

Polycyclic Aromatic Hydrocarbons (PAHs) in wood smoke used for production of traditional smoked meat products in Serbia

Polycyclische Aromatische Kohlenwasserstoffe (PAK) in Räucherrauch bei der Herstellung von traditionellen geräucherten Fleischerzeugnissen aus Serbien

J. DJINOVIC¹, A. POPOVIC² and W. JIRA

¹Institute of Meat Hygiene and Technology, Belgrade, Serbia

²Faculty of Chemistry, University of Belgrade, Serbia

Summary

During smoking of meat products polycyclic aromatic hydrocarbons (PAHs) are generated by incomplete combustion of wood. About 660 different compounds belong to the PAH group. Some of them are contaminants of great environmental concern due to their toxic, mutagenic and carcinogenic properties.

In this study, PAHs from smoke produced by beech wood combustion in two traditional meat smokehouses (SHs), from Zlatibor region, Serbia, were collected during the smoking process using two types of tubes (PUF and XAD-2). The following 16 EU priority PAHs were analysed by Fast-GC/HRMS: Benzo[c]fluorene (BcL), benzo[a]anthracene (BaA), cyclopenta[c,d]pyrene (CPP), chrysene (CHR), 5-methylchrysene (5MC), benzo[b]fluoranthene (BbF), benzo[j]fluoranthene (BjF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), benzo[g,h,i]perylene (BgP), dibenzo[a,h]anthracene (DhA), indeno[1,2,3-cd]pyrene (IcP), dibenzo[a,e]pyrene (DeP), dibenzo[a,h]pyrene (DhP), dibenzo[a,i]pyrene (DiP) and dibenzo[a,l]pyrene (DlP). Smoke was collected in the middle of the smokehouses at a height of 2 m (SH I) and 5 m (SH II) distant from firebox. Results show a great variability in PAH concentrations. Total emission of 16 EU priority PAHs was $6.7 \pm 6.8 \text{ mg m}^{-3}$ and $7.4 \pm 6.0 \text{ mg m}^{-3}$, in PUF and XAD-2 tubes, respectively, in the SH I. At a height of 5 m (SH II), PAH emission was $2.4 \pm 0.8 \text{ mg m}^{-3}$ and $4.3 \pm 0.7 \text{ mg m}^{-3}$, in PUF and XAD-2 tubes, respectively.

The patterns of the 16 EU priority PAHs in wood smoke were compared with PAH patterns in smoked meat products (beef ham, pork ham, cajna sausage and sremska sausage). Meat products were logically smoked in the smokehouses where smoke samples were collected during the smoking procedure. PAH fingerprints showed that BcL was the most predominant PAH, both in smoke and smoked meat products. For all PAHs, except for dibenzopyrenes (DeP, DhP, DiP and DlP), there is a very similar fingerprint in smoke and smoked meat products.

Schlüsselwörter 16 EU PAK – Räucherrauch – PAK-Muster – Serbien

Key Words 16 EU priority PAHs – wood smoke – PAH patterns – Serbia

Zusammenfassung

Während der Räucherung von Fleischerzeugnissen entstehen Polycyclische Aromatische Kohlenwasserstoffe (PAK) durch unvollständige Verbrennung von Holz. Zu der Gruppe der PAK zählen etwa 660 verschiedene Verbindungen, von denen einige aufgrund ihrer toxischen, mutagenen und Krebs erregenden Eigenschaften von großer Bedeutung sind.

Im Rahmen einer Studie wurden PAK in Räucherrauch während des Räuchervorgangs untersucht. Der aus der Verbrennung von Buchenholz resultierende Rauch stammte aus zwei traditionellen Räucherammern in der Region Zlatibor (Serbien) und wurde in zwei verschiedenen Kartuschen (PUF and XAD-2) gesammelt. Analysiert wurden die 16 von der EU als prioritär eingestuften PAK mit Hilfe einer Fast-GC/HRMS-Methode. Folgende PAK wurden untersucht: Benzo[c]fluoren (BcL), Benzo[a]anthracen (BaA), Cyclopenta[c,d]pyren (CPP),

Chrysen (CHR), 5-Methylchrysen (5MC), Benzo[b]fluoranthen (BbF), Benzo[j]fluoranthen (BjF), Benzo[k]fluoranthen (BkF), Benzo[a]pyren (BaP), Benzo[g,h,i]perylene (BgP), Dibenz[a,h]anthracen (DhA), Indeno[1,2,3-cd]pyren (IcP), Dibenzo[a,e]pyren (DeP), Dibenzo[a,h]pyren (DhP), Dibenzo[a,i]pyren (DiP) und Dibenzo[a,l]pyren (DlP). Der Rauch wurde in der Mitte der Räucherammer in einer Entfernung von 2 Metern (Räucherammer I) bzw. 5 Metern (Räucherammer II) vom Raucherzeuger gesammelt. Die Untersuchungen ergaben große Schwankungen in den PAK-Gehalten. Die PAK-Gesamtgehalte der 16 EU-PAK in Räucherammer I lagen bei $6,7 \pm 6,8 \text{ mg m}^{-3}$ (PUF) und $7,4 \pm 6,0 \text{ mg m}^{-3}$ (XAD-2). In Räucherammer II waren PAK-Summengehalte von $2,4 \pm 0,8 \text{ mg m}^{-3}$ (PUF) und $4,3 \pm 0,7 \text{ mg m}^{-3}$ (XAD-2) nachweisbar.

Die in Räucherrauch gefundenen Muster der 16 EU-PAK wurden mit den PAK-Mustern der in derselben Räucherammer geräucherten Fleischerzeugnisse (Rinderschinken, Schweineschinken, Teesalami und Rohwurst Hausmacher Art) verglichen. Dabei zeigte sich, dass sowohl in Räucherrauch als auch in geräucherten Fleischerzeugnissen BcL die dominierende PAK-Verbindung darstellte. Für alle untersuchten PAK mit Ausnahme der Dibenzpyrene (DeP, DhP, DiP und DlP) ergaben sich sehr ähnliche PAK-Muster.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a large group of persistent organic compounds, which are usually released to environment by anthropogenic activities such as different combustion processes. Wood combustion is one of the most important sources of a large number of pollutants, such as aldehydes, ketones, benzene, toluene, xylenes, polycyclic aromatic hydrocarbons (PAHs), organic acids and particulate matter [1]. PAHs are among the most harmful products of incomplete wood combustion. Total PAH concentrations are different in smoke extracts from different wood smoke [2]. PAH content in wood smoke became of public health concern because of negative effects to humans [3, 4].

Benzo[a]pyrene (BaP) is used as a marker and as the main indicator of PAH occurrence and carcinogenicity, capable of tumor initiation, promotion and progression. It is abundantly distributed in the environment [5]. Carcinogenic and mutagenic properties of BaP have been investigated in many studies [6, 7]. BaP is in the spotlight of scientific interest concerning the fact that it is still used as a marker compound of PAHs occurrence and carcinogenicity. Recently, European Food Safety Authority (EFSA) published a scientific opinion concerning PAH in food [8]. It was concluded that BaP is not a suitable indicator for the occurrence of PAHs in food and that

“PAH4” (BaP, CHR, BaA and BbF) and “PAH8” (BaP, BaA, BbF, BkF, BgP, CHR, DhA and IcP) are the most suitable indicators in food.

Toxic equivalency factors (TEFs) are usually used to denote cancer potency of specific PAH compounds in relation to carcinogenicity of BaP [9, 10]. Also, TEF values were used to estimate relative contribution of individual PAHs to total carcinogenicity of the measured PAHs in air. TEFs described by NISBET and LaGOY [10] and LARSEN and LARSEN (cit. BOSTRÖM *et al.* [9]) are widely used.

In this study 16 EU priority PAHs have been analysed as recommended by the Scientific Committee on Food (SCF) [11] and the European Food Safety Authority (EFSA). The European Food Safety Authority (EFSA) recommended to analyze benzo[c]fluorene, assessed to be relevant by the Joint Food and Agriculture Organization of the United Nations/World Health Organization (FAO/WHO) Experts Committee on Food Additives (JECFA), [12]. The 16 EU priority PAHs to be analysed are: benzo[c]fluorene (BcL), benzo[a]anthracene (BaA), cyclopenta[c,d]pyrene (CPP), chrysene (CHR), 5-methylchrysene (5MC), benzo[b]fluoranthene (BbF), benzo[j]fluoranthene (BjF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), benzo[g,h,i]perylene (BgP), dibenzo[a,h]anthracene (DhA), indeno[1,2,3-cd]pyrene (IcP), dibenzo[a,e]pyrene (DeP), dibenzo[a,h]py-

rene (DhP), dibenzo[a,i]pyrene (DiP) and dibenzo[a,l]pyrene (DlP).

Carcinogenic and mutagenic properties of some polycyclic aromatic hydrocarbons justify the necessity to determine their contents in smoke used for smoking of food. Twelve of sixteen EU priority PAHs have been classified by the International Agency for Research on Cancer (IARC) to be probably carcinogenic to humans (BaA, BaP, DhA) or possibly carcinogenic to humans (5MC, BbF, BjF, BkF, IcP, DeP, DhP, DiP, DlP), [13-15]

In the south-west region of Serbia (Zlatibor) smoked meat products are still produced in a traditional way. Tradition of producing smoked meat products on Zlatibor region lasts over centuries. Step by step, this tradition was developed and became a trademark of the region.

The aim of this study was to quantify and characterize the emission of the 16 priority EU PAHs in smoke produced by beech wood combustion in traditional meat smokehouses, as well as to investigate the influence of the distance between sampling point (meat smoking position) and firebox on PAH concentration. In addition, BaP equivalent concentration (BaP_{eq}) of PAHs in smoke samples are calculated.

Materials and Methods

Smoke Collection

Smoke collection was performed by a low volume pump (Proekos Aerotest AT 401) situated in the middle of SH at a height of 2 m (SH I) and 5 m (SH II) from the ground. Smoke sample collecting points were at the same distance as the distance between meat products and firebox in the smokehouses. In both cases smoke was produced by beech wood combustion. The pump flow was set at 1 dm³/min. Smoke was collected into an adsorbent tube containing polyurethane foam (PUF), (22 x 100 mm size, 1-section, 76 mm sorbent, SKC, Dorset, UK), on the first pump line. A tube containing XAD-2 resin (8 x 110 mm size, 2-section, 200/400 mg sorbent, SKC, Dorset, UK) was set up on the second pump line. Smoke samples were collected

on both pump lines at the same time. Samples have been collected during 15 min daily, successively five days, in the middle of the smoking period lasting 15 days, in winter time (February). After sampling, tubes have been covered with aluminium foil and stored at ≤ 4 °C in the dark, up to 7 days, prior to extraction.

Reagents

All solvents were obtained in picograde quality from Promochem (Wesel, Germany). Drying material (poly(acrylic acid), partial sodium salt-graft-poly(ethylene oxide)) was purchased from Sigma Aldrich (Munich, Germany). Bio Beads S-X3 (200-400 mesh) was purchased from Bio-Rad Laboratories (Munich, Germany) and silica gel 60 (70-230 mesh) from Merck (Darmstadt, Germany). Glass microfibre filters (18 mm i.d.) were obtained from Dionex (Idstein, Germany). PTFE-Filters (1 µm pore size, 25 mm i.d.) and the SPE-Cartridges (12 mm i.d.) were purchased from Alltech (Unterhaching, Germany).

A PAH standard mixture containing isotope labelled (¹³C and ²H) PAH compounds (benzo[a]anthracene-¹³C₆, chrysene-¹³C₆, 5-methylchrysene-d₃, benzo[b]fluoranthene-¹³C₆, benzo[k]fluoranthene-¹³C₆, benzo[a]pyrene-¹³C₄, dibenzo[a,h]anthracene-d₁₄, indeno[1,2,3-cd]pyrene-d₁₂, benzo[g,h,i]perylene-¹³C₁₂, dibenzo[a,e]pyrene-¹³C₆ and dibenzo[a,i]pyrene-¹³C₁₂ in isooctane) and recovery PAH standard mixture (benzo[a]anthracene-d₁₂, benzo[a]pyrene-d₁₂ and benzo[g,h,i]perylene-d₁₂ in isooctane) were obtained as single compounds from Promochem (Wesel, Germany). Fluorinated PAH standards (13-fluorodibenzo[a,l]pyrene and 5-fluorobenzo[c]fluorine in isooctane) were obtained from the Biochemical Institute for Environmental Carcinogens (Grosshansdorf, Germany).

Soxhlet extraction

After sampling, PUF and XAD-2 resin were separately extracted with 250 mL n-hexane, for 18 h in a Soxhlet apparatus. Before extraction 50 µL of the PAH standard mixture, containing isotope labeled (¹³C and ²H) and fluorinated PAH compounds, were added to the Soxhlet solvent (n-hexane) as internal standard.

Gel permeation chromatography (GPC)

The evaporated Soxhlet extract was dissolved in 4.5 mL cyclohexane/ethylacetate (50:50 v/v) and filtered through a PTFE filter with 1 µm pore size. A GPC column (25 mm i.d.) was filled with 60 g Bio-Beads S-X3. Samples were eluted with cyclohexane/ethylacetate (50:50 v/v) at a flow rate of 5 mL/min (dump time 0-36 min, collecting time 36-65 min). The solvent was removed with a rotary evaporator. The eluate was dried in nitrogen stream. The dried GPC eluate was dissolved in 1 mL cyclohexane.

Solid phase extraction (SPE)

This clean-up step to remove more polar substances was performed automatically with a modified ASPEC Xli. The system was modified with a fitting rack, teflon fun-

nels and teflon tubes. Silica, dried for 12 h at 550 °C, was deactivated with 15 % of water. 1 g of dried deactivated silica was filled into commercial 8-mL SPE columns (12 mm i.d.). After column conditioning with 3 mL cyclohexane the sample was applied and eluted with 10 mL cyclohexane.

Results and Discussion

The average concentration of PAHs [mg m⁻³] in beech wood smoke samples simultaneously collected with PUF and XAD-2 tubes from smokehouse (SH) I and II, as well as BaP equivalent concentration (BaPeq) of analysed PAHs [mg m⁻³] are presented in Tables 1 and 2.

Table 1: Average concentrations of PAHs [mg m⁻³] in beech wood smoke samples (n = 5) simultaneously collected with PUF and XAD-2 tubes from SH I^a and BaP equivalent concentration (BaPeq) of PAHs [mg m⁻³]

Tab. 1: Durchschnittliche PAK-Gehalte [mg m⁻³] in Buchenholz-Räucherrauch (n = 5) bei simultaner Absorption in PUF- und XAD-2-Kartuschen in Räucherkerammer I und BaP-Toxizitäts-äquivalente (BaPeq) der PAK [mg m⁻³]

PAH	PUF (Mean ± SD) [mg m ⁻³]	XAD-2 (Mean ± SD) [mg m ⁻³]	TEF 1 ^b	TEF 2 ^c	BaPeq 1 ^d [mg m ⁻³]		BaPeq 2 ^e [mg m ⁻³]		
					PUF	XAD-2	PUF	XAD-2	
4-ring	BcL	0.627 ± 0.284	1.080 ± 0.487	--	--	--	--	--	--
	BaA	0.618 ± 0.383	1.149 ± 0.980	0.1	0.005	0.062	0.115	0.003	0.006
	CHR	1.592 ± 1.853	1.801 ± 1.254	0.01	0.03	0.016	0.018	0.048	0.054
	5MC	0.099 ± 0.106	0.118 ± 0.005	--	--	--	--	--	--
5-ring	CPP	0.221 ± 0.242	0.559 ± 0.914	--	0.02	--	--	0.004	0.011
	BbF	1.630 ± 2.983	0.593 ± 0.472	0.1	0.1	0.163	0.059	0.163	0.059
	BjF	0.525 ± 0.808	0.320 ± 0.283	--	0.05	--	--	0.026	0.016
	BkF	0.420 ± 0.665	0.238 ± 0.226	0.1	0.05	0.042	0.024	0.021	0.012
6-ring	BaP	0.264 ± 0.165	0.619 ± 0.581	1	1	0.264	0.619	0.264	0.619
	DhA	0.173 ± 0.298	0.059 ± 0.046	5	1.1	0.863	0.294	0.190	0.065
	BgP	0.259 ± 0.068	0.362 ± 0.258	0.01	0.02	0.003	0.004	0.005	0.007
	IcP	0.207 ± 0.111	0.412 ± 0.362	0.1	0.1	0.021	0.041	0.021	0.041
	DeP	0.022 ± 0.013	0.044 ± 0.036	--	0.2	--	--	0.004	0.009
	DhP	0.003 ± 0.002	0.006 ± 0.004	--	1	--	--	0.022	0.006
	DiP	0.027 ± 0.023	0.058 ± 0.057	--	0.1	--	--	0.003	0.006
DIP	0.007 ± 0.005	0.015 ± 0.013	--	1	--	--	0.007	0.015	
Total emission	6.692	7.430							
Total BaPeq					1.433	1.174	0.781	0.926	

^a The distance between the point of smoke sampling and firebox was 2 m in the smokehouse (SH) I;

^b TEF 1 described by NISBET and LaGOY 1992; ^c TEF 2 described by LARSEN and LARSEN 1998

(cit. BOSTRÖM *et al.* 2002); ^d BaPeq 1 calculated using TEF 1; ^e BaPeq 2 calculated using TEF 2

The percentages of individual PAH compounds [%] to the sum contents of 16 EU priority PAHs in smoke from different smokehouses (SHs), collected with PUF and XAD-2 tubes, are shown in Table 3. Distribution of PAHs in smoke samples collected with PUF and XAD-2 tubes in two different SHs (I and II) are shown in Figure 1. Figure 2 and 3 show PAH fingerprints for smoke and smoked meat products, from both SHs. Data for contents of individual 16 EU PAHs in smoked meat products were published elsewhere [16].

16 EU priority PAHs in smoke from meat smokehouses (SHs)

PAH concentrations in smoke samples, collected from both smokehouses, are presented as mean value \pm standard deviation (SD) in Tables 1 and 2. All of the 16 EU priority PAHs were detected in the analysed smoke samples. The obtained results show a large variability (high SD) in

concentration of PAHs during the sampling period of five successive days, in the middle of the meat smoking period. Differences in PAH emission could be explained by differences in the content of smoke during smoking, as well as by different concentrations of PAHs in smoke during wood combustion. Namely, smoke samples have been collected from traditional meat SHs, where smoking conditions were not electronically controlled. Temperature in the smoking chamber ranged between 18-20 °C. Total PAH emission in SH I, where distance between the point of smoke sampling and firebox was 2 m, was 6.7 mg m⁻³ and 7.4 mg m⁻³ (Tab. 1), measured with PUF and XAD-2 tubes, respectively. In SH II, where the distance between the point of smoke sampling and firebox was 5 m, total PAH emission was 2.4 mg m⁻³ and 4.3 mg m⁻³ (Tab. 2), collected with PUF and XAD-2 tubes, respectively.

Table 2: Average concentrations of PAHs [mg m⁻³] in beech wood smoke samples (n = 5) simultaneously collected with PUF and XAD-2 tubes from SH II^a and BaP equivalent concentration (BaP_{eq}) of PAHs [mg m⁻³]

Tab. 2: Durchschnittliche PAK-Gehalte [mg m⁻³] in Buchenholz-Räucherrauch (n = 5) bei simultaner Absorption in PUF- und XAD-2-Kartuschen in Räucherkerammer II und BaP-Toxizitäts-äquivalente (BaP_{eq}) der PAK [mg m⁻³]

PAH		PUF	XAD-2	TEF 1 ^b	TEF 2 ^c	BaP _{eq} 1 ^d [mg m ⁻³]		BaP _{eq} 2 ^e [mg m ⁻³]	
		(Mean \pm SD) [mg m ⁻³]	(Mean \pm SD) [mg m ⁻³]			PUF	XAD-2	PUF	XAD-2
4-ring	BcL	0.575 \pm 0.220	0.806 \pm 0.214	--	--	--	--	--	--
	BaA	0.278 \pm 0.093	0.611 \pm 0.097	0.1	0.005	0.028	0.061	0.001	0.003
	CHR	0.610 \pm 0.237	1.213 \pm 0.309	0.01	0.03	0.006	0.012	0.018	0.036
	5MC	0.043 \pm 0.012	0.082 \pm 0.017	--	--	--	--	--	--
5-ring	CPP	0.032 \pm 0.009	0.086 \pm 0.090	--	0.02	--	--	0.001	0.002
	BbF	0.194 \pm 0.064	0.363 \pm 0.077	0.1	0.1	0.019	0.036	0.019	0.036
	BjF	0.085 \pm 0.019	0.155 \pm 0.043	--	0.05	--	--	0.004	0.008
	BkF	0.058 \pm 0.012	0.109 \pm 0.034	0.1	0.05	0.006	0.011	0.003	0.005
	BaP	0.142 \pm 0.041	0.311 \pm 0.047	1	1	0.142	0.311	0.142	0.311
6-ring	DhA	0.021 \pm 0.006	0.034 \pm 0.008	5	1.1	0.105	0.169	0.023	0.037
	BgP	0.197 \pm 0.039	0.247 \pm 0.061	0.01	0.02	0.002	0.003	0.004	0.005
	IcP	0.120 \pm 0.032	0.216 \pm 0.050	0.1	0.1	0.012	0.022	0.012	0.022
	DeP	0.013 \pm 0.004	0.024 \pm 0.004	--	0.2	--	--	0.003	0.005
	DhP	0.003 \pm 0.001	0.003 \pm 0.001	--	1	--	--	0.003	0.003
	DiP	0.015 \pm 0.005	0.026 \pm 0.009	--	0.1	--	--	0.002	0.003
	DIP	0.004 \pm 0.001	0.008 \pm 0.002	--	1	--	--	0.004	0.008
Total emission	2.388	4.290							
Total BaP _{eq}					0.320	0.624	0.238	0.483	

^a The distance between the point of smoke sampling and firebox was 5 m in the smokehouse (SH) II;

^b TEF 1 described by NISBET and LaGOY 1992; ^c TEF 2 described by LARSEN and LARSEN 1998 (cit. BOSTRÖM *et al.* 2002); ^d BaP_{eq} 1 calculated using TEF 1; ^e BaP_{eq} 2 calculated using TEF 2

Table 3: Percentages of individual PAH compounds [%] to the sum contents of 16 EU PAHs in smoke from different smokehouses (SH) collected with PUF and XAD-2 tubes

Tab. 3: Anteile der einzelnen PAK-Verbindungen [%] zum Summengehalt der 16 EU-PAK in Räucherrauch aus verschiedenen Räucherarkammern, absorbiert mit PUF- und XAD-2-Kartuschen

		SH I PUF	SH II PUF	SH I XAD-2	SH II XAD-2
The percentage of each PAH in 16 EU PAHs, [%]					
4-ring	BcL	9.37	24.07	14.53	18.78
	BaA	9.23	11.63	15.46	14.23
	CHR	23.78	25.55	24.24	28.27
	5MC	1.48	1.79	1.58	1.90
5-ring	CPP	3.31	1.34	7.52	2.00
	BbF	24.36	8.11	7.99	8.46
	BjF	7.84	3.54	4.29	3.61
	BkF	6.27	2.42	3.20	2.54
6-ring	BaP	3.95	5.96	8.33	7.25
	DhA	2.58	0.88	0.79	0.79
	BgP	3.87	8.26	4.88	5.75
	IcP	3.09	5.03	5.55	5.02
	DeP	0.33	0.55	0.59	0.55
	DhP	0.04	0.10	0.07	0.07
	DiP	0.40	0.61	0.78	0.59
	DIP	0.11	0.15	0.21	0.19
sum of 4-ring		43.86	63.04	55.81	63.18
sum of 5-ring		48.31	22.25	32.12	24.64
sum of 6-ring		7.84	14.72	12.07	12.17
PAH ^a		61.31	51.25	56.02	58.21
PAH ⁸		77.14	67.84	70.43	72.31

^a PAH⁴ = (BaP + CHR + BaA + BbF); PAH⁸ = (BaP + BaA + BbF + BkF + BgP + CHR + DhA + IcP)

It was shown that XAD-2 tubes have a stronger PAH adsorption than PUF tubes. In SH I concentrations of 12 PAH were higher in XAD-2 than in PUF tubes. Only concentrations of four 5-ring PAHs (BbF, BjF, BkF and DhA) were higher in PUF

tubes. In SH II concentrations of all 16 EU PAHs were higher in XAD-2 tubes. In SH I, BbF is detected in the highest concentration in smoke samples collected with PUF tubes, followed by CHR and BcL.

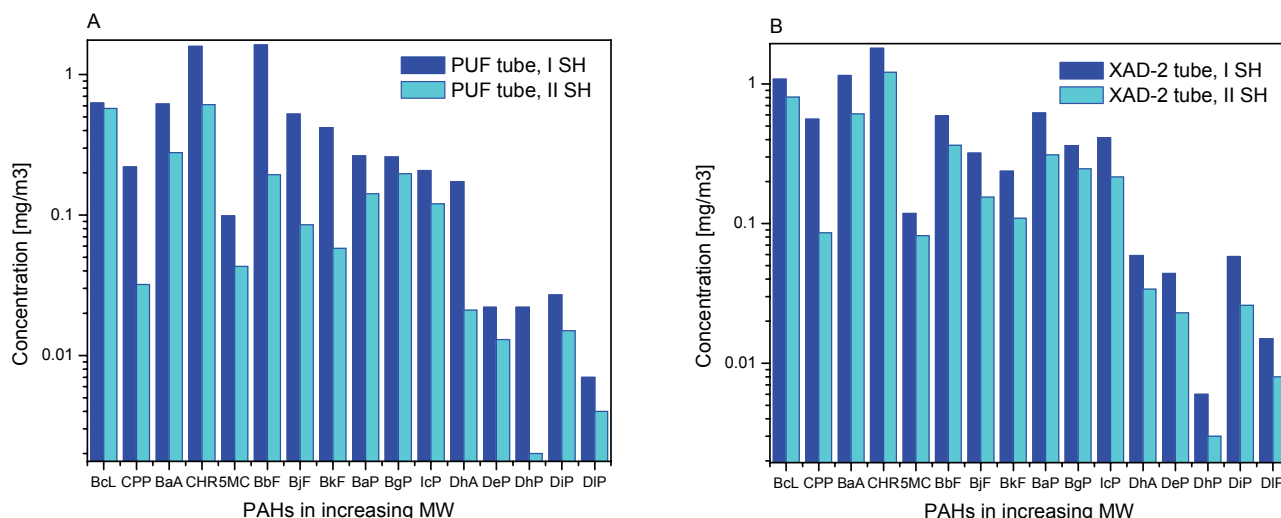


Fig. 1: Distribution of PAHs in smoke samples collected with PUF and XAD-2 tubes in two different smokehouses (SHs)

Abb. 1: Verteilung der PAK in Räucherrauch, absorbiert mit PUF- und XAD-2-Kartuschen in zwei unterschiedlichen Räucherarkammern

In case of XAD-2 tubes, the highest PAH concentrations (in decreasing order) were detected for CHR, BaA and BcL. In SH II the maximum concentrations, both in PUF and XAD-2 tubes, belonged to CHR, followed by BcL and BaA. Figure 1 shows the distribution of PAHs in smoke samples collected with PUF and XAD-2 tubes in two different SHs.

From the presented data it can be seen that BaP contributes with 4.0 % and 8.3 % to the total sum of 16 EU priority PAHs in PUF and XAD-2 smoke collecting tubes, respectively, in SH I. Detected values in PUF and XAD-2 tubes from SH II are 5.0 % and 7.2 %, respectively. Percentages of DIP in 16 EU PAHs are similar for the same tubes with smoke collected in different SHs (in average, PUF - 0.13 % and XAD-2 - 0.20 %). Percentages of the

sum contents of 4-ring, 5-ring and 6-ring PAHs in PUF and XAD-2 tubes are mostly decreasing with increasing ring number (Tab. 3). The presented results show that PAHs with a lower number of rings contribute with a higher percentage to the sum content of analysed PAHs. The obtained data indicate that distribution of PAH compounds depends on the molecular weight of the analysed PAHs. PAH compounds with lower molecular weight are transported for a longer distance away from the firebox than compounds with higher molecular weight during meat smoking process.

Concerning the fact that EFSA (EFSA, 2008) recommended investigation and discussion of the sum of "PAH4", as well as the sum of "PAH8" in food, as a more suitable indicator of PAH presence in food

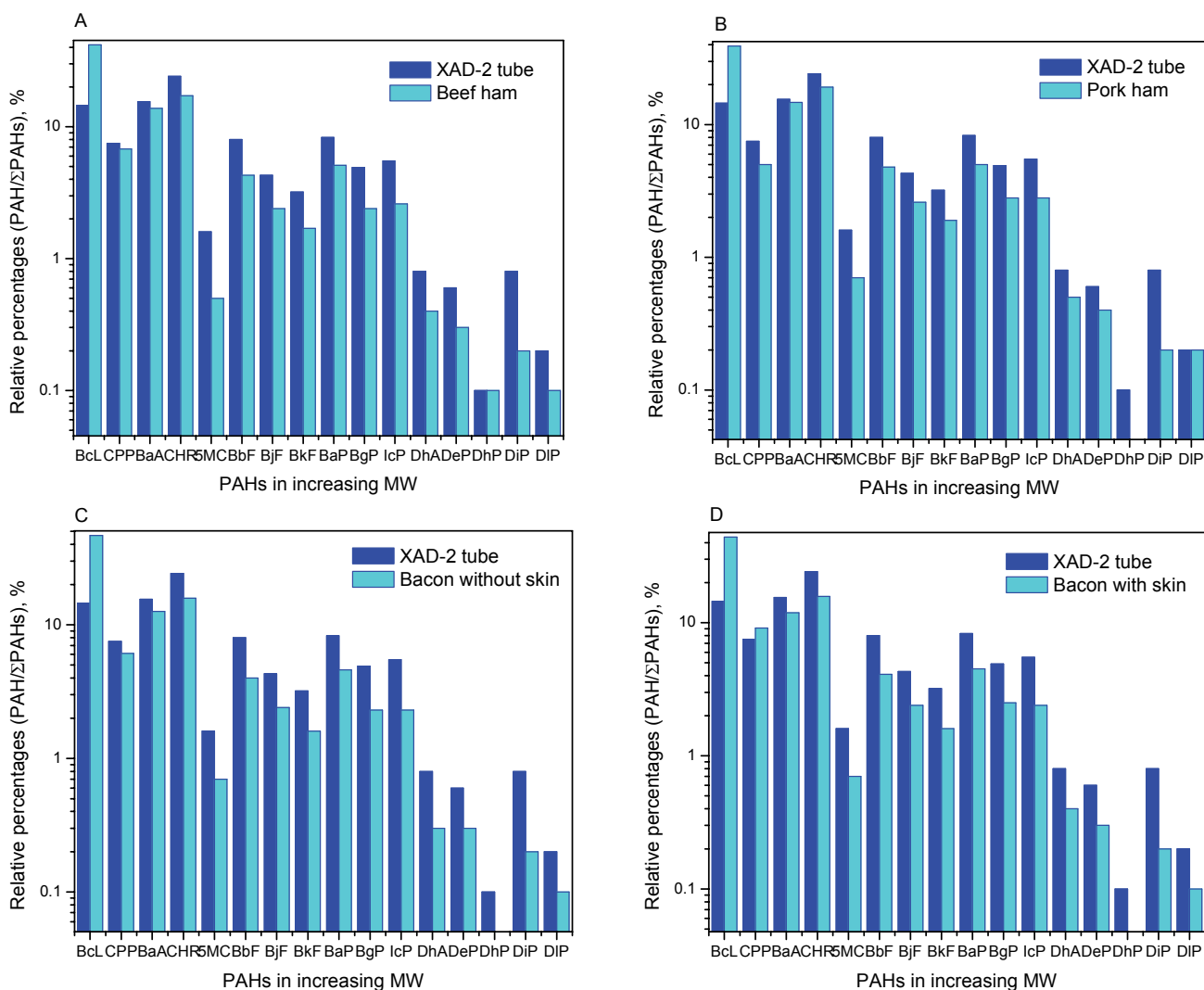


Fig. 2: PAH fingerprints for smoke and smoked meat products from smokehouse I (SH I)
 Abb. 2: PAK-Muster von Räucherrauch und geräucherten Fleischerzeugnissen in Räucherhammer I

than BaP only, the percentages of PAH4 and PAH8 in smoke used for meat smoking are also presented in this study (Tab. 3). In SH I, the percentages of "PAH4" to the sum content of 16 EU PAHs, smoke samples collected with PUF and XAD-2 tubes are 61 % and 56 %, respectively, while the mentioned percentages in SH II are 51 % and 58 %, respectively. PAH8 contributes with percentages in the range of 68-77 % (SH I: 77 % - PUF, 70 % -XAD-2; SH II: 68 % - PUF, 72 % - XAD-2) than "PAH4" to the total sum of 16 EU PAHs.

PAH fingerprints for smoke and smoked meat products

Considering the fact that XAD-2 tubes had higher PAHs capacity for smoke than PUF tubes, only smoke samples collected with XAD-2 tubes were considered for fingerprint evaluation. Figure 2 and 3 show PAH fingerprints for smoke and smoked meat products. During smoking, pork ham, beef ham, bacon without skin and bacon with skin have been placed in SH I, whereas cajna and sremaska sausages were placed in SH II.

Fingerprints for smoke and smoked meat products were determined by calculating the mean percentage contribution of the individual PAHs to the sum of 16 analysed PAH compounds.

Relative percentages of BcL are higher in all smoked meat products in comparison to smoke samples (Fig. 2, 3). Relative percentages of other analysed PAHs are higher in smoke than in smoked meat products, except for CPP in cajna and sremaska sausages. In all analysed samples a very similar pattern for the majority of analysed PAHs is observed. Concerning relative percentages of PAH with low molecular weight (CPP, BaA, CHR and 5MC) in both SHs, smoke samples and smoked meat products showed similar patterns. For PAH compounds with molecular weight (MW) 252 similar PAH patterns were observed. Relative percentages for all three benzofluoranthenes were increasing in the following order: BkF, BjF, BbF, both for smoke and smoked meat samples in both smokehouses. BaP showed similar relative percentages like BbF. In the SH I, BgP and IcP (PAHs with MW 276) had similar relative percentages, while the relative percentage of DhA (MW 278) was significantly lower. In SH II, decreasing of relative percentages could be noticed in the following order: BgP, IcP, DhA. For dibenzopyrenes, no correlations between smoke and beef ham, pork ham, cajna sausage and sremaska sausage were found in any SH, but similar fingerprints for dibenzopyrenes in smoke samples and bacon without skin, and bacon with skin were observed (Fig. 2C, 2D). If relative

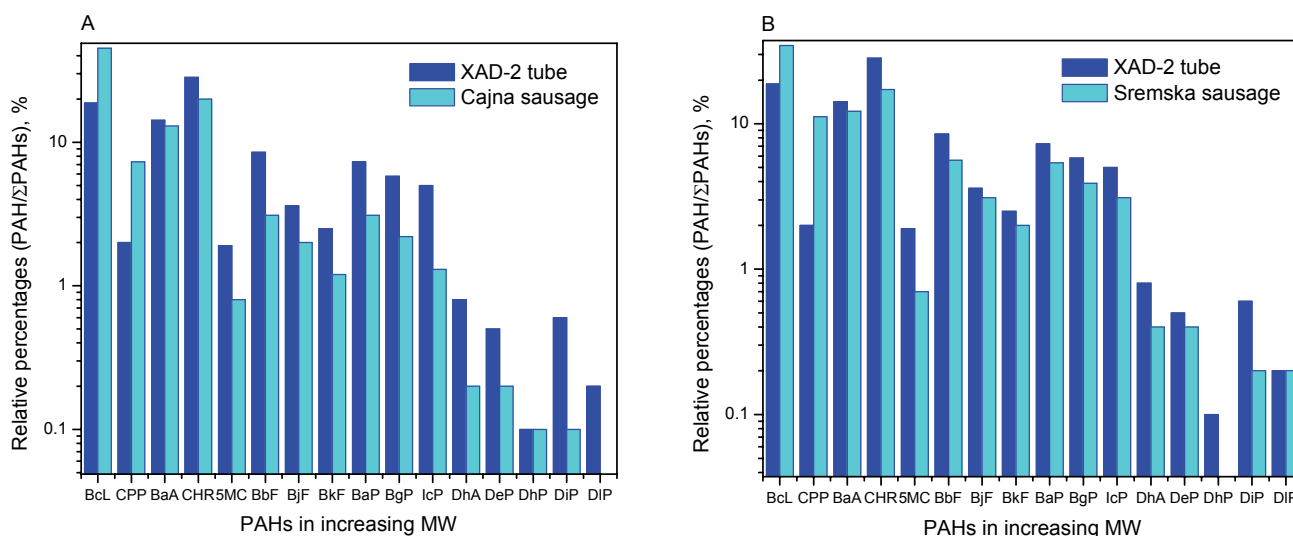


Fig. 3: PAH fingerprints for smoke and smoked meat products from smokehouse II (SH II)
 Abb. 3: PAK-Muster von Räucherrauch und geräucherten Fleischerzeugnissen in Räucherhammer II

percentages are compared in all investigated smoked samples from both SHs, the maximum relative percentage within the group of dibenzopyrenes belonged to DiP.

BaP equivalent concentrations for smoke

In the majority of studies BaP is used as a reference substance to express carcinogenic potency of PAHs, because this compound has carcinogenic potency 10-100 times higher than many other PAHs. The TEF approach is not scientifically valid, because of the lack of data from oral carcinogenicity studies on individual PAHs, their different modes of action and the evidence of poor predictivity of the carcinogenic potency of PAH mixtures based on the currently proposed TEF values (EFSA, 2008). Nevertheless in the present study TEFs were used in order to compare the contents of different PAH compounds by considering their different carcinogenic potencies. In order to assess the potential health risk of PAHs in smoke, concentrations of PAHs are transformed to BaP equivalent concentrations by using TEFs for PAHs, according to NISBET and LaGOY (1992) and LARSEN and LARSEN (1998) (cit. BOSTRÖM *et al.*, 2002) (Tab. 1, 2).

The total BaP_{eq} concentration in smoke samples collected with PUF tubes in SH I, where the distance between sample collecting point and firebox was 2 m, is 1.43 mg m⁻³, using TEFs according to NISBET and LaGOY (TEF 1) and 0.78 mg m⁻³, using TEFs according to LARSEN and LARSEN (TEF 2). In case of XAD-2 tubes total BaP_{eq} concentration is 1.17 mg m⁻³, using TEF 1 and 0.93 mg m⁻³, using TEF 2.

The total BaP_{eq} concentration in smoke samples collected with PUF tubes in SH II, where distance between sample collecting point and firebox was 5 m, is 0.32 mg m⁻³, using TEF 1 and 0.24 mg m⁻³, using TEF 2. In case of XAD-2 tubes total BaP_{eq} concentration is 0.62 mg m⁻³, using TEF 1 and 0.48 mg m⁻³, using TEF 2.

In SH II, the total BaP_{eq} value is about 2-fold higher in XAD-2 than in PUF smoke sample collecting tubes, taking into consideration TEF 1 and TEF 2 for expressing total BaP_{eq} concentration.

In smoke samples collected with XAD-2, total BaP_{eq} value is about 1.2 fold higher than for samples collected with PUF tubes, using TEF 2 for expressing total BaP_{eq} concentration in SH I. Opposite results are obtained for the same samples when total BaP_{eq} concentrations are calculated using TEF 1. Namely, total BaP_{eq} value is 1.2 fold higher in PUF than in XAD-2 smoke samples.

The total BaP_{eq} concentration in smoke samples collected in SH I is much higher than BaP_{eq} concentration for samples collected in SH II. Considering the fact that distances between smoke collecting points and fireboxes were 2 m and 5 m in smokehouses I and II, respectively, it could be concluded that smoking of meat at a higher distance from the firebox is more acceptable for protecting meat products from contamination with PAHs.

Conclusions

PAH concentrations in smoke samples from smokehouses are different in different tubes (PUF and XAD-2) and depend on the distance between sampling point and firebox. XAD-2 tubes have stronger PAH adsorptive properties than PUF tubes. PAH compounds with lower molecular weight are transported to a longer distance from the firebox than compounds with higher molecular weight during the meat smoking process. Generally, PAHs with a lower number of rings contribute with a higher percentage to the sum content of 16 EU priority PAHs.

In both SHs, BaP contribution to the total sum of 16 EU priority PAHs, is 4 % and 5 % in PUF tubes and 7 % and 8 % in XAD-2 tubes. The percentage contribution of DiP to the sum content of 16 EU PAHs is also depending on the used type of tube (PUF: 0.1 % and XAD-2 – 0.2 %). These results indicate that toxic effect of PAHs emission in atmosphere might be of great environmental concern.

Total BaP_{eq} concentration in smoke samples collected in SH I (PUF: 1.43 mg m⁻³, XAD-2: 1.17 mg m⁻³ calculated by using TEF 1, and PUF: 0.78 mg m⁻³, XAD-2:

0.93 mg m⁻³ calculated by using TEF 2) is much higher than BaP_{eq} concentration for samples collected in SH II (PUF: 0.32 mg m⁻³, XAD-2: 0.62 mg m⁻³ calculated using TEF 1, and PUF: 0.24 mg m⁻³, XAD-2: 0.48 mg m⁻³ calculated using TEF 2). Considering the fact that distances between smoke collecting points and fireboxes were 2 m and 5 m in SH I and II, respectively, it could be concluded that smoking of meat at a higher distance from the firebox is more acceptable for protecting meat products from contamination with PAHs and consequently for protecting consumers from intake of contaminated meat products.

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