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Final conclusions and outlook

The original search for a reliable tracer compound for the indication of a wastewater impact in a SAT-field in Israel identified artificial sweeteners as emerging contaminants. The developed analytical method, based on LC-MS/MS, allows for the rapid and sensitive analysis of seven artificial sweeteners in aqueous environmental matrices, such as wastewater, surface water, groundwater, and drinking water. Accurate quantification could be achieved by the use of deuterated standards and appropriate sample dilution. The first application of this method demonstrated the ubiquitary occurrence of acesulfame, sucralose, saccharin, and cyclamate in German wastewaters and surface waters. Although all four sweeteners are mainly excreted unchanged by humans, their behavior in WWTPs is different. A very good biodegradability was observed for saccharin and cyclamate, but due to high influent concentrations they are still released into recipient waters with concentrations up to the µg/L range. The limited use of sucralose in consumer products in Germany constrains its relevance, although the compound showed a pronounced stability during wastewater treatment. However, in other countries sucralose is already the dominant sweetener with concentrations more than one order of magnitude higher than in Germany. Acesulfame is by far the most important sweetener of this study. The compound has high concentrations in wastewater and is practically not removed by secondary or even tertiary treatment by powdered activated carbon.

As a direct consequence of their stability and mobility only sucralose and acesulfame are relevant for drinking water treatment plants, whereas remaining traces of saccharin and cyclamate are effectively removed during river bank filtration (RBF). The multi-barrier treatment system is essential and only effective for the removal of sucralose and acesulfame from raw water sources if certain boundary conditions are met. For sucralose activated carbon filtration is very effective and no detectable traces can be expected in drinking water at this stage of usage in Germany. However, for other countries, where the concentrations of sucralose are much higher, the effectiveness of single treatment steps in waterworks should be further investigated as other treatment steps seem to be ineffective. Chemical treatment with ozone is more effective for acesulfame, but the applied ozone doses and contact times in waterworks are not sufficient for a complete oxidation of the compound. It was shown for the first time within this thesis that acesulfame is only removed by activated carbon with a low pre-load and that it can break through into finished drinking water. Concerns about the formation of undesired compounds during ozonation of acesulfame were allayed by the structural elucidation of acetic acid and dihydroxyacetyl sulfamate, a compound with an aldehyde hydrate moiety, as major oxidation products. In fact, the latter was detected in a full scale waterworks after the ozonation of river bank filtrate, but also effectively eliminated by activated carbon filtration, most likely by biological degradation in the filter.

The most important outcome of this thesis is the identification of acesulfame as an almost ideal tracer for contaminations of water sources by domestic wastewater. The usage of acesulfame implicates a high specificity to wastewater and its persistence and mobility enables the evaluation of a contamination in a quantitative manner. Based on an average concentration of about 20 µg/L in treated wastewater and on a limit of quantification of 10 ng/L the detection of only 0.05 % of wastewater derived water is possible. Contemplating all four sweeteners found in wastewater it might be even possible to use this compound class for the differentiation of untreated and treated sewage. Saccharin and cyclamate are short-lived when passing WWTPs and can therefore indicate an impact of untreated wastewater when they are detected in high concentrations comparable to the levels found in WWTP influents.

Further work is worthwhile for sucralose. The compound proved to be rather persistent during aerobic RBF but the concentrations decreased during extended residence time in the subsurface of the SAT field in Israel. As sucralose is used in much higher quantities in Israel compared to Germany, it was still detected in the µg/L-range even after a reduction of about 90 % of the initial concentrations and after almost two years in the subsurface. This fact should be studied carefully in future research as sucralose could be one of very few compounds providing information about the age of SAT treated wastewater depending on the degradation extend. By using acesulfame as a wastewater tracer it was possible to assess the purification power of the Israeli SAT process regarding organic trace pollutants. A very effective removal of a broad range of compound classes like pharmaceuticals, X-ray contrast agents, aromatic sulfonates, etc. was observed (Lange et al., 2011), whereas the acesulfame concentrations remained constant even after a residence time of more than one year in the subsurface.

The publication in chapter 2 and the contemporaneously published article of Buerge et al. (2009) were the first putting forward the research on artificial sweeteners in common and on sucralose and acesulfame in particular. They were followed by numerous other studies on artificial sweeteners in the environment during the last two years. Mead and co-workers (2009) presented the first data for sucralose for North America. Sucralose was found in two orders of magnitude higher concentrations in wastewater compared to Europe and was even detected in oceanic waters. The presence of sucralose was attributed to its persistence against bacterial decomposition in coastal environments and it was suggested as a potential tracer for anthropogenic activities and for the oceanic circulation. The presence in U.S. inland surface waters, its suitability as an anthropogenic marker and the ineffectiveness of advanced wastewater treatment techniques for the removal of sucralose was demonstrated in subsequent publications (Oppenheimer et al., 2011; Torres et al., 2011; Soh et al., 2011). The sucralose emissions for the Swedish city of Linköping were evaluated by Schmidt Neset et al. (2010). The authors proved that the removal of only one sucralose-sweetened product from the market (Coca Cola light) reduced the daily household emissions by more than 60 %. This has to be considered when using artificial sweeteners as anthropogenic markers and one should keep in mind that the wastewater load might also be a matter of the market launch or removal of sweetened products. In a wastewater plume in a Canadian aquifer acesulfame correlated positively with chloride, revealing its abundance and prediction power also for North America (Van Stempvoort et al., 2011). In Switzerland acesulfame was used to confirm the correlation of perfluoroalkyl acids in river water with the population living in the catchment area (Müller et al., 2011).

However, further work about artificial sweeteners is still needed to fill gaps concerning their behavior under different redox conditions and to identify possible degradation products. If acesulfame proves to be stable in any environmentally relevant redox environment, it could even indicate changing redox conditions, e.g. when concentration ratios with other persistent trace pollutants, which are degraded only anaerobically, are shifted. This is becoming apparent by first own measurements at anaerobic river bank filtration sites.

In the Israeli study area a pronounced decrease of the sucralose concentration was observed, but no degradation products are identified yet. Both, aerobic as well as anaerobic degradation, e.g. by dehalogenation, have to be taken into account in future research.

Although acesulfame concentrations correlated well with the levels of other conservative markers like CBZ and chloride, uncertainty studies about its prediction power are still missing. The wastewater specificity of acesulfame could be slightly lower compared to other organic trace pollutants due to its widespread usage and possible spills. Even a seasonal fluctuation seems possible. This should be evaluated in terms of the variability of WWTP effluent and background concentrations. For this reason two projects financially supported by the German Technical and Scientific Association for Gas and Water (DVGW) and the Federal Ministry of Education and Research (BMBF) are already approved or proposed to fill these gaps of knowledge.

Apart from the fate and the tracer function of sucralose and acesulfame first research groups already addressed their work to ecotoxicological effects of artificial sweeteners. As used as food additives, sweeteners have already undergone intensive testing about potential harmful effects on humans. However, the facts that sucralose is a chlorinated compound and proved to be rather persistent seem to push the research compared to former years, when eco-toxicologists were always years behind after analytical chemists identified new emerging contaminants. In fact, there seems to be little evidence of acute adverse effects on the aquatic environment so far. The chronic exposure at ecotoxicologically relevant concentrations led to an increased mortality of juvenile gammarideans (Adolfsson-Erici et al., 2009) and sucralose was also identified to inhibit the sucrose transport in sugarcane (Reinders et al., 2006). For acesulfame ecotoxicological studies are still missing in the scientific literature.

Consequently the question arises if merely the pronounced persistence of a compound, without a bioaccumulative or toxic potential, is reason enough to ban it or to regulate its use. In this context artificial sweeteners are simply another class of contaminants for which the tenth principle of green chemistry (the breaking down into harmless degradation products after usage) (Anastas and Warner, 1998) was not taken into account before their market launch. The precautionary protection of the environment, water resources and consequently the human health should be strongly considered in the future for newly designed chemicals, because aquatic organisms, WWTPs, and drinking water treatment facilities already have to deal with countless organic trace pollutants awaiting their discovery.

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Ich versichere, dass ich die eingereichte Dissertation „Artificial sweeteners - Studies of their environmental fate, drinking water relevance, use as anthropogenic markers, and ozonation products“ selbständig und ohne unerlaubte Hilfsmittel verfasst habe. Anderer als der von mir angegebenen Hilfsmittel und Schriften habe ich mich nicht bedient. Alle wörtlich oder sinngemäß den Schriften anderer Autorinnen oder Autoren entnommenen Stellen habe ich kenntlich gemacht.

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Marco Scheurer Karlsruhe, 03.02.2012