

Musk compounds in fish from Elbe River

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Introduction

While the contamination of aquatic ecosystem by persistent organochlorine contaminants such as OCPs, PCBs, PCDDs and PCDFs has been well documented over the past decades, "musk compounds" have so far escaped from appropriate attention. Synthetic musks are widely used as fragrance substances in detergents, cleaning agents and cosmetic products.

Extensive release of musk compounds from household use as well as from industry (contaminated waste waters) occurred during the years of their use. The first report on the presence of these substances in aquatic ecosystem dates from 1981: Japanese (1) identified musk ketone and musk xylene in carp and subsequently in shellfish from Tokyo bay. In following years musk compounds were found as contaminants not only in freshwater fish (2-5) but also in human milk and adipose tissue (6, 7). Since the biodegradability of nitro musks is low and their lipophilicity (8) is relatively high ($\log K_{ow}$ for musk ketone is 4.9 and for musk xylene 4.2), accumulation in food chains may easily occur.

Methods used for determination of musk compounds usually consist from extraction of analytes from different matrices with mixtures of non- and semipolar solvent (namely n-hexane and acetone), clean-up step utilizing adsorption chromatography on sorbents such as silica (3, 9, 10) or florisil (11) follows. Alternatively, GPC (12) is employed. Quantitation of analytes can be carried out either by GC-ECD (9) (only nitro musks are determined) or by HRGC-MSD (4-5).

Although, as shown above, several studies concerned with discussed contaminants in biotic samples exist, the data on the levels of both groups of musks in freshwater fish are rather sporadic (two existing studies were conducted in Germany) the routine monitoring of these biota for musks is not common. Similarly to many other countries, no comprehensive information on environmental musks is available in Czech Republic. The aim of presented study was to implement analytical method applicable for simultaneous determination of musk xylene, musk ketone (the nitro musk group), galaxolide and tonalide (the polycyclic musk group) in fish samples collected at Elbe river. Two localities upstream and downstream from industrial cities (representing potential sources of pollution) were sampled.

Material and Methods

Samples of fish were collected from Elbe river at: A - locality Pardubice, upstream from the city; B - locality Pardubice, downstream from the city; C - Střekov; D - Hřensko (exit of Elbe river from Czech Republic). Breams, perches and chubs, 20 pieces each, were collected in these localities. The length and weight of each fish was recorded and then pooled samples of skinned fillets were prepared (aliquot portion of each fish was left for individual examination).

Representative sample (approx. 50g) was homogenised with anhydrous sodium sulphate to obtain a free-flowing powder. Analytes were extracted with three portions of hexane : acetone mixture (2:1, v/v) using sonication (lipids extracted under these conditions were determined gravimetrically). Approx. 150 mg of lipids were dissolved in GPC mobile phase and loaded onto BioBeads SX-3 column (500 × 8 mm, ethyl acetate : cyclohexane, 1:1, v/v, 0.8 ml/min). Fraction 16-24 ml was collected, evaporated to dryness and the residue dissolved in 1 ml of isoctane.

Quantification of analytes was carried out by HRGC-LRMS in SIM mode. GC conditions are summarized in Table 1., ions selected for quantitation and confirmation are presented in Table 2.

Table 1: GC conditions used for analysis of musk compounds - corresponds to (2)

<i>Parameter</i>	<i>Conditions</i>
column	HP-5ms, 30m × 0.25mm I.D., 0.25µm phase
inlet temperature	250°C
splitless time	2 min
injected amount	1 µl
oven program	60°C (2 min), 10°C/min do 180°C, 1.5°C/min do 220°C, 30°C/min do 280°C (12 min)
analysis time	55 min
carrier gas	helium
linear velocity of carrier gas	37 cm/min (constant)
MS quadrupole temperature	106°C
MS source temperature	230°C
dwel time	100 ms

Table 2: Ions selected for quantification and confirmation of analytes

<i>Time group (min)</i>	<i>Retention time (min)</i>	<i>Analyte</i>	<i>Monitored ions, m/z</i>
10 - 19	18.88	Galaxolide	213, 243, 258
19 - 21	19.14 (coelution)	Tonalide	243, 244, 258
		Musk xylene	282, 283, 297
21 - 55	22.09	Musk ketone	279, 280, 294

Results and Discussion

In all the examined fish samples collected from Elbe river, the presence of targeted nitro- and polycyclic musks was proved. In Figure 1. there are shown the results obtained by analysis of pooled bream samples from different localities. The levels of galaxolide and tonalide were generally distinctly higher than those of nitro musks (similar findings were obtained for all other fish species). Highest concentration of tonalide and galaxolide (3194 mg/kg and 1289 mg/kg, on the fat basis) were recorded at locality Hrensko (D). This may be due to the wastes from detergents producing factory located upstream from this locality. This assumption corresponds to lower levels of analytes found in fish upstream from this potential source of pollution (C, locality Střekov). Similarly, comparing localities A and B in Figure 1., increased levels of polycyclic musks, probably due to the municipal wastes, were determined in fish collected downstream from urban area Pardubice (locality A).

As shown in Figure 2., some differences, both qualitative and quantitative, were found in fish representing various trophic levels. Nevertheless, the contribution of food chain (biomagnification) to the bioaccumulation of musk compounds in examined fish was not statistically significant. The levels of musks in "young" and "old" fish were almost the same, some biodegradation and/or elimination of these contaminants occurs.

Relationship between the data obtained in this study and all fish characteristics recorded were tested by general linear model procedure using a linear regression analysis (all assessments at confidence level $p = 0.05$). No correlations were found except for concentrations of galaxolide and tonalide ($R = 0.835$).

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Figure 1: Average levels of musk compounds in bream from Elbe river (localities: A-upstream from Pardubice, B-downstream from Pardubice, C-Střekov, D-Hřensko)

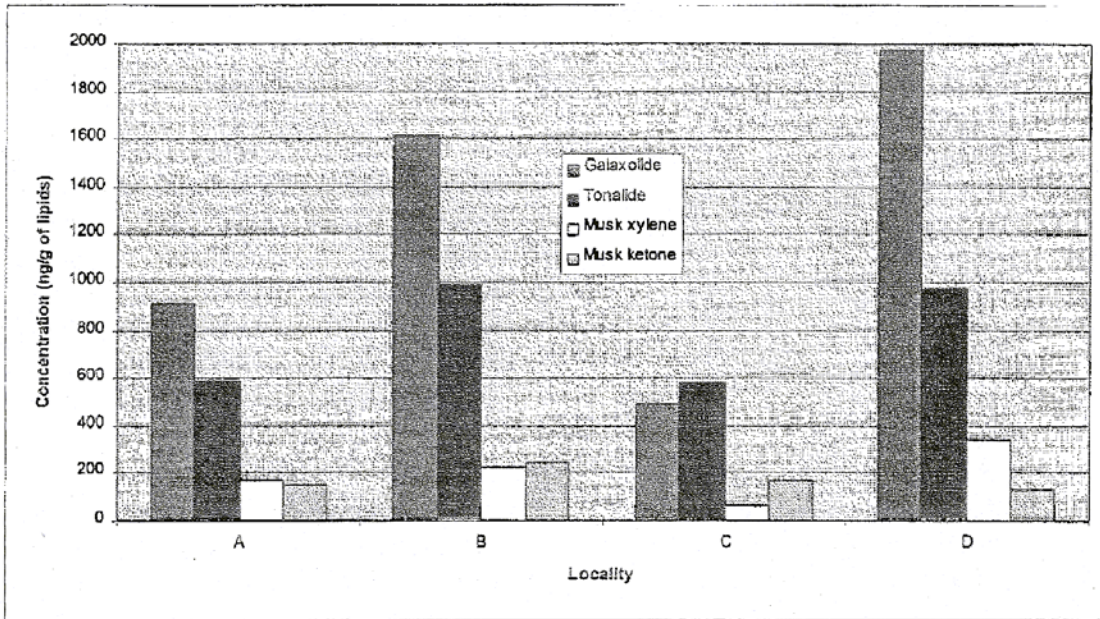


Figure 2: Musk compounds in various fish species collected downstream from Pardubice

