion on dissipation of EC 407-000-3

SFO is not suitable to model the measured data as deviation of the residuals is systematic. FOMC and DFOP both fit well. However, FOMC shows systematic deviation while DFOP does not. Additionally, Chi^2-error of DFOP is smaller than Chi^2-error of FOMC, i.e. overall deviations are smaller. DFOP describes data better than FOMC.

3.2. Pond system: Model fitting of M1 dissipation in water and sediment phase

3.2.1. Limitations to modelling the dissipation of EC 407-000-3

As discussed in section 3.1.1. it is impossible to calculate the dissipation of EC 407-000-3 in water or sediment phase separately. Therefore, modelling the whole system has to be considered.

3.2.2. M1 SFO in water and sediment phase

3.2.2.1. Preliminary notes on modelling

As discussed earlier M1 is the first metabolite of the parent EC 407-000-3. Following FOCUS guidance (FOCUS 2006) SFO was used for modelling of M1 dissipation (level M-I calculation).

Figure 62 shows the model setup used. In addition to the sink for water or sediment phase Non Extractable Residues are considered. In contrast to the aerobic study a NER formation of only approximately 10 % had been observed. Nevertheless, to foster comparability of data from aerobic and anaerobic study NER was included as an additional sink in the model set. From a mathematical point of view this means that the resulting DT_{50} values are shorter than if NER were not considered. Please note that for technical reasons a rate constant for NER has to

be calculated (k_{NER}). It has no physical meaning and has to be zero, nevertheless information on it is given as well. The chosen setup is no worst case but because of the reasons mentioned this set is considered justified. All metabolites and CO_2 evolution are subsumed in the sink.

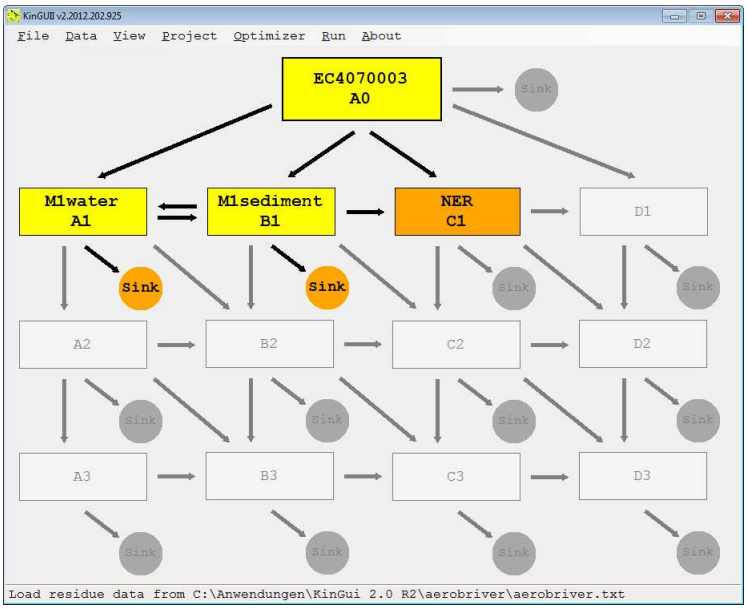


Figure 62: Considered compartments and sinks in pond system under anaerobic conditions

3.2.2.2. EC 407-000-3 in whole system

Data of EC 407-000-3 are well described by DFOP kinetic. The curve fits to the measured data and matches the observed behaviour (see Figure 63). The residuals are small and randomly scattered around the zero line except day 3 to 14 which are systematically underestimated (see Figure 64). Chi^2-error is acceptable (see Table 35). Visual fit shows that the fit is acceptable.

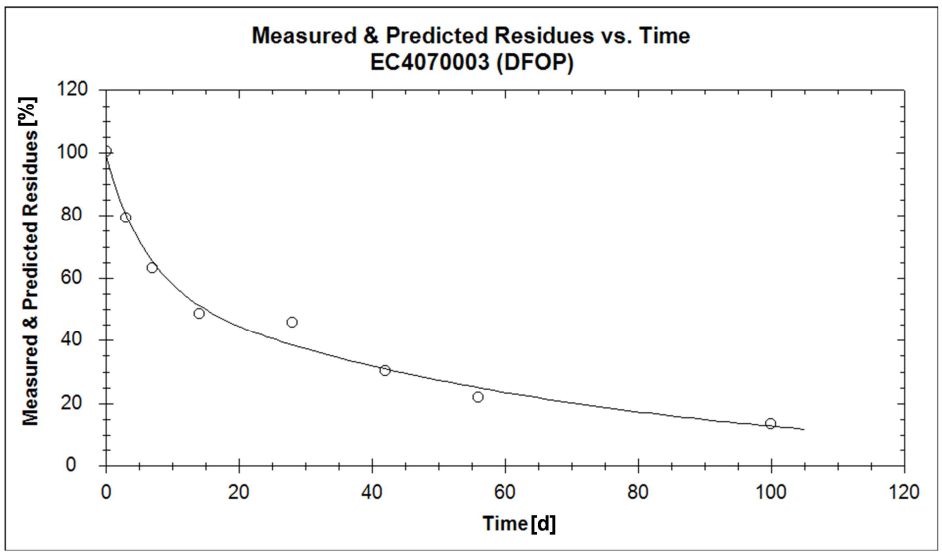


Figure 63: Measured and predicted residues of EC-407-000-3 vs. time in the whole system of an anaerobic pond – DFOP.

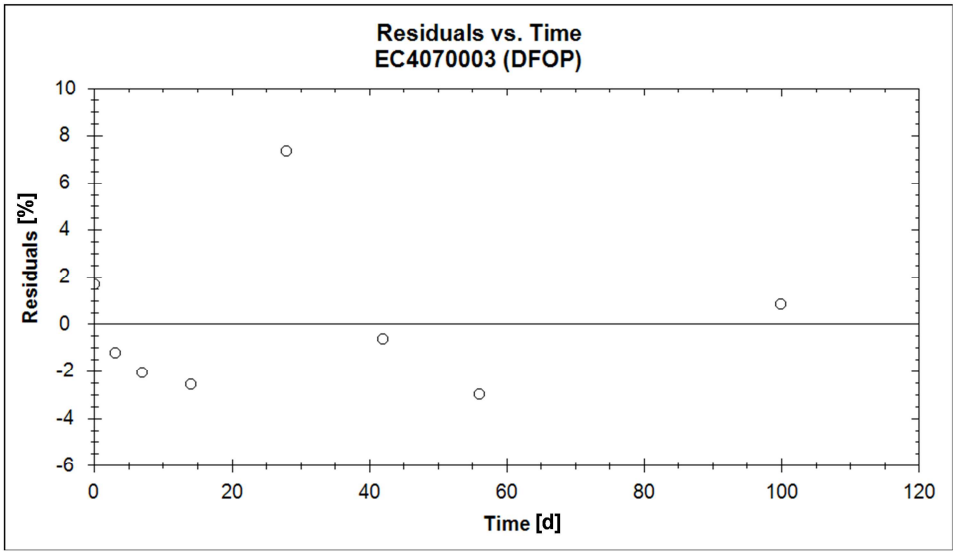


Figure 64: Residuals of EC-407-000-3 vs. time in the whole system of an anaerobic pond – DFOP.

3.2.2.3 M1 in water

Data of M1 in the water phase are acceptably well described by SFO kinetic (see Figure 65). The residuals are small and there is no systematic deviation. However, neither the maximum value at day 14 is well modelled nor are the last four data points (see Figure 66). As a consequence Chi^2 is elevated (above 15) but still acceptable. (see Table 35).

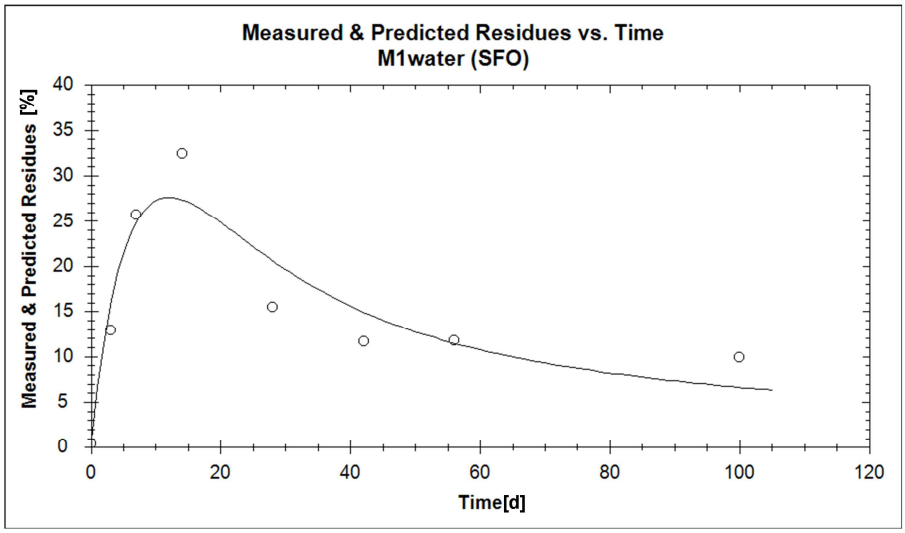


Figure 65: Measured and predicted residues of M1 vs. time in the water phase of an anaerobic pond – SFO

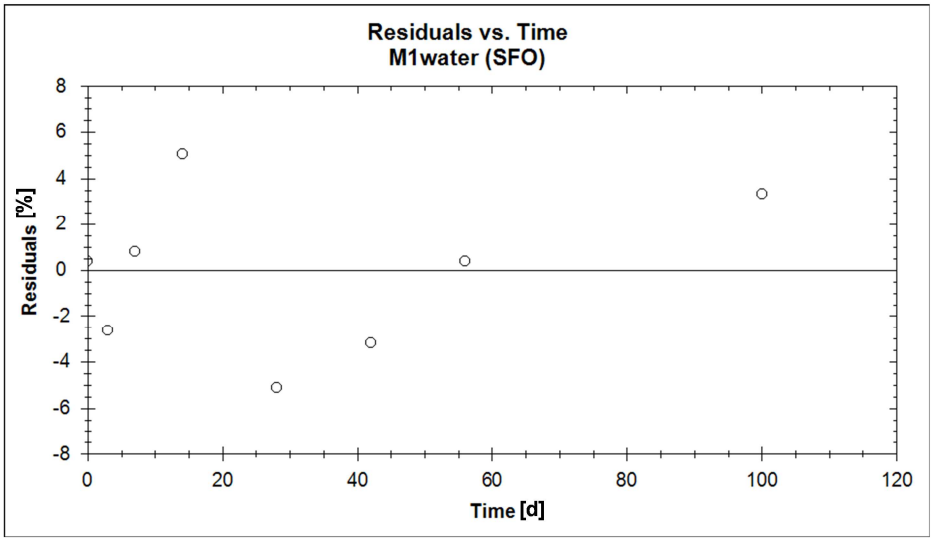


Figure 66: Residuals of M1 vs. time in the water phase of an anaerobic pond – SFO.

3.2.2.4. M1 in sediment

Data of M1 in the sediment phase are well described by SFO kinetic and the curve fits well to the measured data (see Figure 67). Residuals are small and do not show systematic deviation (see Figure 68). Chi^2 is small (see Table 35).

Please note that the kinetic Parameter for M1 in sediment is very small and essentially zero (see results of t-test). This can be understood as the concentration of M1 constantly rises during the experiment (i.e. only the first part of the degradation curve of M1 in sediment was monitored). This also means that the absolute DT_{50}-value has to be taken with care as it could differ from the calculated value (depending on how the rest of the curve will look like).

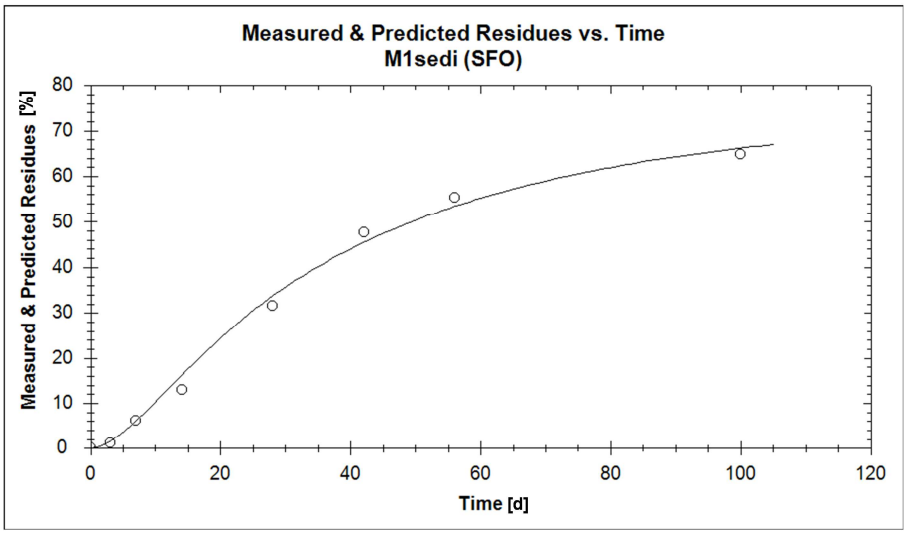


Figure 67: Measured and predicted residues of M1 vs. time in the sediment phase of an anaerobic pond – SFO.

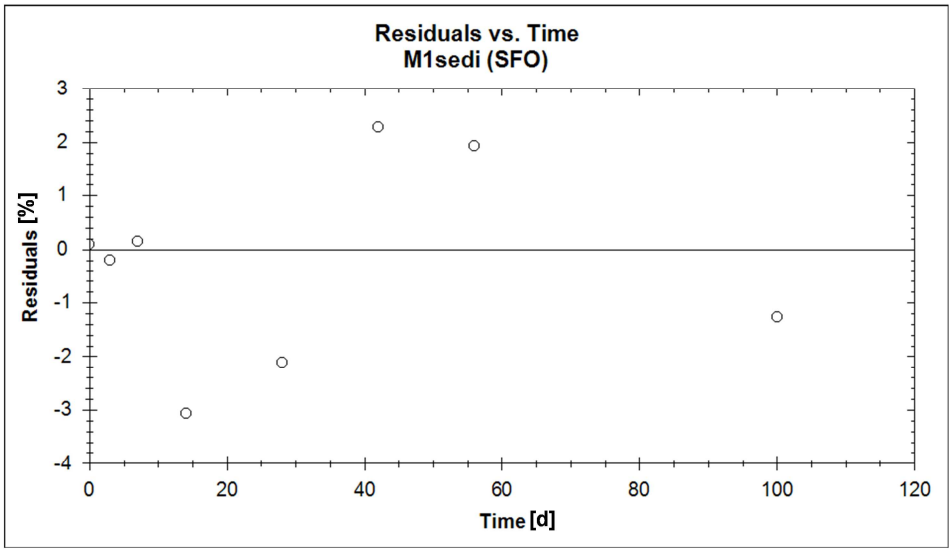


Figure 68: Residuals of M1 vs. time in the sediment phase of an anaerobic pond – SFO.

3.2.2.5. NER in whole system

Data of NER are acceptably well described by SFO kinetic (see Figure 69). Residuals are small but there is a systematic overestimation from day 3 to 14. Nevertheless, the visual fit and the acceptable Chi^2 (see Table 35) show that the fit is adequate.

Please note that the kinetic constant for NER is in this case very low and essentially zero. This can be understood when looking at the experimental results and the way the kinetic model is composed: Up to the end of the experiment NER is constantly formed.

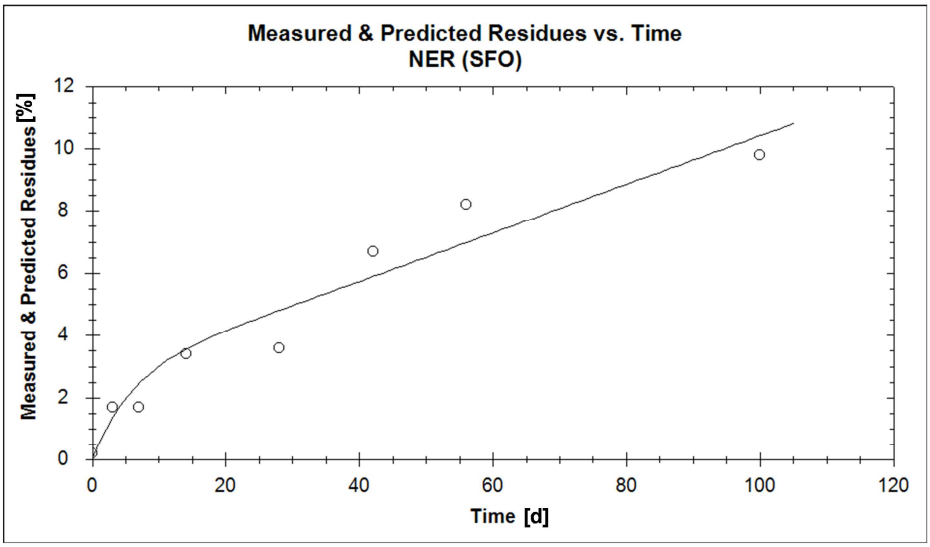


Figure 69: Measured and predicted residues of NER vs. time in the whole system of an anaerobic pond – SFO.

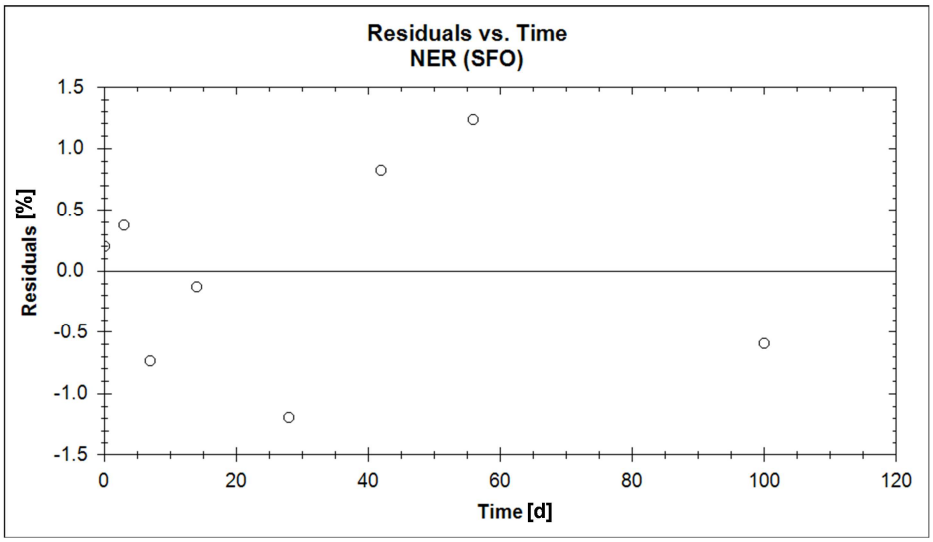


Figure 70: Residuals of NER vs. time in the whole system of an anaerobic pond – SFO.

Figure 71 gives an overview of the measured and predicted data of EC 407-000-3, M1 and NER.

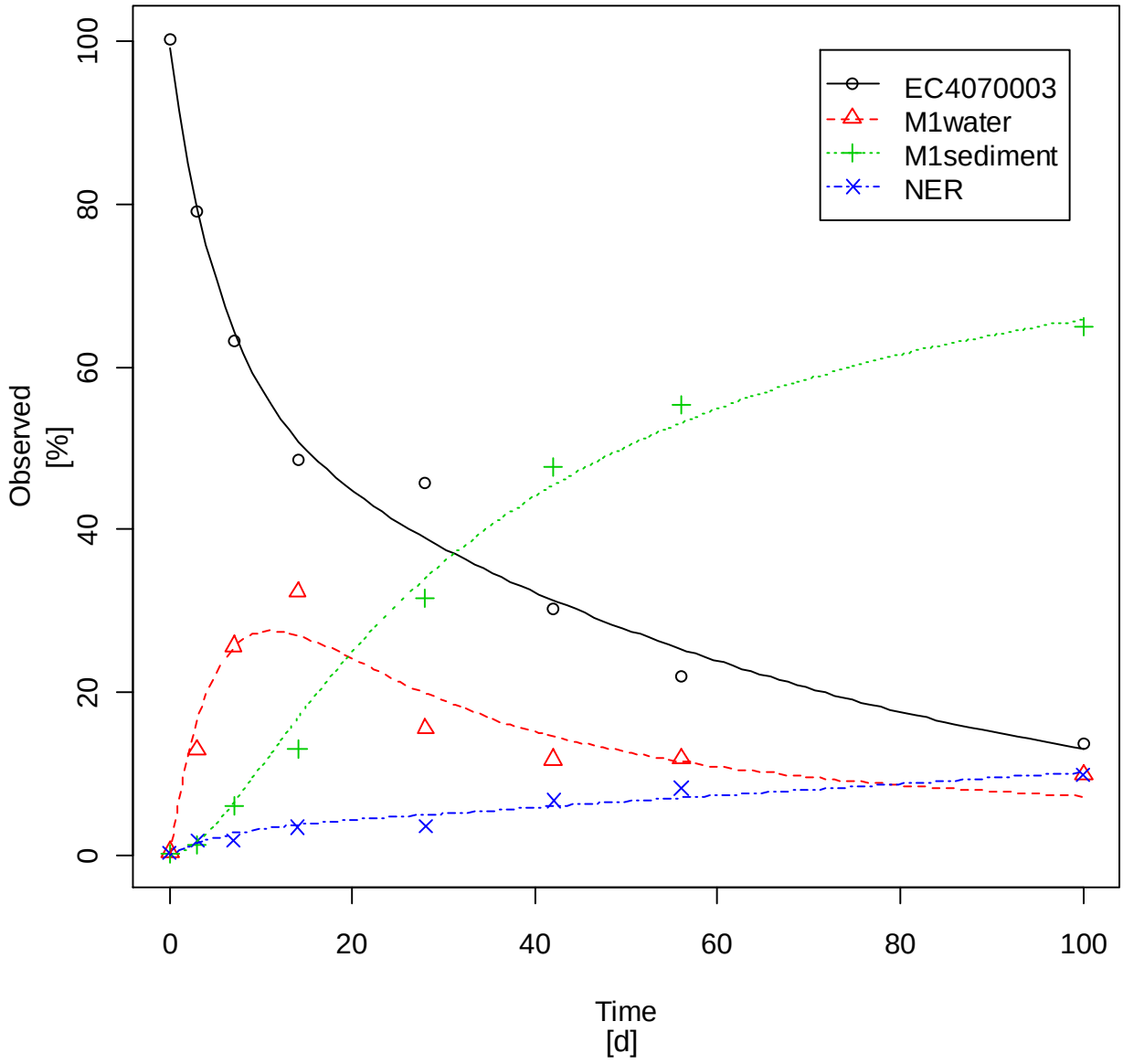


Figure 71: Combined diagram of measured data and respective trends in a pond system under anaerobic conditions.

Table 35: Chi^2-error and dissipation times of EC-407-000-3, M1 and NER in an anaerobic pond system.

	EC4070003	M1water	M1sediment	NER	All
Chi2Err%	7.200	16.817	5.423	13.114	10.075
DT50 in d	15.383	12.224	237.65	15,219,328	
DT90 in d	116.90	40.608	789.46	50,557,513	
Kinetic model	DFOP	SFO	SFO	SFO	

Table 36: Parameter estimation (Degrees of Freedom: 20)

Parameter	Estimate	Lower 95% CI	Upper 95% CI	St.Dev	Result t-test
M0 EC4070003	9.87E+01	9.35E+01	104.001	2.69E+00	$< 2.0*10^{-16}$

k1 EC4070003	1.64E-01	7.58E-02	0.251	4.47E-02	$7.9*10^{-4}$
k2 EC4070003	1.52E-02	8.72E-03	0.022	3.30E-03	$8.6*10^{-5}$
g EC4070003	4.10E-01	2.67E-01	0.554	7.34E-02	$8.9*10^{-6}$
k M1water	5.67E-02	4.36E-02	0.070	6.67E-03	$2.3*10^{-8}$
k M1sediment[14,15]	2.92E-03	-2.47E-03	0.008	2.75E-03	**$1.5*10^{-1}$**
k NER[16]	4.55E-08	-3.94E-02	0.039	2.01E-02	**$5.0*10^{-1}$**

Table 37: Measured vs. predicted values

Time [d]	variable	Observed [%]	err-std [%]	Predicted [%]	Residual [%]
0	EC4070003	100.4	3.1221	98.7262	1.6738
3	EC4070003	79.2	3.1221	80.4264	-1.2264
7	EC4070003	63.2	3.1221	65.2402	-2.0402
14	EC4070003	48.6	3.1221	51.1716	-2.5716
28	EC4070003	45.8	3.1221	38.4714	7.3286
42	EC4070003	30.2	3.1221	30.8124	-0.6124
56	EC4070003	21.9	3.1221	24.8841	-2.9841
100	EC4070003	13.6	3.1221	12.7589	0.8411
0	M1water	0.4	3.1708	0	0.4000
3	M1water	12.9	3.1708	15.5174	-2.6174
7	M1water	25.7	3.1708	24.8724	0.8276
14	M1water	32.4	3.1708	27.3618	5.0382
28	M1water	15.5	3.1708	20.607	-5.1070
42	M1water	11.7	3.1708	14.8956	-3.1956
56	M1water	11.8	3.1708	11.4266	0.3734
100	M1water	9.9	3.1708	6.5809	3.3191
0	M1sediment	0.1	1.7630	0	0.1000
3	M1sediment	1.2	1.7630	1.4047	-0.2047
7	M1sediment	6.1	1.7630	5.9577	0.1423
14	M1sediment	13	1.7630	16.0747	-3.0747
28	M1sediment	31.5	1.7630	33.6079	-2.1079
42	M1sediment	47.7	1.7630	45.4116	2.2884
56	M1sediment	55.3	1.7630	53.3617	1.9383
100	M1sediment	64.9	1.7630	66.1710	-1.2710
0	NER	0.2	0.7673	0	0.2000
3	NER	1.7	0.7673	1.3274	0.3726
7	NER	1.7	0.7673	2.4412	-0.7412
14	NER	3.4	0.7673	3.5336	-0.1336
28	NER	3.6	0.7673	4.7914	-1.1914
42	NER	6.7	0.7673	5.8778	0.8222

[14] Please note that the Chi-square values for k M1water, k M1sediment and kNER are elevated. Therefore the absolute values of the reaction constants should be interpreted with caution. See also remark on t-test.
[15] According to the t-test this values is essentially zero, meaning that there is no degradation in M1 Sediment. The resulting endpoint M1 DT50 has to be taken with care.
[16] According to the t-test this values is essentially zero, meaning that there is no degradation in NER.

56	NER	8.2	0.7673	6.9681	1.2319
100	NER	9.8	0.7673	10.3924	-0.5924

4. Simulation of UV-328 with data from the soil study of Lai et al. (2014)

4.1. SFO: Treatment 1 (one time application in 2007) during spring to autumn 2011

The model setup considered in this case is very simple. All UV-328 disappears into a sink. (see Figure 72).

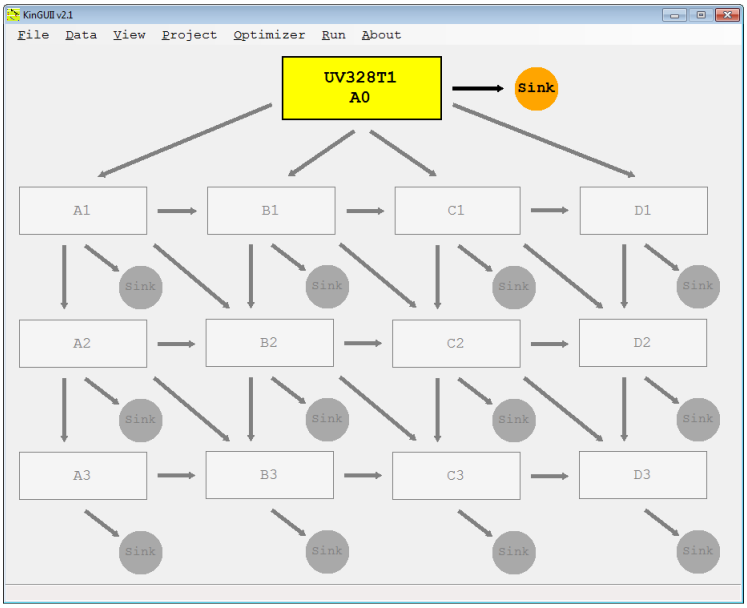


Figure 72: Overview of the model system for simulating treatment 1 according to Lai.

The data shown in Figure 73 are adequately described by SFO as Figure 74 shows that the residuals are random and non systematic. Chi^2 is acceptable.

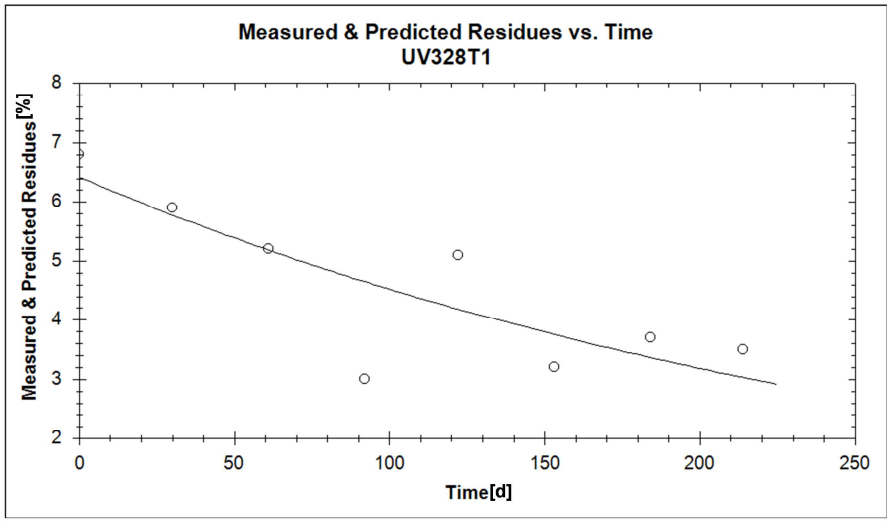


Figure 73: Measured and predicted residues of UV-328 in Treatment 1 vs. time – SFO.

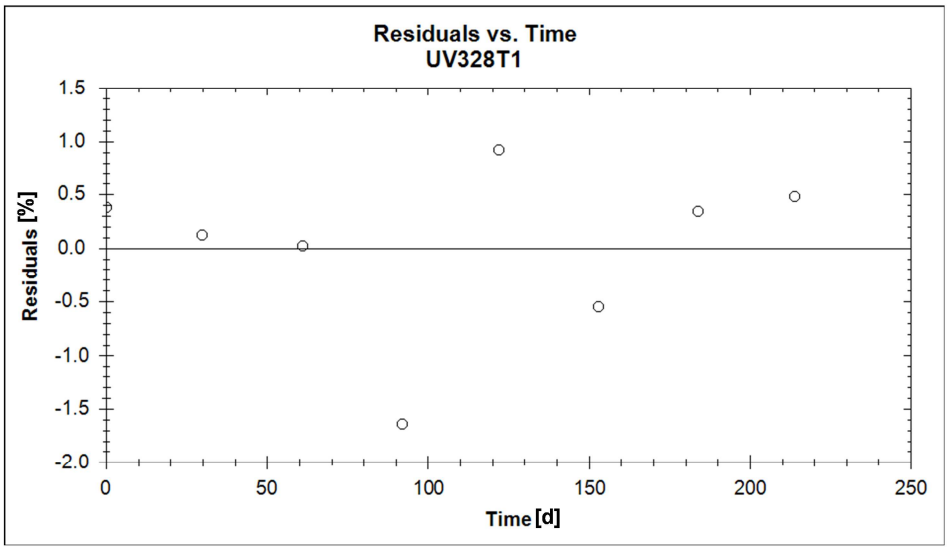


Figure 74: Residuals of UV-328 in Treatment 1 vs. time- SFO.

Table 38: Chi^2 and dissipation times of UV-328 in treatment 1 using SFO kinetic

Parameter	UV328T1	All	Kinetic model
Chi2Err%	12.92	12.92	SFO
DT50 in d	196.96		
DT90 in d	654.30		

Table 39: Kinetic Parameters of the simulation (Degrees of Freedom: 6)

Parameter	Estimate	Lower 95% CI	Upper 95% CI	St.Dev	Result t-test
M0 UV328T1	6.42	5.20	7.65	0.62	$2.5*10^{-5}$
k UV328T1	3.5197 E-03	1.5858 E-03	5.0 E-03	9.867 E-04	$5.9*10^{-3}$

Table 40: Measured vs. predicted values

Time [d]	Observed [%]	err-std [%]	Predicted [%]	Residual [%]
0	6.8	0.7887	6.4204	0.3796
30	5.9	0.7887	5.7770	0.1230
61	5.2	0.7887	5.1798	0.0202
92	3.0	0.7887	4.6444	-1.6444
122	5.1	0.7887	4.1790	0.9210
153	3.2	0.7887	3.7470	-0.5470
184	3.7	0.7887	3.3597	0.3403
214	3.5	0.7887	3.0230	0.4770

4.2. SFO: Treatment 2 (yearly repeated application between 2007 and 2010) during spring to autumn 2011

Again the model setup considered in this case is very simple. All UV-328 disappears into a sink. (see Figure 75).

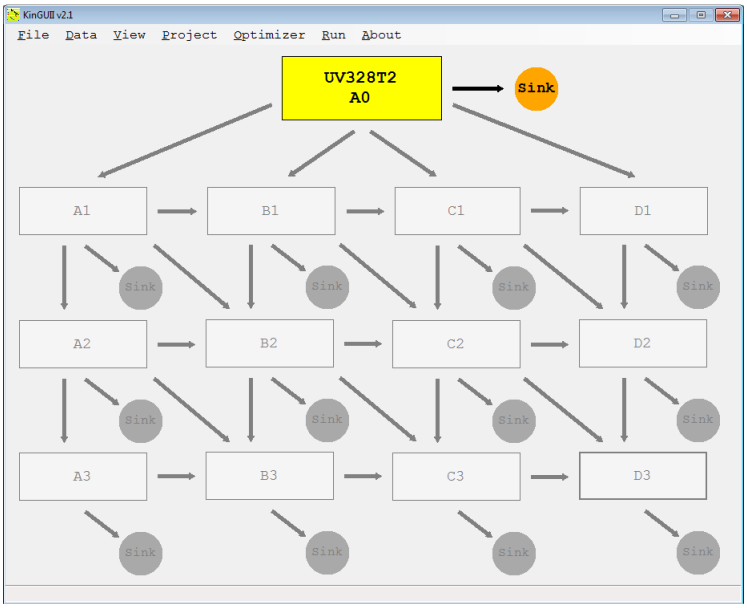


Figure 75: Overview of the model system for simulating treatment 2 according to Lai

The data shown in Figure 76 are adequately described by SFO as Figure 77 shows that the residuals are random and non systematic. Chi^2 is acceptable.

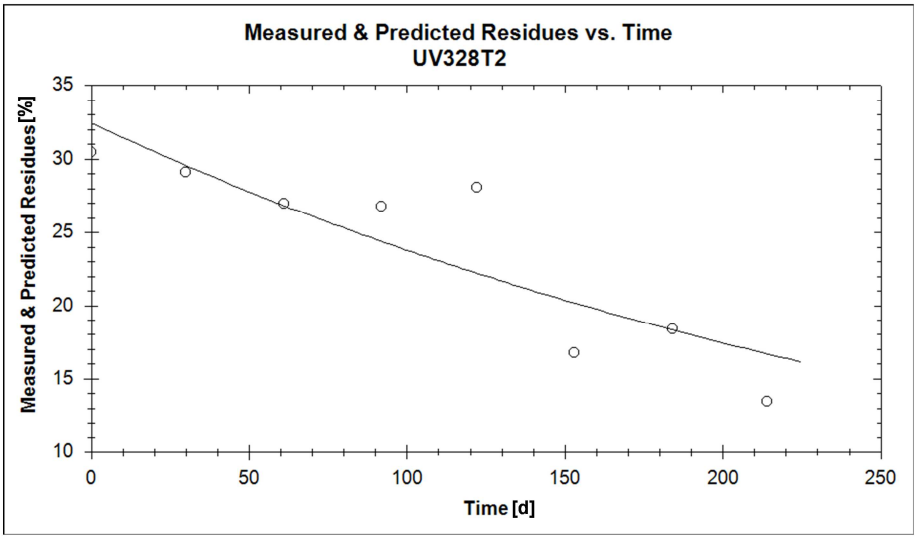


Figure 76: Measured and predicted residues of UV-328 in treatment 2 vs. time – SFO.

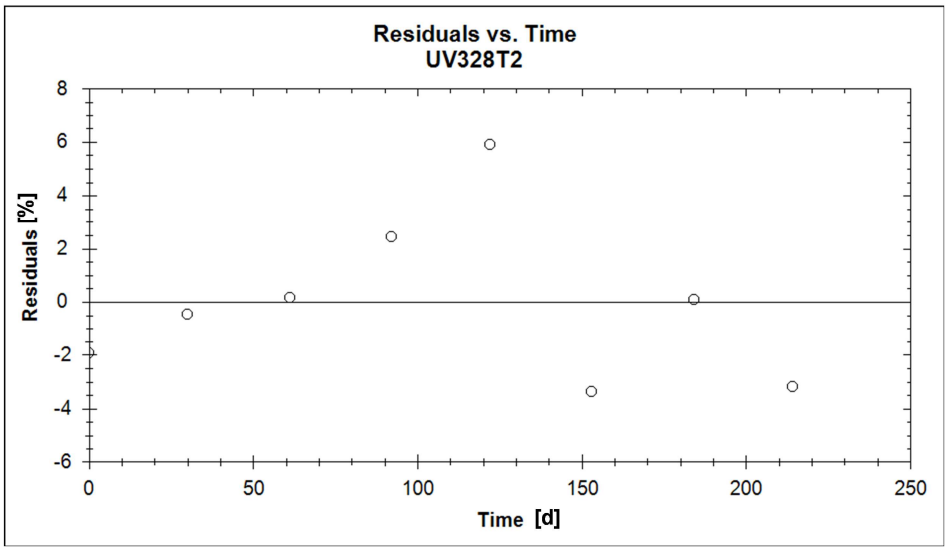


Figure 77: Residuals of UV-328 in Treatment 2 vs. time- SFO.

Table 41: Chi^2 and dissipation times of UV-328 in treatment 2 using SFO kinetic

Parameter	UV328T2	All	Kinetic model
Chi2Err%	9.637	9.637	SFO
DT50 in d	222.830		
DT90 in d	740.230		

Table 42: Kinetic Parameters of the simulation (Degrees of Freedom: 5)

Parameter	Estimate	Lower 95% CI	Upper 95% CI	St.Dev	Result t-test
M0 UV328T2	3,24E+01	2,77E+01	37,149	2,40E+00	$5.1*10^{-6}$
k UV328T2	3,11E-03	1,69E-03	0,005	7,26E-04	$2.6*10^{-3}$

Table 43: Measured vs. predicted values

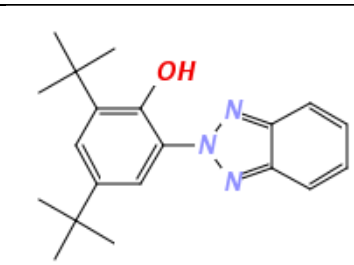
Time [d]	Observed [%]	err-std [%]	Predicted [%]	Residual [%]
0	30.5	3.0727	32.4400	-1.9400
30	29.1	3.0727	29.5494	-0.4494
61	27.0	3.0727	26.8328	0.1672
92	26.8	3.0727	24.3660	2.4340
122	28.1	3.0727	22.1948	5.9052
153	16.8	3.0727	20.1544	-3.3544
184	18.4	3.0727	18.3015	0.0985
214	13.5	3.0727	16.6707	-3.1707

ANNEX 2: Analysis of QSAR Application: Prediction of log KOC for UV-320 and UV-328

A Information on substances and purpose

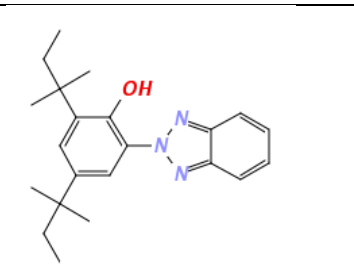
Molecule 1:

Name:	2-benzotriazol-2-yl-4,6-di-tert-butylphenol (UV-320)
CAS Nr.	3846-71-7
EU Nr.	223-346-6
Smiles	c1(c(c(cc(c1)C(C)(C)C)C(C)(C)C)O)N(N=C2C=C3)N=C2C=C3



Molecule 2:

Name:	2-(2H-benzotriazol-2-yl)-4,6-ditertpentylphenol (UV-328)
CAS Nr.	25973-55-1
EU Nr.	247-384-8
Smiles	c1(c(c(cc(c1)C(C)(C)CC)C(C)(C)CC)O)N(N=C2C=C3)N=C2C=C3



Endpoint	Logarithmic Partition coefficient of soil organic carbon and water
Regulatory purpose	PBT-Assessment, supporting information for a weight of evidence approach to identify the substances as vP

B Relevant structure information

Parameter	**Result**	**Rationale**
Structure identification		
Structure of concern	parent	Substances are mono-constituents
Descriptors used for QSAR prediction		
Correction factors (KOCWIN KOW/MCI)	Applicable	All fragments are represented by the model
σ (COSMOtherm)	Applicable	The polarity was calculated on molecular structures geometrically optimized with Density-Functional-Theory (functional: Becke-Perdew 86, basis set of Triple-Zeta-Valence-Polarization-quality), all parameters for this method and all elements of the molecules are implemented
Other relevant information		
-	-	-

C QSAR models used

Model	Version	Endpoint	QMBI
(PC)KOCWIN - KOW method	V2.0	log K_{OC}	Annex 2.1
(PC)KOCWIN - MCI method	V2.0	log K_{OC}	Annex 2.2
COSMOtherm (K_{OC})	v. C30_1201	log K_{OC}	Annex 2.3

D Analysis of QSAR model performance

Model	QSAR result	Overall model performance	QPREF
KOCWIN KOW method	UV-320: 4.63	Reliable with restrictions	Annex 2.4
	UV-328: 5.18		
KOCWIN MCI method	UV-320: 5.07	Reliable with restrictions	Annex 2.4
	UV-328: 5.65		
COSMOtherm (K_{OC})	UV-320: 5.17	Reliable with restrictions	Annex 2.4
	UV-328: 5.46		

E Overall conclusion

Overall QSAR Result	Irrespective of the employed model all four substances have a high log K_{OC}. There does not seem to be a general systematic shift between the models and there is also no general order of the values when comparing the relative order of the results in the three models.
Rational	The log K_{OC} for the substances and all models is in the range of 4.63 to 5.65 log-units
Reliability	Reliable with restrictions.

Conclusion with regard to the regulatory purpose
The log K_{OC}-values for both substances are high in all three models. The predictions are all in the same region, therefore these substances are similar in their behaviour. According to the prediction the substances will bind strongly to (sediment, soils, particulate matter) in the environment and therefore will mostly not be available for degradation processes.

ANNEX 2.1: QMBI KOCWIN KOW-method

	Information	Literature references or Links	Remarks
0 - General			
Model name and version	(PC)KOCWIN v.2 - KOW method	Online Help of KOCWIN	The KOCWIN – KOW method is essentially an extension of the MCI method were the descriptor MCI was replaced with K_{OW}. The same Trainings Sets and Validation Sets as for the MCI method were used and also the same Correction factors are applied. Overall the statistical performance of the KOW method is not quite as good as the MCI method.
W.a.[17]: software package	EPISUITE Estimation Programs Interface Suite™ for Microsoft® Windows, v4.10	http://www.epa.gov/oppt/exposure/pubs/episuite.htm	
1 - Definition of Endpoint			
Endpoint [units] (w.a. species and other relevant information)	Soil adsorption coefficient K_{OC} given as a logarithmic value		Definition of K_{OC} according to Lyman et al, 1990: "the ratio of the amount of chemical adsorbed per unit weight of organic carbon (oc) in the soil or sediment to the concentration of the chemical in solution at equilibrium" Koc = (µg adsorbed/g organic carbon) / (µg/mL solution) [L/kg or mL/g]
2 – Definition of Algorithm			
Brief description of algorithm and/or link to full definition	Non-polar chemicals (i.e. compounds where no correction factor is needed): log K_{oc} = 0.8679 Log K_{ow} - 0.0004 Polar chemicals (i.e. compounds where a correction factor is needed): log K_{oc} = 0.55313 Log K_{ow} + 0.9251 + $\Sigma P_f N$	See Online Help of KOCWIN	The equations were developed in a two separate regression calculations since this approach is statistically more accurate than the approach taken in the MCI-method

[17] w.a.: when applicable

List of employed descriptors with units	Log KOW: logarithm of the n-octanol/water partition coefficient; P_f: correction factor for chemical class of functional group f; N: number of times chemical class or functional group f occurs	List of P_f available in Online Help of KOCWIN, Appendix D	
Number of Chemicals in Training Set and Brief description of it	Training Set comprises of non-polar set (68 chemicals) and a polar set (447 chemicals) taken from several literature sources. One compound of the original non-polar training set (hexabromobiphenyl) was not considered since there was no recommended experimental log K_{OW}.		Training Estimation Error: within <= 0.20 - 44.2% within <= 0.40 - 76.9% within <= 0.60 - 93.0% within <= 0.80 - 98.6% within <= 1.00 - 100% non-polar Training Set (n=68): r^2=0.877; std. dev.=0.478; avg. dev.= 0.371 polar Training Set (n=447): r^2=0.855; std. dev.=0.396; avg. dev.= 0.307
W.a.: Training set available at		Non-Polar Training Set: Online Help of KOCWIN, Appendix E Polar Set: Online Help of KOCWIN, Appendix F	
3 – Definition of the Applicability Domain			
W.a.: Definition of the Applicability Domain	Currently there is no universally accepted definition of model domain. Log Koc estimates are less accurate for compounds outside the MW range of the training set compounds and/or that have more instances of a given fragment than the maximum for all training set compounds. It is also possible that a compound may have a functional group(s) or other structural features not represented in the training set, and for which no fragment coefficient or correction factor was developed	List of correction factors available in Online Help of KOCWIN, Appendix D Non-Polar Training Set: Online Help of KOCWIN, Appendix E Polar Training Set: Online Help of KOCWIN, Appendix F	
Limits of the Applicability Domain	Molecular weight: 32.04-665.02 g/Mol Fragments and Functional groups according to Training Sets and correction factors for best results		

4 – Information on the Validation of the Model			
Validation Set Type	Internal, 150 compounds from the same sources as the Training Set. Eight ammonium and metal salt compounds were removed from the original Validation dataset of the MCI method. Compound Pool was split before regression into Training Set and Validation Set.		
W.a.: Validation available at		Online Help of KOCWIN, Appendix G	
Statistical information on validity	r^2=0.778; std. dev.=0.679; avg. dev.= 0.494		
5 – Mechanistic Interpretation of the model			
W.a.: Mechanistic basis of model	The tendency of a compound to adsorb itself on organic carbon is linked with its lipophilicity. The n-octanol/water partition coefficient is one descriptor for lipophilicity.		

ANNEX 2.2: QMBI KOCWIN MCI-method

	Information	Literature references or Links	Remarks
0 – General			
Model name and version	(PC)KOCWIN v.2 - MCI method	Meylan, W., P.H. Howard and R.S. Boethling, "Molecular Topology/Fragment Contribution Method for Predicting Soil Sorption Coefficients", *Environ. Sci. Technol*. 26: 1560-7 (1992)	Besides the MCI method there is also the KOW method implemented in KOCWIN. Overall the statistical performance of the MCI method is better than the KOW method.
W.a.[18]: software package	EPISUITE Estimation Programs Interface Suite™ for Microsoft® Windows, v4.10	http://www.epa.gov/oppt/exposure/pubs/episuite.htm	
1 - Definition of Endpoint			
Endpoint [units] (w.a. species and other relevant information)	Soil adsorption coefficient K_{OC} given as a logarithmic value		Definition of K_{OC} according to Lyman et al, 1990: "the ratio of the amount of chemical adsorbed per unit weight of organic carbon (oc) in the soil or sediment to the concentration of the chemical in solution at equilibrium" Koc = (µg adsorbed/g organic carbon) / (µg/mL solution) [L/kg or mL/g]
2 – Definition of Algorithm			
Brief description of algorithm and/or link to full definition	log Koc = 0.5213 MCI + 0.60 + $\Sigma(P_f*N)$; MCI = $\Sigma\delta i*\delta j)^{-0.5}$	See Online Help of KOCWIN	MCI: Molecular Connectivity Index (in this case: First Order) mathematical approach to describe molecular topology The equation was developed in a two step regression approach: 1. Derivation of equation

[18] w.a.: when applicable

			without correction factors using a set of non polar chemicals 2. Derivation of final equation using a set of non-polar chemicals
List of employed descriptors with units	δi: δ-value of atom i, i.e. the number of adjacent non-hydrogen atoms; δj: δ–value of atom j, i.e. the number of adjacent non-hydrogen atoms; P_f: correction factor for chemical class of functional group f; N: number of times chemical class or functional group f occurs	List of P_f available in Online Help of KOCWIN, Appendix D	
Number of Chemicals in Training Set and Brief description of it	Training Set comprises of non-polar set (69 chemicals) and a polar set (447 chemicals) taken from several literature sources		Training Set Estimation Error: within <= 0.20 - 44.2% within <= 0.40 - 76.9% within <= 0.60 - 93.0% within <= 0.80 - 98.6% within <= 1.00 - 100% non-polar Training Set (n=69): r^2=0.967; std. dev.=0.247; avg. dev.= 0.199 polar Training Set (n=447): r^2=0.90; std. dev.=0.34; avg. dev.= 0.273
W.a.: Training set available at		Non-Polar Training Set: Online Help of KOCWIN, Appendix E Polar Set: Online Help of KOCWIN, Appendix F	
3 – Definition of the Applicability Domain			
W.a.: Definition of the Applicability Domain	Currently there is no universally accepted definition of model domain. Log Koc estimates are less accurate for compounds outside the MW range of the training set compounds and/or that have more instances of a	List of correction factors available in Online Help of KOCWIN, Appendix D Non-Polar Training Set: Online Help of KOCWIN, Appendix E Polar Training Set: Online Help of KOCWIN, Appendix F	

	given fragment than the maximum for all training set compounds. It is also possible that a compound may have a functional group(s) or other structural features not represented in the training set, and for which no fragment coefficient or correction factor was developed		
Limits of the Applicability Domain	Molecular weight: 32.04-665.02 g/Mol Fragments and Functional groups according to Training Sets and correction factors for best results		
4 – Information on the Validation of the Model			
Validation Set Type	Internal, 158 compounds from the same sources as the Training Set. Compound Pool was split before regression into Training Set and Validation Set.		
W.a.: Validation available at		Online Help of KOCWIN, Appendix G	
Statistical information on validity	r^2=0.850; std. dev.=0.583; avg. dev.= 0.459		
5 – Mechanistic Interpretation of the model			
W.a.: Mechanistic basis of model	The tendency of a compound to adsorb itself on organic carbon is linked with the chemical structure. In the Molecular Correction Index information on the chemical structure, i.e. molecular size, branching, cyclization, unsaturation and (to a certain extent) heteroatom content are encoded. The different influences of chemical classes or functional groups are considered by correction factors.		

ANNEX 2.3: QMBI COSMOtherm (K_{OC})

	Information	Literature references or Links	Remarks
0 - General			
Model name and version	COSMOtherm v C30_1201		The COSMOtherm model allows in principle the calculation of all partition properties of molecules. In this QMBI only the calculation of the K_{OC} will be addressed
W.a.[19]: software package	COSMOtherm		
1 - Definition of Endpoint			
Endpoint [units] (w.a. species and other relevant information)	n-octanol/organic carbon partition coefficient given as a logarithmic value		
2 – Definition of Algorithm			
Brief description of algorithm and/or link to full definition	Log K_{OC} = 0.0168*M_0^X – 0.017*M_2^X – 0.040*M_3^X + 0.19*PM_{acc}^X – 0.27*M_{don}^X + 0.37 with $M_i^X = \int p^X \sigma^i d\sigma$ for i = 0, 2, 3. M_{acc}^X = 0 if $\sigma < 1$ e/nm^2 or = σ – 1 e/nm^2 if σ > 1 e/nm^2 and M_{don}^X = 0 if $-\sigma < 1$ e/nm^2 or = -σ – 1 e/nm^2 if $-\sigma > 1$ e/nm^2	"COSMO-RS: From Quantum Chemistry to Fluid Phase Thermodynamics and Drug Design", Andreas Klamt, Elsevier Science Ltd., Amsterdam, The Netherlands (2005), ISBN: 0-444-51994-7. "Prediction Of Soil Sorption Coefficients With A Conductor-Like Screening Model For Real Solvents", Andreas Klamt, Frank Eckert and Michael Diedenhofen, *Environmental Toxicology and Chemistry*, **21**, 2562-2566 (2002).	COSMOtherm implements the COSMO-RS theory. This theory interprets the interaction of molecules as an interaction of a larger ensemble of molecular surfaces calculated with Quantum Mechanical methods. Due to a treatment with statistical thermodynamics the macroscopic properties of interacting molecules like partition coefficients become available. If the partition is with a phase that is ill defined like organic carbon, the so called σ-moment approach is employed where a solvent is represented as a linear combination of six σ-functions. The coefficients to these functions are fitted with experimental data.
List of employed descriptors with units	σ: Screening charge density or polarity, i.e. the electrostatic screening of a solute molecule by its surrounding and its back polarization in a region with radius of ca. 0.5 Å ; p^X: sigma profile of molecule X, i.e. the sum of the probability distributions of all		

[19] w.a.: when applicable

	possible σ		
Number of Chemicals in Training Set and brief description of it	Original parameterization for COSMOtherm: 225 small- and medium-sized organic compounds with H, C, O, N, Cl atoms. The fitting was done for 650 experimental room-temperature parameters (ΔG_{hydr}, log(vapour pressure), log $K_{octanol-water}$, log $K_{hexane-water}$, log $K_{benzene-water}$, log $K_{diethyl\ ether-water}$ log K_{OC}-formula: 387 molecules (performance: r^2 = 0.72, rms = 0.62 log-units)		While the principle theory is applicable for all elements, the practical implementation needs some specific parameters to the QM-method used and the elements of the substance in question like the employed ratio for scaling the bonds of the QM-method and the van der Waals-coefficients
W.a.: Training set available at		Original parameterization for COSMOtherm: "Refinement and Parameterization of COSMO-RS", Andreas Klamt, Volker Jonas, Thorsten Bürger and John C. W. Lohrenz, *J. Phys. Chem. A* **102**, 5074-5085 (1998). Log K_{OC}-formula: "Prediction Of Soil Sorption Coefficients With A Conductor-Like Screening Model For Real Solvents", Andreas Klamt, Frank Eckert and Michael Diedenhofen, *Environmental Toxicology and Chemistry*, **21**, 2562-2566 (2002).	Original parameterization for COSMOtherm: Since the original parameterization was done further adjustments were made and parameters for further elements were introduced. While the parameters are available in the software, to our knowledge the details of the new parameterisations were not disclosed
3 – Definition of the Applicability Domain			
W.a.: Definition of the Applicability Domain	There is no formal definition of the applicability domain		
Limits of the Applicability Domain	In principle the method is completely based on first-principles meaning there is no limit of the Applicability Domain.		
4 – Information on the Validation of the Model			
Validation Set Type	The KOC-model was tested against 53 demanding chemicals achieving a rmd of 0.72		
W.a.: Validation		"Prediction Of Soil Sorption	

available at		Coefficients With A Conductor-Like Screening Model For Real Solvents", Andreas Klamt, Frank Eckert and Michael Diedenhofen, *Environmental Toxicology and Chemistry*, **21**, 2562-2566 (2002).	
Statistical information on validity	-		
5 – Mechanistic Interpretation of the model			
W.a.: Mechanistic basis of model	The interaction of a solute and a solvent is calculated in terms of a chemical potential. The difference of the chemical potentials of the solute in two different solvents is the mechanistic reason for partition effects.		

ANNEX 2.4: Analysis of QSAR prediction for UV-320 and UV-328

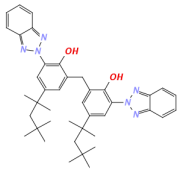
QSAR Model: KOCWIN KOW-method, KOCWIN MCI-method and COSMOtherm (K_{OC})

Overall performance

	Result		Further description
Endpoint results [unit]	KOCWIN KOW-method	UV-320: 4.63	All log KOC-values are high and in a similar region.
		UV-328: 5.18	
	KOCWIN MCI-method	UV-320: 5.07	
		UV-328: 5.65	
	COSMOtherm (K_{OC})	UV-320: 5.17	
		UV-328: 5.46	
Applicability domain	Yes		The molecules are in the range of all descriptors employed in the models.
Similarity with trainings set	Yes		All fragments or elements of the molecules are represented in the Training Set of KOCWIN. COSMOtherm has no training set but is generally applicable.
Similar substances	One		See table next side, substance is not very similar
Model performance for similar substances	Mediocre		There is just one experimental value of unknown quality for a substance not very similar to the substances at hand. The prediction for this substance is much higher than the experimental value but both values are high.
Other uncertainties	No		-

Overall conclusion	Reliable
Rational	As the models are applicable and results for similar molecules and two of the four models at hand show values in the same range it can be expected that the range is correctly predicted.

Results for similar substances

	Substance 1
Structure	
CAS-Nr.	103597-45-1
EU-Nr.	403-800-1
(Trade-)Name	UV-360
Descriptor value	KOCWIN KOW-method : log K_{OC} = 11.08 KOCWIN KOW-method : log K_{OC} = 8.22 COSMOtherm: log K_{OW} = 7.91
Predicted endpoint	See above

Experimental endpoint	5.63
Statistical performance	-

Rationale for the selection of similar substances

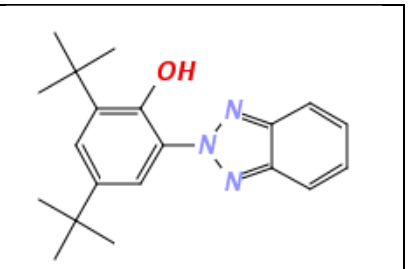
Substance 1 is a phenolic benzotriazole as the target molecule but it is a molecule comprised of two phenolic benzotriazole bodies therefore the similarity is not very high. Since the functional groups are nevertheless the same and since there are no other phenolic benzotriazoles where an experimental log K_{OC} is reported, UV-360 was chosen as point of reference.

ANNEX 3: Analysis of QSAR Application: Prediction of log KOW for UV-320 and UV-328

A Information on substances and purpose

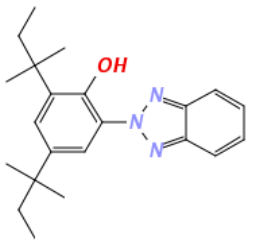
Molecule 1:

Name:	2-benzotriazol-2-yl-4,6-di-tert-butylphenol (UV-320)
CAS Nr.	3846-71-7
EU Nr.	223-346-6
Smiles	c1(c(c(cc(c1)C(C)(C)C)C(C)(C)C)O)N(N=C2C=C3)N=C2C=C3



Molecule 2:

Name:	2-(2H-benzotriazol-2-yl)-4,6-ditertpentylphenol (UV-328)
CAS Nr.	25973-55-1
EU Nr.	247-384-8
Smiles	c1(c(c(cc(c1)C(C)(C)CC)C(C)(C)CC)O)N(N=C2C=C3)N=C2C=C3



Endpoint	Logarithmic Partition coefficient of octanol-water
Regulatory purpose	PBT-Assessment, supporting information

B Relevant structure information

Parameter	**Result**	**Rationale**
Structure identification		
Structure of concern	parent	Substances are mono-constituents
Descriptors used for QSAR prediction		
Fragment descriptors (KOWWIN)	applicable	All fragments are represented by the model
σ (COSMOtherm)	applicable	The polarity was calculated on molecular structures geometrically optimized with employing Density-Functional-Theory (functional: Becke-Perdew 86, basis set of Triple-Zeta-Valence-Polarization-quality), all parameters for this method and all elements of the molecules are implemented
Other relevant information		
-	-	-

C QSAR models used

Model	**Version**	**Endpoint**	**QMBI**
KOWWIN	v1.68	log K_{OW}	Annex3.1

COSMOtherm (K_{OW})	v. C30_1201	log K_{OW}	Annex 3.2

D Analysis of QSAR model performance

Model	QSAR result	Overall model performance	QPREF
KOWWIN	UV-320: 6.27	Reliable	Annex 3.3
	UV-327: 6.91		
	UV-328: 7.25		
	UV-350: 6.31		
COSMOtherm (K_{OW})	UV-320: 7.39	Reliable	Annex 3.3
	UV-327: 7.91		
	UV-328: 7.89		
	UV-350: 7.11		

E Overall conclusion

Overall QSAR Result	Both substances have a very high log K_{OW} that is above the screening criterion for bioaccumulation in the PBT-assessment. The substances behave similar. Also KOWWIN predicts log KOWs approximately 0.8-1.0 log units smaller than COSMOtherm. The values of KOWWIN are nearer to the available experimental values.
Rationale	Not B-Screening criteria according to ECHA Guidance R.11 is log K_{OW} < 4.5
Reliability	Reliable

Conclusion with regard to the regulatory purpose
The log K_{OW}-values for all four substances are high and therefore a high bioaccumulation potential is expected. This expectation is confirmed by the available experimental BCF-values. All four substances have log K_{OW}-values in the same region. While there seems to be a systematic shift between the results there is no such shift observed for the relative order of the values.

ANNEX 3.1: QMBI KOWWIN

	Information	Literature references or Links	Remarks
0 - General			
Model name and version	KOWWIN 1.68	Meylan, W.M. and P.H. Howard. 1995. Atom/fragment contribution method for estimating octanol-water partition coefficients. J. Pharm. Sci. 84: 83-92.	
W.a.[20]: software package	EPISUITE Estimation Programs Interface Suite™ for Microsoft® Windows, v4.10	http://www.epa.gov/oppt/exposure/pubs/episuite.htm	
1 - Definition of Endpoint			
Endpoint [units] (w.a. species and other relevant information)	n-octanol/water partition coefficient given as a logarithmic value		
2 – Definition of Algorithm			
Brief description of algorithm and/or link to full definition	Log K_{OW} = $\Sigma(f_i*n_i)+ \Sigma (c_j*n_j)$ + 0.229	See Online help of KOWWIN	Derived by multiple regression of training set in a two step procedure: 1. Derivation of f_i 2. Introduction of c_j
List of employed descriptors with units	f_i: coefficient for each atom or fragment i; n_i: number of times fragment/atom i occurs; c_j: coefficient for correction instance j; number of times a structure that leads to a correction instance occurs	See Online help of KOWWIN, Appendix D	There are 157 different atoms and fragments defined and 278 correction factors that are employed when certain chemical classes or functional groups are present in the molecule for which an estimation is made
Number of Chemicals in Training Set and Brief description of it	2447 chemicals with measured log K_{OW}-values from the PhysProp Database		Training Set Estimation Error: within <= 0.10 - 45.0% within <= 0.20 - 72.5% within <= 0.40 - 92.4% within <= 0.50 - 96.4% within <= 0.60 - 98.2%
W.a.: Training		List available at	

[20] w.a.: when applicable

set available at		http://esc.syrres.com/interkow/KowwinData.htm	
3 – Definition of the Applicability Domain			
W.a.: Definition of the Applicability Domain	Currently there is no universally accepted Applicability Domain, but in principle by molecular weight range and by fragments and their maximum occurrence, both defined by the Training Set; while also substances with specific behaviour in liquids like dissociation or surfactant-specific properties were included, these are not explicitly considered in the model		With exceedingly high or low log K_{OW} the experimental errors for determination of log K_{OW} will become larger and therefore the uncertainty. In such cases the predicted values will be more uncertain as well.
Limits of the Applicability Domain	18.02 to 719.92 [g/Mol], for Structural Domain see Training Set		
4 – Information on the Validation of the Model			
Validation Set Type	Approximately 10.946 chemicals from different sources		
W.a.: Validation available at		List available at http://esc.syrres.com/interkow/KowwinData.htm	
Statistical information on validity	Validation Set Estimation Error: within <= 0.20 - 39.6% within <= 0.40 - 66.0% within <= 0.50 - 75.6% within <= 0.60 - 82.5% within <= 0.80 - 91.6% within <= 1.00 - 95.6% within <= 1.20 - 97.7% within <= 1.50 - 99.1%		Details available in Online help of KOWWIN
5 – Mechanistic Interpretation of the model			
W.a.: Mechanistic basis of model	Fragment coefficients and correction factors reflect the impact of certain chemical fragments or functional groups on lipophilicity and thus on the log K_{OW}.		

ANNEX 3.2: QMBI COSMOtherm KOW

	Information	Literature references or Links	Remarks
0 - General			
Model name and version	COSMOtherm v C30_1201		The COSMOtherm model allows in principle the calculation of all partition properties of molecules. In this QMBI only the calculation of the K_{OW} will be addressed
W.a.[21]: software package	COSMOtherm		
1 - Definition of Endpoint			
Endpoint [units] (w.a. species and other relevant information)	n-octanol/water partition coefficient given as a logarithmic value		
2 – Definition of Algorithm			
Brief description of algorithm and/or link to full definition	log K_{OW} (T)= $\int p^i(\sigma)(\mu_{water}(\sigma;T) - \mu_{octanol}(\sigma;T))d\sigma + \mu_i^C$(water, T) - μ_i^C(octanol,; T), where μ_i^C(S, T) = RT* [λ_0* ln r_i + λ_1*(1-(r_i/$\underline{r}$ –ln $\underline{r}$)+ λ_2*(1-q_i/$\underline{q}$ –ln $\underline{q}$)] and $\underline{r}$ = Σ_I x_i*r_i and $\underline{q}$ = Σ_i x_i*q_i	"COSMO-RS: From Quantum Chemistry to Fluid Phase Thermodynamics and Drug Design", Andreas Klamt, Elsevier Science Ltd., Amsterdam, The Netherlands (2005), ISBN: 0-444-51994-7.	COSMOtherm implements the COSMO-RS theory. This theory interprets the interaction of molecules as an interaction of a larger ensemble of molecular surfaces calculated with Quantum Mechanical methods. Due to a treatment with statistical thermodynamics the macroscopic properties of interacting molecules like partition coefficients become available.
List of employed descriptors with units	R: Ideal gas constant [kcal/(mol K)], T: temperature [K]; σ: Screening charge density or polarity, i.e. the electrostatic screening of a solute molecule by its surrounding and its back		

[21] w.a.: when applicable

	polarization in a region with radius of ca. 0.5 Å ; $p^i(\sigma)$: sigma profile of molecule i, i.e. the sum of the probability distributions of all possible σ; $\mu_{water}(\sigma;T)$: sigma potential of water at temperature T, a sigma potential can be interpreted as the affinity of a molecule for a surface of polarity σ; $\mu_{octanol}(\sigma;T)$: sigma potential of octanol at temperature T; $\mu_i^C(S;T)$: combinatorial contribution to the chemical potential of molecule i in solvent S at temperature T; λ_0, λ_1, λ_2: adjustable parameters, r_i: molecular volume of substance i, q_i: molecular area of substance i, r: overall volume of the mixture, g: overall area of the mixture.		
Number of Chemicals in Training Set and brief description of it	Original parameterisation: 225 small- and medium-sized organic compounds with H, C, O, N, Cl atoms. The fitting was done for 650 experimental room-temperature parameters (ΔG_{hydr}, log(vapour pressure), log $K_{octanol-water}$, log $K_{hexane-water}$, log $K_{benzene-water}$, log $K_{diethyl\ ether-water}$		While the principle theory is applicable for all elements, the practical implementation needs some specific parameters to the QM-method used and the elements of the substance in question like the employed ratio for scaling the bonds of the QM-method and the van der Waals-coefficients
W.a.: Training set available at		"Refinement and Parameterization of COSMO-RS", Andreas Klamt, Volker Jonas, Thorsten Bürger and John C. W. Lohrenz, *J. Phys. Chem. A* **102**, 5074-5085 (1998).	Since the original parameterization was done further adjustments were made and parameters for further elements were introduced. While the parameters are available in the software, to our knowledge the details of the new parameterisations were not disclosed
3 – Definition of the Applicability Domain			
W.a.: Definition of	There is no formal definition of the applicability domain		

the Applicability Domain			
Limits of the Applicability Domain	In principle the method is completely based on first-principles meaning there is no limit of the Applicability Domain.		
4 – Information on the Validation of the Model			
Validation Set Type	To our knowledge there is no single validation set but there are several citations in literature on the accuracy/validity of the model		
W.a.: Validation available at		Overview over publications: http://www.cosmologic.de/index.php?cosId=4150&crId=10	
Statistical information on validity	-		
5 – Mechanistic Interpretation of the model			
W.a.: Mechanistic basis of model	The interaction of a solute and a solvent is calculated in terms of a chemical potential. The difference of the chemical potentials of the solute in two different solvents is the mechanistic reason for partition effects.		

ANNEX 3.3: Analysis of QSAR prediction for UV-320 and UV-328

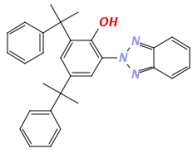
QSAR Model: KOWWIN and COSMOtherm (K_{OW})

Overall performance

	Result		Further description
Endpoint results [unit]	KOWWIN	UV-320: 6.27	All log KOW-values are high and in a similar region. There seems to be a systematic shift between the two models where KOWWIN predicts in general lower values.
		UV-328: 7.25	
	COSMO-therm (K_{OW})	UV-320: 7.39	
		UV-328: 7.89	
Applicability domain	Yes		The molecules are in the range of all descriptors employed in the models and in the range of the molecular weight of the molecules in the training set of KOWWIN.
Similarity with trainings set	Yes		All fragments or elements of the molecules are represented in the Training Set of KOWWIN. COSMOtherm has no training set but is generally applicable.
Similar substances	Yes		See table next side
Model performance for similar substances	Concerning the range of values good, but absolute values seem to be slightly overestimated		Experimental Values and predictions show a systematic shift but caution has to be advised as the experimental values were not validated.
Other uncertainties	No		-

Overall conclusion	Reliable
Rational	As the models are applicable and results for similar molecules and two of the four models at hand show values in the same range it can be expected that the range is correctly predicted.

Results for similar substances

	Substance 1
Structure	
CAS-Nr.	70321-86-7
EU-Nr.	274-570-6
(Trade-)Name	UV-234
Descriptor value	KOWWIN : log K_{OW} = 7.67 COSMOtherm: log K_{OW} = 8.30
Predicted endpoint	See above
Experimental endpoint	> 6.5
Statistical performance	-

Rationale for the selection of similar substances

Substance 1 is structurally similar as it is a phenolic benzotriazole as the target molecule. It also has a sterical demanding side chain in ortho- and one in para-position to the hydroxyl group. The difference lies in the substitution of a phenyl group for a methyl group. Therefore, it is probably to some degree more lipophilic as UV-320 and UV-328.

ANNEX 4: Monitoring Study Results for Phenolic Benzotriazoles

Monitoring of phenolic benzotriazoles

Monitoring studies are summarized concerning the following phenolic benzotriazoles:

UV-234 (CAS 70-321-86-7), -320 (CAS 3846-71-7), -326 (CAS 3896-11-5), -327 (CAS 3864-99-1), -328 (CAS 25973-55-1), -329 (CAS 3147-75-9), -350 (CAS 36437-37-3), -360 (CAS 103597-45-1) and -571 (CAS 125304-04-3). No monitoring studies were found for UV-928 (CAS 73936-91-1).

European studies:

Brorström-Lundén et al. (Brorström-Lundén et al., 2011) published a screening study on benzotriazoles (UV-234, -320, -327, -328, -329, -360). Phenolic benzotriazoles may to a large extent enter Sweden through imported finished goods. Emissions via diffuse sources were assumed as the main pathway of benzotriazole UV-absorbers to the environment. The sampling program was therefore focused on emissions in urban environments (Stockholm area and smaller city Borås). In addition, background sites were included and two sites with potential point sources. Benzotriazoles were analysed using an LC-MS system including a tandem mass-spectrometer. Detection limits vary with analysed substance and sample. Compared to other studies the detection limits for sediment, soil, particles, WWTP sludge and fish are high.

Table 44: Detection limits in the investigation of Brorström-Lundén et al.

Compartment	Detection limits	Compartment	Detection limits
Air	0.01 – 0.48 ng/m³	storm water	0.03 – 0.1 ng/L
air deposition	30 – 200 ng/m² day	landfill effluent particles	0.7 -1.6 µg/g dw
surface water	0.03 – 0.09 ng/L	landfill effluent	0.08 – 0.5 ng/L
Sediment	0.2 – 12 µg/g dw	WWTP effluent particles	61 – 130 µg/g dw
Soil	0.1 – 0.9 µg/g dw	WWTP effluent	0.04 – 0.1 ng/L
Fish	0.3 – 1.9 µg/g dw	Sludge	0.1 – 0.6 µg/g dw

In air samples four benzotriazole UV-absorbers were detected (UV-320, -327, -329, -360). Concentrations were similar in background and urban air. However, the highest concentration was measured in Stockholm. Only two compounds were detected in atmospheric deposition (UV-327, -329). The deposition was higher at the urban site.

Table 45: Concentrations of phenolic benzotriazoles in air and atmospheric deposition in Sweden

Substance	Air		Deposition	
	detected in x of y samples [x/y]	concentration [ng/m³]	detected in x of y samples [x/y]	deposition flux [ng/m² day]
UV-234	0/8	-	0/4	-
UV-320	3/8	0.024 – 0.67	0/4	-
UV-327	6/8	0.40 - 25	3/4	<100-320
UV-328	0/8	-	0/4	-
UV-329	5/8	< 0.15 – 3.0	3/4	<100-331
UV-360	1/8	0.40	0/4	-

Several benzotriazoles were found in soil, in rather similar concentrations at the background and the urban locations (UV-320, -327, -328, -329). There were differences in the occurrence among the individual substances at the different locations. According to the authors, the highest concentration of a single substance (UV-329) was found in soil 500 m from a busy road in the Stockholm area. However, according to the annex of the study such a high concentration

was also found for UV-327 in another urban sample. Since only four samples were analysed altogether, the results should generally be interpreted with care.

Several of the benzotriazoles were frequently detected in surface water (UV-320, -327, -328, -329). The concentrations were mostly similar at background and urban locations. In sediments the distribution among different substances varied for the different sampling sites. Peaks of single substances occurred both at background and urban locations; the lower concentration levels were similar at different locations.

Three of the benzotriazoles were found in fish, both at urban and background locations (UV-324, -327, -329). The highest concentration was found at the background location (UV-327). The concentrations found in Swedish fish are 1000fold higher than those found in Japanese fish. The reason for this is unknown. The authors note however that most substances are not detected and the levels found are quite close to the detection limit of the method used.

Table 46: Concentrations of phenolic benzotriazoles in soil and fish in Sweden

Substance	**Soil**		**Fish**	
	detected in x of y samples [x/y]	concentration [µg/g dw]	detected in x of y samples [x/y]	concentration [µg/g dw]
UV-234	0/4	-	1/4	0.26
UV-320	1/4	0.91	0/4	-
UV-327	3/4	0.66-3.7	3/4	2.3-9.8
UV-328	1/4	0.74	0/4	-
UV-329	3/4	0.79-3.7	3/4	1-2.5
UV-360	0/4	-	0/4	-

Table 47: Concentrations of phenolic benzotriazoles in surface water and sediment in Sweden

Substance	**Surface water**		**sediment**	
	detected in x of y samples [x/y]	concentration [ng/L]	detected in x of y samples [x/y]	concentration [µg/g dw]
UV-234	0/6	-	0/6	-
UV-320	3/6	0.55-0.94	5/6	0.16-3
UV-327	4/6	0.11-0.39	6/6	1.6-35
UV-328	6/6	1.3-10	4/6	0.65-1.3
UV-329	6/6	0.25-2.4	4/6	0.81-33
UV-360	1/6	0.16	3/6	0.42-2.9

All benzotriazoles but UV-360 were detected in WWTP effluent and all substances were detected in sludge from WWTPs. However, there were differences both in concentration levels and in distribution among the different benzotriazoles between the WWTPs. A different distribution among the substances was also found in effluent and sludge. Only one sample of WWTP effluent particles was analyzed and only UV-327 was detected in this sample (270 µg/g dw).

Table 48: Concentrations of phenolic benzotriazoles in WWTP effluent and sludge in Sweden

Substance	**effluent WWTP**		**sludge WWTP**	
	detected in x of y samples [x/y]	concentration [ng/L]	detected in x of y samples [x/y]	concentration [µg/g dw]
UV-234	1/5	0.11	8/8	2.1-7.3
UV-320	1/5	4	6/8	0.84-2
UV-327	4/5	0.12-0.48	7/8	0.54-17
UV328	5/5	6.8-15	4/8	2.8-37
UV-329	5/5	0.87-4.9	7/8	2.3-15
UV-360	0/5	-	8/8	4.6-23

All substances but UV-360 were found in landfill leachates, all substances but UV-329 occurred in storm water. In one sample of landfill effluent particles UV-327, -328 and -329 were

detected in concentrations of 4.3, 3.1 and 6.1 µg/g dw, respectively.

Table 49: Concentrations of phenolic benzotriazoles in effluent landfill and storm water in Sweden

Substance	effluent landfill		storm water	
	detected in x of y samples [x/y]	concentration [ng/L]	detected in x of y samples [x/y]	concentration [ng/L]
UV-234	2/3	0.16 and 0.5	4/4	0.06-0.31
UV-320	2/3	7.3 and 23	1/4	0.73
UV-327	2/3	0.45 and 1.3	3/4	0.13-0.17
UV-328	3/3	7-91	3/4	0.19-1.3
UV-329	1/3	17	0/4	-
UV-360	0/3	-	2/4	0.17 and 0.28

In summary widespread occurrence of benzotriazoles in the Swedish environment was observed both in background and urban areas. The substances occurred in all environmental matrices included in the study: air, deposition, surface water, sediment, soil and biota. Diffuse spreading through WWTPs, landfills and storm water may be important for the occurrence in the environment. Levels measured in WWTP effluents and sludge indicate widespread diffusive sources via use of products. The benzotriazoles with the highest usage volume in Sweden (UV-327, UV-328) were also most often found in the highest concentrations.

The authors conclude that on a national scale air transport may be a significant source of the compounds and that the substances are stable enough to undergo atmospheric long range transport.

Carpinteiro et al. (Carpinteiro et al., 2010a) used headspace solid-phase microextraction followed by gas chromatography tandem mass spectrometry for the sensitive determination of benzotriazole UV-stabilisers in water samples (UV-326, -327, -328). The limit of quantification was < 2 ng/l. The developed methodology was used to investigate the presence of benzotriazoles in filtered river water (three samples), two samples taken in the inlet and outlet streams of an urban WWTP and four additional specimens of raw wastewater provided by a local laboratory. Phenolic benzotriazoles were not detected in river water and treated wastewater. In raw wastewater samples UV-327 was not detected, whereas UV-326 and -328 were each found in four of five samples in concentrations ranging from 3.5-57 ng/L and 1-19 ng/L, respectively.

Carpinteiro et al. (Carpinteiro et al., 2010b) also investigated benzotriazole UV-stabilisers in indoor dust samples (UV-326, -327 and -328). Pressurized liquid extraction and gas chromatography followed by tandem in time mass spectrometry were used. The limits of quantification were between 4 and 9 ng/g. Procedural blanks showed small peaks at the retention time of some species. The source of this contamination may be related to the trend of target compounds to be retained on solid surfaces. Glass material, extraction cells and connections in the extraction system might contribute to the presence of benzotriazole UV-stabilisers in procedural blanks due to carry over problems.

Dust was collected with domestic vacuum cleaners equipped with paper filter bags from several private houses (five samples), vehicle cabins (three samples) and an administrative building (one sample). It is not stated in which country the dust was collected. However, it was assumed that it was collected in Spain. The dust fraction < 60 µm was used for the study. In addition a house dust reference material from USA was acquired. This sample was used to confirm the ubiquity of benzotriazole UV-stabilisers in dust although no certified or indicative values of their levels in the reference material were available.

UV-326, -327 and -328 were found to be ubiquitous in dust, with measured values from 22 to >600 ng/g. Moreover, UV-326 was found in one car cabin dust sample at a concentration of almost 5 µg/g.

Table 50: Levels of benzotriazole light stabilisers in dust samples (n = 3 replicates) [ng/g]

	UV-326	UV-327	UV-328
private house 1	42	86	46
private house 2	58	101	127
private house 3	333	29	100
private house 4	73	22	68
private house 5	269	52	149
public building	676	131	62
car cabin 1	4880	48	88
car cabin 2	522	127	124
car cabin 3	170	43	52
US dust reference material	121	322	259
Min-Max (Mean) of all samples except US material	42 – 4883 (780)	22 – 127 (71)	46 – 149 (91)

Carpinteiro et al. (Carpinteiro et al., 2012b) combined stir-bar sorptive extraction and liquid desorption with large volume injection-gas chromatography-mass spectrometry for the determination of benzotriazole UV-stabilisers in wastewater matrices. UV-320, -326, -327 and -328 were measured in urban sewage waters. Grab samples of wastewater were obtained from inlet and outlet streams of two urban WWTPs, equipped with primary and activated sludge treatment units, located in Portugal and Spain. The limits of quantification were between 4 and 10 ng/L. Because of the existence of significant concentrations of phenolic benzotriazoles associated with dust particles it is highly recommended to protect laboratory material from deposition of particulate matter. The efficiency of the extraction is sample dependent; therefore, the standard addition method is required for the accurate quantification of the substances in wastewater matrices.

Table 51: Average concentrations of phenolic benzotriazoles in wastewater matrices (n = 3 replicates) [ng/L]

Place, date	Type	UV-320	UV-326	UV-327	UV-328
Portugal, Nov. 2010	raw wastewater	24	26	85	76
	treated wastewater	n.d.	n.d.	31	21
Spain, Jan. 2011	raw wastewater	n.d.	40 (6)	n.d.	53
	treated wastewater	n.d.	n.d.	n.d.	n.d.
Spain, Feb. 2011	raw wastewater	n.d.	34	22	65
	treated wastewater	n.d.	n.d.	n.d.	n.d.

n.d. = not detected

Carpinteiro et al. (Carpinteiro et al., 2012a) (personal communication July 2014) also measured benzotriazole UV-absorbers in sediments. Matrix solid-phase dispersion followed by gas chromatography tandem mass spectrometry was used. The limit of quantification of the method was 3 ng/g dw for UV-320, -326, -327 and -328. Ten samples of river and estuarine sediments with different carbon contents were investigated. Fresh sediment samples were air-dried in the hood for several days then sieved. The fraction with the particle size < 0.3 mm was considered in the study. In six of the ten sediment samples quantifiable levels of UV-absorbers were detected:

Table 52: Concentrations of benzotriazole UV-absorber species measured in sediment samples (particle fraction < 0.3 mm, n=3 replicates, - = not detected)

Sample	total carbon [%]	UV-320 [ng/g dw]	UV-326 [ng/g dw]	UV-327 [ng/g dw]	UV-328 [ng/g dw]
1	3.0	5.6	32	15	56
2	3.9	-	-	10.3	10
3	5.5	-	7.8	-	8.3
4	4.6	-	-	9.5	11.2
5	2.2	-	-	-	7.9

6	8.0	-	15	-	8

Unfortunately the origin of the sediment samples is not mentioned in the study. According to the acknowledgements some of the analyzed sediment samples were supplied by the German Federal Institute of Hydrology. However, the authors could not specify which samples were from Spain and which were from Germany (personal communication April 2012).

Montesdeoca-Esponda et al. (Montesdeoca-Esponda et al., 2012) used on-line solid-phase extraction coupled to ultra-performance liquid chromatography with tandem mass spectrometry detection (SPE-UPLC-MS/MS) for the determination of UV-326, -327, -328, -329, -360 and -571 in samples from WWTP effluents and coastal marine water from Spain. The detection limits and quantification limits achieved were in the range of 0.6-4.1 ng/L and 2.1-14 ng/L. The analytical method allowed simultaneous determination of the compounds in liquid samples with satisfactory recoveries and reproducibility, except for UV-360, which cannot be completely eluted from the cartridge due to its high octanol-water partition coefficient and molecular mass.

Seawater samples were collected from six beaches around the Gran Canaria Island in Spain (two samples per beach), wastewater samples were collected from seven WWTPs of Gran Canaria Island. All substances studied were detected in the wastewater samples (see table). In seawater samples only UV-360 was found (six of twelve samples, 3.6 – 5.2 ng/L).

Table 53: Concentrations of phenolic benzotriazole UV-absorbers in samples of WWTP effluents of Gran Canaria Island

	detection frequency	**concentration(s) [ng/L]**
UV-326	1/7	11
UV-327	1/7	4.8
UV-328	5/7	6.2 – 13
UV-329	1/7	4.0
UV-360	2/7	5.9 and 6.6
UV-571	0/7	not detected

Soil and suspended solids samples from the German Environmental Specimen Bank were analysed for UV-234, -320, -326, -327, -328, -329 and -350 at the University of Santiago de Compostela (Rodríguez Pereiro and Casado Agrelo, 2012). Samples were extracted using the matrix solid-phase dispersion (MSDP) technique, with an integrated clean-up step. A GC-MS/MS method was used with a hybrid quadrupole time-of-flight mass spectrometer furnished with an electronic impact source. The limits of quantification were 2 ng/g per compound.

Soil samples were from sites with high anthropogenic influence and from background sites. Sampling sites for suspended particulate matter were chosen depending on the contamination with other substances found in previous studies at these sites. Sites with high and low contamination were selected. Five soil samples taken in 2010 and five samples of suspended particulate matter taken in 2011 were analysed. Soil samples were three litter samples, one root network sample and one top soil sample. All soil samples revealed target compound levels below the limits of quantification, also for the soils from Saarbruecken-Staden (root network) and Duebener Heide/Leipzig (litter, top soil) which are assumed to be more anthropogenically influenced. Concentrations of phenolic benzotriazoles in suspended solids samples are shown in Table 54.

Table 54: Concentrations of phenolic benzotriazoles in suspended solids samples from Germany

Suspended solids sample	**UV-234 [ng/g dw]**	**UV-320 [ng/g dw]**	**UV-326 [ng/g dw]**	**UV-327 [ng/g dw]**	**UV-328 [ng/g dw]**	**UV-329 [ng/g dw]**	**UV-350 [ng/g dw]**
Danube / Jochenstein	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Rhine /Weil	n.d.	n.d.	26	n.d.	26	n.d.	n.d.

Elbe / Cumlosen	8.1	n.d.	4.6	n.d.	n.d.	n.d.	n.d.
Saale / Wettin	15	n.d.	17	n.d.	n.d.	n.d.	n.d.
Saar / Rehlingen	17	n.d.	17	n.d.	n.d.	2.0	n.d.

n.d. = not detected

Suspended solids from the river Elbe and its tributary Saale showed similar patterns, with higher levels for the tributary Saale. Patterns for suspended solids from the rivers Saale and Saar are comparable. Both rivers revealed high burdens also for other substances. The Rhine site Weil downstream Basel is influenced by the Swiss chemical industry and has a different pattern (higher level of UV-326, only site with UV-328). The Danube site at Jochenstein was selected because of low burdens and displayed levels below the limits of quantification.

Casado et al. (2013) analysed phenolic benzotriazoles in eight samples of non-digested sludge obtained from several WWTPs located in the Northwest of Spain, in two reference materials of WWTP sludge from Belgium and USA and in one sediment sample collected close to the discharge of an urban WWTP. They used matrix solid-phase dispersion technique for extraction and gas chromatography with quadrupole time-of-flight mass spectrometry for further determination of analytes. Limits of quantification were 2-10 ng/g dw, recoveries were 70-111% with standard deviations of 2-13%. Of the nine phenolic benzotriazoles investigated UV-234, -326 and -328 displayed the highest occurrence frequencies and individual concentrations above 100 ng/g dw in several samples.

Table 55: Concentrations of phenolic benzotriazoles in WWTP sludge from Spain, sludge reference materials and a sediment sample close to a WWTP discharge

sample	UV-234 [ng/g dw]	UV-320 [ng/g dw]	UV-326 [ng/g dw]	UV-327 [ng/g dw]	UV-328 [ng/g dw]	UV-329[ng/g dw]	UV-350[ng/g dw]
biological sludge 1	126 ± 6	41 ± 6	171 ± 10	33 ± 2	152 ± 11	23 ± 1	n.d
biological sludge 2	98 ± 8	n.d.	129 ± 8	12 ± 1	124 ± 24	14.8 ± 0.8	n.d.
biological sludge 3	37 ± 8	n.d.	90 ± 5	n.d.	28 ± 3	n.d	n.d
biological sludge 4	50 ± 9	n.d.	75 ± 4	n.d	44 ± 2	n.d.	n.d.
primary sludge 1	41 ± 1	n.d.	56 ± 5	n.d.	60 ± 1	n.d	n.d
primary sludge 2	63 ± 2	n.d.	80 ± 2	n.d	74 ± 6	n.d.	n.d.
primary sludge 3	42 ± 1	n.d.	44 ± 1	n.d.	59 ± 2	n.d	n.d.
stabilised sludge	11 ± 2	n.d.	9.4 ± 0.3	n.d.	n.d.	n.d.	n.d.
reference material Belgium	30 ± 3	19 ± 1.4	154 ± 9	111 ± 3	231 ± 12	n.d.	28 ± 4
reference material USA	96 ± 13	n.d.	83 ± 7	67 ± 1	292 ± 24	64 ± 7	n.d
sediment close to WWTP	15 ± 1	n.d.	17 ± 2	n.d.	20 ± 5	n.d.	n.d.

According to the authors the most abundant phenolic benzotriazoles found in this study (UV-234, -326 and -328) matched with those reported for a larger research performed with sludge

from 60 WWTPs in China (Ruan et al., 2012). However, the detection frequency of UV-329 in this research was lower than that reported by Ruan et al.

Montesdeoca-Esponda et al. (Montesdeoca-Esponda et al., 2013) (personal communication July 2014) analysed phenolic benzotriazoles in marine sediments and sewage sludges using microwave-assisted extraction followed by a clean-up step based on on-line solid phase extraction coupled to ultra-high-performance liquid chromatography with MS/MS detection. Limits of detection were 53.3-146 ng/kg and limits of quantification 176-486 ng/kg. Recoveries were 46.1-83.9% (sludges) and 50.1-87.1% (sediments). Recoveries were satisfactory for all phenolic benzotriazoles except UV-360. Relative standard deviations were 7.8-15.5% (sludges) and 8.83-16.3% (sediments). Compounds investigated included UV-326, -327, -328, -329, -360, -571. Marine sediment samples were taken close to shore of three tourist beaches of Gran Canaria Island (Spain). In addition, a marine outfall was selected that discharges the depurated waters from a WWTP. This marine outfall is located in the southern region of Gran Canaria Island. Four sediment samples were taken at different distances from the coast (sample 1 is closest to the marine outfall, sample 4 is the farthest) Sludge samples were from three different WWTPs.

In the beach sediment samples (sand) all phenolic benzotriazoles were below the limits of detection. UV-326, -327 and -571 were below the limits of detection in all samples investigated. UV-329 was detected in both outfall marine sediments and sludges but were not quantified because their concentrations were below the limit of quantification. only UV-328 and UV-360 were detected in concentrations above the limit of quantification in marine outfall sediments and sewage sludges.

Table 56: Concentrations of phenolic benzotriazoles in marine sediments and WWTP sludge from Spain

sample	UV-326 [ng/g dw]	UV-327 [ng/g dw]	UV-328 [ng/g dw]	UV-329 [ng/g dw]	UV-360 [ng/g dw]	UV-571 [ng/g dw]
beach 1	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
beach 2						
beach 3						
marine outfall 1			24.0 ± 2.43	< LOQ	0.33 ± 0.04	
marine outfall 2			22.0 ± 2.33	< LOQ	0.19 ± 0.02	
marine outfall 3			20.7 ± 1.95	< LOD	0.18 ± 0.02	
marine outfall 4			< LOQ	< LOQ	< LOQ	
sewage sludge 1			12.2 ± 1.49	< LOD	6.32 ± 0.92	
sewage sludge 2			< LOD	< LOQ	2.30 ± 0.31	
sewage sludge 3			0.94 ± 0.11	< LOQ	< LOQ	

LOD = limit of detection, LOQ = limit of quantification

Table 57: Limits of detection and quantification

substance	limit of detection [ng/kg dw]		limit of quantification [ng/kg dw]	
	sediment	**sludge**	**sediment**	**sludge**
UV-326	99.3	146	327	486
UV-327	84.1	106	280	353
UV-328	78.4	108	260	360
UV-329	73.8	98.2	243	326

UV-360	53.3	70.7	176	233
UV-571	106	108	353	360

The Norwegian Environment Agency (2014) published results of a screening program on several substance groups including UV-234, -327, -328, -329, -360 and -571 (http://www.miljodirektoratet.no/Documents/publikasjoner/M176/M176.pdf). In 2013 samples were taken from 3 WWTPs (effluent, sludge) with different sewage treatment procedures, 2 landfills (leachate), the Oslofjord and lake Mjøsa (sediments, biota). Detection limits vary for the different compounds and different sample matrices. This has to be taken into account when considering the study results.

In WWTP effluent only UV-234 was found in a WWTP with only mechanical sewage treatment (Table 58). UV-327 and an order of magnitude higher concentrations of UV-329 were detected in sludge of two WWTPs with mechanical, chemical and biological sewage treatment.

Table 58: Concentrations of phenolic benzotriazoles in three Norwegian WWTPs. (x/y) = detection frequency; concentrations detected in x of y samples

substance	concentrations in effluents of 3 WWTPs [ng/L]	concentrations in sludge of 2 WWTPs [ng/g dw]
UV-234	81 (1/5) ?? <5 (0/5) **5-6 (3/5)**	<10.9 <13.1
UV-327	81 (1/5) ?? <10 (0/5) <10 (0/5)	**30-77 (5/5)** **83-160 (5/5)**
UV-328	81 (1/5) ?? <5 (0/5) <5 (0/5)	<10.7 (0/5) <25 (0/5)
UV-329	81 (1/5) ?? <5 (0/5) <5 (0/5)	**1172-3075 (5/5)** **1493-3303 (5/5)**
UV-360	81 (1/5) ?? <50 (0/5) <50 (0/5)	<125 (0/5) <125 (0/5)
UV-571	81 (1/5) ?? <125 (0/5) <125 (0/5)	<125 (0/5) <125 (0/5)

?? = this value is given in the report for all substances and therefore is probably an error

UV-234 was the only phenolic benzotriazole detected in leachate of a landfill in the particulate matter(**Table 59**). The levels detected were just above the detection limit. Detection limits for most other phenolic benzotriazoles were higher. Particulates of the leachate were analysed for one landfill, only. Ath the other landfill the leachate had a very low particulate content.

Table 59: Concentrations of phenolic benzotriazoles in leachate of two Norwegian landfills; (x/y) = detection frequency; concentrations detected in x of y samples

substance	concentrations in leachate of 2 landfills [ng/L]	concentrations in particulate of leachate of 1 landfill [ng/g dw]
UV-234	<5 (0/3) <5 (0/3)	**16 and 19 (2/3)**
UV-327	<10 (0/3) <10 (0/3)	<65 (0/3)
UV-328	<5 (0/3) <5 (0/3)	<25 (0/3)
UV-329	<5 (0/3) <5 (0/3)	<15 (0/3)

UV-360	<50 (0/3) <50 (0/3)	<125 (0/3)
UV-571	<125 (0/3) <125 (0/3)	<125 (0/3)

In sediments of the Oslofjord UV-327 and UV-328 were found. Concentrations were slightly higher in the vicinity of the discharge diffuser of a WWTP. In sediments of Lake Mjøsa no phenolic benzotriazoles could be detected. However, detection limits for Lake Mjøsa were higher. There was also a WWTP located at Lake Mjøsa, but its size was an order of magnitude smaller than the size of the WWTP located near the sampling stations in the Oslofjord.

Table 60: Concentrations of phenolic benzotriazoles in sediments of the Oslofjord and Lake Mjøsa. (x/y) = detection frequency; concentrations detected in x of y samples

substance	concentrations in sediments of the Oslofjord [ng/g dw]	concentrations in sediments of Lake Mjøsa [ng/g dw]
UV-234	<15 (0/5)	<4 (0/5)
UV-327	**4-8 (4/5)**	<65 (0/5)
UV-328	**3-25 (5/5)**	<25 (0/5)
UV-329	<15 (0/5)	<15 (0/5)
UV-360	<125 (0/5)	<125 (0/5)
UV-571	<125 (0/5)	<125 (0/5)

In biota of the Oslofjord UV-327 was detected in one of 15 samples of Northern shrimps and UV-328 was detected in three of 15 samples of cod liver. In biota samples of Lake Mjøsa (soft tissue of burbot, perch and whitefish) no phenolic benzotriazoles were detected. The respective detection limits are given in Table 62.

Table 61: Concentrations of phenolic benzotriazoles in biota of the Oslofjord; (x/y) = detection frequency; concentrations detected in x of y samples

substance	concentrations in cod liver [ng/g ww]	concentrations in shore crabs [ng/g ww]	concentrations in northern shrimps [ng/g ww]
UV-234	<10 (0/15)	<10 (0/15)	<10 (0/15)
UV-327	<50 (0/15)	<10 (0/15)	**52 (1/15)**
UV-328	**13-19 (3/15)**	<10 (0/15)	<10 (0/15)
UV-329	<25 (0/15)	<25 (0/15)	<25 (0/15)
UV-360	<250 (0/15)	<250 (0/15)	<250 (0/15)
UV-571	<250 (0/15)	<250 (0/15)	<250 (0/15)

Table 62: Concentrations of phenolic benzotriazoles in biota of Lake Mjøsa. (x/y) = detection frequency; concentrations detected in x of y samples

substance	concentrations in burbot soft tissue [ng/g ww]	concentrations in perch soft tissue [ng/g ww]	concentrations in whitefish soft tissue [ng/g ww]
UV-234	<10 (0/15)	<10 (0/15)	<10 (0/15)
UV-327	<50 (0/15)	<5 (0/15)	<50 (0/15)
UV-328	<10 (0/15)	<10 (0/15)	<10 (0/15)
UV-329	<25 (0/15)	<25 (0/15)	<25 (0/15)
UV-360	<250 (0/15)	<250 (0/15)	<250 (0/15)
UV-571	<250 (0/15)	<250 (0/15)	<250 (0/15)

The authors of the study conclude that

- Uv-234, UV-327 and UV-329 are entering the environment through WWTP effluent and sludge.
- landfill leachate is a source of UV-234.
- UV-327 and -328 accumulate in marine and freshwater sediments receiving treated wastewater.
- UV-327 and -328 accumulate in Oslofjord biota.

Japanese studies:

Nakata et al (Nakata et al., 2009a) studied occurrence and concentrations of UV-320, -326, -327 and -328 in marine organisms and sediments from the Ariake Sea, western Japan. 16 coastal and river sediments were collected during 2006-2007. Five of the sediment samples were taken in a heavily polluted river. 55 biota samples were collected during 2004 and 2007:

- tidal flat organisms: lugworm, lamp shell, oyster, clam, gastropod, crustaceans (crab, shrimp), fishes (herbivorous and omnivorous mudskippers)

- shallow water species: crustaceans (crab, shrimp), teleost fish (flathead, solefish, right eye flounder, sandperch, sweetlips, mullet, sea bass, hairtail), cartilaginous fish (eagle ray, hammerhead shark)

- coastal birds (spot-billed duck, mallard).

Depending on the species, the whole body, soft tissue, hepatopancreas and liver samples were analysed. 16 coastal and river sediments were also collected around the Ariake Sea during 2006-2007. UV-stabilisers were detected in all biota and sediment samples. In biota UV-326, -327 and -328 were the dominant compounds at levels of 0.1-55 ng/g ww. Concentrations of UV-320 in samples were low, it could be detected only in tidal flat organisms and some shallow water species. This may be due to small amounts of use of this compound in Japan since its domestic production and use have been restricted.

In general, concentrations of UV-stabilisers in tidal flat organisms were greater than those in shallow water species. The average concentrations of UV-320 and UV-326 in tidal flat species were approximately 10- to 20-fold higher than those in shallow water organisms. The tidal flat

clam showed the highest concentrations of UV-320 and UV-326 at 74 ng/g and 219 ng/g (lw) respectively. Elevated concentrations of UV-326 were also found in oysters and gastropods in tidal flat area. These results imply the presence of phenolic benzotriazoles in sediment, resulting in accumulation of these compounds in benthic organisms. The low concentrations of UV-326 in shallow water species might be explained by low BCF of this compound, as compared with other benzotriazole UV-filters. In addition, the authors speculate that biodegradation of UV-326 in shallow water organisms may be a possible reason for low accumulation of this compound.

UV-327 was most frequently detected in the organisms investigated. The average concentrations of UV-327 in tidal flat organisms were only twofold higher than those in shallow water species. The tidal flat clam, crab and herbivorous mudskipper contained high concentrations of UV-327 (> 100 ng/g lw), followed by gastropods and oysters. In shallow water fishes such as mullet, sea bass and young sea bass, concentrations of UV-327 were three- to fourfold higher in liver than in carcass. These results are consistent with the concentration profiles of UV-328 in mullet, suggesting the preferential accumulation and less biodegradation of this compound in the liver of some fish species. Omnivorous birds accumulate UV-327 in the liver, at average concentrations of 90 ng/g (lw) in a spot-billed duck and 59 ng/g in mallards. This suggests bioaccumulation in higher trophic species in the aquatic food chain.

Concentrations of UV-328 in biota were variable and species-specific. The highest concentration was found in tidal flat gastropod at 460 ng/g (lw), followed by mullet (120 ng/g lw in whole body and 250 ng/g lw in liver) and hammerhead shark (130 ng/g lw in liver) collected from shallow waters. The oysters and clams in tidal flat contained high concentrations of UV-328, at >100 ng/g lw. The large variations in UV-328 concentrations observed in this study might be due to differences in retention and metabolism of this compound in marine organisms.

As described above, the concentrations of benzotriazole UV-stabilisers in tidal flat organisms were higher than those in shallow water species. In addition, clams, oysters and gastropods presented high concentrations of UV-320, UV-326 and UV-328 rather than crabs and fishes, although the former species are at lower trophic levels in the tidal flat ecosystems. There is no positive correlation between the concentrations and the trophic status of organisms in marine ecosystems.

The benzotriazole UV-stabilisers were detected in eleven coastal sediments analysed, at total concentrations of several ng/g dw. UV-328 was found at the highest concentrations (average 6.4± 4.0 ng/g dw), followed by UV-326 (3.7 ± 3.0 ng/g dw), UV-327 (3.2 ± 2.6 ng/g dw) and UV-320 (0.9 ± 0.6 ng/g dw). The composition of the UV-stabilisers among the sediment samples was less variable than in biota. Extremely high concentrations were found in five sediments from the highly polluted Omuta River. Highest concentrations of UV-320, -326, -327 and -328 reached 14, 200, 190 and 320 ng/g dw, respectively. Significant correlations were found in sediment concentrations between UV-326 and 327, UV-326 and 328, and UV-327 and 328 in the Ariake Sea. Significant correlations were also found between UV-stabiliser concentrations and organic carbon contents in sediment.

Table 63: Concentrations of benzotriazole UV-stabilisers in tidal flat and shallow water organisms collected in Japan

	UV-320 [ng/g ww]	**UV-326 [ng/g ww]**	**UV-327 [ng/g ww]**	**UV-328 [ng/g ww]**
10 tidal flat organisms	< 0.05 – 0.60	< 0.10 – 2.5	< 0.12 – 3.6	0.35 - 14
10 marine shallow water organisms	< 0.05 – 0.09	< 0.10 – 0.32	< 0.12 – 2.3	0.19 – 8.7
6 marine shallow water organisms (liver)	< 0.05 – 7.0	< 0.10 – 5.6	2.4 - 13	< 0.15 - 55
2 species of water fowl	< 0.05	< 0.10	2.6	< 0.15

(liver)			3.4	

Table 64: Concentrations of benzotriazole UV-stabilisers in sediments in Japan

	UV-320 [ng/g dw]	**UV-326 [ng/g dw]**	**UV-327 [ng/g dw]**	**UV-328 [ng/g dw]**
marine and estuarine sediments (n = 11)	0.3 – 2.3	1.5 – 12	1.6 – 9.9	7.9 - 40
Omuta River sediments (n = 5)	2.6 - 14	23 – 200	16 – 190	18 - 320

Nakata et al. (Nakata et al., 2009b) also investigated occurrence and concentrations of UV-320, 326, 327 and 328 in marine organisms collected from the Ariake Sea, western Japan. 51 marine organisms, such as lugworms, mussels, oysters, crustaceans, fish, birds and marine mammals were collected during 2001 and 2005. Twelve sediments were collected from the same region in 2007. Analyses were done via GC-MS.

UV-filters were detected in most marine organisms in the study. Highest concentrations were found in lower benthic organisms, gastropods, collected from the tidal flat area (UV-328 > 400 ng/g lw). UV-328 and -326 were the dominant components in these organisms. In shallow water species, elevated levels were found in the liver of mullet, a benthic fish (UV-328 > 200 ng/g lw). Higher trophic species, such as sharks, marine mammals and birds accumulate organic UV-filters. UV-328 and -327 were dominant in finless porpoises and mallards, respectively. The results suggest significant bioaccumulation of UV-filters through the marine food-webs.

The substances were also detected in surface sediments from the Ariake Sea (average concentration: several ng/g dw). High concentrations of UV-filters were found in the Omuta River sediments, at levels ranging from 2.3-320 ng/g dw. Significant correlations were found between concentrations and organic carbon contents in sediments. No more details are given.

In order to understand the geographical distribution of UV-filters, blue and green mussels from ten Asian countries and regions were collected during 1998 and 2005 and analysed (Cambodia, China, Hong Kong, India, Indonesia, Japan, Korea, Malaysia, the Philippines, Vietnam). Only qualitative information is given on this investigation. UV-filters were detected in most mussel samples, indicating the widespread use of these compounds in Asian coastal regions. In general, UV-326 was the dominant compound, whereas UV-320 was detected only in several samples collected from Japan. The UV-filters concentrations were high in mussels from Korea, Japan and Hong Kong. Low residue levels of UV-filters were found in samples from India and Vietnam. These results suggest different usage values of UV-filters among countries and regions in Asia. Concentrations in mussels showed great spatial variations in Korea and Japan, which may be due to the distance between the sampling points and the sources of UV-filters, such as WWTPs. Significant positive correlation was determined in concentrations between UV-327 and UV-328 in mussels.

Nakata and Shinohara (Nakata and Shinohara, 2010) analysed UV-320, -326, -327 and -328 in influent, effluent and sewage sludge samples collected from five WWTPs located in a town (population 680,000) in Japan. Samples were taken in May and October 2009. The wastewater flows were 140,000, 29,300, 9,300, 53,300 and 63,200 m^3/d, respectively. The treatment process included activated sludge method in all WWTPs. In the biggest WWTP (East WWTP) influent samples were collected at 9:00, 12:00, 15:00, 18:00 and 21:00 (n = 5), to study time-dependent variations of target substance concentrations. Influent and effluent samples were also obtained from the four other WWTPs (n = 1 / sample). Two sewage sludge samples were also collected from each of the five WWTPs (n = 10). The detection limits ranged from 2.1 to 8.7 ng/L in this study (limits of quantification not given).

Benzotriazole UV-stabilisers were detected in all influents collected from East WWTP at every three hours during 9:00 to 21:00. UV-326 showed the highest concentrations in influents,

followed by UV-328 and -327.

Table 65: Concentrations [ng/L] of benzotriazole UV-stabilisers in influents of East WWTP

Time of sampling	9:00	12:00	15:00	18:00	21:00	Average ± standard deviation
UV-326	26	24	23	19	28	24 ± 3.7
UV-327	17	11	10	20	5.6	12 ± 5.6
UV-328	23	20	17	14	15	18 ± 3.9

Table 66: Concentrations of benzotriazole UV-stabilisers in five WWTPs in Japan

Concentration in	UV-326	UV-327	UV-328
influent (9 samples) [ng/L]	24 - 78	< 8.7 - 12	18 - 52
effluent (5 samples) [ng/L]	3.0 - 4.5	< 8.7	2.1 – 2.9
sludge (10 samples) [ng/g dw]	760 - 1800	120 - 200	430 - 570

Benzotriazole UV-stabilisers were detected in most samples analysed and UV-326 was the dominant compound in influents (mean: 46 ng/L), followed by UV-328 (34 ng/L). UV-327 was detected in two influents at concentrations of 9.2 and 12 ng/L. UV-320 was not identified in any of the samples, probably because its domestic production and use have been restricted in Japan. These results imply a large amount of production and usage of UV-326 compared with other benzotriazole UV-stabilisers in Japan. Concentrations in the effluents were generally < 5 ng/L, suggesting an elimination of these compounds during wastewater treatment. The removal rates of UV-326 and -328 were >90% in the effluents, but high concentrations of benzotriazole UV-stabilisers were detected in sewage sludge samples of WWTPs, at high levels indicating adsorption to organic carbon in sewage sludge. The mean carbon percentage of sewage sludges was 31 ± 2.2 %. Partition coefficients (Kp) were calculated at a moisture content of 80% in sludges. The values are 7,200 ± 3,900 L/kg for UV-326 and 4,200 ± 970 L/kg for UV-328.

Nakata et al. (Nakata et al., 2010) also detected benzotriazole UV-stabilisers in the blubber of marine mammals. They analysed UV-320, -327 and -328 in five finless porpoises (*Neophocaena phocaenoides*) collected from the Yatsushiro Sea, Ariake Sea and Tachibana Bay, Japan, in 1999, 2008 and 2009, respectively. All animals were stranded or accidentally caught by fishing net. Detection limits were 0.05, 0.12, 0.15 ng/g ww for UV-320, -327 and -328, respectively.

Table 67: Concentrations of benzotriazole UV-stabilisers [ng/g ww] in the blubber of finless porpoises

sample no.	1	2	3	4	5
sampling year	1999	1999	2008	2009	2009
lipid content [%]	81	83	87	59	91
UV-327	4.5	9.5	6.3	31	18
UV-328	20	64	11	34	16

UV-320 was not detected in the samples, which is attributed to its restriction in Japan in 2007. The mean concentrations and standard deviations of UV-327 and UV-328 in five blubber samples were 19 ± 19 ng/g lw and 38 ± 28 ng/g, respectively, reflecting the higher consumption of UV-328 in Japan.

The authors cite a study showing a high concentration of UV-327 in the liver of a common cormorant (220 ng/g) collected from Hokkaido, northern Japan (respective reference in Japanese). While the concentrations of UV-327 in finless porpoises were lower than those in seabirds, the occurrence of UV-327 in marine mammals suggests the potential bioaccumulation in higher trophic species through the aquatic food chain.

According to the authors it has been reported that UV-327 concentrations in seawater from four coastal areas of Tokyo Bay were less than 0.5 ng/L and that the geometric mean concentration in river, lake and coastal water samples (n = 44) was 0.12 ng/L (respective references in Japanese). On the basis of these water concentrations the BAF of UV-327 between water and finless porpoises was estimated to be 33,300. Applying the same water concentrations to the calculation of a BAF of UV-327 in small fish inhabiting the same regions results in a value of 3250, which is comparable to the values found under laboratory conditions (3400 to 9000).

UV-328 was not detected in the liver of seabirds, although UV-327 was present in the samples (Nakata et al. 2010). The log K_{ow} of UV-328 is the highest (8.28 reported in study) among the analysed substances, "but the BCF in fish was relatively low, 570-1400 and 620-2700 at the exposure concentrations of 0.1, 0.01 for 60 days, respectively" (unit not given but probably the dimensionless BCF, respective reference in Japanese). However, UV-328 showed a very high BCF, 36,000, between water and innards of fish (respective reference in Japanese). The authors conclude that the bioaccumulation profiles of UV-328 in marine organisms might be related to different retention and metabolism of this compound among species. The occurrence of UV-328 in finless porpoise may imply a low potential for biotransformation of this compound in this species. Finally it is stated that benzotriazole UV-stabilisers appear to be persistent and bioaccumulative in the aquatic food chain.

Kameda et al. (Kameda et al., 2011) measured 18 sun-blocking agents, among them UV-234, -326, -327, -328 and -329 in water and sediment collected from 22 rivers, four WWTP effluents and three lakes in August and September 2008 in Japan. Phenolic benzotriazoles are the most widely used UV-light stabilisers in Japan. WWTP sediment samples were collected from the river at the point of WWTP effluent discharge. In order to estimate contribution of sun-blocking agents from domestic wastewater to those in surface water and sediment, an indicator chemical for domestic wastewaters and WWTP effluents was also measured (HHCB = 1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta-[g]-2-benzo-pyrane, a polycyclic musk, CAS 1222-05-5). The sampling sites represent 5 different groups:

- two streams with direct inputs of domestic wastewater (S1,S2)
- four WWTP effluents (ST1-ST4), conventional activated sludge treatment plants,
- six rivers heavily polluted by industrial and domestic wastewaters (H1-H6),
- twelve moderately contaminated rivers (M1-M12),
- two little rivers and three lakes as background sites (BG1-BG5).

Background sites did not receive domestic or industrial wastewater, but have possible slight sources (atmosphere deposition, recreational activities). In spite of considerable care, UV-328 was detected in blank samples. According to the authors this contamination was caused by analyte in indoor floor dust in the laboratory during experiments. The measured concentrations were corrected by the use of blanks upon each analysis. The limits of detection ranged from 0.1 ng/l to 3.0 ng/l and from 0.05 ng/g dw to 1.0 ng/g dw except for UV-328 which had a LOD of 10 ng/g dw.

The profiles of sun-blocking agents in surface water demonstrated site-specific differences at each sampling site. UV-328 was one of the dominant sun-blocking agents measured in water samples from heavily and moderately polluted rivers. The maximum level of UV-328 in heavily polluted rivers was near the lowest chronic NOEC of the substance estimated by EPI Suite (7 µg/L). UV-234 and UV-329 were neither detected in water samples from surface waters nor from WWTP effluents. At the background sites none of the phenolic benzotriazoles analysed were found in water samples.

Table 68: Concentrations of phenolic benzotriazoles in water samples. UV-234 and 329 were not detected.

Analyte		UV-326	UV-327	UV-328
streams (S1, S2)	Occurrence	1/2	1/2	1/2
	mean detected [a] [ng/L]	16	5	70
	range [ng/L]			
WWTP effluents (ST1-ST4)	Occurrence	1/4	1/4	3/4
	mean detected [ng/L]	13	2	62
	range [ng/L]			47-88
heavily polluted rivers (H1-H6)	Occurrence	1/6	1/6	4/6
	mean detected [ng/L]	9	1	701
	range [ng/L]			149-4780
moderately polluted rivers (M1-M12)	Occurrence	5/12	6/12	8/12
	mean detected [ng/L]	2	1	152
	range [ng/L]	1-22	1-6	30-583
background sites (BG1-BG5)	Occurrence	0/5	0/5	0/5
	mean detected [ng/L]			
	range [ng/L]			

[a] geometric mean calculated from detected samples

Table 69: Concentrations of phenolic benzotriazoles in sediment samples

Analyte		UV-234	UV-326	UV-327	UV-328	UV-329
streams (S1, S2)	Occurrence	1/2	2/2	2/2	2/2	1/2
	mean detected [a] [µg/kg[b]]	1266	7.8	4.7	102	16
	range [µg/kg[b]]		0.1-110	0.6-37	10-1146	
WWTP effluents (ST1-ST4)	Occurrence	0/4	4/4	4/4	3/4	0/4
	mean detected [µg/kg]		0.8	0.5	13	
	range [µg/kg]		0.4-5.4	0.3-1.0	10-85	
heavily polluted rivers (H1-H6)	Occurrence	4/6	5/6	5/6	6/6	3/6
	mean detected [µg/kg]	99	4.7	2.4	117	26
	range [µg/kg]	38-324	0.9-45	0.7-18	21-1735	7.4-269
moderately polluted rivers (M1-M12)	Occurrence	8/12	12/12	10/12	9/12	3/12
	mean detected [µg/kg]	47	1.8	0.9	59	0.6
	range [µg/kg]	18-315	1.0-5.0	0.4-2.6	10-213	0.1-4.3
background sites (BG1-BG5)	Occurrence	3/5	2/5	2/5	3/5	0/5
	mean detected [µg/kg]	39	1.2	0.7	58	
	range [µg/kg]	8.3-113	1.1-1.3	0.5-1.1	29-89	

[a] geometric mean calculated from detected samples
[b] µg/kg dw

UV-234, -326, -327 and -328 were detected in most sediments. The compositions of sun-blocking agents in sediment were quite similar among the five sampling site groups. The highest geometric mean concentrations of 18 sun-blocking agents in sediments were detected in streams and in heavily polluted rivers. The highest contributions to the total concentrations were those of UV-234 and -328. These two substances accounted for 70-80% of the total contaminants identified at all sediment sampling sites.

The results demonstrate that high concentrations of phenolic benzotriazoles were accumulated in sediment receiving not only chemical plants effluent, but also residential wastewaters, WWTP effluent and surface runoff.

UV-234, -326, -327 and -328 were significantly correlated with HHCB in sediments from rivers and lakes. According to the authors this shows that a large input of these substances is from domestic wastewater or WWTPs. It also suggests that their behaviour in rivers and lakes, such

as partitioning and attenuation, is similar to that of HHCB. UV-329 had no significant correlation with HHCB in sediments.

UV-326 had a strong linear correlation between UV-327 as well as UV-328 in all sediments. Since UV-stabilisers are often used as mixtures, the ratios observed in sediments may reflect their compositions in the products. The authors suggest that their (degradation) behaviour may be also quite similar.

In a presentation Nakata (Nakata, 2011) showed graphs with concentrations of UV-326, -327 and -328 in mussels from ten Asian countries and in mussels from the USA mussel watch program. All data cited are taken from the graphs. 45 samples were taken during 2003 and 2005.

UV-326 was detected in mussels from seven of the ten Asian countries. Highest concentrations were detected in mussels from Japan and Korea (ca. 1.5 and ca. 1.2 µg/g lw, respectively). UV-327 was detected in six of the ten countries with highest concentrations in Hong Kong and Korea (ca. 0.3 µg/g lw). UV-328 was detected in eight of the ten countries with highest concentrations in Hong Kong and Korea (ca. 0.8 µg/g lw).

In the USA samples were taken from blue mussels at 17 locations (n = 34) on the west coast (Alaska, Oregon, California) in 1994/95 and 2004/05. UV-326 and -327 were detected in most samples (14/17). Concentrations of UV-326 were similar to those measured in Japan and Korea. However, the maximum concentration was lower (ca. 0.7 µg/g lw). Concentrations of UV-327 were higher than in Japan, but slightly lower than in Korea and had a maximum of ca. 0.25 µg/g lw. UV-328 was detected in few samples, only, and showed a maximum of ca. 0.3 µg/g lw.

In an article Nakata et al. (Nakata et al., 2012) published more details on the mussel analyses. However, some more samples were included and other samples were excluded, so the results published in the article differ somewhat from those given in the presentation. Compounds analysed were UV-320, -326, -327 and -328. 53 samples of blue and green mussels were collected from Cambodia, China, Hong Kong, India, Indonesia, Japan, Korea, Malaysia, Philippines and Vietnam during 2003 and 2007. In addition the analysis comprised 15 samples of blue mussels from the Pacific coast of the USA collected during 2004 and 2005. Liquid extraction and GC-MS in selective ion monitoring (SIM) mode was used. The limits of detection are given as 0.05, 0.1, 0.12 and 0.15 ng/g ww for UV-320, -326, -327 and -328, respectively.

Table 70: Mean concentrations of phenolic benzotriazoles in blue and green mussels [ng/g lw]. Geometric means in parenthesis.

	UV-320		**UV-326**		**UV-327**		**UV-328**	
Cambodia	0/2	n.d.	0/2	n.d.	0/2	n.d.	2/2	120 (110)
China	0/5	n.d.	2/5	60 (33)	4/5	84 (65)	3/5	96 (52)
Hong Kong	0/8	n.d.	2/8	91 (18)	6/8	93 (48)	6/8	200 (75)
India	0/3	n.d.	0/3	n.d.	0/3	n.d.	0/3	n.d.
Indonesia	0/2	n.d.	1/2	33 (22)	2/2	58 (45)	2/2	120 (110)
Japan	4/7	33 (13)	7/7	450 (260)	3/7	38 (15)	7/7	120 (93)
Korea	0/17	n.d.	13/17	210 (90)	11/17	100 (56)	16/17	220 (150)
Malaysia	0/4	n.d.	1/4	42 (12)	0/4	n.d.	1/4	24 (14)
Philippines	0/2	n.d.	1/2	120 (50)	2/2	150 (150)	2/2	170 (140)
USA	0/15	n.d.	12/15	130 (79)	11/15	61 (45)	3/15	69 (33)
Vietnam	0/3	n.d.	0/3	n.d.	0/3	n.d.	0/3	n.d.

Analytical results demonstrate ubiquitous contamination and widespread distribution of phenolic benzotriazoles. Levels were comparable to those of PCBs, DDTs and PBDEs. However, spatial variation of the concentrations was often high. Significant correlations were found between the concentrations of several phenolic benzotriazoles, which suggests similar sources

and compositions of these compounds in commercial and industrial products. While Kameda et al. (2011) reported correlations of UV-326, -327 and -328 with the polycyclic musk HHCB, such correlations were not always found by Nakata et al. (2012). HHCB is an indicator substance for WWTP effluent. It is concluded that in addition to WWTP effluents there may be point sources or other sources, e.g. road dust, influencing the phenolic benzotriazoles concentrations in mussels.

The authors report that the domestic production and import of UV-327 in Japan decreased dramatically from 2436 tons between 2004 and 2009 to only three tons in 2010. They assume that this is due to the availability of an alternative in the Japanese market.

Yanagimoto et al. (Yanagimoto et al., 2011) studied the occurrence of UV-327 and -328 in human adipose tissues collected from Japan (2004-2005, n = 22), South Korea (2005-2006, n = 18), China (2002, n = 12), India (2008, n = 5), Spain (2006, n = 12), Poland (1990, n = 12) and the USA (2003-2004, n = 24). In addition foodstuffs collected from Japan were analysed for UV-326, -327 and -328 (seafood, meat, eggs, vegetables, dairy products, potatoes, pulses, cereals, fruits, n = 32). Some of the foodstuffs originated from other countries than Japan. GC-HRMS/LRMS was used. All data cited are taken from graphs.

The highest concentrations in human adipose tissue were found In Japan and South Korea. In Japan up to ca. 60 ng/g lw UV-327 were detected in human adipose tissues, in South Korea the concentrations reached ca. 45 ng/g, whereas those in Europe were lower (up to ca. 17 ng/g in Spain, up to ca. 11 ng/g in Poland). Lowest concentrations were observed in the USA (up to ca. 5 ng/g lw). Concentrations of UV-328 were generally lower than those of UV-327: up to ca. 35 ng/g lw in Japan, up to ca. 20 ng/g in South Korea and up to ca. 6 ng/g in Spain, whereas UV-328 was not detected in samples from Poland and only in few samples at low concentrations in the USA (up to ca. 2 ng/g lw). No gender- and age-related differences in concentrations were observed.

In foodstuffs ubiquitous contamination with benzotriazole UV-stabilisers was found. Highest concentrations were detected in seafood (up to ca. 1.2 ng/g ww UV-326, 1.4 ng/g UV-327 and 1.7 ng/g UV-328) and meat (up to ca. 1.5 ng/g ww UV-326, 1.2 ng/g UV-327 and 1.0 ng/g UV-328). Meat with high concentrations was imported from the USA and Australia. Lower concentrations were detected in vegetables (up to ca. 1.0 ng/g ww UV-326, 0.3 ng/g UV-327 and 0.2 ng/g UV-328) and some fruit (up to ca. 0.5 ng/g ww each UV-326, 327 and 328). In dairy products no benzotriazole UV-stabilisers were found. The estimated daily intake of benzotriazole UV-stabilisers through food consumption was 861 ng/person/d. Contamination was mainly due to meat and vegetables (> 50%), which may imply the transfer of benzotriazole UV-stabilisers from plastic trays and wraps.

By way of a poster Nakata et al. (Nakata et al., 2011) reported temporal trends of UV-327 and -328 in archived marine mammal tissues. In addition, temporal trends of UV-326, -327 and -328 in sediment cores were analysed. Marine mammals sampled were finless porpoises and striped dolphins from Japanese coastal waters (n = 33). Sediment cores were taken from two sample stations at Tokyo Bay, Japan (n = 12). The sedimentation periods (1930-1999) were determined by 210Pb and the particle fraction < 500 µm was investigated. All data cited are taken from graphs.

UV-327 and -328 were not detected in blubber samples collected around 1980, but in samples taken in 1990 and later. Maximum concentrations of UV-327 and -328 were ca. 45 ng/g lw and ca. 70 ng/g lw, respectively. An increasing trend is identified for UV-327 as well as UV-328.

Sediment cores showed an increasing temporal trend for UV-326, -327 and -328. Results are presented for two different sampling stations. At both sampling stations concentrations start to rise around 1970. Highest concentrations are found for UV-326 (maximum ca. 17 ng/g dw at station A, ca. 31 ng/g at station B), whereas concentrations of UV-327 and -328 were lower (UV-327 maximum ca. 8 ng/g dw at station A, ca. 4 ng/g at station B, UV-328 ca.10 ng/g at

station A, ca. 4 ng/g at station B).

UV-320, -326, -327 and -328 were also detected in road dusts. Samples were collected in December 2010 at nine stations of Route 57, Kumamoto, with a traffic density of approx. 5,000 to 60.000 cars/d (Nakata Presentation, 2011). All data are taken from graphs.

Concentrations were low for UV-320 (n.d. - ca. 3 ng/g dw), higher for UV-328 (ca.2.5 - ca. 40 ng/g) and UV-326 (ca. 8 - ca. 55 ng/g) and at a single sampling point 116.9 ng/g UV-327 was detected (minimum ca. 8 ng/g dw). Concentrations of UV-320, -326 and -328 correlated with traffic density. The authors conclude that that automobile equipment might be a possible source of benzotriazole stabilisers in the environment.

Based on the data set obtained and the physicochemical properties of benzotriazole UV-stabilisers, the authors conclude that UV-327 will be a candidate of the POP Convention.

Watanabe and Noma (Watanabe and Noma, 2010) performed thermal treatment experiments using pilot-scale equipment and waste containing UV-320 as an input material to determine the destruction behaviour of UV-320 and possible formation of UV-327 and NOx.

UV-320 was classified as a "Class I Specified Chemical Substance" under the Chemical Substance Control Law in Japan in 2007, which means that it is comparable in nature and toxicity to POPs (Watanabe and Noma, 2010). Manufacture and import of this substance have to be permitted, only specified uses are allowed and import of certain products specified by cabinet orders is prohibited. Therefore, production, import and use of UV-320 have declined in Japan. However, it is still used in some countries, such as Korea and China and in Japan it may still be leached from long-life products. It is expected that incineration may be the predominant method of treatment for wastes containing UV-320.

Concentrations of UV-320 and -327 in "refuse derived fuels" obtained from Japanese municipal solid waste after removing the incombustible materials were 7.1 and 20 µg/kg, respectively. After treatment in the pilot-scale incinerator with two combustion units, bag filter, activated carbon adsorption tower and wet scrubber concentrations in the flue gas (final exit) were 0.0020 µg/m³ and 0.0042 µg/m³ for UV-320 and -327, respectively. Bottom ash contained 0.52 µg/kg UV-320 and 0.063 µg/kg UV-327, fly ash 0.36 µg/kg UV-320 and 0.049 µg/kg UV-327. After increasing the input concentration to 5000 mg/kg UV-320 concentrations of UV-320 and 327 in flue gas, bottom ash and fly ash were of the same order of magnitude as those observed at low input concentrations of UV-320.

UV-320 was destroyed mainly in the primary combustion zone. Overall destruction efficiency of UV-320 in input at a concentration of 5000 mg/kg was > 99.9999%. The input amount of UV-320 did not affect the formation and destruction behaviour of UV-327 and NOx.

Other Asian studies:

Kim et al. (Kim et al., 2011a) developed a multiresidue analytical method for the determination of emerging pollutants including UV-234, -320, -326, -327, -328 and -329 in fish. The concentrations in fish muscle tissue were given on a lipid weight (lw) basis and the method detection limits were 0.3 – 9 pg/g for the UV-stabilisers mentioned above. Five individual fish samples belonging to three species of fish from Manila Bay, the Philippines were analysed. Samples were collected during June 2008. Concentrations ranged from below the method detection limit to 179 ng/g lw, suggesting the ubiquitous contamination in Manila Bay.

Table 71: Concentrations of phenolic benzotriazoles in fish muscle tissue [ng/g lw]

	bluetail mullet *V. buchanani* (n=1)	**coral grouper *E. corallicola* (n=1)**	**flathead grey mullet *M. cephalus* (n=3)**	
			mean	Min-Max
UV-234	not detected	14.3	34.6	22-47.1

UV-320	9.60	0.78	6.88	4.11-9.15
UV-326	211	n.d.	18.9	no data given
UV-327	2.57	18.5	14.6	10.5-18.5
UV-328	18.4	21.1	105	30.2-179
UV-329	not detected	39.4	7.29	6.69-7.89

Using the same method Kim et al. (Kim et al., 2011b) studied contamination of fish from Manila Bay, the Philippines, with benzotriazole UV-stabilisers including UV-234, -320, -326, -327, -328 and -329. Manila Bay is one of the pollution hot spots in the seas of East Asia with a very dense population and significant fisheries and aquaculture activities. It serves as a sink and transit area for the domestic and industrial wastes from metro Manila and the surrounding provinces. Many people depend on fish from the bay for food. During January and June 2008 58 fish specimens belonging to 20 species were collected from the local fish markets. Only fishes from Manila Bay were selected and analysed. The method quantification limits were 1-27 pg/g lw.

Benzotriazole UV-stabilisers were detected, each at ng/g level in almost all fish samples, indicating ubiquitous contamination in coastal waters. Among the eight targeted substances UV-328 was predominantly found with a mean concentration of 34.2 ng/g lw, implying large scale production and use of this compound in the Philippines. UV-328 was found in 88% of analysed specimens (n = 58), UV-320 and UV-234 in 79% and 55%, respectively. UV-326, -327 and -329 were detected in less than half of the samples suggesting smaller amount of use or lower bioavailability. Generally concentrations of UV-320, -326, -327 and -328 in fish samples from the Philippines were higher than those reported in marine fish from shallow waters of Japan (Nakata et al., 2009a), which is attributed to large scale usage of the substances and/or the release of untreated wastewater containing the substances. In line with the results of Nakata et al. (2009a) concentrations of UV-320, though frequently detected, were lower than that of UV-234 and -328. According to the authors this may indicate the differences in accumulation and biodegradability of UV-320. Significant positive correlations were found between UV-234 and -328, UV-234 and -329, UV-320 and -327 and UV-320 and UV-328. From this it is suggested that fish in Manila Bay are exposed to benzotriazole UV-stabilisers originating from the same sources which are distributed homogenously in the bay. Examination of the relative contributions of each analyte to the total concentrations of analytes revealed that from the substances relevant for the SVHC dossier UV-328 was predominant. Compositions of the benzotriazole UV-stabilisers were different even in fishes belonging to the same family whereas some composition pattern was observed in fishes belonging to different families. This may be due to different availability, different metabolic capacity or selective uptake of the substances.

Concentrations of UV-234, -320, -326, -327, -328 and -329 did not show any relation with fish length and weight. Therefore, differences in accumulation/exposure pattern indicate the species specificity in fish samples. Concentrations measured in the different fish species varied greatly depending on the species within one to two orders of magnitude. This wide variation in concentrations indicates species-specific accumulation and elimination of the substances.

High concentrations of the sum of the investigated eight substances were found in bumpnose trevally (*Caranoides hedlandensis*, n = 3), bluetail mullet (adult) (*Valamugil buchanani*, n = 1), common ponyfish (*Leiognathus equulus*, n = 3) and coral grouper (adult) (*Ephinephelus corallicola*, n = 1). These high concentrations (several hundred ng/g lw) indicate that these compounds are preferably accumulated by these species and/or that these species may have low metabolic capacity to eliminate benzotriazole UV-stabilisers. All these fishes belong to the demersal habitat.

Table 72: Concentrations of benzotriazole UV-stabilisers in marine species from Manila Bay, the Philippines

	lipid content	**UV-234 [ng/g**	**UV-320 [ng/g**	**UV-326 [ng/g**	**UV-327 [ng/g**	**UV-328 [ng/g**	**UV-329 [ng/g**	**Σ 8 benzotriazole**

	[%]	lw]	lw]	lw]	lw]	lw]	lw]	UV-stabilisers
detection frequency [%]	---	55	79	19	43	88	41	---
Min. – Max. in 20 fish species (n = 58)	0.13-2.61	n.d. - 126	n.d. – 28.7	n.d. - 211	n.d. - 221	n.d. – 563	n.d. - 96.7	6.5 ± 11.1 - 316 ± 460

Kim et al. (Kim et al., 2012) used the same method for determining UV-234, -320, -326, -327 and -328 in house dust from the Philippines. During August 2008 house dust samples were collected from a residential area (Malate, n = 17) and near a large-scale open dumping area of municipal wastes (Payatas, n = 20) in Manila. People live directly at and even on the dumping area (http://www.dr-koelsch.de/html/payatas.html). House dust was collected in separate vacuum-cleaner bags used in each of the sampled house, which consist of dust from living room, kitchen and bedrooms. Dust was not collected from under furniture or in crevices between cushions. Obtained dust samples were combined individually for each house and sieved with a 500 µm mesh. Data on the details of the house, the possible sources of dust, floor area, number of computers/televisions, furniture and type of flooring were documented in a questionnaire at the time of sample collection.

Table 73: Concentrations of benzotriazole UV-stabilisers in house dust samples from Malate and Payatas in the Philippines

Target compounds	Malate					Payatas				
	DF[a] [%]	Median [ng/g]	Average [ng/g]	Min. [ng/g]	Max. [ng/g]	DF[a] [%]	Median [ng/g]	Average [ng/g]	Min. [ng/g]	Max. [ng/g]
UV-234	94	84	148	n.d.[b]	817	95	41	63	n.d.	212
UV-320	82	4.7	6.6	n.d.	25	65	3.0	6.9	n.d.	75
UV-326	88	50	53	n.d.	275	65	6.2	17	n.d.	133
UV-327	88	19	28	n.d.	73	80	10	10	n.d.	32
UV-328	82	27	50	n.d.	304	85	12	18	n.d.	48
Σ	---	147	285	n.d.	1020	---	118	115	n.d.	277

[a] DF: detection frequency
[b] n.d. = not detected

UV-234, -320, -326, -327 and -328 were frequently detected indicating ubiquitous contamination of the indoor environments. Among the target compounds, UV-234, -326 and -328 were the predominant compounds. The most abundant was UV-234, with a median value of 84 ng/g in Malate and 41 ng/g in Payatas. Significantly higher concentrations of UV-326 and -327 were found in house dust samples from Malate than those from Payatas, indicating possible differences in usage patterns of household products such as TV, waxes, coating materials, paints etc. between the two locations. Household products are considered the major source of contamination in the indoor microenvironment. The composition of phenolic benzotriazoles differed among the houses even within the same sampling region. It was not possible to distinguish the sources of the contamination. However, the correlations found for most of the benzotriazole UV-stabilisers in house dust samples indicate a common source. This is in line with the results from other investigations (Kim et al.2011a, Nakata et al. 2009a)

Generally, levels of benzotriazole UV-stabilisers in dust from the Philippines are comparable to or lower than those measured by Carpinteiro et al. (2010b) in dust from Spain or the USA. Lower levels are attributed to lesser usage of the respective compounds in the Philippines.

Zhang et al. (Zhang et al., 2011) investigated UV-326, UV-327 and UV-328 in surface

sediment samples (0-20 cm) collected from rivers in China (six samples from river Songhua in 2009) and the U.S. (three samples both from river Saginaw in 2002 and river Detroit in 1998). Five sewage sludge samples were collected from five WWTPs serving large cities located along the Songhua River in China in July 2009. Sediment and sludge samples taken from four to six spots within 10 m at a given sampling location were pooled to obtain a representative sample. UV-326, UV-327 and UV-328 were determined by use of a GC-MS.

The limit of detection (LOD) and the limit of quantification (LOQ) for sediment analysed in this study were 0.02 and 0.06 ng/g for UV-327 and 0.1 and 0.33 ng/g for both UV-326 and UV-328. The method LOD and LOQ values for sludge samples were 0.1 and 0.3 ng/g for UV-327 and 0.5 and 1.65 ng/g for both UV-326 and UV-328. Because measured values are reported in relation to dry weight it is assumed that the LODs LOQs given also relate to dry weight.

UV-326 was detected in two of six sediment samples from the Chinese River (1.71 and 2.01 ng/g dw) in one of six sediment samples from the U.S. (5.88 ng/g dw) and in all five sewage sludge samples from China (23.3-136 ng/g dw, mean 77.4 ng/g dw).

UV-327 was detected in one of six sediment samples from the Chinese River (0.310 ng/g dw) in three of six sediment samples from the U.S. (0.22-1.90 ng/g dw, mean 0.850 ng/g dw) and in four of five sewage sludge samples from China (1.80-8.40 ng/g dw, mean 3.68 ng/g dw).

UV-328 was detected in all six sediment samples from the Chinese River (2.06 - 7.12 ng/g dw, mean 3.81 ng/g dw) in five of six sediment samples from the U.S. (0.72-224 ng/g dw, mean 116 ng/g dw) and in all five sewage sludge samples from China (40.6-5920 ng/g dw, mean 1300 ng/g dw).

The concentration of UV-328 in sludge was the highest (mean: 1300 ng/g dw) among the target compounds.

Ruan et al. (Ruan et al., 2012) analysed UV-234, -320, -326, -327, -328, -329 and -350 in municipal sewage sludge in China using an HPLC-MS/MS method. The method quantification limits were from 0.15 (UV-234) to 0.77 (UV-320) ng/g dw. Sixty sewage sludge samples from WWTPs in 33 cities were collected in 2010 and 2011. Most of the WWTPs are located in economically developed provinces in China. Samples were taken from freshly digested sludge at the dewatering process. The most dominant analogue was UV-234 at a median concentration of 116 ng/g dw. The abundance was successively followed by UV-329, -326 and -328 with median concentrations of 66.8, 67.8 and 57.3 ng/g dw respectively. UV-327 and UV-350 had low detection frequency, while UV-320 was not detectable in any sample. According to the authors the observed composition pattern in the sludge samples was quite consistent with the global production volumes of benzotriazole UV-stabilisers (according to the OECD and US EPA HPV databases).

Significant correlations were found among the phenolic benzotriazole concentrations and the daily treatment volume of the WWTPs was moderately correlated UV-329 and UV-328. Results from degradation prediction and multimedia fate simulation based on a quantitative structure-property-relationship (QSPR) model at screening level based on EPISuite and therefore comparable with the simulations done for the presented dossiers implied that the commercial benzotriazole stabilisers and their plausible transformation products might be persistent in the environment.

Table 74: Concentrations of benzotriazole UV-stabilisers in sludge from Chinese municipal WWTPs

Analyte	Detection frequency	Concentrations [ng/g dw]	Median [ng/g dw]
UV-234	58/60	0.96 – 235	116
UV-320	0/60	n.d.	-
UV-326	59/60	4.00 – 319 two extreme values: 2930 and 3390	67.8

UV-327	24/60	1.53 – 133	14
UV-328	58/60	3.54 – 213 one extreme value: 24,700	20.6
UV-329	59/60	0.57 – 757	66.8
UV-350	5/60	1.88 – 42.7	13.8

Australian studies:

Liu et al. (Liu et al., 2011; Liu et al., 2012) developed a method for simultaneous determination of benzotriazoles and UV-filters (including UV-326 and -329) in ground water and WWTP effluent and biosolid samples using GC-MS/MS. The method was applied to screen the selected substances in samples from Bolivar WWTP in Adelaide, South Australia. The WWTP serves a population of 1,300,000 and is designed to have dry weather flow of 148.5 ML/d. About 75% of the inflow is from domestic sources, 25 % from industrial sources. The WWTP consists of primary sedimentation, secondary activated sludge treatment, stabilisation lagoons and dissolved air flotation/filtration. The effluent is piped to a vegetable growing region for irrigation, or recharged into aquifer on site. The sludge line comprises mesophilic anaerobic digestion and sludge stabilisation lagoons.

Groundwater samples were collected from an aquifer storage and recovery well at a depth of 300 m below ground within the WWTP site. Biosolid samples were collected from different sludge treated process (sludge is dewatered and dried using a combination of sludge drying lagoons, centrifugation and agitated air drying). Three parallel samples were collected for each sample type.

In groundwater and effluent water concentrations of UV-326 and -329 were below the limits of quantification (LOQ). The LOQ were: 4.9 ng/L in tap water and 11.0 ng/L in effluent for UV-326 and 18.6 ng/L in tap water and 16.0 ng/L in effluent for UV-329. The concentration in biosolid samples was 49.9±7.4 ng/g for UV-326 (LOQ 1.1 ng/g) and 122.9±7.1 ng/g for UV-329 (LOQ 27.4 ng/g).

Results published in 2012 focus on the removal processes in the WWTP. 24 h composite water samples and samples of sludge (24 h composite or grab) and influent suspended solids were collected in April and October 2010. The average removal efficiencies of suspended solids, BOD_5 and NH_4-N were above 99% during the sampling periods. The highest value of LOD for the target analytes (four benzotriazoles and six UV-filters including UV-326 and -329), were 16.3 ng/L in the influent, 14.1 ng/L in the effluent and 8.2 ng/g in biosolid samples.

All water and sludge concentrations are taken from graphs. UV-326 was detected in the influent in concentrations of ca. 35 ng/L (April) and ca. 20 ng/L (October), UV-329 in concentrations of ca. 230 ng/L (April) and ca. 420 ng/L (October). According to the authors both substances were completely removed from the water phase. However, removal rates of both > 100% and < 0% were noticed in some treatment stages, which might be due to variations in the input and output concentrations. Concentrations of UV-326 and UV-329 in influent suspended solids were always near 100 ng/g. Both substances are further detected in all other sludge samples taken after different treatment steps.

A mass balance analysis was applied to establish mass flux in the plant and removal mechanisms. However, few data were available, concentrations in water and sludge varied considerably with different treatment stages. The authors discuss plenty uncertainties associated with the mass balance analysis, but nevertheless state that sorption onto sludge played a dominant role in the removal of UV-326 in the WWTP whereas biological degradation played a significant role for UV-329.

American studies investigating the environmental impact of a certain industrial point source:

Jungclaus et al. (Jungclaus et al., 1978) analysed industrial WWTP effluent and receiving waters and sediments from an American specialty chemicals manufacturing plant producing organic compounds and running a badly performing WWTP. 16 water samples and 19 sediment samples were taken in 1975 and 1976 and the compounds contained were identified, beside others UV-320, -327 and -328. River water and sediments were collected in Providence River and its tributary Pawtuxet River (Pruell et al., 1984).

UV-328 was detected in industrial WWTP effluent (0.55 – 4.7 ppm), in river water (7 – 85 ppb) and in sediments (1-100 ppm) (Jungclaus et al., 1978). UV-320 and UV-327 were detected only in sediment, with concentrations of 40 ppm and 2 – 300 ppm, respectively. It is not mentioned whether the measured concentrations refer to dry or wet weight.

In another publication Hites et al. (Hites et al., 1979) describe the same chemicals manufacturing plant as a case study and mention the same measured values. The plant operated in a batch production mode, generally following a weekly schedule and produced a wide range of compounds including pharmaceuticals, herbicides, antioxidants, thermal stabilisers, UV absorbers, optical brighteners and surfactants. Only about one fourth of the total BOD was removed by the waste treatment system. Wastewater samples were collected as the water spilled over from the clarifier. River water samples were collected both upstream and downstream from the plant. Sediment samples were taken at the plant and downstream from it. Analysis was done by GCMS and 123 compounds were identified. The individual concentrations have an estimated error of 20%. Two substituted benzotriazoles (UV-P and UV-328) were generally the most abundant anthropogenic compounds in the water and sediment samples. The former product UV-327 was only found in sediment samples. The other benzotriazoles, present in much lower concentrations, are suspected to be impurities in the major products. These benzotriazoles are characterized by resonance-stabilised internal hydrogen binding of the phenolic hydroxyl to the benzotriazole ring, apparently resulting in compounds with a high degree of environmental stability. For UV-328 a sediment accumulation factor of 500 is calculated. Fewer of the plant's compounds, including UV-P, UV-327 and UV-328, were detected in sediment from the channel where the Pawtuxet Cove leads into the brackish Providence River. The only compounds from the plant detected in the sediment sample from the Providence River were UV-327, UV-328 and methyl 3-(3',5'-di-t-butyl-4'-hydroxphenyl) propionate.

Lopez-Avila and Hites (Lopez-Avila and Hites, 1980) investigated transport of pollutants in sediments in the USA. The wastewater from a small specialty chemicals manufacturing plant located on the Pawtuxet River (Rhode Island) contaminated the water and sediment of that river, which flows into the brackish Providence River and Narragansett Bay. The plant was the same as the one studied in the studies mentioned above. UV-328 had been manufactured in the plant since 1970. Wastewater samples from the clarifier tank, water samples and sediment cores were taken. Reported concentrations represent minimum values since they had not been corrected for solvent extraction efficiencies. Average water concentrations for UV-328 (geometric averages of two to five values measured at the specified locations at different times) were 3000 ppb in the wastewater of the plant, 40 ppb in river water near the plant, 10 ppb in more distant river water, 8-9 ppb in the mouth of the Pawtuxet River and 0.5-2 ppb in the Providence River. The concentrations follow the rules of simple dilution. UV-327 was manufactured at the plant between 1963 and 1972. It was not detected in any of the water samples.

Eight sediment cores were taken at three locations in the Pawtuxet River. The sites were selected for an abundance of fine-grained material. Further sediment cores were taken at four locations in the Pawtuxet Cove and 13 locations in the Providence River and Narragansett Bay. The core concentrations of the compounds in the sediment have been condensed into a single number. However, the authors feel the values given are representative of the sediment concentrations. Concentrations decrease both with depth in the sediment and with increasing distance from the discharge.

Table 75: Concentrations of phenolic benzotriazoles in sediment cores (ppm)

	Pawtuxet River			Pawtuxet Cove	Providence River		
	near plant	mid river	near dam		near	far	bay
UV-327	300	400	20	80	20	2	0.5
UV-328	300	300	70	100	10	5	0.6

Pruell et al. (Pruell et al., 1984) developed an analytical method for the determination of PAH and phenolic benzotriazoles in clams. Concentrations of UV-327 and -328 were measured in hard shell clams (*Mercenaria mercenaria*) purchased from Rhode Island seafood stores in 1979. Personnel in nine of the 13 stores surveyed indicated that the clams were harvested from Narragansett Bay. Three seafood stores were sampled a second time to determine if the higher values obtained at these establishments were representative of their usual stock. As controls, clams were collected from a relatively unpolluted site in lower Narragansett Bay. The detection limit for specific compounds was ca. 0.1 ng/g ww.

The levels in purchased clams were generally higher than the concentrations found in clams collected from a lower Narragansett Bay control location. However, also in control samples both substances were detected. In summary UV-328 and UV-327 were present in clam tissue in concentrations ranging from 7 – 65 ng/g ww and from 1.0 – 8.5 ng/g ww (including controls). The ratio of UV-328 to UV-327 in clams varied from 2.7 to 9.5. This is similar to the ratio in surface sediments of the bay which ranges from 2.0 to 7.6. A significant correlation existed between UV-327 and UV-328.

Pruell and Quinn (Pruell and Quinn,1985) analysed organic contaminants from several different chemical classes in surface sediments along a transect from the head to the mouth of Narragansett Bay. Sediment concentrations of all compounds (total hydrocarbons, PAH, substituted benzotriazoles, phthalates) were highest in the Providence River and decreased with distance downbay. Maximum concentrations for phenolic benzotriazoles were ca. 1 µg/g dw for UV-327 and ca. 10 µg/g dw for UV-328. The authors emphasize that UV-327 and UV-328 "have a unique source, a known history of inputs, are strongly partitioned to particulate material and are environmentally persistent".

Depth distribution of UV-327 and -328 was investigated in three sediment cores taken in 1979/80 along a transect from the head (Providence River) to the mouth of Narragansett Bay. About 1 cm was scraped from the outside of the cores to prevent contamination from the plastic core liner. The core collected near the head of the bay showed a well defined historical record of contaminant input to the bay: UV-328 concentration was highest in the surface (ca. 7.5 µg/g dw) followed by decrease with depth, while UV-327 displayed a subsurface concentration maximum (ca. 6 µg/g dw) in the 10-15 cm horizon and then decreased with depth. Both compounds could not be detected below 20 cm in the core. At a mid-bay location the record was smeared because of extensive bioturbation. Maximum concentrations were ca. 8 ng/g dw for UV-327 and ca. 75 ng/g dw for UV-328. A sediment core collected near the mouth of the bay showed a subsurface increase of the compounds with maximum concentrations of ca. 2 ng/g dw for UV-327 and ca. 4.5 ng/g dw for UV-328. It is suggested that this horizon may have been influenced by dredge spoil material. The authors recommend UV-327 and UV-328 as "unique geochemical markers in Narragansett Bay sediments".

There was and still is a municipal wastewater treatment plant situated a certain distance upstream of the (former) chemical plant (Oviatt et al. 1987, http://www.dem.ri.gov/programs/benviron/water/permits/wtf/potwops.htm). Oviatt et al. found UV-327 (7.88 ± 6.49 µg/g dw) and UV-328 (180 ± 103 µg/g dw) in the sewage sludge of this WWTP. They used this sludge in mesocosms to investigate its fate and effects in the coastal marine environment. However, degradation was not considered.

Reddy et al. (Reddy et al., 2000) examined the free and bound fractions of different substituted benzotriazoles in sediment cores from the Pawtuxet River and Narragansett Bay in the U.S. The chosen benzotriazoles were produced from 1961 to 1985 by the chemical plant

located on the Pawtuxet River discussed already. Beside others, UV-326, -327 and -328 were investigated. Previous research has used these compounds as specific tracers of inputs from the Pawtuxet River into Narragansett Bay sediments and they are highly enriched in the sediments of both.

The Pawtuxet River sediment core was collected in 1989 and sectioned at 2-3 cm intervals. Eleven sections from 0-2 cm to 50-52 cm were analyzed. The sedimentation rates in this section of the river are 2-3 cm/year. The redox discontinuity, determined visually, was in the top 2 cm of the core. The Narragansett Bay core was collected in 1997. Six sections from the top 13 cm of the core were analysed. The sediments in this area become anoxic within a few millimetres of the surface and have a sedimentation rate of about 0.3 cm/year. The deepest sections of both cores were the approximate depths of where the phenolic benzotriazoles were no longer detected and should roughly be equivalent to the initial date of production of these compounds (1961-1979). The method detection limit was ca. 20 ng/g dw for each (free and bound) fraction.

In the Narragansett Bay core UV-327 and -328 were detected at trace levels in the 10-13 cm section and their concentrations generally increased up-core (with concentrations as high as 25 µg/g dw). UV-326 was detected at much lower concentrations. UV-327 and -328 were not detected in the bound fraction in the Narragansett Bay core.

In the Pawtuxet River core all benzotriazoles were detected in the free fraction. UV-327 was most abundant: the highest concentration was ca. 5 mg/g dw and it was observed down to 50-52 cm. The other benzotriazoles were only present in the top 20 cm of the core. UV-326 and -327 were also found in the bound fraction of the Pawtuxet River core in at least the top 15 cm. However, the maximum percentage bound was 0.04%.

Benzotriazoles that had alkyl substitution in ortho position to the hydroxyl group were less likely to be found in the operationally defined bound fraction than compounds that did not have this substitution.

Hartmann et al. (2005) took sediment cores at three locations in Narragansett Bay in 1997 (Apponaug Cove, Seekonk River, Quonset Point). The cores were analysed for several contaminants including UV-327 and UV-328. The phenolic benzotriazoles were used as markers indicating the years of their introduction (1963 for UV-327 and 1970 for UV-328). Two of the cores were split into 2 cm sections, and the third core (Quonset Point) was split into 10 cm sections.

Sharp breaks in the concentrations of UV-327 and UV-328 marking their introduction were successfully used to determine the sedimentation rate at Quonset Point. Both the Quonset Point and Seekonk River cores had subsurface maximums for phenolic benzotriazoles, which were consistent with expected inputs to the environment. The Apponaug Cove core showed an increase of the contaminants at the surface indicating a recent event in which more contaminated sediments were deposited at that location. The distributions of phenolic benzotriazoles at Apponaug Cove and in the Seekonk River indicate that there was a disturbance in the depositional environment relative to cores collected at these locations in 1986, demonstrating the potential for buried contaminants to be remobilized in the environment even after a period of burial.

At Quonset Point the phenolic benzotriazole profile increased down core through the 40-50 cm section before decreasing in the 50-60 cm section. Below the 50-60 cm section, UV-327 and UV-328 were below the detection limit of 10 ng/g dw. In the 50-60 cm section UV-327 is much more prominent than UV-328. Moving up core, UV-328 progressively accounts for more of the sum of both phenolic benzotriazoles. This reflects the earlier introduction (1963) and subsequent earlier discontinuation (1972) of UV-327 relative to UV-328 (1970 and 1985, respectively).

At Apponaug Cove surface concentrations were higher than the lower sections of the core. There could be degradation in the oxic surface layer of the sediments with subsequently lower concentrations in the deeper sections. However, data from a core taken in 1986 had a profile more consistent with the appearance of the different analytes. Therefore, the authors assume that the distribution of phenolic benzotriazoles represents resuspended sediment transport and deposition of materials with high concentrations.

Data from the Seekonk River core also show high concentrations in the surface layer. Another core taken in the same area in 1986 showed a more orderly decrease down to 70 – 80 cm. The authors assume that some sedimentary layers were removed. Additional evidence of a disturbance is found in the ratio of the phenolic benzotriazoles. The lowest core section with phenolic benzotriazoles (12 – 14 cm) should have high ration of UV-327 to UV-328 due to their production history, but in this case actually had a lower ratio of UV-327 to UV-328 than the sections above it.

Table 76: Concentrations of phenolic benzotriazoles in sediment cores from Narragansett Bay (concentrations taken from a graph)

Quonset Point core			**Apponaug Cove core**			**Seekonk River core**	
depth [cm]	**UV-327 [ng/g dw]**	**UV-328 [ng/g dw]**	**depth [cm]**	**UV-327 [ng/g dw]**	**UV-328 [ng/g dw]**	**UV-327 [ng/g dw]**	**UV-328 [ng/g dw]**
0 - 2	ca. 40	ca. 160	0 – 2	ca. 130	ca. 270	ca. 30	ca. 120
0 - 10	ca. 60	ca. 260	2 – 4	ca. 30	ca. 80	ca. 20	ca. 70
10 - 20	ca. 80	ca. 360	6 – 8	ca. 50	ca. 140	ca. 30	ca. 140
20 - 30	ca. 100	ca. 840	10 – 12	ca. 70	ca. 120	-	-
30 - 40	ca. 130	ca. 1100	12 - 14	-	-	ca. 5	ca. 20
40 – 50	ca. 690	ca. 1180	20 – 22	n.d.	n.d.	n.d.	n.d.
50 - 60	ca. 480	ca. 40	30 – 32	n.d.	n.d.	-	-
60 - 70	n.d.	n.d.	38 – 40	-	-	n.d.	n.d.
80 - 90	n.d.	n.d.	40 – 42	n.d.	n.d.	-	-
100 - 110	n.d.	n.d.	48 - 50	-	-	n.d.	n.d.
119 - 129	n.d.	n.d.					

n.d. = not detected
- = not measured

At Apponaug Cove the phenolic benzotriazole profile indicates a much higher surface concentration than the lower sections of the core. Because the production of UV-328 was discontinued 12 years before the core was taken and the production of UV-327 25 years before that date, the authors attribute the high surface concentrations to resuspended sediment transport and deposition of materials in Apponaug Cove with relatively high concentrations of phenolic benzotriazoles. The ratio of UV-327 to UV-328 also increases in the surface section and may indicate a disturbance of older sediments having higher UV-327 levels.

White et al. (White et al., 2008) analysed three sediment samples from the Pawtuxet River, which were taken in 2003. Several benzotriazole compounds including UV-P, UV-326, UV-327 and UV-328 were isolated from the sediments taken from stations one and two. UV-P dominated with maximum concentrations of 6 µg/g dw sediment (0.33mg/g OC) and 100µg/g dw (1.9 mg/g OC), respectively. Benzotriazole compounds were not identified at station three due to its location upstream of the chemical plant that released benzotriazole compounds into the river.

ANNEX 5: Abbreviations

°C	Degrees centigrade
Å	Angstrom
avg.	Average
B	Bioaccumulative
BAF	Bioaccumulation factor
BCF	Bioconcentration factor
BOD_x	Biological oxygen demand in x days
CAS	Chemical Abstracts Service
CLP	Classification, labelling and packaging (of substances and mixtures)
C&L	Classification and labelling
cm	Centimetres
cm²	Centimetres squared
cm³	Cubed centimetres
CMR	Carcinogenic, mutagenic, toxic to reproduction
d	Day
DDT	Dichlorodiphenyltrichloroethane
$DegT_{50}$	Time interval after which 50% of a substance is degraded
DF	Detection frequency
DFOP	Double First Order in Parallel kinetic model
DT_{50}	Time interval after which 50% of a substance is degraded or disappeared otherwise from the test medium
dw	Dry weight
EC	European Community
ECHA	European Chemicals Agency
EPA	Environmental Protection Agency
EU	European Union
FOMC	First Order Multiple Compartments kinetic model
g	grammes
GC	Gas chromatography
GC/MS	Gas chromatography – mass spectrometry
GC-MS/MS	Gas chromatography – tandem mass spectrometry
GC-HRMS/LRMS	Gas chromatography – high resolution mass spectrometry/low resolution mass spectrometry
GLP	Good laboratory practice
h	Hour
H 351	Classification: suspected of causing cancer
H 373	Classification: May cause damage to organs through prolonged or repeated exposure
H 412	Classification: Harmful to aquatic life with long lasting effects
HALS	Hindered Amine Light Stabilisers
HHCB	1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta-[g]-2-benzo-pyrane, a polycyclic musk, CAS 1222-05-5
HPLC	High performance liquid chromatography
HPLC-MS/MS	High performance liquid chromatography – tandem mass spectrometry
IUPAC	International Union of Pure and Applied Chemistry
K	Rate constant (e.g. for biodegradation in sewage treatment plants)
$K_{air\text{-}water}$	Air-water partition coefficient
Kg	Kilograms
Km	Kilometres
Koc	Organic carbon-water partition coefficient
Kow	Octanol/water partition coefficient (log value)
Kp	Partition coefficient
KPa	Kilopascals

L (or l)	Litres
LC	Liquid chromatography
LC-MS	Liquid chromatography – mass spectrometry
LC-MS/MS	Liquid chromatography – tandem mass spectrometry
LC50	Lethal concentration for 50% of the test organisms
LOD	Limit of detection
LOQ	Limit of quantification
lw	Lipid weight
M	Molar
m^2	Metres squared (area)
m^3	Cubed metres (volume)
Max	Maximum
Min	Minimum
MITI	Ministry of International Trade and Industry (Japan)
mg	Milligrams
ml	Millilitres
ML	Megalitre
Mol	Moles
Mmol	Millimoles
MS	Mass spectrometry
µg	Micrograms
n	Number (e.g. number of samples)
n.d.	Not detected
NER	Non-extractable residues
NITE	National Institute of Technology and Evaluation, Japan
nm	Nanometres
NOEC	No-observed effect concentration
oc	Organic carbon
OECD	Organisation for Economic Co-operation and Development
P	Persistent
Pa	Pascals
PBDE	Polybromodiphenyl ether
PBT	Persistent, bioaccumulative and toxic
PCB	Polychlorinated biphenyl
POP	Persistent organic pollutant
PPB	Parts per billion
PPM	Parts per million
QSAR	Quantitative structure-activity relationship
QPREF	QSAR Prediction Reference Format
QSPR	Quantitative structure-property-relationship
r^2	Correlation coefficient
REACH	Registration, Evaluation, Authorisation and restriction of Chemicals Regulation (EC 1907/2006)
Rel.	Reliability according to the Klimisch Score
s	Seconds (time)
SFO	Single First Order kinetic model
SIM	Selective ion monitoring
SPIN	Database of substances in products in the Nordic countries
std.dev.	Standard deviation
STOT-RE	Specific target organ toxicity – repeated exposure
SVHC	Substances of very high concern
Σ	Sum
T	Toxic (hazard classification)
US or USA	United States of America
UV	Ultraviolet
UV-234	A phenolic benzotriazole UV stabiliser, CAS 70321-86-7
UV-320	A phenolic benzotriazole UV stabiliser, 2-benzotriazol-2-yl-4,6-di-

	tert-butylphenol, CAS 3846-71-7
UV-326	A phenolic benzotriazole UV stabiliser, CAS 3896-11-5
UV-327	A phenolic benzotriazole UV stabiliser, 2,4-di-tert-butyl-6-(5-chlorobenzotriazol-2-yl)phenol, CAS 3864-99-1
UV-328	A phenolic benzotriazole UV stabiliser, 2-(2H-benzotriazol-2-yl)-4,6-ditertpentylphenol, CAS 25973-55-1
UV-329	A phenolic benzotriazole UV stabiliser, CAS 3147-75-9
UV-350	2-(2H-benzotriazol-2-yl)-4-(tert-butyl)-6-(sec-butyl)phenol, CAS 36437-37-3
UV-360	A phenolic benzotriazole UV stabiliser, CAS 103597-45-1
UV-571	A phenolic benzotriazole UV stabiliser, CAS 125304-04-3
UV-928	A phenolic benzotriazole UV stabiliser, CAS 73936-91-1
UV-P	A phenolic benzotriazole UV stabiliser, CAS 2440-22-4
vB	Very bioaccumulative
vP	Very persistent
vPvB	Very persistent, very bioaccumulative
w.a.	When applicable
ww	Wet weight
WWTP	Waste water treatment plant