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Case study

The influence of baking fuel on residues of polycyclic aromatic hydrocarbons and heavy metals in bread

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Abstract

The influence of fuel type used to bake bread on the spectrum and concentrations of some polycyclic aromatic hydrocarbons and heavy metals in baked bread was assessed. Bread samples were collected from different bakeries operated by either electricity, solar, mazot or solid waste and their residue content of PAHs and heavy metals was assessed. The total concentration of PAHs detected in mazot, solar, solid waste and electricity operated bakeries had an average of 320.6, 158.4, 317.3 and 25.5 $\mu g\,kg^{-1}$, respectively. Samples collected from mazot, solar and solid waste operated bakeries have had a wide spectrum of PAHs, in comparison to that detected in bread samples collected from electricity operated bakeries. Lead had the highest concentrations in the four group of bread samples, followed by nickel, while the concentrations of zinc and cadmium were the least. The concentration of lead detected in bread samples produced from mazot, solar, solid waste and electricity fueled bakeries were 1375.5, 1114, 1234, and 257.3 $\mu g\,kg^{-1}$, respectively. Estimated daily intake of PAHs based on bread consumption were 48.2, 28.5, 80.1, and 4.8 μg per person per day for bread produced in bakeries using mazot, solar, solid waste and electricity, respectively. Meanwhile, the estimated daily intake of benzo (a) pyrene were 3.69, 2.65, 8.1, and 0.81 μg per person per day for bread sample baked with mazot, solar, solid waste and electricity, respectively. The daily intake of lead, based on bread consumption was 291, 200.5, 222, and 46.31 μg per person per day for bread sample baked with mazot, solar, solid waste and electricity, respectively. The present work has indicated the comparatively high level of daily intake of benzo (a) pyrene and lead in comparison to levels reported from many other countries and those recommended by international regulatory bodies. It is probable that residues detected in bread samples are partially cereal-borne

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but there is strong evidence that the process of baking and the gases emitted are responsible for most of the contamination load.

Keywords: Polycyclic aromatic hydrocarbons; Baking fuel; Bread

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) is a group of organic compounds formed by incomplete combustion of organic matter. They are omnipresent in all environmental segments, including air, water and soil. The acute toxicity of PAHs is low, however, several PAHs have been shown to be carcinogenic in a number of different species [1,2].

The human exposure to PAHs comes through inhalation, dermal contact and consumption of contaminated foods. In foodstuffs, PAHs can be found in cereals, vegetables, fruits, oil and butter, meat, fish and seafood. However, the foodstuff that contributes most to the PAHs intake of humans is grain and cereals, because of their high rate of consumption.

Similarly, heavy metals are among the most frequently encountered contaminants in the environment. Several reports have focused on residues of numerous heavy metals in foodstuffs [3,4]. Other reports have delineated on the contamination of cereal products, including bread with heavy metals. Hubbard and Lindsay [5] reported that the major route of man's exposure to heavy metal was ingestion. Even in the case of lead where the use of leaded petrol produces ambient lead levels higher than other heavy metals pollutants, direct inhalation contributes less to the total body burden than ingested lead. The main contributors, therefore, to heavy metals in the body were the foods consumed.

In Egypt, bread is a major component of people's diet. The per capita consumption of bread is among the highest in the world, and bread is one of the few commodities still on the government's subsidy list. Local bread is produced in a number of different types of bakeries. In cities, most of the bakeries are either fully or partially automated. Solar and natural gas are main sources of energy used to operate these bakeries, although a considerable number of bakeries are using mazout, a heavy fraction of petroleum product (fuel no. 6). Electricity operated bakeries are also available, though in relatively small numbers. On the other hand, bakeries in the country side are less well equipped and many of them are fueled with agricultural and municipal solid waste.

The concentration level of PAHs and some heavy metals in bread and cereal have been studied in different parts of the world because of the paramount importance of these food materials and the heavy reliance of some societies on them [6,7]. On the other hand and despite the high magnitude of bread consumption in Egypt, meagre attempts were conducted to map out the concentration levels of these contaminants in bread [8].

In the present study, the influence of the type of fuel used to bake bread on the residues of some PAHs and heavy metals was investigated. Samples of bread baked in different bakeries, using different sorts of fuels, that include solar, mazot, solid waste and electricity were collected. Residues of some PAHs and heavy metals were mapped out. Moreover, the daily intake of PAHs, benzene (a) pyrene and some heavy metals, based on bread consumption was ascertained.

2. Materials and method

2.1. Sampling

Bread samples collected in this study were Balady brand, baked from the same type of wheat, 'Giza'. Samples, each of 10 loaves were collected from bakeries using different types of fuel. Samples were collected from a minimum of three bakeries using the same type of fuel, kept in clean clothes and taken to the laboratory. Samples were taken directly after being baked not to let them exposed to other source of contamination. Bread samples of each bakery were separately cut into small pieces and mixed thoroughly, before three subsamples, each of 50 g were taken from each bakery for analysis.

2.2. Reagents

All organic solvents used were glass distilled or analytical grade (Fisons scientific equipment, England or Honil Ltd., London). Potassium hydroxide pure pellets were reagent grade (BDH). Aluminum oxide 90 and silica gel 60 (70–230 mesh) for column chromatography were obtained from Merck.

Authentic PAHs standard was purchased from Alltech (USA) as a mixture dissolved in acetone, containing 13 compounds.

2.3. Extraction and clean up

Samples extraction and clean up was conducted according to the method reported by Mohamed Tawfic et al. [9]. Bread subsamples, each of 50 g were reflex extracted for 10 h in a soxhlet unit with 200 ml of *n*-hexane. The extract was concentrated to 2 ml, using a rotary evaporator. The concentrated extract was transferred to a round bottom flask, and saponified, using 100 ml of aqueous methanolic KOH (30 g KOH dissolved in 30 ml of distilled water and 270 ml of methanol), to eliminate possible fat material, and the mixture was refluxed again for 2 h. Saponified material was quantitatively transferred to a separatory funnel, using 100 ml of a methanol–distilled water mixture (4-1) and 100 ml of *n*-hexane and the funnel was shaken for 5 min, left to settle and phases were allowed to separate. Aqueous layer was drained out in a beaker and extracted again with 100 ml of *n*-hexane. Aqueous layer was discarded, while organic layers were combined and evaporated using a rotary evaporator, and residues were quantitatively transferred on top of glass column, ready for clean up. Adsorption column chromatography was performed to separate aliphatic hydrocarbons from aromatics and other components. A slurry of alumoxide (14 g), Merck, Darmstadt, particle size 0.063–0.2 mm, in *n*-hexane was made to pack a glass column (22 cm $\times$ 1.5 cm, i.d.). Another slurry of silica gel (14 g) was made and loaded over the aluminum oxide layer. The column was then topped with 2 g of anhydrous sodium sulfate. The column was eluted with 50 ml of toluene. Polycyclic aromatic hydrocarbon fractions were concentrated to 1 ml by a rotary evaporator. The concentrated sample was transferred to a capped glass tube and wrapped in aluminum foil ready for analysis.

2.4. Capillary gas liquid chromatography

A Pye Unicam 304 model gas chromatograph, equipped with a flame ionization detector was used in this study. An analytical capillary column (AT 5, 30 m × 0.53 mm), with film thickness of 1.2 μm was used to separate polycyclic aromatic hydrocarbons. Column conditions, temperature programme, quantification were performed according to the method reported by Tawfic Ahmed et al. [9].

2.5. Validation study

Control bread samples were fortified with a standard solution of PAHs in hexane (10 mg l^{-1}) at three levels. To 50 g of bread control bread sample, 5, 50, and 100 μl standard solution. Final concentration of PAHs in control samples were 1, 10, and 20 μl. Each fortification level was replicated three times. Extraction of control samples was performed as mentioned earlier. The average rate of recovery was 82% (standard error of the mean (S.E.M.), 6.7). Results were not corrected according to recovery rate.

3. Heavy metal analysis

For heavy metal analysis bread samples were left to air dry before sub-samples of 50 g each were taken from each group. Sub-samples were ground in Titanium knives and stored in high density polyethylene bottles, 100 ml capacity, with screw caps. Bottles were prewashed with nitric acid, rinsed with deionized water, dried and tested for contamination by leaching with 5% nitric acid. The bottles contained no metal liners that can contaminate the samples

About 0.5 g finely ground samples were precisely weighed in test tubes and 3 ml of nitric acid were added to each tube, and tubes were allowed to remain over night at room temperature, protected from dusts. Tubes were heated up to 130°C for 4 h using a metal block thermostat unit (Gebr. Liebisch, Bielefeld 14 Germany). Tubes were left to cool down before 2 ml of nitric acid and 0.7 ml of perchloric acid and 43 ml distilled water were added to each tube. A programmable circuit was used to raise temperature up to 230°C within 33.5 h. The clear wet ash in each tube was dissolved in 2 ml of distilled water and tubes were stored until flame atomic absorption spectrophotometery was performed.

Elements measurements were carried out using a Perkin-Elmer, model 3030 atomic absorption spectrophotometer equipped with HGA-600 transverse-heated graphite furnace, AS-60 autosampler, closed circuit cooling system, fume extraction system, and an electrodeless discharge lamp power supply.

4. Results and discussion

Residues of polycyclic aromatic hydrocarbons detected in bread samples collected from bakeries using different types of fuel are shown in Table 1. The total concentration of PAHs detected in bread samples from mazot, solar, solid waste and electricity operated bakeries had an average of 320.6, 158.4, 317.3 and 25.5 μg kg^{-1}, respectively.

Table 1
Residues of polycyclic aromatic hydrocarbons ($\mu g\,kg^{-1}$) detected in bread baked with different types of fuel[a]

Compound	Heavy oil (mazot)	Light oil (solar)	Solid waste	Electricity
Fluorene	58 a	4.7 c	27.5 b	0.00 c
Phenanthrene	5.3 b	2.3 c	8 a	0.00 d
Anthracene	50.3 a	1.3 b	0.9 b	0.00 b
Pyrene	25.7 a	13 b	16.2 b	0.00 c
Chrysene	59.3 a	28.8 b	32.9 b	0.00 c
Benzo a anthracene	27.6 a	16.9 b	26 a	0.45 c
Benzo b fluoranthene	19.6 a	23.9 a	11.5 b	9.6 b
Benzo k fluoranthene	8.5 a	2.2 bc	3 b	1.1 c
Benzo a pyrene	20.6 b	14.7 c	45.1 a	4.4 d
Dibenzo a,h, anthercene	24.4 b	8.0 c	88.1 a	0.00 d
Benzo g,h,i, pyrelene	15.7 bc	17.6 b	58.2 a	14.5 c
Indeno 1,2,3-cd pyrene	26.4 c	37.2 b	57.4 a	0.00 d
Total	320.6a	158.4 b	317.3 a	26.9 c

[a] Figures followed with the same letters are not significantly different.

Samples collected from mazot, solar and solid waste operated bakeries have had a wide spectrum of PAHs, but concentrations of individual compounds varied to a considerable extent. On the other hand, residues of PAHs detected in bread collected from electricity operated bakeries have had a much smaller spectrum and concentrations. Significantly, higher concentrations of high molecular weight PAHs such as benzo (a) antheracene, benzo (a) pyrene, dibenzo (a,h) antheracene and indeno (1,2,3-cd) pyrene were detected in bread samples collected from mazot and solid waste operated bakeries. This may indicate that combustion gases emitted from mazot and solid waste during bread baking are the major source of such high concentrations of such PAHs. However, the presence of such heavy PAHs residues, though in much smaller concentrations in bread samples baked in electricity operated bakery may reflect the ingredients. This finding would give some support to the assumption that some part of the residues detected in all samples are cereal-borne residues and not necessarily the product of baking process.

Various studies have indicated that wheat may contain appreciable levels of PAHs that impinge on various part of the crop during growing season [10–12].

However, considering the significant difference in the concentration of heavy PAHs in bread samples baked in solid waste and mazot with samples obtained from electricity operated bakeries, it is rather likely that processing and combustion gases are major source of PAH contamination.

Residues of PAHs detected in all bread samples in this study are much higher than residues reported from other European countries. In England, Dennis et al. [13] reported that the level of benzo (a) pyrene was $<0.1\,\mu g\,kg^{-1}$ in white flour and similar amount was found in bread, meanwhile they reported that higher concentrations of up to $2.2\,\mu g\,kg^{-1}$ of B(a)P were detected in cereal-derived products containing higher levels of edible oils such as pudding-based desserts and cakes. In Finland, Tuominen et al. [14] found that the level of PAHs in bolted flours, milled oats and wheat ranged from 25 to $38\,\mu g\,kg^{-1}$, while the average concentration in rolled oat was $64\,\mu g\,kg^{-1}$. In Canada, Lawrence and Webber [15]

Table 2
Residues of some heavy metals ($\mu g\,kg^{-1}$) detected in bread baked with different types of fuel[a]

Metal	Heavy oil (mazot)	Light oil (solar)	Solid waste	Electricity
Lead	1375.5 a	1114.0 b	1234.1 b	257.3 d
Cadmium	15.9 c	44.10 a	27.6 b	8.6 d
Zinc	21.2 b	17.6 c	25.6 a	13.5 d
Nickel	257.4 a	99.6 c	152.6 b	174.5 b

[a] Figures followed with the same letters are not significantly different.

showed that in breakfast cereals the wheat products contained levels of PAH ranging from 18.6 to 59.5 $\mu g\,kg^{-1}$, while corn or oats cereals contained a range of 5.7–6.9 $\mu g\,kg^{-1}$.

Residues of lead, cadmium, zinc and nickel detected in bread samples collected from bakeries using different types of fuel are shown in Table 2. Lead had the highest concentrations in the four groups of bread samples, followed by nickel, zinc and cadmium. The concentration of lead in bread samples produced by electricity operated bakeries was substantially less than residues detected in the other three groups. Since wheat used in bread production has one origin, it is rather likely that variation in lead concentrations is due to the baking process rather than precipitation of atmospheric lead during cereal growth or storage in open heaps before baking. This trend of results was also observed in the case of cadmium, and to a lesser extent in zinc residues. On the other hand, residues of nickel detected in bread samples produced in electricity operated bakeries were rather comparable to residues detected in other bread samples. Hence, it may be suggested that baking process was not the reason for such nickel residues detected in all samples alike, but such residues were likely to have originated during some other stage of cereal and/or bread production.

Cabrera et al. [3] reported that atmospheric contamination, excessive use of fertilizers and pesticides and irrigation with residual water were among causes of contamination of raw foodstuffs.

Table 3 portrays the estimated daily intake of total PAHs and B(a)P, based on consumption of bread baked with different types of fuel. Benzo (a) pyrene, the most regulated PAH compound by law in many countries has often been measured as an indicator of PAH level in foodstuffs.

In the present study, the estimated intake of B(a)P based on bread consumption only is 0.81 μg per person per day. Reports of daily intake of B(a)P from other countries, based on all

Table 3
Estimated intake (μg per person per day) of total PAHs, benzo (a) pyrene, lead, cadmium, zinc and nickel of bread baked with different types of fuel

Type of fuel	Daily intake					
	Total PAH	B(a)P	Pb	Cd	Z	Ni
Heavy oil	48.21	3.69	291.1	2.4	4.22	44.71
Light oil	28.51	2.65	200.5	7.94	3.18	17.93
Solid waste	80.18	8.12	222.1	4.97	4.62	27.47
Electricity	4.86	0.81	46.31	1.55	2.44	31.41

types of food consumption vary between 0.36 μg per person and day in Austria [16], 0.25 μg per person and day in the UK [17], 0.5 μg per person and day in the Netherlands [6] and 0.1–0.3 μg per person and day in Italy [18]. The present results indicated the comparatively high level of the daily intake of B(a)P in the study area, though it is only based on bread consumption. It must be inferred that if based on multiple diet, daily intake estimate of B(a)P in Egypt would be even higher.

The estimated daily intake of lead, zinc, cadmium and nickel based on bread consumption under local Egyptian conditions are shown in Table 3. Results indicated that the daily intake of lead based only on bread consumption is in the range of 214 μg per person per day. Such level is much higher than level recommended by WHO [19], based on all type of diet. Meanwhile, the residues of zinc, nickel and cadmium detected are well below WHO recommendations.

5. Conclusion

Results of the present work indicate the influence of fuel type used in bread processing on bread contamination with PAH and heavy metals is significant. However, there is also some indications that some of the contamination load is related to the quality of seeds used. Results has also indicated the comparatively high level of daily intake of benzo (a) pyrene and lead in comparison to levels reported from many other countries and those recommended by international regulatory bodies.

The present results suggest that some special care should be taken in bakeries using fuel source other than electricity in order to minimize bread contamination with PAHs and heavy metals.

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