

Supplementary Information

Helping WWTP managers to address the volatile methylsiloxanes issue -
behaviour and complete mass balance in a conventional plant

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	Water		Air		Biogas LMC ($\mu\text{g}/\text{m}^3$)	Solid Sludge		Liquid Sludge	
	LOD (ppb)	LMC (ng/L)	LOD (ppb)	LMC (pg/m ³)		LOD (ppb)	LMC (ng/g dw)	LOD (ppb)	LMC (ng/L ww)
D3	1.97E-01	6.58E+00	3.06E-01	5.47E+01	3.00E+01	4.17E-01	9.11E-01	4.20E-01	2.10E+01
D4	1.27E-02	4.24E-01	2.03E-02	3.63E+00	3.00E+01	5.47E-02	1.20E-01	5.00E-02	2.50E+00
D5	2.20E-03	7.34E-02	2.63E-03	3.99E-01	3.00E+01	5.09E-03	1.11E-02	1.00E-02	5.00E-01
D6	4.16E-02	1.39E+00	2.00E-02	3.04E+00	N.M.*	1.10E-01	2.41E-01	1.10E-01	5.50E+00
L3	2.34E-01	7.81E+00	1.90E-01	2.83E+01	3.00E+01	7.89E-01	1.73E+00	7.90E-01	3.95E+01
L4	1.03E-01	3.45E+00	5.62E-02	9.12E+00	3.00E+01	1.58E-01	3.45E-01	1.60E-01	8.00E+00
L5	4.29E-01	1.43E+01	1.36E-01	2.07E+01	3.00E+01	2.73E-01	5.96E-01	2.70E-01	1.35E+01

N.M - not measured; dw – dry weight; ww – wet weight

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1. Supplementary Materials and Methods

1.1. Chemicals and materials

Linear (L3-L5) and cyclic (D3-D6) volatile methylsiloxanes, as well as tetrakis(trimethylsilyloxy) silane (M4Q), used as surrogate standard, were purchased from Sigma-Aldrich (St. Louis, MO, USA) with purity >97%. From the commercial standards, individual stock solutions of 1.00 g/L were prepared in hexane. For M4Q, a 10 mL standard solution in n-hexane (HEX) with a concentration of 5.00 mg L⁻¹ was prepared from a stock solution of 1 g/L and 100 mg/L, respectively. All solutions were stored at -20°C and protected from light.

The solvents used were HEX, dichloromethane (DCM), ethyl acetate (EA) and acetone, purchased from VWR International (Leuven, Belgium), all analytical grade. Nitrogen for extract blow-down was supplied by Linde (Maia, Portugal). To perform the QuEChERS (quick, easy, cheap, effective, rugged and safe) extraction, anhydrous magnesium sulfate (MgSO_4) was used, previously baked at 450 °C for 12 h, obtained from Panreac (Darmstadt, Germany), while PSA (primary and secondary amine) and C18 (“octadecyl-silica”) sorbents were obtained from Supelco (Bellefonte, PA, USA). To clean the XAD-2 resin (also from Supelco) before use, a mixture of HEX:DCM (1:1). Polytetrafluoroethylene (PTFE) bottles (250 mL) from VWR were used to collect sludge and wastewater, whereas biogas was sampled with 1 L Tedlar bags from Supelco. 50 mL conical bottom Falcon-type polypropylene (PP) tubes, and 1.5 mL injection vials were obtained from VWR, as were the glass amber vials of different volumes (i.e., 12, 15, and 60 mL) and the glass separation funnels.

1.2. Processing conditions details and plant limitations

Detailed information on processing conditions can be consulted in the literature (Cunha, 2017; Moura Fernandes, 2015; Silva Lopes, 2017). In brief, the WWTP receives both, domestic and industrial wastewater from four different pipes. The discharge of these pipes takes place in an equalization tank. This tank is equipped with a bypass pipe, designed to send the excess water directly to the effluent in case maximum treatment capacity of the ETAR (i.e., 800 L/s) is exceeded (in situations of extremely high pluviosity). Afterwards, the wastewater is conducted through to sieves (20 and 5 mm) to the pretreatment step, consisting of two tanks of 308 m³ used to remove sands and fats. This unit is also equipped with a bypass pipe, connected to the secondary treatment, which works when the wastewater flow is higher than 190 L/s. The wastewater is then conducted to the primary treatment, consisting of two decanters (having each one a diameter of 31.5 m and a volume of 2750 m³). The average retention time in these units is 6.4 ± 0.5 h. Then, wastewater is sent to the secondary treatment, while sludge is conducted to thickening. This treatment consists of two different installations: two aeration tanks (having each one a volume of 3882 m³ and an aeration flow of 562 kg- O_2 /h), where the activated sludge biological treatment takes place, and two secondary decanters (having each one a diameter of 38 m and a volume of 4150 m³). Average retention times are, respectively, 5.2 ± 0.2 h and 9.9 ± 0.7 h. The entrance of the secondary treatment has also a bypass pipe, connected to the effluent, that works in cases of extremely high pluviosity to avoid malfunction in aeration tanks. The treated wastewater is then pumped to the effluent pipe from the secondary decanters to the ocean, and the secondary sludge is sent to the equalization tank. Regarding sludge, the product from the primary decanters arrives to two thickeners (having each one a volume of 276 m³, with a retention time of 1.6 ± 0.3 d), and a subsequent step of FeCl_3 addition. After this, the sludge is sent to two anaerobic digesters (having each one a volume of 3000 m³) where it remains for 21.0 ± 0.4 d at constant temperature of approximately 36 °C. Biogas generated in this unit is storage in a 1720 m³ gasometer. Digested sludge is dehydrated in two centrifuges, and subsequently stored in a 100 m³ silo.

As can be deduced from the information above, the management of the WWTP presents a series of technical and environmental challenges to cope with. First, the volume and composition of the industrial discharges entering the plant is unknown and variable. This fact can affect the performance of the plant, as well as the need of more intensive treatments. Second, three bypass pipes are present in the WWTP. This technology is meant to secure the correct functioning of the different treatments, but at the same time implies that part of the wastewater will be discharged into the ocean without proper treatment. Finally, the fact that the temperature is not controlled in any unit (except the anaerobic digesters) may negatively impact the efficiency of the treatment, especially in the processes more sensitive to thermal changes (such as aeration or centrifugation).

1.3. Quality Assurance/Quality Control (QA/QC)

VMSs are ubiquitous compounds and to prevent and/or reduce any cross contamination during the sampling and extraction process, the use of products containing siloxanes in the laboratory was avoided by the researchers (especially personal care products (PCPs) and common cleaning detergents). Moreover, the needles used to reduce the volume with nitrogen were submerged in acetone and taken to the ultrasound bath for 15 min, while microsyringes from Hamilton (Reno, USA) were washed with acetone and HEX, before and after use. The rest of the material used was washed with a VMS-free detergent, and rinsed with water, distilled water, and acetone. After washing, this material was dried at 40 °C in an WTC Binder 7200 E115 oven (Tuttlingen, Germany). All non-volumetric glassware (amber vials, beakers, GC-MS injection vials, Pasteur pipettes and separation funnels), and aluminum foil used in the extraction method were baked at 400 °C for 4 h before used in a Nabertherm furnace (Lilienthal, Germany), to eliminate possible residues/contaminants in the material.

For wastewater, sludge and passive air analysis, two laboratory blanks were prepared for each day of extractions to detect any external contamination. For the passive air samples, upon deployment, a field blank (consisting of a cylinder with 10 g of XAD-2) was also performed in each site, exposing the cylinder during the deployment process to uncover any contamination from sample manipulation and transportation. Whenever blanks revealed detected levels of VMSs, the pertinent correction was made, subtracting the blank concentration to the final extract concentration. Injections with HEX were performed in the GC-MS every four sample injections to avoid carry-over issues, which were not relevant in this case.

The method limits of detection (LOD) and lowest measurable concentrations (LMCs) varied depending on matrix and congener analyzed. To calculate LMCs for wastewater and liquid sludge, the following equation was used:

$$LMC_{i,k} \left(\frac{ng}{L} \right) = \frac{LOD_{i,k} (ppb)}{SV_k (mL)} \times 1000 (mL/L) \quad \text{Eq S1}$$

Where $LOD_{i,k}$ is the limit of detection of compound “i” in injection vial of matrix “k”, and SV_k is the sample volume of matrix “k” (30 mL for wastewater and 20 mL for sludge).

In the case of solid sludge, the following equation was followed:

$$LMC_i \left(\frac{ng}{g} \text{ dry weight} \right) = \frac{LOD_i (ppb)}{SM (g) \times \%DR} \quad \text{Eq S2}$$

Where LOD_i is the limit of detection of compound “i” in injection vial, SM is the sample mass (2.5 g), and $\%DR$ is the average dry residue of solid sludge (0.183).

For air calculations, the expression below was used:

$$LMC_i \left(\frac{pg}{m^3} \right) = \frac{LOD_i (ppb)}{SR_i \left(\frac{m^3}{d} \right) \times 14 d} \times 1000 (pg/ng) \quad \text{Eq S3}$$

Where LOD_i is the limit of detection of compound “i” in injection vial, SR_i is the maximum sampling calculated volume for compound “i” (0.40 for D3 and D4, 0.47 for D5, D6, and L5, 0.48 for L3, and 0.44 for L4 (Sánchez-Soberón and Ratola, 2022)), and 14 is the number of sampling days.

In the case of biogas, the LODs are the same as the LMCs, since the sample is directly analyzed in the GC-IMS SILOX.

The results from these calculations are detailed in **¡Error! No se encuentra el origen de la referencia.2**.

1.4. Statistical analyses

Statistical analyses were performed using the R studio package Version 3.5.2. The Levene test were used to study the equality of variances. If the variables presented equal variances, the Saphiro-Wilk test were applied to see if the variables followed a normal distribution. To study the significance of differences between two different groups, the Student's t-test (in case of equality of variances and normally distributed data) and the Mann-Whitney test (in the rest of cases) were used. To study correlations among variables, the Pearson correlation tests were applied. The results of the statistical tests were considered significant for p values smaller than 0.05 ($p < 0.05$).

Table S1: %Recoveries (n=3) and relative standard deviations for the different media analyzed in this study (spike levels are detailed below their correspondent matrix). N.B.: biogas values are not showed, since they are not provided by the GC-IMS-SILOX manufacturer.

	Liquid Sludge		Water		Solid Sludge		Air	
	500 µg/L		2.5 µg/L		100 ng/g		25 ng/g XAD	
	%Rec	%RSD	%Rec	%RSD	%Rec	%RSD	%Rec	%RSD
D3	87%	14%	44%	14%	81%	9%	101%	13%
L3	110%	13%	24%	6%	90%	7%	93%	2%
D4	94%	8%	104%	30%	92%	3%	94%	5%
L4	95%	7%	64%	7%	93%	3%	112%	4%
D5	69%	7%	108%	9%	104%	7%	92%	2%
L5	105%	7%	92%	4%	92%	4%	92%	2%
D6	101%	12%	75%	7%	97%	6%	95%	2%

Table S2: Limits of Detection (LOD) and Lowest Measurable Concentrations (LMC) for the different matrices and VMS congeners (GC-IMS-SILOX only displays LMC values).

	Water		Air		Biogas LMC (µg/m ³)	Solid Sludge		Liquid Sludge	
	LOD (ppb)	LMC (ng/L)	LOD (ppb)	LMC (pg/m ³)		LOD (ppb)	LMC (ng/g dw)	LOD (ppb)	LMC (ng/L ww)
D3	1.97E-01	6.58E+00	3.06E-01	5.47E+01	3.00E+01	4.17E-01	9.11E-01	4.20E-01	2.10E+01
D4	1.27E-02	4.24E-01	2.03E-02	3.63E+00	3.00E+01	5.47E-02	1.20E-01	5.00E-02	2.50E+00
D5	2.20E-03	7.34E-02	2.63E-03	3.99E-01	3.00E+01	5.09E-03	1.11E-02	1.00E-02	5.00E-01
D6	4.16E-02	1.39E+00	2.00E-02	3.04E+00	N.M.*	1.10E-01	2.41E-01	1.10E-01	5.50E+00
L3	2.34E-01	7.81E+00	1.90E-01	2.83E+01	3.00E+01	7.89E-01	1.73E+00	7.90E-01	3.95E+01
L4	1.03E-01	3.45E+00	5.62E-02	9.12E+00	3.00E+01	1.58E-01	3.45E-01	1.60E-01	8.00E+00
L5	4.29E-01	1.43E+01	1.36E-01	2.07E+01	3.00E+01	2.73E-01	5.96E-01	2.70E-01	1.35E+01

N.M - not measured; dw – dry weight; ww – wet weight

Table S3: Flows (Q_{i,j,k}) for the different matrices and sampling days (m³/d)

	W1 and W2	W3	W4	S1 and S2	S3 and S4	S5	S6	B1
03/08/2020	21454.6	20700.0	20120.0	361.0	324.0	409.0	777.6	1371.9
04/08/2020	21405.0	20491.0	20115.0	369.0	302.0	386.0	779.0	1583.0
05/08/2020	23404.5	21961.5	22129.5	345.0	336.5	360.5	785.5	1767.0
06/08/2020	23379.5	21961.5	22129.5	345.0	336.5	360.5	785.5	1735.0
07/08/2020	21800.4	20140.6	20587.7	320.6	275.6	353.6	770.6	1739.0
08/08/2020	21426.9	20472.7	20393.6	322.6	327.3	159.7	780.3	1380.5
09/08/2020	20511.7	19769.8	19317.6	316.8	334.1	261.7	828.1	1684.3
10/08/2020	20776.0	19762.0	19637.0	309.0	326.0	282.0	766.0	2037.1
11/08/2020	22062.0	20806.0	20747.0	314.0	327.0	431.0	770.0	2111.0
12/08/2020	22203.0	20866.0	20926.0	329.0	330.0	372.0	805.0	2308.0
13/08/2020	21810.0	20774.0	20729.0	321.0	324.0	208.0	794.0	2311.0
14/08/2020	21913.0	20851.0	20874.0	314.0	327.0	180.0	771.0	3044.0
15/08/2020	21525.0	20353.0	20197.0	320.0	319.0	427.0	775.0	1856.0
16/08/2020	21000.6	20023.6	19729.3	324.5	327.6	363.1	779.0	2392.0

W1 - entry water, W2 - post-preliminary treatment, W3 - post-primary treatment, W4 – effluent, S1 - primary sludge; S2 - thickened sludge; S3 - chlorinated sludge; S4 - digested sludge; S5 - dewatered sludge; S6, secondary sludge, B1 - biogas

Table S4: Mean VMS concentrations (in ng/L) and standard deviation (S.D.; n=2) of daily composite wastewater samples in the different sampling points.

		W1		W2		W3		W4	
		Conc (ng/L)	S.D.	Conc (ng/L)	S.D.	Conc (ng/L)	S.D.	Conc (ng/L)	S.D.
03-ago	D3	0.43	0.12	0.33	0.04	0.77	0.12	1.14	0.26
	D4	0.67	0.12	0.50	0.13	0.88	0.23	1.45	0.28
	D5	3.67	0.16	7.89	0.18	1.52	0.14	0.43	0.18
	D6	1.05	0.15	2.19	0.22	1.05	0.18	0.83	0.34
	L3	0.07	0.02	0.05	0.01	0.12	0.01	0.20	0.09
	L4	0.02	0.00	0.03	0.01	0.03	0.01	0.04	0.01
	L5	0.08	0.01	0.18	0.02	0.03	0.01	N.A.*	N.C.†
04-ago	D3	0.89	0.42	0.69	0.02	1.68	0.15	N.S.‡	N.C.
	D4	0.84	0.44	0.88	0.09	2.00	0.21	N.S.‡	N.C.
	D5	5.21	1.43	10.96	0.98	6.73	0.97	N.S.‡	N.C.
	D6	1.40	0.35	3.35	0.03	2.61	0.73	N.S.‡	N.C.
	L3	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.S.‡	N.C.
	L4	0.01	0.01	0.02	0.00	0.02	0.00	N.S.‡	N.C.
	L5	0.10	0.02	0.22	0.01	0.12	0.05	N.S.‡	N.C.
05-ago	D3	0.08	0.10	0.25	0.26	N.A.*	N.C.†	N.A.*	N.C.†
	D4	0.23	0.16	0.34	0.03	0.14	0.14	0.01	0.02
	D5	3.40	0.39	3.78	0.12	1.52	0.33	0.00	0.01
	D6	0.56	0.06	1.11	0.07	0.75	0.16	N.A.*	N.C.†
	L3	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	L4	0.01	0.00	0.00	0.00	N.A.*	N.C.†	N.A.*	N.C.†
	L5	0.07	0.00	0.07	0.00	0.04	0.00	N.A.*	N.C.†
06-ago	D3	5.54	7.37	2.75	2.26	0.57	0.07	N.A.*	N.C.†
	D4	0.46	0.65	0.69	0.08	0.35	0.14	N.A.*	N.C.†
	D5	4.50	0.74	4.67	1.27	1.47	0.04	N.A.*	N.C.†
	D6	0.47	0.11	1.32	0.26	0.91	0.05	0.13	0.04
	L3	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	L4	0.01	0.00	0.01	0.00	0.01	0.01	N.A.*	N.C.†
	L5	0.09	0.00	0.10	0.01	0.04	0.00	N.A.*	N.C.†
07-ago	D3	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	D4	0.30	0.19	0.66	0.05	N.A.*	N.C.†	0.11	0.16
	D5	5.80	0.87	6.20	0.70	1.21	0.01	0.10	0.07
	D6	0.82	0.25	2.17	0.24	0.46	0.04	0.20	0.01
	L3	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	L4	0.01	0.00	0.01	0.00	N.A.*	N.C.†	N.A.*	N.C.†
	L5	0.08	0.01	0.10	0.01	0.02	0.00	N.A.*	N.C.†
08-ago	D3	N.S.*	N.C.	4.32	0.98	N.A.*	N.C.†	N.A.*	N.C.†
	D4	N.S.*	N.C.	1.12	0.07	0.22	0.10	N.A.*	N.C.†
	D5	N.S.*	N.C.	4.44	0.09	2.81	1.70	0.06	0.02
	D6	N.S.*	N.C.	2.29	0.11	0.92	0.18	0.15	0.00
	L3	N.S.*	N.C.	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	L4	N.S.*	N.C.	0.02	0.00	N.A.*	N.C.†	N.A.*	N.C.†
	L5	N.S.*	N.C.	0.10	0.00	0.04	0.01	N.A.*	N.C.†
09-ago	D3	N.S.*	N.C.	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	D4	N.S.*	N.C.	0.26	0.10	0.14	0.10	0.05	0.07
	D5	N.S.*	N.C.	2.83	0.26	1.52	1.07	0.15	0.07
	D6	N.S.*	N.C.	1.59	0.20	0.84	0.60	0.23	0.08
	L3	N.S.*	N.C.	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	L4	N.S.*	N.C.	0.01	0.00	N.A.*	N.C.†	0.00	0.00
	L5	N.S.*	N.C.	0.06	0.00	0.03	0.02	N.A.*	N.C.†

10-ago	D3	4.56	6.45	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	D4	1.86	2.06	0.22	0.31	0.05	0.07	0.05	0.07
	D5	4.36	0.84	3.04	0.08	1.54	0.18	0.17	0.02
	D6	1.37	0.84	1.59	0.04	0.79	0.14	0.22	0.02
	L3	0.03	0.04	N.A.*	N.C.†	N.A.*	N.C.†	0.01	0.00
	L4	0.01	0.01	0.01	0.00	N.A.*	N.C.†	0.00	0.00
	L5	0.08	0.02	0.06	0.00	0.03	0.00	N.A.*	N.C.†
11-ago	D3	N.S.*	N.C.	46.14	46.95	52.70	11.01	13.49	5.18
	D4	N.S.*	N.C.	1.31	0.54	0.66	0.03	0.07	0.09
	D5	N.S.*	N.C.	4.81	0.01	1.66	0.23	0.23	0.03
	D6	N.S.*	N.C.	2.46	0.06	0.71	0.13	0.26	0.01
	L3	N.S.*	N.C.	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	L4	N.S.*	N.C.	0.01	0.01	0.00	0.00	N.A.*	N.C.†
	L5	N.S.*	N.C.	0.18	0.16	0.03	0.01	N.A.*	N.C.†
12-ago	D3	45.44	24.80	20.32	2.55	17.17	3.91	1.15	1.62
	D4	0.78	0.36	0.48	0.44	0.40	0.05	0.05	0.06
	D5	4.31	0.61	3.35	1.56	2.06	0.11	0.31	0.06
	D6	0.76	0.23	2.16	0.63	0.96	0.22	0.25	0.04
	L3	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	L4	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	L5	0.07	0.01	0.06	0.01	0.04	0.01	N.A.*	N.C.†
13-ago	D3	19.58	6.73	N.S.*	N.C.	6.65	1.69	N.A.*	N.C.†
	D4	0.51	0.29	N.S.*	N.C.	0.26	0.08	0.14	0.04
	D5	3.88	1.40	N.S.*	N.C.	2.11	0.35	0.42	0.09
	D6	0.73	0.24	N.S.*	N.C.	1.27	0.32	0.77	0.44
	L3	0.01	0.00	N.S.*	N.C.	N.A.*	N.C.†	N.A.*	N.C.†
	L4	0.01	0.00	N.S.*	N.C.	0.00	0.00	0.00	0.00
	L5	0.07	0.02	N.S.*	N.C.	0.04	0.01	N.A.*	N.C.†
14-ago	D3	23.99	5.83	10.10	11.42	7.27	9.53	0.96	1.35
	D4	2.18	1.15	4.49	0.30	3.14	1.44	2.95	4.11
	D5	10.08	4.23	9.88	2.47	4.95	1.27	1.91	2.19
	D6	2.42	1.16	6.84	1.38	2.86	1.13	2.45	2.93
	L3	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	L4	0.02	0.01	0.03	0.01	0.01	0.00	0.01	0.01
	L5	0.19	0.07	0.25	0.04	0.13	0.03	0.02	0.02
15-ago	D3	5.37	3.40	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	D4	0.36	0.24	N.A.*	N.C.†	0.01	0.01	N.A.*	N.C.†
	D5	4.19	1.33	1.78	0.23	2.85	0.55	0.11	0.02
	D6	0.85	0.36	0.35	0.01	0.55	0.21	0.16	0.10
	L3	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	0.01	0.00
	L4	0.01	0.00	0.00	0.00	0.00	0.00	N.A.*	N.C.†
	L5	0.08	0.01	0.04	0.00	0.07	0.01	N.A.*	N.C.†
16-ago	D3	48.95	6.27	15.93	3.86	N.A.*	N.C.†	7.15	5.37
	D4	5.49	1.27	4.24	0.28	2.48	0.26	2.53	0.62
	D5	24.05	5.88	10.66	0.56	1.76	0.46	3.90	0.10
	D6	4.20	1.22	5.86	0.15	3.75	1.18	2.31	0.12
	L3	0.04	0.03	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	L4	0.05	0.00	0.02	0.00	0.01	0.01	0.01	0.01
	L5	0.55	0.15	0.23	0.04	0.01	0.01	0.07	0.01

W1 - entry water, W2 - post-preliminary treatment, W3 - post-primary treatment, W4 - effluent, *N.A. - not acquired (values under LOD); †N.C. - not calculated; ‡N.S. - not sampled (sample not taken)

Table S5: Mean VMS concentrations (in ng/L) and standard deviation (S.D.; n=2) of six-hour composite wastewater samples in W1.

		0h		6h		12 h		18 h	
		Conc (ng/L)	S.D.	Conc (ng/L)	S.D.	Conc (ng/L)	S.D.	Conc (ng/L)	S.D.
03-ago	D3	1.08	0.20	0.56	0.09	N.S.‡	N.C.†	0.50	0.15
	D4	1.04	0.32	0.85	0.20	N.S.‡	N.C.†	0.58	0.29
	D5	8.25	0.96	5.22	0.83	N.S.‡	N.C.†	4.05	0.34
	D6	1.73	0.24	1.43	0.24	N.S.‡	N.C.†	0.95	0.05
	L3	0.06	0.02	0.04	0.01	N.S.‡	N.C.†	0.06	0.02
	L4	0.02	0.00	0.02	0.01	N.S.‡	N.C.†	0.02	0.00
	L5	0.16	0.02	0.10	0.01	N.S.‡	N.C.†	0.10	0.00
04-ago	D3	0.52	0.23	0.72	0.14	1.06	0.22	0.78	0.02
	D4	0.77	0.47	1.15	0.15	1.06	0.30	0.99	0.02
	D5	4.29	0.31	4.05	0.73	5.49	0.47	7.37	1.23
	D6	1.00	0.06	0.99	0.26	1.31	0.26	2.59	0.06
	L3	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	L4	N.A.*	N.C.†	0.01	0.00	0.01	0.01	N.A.*	N.C.†
	L5	0.09	0.01	0.09	0.00	0.11	0.01	0.11	0.00
05-ago	D3	0.04	0.01	0.17	0.10	0.13	0.01	0.25	0.03
	D4	0.31	0.02	0.32	0.13	0.37	0.04	0.40	0.05
	D5	2.96	0.12	2.91	0.45	5.72	0.07	3.91	0.14
	D6	0.53	0.07	0.45	0.15	1.03	0.14	0.57	0.06
	L3	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	L4	0.01	0.00	0.00	0.00	0.01	0.00	0.01	0.00
	L5	0.06	0.00	0.05	0.01	0.09	0.02	0.07	0.01
06-ago	D3	18.50	0.41	9.52	7.13	3.31	3.91	6.46	1.57
	D4	1.28	0.13	0.53	0.27	0.62	0.16	0.38	0.27
	D5	9.17	4.54	5.78	1.20	4.12	0.51	4.79	0.31
	D6	0.70	0.13	0.66	0.10	0.66	0.10	0.47	0.08
	L3	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	L4	0.01	0.00	0.02	0.00	0.01	0.00	0.01	0.00
	L5	0.14	0.03	0.11	0.01	0.08	0.02	0.07	0.00
07-ago	D3	5.86	2.81	1.10	1.56	3.15	1.07	N.A.*	N.C.†
	D4	0.59	0.03	0.94	0.92	0.62	0.01	N.A.*	N.C.†
	D5	6.80	0.27	5.69	3.14	8.24	1.34	0.74	0.15
	D6	0.92	0.06	3.04	3.54	0.84	0.19	0.20	0.10
	L3	N.A.*	N.C.†	0.02	0.02	N.A.*	N.C.†	N.A.*	N.C.†
	L4	0.02	0.00	0.04	0.04	0.02	0.00	N.A.*	N.C.†
	L5	0.10	0.02	0.07	0.02	0.09	0.00	0.02	0.00
08-ago	D3	4.56	1.69	1.11	1.57	N.A.*	N.C.†	2.12	3.00
	D4	0.28	0.10	0.26	0.34	0.11	0.16	0.45	0.19
	D5	3.42	0.77	3.67	1.52	2.07	0.13	3.43	1.52
	D6	0.68	0.08	0.59	0.21	0.31	0.10	0.62	0.35
	L3	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	L4	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
	L5	0.06	0.00	0.05	0.02	0.04	0.01	0.12	0.05
09-ago	D3	N.S.‡	N.C.	N.S.‡	N.C.†	N.S.‡	N.C.	N.S.‡	N.C.†
	D4	N.S.‡	N.C.	N.S.‡	N.C.†	N.S.‡	N.C.	N.S.‡	N.C.†
	D5	N.S.‡	N.C.	N.S.‡	N.C.†	N.S.‡	N.C.	N.S.‡	N.C.†
	D6	N.S.‡	N.C.	N.S.‡	N.C.†	N.S.‡	N.C.	N.S.‡	N.C.†
	L3	N.S.‡	N.C.	N.S.‡	N.C.†	N.S.‡	N.C.	N.S.‡	N.C.†
	L4	N.S.‡	N.C.	N.S.‡	N.C.†	N.S.‡	N.C.	N.S.‡	N.C.†
	L5	N.S.‡	N.C.	N.S.‡	N.C.†	N.S.‡	N.C.	N.S.‡	N.C.†

*N.A. - not acquired (values under LOD); †N.C. - not calculated; ‡: N.S. - not sampled (sample not taken)

Table S6: Mean VMS concentrations (in ng/L) and standard deviation (S.D.; n=2) of six-hour composite samples in W2.

		0h		6h		12 h		18 h	
		Conc (ng/L)	S.D.	Conc (ng/L)	S.D.	Conc (ng/L)	S.D.	Conc (ng/L)	S.D.
03-ago	D3	0.57	0.56	0.18	0.17	0.38	0.17	0.45	0.22
	D4	0.90	0.58	0.48	0.15	0.53	0.43	0.72	0.45
	D5	11.69	2.59	6.04	2.43	4.81	2.38	10.74	1.58
	D6	2.70	0.48	1.88	0.30	2.05	0.02	2.26	0.13
	L3	0.04	0.01	0.05	0.02	0.02	0.01	0.03	0.00
	L4	0.04	0.02	0.09	0.10	0.01	0.00	0.02	0.01
	L5	0.25	0.03	0.23	0.04	0.15	0.01	0.19	0.03
04-ago	D3	0.18	0.15	0.20	0.27	1.19	0.09	0.95	0.31
	D4	0.60	0.02	0.48	0.50	1.51	0.37	1.11	0.52
	D5	4.82	1.41	1.96	0.15	9.33	1.70	9.49	0.03
	D6	1.61	0.33	1.17	0.01	3.04	0.54	3.14	0.27
	L3	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	L4	0.01	0.00	0.01	0.00	0.01	0.00	0.01	0.00
	L5	0.10	0.03	0.03	0.03	0.19	0.05	0.20	0.02
05-ago	D3	0.35	0.34	N.A.*	N.C.†	0.25	0.23	0.14	0.19
	D4	0.65	0.25	0.13	0.19	0.56	0.16	0.44	0.11
	D5	4.21	1.04	2.65	0.03	9.60	0.07	6.26	0.49
	D6	1.11	0.31	0.88	0.02	3.08	0.51	1.59	0.26
	L3	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	L4	0.01	0.00	0.00	0.00	0.02	0.00	0.01	0.00
	L5	0.10	0.01	0.06	0.00	0.20	0.01	0.12	0.01
06-ago	D3	2.90	2.01	0.54	0.04	5.11	1.56	0.52	0.04
	D4	0.72	0.27	0.20	0.04	0.43	0.00	0.46	0.20
	D5	3.43	0.81	3.20	0.27	2.80	0.19	5.61	1.23
	D6	1.72	0.34	0.76	0.12	1.25	0.09	1.50	0.23
	L3	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	L4	0.01	0.00	0.00	0.00	0.01	0.00	0.02	0.01
	L5	0.08	0.02	0.07	0.01	0.06	0.00	0.13	0.05
07-ago	D3	N.A.*	N.C.†	N.A.*	N.C.†	N.S.*	N.C.	N.A.*	N.C.†
	D4	0.43	0.16	0.28	0.33	N.S.*	N.C.	0.46	0.07
	D5	4.56	2.08	3.83	1.97	N.S.*	N.C.	2.75	0.10
	D6	1.66	0.29	1.54	0.57	N.S.*	N.C.	1.46	0.06
	L3	N.A.*	N.C.†	N.A.*	N.C.†	N.S.*	N.C.	N.A.*	N.C.†
	L4	0.01	0.00	0.01	0.00	N.S.*	N.C.	0.00	0.00
	L5	0.06	0.01	0.05	0.02	N.S.*	N.C.	0.06	0.00
08-ago	D3	1.77	2.50	1.24	1.69	N.A.*	N.C.†	0.02	0.02
	D4	0.92	0.23	0.80	0.26	0.35	0.25	0.84	0.03
	D5	5.62	1.99	3.48	0.81	2.45	0.05	4.33	1.15
	D6	2.13	0.34	1.57	0.30	2.13	0.60	2.92	0.63
	L3	N.A.*	N.C.†	0.01	0.01	N.A.*	N.C.†	N.A.*	N.C.†
	L4	0.01	0.01	0.01	0.00	0.01	0.00	0.01	0.00
	L5	0.09	0.01	0.06	0.01	0.08	0.01	0.10	0.02
09-ago	D3	2.68	1.78	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	D4	0.34	0.09	0.07	0.05	0.22	0.30	0.06	0.03
	D5	3.74	0.62	3.08	0.29	2.66	0.19	4.09	0.54
	D6	1.83	0.32	2.52	0.12	1.91	0.25	1.82	0.15
	L3	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	L4	0.00	0.00	0.01	0.01	N.A.*	N.C.†	0.01	0.00
	L5	0.07	0.00	0.07	0.00	0.06	0.01	0.07	0.01

*N.A. - not acquired (values under LOD); †N.C. - not calculated; ‡: N.S. - not sampled (sample not taken)

Table S7: Mean VMS concentrations (in ng/L) and standard deviation (S.D.; n=2) of six-hour composite samples in W3.

		0h		6h		12 h		18 h	
		Conc (ng/L)	S.D.	Conc (ng/L)	S.D.	Conc (ng/L)	S.D.	Conc (ng/L)	S.D.
03-ago	D3	1.09	0.48	1.01	0.13	0.81	0.16	0.60	0.07
	D4	1.58	0.35	1.29	0.15	1.25	0.57	0.77	0.19
	D5	2.13	0.33	3.20	1.31	1.43	0.28	1.61	0.00
	D6	1.29	0.21	1.55	0.16	1.14	0.05	1.11	0.07
	L3	0.10	0.01	0.30	0.01	0.11	0.15	0.11	0.03
	L4	0.02	0.01	0.06	0.01	0.03	0.05	0.03	0.01
	L5	0.08	0.05	0.05	0.01	0.03	0.01	0.04	0.00
04-ago	D3	0.93	0.09	0.48	0.20	0.92	0.12	0.55	0.24
	D4	0.63	0.03	0.44	0.39	0.73	0.03	0.37	0.32
	D5	1.86	0.24	2.05	0.77	2.56	0.18	2.13	0.18
	D6	1.12	0.15	1.12	0.42	1.26	0.12	1.22	0.28
	L3	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	L4	0.00	0.00	N.A.*	N.C.†	0.00	0.00	0.01	0.00
	L5	0.05	0.01	0.05	0.02	0.06	0.00	0.05	0.01
05-ago	D3	0.04	0.05	N.A.*	N.C.†	N.S.*	N.C.	0.36	0.16
	D4	0.09	0.02	0.22	0.06	N.S.*	N.C.	0.42	0.03
	D5	1.49	0.08	1.46	0.12	N.S.*	N.C.	1.36	0.11
	D6	0.69	0.08	0.62	0.05	N.S.*	N.C.	0.88	0.01
	L3	N.A.*	N.C.†	N.A.*	N.C.†	N.S.*	N.C.	N.A.*	N.C.†
	L4	N.A.*	N.C.†	0.01	0.00	N.S.*	N.C.	0.00	0.00
	L5	0.05	0.00	0.03	0.00	N.S.*	N.C.	0.04	0.01
06-ago	D3	0.58	0.10	0.34	0.01	0.24	0.07	0.35	0.11
	D4	0.51	0.04	0.30	0.26	0.10	0.09	0.30	0.04
	D5	1.56	0.01	1.32	0.28	1.42	0.36	1.76	0.00
	D6	0.84	0.01	0.58	0.04	0.54	0.14	0.87	0.03
	L3	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	L4	0.01	0.00	0.00	0.00	N.A.*	N.C.†	0.01	0.00
	L5	0.04	0.01	0.03	0.00	0.03	0.01	0.04	0.00
07-ago	D3	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	D4	0.01	0.01	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	D5	1.40	0.09	1.10	0.09	1.12	0.20	2.34	0.07
	D6	0.71	0.07	0.59	0.03	0.64	0.17	0.96	0.08
	L3	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	L4	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	L5	0.03	0.00	0.02	0.00	0.03	0.00	0.05	0.01
08-ago	D3	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	D4	0.16	0.17	N.A.*	N.C.†	N.A.*	N.C.†	0.10	0.15
	D5	1.45	0.10	0.84	0.10	1.95	0.28	1.56	0.00
	D6	0.85	0.32	0.48	0.01	0.77	0.08	1.10	0.18
	L3	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	L4	N.A.*	N.C.†	N.A.*	N.C.†	0.01	0.00	N.A.*	N.C.†
	L5	0.03	0.00	0.02	0.00	0.04	0.00	0.06	0.02
09-ago	D3	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	D4	N.A.*	N.C.†	0.14	0.07	0.37	0.25	0.10	0.08
	D5	1.23	0.17	1.68	0.01	1.32	0.04	1.85	0.37
	D6	0.68	0.08	0.90	0.05	0.82	0.16	0.77	0.21
	L3	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	L4	N.A.*	N.C.†	N.A.*	N.C.†	0.00	0.00	0.00	0.00
	L5	0.03	0.00	0.03	0.00	0.02	0.00	0.04	0.01

*N.A. - not acquired (values under LOD); †N.C. - not calculated; ‡: N.S. - not sampled (sample not taken)

Table S8: Mean VMS concentrations (in ng/L) and standard deviation (S.D.; n=2) of six-hour composite samples in W4.

		0h		6h		12 h		18 h	
		Conc (ng/L)	S.D.	Conc (ng/L)	S.D.	Conc (ng/L)	S.D.	Conc (ng/L)	S.D.
03-ago	D3	1.05	0.13	0.86	0.03	0.40	0.12	0.55	0.17
	D4	1.28	0.52	1.29	0.23	0.33	0.20	0.54	0.20
	D5	0.52	0.25	0.60	0.09	0.25	0.19	0.18	0.07
	D6	0.61	0.40	1.21	0.20	1.46	0.63	0.18	0.03
	L3	0.09	0.11	0.14	0.18	0.03	0.03	0.16	0.08
	L4	0.01	0.01	0.02	0.03	N.A.*	N.C.†	0.04	0.02
	L5	N.A.*	N.C.†	N.A.*	N.C.†	0.01	0.00	N.A.*	N.C.†
04-ago	D3	N.S.‡	N.C.†	N.S.‡	N.C.†	N.S.‡	N.C.†	N.S.‡	N.C.†
	D4	N.S.‡	N.C.†	N.S.‡	N.C.†	N.S.‡	N.C.†	N.S.‡	N.C.†
	D5	N.S.‡	N.C.†	N.S.‡	N.C.†	N.S.‡	N.C.†	N.S.‡	N.C.†
	D6	N.S.‡	N.C.†	N.S.‡	N.C.†	N.S.‡	N.C.†	N.S.‡	N.C.†
	L3	N.S.‡	N.C.†	N.S.‡	N.C.†	N.S.‡	N.C.†	N.S.‡	N.C.†
	L4	N.S.‡	N.C.†	N.S.‡	N.C.†	N.S.‡	N.C.†	N.S.‡	N.C.†
	L5	N.S.‡	N.C.†	N.S.‡	N.C.†	N.S.‡	N.C.†	N.S.‡	N.C.†
05-ago	D3	N.A.*	N.C.†	N.A.*	N.C.†	N.S.‡	N.C.†	N.A.*	N.C.†
	D4	N.A.*	N.C.†	0.03	0.04	N.S.‡	N.C.†	N.A.*	N.C.†
	D5	0.09	0.11	0.04	0.06	N.S.‡	N.C.†	0.07	0.09
	D6	N.A.*	N.C.†	0.11	0.08	N.S.‡	N.C.†	1.46	0.38
	L3	N.A.*	N.C.†	N.A.*	N.C.†	N.S.‡	N.C.†	N.A.*	N.C.†
	L4	N.A.*	N.C.†	N.A.*	N.C.†	N.S.‡	N.C.†	N.A.*	N.C.†
	L5	N.A.*	N.C.†	N.A.*	N.C.†	N.S.‡	N.C.†	N.A.*	N.C.†
06-ago	D3	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	D4	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	0.02	0.02
	D5	0.03	0.05	N.A.*	N.C.†	0.00	0.00	0.06	0.02
	D6	0.03	0.04	N.A.*	N.C.†	0.72	0.16	0.20	0.03
	L3	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	L4	0.00	0.00	N.A.*	N.C.†	N.A.*	N.C.†	0.00	0.00
	L5	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
07-ago	D3	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	D4	0.03	0.05	N.A.*	N.C.†	N.A.*	N.C.†	0.03	0.05
	D5	0.27	0.13	0.04	0.05	0.09	0.03	0.18	0.11
	D6	0.66	0.19	0.05	0.04	0.15	0.02	0.60	0.08
	L3	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	L4	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	0.00	0.00
	L5	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
08-ago	D3	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	D4	0.04	0.05	N.A.*	N.C.†	0.01	0.01	N.A.*	N.C.†
	D5	0.09	0.01	0.06	0.01	0.04	0.05	0.08	0.02
	D6	0.21	0.01	0.08	0.05	0.25	0.07	0.29	0.11
	L3	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	L4	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	L5	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
09-ago	D3	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	D4	N.A.*	N.C.†	0.04	0.06	0.10	0.14	0.04	0.05
	D5	0.10	0.05	0.14	0.13	0.21	0.08	0.17	0.03
	D6	0.12	0.07	0.37	0.19	0.19	0.07	0.10	0.04
	L3	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	L4	0.00	0.00	N.A.*	N.C.†	0.00	0.00	0.00	0.00
	L5	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†

*N.A. - not acquired (values under LOD); †N.C. - not calculated; ‡: N.S. - not sampled (sample not taken)

Table S9: Mean VMS concentrations (in µg/g dry weight) and standard deviation (S.D.; n=2) of composite daily samples of sludge in the different sampling points.

		S1		S2		S3		S4		S5		S6	
		Conc (µg/g dw)	S.D.	Conc (µg/g dw)	S.D.	Conc (µg/g dw)	S.D.	Conc (µg/g dw)	S.D.	Conc (µg/g dw)	S.D.	Conc (µg/g dw)	S.D.
03-ago	D3	0.20	0.12	0.05	0.05	0.01	0.01	N.A.*	N.C.†	0.06	0.01	N.A.*	N.C.†
	D4	0.13	0.02	0.14	0.04	0.06	0.00	0.03	0.01	0.18	0.02	0.00	0.00
	D5	3.03	0.31	3.93	1.39	1.76	0.34	1.75	0.12	4.28	0.51	0.12	0.05
	D6	0.33	0.06	0.46	0.23	0.16	0.03	0.15	0.02	0.70	0.09	0.00	0.00
	L3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	L4	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
	L5	0.05	0.01	0.07	0.03	0.03	0.00	0.03	0.00	0.10	0.01	0.00	0.00
04-ago	D3	0.06	0.03	0.04	0.01	0.02	0.01	N.A.*	N.C.†	0.04	0.01	0.00	0.00
	D4	0.13	0.01	0.11	0.04	0.04	0.01	0.03	0.00	0.15	0.01	0.00	0.00
	D5	3.63	0.22	2.63	0.74	1.39	0.08	1.32	0.14	4.53	0.19	0.27	0.07
	D6	0.40	0.01	0.29	0.08	0.16	0.00	0.14	0.02	0.75	0.00	0.03	0.00
	L3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	N.A.*	N.C.†	0.00	0.00
	L4	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
	L5	0.06	0.00	0.04	0.01	0.02	0.00	0.02	0.00	0.11	0.00	0.01	0.00
05-ago	D3	N.A.*	N.C.†	0.00	0.00	0.01	0.01	N.A.*	N.C.†	0.05	0.01	N.A.*	N.C.†
	D4	0.09	0.01	0.23	0.01	0.19	0.04	0.03	0.00	0.19	0.02	0.01	0.00
	D5	3.06	0.48	7.56	0.91	5.32	1.31	2.18	0.49	5.44	0.22	0.53	0.03
	D6	0.33	0.06	0.74	0.00	0.59	0.17	0.25	0.06	0.89	0.04	0.05	0.00
	L3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	L4	0.01	0.00	0.02	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00
	L5	0.05	0.01	0.12	0.00	0.09	0.03	0.04	0.01	0.14	0.01	0.01	0.00
06-ago	D3	0.08	0.05	0.24	0.14	0.10	0.05	0.09	0.01	0.05	0.01	N.A.*	N.C.†
	D4	0.16	0.02	0.31	0.08	0.23	0.01	N.A.*	N.C.†	0.17	0.01	N.A.*	N.C.†
	D5	5.45	0.09	8.51	2.22	6.55	0.48	1.03	0.07	4.01	0.27	0.36	0.07
	D6	0.54	0.00	0.95	0.28	0.76	0.08	N.A.*	N.C.†	0.64	0.06	0.03	0.00
	L3	0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	L4	0.01	0.00	0.02	0.01	0.02	0.00	0.00	0.00	0.01	0.00	0.00	0.00
	L5	0.10	0.00	0.16	0.05	0.14	0.01	0.02	0.00	0.10	0.01	0.01	0.00
07-ago	D3	0.03	0.03	0.04	0.04	0.13	0.13	N.A.*	N.C.†	0.05	0.01	N.A.*	N.C.†
	D4	0.12	0.04	0.25	0.15	0.12	0.05	0.03	0.03	0.15	0.04	0.00	0.00

	D5	3.80	1.05	7.17	4.71	2.90	0.99	2.28	0.53	3.57	0.66	0.67	0.06
	D6	0.45	0.14	0.99	0.66	0.34	0.11	0.23	0.08	0.60	0.09	0.07	0.01
	L3	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
	L4	0.01	0.00	0.02	0.01	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00
	L5	0.07	0.02	0.14	0.10	0.05	0.02	0.04	0.01	0.09	0.02	0.01	0.00
	D3	0.08	0.08	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	0.06	0.01	0.00	0.00
	D4	0.23	0.01	0.15	0.03	0.07	0.03	0.05	0.04	0.22	0.01	0.01	0.01
	D5	8.11	0.49	4.47	1.03	2.76	0.57	2.11	0.40	5.48	0.42	0.88	0.03
08-ago	D6	0.88	0.11	0.42	0.14	0.19	0.07	0.07	0.04	0.91	0.03	0.06	0.01
	L3	0.00	0.00	0.00	0.00	0.00	0.00	N.A.*	N.C.†	0.00	0.00	0.00	0.00
	L4	0.01	0.00	0.00	0.00	N.A.*	N.C.†	N.A.*	N.C.†	0.01	0.00	N.A.*	N.C.†
	L5	0.12	0.01	0.06	0.01	0.04	0.01	0.03	0.00	0.14	0.01	0.01	0.00
	D3	N.S.*	N.C.	0.13	0.07	0.06	0.02	0.09	0.00	0.02	0.02	0.02	0.00
	D4	N.S.*	N.C.	0.33	0.07	0.19	0.03	0.15	0.00	0.11	0.07	0.02	0.00
	D5	N.S.*	N.C.	8.01	2.05	3.85	0.10	1.96	0.53	4.12	0.97	0.66	0.03
09-ago	D6	N.S.*	N.C.	1.09	0.28	0.49	0.00	0.25	0.10	0.75	0.12	0.08	0.00
	L3	N.S.*	N.C.	0.00	0.00	0.00	0.00	N.A.*	N.C.†	0.00	0.00	N.A.*	N.C.†
	L4	N.S.*	N.C.	0.02	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00
	L5	N.S.*	N.C.	0.14	0.05	0.06	0.00	0.03	0.01	0.11	0.02	0.01	0.00
	D3	0.06	0.01	0.07	0.01	0.06	0.01	0.06	0.00	0.08	0.01	0.02	0.00
	D4	0.40	0.03	0.39	0.01	0.31	0.01	0.11	0.02	0.24	0.01	0.02	0.00
	D5	12.55	0.13	11.03	0.21	8.30	0.44	2.91	0.67	6.20	0.01	0.84	0.05
10-ago	D6	1.67	0.09	1.45	0.01	1.08	0.05	0.38	0.07	1.04	0.01	0.10	0.01
	L3	0.01	0.00	0.01	0.00	0.01	0.00	N.A.*	N.C.†	0.00	0.00	0.00	0.00
	L4	0.03	0.01	0.02	0.00	0.02	0.00	0.00	0.00	0.01	0.00	0.00	0.00
	L5	0.23	0.00	0.19	0.01	0.14	0.01	0.04	0.01	0.15	0.00	0.01	0.00
	D3	0.03	0.03	0.04	0.01	0.07	0.00	0.01	0.01	0.05	0.02	0.01	0.00
	D4	0.38	0.06	0.46	0.02	0.32	0.00	0.11	0.00	0.17	0.01	0.01	0.00
	D5	12.50	1.61	13.54	0.31	9.24	0.04	3.78	1.17	4.12	0.42	0.76	0.03
11-ago	D6	1.59	0.20	1.76	0.10	1.13	0.01	0.47	0.17	0.71	0.06	0.09	0.00
	L3	0.01	0.00	0.01	0.00	0.01	0.00	N.A.*	N.C.†	0.00	0.00	N.A.*	N.C.†
	L4	0.03	0.00	0.03	0.00	0.02	0.00	0.01	0.00	0.01	0.00	0.00	0.00
	L5	0.23	0.04	0.24	0.01	0.15	0.00	0.06	0.02	0.10	0.01	0.01	0.00
12-ago	D3	0.02	0.01	0.02	0.00	0.03	0.01	0.01	0.01	0.08	0.01	0.00	0.00
	D4	0.31	0.04	0.24	0.00	0.18	0.03	0.12	0.04	0.20	0.01	0.01	0.00

	D5	10.20	1.36	7.96	0.19	5.89	0.86	4.07	1.09	4.57	0.92	0.85	0.04
	D6	1.28	0.17	0.89	0.04	0.71	0.04	0.51	0.12	0.80	0.16	0.09	0.00
	L3	0.01	0.00	0.01	0.00	0.00	0.00	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	L4	0.02	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.00	0.00
	L5	0.18	0.03	0.12	0.00	0.09	0.01	0.06	0.02	0.11	0.03	0.01	0.00
13-ago	D3	0.01	0.01	0.01	0.00	0.03	0.00	N.A.*	N.C.†	0.08	0.02	0.00	0.00
	D4	0.26	0.02	0.12	0.03	0.10	0.04	0.03	0.00	0.17	0.01	0.01	0.00
	D5	8.84	0.80	4.88	1.22	3.83	0.96	4.76	0.23	3.43	0.07	0.96	0.01
	D6	0.96	0.11	0.41	0.13	0.31	0.10	0.44	0.04	0.57	0.02	0.07	0.00
	L3	0.00	0.00	0.00	0.00	0.00	0.00	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	L4	0.02	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.00	0.00
	L5	0.15	0.02	0.07	0.02	0.06	0.02	0.08	0.00	0.08	0.00	0.01	0.00
14-ago	D3	0.12	0.10	0.06	0.00	0.06	0.03	0.02	0.01	0.08	0.00	0.00	0.00
	D4	0.19	0.07	0.21	0.06	0.16	0.05	0.03	0.01	0.13	0.02	0.00	0.00
	D5	5.83	1.38	6.63	1.79	5.50	1.02	3.23	1.03	2.58	0.05	1.00	0.00
	D6	0.59	0.15	0.71	0.24	0.49	0.14	0.20	0.14	0.45	0.00	0.08	0.01
	L3	0.00	0.00	0.00	0.00	0.00	0.00	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	L4	0.01	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	L5	0.11	0.03	0.11	0.03	0.09	0.02	0.06	0.02	0.06	0.00	0.02	0.00
15-ago	D3	0.04	0.02	0.02	0.00	0.02	0.01	0.01	0.01	0.07	0.01	0.01	0.00
	D4	0.25	0.01	0.25	0.02	0.22	0.00	0.05	0.02	0.22	0.04	0.01	0.00
	D5	7.37	0.41	9.15	0.21	7.92	0.28	4.53	1.72	4.99	0.76	0.90	0.05
	D6	0.87	0.07	1.06	0.07	0.94	0.05	0.38	0.23	0.84	0.15	0.07	0.00
	L3	0.01	0.00	0.01	0.00	0.01	0.00	N.A.*	N.C.†	0.00	0.00	N.A.*	N.C.†
	L4	0.02	0.00	0.02	0.00	0.02	0.00	0.01	0.00	0.01	0.00	0.00	0.00
	L5	0.14	0.01	0.18	0.01	0.17	0.01	0.08	0.03	0.12	0.02	0.01	0.00
16-ago	D3	0.03	0.02	0.02	0.01	0.02	0.01	N.A.*	N.C.†	0.07	0.01	0.02	0.01
	D4	0.19	0.05	0.16	0.00	0.14	0.03	0.00	0.00	0.21	0.02	0.01	0.00
	D5	6.69	1.50	5.76	0.07	4.62	0.29	3.29	0.68	5.10	0.15	0.75	0.04
	D6	0.77	0.23	0.56	0.00	0.45	0.08	0.23	0.10	0.74	0.06	0.05	0.01
	L3	0.00	0.00	0.00	0.00	0.00	0.00	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
	L4	0.01	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00
	L5	0.13	0.03	0.10	0.00	0.09	0.01	0.06	0.01	0.10	0.01	0.01	0.00

S1 - primary sludge; S2 - thickened sludge; S3 - chlorinated sludge; S4 - digested sludge; S5 - dewatered sludge; S6, secondary sludge, *N.A. - not acquired (values under LOD); †N.C. -not calculated.

Table S10: Mean VMS concentrations (in ng/m³) and standard deviation (S.D.; n=2) of 14-day exposure samples of passive air in the different sampling points.

	A1		A2		A3		A4		A5		A6		A7		A8		A8	
	Conc. (ng/m ³)	S.D.	Conc. (ng/m ³)	S.D.	Conc. (ng/m ³)	S.D.	Conc. (ng/m ³)	S.D.	Conc. (ng/m ³)	S.D.	Conc. (ng/m ³)	S.D.	Conc. (ng/m ³)	S.D.	Conc. (ng/m ³)	S.D.	Conc. (ng/m ³)	S.D.
D3	3.82	0.16	1.72	2.39	6.31	1.68	42.70	3.31	208.82	0.82	1102.31	143.07	649.75	64.06	3250.82	52.77	N.A.*	N.C.†
D4	88.81	9.76	11.45	4.74	163.54	5.68	123.04	0.53	89.39	4.47	673.21	68.87	386.37	43.76	1652.21	249.10	0.67	0.32
D5	1012.01	99.08	42.85	2.22	1091.42	35.70	1189.39	16.48	29.93	0.36	106.34	25.36	87.30	14.20	242.34	40.00	5.71	0.68
D6	44.82	4.53	N.A.*	N.C.†	22.08	2.05	79.12	5.11	11.08	2.14	35.58	19.67	42.45	7.55	136.26	21.05	1.15	1.63
L3	3.43	0.61	0.83	1.15	4.80	1.05	2.12	0.43	7.25	0.73	0.45	0.59	2.44	0.18	5.21	0.12	0.46	0.36
L4	2.70	0.18	0.23	0.00	2.91	0.13	3.98	0.17	0.17	0.00	1.08	0.24	0.80	0.09	1.71	0.27	N.A.*	N.C.†
L5	11.53	0.55	0.29	0.14	7.86	0.47	13.65	0.50	1.14	0.02	2.46	0.77	2.32	0.28	3.18	0.43	0.11	0.02

*N.A. - not acquired (values under LOD); †N.C. - not calculated.

Table S11: Mean VMS concentrations (in mg/m³) and standard deviation (S.D.; n=2) of biogas samples.

	03-ago		06-ago		10-ago		13-ago		17-ago	
	Conc. (mg/m ³)	S.D.	Conc. (mg/m ³)	S.D.	Conc. (mg/m ³)	S.D.	Conc. (mg/m ³)	S.D.	Conc. (mg/m ³)	S.D.
L3	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
L4	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
L5	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
D3	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†	N.A.*	N.C.†
D4	0.725	0.007	0.835	0.007	0.880	0.007	0.870	0.000	0.730	0.000
D5	7.200	0.000	7.090	0.172	7.230	0.002	7.207	0.072	6.835	0.276

*N.A. - not acquired (values under LOD); †N.C. - not calculated.

Table S12: Mean VMS mass flows (in g/d) and standard deviation (S.D.; n=14) of water samples in the different sampling points.

	W1		W2		W3		W4	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
D3	305.41	393.29	169.99	294.11	129.13	296.23	37.59	82.37
D4	26.63	32.33	25.31	31.45	15.77	20.85	11.57	21.24
D5	144.44	126.13	124.02	66.70	49.65	32.32	12.11	22.06
D6	28.66	22.94	55.39	39.56	27.10	20.26	12.47	16.68
L3	0.36	0.48	0.16	0.25	0.25	0.64	0.40	1.11
L4	0.32	0.27	0.30	0.21	0.13	0.17	0.12	0.20
L5	2.88	2.95	2.72	1.58	0.98	0.73	0.26	0.35
Total	507.86	530.27	377.34	343.02	221.88	299.35	72.74	112.43

W1 - entry water, W2 - post-preliminary treatment, W3 - post-primary treatment, W4 - effluent

Table S13: Mean VMS mass flows (in g/d) and standard deviation (S.D.; n=14) of sludge samples in the different sampling points.

	S1		S2		S3		S4		S6	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
D3	0.48	0.48	0.36	0.47	0.32	0.27	0.07	0.13	0.33	0.43
D4	1.74	0.72	1.69	0.72	1.25	0.69	0.22	0.18	0.52	0.03
D5	55.70	24.63	52.14	20.42	38.59	19.50	13.14	5.40	53.30	0.42
D6	6.51	3.38	5.97	2.94	4.27	2.63	1.22	0.73	4.76	0.04
L3	0.04	0.02	0.04	0.02	0.03	0.02	0.01	0.00	0.03	21.21
L4	0.11	0.06	0.10	0.05	0.08	0.05	0.02	0.01	0.09	0.29
L5	0.99	0.45	0.91	0.39	0.68	0.37	0.22	0.10	0.75	2.10
Total	65.57	29.05	61.74	23.68	44.59	22.48	14.65	6.01	59.77	23.74

S1 - primary sludge; S2 - thickened sludge; S3 - chlorinated sludge; S4 - digested sludge; S5 - dewatered sludge; S6, secondary sludge

Table S14: Mean VMS mass flows (in g/d) and standard deviation (S.D.; n=5) of biogas samples.

	B1	
	Mean	SD
D3	0.03	0.00
D4	1.57	0.01
D5	13.81	0.01
D6	0.03	0.00
L3	0.03	0.00
L4	0.03	0.00
L5	0.03	0.00
Total	15.52	0.02

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