Substance Name: 2-(2H-benzotriazol-2-yl)-4-(tert-butyl)-6-(sec-butyl)phenol (UV-350)

EC Number: 253-037-1

CAS Number: 36437-37-3

SUPPORT DOCUMENT FOR IDENTIFICATION OF

2-(2H-BENZOTRIAZOL-2-YL)-4-(TERT-BUTYL)-6-(SEC-BUTYL)PHENOL (UV-350)

AS A SUBSTANCE OF VERY HIGH CONCERN BECAUSE OF ITS VPVB (ARTICLE 57 E) PROPERTIES

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IDENTIFICATION OF A SUBSTANCE OF VERY HIGH CONCERN ON THE BASIS OF THE CRITERIA SET OUT IN REACH ARTICLE 57

Substance Name: 2-(2H-benzotriazol-2-yl)-4-(tert-butyl)-6-(sec-butyl)phenol (UV-350)

EC Number: 253-037-1

CAS number: 36437-37-3

- 2-(2H-benzotriazol-2-yl)-4-(tert-butyl)-6-(sec-butyl)phenol (UV-350) is identified the substance as very persistent and very bioaccumulative (vPvB) according to Article 57 (e) of Regulation (EC) No 1907/2006 (REACH).

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

UV-320 (EC 223-346-6) and UV-328 (EC 247-384-8), that are used in a read-across assessment for UV-350, were identified as Substances of Very High Concern (SVHC) due to their PBT/vPvB properties, according to article 57 d and e of Regulation (EC) No 1907/2006 (REACH), and were therefore included in the Candidate List for Authorisation on 17 December 2014, following ECHA's decision ED/108/2014.

Persistence

The persistence of UV-350 has been assessed by using a weight-of-evidence approach.

Conclusions of the weight-of-evidence approach:

- There is no biodegradation screening test for UV-350. The ready biodegradation tests on UV-320 and UV-327 following OECD Guideline 301 C indicate no biodegradation at all (0% after 28 days). An OECD 301 B test with UV-328 resulted in 2-8 % $ThCO_2$ evolution. All of these UV protection substances are "not readily biodegradable". Due to the structural similarity of UV-350 to UV-320, UV-327, and UV-328, it may be assumed that UV-350 is also "not readily biodegradable".

- UV-350 was tested in a water/sediment system based on OECD Guideline 308. UV-350 rapidly and completely adsorbs to sediment and hardly degrades over a period of 100 days ($DT_{50, sed.}$ >> 100 d).

- 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 an OECD 308 simulation test in several systems. In these studies, a major degradation product M1 wasdetected. This metabolite is structurally similar to UV-350 and other phenolic benzotriazoles. Therefore, its behaviour in the simulation test is used in a read-across assessment for UV-350. 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 (at 20 °C) 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 DT_{50}-values. The differing side chain of M1 will be degraded faster than that of UV-350. Therefore, and assuming that the fate properties of UV-350 and M1 are similar in a degradation simulation test, the results on M1 can be considered to constitute a best-case read across for disappearance and degradation of UV-350.

- In a recent field study, dissipation of several UV substances in soil other than UV-350 was tested. Using the results of this test, a DT_{50} of 151 to 192 days was calculated. The reported range of DT_{50}-values exceeds the trigger value for persistence in soil. As the time required for disappearance cannot be longer than the time required for degradation, the respective $DegT_{50}$-values will exceed this value range, i.e. they will be over 192 days for the worst case reported. Thus, this study indicates that the other phenolic benzotriazoles meet the numerical vP-criterion of 180 days for the soil compartment as defined in Annex XIII. These results were taken as a read-across on UV-350;

- For UV-327 and the similar substance UV-328, available monitoring studies indicate presence of the substances in sediments decades after environmental releases 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 are taken as a read-across on UV-350. The read across substances UV-320 and UV-328 were already concluded as “vP” (ECHA’s decision ED/108/2014);

- Thus, considering the evidence available, including direct evidence from the water/sediment-study, it is concluded that UV-350 fulfils the P- and vP-criteria as defined under Sections 1.1.1 and 1.2.1 of REACH Annex XIII.

Bioaccumulation

Next to the other UV substances, also UV-350 was tested in an OECD 305 C bioaccumulation test in fish. For the two concentration levels (1.0 and 0.1 µg/L), the reported BCF-values were 7,700 and 13,000, respectively; the lipid-normalised BCF-values were 20,370 and 34,391, respectively. Therefore, UV-350 fulfils the B (BCF >2000) and vB criterion (BCF >5000) as defined under Sections 1.1.2 and 1.2.2 of REACH Annex XIII. The results are in line with the bioaccumulative properties of the read across substances UV-320 and UV-328 (ECHA’s decision ED/108/2014).

Conclusion

In conclusion, UV-350 meets the criteria for a vPvB substance according to Article 57(e) of REACH.

Registration dossiers submitted for the substance: No

Justification

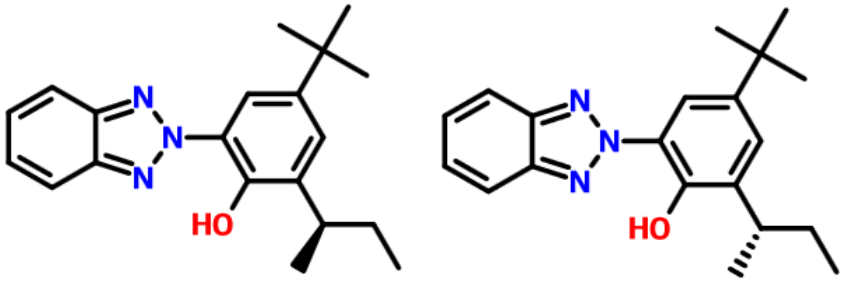
1. Identity of the substance and physical and chemical properties

1.1. Name and other identifiers of the substance

Table 1: Substance identity

EC number:	253-037-1
EC name:	2-(2H-benzotriazol-2-yl)-4-(tert-butyl)-6-(sec-butyl)phenol
SMILES code:	Oc(c(cc(c1)C(C)(C)C)C(CC)C)c1N(N=C(C=2C=CC=3)C3)N2
CAS number (in the EC inventory):	36437-37-3
CAS number: **Deleted CAS numbers:**	36437-37-3 122245-62-9, 142513-61-9, 153613-76-4, 188025-37-8, 189456-67-5
CAS name:	phenol, 2-(2H-benzotriazol-2-yl)-4-(1,1-dimethylethyl)-6-(1-methylpropyl)-
IUPAC name:	2-(2H-benzotriazol-2-yl)-6-sec-butyl-4-tert-butylphenol
Index number in Annex VI of the CLP Regulation	-
Molecular formula:	$C_{20}H_{25}N_3O$
Molecular weight range:	323.43 g/mol
Synonyms:	UV 350 Reaction mass of 2-(2H-benzotriazol-2-yl)-6-[(2R)-butan-2-yl]-4-tert-buthylphenol and 2-(2H-benzotriazol-2-yl)-6-[(2S)-butan-2-yl]-4-tert-buthylphenol 2-(2-hydroxy-3-sec-butyl-5-tert-butylphenyl) benzotriazole; 2-(2-hydroxy-3-sec-butyl-5-tert-butylphenyl)-2H-benzotriazole; 2-(2H-benzotriazol-2-yl)-4-(tert-butyl)-6-(sec-butyl)phenol; 2-(3-sec-butyl-5-tert-butyl-2-hydroxyphenyl)benzotriazole; 2-(3'-sec-butyl-5'-tert-butyl-2'-hydroxyphenyl)benzotriazole; 4-tert-butyl-6-sec-butyl-2-(2H-benzotriazol-2-yl)phenol; Chisorb 350; Eversorb 79

Structural formula:



1.2. Composition of the substance

Name: 2-(2H-Benzotriazol-2-yl)-6-sec-butyl-4(2-methyl-2-propanyl)phenol

Description: organic

Substance type: multi-constituent

Table 2: Constituents

Constituents	Typical concentration	Concentration range	Remarks
2-(2H-benzotriazol-2-yl)-6-[(2R)-butan-2-yl]-4-tert-butylphenol		10-80%	
2-(2H-benzotriazol-2-yl)-6-[(2S)-butan-2-yl)-4-tert-butylphenol		10-80%	

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

Table 3: Structurally related substance identity of UV-320

EC number:	223-346-6
EC name:	2-benzotriazol-2-yl-4,6-di-tert-butylphenol
SMILES:	Oc(c(cc(c1)C(C)(C)C)C(C)(C)C)c1n(nc(c2ccc3)c3)n2
CAS number (in the EC inventory):	3846-71-7
CAS number:	3846-71-7
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

Substance type: mono-constituent

Structurally related substance(s) formula:

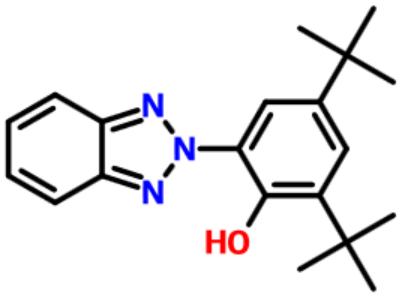


Table 4: Structurally related substance identity of UV-327

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-2*H*-benzotriazol-2-yl)-4,6-bis(1,1-dimethylethyl)-
IUPAC name:	2-(5-chloro-2H-benzotriazol-2-yl)-4,6-bis(2-methyl-2-propanyl)phenol
Index number in Annex VI of the CLP Regulation	-
Molecular formula:	$C_{20}H_{24}ClN_3O$
Molecular weight range:	357.88 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; Hisorp 327; Kemisorb 72; LA 34; Lowilite 27; Mark LA 34; Seesorb 702; TNV 327;

	Tinuvin 327; UV 2; UV 2 (UV stabilizer); UV-327; UV-Chek AM 607; Viosorb 580

Substance type: mono-constituent

Structurally related substance(s) formula:

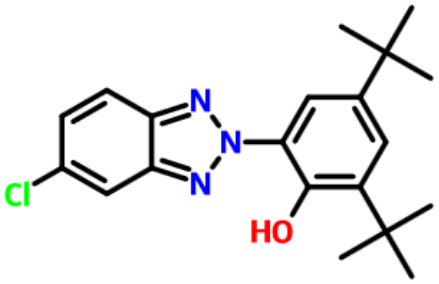
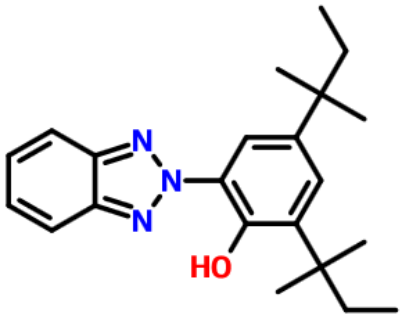


Table 5: Structurally related substance identity of UV-328

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:	$C_{22}H_{29}N_3O$
Molecular weight range:	351.50 g/mol
Synonyms:	UV 328 phenol, 2-(2H-benzotriazol-2-yl)-4,6-di-tert-pentyl-(7CI,8CI) 2-(2-hydroxy-3,5-di-tert-amylphenyl)-2H-benzotriazole 2-(2-hydroxy-3,5-di-tert-amylphenyl)benzotriazole 2-(2-hydroxy-3,5-di-tert-pentylphenyl)benzotriazole 2-(2H-benzotriazol-2-yl)-4,6-bis(1,1-dimethylpropyl)phenol 2-(2H-benzotriazol-2-yl)-4,6-di-tert-pentylphenol 2-(2'-hydroxy-3',5'-di-tert-amylphenyl)benzotriazole 2-(3,5-di-tert-amyl-2-hydroxyphenyl)-2H-benzotriazole 2-(3,5-di-tert-amyl-2-hydroxyphenyl)benzotriazole 2-(3,5-di-tert-pentyl-2-hydroxyphenyl)-2H-benzotriazole 2-(3,5-di-tert-pentyl-2-hydroxyphenyl)benzotriazole 2-(3',5'-di-tert-amyl-2'-hydroxyphenyl)benzotriazole Chisorb 328 Cyasorb UV 2337 Eversorb 74 Kemisorb 74 Lowilite 28 Seesorb 704 Sumisorb 350

Substance type: mono-constituent

Structurally related substance(s) formula:



1.4. Physicochemical properties

Table 6: Overview of physicochemical properties

Property	Value	Reference / source of information
Physical state at 20°C and 101.3 kPa	-	-
Melting / freezing point	81 – 83 °C	Rosevear, Judi; Australian Journal of Chemistry 1985, V 38(8), P1163-76; Condition: Solv: ethanol (64-17-5)
Boiling point	458.0±55.0 °C	Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2015 ACD/Labs)
Vapour pressure	6.96E-7 Pa at 25 °C	Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2015 ACD/Labs)
Density	1.12±0.1 g/cm^3 at 20 °C and 1013.25 hPa	Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2015 ACD/Labs)
Water solubility	0.1395 mg/L at 25 °C	QSAR estimation from log KOW with the EPISuite module WSKOW v1.41; log K_{ow} used for calculation: 6.31 (also estimated, see below)
Partition coefficient n-octanol / water (log value)	6.951 ± 1.251 at 25 °C	Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2015 ACD/Labs)
	6.31	EPISuite result (SRC): Log K_{ow} (KOWWIN v1.67 estimate)
	7.11	COSMOtherm v. C30_1201

2. Harmonised classification and labelling

None.

3. Environmental fate properties

Studies/paragraphs in this chapter, which were already used in the SVHC dossiers on UV-320 and/or UV-328 (ECHA 2014a, ECHA 2014b), are marked with a turquoise background. The dossiers on UV-320 and UV-328 were discussed by the Member State Committee and both substances identified as SVHC in December 2014.

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-350.

3.1.1.2. Oxidation

There are no studies on oxidation of UV-350 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. However, to the knowledge of the dossier submitter there are no experimental studies in the literature available showing a reaction of UV-350 and atmospheric Nitrate radicals.

Phenolic benzotriazoles are mainly used as UV absorbers. Given their chemical structure, degradation through oxidation can be regarded as negligible.

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 radiation-less 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

Overall, abiotic degradation is not relevant for UV-350.

3.1.2. Biodegradation

3.1.2.1. Biodegradation in water

3.1.2.1.1. Estimated data

Since no experimental data are available on the biodegradation of UV-350 in water, a QSAR-calculation with the BIOWIN module of EPISuite v4.10 (U.S. EPA, 2011) was performed. The numerical results are shown in Table 7. For details of these calculations, see Annex I.A. These estimations are considered to be reliable with restrictions, as one inhibiting structural motif (the triazole group) is not represented in the BIOWIN models.

Table 7: Results of BIOWIN 2, 3, and 6 predictions of biodegradability for UV-350

Model	QSAR result	Overall model performance	Reference
BIOWIN 2 (non-linear)	**0.1329** (does not biodegrade fast)	Reliable with restrictions (Klimisch 2)	Annex I.A.9
BIOWIN 3 (ultimate survey)	**2.2538** (weeks to months)	Reliable with restrictions (Klimisch 2)	Annex I.A.9
BIOWIN 6 (MITI non-linear)	**0.012** (does not biodegrade fast)	Reliable with restrictions (Klimisch 2)	Annex I.A.9

The results of the prediction indicate that UV-350 is a borderline case for meeting the screening criteria of the ECHA Guideline R.11 for persistence. In the light of the available experimental results of similar structures (UV-320, UV-327 and UV-328), the simulation of the prediction pathway and the discrepancies of the BIOWIN fragment approach considering the triazole group, it is concluded that UV-350 would meet the experimental screening criteria.

3.1.2.1.2. Screening tests

No screening tests on the biodegradability of UV-350 are available. However, studies on the structurally related benzotriazoles UV-320, UV327 and UV-328 are available, all showing little or no degradation. The results are shown in Table 8.

Table 8: Results of the Degradation Screening Tests on UV-320, UV-327 and UV-328

Substance	Result Screening Test	Test protocol	Reliability	Reference
UV-320	Non-biodegradable, BOD = 0	OECD 301C	Klimisch 2	(NITE, 2012)
UV-327	Non-biodegradable, BOD = 0	OECD 301C	Klimisch 2	(NITE, 2012)
UV-328	not readily biodegradable (2-8 % after 28 days)	OECD 301B	Klimisch 2	(Phenolic Benzotriazoles Association, 2001)

As UV-350 is expected to follow the same degradation pattern (cf. below), it is concluded in a read-across approach that it is “not readily biodegradable”, too.

3.1.2.1.3. Simulation tests (water and sediments)

Wick et al. (in preparation, 2015) investigated the biodegradation of several phenolic benzotriazoles including UV-350 in a water-sediment study. This non-GLP study shows some variations to the OECD Guideline 308: (a) Only one sediment was used with a relatively high TOC of 4.22 % (fine texture, as required); (b) the sediment was freshly collected at a site where previous contamination with organic chemicals may be expected, resulting in possible pre-adaptation of micro-organisms; (c) volatiles were not collected. Besides that, test conditions were in accordance with OECD 308: equilibration time 4 weeks; test temperature 20 °C; constant pH and 0_2 levels (> 95 %); initial test substance concentration approx. 10 µg/L UV-350; spiking of the radioactively non-labelled test substance into the water phase with the help of a solvent; triplicate sampling at 30 min, 2, 4, 8, 16, 25, 50 and 100 days after spiking; test duration was 100 days. Extraction of the freeze-dried sediment samples was done by pressurised liquid extraction (PLE) followed by silica clean-up. Analysis of UV-350 was accomplished by LC-MS/MS measurements. An external standard calibration with 14 calibration points ranging from 0 to 100 µg/L and a linear fitting were used for quantification. The limit of quantification (LOQ) for UV-350 was determined to be 0.4 ng/g in sediment, thus being lower than 1 % of the initial amount. A parallel test with the reference substance Lenacil showed degradation of up to 50 % on 100 d, thus demonstrating the microbial viability of the test system. Results for this test are presented in Figure 1 (the error bars represent the standard deviation).

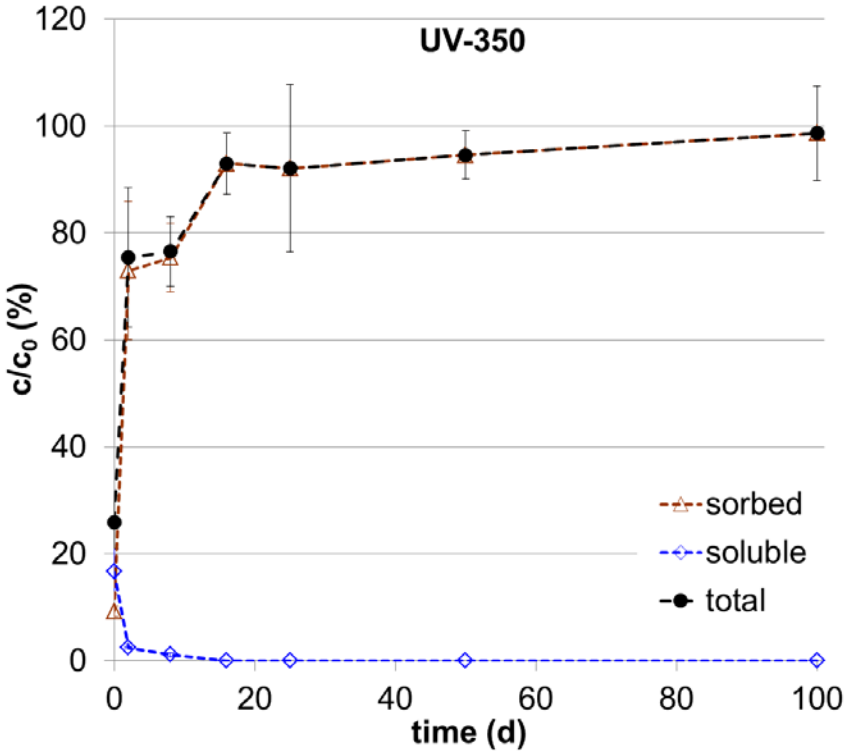


Figure 1: Average relative concentrations (% of c_0) of UV-350 in sediment-water systems incubated for 100 d at 20 °C; the initial spike concentration was 10 µg/L.

Recoveries of 92 to 99 % UV-350 between incubation day 16 and 100 were in the required

range of 70 to 110 % and confirmed that the mass balance was closed after the sorption equilibrium had been established. Recoveries determined after day 16 were fairly constant over time and standard deviations were mainly less than 15 % suggesting a good uniformity and repeatability of the results.

Analysis of the soluble and sorbed concentrations confirmed a high sorption affinity of UV-350. After about 16 days, UV-350 could not be detected in the water phase anymore and recoveries in sediments reached values of approximately 95 %, which remained fairly constant for whole incubation period. Based on the quantification limit for the water phase (0.08 ng/mL), it can be expected that more than 99.25 % of the applied amount of UV-350 was sorbed to the sediment after 16 days. Due to the intensive extraction method, which was specifically designed to recover as much of the non-radioactive test substance as possible, there were practically no “non-extractable residues” (NER). No significant loss of UV-350 could be observed until the end of the incubation period. The DT_{50} in water can be expected to be < 2 days, while DT_{50} in sediment and in the total system was far beyond 100 days. The formation of transformation products contributing to more than 10 % of the applied amount of parent compound cannot be expected, because the mass balance for UV-350 itself did not show any trend to decline after day 16.

In conclusion, UV-350 rapidly and nearly completely adsorbs to sediment in a water / sediment system and hardly degrades over a period of 100 days ($DT_{50,sed.}$ >> 100 d).

Besides that, 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-hydroxy-phenyl]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 350.

Rationale for read-across assessment:

Please note that the rationale for read-across assessment between M1 and UV-327, UV-320, UV-328, and UV-350 has already been discussed and accepted by the Member State Committee (ECHA 2014a, ECHA 2014b). 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 2).

As can be seen in Figure 2, UV-320, UV-327, UV-328, and UV-350, as well as M1 are structurally similar and differ only slightly in the substitution groups in position 4 (and 6) of the phenolic ring. UV-327 differs from the others by the substitution of one hydrogen atom with a chlorine atom in the benzotriazole moiety. Based on this structural relationship these substances should have similar physicochemical properties (cf. Table 9). In the case of EC 407-000-3, the side-chain in position 4 contains an ester. Two simulation studies with EC 407-000-3 are discussed below.

A comparison of physico-chemical properties of the UV substances is difficult, because only few experimental data are available on UV-328 and UV-327 and none on the other substances (UV-320, UV-350, M1). Nevertheless, the missing experimental data were simulated with the QSAR-methods provided by EPISuite and COSMOtherm, in order to at least estimate the respective ranges (cf. Annex I.C for K_{OW} and Annex I.D for K_{oc}). The comparison in Table 9 shows that all the substances are lipophilic with a strong tendency for binding to organic

carbon. M1 is more water soluble and thus less lipophilic than the other substances and is therefore likely to distribute slightly differently in the environment. However, more water-soluble substances can be assumed to degrade faster in the environment since they are more bioavailable. If there is a certain effect on the degradation time, it should therefore result in shorter DT_{50}-values for M1.

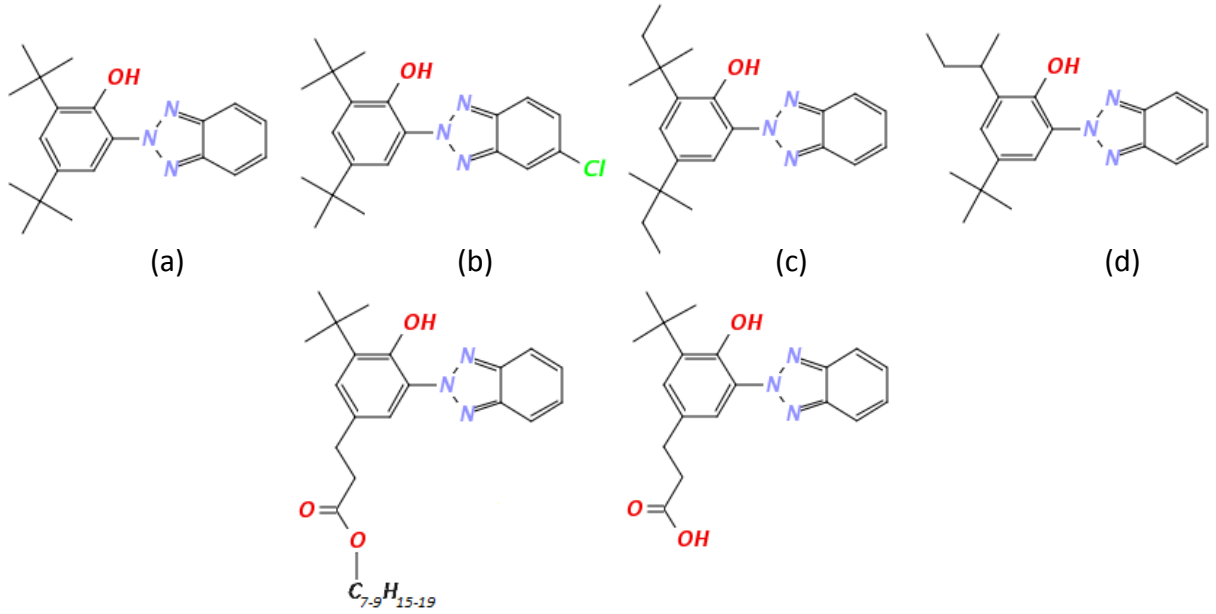


Figure 2: Chemical structure of UV-320 (a), UV-327 (b), UV-328 (c), UV-350 (d), EC 407-000-3 (e) and its first degradation product M1 (f)

Table 9: Overview of available physico-chemical data for UV-320, UV-327, UV-328, UV-350, EC 407-000-3, and metabolite M1

Substance	**UV-320**			**UV-327**			**UV-328**		
EC-No.	223-346-6			223-383-8			247-384-8		
CAS-No.	3846-71-7			3864-99-1			25973-55-1		
SMILES	Oc(c(cc(c1)C(C)(C)C)C(C)(C)C)c1n(nc(c2ccc3)c3)n2			Oc(c(cc(c1)C(C)(C)C)C(C)(C)C)c1n(nc(c2cc(c3)Cl)c3)n2			Oc(c(cc(c1)C(CC)(C)C)C(CC)(C)C)c1n(nc(c2ccc3)c3)n2		
Mol. Weight [g/mol]	323.4			357.9			351.5		
	Exp.	*EPISuite*	*COSMO therm*	*Exp.*	*EPISuite*	*COSMO therm*	*Exp.*	*EPISuite*	*COSMO therm*
Log K_{OW}	n.a	6.3	7.4	n.a	6.9	7.9	>6.5 [a]	7.3	7.9
Log K_{OC}	n.a.	5.1/4.6	5.2	n.a.	5.3/5.0	5.7	n.a.	5.7/5.2	5.5
Water solubility [mg/L] (exp. data at 20°C)	n.a.	0.2/4.6	9.0E-4	0.022	3E-2/1	2.0E-4	0.015 [b] <0,001	1.0E-2/ 0.4	3.0E-4
Vapour pressure [Pa] (exp. data at 20°C)	n.a.	8.2E-6	5.4E-5	n.a.	3.6E-8	1.1E-5	5.0E-6	2.6E-6	2.4E-5
Substance	**UV-350**			**EC 407-000-3**			**M1**		
EC-No.	253-037-1			407-000-3			-		
CAS-No.	36437-37-3			127519-17-9			84268-36-0		
SMILES	Oc(c(cc(c1)C(C)(C)C)C(CC)C)c1N(N=C(C=2C=CC=3)C3)N2			O=C(CCc1cc(c(c(c1)n3nc2c(n3)cccc2)O)C(C)(C)C)OCCCC(C)CC			CC(C)(C)c3cc(CCC(=O)O)cc(n2nc1ccccc1n2)c3O		
Mol. Weight [g/mol]	323.4			437.6			339.4		
	Exp.	*EPISuite*	*COSMO therm*	*Exp.*	*EPISuite*	*COSMO therm*	*Exp.*	*EPISuite*	*COSMO therm*
Log K_{OW} [d]	n.a	6.3	7.1	n.a	7.8	n.a	n.a	3.3	3.0 [c]
Log K_{OC} [e]	n.a.	5.2/4.66	4.9	n.a.	5.9/5.4	n.a.	n.a.	3.8/2.2	3.96
Water solubility [mg/L] (exp. data at 20°C)	n.a.	0.14/3.1	n.a.	n.a.	1.45E-3/ 0.033	n.a.	n.a.	102/213	1.29
Vapour pressure [Pa] (exp. data at 20°C)	n.a.	1.04E-7	n.a.	n.a.	7.1E-11	n.a.	n.a.	6.9E-10	1.0E-7

n.a.: not available

Footnotes to Table 9:
a) According to the registration dossier
b) According to Lopez-Avila and Hites (1980)
c) Using a pKA of 4.65 as calculated by ACDLabs
d) For an analysis of the QSAR prediction of log K_{OW} for UV-327 and UV-350, see Annex I.C.
e) For an analysis of the QSAR prediction of log K_{oc} for UV-327 and UV-350, see Annex I.D. The two estimated log K_{oc}-values refer to the K_{OW}/MCI-method.

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(2) Common precursors and/or the likelihood of common breakdown products via physical and biological processes, which result in structurally similar chemicals (see Figure 3)

According to the simulation of the biodegradation pathway with the Biocatalysis/ Biodegradation Prediction System PPS[1], the breakdown products are similar. Three generalised 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 3a).

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 3b).

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 3c).

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.

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

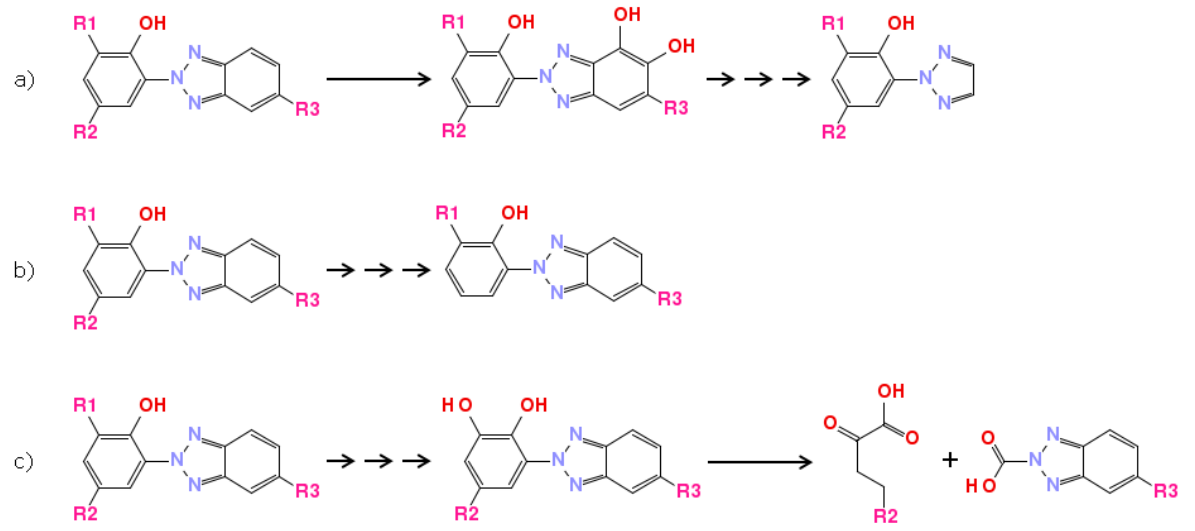

Figure 3: Simulated simplified mechanisms for the degradation of the phenolic benzotriazoles. a) Degradation of the benzotriazole moiety; b) Degradation of side chain R2; c) Degradation of side chain R1 leading to the ring cleavage of the phenolic ring R1, R2: alkyl; R3: H or Cl. Side reactions are for the sake of simplicity not considered here

(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 considered phenolic benzotriazoles and M1.

The following conclusion is drawn:

$DegT_{50}(M1) < DegT_{50}(UV\text{-}350) < DegT_{50}(UV\text{-}320) \approx DegT_{50}(UV\text{-}328) < DegT_{50}(UV\text{-}327)$.

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 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 of these molecules (UV-350 has a tertiary C at R1 instead of a quaternary C) and thus will have a minor influence on degradation. R2 of M1 is different to R2 of UV-320, UV-327, UV-328, and UV-350. R2 of M1 is a linear n-propionic acid, which degrades easier than R2 of the other substances. As the degradation of M1 should be faster than for the other phenolic benzotriazoles, the results of M1 can be regarded as a best case-scenario for the degradation half-lives of UV-350 and the other UV-substances. The structures of UV-320 and UV-327 are nearly identical except for the additional chlorine in UV-327 (cf. Figure 2). Thus, degradation of UV-327 needs dechlorination which adds an additional degradation step as compared to UV-320. Hence, degradation of UV-327 will be slower than degradation of UV-320.

This can also be verified by looking at the incremental values of the respective side chains (Table 10) in common QSAR-models. For example, BIOWIN3 (ultimate degradation) predicts a value of 3.07 for a tert-butyl group (UV-320, UV-327; meaning a degradation in weeks); for a tert-pentyl group (UV-328) a value of 3.04 (also meaning weeks); for a sec-butyl group (UV-350) a value of 3.37 (meaning days to weeks); and for an 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.

Table 10: Fragments to be considered for qualitative assessment of degradation times; substances are ordered by decreasing degradability (cf. above)

Substance	**R1**	**R2**	**R3**
M1	tert-butyl [a]	n-propionic acid [d]	H
UV-350	sec-butyl [b]	tert-butyl [a]	H
UV-320	tert-butyl [a]	tert-butyl [a]	H
UV-327	tert-butyl [a]	tert-butyl [a]	Cl
UV-328	tert-pentyl [c]	tert-pentyl [c]	H

a) Smiles-code for tert-butyl: CC(C)(C)
b) Smiles-code for sec-butyl: CCC(C)
c) Smiles-code for tert-pentyl: CC(C)(CC)
d) Smiles-code for n-propionic acid: CCC(=O)O

In conclusion, the general rules for applying a read-across approach under REACH seem to be met as far as can be evaluated without availiability of 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 behaviour of the phenolic benzotriazoles 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 disappearance half-life.

$DegT_{50}$: Degradation half-life time; used to express the half-life for true 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 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 Persistence 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 the specific case of EC 407-000-3, there is no unlimited reservoir of the parent substance. It is known from monitoring data, that the decline of concentration of the parent is fast; already after 14 days, most of EC 407-000-3 has degraded and its concentration is low in comparison to the concentration of M1. Nevertheless, it should be kept in mind that the calculated

DT_{50}-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 the test system

Test conditions of this water/sediment study 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. Chi² 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 a 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. It could be assumed for both systems 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 radiolabelled 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 drop wise onto the water surface. Samples were taken and water and sediment were analysed separately on six occasions. Two traps were employed for volatile substances. Further information on test conditions is given in Table 11.

Table 11: Detailed conditions for the water/sediment simulation test (aerobic)

System	org. C in %	Temperature in °C	Substance concentration in µg/L	Test duration (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 %)	

Test duration was 100 days, i.e. shorter than the trigger values for P and vP in sediment, and test temperature was 20 ± 2 °C. As this is higher than 12 °C, PBT-guidance recommends employing a temperature correction for degradation times with a Q10-factor of 2.2.

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. In both systems, mineralisation of EC 407-000-3 was negligible with 1.2 % and 1.3 %. Volatile substances were not detected.

As stated above it is not possible to differentiate between degradation and mere

dissipation processes, because of missing information on real degradation and the unknown identities of the further metabolites and thus the $DisT_{50}$ of M1 for the sediment phase represents all processes. Another aspect that hampers differentiation is the relatively high level of non-extractable residues (NER), because it remains unknown to which extent parent or metabolites contributed to NER formation. NER reached 36 % in the river system and 25 % in the pond system. They were mainly bound to the humic fraction and humic acids and to a lesser part to fulvic acids. Phenolic benzotriazoles have a high log K_{OC}. Therefore, they have in general a high tendency to adsorb.

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 (cf. Figure 4).

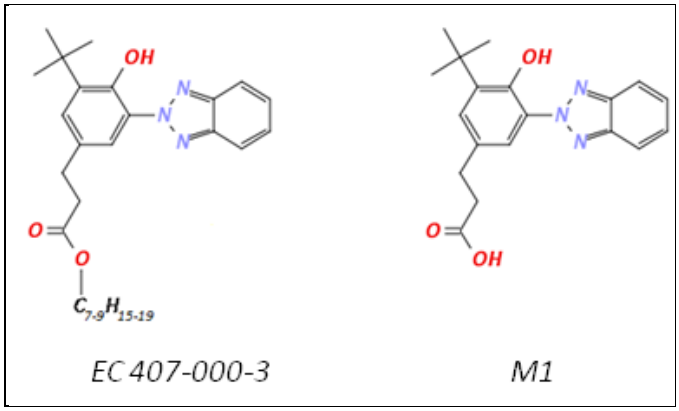

Figure 4: Molecular structure of EC 407-000-3 and M1 in comparison

Results of the kinetic modelling (cf. Annex I.B):

There are two studies, which were assessed (cf. Dossier on EC 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 Persistence and Degradation Kinetics (FOCUS, 2006) using the software KinGUI. This means that the calculated DT_{50}-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 non-extractable residues NER. For further details, see Annex I.B.

Figure 5 and Figure 6 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.

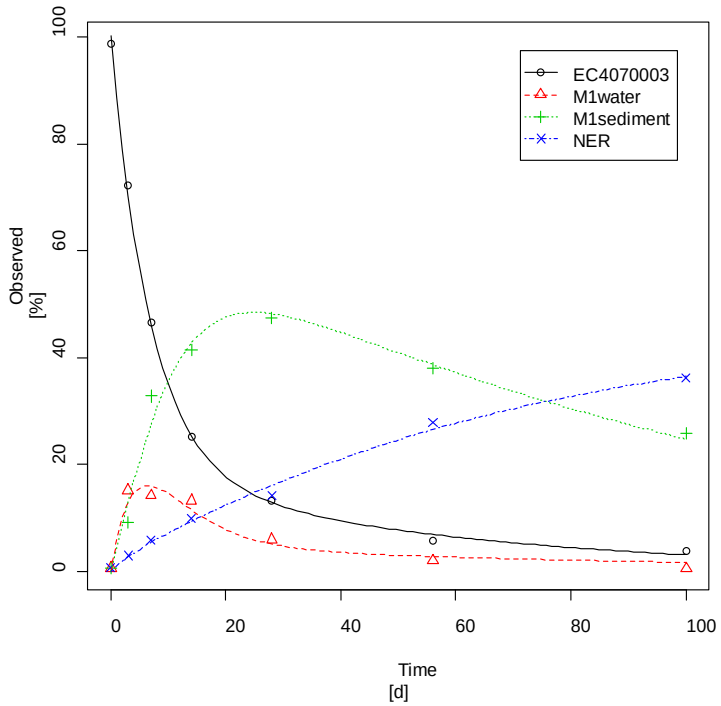

Figure 5: Measured and predicted (kinetic model) residues vs. time for the river system under aerobic conditions

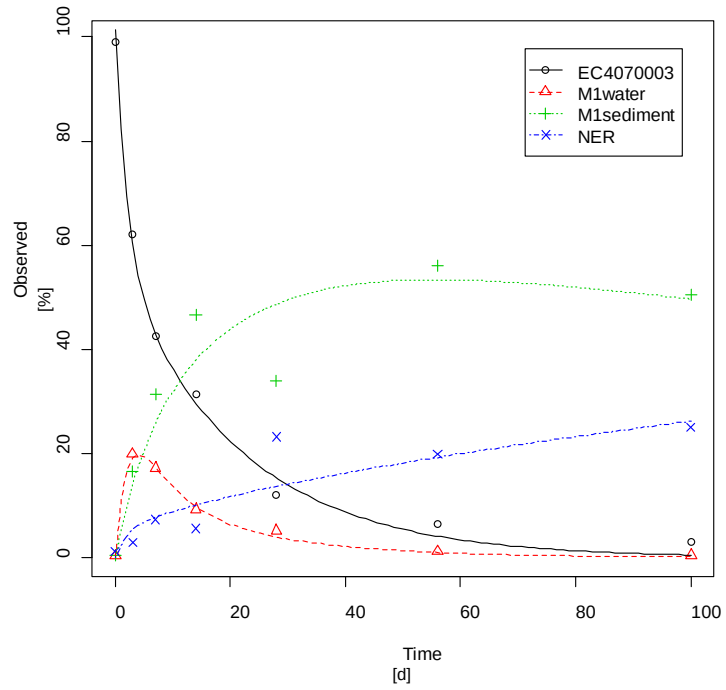

Figure 6: Measured and predicted (kinetic model) residues vs. time for the pond system under aerobic conditions

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 (cf. Figure 7).

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 7) and Chi² of 15 show that the model used describes the data well. This reflects the dissipation of M1 from water to sediment starting after a maximum at day 3.

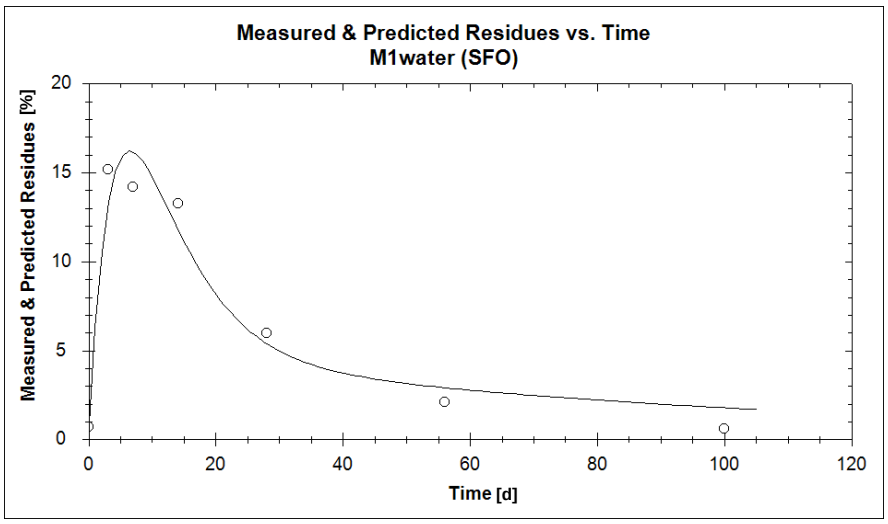

Figure 7: Measured and predicted (SFO model) residues of M1 vs. time in the water phase of the river system under aerobic conditions

For further details, please refer to Section 2.2.2.3. and Table 29 to Table 31 in Annex I.B.

In the river system under aerobic conditions, M1 shows a DT_{50} of 3.4 days in the water phase.

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 8).

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 8) and Chi² of 5.2 show that the used model describes the data well. As in the river system, M1 dissipates from water to sediment.

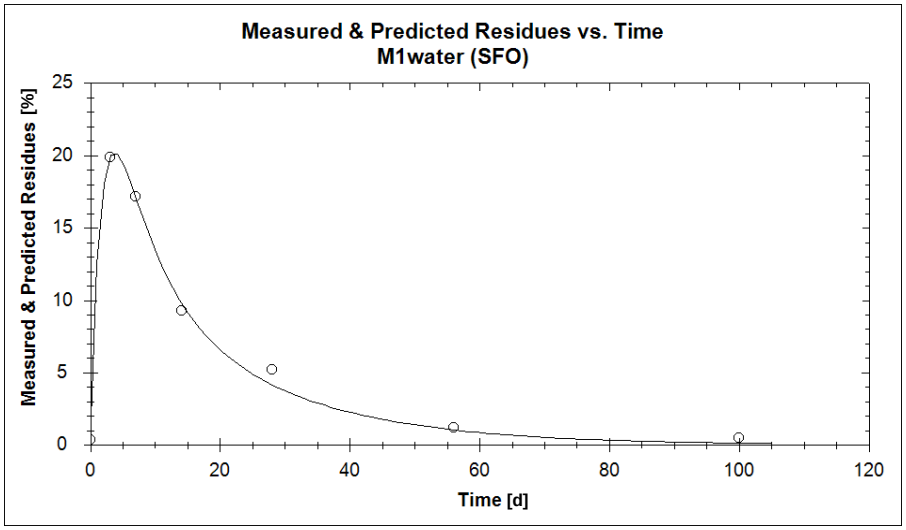

Figure 8: Measured and predicted (SFO model) residues of M1 vs. time in the water phase of the pond system under aerobic conditions

For further details, please refer to Section 2.4.2.3 and Table 35 to Table 37 in Annex I.B.

In the pond system under aerobic conditions, M1 shows a DT_{50} of 3.9 days in the water phase.

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 an SFO DT_{50} of 31.6 days. Visual fit (see Figure 9) and Chi^2 of 8.3 show that the used model describes data well.

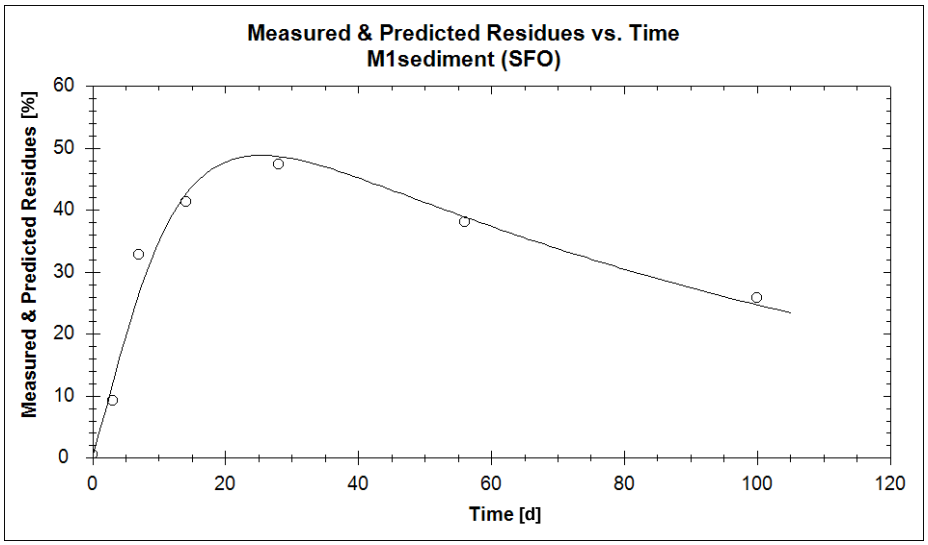

Figure 9: Measured and predicted (SFO model) residues of M1 vs. time in the sediment phase of the river system under aerobic conditions

For further details, please refer to Section 2.2.2.4. and Table 29 to Table 31 in Annex I.B.

In the river system under aerobic conditions, M1 shows a DT_{50} of 31.6 days in the sediment phase.

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. 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 10) 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.

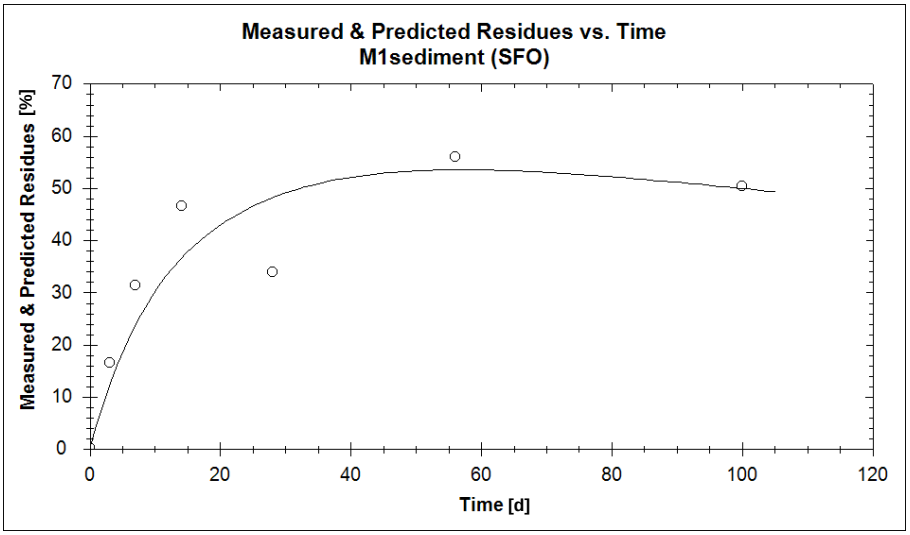

Figure 10: Measured and predicted (SFO model) residues of M1 vs. time in the sediment phase of the pond sediment under aerobic conditions

For further details, please refer to Section 2.4.2.4 and Table 35 to Table 37 in Annex I.B.

In a pond system under aerobic conditions, M1 shows a DT_{50} of 248.2 days in the sediment phase.

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 I.B.

Figure 11 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.

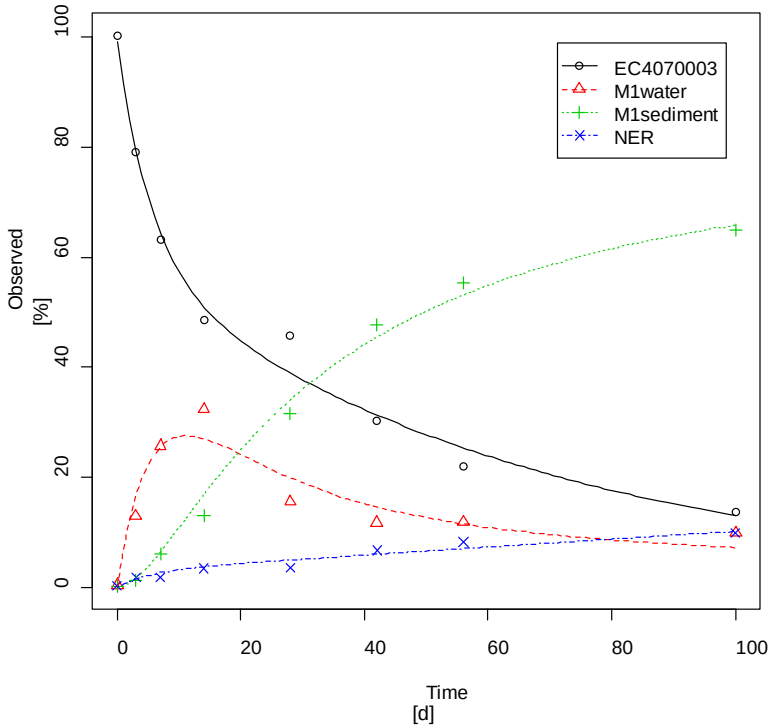

Figure 11: Measured and predicted (kinetic model) residues vs. time in the pond system under anaerobic conditions

M1 in the water phase under anaerobic conditions:

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 an SFO DT_{50} of 12.2 days. Visual fit (see Figure 12) and Chi^2 of 16.8 show that the used model describes data well though Chi^2 is slightly elevated.

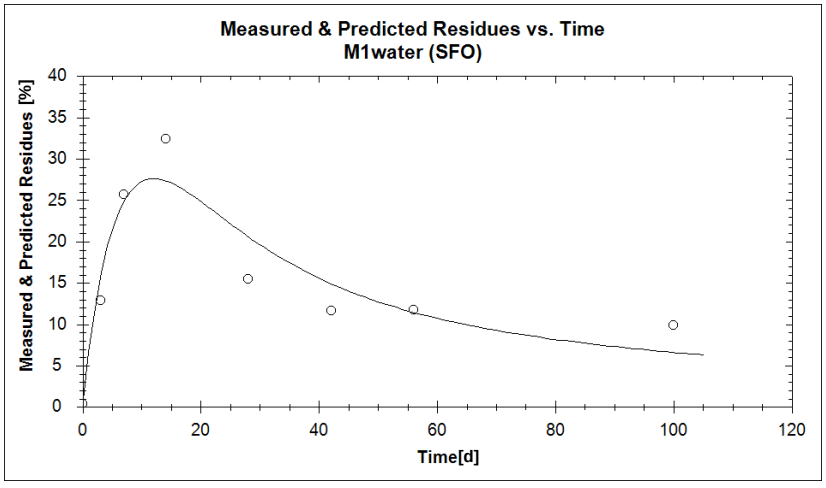

Figure 12: Measured and predicted (SFO model) residues of M1 vs. time in the water phase of the pond system under anaerobic conditions

For further details, please refer to Section 3.2.2.3. and Table 41 to Table 43 in Annex I.B.

In a pond system under anaerobic conditions, M1 shows a DT_{50} of 12.2 days in

the water phase.

M1 in the sediment phase under anaerobic conditions

M1 concentration in sediment rose steadily up to day 42 (see Figure 13). Thereafter, the increase was less pronounced but stayed steady up to the test end. M2-9, which represented the next degradation steps, did not exceed 2.2 %. This level 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 an SFO DT_{50} of 237.7 days. Visual fit (see Figure 13) and Chi² 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.

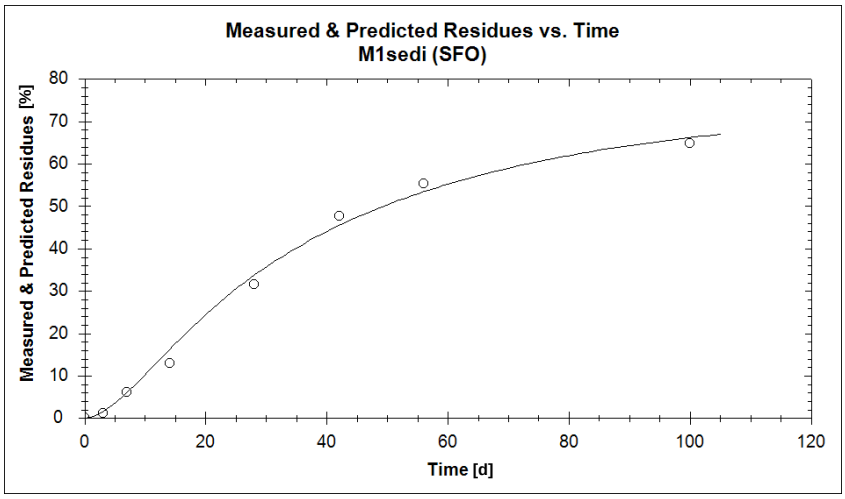

Figure 13: Measured and predicted (SFO model) residues of M1 vs. time in the sediment phase of the pond system under anaerobic conditions

For further details, please refer to section 3.2.2.4. and Table 41 to Table 43 in Annex I.B.

In a pond system under anaerobic conditions, M1 shows a DT_{50} of 237.7 days in the sediment phase.

3.1.2.2. Biodegradation in soil

3.1.2.2.1. Simulation tests

Assessment of a simulation field study

Recently, a study by Lai et al. (Lai et al., 2014) 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 fertilisers in agricultural land might be a relevant pathway for environmental contamination. In the following, particular reference is made to values for UV-327 and UV-328, as these substances are similar to UV-350.

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 12. 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 (3 m x 2 m each). In addition, 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 trial sites and the treatments is summarised in Table 12.

Table 12: Detailed information on the field trial sites and treatments according to Lai et al. (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[2]	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 limits were 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 variability (i.e. a rise) of the concentrations was reported by Lai et al. (2014). The authors attribute this 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 variability and how this problem was finally solved. Beginning with March 2011, the problem was eliminated. Therefore, the authors only fitted the data starting from March 2011 to October 2011.

In all the control samples, only trace concentrations at the limit of quantification of

[2] 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.

Benzotriazole, Tolyltriazole and UV-327 were detected, but other phenolic benzotriazoles were not found. The reported concentrations for UV-328 are shown in Figure 14 and Figure 15.

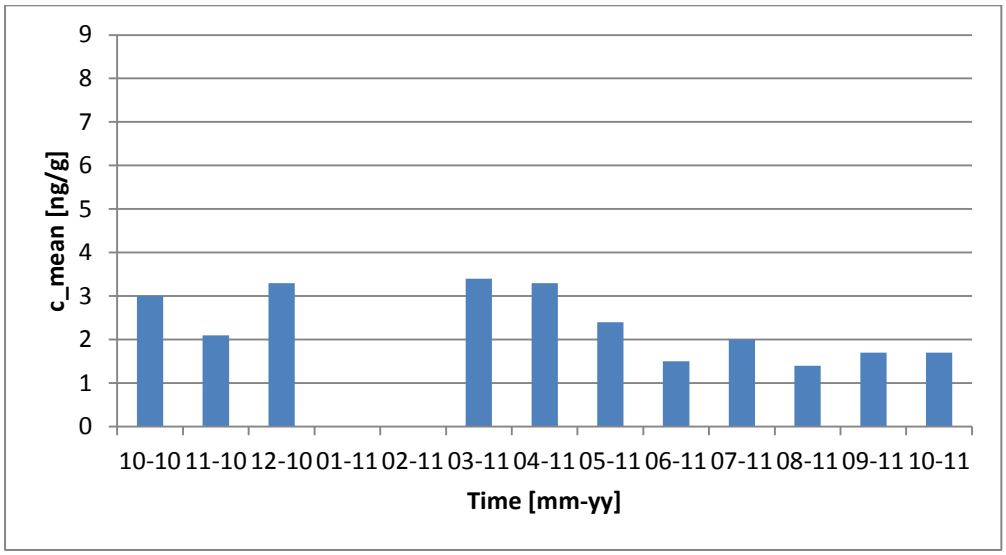

Figure 14: Reported concentrations of UV-328 during the one-year monitoring of Treatment 1 (one time application of sludge in October 2007); standard errors where calculated and lie between 0.1 and 1.7 %. As the errors are so small, they are not shown in the figure

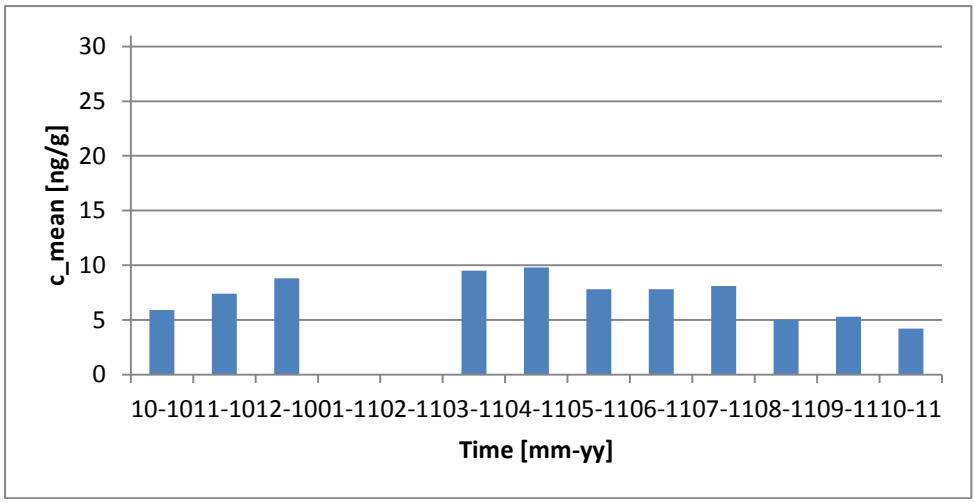

Figure 15: Reported concentrations of UV-328 during the one-year monitoring of Treatment 2 (yearly application of sludge from October 2007 to October 2010); standard errors where calculated and lie between 2 and 10.4 %. As the errors are so small, they are not shown in the figure

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 13: Overview of reported DT_{50}-values (dissipation in the field) 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 DT_{50}-values between T1 and T2 as this kinetic model is independent of concentration. As can be seen in Table 13, in some cases T1 is larger and in some T2, but when additionally 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 passed between (first) application and measurements, therefore potentially allowing micro-organisms to adapt;
- only dissipation was monitored;
- NER were not considered at all.

In a field dissipation study, treatment 1 (one time application of UV-328) in soil resulted in a DT_{50} of 179 days (SFO).

In a field dissipation study, treatment 2 (repeated application of UV-328) in soil resulted in a DT_{50} of 218 days (SFO).

These values may be transferred to UV-350.

3.1.2.3. Summary and discussion on biodegradation

Screening Tests:

There is no biodegradation screening test for UV-350. The ready biodegradation tests on UV-320 and UV-327 following OECD Guideline 301 C indicate no biodegradation at all (0 % after 28 days). An OECD 301 B test with UV-328 resulted in 2-8 % $ThCO_2$ evolution. All of these UV protection substances are “not readily biodegradable”. Due to the structural similarity of UV-350 to UV-320, UV-327, and UV-328, it may be assumed that UV-350 is also “not readily biodegradable”.

Simulation Tests Water/Sediment:

UV-350 was tested in a water/sediment system based on OECD Guideline 308. UV-350 rapidly and completely adsorbs to sediment and hardly degrades over a period of 100 days ($DT_{50,\ sed.}$ >> 100 d).

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 to UV-350. These tests were conducted according to OECD 308. One test was performed under aerobic conditions in a river system and a pond system, the other test was conducted under anaerobic conditions in 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 system have to be considered with care as only part of the degradation curves of M1 were monitored.

Depending on the test system, the observed dissipation half-lives for M1 varied (see Table 14).

Table 14: Summary of dissipation half-lives of M1 for water and sediment under different test conditions (DT_{50}-values for 20 °C)

Water/Sediment Study (OECD 308) for metabolite M1 of EC 407-000-3		**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**

Dissipation half-lives in Table 14 were derived in a test at 20 °C. For assessment of persistence under REACH, these values may be recalculated for an environmental temperature of 12 °C, resulting in even longer DT_{50}-values. However, already the non-extrapolated DT_{50} values obtained at 20 °C indicate fulfilment of the P/vP-criterion for sediment.

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 determined (Lai et al., 2014). 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. The results have to be considered as best case estimations for degradation in the environment as only dissipation was monitored, pre-adaptation of micro-organisms cannot be ruled out, only the warmer period of the year was simulated and NER were not considered at all. The results show that UV-328 is very persistent in soils. These results may be used for read-across to UV-350, which has a similar structure (cf. Figure 2).

Overall assessment of biodegradation testing results:

Direct evidence of the persistence of UV-350 has been presented in the water/sediment-study according to OECD 308. UV-350 rapidly and completely adsorbs to sediment and hardly degrades over a period of 100 days ($DT_{50,\ sed.}$ >> 100 d).

From the read-across approach, it can be concluded that UV-350, which has only slightly different side-chains compared to M1, is at least as hard to degrade as M1. Accordingly, the degradation half-life is inferred to be at least as long as that of M1 (more than 238 days in sediment). Other similar phenolic benzotriazoles are very persistent in soil, too. The predicted degradation pathway also supports the read-across to UV-350.

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). This information can be used as an indication for the degradation potential of UV-327, -328 and similar phenolic benzotriazoles like UV-350 in environmental sediments.

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., 1978; 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 (1985), 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). 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. (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 of UV-327:

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/L) 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 µg/g.

Lopez-Avila and Hites (1980) 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. Average values were calculated for each substance analysed in the sediment cores. 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 15: Concentrations of phenolic benzotriazoles in sediment cores (in µg/g) according to Lopez-Avila and Hites (1980).

	Pawtuxet River			**Pawtuxet Cove**	**Providence River**		
	near to the 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://echa.europa.eu/documents/10162/e614617d-58e7-42d9-b7fb-d7bab8f26feb, DEHP Risk Assessment Report 2008, accessed 19.06.2015).

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.), and interaction between chemicals. Pruell et al. (1984) 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, 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. (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 16, assumption according to the literature: 2.5 cm depth reflects 1 year).

Table 16: 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	$2.0*10^{-6}$

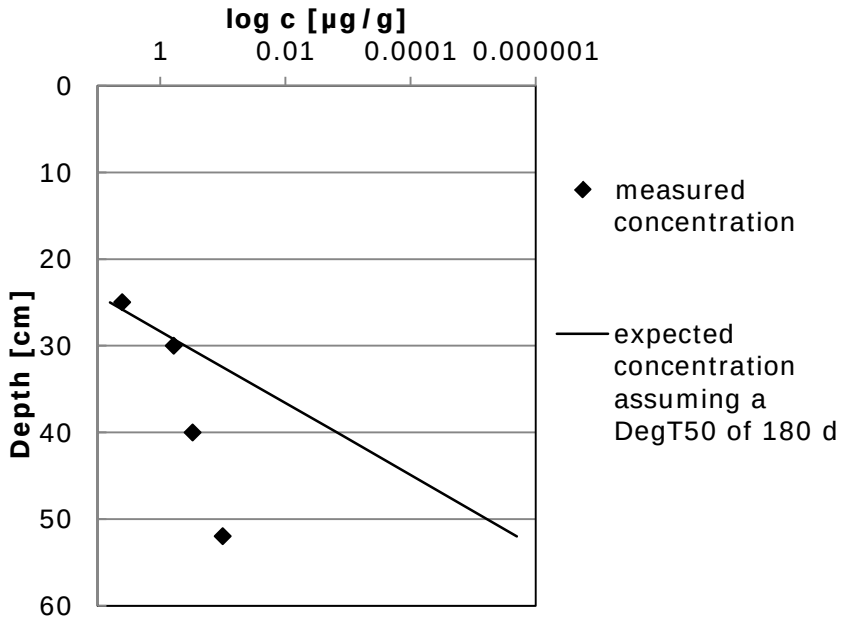

Figure 16: Graphical plot of the measured concentrations in different depths. Also included is a comparison with the concentrations that would be measured, if UV-327 had a $DegT_{50}$ of 180 days. Please note that the concentration scale is logarithmic

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 in Table 17.

Table 17: 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 summarised in Table 18.

It 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 $DegT_{50}$ 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.

Table 18: Comparison of concentrations from literature after and during the respective production periods

Study	Detection limit [µg/g]	Site	Year of collection	Sediment-ation rate [cm]	Layer assumed to reflect production period [cm]	c at that layer [ppm]	c (historical, but probably not at exactly the 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., 1978; 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 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 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 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 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-350, if degradation might occur.

Weight of evidence of the information presented in Sections 3.1.2 and 3.1.3 indicates that UV-350 does persist in the environment. This conclusion is based on the following findings and read-across from UV-327 and UV-328:

The ready biodegradation tests on UV-320 and UV-327 following OECD Guideline 301 C indicates no biodegradation at all (0 % ThO_2 after 28 days). An OECD 301 B test with UV-328 resulted in 2-8 % $ThCO_2$ evolution. All of these UV protection substances are "not readily biodegradable". Due to the structural similarity of UV-350 to UV-320, UV-327, and UV-328, it may be assumed that UV-350 is also "not readily biodegradable".

Direct evidence of the persistence of UV-350 has been presented in the water/sediment-study according to OECD 308. UV-350 rapidly and completely adsorbs to sediment in a water/sediment system (OECD 308) and hardly degrades over a period of 100 days ($DT_{50,sed.}$ >> 100 d).

From the simulation studies on radiolabelled EC 407-000-3, the first metabolite of the substance (M1), which is its carboxylic acid and structurally very similar to UV-350, is used for a read-across assessment. This metabolite is considered as a best-case example, because it presumably is more easily degradable than UV-350. Relevant for the assessment of the persistence of M1 are the sediment DT_{50}-values obtained in the aerobic pond system, which was calculated to be 248 days, and in the anaerobic pond system ($DT_{50,sed}$ 238 days).

In addition, a field dissipation study in soil treated with sludge contaminated with several phenolic benzotriazoles (UV-326, UV-327, UV-328, UV-329, UV-P) is available. 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 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. 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.). Furthermore, we have no detailed information on microbial viability. Given the history and state of pollution, there might not be many micro-organisms in the sediment. On the other hand, the studies show that other contaminants are at least partially degraded. Overall, with the available data, it is nevertheless possible to semi-quantitatively model the concentration curve assuming slow degradation. Results suggest that the $DegT_{50}$ of UV-327 should be larger than 180 days. Furthermore, the concentration levels found up to 25 years after the production of the substances ceased, were of comparable level or only an order of magnitude lower than at the time of manufacture.

Summary on remaining uncertainty

The results of the tests on ready biodegradability are not appropriate for benchmarking with the numerical criteria on persistence of Annex XIII, since they only indicate

potential persistence.

According to Annex XIII, the ultimate decision on the persistence of a substance is based on degradation 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 results in an experimental complexity, which renders the subsequent assessment difficult. In relation to the phenolic benzotriazole assessed, the metabolite M1 is more water soluble due to its carboxylic acid group. This will probably lead to a slightly different behaviour in the environment compared to the target molecules. However, with regard to DT_{50}-values, more water-soluble substances can be assumed to be more bio-available and therefore faster degraded. Therefore, the DT_{50}-values calculated might be lower for M1 than could be expected for UV-350 or the other UV substances.

The highest uncertainty in this particular study on the degradation of EC 407-000-3 is associated with the very high fraction of non-extractable residues (NER). While NER are already high for M1, they would probably be even higher for the parent 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 mineralisation 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. 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 at 100 days). In addition, information on standard errors for the measured concentrations is missing. This limits the explanatory power of the quantitative DT_{50}-values.

The difference of the DT_{50}-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 were 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 DT_{50}-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. Given the available information, the derived numeric value should be considered with caution, as it might vary, but it is unknown by how much, since the test duration was considerably shorter than the estimated DT_{50} (100 vs. around 240 days).

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

Nevertheless, the DT_{50} values obtained with the aerobic and anaerobic pond test systems are very high and they can be considered as best case estimations. The real degradation half-lives of the phenolic benzotriazoles are expected to be higher than the estimated disappearance half-lives of the proxy substance, but it is uncertain to which extent. It should also be noted that in cases where divergent 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 using the results giving rise to the highest concern, to draw the conclusion. This is application of the 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 are missing and no initial concentration values for the different field trials after the first (and in case of T2 the subsequent) applications of the biosolids are given. In addition, 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 also have been 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 the study gives information on primary disappearance only, since none of the metabolites were determined.

The case study of degradation of phenolic benzotriazoles in the Pawtuxet River and the Narragansett Bay comprises several different studies by different authors. Drawing overall conclusions is associated with some uncertainty. The 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 generalised, 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 (with anaerobic layers) 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 used in the read-across approach shows limitations, deficiencies or uncertainties. Considering each information source on its own would make it difficult to conclude with the required confidence that phenolic benzotriazoles are persistent in the environment. However, as all pieces of information presented are independent of each other, it is possible to combine the bits to a broader picture, neutralising shortcomings associated with the individual pieces of information. With this approach, the overall level of uncertainty becomes much lower: All individual results point to a considerable potential for high persistence in the environment.

However, the most compelling evidence of the persistence of UV-350 is provided by the water/sediment-study according to OECD 308. Recovery of the parent UV-350 was near

to 100 % after 100 days in this test, with no tendency for decrease of concentration in the sediment after day 16.

In conclusion, the available data indicate that the substance UV-350 is very persistent in the environment.

3.2. Environmental distribution

3.2.1. Adsorption / desorption

QSAR-based calculations were performed to estimate the adsorption behaviour to soil or suspended organic matter. Details of the prediction are presented in Annex I.D. The default input parameters were used.

Table 19: Results adsorption behaviour predictions of UV-350

Model	QSAR result	Overall model performance	QPREF
EPISuite 4.1 Kow-method	K_{OC} (L/kg): 4.57 10^4 Log K_{OC}: 4.66	Reliable with Restrictions (Klimisch 2)	Annex I.D.9
EPISuite 4.1 MCI-method	K_{OC} (L/kg): 1.55 10^5 Log K_{OC}: 5.19	Reliable with Restrictions (Klimisch 2)	Annex I.D.9
COSMOtherm	K_{OC} (L/kg): 7.94 10^4 Log K_{OC}: 4.90	Reliable with Restrictions (Klimisch 2)	Annex I.D.9

The results of the estimation of the adsorption behaviour lead to the conclusion that UV-350 will strongly adsorb to organic material. Estimated values for UV-350 are slightly lower than for UV-327 (cf. Table 9).

3.2.2. Volatilisation

The tendency for volatilisation from the water phase was estimated by calculation of the Henry constant. Using the molecular weight and the water solubility and vapour pressure as estimated by EpiSuite (see Table 9), the calculated Henry constant[3] was determined to be $1.614*10^{-3}$ Pa*m³*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 $6.81*10^{-7}$ 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-350 from aquatic systems and it is unlikely that the substance will be transported very far in the atmosphere (based on its atmospheric half-life estimated to be 8.14 hours).

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

3.2.3. Distribution modelling

Fugacity Level III distribution modelling

When released to the environment, UV-350 will be distributed to the environmental compartments in different amounts. Table 20 shows the result of Fugacity Level III distribution modelling using EPI Suite v4.10 with the substance properties calculated within EPI Suite and assuming multiple Level III output with identical initial release rate to the compartments air, water and soil. The reliability of the result from the EPI Suite calculation is rated Klimisch 2.

Table 20: Distribution of UV-350 according to Mackay Level III Fugacity Model (estimation with standard parameters as provided by EPI Suite v4.10)

Compartment	**mass amount (percent)**
air	$4.64*10^{-5}$
water	5.21
soil	58.5
sediment	36.3

The results of the distribution modelling and physical-chemical substance properties lead to the conclusion that the overall amount of UV-350 will adsorb to the soil (58.5 %) and the sediment (36.3 %) when it is released to the environment.

Distribution in wastewater treatment plants

The dominant route of exposure for UV-350 is expected to be wastewater that is treated in sewage treatment plants. Therefore, distribution modelling based on the molecular weight of 323.43 g/mol, the physical-chemical data from Table 6, and the log K_{OC} of $1.55*10^{5}$ taken from Table 20 has been conducted with the help of SimpleTreat to estimate the distribution of the substance in municipal sewage treatment plants (Table 21). The calculation was done assuming that the substance is not readily biodegradable (k=0/h) and the reliability of the result was rated Klimisch 2.

Table 21: Distribution of UV-350 in sewage treatment plants (acc. to SimpleTreat 3.0, debugged version; 7 Feb 1997)

Summary of distribution	**percent**
to air	0.0
to water	12.1
via primary sludge	63.6
via surplus sludge	24.3
degraded	0.0
total	*100*

The results of the calculation lead to the following conclusion: When the substance is released into wastewater, it will predominantly concentrate in sewage sludge. This is in agreement with experimental findings (see Ruan et al., 2012). 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, the substance might be released into

agricultural soil.

3.2.4. Field data

See Annex I.E .

3.2.5. Summary and discussion of environmental distribution

The available data indicate that UV-350 will predominately distribute to soil and suspended organic matter. Please note that the potential for dissociation was not considered due to a lack of available experimental data.

3.3. Data indicating potential for long-range transport

None.

3.4. Bioaccumulation

To the knowledge of the dossier submitter, no experimental log K_{OW}-values for UV-350 are available. Therefore, the value was calculated with the QSAR model KOWWIN of EPISuite 4.10 and with COSMOtherm (Table 22). Details on these calculations can be found in Annex I.C.

Table 22: QSAR-Results for log KOW-predictions of UV-350

Model	QSAR result	Overall model performance	QPREF
EPISuite 4.1 KOWWIN	Log K_{OW}: 6.31	Reliable	Annex I.C.8
COSMOtherm	Log K_{OW}: 7.11	Reliable	Annex I.C.8

The estimated log K_{OW}-values are larger than 4.5, thus it is expected that UV-350 tends to bioaccumulate.

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

UV-350 was tested in a bioconcentration study on fish according to OECD 305 C (NITE, 2012; reliability rated Klimisch 2). Not all test conditions can be reported because the summary of the studies does not list them. Two substance concentrations were tested steady-state in common carp (*Cyprinus carpio*). The uptake duration was 60 days. Like in two similar studies with UV-327, which also has a low water solubility, dispersants were used.

Please note that most of the protocol is in Japanese language and only a minor part was translated; therefore, some information on test conditions remain unknown, e.g.

information on toxicity control or a rationale for the use of a dispersant. Nevertheless, data are believed to be reliable as they have been collected and reviewed by experts from the Japanese Agency.

Use of solubilising agents is generally not recommended but may be acceptable in order to produce a suitably concentrated stock solution (OECD, 2012). This restraint is well founded because solubilising agents may potentially interact with the test substance resulting in an altered response in the test. For instance, dispersants emulsify the test substance and may falsify BCF results if the concentration of the test substance is elevated above its true limit of water solubility. However, substance concentrations in the tests referred to, were below the limit of water solubility of UV-350. Thus, use of dispersants is not thought to have influenced the reported BCFs.

Some solvents and solubilising agents are mentioned in the guideline on bioaccumulation in fish according to OECD 305 (OECD, 2012). HCO-40 is one of the designated solvents, if its concentration does not exceed its toxicity threshold, which probably is in the upper mg/L range, because the guideline allows a maximum solvent concentration of 100 mg/L. HCO-40 was used in very small concentrations of 2 – 20 µg/L. Furthermore, EMEA (1999) reports a lack of adverse effects for mammals for HCO-30 to -40. Thus, we conclude that HCO-40 probably was not toxic to fish in this bioaccumulation study.

Hence, we conclude that the use of dispersants does not question the significance of the referred bioconcentration study.

Table 23 lists the reported steady-state BCF-data amended with the BCF normalised to 5 % lipid content calculated with the averaged lipid content of fish of 1.89 % (lipid content 1.47 % at start, and 2.31 % at the end of the test).

Table 23: Steady-state BCF of UV-350; BCF reported and BCF lipid-normalised of UV-350 (values refer to whole body wet weight basis or 5% normalised lipid content) (NITE 2012)

Test concentration in µg/L	**$BCF_{reported}$**	**$BCF_{lipid\text{-}normalised}$**
1.0	7,700	20,370
0.1	13,000	34,391

Additional BCF data for skin, head, innards and edibles and depuration data for UV-350 were reported by NITE (2012):

Table 24: Reported tissue BCF for UV-350

Test concentration in µg/L	**Skin**	**Head**	**Innards**	**Edible**
1.0	16000; 8900	17000; 11000	29000; 17000	11000; 5500
0.1	13000; 17000	18000; 25000	31000; 52000	9000; 12000

Clearance half-lives of 15 and 14 days were reported for the two test concentrations in the order stated above.

In a similar test, UV-327 bioconcentrates with $BCF_{lipid\text{-}norm.}$-values of 7540, 8817, 6283, and 1203 (L/kg_{lip}) at test concentrations of 0.01, 0.1, 0.1, and 1.0 µg UV-327/L, respectively. This confirms the similar bioaccumulation behaviour of UV-327 and UV-350.

3.4.2. Field data

For comparison, field bioaccumulation data for UV-327 are presented here. Nakata et al. (2010) studied occurrence of several benzotriazoles in blubber of finless porpoise (*Neophocaena phocaenoides*) of the Ariake Sea. They report a mean body concentration of 4.0 ng g-1 (wet wt) for UV-327 as average for 5 individuals sampled from 1998 to 2009. By relating this to the average water concentration of UV-327 (0,12 ng/L), a BAF value of 33,000 was calculated by the authors. The study has some deficiencies, e.g. a long time period over which the samples were taken. Besides, only a low number of samples was available and a recalculation to the whole body was necessary which is not uncommon in case of mammalian samples in monitoring studies. Some further aspects should be considered when evaluating the study. The Ariake Sea is a large bay with a maximum depth of 50 meters. Such shallow waters are preferred by finless porpoises. The bay is surrounded by several cities, e.g. Nagasaki. Therefore, it is probable that there has been a steady exposition to phenolic benzotriazoles in this region in recent years. Monitoring studies confirm this assumption (cf. Annex I.E). As phenolic benzotriazoles adsorb strongly to suspended matter and sediment it is probable that the entry path into the food chain is via benthic animals taking up UV-327 from sediment.

Considering nutrition behaviour of finless porpoises and its prey creates a plausible picture of transport scenario of UV-327 through the food chain. Finless porpoises feed on small fish but also on shrimps and cephalopods, e.g. squids. Squids are carnivorous and feed on fish, but also on crabs which are benthic omnivores, feeding e.g. on carrion. Shrimps feed on detritus and algae, which have a large adsorption surface and are known to have weak elimination capabilities. Finless porpoises of this region also feed on sand eels (*Amodytes tobianus*) which again feed on crabs and cephalopods. Thus, UV-327 (and UV-328) are enriched in top predators (cf. Nakata et al., 2010).

Though no direct proof is given in the study of Nakata et al. (2010) itself, the habitat may be assumed as having been continuously exposed to phenolic benzotriazoles and such has been the prey. Several biomonitoring studies suggest that as well (see Annex I.E). Moreover, absorptivity of UV-327 and information on the diet of finless porpoise and its prey show a plausible and very probable transport scenario of the substance through the food chain. This is supported to some extent by the appearance of the substance in foodstuff and (in higher concentrations) in human adipose tissue (Yanagimoto et al., 2011). However, uptake by humans could also take place via air, dust etc.

In marine fish and marine tidal flat organisms, concentrations of more than one hundred ng/g lw were found (Kim et al., 2011 a and b; Nakata et al., 2009a). In mussels, such high concentrations were found regularly (Nakata et al., 2012). Concentrations were lower, but still regularly found in marine shallow water organisms (Nakata et al., 2009a) and in human adipose tissue (Yanagimoto et al., 2011). UV-327 is accumulated in the blubber of marine mammals and an increasing temporal trend is stated for marine mammals in Japan (Nakata, 2011).

In Sweden, concentrations in fish in the µg/g dw range were reported, even in samples from background sites (Brorström-Lundén et al., 2011). On the other hand, the Swedish study is the only one with measured concentrations of that level. The authors do not offer an explanation for this. It should also be noted that the detection limits for biota were very high in the Swedish study.

3.4.3. Summary and discussion of bioaccumulation

In a fish bioaccumulation study, UV-350 showed lipid-normalised bioconcentration factors far above 5000; therefore, UV-350 is considered to be very bioaccumulative. The structurally similar substances UV-320 (CAS 3846-71-7) and UV-328 (CAS 25973-55-1) are very bioaccumulative as well and confirm the overall assessment.

Field bioaccumulation studies and environmental monitoring data on UV-350 and related phenolic benzotriazoles give an indication that bioaccumulation and trophic transfer takes place in some food chains.

In conclusion, the data presented in the assessed studies suggest that UV-350 bioaccumulates strongly.

4. Human health hazard assessment

Not relevant for the identification of the substance as SVHC in accordance with Article 57(e) REACH.

5. Environmental hazard assessment

Not relevant for the identification of the substance as SVHC in accordance with Article 57(e) REACH.

6. Conclusions on the SVHC Properties

6.1. CMR assessment

Not relevant for the identification of the substance as SVHC in accordance with Article 57(e) REACH.

6.2. PBT and vPvB assessment

6.2.1. Assessment of PBT/vPvB properties

6.2.1.1. Persistence

The persistence of UV-350 has been assessed by using a weight-of-evidence approach.

Conclusions of the weight-of-evidence approach:

- There is no biodegradation screening test for UV-350. The ready biodegradation tests on UV-320 and UV-327 following OECD Guideline 301 C indicate no biodegradation at all (0 % after 28 days). An OECD 301 B test with UV-328 resulted in 2-8 % $ThCO_2$ evolution. All of these UV protection substances are “not readily biodegradable”. Due to the structural similarity of UV-350 to UV-320, UV-327, and UV-328, it may be assumed that UV-350 is also “not readily

biodegradable".

- UV-350 was tested in a water/sediment system based on OECD Guideline 308. UV-350 rapidly and completely adsorbs to sediment and hardly degrades over a period of 100 days ($DT_{50, sed.}$ >> 100 d).

- 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-hydroxy-phenyl]-propionates) was studied in an OECD 308 simulation test in several systems. In these studies, a major degradation product M1 was identified. This metabolite is structurally similar to UV-350 and other phenolic benzotriazoles. Therefore, its behaviour in the simulation test is used in a read-across assessment for UV-350. 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 (at 20 °C) 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 DT_{50}-values. The differing side chain of M1 will be degraded faster than that of UV-350. Therefore, and assuming that the fate properties of UV-350 and M1 are similar in a degradation simulation test, the results on M1 can be considered to constitute a best-case read across for disappearance and degradation of UV-350. Consequently, UV-350 is considered to be "very persistent" (vP) in sediment, too.

- In a recent field study, dissipation in soil of several UV substances other than UV-350 was tested. Using the results of this test, a DT_{50} of 151 to 192 days was calculated. The reported range of DT_{50}-values exceeds the trigger value for persistence in soil. As the time required for disappearance cannot be longer than the time required for degradation, the respective $DegT_{50}$-values will exceed this value range, i.e. they will be over 192 days for the worst case reported. These results were taken as a read-across on UV-350.

- For UV-327 and the similar substance UV-328, available monitoring studies indicate presence of the substances in sediments decades after environmental releases 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 are taken as a read-across on UV-350.

- The read-across substances UV-320 (EC 223-346-6) and UV-328 (EC 247-384-8) were already concluded as "vP" (ECHA's decision ED/108/2014) and were identified as Substances of Very High Concern (SVHC) due to their PBT/vPvB properties according to Article 57 (d) and (e) of Regulation (EC) No 1907/2006 (REACH); this provides evidence for UV-350 itself.

- Thus, considering the evidence available, it is concluded that UV-350 fulfils the P- and vP-criteria as defined under Sections 1.1.1 and 1.2.1 of REACH Annex XIII.

6.2.1.2. Bioaccumulation

Next to the other UV substances, also UV-350 was tested in an OECD 305 C bioaccumulation test in fish. For the two concentration levels (1.0 and 0.1 µg/L), the reported BCF-values were 7,700 and 13,000, respectively; the lipid-normalised BCF-values were 20,370 and 34,391, respectively. Therefore, UV-350 fulfils the B (BCF >2000) and vB criterion (BCF >5000) as defined under Sections 1.1.2 and 1.2.2 of REACH Annex XIII.

The results are in line with the bioaccumulative properties of the read-across substances UV-320 and UV-328 (ECHA's decision ED/108/2014).

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

In conclusion, UV-350 meets the criteria for a vPvB substance according to Art. 57(e) of REACH.

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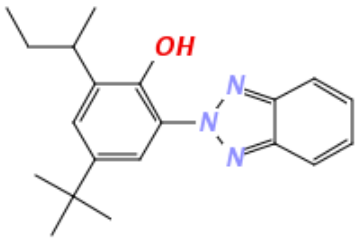
Annex I - Additional Information on UV-350

Annex I.A – Analysis of QSAR Application: Prediction of Potential Persistent Properties in the Environment for UV-350

1. Information on substance and purpose

Name:	2-(2H-Benzotriazol-2-yl)-6-sec-butyl-4-(2-methyl-2-propanyl)phenol (UV-350)
CAS Nr.	36437-37-3
EU Nr.	253-037-1
Smiles	c1(c(c(cc(c1)C(C)(C)C)C(C)CC)O)N(N=C2C=C3)N=C2C=C3



Endpoint	Screening on Persistence in the Environment
Regulatory purpose	PBT-Assessment, used in a weight of evidence approach to justify vP-assessment of a group of phenolic benzotriazoles

2. Relevant structure information

Parameter	**Result**	**Rationale**
Structure identification		
Structure of concern	parent	Substance is a mono-constituent, question to be answered is, if this substance itself fulfils the P-Screening criteria.
Descriptors used for QSAR prediction		
Fragment descriptors of BIOWIN2 and BIOWIN 3	applicable but probably slightly underestimating	All fragments are represented by the model with exception of the triazole group which has probably an inhibiting influence
Fragment descriptors of BIOWIN6	applicable but probably slightly underestimating	All fragments are represented by the model with exception of the triazole group which has probably an inhibiting influence.
Molecular Weight	applicable	Molecular weight in the range of the weights in the Training Set
Other relevant information		
-	-	-

3. QSAR models used

Model	Version	Endpoint	QMBI
BIOWIN2	v4.1	Probability of rapid biodegradation	Annex I.A.6
BIOWIN3	v4.1	Time to Ultimate Biodegradation given as a numerical value between 1 and 5	Annex I.A.7
BIOWIN6	v4.1	Probability of rapid biodegradation	Annex I.A.8

4. Analysis of QSAR model performance

Model	QSAR result	Overall model performance	Reference
BIOWIN2	**0.1329** (does not biodegrade fast)	Reliable with restrictions	Annex I.A.9
BIOWIN3	**2.2538** (weeks to months)	Reliable with restrictions	Annex I.A.9
BIOWIN6	**0.012** (does not biodegrade fast)	Reliable with restrictions	Annex I.A.9

5. Overall conclusion

Overall QSAR Result	Borderline case for meeting the criteria on persistence
Rationale	Both QSAR-criteria according to ECHA Guidance R.11 are not met ((BIOWIN2 < 0.5 AND BIOWIN3 < 2.2) OR (BIOWIN6 < 0.5 AND BIOWIN 3 < 2.2))). The reason for this is that the BIOWIN3-result is larger by 0.0538, which indicates a borderline case. The model performance and read-across on similar substances supports the result of the QSAR model (see Annex I.A.10).
Reliability	Reliable with restrictions. The triazole group is not a descriptor fragment of the three models, therefore the actual persistence might be underestimated. The comparison of experimental data for similar structures with BIOWIN3 results for them can be interpreted as showing a slight underestimation of the Ultimate Biodegradation time, therefore the actual degradation time might probably be longer and the criterion fulfilled.

Conclusion with regard to the regulatory purpose
When combining the evidence of the QSAR results with the information known from similar structures it can be concluded that UV-350 meets the Persistence criterion on a Screening level. Note that the information obtained in this way is on its own not sufficient for assessing the actual P/vP-criterion. This will be done in a weight of evidence approach where this QSAR result is used as supporting evidence.

6. QMBI BIOWIN2

	Information	Literature References or Links[4]	Remarks
0 – General			
Model name and version	BIOWIN2 (nonlinear probability model), v4.10	Howard, P.H., Boethling, R.S., Stiteler, W.M., Meylan, W.M., Hueber, A.E., Beauman, J.A., Larosche, M.E. 1992. Predictive model for aerobic biodegradability developed from a file of evaluated biodegradation data. Environ. Toxicol. Chem. 11:593-603. Boethling, R.S., Howard, P.H., Meylan, W., Stiteler, W., Beaumann, J., Tirado, N. 1994. Group contribution method for predicting probability and rate of aerobic biodegradation. Environ. Sci. Technol. 28:459-65.	
w.a.[5]: 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)	Probability of Rapid Degradation (0.0-1.0)		Values > 0.5 are interpreted as 'biodegrades fast'
2 – Definition of Algorithm			
Brief description of algorithm and/or link to full definition	*Probability = Exp (Y_j) / (1 + Exp (Y_j)), $Y_j = a_0 + a_1 * f_1 + a_2 * f_2 + \ldots + a_{36} * f_{36} + a_m * MW_j$*	Online documentation of BIOWIN	-
List of employed descriptors with units	a_0=3.0087; $a_1 \ldots a_{36}$: fragment coefficients, $f_1 \ldots f_{36}$: instances of fragment, a_m: molecular weight coefficient, MW_j : molecular weight of substance j [g/mol]	List of the 36 fragments employed and all their coefficients can be found in online documentation of BIOWIN	-

[4] References given here are not substance-specific but related to the EPISUITE software.

[5] w.a.: when applicable

	Information	Literature References or Links[4]	Remarks
Number of Chemicals in Training Set and brief description of it	295 chemicals of the BIODEG database		-
w.a.: Training set available at		Online documentation of BIOWIN	
3 – Definition of the Applicability Domain			
w.a.: Definition of the Applicability Domain	-	-	-
Limits of the Applicability Domain	The target molecule should be composed of fragments that are used in this model, otherwise only molecular weight will be considered; MW = 30.02-959.2	Online documentation of BIOWIN	-
4 – Information on the Validation of the Model			
Validation Set Type	internal and external		-
w.a.: Validation available at		Several available, see for example: Posthumus, R., Traas, T.P., Peijnenburg, W.J.G.M., Hulzebos, E.M. 2005. External validation of EPIWIN biodegradation models. SARQSAR Environ. Res. 16:135-148	-
Statistical information on validity	Total correct: 275 / 295 (93.2%)		-
5 – Mechanistic Interpretation of the model			
w.a.: Mechanistic basis of model	Biodegradation is a stepwise reaction cascade therefore individual fragments contribute to the probability that a substance is degraded fast	-	-

7. QMBI BIOWIN3

	Information	Literature References or Links[6]	Remarks
0 – General			
Model name and version	BIOWIN3 (ultimate survey model), v4.10	Boethling, R.S., Howard, P.H., Meylan, W., Stiteler, W., Beaumann, J., Tirado, N. 1994. Group contribution method for predicting probability and rate of aerobic biodegradation. Environ. Sci. Technol. 28:459-65.	-
w.a.[7]: 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)	Expert Rating for time to Ultimate Biodegradation given as a numerical value between 1 and 5		>4.75 – 5: hours; >4.25 - 4.75: hours to days; >3.75 - 4.25: days; >3.25 - 3.75: days to weeks; >2.75 - 3.25: weeks; >2.25 - 2.75: weeks to months; >1.75 - 2.25: months; <1.75: recalcitrant
2 – Definition of Algorithm			
Brief description of algorithm and/or link to full definition	$Rating_j = a_0 + a_1 * f_1 + a_2 * f_2 + \ldots + a_{36} * f_{36} + a_m * MW_j$	Online documentation of BIOWIN	-
List of employed descriptors with units	a_0=3.1992; $a_1 \ldots a_{36}$: fragment coefficients, $f_1 \ldots f_{36}$: instances of fragment, a_m: molecular weight coefficient, MW_j : molecular weight of substance j [g/mol]	List of the 36 fragments employed and all their coefficients can be found in online documentation of BIOWIN	-
Number of Chem-icals in Training Set and Brief descript-tion of it	200 substances		17 Experts reviewed 200 substances and assigned a degradation rating of 1 to 5 for them. Based on this rating the coefficients for the fragments were derived
w.a.: Training set available at		Online documentation of BIOWIN	-

[6] References given here are not substance-specific but related to the EPISUITE software.
[7] w.a.: when applicable

	Information	Literature References or Links[6]	Remarks
3 – Definition of the Applicability Domain			
w.a.: Definition of the Applicability Domain	-	-	-
Limits of the Applicability Domain	The target molecule should be composed of fragments that are used in this model, otherwise only molecular weight will be considered; Prediction Range for Expert Rating : 1.44 – 3.89	Online documentation of BIOWIN	-
4 – Information on the Validation of the Model			
Validation Set Type	internal and external		-
w.a.: Validation available at		Several available, see for example: Posthumus, R., Traas, T.P., Peijnenburg, W.J.G.M., Hulzebos, E.M. 2005. External validation of EPIWIN biodegradation models. SARQSAR Environ. Res . 16:135-148	-
Statistical information on validity	Total correct: 167/200 (83.5%)		-
5 – Mechanistic Interpretation of the Model			
w.a.: Mechanistic basis of model	Biodegradation is a stepwise reaction cascade therefore individual fragments contribute to the probability that a substance is degraded fast	-	-

8. QMBI BIOWIN6

	Information	Literature References or Links[8]	Remarks
0 – General			
Model name and version	BIOWIN6 (non-linear MITI model), v4.10	Tunkel, J., Howard, P.H., Boethling, R.S., Stiteler,W., Loonen, H. 2000. Predicting Ready Biodegradability in the Japanese Ministry of International Trade and Industry Test. *Environ. Toxicol. Chem.* 19:2478-2485.	
w.a.[9]: 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)	Probability of Rapid Degradation (0.0-1.0)		Values > 0.5 are interpreted as “biodegrades fast”
2 – Definition of Algorithm			
Brief description of algorithm and/or link to full definition	*Probability = Exp (Y_j) / (1 + Exp (Y_j)), $Y_j = a_0 + a_1 * f_1 + a_2 * f_2 + \ldots + a_{42} * f_{42} + a_m * MW_j$*	Online documentation of BIOWIN	-
List of employed descriptors with units	a_0= 2.5257; $a_1 \ldots a_{42}$: fragment coefficients, $f_1 \ldots f_{42}$: instances of fragment, a_m: molecular weight coefficient, MW_j : molecular weight of substance j [g/mol]	List of the 42 fragments employed and all their coefficients can be found in online documentation of BIOWIN	-
Number of Chem-icals in Training Set and Brief descript-tion of it	589 chemicals of 884 chemicals that were tested under the Japanese Chemical Substances Control Law		The other 295 substances were used as Validation Set
w.a.: Training set available at		Online documentation of BIOWIN	-

[8] References given here are not substance-specific but related to the EPISUITE software.

[9] w.a.: when applicable

	Information	Literature References or Links[8]	Remarks
3 – Definition of the Applicability Domain			
w.a.: Definition of the Applicability Domain	-	-	-
Limits of the Applicability Domain	The target molecule should be composed of fragments that are used in this model, otherwise only molecular weight will be considered	Online documentation of BIOWIN	-
4 – Information on the Validation of the Model			
Validation Set Type	internal and external		-
w.a.: Validation available at		Internal: Online documentation of BIOWIN External: Several available, see for example: Posthumus, R., Traas, T.P., Peijnenburg, W.J.G.M., Hulzebos, E.M. 2005. External validation of EPIWIN biodegradation models. SARQSAR Environ. Res. 16: 135-148	
Statistical information on validity	Total correct Training Set: 488 / 589 (82.9%) Total Correct Validation Set: 238 / 295 (80.7%)		-
5 – Mechanistic Interpretation of the model			
w.a.: Mechanistic basis of model	Biodegradation is a stepwise reaction cascade therefore individual fragments contribute to the probability that a substance is degraded fast		-

9. Analysis of QSAR prediction for UV-350

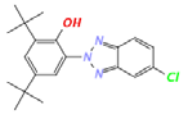
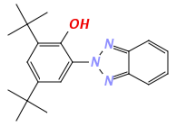
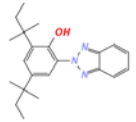
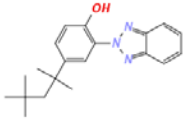
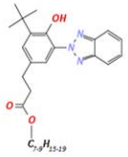
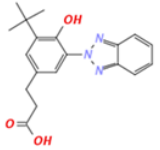
QSAR Model: BIOWIN 2/3/6

Overall performance

	Result	**Further description**
Endpoint result [unit] for UV-350	BIOWIN2: 0.1329 BIOWIN3: 2.2538 BIOWIN6: 0.012 **Borderline Case of Persistence Criterion met**	According to the ECHA Guideline R.11 the Screening Criterion is met, when (BIOWIN2 < 0.5 AND BIOWIN3 < 2.25) OR (BIOWIN6 < 0.5 AND BIOWIN3 < 2.25), this is not the case here since the BIOWIN3 result is slightly above the trigger value.
Applicability domain	Yes, with restrictions	The molecule is in the range of molecular weights of the training sets of the three models. Also, most of the fragments of UV-350 are represented in the fragment descriptors of the molecule (with the exception of the triazole group). The prediction of BIOWIN 3 is in the range of the predictions of the Training Set as well.
Similarity with trainings set	Yes	Most fragments of UV-350 are present in the Training Set (with the exception of the triazole group)
Similar substances	Yes	See table next side
Model performance for similar substances	Good	Experimental Values and Assessment are in agreement
Other uncertainties	No	-

Overall conclusion	Reliable with restrictions (but used in a weight of evidence approach)
Rationale	The result is very near the trigger value for BIOWIN3 (< 2.25). One essential group for the degradation, the triazole group, is not represented. As the group is known to be difficult to degrade its contribution should probably be inhibiting. Hence, it can be assumed that UV-350 will be indeed not readily biodegradable. This assumption is supported by the known experimental values of other phenolic benzotriazoles. The comparison of experimental data for similar structures with BIOWIN3 results for them can be interpreted as showing a slight underestimation of the Ultimate Biodegradation time.

10. Results for similar substances

	Substance 1	**Substance 2**	**Substance 3**
Structure	 **UV 327**	 **UV-320**	 **UV-328**
CAS-Nr.	3864-99-1	3846-71-7	25973-55-1
EU-Nr.	223-383-8	223-346-6	247-384-8
(Trade-)Name	**UV-327**	**UV-320**	**UV-328**
Descriptor value	BIOWIN 2 : 0.0013; BIOWIN 6 : 0.0024; BIOWIN 3 : 1.8338 (months)	BIOWIN 2 : 0.016; BIOWIN 6 : 0.0091; BIOWIN 3 : 2.1165 (months)	BIOWIN 2 : 0.0108; BIOWIN 6 : 0.0096; BIOWIN 3 : 2.0546 (months)
Predicted endpoint	P-Screening criterion met	P-Screening criterion met	P-Screening criterion met
Experimental endpoint	Non-biodegradable, BOD = 0	Non-biodegradable, BOD = 0	not readily biodegradable (2-8% after 28 days)
	Substance 4	**Substance 5**	**Substance 6**
Structure	 **UV-329**	 **EC 407-000-3**	 **Metabolite M1**
CAS-Nr.	3147-75-9	127519-17-9	84268-36-0
EU-Nr.	221-573-5	407-000-3	-
(Trade-)Name	**UV-329**	**-**	**M1**
Descriptor value	BIOWIN 2 : 0.016; BIOWIN 6 : 0.0154; BIOWIN 3 : 2.1165 (months)	BIOWIN 2 : 0.6541; BIOWIN 6 : 0.0174; BIOWIN 3 : 2.1418 (months)	BIOWIN 2 : 0.1970; BIOWIN 6 : 0.0153; BIOWIN 3 : 2.5832 (weeks-mon.)
Predicted endpoint	P-Screening criterion met	P-Screening criterion BW 6/3 met	P-Screening criterion not met
Experimental endpoint	not readily biodegradable (0-1% after 28 days)	Water/Sed. study: degradation to M1 and dissipation to NER	Water/Sed. Study: DT_{50} sed. 238-248 days; dissipation to NER

Rationale for the selection of similar substances:
Substances 1 to 4 are structurally similar phenolic benzotriazoles to UV-350. The largest similarity is with substances 2 and 3.

Annex I.B – Degradation kinetic modelling of two W/S-simulation studies

This Annex was already part of the Support Documents of UV-320 and UV-320 (ECHA 2014a; ECHA 2014b).

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 Persistence and Degradation Kinetics (FOCUS, 2006) was followed. Data used were taken from the dossier on EC 407-000-3. The final degradation kinetic modelling considered parent EC 407-000-3 for the whole system, main metabolite M1 separately for water and sediment phase, and NER. For a better understanding, more details on the stepwise procedure are given in each section below 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 considered here 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:	$M = M_0*[g*e^{-k1*t} + (1-g)*e^{-k2*t}]$
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 possibly systematic deviations. Secondly, 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 has also been done by the dossier submitter. 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 the case and consequently the 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 DT_{50} 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 17 – river system, and Figure 18 – pond system).

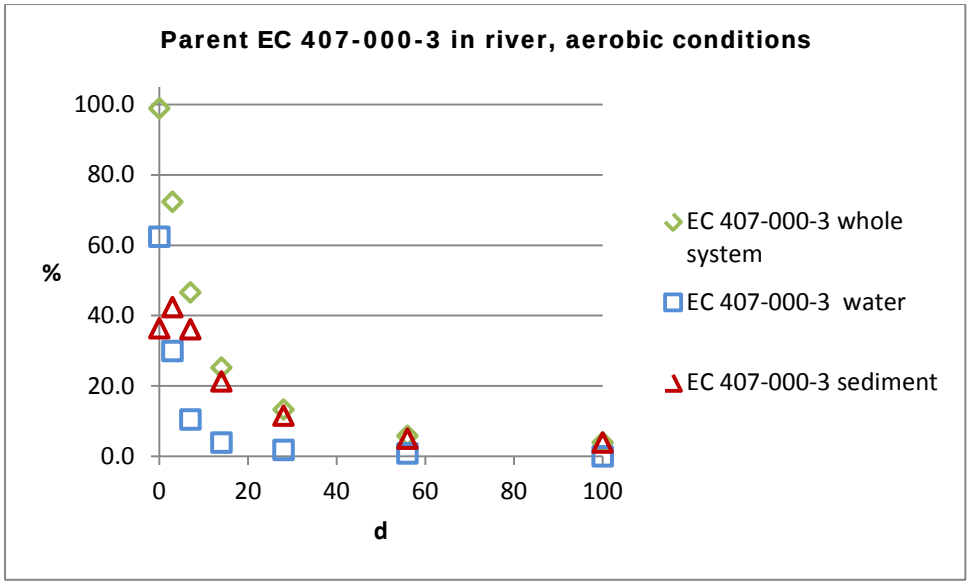


Figure 17: Distribution of EC 407-000-3 in a river system under aerobic conditions

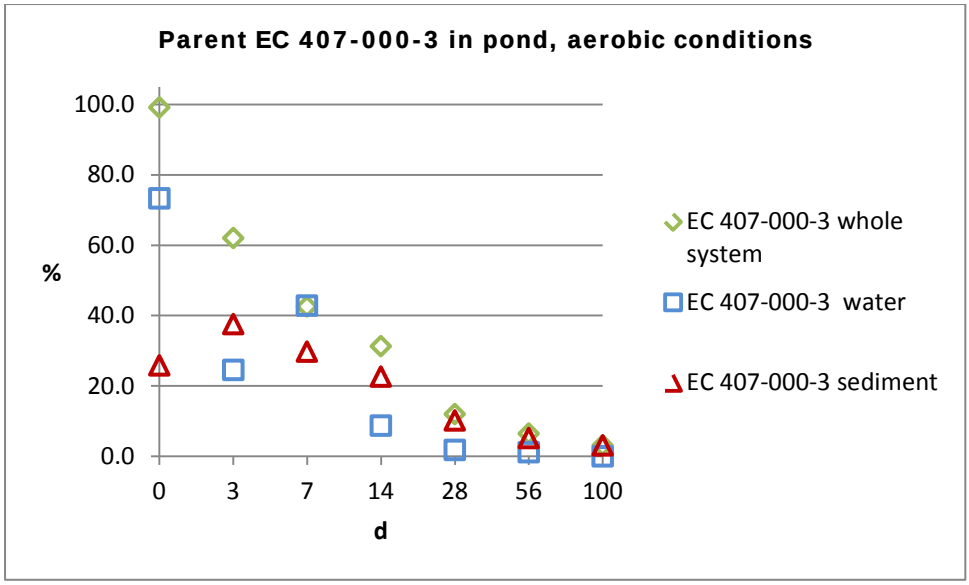


Figure 18: Distribution of EC 407-000-3 in a pond system under aerobic conditions

Unfortunately, test protocols do not give information on 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 could not be circumvented if the concentration of the parent was 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 river system

The model setup used in all kinetic modelling of parent substance EC 407-000-3 is shown in Figure 19. It is simple and considers one sink only, without differentiating it further.

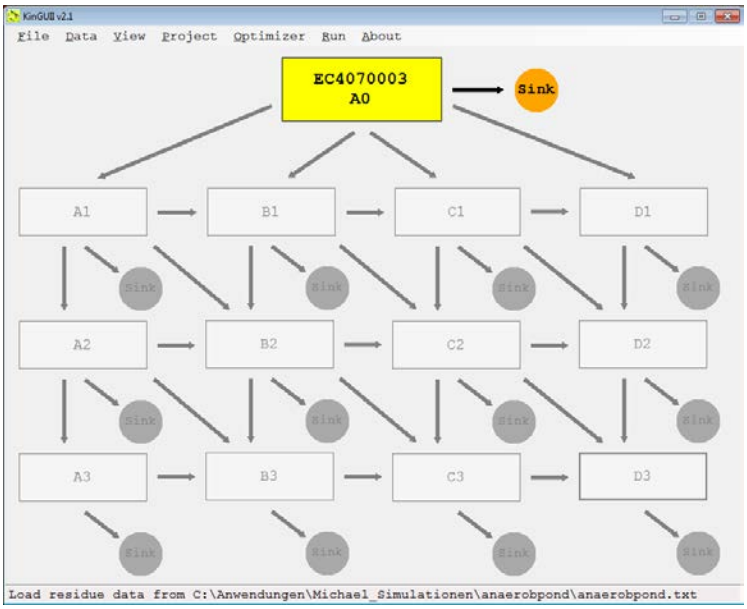


Figure 19: Model setup for dissipation modelling of EC 407-000-3 in river system under aerobic conditions

2.1.3. EC 407-000-3 SFO (whole aerobic river system)

The data shown in Figure 20 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 21). Chi²-error is acceptable. SFO-calculated DT_{50} is 7.3 days and DT_{90} is 24.1 days (Table 26) for the whole river system.

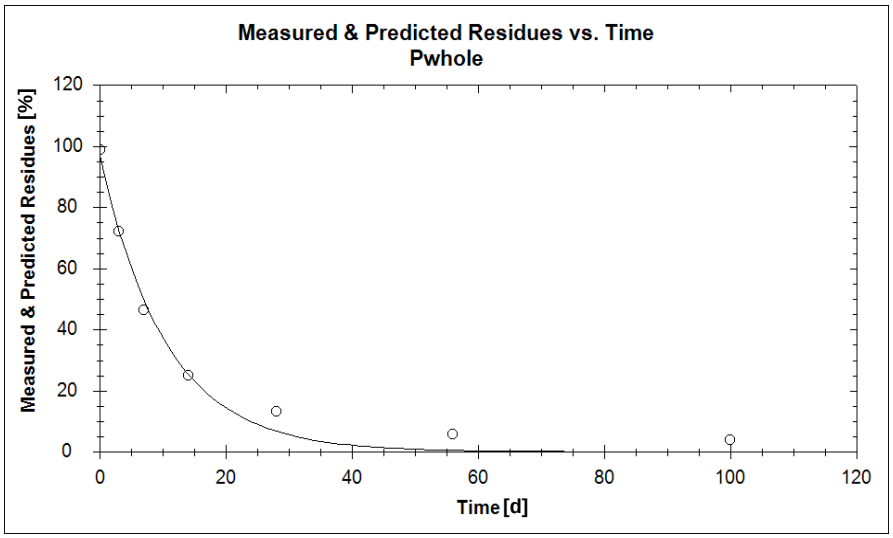


Figure 20: Measured and predicted residues of EC 407-000-3 vs. time in the whole system of an aerobic river – SFO

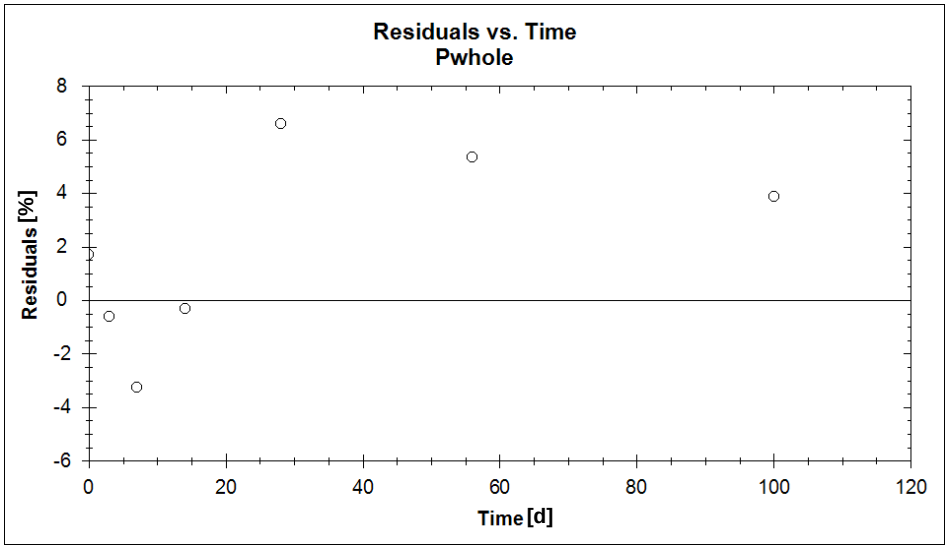


Figure 21: Residuals of EC 407-000-3 vs. time in the whole system of an aerobic river – SFO

Table 25: Chi² 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
DT_{50} in d	7.2613		
DT_{90} in d	24.1220		

2.1.4. EC 407-000-3 FOMC (whole aerobic river system)

Data are well described by FOMC kinetic. The curve fits closely to the measured data (Figure 22). The residual plot shows that data initially scatter around the zero line (Figure 23). Chi²-error is acceptable. FOMC-calculated DT_{50} is 6.4 days and DT_{90} is 33.9 days (Table 27) for the whole river system.

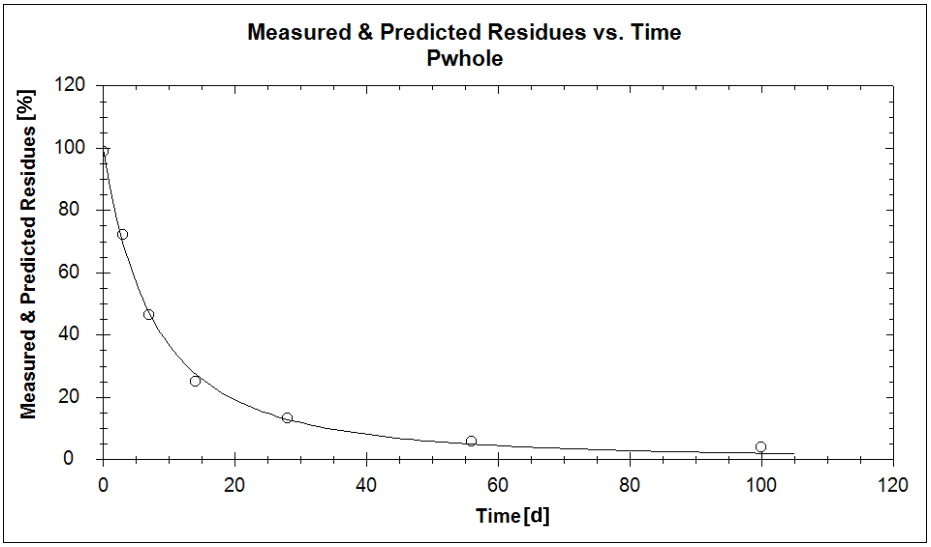


Figure 22: Measured and predicted residues of EC 407-000-3 vs. time in the whole system of an aerobic river – FOMC

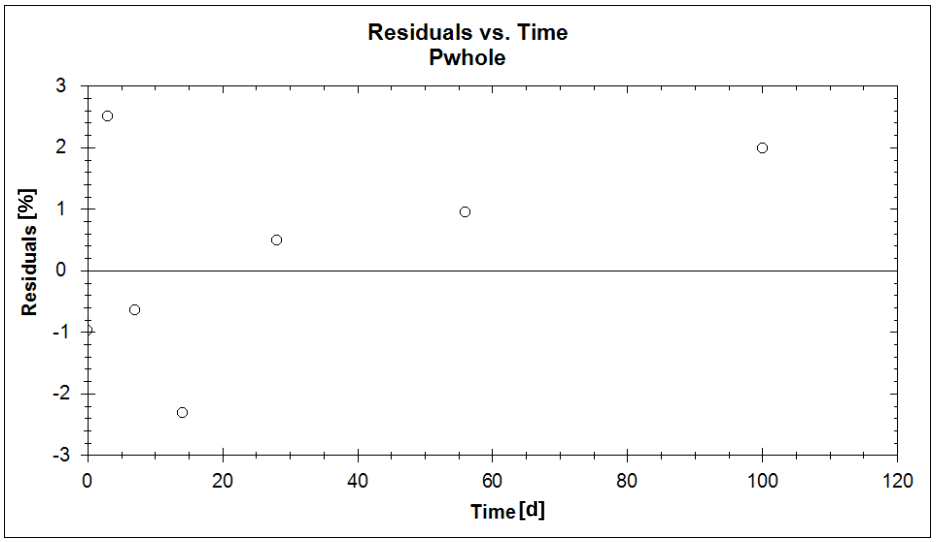


Figure 23: Residuals of EC 407-000-3 vs. time in the whole system of an aerobic river – FOMC

Table 26: Chi² 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
DT_{50} in d	6.3731		
DT_{90} in d	33.8950		

2.1.5. EC 407-000-3 DFOP (whole aerobic river system)

Data are well described by DFOP kinetic and the curve fits closely to the measured data (Figure 24). 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 (Figure 25). Chi²-error is acceptable. DFOP-calculated DT_{50} is 6.5 days and DT_{90} is 35.3 days (Table 28) for the whole river system.

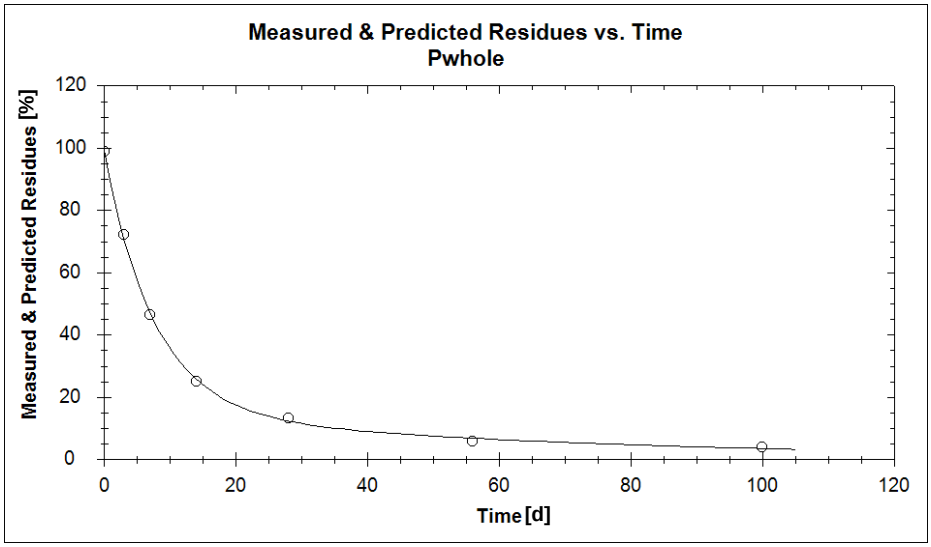


Figure 24: Measured and predicted residues of EC 407-000-3 vs. time in the whole system of an aerobic river – DFOP

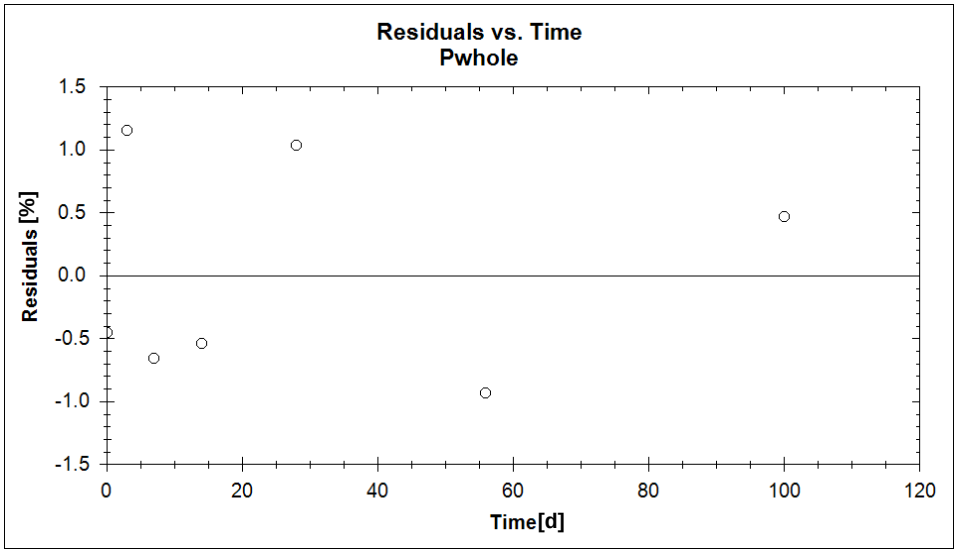


Figure 25: Residuals of EC 407-000-3 vs. time in the whole system of an aerobic river – DFOP

Table 27: Chi² 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
DT_{50} in d	6.480		
DT_{90} in d	35.296		

2.1.6. Conclusion on dissipation of EC 407-000-3 (whole aerobic river system)
SFO is not suitable to model the measured data, as deviation of the residuals is systematic. FOMC and DFOP both fit well. However, DFOP is the slightly better choice because only two of the last residuals show a 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 is considered as DFOP in the following modelling of M1.

2.2.2 M1 SFO for water and sediment (aerobic river system)

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 submitter followed its advice and used SFO for modelling of M1 dissipation (level M-I calculation).

Figure 26 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 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 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.

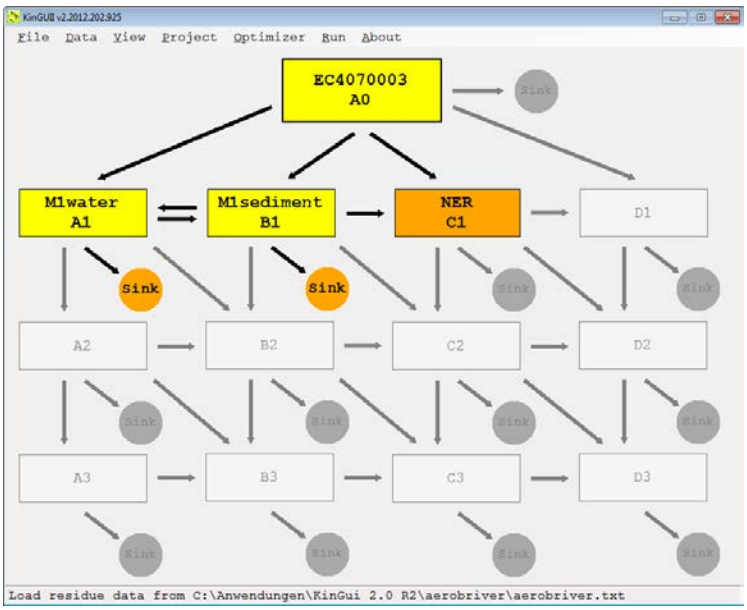


Figure 26: Considered compartments and sinks in river system under aerobic conditions

2.2.2.2. EC 407-000-3 in whole aerobic river 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 (Figure 27). The residuals are small and randomly scattered around the zero line (Figure 28). Chi²-error is acceptable (see Table 29). DFOP-calculated DT_{50} is 6.4 days and DT_{90} is 35.7 days (Table 29) for the parent substance the whole river system.

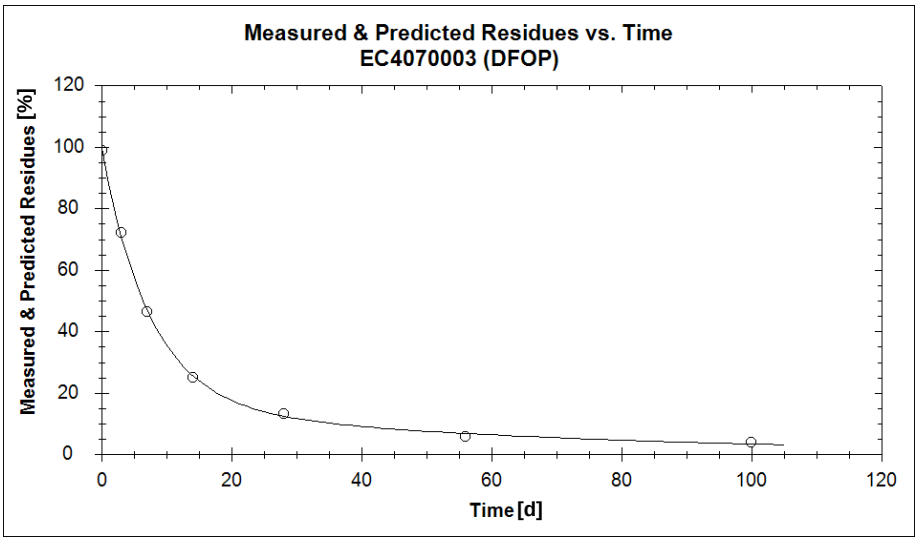


Figure 27: Residuals of EC 407-000-3 vs. time in the whole system of an aerobic river – DFOP

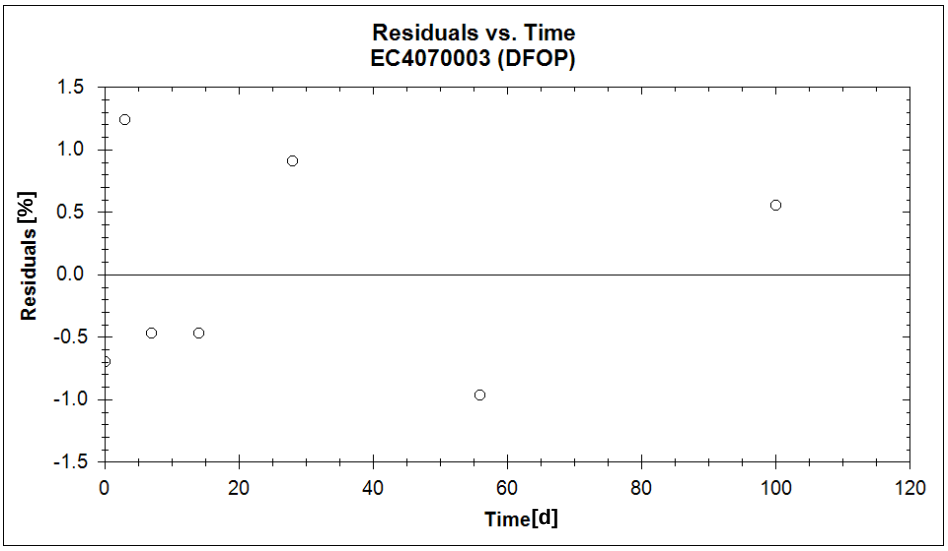


Figure 28: Measured and predicted residues of EC 407-000-3 vs. time in the whole system of an aerobic river – DFOP

2.2.2.3. M1 in water (aerobic river system)

Data of M1 in the water phase are well described by SFO kinetic (see Figure 29). The curve fits well to the measured data. The residuals are small and there is no systematic deviation (see Figure 30). 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 Chi²-value show that the fit is acceptable (see Table 29). SFO-calculated DT_{50} is 3.4 days and DT_{90} is 11.3 days (Table 29) for metabolite M1 in water (river system).

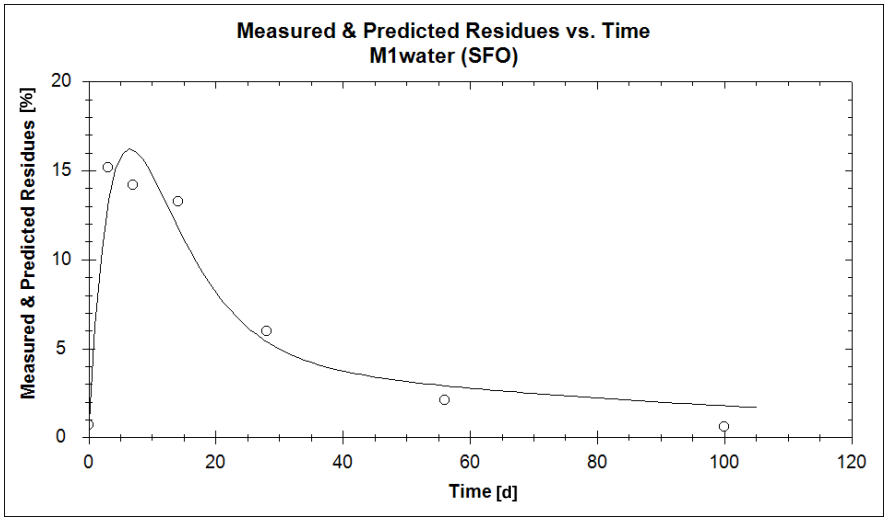


Figure 29: Measured and predicted residues of M1 vs. time in the water phase of an aerobic river – SFO

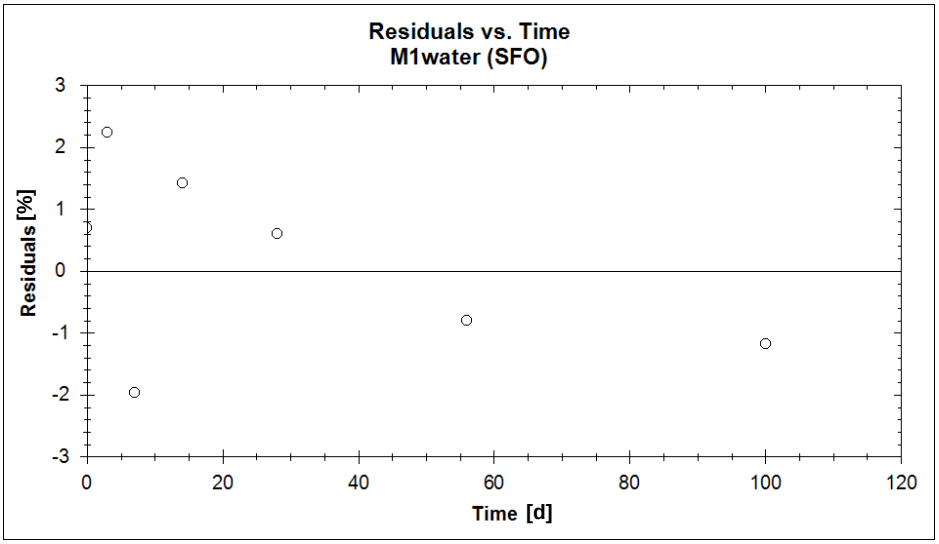


Figure 30: Residuals of M1 vs. time in the water phase of an aerobic river – SFO

2.2.2.4. M1 in sediment (aerobic river system)

Data of M1 in the sediment phase are well described by SFO kinetic (see Figure 31). The curve fits to the measured data. Residuals show a small overestimation for day 14 to 56 (see Figure 32). 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. Chi² is acceptable (see Table 29). It is concluded that the fit is acceptable. SFO-calculated DT_{50} is 31.6 days and DT_{90} is 105.1 days (Table 29) for metabolite M1 in sediment (river system).

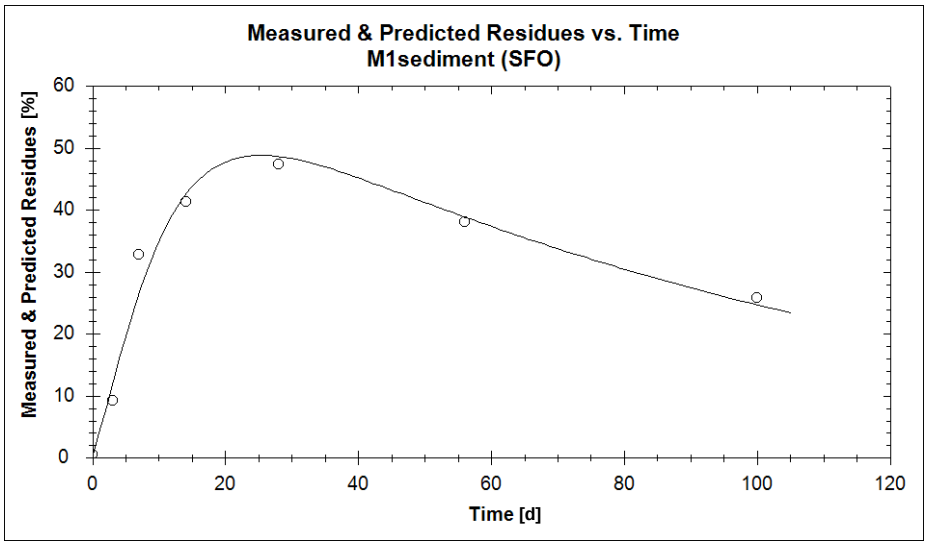


Figure 31: Measured and predicted residues of M1 vs. time in the sediment phase of an aerobic river – SFO

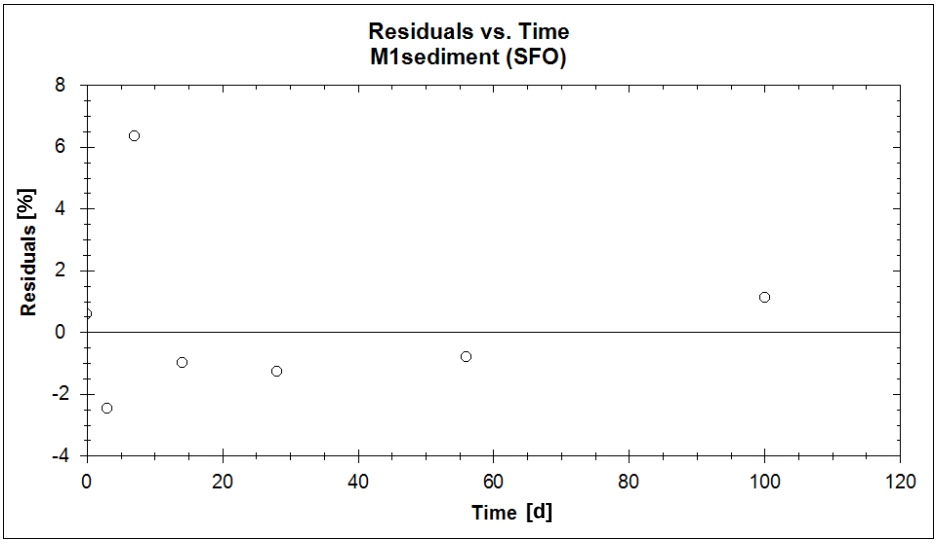


Figure 32: Residuals of M1 vs. time in the sediment phase of an aerobic river – SFO

2.2.2.5. NER in whole system (aerobic river system)

Data of NER are well described by SFO kinetic (see Figure 33). Residuals are small but there is an underestimation from day 0 to 14. Chi² is acceptable (see Table 29). 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. SFO-calculated DT_{50} is 275.5 days and DT_{90} is 915.3 days (Table 29) for NER in the whole river system.

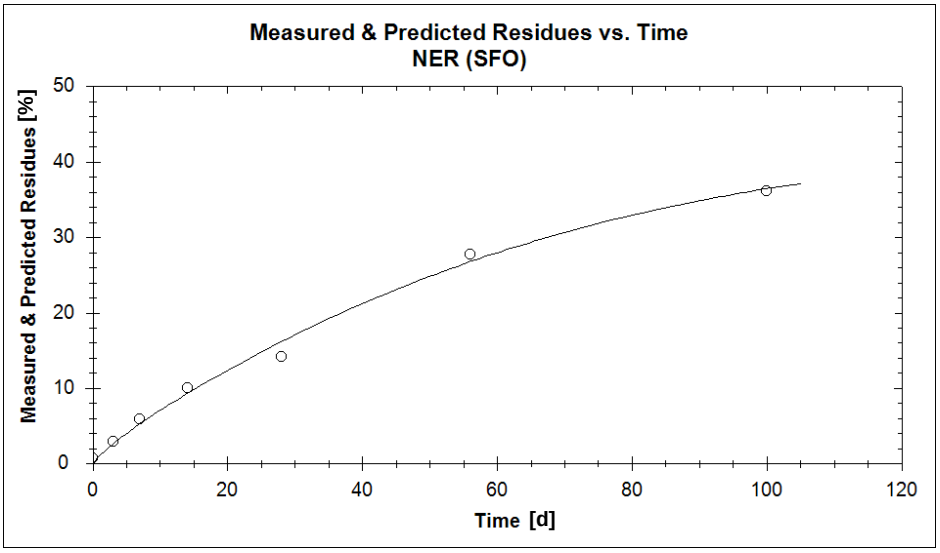


Figure 33: Measured and predicted residues of NER vs. time in the whole system of an aerobic river – SFO

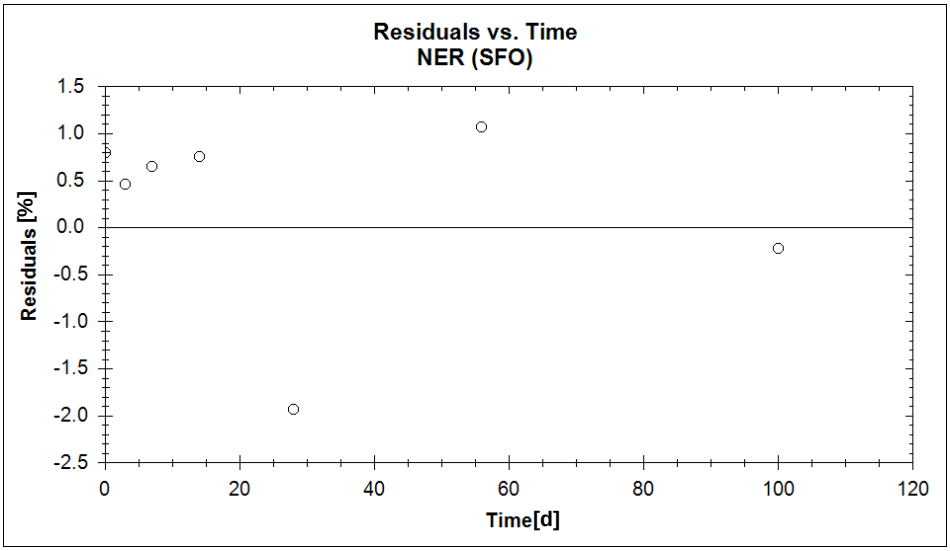


Figure 34: Residuals of NER vs. time in the whole system of an aerobic river – SFO

Figure 35 gives an overview of the measured and predicted data of EC 407-000-3, M1 and NER (aerobic river system).

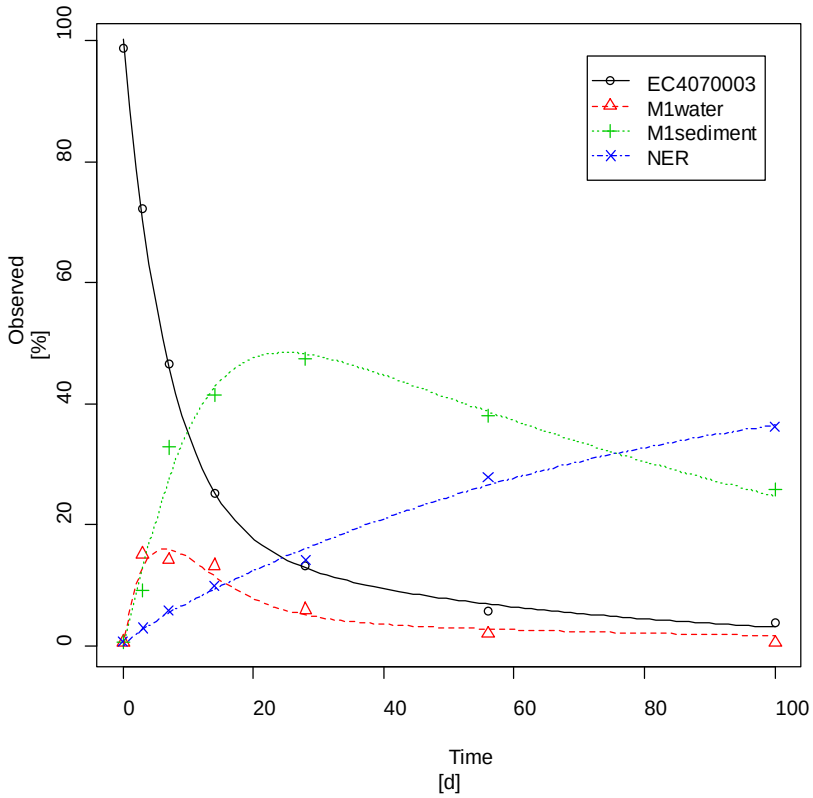


Figure 35: Combined diagram of measured data and respective trends in a river system under aerobic conditions

Table 28: Chi²-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
DT_{50} in d	6.4174	3.4002	31.635	275.53	
DT_{90} in d	35.730	11.295	105.09	915.30	
Kinetic model	DFOP	SFO	SFO	SFO	

Table 29: 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[10]	2.52E-03	-3.82E-03	0.009	3.23E-03	**$2.2*10^{-1}$**

[10] According to the t-test, the value is essentially zero, meaning that there is no degradation in the NER.

Table 30: 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

2.3. Pond System: Dissipation of EC 407-000-3 in whole system (aerobic pond)

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 aerobic pond system

The model setup used in all kinetic modelling of the parent substance EC 407-000-3 is shown in Figure 36. It is simple and considers one sink only, without differentiating it further.

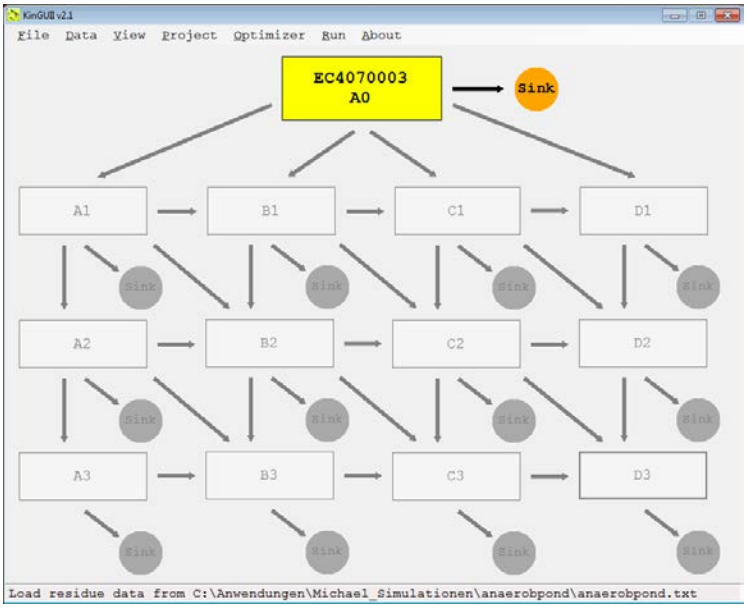


Figure 36: Model setup for modelling dissipation of EC-407-000-3 in pond system under aerobic conditions

2.3.3. EC 407-000-3 SFO (whole aerobic pond system)

The data shown in Figure 37 are adequately described by SFO up to day 7. Concentrations measured at later dates are underestimated by SFO kinetics and the residual plot shows deviations (see Figure 38). From day 14 on all residuals remain positive. Chi²-error is acceptable (see Table 32). SFO-calculated DT_{50} is 7.3 days and DT_{90} is 24.4 days (Table 32) for the whole aerobic pond system.

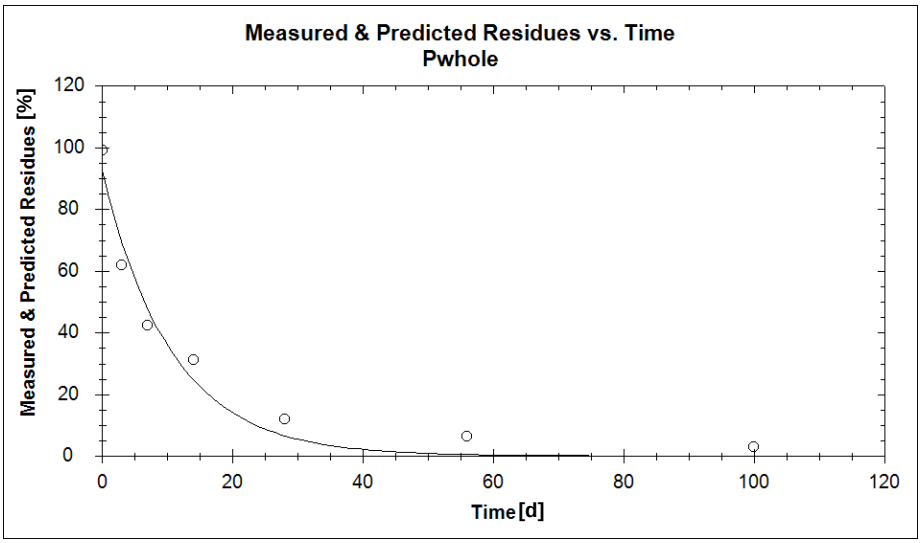


Figure 37: Measured and predicted residues of EC 407-000-3 vs. time in the whole system of an aerobic pond – SFO

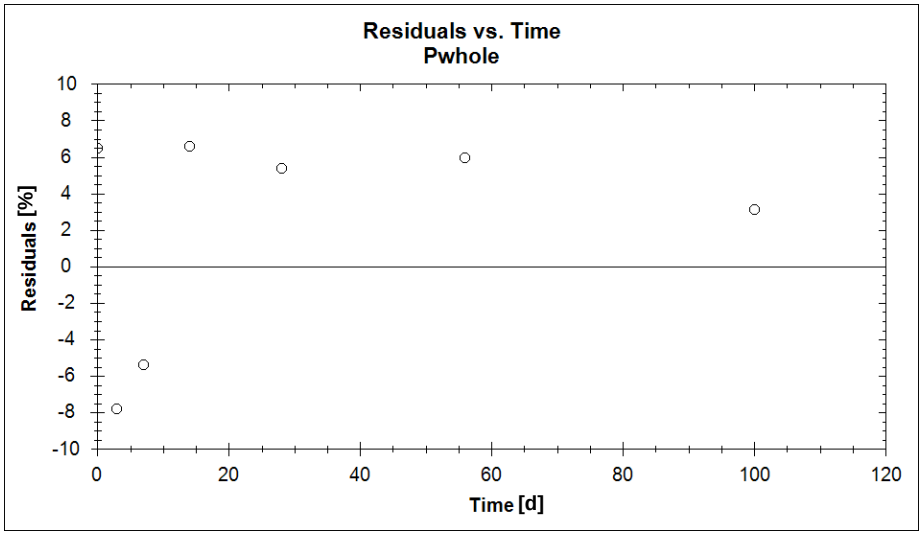


Figure 38: Residuals of EC 407-000-3 vs. time in the whole system of an aerobic pond – SFO

Table 31: Chi² and dissipation times of EC 407-000-3 using SFO kinetic (aerobic pond system)

Parameter	EC 407-000-3	All	Kinetic model
Chi²Err %	12.9300	12.9300	SFO
DT_{50} in d	7.3499		
DT_{90} in d	24.4160		

2.3.4. EC 407-000-3 FOMC (whole aerobic pond system)

Data are well described by FOMC kinetic. The curve fits closely to the measured data Figure 39. 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 (Figure

40). Nevertheless, it is obvious that there is a overestimation from day 28 on. Chi²-error is small and acceptable. FOMC-calculated DT_{50} is 5.4 days and DT_{90} is 42.0 days (Table 33) for the whole aerobic pond system.

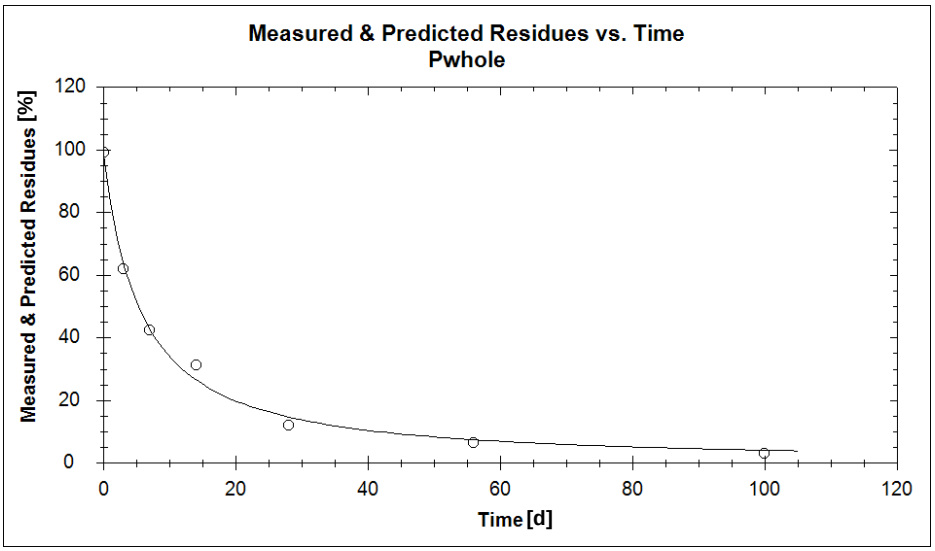


Figure 39: Measured and predicted residues of EC 407-000-3 vs. time in the whole system of an aerobic pond – FOMC

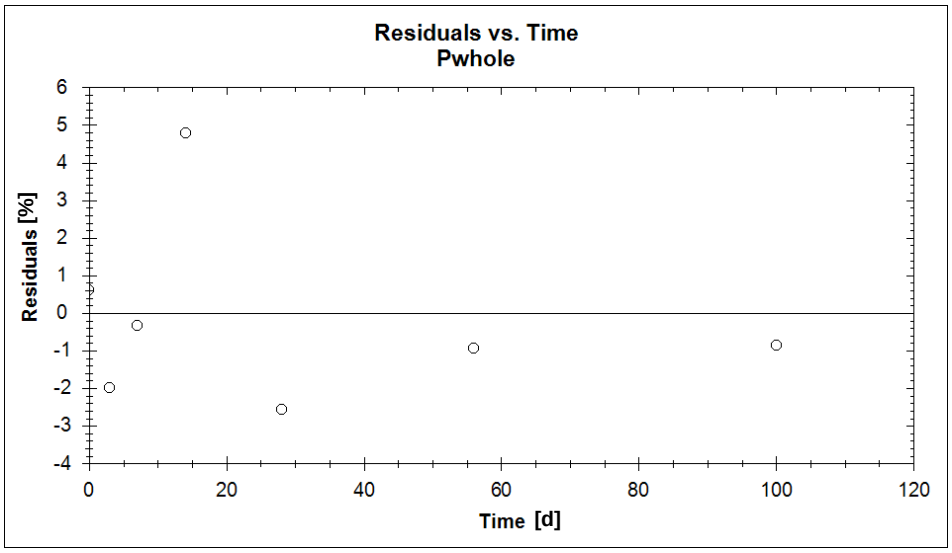


Figure 40: Residuals of EC 407-000-3 vs. time in the whole system of an aerobic pond – FOMC

Table 32: Chi² and dissipation times of EC 407-000-3 using FOMC kinetic (aerobic pond system)

Parameter	EC 407-000-3	All	Kinetic model
Chi²Err %	5.2810	5.2810	FOMC
DT_{50} in d	5.4485		
DT_{90} in d	41.9500		

2.3.5. EC 407-000-3 DFOP (whole aerobic pond system)

Data are well described by DFOP kinetic. The curve fits closely to the measured data (Figure 41). The calculated curve matches the observed behaviour well. The residuals are small and randomly scattered around the zero line (Figure 42). Chi²-error is acceptable and with 4.994 smaller than Chi²-error of 5.281 of FOMC, i.e. overall deviations are smaller and DFOP describes data better than FOMC. DFOP-calculated DT_{50} is 5.2 days and DT_{90} is 36.7 days (Table 34) for the whole aerobic pond system.

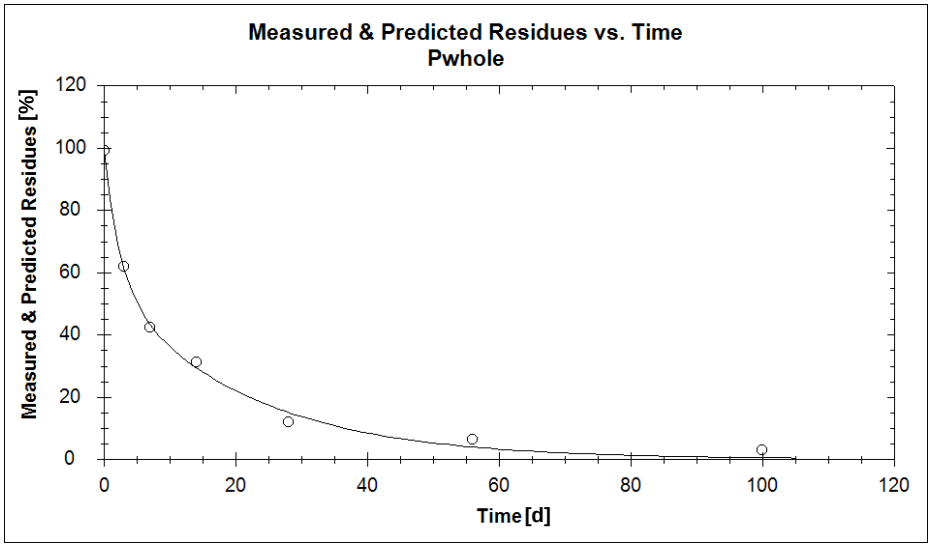


Figure 41: Measured and predicted residues of EC 407-000-3 vs. time in the whole system of an aerobic pond – DFOP

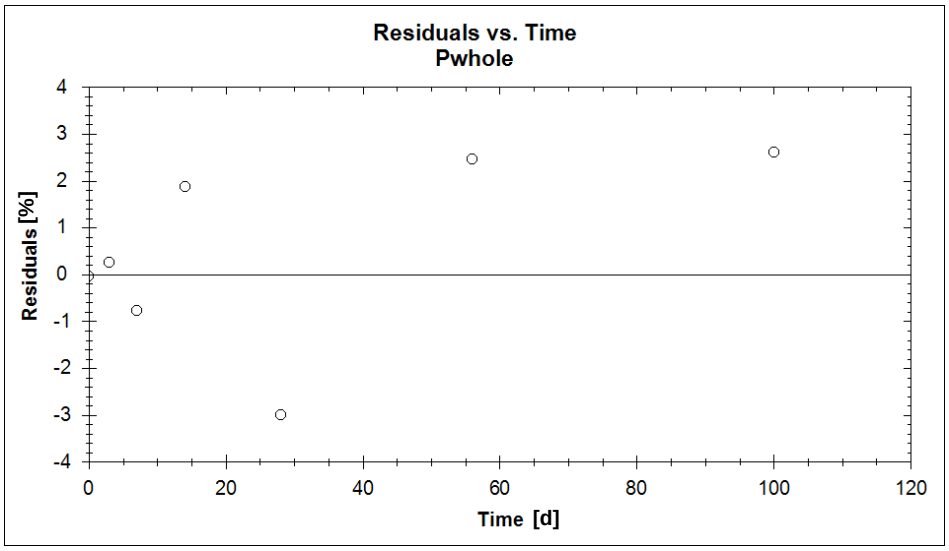


Figure 42: Residuals of EC 407-000-3 vs. time in the whole system of an aerobic pond – DFOP

Table 33: Chi² and dissipation times of EC 407-000-3 using DFOP kinetic (whole aerobic pond system)

Parameter	EC 407-000-3	All	Kinetic model
Chi²Err %	4.9940	4.9940	DFOP
DT_{50} in d	5.1916		
DT_{90} in d	36.6510		

2.3.6. Conclusion on dissipation of EC 407-000-3 (whole aerobic pond system)
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 38) shows that Single First Order Kinetic (SFO) cannot be accepted although Chi² 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. Aerobic 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 (aerobic pond system)

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 submitter followed its advice and used SFO for modelling of M1 dissipation (level M-I calculation).

Figure 43 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 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 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.

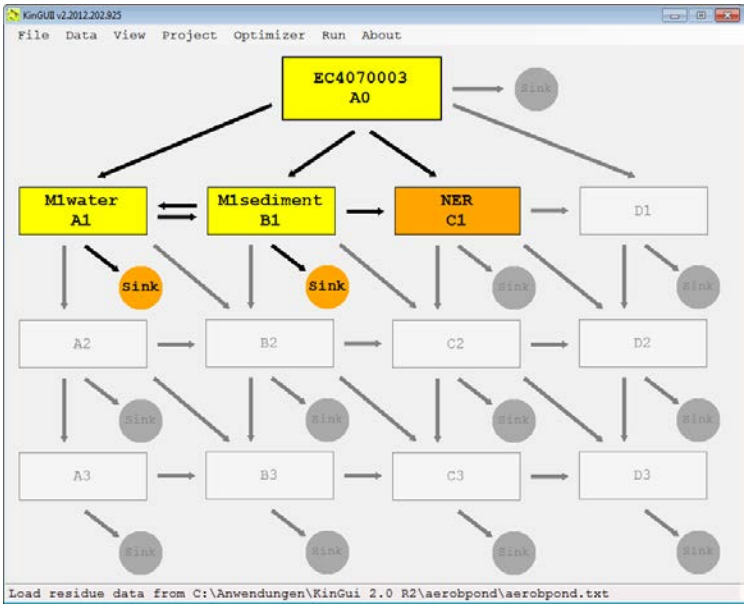


Figure 43: Considered compartments and sinks in pond system under aerobic conditions

2.4.2.2. EC 407-000-3 (whole aerobic pond 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 44). The residuals are small and randomly scattered around the zero line except day 56 and 100, which both are underestimated (see Figure 45). Chi²-error is acceptable (see Table 35). DFOP-calculated DT_{50} is 5.0 days and DT_{90} is 37.1 days (Table 35) for the whole aerobic pond system.

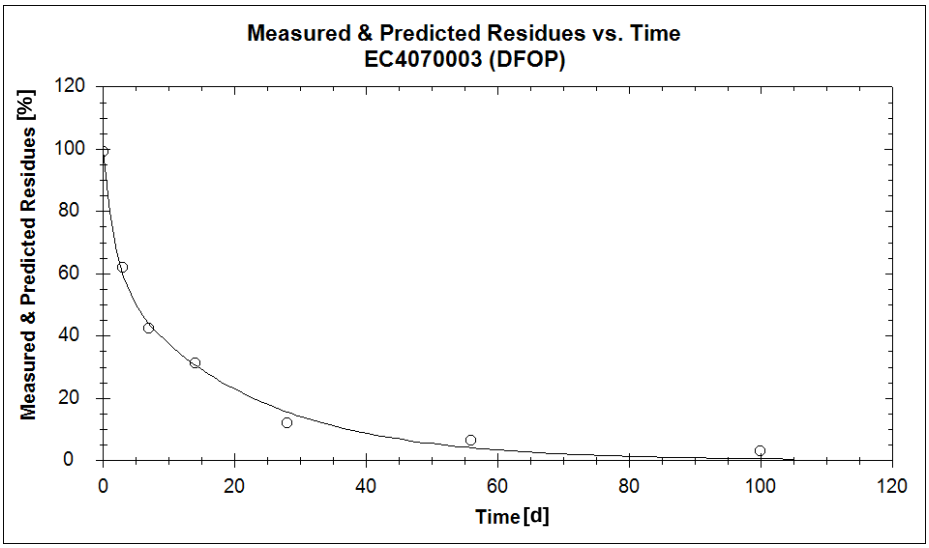


Figure 44: Measured and predicted residues of EC 407-000-3 vs. time in the whole system of an aerobic pond – DFOP

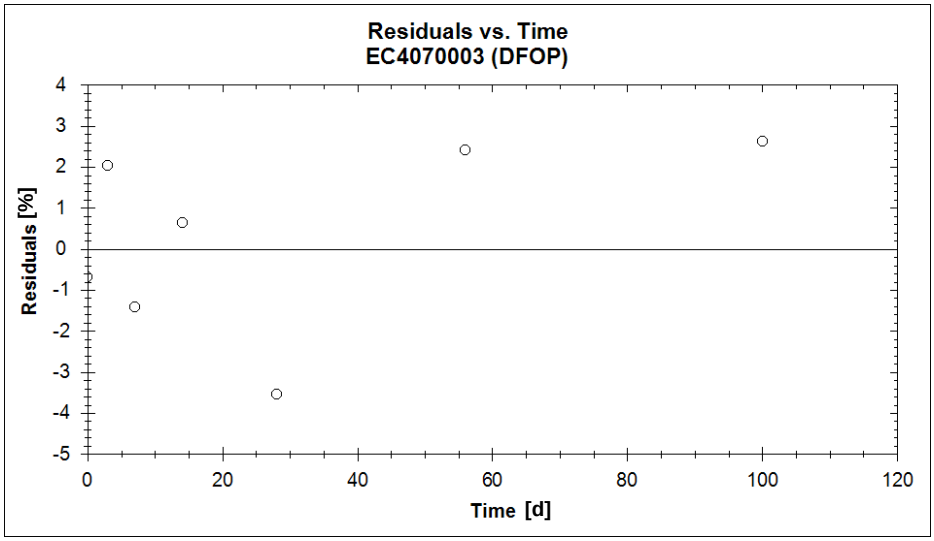


Figure 45: Residuals of EC 407-000-3 vs. time in the whole system of an aerobic pond – DFOP

2.4.2.3. M1 in water (aerobic pond system)

Data of M1 in the water phase are well described by SFO kinetic (see Figure 46). The curve fits to the measured data. The residuals are small but there is a constant underestimation except on day 14 (see Figure 47). 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 deviation. However, data from day 28 to day 100 clearly show a deviation and measured data are underestimated. The reason is that an 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. SFO-calculated DT_{50} is 3.9 days and DT_{90} is 13.0 days for metabolite M1 in water (Table 35) for the aerobic pond system.

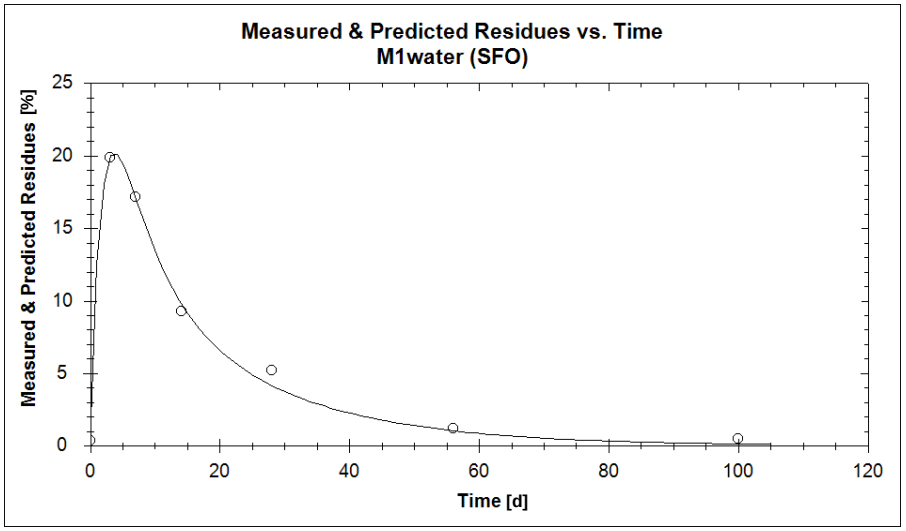


Figure 46: Measured and predicted M1 concentrations in pond water under aerobic conditions

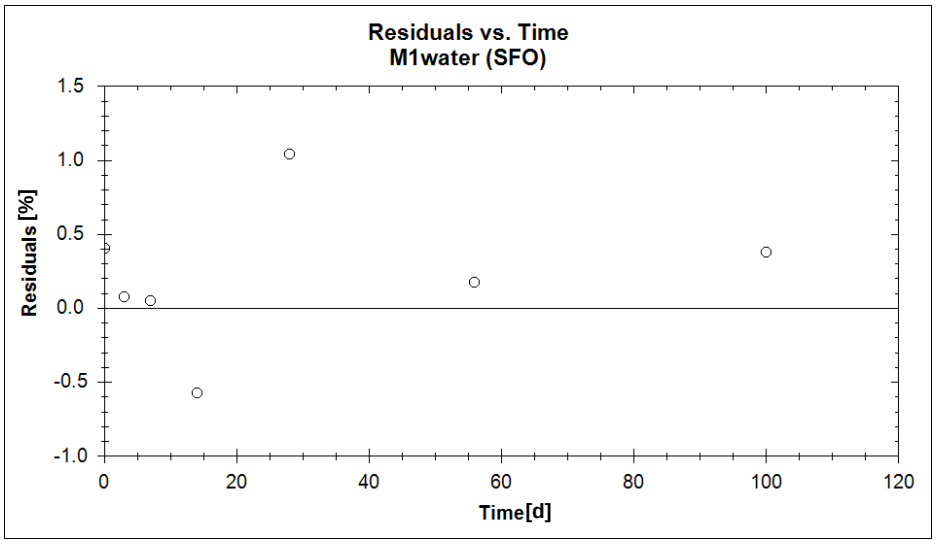


Figure 47: Residuals of M1 concentrations in pond water under aerobic conditions

2.4.2.4. M1 in sediment (aerobic pond system)

Data of M1 in the sediment phase are well described by SFO kinetic (see Figure 48). 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 49). The last two data points are well represented by model although SFO kinetic frequently tends to underestimate the last data points. Chi² is only slightly elevated (see Table 35). 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. SFO-calculated **DT_{50} is 248.2 days** and DT_{90} is 824.5 days for metabolite M1 in sediment (Table 35) for the aerobic pond system.

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 data points 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.

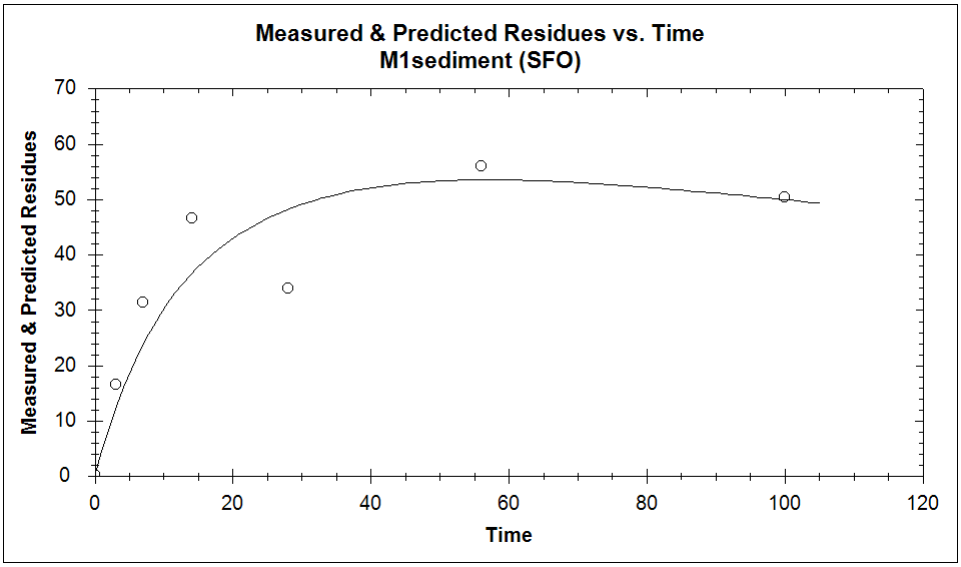


Figure 48: Measured and predicted M1 concentrations in pond sediment under aerobic conditions

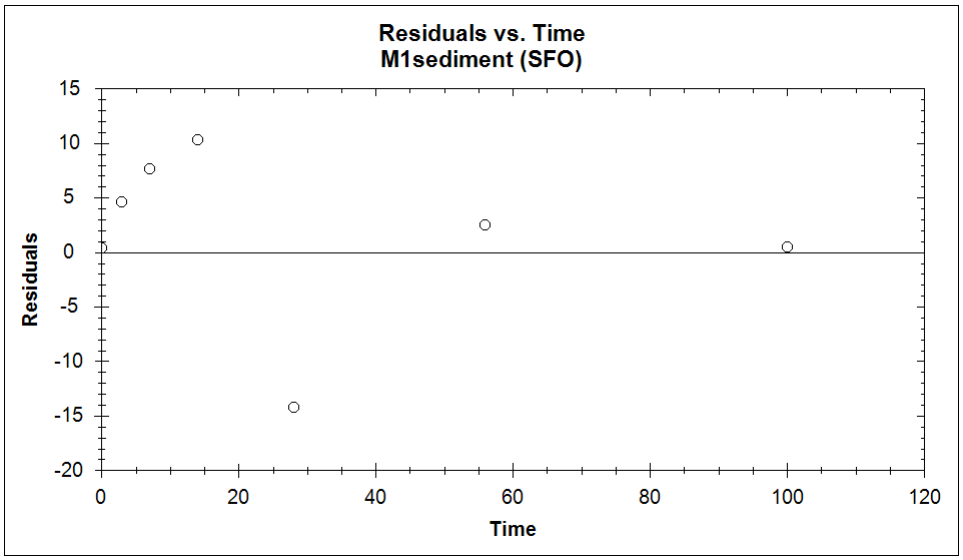


Figure 49: Residuals of M1 concentrations in pond sediment under aerobic conditions

2.4.2.5. NER in whole aerobic pond system

Data of NER are sufficiently well described by SFO kinetic (see Figure 50). Most residuals are small (see Figure 51). 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. Chi²-error is elevated, i.e. above 15, especially for M1 in sediment and the NER (see Table 35). 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. SFO-calculated DT_{50} is $1.1*10^{10}$ days and DT_{90} is $3.5*10^{10}$ days for NER (Table 35) for the whole aerobic pond system.

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.

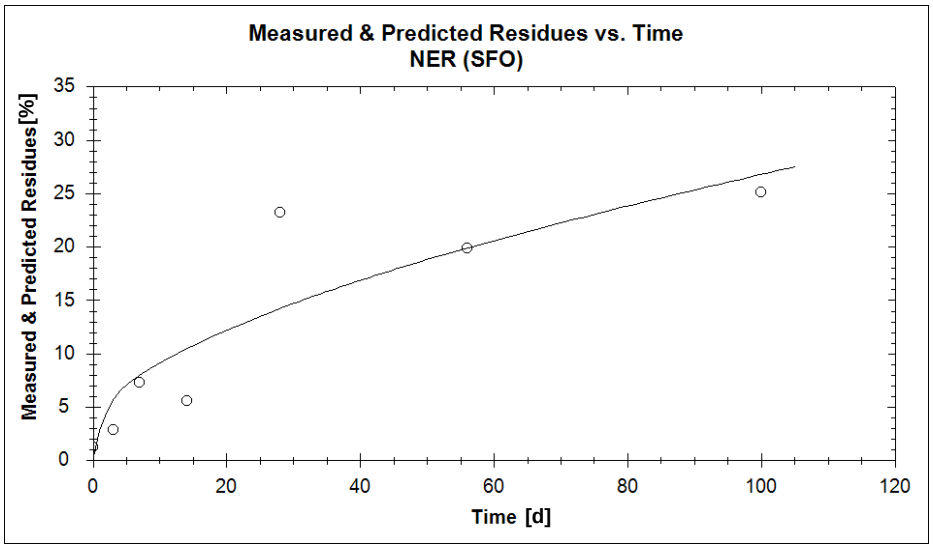


Figure 50: Measured and predicted NER concentrations in pond sediment under aerobic conditions

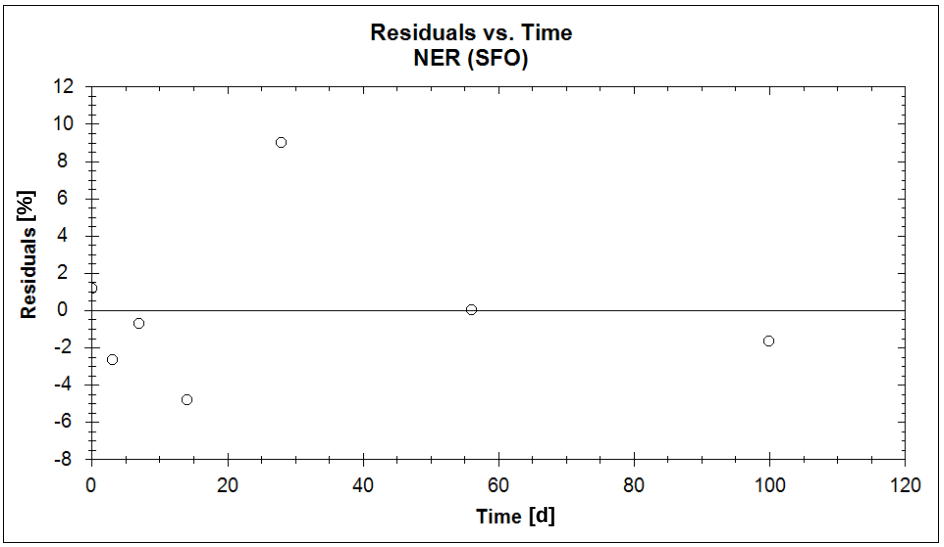


Figure 51: Residuals of NER concentrations in pond sediment under aerobic conditions

Figure 52 gives an overview of the measured and predicted data of EC 407-000-3, M1 and NER.

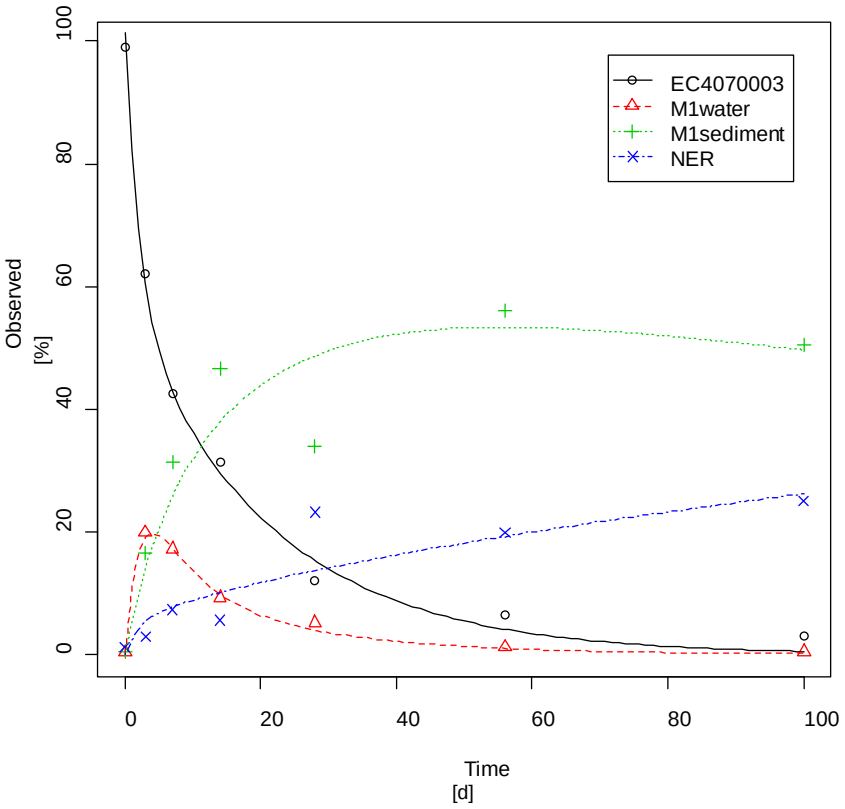


Figure 52: Combined diagram of measured data and respective trends in a pond system under aerobic conditions

Table 34: Chi²-error and dissipation times of EC 407-000-3, M1 and NER in an aerobic pond system

	EC 4070003	**M1 water**	**M1 sediment**	**NER**	**All**
Chi²Err %	7.908	5.186	19.170	24.924	20.195
DT_{50} in d	5.0379	3.9189	248.190	1.0678E+10	
DT_{90} in d	37.123	13.018	824.480	3.547E+10	
Kinetic model	DFOP	SFO	SFO	SFO	

Table 35: 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[11]	NA	NA	NA	NA

[11] This value is essentially zero.

Table 36: 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

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 anaerobic 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.

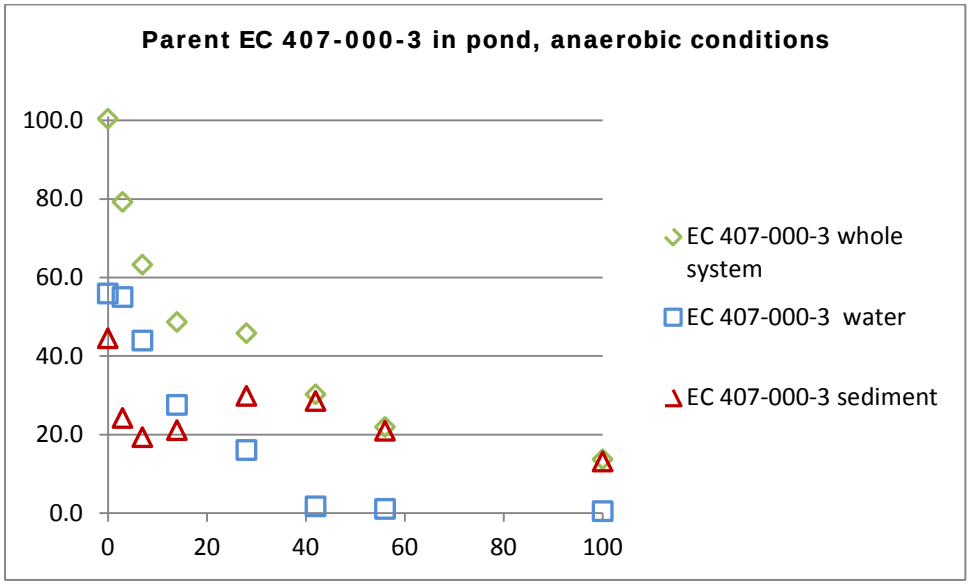


Figure 53: Distribution of EC 407-000-3 in a pond system under anaerobic conditions

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 anaerobic system

The model setup used in all kinetic modelling of EC 407-000-3 is shown in Figure 54. It is simple and considers one sink, only, without differentiating it further.

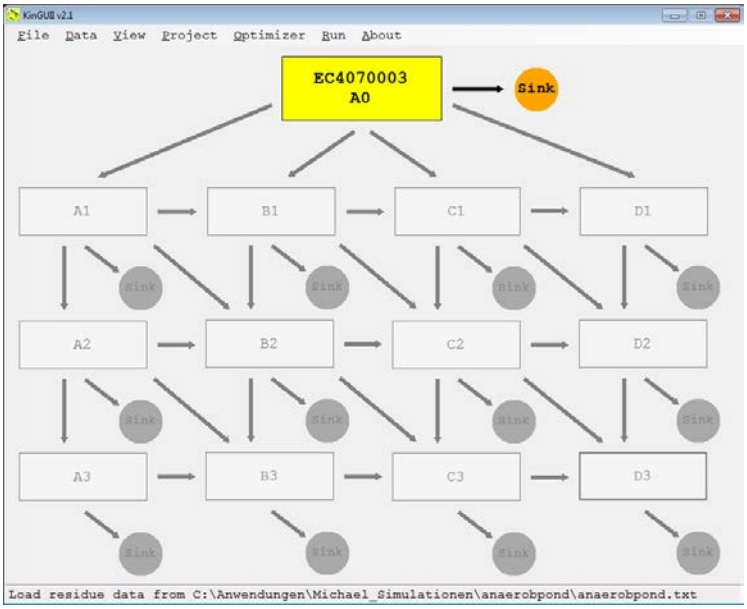


Figure 54: Model setup for modelling of EC 407-000-3 in pond system under anaerobic conditions

3.1.3. EC 407-000-3 SFO (whole anaerobic pond system)

The data shown in Figure 55 are adequately described by SFO but residuals show underestimation from day 28 to 100 (see Figure 56). Chi²-error is acceptable (see Table 38). SFO-calculated DT_{50} is 25.9 days and DT_{90} is 86.0 days (Table 38) for the whole anaerobic pond system.

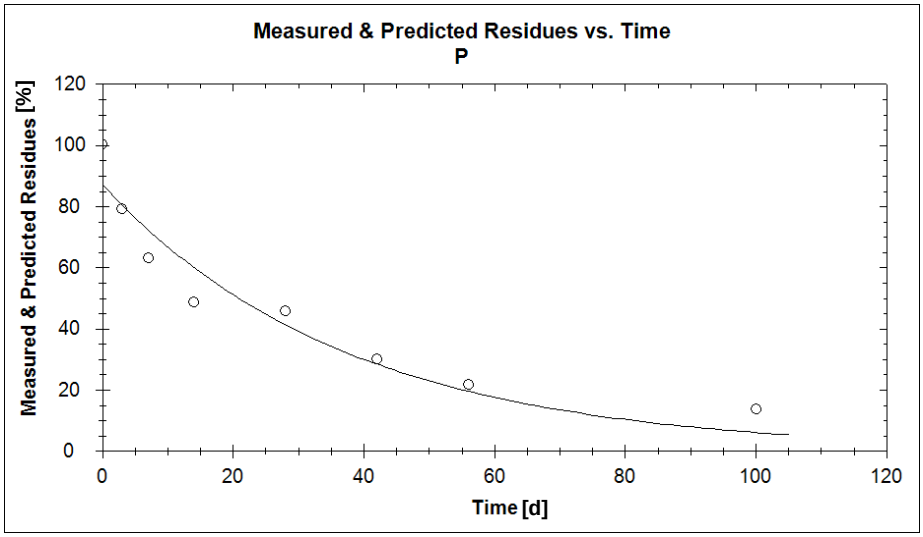


Figure 55: Measured and predicted residues of EC 407-000-3 vs. time in the whole system of an anaerobic pond – SFO

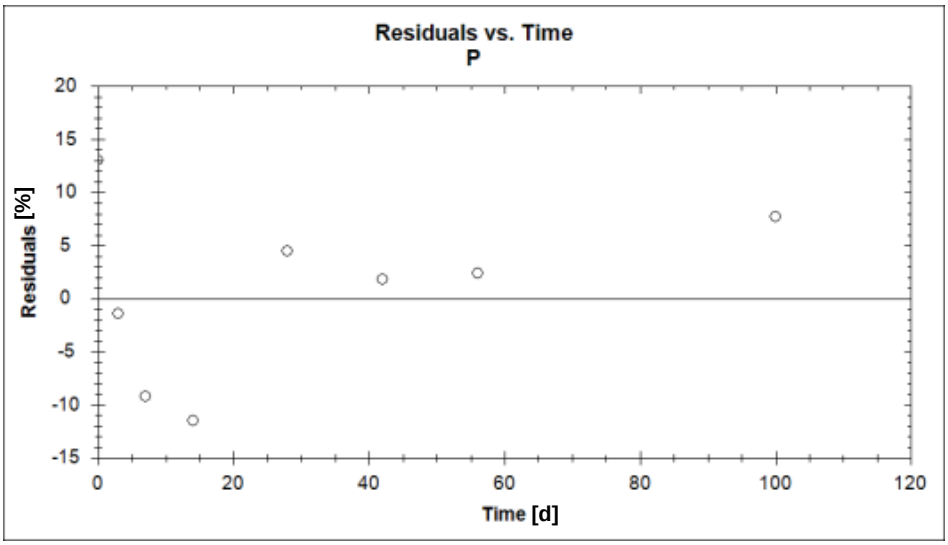


Figure 56: Residuals of EC 407-000-3 vs. time in the whole system of an anaerobic pond – SFO

Table 37: Chi² and dissipation times of EC 407-000-3 using SFO kinetic (whole anaerobic pond system)

Parameter	EC 407-000-3	All	Model
Chi²Err %	12.220	12.220	SFO
DT_{50} in d	25.884		
DT_{90} in d	85.986		

3.1.4. EC 407-000-3 FOMC (whole anaerobic pond system)

Data are well described by FOMC kinetic and the curve fits closely to the measured data (see Figure 57). Residuals show an overestimation for day 3 to 14 (see Figure 58). Chi² is small and acceptable (see Table 39). FOMC-calculated DT_{50} is 14.7 days and DT_{90} is 247.8 days (Table 39) for the whole anaerobic pond system.

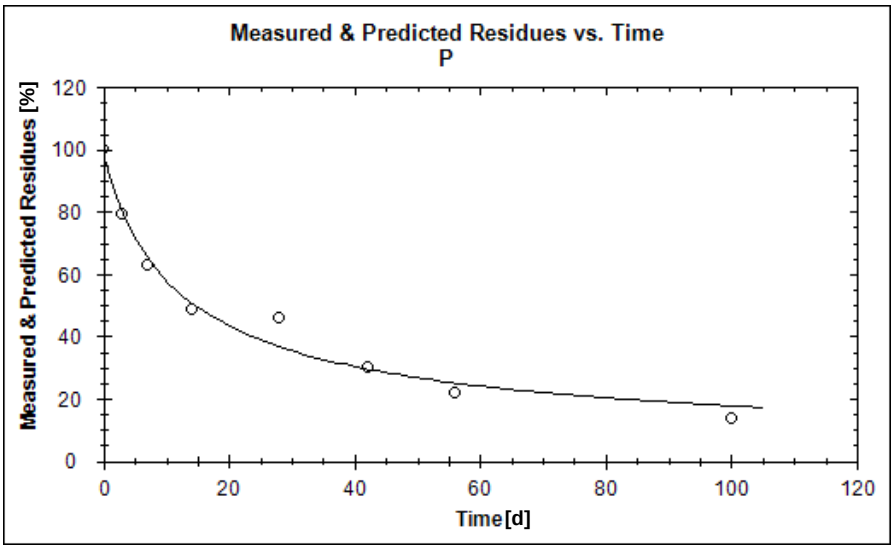


Figure 57: Measured and predicted residues of EC 407-000-3 vs. time in the whole system of an anaerobic pond – FOMC

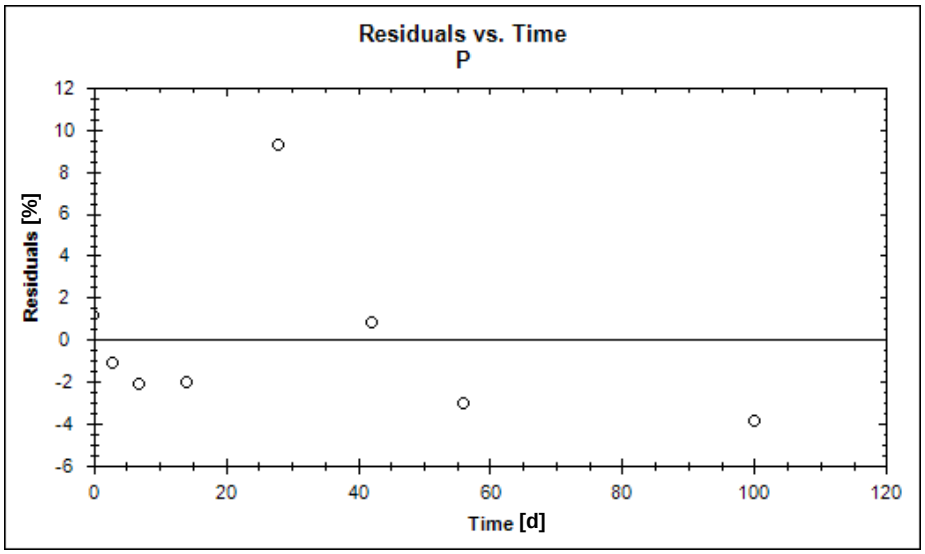


Figure 58: Residuals of EC 407-000-3 vs. time in the whole system of an anaerobic pond – FOMC

Table 38: Chi² and dissipation times of EC 407-000-3 using FOMC kinetic (whole anaerobic pond system)

Parameter	EC 407-000-3	All	Model
Chi²Err %	6.604	6.604	FOMC
DT_{50} in d	14.677		
DT_{90} in d	247.830		

3.1.5. EC 407-000-3 DFOP (whole anaerobic pond system)

Data are well described by DFOP kinetic. The curve fits closely to the measured data and matches the observed behaviour well (see Figure 59). The residuals are small and randomly scattered around the zero line (see Figure 60). Chi²-error is small and

acceptable and with 4.937 (see Table 40) smaller than Chi²-error of 6.604 of FOMC. DFOP-calculated DT_{50} is 15.1 days and DT_{90} is 110.8 days (Table 40) for the whole anaerobic pond system.

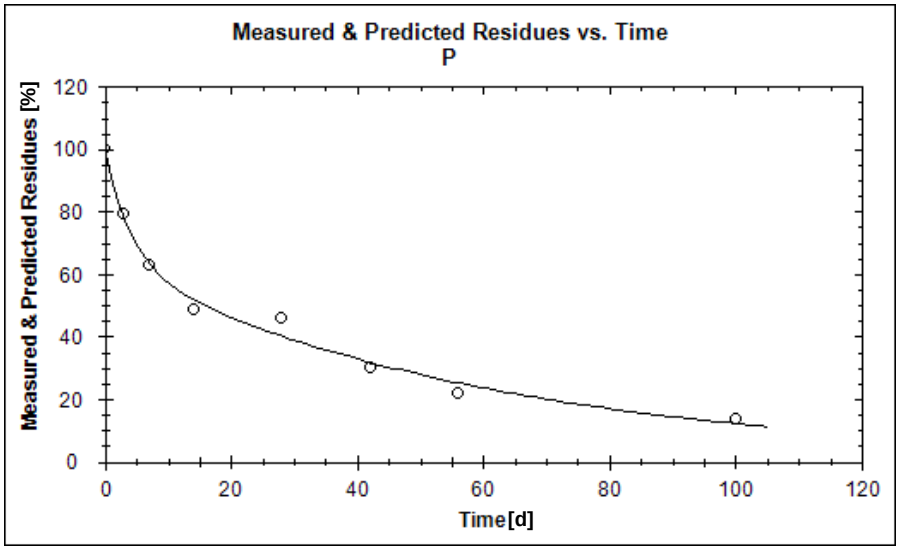


Figure 59: Residuals of EC 407-000-3 vs. time in the whole system of an anaerobic pond – DFOP

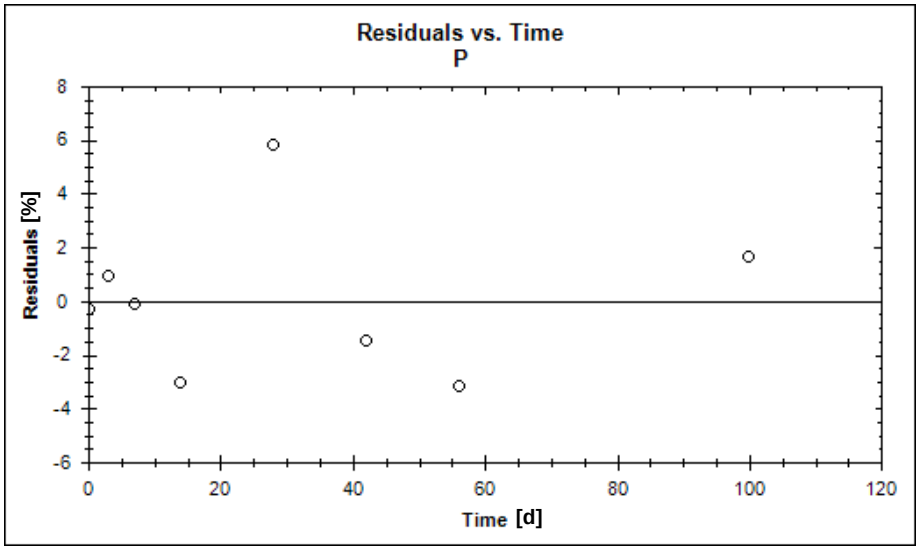


Figure 60: Measured and predicted residues of EC 407-000-3 vs. time in the whole system of an anaerobic pond – DFOP

Table 39: Chi² and dissipation times of EC 407-000-3 using DFOP kinetic (whole anaerobic pond system)

Parameter	EC 407-000-3	All	Kinetic model
Chi²Err %	4.937	4.937	DFOP
DT_{50} in d	15.179		
DT_{90} in d	110.830		

3.1.6. Conclusion on dissipation of EC 407-000-3 (whole anaerobic pond system)

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 a possibly systematic deviation, while DFOP does not. Additionally, Chi²-error of DFOP is smaller than Chi²-error of FOMC, i.e. overall deviations are smaller. DFOP describes data better than FOMC.

3.2. Anaerobic 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 (anaerobic pond system)

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 61 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.

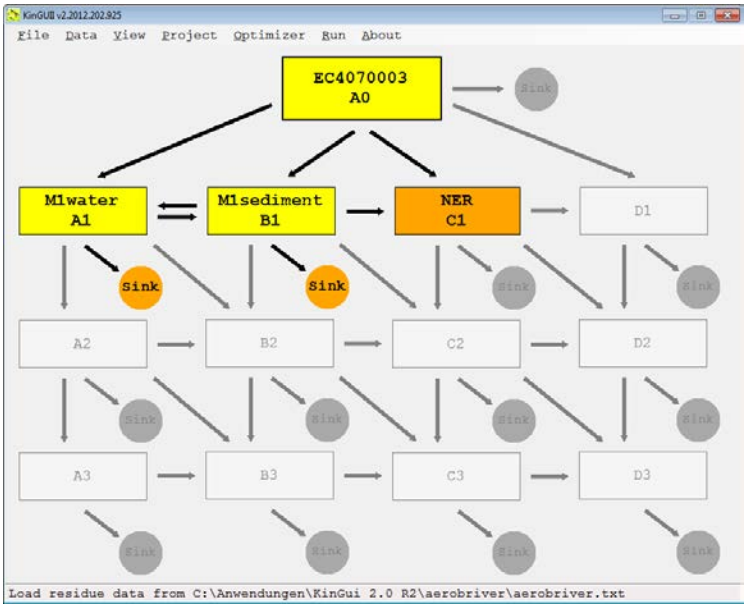


Figure 61: Considered compartments and sinks in pond system under anaerobic conditions

3.2.2.2. EC 407-000-3 in whole anaerobic pond 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 62). The residuals are small and randomly scattered around the zero line except day 3 to 14 which are underestimated (see Figure 63). Chi²-error is acceptable (see Table 41). Visual fit shows that the fit is acceptable. DFOP-calculated DT_{50} is 15.4 days and DT_{90} is 116.9 days for the parent substance (Table 41) for the whole anaerobic pond system.

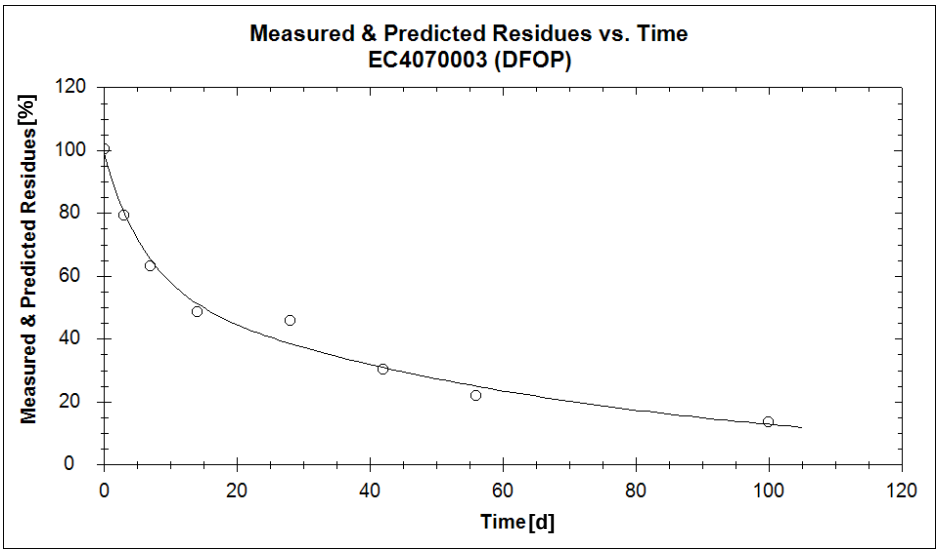


Figure 62: Measured and predicted residues of EC-407-000-3 vs. time in the whole system of an anaerobic pond – DFOP

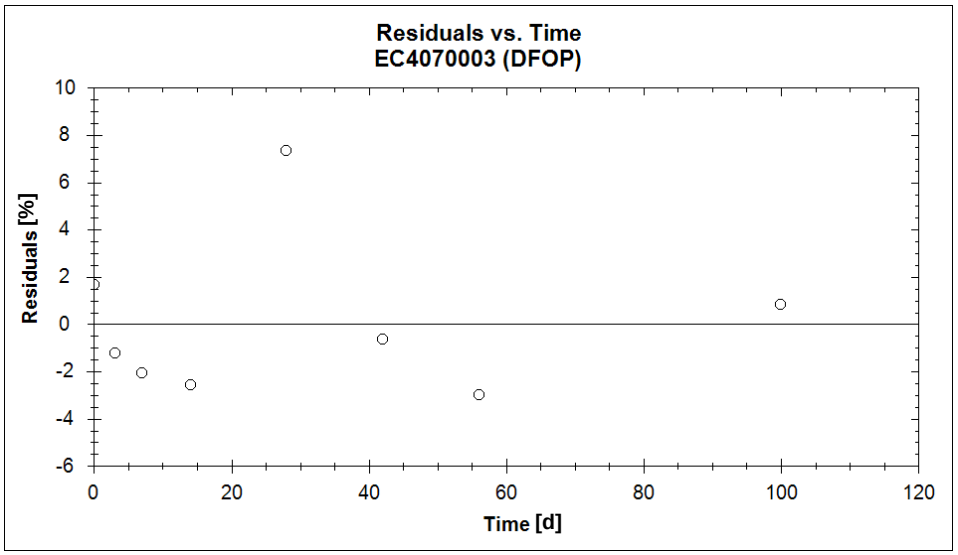


Figure 63: Residuals of EC-407-000-3 vs. time in the whole system of an anaerobic pond – DFOP

3.2.2.3 M1 in water (anaerobic pond system)

Data of M1 in the water phase are acceptably well described by SFO kinetic (see Figure 64). 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 65). As a consequence, Chi² is elevated (above 15) but still acceptable (see Table 41). SFO-calculated DT_{50} is 12.2 days and DT_{90} is 40.6 days for the metabolite M1 in water (Table 41) for the anaerobic pond system.

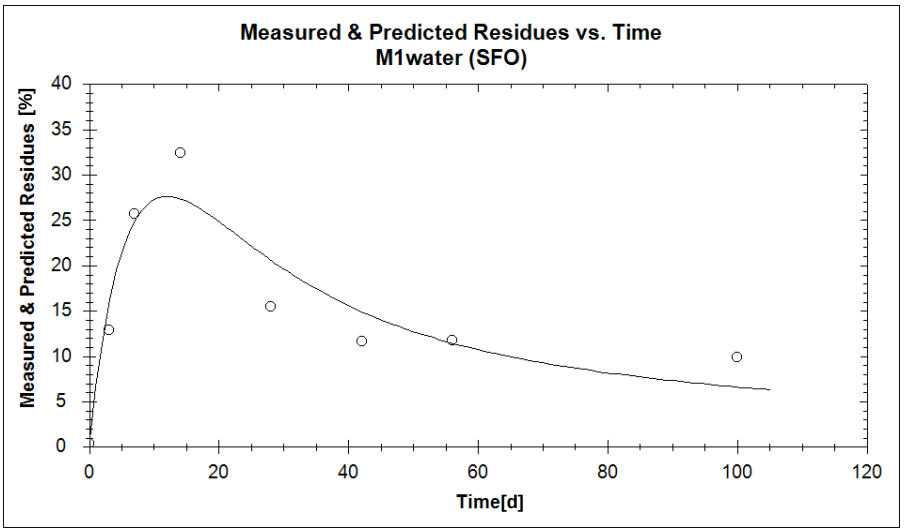


Figure 64: Measured and predicted residues of M1 vs. time in the water phase of an anaerobic pond – SFO

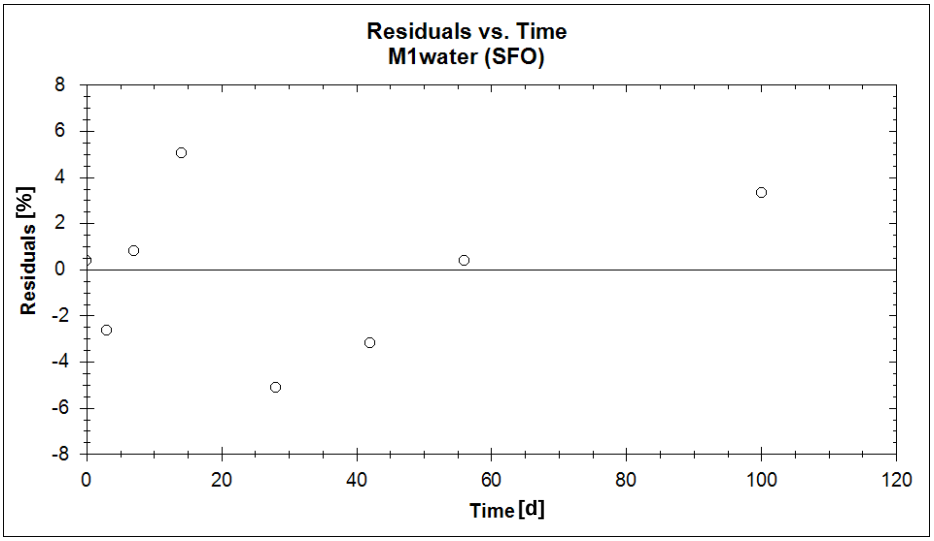


Figure 65: Residuals of M1 vs. time in the water phase of an anaerobic pond – SFO

3.2.2.4. M1 in sediment (anaerobic pond system)

Data of M1 in the sediment phase are well described by SFO kinetic and the curve fits well to the measured data (see Figure 66). Residuals are small and do not show systematic deviation (see Figure 67). Chi² is small (see Table 41). SFO-calculated **DT_{50} is 237.7 days** and DT_{90} is 789.5 days for the metabolite M1 in sediment (Table 41) for the anaerobic pond system.

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).

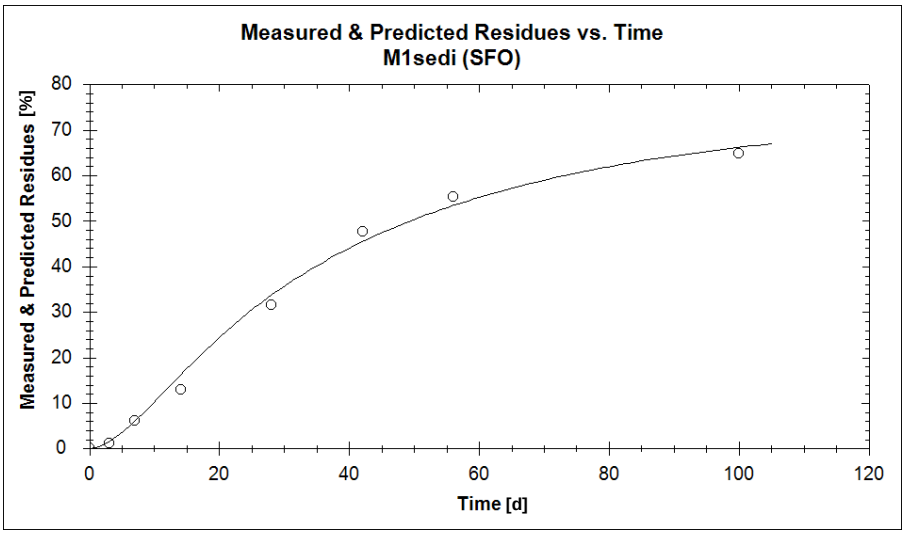


Figure 66: Measured and predicted residues of M1 vs. time in the sediment phase of an anaerobic pond – SFO

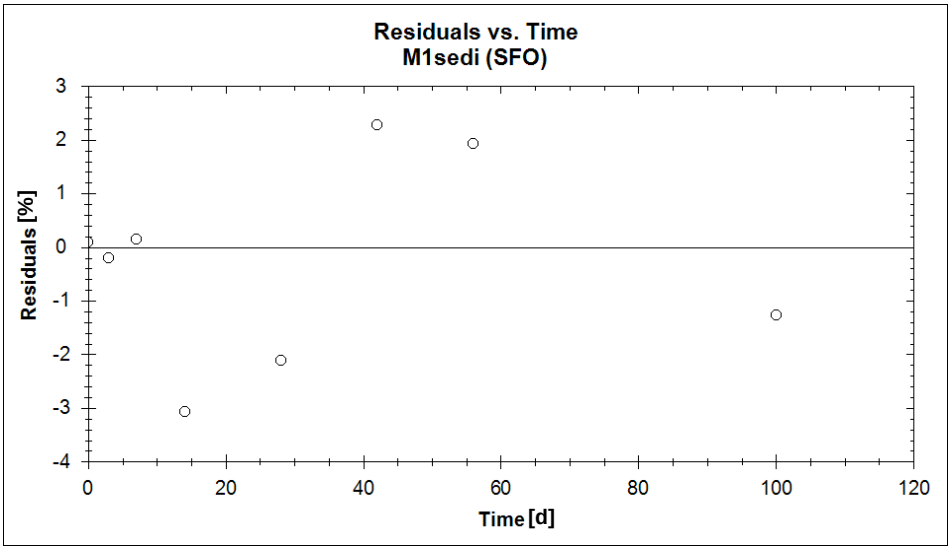


Figure 67: Residuals of M1 vs. time in the sediment phase of an anaerobic pond – SFO

3.2.2.5. NER in whole system (anaerobic pond system)

Data of NER are acceptably well described by SFO kinetic (see Figure 68). Residuals are small but there is an overestimation from day 3 to 14 (see Figure 69). Nevertheless, the visual fit and the acceptable Chi² (see Table 41) show that the fit is adequate. SFO-calculated DT_{50} is $1.5*10^7$ days and DT_{90} is $5.1*10^7$ days for NER (Table 41) for the whole anaerobic pond system.

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 70).

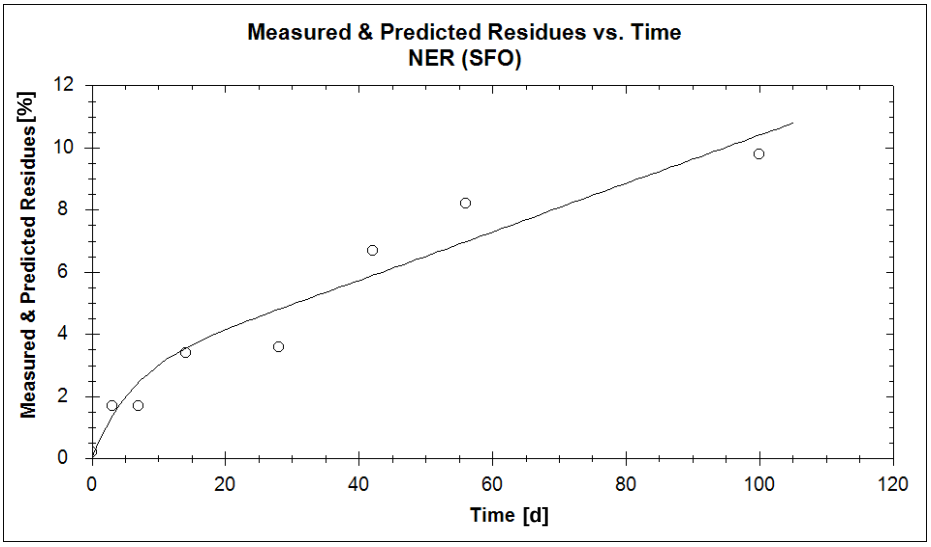


Figure 68: Measured and predicted residues of NER vs. time in the whole system of an anaerobic pond – SFO

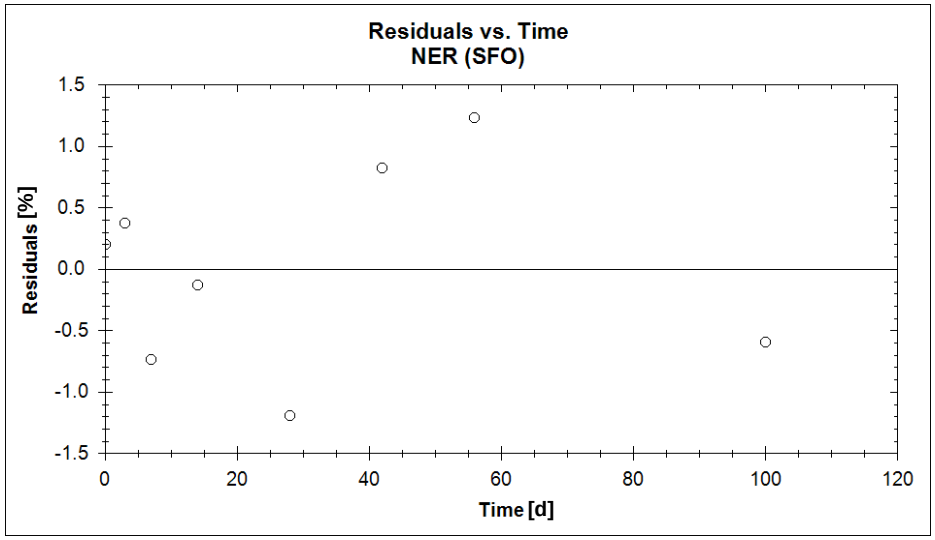


Figure 69: Residuals of NER vs. time in the whole system of an anaerobic pond – SFO

Figure 70 gives an overview of the measured and predicted data of EC 407-000-3, M1 and NER in an anaerobic pond system.

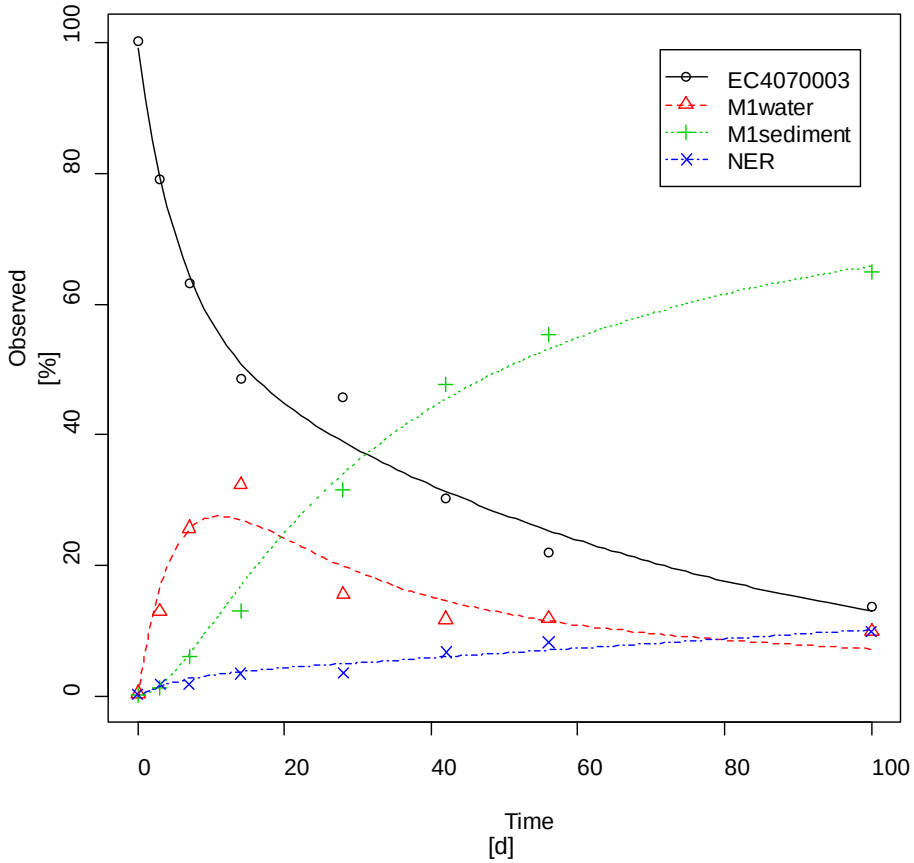


Figure 70: Combined diagram of measured data and respective trends in a pond system under anaerobic conditions.

Table 40: Chi²-error and dissipation times of EC-407-000-3, M1 and NER in an anaerobic pond system

	EC 4070003	**M1 water**	**M1 sediment**	**NER**	**All**
Chi²Err %	7.200	16.817	5.423	13.114	10.075
DT_{50} in d	15.383	12.224	237.65	15,219,328	
DT_{90} in d	116.90	40.608	789.46	50,557,513	
Kinetic model	DFOP	SFO	SFO	SFO	

Table 41: 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[12,13]	2.92E-03	-2.47E-03	0.008	2.75E-03	**$1.5*10^{-1}$**
k NER[14]	4.55E-08	-3.94E-02	0.039	2.01E-02	**$5.0*10^{-1}$**

Table 42: 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

[12] Please note that the Chi-square values for k M1water, k M1sediment and k NER are elevated. Therefore the absolute values of the reaction constants should be interpreted with caution. See also remark on t-test.
[13] According to the t-test this values is essentially zero, meaning that there is no degradation in M1 Sediment. The resulting endpoint M1 DT_{50} has to be taken with care.
[14] According to the t-test this values is essentially zero, meaning that there is no degradation in NER.

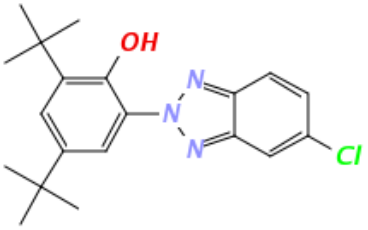
Time [d]	variable	Observed [%]	err-std [%]	Predicted [%]	Residual [%]
0	M1sediment	0.1	1.7630	0	0.1000
3	M1sediment	1.2	1.7630	1.4047	-0.2047
7	M1sediment	6.1	1.7630	5.9577	0.1423
14	M1sediment	13	1.7630	16.0747	-3.0747
28	M1sediment	31.5	1.7630	33.6079	-2.1079
42	M1sediment	47.7	1.7630	45.4116	2.2884
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
56	NER	8.2	0.7673	6.9681	1.2319
100	NER	9.8	0.7673	10.3924	-0.5924

Annex I.C – Analysis of QSAR Application: Prediction of log Kow for UV-327 and UV-350

1. Information on substances and purpose

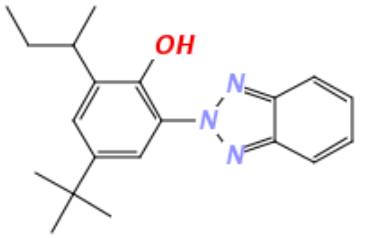
Molecule 1: UV-327

Name:	2,4-di-tert-butyl-6-(5-chlorobenzotriazol-2-yl)phenol (UV-327)
CAS Nr.	3864-99-1
EU Nr.	223-383-8
Smiles	(c(cc(c1)C(C)(C)C)C(C)(C)C)O)N(N=C2C=C3)N=C2C=C3Cl



Molecule 2: UV-350

Name:	-(2H-benzotriazol-2-yl)-4-(tert-butyl)-6-(sec-butyl)phenol (UV-350)
CAS Nr.	36437-37-3
EU Nr.	253-037-1
Smiles	c1(c(c(cc(c1)C(C)(C)C)C(C)CC)O)N(N=C2C=C3)N=C2C=C3



Endpoint	Logarithmic octanol-water partition coefficient (log K_{OW})
Regulatory purpose	PBT-Assessment, supporting information

2. 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 optimised with employing Density-Functional-Theory (functional: Becke-Perdew 86, basis set of

Parameter	Result	Rationale
		Triple-Zeta-Valence-Polarisation-quality), all parameters for this method and all elements of the molecules are implemented
Other relevant information		
n/a	n/a	n/a

3. QSAR models used

Model	Version	Endpoint	QMBI
KOWWIN	v1.68	log K_{OW}	Annex I.C.6
COSMOtherm (K_{OW})	v. C30_1201	log K_{OW}	Annex I.C.7

4. Analysis of QSAR model performance

Model	QSAR Result	Overall Model Performance	Reference
KOWWIN	**UV-327: 6.91**	Reliable with restrictions	Annex I.C.8
	UV-350: 6.31		
COSMOtherm (K_{OW})	**UV-327: 7.91**	Reliable with restrictions	Annex I.C.8
	UV-350: 7.11		

5. 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. In addition, KOWWIN predicts log K_{OW} approximately 0.6-0.8 log units smaller than COSMOtherm. The values of KOWWIN are nearer to the available experimental values.
Rationale	According to the B-Screening criteria in ECHA Guidance R.11, a log K_{OW} < 4.5 means that the respective substance is not suspected to be 'B'.
Reliability	Reliable with restrictions.

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

6. QMBI KOWWIN

	Information	Literature References or Links[15]	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.[16]: 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 set available at		List available at http://esc.syrres.com/interkow/KowwinData.htm	

[15] References given here are not substance-specific but related to the EPISUITE software.
[16] w.a.: when applicable

	Information	Literature References or Links[15]	Remarks
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}.		

7. QMBI COSMOtherm KOW

	Information	Literature References or Links[17]	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.[18]: 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		Log K_{OW}
2 – Definition of Algorithm			
Brief description of algorithm and/or link to full definition	$\log K_{OW}(T) = \int p^i(\sigma)(\mu_{water}(\sigma;T) - \mu_{octanol}(\sigma;T))d\sigma + \mu_i^C(water, T) - \mu_i^C(octanol,; T)$, where $\mu_i^C(S, T) = RT^* [\lambda_0^* \ln r_i + \lambda_1^*(1-(r_i/\underline{r} - \ln \underline{r}) + \lambda_2^*(1-q_i/\underline{q} - \ln \underline{q})]$ and $\underline{r} = \Sigma_i x_i^* r_i$ and $\underline{q} = \Sigma_i x_i^* q_i$	"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 polarisation 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, $\underline{r}$: overall volume of the mixture, $\underline{q}$: overall area of the mixture.		
Number of Chemicals in	Original parameterisation: 225 small- and medium-sized organic compounds with H, C,		While the principle theory is applicable for all elements, the practical implementation needs

[17] References given here are not substance-specific but related to the EPISUITE software.
[18] w.a.: when applicable

	Information	**Literature References or Links**[17]	**Remarks**
Training Set and brief description of it	O, N, Cl atoms. The fitting was done for 650 experimental room-temperature parameters (ΔG_{hydr}, log(vapour pressure), log $K_{octanol\text{-}water}$, log $K_{hexane\text{-}water}$, log $K_{benzene\text{-}water}$, log $K_{diethyl\ ether\text{-}water}$		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 Parameterisation 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 parameterisation 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	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	n/a		
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.		

8. Analysis of QSAR prediction for K_{ow} for UV-327 and UV-350

Overall performance of QSAR Models KOWWIN and COSMOtherm (K_{ow})

	Result		Further description
Endpoint results [unit]	KOWWIN	**UV-327: 6.91**	All log K_{OW}-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-350: 6.31	
	COSMO-therm (K_{OW})	**UV-327: 7.91**	
		UV-350: 7.11	
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 9
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, however, the experimental values were not validated.
Other uncertainties	No		-

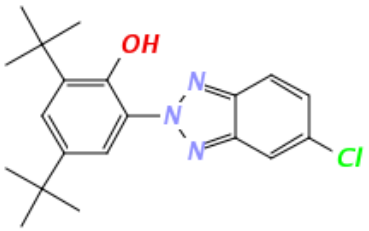
Overall conclusion	Reliable with restrictions
Rationale	As the models are applicable and results show values in the same range it can be expected that the range is correctly predicted.

Annex I.D – Analysis of QSAR Application: Prediction of log Koc for UV-327 and UV-350

1. Information on substances and purpose

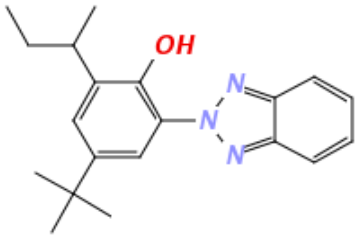
Molecule 1: UV-327

Name:	2,4-di-tert-butyl-6-(5-chlorobenzotriazol-2-yl)phenol (UV-327)
CAS Nr.	3864-99-1
EU Nr.	223-383-8
Smiles	(c(cc(c1)C(C)(C)C)C(C)(C)C)O)N(N=C2C=C3)N=C2C=C3Cl



Molecule 2: UV-350

Name:	-(2H-benzotriazol-2-yl)-4-(tert-butyl)-6-(sec-butyl)phenol (UV-350)
CAS Nr.	36437-37-3
EU Nr.	253-037-1
Smiles	c1(c(c(cc(c1)C(C)(C)C)C(C)CC)O)N(N=C2C=C3)N=C2C=C3



Endpoint	Logarithmic soil adsorption coeffiecient (log K_{oc}) of organic compounds
Regulatory purpose	PBT-Assessment, supporting information

2. Relevant structure information

Parameter	**Result**	**Rationale**
Structure identification		
Structure of concern	parent	Substances are mono-constituents
Descriptors used for QSAR prediction		
Fragment descriptors (KOCWIN)	applicable	The first-order molecular connectivity index (MCI) and a series of group contribution factors (correction factors) are used to predict K_{oc} values for hydrophobic organic compounds. Separately, K_{oc} estimate is based upon log K_{ow} (rather than MCI).
σ (COSMOtherm)	applicable	The polarity was calculated on molecular

Parameter	Result	Rationale
		structures geometrically optimised with employing Density-Functional-Theory (functional: Becke-Perdew 86, basis set of Triple-Zeta-Valence-Polarisation-quality), all parameters for this method and all elements of the molecules are implemented
Other relevant information		
n/a	n/a	n/a

3. QSAR models used

Model	Version	Endpoint	QMBI
KOCWIN (K_{OW}) KOCWIN (MCI)	V2.00 (Sep. 2010)	log K_{oc}	Annex I.D.6 Annex I.D.7
COSMOtherm (K_{OW})	v. C30_1201	log K_{oc}	Annex I.D.8

4. Analysis of QSAR model performance

Model	QSAR Result UV-327	QSAR Result UV-350	Overall Model Performance	Reference
KOCWIN (K_{OW}-method)	**4.99**	**4.66**	Reliable with restrictions	Annex I.D.9
(MCI-method)	**5.28**	**5.19**		
COSMOtherm (K_{oc})	**5.64**	**4.90**	Reliable with restrictions	Annex I.D.9

5. Overall conclusion

Overall QSAR Result	Both substances have a high log K_{oc}. The substances behave similar. 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.
Rationale	The log K_{OC} for both substances and all models is in the range of 4.66 to 5.64 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 range; therefore, these substances are similar in their behaviour. According to the prediction, the substances will bind strongly to sediment in the environment, and therefore will mostly not be available for biodegradation processes.

6. QMBI KOCWIN (K_{OW}-method)

	Information	Literature References or Links[19]	Remarks
0 – General			
Model name and version	(PC)KOCWIN v.2 - KOW method	Online Help of KOCWIN: The KOCWIN – KOW method is 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 K_{OW} method is not quite as good as the MCI method.	
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]	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" K_{oc} = (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
List of employed descriptors with units	Log K_{OW}: 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	

[19] References given here are not substance-specific but related to the EPISUITE software.
[20] w.a.: when applicable

	Information	Literature References or Links[19]	Remarks
w.a.: Training set available at		Non-Polar Training Set: Online Help of KOCWIN, Appendix E Polar Set: Online Help of KOCWIN, Appendix F 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	
3 – Definition of the Applicability Domain			
w.a.: Definition of the Applicability Domain	Currently, there is no universally accepted definition of model domain. Log K_{oc} 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		
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 to organic carbon is linked with its lipophilicity. The n-octanol/water partition coefficient is one descriptor for lipophilicity.		

7. QMBI KOCWIN (MCI-method)

	Information	Literature References or Links[21]	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)	Overall, the statistical performance of the MCI-method is better than the K_{OW}-method of KOCWIN.
w.a.[22]: 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" K_{oc} = (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	$\log K_{oc} = 0.5213\ MCI + 0.60 + \Sigma(P_f*N)$; $MCI = \Sigma\delta i*\delta j)^{-0.5}$	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 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	

[21] References given here are not substance-specific but related to the EPISUITE software.
[22] w.a.: when applicable

	Information	Literature References or Links[21]	Remarks
w.a.: Training set available at		Non-Polar Training Set: Online Help of KOCWIN, Appendix E Polar Set: Online Help of KOCWIN, Appendix F List of correction factors available in Online Help of KOCWIN, Appendix D	
3 – Definition of the Applicability Domain			
w.a.: Definition of the Applicability Domain	Currently, there is no universally accepted definition of model domain. Log K_{oc} 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		
Limits of the Applicability Domain	Molecular weight: 32 - 665 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, cyclisation, unsaturation and (to a certain extent) heteroatom content are encoded. The different influences of chemical classes or functional groups are considered by correction factors.		

8. QMBI COSMOtherm (K_{oc})

	Information	Literature References or Links[23]	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.[24]: software package	COSMOtherm		
1 - Definition of Endpoint			
Endpoint [units]	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 –σ > 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 polarisation 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 possible σ		

[23] References given here are not substance-specific but related to the EPISUITE software.
[24] w.a.: when applicable

	Information	Literature References or Links[23]	Remarks
Number of Chemicals in Training Set and brief description of it	Original parameterisation for COSMOtherm: 225 small- and medium-sised organic compounds with H, C, O, N, Cl atoms. The fitting was done for 650 experimental room-temperature parameters (ΔG_{hydr}, log(vapor pressure), log $K_{octanol\text{-}water}$, log $K_{hexane\text{-}water}$, log $K_{benzene\text{-}water}$, log $K_{diethyl\ ether\text{-}water}$ log K_{OC}-formula: 387 molecules (performance: r^2 = 0.72, rms = 0.62 log-units)		Original parameterisation for COSMOtherm: Since the original parameter-sation was done further ad-justments were made and parameters for further ele-ments were introduced. While the parameters are available in the software, to our know-ledge the details of the new parameterisations were not disclosed
	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 parameterisation for COSMOtherm: "Refinement and Parametrisation 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).		
3 – Definition of the Applicability Domain			
w.a.: Definition of 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 available at		"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).	
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.		

9. Analysis of QSAR prediction for K_{oc} for UV-327 and UV-350

Overall performance of QSAR Models KOCWIN and COSMOtherm (K_{oc})

	Result		Further description
Endpoint results [unit]	KOCWIN (K_{OW}-method)	**UV-327: 4.99**	All log K_{oc}-values are high and in a similar range.
		UV-350: 4.66	
	KOCWIN (MCI-method)	**UV-327: 5.28**	
		UV-350: 5.19	
	COSMO-therm (K_{oc})	**UV-327: 5.64**	
		UV-350: 4.90	
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	Yes		See Table 9
Model performance for similar substances	Good		Results are in a similar range.
Other uncertainties	No		-

Overall conclusion	Reliable with restrictions
Rationale	As the models are applicable and results for similar substances show values in the same range, it can be expected that the range is correctly predicted.

Annex I.E – Monitoring Study Results for Phenolic Benzotriazoles

Monitoring of phenolic benzotriazoles

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

European studies:

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 43: 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, UV-327, UV-329, UV-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, UV-329). The deposition was higher at the urban site.

Table 44: 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, UV-327, UV-328, UV-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, UV-327, UV-328, UV-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, UV-327, UV-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 45: 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 46: 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 except 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 47: Conc. 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, UV-328 and UV-329 were detected in concentrations of 4.3, 3.1 and 6.1 µg/g dw, respectively.

Table 48: Conc.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. (2010a) used headspace solid-phase micro-extraction followed by gas chromatography tandem mass spectrometry for the sensitive determination of benzotriazole UV-stabilisers in water samples (UV-326, UV-327, UV-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 UV-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. (2010b) also investigated benzotriazole UV-stabilisers in indoor dust samples (UV-326, UV-327 and UV-328). Pressurised 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, UV-327 and UV-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 49: 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

	UV-326	UV-327	UV-328
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. (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, UV-326, UV-327 and UV-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 50: 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. (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, UV-326, UV-327 and UV-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, and 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 51: 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 analysed 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. (2012, 2013) 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, UV-327, UV-328, UV-329, UV-360 and UV-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 52: 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, UV-320, UV-326, UV-327, UV-328, UV-329 and UV-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 quadruple

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 53: 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 54: 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]**

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, UV-326 and UV-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. (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, UV-327, UV-328, UV-329, UV-360, UV-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, UV-327 and UV-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 55: 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 56: 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) and Langford et al. (2015) published results of a screening program on several substance groups including UV-234, UV-327, UV-328, UV-329, UV-360 and UV-571. 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 57: 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	<5 (0/5) <5 (0/5) **5-6 (3/5) (only primary treatment)**	<10.9 <13.1
UV-327	<10 (0/5) <10 (0/5) <10 (0/5) (only primary treatment)	**30-77 (5/5)** **83-160 (5/5)**
UV-328	<5 (0/5) <5 (0/5) <5 (0/5) (only primary treatment)	<10.7 (0/5) <25 (0/5)
UV-329	<5 (0/5) <5 (0/5) <5 (0/5) (only primary treatment)	**1172-3075 (5/5)** **1493-3303 (5/5)**
UV-360	81 (1/5) ?? <50 (0/5) <50 (0/5) (only primary treatment)	<125 (0/5) <125 (0/5)
UV-571	81 (1/5) ?? <125 (0/5) <125 (0/5) (only primary treatment)	<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. At the other landfill the leachate had a very low particulate content.

Table 58: 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)

Substance	Concentrations in leachate of 2 landfills [ng/L]	Concentrations in particulate of leachate of 1 landfill [ng/g dw]
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 59: 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 60: 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 61: 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 UV-328 accumulate in marine and freshwater sediments receiving treated wastewater.
- UV-327 and UV-328 accumulate in Oslofjord biota.

Japanese studies:

Nakata et al. (2009a) studied occurrence and concentrations of UV-320, UV-326, UV-327 and UV-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, UV-327 and UV-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, UV-326, UV-327 and UV-328 reached 14, 200, 190 and 320 ng/g dw, respectively. Significant correlations were found in sediment concentrations between UV-326 and UV-327, UV-326 and UV-328, and UV-327 and UV-328 in the Ariake Sea. Significant correlations were also found between UV-stabiliser concentrations and organic carbon contents in sediment.

Table 62: 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

	UV-320 [ng/g ww]	**UV-326 [ng/g ww]**	**UV-327 [ng/g ww]**	**UV-328 [ng/g ww]**
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 (liver)	< 0.05	< 0.10	2.6 3.4	< 0.15

Table 63: 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. (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 UV-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 UV-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 (2010) analysed UV-320, UV-326, UV-327 and UV-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 UV-327.

Table 64: 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 65: 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 UV-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. (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 66: 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. (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 67: 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 68: Concentrations of phenolic benzotriazoles in sediment samples

Analyte		**UV-234**	**UV-326**	**UV-327**	**UV-328**	**UV-329**
streams	Occurrence	1/2	2/2	2/2	2/2	1/2

Analyte		UV-234	UV-326	UV-327	UV-328	UV-329
(S1, S2)	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 (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. (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 69: 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. (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. (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 (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. (2011a) developed a multi-residue 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 70: 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. (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 71: Concentrations of benzotriazole UV-stabilisers in marine species from Manila Bay, the Philippines

	lipid content [%]	**UV-234 [ng/g lw]**	**UV-320 [ng/g lw]**	**UV-326 [ng/g lw]**	**UV-327 [ng/g lw]**	**UV-328 [ng/g lw]**	**UV-329 [ng/g lw]**	**Σ 8 benzotriazole 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. (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 72: 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., 2011b; 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. (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. (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 73: 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

Peng et al. (2015) developed a method for multi-target determination of 13 most widely used organic UV absorbents in aquatic organism tissues. UV absorbents were extracted using ultrasonic-assisted extraction, purified via gel permeation chromatography coupled with silica gel column chromatography and determined by ultra-high performance liquid chromatography – tandem mass spectrometry. Recoveries mostly ranged from 70% to 120% from fish filet with satisfactory reproducibility. The authors assume that lower recoveries from the fish “belly” sample could be ascribed to the higher lipid content and subsequently stronger matrix effect, especially for compounds with high lipophilicity such as UV-327. Method quantification limits were 0.003 – 1.0 ng/g dw. The method was applied to analyze UV absorbents in different wild aquatic organisms (e.g. hairtail, squid, goby, pomfret, squilla) in April 2013 and farmed red snappers collected from the Pearl River Estuary, South China. The phenolic benzotriazoles UV-234, -326, -327, -328, -329 and –P were analyzed. UVP was frequently detected in wild and farmed marine organisms at low ng/g dw concentrations. Most of the benzotriazole UV stabilisers were also frequently detected in maricultured fish.

Analyte	Concentrations in wild aquatic organisms (carcasses without heads and internal organs) [ng/g dw]	Detection frequency (11 different species)	Concentrations in farmed red snapper [ng/g dw]
UV-234	n.d.	0/11	0.202 ± 0.031 (filet) 0.260 ± 0.029 (“belly”)

UV-326	n.d.	0/11	7.95 ± 1.01 (filet) 11.38 ± 1.04 (“belly”)
UV-327	n.d.	0/11	1.0 ± 0.1 (filet) 1.8 ± 0.1 (“belly”)
UV-328	n.d.	0/11	< LOQ (filet) 0.8 ± 0.1 (“belly”)
UV-329	0.105 and 0.225	2/11	n.d.
UV-P	0.03 – 3.33	8/11	0.4 ± 0.02 (filet) 0.67 ± 0.02 (“belly”)

Australian studies:

Liu et al. (2011; 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. (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., 1985).

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. (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 characterised 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 (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 74: 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. (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 (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 emphasise 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. (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 analysed. 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 remobilised 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 75: 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. (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.