GHENT UNIVERSITY

FACULTY OF BIOSCIENCE ENGINEERING

RISK ASSESSMENT ON PAH4 IN SMOKED FISH (GHANA REGION 3)

Case Study of Chemical Risk Assessment presented by:

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1. HAZARD IDENTIFICATION

Polycyclic aromatic hydrocarbons (PAHs) are semi-volatile organic compounds which have various pyrogenic and petrogenic origins. Benzo(a)pyrene (BaP), chrysene, benzo(a)anthracene, and benzo(b)fluoranthene are forms of PAHs associated with food safety. These substances are commonly referred to as PAH4.

A variety of food categories such as fruits, vegetables, meat and fish are a significant source of exposure to PAHs. They cause severe respiratory and cardiovascular disorders, reduce lung capacity, provoke myocardial infarction, asthma, and possibly cancer, as well as immune system failure. Furthermore, PAHs have been reported to be extremely mutagenic and carcinogenic in humans.

Food processing methods such as curing, drying, smoking, roasting, grilling, barbecuing, and refining are known to produce and raise the level of PAHs in the food.
Smoked fish is a substantial food source of PAHs. Smoke not only adds fish flavor and aroma, but it also improves preservation thanks to its dehydrating and antibacterial qualities, extending shelf life, enhancing flavor, and increasing utilization. Smoked fish is a common source of protein in most diets in underdeveloped nations.
Africa is known for employing fuelwood in traditional smoking techniques. High levels of polycyclic aromatic hydrocarbon (PAH) pollution result from this processing method.
The formation of PAH is also related to exposure of organic matter to high temperature in reduced oxygen conditions. 60% of the animal protein consumed in Ghana comes from fish in general. Among this 60%, 70-80% of the fish is consumed in the smoked form. Hot smoking (T≥80°C) is the preferred method used in Ghana to process fish. Hot smoking can be performed in the soft form, creating a product with a very short shelf life, or in the dried form, creating a product with a much longer shelf life.

2. EXPOSURE ASSESSMENT

To perform the probabilistic risk assessment of benzopyrene and PAH4 in smoked fish from Ghana (region 3), @Risk version 7 has been used.

2.1. DISTRIBUTION OF THE DATA

The best fit was both chosen for consumption data (kg/kg BW/day) and concentration of benzopyrene and PAH4 data (µg/kg). The choice was first based on chi square statistic: the five lowest chi square value were taken into consideration. Secondly, the minimum, maximum, mean and the 99% percentile were evaluated with respect to the input values. Values that were too distant from those of the input were discarded. Thirdly, the plot percentile-percentile was used. One example of the procedure is reported next, showing the best fitting distribution of PAH4 concentration in soft herring.

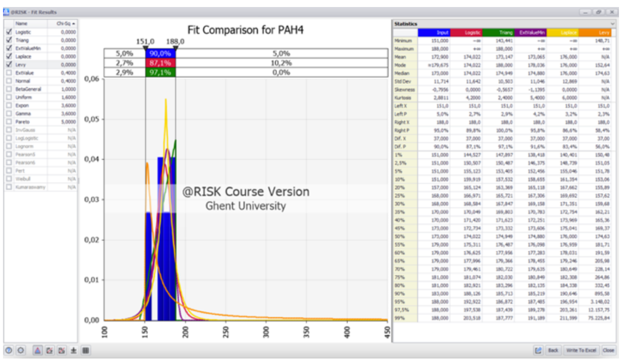

Figure 1: First step for choosing the best fitting distribution

The fit ranking has been set as Chi-square statistics. The top 5 five distributions have been taken into consideration. The distributions with a minimum equal to -∞ have been discarded (*Laplace, Logistic, ExtValueMin*).

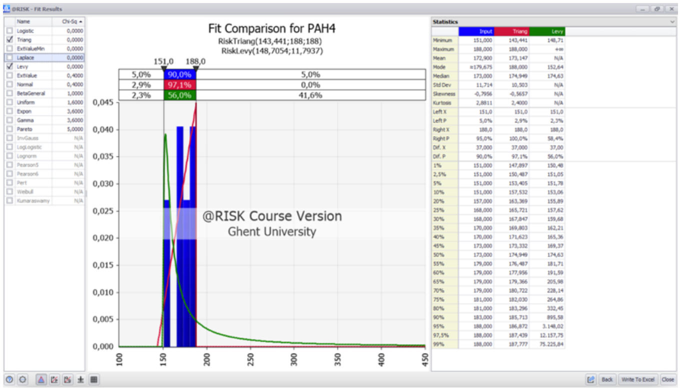

Figure 2: Second step for choosing the best fitting distribution

By comparing the min, max, mean and P99 of each distribution in respect with the input values, it is possible to verify the nearest values to the input. In this case, *Triang* is the best fitting distribution.

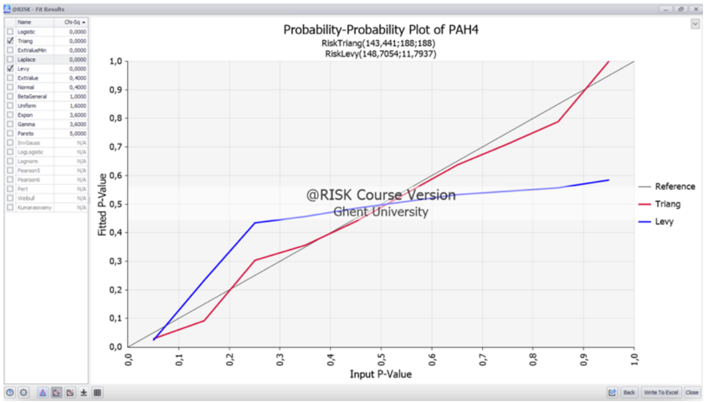

Figure 3: Third step for choosing the best fitting distribution

It is possible to verify the choice by using the P/P plot, in which *Triang* is closer to the input line.

The distributions of the consumptions of each type of fish and the distributions of the different concentrations of benzopyrene and PAH4 have been chosen according to the previous method. The following tables show the best fitting distributions for each dataset.

	Smoked soft herring		**Smoked dry herring**		**Smoked dry barracuda**			
	Consumption		**Consumption**		**Consumption total population**		**Consumption consumers**	
	Input	*BetaGeneral*	Input	*Triang*	Input	*Triang*	Input	*Uniform*
Minimum	2,500E-005	2,500E-005	2,500E-005	2,500E-005	0,00000000	0,00000000	2,500E-005	1,103E-005
Maximum	7,500E-005	7,500E-005	0,00035000	0,00041464	0,00050000	0,00050168	0,00050000	0,00051397
Mean	4,717E-005	4,596E-005	0,00012622	0,00015488	4,500E-006	0,00016723	3,857E-005	0,00026250
P99	7,500E-005	7,500E-005	0,00035000	0,00037568	2,500E-005	0,00045151	0,00050000	0,00050894

Table 1: Best fitting distribution for consumption data

The distribution for the consumption of smoked dry barracuda of the total population has been calculated through the use of the IF function, since the dataset contained values equal to 0, when the random number is lower than the chance of zero in the dataset (amount of zero in the population/total number of data) the consumption will be equal to 0. The consumption distribution was also found for consumers, by eliminating the values equal to 0.

	Smoked soft herring				**Smoked dry herring**				**Smoked dry barracuda**			
	Benzo(a)pyrene		**PAH4**		**Benzo(a)pyrene**		**PAH4**		**Benzo(a)pyrene**		**PAH4**	
	Input	*Triang*	Input	*Triang*	Input	*InvGauss*	Input	*BetaGeneral*	Input	*Uniform*	Input	*InvGauss*
Minimum	13,00	13,00	151,00	143,44	12,00	9,54	68,00	68,00	48,000	44,333	297,00	279,36
Maximum	20,00	21,43	188,00	188,00	58,00	+∞	391,0	391,00	81,000	84,667	801,00	+∞
Mean	15,80	15,81	172,90	173,14	30,20	30,20	195,1	219,69	66,300	64,500	476,00	476,00
P99	20,00	20,59	188,00	187,77	58,00	132,77	391,0	391,00	81,000	84,263	801,00	1.624,04

Table 2: Best fitting distribution for concentration data

2.2. EXPOSURE CALCULATION

The exposure to PAH and benzopyrene for each type of fish was calculated through the use of the risk output function plus the distribution of consumption times the distribution of the concentration of BaP or PAH4 as shown in the following formula:

Exposure = RiskOutput() + Distribution of the consumption x Distribution of concentration (BaP or PAH4)

Exposure is expressed in µg/kg bw/day; distribution of consumption is expressed in kg/kg bw/day; distribution of concentration of BaP or PAH4 is expressed in µg/kg. Exposure is intended as chronic exposure to benzopyrene and PAH4 in each product. The results of exposure are shown in the following table:

	EXPOSURE			
	***EXPOSURE BENZO(A)PYRENE* (µg/kg BW/day)**		***EXPOSURE PAH4* (µg/kg BW/day)**	
Smoked soft herring	0,0007269		0,00796	
Smoked dry herring	0,00467		0,034	
Smoked dry barracuda	**Total population**	**Consumers**	**Total population**	**Consumers**
	0,01079	0,0169	0,079	0,1249

Table 3: Exposure for each type of fish

With the data at our disposal, it was not necessary to make scenarios using lower, medium and upper bound since all concentrations' values are above LOQ (0.2 µg/kg). After calculating exposure, 10.000 interactions have been selected and simulations were run. All simulations are shown in the following figure:

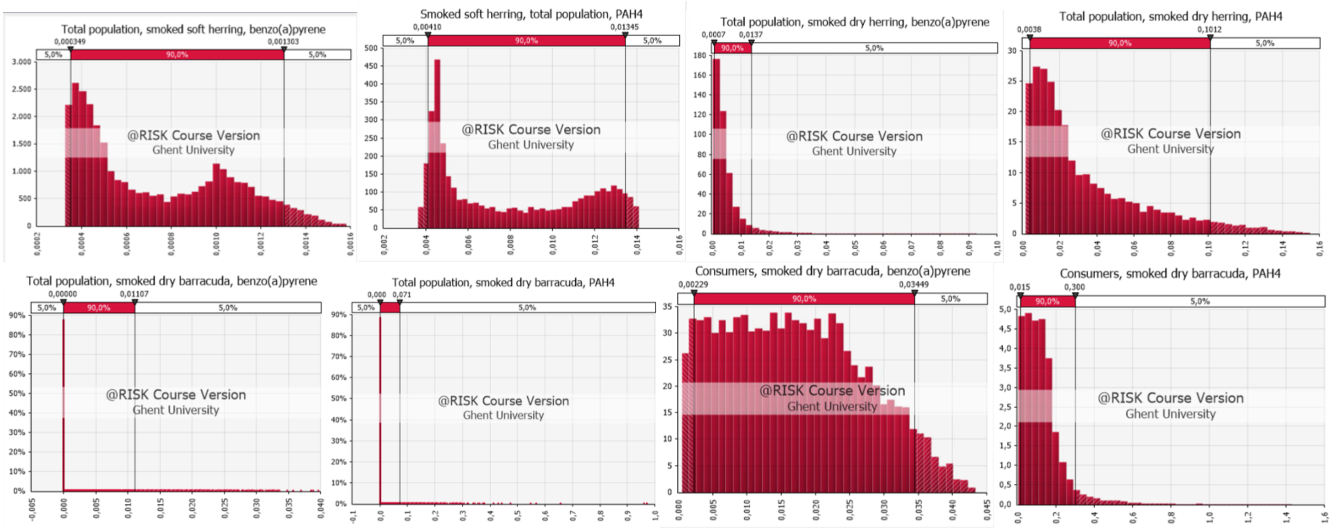

Figure 4: Results of the simulations

According to the simulations shown in figure 4, 90% of consumers (=total population) that consume smoked-soft herring are exposed to 0,000349 – 0,001303 µg/kg bw/day of benzo(a)pyrene and 0,00410 – 0,01345 µg/kg bw/day of PAH4; 90% of consumers (=total population) that consume smoked dry herring are exposed to 0,0007 – 0,0137 µg/kg bw/day of benzo(a)pyrene and 0,0038 – 0,1012 µg/kg bw/day of PAH4; 90% of the total population that consumes smoked dry barracuda are exposed to 0,00000 - 0,01107 µg/kg bw/day of benzo(a)pyrene and 0,00229 – 0,03449 µg/kg bw/day of PAH4 while for the 90% of consumers that intake smoked dry barracuda the exposure goes from 0,00229 to 0,03449 for benzo(a)pyrene while it goes from 0,015 to 0,300 for PAH4.

2.3. P50, P90, MAXIMUM, AVERAGE AND MINIMUM EXPOSURE

The average, minimum, maximum exposure has been also calculated as well as exposure at P50 and P90. The results are shown in the following table:

Exposure (µg/kg BW/day)	Smoked-soft herring		Smoked-dry herring		Smoked-dry barracuda Total population		Smoked-dry barracuda Consumers	
	Benzo(a) pyrene	PAH4	Benzo(a) pyrene	PAH4	Benzo(a) pyrene	PAH4	Benzo(a) pyrene	PAH4
P50 (µg/kg BW/day)	0,00064	0,0068	0,00327	0,01934	0	0	0,0172	0,1041
P90 (µg/kg BW/day)	0,00117	0,0129	0,0099	0,06067	0,00309	0,01021	0,0320	0,241
Average (µg/kg BW/day)	0,000727	0,00795	0,0051	0,0289	0,00126	0,00984	0,0176	0,128
Maximum (µg/kg BW/day)	0,00159	0,01409	0,183	0,3265	0,0359	1,4049	0,0416	1,739
Minimum (µg/kg BW/day)	0,000325	0,0036	0,000302	0,00152	0	0	0,000511	0,00352

Table 4: P50, P90, mean, maximum and minimum exposure for each type of fish

It is clearly visible how the exposure to PAH4 is higher than the exposure to benzo(a)pyrene, due to their higher concentrations' values.

3. HAZARD CHARACTERIZATION

PAHs are classified as possible (group 2B), probable (group 2A), and human (group 1) carcinogens. BaP is the only PAHs classified in group 1. To date, the most potent genotoxic and carcinogenic PAH is dibenzo[al]pyrene (Group 2A), but it has not yet been reported as a human carcinogen owing to a lack of studies (*World Health Organisation, 2021*).

Regarding hazard characterization, the most appropriate approach used to evaluate the risk for PAH4 is the margin of exposure.

MOE is estimated using the following formula:

$$MOE = BMDL_{10} / Exposure$$

In this case in particular, a $BMDL_{10}$ of 70 µg/kg bw/day and 340 µg/kg bw/day have been used for carcinogenic BaP and PAH4 in food, respectively (*EFSA, 2008*).

These $BMDL_{10}$ values and the previously calculated exposure have been used to determine the MOE.

To interpret the MOE, it is necessary to know that for carcinogenic compounds, a MOE lower than 10.000 is considered to be highly concerning and for this reason it should be addressed for risk management; while a MOE higher than 10.000 is of low concern, making the hazard not priority for risk management.

4. RISK CHARACTERIZATION

To check the percentile at which the MOE exceeds 10.000, the calculations to determine MOE have been performed for each different percentile for each type of fish (smoked soft herring=SSH, smoked dry herring=SDH, smoked dry barracuda=SDB):

PERCENTILE	MOE BaP SSH	MOE PAH4 SSH	MOE BaP SDH	MOE PAH4 SDH	MOE BaP SDB (total population)	MOE PAH4 SDB (total population)	MOE BaP SDB (consumers)	MOE PAH4 SDB (consumers)
1	211034	88564	157657	149779	/	/	70000	53797
2,5	206672	85771	126582	116438	/	/	47586	34447
5	200171	82906	101156	89005	/	/	31138	22972
10	189547	79235	74231	60390	/	/	18464	13492
20	171779	74791	48143	36324	/	/	10103	7505
25	163627	73275	40863	30797	/	/	8201	6071
30	155555	71458	35371	26377	/	/	6927	5112
35	146535	67513	30959	22895	/	/	5990	4456
40	137093	61750	27365	20011	/	/	5271	3930
45	125201	55829	24297	17382	/	/	4704	3494
50	111856	48991	21766	15461	/	/	4284	3165
55	98286	43059	19712	13589	/	/	3916	2874
60	86784	38288	17766	11655	/	/	3596	2645
65	78098	34437	15952	9789	/	/	3316	2442

70	72269	31481	14233	8288	/	/	3090	2278
75	69149	29645	12569	6968	/	/	2879	2119
80	66006	28321	10767	5881	/	/	2674	1947
90	58270	26198	7290	4106	26168	25185	2271	1478
95	53742	25280	5107	3297	6307	4625	2040	1111
97,5	50872	24732	3853	2905	4000	3025	1894	851
99	48479	24428	2740	2592	3037	2026	1779	636

Table 5: MOE in each percentile for BaP and PAH4 in smoked dry herring and smoked dry barracuda

The values highlighted in red show that risk is present at that percentile. So, the exact percentile in which the MOE is firstly exceeded will be between the first percentile highlighted in red and the previous one.

In the first type of fish, the smoked soft herring, for both benzo(a)pyrene and PAH4, MOE is not exceeded even at P99. This means that no risk is present regarding the first type of fish.

It is also visible that the risk for consumers of smoked dry barracuda is much higher than the one of the total population, due to the higher consumption data.

Also, by using the inverted formula of $MOE = BMDL_{10} / Exposure$, it is possible to know the exposure values in which the MOE exceeds 10.000, as shown in the following:

$Exposure = BMDL_{10} / MOE$; in which $BMDL_{10}$ is 70 for BaP and 340 for PAH4 and MOE is 10.000.

The values obtained from the inverted formula are 0,007 and 0,034 respectively for BaP and PAH4. By checking the output of the simulations using @Risk, is it possible to verify between which percentiles exposure is above these values.

PAHs residues if present in smoked fish above recommended levels could pose serious public health concerns; according to the commission regulation EU No. 835/2011 of 19 August 2011, the maximum levels (µg/kg) are respectively 2.0 for benzopyrene and 12 for PAH4. By comparing these values with the values of the concentrations in our possession, it is clearly visible that the latter are highly above the limits of the EU regulation.
Due to the absence of Codex standards on PAH4, the Ghana Standards Authority adopts EU regulations for the management of PAH4 in smoked fish for export (GSA, 2014). At present, PAHs in smoked fish for domestic consumption are not regulated.

5. REFERENCES

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