THE ENVIRONMENTAL RISK ASSESSMENT OF BIOCIDES

REGULATORY CHALLENGES AND SCIENTIFIC SOLUTIONS

Fate of chemicals in the sewage treatment plant

Opportunities and limitations with SimpleTreat

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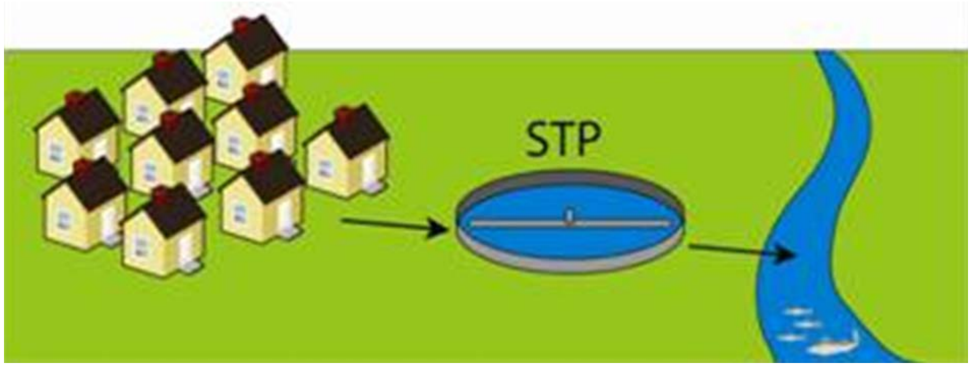
Importance of STP

Sewage Treatment Plant (STP): barrier between down-the-drain home and personal care (HPC) products and the aquatic ecosystem



Presentation outlook

1. Overview of STP model SimpleTreat
2. Validation study with selected chemicals
3. Research priorities

Objectives

STP modelling to support risk assessment by:

- Understanding key processes and parameters controlling chemical removal
- Refining predicted environmental concentrations (PECs):

  - screening level (base datasets)

  - higher tier probabilistic assessment
- Integrating assessments: simulation studies + monitoring
- Predicting future trends (increasing infrastructure)

SimpleTreat: model concept

SimpleTreat simulates the fate of trace organic xenobiotics (parent structure) in the treatment plant

Input:
- Chemical properties (MW, H, K_{OW}, K_{OC})
- STP scenario discharge
- First order biodegradation rates (k)

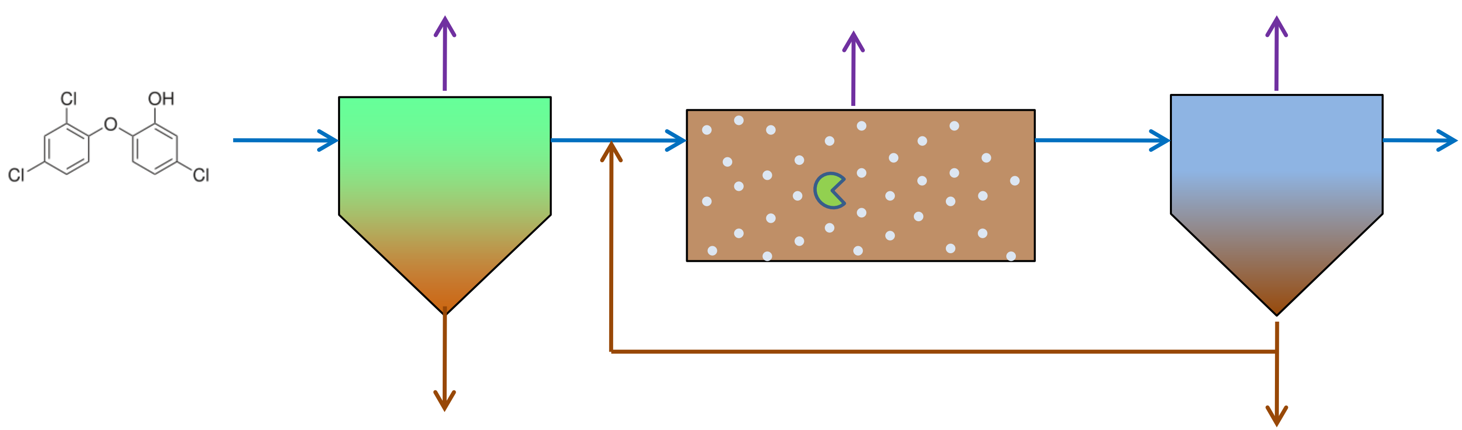
→ SimpleTreat →

Output:
- $C_{EFFLUENT}$
- C_{SLUDGE}
- Relative emissions

Modelled processes:

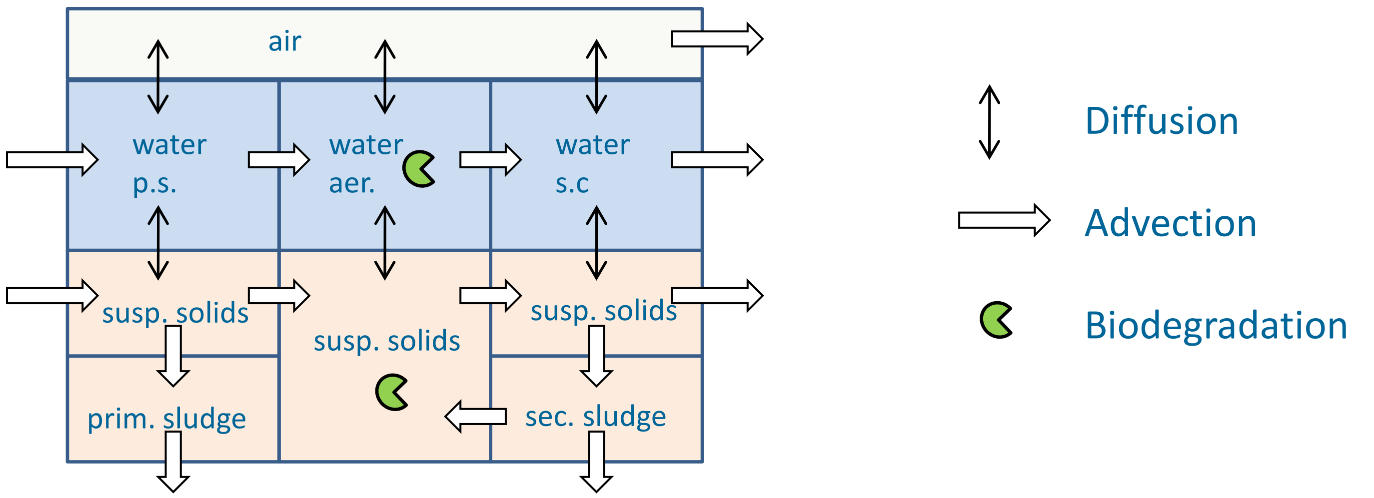
Physical
- Advection: water, sludge and air flows
- Diffusion: water-solids (sorption) and water-air (volatilization + stripping)

Biological
- Degradation: (primary) biodegradation in aeration tank



SimpleTreat: model structure

9-box representation of a conventional activated-sludge sewage treatment plant with primary sedimentation (p.s) and secondary clarifier (s.c).



Mass balance system of 9 linear equations solved at steady-state (dC/dt=0)

$$V_i \cdot \frac{dC_i}{dt} = -k_i C_i V_i + \sum Adv_{i,j} \cdot C_i + \sum Diff_{i,j} \cdot C_i$$

SimpleTreat: model assumptions

Applicability

- Organic chemicals with basic physicochemical properties and biodegradability profile

Key assumptions:

- Non-equilibrium, Steady-state (level III)
- Homogeneous, well mixed compartments (CSTR)
- First order biodegradation in aeration tank (low concentrations)

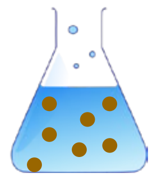
Modelled scenario does not consider:

- Chemical treatment units
- Abiotic degradation
- Biodegradation in settlers
- Parent compound formation / degradation products
- Other?

SimpleTreat processes: biodegradation

Tier 1

Input: from ready biodegr. tests (OECD 301)



OECD 301 Result	rate* (h-1)
Ready biodegr (fulfilling 10 d window)	$k_W = 1$
Ready biodegr, not fulfiling	$k_W = 0.3$
Inherently biodegr.	$k_W = 0.1$
Non biodegr.	$k_W = 0$

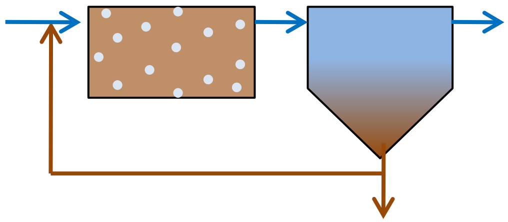
* Values assigned based on a reasonable worst-case scenario (EUSES)

Assumption:
First order biodegradation, only in water phase

Limitations: unrealistic high concentrations

Tier 2

Input: biodegradation rates derived from continuously-stirred activated sludge simulation study (OECD 303A)



Assumption:
First order biodegradation in water and solid phase

Limitations:
Expensive, strict criteria (realistic, representative conditions must be met)

SimpleTreat processes: sorption

Sorption model

$K_d = K_{OC} \times OC$

Tier 1:

K_{OC} calculated from K_{OW}

$\log K_{OC} = a \log K_{OW} + b$

Tier 2:

From adsorption/desorption study (OECD 106, OECD 121)

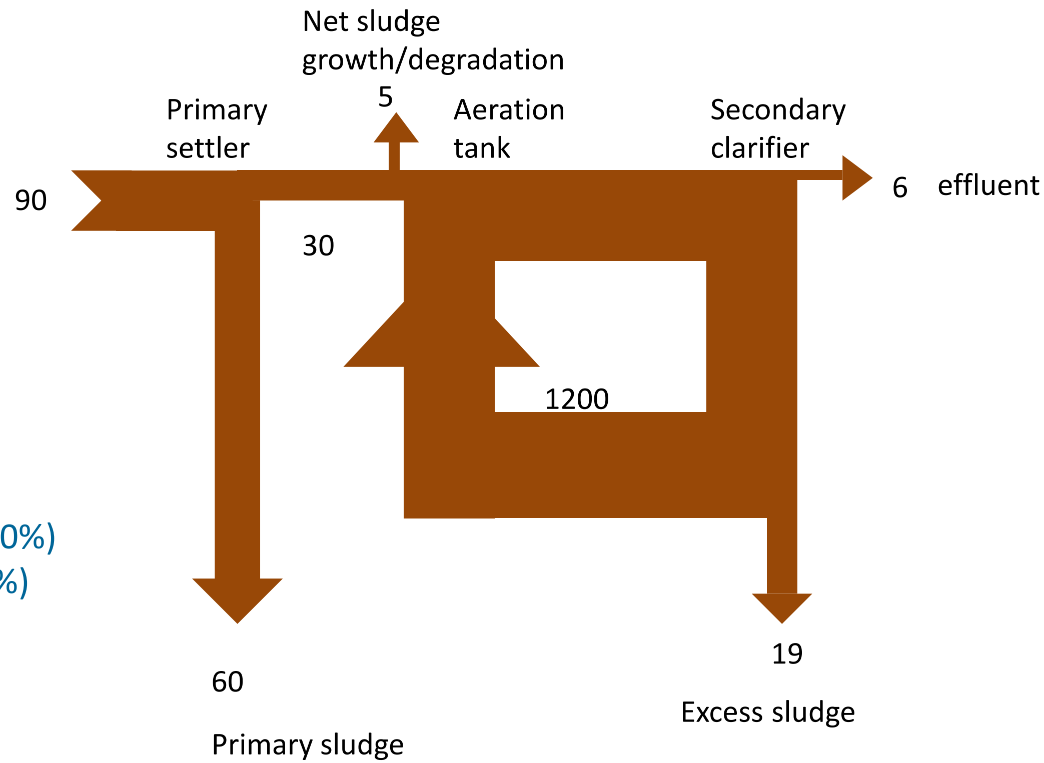
Removal by adsorption:

Log $K_{OC} > 3$ significant partitioning to sludge (>10%)

Log $K_{OC} > 5$ almost totally bound to sludge (>90%)

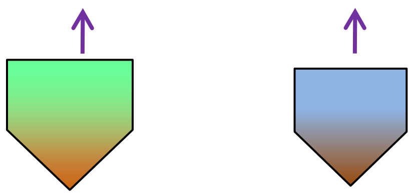
solids to effluent = (1/3)*(6/25) *100 = 7.9%

Solids mass balance according to SimpleTreat (g_{dwt}/PE/d)



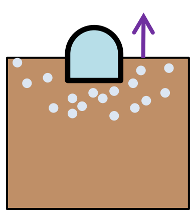
SimpleTreat processes: volatilization

Primary settler and secondary clarifier

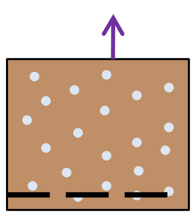


Two films model f (Henry's Law constant, molecular permeability in air and water)

Aeration tank



Surface aeration

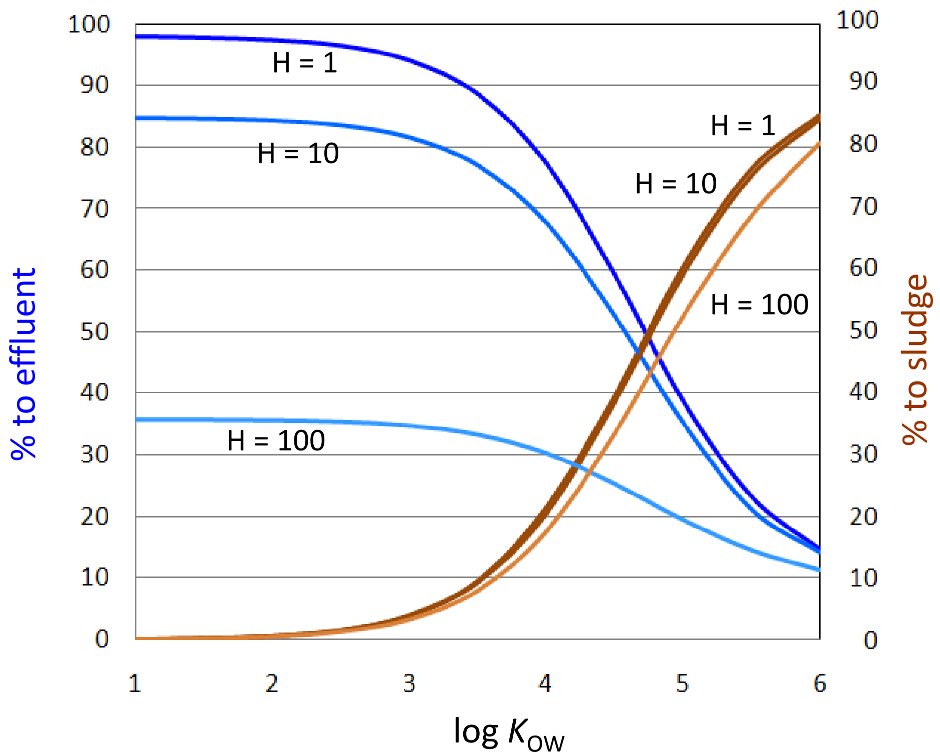


Bubble aeration

Empirical equations f (oxygen requirement, Henry's Law constant, hydraulic retention time)

Relative emissions to effluent and sludge

Relative emission to water and sludge for a neutral, persistent chemicals vs. log K_{OW} for varying volatility (H, Pa m^3 mol^{-1})



SimpleTreat: default parameterisation (EUSES)

Model Scenario	Default scenario
With/without primary sedimentation	9-boxes (with primary sedimentation)
Surface/bubble aeration	Surface aeration

Input data	Default input
Biodegradation rate	Assigned based on readily biodeg. test
Sludge-water sorption coefficient	Calculated from Kow

Treatment unit	Parameters	values
Raw sewage composition	T, TSS_{IN}, BOD, OC_{SLUDGE}	Typical range
Primary settler	geometrical-hydraulic parameters and efficiency	Typical range
Activated sludge system	Volume and HRT aerator, BOD removal, excess sludge	Based on Sludge Loading Rate SLR = 0.15 $kg_{BOD}/Kg_{dwt}/d$
	OC, VSS	Typical range
Secondary settler and effluent	Geometry, HRT	typical range
	$TSS_{EFFLUENT}$	$TSS_{EFFLUENT} = 30$ mg/L (EU legal limit)

SimpleTreat: limitations

- **One scenario – one parameterisation**:. For example, is the modelled scenario (9-box system activated sludge) representative of existing infrastructure? Are parameters representative of activated sludge secondary treatment systems?
- **Input data**: do they represent real conditions in the system (e.g. tests at low concentrations)
- **Phase partitioning concept:** is the $K_{OC} = f(K_{OW})$ approach applicable to ionisable chemicals, surfactants, organic ligands? Are soil/sediment K_{OC} data useful for sludge?
- **Abiotic degradation**: overlooked removal processes (chemicals treatment, UV/light)?

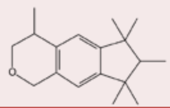
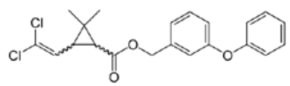
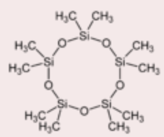
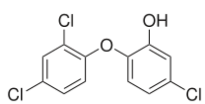
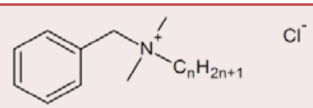
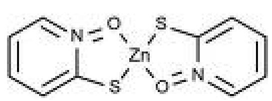
Validation study

→ **Model evaluation**: simulation results vs. measured data for 6 HPC ingredients

→ **Identify research priorities**

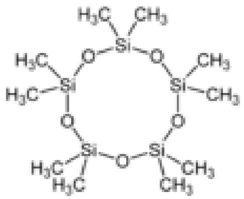
Validation study: test chemicals

Input properties of test chemicals

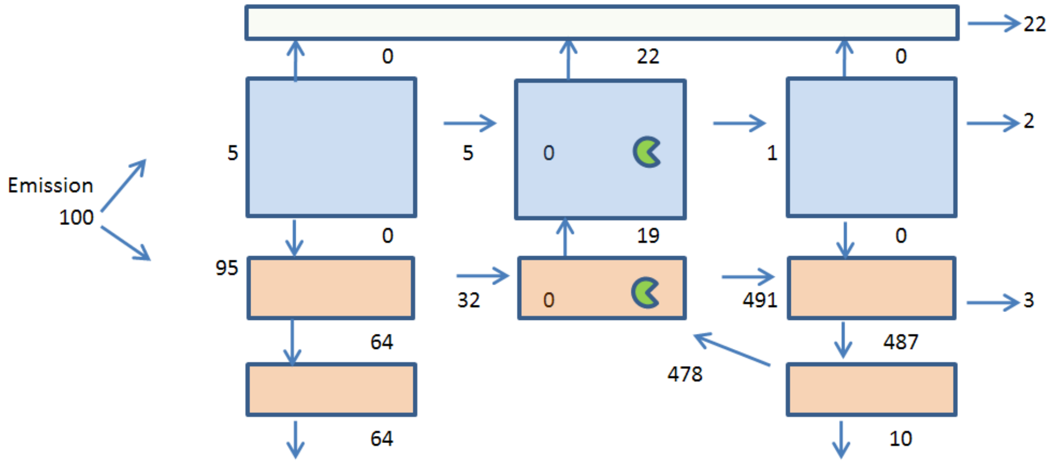
Chemical	Structure	pK_a	H Pa m^3 mol^{-1}	Log $K_{OW,n}$	Log K_{OC}	Ready biodeg.
Galaxolide (HHCB)		-	36.9	5.3	3.82	No
Permethrin (PMT)		-	0.19	6.10	4.00	Yes, not fulfilling 10 d window
Decamethyl-cyclopentasiloxane (D5)		-	3.34 x 10^6	8.03	5.17	No
Triclosan (TCS)		8.1 (acid)	2.27x 10^{-3}	4.76	4.67	No
Benzalkonium chloride (BAC)	 n = 8, 10, 12, 14, 16, 18	base	5.03 x 10^{-7}	-	4.12	Yes, fulfilling 10 d window
Zinc pyrithione (ZPT)		4.7 (acid)	5.29 x 10^{-9}	0.97	3.55	No

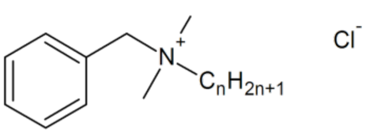
Validation study: model results

Calculated mass fluxes (%) throughout SimpleTreat nine compartments for two test chemicals



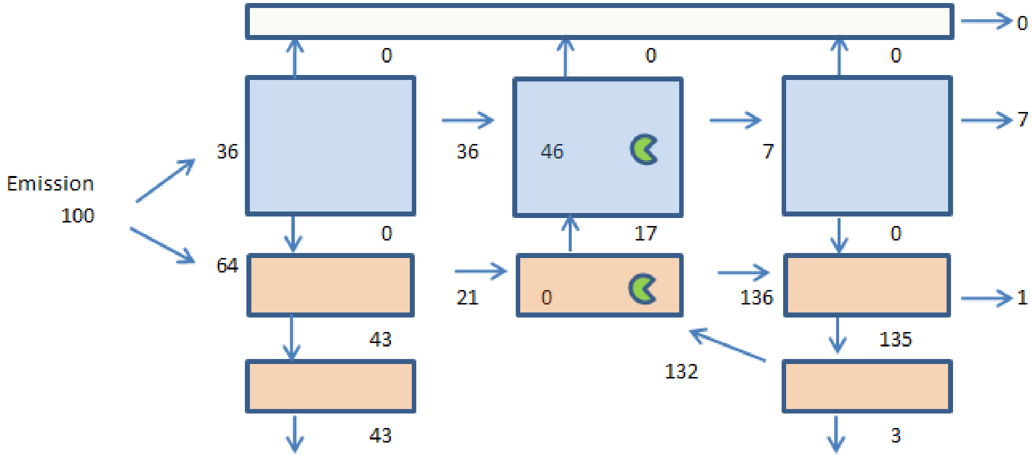
D5





n = 8, 10, 12, 14, 16, 18

Benzalkonium chloride



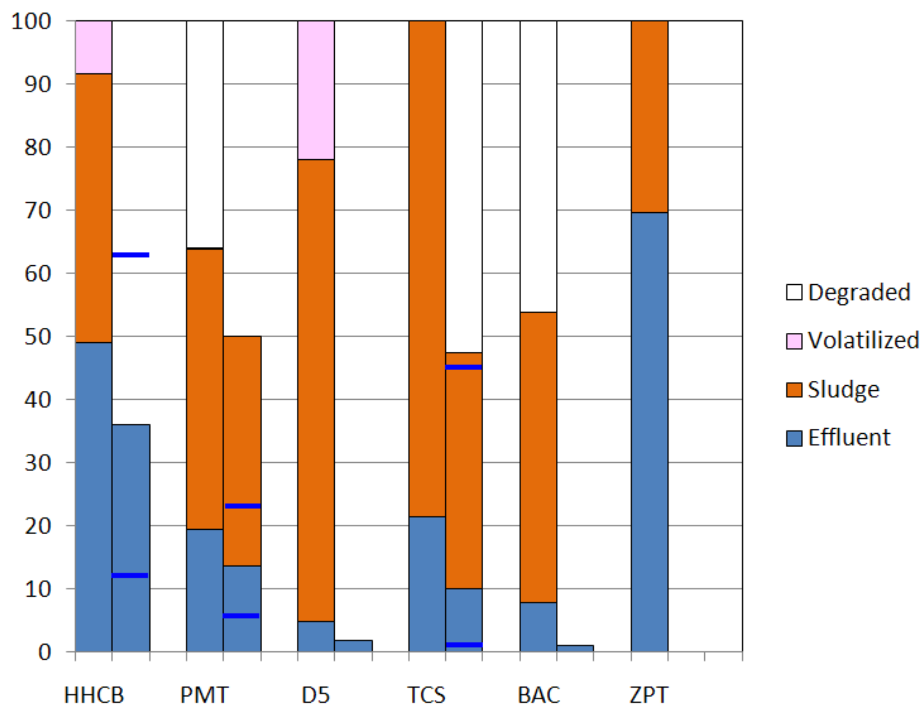
Mass flows measured in STPs

Mass balance of test chemicals measured in activated sludge STP (% of influent load)

Chemical	Effluent Min	Effluent Avg	Effluent Max	Sludge	Degraded	n STP	Reference
Galaxolide	40	54	68			3	Artola-Garicano 2003
	1.5	12.2	23			2	Horii et al 2007
	15	22.5	30			1	Carballa et al 2004
		18		70		1	Kupper et al 2006
		63				1	Bester 2004
		47				1	Lee et al 2010
Permethrin	11	23	35	43		2	Santos et al 2010
	10	20	30			1	Abram et al 1980
		7		30		1	Kupper et al 2006
		12					Gomez et al 2007
		6					Plagellat 2004
D5		1.78				1	Sparham et al 2011
Triclosan	1	10	45	37.5	52.5	36	Bock et al 2010
Benzalkonium chloride		1				9	Clara et al 2007
Zinc pyrithione							

Comparison with measured data

Comparison of mass fluxes (%) estimated by SimpleTreat (left bars) with average (and min-max range) values measured in STPs (right bars)



Key results:

- Reasonable agreement with measurements, consistent with the model conservative parameterisation
- Measured K_{OC} necessary for organic ions (BAC)
- Speciation of organic ligands overlooked
- Tier 2 biodeg data can refine assessments (TCS)
- Cannot represent large variability in measured data

Research priorities

Applicability domain

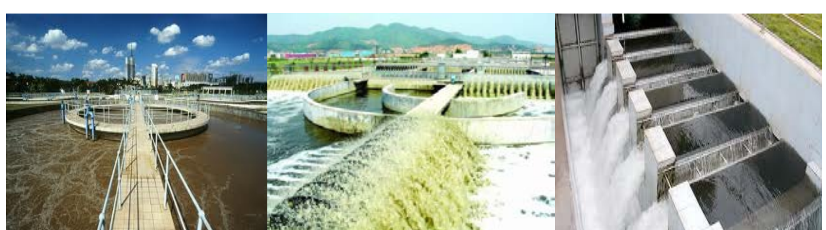
- Does SimpleTreat capture the chemistry of **organic ions** (sorption), **surfactants** (interface enrichment), **ligands** (speciation)?

SimpleTreat model refinement

- Investigate the impact of **abiotic processes** (flotation, photolysis)
- **Probabilistic parameterisation** of a conventional STP (activated sludge) for high tier exposure assessment
- Fate of **degradation products**

Scenario uncertainty

- **Other types of STPs** (e.g. trickling filters)
- Advantages of other **existing models** (water industry)

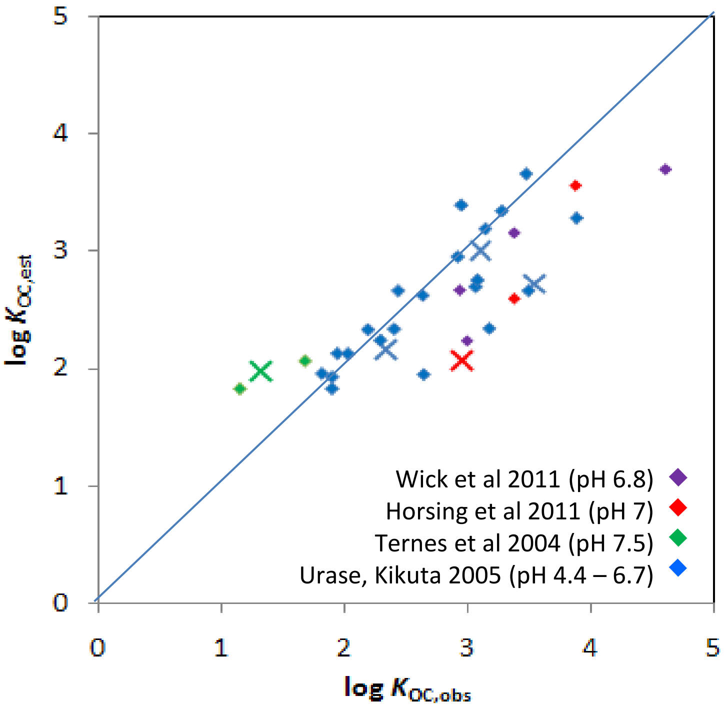


Applicability domain: organic ions

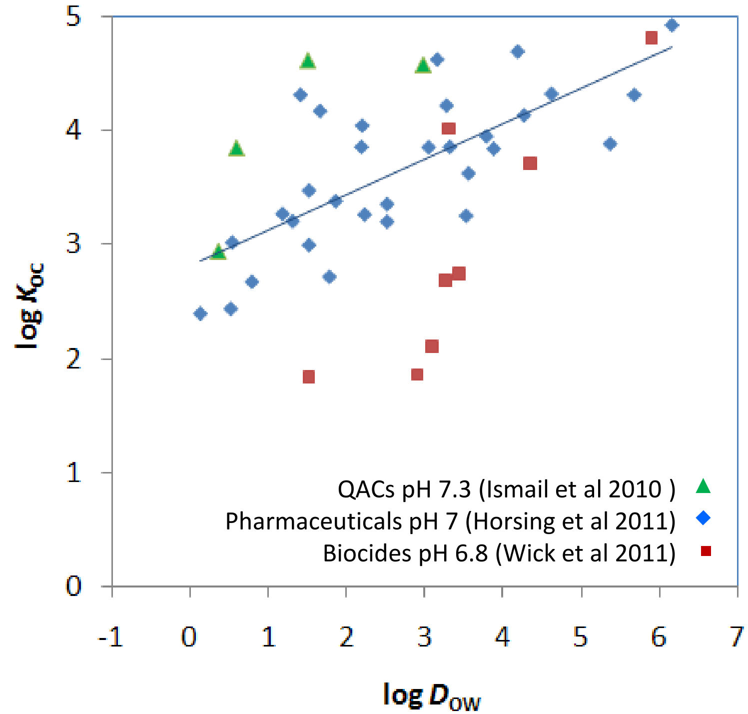
Organic Acids and Bases:

SimpleTreat 3.0: $K_{OC,ion} = 0$ SimpleTreat 3.1: **see poster**

Regression tested against 34 sludge K_{OC} values for 14 monovalent organic acids



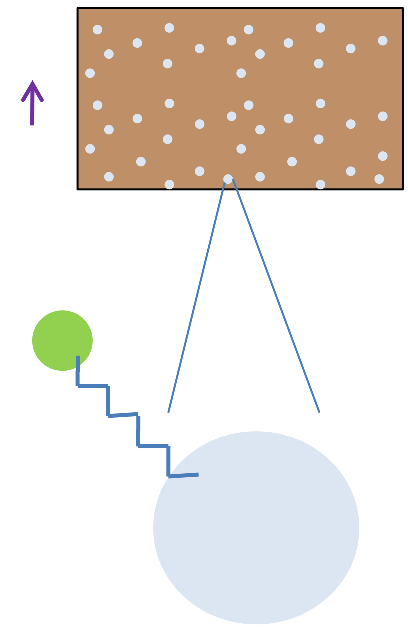
Correlation of apparent octanol water partition coefficient (D_{OW}) with K_{OC} for 43 monovalent bases



Applicability domain: surfactants

Surfactants

- Homogeneous distribution is assumed throughout the system.
- Concentrations typically << critical micelle concentrations.
- Surface active molecules may be enriched at the surface when specific interface area is high (during flotation/aeration).
- Interface enrichment depends on air/water K_{IW} and on the specific surface area.



Test calculation with SimpleTreat for BAC assuming $K_{IW} = 10^{-5}$ m (10 µm)
$V_{bubble,aer} = 0.4\%$, $d_{bubble} = 3$mm (Gresch et al. 2011)

Fraction adsorbed to bubbles <0.1%
Fraction transported to the surface <1% (3.8% assuming no degradation, 10% assuming $K_{OC} = 0$)

Applicability domain: organic ligands

Organic ligands

Undergo transchelation by metal ions. Speciation depends on:

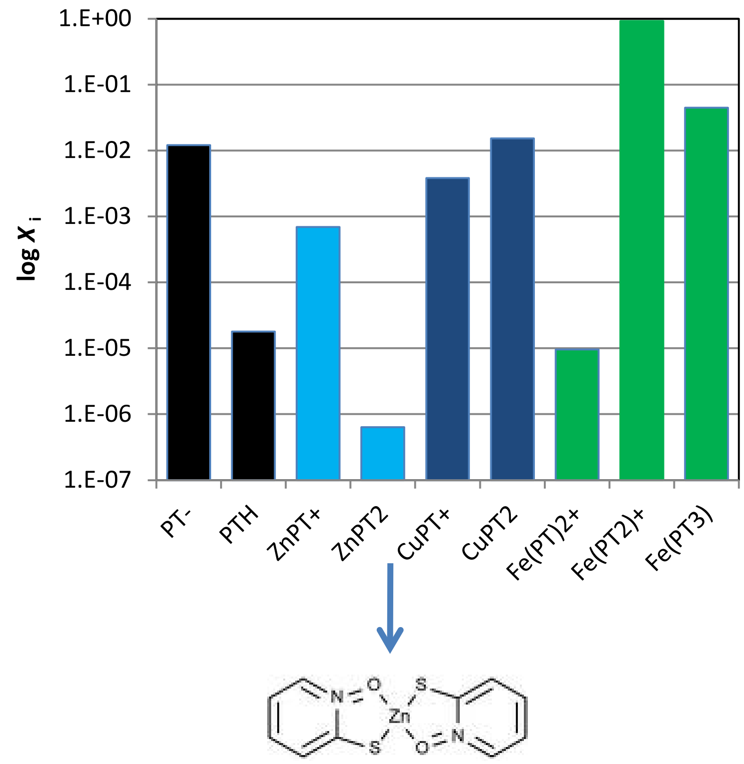
- Binding constant
- Metal concentrations
- pH, ionic strength, DOC

Example: ZPT
The 1:2 complex with iron is likely the dominating species in STP

Model limitations:

- Species-specific modelling hindered by lack of data
- Single-species simulation valid only if input data were generated in a media that well represents STP. (e.g. log K_{OC} = 3.55 in soil)
- Rapidly photodegraded $t_{1/2,photo}$ = 15 min

Estimated speciation of pyrithione in freshwater



Higher tier assessment

Tier 1 – Ready biodegradability – SimpleTreat default – conservative, possibly unrealistic

Tier 2 – Simulation study - ?

Problem: The use of higher tier biodegradation data (OECD 303A CAS study) in exposure assessments is debated because the representativeness of these studies is unknown. Can a realistic **endpoint replace a conservative estimate?**

Worst case point estimate ➡ **Probabilistic exposure assessment**

How can STP modelling support higher tier exposure assessments? A case study with triclosan

1. Derive degradation rates in activated sludge from the mass balance of an OECD 303A study (e.g. 6-box SimpleTreat of a CAS system).
2. Define probability density distributions for SimpleTreat inputs and model parameters.
3. Run probabilistic simulations with SimpleTreat.
4. Probabilistic exposure assessment and uncertainty analysis.

SimpleTreat: probabilistic parameterisation

Test substance: triclosan

Substance inputs	unit	SimpleTreat default	Type of distribution	min (T) location (L)	likeliest (T) mean (N, L)	max (T) st. dev. (N, L)	95%-ile (N, L)
pK_a			N		8	0.1	
$\log K_{OC,n}$			N		4.67	0.2	
$\log K_{OC,a}$			N		2.06	0.5	
k_{biodeg}	h^{-1}	0	L	0.02*	0.11*		0.36*
STP parameters**							
Inflow	L/PE/d	200	L	90	153	58	
Sludge loading rate	$kg_{BOD}/kg_{dwt}/d$	0.15	T	0.04	0.15	0.6	
T water	°C	15	N		15		25
Solids inflow	g/PE/d	90	L	50	90		150
OC raw sewage	g/g	0.3	N		0.4	0.03	
BOD raw sewage	$g_{BOD}/PE/d$	54	L	45	60		82
pH		7	N		7.5	0.35	
depth ps	m	4	T	3	4	4.9	
depth aer	m	3	T	2	3	6	
depth sc	m	3	T	2.5	3	4.5	
OC sc	g/g	0.37	N		0.37	0.03	
C solids effluent	mg/L	30	T	3	9		30
TSS rem primary		0.66	N		0.55	0.07	
O_2 in aerator	mg/L	2	T	1	2	2.5	

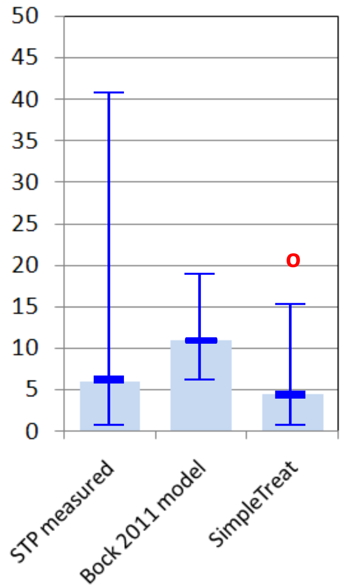
* Measured range calculated from Federle et al. 2002 – CAS study at different (low) concentrations, T = 22 °C

** STP parameters and variability based on Tchobanoglous et al. 2004 – Wastewater Engineering – Treatment and Reuse

Probabilistic exposure assessment

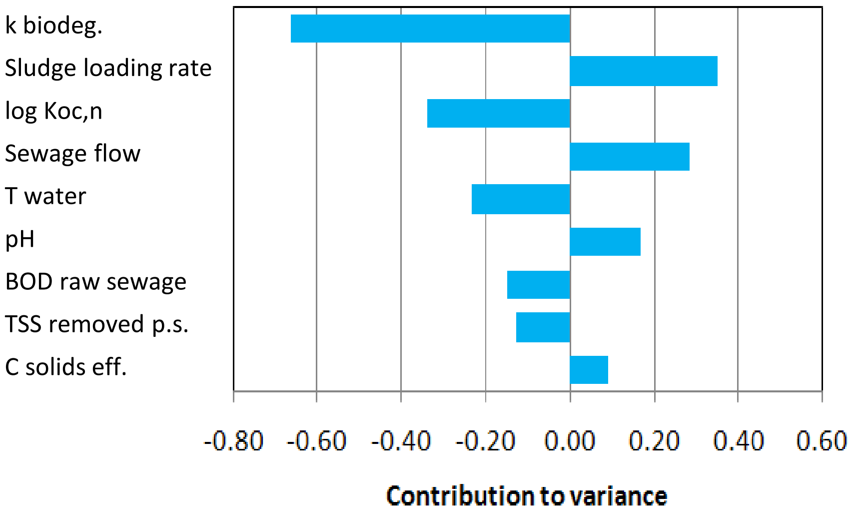
Triclosan probabilistic STP modelling:
Comparison of modelled estimated fraction released to effluent with measured (n = 23, activated sludge) and model results from Bock et al. 2010.

	STP Measured	Bock 2011 model	SimpleTreat
default			21.4
5 %-ile	1	7	0.5
50 %-ile	6	11	4.4
95 %-ile	40.9	18	16.0



Uncertainty analysis:
Identification of most important (uncertain) parameters.

Contribution to variance of most sensitive parameters on the fraction released to effluent



Conclusions

- **SimpleTreat applicability domain**

  Organic ionics: new version SimpleTreat 3.11 includes algorithm for organic acids; measured K_{OC} recommended for organic bases.

  Surfactants: model OK (may be enriched at the surface). Default K_{OC} estimations not valid.

  Organic ligands: model validity limited, depending on input data (test media).

- **Interpretation of results**

  Default (Tier 1) SimpleTreat is a tool for risk assessment, not designed to represent a realistic scenario. Simulation test data on biodegradation can support high tier model simulation, but it is important to describe variable STP conditions (probabilistic exposure assessment).

  Limitation: only represents activated sludge, other scenarios currently not included (e.g. photodegradation, attached biomass, tertiary treatment).

- **Implications for risk assessment**

  BPD current TGD recommends 1) Measured data in full scale STP 2) Simulation test data 3) Modelling STP.

  Model simulations and experimental data can support each other. No single method alone is fully reliable and representative. Opportunities for probabilistic risk assessments, as in REACH.

Thanks

Applicability domain: organic ions

Acids:

SimpleTreat 3.0: $K_{OC,ion} = 0$

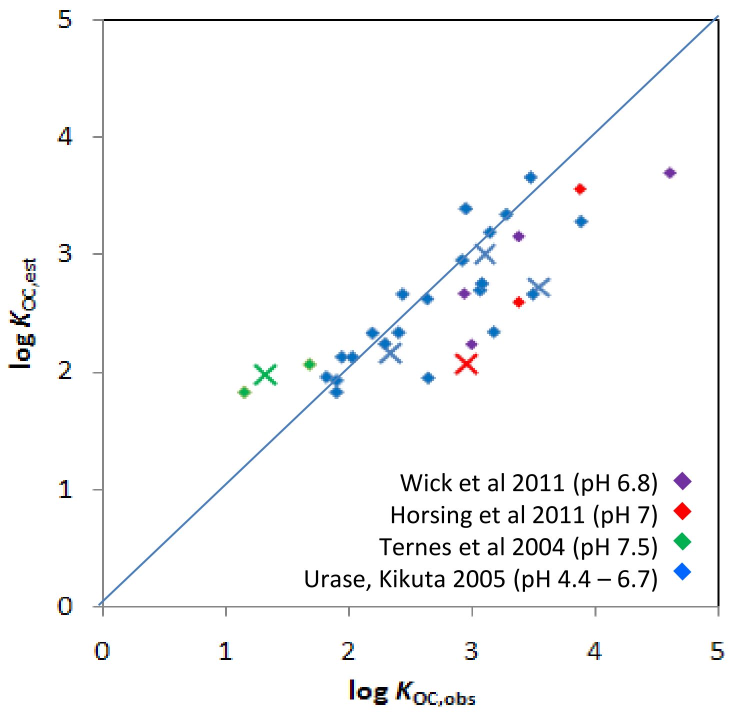
SimpleTreat 3.1:

$$K_{OC} = \phi_n \cdot K_{OC,n} + \phi_{ion} \cdot K_{OC,ion} \qquad (1)$$

$$K_{OC} = \frac{10^{0.54 \cdot \log K_{OW,n} + 0.11}}{1 + 10^{(pH - 0.6 - pK_a)}} + \frac{10^{0.11 \cdot \log K_{OW,n} + 1.54}}{1 + 10^{(pK_a - pH + 0.6)}} \qquad (2)$$

- The species-specific hydrophobicity-based model (Eq. 2) reasonably estimates sorption to sludge and can be incorporated into SimpleTreat.
- Mean absolute error on $\log K_{OC}$: MAE = 0.33
- Some inconsistencies were found between data from different studies (x = diclofenac)
- Two anionic surfactants identified as outliers (not shown).

Regression tested against 34 sludge K_{OC} values for 14 monovalent organic acids



Applicability domain: organic ions

Bases:

SimpleTreat 3.0: $K_{OC,ion} = 0$

SimpleTreat 3.1:

- Sorption is generally high, even at low D_{OW}.
- At equal D_{OW}, logK_{OC} (QACs) > logK_{OC} (pharmaceutical, pK_a 7-10) > logK_{OC} (biocides, pKa 3-5).

- Correlation of sorption with hydrophobicity is significant but other factors influence adsorption.
- The correlation with logD_{OW} improves when pK_a and calculated logD_{OW} values are checked for quality assurance.

Correlation of apparent octanol water partition coefficient (D_{OW}) with K_{OC} for 43 monovalent bases