

Artificial sweeteners—a recently recognized class of emerging environmental contaminants: a review

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Abstract An overview is given of existing trace analytical methods for the determination of seven popular artificial sweeteners [acesulfame (ACE), aspartame, cyclamate (CYC), neotame, neohesperidine dihydrochalcone, saccharin (SAC), and sucralose (SUC)] from aqueous environmental samples. Liquid chromatography–electrospray ionization tandem mass spectrometry and liquid chromatography–electrospray ionization high-resolution mass spectrometry are the methods most widely applied, either directly or after solid-phase extraction. Limits of detection and limits of quantification down to the low nanogram per liter range can be achieved. ACE, CYC, SAC, and SUC were detected in wastewater treatment plants in high microgram per liter concentrations. Per capita loads of individual sweeteners can vary within a wide range depending on their use in different countries. Whereas CYC and SAC are usually degraded by more than 90% during wastewater treatment, ACE and SUC pass through wastewater treatment plants mainly unchanged. This suggests their use as virtually perfect markers for the study of the impact of wastewater on source waters and drinking waters. In finished water of drinking water treatment plants using surface-water-influenced source water, ACE and SUC were detected in concentrations up to 7 and 2.4 $\mu\text{g/L}$, respectively. ACE was identified as a precursor of oxidation byproducts during

ozonation, resulting in an aldehyde intermediate and acetic acid. Although the concentrations of ACE and SUC are among the highest measured for anthropogenic trace pollutants found in surface water, groundwater, and drinking water, the levels are at least three orders of magnitude lower than organoleptic threshold values. However, ecotoxicology studies are scarce and have focused on SUC. Thus, further research is needed both on identification of transformation products and on the ecotoxicological impact of artificial sweeteners and their transformation products.

Keywords Artificial sweeteners · Acesulfame · Sucralose · Wastewater · Surface water · Groundwater · Drinking water · Ozonation

Introduction

Artificial sweeteners are used worldwide as sugar substitutes in remarkable amounts in food, beverages, and also in drugs and sanitary products, such as mouthwashes. They provide no or negligible energy and thus are ingredients of dietary products [1].

The structures of the artificial sweeteners treated in this review are depicted in Table 1 together with additional data on physicochemical properties, intensity figures for their sweetness (sugar equivalents), and their acceptable daily intake values that a person can safely consume on average every day without risk to health.

Like natural sugars and other chemicals with a sweet taste, artificial sweetener structures possess a special molecular feature, the so-called *AH*, *B* system [2, 3], which is responsible for a molecular interaction between the sweetener and the receptor site for the generation of the sweet taste. *A* and *B* are electronegative atoms and the *AH* group is

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a weakly acidic group, e.g., an OH or NH group with a specific *AH* proton–*B* orbital distance of about 3 Å. For examples, see Table 1.

Artificial sweeteners are water contaminants that are highly specific to wastewater. In contrast to other emerging trace contaminants, such as pharmaceuticals and personal care products (PPCPs), artificial sweeteners have been considered in environmental sciences only recently [4–14]. Since 2009 the number of scientific articles on the environmental occurrence, fate, and ecotoxicological effects of artificial sweeteners has been rapidly increasing. Especially, the two artificial sweeteners acesulfame (ACE) and sucralose (SUC) were found to appear in the aquatic environment in much higher concentrations than most PPCPs and other wastewater-specific anthropogenic organic chemicals.

These high environmental concentrations of ACE and SUC combined with their persistence, high water solubility, low adsorbability to solids, and the high sensitivity of modern trace analytical methods for the detection of artificial sweetener traces make them virtually ideal anthropogenic wastewater markers [12, 15–17]. Using ACE as a marker, one can detect even wastewater-derived proportions of a water resource of less than 1 % in this way [12].

Besides their useful function as wastewater markers, like other organic contaminants, some artificial sweeteners are also precursors of oxidation products which can be formed during advanced wastewater treatment by ozone or during the ozonation processes in waterworks [18].

Owing to their use as food additives, artificial sweeteners are extensively tested for potential adverse health effects on humans [1, 19–22]. Although the measured concentrations of some artificial sweeteners range up to microgram per liter levels in surface water, groundwater, and drinking water, there is a huge safety margin regarding potential adverse health effects. Acceptable daily intake values of artificial sweeteners are in the range from 5 to 50 mg/kg of body weight per day and are thus three to four orders of magnitude above the maximum possible daily human intake by drinking water [1, 23]. However, their ecotoxicological profiles have only been scarcely investigated.

This review aims at compiling current knowledge in this emerging and rapidly increasing field of research. In particular, the following three topics will be addressed: (1) trace analysis, (2) occurrence in the aquatic environment, and (3) elimination and transformation processes in the environment and during water treatment processes.

Table 1 Structures and selected properties of the seven artificial sweeteners discussed in this review

	ACE	CYC	SAC	SUC	Aspartame	Neotame	NHDC
CAS no.	33665-90-6	100-88-9	81-07-2	56038-13-2	22839-47-0	165450-17-9	20702-77-6
Structure							
Molecular formula	C ₄ H ₅ NO ₂ S	C ₆ H ₁₃ NO ₃ S	C ₇ H ₅ NO ₃ S	C ₁₂ H ₁₉ Cl ₃ O ₈	C ₁₄ H ₁₈ N ₂ O ₅	C ₂₀ H ₃₀ N ₂ O ₅	C ₂₈ H ₃₆ O ₁₅
Molecular weight in (g/mol)	163.15	179.24	183.19	397.63	294.31	378.47	612.58
Sugar equivalence	200 [66]	30 [67]	300 [68]	600 [69]	160–220 [68]	7,000–13,000 [70]	up to 1,800 [71]
Water solubility in (g/L)	270 (20 °C) [66]	1,000 [69], 133 [67]	4 [69]	283 (20 °C) [72]	~10 (25 °C) [73]	12.6 [74]	0.4–0.5 [71]
pK _a ^a	2.0 [75]	1.9 [76]	2.2 [76]	11.8 ^c [77]	3.19 and 7.87 [78]	3.01 and 8.02 [79]	9.7 ^c [77]
log K _{OW} ^b	-1.33 [69]	-1.61 [69]	0.91 [69]	-1.00 [69] -0.51±0.05 [72]	0.07 [69]	2.39 (nonionic species) [77]	0.75 (nonionic species) [77]
Human excretion	100 % unchanged [66], mainly unchanged [19]	mainly unchanged [19], inter-individual variations in conversion to cyclohexylamine [80]	mainly unchanged [19]	>92 % unchanged [81]	complete metabolic breakdown into aspartic acid, phenylalanine, and methanol [82]	<2 % [70] (deesterification major metabolic pathway)	complete metabolism by hydrolysis and conjugation is anticipated [83]
ADI mg/kg body weight	9 (potassium salt) [84]	7 [80]	5 (sodium salt), 3.8 (free acid) [85]	15 [86]	40 [82]	2 [87]	5 [83]

The yellow background indicates artificial sweeteners detected in the aquatic environment

ACE acesulfame, ADI acceptable daily intake, CAS Chemical Abstracts Service, CYC cyclamate, NHDC neohesperidine dihydrochalcone, SAC saccharin, SUC sucralose

^a pK_a is the negative logarithm of the dissociation constant

^b log K_{OW} is the logarithm of the octanol–water partition coefficient

^c Calculated pH where 50% of the neutral molecules are dissociated into several corresponding bases

Trace analysis of artificial sweeteners from aqueous samples

Overview of analytical methods

Long before artificial sweeteners were recognized as emerging environmental chemicals numerous techniques were reported for their analysis from foodstuffs. They comprise high-performance liquid chromatography (HPLC), ion chromatography, thin-layer chromatography, gas chromatography, capillary electrophoresis, flow injection analysis, electroanalysis, and spectroscopy. These methods can be grouped into methods for determination of individual artificial sweeteners and multianalyte approaches, sometimes also including other food additives, such as colorants or preservatives [24].

For the artificial sweeteners as emerging environmental chemicals, there is no existing national or international standard method for their determination from aqueous environmental samples, but several methods have been described in the scientific literature.

Owing to the ionic nature of the weakly acid artificial sweeteners and the high sensitivity and selectivity of tandem mass spectrometry, most methods of analysis for the determination of artificial sweeteners at trace levels in the nanogram per liter to microgram per liter range are based on the following coupling techniques: liquid chromatography (LC)–tandem mass spectrometry (MS/MS) [12, 13, 15, 17, 25–28], LC–high-resolution mass spectrometry (HRMS) [29, 30], and ion chromatography–MS/MS [16]. These methods comprise the analysis of the seven artificial sweeteners ACE, aspartame (ASP), cyclamate (CYC), saccharin (SAC), neohesperidine dihydrochalcone (NHDC), neotame (NEO), and SUC by HPLC–MS/MS, the analysis of SUC, ASP, and SAC by HPLC–HRMS [29, 30], and the determination of ACE, SAC, and CYC by ion chromatography–MS/MS [16]. In addition, one gas chromatography–mass spectrometry approach for the analysis of SUC after derivatization with *N*-methyl-*N*-trimethylsilyltrifluoroacetamide has been described [14]. In addition, thin-layer chromatography was recently used for the determination of SUC in sewage effluent, surface water, and drinking water [31].

LC-MS/MS and LC-HRMS methods

These methods are the most widely applied and can be divided into methods based on direct analysis of an aqueous sample or a sample made up with an appropriate solvent and methods including sample preparation by solid-phase extraction (SPE). By application of these methods (Table S1), limits of detection (LODs) and limits of quantification (LOQs) down to the low nanogram per liter range can be

achieved depending on the concentration factors and on the sensitivity of the mass spectrometers used.

Direct injection after filtration was reported in [16, 27, 32, 33]. Other authors [12, 29, 34] applied online SPE prior to HPLC–electrospray ionization (ESI) MS/MS analysis. Without a preceding sample preparation procedure to minimize interferences of sample matrix constituents, the use of isotopically labeled standards is mandatory for correct quantification. Also, in most of the methods involving SPE, labeled standards are used and are recommended to compensate for matrix effects. ACE-*d*₄ potassium [15, 16, 25], cyclamic acid-*d*₁₁ [16], SAC-¹³C₆ [16], and SUC-*d*₆ [12, 13, 15, 16, 28, 29] have been used for analysis of aqueous environmental samples. Another option when using direct injection is the application of the standard addition approach [27], which, however, is more appropriate for research than for routine analysis.

For the mass-spectrometric detection in LC-MS/MS and LC-HRMS, most often negative ESI mode was applied (Table 2).

In one study positive ionization of ASP, SAC, and SUC was used in time-of-flight mass-spectrometric measurements [30]. Positive ionization of the artificial sweeteners studied has the advantage of more fragmentation information compared with negative ionization, which might be important for confirmation purposes in environmental samples. In this study, ASP and SAC were measured as [M+H]⁺ base peak ions and SUC was measured as [M+Na]⁺. Application of so-called pseudo multiple reaction monitoring in positive ionization mode with the [M+Na]⁺ adduct of SUC was reported in [28]. In pseudo multiple reaction monitoring, the same *m/z* values are selected in the first and third quadrupoles, which in the case of hardly fragmenting molecules, such as SUC, reduces the background by collision-induced dissociation of coeluted isobaric matrix interferences. This gives lower LODs in wastewater effluent and river water matrix compared with selected ion recording of the [M+Na]⁺ adduct. However, the strong matrix suppression observed by analyzing wastewater samples (–58 to –93%) and receiving surface waters (–94 to –98%) makes accurate quantification by this method questionable.

In LC-ESI(–)-MS/MS analysis, the response of SUC with its very weakly basic OH groups is much lower by approximately two orders of magnitude compared with that of the other artificial sweeteners, e.g., ACE. To overcome this problem in part, its response and also the response of other artificial sweeteners can be enhanced by postcolumn addition of the weakly basic buffer tris(hydroxymethyl)aminomethane [13]. Owing to the improved proton abstraction from the sweetener molecules, the sensitivity of the mass-spectrometric detection could be enhanced within a range from 30% (NHDC) to 290% (SAC), by introducing 20 mM tris(hydroxymethyl)aminomethane at a flow rate of 5 μL/min post column into the HPLC effluent (0.8 mL/min).

Table 2 Ionization mode and precursor and product ions of artificial sweeteners measured in the aquatic environment and their mass-labeled standards

Compound	Precursor ion <i>m/z</i>	Product ions <i>m/z</i>	ESI mode	Reference	
ACE	161.8 ^a	82/78	–	[32]	
	162	82/78	–	[12]	
	161.8	81.8/77.9	–	[13]	
	162.1	81.8/77.8	–	[16]	
	162	82/78	–	[27]	
	ACE- <i>d</i> ₄	165.8	85 ^b	–	[16]
	CYC	178	80/96	–	[12]
		177.9	79.9	–	[13]
		177.9	79.8/96.0	–	[16]
	CYC- <i>d</i> ₁₁	189.0	79.9	–	[16]
	SAC	182	106/62	–	[12]
		181.8	41.9/105.9	–	[13]
		181.8	106.0/61.7	–	[16]
		184.0061	165.9956	+	[30]
SAC- ¹³ C ₆	187.9	106	–	[16]	
SUC	395.0 ^c			[8]	
	397.0 ^d		–	[8]	
	395	359	–	[11]	
	397	359			
	395	359	–	[12]	
	397	361			
	394.7	358.8	–	[13]	
	396.8	360.8	–		
	441.0128 ^e	395.0073 ^f	–	[29]	
	395.2	359.0	–	[16]	
	396.8	361.0			
	395.3	359.0	–	[39]	
	397.2	361.1			
ESI electrospray ionization	419 ^g	419 ^g	+	[28]	
^a Personal communication (Carsten Prasse)	421 ^g	421 ^g			
^b <i>m/z</i> is expected to be 86 according to our own data	419.0038 ^h	238.9849/198.9923/180.9822/163.0160/145.0055	+	[30]	
^c Used as a qualifier (time-of-flight mass spectrometry)	SUC- <i>d</i> ₆	401	365	–	[11]
^d Used as a quantifier (time-of-flight mass spectrometry)		403	367		
^e Formic acid adduct (LTQ Orbitrap full scan)		401	365	–	[12]
^f Tandem mass spectrometry of the formic acid adduct		447.0504 ^e	401.0449 ^f	–	[29]
^g Sodium adducts and pseudo multiple reaction monitoring		401.1	365.0	–	[16]
^h Sodium adduct		427 ^g	427 ^g	+	[28]
	Aspartame	293.0	260.8/199.9	–	[13]
		295.1295	260.0921/235.1082/180.1024/120.0813	+	[30]
	Neotame	377.1	345.0/199.9	–	[13]
	NHDC	611.2	303.1/125.1	–	[13]

Except for the work reported in the aforementioned articles [16, 27, 32, 33], most groups extract artificial sweeteners by online or offline SPE from aqueous environmental samples. Besides concentrating the artificial sweeteners, this step removes matrix constituents, which may affect LC-MS/MS detection by matrix suppression or enhancement. A

summary of existing analytical methods for the determination of artificial sweeteners from aqueous environmental samples is given in Table S1. One additional study compared the recoveries of nine sweeteners in seven different buffer solutions [35] during extraction of 2 mL of the respective buffer solution. The best recoveries (more than

92%) were obtained using formic acid–*N,N*-diisopropylethylamine buffer adjusted to pH 4.5 and C₁₈-bonded silica sorbents. However, no application to real aqueous samples was reported.

In contrast to the application of expensive and modern instruments for trace analysis of artificial sweeteners from aqueous samples, there is little published data on stability tests in real environmental samples. Stabilization is of special importance for the nonpersistent sweeteners, such as SAC and CYC, and when dealing with wastewater samples. Oppenheimer et al. [34] reported the use of 5 mg ascorbic acid and 50 mg sodium azide or 5 mg ascorbic acid and 3 mg sodium omadine in 40-mL amber glass vials; the samples were transported on blue ice to the laboratory. However, the applicability of this stabilization procedure was only made plausible by comparison with stabilization procedures for PPCPs and was not explicitly experimentally tested for SUC. Van Stempvoort et al. [16, 36] compared refrigerated and frozen samples for the stability of ACE, CYC, SAC, and SUC and found ACE and SUC to be stable over a storage time of 13.5 months. The concentration of CYC declined within 3 weeks in refrigerated samples, whereas ACE and SAC were stable during this period. After more than 1 year of storage, CYC and SAC were nearly completely lost from refrigerated groundwater samples, likely because of microbial degradation.

Unpublished data from our own group proved the artificial sweeteners ACE, CYC, SAC, and SUC were stable for 21 days in reagent-grade water, tap water (Karlsruhe, without disinfectant), and wastewater-influenced surface water (Rhine river) under different stabilization conditions, i.e., without chemical stabilization, addition of 100 mg/L sodium azide, and addition of 1 mL 37% HCl (data not shown). All samples were stored in glass bottles at 6±2 °C. The initial concentration (1 µg/L) of all these four sweeteners did not significantly decline (usually below 3%, in one instance up to 11%). However, whereas ASP was stable for 3 weeks in reagent-grade water and tap water under all conditions tested, in Rhine river water its concentration was stable only after the pH had been lowered with HCl, but it was unstable (recoveries below 11%) after 1 week.

Occurrence in the aquatic environment

Municipal wastewater and sludge

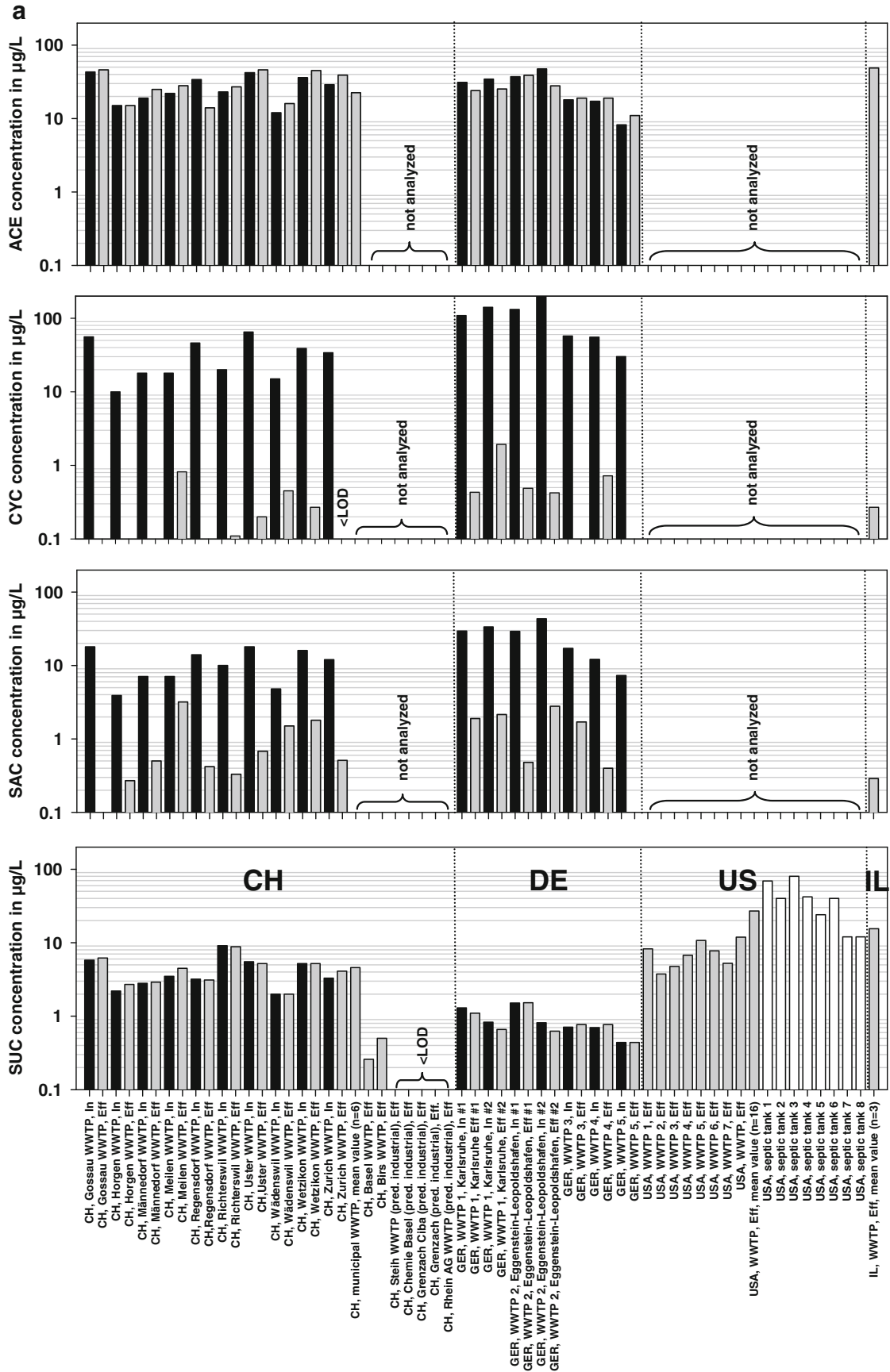
Wastewater

Of the seven artificial sweeteners that have been analyzed in wastewater influents and effluents, only ACE, CYC, SAC, and SUC have been positively detected. An overview is given in Fig. 1 and Table S2. In the USA, five additional

wastewater samples from three different locations were analyzed for ASP, SAC, and SUC by Ferrer and Thurman [30] downstream of municipal wastewater effluents. SAC was detected at one location at 5 µg/L (LOD = 0.5 µg/L) and SUC was detected in all samples at levels between 0.8 and 1.8 µg/L. However, dilution with surface water was not specified. Additional sweetener concentrations in some Canadian wastewaters were reported by Van Stempvoort et al. [16] as box plots. These measurements showed SUC as the prevailing sweetener (lower and upper quartiles approximately between 20 and 40 µg/L), similar to the levels found in US wastewaters. In their article, sampling sites, treatment stages, and concentrations were not given in detail. For the aforementioned reasons, the wastewater data in [16, 30] were not included in Fig. 1 and Table S2.

Most data on the occurrence of artificial sweeteners in wastewater are available for SUC, which has been analyzed in wastewater treatment plant (WWTP) effluents and/or influents in Sweden [8, 9, 29], Switzerland [12, 37, 38], Germany [13, 15, 38], Austria [38], Canada [16, 36], and Israel [13]. For the USA, only effluent data and concentrations in eight septic tanks are available [14, 34, 39]. From the effluent levels, country-specific differences in the consumption of SUC can clearly be recognized [29]. This is likely due to the different time since approval in individual countries and due to different usage patterns. SUC was discovered in 1976 and today is approved as a food and beverage additive in more than 80 countries. In the USA, SUC has been approved since 1998 [40] and its use was extended to all categories of food and beverages in 1999 [41]. It has been approved for general use in Switzerland since 2005 [42]; however, it was approved for individual products in 2003 (E. Ilg Hampe, BAG, personal communication). SUC has been approved as a food additive in Sweden since 2004 [43]. In Germany [44], SUC was approved in 2005. Thus, the early market introduction and the wide field of applications in the USA and the slightly earlier approval in Switzerland and Sweden might explain the higher wastewater concentrations of SUC of up to one and two orders of magnitude in these countries compared with Germany.

A direct comparison of the sweetener consumption in different countries is only possible on the basis of per capita loads, because the per capita loads are independent of the number of households connected to a WWTP. Per capita loads to WWTPs have been estimated for Switzerland in 2008 [12, 38] and 2009 [38], Germany in 2009 [13, 38] and 2010 [15], Austria in 2009 [38], and Sweden in 2007 [8], and 2009 [29]. The following per capita loads (in milligrams per person and day) were evaluated: 5.7–17.6 (Switzerland), 5.8–12.7 (Germany), and 4.9 (Austria) for ACE, 4.4–27.2 (Switzerland) and 32.3–38.7 (Germany) for CYC, 1.7–7.5 (Switzerland) and 7.3–9.3 (Germany) for SAC, and 1.0–2.9 (Switzerland), 0.14–0.23 (Germany), 0.49 (Austria), 1.7–2.1



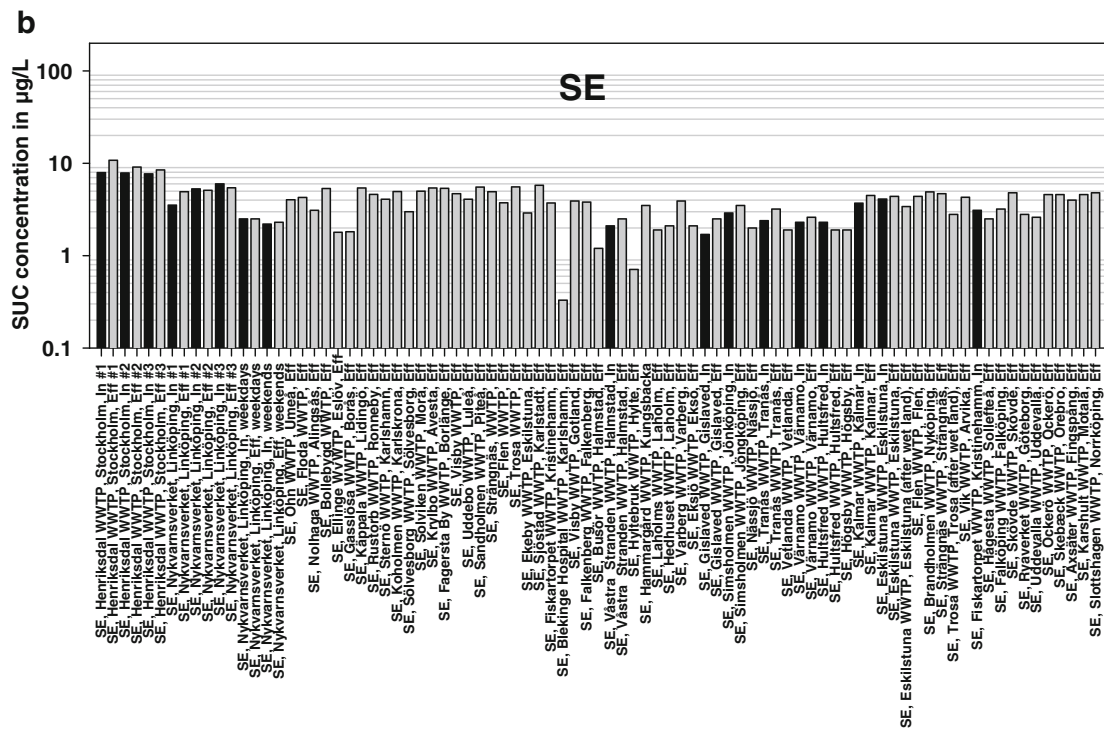


Fig. 1 continued.

(Sweden, 2007), and 0.76 ± 0.1 (Sweden, 2009) for SUC. Especially from the SUC per capita loads it is obvious that the food and beverage industries in the countries investigated prefer different artificial sweeteners in their products. Even the removal of a single important product, Coca-Cola light, from the Swedish market decreased the per capita loads significantly from 2007 to 2009 [29].

Comparison of 24-h composite samples in Swiss [12] and German [13, 15] studies shows that there is no significant removal of SUC during mechanical–biological wastewater treatment. As in these investigations SUC- d_6 was used as an internal standard for quantification by HPLC-ESI(-)-MS/MS, these data can be considered as highly reliable. WWTP influents and effluents have also been studied in the most extensive study on the environmental occurrence of SUC in Sweden [8, 9]. However, in this early study no internal standard was applied in the analysis by HPLC-ESI(-)-HRMS. Thus, less ion suppression in the cleaner effluent samples than in the influent samples might have been the reason for the apparently

systematically higher SUC concentrations in the Swedish effluent samples.

The second very persistent artificial sweetener which is not removed in conventional WWTPs is ACE, which was found in WWTP influents and/or effluents in Switzerland [12, 38], Germany [13, 15, 38], Austria [38], Canada [16, 36], and Israel [13, 15]. The ACE levels in some countries, e.g., Switzerland and Germany, were about one to two orders of magnitude higher than the SUC levels. This means, on the basis of the higher environmental concentrations in these countries combined with the much higher sensitivity of ACE detection by LC-ESI(-)-MS/MS, ACE is superior to SUC regarding its suitability as an environmental marker for municipal wastewater. This specificity of SUC and ACE for municipal wastewater was also recognized from the analysis of five WWTPs in Switzerland which treat predominantly industrial wastewaters [45] and from SUC analysis of hospital wastewater in Sweden [9]. In the first case, the concentration of SUC was below the LOQ (below 10 ng/L). In the Swedish example, the SUC concentration of $0.33 \mu\text{g/L}$ in the hospital wastewater was about one order of magnitude lower than the median level of $3.5 \mu\text{g/L}$ found in municipal WWTP effluents [37].

CYC showed high influent concentrations, typically between 10 and $200 \mu\text{g/L}$, in Swiss and German WWTPs [12, 13]. This might be attributed to the low sugar equivalent number of CYC compared with ACE, SAC, and SUC, which means that higher concentrations of CYC in foods

◀ Fig. 1 a Acesulfame (ACE), cyclamate (CYC), saccharin (SAC), and sucralose (SUC) concentrations in municipal wastewater influents (black bars) and effluents (gray bars) in Switzerland (CH) [12, 37, 45], Germany (GER) [13, 15], the USA (US) [14, 34, 39], and Israel (IL) [15]. b SUC concentration in Sweden (SE) [8, 9, 29]; for better comparability, data from [39] have been corrected for SUC recovery. Eff effluent, In influent, LOD limit of detection, WWTP wastewater treatment plant

or beverages are needed to obtain the same intensity of sweet taste. During secondary or tertiary wastewater treatment, more than 99% of CYC was removed.

Removal of SAC is quite similar to removal of CYC. In Switzerland and Germany, influent concentrations up to several tens of microgram per liter were observed. Typically, the removal rates are more than 90%, leading to effluent SAC levels of the order of 1 µg/L or lower. So far, no degradation products of CYC and SAC have been identified in WWTPs. Further information on the biodegradation potential of artificial sweeteners is given in “[Occurrence of and treatment options for the removal of artificial sweeteners and oxidation products in drinking water.](#)”

Temporal trends of sweetener concentrations have been scarcely investigated. In a Swedish study, no significant difference between weekday and weekend SUC levels in influents and effluents was observed [29]. However, there is still a lack of data on other temporal trends (intraday, day to day, summer/winter) of the artificial sweetener concentrations in WWTPs.

Sludge

Sludge investigations have been reported from Sweden (two WWTPs, three samples each) [8, 9] and Switzerland (digested sludge from four WWTPs) [26]. These studies agree that there is no significant adsorption of the sweeteners ACE, CYC, SAC [26], and SUC [8, 9, 26] to sludge particles, as can be expected on the basis of the values for water solubility and octanol–water partition coefficients (Table 1). In the Swiss study, the measured concentrations in the digested sludge were similar to the concentrations in the untreated wastewater, except for CYC, which was obviously degraded by approximately 90% in the digestion tanks. In the Swedish studies [8, 9], the measured SUC levels ranged from below the LOQ (0.3 and 1 µg/kg ww) to 19 µg/kg ww. Thus, the small residuals of sweeteners found in sludge correspond to the SUC concentration in the WWTP effluents (0.7–10 µg/L).

Surface water

Investigations on the occurrence of artificial sweeteners in surface waters include freshwater and seawater. A summary of the results on surface water measurements for artificial sweeteners is given in Table 3. The concentration of the persistent sweeteners ACE and SUC lie in the nanogram per liter to microgram per liter range in rivers and lakes.

Like with wastewater, the mainly studied sweetener in surface waters is SUC. SUC concentrations in rivers were determined in the most extensive monitoring in Europe [11], including 120 river water samples in 23 countries. The SUC concentrations ranged up to 1 µg/L. A direct comparison

between countries on the basis of per capita loads was not made in this study, but the results suggest a predominant SUC usage in the UK, Belgium, the Netherlands, France, Switzerland, Spain, Italy, Norway, and Sweden. However, this picture might be somewhat distorted, because the population connected to the WWTPs discharging to these receiving rivers and the river discharge were not taken into account by comparison only on a concentration basis. For example, a high discharge such as in the Danube river (2,000 m³/s) can lead to a value below the LOD (below 10 ng/L), whereas the highest SUC concentrations up to 920 ng/L measured in this study were found in the small rivers in the UK (discharge between 10.4 and 53 m³/s).

In the first measurements on four lakes in Switzerland in 2008, SUC was not detected [12]. This might be attributed to the comparably high LOQ (0.2 µg/L) and likely also to the late market introduction of SUC compared with other sweeteners in combination with the long residence times (1–15 years) of the water in the lakes. Low measured concentrations of 0.013 and 0.009 µg/L were reported in the epilimnion and the hypolimnion, respectively, of Lake Constance [38]. Owing to the long residence time of about 4.3 years of the water in this lake, it is expected that the SUC concentrations will increase in the next few years. By modeling the SUC concentration in the lake, the authors predicted an increase within the next 20 years of up to a factor of 8 compared with the concentration in 2009.

In general, at reference sites without a known impact of municipal wastewater, no artificial sweetener traces can be detected. This can clearly be seen, e.g., from measurement of ACE in Alpine lakes in Switzerland, where no sweeteners could be detected [12, 27], or from the absence of positive SUC detections in river water without wastewater impact in the USA [34].

Typically, concentrations and loads increase in rivers and streams with increasing wastewater contribution [12, 46, 47]. An example is shown for the Rhine in Fig. 2 [46, 47]. Like for other conservative wastewater markers with a more or less constant input into the receiving waters, the concentrations for the persistent sweeteners ACE and SUC also show an inversely proportional trend with the river discharge (see the examples in Fig. 3), meaning they depend on the degree of dilution. Good and fairly good log–log correlation of the ACE concentration with population equivalents ($R^2=0.94$) and the catchment area ($R^2=0.56$), both normalized by the river discharge, were found in a Swiss investigation including 80 samples from 44 sampling sites [27].

According to the Danube, Meuse and Rhine Memorandum of the waterworks associations IAWD, RIWA Meuse, and IAWR, the target value for anthropogenic, nonnatural substances without known adverse effects is 1.0 µg/L per individual compound [48]. Compared with this value, the median ACE concentration in the Rhine exceeds this target

Table 3 Concentrations ($\mu\text{g/L}$) of the artificial sweeteners ACE, CYC, SAC, and SUC in surface waters

Sites	Year	Sample type	No. of samples	ACE	CYC	SAC	SUC	Reference
EU wide	2007/2008	Grab samples	120	–	–	–	<0.10 to 0.92	[11]
Switzerland	2008	Flow-proportional 7-day composite samples	12	$\approx 0.2\text{--}6.9$	–	–	<LOD ^a to 0.6	[12]
		Grab samples	9	<LOD ^a to 2.8	<LOD ^a to 0.13	<LOD ^a to 0.18	<LOD ^a	
	2009	Grab samples	80 samples from 44 sites	<LOD to 12.7	–	–	–	[27]
Lake Constance	2008	Grab samples	2	0.28 ^b	–	–	0.013 ^b	[38]
			2	0.27 ^b	–	–	0.009 ^b	
Switzerland, Germany, Austria	2009	Grab samples	12	0.29–25	–	–	0.02–3.4	[38]
Germany	2009	Not specified	7	3.1–10	–	–	–	[50]
	2010	Grab samples	13	0.40–1.1	0.01–0.13	0.01–3.8	<LOQ ^c to 0.10	[46]
	2010	Grab samples	13	0.49–4.2	<LOQ ^c to 1.0	0.03–0.47	<LOQ ^c to 0.18	[47]
	2010	Grab samples	3 samples at 1 site	12.4	–	–	–	[32]
USA	Not specified	Not specified	1 site	23	–	–	–	[33]
	2008	Grab samples	8	–	–	–	0.0008–2.0	[14]
		Grab samples	7	–	–	–	<LOD ^d to 0.39	
	Not specified	Not specified	11	–	–	–	0.12–10	[34]
	Not specified	Not specified	15	–	–	–	<MRL ^e	
	2008/2009	Not specified	5 from each river	–	–	–	0.032 \pm 0.017	[39]
							0.30 \pm 0.030	
							0.004 \pm 0.006	
							0.047–0.081	[54]
Sweden	2006/2007	Not specified	4	–	–	–	–	
	2007	Not specified	3	–	–	–	–	
							0.41 \pm 0.30	[28]
							0.07 \pm 0.01	
							0.11 \pm 0.04	
Serbia	2009	Grab samples	2	0.09–0.31	0.09–0.13	0.06–0.08	<LOQ	[51]

LOD limit of detection, LOQ limit of quantification, MRL maximum reporting limit, WW wastewater

^a LOD of 0.01, 0.02, 0.03, and 0.2 $\mu\text{g/L}$ for ACE, CYC, SAC, and SUC, respectively

^b Mean of samples from 1 and 2.5 m (epilimnion) and from 100 and 230 m (hypolimnion)

^c LOQ of 0.01, 0.01, 0.01, and 0.05 $\mu\text{g/L}$ for ACE, CYC, SAC, and SUC, respectively

^d LOD not specified

^e MRL of 0.1 $\mu\text{g/L}$

value in the lower stretch of the Rhine downstream of Mainz (Fig. 2). However, a decrease of the ACE concentration is only possible by either a change of consumer habits or a change in foodstuff or beverage composition by the producers. Both changes will be difficult to achieve voluntarily, and most likely only a restriction of the approval situation will lower the environmental levels.

In addition to the freshwater studies, there are also some publications on the occurrence of SUC in seawater [14, 49]. SUC was detected in concentrations ranging from 0.0008 to 0.39 $\mu\text{g/L}$ in coastal seawaters in the USA [14]. Even in two Gulf Stream samples it was found in low concentrations of 0.0008 and 0.068 $\mu\text{g/L}$, respectively. In another measurement program, no SUC (below 0.0005 $\mu\text{g/L}$) was found in three seawater samples from the Norwegian arctic with no or negligible wastewater influence [49].

Groundwater and riverbank filtrate

Different direct and indirect routes of groundwater contamination with artificial sweeteners from wastewater or waste sources have been considered in the literature: infiltration of wastewater-influenced surface waters [12, 15, 25, 32, 33,

50, 51], percolation of treated wastewater in soil aquifer treatment (SAT) [13, 15], impact of landfill leachate [16], septic systems [16, 36], municipal wastewater ponds [16], municipal wastewater exfiltration cells [16], and percolation of manure on agricultural land [26].

Accordingly, all four artificial sweeteners ACE, CYC, SAC, and SUC which were detected in wastewater were also found in groundwater aquifers. The persistent ACE was most frequently detected in groundwater samples and in the highest concentrations of all sweeteners analyzed, up to the microgram per liter range. An extensive study on groundwater was conducted by Buerge et al. [12]. In the area of Zurich, ACE was found in 65 of the 100 samples investigated at concentrations up to 4.7 $\mu\text{g/L}$. Similar values (0.05–2.6 $\mu\text{g/L}$) were found in a groundwater monitoring program in Bavaria, Germany [50]. Even higher ACE concentrations were reported by Prasse et al. [32] in two German groundwater samples, 12 and 6.9 $\mu\text{g/L}$, for an oxic and an anoxic groundwater, respectively, and by Engelhard et al. [33] (approximately 8–13.5 $\mu\text{g/L}$, from Fig. 10 in [33]) below the Schwarzbach, a creek with a wastewater burden of about 50%. The highest values of artificial sweeteners in groundwater found in the literature were measured in Canada [16,

Fig. 2 Median values of concentrations and daily loads of ACE, CYC, SAC, and SUC in the Rhine in the flow direction from left to right. (Concentration data from [46, 47])

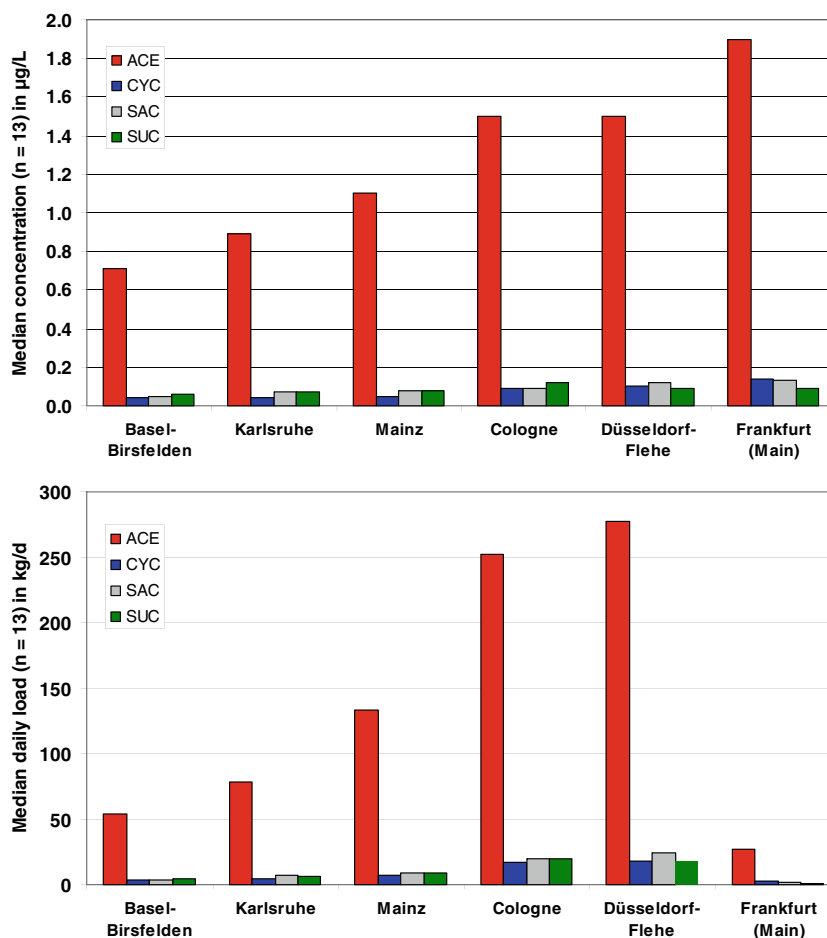
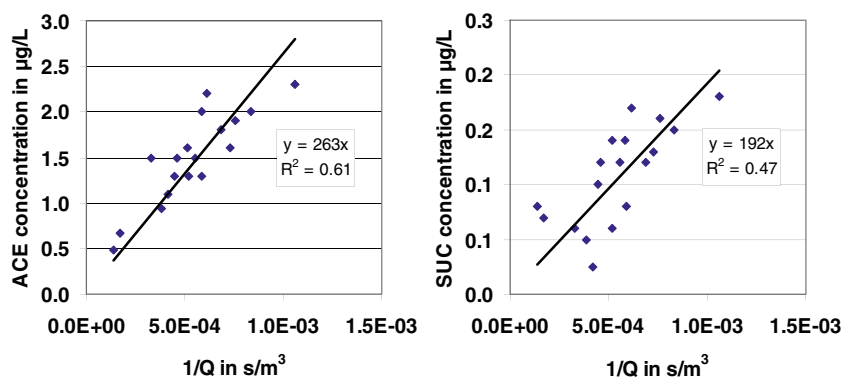


Fig. 3 Correlation of ACE and SUC concentrations in the Rhine at Cologne with the reciprocal of the discharge. (Data from [47])



[36]. Maximum values of 34 µg/L for ACE, 0.98 µg/L for CYC, 10 µg/L for SAC, and 24 µg/L for SUC were given by Van Stempvoort et al. [16] for groundwater aquifers with known wastewater impact or in shallow groundwater samples along wastewater-impacted streams. Van Stempvoort et al. [36] detected high ACE levels in the wastewater plume of a septic tank of a campground of the order of several tens of micrograms per liter. In contrast to the other sweeteners investigated (CYC, SAC, and SUC), the ACE concentration decreased only smoothly with depth below a tile field and downstream from a septic tank, suggesting dilution as the main attenuation process for ACE.

The second persistent sweetener, SUC, was much less frequently detected in groundwater or riverbank filtrate. However, this might be a consequence of several factors: its higher LOD, its later introduction in different countries, and the greater sweetness of SUC compared with ACE (sugar equivalence values of 600 for SUC and 200 for ACE; see Table 1), resulting in lower amounts of SUC needed to achieve comparable sweetness in foods and beverages.

Although trace concentrations of CYC and SAC were also detected in groundwater and riverbank filtrates [16, 25, 36], the information available on their stability in these water bodies does not give a unique picture. One problem which might hamper comparison is potential degradation during the time between sampling and analysis (see the last two paragraphs in “LC-MS/MS and LC-HRMS methods”) [36]. This could also be one reason for a bad correlation between SAC and CYC concentrations with the concentration of the wastewater marker chloride (for SAC vs. Cl^- $R^2=0.13$ [16] and $R^2=0.22$ [36], for CYC vs. Cl^- $R^2=0.26$) in contrast to the good ACE–chloride correlation ($R^2=0.93$ [16] and $R^2=0.92$ [36]).

In a SAT field in Israel, Scheurer et al. [13, 15] found a larger decrease of SUC concentrations relative to ACE with increasing distance from the wastewater percolation basin. In their study, the residence time of the treated wastewater at the remote sampling sites was up to about 1.5 years. The recent results of Van Stempvoort et al. [36] support this finding. The attenuation of SUC can have different origins, e.g., adsorption in the subsoil or, most likely, partial

degradation in the aquifer. The possible mechanisms for the removal of SUC and further sweeteners by biodegradation and other processes are discussed in more detail in “Occurrence of and treatment options for the removal of artificial sweeteners and oxidation products in drinking water.” Unusually high SAC concentrations (up to 10.3 µg/L) in groundwater samples, even higher than the ACE concentrations, were found by Van Stempvoort et al. [16]; the high SAC concentrations mutually stemmed from an old landfill adjacent to the sampled sites. Other possible entry pathways of SAC into groundwater were compared by Buerge et al. [26]. These include application of manure to farmland, degradation of sulfonylurea herbicides to SAC, irrigation with wastewater-impacted surface water, application of digested sewage sludge as a fertilizer, and leaks in sewers. SAC is not used only as sweetener for human consumption, but is also registered as a piglet feed additive, e.g., in Switzerland. Buerge et al. [26] measured high SAC concentrations of up to 12 mg/L in liquid manure, where it was stable during 2 months of storage. By computer simulations they found manure application to be by far the most likely entry pathway of SAC into Swiss groundwater. The observed SAC concentration in groundwater ranged up to 0.26 µg/L.

The role of important boundary conditions in the aquifer, in particular, redox conditions, on the degradation of artificial sweeteners has not been investigated systematically. There is still urgent need for additional field and laboratory research. One important aspect for marker applications of ACE is the question of whether it could also be used under anaerobic conditions, e.g., under iron and manganese reducing conditions in groundwater aquifers. This issue is currently being investigated in a research project of TZW [52].

Occurrence of and treatment options for the removal of artificial sweeteners and oxidation products in drinking water

The first sweetener detected in tap water was ACE. It was detected in Swiss tap waters of groundwater origin in concentrations up to 2.6 µg/L [12]. It is also the sweetener with

the highest measured level ($7.2 \pm 1.7 \mu\text{g/L}$, $n=3$) in finished drinking water (Fig. 5 in [32], exact values from C. Prasse, personal communication). Such high levels of an anthropogenic and xenobiotic chemical in drinking water are rare. Comparable levels have been measured only for a few chemicals, e.g., the chelating agent ethylenediaminetetraacetic acid [53], which is included in many household and industrial products, e.g., in cleaning products.

There have been two detailed studies on the behavior of artificial sweeteners during drinking water production [25, 54] in full-scale drinking water treatment plants (DWTPs). In the German study of Scheurer et al. [25], the behavior of ACE, CYC, SAC, and SUC was investigated in six waterworks with surface-water-derived raw water sources, i.e. river water or riverbank filtrate, sometimes partly mixed with landside groundwater. Only ACE was detected in finished waters, at levels up to $0.76 \mu\text{g/L}$. In the USA, Mawhinney et al. [54] studied the fate of SUC from source water to the distribution system. They analyzed samples from 19 DWTPs and found SUC concentrations up to $2.4 \mu\text{g/L}$ in finished waters and in distribution systems.

Water treatment in DWTPs, which process surface-water-influenced source waters, usually consists of a multibarrier treatment system. Several treatment steps involved in conventional water treatment have been investigated in laboratory experiments and in full-scale DWTPs. From the qualitative summary in Table 4, it is obvious that only a few removal options exist for individual sweeteners, in particular for the persistent ACE and SUC. Only the processes of natural attenuation, ozonation, and granular activated carbon (GAC) filtration, which are most common to conventional DWTPs and which result in partial removal of at least one of the sweeteners given in Table 4, are discussed in the following.

Natural attenuation processes

Natural attenuation processes occurring in treatment steps such as bank filtration, underground passage, and in biological active filters, e.g., in slow sand filters, include biological degradation and adsorption. Owing to the good water solubility of the artificial sweeteners and their low soil adsorption tendency [17, 26], adsorption processes can be neglected. Generally speaking, of the four sweeteners listed in Table 4, only CYC and SAC can be effectively removed in such treatment steps. In the study of Scheurer et al. [25], three of the six DWTPs investigated use Rhine riverbank filtrate as source water. In the river itself, CYC and SAC were permanently present in low concentrations (see Fig. 2), but both sweeteners could not be detected (below 10 ng/L) in the source waters. The removal can be understood as resulting from biological degradation. This was confirmed in a fixed-bed bioreactor experiment (initial sweetener

concentration of $1 \mu\text{g/L}$) with Rhine water [25] which was designed to simulate aerobic biodegradation processes during bank filtration. In this experiment, after a lag phase of about 1 week, the degradation rapidly proceeded and CYC and SAC were completely removed after 15 and 20 days, respectively. These results are consistent with the good degradation observed in WWTPs (see “Municipal wastewater and sludge”) and in incubation experiments by Buerge et al. [12] with activated sludge. They found dissipation of CYC and SAC following first-order kinetics and elimination efficiencies of 99 and 78% after 3 h, respectively. A few years before the publication of the abovementioned articles, Schleheck and Cook [55] enriched and isolated a bacterium, strain SKN, that was able to utilize SAC as the sole source of carbon and energy for aerobic growth. They also identified catechol as an intermediate during degradation of SAC.

In incubation experiments with sweeteners in soils, Buerge et al. [26] evaluated half-lives (DT_{50}) of 6.1, 0.8, 3.3, and 9.0 days for ACE, CYC, SAC, and SUC, respectively. No degradation occurred in sterile batches. The degradation of CYC and SAC in these soil incubation experiments is consistent with the aforementioned extensive elimination in WWTPs, during bank filtration, and in the fixed-bed bioreactor experiment. However, the degradation of ACE and SUC is apparently contrary to the finding of the other investigations. Buerge et al. suggested a difference in microbial communities in activated sludge and soil and the much shorter residence time in activated sludge basins as possible explanations. Nevertheless, it has also to be taken into account that the sweetener concentrations in these soil incubation experiments (initial individual sweetener concentrations of 1 mg/kg) were comparatively high. For example, they exceeded the highest measured concentration in WWTPs and were even three orders of magnitude above the initial concentration in the fixed-bed reactor experiment of Scheurer et al. [25] and three to five orders of magnitude higher than in the Rhine. In addition, a high concentration of organic matter in soils could also have been responsible for the degradation of ACE and SUC, tentatively due to cometabolic degradation. Labare and Alexander [56, 57] found that SUC can be mineralized in natural environments, such as lake sediments (4.4–18.8%, 96–126 days), sewage (23.2%, 123 days), and surface waters (1.1–4%, 42–132 days), but at lower rates and to lesser extents than in soils (32.6–60.4%, 20–101 days). The mineralization in surface waters was in the range of the impurities of the ^{14}C -labeled SUC, and therefore, was not significant. Labare and Alexander provided good experimental evidence that SUC mineralization is a cometabolic process, which is supported by the higher amount of organic matter in soil samples. These findings could explain the dissipation of SUC in the SAT process after long residence times of up to about 1.5 years

Table 4 Qualitative representation of efficiency of different water treatment processes for the removal of artificial sweeteners

	ACE	CYC	SAC	SUC	References
Bank filtration/underground passage/SAT	–	+	+	0/–	[13, 15, 25, 36]
Flocculation	–	–	–	–	[25]
Ozonation	0/+	0	–	0/–	[17, 25, 39, 58, 60, 88]
GAC filtration	–/0	–	+	0/+	[17, 25, 28]
Reverse osmosis				+	[88]
Chlorination/chloramination	–	–	–	–	[17, 25, 39, 54]
UV radiation				0	[17, 39]

SAT soil aquifer treatment,
GAC granular activated carbon,
+ high removal potential,
0 medium removal potential,
– low removal potential

[13, 15] and also the attenuation of SUC in a large septic plume [36]. The intermediate of soil microbial degradation of SUC proposed by Labare and Alexander [56, 57], either the aldehyde or the uronic acid of SUC, could not be detected in soil incubation experiments by Soh et al. [17], maybe owing to the lower concentration of SUC and consequent byproducts or because the formation of this intermediate depends on soil conditions, as reported by Labare and Alexander. Also, in environmental samples the occurrence of such intermediates is still to be reported.

Ozonation

Buerge et al. [12] reported that ACE was partly removed during ozonation of groundwater in a DWTP and found detectable concentrations also in finished drinking water (0.02–0.07 µg/L) after ozonation of lake water. Similar findings were obtained in the systematic field studies of Scheurer et al. [25]. The results were confirmed by bench-scale experiments [18].

The kinetics of the reaction of ACE with ozone was evaluated under realistic conditions (tap water matrix, 0.5–5.0 mg/L ozone). The rate constants of the first-order reaction kinetics ranged from $5.5 \times 10^{-4} \text{ s}^{-1}$ at 0.5 mg/L ozone to $9.7 \times 10^{-3} \text{ s}^{-1}$ at 5.0 mg/L ozone and there was fairly good consistency of field and laboratory results. During ozonation, different oxidation products were formed. The reaction of the ozone molecule according to the Criegee mechanism (Fig. 4) led to the formation of an aldehyde, which appears as aldehyde hydrate with $m/z=170$ in aqueous solution, and acetic acid. Further oxidation of this aldehyde gives the corresponding acid with $m/z=168$. Measurements in a full-scale DWTP with a known source water contamination with ACE detected the aldehyde after the ozonation step. This intermediate was removed by a subsequent activated carbon filter and no identified oxidation products were detected in the finished water.

CYC reacts with ozone in DWTPs at typical ozone concentrations between 0.5 and 2.0 mg/L, and different oxidation products of CYC were identified by several analytical coupling techniques and also nuclear magnetic resonance spectroscopy [18]. However, the reaction of CYC might

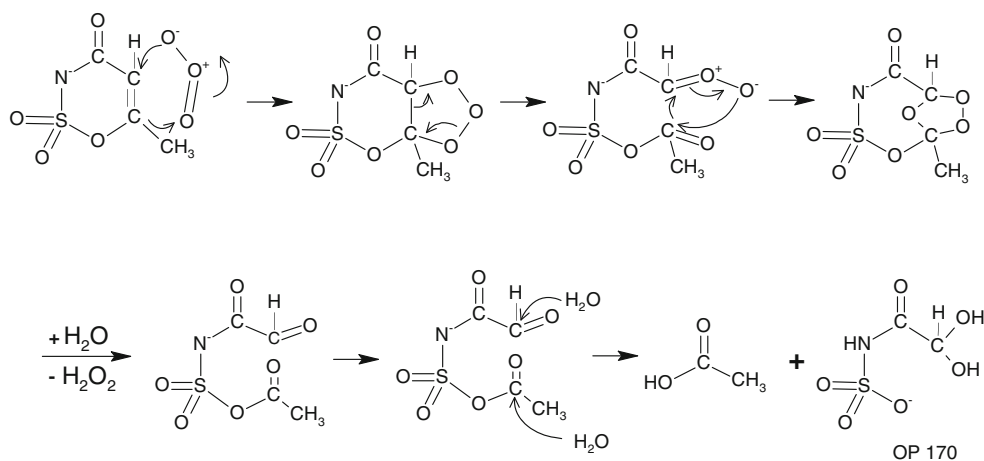
only be relevant to DWTPs applying direct surface water abstraction or to WWTPs with an advanced wastewater treatment by ozone. Such additional ozonation steps will soon be installed in a number of Swiss WWTPs. The main products formed in laboratory ozonation experiments were cyclohexanone and amidosulfonic acid, which result from ozone attacking the C–N bond between the sulfonamide moiety and the cyclohexyl ring (see the structure of CYC in Table 1). Minor oxidation products were three isomers of a ketone, which was formed via oxidation at one of the symmetrically different carbon atom positions in the cyclohexyl ring. It needs still to be tested if such oxidation products are also formed in DWTPs with a source water contaminated with CYC.

SUC was stable at low ozone concentrations of 0.5 and 1.0 mg/L in tap water, but approximately 20% was removed with an ozone concentration of 5 mg/L. In treatment of wastewater effluents at ozone concentrations of 5 and 15 mg/L, 28 and 62% SUC removal was reported by Minten et al. [28] in a pilot-scale plant (the ozone contact time was not given). A similar value (57%) was given by Lee et al. [88] for an ozone concentration of 8 mg/L, and Hollender et al. [60] found $31 \pm 6\%$ elimination with approximately 0.6 mg ozone per gram of dissolved organic carbon (dissolved organic carbon concentration $5.2 \pm 0.6 \text{ mg/L}$). Thus, under typical conditions for DWTPs and WWTPs, only partial SUC removal can be expected.

GAC filtration

GAC filtration is not the method of choice for the removal of artificial sweeteners in DWTPs. Among the sweeteners ACE, CYC, SAC, and SUC which occur in the aquatic environment, significant removal by GAC filtration is only possible for SAC (with an aromatic ring) and SUC (three-fold chlorinated) [25]. This is in accordance with their octanol–water partition coefficients, which are the highest of these four sweeteners (see Table 1). In a small-scale filter test, SAC breakthrough was 10% or lower until about 20,000 bed volumes treated (BVT). According to the definition of “drinking water relevance” by Marcus [61] a compound is termed “relevant to drinking water” if it shows

Fig. 4 Formation of oxidation product OP 170, an aldehyde hydrate, through reaction of ACE with ozone according to the Criegee mechanism (reproduction from [18] with kind permission of Springer 2012)



a breakthrough above 10% below 15,000 BVT, i.e., SAC is close to being a “drinking water relevant” compound.

SUC would be such a “drinking water relevant” compound because it exceeds the 10% line below 10,000 BVT. However, it shows a smooth breakthrough curve, and thus breakthrough in the small-scale filter experiment was only about 30% at 25,000 BVT. A substantial reduction of SUC concentration was also observed in advanced wastewater treatment by activated carbon. With Filtrasorb 400 carbon and an empty bed contact time of 1 h, the SUC concentration decreased from 11 ± 3.2 to 0.03 ± 0.0 $\mu\text{g/L}$ [28]. However, the running time and the load were not further specified.

Soh et al. [17] evaluated the sorption isotherm of SUC on GAC and reported the Freundlich coefficient $K_f = 78.6$ (mg/g) $(\text{L/mg})^{1/n}$ and $1/n = 0.364$. From these equilibrium data, adsorption of SUC is less likely than that of compounds with similar $1/n$ values, e.g., chlordane, naphthalene, and toluene, with K_f values of 190, 132, and 97 (mg/g) $(\text{L/mg})^{1/n}$.

Conclusions

Seven artificial sweeteners were analyzed in the aquatic environment, and of them ACE, CYC, SAC, and SUC were found in the water cycle. High levels, sometimes exceeding 100 $\mu\text{g/L}$, appear in wastewater influents. Their concentration in the environment decreases mainly as a result of biological degradation (CYC, SAC, partly SUC) or dilution (ACE, SUC). The levels of ACE and SUC in wastewater-impacted surface waters and groundwater aquifers and in derived drinking waters range up to the microgram per liter level. The concentrations of ACE and SUC found in some drinking waters are among the highest concentrations of anthropogenic trace pollutants known. In spite of the comparatively high ACE and SUC concentrations in some drinking waters, these values are about three orders of

magnitude lower than organoleptic threshold values of artificial sweeteners [12].

The occurrence of individual sweeteners strongly depends on the approval situation and usage pattern and can differ greatly between countries.

The most persistent compounds are ACE and SUC. They were proposed as anthropogenic markers in most of the publications on their environmental occurrence. Their use as anthropogenic markers for municipal wastewater impact is only valid on a regional or national scale and within a certain time. Sudden changes of important product compositions, e.g., Coca-Cola light in Sweden [29], can change the concentrations in wastewater and surface waters immediately. As long as the consumption situation does not change much, the ACE and SUC concentrations will remain highly correlated with the levels of other anthropogenic wastewater trace pollutants, e.g., perfluorooctanoic acid and perfluorooctane sulfonate [27], carbamazepine (pharmaceutical), and 1*H*-benzotriazol (corrosion inhibitor, e.g., in household dishwashers) [15]. Such correlations can also be used to detect unusual concentration ratios, which indicate other sources, such as individual point sources. ACE and SUC are ideal markers regarding specificity for wastewater and, owing to negligible background concentrations, are superior to natural markers such as chloride. The first applications of LC-ESI-MS/MS measurements of ACE have been reported on mineral waters [62], and as a first consequence an individual well was shut down because of proof of an anthropogenic influence.

Sweeteners which occur in source waters of waterworks must be regarded not solely as anthropogenic markers, but also as precursors for oxidation products occurring in DWTPs. This was demonstrated for ACE and CYC. One ozonation byproduct of ACE was identified as an intermediate in the water treatment process [18].

There have been a few studies on the ecotoxicological impact of SUC [17, 58, 63–65], which was detected first

among the artificial sweeteners in the environment. However, there have been no similar studies for the second persistent sweetener, ACE. The existing ecotoxicology studies on SUC give the picture that no bioaccumulation occurs and most end points indicate no or only small environmental effects. Nevertheless, the environmental impact of the not fully identified transformation products of SUC [56, 57] and the potential transformation products of other sweeteners is not understood and needs further research.

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