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Polycyclic aromatic hydrocarbons in smokehouses

by Lars Nordholm, PhD, Inge-Merete Espensen, Hanne S Jensen, Erik Holst, PhD¹

NORDHOLM L, ESPENSEN I-M, JENSEN HS, HOLST E. Polycyclic aromatic hydrocarbons in smokehouses. *Scand J Work Environ Health* 12 (1986) 614–618. The level of exposure to polycyclic aromatic hydrocarbons (PAH) from smoking kilns in Danish smokehouses was determined. Of 60 smokehouses curing fish with hot smoke from smoldering alder chips, 10 companies were selected for the analysis of workzone air. The amount of PAH, determined as the sum of 11 selected compounds, varied from 2.2 $\mu\text{g}/\text{m}^3$ to 2 472 $\mu\text{g}/\text{m}^3$ above the kiln doors. Samples taken approximately 2 m in front of the kiln doors contained 0–19.2 $\mu\text{g}/\text{m}^3$.

Key terms: high-performance liquid chromatography, diode-array detection, curing smoke, work environment, smokehouse, PAH, benzo(a)pyrene.

Smoke curing is one of the oldest preservation processes. The classical way of performing this process is by placing the foodstuff over smoldering wood. Depending on the kind of foodstuff, either hot-smoke curing or cold-smoke curing is used. For cold-smoke curing, which is typically used for, for instance, sea trout, salmon or various kinds of meat, sawdust is used for smoke generation. In Denmark hot-smoke curing is mainly used for eel, herring, and mackerel, and chip-ped wood (alder or sometimes beech) is used for smoke generation. While hot-smoke curing is a process that lasts a maximum of 3 or 4 h, cold-smoke curing will typically last for at least 12 h. The presence of smoke in the work area will typically be the most pronounced during hot-smoke curing. Today, the smoke curing of especially meat products and salmon is mainly performed in modern smoking kilns of high technology and under strictly controlled temperature, moisture, and smoke generation, where also the exposure in the work area is minimized. But the classical smoking method is still widely used in Danish smokehouses. It is claimed to give tastier results than the modern technique, and also the fact that many smokehouses are situated in tourist areas may play an important role. The generation of smoke by smoldering takes place at temperatures which are optimum for the formation of polycyclic aromatic hydrocarbons (PAH) (7). It has been known for many years that the burning of wood produces a considerable amount of PAH, and reviews concerning the presence of PAH in curing smoke are also classical (6, 7). It is, however, the presence of PAH in smoked foodstuff which has attracted the most attention. Smoked food contributes considerably to the oral intake of PAH (4, 6, 7). To our knowledge studies concerning the exposure of smokehouse workers to PAH are rather scarce. Lately, however, Colmsjo

et al (3) investigated the content of PAH in a smokehouse by taking samples inside and just outside the kiln. The authors considered the process to be cold-smoke curing because the temperature of the smoke did not exceed 30°C, although alder chips were used as fuel. A considerable amount of methylphenanthrenes was found in the smoke, while PAH of higher molecular weight were below the detection limits.

Denmark has too few smokehouses to provide sufficient information for epidemiologic studies on cancer related to work in smokehouses. A related type of exposure is found in Finnish smoke saunas (5). Häsänen et al (5) assumed that the PAH exposure from this type of sauna, common in Finnish rural areas, may contribute to the unusually high incidence of lung cancer in these areas in comparison to urban areas. In their study 18 PAH compounds were measured, the total PAH level being 170–1 550 $\mu\text{g}/\text{m}^3$ [benzo(a)pyrene 4.6–20 $\mu\text{g}/\text{m}^3$] in the smoke saunas.

In the present study we have determined the level of PAH concentrations in a representative part of Danish smokehouses where classical hot-smoke curing takes place. Furthermore, results from two smokehouses using modern controlled kilns with separate smoke generators were included.

Materials and methods

Smokehouses

Ninety smokehouses found through the Danish Central Occupation Register and through the telephone book were contacted, by telephone, for information about their smoke curing techniques. Only companies which were registered as smokehouses and companies listed as such in the telephone book were included. Smoke curing in slaughterhouses was not included in the investigation. Sixty smokehouses used the classical technique of smoldering wood beneath the foodstuff for hot-smoke curing. Several others used this technique for cold-smoke curing, but, since it is our

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experience that hot-smoke curing produces the highest concentration of smoke in the work area, only this procedure was intensively investigated in the present work.

Air samples were taken in 10 smokehouses, mainly situated in Zealand. All smokehouses used the classical technique of smoldering wood beneath the food-stuff for hot-smoke curing. Smoking kilns were, in all cases, built into a wall and provided with ventilation in the wall or the ceiling above. Usually one or two workers tended the kilns either full- or part-time. Room sizes varied but were, as a rule, dependent on the number of smoking kilns. Alder chips were used in all cases. Results from two modern smoking kilns treating salmon and pork, respectively, were included for comparison.

Sampling

The method used for sampling and extraction was a modification of a method developed by Andersson et al (1). The sampling equipment consisted of a 37-mm glass fiber filter (Millipore AP 4003-705) placed in a standard cassette of polystyrene for the collection of particulate PAH. The filter was, by use of a 10-cm tube made of polyvinyl chloride, connected in series to a double-zone styrene-divinylbenzene adsorption tube (ORBO 43 from Supelco, Gland, Switzerland) for the collection of gaseous phase PAH. Air was sucked through the system at a rate of 1.9 l/min with a DuPont pump (DuPont Constant Flow Sampler model P 2500, Wilmington, Delaware, United States). Whenever possible 500 l of air was sampled. Samples were taken just above each kiln door. Two samples were taken in the workzone in front of the kilns (usually at a height of about 2 m in order not to disturb the work). Personal samplings were omitted because of too big a difference in the smokehouses as to the work routines of the individual workers. Because of an excessive amount of particles sampled, it was often not possible to collect more than 100–200 l of air above the kiln doors. All sampling was performed with the filter cassettes wrapped in aluminum foil for protection against light. Samples were placed in a refrigerator until the extraction could be performed (maximum overnight).

Instrumentation

High-performance liquid chromatography was performed with two model 6000A pumps, a WISP 710B autosampler, a model 720 system controller and a model 730 data module, all from Waters (Waters Associates Inc, Milford, United States). Detection was carried out with a Waters model 440 absorbance detector (254 nm) and a Hewlett-Packard 1040A diode-array detector with the aid of a Hewlett-Packard HP 85 and a Hewlett-Packard 9121 disc drive (Hewlett-Packard, Waldbronn, Federal Republic of Germany). The column (250 × 4.6 mm inner diameter) was a Supelcosil LC-PAH column (5- μ m packing) protected with a Wa-

ters guard column packed with Bondapak C₁₈/Corasil (37–50 μ m). The mobile phase was acetonitrile-water (2 : 3) the first 5 min, 5–25 min a linear gradient to 100 % acetonitrile, 25–40 min 100 % acetonitrile. The flow rate was 1 ml/min, and the injection volumes were 10–50 μ l.

Peaks were identified through comparison of ultraviolet spectra in the range 210–400 nm with standard ultraviolet spectra. The Waters 440 ultraviolet detector was used for quantitation (manual peak-height measurements).

Chemicals

The acetonitrile used was LiChrosolv (Merck, Darmstadt, Federal Republic of Germany). Every new batch was checked for excessive ultraviolet absorbance around 254 nm.

All water was obtained from a Milli-Q water-purification system (Millipore).

A PAH standard solution containing naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(ghi)perylene, and indeno(1,2,3-cd)pyrene was purchased from Supelco.

Technical potassium permanganate and oxalic acid were used for treating glassware contaminated with carcinogens.

Analysis

Filters and both tube zones were each ultrasonically extracted (1 h) with 10 ml of acetonitrile in 25-ml Erlenmeyer flasks sealed with laboratory film. Ice was added to the ultrasonic bath to prevent excessive heating. The extracts were filtered through 0.45- μ m HV-filters (Millipore) before the high-performance liquid chromatography.

Each sample was examined for the 16 priority pollutant PAH through comparisons with standard chromatograms and ultraviolet spectra in the range 210–400 nm (diode-array detection).

Recovery studies were performed and standard curves determined for unexposed filters and tubes spiked with at least three to four concentration levels for each PAH component (generally six determinations at each level).

Results

The detection limits determined for the 16 priority pollutant PAH with the Waters 440 detector and the maximum concentrations observed in the smokehouses are presented in table 1. The detection limits are valid for 500-l samples and 50- μ l injections (signal/noise = 3). Because of the excessive adsorption of smoke particles it was sometimes impossible to collect more than

Table 1. Detection limits of the polycyclic aromatic hydrocarbons and the maximum concentrations observed in the smokehouses.

Compound	Detection limit ($\mu\text{g}/\text{m}^3$) ^a	Maximum concentration ($\mu\text{g}/\text{m}^3$) observed in the smokehouses ^b
Naphthalene	1	2 918 ^c
Acenaphthylene	1	.. ^d
Acenaphthene	Not determined	.. ^d
Fluorene	0.1	166
Phenanthrene	0.04	746
Anthracene	0.02	188
Fluoranthene	0.1	460
Pyrene	0.2	574
Benzo(a)anthracene	0.04	92
Chrysene	0.03	78
Benzo(b)fluoranthene	0.06	64
Benzo(k)fluoranthene	0.08	.. ^e
Benzo(a)pyrene	0.2	78
Dibenzo(a,h)anthracene	0.4	59
Benzo(ghi)perylene	0.4	86
Indeno(1,2,3-cd)pyrene	0.2	..

^a Valid for a 500-l sample.

^b Sum of the particulate and gas phase.

^c Breakthrough was observed in several cases.

^d Not determined due to interference in most samples.

^e No observations.

Figure 1. High-performance liquid chromatogram of an extract of polycyclic aromatic hydrocarbons from a spiked glass-fiber filter. For information on the experimental conditions, see the text. (Peak identification: 1 naphthalene, 2 acenaphthylene, 3 acenaphthene, 4 fluorene, 5 phenanthrene, 6 anthracene, 7 fluoranthene, 8 pyrene, 9 benz(a) anthracene, 10 chrysene, 11 benzo(b)fluoranthene, 12 benzo(k)fluoranthene, 13 benzo(a)pyrene, 14 dibenzo(a,h)anthracene, 15 benzo(ghi)perylene, 16 indeno(1,2,3-cd)pyrene) (Rel Int = relative intensity, MeCN = acetonitrile)

100–200 l of air without a drop in the sampling flow rate. For positive identification, with the diode-array detector, about five times the detection limits is necessary.

Recoveries from the spiked filters and tubes were in the range of 90–100 % for most compounds [about 75 % for benzo(a)pyrene]. A chromatogram of a spiked filter is shown in figure 1. Linearity of standard curves was found for all compounds in the concentration ranges observed in the smokehouses. Typical chromatograms are shown in figures 2 and 3. The

Figure 2. High-performance liquid chromatogram of an extract of polycyclic aromatic hydrocarbons from a glass-fiber filter exposed to curing smoke. The peak identification and abbreviations are the same as in figure 1.

Figure 3. High-performance liquid chromatogram of an extract of polycyclic aromatic hydrocarbons from an ORBO43 tube exposed to curing smoke. The peak identification and abbreviations are the same as in figure 1. An asterisk indicates excessive interference from other components in the sample.

Figure 4. Typical profile of the polycyclic aromatic hydrocarbons in the air above the kiln doors. Acenaphthene and acenaphthylene are not included due to interference. Apart from the compounds shown in this diagram, dibenzo(a,h)anthracene and benzo(ghi)perylene were found in some samples. (Conc = concentration)

Table 2. Amount of polycyclic aromatic hydrocarbons (PAH) found in 10 Danish smokehouses. Total PAH include both the gas phase and particulate phase. Naphthalene, acenaphthylene, acenaphthene, fluorene, and fluoranthene are not included in the total PAH.

Smoke-houses	Total PAH					
	Above kiln doors			In front of kilns		
	Number of samples	Mean	Concentration range ($\mu\text{g}/\text{m}^3$)	Number of samples	Mean	Concentration range ($\mu\text{g}/\text{m}^3$)
1	4	34.0	18.8–50.2	0	..	..
2	7	1 487	870–2 472	2	1.9	1.9–1.9
3	5	112	21.2–162	2	1.4	1.3–1.4
4	1	2.2	2.2	1	0.4	0.4
5	4	35.6	11.8–65.1	2	0.2	0–0.3
6	1	41.9	41.9	2	0.4	0.2–0.6
7	3	126	61.4–218	2	15.1	10.9–19.2
8	1	18.0	18.0	2	0.3	0.1–0.4
9	3	136	52.3–213	2	0	0
10	1	87.8	87.8	2	1.7	1.7–1.7

PAH profile of the air above the kiln doors is presented in figure 4. The air approximately 2 m in front of the smoking kilns was dominated by two- and three-ring compounds. In a few cases also higher PAH were detected.

For convenience a simple extraction procedure was employed. This method gave rise to problems with ambiguous determinations of acenaphthene, acenaphthylene, fluorene, and fluoranthene in some samples due to interfering compounds. Furthermore a breakthrough of naphthalene was observed in several cases. Therefore for the comparison of data these compounds were not included in the total PAH (table 2).

In the two smokehouses using modern technology, only small amounts of the low-boiling PAH were observed, ie, naphthalene < $15 \mu\text{g}/\text{m}^3$, fluorene < $2.9 \mu\text{g}/\text{m}^3$, phenanthrene < $0.4 \mu\text{g}/\text{m}^3$, anthracene < $0.1 \mu\text{g}/\text{m}^3$.

Discussion

Colmsjö et al (3) reported that both the vapor phase and the particulate phase of a sample derived from curing smoke are dominated by phenanthrene and methylphenanthrenes when the smoke temperature is below 30°C and alder chips are used for smoke production. The present study indicates, however, that smoldering alder chips at smoke temperatures of 50 – 70°C results in the formation of other PAH, as seen in figures 2 and 3, although phenanthrene is still one of the dominating peaks in the chromatograms. Major unidentified peaks were investigated for similarity with the ultraviolet spectrum of phenanthrene, but generally no indications of the presence of methylphenanthrenes were found.

The PAH profile of the air above the smoking kilns showed a strikingly high amount of particulate PAH, including low-boiling compounds. This finding is different from the profile seen in studies of other work environments (1, Nordholm, unpublished results). An explanation might be that the process is a kind of sup-

pressed combustion giving a relatively large amount of particles in the smoke.

Air samples taken a distance away from the smoking kilns showed that the concentrations of particulate PAH drop dramatically with distance to the kilns. With respect to PAH exposure, inspection and stoking of the kilns are therefore much more unhealthy than just staying in the room.

The results from the two smokehouses with smoke-generators showed, as expected, very low PAH concentrations in comparison to smokehouses using the classical technique. The smoke generation is, in this type of smokehouse, controlled, and smoke is automatically removed before the kilns are opened.

As seen in table 2, there were large variations in the PAH concentrations between smokehouses, while the variations between smoking kilns were less pronounced. In all the smokehouses except those supplied by smoke generators, the removal of smoke from the work environments took place through air shafts over the smoking kilns, generally by means of a ventilator. The presence of much smoke in some of the workzones was possibly due to a combination of poor chimney draw and leaky kiln doors. Some directors of smokehouses are not very keen on altering these conditions because the result could lead to alterations in the product quality of the smokehouses concerned, and therefore attempts to remove the smoke after it has penetrated the work environment are more often seen. However, when new smokehouses are established, we have seen that it is possible to exclude the smoke almost completely from the work environment, even where the classical smoke curing technique is still performed. Smokehouse number 4 in table 2 is an example of such a place.

In conclusion the exposure of smokehouse workers to PAH varies, and in the worst cases the amount of PAH is comparable to, for instance, the high exposures found in some aluminum and coke plants (2). The largest PAH concentrations were found in smokehouses with leaky kiln doors and those in which the workers, in busy periods, did not efficiently evacuate

the smoke through the chimney before the kiln doors were opened. The exposure of smokehouse workers to PAH can thus probably be maintained on an acceptable level through good work habits and proper maintenance of the kilns.

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