Surfactants and their TPs discharged from WWTPs: Germany case study

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Surfactants in detergents - an obvious problem „in former times“

- First generation surfactants used in detergents not easily degradable
- Visible „foam mountains“ on rivers and lakes - the first German environmental law enacted in 1964; required the complete degradation of the surfactants

➔ Still a problem?

Bild: „Schaumberge durch schlecht abbaubare Tenside“ vor dem Jahr 1964

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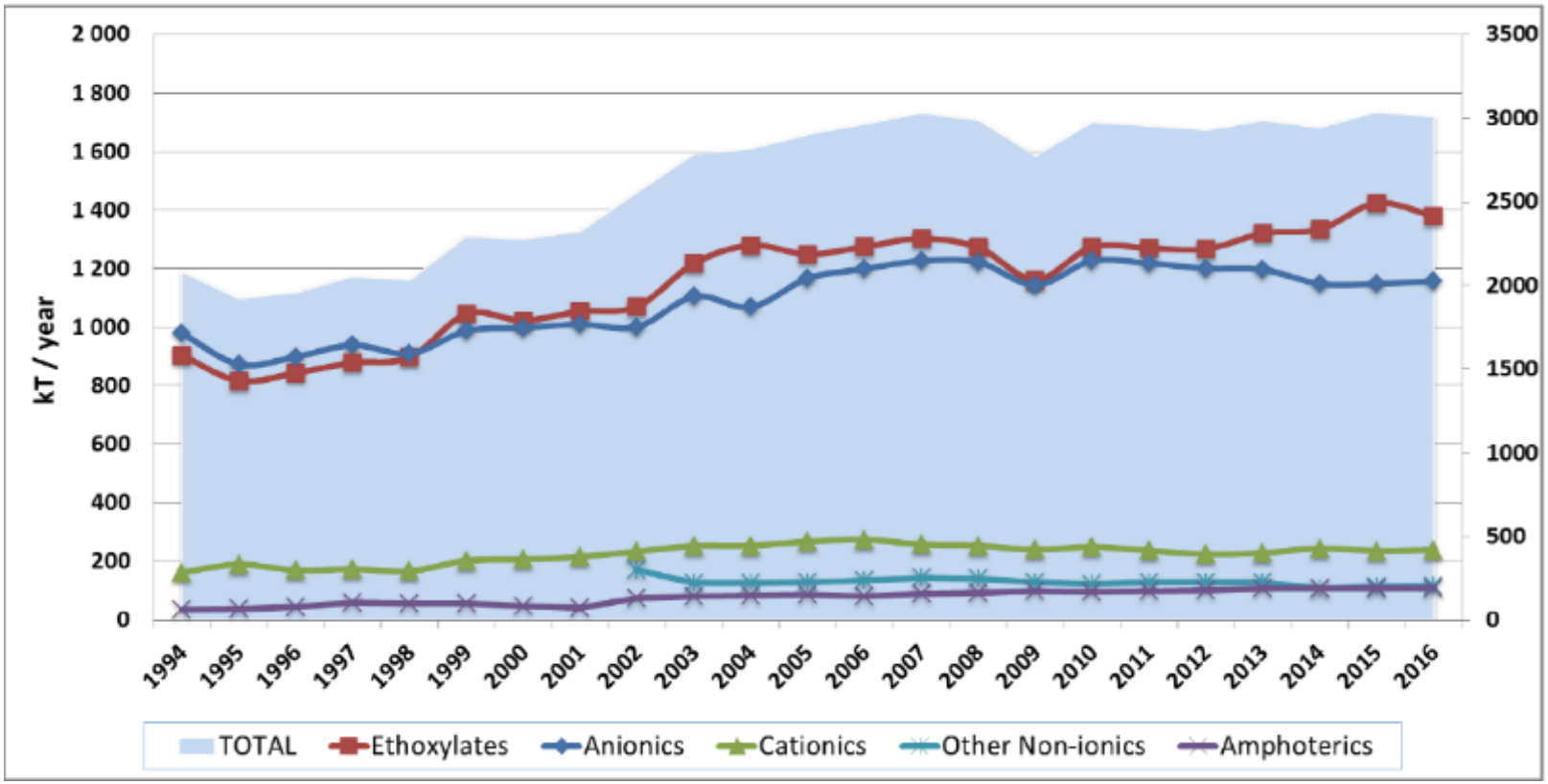
High usage of detergents

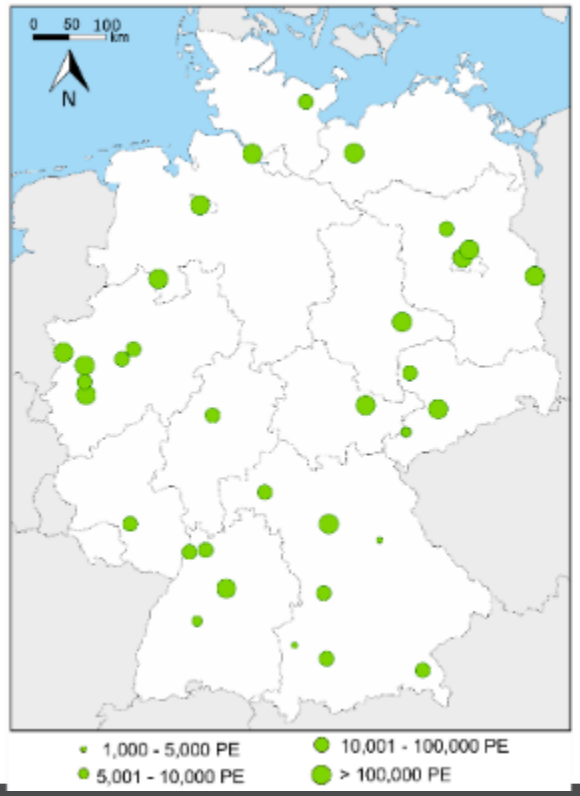
- Europe: ca. 3 million tons/a
- Globally: ca. 15 million tons/a



(CESIO, 2016)

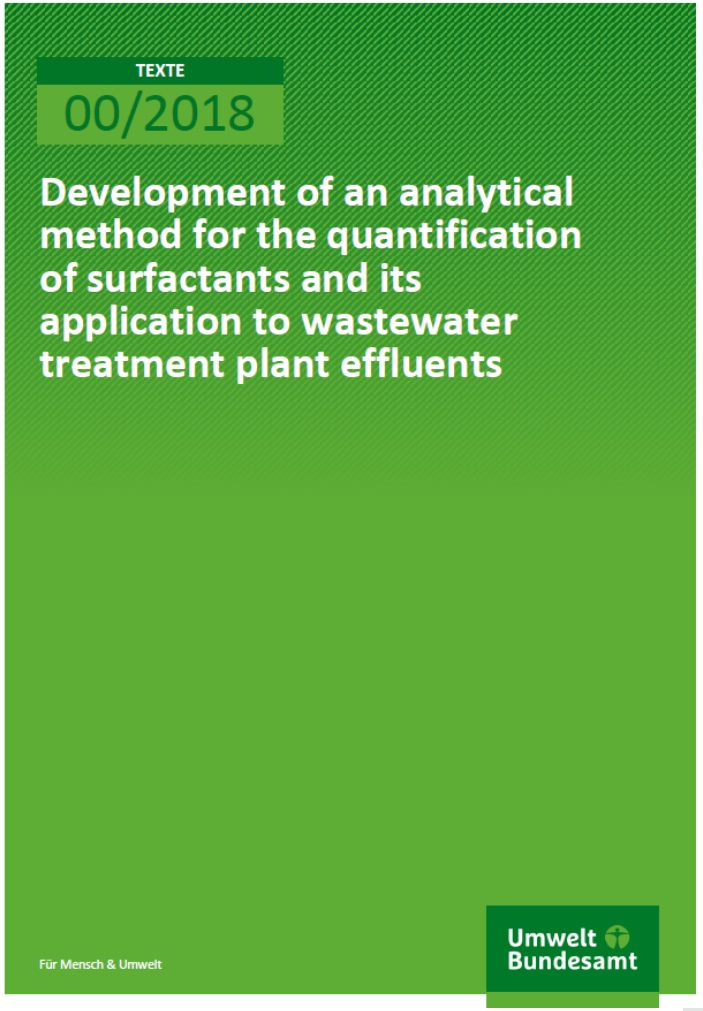
Prioritisation of surfactants

Anlayse common surfactants and their TPs in wastewater samples to determine the potential risk to the aquatic environment

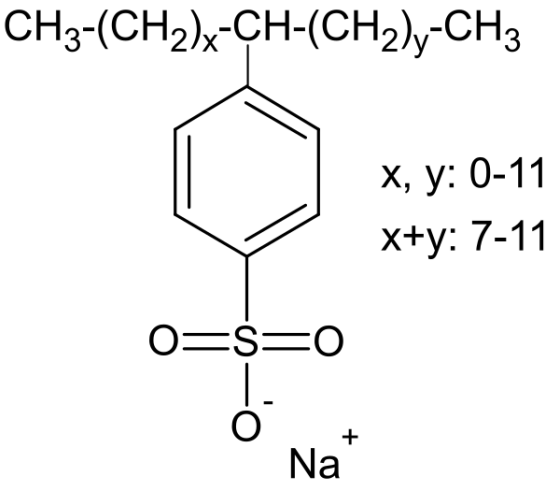


33 wastewater samples

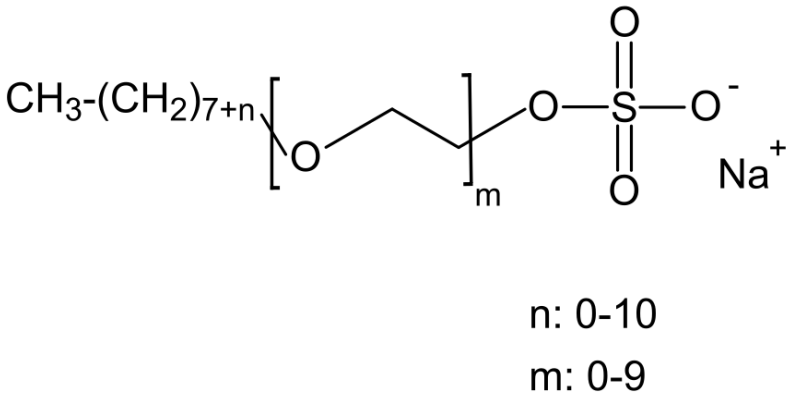
March-April 2018



Target analytes: structures



linear alkylbenzosulfonate (LAS):
C10, C11, C12, C13



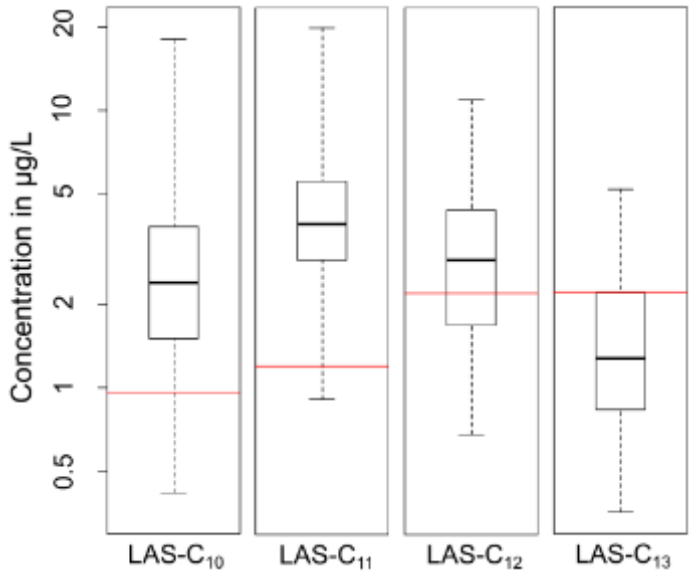
alkylethersulfate (AES):
C12, C14 with each 0-9 ethoxy-groups

Target analytes AES: analytical standard

	AES-C_{12}				AES-C_{14}			
Number of EO units	Counts	MW	Counts x MW	Fraction in %	Counts	MW	Counts x MW	Fraction in %
0	2.94E+09	265.1	7.80E+11	**14.7**	1.15E+09	293.1	3.37E+11	**6.3**
1	2.17E+09	309.1	6.71E+11	**12.6**	8.49E+08	337.1	2.86E+11	**5.4**
2	1.79E+09	353.1	6.32E+11	**11.9**	6.36E+08	381.2	2.42E+11	**4.6**
3	1.44E+09	397.2	5.74E+11	**10.8**	4.93E+08	425.2	2.10E+11	**3.9**
4	8.43E+08	441.2	3.72E+11	**7.0**	2.69E+08	469.3	1.26E+11	**2.4**
5	5.39E+08	485.3	2.62E+11	**4.9**	1.78E+08	513.3	9.14E+10	**1.7**
6	3.40E+08	529.3	1.80E+11	**3.4**	1.24E+08	557.3	6.92E+10	**1.3**
7	2.45E+08	573.3	1.40E+11	**2.6**	1.01E+08	601.3	6.06E+10	**1.1**
8	1.99E+08	617.3	1.23E+11	**2.3**	7.55E+07	645.3	4.87E+10	**0.9**
9	1.23E+08	661.3	8.16E+10	**1.5**	4.24E+07	689.4	2.93E+10	**0.6**

Results

a) **LAS**



- Mean effluent concentration: **14,4 µg/L** (n=33)

e.g. McDonough et al. (2016): **15,3 µg/L** (n=44)
Clara et al. (2007): **13,3 µg/L** (n= 7)

- Mean influent concentration: **3.200 µg/L** (n=4)

➔ Mean LAS removal: **99,6%**

b) **AES**

- Mean effluent concentration: **0,57 µg/L** (n=33)

Generally lower concentrations than other studies:
z.B. McDonough et al. (2016): **1,95 µg/L** (n=44)
Matthijs et al. (1999): **6,5 µg/L** (n=7)

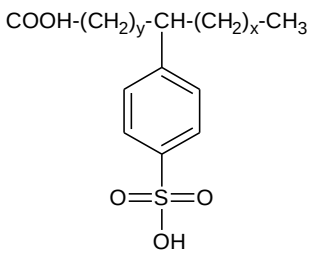
- Mean influent concentration: **680 µg/L** (n=4)

➔ Mean AES removal: **99,9%**

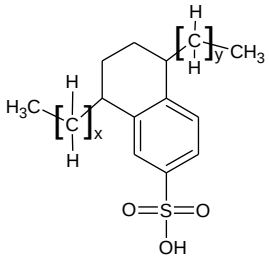
Screening analyses: Structures I

Transformation products (TPs) and impurities of LAS

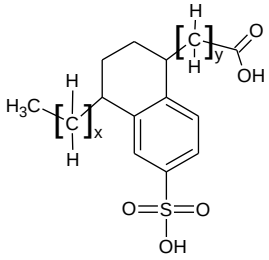
Sulfophenylalkyl-
Carbonic acids (SPACs)



Dialkyltetralin-
sulfonates (DATSs)



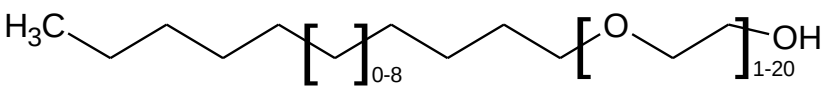
Sulfotetralinalkyl-
carbonic acid (STACs)



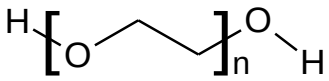
In many cases:
SPACs + DATSs + STACs > LAS

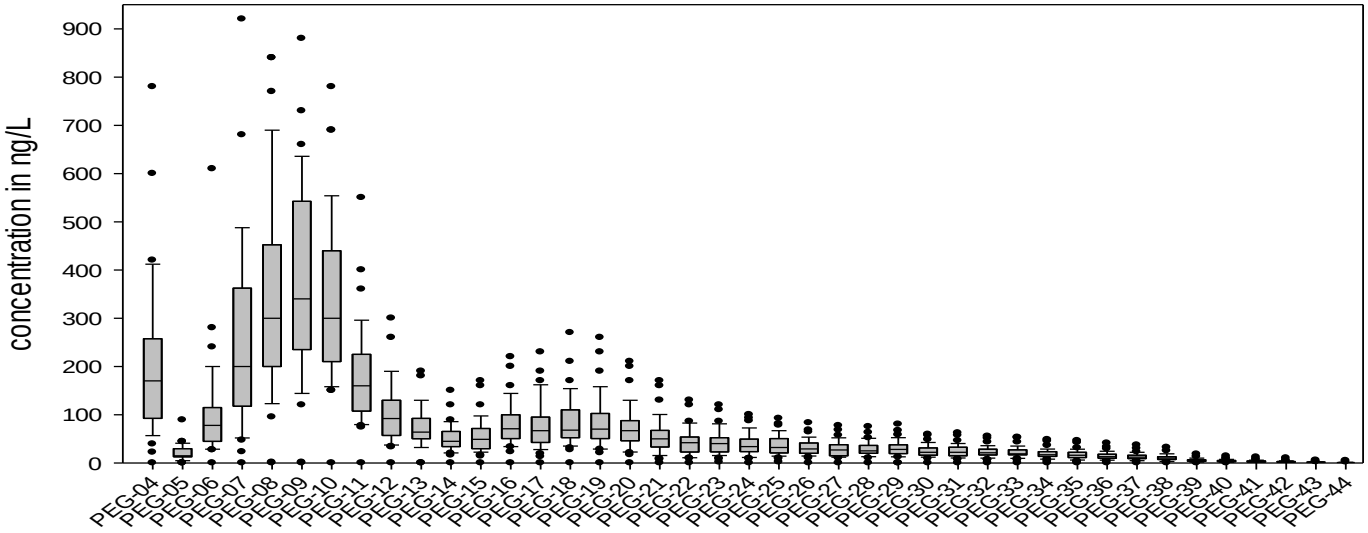
Screening analyses: Structures II

- High concentrations of alcoholethoxylates (AEOs) up to 6,6 µg/L



- High concentrations of polyethylenglycoles (PEGs) up to 7,4 µg/L



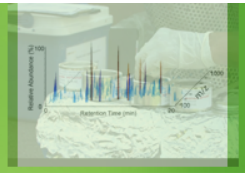


- Total concentration of **all** (semi-)quantified surfactants and TPs: up to **82 µg/L**

NORMAN SUSPECT LIST EXCHANGE AND RELATED LISTS SCREENED IN THE SAMPLES

NORMAN

Network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances



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NORMAN Suspect List Exchange

In September 2014, NORMAN members expressed the need to exchange various lists of substances to improve their suspect screening efforts. This website was established aspart of the 2015 Joint Programme of Activities as a central access point for NORMAN members (and others) to find suspect lists relevant for their environmental monitoring question. All suspect lists currently available are compiled in the table below and on the US EPA CompTox Chemistry Dashboard (**website**, **downloads**, **chemical lists**).

The "Link to full list" column below contains an excel or comma-separated file (csv) with all available information, e.g. as provided as supporting information for the publication, while the third column provides a list of the structures as InChIKeys only, which allows suspect searching using MetFrag or other workflows. The fourth column contains references for the data: please cite these references if you use the respective datasets.

Recent Suspect Exchange and Dashboard presentations/publications include: **ICCE Oslo 2017**: **NORMAN Suspects meet the Dashboard** and **NORMAN MassBank and Suspect Exchange**; SETAC **Mixtures** Denver: **Identifying Complex Mixtures with Cheminformatics and HR-MS**; ACS Fall 2017: **Markush Enumeration for UVCBs** and a **viewpoint article**.

S7	EAWAGSURF	**Eawag Surfactants Suspect List**	Suspect formulas: **CSV**, **XLSX** CompTox **EAWAGSURF List**	(in progress…)	Schymanski *et al.* 2014. DOI: **10.1021/es4044374**

Interactive merged list of all suspect substances (update in progress)

NEW (March 2018): SusDat is now at >40,000 chemicals; new US EPA Consumer Product Suspect List, Uni Athens Target List.

DISCLAIMER: SusDat is a compilation of information provided by NORMAN network members and it is a "living document" undergoing constant curation and improvement. NORMAN SusDat

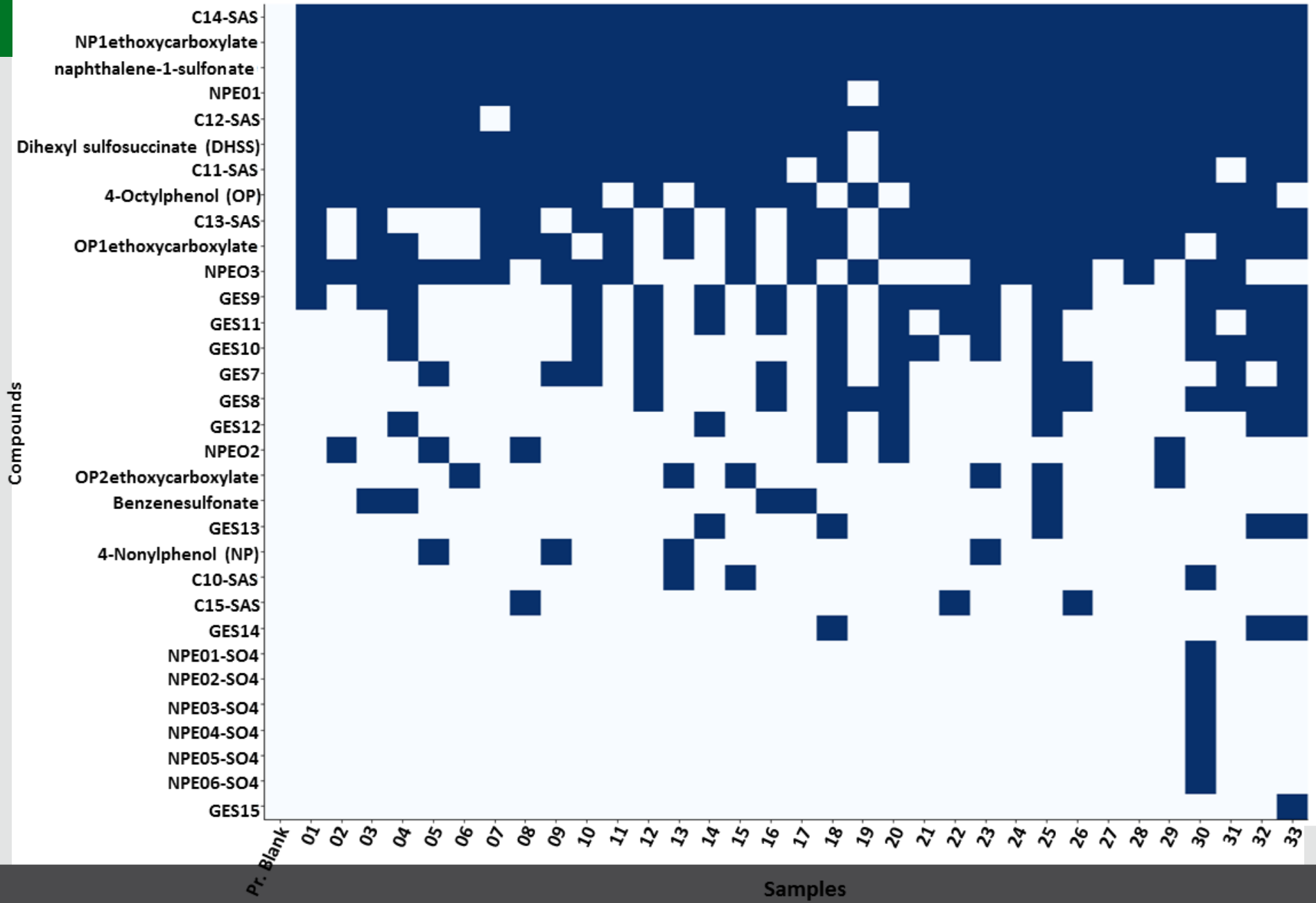
S8	ATHENSSUS	**University of Athens Surfactants and Suspects List**	Gago Ferrero *et al* **CSV**, **XLSX** (3/10/2017) CompTox **ATHENSSUS List**	**UniAthens InChIKeys** (28/01/2016)	Gago-Ferrero*et al.* 2015. DOI: **10.1021/acs.est.5b03454**

	SUSDAT	**Merged NORMAN Suspect List: SusDat**	**Interactive Data table** (updating…)	**MS-ready InChIKeys** (1/03/2018)	A merged list of >40,000structures from suspect lists. See **interactive version**. Compiled by Reza Aalizadeh, University of Athens, including RTI and toxicity values, support by Nikiforos Alygizakis, EI. *Work in progress … please report any issues!*

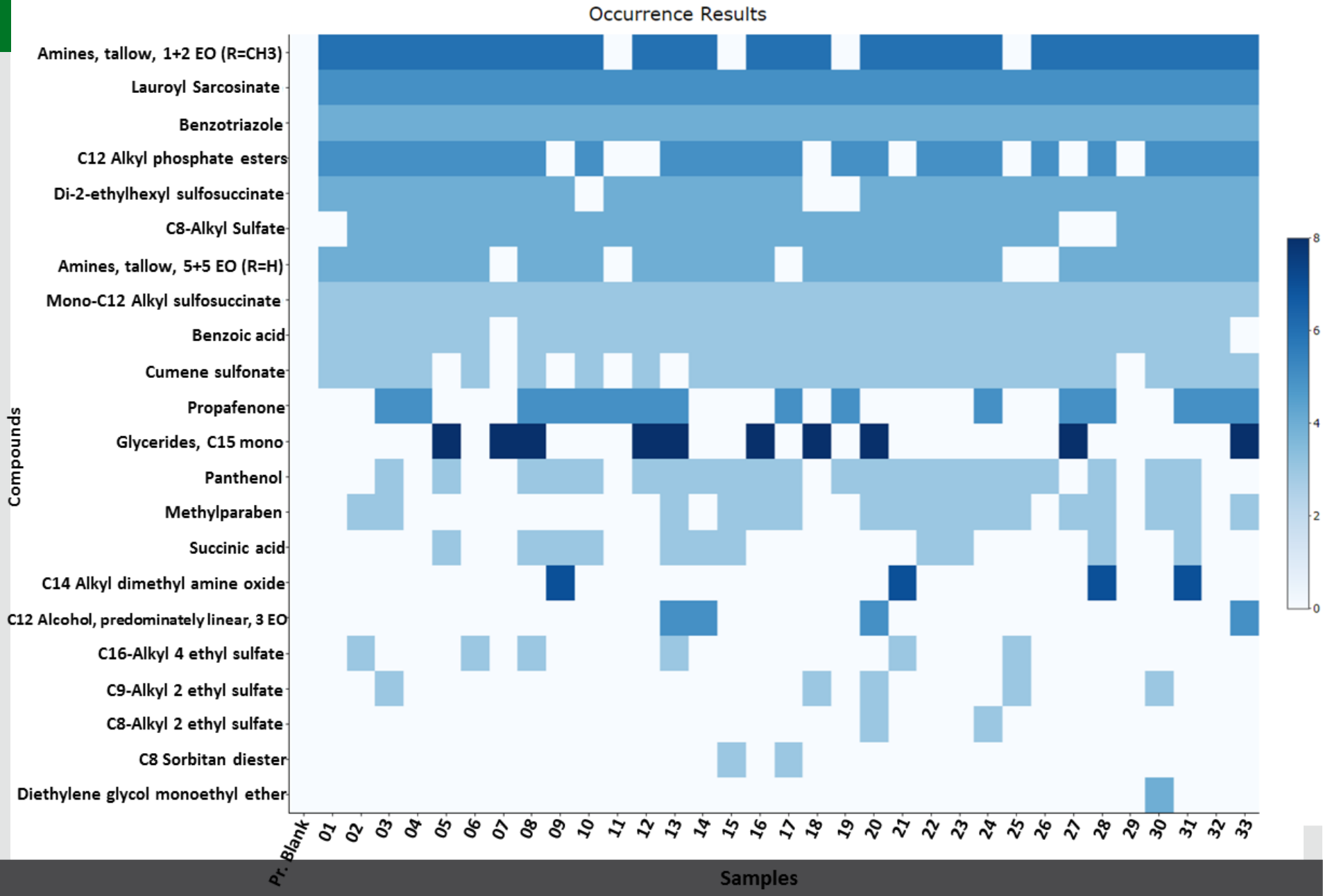
S23	EIUBASURF	**Surfactant Suspect List from EI and UBA**	Surfactant List **XLSX** (19/06/2018) Surfactant List **CSV** (19/06/2018) CompTox **EIUBASURF List**	EI UBA Surfactant **InChIKeys** (19/06/2018)	A compiled list of eco-labeled surfactants from Environmental Institute (EI, SK) and the German Federal Environmental Agency (UBA, DE) assigning chemical structures to UVCB chemicals based on names and prior knowledge. Provided by Nikiforos Alygizakis, EI.

			Further curation in progress…		free; batch search after free registration).
S3	NORMANCT15	**NORMAN Collaborative Trial Targets and Suspects**	LC-MS: **CSV**, **XLSX** (3/10/2017) GC-MS: **CSV**, **XLSX** (3/10/2017) CompTox **NORMANCT15 List**	**LC-MS InChIKeys** (31/10/2016) **GC-MS InChIKeys**	Schymanski *et al.* 2015. DOI: **10.1007/s00216-015-8681-7**

Suspect screening of other known surfactants and their TPs



Suspect screening of DID list



ON-LINE DATABASE

Analysis of surfactants in effluent wastewater from Germany: May 2018

Screening - 1564 suspected surfactants

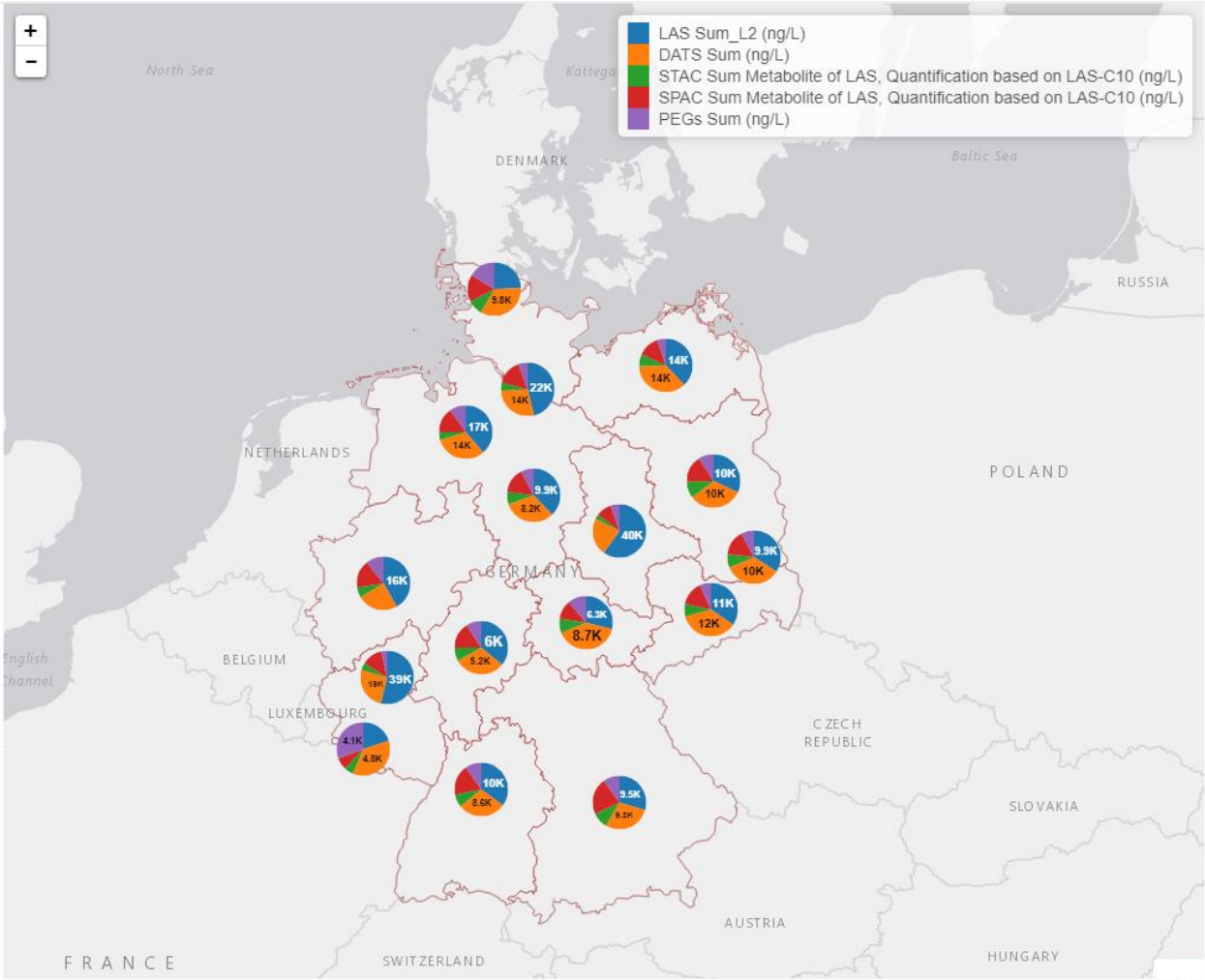
Select emerging contaminants

LAS Sum_L2 DATS Sum STAC Sum SPAC Sum PEGs Sum

Chart type

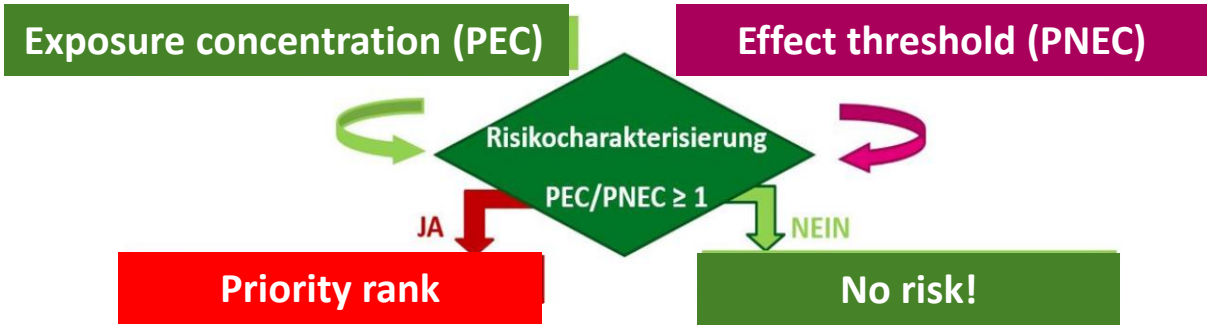
pie

Show values



Prioritisation of surfactants: concept

Using the classical PEC/PNEC ratio!



PEC / PNEC < 1 ➔ contribution to mixture toxicity?

PEC / PNEC > 1 ➔ risk mitigation measures

Prioritisation of surfactants: input data

Expo: $PEC_{surface\ water}$ based on measured effluent concentrations devided by the local dilution factor!

Effects: PNEC based on existing risk assessment reports and available experimental data

	Compound	CAS	DID-List #	TF_{acute} [mg/L]	AF	$TF_{chronic}$ [mg/L]	AF	$LC50_{Daphnia}$ [mg/L]	Validation level		PNEC type	value [mg/L]	AF	Endpoint	Reference
LAS-C10-13	LAS-C10-13		2001	0,0041	1000	0,069	10	2.35 - 16.7	exp.	HERA report 2013	$PNEC_{chronic}$	0,0230	10	NOEC	Temra et al. 2001
DATS	DATS C7-10	-	-	-	-	-	-	59,000 - 925,000	pred.	EPI Suite	P-PNEC	0,3755	1000	LC50	EPI Suite 2018
	DATS C11-14	-	-	-	-	-	-	1,440 - 23,000	pred.	EPI Suite	P-PNEC	0,0093	1000	LC50	EPI Suite 2018
STAC C3-8	STAC C3-5	-	-	-	-	-	-	744 - 4,736	pred.	EPI Suite	P-PNEC	2,4530	1000	LC50	EPI Suite 2018
	STAC C6-8	-	-	-	-	-	-	4.6 - 294	pred.	EPI Suite	P-PNEC	0,1520	1000	LC50	EPI Suite 2018
SPAC	SPAC C4-5	-	-	-	-	-	-	23,296 - 58,301	pred.	EPI Suite	P-PNEC	40,8000	1000	LC50	EPI Suite 2018
	SPAC C6-10	-	-	-	-	-	-	229 - 9,283	pred.	EPI Suite	P-PNEC	0,3050	1000	LC50	EPI Suite 2018
	SPAC C11-13	-	-	-	-	-	-	14 - 90.0	pred.	EPI Suite	P-PNEC	0,0465	1000	LC50	EPI Suite 2018
AES C12-14 Ethoxy 0-9	AES-C12 EO 0	151-41-7	2005	0,0028	1000	0,039	10	5.71	pred.	Alizadeh et al. 2017	$PNEC_{chronic}$	0,0391	10	NOEC	DID 2016
	AES-C12 EO 1-3	201686-09-1	2008	0,0071	1000	0,038	50	2.08 - 3.39	pred.	Alizadeh et al. 2017	$PNEC_{chronic}$	0,0270	10	NOEC	Maki et al. 1979
	AES-C12 EO 4-9	-	-	-	-	-	-	2.70 - 23.0	pred.	Alizadeh et al. 2017	$PNEC_{chronic}$	0,1950	10	NOEC	Dyer et al 2000
	AES-C14 EO 0	4754-44-3	2005	0,0028	1000	0,039	10	5.18	pred.	Alizadeh et al. 2017	$PNEC_{chronic}$	0,0391	10	NOEC	DID 2016
	AES-C14 EO 1-3	68891-38-3	2009	0,0046	1000	0,014	10	1.17	exp.	Maki 1979	$PNEC_{chronic}$	0,0270	10	NOEC	Maki et al. 1977
	AES-C14 EO 4-9	-	-	-	-	-	-	1.50 - 9.20	pred.	Alizadeh et al. 2017	$PNEC_{chronic}$	0,1100	10	NOEC	Dyer et al. 2000
PEG 4-44	PEG EO ≥ 4 - ≤44	-	2539	0,1	10000	-	-	5,405 - 28,616	pred.	Alizadeh et al. 2017	P-PNEC	20,3320	1000	LC50	Alizadeh et al. 2017
FAE C8-18 Ethoxy 3-20	FAE C08-11 EO > 2 - ≤10	-	2156	0,00500	1000	0,1500	10	8.4-669	predicted	Alizadeh et al. 2017	$PNEC_{chronic}$	0,0730	10	NOEC	Harrelson et al. 1997
	FAE C08-11 EO >10 - ≤20	-	2157	0,05000	1000	2,5000	10	153 - 1608	predicted	Alizadeh et al. 2017	$PNEC_{chronic}$	2,5000	10	NOEC	DID 2016
	FAE C12-16 EO > 2 - ≤ 5	-	2162	0,00043	1000	0,0370	10	2.78 - 16.3	predicted	Alizadeh et al. 2017	$PNEC_{chronic}$	0,0082	10	NOEC	Mank et al. 1999
	FAE C12-16 EO > 5 - ≤10	-	2163	0,00040	1000	0,0270	10	4.20 - 70.4	predicted	Alizadeh et al. 2017	$PNEC_{chronic}$	0,0140	10	NOEC	Mank et al. 1998a
	FAE C12-16 EO >10 - ≤20	-	2166	0,00070	1000	0,4860	10	21.0 - 210	predicted	Alizadeh et al. 2017	$PNEC_{chronic}$	0,4860	10	NOEC	DID 2016
	FAE C16-18 EO > 2 - ≤8	-	2175	0,00320	1000	0,0082	10	1.92 - 4.87	predicted	Alizadeh et al. 2017	$PNEC_{chronic}$	0,0082	10	NOEC	DID 2016
	FAE C16-18 EO > 9 - ≤19	-	2176	0,00072	1000	0,0110	10	4.25 - 29.1	predicted	Alizadeh et al. 2017	$PNEC_{chronic}$	0,0110	10	NOEC	DID 2016

Prioritisation of surfactants: LAS, impurities and their TPs

	LAS	DATs	SPACs	STACs
PEC_{Target}	MEC_{95} = 10 µg/L	-	-	-
$PEC_{Screening}$	-	MEC_{95} = 3,3 µg/L	MEC_{95} = 0,77 µg/L	MEC_{95} = 0,35 µg/L
$PEC_{Literatur}$	Max = 23 µg/L	-	-	-
PNEC	25 µg/L (AF=10)	9,3 µg/L (AF=1000)	4653 µg/L (AF=1000)	152 µg/L (AF=1000)
$PEC/PNEC_{Tar.}$	0,40	-	-	-
$PEC/PNEC_{Screen.}$	-	0,35	0,0002	0,002
$PEC/PNEC_{Lit.}$	1	-	-	-

LAS concentrations reach almost half of the PNEC and might contribute to mixture effects

Total concentrations, including mostly DATs, exceeded the PEC/PNEC sum at one site

Prioritisation of surfactants: AESs, FAEs, PEGs

	AESs	FAEs	PEGs
PEC_{Target}	MEC_{95} = 2,1 µg/L	-	-
$PEC_{Screening}$	-	MEC_{95} = 0,23 µg/L	MEC_{95} = 2,0 µg/L
$PEC_{Literatur}$	Max = 73 µg/L		
PNEC	27 µg/L (AF=10)	8,2 µg/L (AF=10)	20233 µg/L (AF=1000)
$PEC/PNEC_{Tar.}$	0,08	-	-
$PEC/PNEC_{Screen.}$	-	0,028	0,0001
$PEC/PNEC_{Lit.}$	2,7		

Despite one very high AES concentration in the literature, the other surfactant classes did not contribute to the overall risk

Summary

- LAS and DAT identified as top priority surfactants
- LAS concentrations are reaching half of the PNEC and should trigger screening campaign
- Total surfactant concentrations are expected to contribute to mixture effects

Outlook

- Routine monitoring of the top priority surfactants
- Derivation of harmonized PNECs for these surfactants
- Investigation of their potential contribution to mixture effects