

Comparison of patterns of 16 EU priority polycyclic aromatic hydrocarbons (PAHs) in the wood smoke as well as in smoked beef and pork ham

J.M. Djinic¹, A.R. Popovic², A.T. Spiric^{3*}, L.R. Turubatovic³ & W.M. Jira¹

¹Max Rubner-Institut (MRI), Federal Research Institute of Nutrition and Food, Analysis Division, E.-C.-Baumann-Str. 20, 95326 Kulmbach, Germany.

²Faculty of Chemistry, University of Belgrade, POB 51, 11158 Belgrade 118, PAK: 105305, Serbia.

³Institute of Meat Hygiene and Technology, Kacanskog 13, 11000 Belgrade, Serbia.

*E-mail: aurelija@inmesbgd.com.

Abstract

Smoked meat products are still produced in traditional way in Zlatibor region, Serbia. Beef and pork ham were smoked by beech wood smoke, both in traditional (TS) and industrial smokehouses (IS). Smoke samples were collected from both smokehouses using different types of tubes (PUF and XAD-2) during meat smoking. The sum of 16 EU priority PAHs in final smoked beef and pork ham was (µg/kg): beef ham - 3.9/TS, 1.9/IS; pork ham - 4.9/TS, 4.2/IS. The total emission of the analysed PAHs in smoke samples was (mg/m³): in PUF 1.1/TS, 3.8/IS and in XAD-2 0.9/TS, 11.0/IS. PAH fingerprints in smoke and smoked beef and pork ham were compared. Chrysene was found to be the most predominant PAH compound in smoke, both in PUF and XAD-2 tubes from TS, while benzo[c]fluorene (BcL) was the most predominant PAH in smoke from IS. For PAHs with lower MW (BcL to BaP) similar fingerprints between smoke-beef and smoke-pork ham were observed, while the fingerprints for dibenzopyrenes (MW=302) were different, both in TS and IS. BaP equivalent concentrations (BaP_{eq}) were calculated, both in smoke and smoked meat products.

Introduction

Polycyclic aromatic hydrocarbons (PAHs), organic compounds which consist of two or more condensed aromatic rings, are widespread in environment. These compounds are found in samples representative of the atmosphere, geosphere, hydrosphere etc. (Qiao *et al.*, 2008). PAH compounds from the incomplete combustion of organic matter are becoming the main source of atmosphere pollution.

Process of meat smoking in smokehouses is one of the main ways of meat contamination with PAH compounds. The PAH content of smoked foods depends on different parameters such as moisture content of the wood used for smoking, the temperature the wood attains during combustion and concentration of oxygen in the combustion chamber (Toth & Blaas, 1972). Investigations on the penetration of PAH compounds into the inside of smoked meat products showed that nearly 99% of all PAHs were found in the outer 22% of the total weight of a cooked sausage (Jira *et al.*, 2006).

Commission Regulation (No 1881/2006) provides maximum levels for benzo[a]pyrene in different food groups. The 16 EU priority PAHs (European Commission, 2005; JECFA, 2005) analysed in this study 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]pyrene (DhP), dibenzo[a,i]pyrene (DiP) and dibenzo[a,l]pyrene (DlP). BaP is usually used as a marker and indicator of carcinogenic PAHs. Toxic equivalency factors (TEFs) are usually used to denote the cancer potency of specific PAH compounds in relation to the carcinogenicity of BaP (Nisbet & LaGoy, 1992; Boström *et al.* 2002).

The aim of this study was comparison of patterns of 16 EU priority PAHs in smoked beef and pork ham as well as in wood smoke used for meat smoking.

Materials and methods

Beef and pork ham as well as smoke samples both from TS and IS were collected from Zlatibor region, Serbia, in February 2007. Packaging and transmission of meat samples followed Commission Directive 2005/10/EC (2005). Smoke samples, that was produced by beech wood combustion, were collected by a low volume pump (Proekos Aerotest AT 401) situated in the middle of SH. Smoke was adsorbed onto different adsorbent tubes (PUF and XAD-2).

Experimental procedure for analysis of PAH compounds in meat products was described in a previous publication (Djinovic *et al.*, in press). In brief, the following steps were applied both for meat and smoke samples: Soxhlet extraction or accelerated solvent extraction, ASE for extraction of lipophilic substances from smoke and meat samples, respectively; gel permeation chromatography, GPC for separation of higher molecular substances; solid phase extraction, SPE to remove more polar substances. Separation, identification and quantification of PAH were performed by gas chromatography/high resolution mass spectrometry (GC/HRMS; DFS High Resolution GC/MS, Thermo Fisher Scientific, Bremen, Germany).

Results and discussion

Table 1 shows the average concentrations of PAHs both in smoke and ham samples, as well as total BaPeq of PAHs. Figures 1, 2 show PAH fingerprints for smoke and smoked ham from TS and IS, respectively. The maximum sum content of 16 PAH (Σ PAH) for meat samples belonged to pork ham from TS ($4.9 \mu\text{g kg}^{-1}$) (Table 1). Ham samples from TS had higher PAH contents than samples from IS. Σ PAH concentration in smoke samples, adsorbed both on PUF and XAD-2 tubes, was higher in samples from IS. It was caused by different regime of smoking in smokehouses. Much higher Σ PAH concentration in smoke adsorbed on XAD-2 (11.0 mg m^{-3}) than on PUF (3.8 mg m^{-3}) tubes from IS indicate that XAD-2 tubes have higher capacity for PAH compounds. Presented PAH fingerprints were made using data of smoke concentration adsorbed on XAD-2 tubes (Figures 1, 2). BaP equivalent concentrations (BaPeq) in analysed smoked ham and smoke were presented in Table 1. Maximal BaPeq values in meat belong to beef ham from TS and pork ham from IS. Maximal BaPeq for smoke samples was calculated for smoke adsorbed on XAD-2 tubes from IS.

Table 1. The average concentration of PAHs [mg m^{-3}] in smoke samples (n=5) simultaneously collected with PUF and XAD-2 tubes from TS and contents of PAHs in the ham samples [$\mu\text{g kg}^{-1}$]; BaPeq of PAHs

	Σ PAH	Total BaPeq 1 ^a	Total BaPeq 2 ^b
Meat samples		[$\mu\text{g kg}^{-1}$]	
Beef ham, TS	3.9	0.43	0.45
Beef ham, IS	1.9	0.16	0.19
Pork ham, TS	4.9	0.31	0.26
Pork ham, IS	4.2	0.46	0.41
Smoke samples		[mg m^{-3}]	
PUF, TS	1.1	0.17	0.11
PUF, IS	3.8	0.58	0.42
XAD-2, TS	0.9	0.11	0.09
XAD-2, IS	11.0	1.68	1.31

^aBaPeq 1 calculated using TEF 1 described by Nisbet and LaGoy 1992

^bBaPeq 2 calculated using TEF described by Larsen and Larsen 1998 (cit Boström et al.

2002)

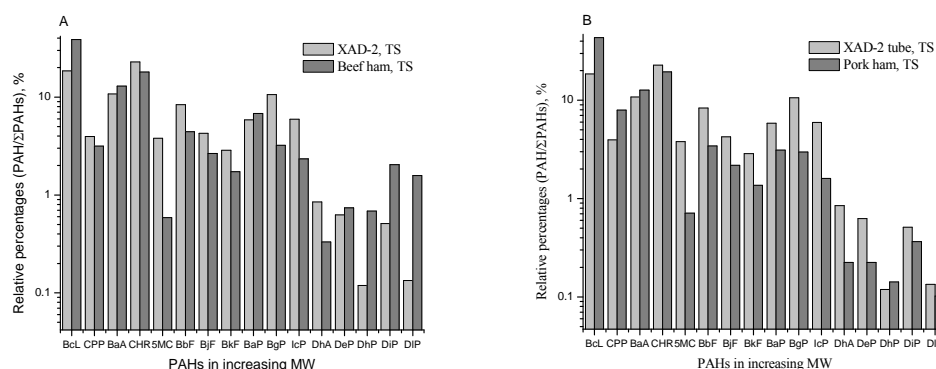


Figure 1. PAH fingerprints for smoke and smoked beef and pork ham from traditional smokehouses, TS.

Similar PAH fingerprints exist between smoke-beef and smoke-pork ham both from TS and IS for most of the 16 EU priority PAH compounds (Figures 1, 2). For BaP and BgP in TS and IS, respectively as well as for dibenzopyrenes (DeP, DhP, DiP and DIP) both in TS and IS no similar PAH fingerprints were existing. The most predominant PAH in ham samples both from TS and IS was BcL. CHR was found to be the

most predominant PAH compound in smoke from TS, while BcL was the most predominant PAH in smoke from IS (Figures 1, 2).

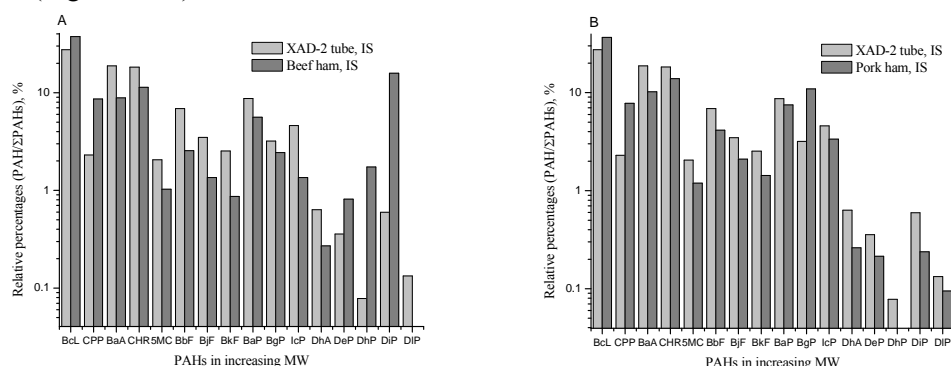


Figure 2. PAH fingerprints for smoke and smoked beef and pork ham from industrial smokehouses, IS.

Conclusions

Regime of meat smoking had influence on Σ PAH content in smoked ham and Σ PAH concentration in smoke samples, as well as on distribution of PAH compound, concerning the fact that for most of analysed PAH compound very similar PAH fingerprints exist between smoke-beef and smoke-pork ham in the same smokehouse.

Acknowledgements

This work was supported by the Ministry of Science, Republic of Serbia (Grant No. 146008). The authors are grateful to Spomenka Zagorac, Gorica Carapic and Miljko Nesanovic from meat industry Zlatibor, Cajetina, Serbia for all the help they have given us.

References

- Barthe, M., Pelletier, E., Breedveld, G.D., & Cornelissen, G., 2008. Passive samplers versus surfactant extraction for the evaluation of PAH availability in sediments with variable levels of contamination. *Chemosphere*, 71, 1486-1493.
- Boström, C.E., Gerde, P., Hanberg, A., Jernstrom, B., Johansson, C., Kyrklund, T., Rannug, A., Tornqvist, M., Victorin, K., Westerholm, R., 2002. Cancer risk assessment, indicators, and guidelines for polycyclic aromatic hydrocarbons in the ambient air. *Environmental Health Perspectives* 110 (Suppl. 3), 451-488.
- Djinovic, J., Popovic, A., Jira, W., 2008. Polycyclic aromatic hydrocarbons (PAHs) in different types of smoked meat products from Serbia, *Meat Science*, doi: 10.1016/j.meatsci.2008.01.008.
- European Commission, 2005. Commission Recommendation 2005/108/EC of 4 February 2005 on the further investigation into the levels of polycyclic aromatic hydrocarbons in certain foods. *Official Journal of the European Union*, L34, 43-45.
- European Commission, 2006. Commission Regulation No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs. *Official Journal of the European Union*, L364, 5-24
- JECFA, 2005. Joint FAO/WHO Expert Committee on Food Additives. (2005). Summary and Conclusion. Sixty-Fourth meeting, Rome, 8-17 February, JECFA/64/SC. <http://www.who.int/ipcs/food/jecfa/summaries/en/>.
- Jira, W., Ziegenhals, K., Speer, K., 2006. PAH in smoked meat products according to EU standards. *Fleischwirtschaft International*, 4, 11-17.
- Nisbet, I.C.T., LaGoy, P.K., 1992. Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). *Regulatory Toxicology and Pharmacology* 16, 290-300.
- Qiao, M., Huang, S., & Wang, Z. 2008. Partitioning characteristics of PAHs between sediment and water in a shallow lake. *Journal of Soils and Sediments*, 8, 69-73.
- Toth, L., Blaas, W., 1972. The effect of smoking technology on the content of carcinogenic hydrocarbons in smoked meat products. II. Effect of smoldering temperature of wood and of cooling, washing and filtering of smoke. *Fleischwirtschaft*, 52, 1419-1422.