**Analysis of emerging organic substances in water, fish, and suspended particulate matter (SPM) in the Joint Danube Survey using solid-phase extraction followed by UHPLC-MS-MS and GC-MS analysis**

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The Danube River is the longest river in the European Union and Europe's second longest river after the Volga.

After the two first Joint Danube Surveys (JDS) in 2001 and 2007, the JDS3 organized by the International Commission for the Protection of the Danube River (ICPDR) was undertaken from 13 August to 25 September 2013 along the Danube River in nine countries from Germany to the Danube Delta in Eastern Europe. 68 sites were sampled by three boats along a 2581 km stretch of the Danube, 15 of which were located in the mouths of tributaries or side arms (Liška et al. 2015).

Within the JDS3 emerging polar water-soluble organic contaminants were analysed in the dissolved liquid water phase of river water samples from the Danube River and its major tributaries. Analyses were performed by solid-phase extraction (SPE) followed by ultra-high pressure liquid chromatography triple-quadrupole mass spectrometry (UHPLC-MS-MS). The polar organic substances selected for analysis were diclofenac, carbamazepine, 10,11-dihydro-10,11-dihydroxy-carbamazepine, sulfamethoxazole, 2,4-D, MCPA (2-methyl-4-chlorophenoxyacetic acid), metolachlor, terbutryn, cybutryne (irgarol), DEET (N,N-diethyl-m-toluamide), 1H-benzotriazole, methyl-benzotriazoles, and several perfluoroalkyl acids (C6-C9; C8 = PFOA) and sulfonates (C4, C8 = PFOS). In addition, several organophosphorus flame retardants were analysed by GC-MS.

The most relevant compounds identified in the 68 water samples in terms of highest median and maximum concentrations were 1H-benzotriazole, methylbenzotriazoles, tris(2-chlorisopropyl)phosphate (TCPP), carbamazepine and its metabolite, tris(isobutyl)phosphate (TiBP), tris(2-butoxyethyl)phosphate (TBEP), tris(2-chloroethyl)phosphate (TCEP), tris(1,3-dichloropropyl)phosphate (TDCPP), DEET, diclofenac, sulfamethox-azole, PFOA, and PFOS. The concentrations found are usually below their environmental quality standard (EQS) threshold values, with the exception of PFOS which exceeded its annual average (AA) water EQS limit of 0.65 ng/L in all cases. The maximum concentrations of diclofenac (255 ng/L) and sulfamethoxazole (141 ng/L) exceeded the proposed AA-EQS limit of 0.1 µg/L.

A trend monitoring comparison was performed with the results of JDS2 of the year 2007. Whereas carbamazepine concentrations in the upstream and middle part of the river (up to Hungary) have been reduced by approximately 20-30 %, sulfamethoxazole levels were twice as high in 2013 in the German part of the Danube (40 ng/L) compared to 2007. These results indicate a rising use of the antibiotic sulfamethoxazole in Germany, and an improved waste water treatment in the area of Budapest or lower use of carbamazepine. In the downstream part of the river, both carbamazepine and sulfamethoxazole levels were identical in 2007 and 2013 (around 20 ng/L).

PFOA contamination from an industrial plant on the Inn River (DE/AT) has been eliminated, so that PFOA levels have decreased along the Danube River. Discharge concentration levels of PFOA at the river mouth in Romania have fallen from 12 ng/L in 2007 to 5 ng/L in 2013. In contrast, PFOS concentrations, showing a relatively uniform concentration profile, remained constant over the time period 2007-2013 (6 ng/L at the Danube estuary). The AA-EQS for PFOS of 0.65 ng/l is exceeded throughout the Danube.

PFOS was also analysed in fish liver of white bream fishes and suspended particulate matter (SPM) taken in JDS3 and JDS2. The biota EQS limit value for PFOS of 9.1 µg/kg was exceeded in all cases (109-1007 µg/kg).

**References:**

Liška, I., Wagner, F., Sengl, M., Deutsch, K., Slobodník, J. (editors), 2015. Joint Danube Survey 3 – A Comprehensive Analysis of Danube Water Quality; ICPDR-International Commission for the Protection of the Danube River, Vienna (Austria), ISBN: 978-3-200-03795-3, 2015.