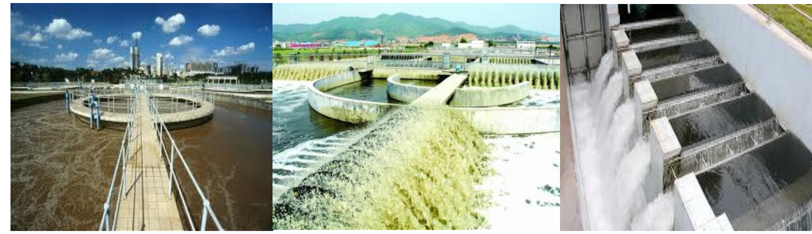

Predicting the fate of emerging contaminants in sewage treatment plants (STPs): evolution of SimpleTreat

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Unilever

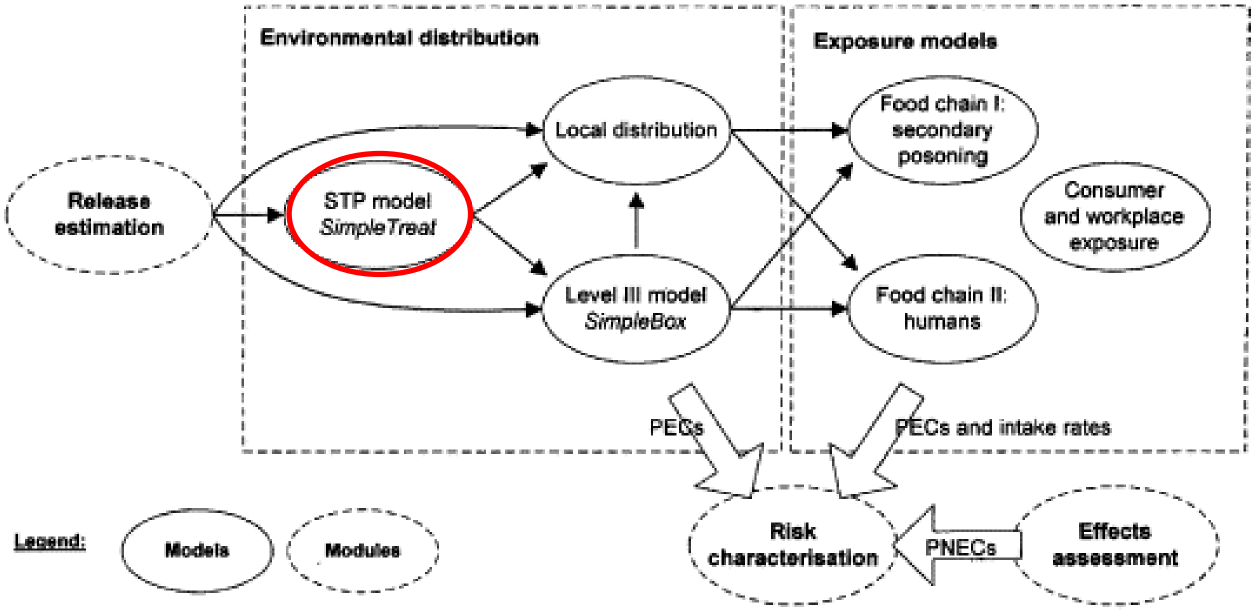
UNILEVER SAFETY AND ENVIRONMENTAL ASSURANCE CENTRE (SEAC)

SEAC - Ecotox group

Environmental risk assessment of chemicals in home and personal care products

SEWAGE TREATMENT PLANT IN REGULATORY RISK ASSESSMENT

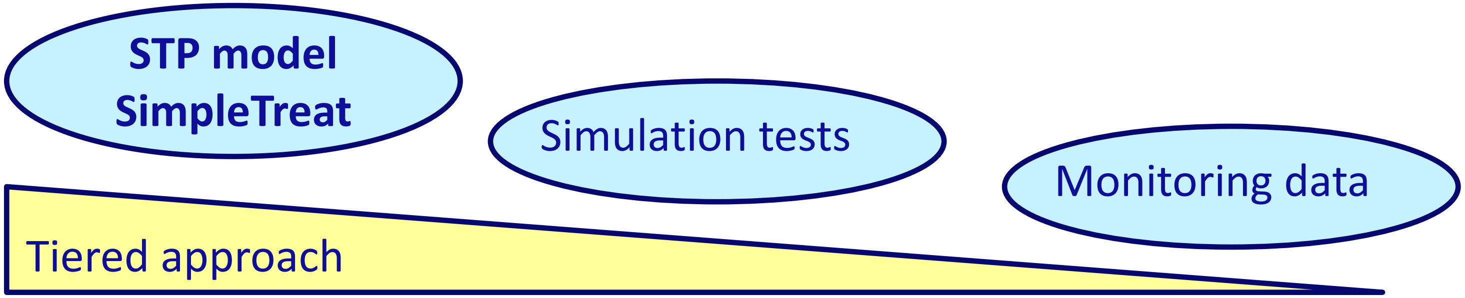
Modelling framework of the European Union System for the Evaluation of Substances (EUSES)



SEWAGE TREATMENT PLANT IN REGULATORY RISK ASSESSMENT

Chemical regulations

- **General chemicals**: REACH
- **Biocides**: Biocidal Products Regulation
- **Pharmaceuticals**: European Medicines Agency guidance for environmental risk assessment



SimpleTreat is used as a predictive tool to support risk assessment. The model represents a standard STP scenario (activated sludge)

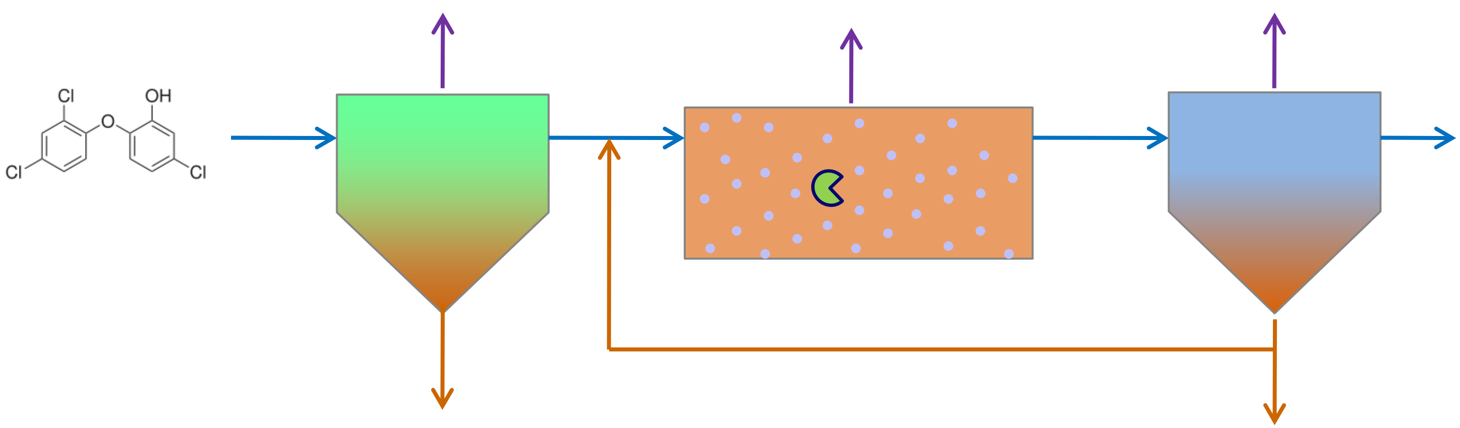
SIMPLETREAT: MODEL CONCEPT

SimpleTreat simulates the fate of trace organic xenobiotics (parent compound) in a STP

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

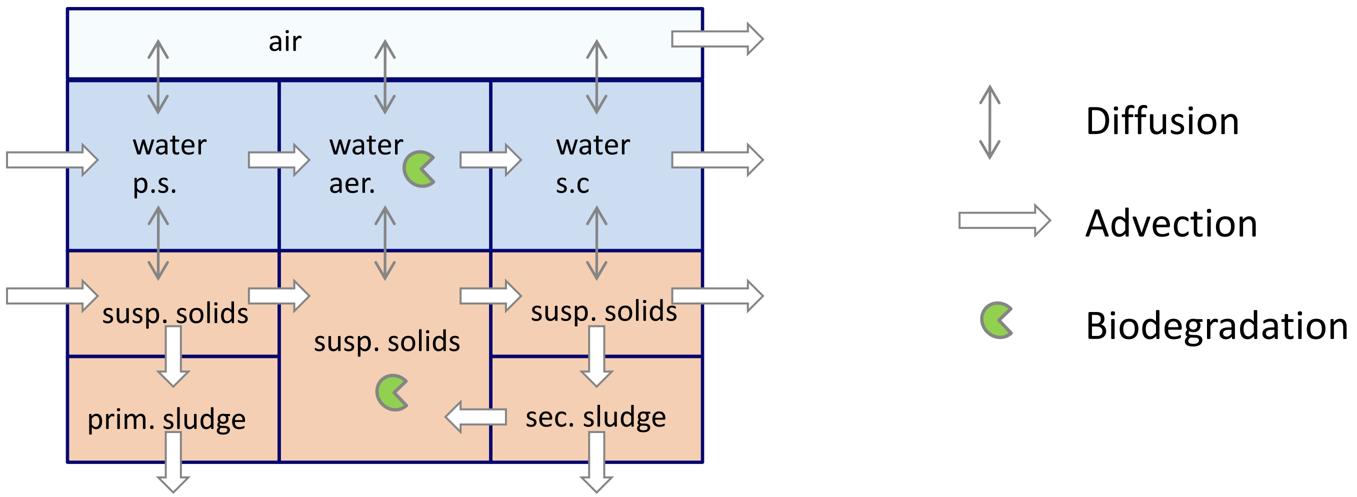
→ **SimpleTreat** →

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



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)

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

MODEL LIMITATIONS

- **One parameterisation** - Are parameters representative of activated sludge secondary treatment systems? Conservative parameterisation to cover “worst case scenario”.
- **Biodegradation**: Biodegradation rates derived from screening test. Are estimates relevant to real conditions in activated sludge?
- **Sludge-water partitioning:** Is the $K_{OC} = f(K_{OW})$ approach applicable to ionisable chemicals? Are soil/sediment K_{OC} data useful for sludge?
- **Abiotic degradation**: other relevant removal processes (ozonation, photodegradation)?
- **One scenario:** Is the modelled scenario (conventional activated sludge) representative of existing infrastructure? Attached biomass and tertiary treatments not included.

SIMPLETREAT EVOLUTION

Unilever (UK) – Radboud University (NL) collaboration

Initiated in 2011 to update/refine SimpleTreat with two main objectives:

- Enlarge (and define) the applicability domain to **ionisable organics**
- Improve model realism by using a **probabilistic parameterisation** with refined input data on **biodegradability**

IMPROVING MODEL REALISM:
FROM WORST-CASE TO PROBABILISTIC ASSESSMENTS

In regulatory risk assessment, more realistic assessments can replace a worst-case scenario only through a comprehensive analysis of uncertainties, embracing most likely as well as worst-case conditions in a statistically robust way

Tier 1:
Deterministic SimpleTreat

- basic input dataset
- default parameterisation
- realistic worst case scenario

Tier 2:
Probabilistic SimpleTreat

new

- refined input dataset
- probabilistic parameterisation
- embraces variability of activated sludge STPs

MODEL UPDATE I: PARTITIONING TO SLUDGE

Tier 1: estimated K_{OC}

Neutral chemicals:
Sabljic regressions (EUSES)
$\log K_{OC} = a \log K_{OW} + b$

Monovalent acids (Franco et al 2009)

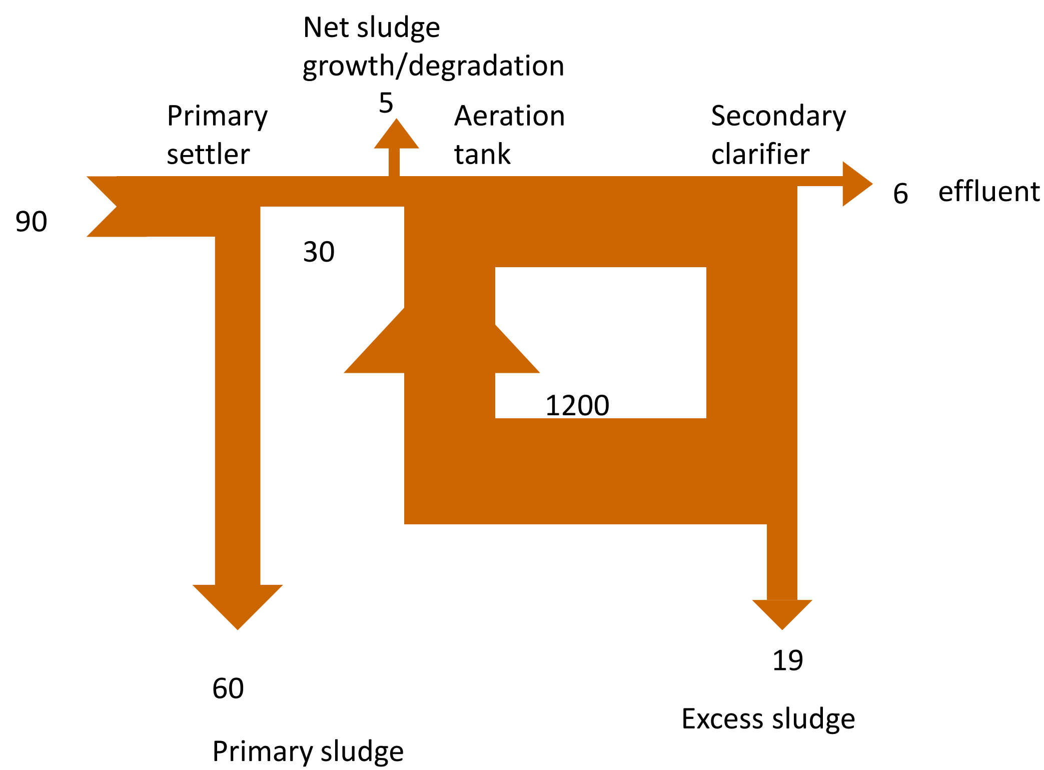
$$K_{OC} = \phi_n \, 10^{0.54 \, logK_{OW,n} + 1.11} + \phi_{-} \, 10^{0.11 \, logK_{OW,n} + 1.54}$$

Monovalent bases (ECETOC 2012 – draft report)

$$K_{OC} = 10^{0.27 \, logD_{OW} + 2.83}$$

Tier 2: measured K_{OC}
From adsorption/desorption study (OECD 106, OECD 121)

Solids mass balance according to SimpleTreat 3.1 (g_{dwt}/PE/d)



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%

MODEL UPDATE II: BIODEGRADATION

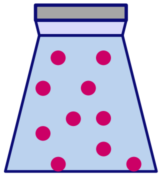
Tier 1

Assumption: first order biodegradation, only in water phase

Input: from ready biodegradability tests (OECD 301)

OECD 301 Result	rate* (h-1)
Ready biodegradable, fulfilling 10 d window	*k* = 1
Ready biodegradable, not fulfilling 10 d window	*k* = 0.3
Inherently biodegradable	*k* = 0.1
Non biodegradable	*k* = 0

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



Limitations: unrealistic high concentrations, low biomass, only chemicals sustaining biomass growth will degrade (no co-metabolism)

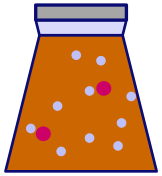
MODEL UPDATE II: BIODEGRADATION

Tier 2

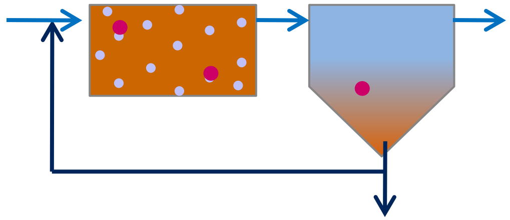
Assumption: first order biodegradation in water and solid phase

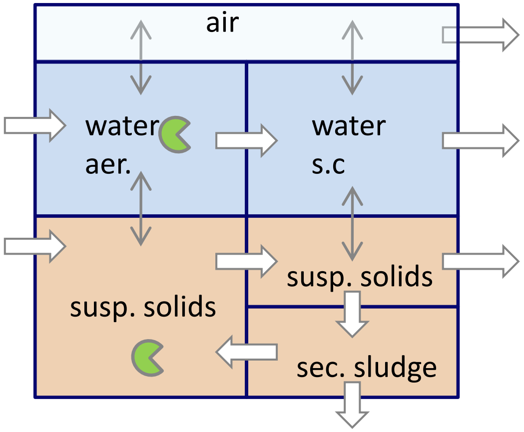
Input: biodegradation rates derived from:

OECD 314B: activated sludge die-away test. Biodegradation rates directly derived from the disappearance of the test material (closed system)



OECD 303A: continuous activated sludge simulation study. Degradation rates can be derived by fitting a first order biodegradation rate to the observed mass balance using the 6-box version of SimpleTreat (representing CAS system). The CAS system can be run at different sludge retention times





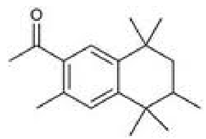
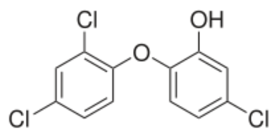
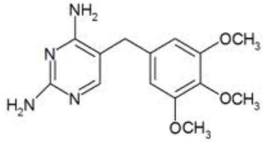
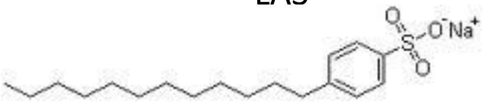
MODEL UPDATE III: PROBABILISTIC STP PARAMETERS

Parameter	Units	SimpleTreat default	SimpleTreat probabilistic		
			Distribution type	Mean / likeliest	Uncertainty parameters
Inflow sewage	L/PE/d	200	L	200	σ = 58, min = 90
Sludge Loading Rate	$kg_{BOD}/kg_{dwt}/d$	0.15	T	0.15	min-max = 0.04-0.6
Water temperature	°C	15	N	15	σ = 6
Solids inflow	g/PE/d	90	L	**66**	σ = 28
OC raw sewage	g/g	0.3	N	**0.4**	σ = 0.03
BOD in	gBOD/PE/d	54	L	54	σ = 10
pH		7	N	**7.5**	σ = 0.35
depth ps	m	4	T	4	min-max = 3-4.9
depth aer	m	3	T	3	min-max = 2-6
depth sc	m	3	T	3	min-max = 2.5-4.5
OC sludge	g/g	0.37	N	0.37	σ = 0.03
C solids effluent	mg/L	**30**	L	**8**	σ = 15
TSS rem primary	%	0.66	N	**0.55**	σ = 0.07
O2 in aerator	mg/L	2	T	2	min-max = 1-2.5

PROBABILISTIC SIMULATIONS AND VALIDATION STUDY

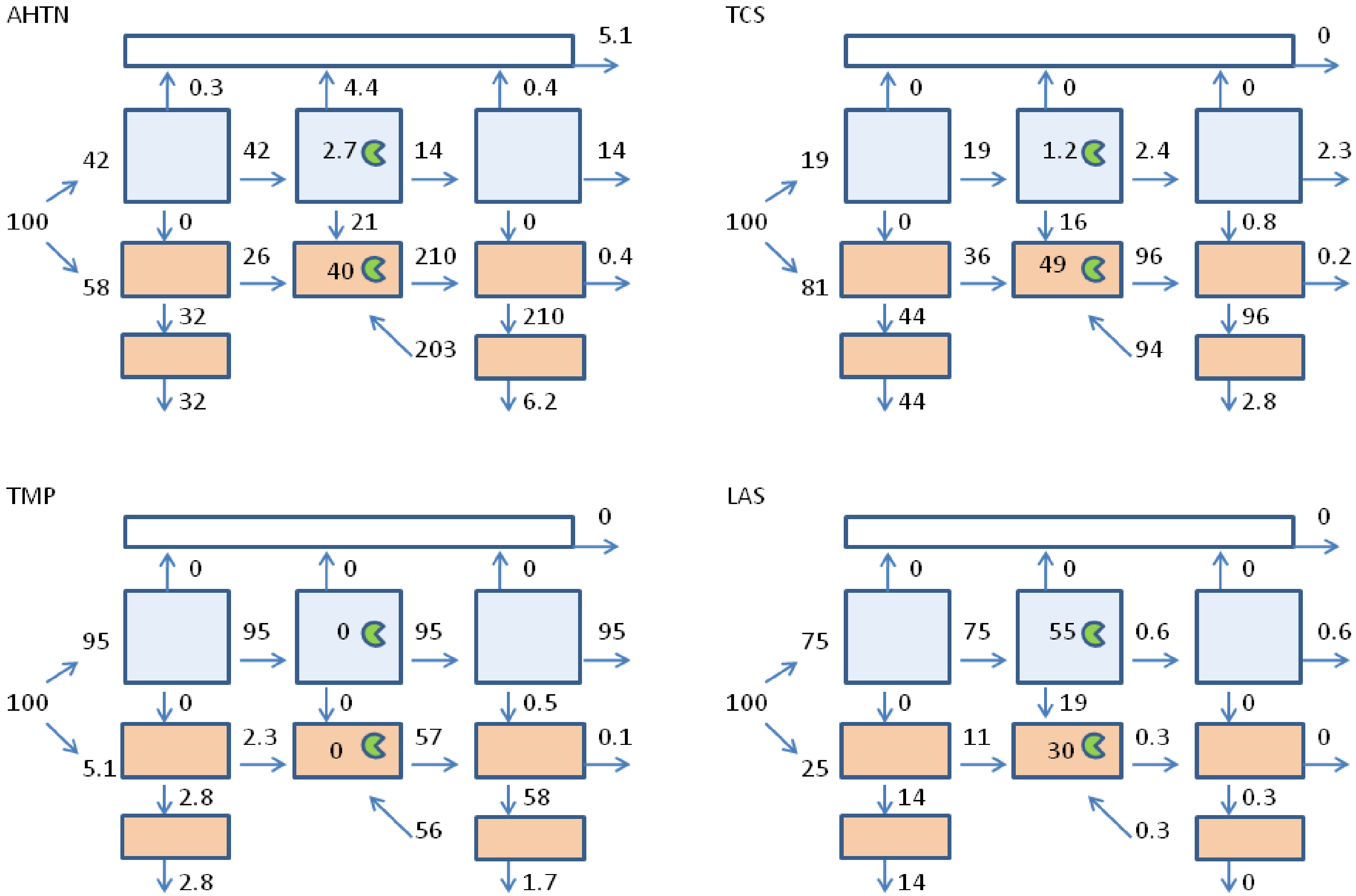
- Four test substances: tonalide, triclosan, trimethoprim and linear alkylbenzene sulfonate
- Input datasets include measured sludge-water sorption and biodegradation rates in activated sludge
- Monitoring data from activated sludge plants in the EU were collected from the literature. Only measurements of total concentrations were considered.
- Probabilistic Monte Carlo simulations with SimpleTreat (at steady-state) were compared to measured data

VALIDATION STUDY: CHEMICALS PROPERTIES

				PDF parameters	
			type	mean	standard deviation
Tonalide 	H	Pa m^{-3} mol^{-1}	L	37.1	σ =20
	$logK_{OC,n}$		N	4.02	σ = 0.5
	$k_{bio,22}$	h^{-1}	L	0.045	σ = 0.034
Triclosan 	$pK_{a,a}$		N	8.00	σ = 0.1
	$logK_{OC,n}$		N	4.67	σ = 0.2
	$logK_{OC,a}$		N	2.06	σ = 0.50
	$k_{bio,22}$	h^{-1}	L	0.12	σ = 0.15
Trimethoprim 	$pK_{a,b}$		N	7.12	σ = 0.67
	$logK_{OC}$		N	2.61	σ = 0.30
	K_{bio}	h^{-1}		0	
LAS 	$logK_{OC,a}$		N	3.40	σ = 0.3
	$k_{bio,22}$	h^{-1}	L	22	σ = 24

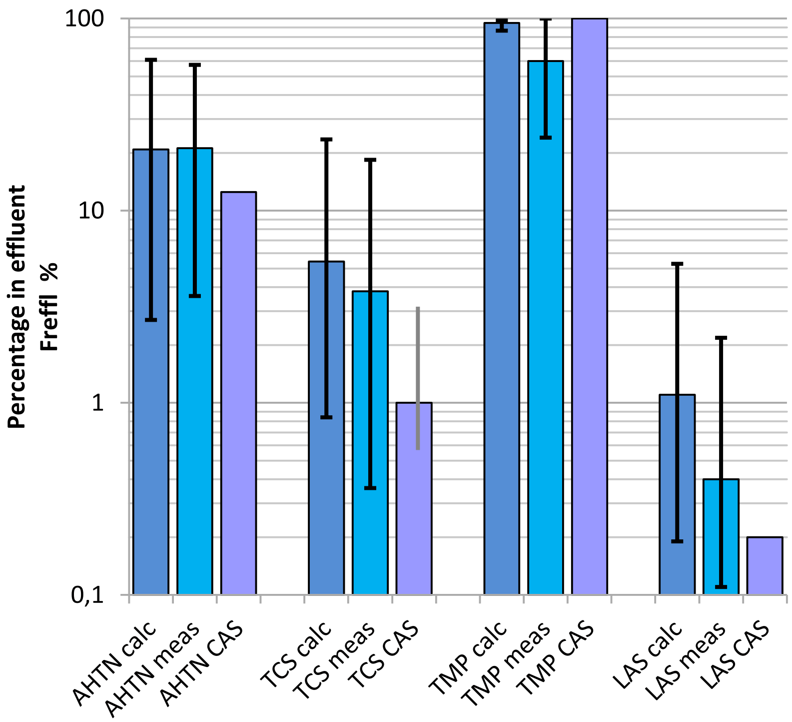
VALIDATION STUDY: ESTIMATED MASS FLUXES

Relative mass fluxes of tonalide (AHTN), triclosan (TCS), trimethoprim (TMP) and linear alkylbenzene sulphonate (LAS) calculated with SimpleTreat 3.2 for the likeliest scenario



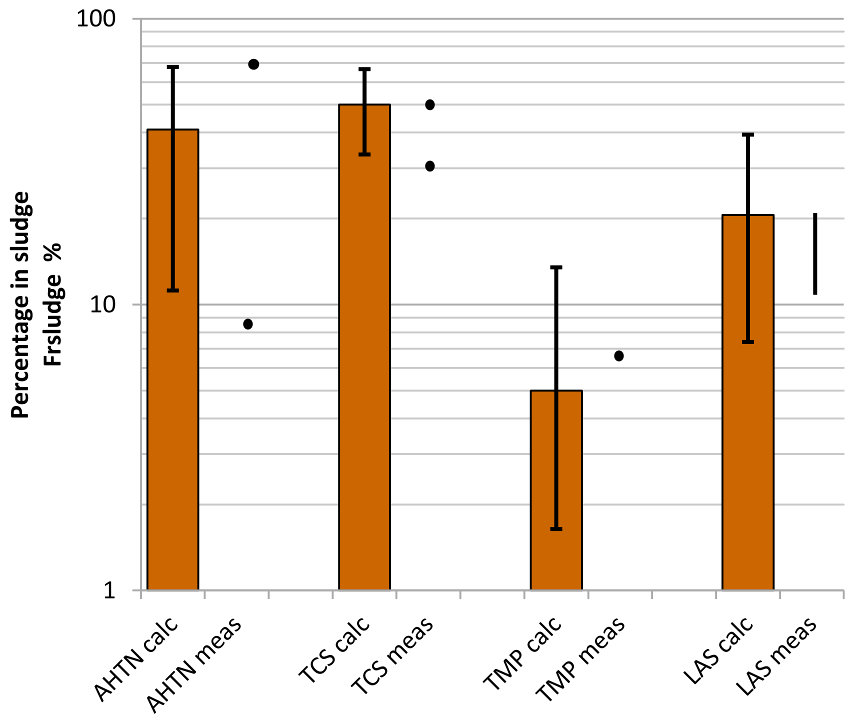
VALIDATION STUDY: MODEL RESULTS VS. OBSERVED DATA

Comparison of percentage released to effluent calculated with SimpleTreat , measured in full scale STPs, and measured in continuous activated sludge (CAS) tests



VALIDATION STUDY: MODEL RESULTS VS. OBSERVED DATA

Comparison of percentage removed via sludge calculated with SimpleTreat 3.2 and measured in full scale STPs



CONCLUSIONS

- **Two versions of SimpleTreat**

  Deterministic: requires only a basic input dataset (screening biodegradability info, Kow, Henry's law constant). This version represents a realistic worst case scenario. SimpleTreat 3.2 includes the new K_{OC} regressions for monovalent acids and bases.

  Probabilistic: requires measured data for K_{OC} and biodegradability in activated sludge.

- **Model evaluation**

  With an accurate input dataset, SimpleTreat 3.2 reasonably predicts most likely estimates and variability ranges of the fate and elimination of organic xenobiotics in activated sludge STPs.

- **Implications for risk assessment and prioritization**

  current TGD recommends 1) Measured data in full scale STP 2) Simulation test data 3) Modelling STP. Simulations and experimental data support each other, no single method alone is reliable/representative.

- **Limitations**

  Scenarios other than activated sludge currently not included (e.g. attached biomass, tertiary treatments). SimpleTreat is not designed to assess and optimize removal efficiency in specific STPs.

THANK YOU

FURTHER INFORMATION:

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APPLICABILITY DOMAIN: ORGANIC IONS

Acids:

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

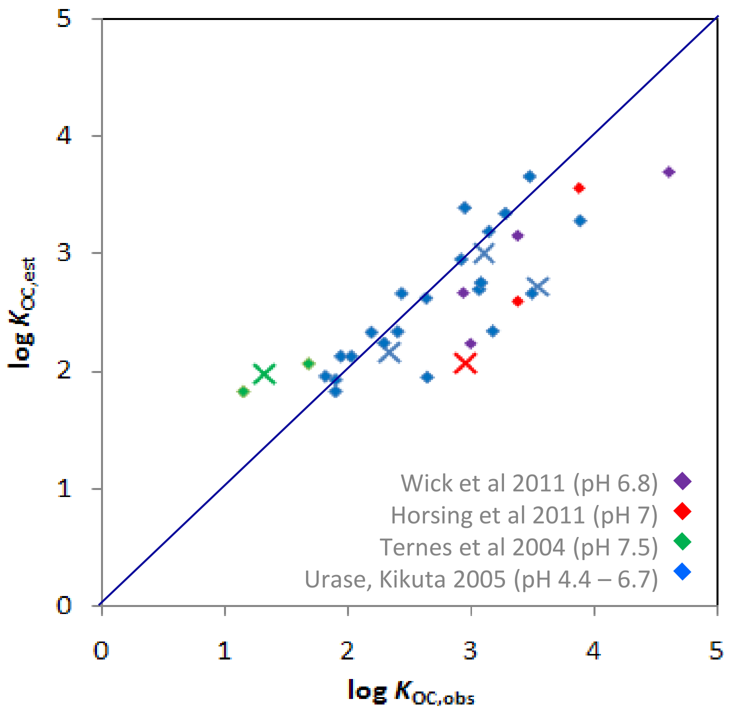
SimpleTreat 3.1:

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

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

- The species-specific hydrophobicity-based model (Eq. 2) reasonably estimates sorption to sludge and can be incorporated into SimpleTreat.
- Mean absolute error on logK_{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.

log log D_{OW} at pH 7 vs. log K_{OC} sludge reported in the literature for basic chemicals (pKa >5).