

## Summary

Oxidative and phototransformation processes frequently contribute to micropollutant degradation in natural or engineered systems. For the remediation of contaminated sites or water treatment processes these may be, e.g., ozone (O<sub>3</sub>), hydroxyl radicals (<sup>•</sup>OH), chlorine dioxide (ClO<sub>2</sub>) or UV/vis light. However, the corresponding reaction mechanisms which are important to assess the formation of undesired transformation products (TPs) are mostly unknown. Currently, TP studies are regularly performed with the analysis by high-resolution mass spectrometry (HRMS) which enables the derivation of the TP sum formulas based on the exact masses. However, the reactive site and point of attack, respectively, remain mostly unknown. Here, compound-specific stable isotope analysis (CSIA) may be a useful tool to enlighten and further investigate reactions of micropollutants since degradation processes may reveal specific isotopic fractionation, which are related to the site of primary attack. Therefore, this study investigates the use of CSIA and HRMS as complementary tools to characterize various transformation processes in order to elucidate the underlying reaction mechanisms.

In the first step, the sulfonamide antibiotic sulfamethoxazole (SMX) is chosen as a model compound in order to systematically investigate the pH dependent transformation caused by the transformation processes listed above. SMX is a widely detected micropollutant in surface, ground- and wastewaters which may occur as neutral or anionic specie at typical pH values of water treatment or in natural waters.

In case of the oxidative processes, O<sub>3</sub> in presence and absence of <sup>•</sup>OH and ClO<sub>2</sub>, the reaction stoichiometry, product formation and reaction mechanisms were systematically investigated for reactions with SMX. Two moles of ClO<sub>2</sub> and approximately three moles of O<sub>3</sub> were consumed per mole SMX degraded. As revealed by HRMS, the oxidation of SMX with O<sub>3</sub> and ClO<sub>2</sub> leads to six major TPs in both cases. Tentatively formulated TP structures from other studies could partly be confirmed by CSIA. However, for one TP, a hydroxylated SMX, by HRMS alone it could not be decided whether hydroxylation occurred at the aromatic ring, as suggested in literature before, or at the anilinic nitrogen. By additional means of CSIA and an analytical standard it was possible to identify sulfamethoxazole hydroxylamine unequivocally as one of the TPs of the reaction of SMX with O<sub>3</sub> as well as with ClO<sub>2</sub>. H-abstraction and electron transfer at the anilinic nitrogen are suggested as likely initial reactions of O<sub>3</sub> and ClO<sub>2</sub>, respectively, leading to its formation. The oxidation of anionic SMX with O<sub>3</sub> did not show any significant isotopic fractionation whereas the other reactions studied resulted in a significant carbon isotope fractionation (e.g.,  $\epsilon_C(\text{O}_3) = -2.2 \pm 0.1 \text{ ‰}$  and  $\epsilon_C(\text{O}_3 + \text{OH}) = -1.2 \pm 0.1 \text{ ‰}$ ).

For the investigation of the phototransformation reactions of the two relevant SMX species, four different irradiation scenarios were employed, i.e., a low, medium, and high pressure Hg lamp as well as simulated sunlight. The observed phototransformation kinetics were faster for the neutral than for the anionic SMX species (from 3.4 (LP lamp) up to 6.6 (HP lamp) times). Furthermore, four phototransformation products (with  $m/z$  189, 202, 242, and 260) were detected by HRMS that have not yet been described for direct photolysis of SMX. Isotopic fractionation occurred only if UV-B and UV-A wavelengths prevailed in the emitted irradiation and was most pronounced for the neutral species with simulated sunlight ( $\epsilon_C = -4.8 \pm 0.1 \text{ ‰}$ ). The phototransformation of SMX with UV-C light did not cause significant isotopic fractionation. Consequently, it was possible to differentiate sunlight and UV-C light induced phototransformation of SMX. Thus, CSIA might be implemented to trace back wastewater point sources or to assess natural attenuation of SMX by sunlight photolysis. In contrast to the wavelength range, pH-dependent speciation of SMX hardly impacted isotopic fractionation. However, regarding phototransformation no further comprehensive insights in the underlying reaction mechanisms could be gained by CSIA. This is attributed inter alia to the presence of sulfur and nitrogen as reactive sites in SMX and the current inability to determine any other but C-isotope values by liquid chromatography isotope-ratio mass spectrometry.

Consequently, much simpler model compounds without nitrogen or sulfur-containing moieties, i.e. benzene and its methylated and methoxylated analogs, were used in order to further systematically characterize the abiotic oxidative processes using  $O_3$ ,  $\cdot OH$  or  $ClO_2$  with CSIA. Carbon isotope enrichments factors ( $\epsilon_C$ ) were determined for reactions with  $O_3$  ( $\epsilon_C = -3.6 \text{ ‰}$  to  $-4.6 \text{ ‰}$ ) and  $\cdot OH$  ( $\epsilon_C = < -1 \text{ ‰}$ ). The differences in isotope fractionation may be used to elucidate the contribution of the reactions with  $O_3$  or  $\cdot OH$  to the overall transformation. Subsequently, apparent kinetic isotope effects (AKIEs) were derived for the reaction with  $O_3$ . This was nontrivial due to challenges in assigning reactive positions in the probe compounds for the monodentate attack leading to an  $O_3$  adduct. Several options for this step are presented and the outcome is compared to quantum chemical characterizations of  $O_3$  adducts. The data show that a general assignment of reactive positions for reactions of  $O_3$  with aromatic carbon in *ortho*, *meta* or *para* positions is not feasible and that AKIEs of this reaction should be derived on a compound-by-compound basis.

In conclusion, this work has illustrated the potential added value of CSIA to characterize oxidative and phototransformation processes. Simultaneously, it became obvious that the chemistry of allegedly simple reactions is not yet fully understood and that further research is required to enable us to understand reaction mechanisms and isotopic fractionation on a more holistic level.