

Screening for Synthetic Pyrethroids in Sediments of European River Estuaries using GC-CI-MS/MS

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Synthetic pyrethroids (sPYR) are a class of pesticides used in crop protection and in biocidal applications. They are of emerging concern because of their high toxicity towards aquatic organisms. Due to their hydrophobicity ($\log K_{ow} > 5$) they sorb to soil organic matter and enter water bodies via run-off. In water bodies they potentially accumulate in aquatic sediments and can affect benthic organisms. LC_{50} values for sediment dwelling *H. azteca* between 2.7 and 125 ng g⁻¹ for different sPYR indicate the need of detection limits in the ppb range (suggested: 10% of LC_{50}). (Amweg 2005)

In this study 12 sPYR were chosen for target analysis based on the approval for agricultural and biocidal application within the European Union.

Current detection methods, e.g. electron capture detection (ECD) and negative chemical ionisation (NCI), make use of halogens present in many sPYR, which excludes non-halogenated sPYR, like allethrin and etofenprox. Therefore it was investigated if positive CI (PCI) is a potential ionisation method for sPYR. Different reactant gases were tested using GC-MS, including methane, methanol, acetone and acetonitrile. Acetone showed best ionisation results and was chosen for comparison with NCI using GC-MS/MS. Non-contaminated sediment was spiked at different concentrations. Although, highly specific precursor ions were chosen for PCI with acetone (mostly molecule ions) the high background did not allow to detect sPYR in low concentrations (lowest detectable concentrations between 1 and 10 ng g⁻¹). NCI showed better performance, detecting concentrations between 0.1 and 0.2 ng g⁻¹. Although etofenprox cannot be detected, NCI is the preferable ionisation method when analysing sediments. Furthermore large volume injection (LVI) was investigated to potentially decrease detection limits. 10 µL LVI showed increased response for sPYR over 10x concentrated 1 µL pulsed splitless injection (PSI), when using spiked solvent samples. However when using sediment matrix, LVI resulted in broad distorted peaks, whereas PSI still resulted in sharp and resolved peaks.

A multi-target method was used for sample preparation, including pressurised liquid extraction with subsequent normal phase column chromatography. Massive signal enhancement of sPYR was observed when analysing sediment matrix. Therefore a matrix-matched calibration was performed with non contaminated sediment. Method detection limits for GC-NCI-MS/MS ranged between 0.02 and 1.43 ng g⁻¹. Recoveries varied between 62 and 82 %. So far, sediments from different sampling spots at the delta of Danube (3 spots) and Po (5 spots) were analysed for the occurrence of sPYR. Results were normalised for total organic carbon (TOC) and are listed in Tab. 1. Sediments of 12 further European river estuaries will be screened for the occurrence and distribution patterns of sPYR. If applicable, toxicity units (TU) will be determined based on Amweg et al (2005).

Tab. 1 Results of target analysis in sediments of Danube and Po

Compound	Danube		Po	
	ng g ⁻¹ d.w.	mg kg ⁻¹ OC	ng g ⁻¹ d.w.	mg kg ⁻¹ OC
Tefluthrin	0.20 - 0.51	0.05 - 0.08	0.27 - 0.55	0.01 - 0.06
Bifenthrin	0.06 - 0.12	0.01 - 0.02	0.12 - 0.32	0.01 - 0.03
λ-Cyhalothrin	0.01 - 0.31	0.03 - 0.05	0.20 - 0.23	0.02 - 0.03
Acrinathrin	< MDL		0.08 (1 spot)	0.01
Cyfluthrin	n.d.		0.15 (1 spot)	0.02
Cypermethrin	0.77 - 1.10	0.12 - 0.18	0.71 - 3.55	0.10 - 0.35

References:

Amweg et al. (2005), Use and toxicity of pyrethroid pesticides in the central valley, california, USA, Environmental Toxicology and Chemistry 24(4), 966-972.