

OCCURRENCE OF POLYCYCLIC MUSKS IN PORE WATER OF THE SEDIMENT-FRESHWATER SYSTEM: PASSIVE SAMPLER APPLICATION

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Abstract

Polycyclic musks are aroma compounds used worldwide as substitutes for natural musks, which have become ubiquitous pollutants in the environment. The land-based input and partition behavior of musks in sediments and fresh water are important for understanding their fate in the aquatic environment. In this study, a 10 sediment samples were collected and used to determine three polycyclic musks: tonalide, galaxolide and cashmeran. All three pollutants were detected in the sediment of the Danube River, but in very low concentrations (< 2 ng/L). In the article, the ex-situ passive methodology of sediment sampling was applied. For this purpose, silicone rubber sheets were used so that, after establishing equilibrium relations between sediment and polymer, the concentration of musk could be determined. Relations of two important parameters for risk assessment- freely dissolved concentration (C_w) in the pore water and the accessible (releasable) concentration in the sediment (C_{AOC}) were deviated the most in the Belegiš locality, with total C_w values of 0.003 ng/L for Galaxolide and Tonalide, and 0.02 ng/L for Cashmeran. The highly significant linear isotherms for musks obtained by the method of equilibrium passive sampling confirmed the partition driven nature of their exchange between water and sediment for the investigated sediments.

Keywords: polycyclic musks, passive sampling, sediment, Danube

Introduction

Synthetic musks (SMs) are aroma compounds that are used worldwide as substitutes for natural musks, and mainly used in the production of household and personal care products (Hua et al., 2023). Due to their low price and widespread availability, the global production and consumption of SMs are increasing rapidly, particularly polycyclic musks (PAMs), galaxolide and tonalide (Hermann et al., 2000). Galaxolide and tonalide have been listed as high volume chemicals by the United States Environmental Protection Agency (Lopez-Gazpio et al., 2012). They can be found in hair care, body washes, toilet soaps, skin lotions as well as makeup products (Lu et al., 2011). Their rapid increase in use worldwide has been primarily due to their economical substitute for natural musk fragrances (Guo et al., 2013). Recently, occurrences of polycyclic musks have been frequently reported in sewage influents, effluents, sludge, surface water and sediments across several major metropolitan regions.

After application, PAMs could be directly discharged into the aquatic environment PAMs in environment are also traced from the effluent of sewage treatment plants, due to the incomplete elimination of SMs in the sewage treatment plants. Despite the application of advanced biological treatment strategies, the removal efficiencies for galaxolide, tonalide, and musk ketone were often lower than 60% (Hong et al., 2021). Also, PAMs have been detected in sediments, surface water, air and biota, suggesting that these contaminants are ubiquitous throughout the environment (Krishnamoorthi et al., 2021). High percentages of PAMs

especially galaxolide and tonalide, were found in blood plasma samples of healthy young adults from Vienna, Austria (Hutter et al., 2009).

Passive sampling methods (PSMs) allow the quantification of the freely dissolved concentration (C_w) of an organic contaminant in pore water even in complex matrices such as sediments. C_w is directly related to a contaminant's chemical activity, which drives spontaneous processes including diffusive uptake into benthic organisms and exchange with the overlying water column. Consequently, C_w provides a more relevant dose metric than total sediment concentration. Recent developments in PSMs have significantly improved our ability to reliably measure even very low levels of C_w (Mayer et al., 2013). Application of PSMs in sediments is preferably conducted in the equilibrium regime, where freely dissolved concentrations in the sediment are well linked to the measured concentration in the sampler via analyte specific partition ratios.

Based on previous research on hydrophobic organic contaminants, it is concluded that C_w allows a direct assessment of 1) contaminant exchange and equilibrium status between sediment and overlying water, 2) benthic bioaccumulation, and 3) potential toxicity to benthic organisms (Mayer et al., 2013; Rusina et al., 2019). Accordingly, the aim of our work was to demonstrate that the use of PSMs to measure C_w of specific emergent contaminants such as polycyclic musks provides an improved basis for mechanistic understanding of fate and transport processes in sediments and has the potential to significantly improve risk assessment and management of contaminated sediments.

Material and Methods

The sampling was performed in Nov 2012. For this investigation, 10 samples of bottom sediment from different sites of Danube River through Serbia (Apatin- D1 (1401 km), Labudnjača- D2 (1367 km), Neštin- D3 (1264 km), Begeč- D4 (1275 km), Ratno Ostrvo- D5 (1257 km), Šangaj- D6 (1250 km), Knićanin- D7 (1214 km), Belegiš- D8 (1199 km), Ritopek- D9 (1141 km), Dubravica- D10 (1103 km)) were collected using a grab sampler (Fig. 1). All sediment samples were analyzed in the laboratory of Research Centre for Toxic Compounds in the Environment - *RECETOX* (Brno, Czech Republic) after two days.

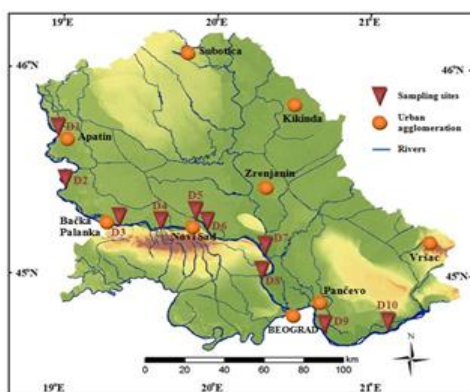


Figure 1. Danube River sampling sites

Passive sampler analysis

As part of the study, transparent strips of silicone rubber, dimensions 300×300 mm and thickness 0.5 mm, were used as sorption media of passive samplers. Before use, the silicone strips were extracted with ethyl acetate in a Soxhlet extractor to remove unpolymerized monomers, followed by methanol extraction to remove other impurities. Sorption media of passive samplers were dosed with performance reference compounds (PRC), using a mixture

of water and methanol. Polycyclic musks were analyzed using a GC 6890 (Agilent, USA) coupled with an MSD 5975 mass spectrometer (Agilent, USA) operating in EI+ mode. Compounds were separated on an HP-5MS column (film 30 m x 0.25 x 0.25 μm) in selected ion mode (SIM). Helium was used as mobile phase at 1.2 mL/min and constant pressure.



Figure 2. Preparation of passive sediment samplers

Results and discussion

Determination of C_w hydrophobic organic compounds in water samples (by active sampling) is often associated with problems of incomplete phase ("unfinished") separation between bound particles and dissolved analyte and adsorption on sampling instruments such as filters and glass bottles. These effects are even more pronounced for pore water, even if it were possible to obtain large amounts of pore water necessary for satisfactory analyte detection. An alternative is the application of passive samplers, which accumulate compounds mainly through the aqueous phase. When equilibrium is reached, C_w can be estimated through the sampler–water partition coefficient (K_{pw}) and the measured concentrations in the sampler (C_p).

The usage of passive sampling providing estimates of both bioavailability parameters, i.e. contaminant's accessibility in sediment (C_{AOC}) and C_w in pore water. Equilibrations of passive samplers with sediment at largely different sampler–sediment mass ratios, allow construction of a part of a (de)sorption isotherm, which yields the C_w in the pore water at a low sampler–sediment ratio (minor depletion of the sediment phase) and the accessible or releasable concentration in the sediment at high sampler–sediment ratio (maximum depletion of the sediment phase).

Table 1. Limit of quantification of selected PAM compounds during passive sampler analysis

Compounds	$\log K_{pw}$	LOQ	
		N_p (ng)	C_w (ng/L)
Galaxolide (HHCB)	5,32	2,2	0,003
Tonalide (AHTN)	5,29	1,9	0,003
Cashmeran (DPMI)	4,50	2	0,02

Plots of freely dissolved concentrations (Δ : $C_w:0$, ng L^{-1} , right y–axis) and accessible concentrations expressed on amorphous organic carbon basis (\circ : $CAS:0/f_{AOC}$, mg kg^{-1} , left y–axis) versus the locations on the x-axis (Fig 3.). The locations are ordered in downstream direction but the distance on the x-axis does not reflect the actual distance, neither do the connecting lines represent the concentrations in between them. Open, gray and black filled markers indicate $f_{AOC} < 0.001$, $f_{AOC} \geq 0.001$ but < 0.002 or $f_{AOC} \geq 0.002$, respectively. Data for a location marked with a "+" passed the quality criterion, QF is "Ok" .

The detected concentration levels of polycyclic musks were very low (< 2 ng/L). At site D8, musk showed some higher $C_{w,0}$ levels but these can only be considered indicative as the results did not qualify. For musk cashmeran, $\log K_{AOC}$ deviated from the unity line but not significantly, considering its large variability ($s = 0.4$ log unit).

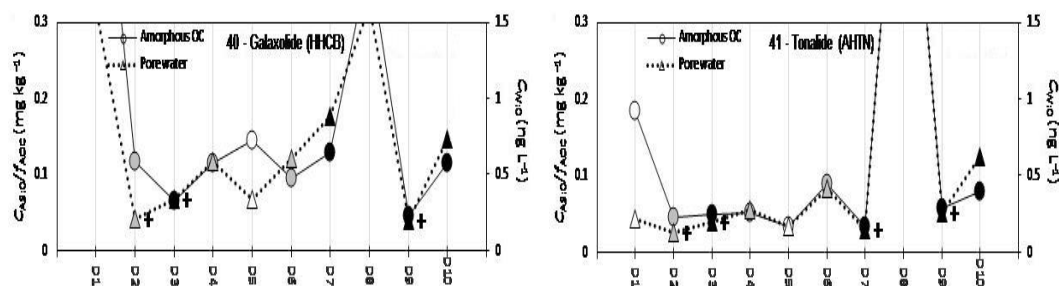


Figure 3. Profiles of freely dissolved concentrations in pore water and available concentrations in the sediment of the Danube River

Conclusion

Based on the overall analysis of the obtained results, it can be established that the Danube riverbank flow at the territory of Serbia have significant potential pollution sources of aquatic systems with polycyclic musks, which is important information to conduct more extensive monitoring and prevent further direct discharge, as well as disposal of ambalage that containing these pollutants by adequate controls, thus diminishing the extremely negative ecotoxicological effects currently present in the aquatic system. Within the framework of such a systematized research process, it would be necessary to include more media (biotic and abiotic) in the analysis as well as more specific points.

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