SUPPLEMENTARY MATERIAL

Synthetic surfactants in Swiss sewage sludges: Analytical challenges, concentrations and per capita loads

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S1. Analytical methods and internal standard mixture

Analysis of SAS, LAS, and AEO

The target analytes SAS, LAS, and AEO were determined using an ultra-performance liquid chromatography (UPLC) system coupled to a Waters Xevo G2-XS time-of-flight mass spectrometer (TOF-MS). The LC-MS parameters were modified based on Lara-Martín et al. (2011) and Lara-Martín et al. (2006). A 10 µL volume of each sample was injected onto a RP-C18 column (Acquity UPLC BEH C18 (Waters); 2.1 mm × 50 mm and 1.7 µm particle size) and eluted with mobile phases of MeOH (A) and 10 mM formic acid (B) at a flow rate of 0.4 mL min^{-1}. The initial solvent mixture of 70% A and 30% B was held for 2 min before ramping up to 100% A within 1 min and holding for 5 min. The initial solvent mixture was then restored and held until column re-equilibration. The MS was operated with electrospray ionization (ESI) in full scan negative and positive modes for detecting anionic and nonionic surfactants, respectively. Desolvation gas flow and temperature were 750 L h^{-1} and 350°C. The source temperature was 150°C. Capillary voltage was 2500 V and 4000 V in negative and positive ESI mode, respectively. The cone gas flow was 10 L h^{-1} and cone voltages were 45 V in negative and 10 V in positive mode. Lock mass was a solution of 200 ng/mL of leu-enkephalin Ions were extracted using MassLynx software.

Analysis of NP, NPEC, and *tert*-OP

The target analytes *tert*-OP, NP, and NPEC were determined using a UPLC system coupled to an Agilent 6495 triplequad MS with a jet stream ESI ion source and ion funnel technology. A 10 µL volume of each sample was injected onto a RP-C18 column (Acquity UPLC HSS T3 3 × 100 mm; 1.8µm) and eluted with MeOH (A) and 10 mM ammonium formate (B) as mobile phases at a flow rate of 0.4 mL min^{-1}. The initial solvent mixture of 100% A and 0% B was held for 15 minutes before ramping up to 80% B within 1 min and holding for 4 min. The initial solvent mixture was restored and held until re-equilibration. A solution of 0.5 mM ammonium fluoride was introduced to the sample post-column at a flow rate of 0.05mL min^{-1}. The MS was operated with electrospray ionization (ESI) in MRM negative mode for monitoring fragmentation reactions of deprotonated molecule ions of *tert*-OP (205.2 → 133), NP (219.2 → 133) and NP1EC (277.2 → 219). Internal standards (D_8-NP and D_2-NP1EC) were used to correct for signal fluctuations. Ions were extracted and quantified using the Agilent Masshunter software. Other MS parameters were: gas temperature 200°C, gas flow 17 L min^{-1}, nebulizer 25 psi, sheath gas heater 400°C, sheath gas flow 12 L min^{-1}, and capillary voltage

3000V. Ion funnel parameters for negative high- and low-pressure radio frequency (RF) were 90 and 60, respectively.

Analysis of NPEO (EO1–3)

The target NP1EO, NP2EO, and NP3EO analytes were analyzed with a UPLC system coupled to a Bruker EvoQ Elite tandem mass spectrometer (MS/MS). The LC-MS parameters were optimized from a previously existing methodology (Lara-Martín et al. 2012). A 10 µL volume of each sample was injected onto a RP-C18 column (Bruker Intensity Solo, 2.1 mm × 100 mm and 2 µm particle size) and eluted with MeOH (A) and 10 mM ammonium formate (B) as mobile phases at a flow rate of 0.4 mL min^{-1}. The initial solvent mixture of 70% A and 30% B was ramped up to 100% A within 1 min and held for 4 min. The initial solvent mixture was restored and held until re-equilibration. The MS was operated with electrospray ionization (ESI) in the MRM positive mode to monitor the fragmentation reactions of the ammonium adduct ions of NP1EO (282 → 127; 282 → 71), NP2EO (326 → 183; 326 → 121), and NP3EO (370 → 227; 370 → 121). Internal standards ($^{13}C_6$-NP1EO and $^{13}C_6$-NP2EO) were used to correct for signal fluctuations. Ions were extracted and quantified using the MS Workstation 8.1 software. Other MS parameters were: spray voltage 4500 V, cone temperature 350°C, and probe temperature 450°C.

Internal standard mixture

The final sludge samples (1 mL) were spiked with 10 µL of an internal standard mixture (before dilution). Blank and calibration samples were spiked, too. The internal standard mixture contained the following analytes in the respective concentrations: C_{16}-LAS (400 µg $µL^{-1}$), C_{10}EO8-AEO (80 µg $µL^{-1}$), C_{12}-SAS (160 µg $µL^{-1}$), D_8-NP (40 µg $µL^{-1}$), D_2-NP1EC (0.4 µg $µL^{-1}$) and $^{13}C_6$-NPEO (160 µg $µL^{-1}$).

Table S 1. Monitored quantifier/qualifier ions and instrumental LOQs of the analyzed surfactants.

Compound	Quantifier m/z	Qualifier m/z	LOQ* (instrumental) ng mL^{-1}
C_{10}-LAS	297.1530	298.1562	1.34
C_{11}-LAS	311.1686	312.1719	3.21
C_{12}-LAS	325.1843	326.1875	3.06
C_{13}-LAS	339.1999	340.2032	2.24
C_{14}-SAS	277.1843	278.1875	3.1
C_{15}-SAS	291.1999	292.2032	3.2
C_{16}-SAS	305.2156	306.2188	2.3
C_{17}-SAS	319.2312	320.2345	1.4
AEO homologues M→ quasi molecular ion	$[M+Na]^+$	$[^{13}C\text{-}M+Na]^+$	10
NP1EO	282 → 127	282 → 71	0.3
NP2EO	326 → 183	326 → 121	0.3
NP3EO	370 → 227	370 → 121	0.3
NP	219.2 → 133	n/a	10
NP1EC	277.2 → 219	n/a	10
tert-OP	205.2 → 133	n/a	1

* LOQ: The limit of quantification refers to the instrumental LOQ and is also the lowest calibration standard. It is at least five times higher than the detected noise.

S2. Recoveries

Recoveries were determined in a preliminary experiment. A sludge sample was spiked (in triplicate) with a known amount of analyte to determine the loss during the sample preparation. The resulting recovery values were then applied to correct the quantified levels in all sludge samples. Recoveries for all target analytes are listed in **Table S 2** to **Table S 6.** Recovery values for AEO are discussed in more detail in the main manuscript. Recovery values for LAS are discussed in the following paragraphs.

For the spiking experiments, the spiked concentration needs to be higher (e.g., 2-fold higher) than the level in the unspiked sample. Sewage sludge is highly contaminated with LAS, so it requires very high spike levels, which can be achieved either by using a highly concentrated spike solution or by using a larger spike volume. The spike solution concentration was limited by the solubility of LAS in solvent. Adding water to the solvent increased the solubility but also resulted in foaming and subsequent irreproducible spiking. The spike volume was further limited by the sample amount (0.2g), since the sample should not be dispersed in the solvent. Ultimately, in this study, the spiked LAS level accounted only for one fifth of the actual environmental level, resulting in uncertain recovery values with high standard deviation. Recoveries were 166 ± 41%, 124 ± 15%, 126 ± 5%, and 284 ± 14% for C_{10}, C_{11}, C_{12}, and C_{13}, respectively. A previous study applied the same preparation method to sediment samples, which are less contaminated; hence, spiking experiments were possible without the mentioned restraints. That study achieved recoveries between 70 and 107% (Lara-Martín et al. 2008). We assume that the method would give similar results when applied to sewage sludge. Applying a conservative approach, a recovery of 100% for LAS homologues is assumed in this study. Due to the high concentrations of LAS in sewage sludge, the final sample extract must be diluted to avoid saturation of the mass spectrometer detector.

C_{10}-SAS was used to verify that no major sample losses occurred during sample preparation. C_{10}-SAS has a good recovery (about 85 ± 13%) with the sample preparation method used here. The sample extract was spiked with C_{10}-SAS before further processing. If the detected C_{10}-SAS deviated by 20% from the average recovery, the sample was excluded from further analysis. Only one sample was ultimately excluded from the data set (deviation of more than 70%). All other samples had deviations of less than 10%.

Table S 2. Recoveries for LAS of different chain lengths (C_{10}-C_{13}).

C10-LAS	C11-LAS	C12-LAS	C13-LAS
166 ± 41%	124% ± 15%	126% ± 5%	284% ± 14%

Table S 3. Recoveries for SAS of different chain lengths (C_{14}-C_{17}).

C14-SAS	C15-SAS	C16-SAS	C17-SAS
67 ± 0.6%	96% ± 2.6%	76% ± 2.4%	74± 3.5%

Table S 4. Recoveries for SAS of different chain lengths (C_{12}, C_{14}, C_{16}, C_{18}) and different ethoxymer units (EO02, EO03, EO06, and EO08).

	EO02	EO03	EO06	EO08
C12	27 ± 2.2%	38 ± 1.7%	54 ± 0.9%	55 ± 3.2%
C14	69 ± 2.3%	74 ± 5.3%	81 ± 5.5%	90 ± 3.3%
C16	56± 3.6%	63 ± 1.9%	73 ± 2.0%	75 ± 2.6%
C18	50 ± 1.7%	63 ± 2.1%	68 ± 2.0%	98 ± 3.9%

Table S 5. Recoveries for NP and NPEO (with 1–3 ethoxymer units).

NP	NP1EO	NP2EO	NP3EO
87 ± 13%	87 ± 18%*	87 ± 24%	79 ± 5.9%

* Estimated by averaging the recoveries of NP and NP2EO.

Table S 6. Recoveries for n-OP and NP1EC. The recovery of linear n-OP is used for *tert*-OP.

n-OP	NP1EC
58 ± 12%	74 ± 4.2%

S3. Mass spectrometric responses of AEO homologues

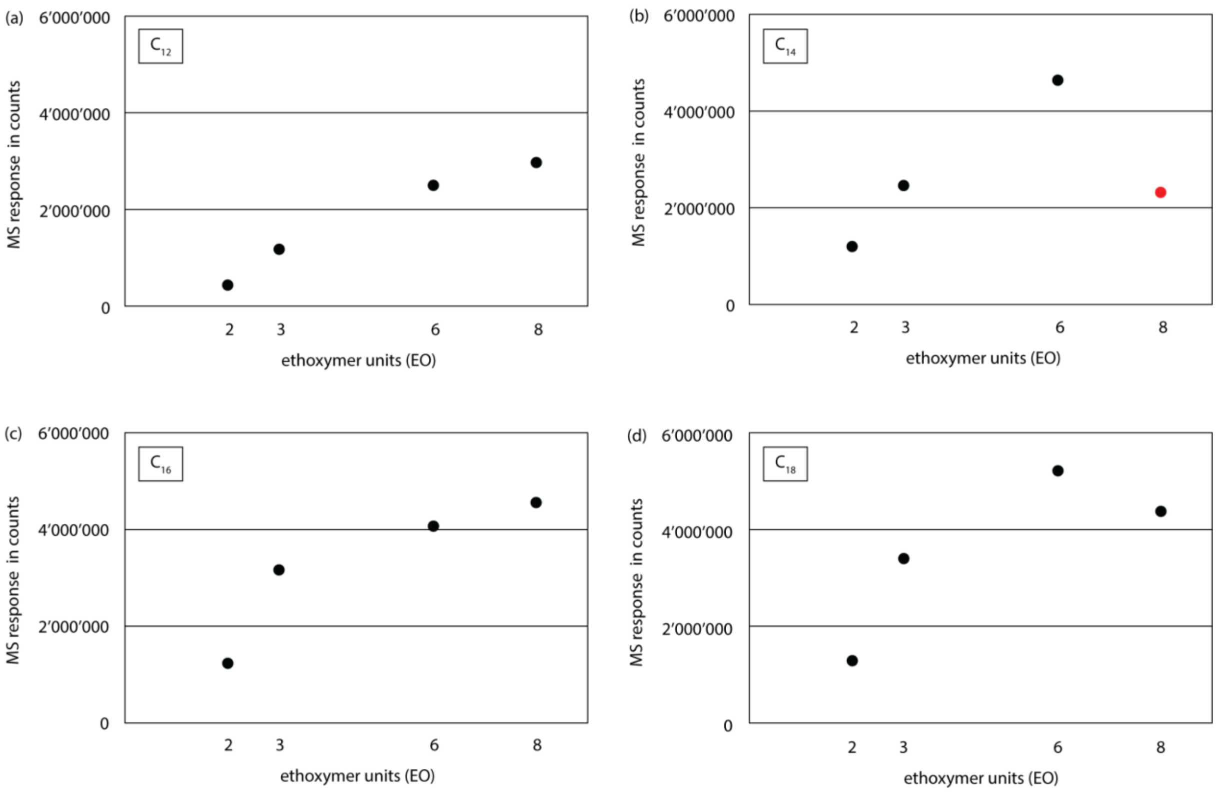

Figure S 1. Mass spectrometric responses for the available AEO standard material at a concentration of 0.1 mg L^{-1}. The responses are plotted for homologues with chain lengths (a) C_{12}, (b) C_{14}, (c) C_{16}, and (d) C_{18} and with ethoxymer units EO2, EO3, EO6, and EO8. The ionization efficiency increases with increasing ethoxylation and, to some degree, with increasing alkyl chain length. The response for C_{14}EO8-AEO is considered an outlier (red). The calibration curve for C_{14}-EO6 was applied to C_{14}-homologues with higher ethoxylation degrees.

The sludge matrix causes a strong signal suppression for AEO in the mass spectrometer. At a strong dilution of 1:100 (i.e., an extract of 0.002 g sludge per mL), the matrix suppression is negligible but the concentration of AEO in sludge is then too low to be detected at this dilution. At a lower dilution of 1:5 (i.e., 0.04 g sludge per mL), AEO can be detected, but with a signal suppression of around 80%. The internal standard C_{10}EO08-AEO is used to account for the varying matrix effects of the sludge extracts.

S4. WWTP and sample specifications

Information about the sampled WWTPs and the samples are provided in the two following tables. Sample containers were sent to the listed WWTPs with the instruction to sample anaerobic sludge from the digester. The requested sludge has preferably spend 25 days (on average) in the digester. The (anaerobic) sludge samples were taken from the digester's outlet by the staff of the WWTPs and then shipped to our lab. Sample sizes were about 50 g or 500 mL, depending on whether the sludge was already dewatered or not.

The WWTPS ZOF, HER,VISP and ZAL do not apply sludge digestion and have provided non-digested sludge.

Table S 7a. Information about the sampled WWTPs and the samples.

Sample ID	Name (location) of WWTP	Stabilized sludge production (kg d^{-1})	Connected population	Sampling year	State of sample	Average residence time in digester (d^{-1})
BUEH	Bühler	280	5000	2019	liquid	45
NEU	Neuchatel	3800	40600	2017	n/a	39
CHDF	La-Chaux-De-Fonds	2300	37500	2017	n/a	50
VEV	Vevey/Aviron	5500	51900	2017	n/a	35
UNT	Unterseen (Interlaken)	1400	25400	2017	n/a	30
WIN	Winterthur	12600	130000	2017	n/a	30
ZOF	Zofingen	8000	34100	2019	dewatered	0 (no anaerobic digestion)
VERN	Vernier/Aire	24500	440800	2017	n/a	n/a
FEH	Fehraltorf-Russikon	860	9600	2019	liquid & dewatered	27
ZUE	Zuerich (Werdhoelzli)	25700	429400	2017	n/a	n/a
CHUR	Chur	7600	54600	2017	n/a	18
BRUE	Bruegg (Muera Biel)	10000	85000	2017	n/a	30
BRI	Brig-Glis (Briglina)	3300	27700	2017	n/a	n/a
POSC	Poschiavo	480	3300	2017	n/a	20
AAR	Aarau	6600	74000	2017	n/a	25
RAM	Ramsen (Bibertal-Hegau)	5100	97600	2017	n/a	35
GLA	Glarnerland	3500	44700	2019	solid	23
OBE	Oberriet	720	8500	2019	liquid	23
UETE	Uetendorf (Thun)	5200	123000	2017	n/a	n/a
BUCH	Buchs	2200	23900	2017	n/a	28
REIN	Reinach (Oberwynental)	1800	17400	2017	n/a	25
OPF	Opfikon-Kloten	2900	37200	2017	n/a	6
DUE	Duebendorf	2600	36200	2017	n/a	14
HER	Herisau Bachwis	150	16200	2019	liquid & dewatered	0 (no anaerobic digestion)
SAM	Samedan	650	3600	2019 (+2020)	liquid & dewatered	23
LAU	Lausanne	23100	235000	2017	n/a	n/a
BIO	Bioggio (Lugano)	13400	125000	2017	n/a	n/a
WEIN	Weinfelden (Mittelthurgau)	2200	30100	2017	n/a	11
MUEN	Münchwilen	1000	20500	2019	liquid & dewatered	21
BAS	Basel	36300	268000	2017	n/a	n/a
RAN	Rancate/Mendrisio	4300	29000	2017	n/a	25
BIRS	Birsfelden (Birs II)	5400	82500	2017	n/a	15
DAVG	Davos (Gadenstatt)	1000	9900	2019 (+2020)	liquid	42
VISP	Visp/Lonza	18600	13000	2019	liquid	0 (no anaerobic digestion)
POR	Porrentruy (Sepe)	1500	16200	2017	n/a	n/a
ZAL	Zala AG	3200	39300	2019	solid	0 (no anaerobic digestion)

Table S 7b. Information about the sampled WWTPs and their treatment processes.

Sample ID	
BUEH	mechanical and biological treatment with phosphorous elimination
NEU	mechanical and biological treatment with advanced phosphorous elimination
CHDF	mechanical and biological treatment with advanced phosphorous elimination
VEV	mechanical and biological treatment with advanced phosphorous elimination
UNT	mechanical and biological treatment with advanced phosphorous elimination
WIN	mechanical and biological treatment with advanced phosphorous elimination, nitrification and denitrification
ZOF	mechanical and biological treatment with phosphorous elimination and nitrification
VERN	mechanical and biological treatment with phosphorous elimination and nitrification
FEH	mechanical and biological treatment with phosphorous elimination, nitrification and denitrification
ZUE	mechanical and biological treatment with advanced phosphorous elimination, nitrification and denitrification
CHUR	mechanical and biological treatment with advanced phosphorous elimination
BRUE	mechanical and biological treatment with advanced phosphorous elimination
BRI	mechanical and biological treatment with advanced phosphorous elimination
POSC	mechanical and biological treatment with advanced phosphorous elimination
AAR	mechanical and biological treatment with advanced phosphorous elimination
RAM	mechanical and biological treatment with phosphorous elimination, nitrification and denitrification
GLA	mechanical and biological treatment with phosphorous elimination, nitrification and denitrification
OBE	mechanical and biological treatment with phosphorous elimination and nitrification
UETE	mechanical and biological treatment with phosphorous elimination, nitrification and denitrification
BUCH	mechanical and biological treatment with phosphorous elimination and nitrification
REIN	mechanical and biological treatment with phosphorous elimination, nitrification and denitrification
OPF	mechanical and biological treatment with advanced phosphorous elimination, nitrification and denitrification
DUE	mechanical and biological treatment with advanced phosphorous elimination, nitrification and denitrification
HER	mechanical and biological treatment with phosphorous elimination
SAM	mechanical and biological treatment with advanced phosphorous elimination
LAU	mechanical and biological treatment with advanced phosphorous elimination
BIO	mechanical and biological treatment with advanced phosphorous elimination, nitrification and denitrification
WEIN	mechanical and biological treatment with phosphorous elimination and nitrification
MUEN	mechanical and biological treatment with phosphorous elimination, nitrification and denitrification
BAS	mechanical and biological treatment with advanced phosphorous elimination
RAN	mechanical and biological treatment with advanced phosphorous elimination and nitrification
BIRS	mechanical and biological treatment with advanced phosphorous elimination
DAVG	mechanical and biological treatment with advanced phosphorous elimination
VISP	mechanical and biological treatment with advanced phosphorous elimination
POR	mechanical and biological treatment with advanced phosphorous elimination
ZAL	mechanical and biological treatment with phosphorous elimination, nitrification and denitrification

S5. Concentrations of surfactants in sludge

This section summarizes the measured concentrations of the target analytes in Swiss sewage sludge. **Table S 8** to **Table S 12** give detailed data for LAS, SAS, AEO, NPEO, NP, NPEC, and *tert*-OP in the different WWTPs. The tables also list maximum, minimum, and average concentrations, as well as median values. **Figure S 2** shows summarizing boxplots for sludge concentrations and per capita loads for individual surfactant classes. **Figure S 3** plots sludge concentrations of (a) *tert*-OP and (b) NPEC for the different WWTPs. **Figure S 4** plots homologue distributions for (a) LAS and (b) SAS. The proportions of NP and *tert*-OP are plotted in **Figure S 5**. More detailed information about AEO homologues is given in the following **section S6**.

Table S 8. Levels of LAS in sewage sludge in µg g^{-1} d.w. (dry weight) and the respective per capita loads.

ID	C_{10}-LAS µg g^{-1} d.w.	C_{11}-LAS µg g^{-1} d.w.	C_{12}-LAS µg g^{-1} d.w.	C_{13}-LAS µg g^{-1} d.w.	Sum LAS µg g^{-1} d.w.	LAS per capita load per capita mg d^{-1}
BUEH	450	2500	3600	2900	9500	540
NEU	300	2100	3400	2600	8400	780
CHDF	340	2100	3100	2100	7800	480
VEV	270	1700	2600	2000	6600	700
UNT	300	1800	2500	1800	6400	360
WIN	300	1700	2500	1800	6300	610
ZOF	360	1700	2400	1800	6200	1500
VERN	250	1600	2400	1800	6000	340
FEH	280	1600	2200	1800	5900	530
ZUE	240	1500	2200	1600	5600	330
CHUR	200	1300	2000	1600	5100	700
BRUE	200	1300	2000	1600	5100	590
BRI	200	1400	2100	1400	5100	600
POSC	200	1300	2000	1400	4800	710
AAR	190	1300	1900	1400	4800	430
RAM	170	1100	1700	1300	4200	220
GLA	160	940	1500	1400	3900	310
OBE	160	870	1300	1000	3300	280
UETE	140	850	1300	970	3300	140
BUCH	74	630	1300	1200	3200	300
REIN	160	880	1200	800	3100	310
OPF	160	830	1200	730	2900	220
DUE	140	810	1100	760	2900	200
HER	120	580	930	990	2600	24
SAM	100	590	920	860	2500	450
LAU	89	530	860	680	2100	210
BIO	50	430	870	790	2100	230
WEIN	93	550	820	630	2100	160
MUEN	65	390	760	760	2000	98
BAS	89	470	720	530	1800	240
RAN	73	430	690	560	1800	260
BIRS	58	320	460	340	1200	76
DAVG	34	170	280	280	770	78
VISP	67	200	180	110	550	780
POR	8	62	130	140	340	31
ZAL	2	17	26	28	74	6
Maximum	**450**	**2500**	**3600**	**2900**	**9500**	**1500**
Minimum	**2**	**17**	**26**	**28**	**74**	**6**
Average	**170**	**1000**	**1500**	**1200**	**3900**	**380**
Median	**160**	**880**	**1300**	**1100**	**3300**	**310**

Table S 9. Levels of SAS in sewage sludge in µg g^{-1} d.w. (dry weight) and the respective per capita loads.

ID	**C_{14}-SAS** µg g^{-1} d.w.	**C_{14}-SAS** µg g^{-1} d.w.	**C_{14}-SAS** µg g^{-1} d.w.	**C_{14}-SAS** µg g^{-1} d.w.	**Sum SAS** µg g^{-1} d.w.	**SAS per capita load** per capita mg d^{-1}
BUEH	46	57	95	64	260	15
NEU	80	120	250	210	660	61
CHDF	76	110	220	180	600	36
VEV	62	87	170	140	460	49
UNT	76	97	170	130	470	26
WIN	53	71	130	97	350	34
ZOF	13	15	29	16	73	17
VERN	50	71	140	120	380	21
FEH	19	27	60	43	150	13
ZUE	46	61	120	90	320	19
CHUR	46	68	140	110	360	50
BRUE	44	63	130	98	330	39
BRI	39	58	120	81	290	35
POSC	25	34	63	44	170	25
AAR	37	56	110	76	270	25
RAM	17	25	52	37	130	6.9
GLA	22	29	67	49	170	13
OBE	24	33	69	44	170	14
UETE	27	37	71	51	190	7.9
BUCH	11	29	79	74	190	18
REIN	29	36	59	36	160	16
OPF	27	31	59	35	150	12
DUE	22	28	51	31	130	9.3
HER	2.2	0.94	1.8	1.2	6.2	0.06
SAM	26	38	81	63	210	38
LAU	9.7	14	30	20	73	7.2
BIO	2.1	5.1	19	18	45	4.8
WEIN	10	13	26	17	66	4.9
MUEN	7.9	11	23	17	59	3.0
BAS	10	12	22	13	56	7.6
RAN	5.9	7.2	15	10	39	5.7
BIRS	8.4	8.5	16	9.8	43	2.8
DAVG	2.8	2.8	7	4.4	17	1.7
VISP	0.09	0.03	0.03	0.01	0.15	0.21
POR	0.31	0.30	0.92	0.97	2.5	0.23
ZAL	0.29	0.04	0.10	0.01	0.44	0.04
Maximum	78	120	250	214	660	61
Minimum	0.09	0.03	0.03	0.01	0.15	0.04
Average	27	38	75	57	200	18
Median	23	30	62	44	160	14

Table S 10. Levels of AEO in sewage sludge in μg g^{-1} d.w. (dry weight) and the respective per capita loads. The average chain lengths and proportion of branched AEO are also listed.

ID	C_{12}-AEO	C_{13}-AEO	C_{14}-AEO	C_{15}-AEO	C_{16}-AEO	C_{17}-AEO	C_{18}-AEO	Sum AEO	AEO per capita load	Average chain length	Proportion of branched AEO
	μg g^{-1} d.w.	μg g^{-1} d.w.	μg g^{-1} d.w.	μg g^{-1} d.w.	μg g^{-1} d.w.	μg g^{-1} d.w.	μg g^{-1} d.w.	μg g^{-1} d.w.	per capita mg d^{-1}		
BUEH	1.46	0.53	0	0.75	6.25	11.2	10.6	30.8	1.73	16.8	99.9
NEU	1.03	0.45	0.25	2.12	7.48	6.22	6.62	24.2	2.24	16.5	92.8
CHDF	0	0.07	0.12	1.46	3.82	4.86	3.76	14.1	0.85	16.7	99.4
VEV	0	0.05	0.05	0.96	3.6	3.37	1.8	9.82	1.05	16.6	99.5
UNT	0	8.74	0	0.71	5.51	5.53	3.8	24.3	1.34	15.4	99.8
WIN	0	0.17	0	0.9	2.14	3.74	2.11	9.06	0.88	16.7	96.3
ZOF	0.09	0.07	0.7	2.44	2.97	2.52	3.46	12.2	2.88	16.4	62.7
VERN	0	0	0	0.62	1.98	2.43	1.92	6.96	0.39	16.8	100.0
FEH	0	0	0	0.46	1.63	2.81	1.88	6.77	0.61	16.9	99.9
ZUE	0	0.01	0	0.39	2.44	2.4	1.62	6.85	0.41	16.8	99.9
CHUR	0	0.02	0	1.02	2.17	3.64	2.29	9.15	1.27	16.8	99.7
BRUE	0	0.02	0	0.28	0.79	1.52	0.98	3.59	0.42	16.9	98.3
BRI	0	0.06	0	0.52	0.81	2.31	1	4.7	0.56	16.8	98.6
POSC	1.71	3.46	0.02	0.03	0.08	1.14	0.67	7.11	1.05	13.9	100.0
AAR	1.13	4.75	0.03	0.47	6.51	1.94	5.55	20.4	1.82	15.7	98.9
RAM	0.64	1.72	0.03	0.33	1.53	2.09	2.27	8.6	0.45	15.8	99.7
GLA	0.01	0	0.37	3.39	6.3	7.24	7.22	24.5	1.92	16.7	100.0
OBE	0	0	0	0.17	0.71	1.27	0.97	3.12	0.26	17.0	100.0
UETE	0	0	0	0.49	1.72	1.92	1.31	5.43	0.23	16.7	100.0
BUCH	0	0	0	0.2	0.67	1.62	0.6	3.08	0.28	16.8	100.0
REIN	0	0	0	0.04	0.22	0.5	0.32	1.09	0.11	17.0	95.2
OPF	0	0	0	0.16	1.09	1.31	1.26	3.82	0.3	17.0	100.0
DUE	1.4	3.73	0	0	0.6	1.12	0.69	7.54	0.53	14.1	100.0
HER	0.11	2.13	0	0.21	1.49	3.09	2.99	10.0	0.09	16.2	97.9
SAM	0	0	0	0.94	1.69	2.44	1.86	6.93	1.26	16.8	98.5
LAU	0.02	0.54	0.08	1.56	0.83	1.1	1.55	5.69	0.56	16.1	53.0
BIO	0.07	0	0	0	0.03	0.66	0.44	1.19	0.13	17.1	94.3
WEIN	1.65	5.48	0.02	0	0.51	1.03	0.76	9.46	0.7	13.8	99.8
MUEN	0	0.3	0	0.14	0.59	1.18	0.53	2.74	0.14	16.4	100.0
BAS	1.06	0.7	0.64	1.72	1.36	0.71	1.39	7.58	1.02	15.2	34.9
RAN	0.02	0.61	0	0	0.81	1.15	1.23	3.82	0.56	16.5	99.6
BIRS	0.94	6.28	0	0.02	1.28	1.25	1.12	10.9	0.71	14.2	99.0
DAVG	0	0	0.06	0.7	0.83	1.62	0.69	3.9	0.4	16.6	100.0
VISP	2.41	8.5	1.21	1.11	0.5	0.56	0.55	14.8	21.3	13.5	55.7
POR	0	0.21	0	0	0	0.02	0.03	0.26	0.02	13.8	78.3
ZAL	0	0	0	0	0	0	0.05	0.05	0.004	18.0	0.0
Maximum	2.41	8.74	1.21	3.39	7.48	11.2	10.6	30.8	21.3	18.0	100.0
Minimum	0	0	0	0	0	0	0.03	0.05	0.004	13.5	0.0
Average	0.38	1.35	0.1	0.67	1.97	2.43	2.11	9.02	1.35	16.1 ± 1.1	90.3 ± 22.1
Median	0	0.07	0	0.46	1.32	1.77	1.35	7.03	0.56	16.7	99.6

Table S 11. Levels of NP, NPEO (EO1-3), NP1EC, and *tert*-OP in sewage sludge in µg g^{-1} d.w. (dry weight). Per capita loads are listed in Table S 12.

ID	NP µg g^{-1} d.w.	NP1EO µg g^{-1} d.w.	NP2EO µg g^{-1} d.w.	NP3EO µg g^{-1} d.w.	Sum NPEO µg g^{-1} d.w.	NP1EC µg g^{-1} d.w.	*tert*-OP µg g^{-1} d.w.
BUEH	18.5	23.6	0.18	0.27	24.1	1.65	2.15
NEU	6.66	13.1	0.32	0.30	13.7	0.20	103
CHDF	13.6	5.4	0.14	0.25	5.8	0.43	4.31
VEV	2.03	32.6	0.33	0.52	33.5	0.41	2.42
UNT	7.94	10.4	0.17	0.31	10.9	0.58	0.98
WIN	4.16	12.8	0.24	0.34	13.4	0.27	0.81
ZOF	0.42	362	0.34	0.68	363	0.02	0.72
VERN	2.81	13.4	0.32	0.34	14.0	0.26	1.33
FEH	2.23	12.6	0.08	0.17	12.9	0.10	0.80
ZUE	4.47	18.1	0.22	0.35	18.7	0.46	2.62
CHUR	2.53	23.2	0.22	0.30	23.7	0.24	1.08
BRUE	9.91	9.4	0.22	0.27	9.9	0.29	2.59
BRI	8.03	15.6	0.31	0.46	16.4	0.40	1.54
POSC	6.24	8.6	0.33	0.43	9.4	0.18	1.15
AAR	2.16	29.8	0.27	0.76	30.9	0.24	1.37
RAM	4.38	12.2	0.16	0.23	12.6	0.08	1.78
GLA	6.93	16.1	0.32	0.35	16.8	0.18	38.1
OBE	6.91	5.2	0.06	0.14	5.4	0.25	0.98
UETE	3.87	20.4	0.26	0.33	21.0	0.36	1.56
BUCH	8.28	5.2	0.07	0.18	5.4	0.69	2.07
REIN	2.88	9.3	0.16	0.27	9.8	0.15	0.58
OPF	4.07	22.8	0.30	0.47	23.6	0.36	3.74
DUE	2.00	14.8	0.19	0.20	15.2	0.23	6.98
HER	1.18	177	0.24	0.21	177	0.57	1.63
SAM	2.71	21.6	0.16	0.29	22.1	0.08	1.07
LAU	0.59	164	0.28	0.47	164	0.04	1.30
BIO	7.91	10.9	0.18	0.25	11.3	1.97	7.09
WEIN	4.82	7.6	0.21	0.21	8.0	0.28	0.85
MUEN	3.50	11.1	0.15	0.22	11.5	0.25	0.78
BAS	0.17	153	0.32	0.52	154	0.36	0.92
RAN	1.65	14.1	0.15	0.20	14.4	0.32	1.41
BIRS	2.05	29.5	0.19	0.22	29.9	0.10	1.36
DAVG	1.05	36.2	0.19	0.35	36.8	0.04	0.61
VISP	0.20	8.6	0.07	0.19	8.9	0	0.19
POR	6.76	4.3	0.10	0.21	4.6	1.30	1.16
ZAL	0.28	74.4	0.11	0.20	74.7	0.10	0.53
Maximum	18.5	362	0.34	0.76	363 (36.8*)	1.97 (1.97**)	103 (7.09***)
Minimum	0.17	4.3	0.06	0.14	4.6 (4.6*)	0 (0.02**)	0.19 (0.19***)
Average	4.55	39.1	0.21	0.32	39.7 (16.0*)	0.37 (0.38**)	5.61 (1.78***)
Median	3.69	14.4	0.20	0.28	14.8 (13.7*)	0.26 (0.26**)	1.34 (1.31***)

* calculated after excluding WWTPs that exceeded the suggested limit value of 50 ug g^{-1} d.w. (n = 5); ** calculated after excluding the WWTP VISP, where NP1EC was not detected;
*** calculated after excluding the two extreme outliers (the WWTPs NEU and GLA)

Table S 12. Per capita loads of NP, NPEO (EO1-3), NP1EC, and *tert*-OP.

ID	NP per capita mg d^{-1}	NP1EO per capita mg d^{-1}	NP2EO per capita mg d^{-1}	NP3EO per capita mg d^{-1}	Sum NPEO per capita mg d^{-1}	NP1EC per capita mg d^{-1}	*tert*-OP per capita mg d^{-1}
BUEH	1.04	1.33	0.010	0.015	1.35	0.09	0.12
NEU	0.62	1.22	0.030	0.028	1.27	0.02	9.58
CHDF	0.82	0.33	0.008	0.015	0.35	0.03	0.26
VEV	0.22	3.48	0.036	0.056	3.57	0.04	0.26
UNT	0.44	0.58	0.010	0.017	0.60	0.03	0.05
WIN	0.40	1.24	0.023	0.033	1.30	0.03	0.08
ZOF	0.10	85.0	0.081	0.159	85.3	0.01	0.17
VERN	0.16	0.74	0.018	0.019	0.78	0.01	0.07
FEH	0.20	1.13	0.007	0.015	1.15	0.01	0.07
ZUE	0.27	1.09	0.013	0.021	1.12	0.03	0.16
CHUR	0.35	3.21	0.031	0.042	3.28	0.03	0.15
BRUE	1.16	1.10	0.026	0.031	1.16	0.03	0.30
BRI	0.96	1.86	0.037	0.055	1.95	0.05	0.18
POSC	0.92	1.28	0.048	0.063	1.39	0.03	0.17
AAR	0.19	2.66	0.024	0.068	2.75	0.02	0.12
RAM	0.23	0.64	0.008	0.012	0.66	0.00	0.09
GLA	0.54	1.26	0.025	0.028	1.31	0.01	2.99
OBE	0.58	0.43	0.005	0.012	0.45	0.02	0.08
UETE	0.16	0.87	0.011	0.014	0.89	0.02	0.07
BUCH	0.77	0.48	0.006	0.016	0.50	0.06	0.19
REIN	0.29	0.94	0.017	0.028	0.98	0.02	0.06
OPF	0.32	1.76	0.024	0.037	1.82	0.03	0.29
DUE	0.14	1.04	0.013	0.014	1.07	0.02	0.49
HER	0.01	1.64	0.002	0.002	1.64	0.01	0.02
SAM	0.49	3.94	0.028	0.053	4.02	0.01	0.19
LAU	0.06	16.1	0.027	0.046	16.1	0.004	0.13
BIO	0.84	1.16	0.019	0.027	1.21	0.21	0.76
WEIN	0.36	0.56	0.016	0.015	0.60	0.02	0.06
MUEN	0.17	0.55	0.008	0.011	0.57	0.01	0.04
BAS	0.02	20.7	0.043	0.071	20.8	0.05	0.12
RAN	0.24	2.07	0.022	0.030	2.12	0.05	0.21
BIRS	0.13	1.93	0.013	0.015	1.96	0.01	0.09
DAVG	0.11	3.17	0.020	0.036	3.77	0.004	0.06
VISP	0.29	12.4	0.094	0.269	12.7	0	0.27
POR	0.63	0.40	0.009	0.019	0.43	0.12	0.11
ZAL	0.02	6.07	0.009	0.016	6.10	0.01	0.04
Maximum	1.16	85.0	0.094	0.269	85.3 (12.7*)	0.21 (0.21**)	9.58 (0.76***)
Minimum	0.01	0.33	0.002	0.002	0.35 (0.35*)	0 (0.003**)	0.02 (0.02***)
Average	0.40	5.14	0.023	0.039	5.20 (1.84*)	0.03 (0.03**)	0.50 (0.16***)
Median	0.29	1.25	0.018	0.027	1.31 (1.21*)	0.02 (0.02**)	0.13 (0.12***)

* calculated after excluding WWTPs that exceeded the suggested limit value of 50 ug g^{-1} d.w. (n = 5); ** calculated after excluding the WWTP VISP, where NP1EC was not detected;
*** calculated after excluding the two extreme outliers (the WWTPs NEU and GLA)

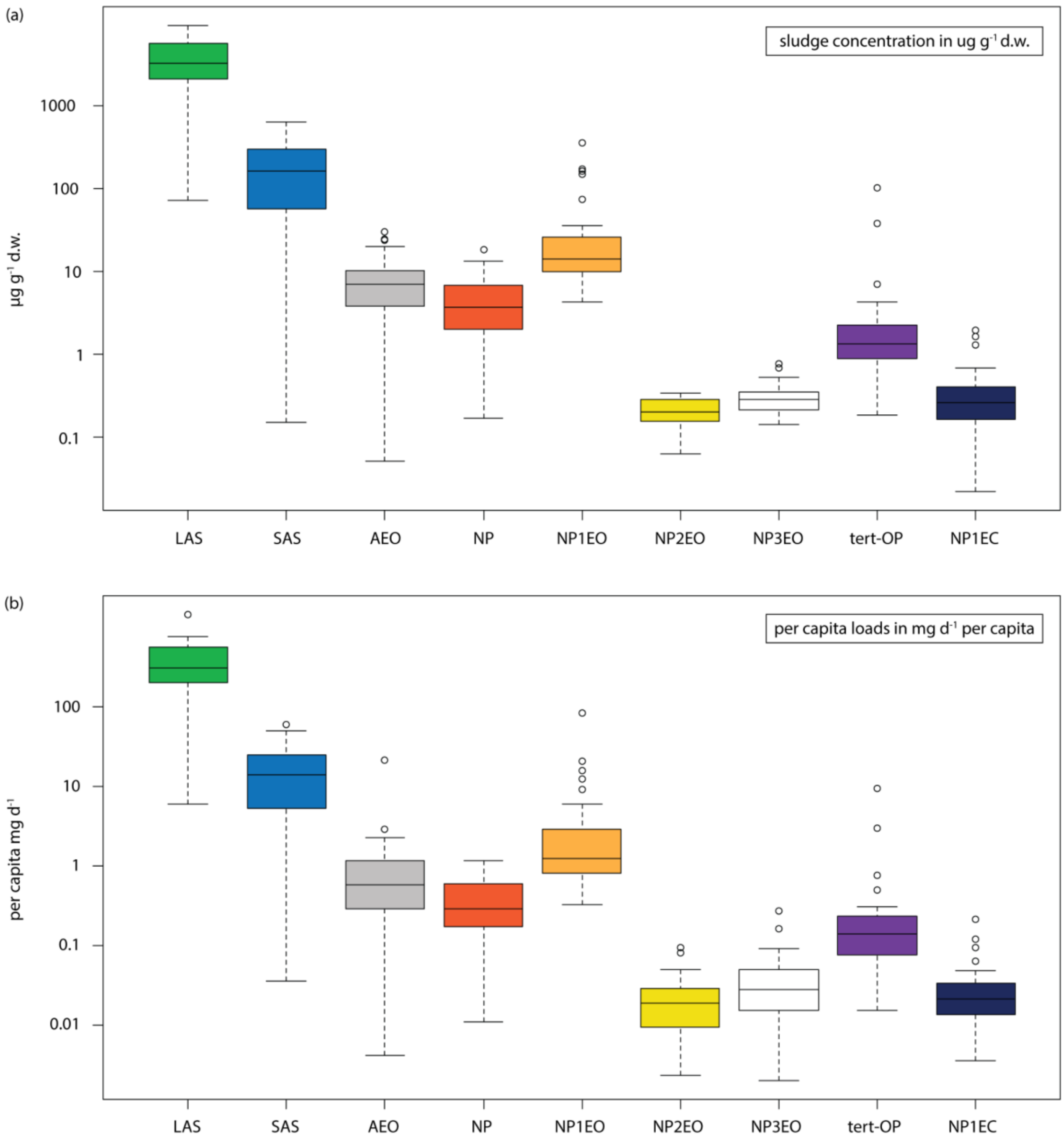

Figure S 2. Summarizing boxplots for levels of target analytes in all sampled WWTPs for (a) sludge concentrations (µg g^{-1} d.w.) and (b) per capita loads (mg d^{-1} per capita).

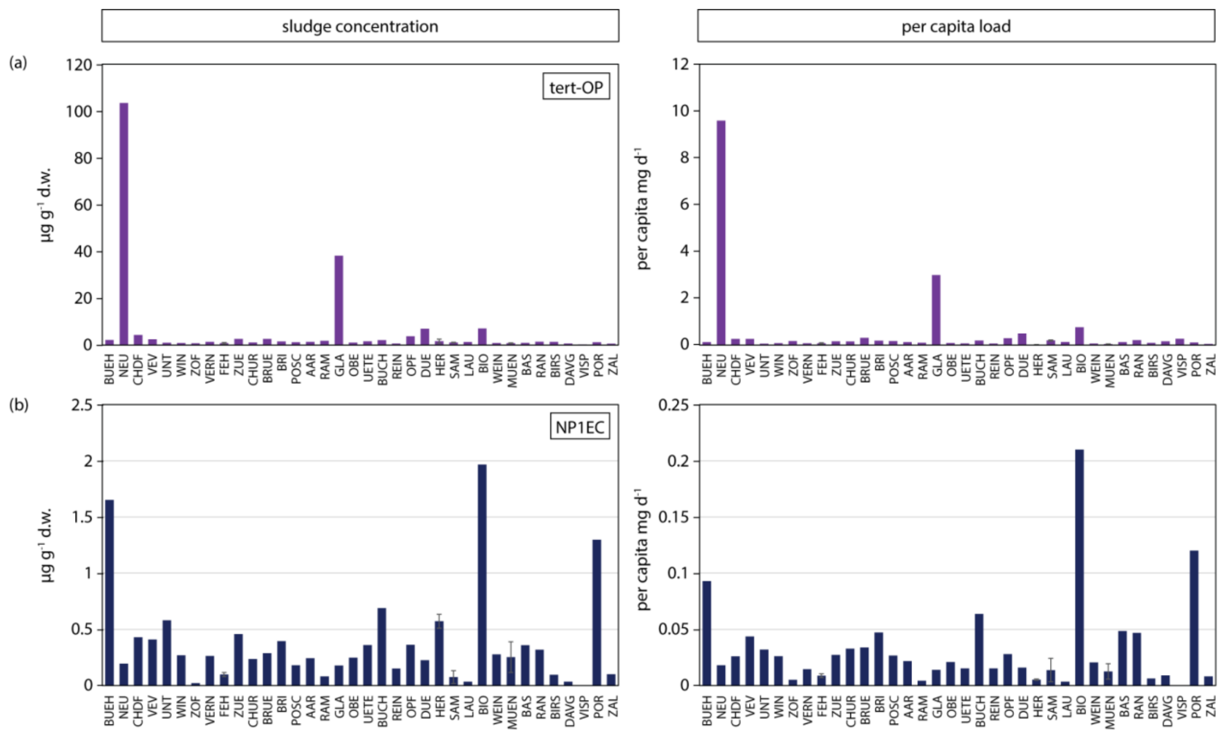

Figure S 3. Concentration levels of (a) *tert*-OP and (b) NP1EC in sampled WWTPs. Right panels show actual sludge concentrations (sludge dry weight, d.w.) whereas left panels show daily per capita loads in sludge. Range bars are depicted for the WWTPs that provided more than one sludge sample.

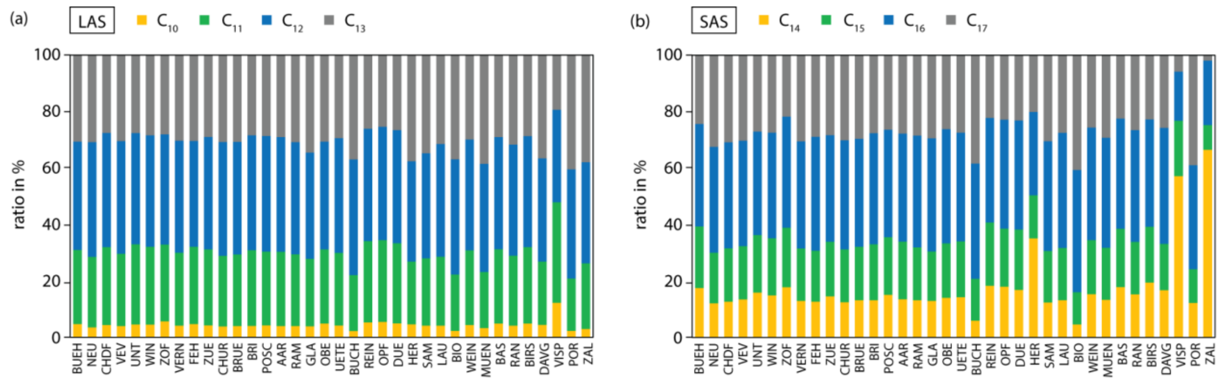

Figure S 4. Carbon chain length distribution of the homologues for (a) LAS and (b) SAS.

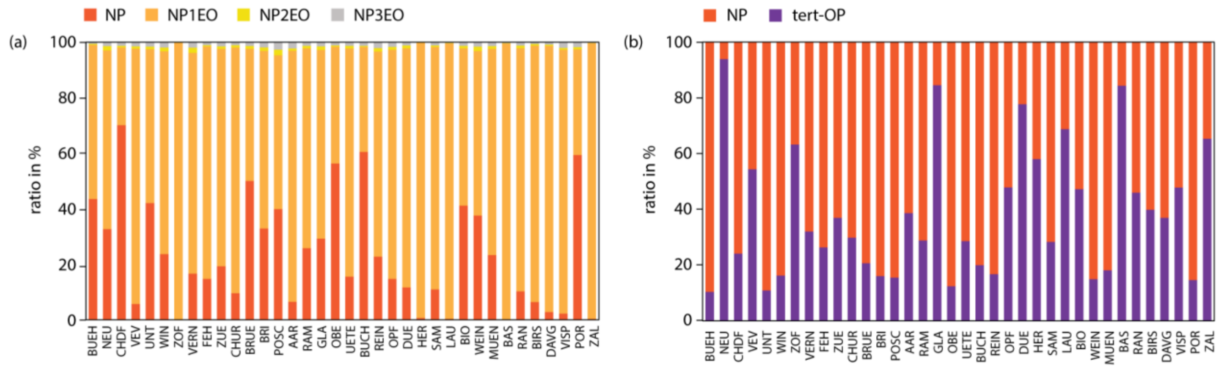

Figure S 5. Distribution of (a) NP and NPEO levels, and (b) NP and *tert*-OP levels in sludge.

S6. AEO homologue data

Table S 13. Average chain lengths of AEO isomers for linear and branched homologues, as well as for the sum of them. The average AEO chain length was derived for each individual sample. These average values were then used to derive the values of the table.

	Linear	**Branched**	**Sum**
Average	14.9 ± 2.0	16.2 ± 1.1	16.1 ± 1.1
Median	14.1	16.7	16.7
Maximum	18.0	17.4	18.0
Minimum	12.0	13.5	13.5

Table S 14. Average ethoxymer units of AEO isomers for linear homologues. The average AEO ethoxymer unit was derived for each individual sample. These average values were then used to derive the values of the table.

Linear	**Average**	**Median**	**Maximum**	**Minimum**
C_{12}	10.3 ± 2.4	9.5	13.5	6.9
C_{13}	8.0 ± 2.2	7.8	12.0	3.0
C_{14}	7.6 ± 1.4	7.8	9.0	5.2
C_{15}	7.0 ± 0.9	7.0	8.4	6.0
C_{16}	6.3 ± 0.9	6.0	7.5	5.3
C_{17}	Not detected	-	-	-
C_{18}	7.5 ± 1.2	7.6	9.8	5.5
All	8.2 ± 1.9	8.0	13.0	3.0

Table S 15. Average ethoxymer units of AEO isomers for branched homologues. The average AEO ethoxymer unit was derived for each individual sample. These average values were then used to derive the values of the table.

Branched	**Average**	**Median**	**Maximum**	**Minimum**
C_{12}	8.9 ± 1.2	8.6	11.0	7.5
C_{13}	9.0 ± 0.7	8.7	10.3	7.9
C_{14}	6.2 ± 1.6	6.9	8.0	4.0
C_{15}	6.3 ± 0.8	6.1	8.0	4.2
C_{16}	7.4 ± 0.9	7.5	9.1	5.0
C_{17}	7.5 ± 0.8	7.5	9.0	4.0
C_{18}	7.4 ± 1.0	7.6	8.7	5.0
All	7.7 ± 0.6	7.7	9.0	6.6

Table S 16. Average ethoxymer units of AEO isomers for the sum of linear and branched homologues. The average AEO ethoxymer unit was derived for each individual sample. These average values were then used to derive the values of the table.

Sum	**Average**	**Median**	**Maximum**	**Minimum**
C_{12}	9.5 ± 1.9	8.8	13.5	6.9
C_{13}	8.3 ± 1.2	8.4	10.5	4.7
C_{14}	6.8 ± 1.7	7.5	9.0	4.0
C_{15}	6.3 ± 0.8	6.1	8.1	4.2
C_{16}	7.3 ± 0.9	7.4	9.1	5.0
C_{17}	7.5 ± 0.8	7.5	9.0	4.0
C_{18}	7.5 ± 1.0	7.6	9.3	5.0
All	7.7 ± 0.7	7.7	9.4	6.6

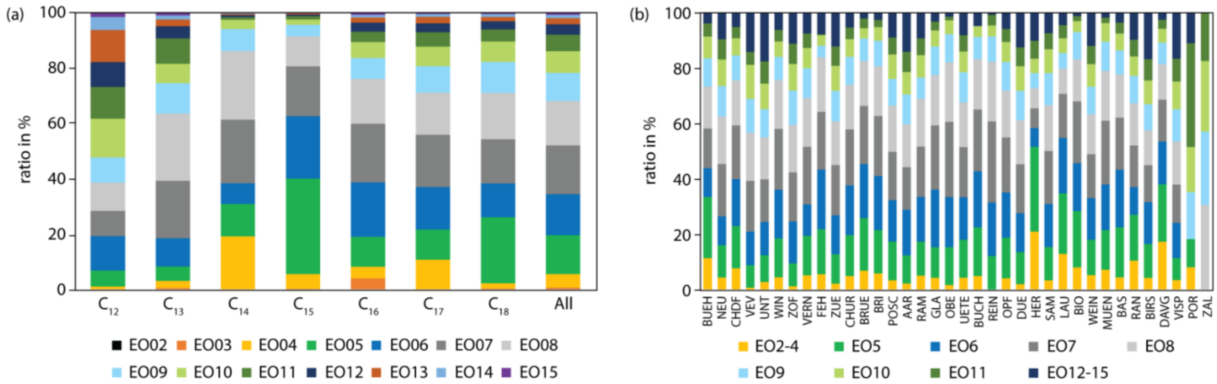

Figure S 6. Relative abundances of different ethoxymer units. (a) Ethoxymer distributions for homologues of different chain lengths. The last bar displays the weighted average of ethoxymer units of all chain length homologues. (b) The average ethoxymer distribution is comparable between most WWTPs.

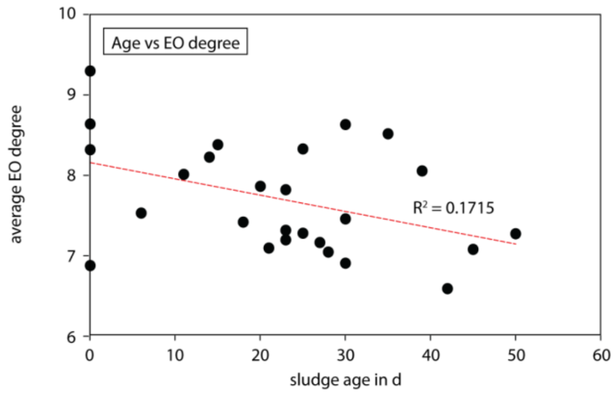

Figure S 7. No apparent relation is observed between the sludge age and the average ethoxylation degree of AEO homologues present in the sludge.

S7. Data correlations

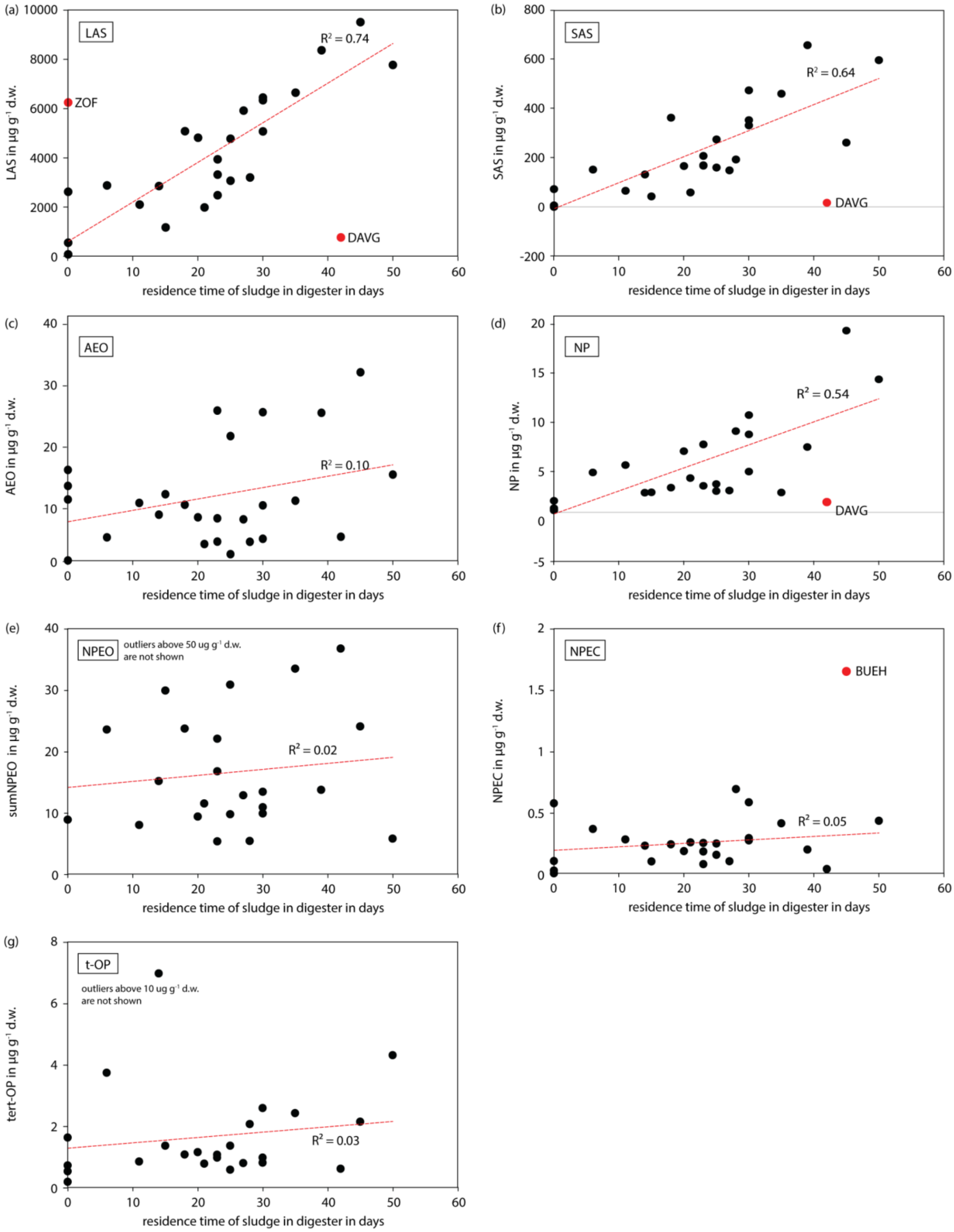

Figure S 8. Correlations between surfactant levels and residence time in the digester (anaerobic). A correlation is evident between sludge age and (a) LAS levels, (b) SAS levels, and (d) NP levels. No correlation is apparent between sludge age and (c) AEO levels, (e) sum NPEO levels, (f) NPEC levels, and (g) *tert*-OP levels. Visually outlying data points that were not considered for the linear regression are highlighted in red.

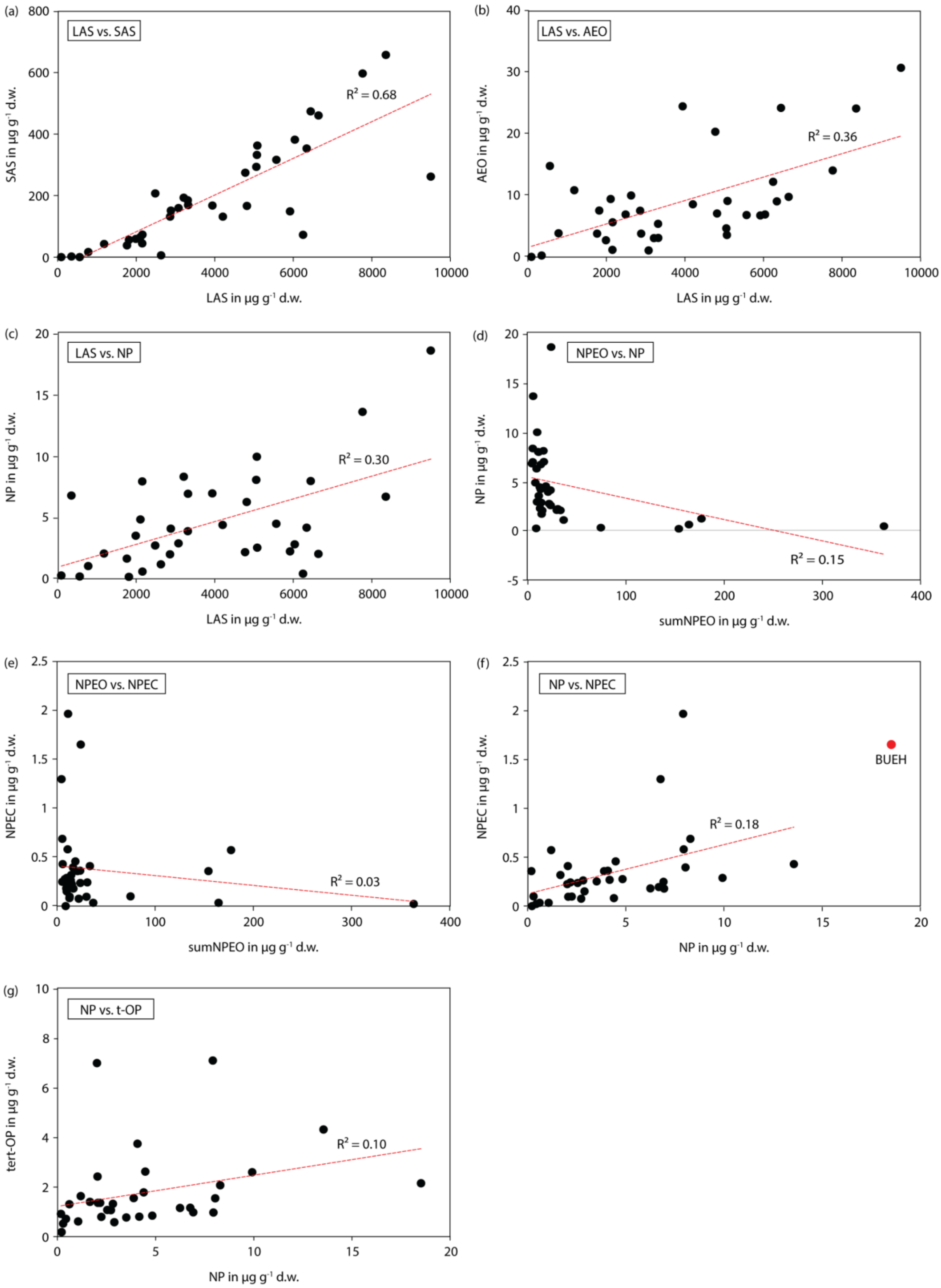

Figure S 9. Correlations between surfactant classes. Levels of surfactants are plotted against each other. A correlation is evident between LAS and (a) SAS levels. A trend toward a linear relationship is evident between (b) LAS levels and AEO levels and (c) (b) LAS levels and NP levels, but with higher dispersion than for LAS vs. SAS. Outlying data points that were not considered for the linear regression are highlighted in red.

S8. References

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