**New insights in the Photolysis of Carbamazepine under environmentally relevant conditions by using a flow system on-line coupled to LC-HRMS**

C. Weidauer, B. Seiwert, T. Reemtsma

Helmholtz Centre for Environmental Research - UFZ, Department of Analytical Chemistry, Permoserstrasse 15, 04318 Leipzig, cindy.weidauer@ufz.de

The chemical fate of a vast number of organic chemicals with diverse molecular structures in the environment is not yet known. Therefore, the detection of transformation products (TPs) in environmental samples and their assignment to specific parent chemicals remains difficult. Our aim is the simulation of transformation processes in the laboratory with systems of gradually increasing complexity. Knowledge of transformation products from such studies eases their subsequent detection in the environment.

One important enviromental relevant process is sunlight photolysis. Therefore we developed a flow system for photochemical investigation under simulated sunlight. Photolysis was studied upon irradiation with a xenon lamp (290-800 nm). This system enables a fast systematic screening of anthropogenic substances and their transformations products. On-line coupling of the flow system to liquid chromatography-high resolution mass spectrometry (LC-HRMS) provides a fast and comprehensive tool allowing for structure elucidation of the formed transformation products, yielding important additional information also for well-studied substances.

The usefulness of the applied method is demonstrated for carbamazepine (CBZ) and some structurally related compounds, including CBZ-TPs. CBZ is a well-known anti-epileptic that is efficiently metabolized (up to 99 %) in the human body and excreted via urine. CBZ and its main metabolites are frequently detected in the effluent of the sewage treatment plant (Miao1) and CBZ and dihydroxy-CBZ (DiOH-CBZ) were occurrence in surface, groundwater and in drinking water (De Laurentiis4). Interestingly the photochemical degradation of carbamazepine is not really established. Different pathways are proposed in literature (Calza2, Chiron3, De Laurentiis4). In the present study we present a comprehensive study on the photolytic degradation of CBZ and its environmentally relevant TPs by the use of the photolysis-LC-MS system.

By comparing the LC-MS chromatograms recorded for irridiated and dark samples (control) an estimation of the general degradability of the original substances is possible. While DiOH-CBZ and CBZ-epoxid proved to be photostable, Ox-CBZ turned out to be more reactive than CBZ. Furthermore we found that one CBZ metabolite degrades through another mechanism than CBZ.

As shown a comprehensive analysis of the obtained LC-HRMS spectra simplified the establishment of reaction pathways. Furthermore the comparison of retention time and fragments of TPS supports structure elucidation.With this approach we have elaborated the sunlight photolysis of CBZ and five related substances. The mass spectrometric data (sum formula, retention time, isotope pattern and fragment ions) of the TPs generated in the flow-photoylsis-LC-MS system are fed into a database of used for the screening of environmental samples by LC-HRMS and, thus, supports the determination of TPs in the environment.

1 Miao, X. S.; Metcalfe, C. D., *Anal Chem* **2003,** *75* (15), 3731-3738.

2 Calza, P.; Medana, C.; Padovano, E.; Giancotti, V.; Minero, C., *Environ Sci Pollut R* **2013,** *20* (4), 2262-2270.

3 Chiron, S.; Minero, C.; Vione, D., *Environ Sci Technol* **2006,** *40* (19), 5977-5983.

4 De Laurentiis, E.; Chiron, S.; Kouras-Hadef, S.; Richard, C.; Minella, M.; Maurino, V.; Minero, C.; Vione, D., *Environ Sci Technol* **2012,** *46* (15), 8164-8173.