

Polycyclic aromatic hydrocarbons (PAHs) in traditional smoked dairy products from Campania (Italy)

Teresa Cirillo, Nunzia Milano, Renata Amodio Cocchieri

Dipartimento di Scienza degli Alimenti, Università degli Studi di Napoli "Federico II", Napoli, Italy

Correspondence to: Teresa Cirillo-Dpt. Scienza degli Alimenti-Via Università, 100- 80055 Portici (NA). E-mail: tcirillo@unina.it

Abstract

The smoked *mozzarella* and *caciocavallo* cheeses occupy a significant area among the traditional products in the Campania region. Smoked and non-smoked *mozzarella* and *caciocavallo* cheeses were screened for the presence of polycyclic aromatic hydrocarbons (PAHs). Total PAH concentration in non-smoked *mozzarella* ranged from 59.11 to 160.05 $\mu\text{g kg}^{-1}$ wet weight (w.w.) and in that smoked from 67.49 to 399.90 $\mu\text{g kg}^{-1}$ w.w. The total PAH content in non-smoked *caciocavallo* was between 36.70 and 248.59 $\mu\text{g kg}^{-1}$ w.w.; in the smoked cheese, it varied from 72.52 to 1643.18 $\mu\text{g kg}^{-1}$ w.w. The benzo(a)pyrene (BaP) values in all cheeses smoked by liquid smoke were higher than the permissible limit for BaP of 0.03 $\mu\text{g kg}^{-1}$ for foods aromatised with liquid smoke.

Key words: PAHs, smoked cheese

Introduction

Smoking is one of the oldest practices used for the preservation and aromatisation of foods, as the smoke is able to inactivate enzymes and microorganisms and to give foods a special organoleptic and sensory profile. It consists on submitting foodstuffs to the smoke generated by thermal pyrolysis of a certain kind of wood during which there is limited access of oxygen.

The composition of the smoke is influenced by the characteristics of the wood used; the type of smoke generator; the combustion temperature and the oxidizing power of the process environment. Smoke contains in the solid phase tars and ashes, on which are adsorbed many organic compounds of high molecular weight, as polycyclic aromatic hydrocarbons (PAHs), and in the vapor phase formic aldehyde and volatile esters of organic acids, chetons, phenols, carbonyls, pyrazines, pyrrols and furane derivatives. The temperature of the smoke generally plays a very important role on the composition of the solid phase. The amount of PAHs in smoke increases linearly with the pyrolysis temperature within the interval of 400-1000°C. Therefore the smoke can be a significant source of food contamination and the amount and the type of PAHs present in the smoked foods can represent a problem for consumer safety.[1,2] The highest concentration of PAHs is produced at the end of the smoking process, then it decreases due to light decomposition and interaction with present compounds. However, PAHs also penetrate into smoked products, where they are protected from light and oxygen, and the concentration stabilizes at a certain constant level. To control PAH contamination, the use of smoking flavour agents

(SFAs) is becoming popular to aromatize food products. These agents are also preferred for the reproducibility of a better taste. SFAs are produced from condensed smoke. Because of the purification process, the use of SFAs is generally considered to be less of a health concern than the traditional smoking process. However, these aromas are not completely free from PAH contamination.[3]

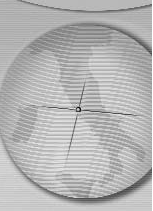
Benzo(a)pyrene (BaP) was chosen as a general indicator of total PAHs presence in smoked foods. The maximum acceptable concentration of 1 $\mu\text{g kg}^{-1}$ BaP in smoked foods was set in Germany, Italy, Austria, Switzerland, Slovak Republic and Czech Republic. For foods aromatised with SFA the EU set a maximum permissible limit for BaP of 0.03 $\mu\text{g kg}^{-1}$ in the Directive 88/388.[4]

In the Campania Region, among a large number of traditional foods, smoked *mozzarella* and *caciocavallo* occupy a significant area of the cheese craft production; the pyrolysis techniques adopted are now quite empirical giving place to a variability in the composition of the smoke and, therefore, in the characteristics of the smoked products.

The aim of the present study was to evaluate the levels of the PAH contamination in the traditional smoked dairy products from the Campania Region.

Materials and methods

Twenty-eight samples of the milk used in the cheese making of white *mozzarella* (seven samples), smoked *mozzarella* (seven samples), white *caciocavallo* (seven samples) and smoked *caciocavallo* (seven samples) were collected from craft producers in the Campania Region (Italy)



during the spring and summer of 2003 and the techniques of the smoking process applied were registered. The cheese samples were analysed with and without the external surface.

The samples, after alkaline hydrolysis with aqueous ethanolic KOH, were extracted in hexane and the extracts purified by ethylethere/hexane elution on silica gel. The eluates were dried under vacuum, 0.5 ml of acetonitrile were added and 20 µl were used for the PAH analysis; 16 priority PAHs pollutants {acenaphthene [AC] acenaphthylene [ACEN]; anthracene [ANT]; benzo(a)anthracene [B(a)A]; benzo(b) fluoranthene [B(b)F]; benzo(k) fluoranthene [B(k)F]; benzo(a)pyrene [B(a)P]; dibenzo(a,h) anthracene [DBA], fluoranthene [FLUO]; fluorene [FLU]; indeno (1,2,3-c,d)pyrene [IND]; naphthalene [NAP]; phenanthrene [PHE]; pyrene [PY]; benzo(g,h,i)perylene[BPE]} were simultaneously separated by high performance liquid chromatography [HPLC] and detected by UV at 254 nm.[5] The detection limits ranged from 0.01 µg kg⁻¹ wet weight (w.w.) for anthracene [ANT] to 0.5 µg kg⁻¹ w.w. for acenaphthylene [ACEN]. Recovery levels ranged from 65% to 90%.

Results

The concentration of total PAHs in milk varied from 11.92 to 102.37 µg kg⁻¹ w.w. The total PAHs in non-smoked *mozzarella* ranged from 59.11 to 160.05 µg kg⁻¹ w.w. and in that smoked from 67.49 to 399.90 µg kg⁻¹ w.w. The total PAH content in non-smoked *caciocavallo* was between 36.70 and 248.59 µg kg⁻¹ w.w.; in the smoked cheese it varied from 72.52 to 1643.18 µg kg⁻¹ w.w. (Table 1).

Among the smoked samples (*mozzarella* and *caciocavallo*) 66% were obtained by the wood smoke and 34% employing liquid smoke.

The PAH content in *mozzarella* and *caciocavallo* smoked by wood smoke varied from 67.49 to 1643.18 µg kg⁻¹ w.w. (median value 173.50 µg kg⁻¹ w.w.); in cheeses smoked by liquid smoke PAHs ranged between 108.12 and 695.23 µg.kg⁻¹ w.w. (median value 209.88 µg kg⁻¹ w.w.) [Table 2].

These results show that under the applied conditions the wood smoke process produces a large variation in the concentrations of total PAH, but the median value is significantly lower (p< 0.05) than that observed in the *mozzarella* and *caciocavallo* obtained by the liquid smoke immersion process. Furthermore, considering the *mozzarella* samples analysed with and without the external surface, the total PAH concentrations ranged between 83.30 and 693.20 µg kg⁻¹ w.w. (median value 527.80 µg kg⁻¹ w.w.), and between 67.50 and 184.40 µg kg⁻¹ w.w. (median 167.85 µg kg⁻¹ w.w.) respectively, in those obtained by wood smoke, and from 200.90 to 640.80 µg kg⁻¹ (median value 235.45 µg kg⁻¹ w.w.) and from 108,10 to 399,90 µg.kg⁻¹ w.w. (median value 172.70 µg kg⁻¹ w.w.) in those smoked by liquid smoke (Table 3).

In *mozzarella* smoked by liquid smoke 25% of the samples were contaminated by Benzo(a)pyrene (BaP) at a mean level of 0.41 ± 0.15 µg kg⁻¹ w.w. (with and without the external surface). These BaP concentrations are higher than the BaP EU admissible limit (0.03 µg kg⁻¹ w.w.).[4]

Table 1. Contents of PAHs (µg kg⁻¹ w.w.) in non smoked and smoked cheeses.

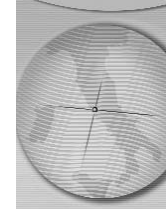
Samples	PAHs (µg kg ⁻¹ w.w.)					
	Mozzarella Cheese			Caciocavallo Cheese		
	Mean ± SD	Median	Range	Mean ± SD	Median	Range
Non-Smoked	118.45 ± 35.35	129.45	59.11 - 160.05	122.5 ± 69.70	124.78	36.70 - 248.59
Smoked	170.30 ± 86.54	163.31	67.49 - 399.90	479.50 ± 555.28	216.29	72.52 - 1643.18

Table 2. Contents of PAHs (µg kg⁻¹ w.w.) in cheeses obtained with different smoking techniques .

Cheese	PAHs (µg kg ⁻¹ w.w.)	
	Median	Range
Wood smoke	173.50	67.49 - 1643.18
Liquid smoke	209.88	108.12 - 695.23

Table 3. Contents of PAHs (µg kg⁻¹ w.w.) in smoked mozzarella cheese obtained by wood and liquid smoke analysed with and without the external surface.

Mozzarella Cheese		PAHs (µg kg ⁻¹ w.w.)	
		Median	Range
Wood smoke	With the external surface	527.80	83.30 - 693.20
	Without the external surface	167.85	67.50 - 184.40
Liquid smoke	With the external surface	235.45	200.90 - 640.80
	Without the external surface	172.70	108.10 - 399.90



The results found in milk and in non-smoked dairy products confirm that the PAHs are ubiquitous environmental pollutants. The smoking process increases significantly their levels in the cheeses, particularly in the external surface both in *mozzarella* and *caciocavallo*. The consumption of the cheeses without the external surface would be advisable in order to reduce the risks associated with such foods.

References

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