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Performance of conventional multi-barrier drinking water treatment plants for the removal of four artificial sweeteners

Due to incomplete removal of artificial sweeteners in wastewater treatment plants some of these compounds end up in receiving surface waters, which are used for drinking water production. The sum of removal efficiency of single treatment steps in multi-barrier treatment systems affects the concentrations of these compounds in the provided drinking water. This is the first systematic study revealing the effectiveness of single treatment steps in laboratory experiments and in waterworks. Six full-scale waterworks using surface water influenced raw water were sampled up to ten times to study the fate of acesulfame, saccharin, cyclamate and sucralose. For the most important treatment technologies the results were confirmed by laboratory batch experiments. Saccharin and cyclamate proved to play a minor role for drinking water treatment plants as they were eliminated by nearly 100 % in all waterworks with biologically active treatment units like river bank filtration (RBF) or artificial groundwater recharge. Acesulfame and sucralose were not biodegraded during RBF and their suitability as wastewater tracers under aerobic conditions was confirmed. Sucralose proved to be persistent against ozone and its transformation was <20 % in lab and field investigations. Remaining traces were completely removed by subsequent granular activated carbon (GAC) filters. Acesulfame readily reacts with ozone (pseudo first-order rate constant $k = 1.3 \cdot 10^{-3} \text{ 1/s}$ at 1 mg/L ozone concentration). However, the applied ozone concentrations and contact times under typical waterworks conditions only led to an incomplete removal (18-60 %) in the ozonation step. Acesulfame was efficiently removed by subsequent GAC filters with a low throughput of less than 30 m³/kg, but removal strongly depended on the GAC preload. Thus, acesulfame was detected up to 0.76 µg/L in finished water.

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4.1 Introduction

Due to the spreading of the liquid chromatography–tandem mass spectrometry (LC–MS/MS) technique in water analysis in the last decade, a strongly increasing number of polar trace pollutants and some of their transformation products were detected in the water cycle (Richardson and Ternes, 2005; Richardson, 2009). Examples comprise different compound classes, such as pharmaceuticals and personal care products (PPCPs) including X-ray contrast media, poly- and perfluorinated chemicals (PFC), and polar pesticide metabolites, such as N,N-dimethylsulfamide (DMS) (Schmidt and Brauch, 2008), desphenyl-chloridazone and methyl-desphenyl-chloridazone (Weber et al., 2007), ethanesulfonic acid (ESA) and oxamylic acid (OSA) metabolites of chloroacetamide herbicides (Hladik et al., 2008). These findings of polar and persistent pollutants pose a new challenge to waterworks treating raw waters, which are directly (*e.g.* unknown sewer leakages) or indirectly (*e.g.* bank filtration or artificial groundwater recharge, AGR) affected by wastewater. Many of these chemicals, which can occur on the ng/L or low µg/L scale in the raw waters are harmless to humans at these trace levels (Snyder et al., 2008), but others are of special concern. The origin of concerns is either due to the toxic properties in animal experiments and accumulation potential in humans (*e.g.* some PFC, such as perfluorooctane sulfonate (PFOS) (Lau et al., 2007; Rumsby et al., 2009)) or because of other reasons, such as increased bacterial resistance through continuing exposure to antibiotics, or disruption of the endocrine system (Jørgensen and Halling-Sørensen, 2000). Another potential risk stems from the transformation potential of precursor compounds into toxic products, such as the carcinogenic N-nitrosodimethylamine (NDMA), generated upon the reaction of non-toxic DMS with ozone (Schmidt and Brauch, 2008).

Another class of compounds, recently detected in the water cycle, are artificial sweeteners (AS). These anthropogenic and xenobiotic compounds are high production volume chemicals, with supplies of saccharin, aspartame, acesulfame K, sucralose, and cyclamate accounting for 4.57 million tons of sucrose equivalents in 2007 in the U.S. (Haley et al., 2008). AS are used world-wide as table-top sweeteners as well as food additives to sweeten diet beverages, pharmaceuticals and some personal care products, such as tooth pastes and mouth washes (Weihrauch and Diehl, 2004; Zygler et al., 2009). Although minor direct inputs into the aquatic environment by improper disposal cannot completely be excluded, the typical entrance pathway of AS is via municipal wastewaters. Sucralose, the active ingredient of the well-known sweetener Splenda[®], was the first AS analyzed as trace impurity in wastewater treatment plant (WWTP) effluents and surface waters in Europe (Brorström-Lundén et al.,

2008; Loos et al., 2009). Recently, three additional AS, acesulfame, cyclamate, and saccharin, were detected in Swiss and German wastewaters (Buerge et al., 2009; Scheurer et al., 2009). In the latter investigations, acesulfame and sucralose turned out to be the most stable of the targeted AS. Traces of all four AS were also found in surface and groundwaters. In Germany and Switzerland the AS measured at the highest level was acesulfame. Its concentrations ranged up to 2.7 µg/L in river water (Neckar river) (Scheurer et al., 2009), 2.8 µg/L in lake water (lake Greifensee) (Buerge et al., 2009), and 4.7 µg/L in groundwaters (Buerge et al., 2009).

A first measurement of AS in a drinking water supply in Switzerland, where aeration of groundwater for iron and manganese removal was the only treatment step, revealed acesulfame to be present in tap water in concentrations up to 2.6 µg/L (Buerge et al., 2009). The toxicological properties of AS are well studied and show that µg/L quantities are harmless to humans (Weihrauch and Diehl, 2004). However, data on ecotoxicological properties of AS are scarce. For example, in the EU there is no obligatory environmental risk assessment for AS according to the European Parliament and Council directive on sweeteners for use in foodstuffs (EU, 1994), which is based on the framework directive for food additives (EU, 1988). Therefore, it is yet unknown, what the occurrence of these trace pollutants means to aquatic biocenoses. In sugarcane, sucralose can even inhibit the transport of the structurally strongly related sugar sucrose, an important transport and signal compound (Reinders et al., 2006). It was also speculated, that sucralose might interfere with plant photosynthesis (Lubick, 2008) or deteriorate functions such as orientation, food or partner localisation.

Both above-mentioned Swiss and German studies suggested acesulfame to be an ideal tracer to quantify the impact of wastewater derived proportions of raw waters. Besides this, there is first evidence that during the ozonation process in waterworks acesulfame readily reacts with ozone to not yet identified products (Buerge et al., 2009).

The aim of this study was to investigate in more detail the fate of the four mentioned AS in conventional multi-barrier treatment plants including bank filtration, artificial recharge, flocculation, ozonation, activated carbon filtration, and disinfection by chlorine and chlorine dioxide as treatment steps. For this purpose, the concentration decrease of AS was studied within six waterworks using river water, bank filtrate, or artificially recharged groundwater as raw water. The focus was directed to those four out of seven AS, which were found in surface waters in a preceding study (Scheurer et al., 2009). To confirm the results obtained from field studies, the main treatment steps were simulated in laboratory experiments.

4.2 Material and methods

4.2.1 Laboratory experiments

Analytical method

The AS were analyzed by high performance liquid chromatography–electrospray tandem mass spectrometry (HPLC–ESI–MS/MS) after solid-phase extraction according to a recently published method (Scheurer et al., 2009). In the present study acesulfame-d₄ was used as an additional internal standard for the quantification of acesulfame. The majority of samples were analyzed according to the described protocol. In addition, some samples of laboratory experiments with elevated concentrations >2 µg/L were analyzed by direct injection (15 µL) LC–ESI–MS/MS with external standard calibration. In the present study reporting limit of AS concentrations was 10 ng/L.

Fixed-bed bioreactor

A laboratory test filter unit, established to simulate aerobic degradation processes during river bank filtration was used to study the biodegradation of artificial sweeteners (Karrenbrock et al., 1999; Knepper et al., 1999a; Knepper et al., 1999b). A glass bottle used as a reservoir was filled with 10 L of unfiltered surface water (Rhine river at Karlsruhe) and spiked at a level of 1 µg/L of the test compounds in aqueous solution. The water was pumped bottom-up in recirculation with a flow rate of 17 mL/min over a filter column filled with sintered glass beads (SIRAN-Carrier no. 023/02/300, Schott Engineering GmbH, Mainz, Germany) used as carrier material. The porous material is non-adsorptive and provides optimum conditions for the formation of a biofilm with similar biological activity as observed in the colmation layer/infiltration zone during river bank filtration. The system was stored in the dark at room temperature (20 ± 2 °C) and aerated with compressed air to ensure aerobic conditions during the running period of over 90 days.

Flocculation

The removal of artificial sweeteners during flocculation was investigated in batch experiments with Karlsruhe tap water and water from the Rhine river. A Stuart flocculator SW6 (Bibby Sterlin Ltd., Stone Staffordshire, UK) was used for batch jar tests. The system consisted of six units with 1 L glass beakers and stirrers with a defined stirring depth. 800 mL of Karlsruhe tap water and river water were spiked at a level of 1 µg/L with the test compounds in aqueous solution. Polyaluminum chloride (AlCl₃) and iron chloride (FeCl₃) were used as flocculants

and added in doses of 5, 10 and 15 mg/L. The batches were stirred at a velocity of 250 rpm for 30 s to achieve an evenly rapid distribution of the flocculation agents. No flocculation aid was added. The velocity was reduced to 50 rpm, held for 5 min and then further reduced to 25 rpm and held for 15 min for the formation and the growth of flocs. After sedimentation of the flocs for 60 min, 100 mL of supernatant was taken for the analysis of artificial sweeteners. The pH was controlled between 7 and 8 to ensure the proper precipitation of the Al or Fe hydroxides and low residual concentrations of dissolved Fe(III) or Al(III) (DVGW, 1998).

Ozonation

Ozonation experiments were performed as batch experiments in 5 L glass vessels filled with Karlsruhe tap water. This water was chosen as a matrix similar to that in waterworks. It had a pH of 7.3, a dissolved organic carbon (DOC) content of 0.9 mg/L, and a hydrogen carbonate concentration of 305 mg/L (5 mmol/L). The initial sweetener concentration was 1 µg/L and four different initial ozone concentrations (0.5, 1, 2, 5 mg/L) were applied. For this purpose 5 mL of a 1 µg/mL aqueous sweetener solution was dissolved in 2 L of tap water and filled up to a total volume of 5 L with tap water and, finally, with the necessary volume of a ozone stock solution (concentration between 17 and 28 mg/L). The test set up was slightly stirred on a magnetic stirrer to spread the ozone evenly. Samples (100 mL) were taken after contact times between 1 and 60 min and residual ozone was reduced by sodium sulfite. Complete ozone removal was confirmed by redox potential measurement.

Activated carbon small-scale filter test

The removability of artificial sweeteners by GAC filtration was investigated using ground (300-400 µm) and washed Filtrasorb 300 (F 300, Chemviron Carbon, Feluy, Belgium), a carbon type often applied in waterworks. To test the removability of artificial sweeteners from running water, a rapid small-scale filter column test, developed by Marcus (2005) and optimized by Happel et al. (2009), was used to assess the adsorbability of sweeteners. Substances were tested using i) a single compound solution with a sweetener concentration of 500 µg/L and ii) a mixture of the four sweeteners each with a concentration of 125 µg/L. To suppress biological activity, 100 mg/L sodium azide were added. The column feed concentrations reflect a compromise between realistic environmental concentrations and the applicability as a rapid laboratory test system. Substances are considered to be relevant for drinking water, if up to the point of 15,000 bed volumes treated (BVT), *i.e.* 30 m³/kg, a breakthrough of more than 10 % of the feed concentration occurs. With a flow rate of

8 mL/min the test can provide information about the general removability of a contaminant by GAC within one week.

Chlorination

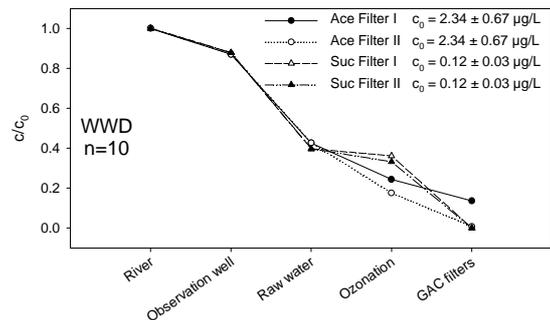
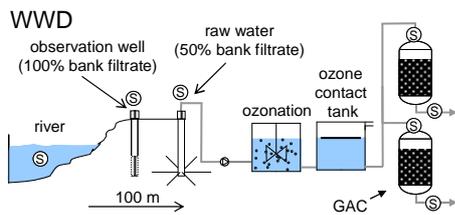
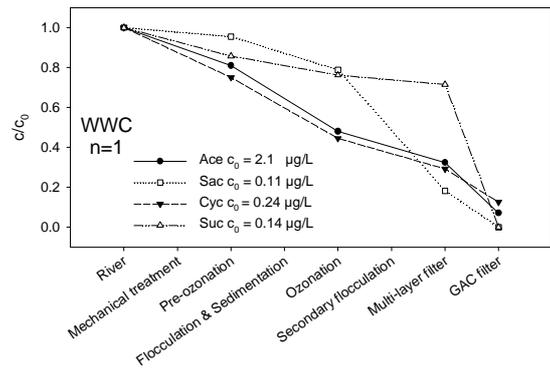
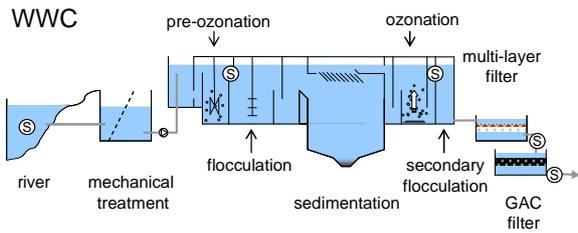
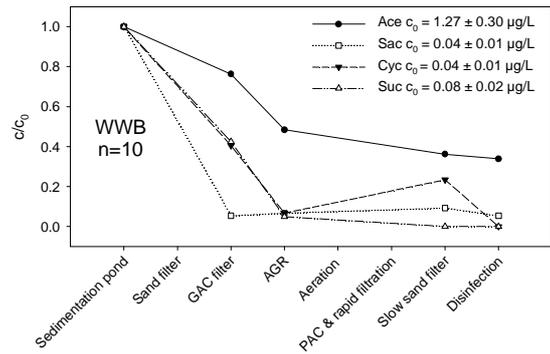
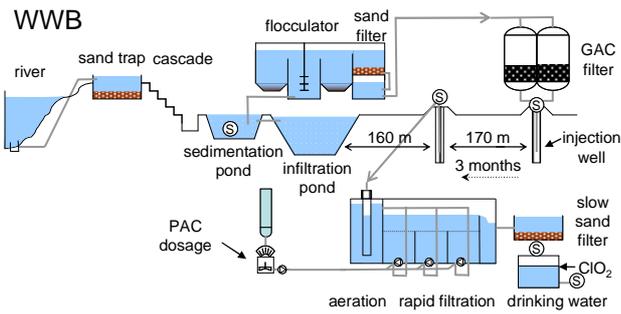
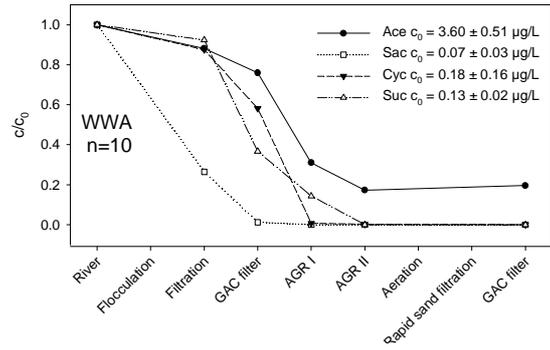
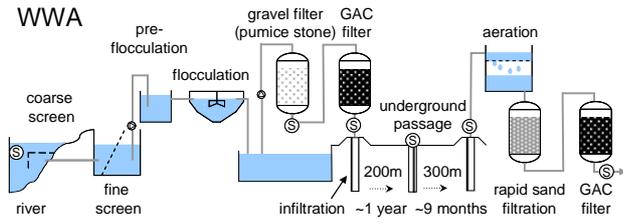
The behavior of artificial sweeteners during chlorination, a method which is frequently used for drinking water disinfection, was determined in a laboratory batch test using drinking water (pH 7) spiked at a level of 1 µg/L of artificial sweeteners. Free chlorine was added at two different levels of 0.2 and 1 mg/L by addition of a commercially available aqueous hypochlorite solution. Prior to use, the concentrations of HOCl stock solutions were determined photometrically after reaction with (N,N-diethyl-p-phenyldiamine, DPD). Samples (100 mL) were taken after contact times of 0.17, 2, 4, 8, 24, and 48 h and residual chlorine was reduced by 50 mg sodium thiosulfate.

4.2.2 Sampling sites and protocols

In order to clarify the behavior of artificial sweeteners under waterworks (WW) conditions, six facilities were sampled up to ten times between August and December 2009. These facilities are briefly described below (Figure 4-1).

Waterworks A (WWA)

The facilities of WWA were mainly set up for groundwater recharge with treated water of the Main river and subsequent treatment of the recovered groundwater for drinking water production. The river water is purified by coarse and fine screens, flocculation, and filtration over a gravel filter and GAC. All eight GAC filters have a diameter of 3 m and were filled with activated carbon to a height of 3 m. The filter velocity was about 10 m/h. Every six months the GAC of four out of eight filters is regenerated when a mean load of approximately 60 m³/kg is reached. The infiltrated water passes a sandy soil layer zone of 500 m horizontal distance and 20 m of vertical distance and is recovered 16 to 24 months (usually about 21 months) after infiltration as a mixture of up to 70 % of infiltrate and 30 % of local groundwater. The recovered raw water is again treated by aeration, rapid sand filtration and an activated carbon filter unit. Sampling points at WWA within the surface water treatment facility were the raw water, the effluents of the gravel filter and the activated carbon filter. Within the groundwater treatment facility, an observation well half way to the recovery well and the recovered raw water before and after its repeated treatment with activated carbon were sampled. Samples were taken weekly over a ten week period (n=10).



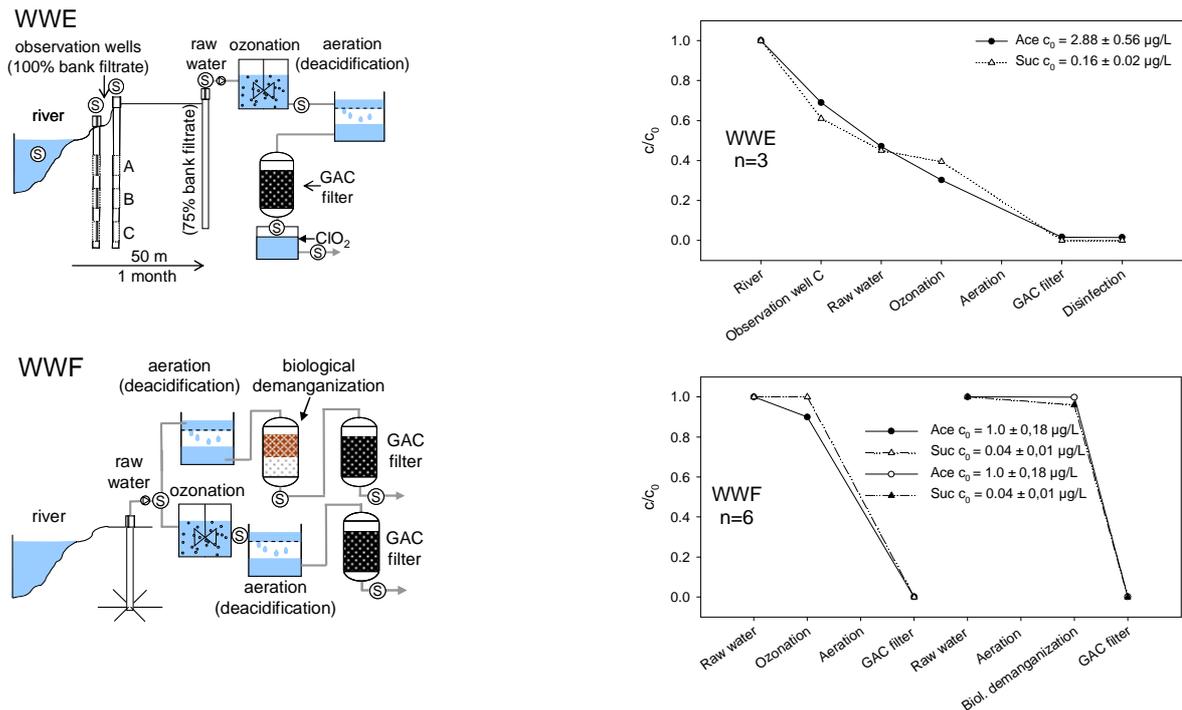


Figure 4-1 Schemes of the investigated water treatment plants and changes in artificial sweeteners concentrations (mean values) along the treatment train; "S" in circle denotes the location of the sampling sites. Ace denotes acesulfame, Sac saccharin, Cyc cyclamate, and Suc sucralose; Standard deviations (STD) of c/c_0 for Ace and Suc were: ≤ 0.12 , and ≤ 0.11 in WWA, WWB, and WWD ($n = 10$), ≤ 0.20 and ≤ 0.19 in WWE ($n = 3$) and ≤ 0.22 and ≤ 0.27 in WWF ($n = 6$), respectively. Sac and Cyc concentrations were low and could only be followed along the treatment in WWA and WWB. Here, STD for Sac and Cyc were ≤ 0.23 , except for three individual sampling points, where Cyc concentration in the raw water fluctuated by a factor of >10 , resulting in a STD of $c/c_0 \leq 0.55$ in WWA (sampling points: filtration, GAC) or was detected only in twice during ten samplings (STD ≤ 0.63 in WWB (sampling point: slow sand filter)

Waterworks B (WWB)

Similar to WWA, WWB consists of the pre-treatment of surface water from the Rhine river prior to infiltration and the final treatment of recovered groundwater. First, the river water passes a sand trap with a flow velocity of 0.3 m/s. Subsequently, the water flows over a cascade in order to increase the oxygen level and to remove volatile organic compounds. The aerated water is stored in sedimentation and infiltration ponds, where a part of it percolates through the ponds' bottom into the subsurface. Most of the water in the sedimentation ponds is pumped to the first treatment facility, which consists of flocculation, sand filtration, and GAC filters. The effluent from the GAC filters is used for the artificial recharge of groundwater. The infiltrated water has a residence time of three months in the aquifer, where it is mixed with local groundwater (20-30 %) and percolating water from the infiltration pond (10-20 %). In the second treatment facility the recovered groundwater is first aerated and then

treated with powdered activated carbon (PAC, 12 g/m³), combined with a refiltration flocculation process. A subsequent sand filter is operated with a filtration velocity of 0.2-0.3 m/h. The last treatment step is disinfection with chlorine dioxide (0.15 mg/L). Sampling points were the river water, the purified surface water prior to infiltration, the recovered water, the effluent of PAC-treatment, and the finished water. Samples were taken weekly (n=10).

Waterworks C (WWC)

WWC represents a wide range of different treatment steps applied in drinking water production without any intermediary artificial groundwater recharge and recovery. First, water from the Rhine river is treated mechanically with different screens before pre-ozonation is applied to improve the subsequent primary flocculation. The next treatment steps are sedimentation, main ozonation (residual concentration 0.3 mg/L), and secondary flocculation. In a multi-layer filter flocks are retained and the remaining ozone is removed. GAC filters complete the treatment before the water is used for surface irrigation and artificial groundwater recharge. Sampling points at WWC were the raw water and the effluents of pre-ozonation, two lines of the main ozonation, the multi layer filter as well as the combined effluent of all activated carbon filters. WWC was sampled three times, but only at the last campaign all above mentioned sampling points were included. Additionally, effluents of four different activated carbon filters were sampled in order to compare the effectiveness at different filter loadings at the last sampling campaign.

Waterworks D (WWD)

In WWD bank filtrate of the Rhine river is used as raw water. The investigated well is located 100 m away of the Rhine's right bank and horizontally screened at 18 m below ground. It yields a mixture of Rhine bank filtrate and landside groundwater (approximately 50 %). Measurements of redox sensitive parameters confirmed aerobic conditions. Sampling points at WWD were surface water, bank filtrate, and the influents (after ozonation) and corresponding effluents of two GAC filters, sampled weekly over a period of ten weeks (n=10). Both GAC filters differed in load and flux. After three of ten sampling campaigns an additional sampling point, unaffected by landside groundwater, was accomplished (n=7) to study the performance of river bank filtration.

Waterworks E (WWE)

WWE was sampled (n=3) in order to check the results from WWC and WWD with respect to the effectivity of ozonation. Additionally, it offered the opportunity to compare different residence times of bank filtrate at the same site. The facility consists of about 100 interconnected wells within a distance of 50 m to the bank of the Rhine. Water mainly infiltrates at the bottom of the river bed into a 10–12 m thick gravelly-sandy aquifer. At mean water level of the Rhine the retention time of the aerobic bank filtrate in the subsurface is about three to four weeks. Besides the Rhine water, two clusters of observation wells, situated between Rhine and the investigated production well, were sampled in three different depths. The approximate retention time to the particular sampling points is 60 d to the deepest observation well (C), 30 d to the second deepest (B), and 12 d to the observation well closest to the surface (A). There is no impact of landside groundwater on these sampling points. The next sampling point was the production well, which typically yields a mixture of 70–75 % of mixed bank filtrate of different retention times and 25–30 % of groundwater. Depending strongly on the surface water level, the proportion of groundwater is highly variable. Raw water is treated with 0.3-0.6 mg/L ozone in a contact tank for six minutes. On its way to the following aeration and subsequent GAC filters oxidation continues for more than 30 min. Additional sampling points were the effluents of two 50 m³ activated carbon filters and the water after disinfection with chlorine dioxide (50-60 µg/L).

Waterworks F (WWF)

WWF also uses bank filtrate from the Rhine river. Here, the investigation focused on the comparison of different treatment technologies. A part of the bank filtrate is treated by ozonation (0.15 mg/L ozone), followed by deacidification and finally by GAC filtration. Alternatively, and in order to abstain from the use of ozone, in WWF an additional synchronized pilot plant line exists, where biological manganese removal and GAC filtration are the only treatment steps after deacidification. Manganese removal is achieved in a two-layer filter filled with filter coal and filter quartz to a height of 1.5 m and operated at a velocity of 9 m/h. The GAC filters are 2.5 m in height and filled with reactivated GAC F 300. Samples for both treatment options were taken every two weeks over a period of ten weeks (n=5). Bank filtrate, effluents of the ozonation and demanganization step, and the GAC filters were sampled.

4.3 Results

4.3.1 Laboratory-scale experiments

Fixed-bed bioreactor

Saccharin and cyclamate were completely microbially degraded in the fixed-bed bioreactor after 20 and 15 days, respectively (Figure 4-2). After a lag-phase of about one week, the degradation rapidly proceeded, likely due to the adaption of microorganisms to the source of nutrition. In contrast, acesulfame and sucralose were not biodegraded even after a prolonged test time of 92 days. The results are in accordance with the reported behavior of artificial sweeteners in wastewater treatment plants (Buerge et al., 2009, Scheurer et al., 2009), even if the aerobic fixed-bed bioreactor experiment is not primarily a model for biodegradation under wastewater treatment conditions, but rather for biodegradation during river bank filtration.

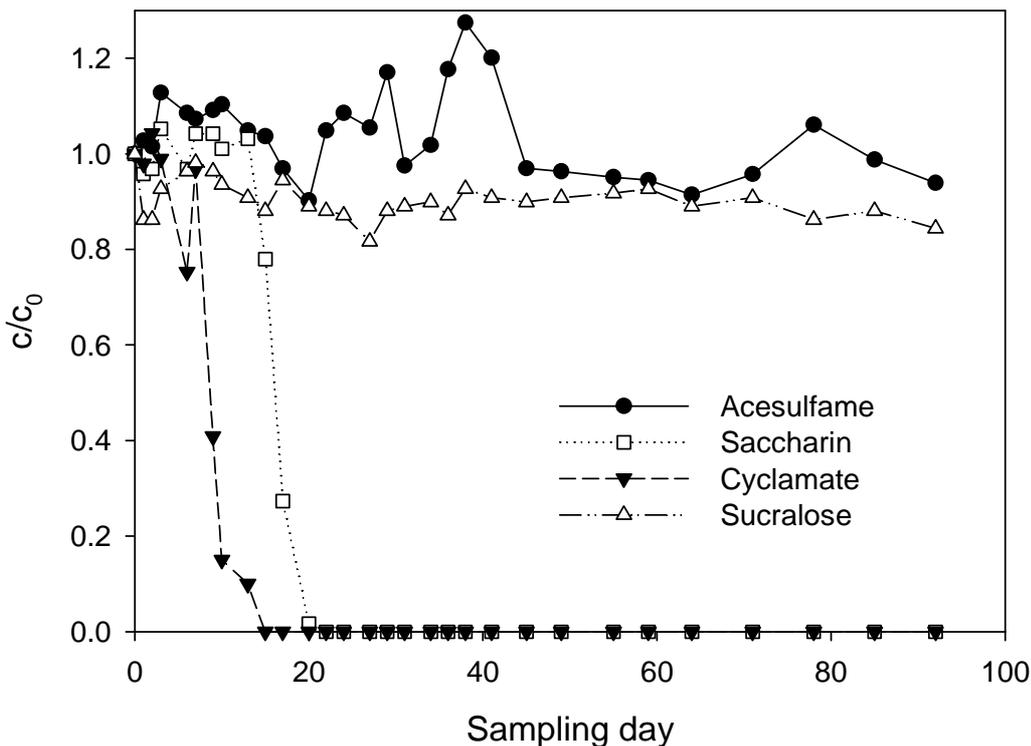


Figure 4-2 Behavior of artificial sweeteners in a fixed-bed bioreactor simulating aerobic river bank filtration. After day 40 the mass-labeled internal standard (IS) acesulfame-d₄ was used to quantify acesulfame. Variations of the acesulfame concentration after that date are mainly due to variations of the test and not due to analytical errors, which were compensated by the IS

Flocculation

Laboratory-scale jar test flocculation experiments with river and tap water and different concentrations of AlCl_3 and FeCl_3 resulted in insignificant elimination of AS from the aqueous phase. After flocculation, AS recoveries were between 79 and 117 % of the spiked concentration. AS background levels in the river water used were subtracted. Although flocculation can remove other dissolved organic contaminants, the results are not surprising, as the removal mechanism is based on precipitation of the compounds or on sorption onto precipitates. Due to high water solubility and low sorption tendency of artificial sweeteners both removal mechanisms are not likely to occur. Log K_{OW} values for AS are scarce, and comprise a range of -1.8 to 0,3 (values from (Jenner and Smithson, 1989; Grice and Goldsmith, 2000), and calculated by ChemAxon, 2010). For comparison, the log K_{OW} of bentazone, a polar herbicidal active ingredient in plant protection products with some structural similarity to the sulfonamido type sweeteners, is -0.46 (EU, 2000b). Like the AS investigated bentazone also has a low sorption tendency (Delle Site, 2000 and references therein). For a graphical presentation of the obtained results see supporting material (Figure 4-5).

Ozonation

Acesulfame was the AS which was oxidized most readily. Its half life was approximately 15 min (Figure 4-3) at an ozone concentration of 0.5 mg/L.

After a contact time of 30–40 min, which is typical for waterworks practice, a residual concentration of ca. 30 % of the initial acesulfame still remained in the test solution. This is in good correlation to the results obtained for WWD (see 4.3.2). For short contact times cyclamate concentration decreased similar to the acesulfame concentration, but the residual concentration of cyclamate after 60 min was more than twice as high. Higher initial ozone concentrations resulted in a faster removal and lower residual concentration of both AS, but usually waterworks avoid ozone doses such high as 5 mg/L, the highest ozone level in these lab experiments. For saccharin and sucralose no significant concentration decrease was observed at an ozone concentration of 0.5 mg/L. This was also true when doubling the applied ozone concentration. Only with 5 mg/L ozone a depletion of about 20 % for saccharin and 30 % for sucralose was achieved.

The results indicate that sucralose and acesulfame are likely to be found in waterworks after ozone treatment, however, for different reasons: sucralose, because it is quite persistent against ozone attack and acesulfame, because it is present in relatively high concentration in

the raw waters and, in addition, is incompletely degraded at typical ozone doses and contact times applied in waterworks.

The reaction of acesulfame with excess ozone followed pseudo first-order kinetics: $c(t) = c_0 * e^{-kt}$; t: time; c(t):concentration at time t; k: rate constant . The coefficients of determination were $R^2 > 0.96$ (Figure 4-6, Table 4-2). At the highest ozone level of 5 mg/L, *i.e.* a molar ratio of ozone:acesulfame of approximately 17,000:1, the reaction was fastest with a rate constant of $9.7 * 10^{-3}$ 1/s, which decreased to $2.6 * 10^{-3}$ 1/s, $1.3 * 10^{-3}$ 1/s and $5.5 * 10^{-4}$ 1/s at 2, 1 and 0.5 mg/L, respectively.

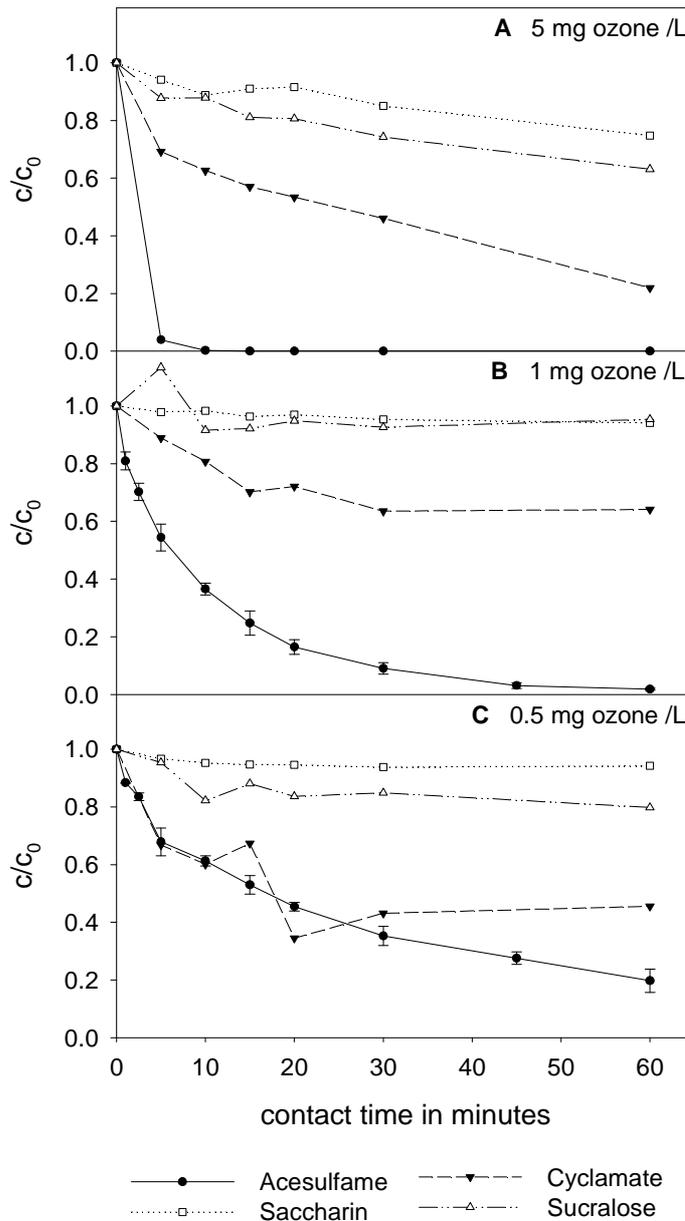


Figure 4-3 Degradation of artificial sweeteners in spiked drinking water treated with different ozone doses. Error bars for acesulfame indicate standard deviations (n=3; for 2.5, 5, and 45 min n=2)

Activated carbon small-scale filter test

A preliminary test with a mixture of all four AS gave a first impression of the suitability of GAC filtration in waterworks for the removal of AS (for graphical presentation see supplementary material, Figure 4-7). Cyclamate was only little retarded in the filter and a 10 % breakthrough occurred already after one day. Acesulfame and sucralose also crossed the 10 % line within 15,000 BVT, i.e. between day two and three. However, whereas for acesulfame and cyclamate a complete breakthrough was observed after about one week, sucralose was still retained by about 50 % after a prolonged runtime of more than 50,000 BVT. All these three sweeteners can be classified as relevant for drinking water in this preliminary test. Saccharin was retained slightly better than sucralose and, therefore, was the only sweetener with no drinking water relevance, based on the above definition. In batch tests with single AS solutions (Figure 4-4) the results of the preliminary test with the AS mixture were confirmed for every sweetener. The results indicate a breakthrough characteristic of cyclamate comparable to diatrizoic acid, an X-ray contrast medium, which is known to have almost no retention in the small-scale filter test and also in full-scale GAC filters in waterworks (Seitz et al., 2006). Saccharin could still be classified as "not relevant to drinking water", but after 30,000 BVT showed a higher breakthrough than in the multi-sweeteners batch experiments. A possible explanation is that sites on the activated carbon suited for saccharin adsorption are limited but still available at the low saccharin concentration of 125 µg/L in the multi-sweeteners batch test. For all AS, data from full-scale plants should be taken into consideration to clarify their behavior under practical conditions, as kinetics and loadings of full-scale filters can vary within a wide range. This is especially true for sucralose, which showed an early but low breakthrough combined with a good retention over weeks in the batch test.

Chlorination

AS were not transformed in chlorination experiments with spiked tap water. Recoveries of the compounds were in a narrow range from 91 to 107 % for all applied contact times and excess chlorine was still present at 1 mg/L Cl₂. The persistence of AS against chlorination was also proved in waterworks (see 4.3.2). For a graphical presentation of the obtained chlorination results see supporting material (Figure 4-8).

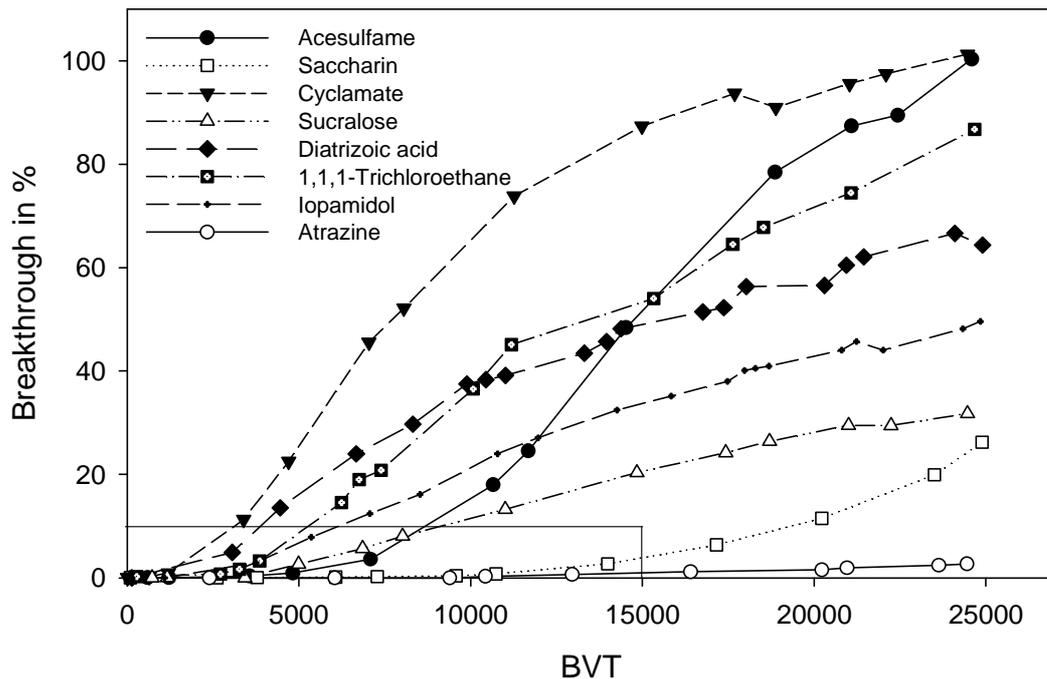


Figure 4-4 Breakthrough behavior of selected organic trace contaminants in an activated carbon small scale filter. Considering treatment with activated carbon filters, compounds are classified as relevant to drinking water, if a 10 % breakthrough occurs within 15,000 BVT (definition and data of diatrizoic acid, 1,1,1-trichloroethane, iopamidol, and atrazine from Marcus (2005))

4.3.2 Field studies

Waterworks A

The elimination of acesulfame and sucralose in the filtration unit of WWA was negligible and might be attributed to non-corresponding sampling and analytical uncertainties (Figure 4-1, WWA). For saccharin the first steps in WWA contributed to the overall elimination (74 % removal), most likely due to microbial activity in the gravel filter. Although the subsequent GAC filter was preloaded at 30–60 m³/kg, it was still effective for the removal of saccharin and sucralose. Saccharin was not detected in the filter effluent and sucralose was retained by more than 60 %. As observed in the batch experiments, acesulfame and cyclamate removal by GAC was limited. As the upper layers of the GAC filters were biological active, cyclamate removal can be understood as the combined effect of biological degradation and adsorption onto GAC. The decrease in the concentration of acesulfame (59 %) and sucralose (61 %) from the infiltration point to the observation well was almost identical for both compounds. Despite the fact that both AS proved to be persistent against microbial degradation in the fixed bed bioreactor experiments and adsorption onto soil should be limited based on their polar nature,

this effect cannot be attributed solely to dilution with landside groundwater, because, according to information of the plant operator, there is almost 100 % infiltration water at this well. Final conclusions for this concentration decrease cannot be drawn, yet because the sampling period of about two months is quite short compared to the residence time of up to two years. Changes in raw water concentrations and/or treatment efficiency of the surface water could be possible explanations. Microbial degradation over such a long underground passage cannot be excluded, although no case of biodegradation of acesulfame has been reported yet. Additional dilution occurred on the way to the recovery well, but a comparison between the further behavior of these two AS was not possible, because sucralose concentrations dropped below the LOD. Acesulfame was the only sweetener detected in the recovered ground water. The GAC in the groundwater facility had a runtime of about four years and was not capable of retaining any acesulfame. In every sampling campaign even slightly higher concentrations in the GAC filter effluent were observed. Accumulation of acesulfame in the past and subsequent elution during the observation period (chromatographic effect), as known also from other trace pollutants, is the most likely explanation for the concentration increase in the filter effluent.

Waterworks B

Three artificial sweeteners were already eliminated by 60–100 % on their way from the river water to the effluent of the GAC filters (Figure 4-1, WWB). For saccharin and cyclamate the elimination was probably due to microbial degradation in the biological active parts of the facility, *i.e.* the sand trap and the sedimentation pond. As proven in the small-scale filter test, cyclamate should not have been adsorbed in the activated carbon filters to a great extent. No conclusion can be drawn, if traces of saccharin were eliminated in the GAC filters of this treatment train, as no sampling point at the influent of the filters was established. However, sampling in other waterworks (see results for WWC) and laboratory experiments proved that GAC had contributed to the elimination of saccharin. For the low biodegradable sucralose adsorption to GAC seemed to be the main elimination process here. Trace concentrations of cyclamate and sucralose were below LOD after recovering the infiltrated water. This can be attributed to dilution and in the case of cyclamate to further microbial degradation. Acesulfame was the most persistent sweetener and could be detected at a level of 34 % (highest value 0.46 µg/L) of the surface water concentration in the finished drinking water. After the GAC filters this compound was removed by about 20 %. Further concentration decrease was achieved by dilution on the way to the recovery well. Taking into account a

known dilution with landside groundwater by 30 % and an impact of 10 % of the infiltration pond a theoretical concentration of 0.69 µg/L can be calculated for the recovered water. The measured mean value was 0.58±0.04 µg/L, which fits rather well to the expected value. The added PAC contributed by approximately 10 % to the overall removal of acesulfame, whereas the dosage of chlorine dioxide had almost no effect.

Waterworks C

In WWC due to a short contact time of 3 min, the pre-ozonation step had only a minor effect on the removal of AS (Figure 4-1, WWC). The AS most resistant to ozone was saccharin, which corresponds well with the ozonation batch experiments. The next sampling point in WWC summarizes the three treatment steps flocculation, sedimentation, and ozonation. Flocculation proved to have no effect on the removal of AS in batch tests, and thus, can be excluded to contribute to the overall elimination. Therefore, the subsequent main ozonation was the major barrier for acesulfame and cyclamate, whereas the oxidation of sucralose and saccharin was not very efficient again. Removal of saccharin can be attributed to microbial degradation in the multi-layer filter, while in this treatment step acesulfame and cyclamate were eliminated to a small proportion only. Sucralose was still detectable at a level of 71 % of the initial concentration after the multi-layer filter, but was completely eliminated in the subsequent GAC filter. GAC contributed by 17 to 25 % of the concentration initially present in the surface water to the removal of acesulfame, cyclamate and saccharin.

Acesulfame was the AS with the highest concentration of about 2 µg/L in the raw water. The entire treatment process removed this compound by about 90 %, but some acesulfame traces (0.15-0.20 µg/L) were still detectable in the finished water. When individual GAC filters were sampled separately, it became obvious, that some adsorbers could not retain this compound anymore due to a high filter load. In four different filters tested, the removal rates for acesulfame ranged from 100 to 43 %, corresponding with filter loads between 7 m³/kg and 127 m³/kg (Figure 4-9). Remaining traces of cyclamate in WWC, the only waterworks without any underground passage, emphasize the importance of a prolonged residence time in a biological active environment in order to remove this AS.

Waterworks D

WWD represents a waterworks, which uses bank filtrate derived from the Rhine river. As the raw water is a mixture of Rhine river bank filtrate and landside groundwater, an additional observation well was sampled, which delivers pure bank filtrate (Figure 4-1, WWD). Bank

filtration proved to be very effective for the removal of saccharin and cyclamate, which were not detected above the LOD in any bank filtrate or raw water sample in WWD. Concentrations of these two sweeteners in the river water were $0.05 \pm 0.03 \mu\text{g/L}$ and $0.10 \pm 0.14 \mu\text{g/L}$, respectively. High standard deviations are due to extremely high concentrations in the last sampling campaign. This phenomenon results from low water levels in the Rhine river and coincidentally heavy rainfalls, which were responsible for the discharge of untreated wastewater in the river. Acesulfame and sucralose concentrations continuously increased during the sampling campaign. Therefore, removal efficiencies of bank filtration were determined from median values (in contrast to Figure 4-1, where mean values are depicted). Recoveries of 102 % and 95 % were calculated for these two persistent AS in the observation well and of 40 % and 41 % in the raw water. These recoveries are largely consistent with the known proportion of bank filtrate in the observation well (100 %) and in the raw water (approximately 50 %), estimated based on historical water quality data.

On its way to the two activated carbon filters the water had different ozone contact times (ozone concentration 0.4 mg/L). The influent of filter I had a contact time of 18 min, filter II of 31 min, resulting in a significantly higher reduction of acesulfame concentration in filter II. This effect was observed in every series of samples and reduced the raw water concentration of acesulfame ($0.95 \pm 0.09 \mu\text{g/L}$) by 44 % ($0.53 \pm 0.10 \mu\text{g/L}$) in the influent of filter I and by 60 % ($0.38 \pm 0.08 \mu\text{g/L}$) in influent of filter II, respectively. The results correlate well with the results obtained in the batch experiments, where a comparable ozone concentration (0.5 mg/L) led to an elimination of acesulfame of 47 % after 15 min and 65 % after 30 min contact time. Sucralose was more refractory against ozone attack, as already found in the batch experiments. Furthermore, the effect of different ozone contact times was less pronounced and not significant for this compound.

The subsequent granular activated carbon filters were differently loaded ($56 \text{ m}^3/\text{kg}$ for filter I and $10 \text{ m}^3/\text{kg}$ for filter II, respectively after 9 of 10 sampling series), but both were still adequate to remove remaining traces of sucralose to concentrations <LOD. However, for acesulfame a decrease of the filter performance over the sampling period of ten weeks was observed for filter I, resulting in an elimination of only approximately 30 % at the last sampling. In the effluent of filter II only traces between 0.01 and $0.03 \mu\text{g/L}$ were observed. These findings suggest that fresh to moderately loaded GAC is an excellent option for the removal of remaining traces of acesulfame after ozonation. However, economic aspects have to be considered, too, before a decision on the frequency of GAC exchange can be made.

Waterworks E

Saccharin and cyclamate were present in every Rhine river water sample at concentrations between 0.03 and 0.18 $\mu\text{g/L}$. Nevertheless, these compounds were found neither in one of the bank filtrate samples from the observation wells, even after the shortest retention time of 12 days at observation well A, nor in the raw water from the production wells (Figure 4-1, WWE).

In contrast to all other investigated waterworks, in WWE apparently lower recoveries than 100 % were found for acesulfame (69 %) and sucralose (61 %) at the observation wells, which supply 100 % bank filtrate. However, this was due to non-corresponding samples and the high variability of the AS concentrations in the river (e.g. acesulfame concentration: $2.88 \pm 0.56 \mu\text{g/L}$) during the observation period. Nevertheless, the recalcitrant nature of these two AS is reflected by the nearly identical concentration decrease of about 32 % for acesulfame and 26 % for sucralose due to dilution from observation well C to the raw water wells, which parallels the observations in WWD.

As in WWC, WWD, and the batch test, acesulfame proved to react more readily with ozone than sucralose. The elimination of both compounds in two different GAC filters was excellent. No sucralose and only traces of acesulfame could be detected in the GAC filter effluents. A subsequent disinfection with chlorine dioxide was not capable of removing residual acesulfame: Therefore, at every sampling date acesulfame was detected in the finished water at concentrations up to 0.05 $\mu\text{g/L}$.

Waterworks F

Cyclamate and saccharin were not detected in the raw water as they were already removed during river bank filtration. The occurrence of acesulfame and sucralose in every raw water sample emphasizes their mobility and persistence. As observed in batch experiments, sucralose was more resistant to ozonation than acesulfame (Figure 4-1, WWF). Due to low ozone concentrations in WWF (0.15 mg/L) the elimination was incomplete (18 % elimination for acesulfame and 9 % for sucralose). The two-layer filter in the pilot plant did not contribute to the elimination of acesulfame and sucralose. However, both AS were removed by the GAC filters in both facilities. These filters were preloaded with about 13 m^3/kg and this load was similar to the load of filter II in WWD (10 m^3/kg after 9 samplings), which also effectively removed acesulfame and sucralose. WWF replaces its GAC at a load of about 30 m^3/kg , which represents a value between the two filter loads in WWD, where the filter loaded at 56 m^3/kg could not retain acesulfame completely anymore.

4.4 Discussion

Saccharin and cyclamate were removed by 100 % in waterworks using bank filtration or artificial groundwater recharge as one of their treatment steps in the multi-barrier system, even at rather short retention times of 12 days as in the case of observation well A at WWE. An aerobic laboratory degradation experiment yielded similar results, with complete removal of cyclamate and saccharin within 13 and 22 days, respectively. Biological active filters in the waterworks were capable of retaining 12–34 % of the cyclamate input and 74–77 % of saccharin. The good biodegradability of these two compounds was already reported for wastewater treatment plants (Buerge et al., 2009; Scheurer et al., 2009) and was thus confirmed by the present study for biological less active compartments like river bank filtration systems and biological active filters in waterworks. However, the biodegradation products of saccharin and cyclamate are still unknown. Therefore, no conclusions can be drawn, if those metabolites are also removed in drinking water treatment facilities.

Ozonation was applicable to a limited extend only to remove traces of both compounds from the raw water, but due to the effective removal at waterworks with bank filtration or artificial groundwater recharge, ozonation had to be studied in laboratory experiments. There, only <10 % of saccharin and 30 to 50 % of cyclamate was transformed within 30 min, requiring ozone concentrations of 5 mg/L.

GAC filters retained 100 % of saccharine and 23 % of cyclamate input at WWA. Consistently, the activated carbon small scale filter test revealed a behavior of cyclamate similar to diatrizoic acid and of saccharin similar to atrazine, but with an earlier breakthrough. However, in GAC filters with prolonged runtimes it is even likely that especially cyclamate is removed due to microbial degradation. As the initial concentrations in the raw waters are relatively low, only traces of both compounds are likely to be found in the finished water, even if treatment in a certain waterworks does not comprise an underground passage. For risk assessment purposes, the identification of oxidation products of cyclamate is of certain interest, as the compound occurs in higher concentrations than saccharin in the raw water and is less recalcitrant during ozone treatment.

Ozonation proved to be very effective for the removal of acesulfame. The compound was detected in the surface or raw waters in concentrations one order of magnitude higher than for all other investigated AS. Thus, the identification of ozonation products should be given high priority to clarify their removability during drinking water treatment and to assess potential health risks. The degradation of acesulfame and the other AS during ozonation is a function of the applied ozone concentration and contact time. This was proven in batch tests and also in

waterworks, where the acesulfame concentrations were very susceptible to small changes in ozone contact times. In the waterworks investigated in this study ozonation incompletely removed acesulfame by 18–60 % due to insufficient ozone doses, but this treatment step contributed to a great extent to the overall elimination.

It is remarkable, that the structurally related sweeteners acesulfame and saccharin, both with a sulfonamide moiety in the ring structure, behaved completely different during the treatment with ozone. As ozonation products of AS are still unknown, it is also unclear what moiety of the molecule would represent the point of ozone attack. For comparison, bentazone a widely used active ingredient of herbicides, which has a structure similar to both sweeteners (phenyl ring plus sulfonamide unit in the ring structure) is very persistent against microbial degradation (Gonzalez et al., 2006) and is removed very well by ozone treatment (Fobbe et al. 2006; Bozkaya-Schrotter et al., 2008). The presence or absence of alkyl side chains play an important role in the reaction of these sulfonamides with ozone. For comparison, in photolysis experiments with bentazone (Peschka et al., 2007), the isopropyl moiety was hydroxylated and also oxidation and subsequent ring cleavage occurred. Similar reaction could be expected for acesulfame with a methyl side chain.

The removal of acesulfame by GAC filters was strongly dependent upon the filter load (compare Figure 4-4, Figure 4-7, and Figure 4-9). Activated carbon provided a very effective tool, as long as the loads were below about 30 m³/kg, which is the limit of an economic use of activated carbon in order to remove single organic compounds in waterworks (Haist-Gulde et al. 1998). As a result, acesulfame was detected up to 0.76 µg/L in effluents of GAC filters, where short or no ozone treatment coincided with high filter loadings. As subsequent disinfection did not contribute to the acesulfame removal, similar concentrations were found in the finished water. Assuming a concentration of 1 µg/L acesulfame (potassium salt) in drinking water, a consumption of 2 L/d, and a body weight of 70 kg, a person would exceed the acceptable daily intake (ADI) of 630 mg/d (EU, 2000a) not until 863 years.

Conclusions of recent publications (Buerge et al., 2009; Scheurer et al., 2009), that acesulfame can be used as a tracer for anthropogenic contaminations, are confirmed by the present study, as its concentrations were only reduced by dilution during aerobic river bank filtration. Additionally, first measurements from anaerobic bank filtration sites at the Sawa river indicate that acesulfame is not degraded at anaerobic sites as well (data not shown). Therefore, this compound represents a new tool in drinking water production to predict the proportion of bank filtrate and landside groundwater in raw water of waterworks and to identify unknown sewer leakages.

The same seems to be true for sucralose, which was also very persistent during bank filtration and an aerobic degradation experiment. It also showed concentration decreases by dilution always in the same range as acesulfame. Brorström-Lundén et al., (2008) reported no significant accumulation for sucralose in sewage sludge, but detailed sorption studies of all AS are still missing. Even though sorption ought to play a minor role for the removal of AS in wastewater treatment or environmental systems, this gap of knowledge should be filled. Two consecutive studies by Labare and Alexander (1993 and 1994) proved that sucralose is not biologically inert, but is degraded in highly variable rates in soils and lake water. These results also have to be confirmed in future research to exclude that its tracer function can only be applied under certain environmental conditions. In waterworks sucralose was more persistent than acesulfame during ozonation, but was well removed in subsequent GAC filters even on activated carbon with higher loads. First comparative analyses of wastewaters from different countries (*e.g.* United States, Israel, Australia; data not presented here) revealed sucralose to still play a minor role among the sweeteners used in foodstuffs, pharmaceuticals and personal care products in Germany, yet. Higher consumption volumes, like in the above-mentioned countries, would cause higher raw water concentrations of this AS in waterworks using bank filtrate. As sucralose proved to be persistent during ozonation (removal of 8–15 % in waterworks and <20 % after 30 min in the batch test), higher influent concentrations in subsequent GAC filters would lead to an earlier detection in the finished drinking water.

In summary, the removal efficiency of single treatment steps applied in multi-barrier drinking water treatment plants can be classified as displayed in Table 4-1. The chance that sweeteners end up in finished drinking water is most likely for acesulfame but also possible for cyclamate and saccharin, when water treatment includes no underground passage.

Table 4-1 Removal efficiency of single treatment steps in multi-barrier drinking water treatment plants for the elimination of artificial sweeteners. + = good, 0 = moderate (also depending on boundary conditions, such as ozone concentration, load of GAC filters, etc.), – = poor

	Acesulfame	Saccharin	Cyclamate	Sucralose
Bank filtration	–	+	+	–
Flocculation	–	–	–	–
Ozonation	0/+	–	0	–
Activated carbon filtration	–/0	+	–	0/+
Chlorination	–	–	–	–

4.5 Conclusions

- The multi-barrier treatment system is effective for the removal of artificial sweeteners from raw water sources if certain boundary conditions are established.
- Saccharin and cyclamate are effectively removed in treatment steps with biological activity.
- Acesulfame and sucralose proved to be very recalcitrant against microbial degradation. Their role as possible tracers for wastewater contamination is confirmed by this study. However, detailed sorption studies are still lacking.
- Applied ozone doses and contact times in waterworks are not sufficient to entirely remove acesulfame, the sweetener with the highest concentrations, from the raw water. Subsequent activated carbon filters are an excellent option for its removal, provided the load is lower than approximately 30 m³/kg.
- Acesulfame was the only artificial sweetener detected in finished drinking water up to several hundred ng/L. Cyclamate was only detected in finished water in a waterworks without any underground passage, which uses the water only for artificial groundwater recharge and irrigation.
- For other countries, where the concentration of sucralose in wastewater is up to two orders of magnitude higher than in Germany, the effectiveness of single treatment steps in waterworks should be further investigated as the only effective treatment for the compound seems to be GAC.
- Priority of research on the field of artificial sweeteners should be given to the identification of unknown transformation products, such as microbial degradation products of saccharin and cyclamate and, in particular, to ozonation products of acesulfame, as this compound occurred in the highest concentrations in the influents of ozonation units and reacted most readily with ozone.

4.6 Acknowledgments

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4.7 Supplementary material

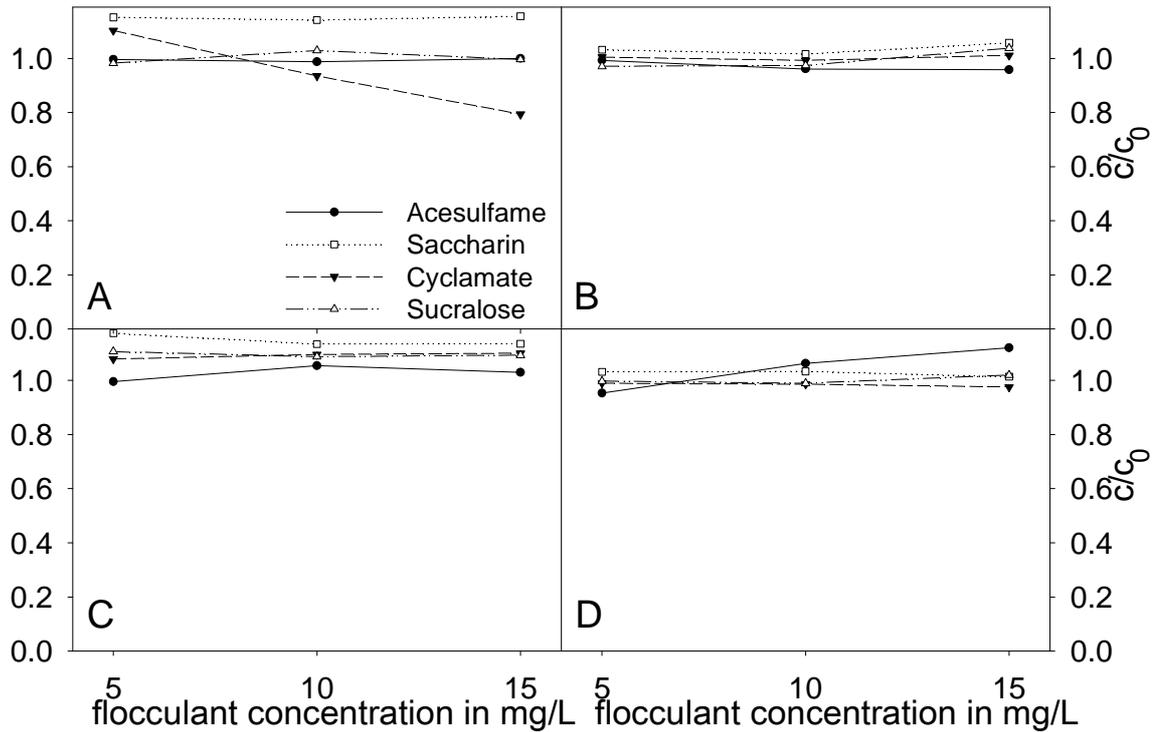


Figure 4-5 Behavior of artificial sweeteners in flocculation batch experiments with different doses of the respective flocculant. A: tap water with iron chloride (FeCl_3), B: river water with FeCl_3 , C: tap water with polyaluminum chloride (AlCl_3) and D: surface water with AlCl_3

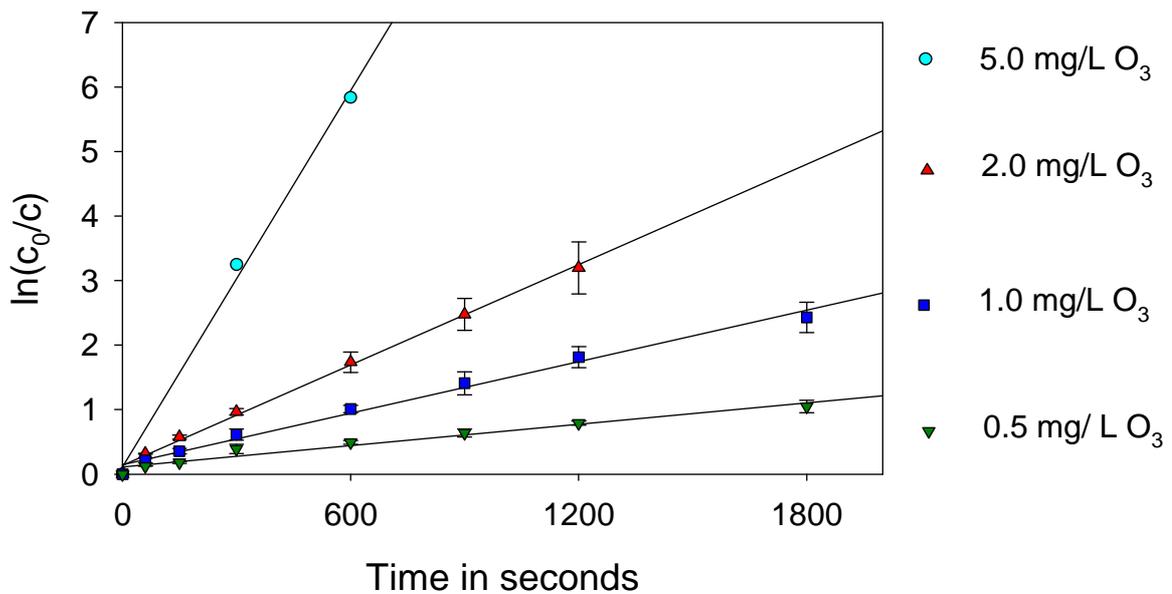


Figure 4-6 Pseudo-first order fit ($c(t) = c_0 \cdot e^{-kt}$ or transformed $\ln(c_0/c(t)) = k \cdot t$) for the reaction of acesulfame with excess ozone; t: time; c(t): concentration at time t; c_0 : initial concentration ($1 \mu\text{g/L}$) at $t = 0$, k: rate constant. For number of experiments (n), rate constants (k), coefficient of determination (R^2) see Table 4-2

Table 4-2 Rate constants (k) of the oxidation of acesulfame for different ozone doses applied and coefficient of determination (R^2) of the linear model used to fit pseudo first-order kinetics; n represent number of batch experiments

Initial ozone concentration (mg/L)	n (-)	k Acesulfame (1/s)	R^2 (-)
5.0	1	$9.7 \cdot 10^{-3}$	0.996
2.0	2	$2.6 \cdot 10^{-3}$	0.997
1.0	3	$1.3 \cdot 10^{-3}$	0.990
0.5	3	$5.5 \cdot 10^{-4}$	0.964

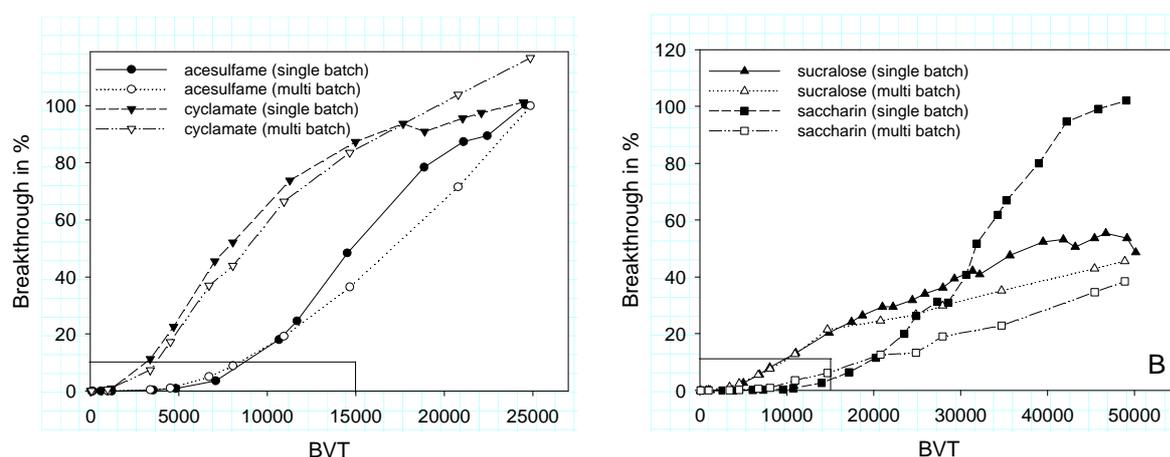


Figure 4-7 Breakthrough curves of acesulfame and cyclamate (A) as well as for sucralose and saccharin (B) in an activated carbon small-scale filter as a function of bed volumes treated (BVT). Spike amount in single batch experiments $500 \mu\text{g/L}$, in multi batch experiments $125 \mu\text{g/L}$ (four sweeteners included). Matrix: drinking water

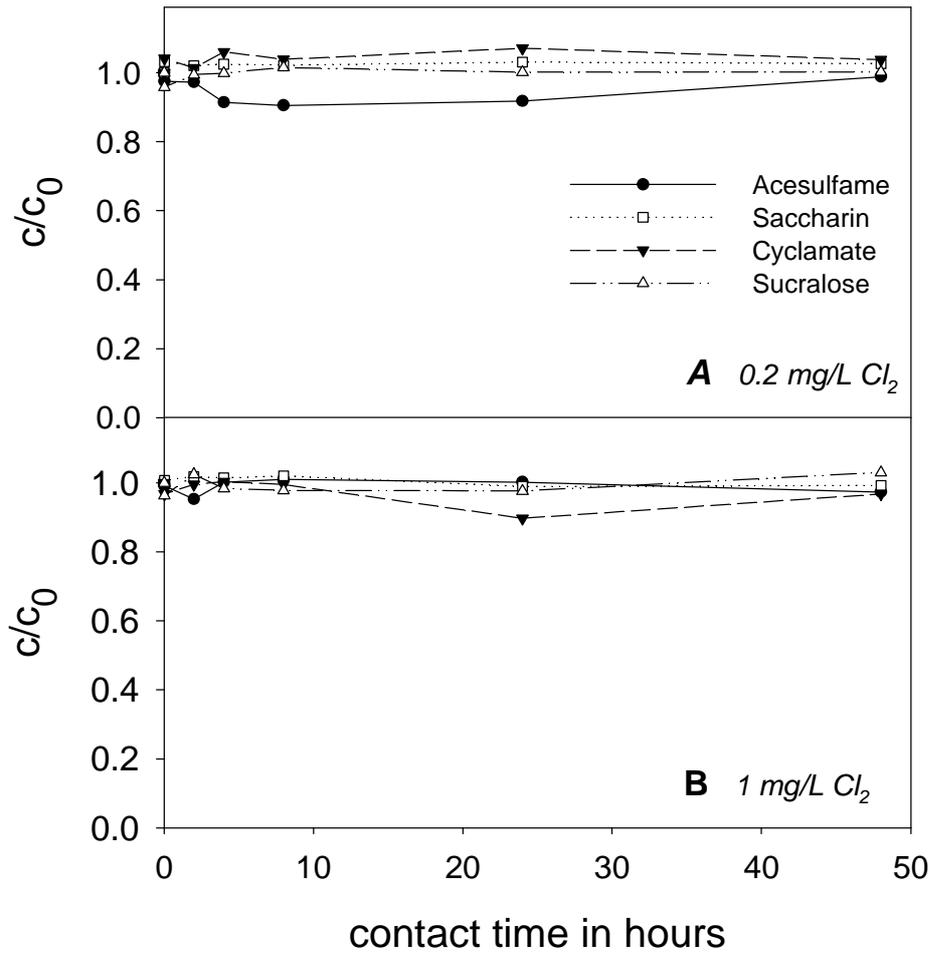


Figure 4-8 Behavior of artificial sweeteners during chlorination at two different chlorine doses in drinking water as function of time

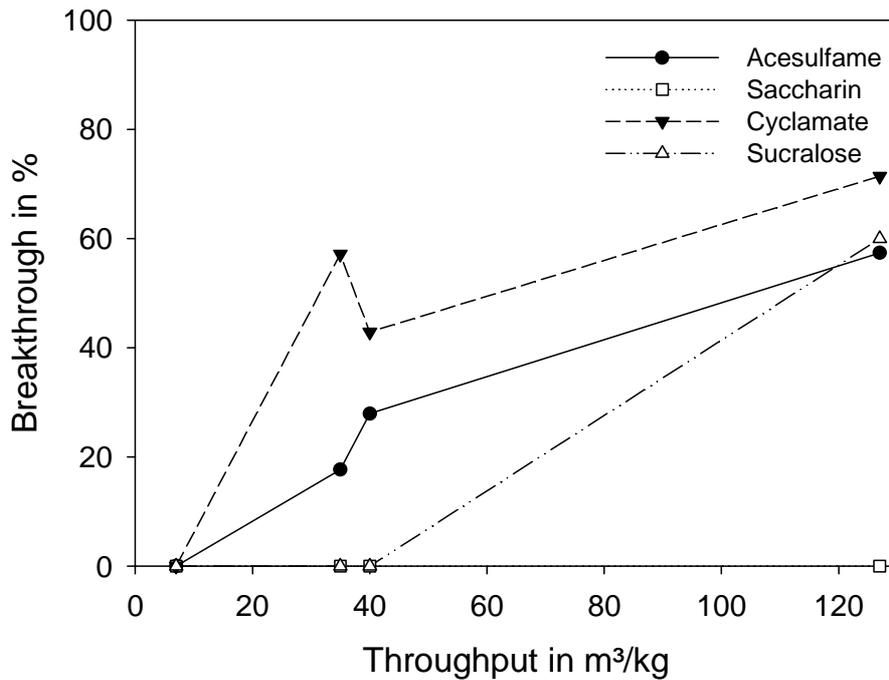


Figure 4-9 Breakthrough of artificial sweeteners through four GAC filters with different loadings in WWC

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