Analysis of pesticides and pharmaceuticals in surface water by liquid chromatography – ultra high resolution mass spectrometry and application to the Münstersche Aa (NRW, Germany)

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A multi-component method for the analysis of pesticides and pharmaceuticals in surface water using liquid chromatography-ultra high resolution time-of-flight mass spectrometry (LC-UHR-TOF-MS) was used in order to understand their occurrence and behavior in the catchment area of a small river in Northwestern Germany.

The method for the determination of 20 pesticides and 6 pharmaceuticals in surface water by LC-UHR-TOF-MS included filtration by 0.7 µm glass fiber filter, pH-adjustment to 8.0, solid phase extraction (SPE) by Oasis HLB cartridges, and pre-concentration. LC was performed in gradient method using a Prominence UFLCXR (Shimadzu) with RP C-18 NucleodurPolarTec column (3 µm x 150 mm, 2 mm ID, Macherey-Nagel, Germany) and precolumn. The mobile phase was composed of Millipore water (A) and acetonitrile mixed with 5% Millipore water (B), both spiked with 0.1% formic acid at flow rates of 0.1 mL/min or 0.2 mL/min (positive and negative ionization mode, respectively). LC was coupled with a MaXis 3G UHR-QTOF-MS (Bruker Daltonics, Germany) for positive and negative electrospray ionization (ESI). To determine recovery rates and evaluate matrix effects, Millipore water, spring water, river water as well as treated waste water samples were spiked, extracted and analyzed according to the method.

For the present study, weekly time-proportional composite water samples were taken with an automated sampling station (Edmund Bühler, Germany) in 30-minute subsampling intervals from the Münstersche Aa over a period of 10 months (2014/2015). Samples were cooled on-site, transported to the laboratory and stored at -20°C until analysis.

The Münsterland region has a long-standing tradition for agriculture and thus the potential contamination of ground and surface water with pesticides and veterinary pharmaceuticals is of special interest. The catchment area of the Münstersche Aa covers 172 km² of which 75% are used for agriculture and intensive animal farming. During earlier monitoring studies (2000-2010) in the catchment area, some pesticides were analyzed and detected in the Münstersche Aa, whereas pharmaceuticals have only rarely been studied and detected (LEVELING 2010, REETZ 2012). In previous sampling campaigns (2011/2012, surface water grab samples) in the catchment area, isoproturon, terbuthylazine, caffeine, carbamazepine and diclofenac were most frequently detected (REINKE 2013).

A discussion of the recovery rates in different matrices as well as the analyses of the weekly composite samples will be presented.

LEVELING, D. (**2010**): Auswertung vorliegender Pestizidkonzentrationen im Aasee und einzelnen Zuflüssen im Zeitraum von 1991 – 2008. Münster, Germany [unpublished Bachelor thesis].

REETZ, S. (**2012**): Hydrochemische Charakterisierung des Einzugsgebietes der Münsterschen Aa (Nordrhein-Westfalen). Münster, Germany [unpublished Diploma thesis].

REINKE, D. (**2013**): Implementation of an analytical method for pharmaceuticals and pesticides in water by liquid chromatography – ultra high resolution mass spectrometry and application to the Münstersche Aa (NRW). Münster, Germany [unpublished Master thesis].