



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



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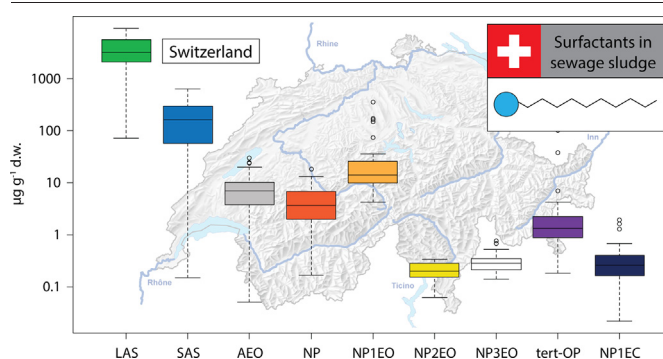
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### HIGHLIGHTS

- Comprehensive study of wastewater treatment plants in Switzerland
- NPEO and NP sludge levels have decreased 10–100 fold since their ban in the 1980s.
- Per capita loads can successfully reveal industrial/commercial emission sources.
- Sludge levels of LAS, SAS, and NP correlate with anaerobic digester residence time.
- <sup>13</sup>C-isotope ions can replace qualifier adduct ions that show strong matrix effects.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Surfactants are high-production-volume chemicals that are among the most abundant organic pollutants in municipal wastewater. In this study, sewage sludge samples of 36 Swiss wastewater treatment plants (WWTPs), serving 32% of the country's population, were analyzed for major surfactant classes by liquid chromatography mass spectrometry (LC-MS). The analyses required a variety of complementary approaches due to different analytical challenges, including matrix effects (which can affect adduct ion formation) and the lack of reference standards. The most abundant contaminants were linear alkylbenzene sulfonates (LAS; weighted mean [WM] concentration of  $3700 \mu\text{g g}^{-1}$  dry weight), followed by secondary alkane sulfonates (SAS;  $190 \mu\text{g g}^{-1}$ ). Alcohol polyethoxylates (AEO;  $8.3 \mu\text{g g}^{-1}$ ), nonylphenol polyethoxylates (NPEO;  $16 \mu\text{g g}^{-1}$ ), nonylphenol (NP;  $3.1 \mu\text{g g}^{-1}$ ), nonylphenol ethoxy carboxylates (NPEC;  $0.35 \mu\text{g g}^{-1}$ ) and *tert*-octylphenol (*tert*-OP,  $1.8 \mu\text{g g}^{-1}$ ) were present at much lower concentrations. This concentration pattern agrees with the production volumes of the surfactants and their fates in WWTPs. Branched AEO homologues dominated over linear homologues, probably due to higher persistence. Sludge concentrations of LAS, SAS, and NP were positively correlated with the residence time in the anaerobic digester. Derivation of the per capita loads successfully revealed potential industrial/commercial emission sources. Comparison of recent versus historic data showed a decrease in NPEO and NP levels by one or two orders of magnitude since their ban in the 1980s. By contrast, LAS still exhibit similar concentrations compared to 30 years ago.

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## 1. Introduction

Surface-active agents (surfactants) are amphiphilic organic compounds containing a hydrophilic head and a hydrophobic tail. This structure imparts solubility in both polar and nonpolar solvents, resulting in surface-active properties. Surfactants are usually classified into non-ionic, anionic, cationic, or zwitterionic (amphoteric) types, based on the ionic charge of the polar head (Tadros, 2005). Surfactants are a diverse group with wide commercial and industrial applications as detergents (laundry detergents, cleaning agents, personal care products), emulsifiers, and wetting agents (Li et al., 2018b). They are high-production-volume chemicals (15 million tons per year), with anionic and non-ionic surfactants accounting for up to 90% of the annual production (Freeling et al., 2019; Lara-Martín et al., 2006).

Linear alkylbenzene sulfonates (LAS) are a high-volume class of anionic surfactants with a yearly consumption of 0.43 million tons in Europe alone (HERA, 2013). They are the most consumed anionic surfactant class apart from soap (Berna et al., 2007). Since the 1960s, LAS have been used as substitutes for the branched alkylbenzene sulfonates that were responsible for foaming in effluents of wastewater treatment plants (WWTPs) and receiving natural waters (Sweeney and Anderson, 1989). Currently, LAS are mainly used as household detergents (e.g., laundry agents), accounting for up to 30% of the active ingredients in respective products. Technical mixtures usually contain homologues with alkyl chains ranging from C<sub>10</sub> to C<sub>13</sub> (HERA, 2013). LAS with C<sub>11</sub> and C<sub>12</sub> are the most abundant.

Secondary alkane sulfonates (SAS) are another important class of anionic surfactants and are mainly used in household cleaning agents (laundry and dishwashing detergents). Technical SAS mixtures mainly contain homologues with chain lengths between C<sub>14</sub> and C<sub>17</sub> (HERA, 2005).

Alkylphenol polyethoxylates (APEO) with nonyl chains (NPEO) were once a major class of non-ionic surfactants (Lara-Martín et al., 2012) and were usually applied as technical mixtures containing isomers with branched nonyl chains and a variety of ethoxylation degrees. In WWTPs, NPEO are transformed into toxic compounds (nonylphenol [NP] and NPEO with one or two ethoxy units) that can end up in receiving waters (Ahel et al., 1994; Brunner et al., 1988; Giger et al., 1984). This has led to a voluntary commitment by the German surfactant industry to no longer use NPEO in washing and cleaning agents (Deutscher Bundestag, 2001). Since 2003, the use of NPEO in commercial products has been legally restricted in the European Union (European Parliament, 2003). In Switzerland, their use was already prohibited in 1986. The use of APEO with octyl chains (OPEO) and their transformation product octylphenol (OP) is also restricted in Switzerland. In general, the use of APEOs and alkylphenols is prohibited at concentrations  $\geq 0.1\%$  in several products, such as washing/cleaning agents, cosmetics, and biocide formulations (Swiss Federal Council, 2021). In the case of OP, the tetramethylbutyl isomer (*tert*-OP) is of primary interest due to registered tonnages between 10,000 and 100,000 t per year in the European Economic Area (ECHA, 2021a). In this case, OP is not a transformation product of OPEO but is directly used in adhesives, coating products, and polymers (ECHA, 2021a).

Alcohol polyethoxylates (AEO) are currently used as more biodegradable substitutes for APEO (Lara-Martín et al., 2012). The AEO are a diverse class of surfactants because their chain length can differ between C<sub>8</sub> and C<sub>18</sub> and they can have up to 13 ethoxymer units, in household products (HERA, 2009). Today, AEO are the most consumed class of non-ionic surfactants (Berna et al., 2007).

In households, surfactant-containing detergents are typically used in down-the-drain applications. Hence, most surfactants are discharged to WWTPs. The WWTPs can remove more than 95% of LAS, SAS, and AEO from the discharged water (Brunner et al., 1988; Field et al., 1995; McAvoy et al., 1998), but surfactants remain ubiquitous pollutants in receiving water bodies because of their high application volume and continuous input. Freeling et al. (2019) have therefore classified surfactants as pseudo-persistent contaminants, although the major surfactant classes used today are considered to pose low or no risk to the environment (Cowan-Ellsberry et al., 2014). Many studies that have reported environmental concentration ranges date back to the 1980s and 1990s (Ahel

et al., 1994; Fendinger et al., 1995; Holt et al., 1989; Marcomini and Zanette, 1996), so current data on environmental concentrations are scarce (Li et al., 2018b; Ruman et al., 2017; Zembrzuska et al., 2016). However, production volumes of surfactants have increased in the last decades (Berna et al., 2007; Freeling et al., 2019), necessitating a reassessment of environmental concentrations.

The average consumption of surfactants in a WWTP catchment area can be assessed by monitoring sewage sludge, as peak concentrations of surfactants have less influence on digested sludge than on wastewater due to the sludge's significantly longer residence time in the WWTP. Furthermore, levels of surfactants in sludge are of interest since the practice of sludge disposal on agricultural lands represents a pathway for surfactant entry to the environment. The addition of sludge to soils has been banned in Switzerland, but many countries still apply nutrient-rich sewage sludge as fertilizer, disregarding the potential hazards posed by sewage-sludge-related pollutants.

Surfactants, such as LAS, SAS, AEO, and APEO, are usually analyzed by liquid chromatography coupled to (tandem) mass spectrometry (LC-MS/MS) using electron spray ionization (ESI) (Baena-Nogueras et al., 2013; Li et al., 2018a; Petrović and Barceló, 2004). AP and APEO with low ethoxylation are often analyzed by gas chromatography MS (GC-MS) after derivatization, but LC-MS methods are also available (Li et al., 2018a). Anionic LAS and SAS are measured in negative ion mode, whereas non-ionic AEO and APEO are determined in positive ion mode. The increasing sensitivity and mass resolution of state-of-the-art mass spectrometers also allows surfactant detection in high-resolution MS (HRMS) full scan mode (Freeling et al., 2019; Li et al., 2018b).

The aims of the presented study were (a) to evaluate the different challenges faced when measuring surfactants in sewage sludge, (b) to conduct a national survey on present-day surfactant levels in Swiss sludge, (c) to link levels to potential industrial inputs, and (d) to compare current levels to historical values. Therefore, sewage sludges from 36 representative WWTPs, distributed across Switzerland (Fig. 1) and with different industry connections, were extracted and analyzed for LAS, SAS, AEO, APEO, and AP using LC-HRMS and LC-MS/MS. A case study is also presented that investigates the impact of off-season and high season activities in tourist regions.

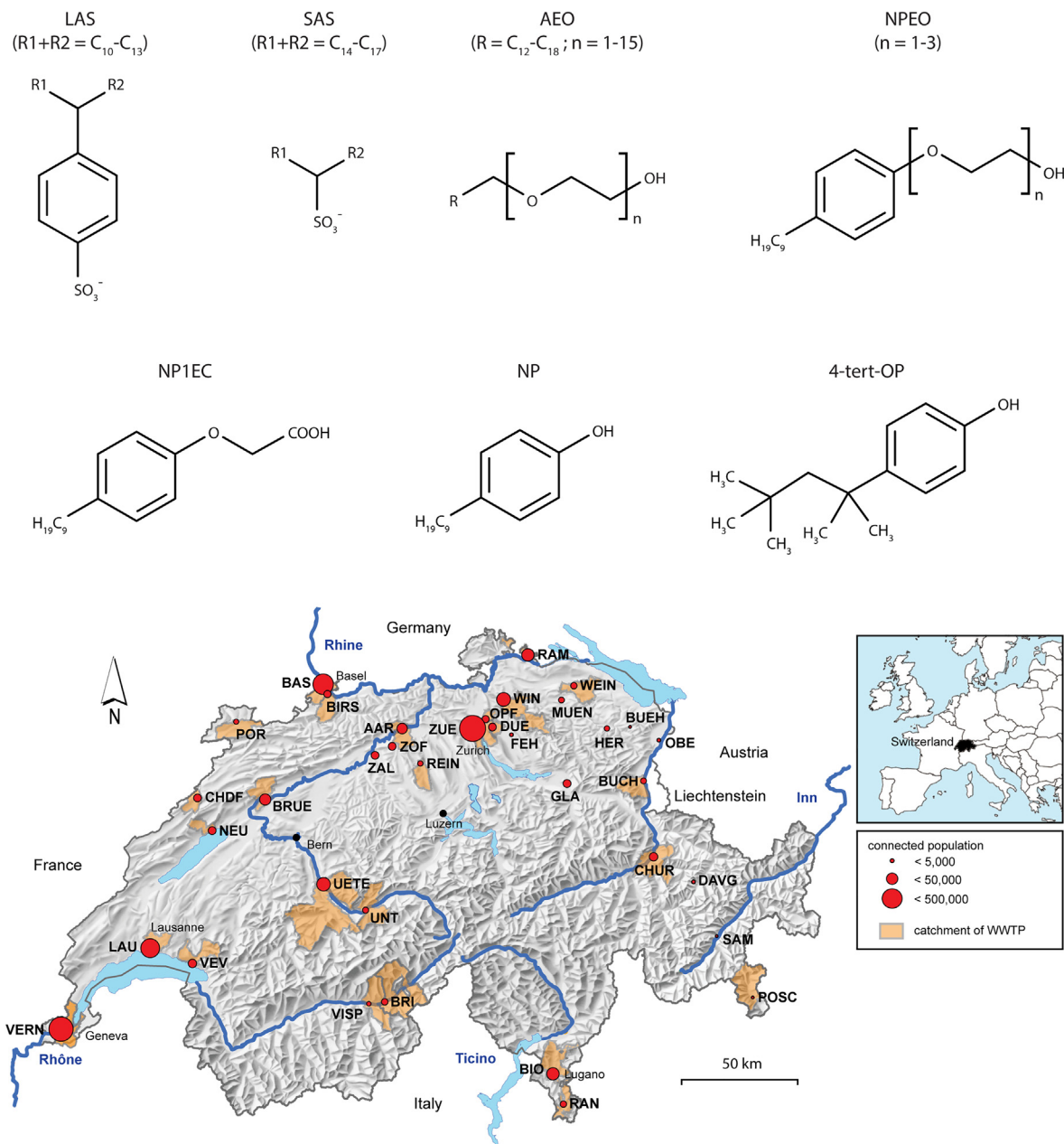
## 2. Materials and methods

### 2.1. Chemicals and standards

LAS were obtained as a technical sodium-LAS mixture from CEPESA (active material = 47.2% with C<sub>10</sub> = 13.4%, C<sub>11</sub> = 32.1%, C<sub>12</sub> = 30.6%, C<sub>13</sub> = 22.4%). SAS were obtained as a technical mixture from Clariant (active material = 18.7% with C<sub>14</sub> = 31%, C<sub>15</sub> = 32%, C<sub>16</sub> = 23%, C<sub>17</sub> = 14%). Individual linear AEO (homologues with carbon chain lengths C<sub>12</sub>, C<sub>14</sub>, C<sub>16</sub> and C<sub>18</sub> and 2, 3, 6 and 8 ethoxymer units) were obtained from Fluka. NP, NPEC, and NPEO (EO1–3) mixtures were purchased from Fluka and from Dr. Ehrenstorfer. *tert*-OP was purchased from Supelco. The structures of the target analytes are displayed in Fig. 1. Internal standards were LAS of chain length C<sub>16</sub>, (C<sub>16</sub>-LAS), SAS of chain length C<sub>12</sub> (C<sub>12</sub>-SAS), AEO of chain length C<sub>10</sub> and 8 ethoxymer units (C<sub>10</sub>EO8-AEO), <sup>13</sup>C<sub>6</sub>-NPEO, D<sub>8</sub>-NP, and D<sub>2</sub>-NP1EC. A SAS standard of chain length C<sub>10</sub> (C<sub>10</sub>-SAS) was used to verify that no major losses occurred during sample preparation. This standard was not used for any corrections. Analytical grade methanol (MeOH, Fischer Chemicals), acetone (Merck), ethyl acetate (EtAc, Honeywell), dichloromethane (DCM, Merck), hydrochloric acid (HCl, 32%, Merck), and nanopure water were used for sample preparation and analysis. Bond Elut C18 cartridges (Agilent Technologies) were used for solid-phase extraction. PTFE micro-centrifugal filters (Thermo Scientific) were used to filter the samples before analysis.

### 2.2. Sampling and sample preparation

Sludge samples were collected during two sampling campaigns. 25 WWTPs were sampled for a previous study in June 2017 (Suess et al., 2020) and 11 WWTPs were sampled in November/December 2019 with



**Fig. 1.** Target analytes and locations of sampled wastewater treatment plants (WWTPs) investigated in this study. Target analytes are non-ionic and anionic surfactants and their potential transformation products. Linear alkylbenzene sulfonates (LAS), secondary alkane sulfonates (SAS), alcohol polyethoxylates (AEO), nonylphenol polyethoxylates (NPEO, with 1 to 3 ethoxymers units), nonylphenol monoethoxy carboxylate (NP1EC), nonylphenol (NP), and *tert*-octylphenol (*tert*-OP) were determined in Swiss sewage sludges. The full names of cities and towns, as well as characteristics of the respective WWTPs, are provided in the supplementary material (Supplementary Table S7).

regard to potential inputs by the textile finishing and pharmaceutical industries. Two WWTPs were sampled again in January 2020 to test for seasonal variations caused by tourist activity in a Swiss skiing region. Fig. 1 shows the locations and catchments of the sampled WWTPs. The obtained samples were mostly anaerobically digested sludge, and the average residence time in the digester was about 27 days. Four of the sampled WWTPs did not have sludge digestion facilities, so non-digested sludge was sampled instead. Some samples were liquid (approximately 95% water), while others had been dewatered. All samples were dried by lyophilization and homogenized before further preparation. Supplementary Table S7 lists information about the sampled WWTPs and the collected samples.

The samples were prepared according to Lara-Martín et al. (2006). Target analytes were extracted from sludge using pressurized liquid extraction (PLE) by mixing 0.2 g of dried sludge with diatomic earth and extracting with methanol (two PLE cycles, 100 °C). The resulting PLE extracts were

spiked with C<sub>10</sub>-SAS before being reduced in volume to 1 mL under nitrogen. Reduced extracts were diluted with 100 mL acidified water (adjusted to pH 2.5 using HCl) and processed by solid-phase extraction (SPE). SPE cartridges were rinsed with 5 mL MeOH and conditioned with 5 mL acidified water. Samples were loaded on the cartridges and then eluted with 5 mL MeOH/acetone (1:1) and 5 mL DCM/EtAc (1:1). SPE extracts were evaporated to dryness under nitrogen and reconstituted in 1 mL. Final samples were spiked with the internal standard mixture, filtered, and diluted 1:100 (for LAS and SAS analysis), 1:10 (for NPEO, NPEC, NP, and OP analysis) and 1:5 (for AEO analysis).

### 2.3. Instrumental and data analysis

Three different analytical methods, based on LC-ESI-HRMS and LC-ESI-MS/MS, were used to detect the target analytes in the sludge extracts. The

methods are described in detail in the supplementary material (Supplementary Chapter S2). LAS, SAS, and AEO were analyzed in full scan mode (HRMS). Molecular ions  $[M]^-$  were extracted for LAS and SAS, whereas  $[M + Na]^+$  ions were extracted for AEO. The corresponding isotopes  $^{13}C-[M]^-$  (LAS and SAS) and  $^{13}C-[M + Na]^+$  (AEO) were extracted as well. OP, NP, NPEC, and NPEO were analyzed by tandem mass spectrometry (MS/MS). Precursor ions were  $[M-H]^-$  for OP, NP, and NP1EC and  $[M + NH_4]^+$  for NPEO (EO1–3). MRM transitions were selected according to Lara-Martín et al. (2012). The dilution process (see Section 2.2) and potential matrix effects were taken into account by correcting the ion response of the analytes by the response of the respective internal standard. Analytes were quantified when the following criteria were fulfilled: (a) the quantifier/qualifier ion ratio was within the chosen tolerance level and (b) the corrected response was at least 2-fold higher than a potential blank value. Blank contamination was observed mainly for LAS. However, the blank levels were small (<2%) compared to the high concentrations in the sludge, and were subtracted from the measured LAS concentration. Calibration standards (spiked with an internal standard mixture) covered a linear range of 0.01–3  $\mu\text{g mL}^{-1}$  for LAS and SAS, 0.01–5  $\mu\text{g mL}^{-1}$  for NPEO and *tert*-OP, 0.001–0.1  $\mu\text{g mL}^{-1}$  for AEO, and 0.01–1  $\mu\text{g mL}^{-1}$  for NP and NP1EC. The calculated concentration levels ( $\mu\text{g mL}^{-1}$ ) were corrected based on recovery values determined by triplicate spiking experiments. Details of the recovery experiments are provided in the supplementary material. Subsequently, the concentrations were normalized to the sludge's dry weight, which was used to calculate the per capita loads.

Per capita loads in sludge were derived by first multiplying the surfactant concentration ( $c_i$ ) by the daily (stabilized) sludge production ( $V_i$ ) to obtain the daily surfactant load for each WWTP. This value was then divided by the connected population ( $N_i$ ) to obtain the daily per capita load.

$$\text{per capita load of WWTP}_i = \frac{c_i * V_i}{N_i}$$

A surfactant's weighted mean (WM) concentration was determined as the sum of all WWTP loads ( $c_i \square V_i$ ) divided by the sum of the WWTPs' daily (stabilized) sludge production ( $V_i$ ).

$$WM = \frac{\sum_n (c_i * V_i)}{\sum_n V_i}$$

The daily loads for Switzerland were derived by multiplying the weighted mean with the daily Swiss sludge production ( $V_{\text{Switzerland}}$ ) of 814  $\text{t d}^{-1}$  (Suess et al., 2020).

$$\text{Daily load for Switzerland} = WM * V_{\text{Switzerland}}$$

### 3. Results and discussion

#### 3.1. Analytical challenges

##### 3.1.1. Dealing with insufficient availability of standard material

Samples of interest are often spiked with isotopically labeled standard materials to ensure a robust quantification of pollutants in environmental samples. During sample analysis, the spiked materials behave similarly to their non-labeled analogues and allow correction for analyte losses. However, despite the high production volumes of LAS, SAS, and AEO, few isotopically labeled standard materials are commercially available and were not available for this study. Instead, we used homologues of LAS, SAS, and AEO that are usually not present in technical mixtures as internal standards (IS) (Baena-Nogueras et al., 2013; Lara-Martín et al., 2006). More specifically,  $C_{16}$ -LAS was used as the IS for LAS with  $C_{10}$ – $C_{13}$ ,  $C_{12}$ -SAS for SAS with  $C_{14}$ – $C_{17}$ , and  $C_{10}$ EO8-AEO for AEO with  $C_{12}$ – $C_{18}$  and EO2–15. In this study, the final sample extracts were spiked with the IS immediately before LC-MS analysis to compensate for matrix effects. Recoveries achieved with the sample preparation method were determined for each analyte in a

preliminary experiment. A detailed description of the recovery experiments, including the challenges of spiking highly contaminated sludge, is provided in the supplementary material (Supplementary Chapter S2).

Reference standards are required for quantification. For AEO, standard material was only available for AEO with even chain lengths and ethoxymer units EO1–3, EO6, and EO8. However, homologues with uneven chain lengths and ethoxymer units of up to EO15 are expected to occur in the environment. Retention times, recoveries, detector sensitivities, and ion ratios are therefore unknown for most of the environmentally relevant AEOs. To resolve this issue, we conducted linear extrapolations from the available standards to determine missing values. Supplementary Table S4 lists the recoveries for the available AEO material. The recoveries ranged from 27% for  $C_{12}$ EO2-AEO to 98% for  $C_{18}$ EO8-AEO. Recoveries increased with increasing ethoxymer units and, to some extent, with increasing chain length. The same pattern was observed for the ionization efficiency in the mass spectrometer (Supplementary Fig. S1) (Lara-Martín et al., 2011). Recoveries for AEO with uneven chain lengths were extrapolated between AEO of even chain lengths. Recoveries for AEO with ethoxymer units of EO4, EO5, and EO7 were extrapolated between AEO standards with ethoxymer units of EO3, EO6, and EO8. Recoveries for AEO with ethoxymer units higher than EO8 were considered to be 100%. Calibration curves were extrapolated using the same approach. Since the MS response seems to level off after an ethoxylation degree of EO6 to EO8 (Supplementary Fig. S1), the calibration curve for AEO with 8 ethoxymer units was applied to homologues with higher ethoxylation degrees.

##### 3.1.2. Ionization of AEO and matrix effects

AEO are ionized by ESI-MS in positive mode to form pseudo-molecular adduct ions, such as  $[M + Na]^+$ ,  $[M + NH_4]^+$ , and  $[M + H]^+$  (Evans et al., 1994; Lara-Martín et al., 2006). The use of LC-MS/MS for detecting AEO often requires that the formation of  $[M + NH_4]^+$  is forced by adding ammonium acetate to the eluent.  $[M + NH_4]^+$  is a labile ion that is favored in MS/MS fragmentation reactions. In this study, full scan HRMS was used, so no fragmentation was required, and we monitored  $[M + Na]^+$ , a very stable and abundant adduct ion (Houde et al., 2002; Lara-Martín et al., 2006).  $[M + NH_4]^+$  and  $[M + H]^+$  can be monitored as qualifier ions for confirmation; however, the abundance of these two qualifier ions is less than 10% of the abundance of the quantifier ion  $[M + Na]^+$ , which is not favorable for the determination of confirming ion ratios. In this case, a tolerance of at least 50% deviation of the theoretical ion ratio (measured in solvent) is recommended (European Commission, 2002). However, even though AEO quantifier ions were detected in most samples, the ion ratios almost never confirmed the presence of AEO.

The formation of adduct ions of AEOs is affected by the homologue chain length and degree of ethoxylation. However, it is also strongly affected by the sample's matrix. Sludge extracts are highly complex matrices that can vary between WWTPs. Hence, the adduct ion formation for AEO can also differ. The ion ratios measured in solvent simply did not apply to the sludge extracts, not even when applying a tolerance of up to 50% deviation. Inspired by an approach with chlorinated organic compounds, where the abundant  $^{37}\text{Cl}$ -isotope is often utilized for confirmation (Minten et al., 2011; Tomy et al., 1997), we used the  $^{13}\text{C}$ -isotope and measured  $[^{13}\text{C}-M + Na]^+$  and  $[^{13}\text{C}_2-M + Na]^+$ . This approach is suitable for molecules with high carbon content, such as AEOs of chain length  $C_{12}$  to  $C_{18}$ . The formation of these ions is independent of the matrix and relies only on the isotope's natural abundance. The ion ratio can therefore be calculated theoretically and does not need measurement. This is beneficial, since not all analyzed homologues are available as standard materials, and determination of their ion ratios would otherwise require extrapolation. However, one consideration when using this approach is that any molecule of the same sum formula will have the same ion ratio; therefore, the presence of a homologous series, in addition to the correct ion ratio, is required to confirm that AEOs are indeed present in the sample (Fig. 2a). In a previous study, Lara-Martín et al. (2011) have also utilized the less abundant  $^{13}\text{C}$ -isotope for quantification when the abundance of the  $^{12}\text{C}$ -isotope of a surfactant was outside the linear range of the MS.

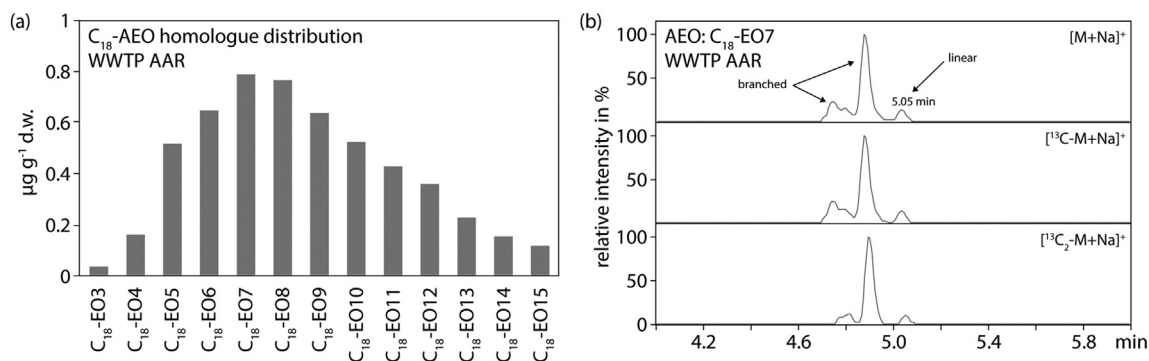


Fig. 2. Both linear and branched AEO were present in sludge samples. (a) The presence of a homologous series (branched  $C_{18}$ -AEO) confirms the detection of AEOs. (b) The extracted ion chromatogram (EIC) for AEO  $C_{18}$ -EO7 ( $[M + Na]^+$  ion) reveals linear isomers at a retention time of 5.05 min. Earlier eluting (multi-)branched isomers are confirmed by the same peak shape of the two qualifier ions  $[^{13}C-M + Na]^+$  and  $[^{13}C_2-M + Na]^+$ .

### 3.1.3. Detection of linear and branched AEO homologues

The available standard material contained AEO homologues with linear chain lengths. Fig. 2b shows the extracted ion chromatogram (EIC) for  $C_{18}$ EO7-AEO for the quantifier ion  $[M + Na]^+$  and the two qualifier ions. As indicated by the arrow, linear  $C_{18}$ EO7-AEO elutes at a retention time of 5.05 min. The three EIC show peaks of the same shape at earlier retention times. The correct ion ratio and the presence of a homologous series suggest that these are also AEO. Similar chromatograms have been observed previously, and the earlier eluting compounds were identified as mono- or multiple-branched AEO (Evans et al., 1997). Branched AEO homologues have been discussed in previous studies on AEO analysis (Evans et al., 1994; Marcomini and Zanette, 1996; Matthijs et al., 1999), but they were often reported with linear AEO as a sum parameter due to insufficient chromatographic separation (Evans et al., 1997). Few studies have reported differences between levels of linear and branched homologues in the environment. Lara Martín et al. (2005) observed an increased proportion of branched AEO with increasing ethoxylation. Matthijs et al. (2004) also detected branched AEO in sludge but stated that linear AEO dominated. Non-household applications have been reported as the major source of branched AEO in WWTPs (Evans et al., 1997).

### 3.1.4. Ionization efficiency of alkylphenols

Alkylphenols (OP and NP) are often analyzed by GC-MS, and this often requires compound derivatization prior to analysis (Li et al., 2018a). However, LC-MS methods are also available and usually allow the simultaneous detection of alkylphenols and alkylphenol polyethoxylates (Li et al., 2018a). When using LC-MS or LC-MS/MS, the monitored (precursor) ion of alkylphenol is the deprotonated molecule ion  $[M-H]^-$ . Originally, in the present study, we applied an LC-MS/MS method published by Lara-Martín et al. (2012). This method analyzes NP and NPEO in sediment extracts by adding formic acid and ammonium formate ( $NH_4HCO_2$ ) to the LC eluent. However, the instrument used in our study (Agilent 6495 Triple Quad, jet stream and ion funnel technology) was not able to provide sufficient sensitivity with the published method parameters, as APs could not be detected in spiked solvent or sludge extracts. Increased deprotonation of a compound in LC-MS requires conditions that are less acidic and more basic. For this reason, formic acid was eliminated from the eluent and ammonium fluoride ( $NH_4F$ ) was introduced post-column to the eluent, prior to MS analysis. This improved the sensitivity for detecting alkylphenols in sludge extracts. Compared to formate (or acetate), fluoride possesses a strong basicity in the gas phase (Yanes et al., 2011), thereby potentially providing a better deprotonation of alkylphenols. The increase in MS sensitivity by adding  $NH_4F$  has previously been shown for other compounds (Pesek and Matyska, 2015; Petrie et al., 2016).

### 3.2. Surfactant concentrations in sewage sludge

#### 3.2.1. Linear alkylbenzene sulfonates (LAS)

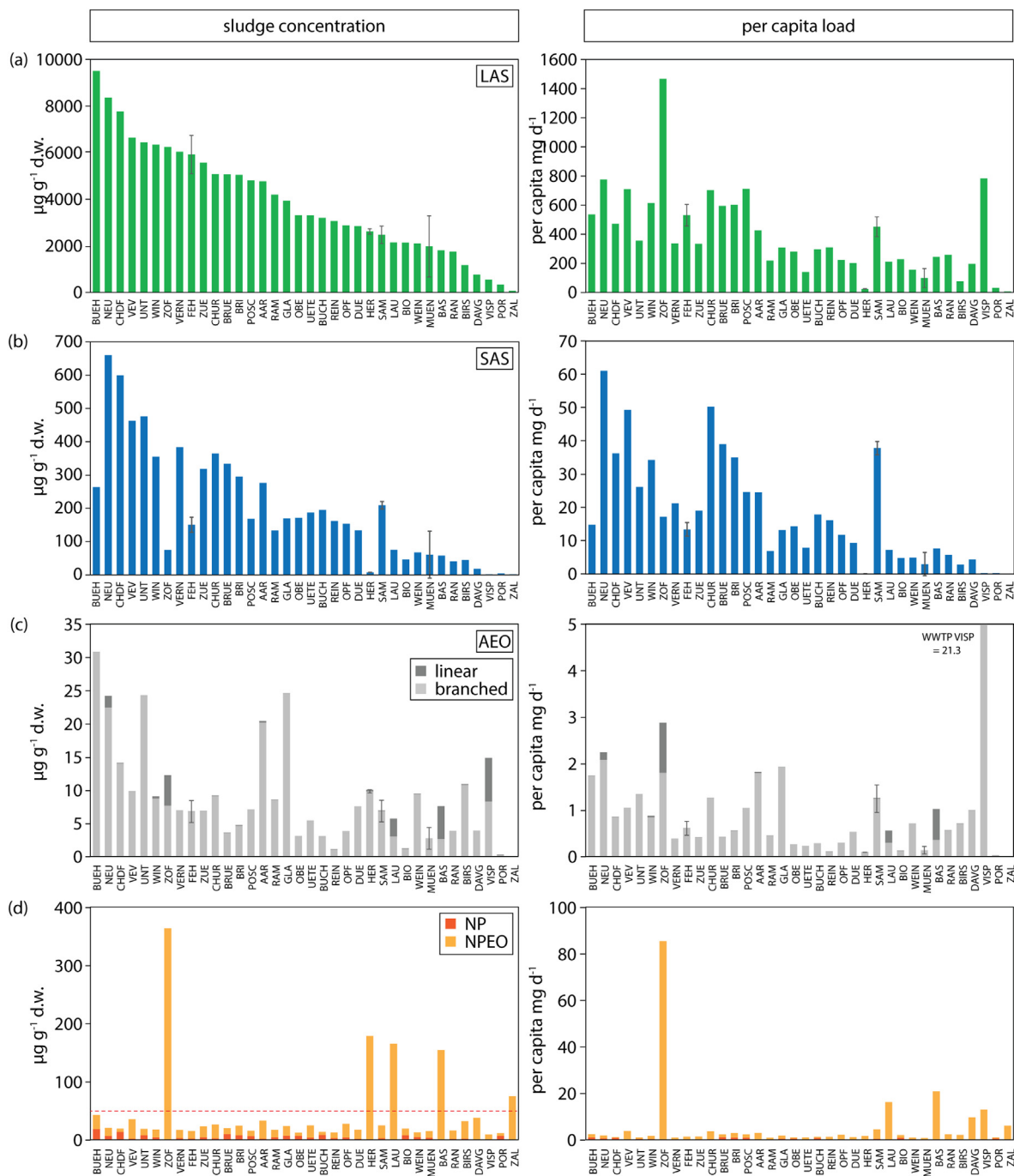
The LAS concentrations measured in the studied WWTPs are plotted in Fig. 3a (left panel). LAS sludge concentrations ranged from 74 to 9500  $\mu g g^{-1}$  dry weight (d.w.) (detailed results are provided in Supplementary Table S8). Hence, the LAS levels in sludge can represent up to 1% of the dry matter. LAS are the most frequently used ionic surfactant class in Europe, so high levels are expected in Swiss sewage sludge (HERA, 2013). With a weighted mean concentration of 3700  $\mu g g^{-1}$  d.w. in sludge (Table 1), LAS are the most abundant surfactant class detected in Swiss sewage sludge (see Section 2.3. for calculations). Multiplying the weighted mean by the daily sludge production in Switzerland resulted in a total daily LAS load of about 3 t in Swiss sewage sludge. Even though most LAS (>99%) are diverted from the wastewater effluent (Brunner et al., 1988), considerable amounts can still end up in receiving waters (Freeling et al., 2019). Therefore, LAS also are the most abundant surfactant class in surface water (Wiest et al., 2021).

In the 1980s, LAS sludge concentrations in Switzerland ranged between 1800 and 12,000  $\mu g g^{-1}$  d.w. (Brunner et al., 1988; McEvoy and Giger, 1985) (Fig. 4). The LAS sludge concentrations have remained relatively stable over the last 30 years, even though the global production volume of surfactants has doubled since the 1990s (Freeling et al., 2019). The observed concentration range is in accordance with concentrations between 2750 and 5754  $\mu g g^{-1}$  d.w. reported in a recent study of six digested sludge samples from one French WWTP (Mailler et al., 2017).

The overall removal efficiency for LAS from wastewater is >99%, whereof 83% is biodegraded during the water treatment, but approximately 16% ends up unaltered in sewage sludge (Brunner et al., 1988). García et al. (2005) observed that LAS do not undergo noteworthy degradation during anaerobic sludge digestion. On the other hand, Mogensen and Ahring (2002) observed anaerobic degradation of LAS under thermophilic conditions. There is an ongoing discussion about the conditions required for a potential anaerobic degradation of LAS. For example, partial anaerobic degradation of LAS has been observed in marine sediments (Lara-Martín et al., 2007) and standardized water/sediment systems (Corada-Fernández et al., 2018), but also in sludge (Sanz et al., 2003).

In the presented study, the daily load in Swiss sewage sludge was extrapolated to the loads reaching the WWTPs, based on the literature data for the fate of LAS in WWTPs (16% of LAS in sewage sludge without considering anaerobic degradation). This results in an estimated Swiss LAS consumption of 19 t  $d^{-1}$  in total, or 2200 mg  $d^{-1}$  per capita. This value is similar to the reported US consumption of about 3600 mg  $d^{-1}$  per capita (Mackay et al., 1996).

The surfactant concentration measured in sludge can be expressed as daily per capita sludge loads for the corresponding WWTP (Fig. 3a, right



**Fig. 3.** Concentrations and per capita loads of (a) LAS, (b) SAS, (c) AEO, and (d) NP and NPEO in the 36 studied Swiss WWTPs. Left panels show actual sludge concentrations (sludge dry weight, d.w.) whereas the right panels show daily per capita loads in sludge. Vertical bars of variability are depicted for the WWTP that provided more than one sludge sample. The red dashed line in panel (d) indicates a suggested limit value of  $50 \mu\text{g g}^{-1} \text{d.w.}$  for the sum of NP, NP1EO, and NP2EO in sludge when used in land applications (EU-Initiative, 2000).

panel) by considering the daily sludge production and the population associated with a particular WWTP. Relatively constant per capita loads are expected for all WWTPs. However, a large industrial input would increase the per capita load, and this increase could reveal potential industrial emissions of surfactants for individual WWTPs. Per capita loads of the studied surfactants in sludge differ by more than two orders of magnitude ( $6\text{--}1500 \text{ mg d}^{-1} \text{ LAS}$ ), with a median of  $310 \text{ mg d}^{-1}$ . The WWTP VISP is an industrial plant operated by a chemical and pharmaceutical company. Up to 2/3 of its wastewater originates from the chemical plant. It is among the three WWTPs with the lowest sludge levels for LAS, but the calculated per capita

load is in the upper range. The chemical company does not report the use of LAS in their production.

The distribution of LAS homologues is relatively constant throughout Switzerland (Supplementary Fig. S4a).  $\text{C}_{11}$ -LAS ( $25.3 \pm 3.1\%$ ),  $\text{C}_{12}$ -LAS ( $39.0 \pm 1.8\%$ ), and  $\text{C}_{13}$ -LAS ( $31.0 \pm 4.3\%$ ) dominate the sludge levels. By comparison,  $\text{C}_{10}$ -LAS ( $4.4 \pm 1.6\%$ ) is much less abundant. Similar distributions have previously been observed in Switzerland in the 1980s (McEvoy and Giger, 1985) and in a recent study in France (Mailler et al., 2017). The average chain length is  $12.0 \pm 0.1$ . A shift toward a higher chain length is expected due to a higher partitioning of LAS with longer

**Table 1**

Weighted mean (WM) surfactant concentrations in sewage sludge of the 36 studied wastewater treatment plants, the average per capita loads, and the total daily loads in sewage sludge extrapolated for the entire country of Switzerland.

	LAS	SAS	AEO	NP	NPEO	NP1EC	<i>tert</i> -OP
WM conc. in sewage sludge ( $\mu\text{g g}^{-1}$ d.w.)	3700	190	8.30	3.1	62 (16) <sup>a</sup>	0.35	3.8 (1.8) <sup>b</sup>
Average per capita load in sludge ( $\text{mg day}^{-1}$ capita <sup>-1</sup> )	380	18	1.4	0.4	5.2 (1.8) <sup>a</sup>	0.03	0.51 (0.17) <sup>b</sup>
Total daily load of Switzerland (in sludge)	3.04 t	0.16 t	6.8 kg	2.6 kg	51 kg (13 kg) <sup>a</sup>	0.29 kg	3.1 kg (1.4 kg) <sup>b</sup>

<sup>a</sup> Calculated after excluding WWTPs that exceeded the suggested limit value of  $50 \mu\text{g g}^{-1}$  d.w. ( $n = 5$ ).

<sup>b</sup> Calculated after excluding the two extreme outliers (WWTP NEU and WWTP GLA).

alkyl chains to organic matter (Lara-Martín et al., 2008; León et al., 2002). Only WWTP VISP shows a slight shift to smaller chain lengths (average chain length of 11.6;  $C_{10} = 12.3\%$ ;  $C_{11} = 35.6\%$ ,  $C_{12} = 32.7\%$ ;  $C_{13} = 19.4\%$ ).

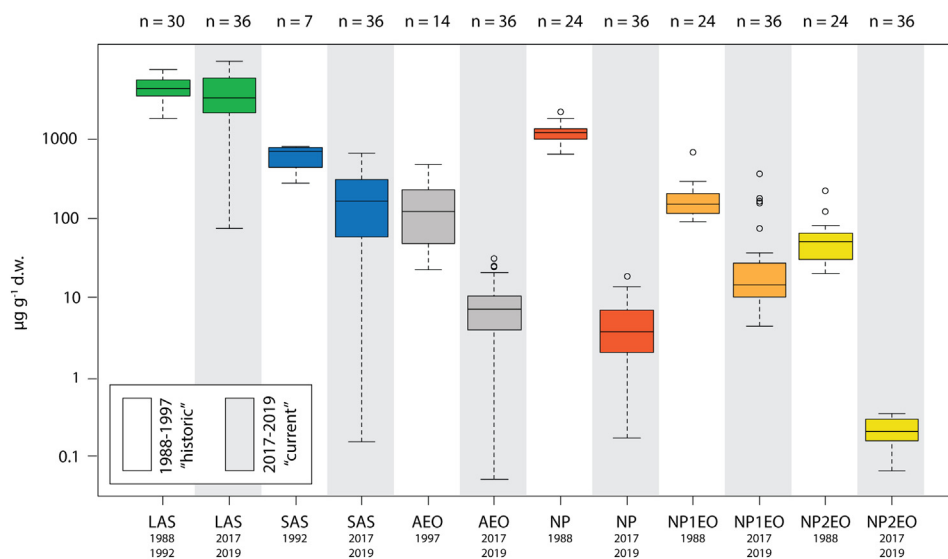
Fig. 5a shows the relationship between LAS levels and the residence time of the sludge in the anaerobic digester. Older sludge had higher LAS concentrations. Most Swiss WWTPs apply anaerobic sludge digestion, as this process reduces the amount of organic matter. However, LAS are resistant to anaerobic digestion (Berna et al., 2007). Hence, LAS are more diluted before sludge digestion. So a broad range of LAS levels is observed in Swiss sludges, influenced by the residence time in the digester. Non-digested sludges are expected to have lower LAS levels (McEvoy and Giger, 1985). This is indeed the case for the WWTPs ZAL, VISP, and HER (0 days of residence time in Fig. 5a). In this plot, aerobic degradation of LAS that occurs before the sludge reaches the digester is not considered. Deviations from the shown plot or scattering can be caused by differences in aerobic treatment among the studied WWTPs. The WWTP ZOF also has no sludge digestion but shows high LAS concentrations (Fig. 3a, left panel) and the highest per capita loads, indicating a strong industrial input of LAS. The WWTP ZOF is known to receive wastewater from two large yarn and textile finishing businesses and a chemical company, all of which potentially consume large amounts of surfactants. Approximately 60–65% of the wastewater treated by the WWTP ZOF is of industrial origin.

### 3.2.2. Secondary alkane sulfonates (SAS)

The detected SAS concentrations are plotted for all WWTPs in Fig. 3b (left panel). SAS sludge concentrations ranged from 0.15–660  $\mu\text{g g}^{-1}$  d.w.

(detailed results are provided in Supplementary Table S9). The weighted mean for Switzerland was  $190 \mu\text{g g}^{-1}$  d.w., resulting in a daily load of 0.16 t of SAS in Swiss sewage sludge. The removal efficiency for SAS from wastewater was >99%. SAS are mostly biodegraded during wastewater treatment, but approximately 16% end up in sewage sludge (Field et al., 1995). Similar to LAS, SAS undergoes negligible degradation during anaerobic digestion (Field et al., 1995). Based on the daily load in Swiss sewage sludge, the SAS consumption in Switzerland is estimated at  $1 \text{ t d}^{-1}$  in total or  $115 \text{ mg d}^{-1}$  per capita. In the 1990s, sludge concentrations in Switzerland ranged between 300 and  $800 \mu\text{g g}^{-1}$  d.w. (Field et al., 1995; Field et al., 1992). Analysis of SAS in sludge from the WWTP OPF in 1992 (Field et al., 1992) and in the present study revealed higher historic SAS levels, at  $800 \text{ mg g}^{-1}$ , than in the present day, at  $150 \text{ mg g}^{-1}$ . Fig. 4 also shows that the average SAS levels in Swiss sludge are currently lower, perhaps indicating either a decreased use of SAS or an improved degradation of SAS during wastewater treatment.

Per capita SAS loads in sludge ranged from 0.04–61  $\text{mg d}^{-1}$ , with a median of  $14 \text{ mg d}^{-1}$  (Fig. 3b, right panel). As expected, the SAS sludge concentration and per capita loads were lower than for LAS, since SAS consumption is lower in Europe (HERA, 2005, 2013). The European Chemicals Agency (ECHA) lists annual tonnages of 10,000 to 100,000 t for SAS versus tonnages of 100,000 to 1,000,000 t for LAS in their respective registration dossiers (ECHA, 2021b, 2021c). The consumption in Switzerland is assumed to correspond to the consumption in Europe. The WWTP SAM shows a pronounced per capita load compared to the actual sludge SAS concentration. The most likely cause is the wastewater from a connected industrial laundry that confirmed a pronounced use of SAS.



**Fig. 4.** Boxplot of recent ( $n = 36$ ) versus historical levels of surfactants in Swiss sewage sludge. Historic concentrations (highlighted in gray) of surfactants in digested sludge were taken from Brunner et al. (1988), Field et al. (1992), Field et al. (1995), and Matthijs et al. (2004). No historic data were available for AEO in Swiss sewage sludge. Historic values for AEO refer to sludge concentrations in the United Kingdom, Germany, Italy, Spain, and the Netherlands. Historic values were not available for NP3EO, NPEC, and *tert*-OP in Swiss or European sewage sludge.

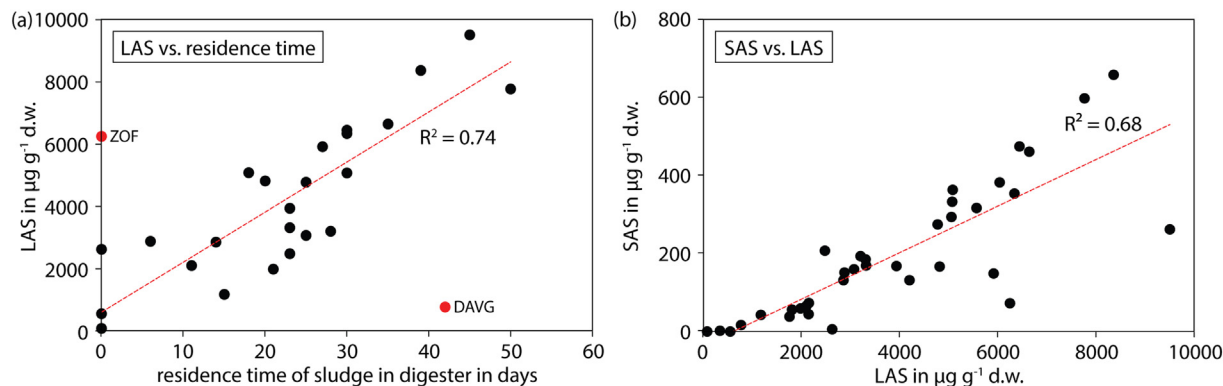


Fig. 5. Correlations between LAS levels and (a) sludge residence time in the anaerobic digester and (b) SAS levels. Longer sludge anaerobic digestion times lead to higher LAS levels. Organic matter is degraded by anaerobic digestion, whereas LAS are not. Similar trends are observed for SAS and NP (Supplementary Fig. S8). Outlying data points (the WWTPs ZOF and DAVG) that were not considered for the linear regression are highlighted in red. The linear relationship between LAS and SAS levels can be explained by their similar sources (household applications) and by their similar behaviors in the WWTPs.

As also observed for LAS, the distribution of SAS homologues was quite constant throughout Switzerland (Supplementary Fig. S4b).  $C_{14}$ -SAS ( $17.4 \pm 11.9\%$ ) and  $C_{15}$ -SAS ( $18.5 \pm 2.9\%$ ) were less abundant than  $C_{17}$ -SAS ( $26.6 \pm 7.2\%$ ) and  $C_{16}$ -SAS ( $37.5 \pm 4.8\%$ ). The enrichment of more hydrophobic SAS homologues (longer alkyl chains) in sludge has been observed previously (Field et al., 1992), but it was even more pronounced in the present study. However, the WWTPs HER, VISP, and ZAL show shifts to shorter chain lengths. These three WWTPs have no sludge digestion, which could indicate that anaerobic digestion causes a partial degradation of SAS, preferentially the shorter chain homologues, in contrast to the findings of a previous study (Field et al., 1995). However, the WWTP ZOF also has no anaerobic digestion, but it showed a similar SAS homologue distribution to that of the WWTPs with sludge digestion. Hence, it is not conclusive whether the shift in homologue pattern is caused by partial anaerobic degradation or by another factor. The use of activated carbon can be eliminated as a cause for the shift in homologue distribution, as the WWTP HER uses an activated carbon treatment, whereas the WWTPs ZAL and VISP do not.

As with LAS, the SAS levels increase with increasing residence time of the sludge in the anaerobic digester (Supplementary Fig. S8b). This study also showed a positive correlation between the LAS and SAS levels (Fig. 5), which is due to their similar origin (mainly household products) and fate (the same removal efficiency and little anaerobic digestion) in the WWTPs.

### 3.2.3. Alcohol polyethoxylates (AEO)

The detected AEO concentrations are plotted for all WWTPs in Fig. 3c (left panel). The sludge AEO concentrations ranged from  $0.05$ – $30 \mu\text{g g}^{-1}$  d.w. (detailed results are provided in Supplementary Table S10). In 2004, a Europe-wide study showed average AEO concentrations of  $167 \mu\text{g g}^{-1}$  d.w. in digested sludge (Matthijs et al., 2004). By comparison, the present-day load of AEO in Swiss sludge is, on average, one order of magnitude lower (Fig. 4).

Per capita surfactant loads in Swiss sludge range from  $0.004$ – $21 \text{ mg d}^{-1}$ , with a median of  $0.58 \text{ mg d}^{-1}$  per capita. A pronounced per capita load suggests input from industrial wastewater. This is apparent for the WWTP VISP, with a per capita load ( $21 \text{ mg d}^{-1}$ ) more than one order of magnitude higher than the average per capita load of  $1.36 \text{ mg d}^{-1}$ . This suggests a high industrial discharge. We were unable to identify a major industrial emission source based on the chemical database of the connected chemical/pharmaceutical company.

The weighted mean of the sludge AEO levels was  $8.3 \mu\text{g g}^{-1}$ , equating to a daily AEO load of  $6.8 \text{ kg}$  in Swiss sewage sludge. This is much lower than the SAS ( $0.16 \text{ t d}^{-1}$ ) and LAS ( $3.04 \text{ t d}^{-1}$ ) loads. AEO are easily degraded during the wastewater treatment process. AEO removal from

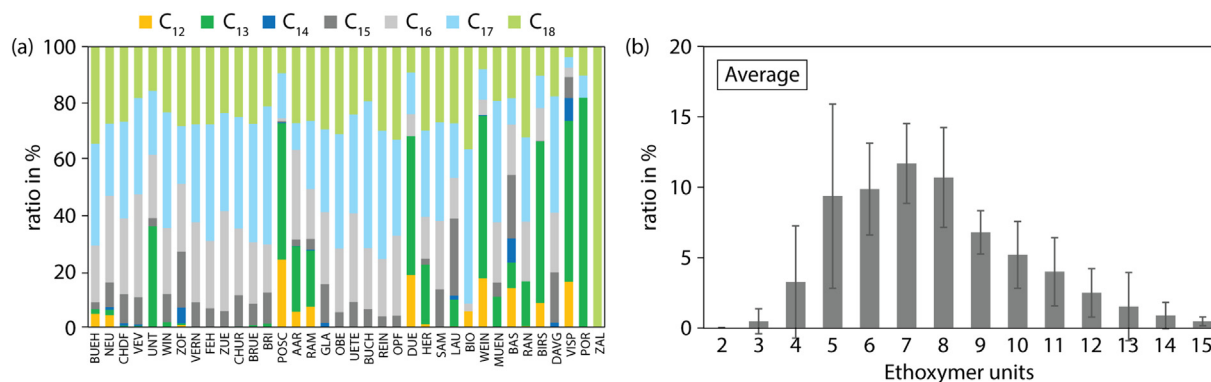
wastewater by degradation is predicted to be  $>99\%$  (Itrich and Federle, 2004) and the AEO remaining in the sludge are subjected to further degradation during sludge digestion. The removal rate of AEO during anaerobic digestion, on average, is  $82\%$  (Matthijs et al., 2004).

Unlike the case for LAS and SAS, the chain length distribution of AEO homologues is not constant throughout Switzerland (Fig. 6a). However, two patterns seem to occur. The most abundant pattern is dominated by AEO with chain lengths of  $C_{16}$ ,  $C_{17}$ , and  $C_{18}$ , with some  $C_{15}$ . The other pattern shows an excess of chain lengths of  $C_{13}$  and some  $C_{12}$ . AEO with a chain length of  $C_{14}$  are rarely detected. Furthermore, AEO with a chain length of  $C_{17}$  occurred only as branched isomers. The average chain length was  $16.1 \pm 1.1$ . Depending on the source of the alcohol used to produce AEO, the carbon chain can be either odd or even numbered. Alcohols of natural origin have even carbon numbers (Talmage, 1994) and only contain linear alcohols (HERA, 2004). If the alcohol is derived from petrochemical sources, AEO homologues with even and odd carbon numbers are possible, and branched chains can occur (HERA, 2004; Talmage, 1994). Compared to LAS and SAS, AEO is a more diverse compound class, and many different formulations are available, registered under many different CAS numbers (Talmage, 1994). The industrial applications of AEO therefore potentially cause the observed differences in homologue distributions in sludges from the different WWTPs.

The distribution of the ethoxymer groups is more or less constant throughout Switzerland (Supplementary Fig. S6b). AEO homologues with 5, 6, 7, and 8 ethoxymer groups dominate in Swiss sewage sludge (Fig. 6b), with an average ethoxylation of  $7.7 \pm 0.7$ . In this study, AEO with 1 and 2 ethoxymers were not analyzed, since their ionization efficiency is low with the chosen method. However, they do exist in wastewater treatment plants and their effluents (Eadsforth et al., 2006). Fig. 6b shows that the ethoxylation pattern in sludge (EO3-EO15) follows a skewed normal distribution. AEO with 3 ethoxymers are very low, indicating that AEO with 1 and 2 ethoxymers are even lower. We concluded that the stated concentrations of AEO in sludge are only slightly underestimated.

The main degradation reaction during activated sludge treatment is central cleavage of the ether group between the alkyl chain and the ethoxymer (Marcomini et al., 2000). This generates linear fatty alcohols and polyethylene glycols (PEG). AEO with lower ethoxylation degrade faster (Marcomini et al., 2000). During anaerobic degradation, a stepwise shortening of ethoxymer units is expected (Huber et al., 2000). However, in the present study, no strong trend was noted toward a lower ethoxylation with increasing sludge age (Supplementary Fig. S7c). The branching of the alcohol moiety sterically hinders the shortening of the ethoxymer units (Mörsche, 2004). The detection of mainly branched AEO homologues in the sewage sludge in the present study can therefore explain the high average ethoxylation.





**Fig. 6.** AEO homologue patterns of the studied sludge samples by (a) chain length. (b) On average ( $n = 36$  WWTPs), sludge samples are dominated by homologues with ethoxymer units of EO5 to EO8.

Branched AEO dominated the investigated sludge samples, with an average proportion of  $90.3 \pm 22.1\%$  (Fig. 3c; branched AEO were quantified using the linear AEO standard material). This could reflect a more pronounced use of branched homologues today or the higher persistence of branched versus linear homologues (Marcomini et al., 2000). The toxicity of AEOs is not influenced by the degree of branching (Bragin et al., 2020; Dorn et al., 1993; Maurer and Kung, 2020) but by the degree of ethoxylation (García et al., 1996). A similar accumulation behavior was observed for branched alkylbenzene sulfonates (BAS), which are less biodegradable than LAS (Gard-Terech and Palla, 1986) and were blamed for major foam formation in natural water bodies in the 1960s (Sweeney and Anderson, 1989). Consequently, BAS were banned, and only LAS can now be used in Europe. AEO levels in sludge were, on average, more than two orders of magnitude lower than LAS levels (Fig. 4). Both LAS and AEO show acute toxicity (*Daphnia magna*) at ranges between 0.26 and  $13.9 \text{ mg L}^{-1}$  and  $0.29\text{--}0.70 \text{ mg/L}^{-1}$ , respectively (Blasco et al., 2003). Due to their similar toxicity ranges, but much lower concentrations, the environmental risk is considered lower for branched AEO than for BAS.

### 3.2.4. Nonylphenol polyethoxylates and their transformation products (NPEO, NP, and NPEC)

The detected NPEO (EO1-3) and NP concentrations are plotted for all WWTPs in Fig. 3d (left panel). Sludge NPEO and NP concentrations ranged between  $4.6$  and  $360 \mu\text{g g}^{-1}$  d.w. and  $0.17\text{--}18.5 \mu\text{g g}^{-1}$  d.w., respectively (detailed results are provided in Supplementary Tables S11 and S12). The weighted mean concentration and the corresponding daily load in Swiss sewage sludge for NPEO were  $16 \mu\text{g g}^{-1}$  d.w. and  $13 \text{ kg}$  ( $0.013 \text{ t}$ ), respectively (these parameters were derived while excluding WWTPs with extreme NPEO levels). The weighted mean for Switzerland was  $3.1 \mu\text{g g}^{-1}$  d.w. for NP, amounting to a total daily load of  $2.6 \text{ kg}$  ( $0.0026 \text{ t}$ ) of NP in Swiss sewage sludge. The dashed red line in Fig. 3d (left panel) indicates a suggested limit value of  $50 \mu\text{g g}^{-1}$  d.w. for the sum of NP, NP1EO, and NP2EO when sludge is used as a soil amendment (EU-Initiative, 2000). Most Swiss WWTPs showed concentrations below this value, indicating low contamination. Only five WWTPs exceeded this limit. The WWTP ZOF showed the highest sludge concentrations for NPEO and elevated per capita loads, indicating an industrial emission source. A major textile finishing company is located within the WWTP catchment, and imported textiles could potentially be contaminated with NPEO. During the finishing process, these NPEO can enter the wastewater cycle, resulting in elevated sludge concentrations. Textiles, yarns, and related products that contain  $\geq 0.01\%$  APEO are banned from the Swiss market and should not be imported (Swiss Federal Council, 2021). The WWTPs HER, LAU and BAS also show elevated NPEO levels. HER receives wastewater from a textile finishing company. LAU and BAS are located in two large Swiss cities (Lausanne and Basel), but no major emission sources could be identified for these two WWTPs.

Technical mixtures of NPEO usually contain a broad range of ethoxylates, with ethoxymer units of up to 15. In WWTPs, they are

degraded to NP by a stepwise shortening of the ethoxymer units. After anaerobic digestion, elevated concentrations of NPEO with low ethoxymer units (e.g., NP1EO to NP2EO) and NP are expected in the sludge, with NP being the most abundant, followed by NP1EO and NP2EO (González et al., 2010). In addition, NP are also transformation products of tris (nonylphenyl)phosphite (TNPP), which is used as an antioxidant in polymer production (Hirai et al., 2011). NP can be detected in plastic particles (Hirai et al., 2011), which could therefore be an additional emission source of NP in WWTPs. The ECHA lists annual tonnages of 10,000 to 100,000 t for TNPP in its registration dossier (ECHA, 2021d).

Brunner et al. (1988) reported tenfold higher concentrations of NP than NP1EO in Swiss sewage sludge. A more recent study observed only slightly higher sludge concentration for NP than for NP1EO, but within the same order of magnitude (González et al., 2010). Fig. 3d and Supplementary Fig. S5a show that the present-day NP concentrations in Swiss sludge are often slightly lower than the NPEO concentrations. Ferguson et al. (2001) observed similar patterns in sewage-impacted sediments.

Compared to the historical data, sludge NP concentrations have decreased by more than two orders of magnitude since their strict regulation in the 1980s (Fig. 4). The sludge concentrations of NP1EO and NP2EO have also decreased by one and two orders of magnitude. The decrease in NP and NPEO in sewage sludge is assumed most likely to correlate with a decrease in NP in the WWTP effluents (Spataro et al., 2019; Stephanou and Giger, 1982). Hence, the receiving waters currently have greatly reduced exposure to endocrine-disrupting NP.

Nonylphenol monoethoxy carboxylate (NP1EC), another transformation product of NPEO, was detected in all WWTPs but one (the WWTP VISP). NP1EC sludge concentrations ranged from  $0.02\text{--}1.97 \mu\text{g g}^{-1}$  d.w., with a median concentration of  $0.26 \mu\text{g g}^{-1}$  d.w. (detailed results are provided in Supplementary Tables S11 and S12). The weighted mean for Switzerland was  $0.35 \mu\text{g g}^{-1}$  d.w., resulting in a daily load of  $0.3 \text{ kg}$  ( $0.0003 \text{ t}$ ) of NP1EC in Swiss sewage sludge. The detected NP1EC concentrations are plotted for all WWTPs in Supplementary Fig. S3b. NP and NP1EC are both expected transformation products of NPEO, but no obvious correlation was observed between the NP1EC and NP levels (Supplementary Fig. S9f). NPEC are aerobic transformation products of NPEO (Lu et al., 2009; Ömeroğlu and Sanin, 2014) and are therefore formed during aerobic wastewater treatment processes, whereas NP can be formed under both aerobic and anaerobic conditions (Lu et al., 2009). Consequently, NP can form during wastewater treatment as well as during anaerobic sludge digestion. In this study, all sampled WWTPs used anaerobic digestion (or no digestion at all). Hence, only low concentrations of NP1EC were observed compared to NP.

### 3.2.5. tert-Octylphenol (tert-OP)

The tert-OP sludge concentrations ranged from  $0.19\text{--}103 \mu\text{g g}^{-1}$  d.w., with a median concentration of  $1.34 \mu\text{g g}^{-1}$  d.w. (detailed results are provided in Supplementary Fig. S3a and Supplementary Tables S11 and

S12). Fernández-Sanjuan et al. (2009) reported similar *tert*-OP concentrations in sludge (0.30–23.5  $\mu\text{g g}^{-1}$  d.w. for 5 WWTPs in Spain). The weighted mean for Switzerland is 3.8  $\mu\text{g g}^{-1}$  d.w., resulting in a daily load of 3.1 kg (0.0031 t) for *tert*-OP in Swiss sewage sludge (parameters were calculated while excluding extreme outliers). Sludge from the WWTPs NEU (103  $\mu\text{g g}^{-1}$  d.w.) and GLA (38  $\mu\text{g g}^{-1}$  d.w.) showed elevated *tert*-OP concentrations, indicating a major emission source in the WWTP catchments. One use of *tert*-OP is in the production of phenolic resin used in tire production or in inks (Miyagawa et al., 2016). It is also a transformation product of *tert*-OPEO. Certain *tert*-OPEO formulations are known by the brand name Triton X, a widely used laboratory detergent for lysing cells and extracting proteins. *tert*-OPEO is also used in the manufacture of biopharmaceuticals. Both the WWTPs NEU and GLA have biopharmaceutical industries located in their catchments, so these industries are identified as potential emission sources for *tert*-OPEO that can be transformed to *tert*-OP in WWTPs.

*tert*-OP concentrations in Swiss sludge fall in the same range as the NP concentrations. Supplementary Fig. S5b plots the proportion of OP and NP in sludge for all WWTPs. On average, the sludges show a 40/60 ratio of OP to NP. A similar average OP/NP ratio was observed in Spanish soils treated with sewage sludges (Andreu et al., 2007). However, in other studies, sludge concentrations have been reported to be at least one order of magnitude lower for OP than for NP (Fernández-Sanjuan et al., 2009; Mailler et al., 2017). NP is a transformation product of the banned NPEO, whereas *tert*-OP is still used in adhesives, coating products, and polymers (ECHA, 2021a). Therefore, a shift toward higher ratios of OP compared to NP is likely to occur in Swiss sewage sludge. Janousek et al. (2020) have also reported on the occurrence of short chain alkylphenols (i.e., butylphenol) in wastewater influent and effluent. This compound, used to manufacture phenolic resins, is of high interest in future monitoring studies of sewage sludge.

### 3.3. Case study: seasonal variation in tourist regions

Two WWTPs (SAM and DAVG) are located in winter tourism regions, and these were sampled once during the off-season (November 2019) and

once during the high season (January 2020). Both WWTPs treat the wastewaters of large areas containing many hotels; therefore, the inhabitant numbers differ substantially between the off and high seasons. In addition, the WWTP SAM receives wastewater from a large industrial laundry facility that serves many hotels in a large tourist region. Tourist activities were hypothesized to influence the surfactant levels in WWTPs; therefore, the potential impact of tourist activity was determined by normalizing the sludge concentrations for the daily sludge production (yearly average) and the known connected population. The resulting per capita loads are plotted for LAS, SAS, AEO, and the sum of NPEO and NP in Fig. 7. For both WWTPs, a trend is evident toward higher levels of LAS, SAS, and AEO during the high season. The WWTP SAM provided three samples per sampling period, and the corresponding range bars indicate significant differences between the seasons for LAS and SAS. For AEO the differences are not significant (*t*-test,  $\alpha = 0.05$ ). The industrial laundry (connected to the WWTP SAM) confirmed the use of detergents that contain SAS and AEO, but not LAS. It was also stated that the consumption of detergent can be up to 8 times higher during the high season than during the off-season. SAS sludge levels were one order of magnitude higher for the WWTP SAM than for the WWTP DAVG. This indicates a strong influence of the industrial laundry. Levels of AEO, NPEO, and NP were generally low in both WWTPs. The combined levels of NPEO and NP showed no apparent seasonal trend in the WWTP SAM, whereas these levels were higher in the WWTP DAVG during the off-season (autumn). Only one sample was available per season for the WWTP DAVG, so we could not determine whether the differences were significant or due to random variation.

## 4. Conclusions

Surfactants are high-production-volume chemicals but their analysis in the environment is a challenging task. LAS, SAS, and AEO are complex chemicals with many homologues, and sufficient (labeled) standard material is not available for all homologues. Hence, the retention times and calibration curves need to be extrapolated for many homologues (e.g., AEO). Considering that surfactants are ubiquitous environmental pollutants, commercially available analytical standards for individual homologues and

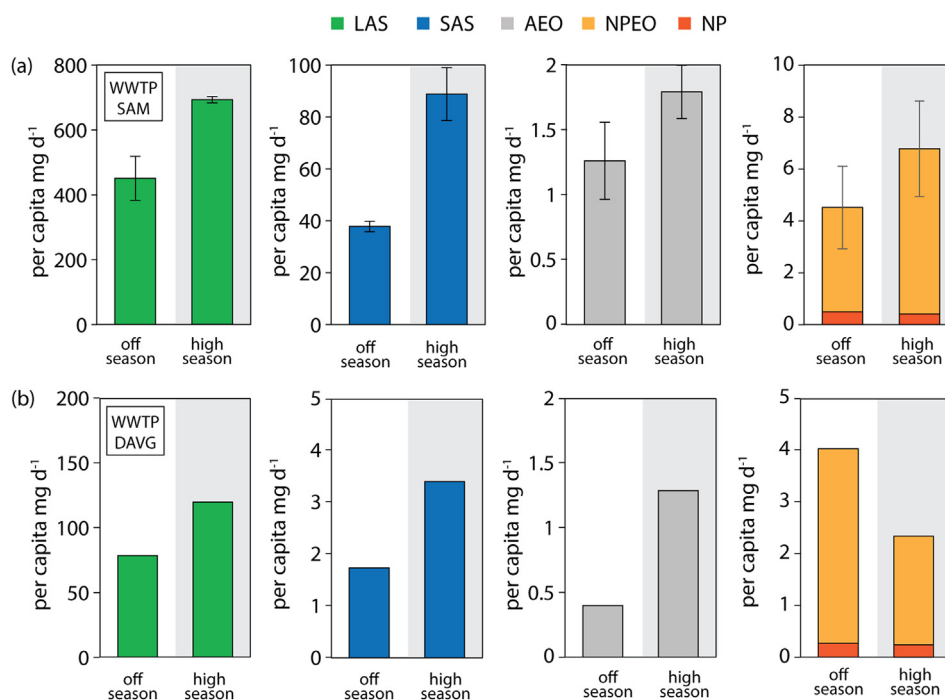


Fig. 7. Seasonal variations of LAS, SAS, AEO, and NPEO and NP in (a) the WWTP SAM and (b) the WWTP DAVG. The selected WWTPs operate in tourist regions (winter tourism). Samples were taken during the off-season (November 2019) and during the high season (January 2020, highlighted in gray). The WWTP SAM provided three sludge samples per sampling period. Range bars indicate ranges for the three samples.

isotopically labeled standards are urgently needed to improve the chemical analysis of surfactants in highly complex sample matrices like, e.g., sludge.

The mass spectrometric detection of non-ionic surfactants depends on the formation of adduct ions. Here, complementary to monitoring a different adduct ion, we recommend monitoring the corresponding  $^{13}\text{C}$ -isotope ion for qualification, as this can ensure a reproducible ion ratio that is independent of matrix effects. A sample's matrix can strongly affect adduct formation and disrupt the quantifier/qualifier ion ratio.

The ubiquitous use of surfactants is reflected by the pronounced LAS and SAS concentrations in Swiss sewage sludge. More than 99% of these surfactants are diverted from the WWTP effluent, either by biodegradation or sorption to sludge. However, due to the high application volumes (Freeling et al., 2019), even the remaining 1% represents a considerable amount that enters the environment. Hence, these surfactants may still pose a risk to receiving water bodies (Johnson et al., 2017) and monitoring concentrations in WWTP effluents and in natural waters is recommended.

Plotting per capita loads in sludge can efficiently reveal the presence or absence of potential industrial applications. Elevated concentrations of *tert*-OP, in particular, could potentially reflect applications of *tert*-OPEO by the biopharmaceutical industry. However, thorough detective work is needed to identify the actual emission sources.

A positive correlation between sludge levels and residence time in the digester was observed for LAS and SAS. These surfactants do not degrade readily during anaerobic sludge digestion, so they accumulate in the sludge. A similar trend was observed for NP. By contrast, AEO are highly biodegradable during anaerobic sludge digestion. The AEO homologues found in sludge were mainly branched forms because they are less readily biodegradable than linear AEO homologues.

Swiss sludge concentrations of common surfactant classes are presently similar to (LAS) or lower than (SAS, AEO) the concentrations reported in the 1980s and 1990s. Concentrations of NPEOs and their transformation product NP have substantially decreased in sewage sludge since their regulation in the 1980s. In Switzerland, sewage sludge is incinerated, but sludge is used as fertilizer in agricultural applications in many other countries. Previous studies indicated a negligible risk of LAS and SAS contamination in sludge-amended soils (Petrović and Barceló, 2004; Schowanek et al., 2007). On average, Swiss sludge concentrations have not increased in the past decades, and a similar pattern is likely in other European countries. Hence, surfactants potentially still do not pose a risk to the environment from sludge as an emission source. However, this study showed that point sources can strongly elevate a surfactant's sludge concentration. As also suggested by other authors (Khakbaz et al., 2020), surfactant levels in sludge should therefore be widely monitored before general conclusions can be drawn regarding the risk of soil and groundwater contamination in the agricultural reuse of sewage sludge.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2021.151361>.

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