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AIS/CESIO Environmental Surfactant Monitoring Programme. Part 1: LAS Monitoring study in "de Meern" sewage treatment plant and receiving river "Leidsche Rijn"

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ABSTRACT

This manuscript reports on the outcome of a 7-day pilot monitoring study on the anionic surfactant linear alkyl benzene sulfonate (LAS) at the "de Meern" municipal sewage treatment plant. The receiving surface water, the Leidsche Rijn is a straight river - about 20 m wide and 1.5 m deep - and dilutes the sewage discharge by a factor 3. The monitoring study illustrates an effective removal of LAS of 99.9% during dry weather and normal operating conditions. The LAS concentrations in daily composite raw sewage samples varied between 3.1 and 7.2 mg/L, with corresponding effluent concentrations generally under the analytical detection limit of 8.1 ug/L. During this same period, total LAS concentrations in the river varied between <2.1 ug/L (detection limit) and 2.9 ug/L in samples taken above the sewage outfall and between <2.1 ug/L and 7.1 ug/L for samples taken below the sewage outfall. Malfunctioning of the primary settler during heavy rainfall conditions, resulted in throughput of primary sludge particles to the aeration tank. The removal of LAS, BOD, SS, and TOC decreased significantly during this period, resulting in higher effluent concentrations. In addition, analyses of river samples taken during and after the rainfall indicated the presence of a sewage overflow which was discharged upstream of the sewage treatment plant outfall.

INTRODUCTION

A scientifically based risk assessment strategy for chemicals requires a comprehensive and integrated assessment of local and regional emissions, and understanding of transport, distribution and transformation processes (ECETOC, 1993). The environmental exposure can be estimated if it is known how and in what quantity a substance enters the environment and how it is subsequently distributed and transformed in these receiving compartments (i.e. air, water, soil). The effect of transport and transformation processes on the distribution and concentration of chemicals in the different environmental compartments may be predicted

by using mathematical models (ECETOC, 1993; ECETOC, 1994), assessed in experimental laboratory simulation models, or possibly measured in actual environmental compartments if specific analytical techniques have been developed for the chemical of interest. The end product of an environmental exposure assessment is typically a predicted or measured concentration for the compartment of interest.

In this context, The European Chemical Industry has commissioned a joint industry Task Force (TF) of the Association International de la Savonnerie et la Détergence (AIS) and the Comité Européen de Agents de Surface et Intermédiares Organiques (CESIO) to develop and apply specific analytical methodology for the environmental monitoring of surfactants. The objectives of the programme were: (1) to establish the fate, distribution and concentrations of major surfactants in relevant environmental compartments and (2) to provide the necessary data for checking the applicability of mathematical models to predict their fate and concentrations in these environmental compartments. The first phase of this AIS/CESIO surfactant monitoring programme was designed (1) to measure LAS concentrations in relevant compartments of the sewage treatment plant and receiving surface waters, and (2) to provide the necessary data to verify mathematical model predictions.

A joint monitoring programme was initiated with the cooperation of the Institute for Inland Water Management and Waste Water (RIZA), the University of Amsterdam (UvA), National Institute of Public Health and Environmental Protection (RIVM), and the Dutch Soap Association (NVZ). This manuscript will report on the first phase of the monitoring programme which was initiated (1) to optimalize sampling parameters and sampling statistics and (2) to examine if the monitoring protocol would be suited for future studies. This first phase focused on linear alkylbenzene sulfonate (LAS) and was executed at one pilot location i.e. "de Meern", a municipal sewage treatment plant discharging in the river "Leidsche Rijn". The sewage treatment plant "de Meern" was monitored in the period 1-7 July 1993. The second phase of the monitoring programme will besides LAS also include alcohol ethoxylates (AE), alcohol ethoxylated sulfates (AES), and soap. This programme will be executed at several representative sites across The Netherlands.

SITE DESCRIPTION

River "Leidsche Rijn"

The Leidsche Rijn is a straight river, about 20 m wide and 1.5 m deep. To the east there is a open connection with the "Amsterdam-Rijn" canal; in the west the "Haanwijker" locks are situated at Harmelen. The sewage treatment plant is located in the middle, at 3.5 km from the locks and 5.4 km from the canal. The flow rate of the river is estimated at 30 m^3/min. During the summer, except during a long period of heavy rain fall, the direction of flow is always from east to west. Along the river several pumping-stations are situated. For the pilot monitoring study, the stations on the west side are the most important. For outlet to polder ditches the station "Vleuterweide" (40 m^3/min, 0.5 km from the discharge point) is normally in use and for the discharge of polderwater on the "Leidsche Rijn" the stations "Harmelerwaard" (9 m^3/min, 1.5 km), "Bijleveld" (2*130 m^3/min, 2.1 km) and also "Vleuterweide" (40 m^3/min, 0.5 km) are used. At Harmelen water of the "Leidsche Rijn" flows during dry weather periods to the side river "Bijleveld". The pumping-station "Vleuterweide" pumps generally 7 hrs per day water from the "Leidsche Rijn" into the canal

"Heycop"; this is about 3 % of the effluent flow of the sewage treatment plant.

Sewage treatment plant "de Meern"

The sewage treatment plant "de Meern" is an activated sludge plant of the Carrousel type. It was constructed in 1988 with a total capacity of 40,000 inhabitant equivalents (i.e.). At the moment 32,000 i.e. are connected with an average sewage flow of 8000 m^3/day. Less than 10 % of the influent consists of industrial waste water. In Table 1 the characteristics and the dimension of the sewage treatment plant are given.

Table 1: Characteristics of flow and dimensions of the sewage treatment plant "de Meern"

Treatment Capacity:	40.000 i.e.		
Dry Weather Flow	560 m^3/h		
Rain Weather Flow	1650 m^3/h		
pre-settling tank:		**post sedimentation tank** :	
surface loading rate	4 $m^3/(m^2.h)$	surface loading rate	0.75 $m^3/(m^2.h)$
volume (excl primary sludge thickener)	775 m3 (50 m^3)	volume	1650 m^3
aeration basin:		**surplus sludge thickener:**	
type	Carrousel	surface loading rate	20 $kg/(m^2.d)$
volume	4000 m^3	volume	240 m^3
sludge content	3.5 kg/m^3		
sludge loading rate	0.1 kg BOD/(kg/d)		

The flow of primary sludge is about 32 m^3/d with a mean suspended solids content of 4 g/l; for the surplus sludge the values are respectively 50 m^3/d and 2.5 g/l.

MATERIALS AND METHODS

Sampling method

Waste water treatment plant

The influent, the settled sewage and effluent are daily flow proportional composite samples. On day 1 there was no sample of settled sewage and effluent. On 6 July 12.00 hr until 7 July 10.00 hr 2 hourly (flow proportional) composite samples of influent and settled raw sewage has been taken. During a part of this monitoring period the automatic sampling device of the settled raw sewage was out of operation; grab samples have been taken instead. According to the estimation of the average flow rate on day 7 from midnight until 18.00 hr also 2 hourly composite samples are taken from the effluent. Analytical measurements of raw sewage included the determination of LAS and boron, total organic carbon (TOC), dissolved organic carbon (DOC), chemical oxygen demand (COD), biological oxygen demand (BOD), suspended solids (SS), nitrate (NO_3), ammonia (NH_4) and N-Kjeldahl (Table 2).

Table 2: Raw sewage, settled sewage, and effluent parameters, preservation and analysis method.

	preservation	analysis method		preservation	analysis method
TOC	4 °C	NPR 6522	NKj	pH 2 (H_2SO_4) 4 °C	NEN 6481
DOC	4 °C	NPR 6522	NH_4	pH 2 (H_2SO_4) 4 °C	NEN 6472
COD	pH 2 (H_2SO_4) 4 °C	NEN 6633	NO_3	4 °C	NEN 6440
BOD	to freeze	NEN 6634	SS	4 °C	NEN 6621
LAS	3 % formaldehyde (37 % v/v), 4 °C		Boron	4 °C	

Primary sludge and surplus sludge were analysed on the parameters LAS, dry solids (% ds; NEN 5747) and ash content (% ds, NEN 6620).

River

Daily grab samples were taken from the river water on the locations 100 m above sewage treatment outlet, 700 m, 1200 m and 2000 m below effluent outlet. The samples were analysed on the specific parameter LAS, the water quality parameters TOC, DOC, BOD, SS, NO_3, NH_4, NKj and Cl, and the directly measurements pH, conductivity, temperature and oxygen. The preservation for analysis of the nitrogen components exist only of cooling at 4 °C.

On July 2nd and July 7th, river sediments have been taken for LAS analyses also on the above mentioned locations. Dry solids (NEN 5747), total organic carbon (IB-method, 1979) and particle size distribution (NEN 5733) have been determined to characterise the sediments. On the 2nd of July sampling was performed with a Beekersampler. The method allows precise sampling of the upper layer (5 cm) of the river sediments. The Van Veen sampler was used during the July 7th sediment sampling. With this method a thicker and disturbed sediment layer is taken as sample.

On July 1st and July 7th river samples were taken for boron analysis and conductivity measurement at 6 locations: 100 m above sewage outfall, and 100 m, 350 m, 700 m, 1200 m and 2000 m below sewage treatment outlet. At each location 4 samples were taken across the river at 2 meters from each border plus 2 samples in between.

LAS Analytical Methodology

Isolation and Concentration Procedures

Representative aliquots of raw sewage (10 mL), settled sewage (10 mL) and effluent (50 mL) were evaporated to dryness on a steambath using a stream of nitrogen. The residue was redissolved in 25 mL of methanol. The extract was passed over a strong anion exchange column and the LAS was then eluted with 2 mL methanol/hydrochloric acid (80:20, v:v). The eluate was brought to a volume of 50 mL with suprapure water after adjusting the pH to 7 with 1 molar sodium hydroxide. This solution was then passed over a C18 solid phase extraction (SPE) column, washed with 2 mL of methanol/water (30:70, v:v) and subsequently eluted with 5 mL of methanol. Similarly, representative aliquots of river water (250 mL) were passed directly over a C18 solid phase extraction (SPE) column. The column was then washed with 2 mL of methanol/water (30:70, v:v) and eluted with 5 mL methanol. Obtained methanol eluates were evaporated to dryness under a stream of nitrogen at approximately 40°C. The residue was then redissolved in 0.5 mL mobile phase and

analysed by HPLC. For influents, the final solution was diluted ten times prior to HPLC analysis.

Wet sludge and sediment samples (± 200 g) were dried at approximately 80°C. Aliquots of well dried and homogenised sludge (0.25 g) were then Soxhlet extracted with 150 mL of methanol for approximately four hours. The extract was then adjusted to a volume of 200 mL with methanol and 10 mL aliquot for sludge and 100 mL for sediment was passed over a strong anion exchange column. The column was then eluted with 2 mL of methanol/hydrochloric acid (80:20, v:v). The eluate was brought to a volume of 50 mL with suprapure water after adjusting the pH to 7 with 1 molar sodium hydroxide. This solution was then passed over a C18 solid phase extraction (SPE) column, washed with 2 mL of methanol/water (30:70, v:v) and subsequently eluted with 5 mL of methanol. The methanol eluate was evaporated to dryness under a stream of nitrogen at approximately 40°C. The residue was then redissolved in 0.5 mL mobile phase and analysed by HPLC.

HPLC analysis and quantition

The HPLC mobile phase consisted of a suprapur water/methanol (16:84,v:v) mixture containing 0.0875M sodium perchlorate. The chromatographic separation is run isocratically on a Chrompack Spherisorb ODS-2 column and using a flow rate of 1 mL/min. Detection is made with a fluorescence detector operating at an excitation wavelength of 232 nm and an emission wavelength of 290 nm. Identification of the LAS alkyl homologues is based on retention time compared to a chromatogram of LAS reference sample. Quantification is made versus an LAS material (Marlon A 390, Huels VA-Nz 172987) with an activity of 89.2% (w:w). Reported chain length distribution for the reference material is 5-10% C10, 40-45% C11, 35-40% C12, 10-15% C13 and <1% C14. A five point calibration curve was made from LAS solutions prepared in mobile phase at concentration levels between 0 and 20 mg/L. The standard work solutions were renewed daily from a 1 g/L LAS stock solution in suprapure water.

The analytical method was validated for its reproducibility and accuracy using control samples spiked with LAS reference material. Control samples and standard LAS addition was used in the analysis for every series of environmental samples. In order to check the efficiency of the sample preservation and the storage efficiency, standard additions of LAS were performed on site, directly after sample collection. The analytical detection limit was calculated from the mean and the standard deviation from blank analyses (Table 3).

Table 3: Main features of the LAS analytical methodology

	Influent	Effluent	River	Sludge	Sediment
Detection Limit	268 ug/L	8.1 ug/L	2.1 ug/L	29 ug/g	2.9 ug/g
Within run variation	9.9%	16%	2.7%	4.2%	4.2%
Recovery analysis	100%	87%	102%	86%	86%
Recovery storage + analysis	85%	90%	110%	-	-

RESULTS AND DISCUSSION

Sewage Treatment Plant

Raw Sewage

The sewage flow entering the treatment plant was recorded as a 24-hours average (Table 4). During the dry weather period the flow varied between 5960 and 7555 m3/day with an average value of 6447 m3/day.

Table 4: Flow rates measured during the monitoring week.

date	time	influent (m3/d)	effluent (m3/d)	primary sludge (m3/d)	secondary sludge (m3/d)
July 1	8.30	7555	7336	32	32
July 2	8.30	6423	6194	8	30
July 3	8.30	6303	6164	33	24
July 4	8.30	6179	5883	32	24
July 5	8.30	5960	5722	33	23
July 6	8.30	19883	20642	32	23
July 7	8.30	6555	6234	48	22
July 8	8.30	6157	5818	32	24

With 32000 equivalents connected to the sewage treatment plant, the average dry weather flow corresponds to a per capita flow of 200 L/day. Heavy rainfall occurred on July 5th which increased the average flow over 24-hours to 19883 m3/day or 600 L/cap.day on July 6th. During this day, the hydraulic residence time decreased from an average value of 14.9 hrs to 4.8 hrs over the whole plant. Due to the heavy rainfall on July 5, the 2 hours composite monitoring was delayed from July 5, till July 6th, starting at 10 am.

Analytical measurements of raw sewage included the determination of LAS and boron, total organic carbon (TOC), dissolved organic carbon (DOC), chemical oxygen demand (COD), biological oxygen demand (BOD), suspended solids (SS), nitrate (NO_3), ammonia (NH_4) and N-Kjeldahl (Table 5).

Table 5: Results of influent of sewage treatment plant "de Meern".

date time	LAS (ug/L)	B (ug/L)	TOC (mg/L)	DOC (mgL)	COD (mg/L)	BOD (mg/L)	SS (mg/L)	NH_4 (mg/L)	NKj (mg/L)
1 July	7160	700	82	32		140			
2 July	6830	780	113	35		160			
3 July	6960	780	158	40	445	185	150	29	46
4 July	6770	770	108	27	410	130	160	28	47
5 July	4220	540	107	28	405	115	200	28	43
6 July 10.00	3100	270	24	20	210	81	120	9.4	19
6 July 12.00	3470	270	27	21	415	155	240	42	54
6 July 14.00	5280	490	29	29	530	200	360	41	59
6 July 16.00	5730	640	97	26	450	140	310	25	48
6 July 18.00	7030	850	83	34	405	135	150	24	44
6 July 20.00	6200	780	82	30	380	130	140	22	39
6 July 22.00	6673	720	75	28	410	160	130	21	41
7 July 0.00	7310	710	105	33	545	220	230	28	48
7 July 2.00	6420	570	110	34	495	210	190	25	44
7 July 4.00	6800	630	105	20	355	210	150	31	55
7 July 6.00	5610	450	94	29	405	125	370	29	51
7 July 8.00	4170	420	69	21	325	88	130	42	44
7 July 10.00	3450	380	13	11	215		65	33	36

Temporal variability of Boron (B) which is used as a tracer for the better understanding of the hydrodynamic behavior of the plant and LAS are given in Figure 1.

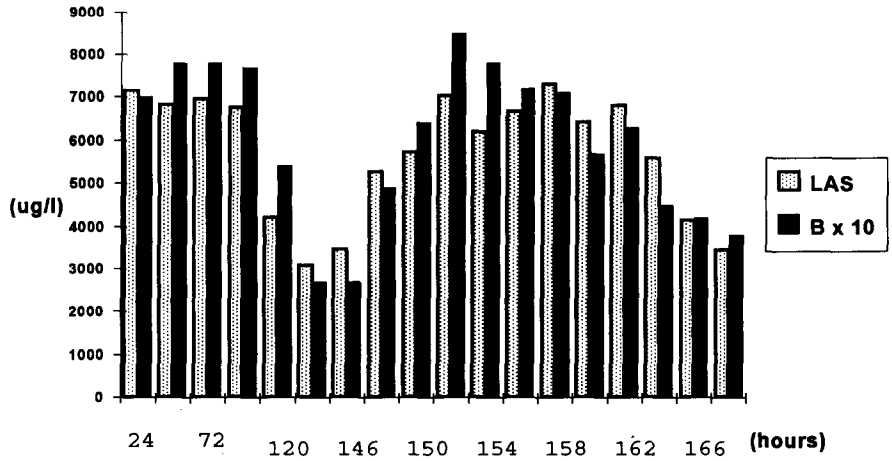

Figure 1: Daily and hourly variability of LAS and boron concentrations in raw sewage

The LAS concentrations in daily composite raw sewage samples varied between 3.1 and 7.2 mg/L. The lowest value represents the concentration measured in the 24-hours composite sample collected during the rain period. The LAS and boron concentration in the 2-hourly composite samples varied between 3.5 and 7.3 mg/L. Over the entire sampling period the LAS and boron concentrations in the raw sewage are highly correlated ($r^2 = 0.90^{**}$), and reflect to a large extent the variability in consumption and/or dilution patterns. Boron and LAS concentrations in raw sewage dropped significantly with the increased sewage flows throug the sewage treatment plant.

The wash-out created a 3-fold increase in sewage flow from about 6500 m3/day to 19000 m3/day resulting in an approximate 3 fold higher internal dilution rate for boron and LAS in the raw sewage. Both boron ($r^2 = -0.73^{*}$) and LAS ($r^2 = -0.71^{*}$) are inversely correlated with sewage flow which explains the variability in influent. Diurnal variation in this treatment plant is small, due to the presence of an in-line buffer tank.

Using dry weather sewage flows of 200 L/capita.day - predicted boron concentrations were in good agreement with measured dry weather boron concentrations (Table 6). However, measured LAS concentrations in raw sewage (3.0 - 7.5 mg/L) were found to be significantly lower than what was predicted on the basis of the annual LAS consumption data. The hydraulic residence time in most Dutch sewers exceeds 10 hours, since several in-line storm tanks are typically present before arrival at the sewage treatment plant. It can therefore be postulated that between 40 to 60% of the LAS load has been removed/biodegraded in the sewers and/or in the in-line storm tanks. In view of the rapid biodegradation of LAS in activated sludge and rivers, it may be assumed that the biodegradation rate in sewers will at least

equal the rate in surface waters.

Table 6: Predicted and measured raw sewage concentrations for LAS and perborates

	1992 -Tonnage ton/yr	Predicted dry weather mg/l	Measured dry weather mg/L	Measured rainy day mg/L
LAS	16420	15.9	7.5	3
PERBORATES (as NaBO3)	7456	0.9	0.9	0.25

Settled Sewage

Similarly to the raw sewage analyses, analytical measurements of settled sewage included the determination of LAS and boron, total organic carbon (TOC), dissolved organic carbon (DOC), chemical oxygen demand (COD), biological oxygen demand (BOD), suspended solids (SS), nitrate (NO_3), ammonia (NH_4) and N-Kjeldahl (Table 7).

Table 7: Results of settled sewage of sewage treatment plant "de Meern".

date time	LAS (ug/L)	TOC (mg/L)	DOC (mg/L)	COD (mg/L)	BOD (mg/L)	SS (mg/L)	NO_3 (mg/L)	NH_4 (mg/L)	NKj (mg/L)
1 July	3190								
2 July	2830						< 0.2		
3 July	3580	57	28	505	86	110	< 0.2	32	53
4 July	4900	100	38	285	145	100	< 0.2	36	53
5 July	5570	74	30	550	135	370	< 0.2	35	59
6 July 10.00	7590	150	32	745	160	720	< 0.2	19	51
6 July 12.00	2140	185	47	186	215	61	< 0.2	20	29
6 July 14.00	2630	39	?	215	68	60	< 0.2	29	42
6 July 16.00	3360	50	40	260	73	55	< 0.2	37	44
6 July 18.00	4680	52	27	265	98	31	< 0.2	36	38
6 July 20.00	4880	29	22	285	93	26	< 0.2	27	38
6 July 22.00	5070	31	29	305	98	46	< 0.2	24	41
7 July 0.00	4470	31	31	315	125	36	< 0.2	37	42
7 July 2.00	3660	32	31	330	135		< 0.2	30	44
7 July 4.00	4180	76	34	315	155	31	< 0.2	31	45
7 July 6.00	3740	49	44	285	145	37	< 0.2	29	75
7 July 8.00	3350	60	33	265	125	18	< 0.2	32	49
7 July 10.00	3050	56	31	255	91	48	< 0.2	59	57

Primary solids removal averaged 68 $\pm$ 23% during the dry weather period. The wash-out during heavy rainfall created an actual negative removal rate of solids in the primary clarifier (up to - 500%), resulting in a wash-over of solids and adsorbed chemicals in the aeration tank.

The combination of mixed sewer system and heavy rain increased the influent flow rate to such an extent that the hydraulic residence time in the primary settler decreased to less than 1 hour. During this period, primary sludge from the buffer tank and primary settler is resuspended and carried-over into the aeration tank. Since the removal of LAS is highly correlated with the removal of primary solids ($r^2 = 0.97^{**}$), a similar picture can be expected for LAS removal in the primary clarifier.

Measured LAS concentrations in the settled sewage indicated that a high fraction of LAS is removed via the primary settling tank under dry weather conditions. During heavy rainfall however, LAS concentration in the

settled sewage were higher than concentrations in the corresponding raw sewage. The presence of primary solids which typically contain high LAS concentrations, resulted in higher LAS readings, since the analytical method measures total LAS (dissolved + adsorbed onto solids). This is reflected in the actual LAS removal figures. LAS removal in the primary settler averaged 38 ± 9 % over the dry weather period, but decreased to -145% during the heavy rainfall period.

Similarly, TOC, COD and BOD removal averaged respectively 49 ± 14, 36 ± 14 and 35 ± 14 % during the dry weather period. Due to the wash-out of July 6th, primary removals of TOC, COD and BOD decreased respectively to - 670%, - 255%, and - 165%. Suspended solids removal and settling of particulate organic matter are positively correlated (r^2= 0.95**), and highly affected by the increased sewage flow.

The concentration of LAS on primary sludge collected from the De Meern plant varied between 3400 and 5930 ug/g with an average concentration of 4336 ug/g (Figure 2). These values correspond very well with other published data for primary sludge (Berna et al. 19989; Giger et al. 1989; de Henau et al. 1989; McAvoy et al. 1993).

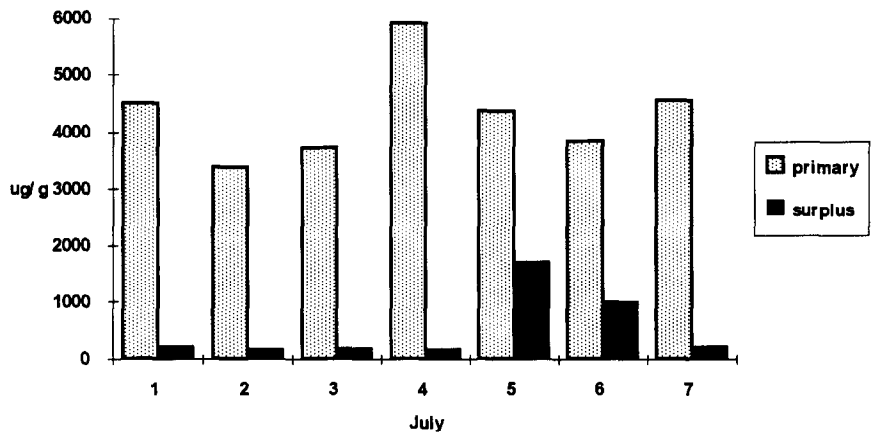

Figure 2: LAS concentrations (ug/g) in primary and surplus sludge

The wash-out of inorganic and organic solids in the storm tank and primary settler during heavy rainfall resulted in an increased LAS concentration in settled sewage and transfer to the aeration tank. This is further substantiated by LAS concentrations analyzed on wasted sludge. The LAS concentration in the wasted sludge averaged 205 ug/g during the dry weather period. However, due to the suspended solids input from the primary settler during high flow conditions, concentrations increased to a value of 1720 ug/g.

The 'solids effect' is still noticeable in the subsequent sampling day as an LAS concentration of 1020 ug/g was measured. However, dry solids and ash contents are not significanlty different for the surplus sludge.

Effluent

Analytical measurements of unfiltered effluent included the determination of total LAS and boron, total organic carbon (TOC), dissolved organic carbon (DOC), chemical oxygen demand (COD), biological oxygen demand (BOD), suspended solids (SS), nitrate (NO_3), ammonia (NH_4) and N-Kjeldahl (Table 8). Dissolved LAS concentration were determined on a sub-set of the samples.

Table 8: Results of effluent of sewage treatment plant "de Meern".

location date	LAS* (ug/L)	B (ug/L)	TOC (mg/l)	DOC (mg/l)	COD (mg/l)	BOD (mg/l)	SS (mg/l)	NO_3 (mg/l)	NH_4 (mg/l)	NKj (mg/l)
1 July	< 8.1	730								
2 July	< 8.1	720	11	9.5		3.0		5.4		
3 July	< 8.1	740	11	11	31	2.0	< 10	4.7	3.4	4.9
4 July	< 8.1	750	16	12	34	3.0	< 10	5.5	-	2.9
5 July	12	710	21	10	28	2.0	< 10	10	2.3	6.5
6 July	491 (410)	410	14	13	48	7.0	< 10	5.5		7.6
7 July 0.00	41 (34)	390	12	9.1	30	9.0	< 10	1.1	1.0	2.0
7 July 2.00	35 (20)	420	11	10	30	1.0	12	0.89	0.76	1.8
7 July 4.00	29 (24)	440	12	9.8	27	2.0	< 10	0.69	1.1	1.6
7 July 6.00	21 (19)	450	11	11	25	2.0	< 10	0.60	0.62	1.5
7 July 8.00	12 (16)	460	12	11	27	2.0	< 10	0.58	0.45	1.4
7 July 10.00	< 8.1	460	11	11	27	2.0	< 10	0.62	0.48	1.6
7 July 12.00	< 8.1	470	12	10	29	1.0	< 10	0.60	0.83	1.8
7 July 14.00	< 8.1	470	12	11	24	1.0	< 10	0.61	1.6	2.4
7 July 16.00	< 8.1	470	12	11	26	1.0	< 10	<0.2	3.3	3.4
7 July 18.00	< 8.1	460	13	11	29	1.0	< 10	1.7	1.0	4.2

* total (dissolved) concentrations

The LAS concentration in the dry weather period was generally under the analytical detection limit of 8.1 ug/L (Table 8). Due to heavy rainfall, the effluent concentration increased to a maximum value of 491 ug/L during one day. The marked increase reflects to a large extent the presence of primary organic and inorganic solids in the activated sludge reactor, containing significant amounts of adsorbed LAS. About 15-20% of the LAS is associated with the inorganic suspended solids. This fraction increased to about 40% in the sample where the highest suspended solids concentrations was measured. The wash-out effect is still visible in the effluent samples during the next 10 hours, when 2-hourly composite samples were collected. After the rain period, measured LAS concentration in the effluent dropped again below the analytical detection limit of 8.1 ug/L. Measured LAS removals during dry weather conditions averaged 99.8%. The removal in the aeration tank decreased to about 93% during periods of heavy rain, and only slowly recovering in the hours following.

Similarly, COD and BOD activated sludge removal averaged respectively 91 $\pm$ 2% and 98.4 $\pm$ 0.5% during the dry weather period. Due to the wash-out of July 6th, activated sludge removals of COD and BOD decreased respectively to 83.9% and 86.5%, i.e. significantly lower than LAS removal.

Boron analyses in effluent showed a different picture as compared to LAS, BOD or COD. The effect of the rain period resulted in higher dilution and lower boron concentrations. Boron which behaves essentially as an inert conservative tracer element is not affected by the increased input of solids in the aeration tank or shorter residence time and exhibits a 3-fold dilution, as predicted by a 3-fold increase in sewage flow.

River Water

During two days (July 1 and July 7) the mixing of the effluent into the receiving water was examined by analysis of samples taken at the river transect. Samples were taken at -100, 100, 350, 700, 1200 and 2000 meter below sewage outfall. The conductivity of the river water was measured in situ at the sampling site using a small boat. Additional characterisation was achieved by boron analysis.

Both conductivity and boron measurements illustrate an homogenous transversal mixing of the top water layer along the river transect. However, boron concentrations increase with distance/time below the sewage outfall, as a result of a very slow vertical mixing of the sewage and receiving water. This is due to submerged discharge of the effluent, as it is located about 70 cm underneath the water surface. Complete vertical mixing of the layers may take at up to 2 km travel time under dry weather conditions.

River water samples taken at 100 m above sewage outfall (ASO), and at 100, 700, 1200 and 2000 m below sewage outfall (BSO) were analysed for total LAS and boron. In addition, the samples were also characterised for TO, DOC, BOD, SS, NO_3/NO_2, NH_4, N-Kjeldahl, phosphates ($PO4^{3-}$) and chloride (Cl^-) (Table 9).

During the dry weather period, total LAS concentration varied between <2.1 ug/L (detection limit) and 2.9 ug/L in samples taken ASO and between <2.1 ug/L and 7.1 ug/L for samples taken BSO. During this period, concentration profiles of LAS and B along the river are quite similar (r^2 = 0.65*). Measured B concentrations varied from 110 to 120 ug/L ASO and from 200 to 290 ug/L BSO.

The picture for LAS and B changes completely as a result of the heavy rain. Measured LAS concentrations above sewage outfall increased to level between 68 and 168 ug/L, while the concentration below sewage outfall remained low, with limit values between <2.1 and 8 ug/L. This was the direct result of the direct discharge of the bypass upstream from the sewage treatment plant.

The water quality parameters and B analyses obtained on samples taken during and after the rainfall did confirmed that direct sewage discharge occurred upstream from the sewage treatment plant. Above sewage outfall concentrations of 280 ug/L B were observed. This in contrast to the dry weather boron concentrations of 70 to 140 ug/L. LAS, NH_4, NK_j, PO_4 concentration measured in the same upstream river samples increased 10-fold, supporting the observation that the sampling point above sewage outfall was impacted by direct untreated sewage discharge. High LAS concentrations are a direct consequence of the limited capacity of the sewering system and malfunctioning of the sewage treatment plant during heavy rainfall, possibly even more accentuated by the presence of higher levels of suspended organic and inorganic solids in effluent and river. The effect of the direct discharge on LAS concentrations is visible during three sampling days. Similarly, NH_4, NK_j, and PO_4 also increased significantly above the sewage outfall to levels of respectively 1.4, 3.0, and 1.2 mg/L during 3 consecutive days.

Table 9 Results of surface water "Leidsche Rijn", 100 m above, 700 m, 1200 m and 2000 m below sewage treatment outlet.

location date	LAS	B	TOC (mg/l)	DOC (mg/l)	BOD (mg/l)	SS (mg/l)	NO_3/NO_2 (mg/l)	NH_4 (mg/l)	NKj (mg/l)	PO_4 (ug/l)	Cl (mg/l)
-100 m											
1 July	2.4	120	2.9	2.9	1	7	2.42	0.12	0.96	318	149
2 July	2.5	110	8.8	7.0	2	7	2.52	0.17	1.11	82	150
3 July	< 2.1	120	7.7	4.6	1	16	2.56	0.15	0.98	94	153
4 July	2.9	110	6.7	4.6	1	14	2.60	0.14	1.19	95	158
5 July	68	210	8.4	4.9	2	10	2.84	1.43	3.02	779	148
6 July	168	260	10	8.7	7	10	2.41	1.00	2.30	1219	112
7 July	142	280	12	7.9	8	11	1.97	1.29	2.13	1278	98
700 m											
1 July	3.8	250	8.0	7.4	1	7	3.32	0.57	1.81	1100	158
2 July	2.7	200	7.8	7.3	1	8	2.65	0.24	1.46	584	157
3 July	< 2.1	260			1	17	2.58	0.90	1.96	984	162
4 July	2.3	220	6.5	6.4	1	11	3.06	0.40	1.43	727	154
5 July	2.1	230	7.7	7.6	2	15	3.78	0.40	1.51	718	150
6 July	3.0	120	12	9.6	4	16	0.86	0.28	1.67	128	108
7 July 8.30	6.0	110	10	8.5	4	13	1.33	0.39	1.42	404	119
10.30	4.8	120									
12.30	14	160									
14.30	23	250									
16.30	62	280									
18.30	69	280									
1200 m											
1 July	5.2	260	9.0	7.9	1	8	3.00	0.45	1.83	1071	158
2 July	3.8	240	7.7	7.5	1	8	3.13	0.37	1.68	611	161
3 July	< 2.1	210	7.3	6.7	1	13	2.44	0.29	1.34	422	155
4 July	< 2.1	210	7.7	6.0	1	10	2.58	0.41	1.29	422	158
5 July	7.0	190	5.7	5.4	2	19	2.83	0.30	1.38	355	156
6 July	3.1	80	13	12	4	12	0.19	0.21	1.29	51	90
7 July	< 2.1	90	12	11	4	15	0.40	0.29	1.43	121	97
2000 m											
1 July	7.1	290	8.3	8.1	2	5	1.66	0.62	1.67	851	141
2 July	5.0	260	6.9	6.9	1	7	3.32	0.47	1.58	310	157
3 July	2.2	250	8.5	8.3	2	10	3.00	0.32	1.59	410	159
4 July	< 2.1	240	6.9	5.0			2.39	0.58	1.60	623	160
5 July	2.1	170	9.6	8.2	5	23	1.81	0.35	1.69	269	133
6 July	5.6	70	16	12	6	15	0.11	0.20	1.17	32	91
7 July	< 2.1	70	14	13	5	18	0.17	0.28	1.48	37	89

At the same sites grab samples of sediment were collected at mid channel. These samples were analysed for LAS, dry solids, TO and particle size distribution. Grab samples of sediments were collected on July 2nd from the top 2 cm layer (Table 10) and on July 7th (Table 11) up to a sampling depth of 15 cm. Sampling was performed 100 m ASO and 700, 1200 and 2000 m BSO.

Table 10: LAS concentrations, dry solids, total organic carbon and particle size distribution (2 cm section)

location date	-100 m 2 July	700 m 2 July	1200 m 2 July	2000 m 2 July
LAS (ug/g)	35	5.3	3.8	4.8
dry solids (w. %)	20.0	15.5	13.3	15.1
tot. organic carbon (% ds)	17	20	23	23
particle size distribution				
< 2 µm (% d.s.)	21	25	25	7.7
< 16 µm (% d.s.)	32	33	32	8.8

Table 11: LAS concentrations, dry solids, total organic carbon and particle size distribution (15 cm section)

location date	-100 m 7 July	700 m 7 July	1200 m 7 July	2000 m 7 July
LAS (ug/g)	12	4.9	4.2	4.4
dry solids (w. %)	17.8	9.1	7.8	14.2
tot. organic carbon (% ds)	18	21	28	22
particle size distribution				
< 2 µm (% d.s.)	9.0	1.6	1.8	1.8
< 16 µm (% d.s.)	11	2.3	2.8	2.4

Measured LAS concentrations BSO did not essentially vary with sampling site nor with sample depth. Concentrations ranged between 3.8 and 5.3 ug/g dry sediment. Highest concentration were measured above sewage outfall, and the impact of the by-pass is clearly visible in the sediment. Dry solids and silt contents indeed confirm the direct discharge situation with higher suspended solids loading and effective settling due to the low flow conditions of the receiving water. The above stream sediment signature confirms the limited capacity of the sewering system and suggests that the direct discharge situation is not a single event. However, extensive LAS removal in sediments can be observed, as LAS levels downstream of the sewage outfall dropped rapidly to 5.3-3.8 ug/g dry sediment.

CONCLUSIONS

The monitoring study in De Meern illustrates an effective removal of LAS of 99.9% during dry weather and normal operating conditions. The LAS concentrations in daily composite raw sewage samples varied between 3.1 and 7.2 mg/L, with corresponding effluent concentrations generally under the analytical detection limit of 8.1 ug/L. During this same period, total LAS concentrations in the river varied between <2.1 ug/L (detection limit) and 2.9 ug/L in samples taken above the sewage outfall and between <2.1 ug/L and 7.1 ug/L for samples taken below the sewage outfall.

Malfunctioning of the sewage treatment plant during heavy rainfall conditions, resulted in throughput of

organic and inorganic suspended solids to the aeration tank. LAS, BOD, and COD removals in the aeration tank decreased significantly, resulting in higher effluent concentrations. Water quality analysis and boron analyses of river samples taken during and after the rainfall indicated that a sewer overflow occurred upstream from the sewage outfall of the treatment plant. The effect of the direct sewer discharge is visible in the river above the sewage treatment plant outfall during three consecutive days. LAS concentrations up to 168 ug/L were measured in the upstream sampling location, and associated mainly by the presence of higher levels of suspended organic and inorganic solids. Concentrations below the sewage outfall decreased rapidly to levels between <2.1 ug/L and 7 ug/L, due to an effective instream removal of LAS. LAS sediment concentrations of 12-35 ug/g above the sewage outfall decreased rapidly downstream to about 3.8 and 5.3 ug/g dry sediment. Significantly higher dry solids and silt contents above the sewage outfall confirm the upstream discharge of raw sewage and settling of solids under low flow conditions.

Similarly to increases of LAS in the receiving surface waters, BOD, NH_4 and PO_4 concentration increased about 10 fold above the sewage outfall to respectively 8 mg/L, 1.4 mg/L and 1.3 mg/L during 3 consecutive days. Further dilution and instream removal below the sewage outfall decreased BOD, NH_4 and PO_4 concentrations respectively to 4 mg/L, 0.3 mg/L and 0.4 mg/L.

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