

Sources for contamination of rapeseed with benzo(a)pyrene

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Abstract. The conducted research has demonstrated that the general rapeseed contamination with benzo(a)pyrene (B(a)P), as the main representative of the PAH family, is at the level of permitted world standards. However, individual cases of dried samples where the B(a)P content was high enough to reach $8.30 \mu\text{g kg}^{-1}$ of seeds, show that the problem of seed pollution by the polynuclear aromatic hydrocarbons is still unsolved and the raw material for further processing should be carefully monitored. Monitoring the PAH risks seems most appropriate given the presence of B(a)P in the samples without any post-harvest treatment. It demonstrates how common the occurrence of the substance is in the human environment. Significant variance between the samples taken directly after the harvest and these after the drying, shows how important the process of drying is on the content of B(a)P. The increased level of the substance in the seeds from the year of adverse weather conditions demonstrates that the drying time and data missing to a great extent affect the quality of the seeds.

Keywords: rapeseeds, benzo(a)pyrene, drying facilities

INTRODUCTION

The continued tendency towards increased intensity of rapeseed growing is forcing producers to apply such amounts of production agents (fertilisers and plant protectors) and to use such methods for post-crop processing and seed conditioning (drying temperature, storage conditions) which heavily affect the nutritional value of seeds delivered to the fat industry. For the above reasons, this process has become more and more important for the consumers, for whom the safe food issue is now even more apparent. This applies as well for the content of heavy metals, pesticides, and polynuclear aromatic hydrocarbons (PAH) in food. The last are particularly dangerous in the sense that, in their chemical

structure, they contain a composition of benzo(a)anthracene chains of which some derivatives exhibit cancerous, mutative and teratogenic impact on living organisms, of which on humans in particular [3–9,13].

The main source of the PAH may, however, be of anthropogenic origin, i.e., extracted in the process of burning and coal, gas, and mineral oil processing as well as in the production of aluminium, ferrum, steel and asphalt, engine burning processes, industrial and commune waste utilisation and through such natural processes as forest fires, volcanic eruptions, and microorganism deterioration of soil [3,6,12].

Emission of the PAH in Poland is estimated to be 800 Mg yr^{-1} , which in conversion to one unit of land in Poland brings it to almost 3 times as high a concentration as it is in the US and almost twice as high a density as in Sweden [1,6,9,12].

Polynuclear aromatic hydrocarbons (PAH) which are present in water are passed there mainly through the waste waters in which the most harmful are carbo-chemical, petrochemical, coal, gas and mine wastes. The PAH reach surface waters through dry and wet dusts in the air and through the dilution of asphalt roads and soil surface. The PAH may also appear as a result of living activity of some water organisms [1–3,6,9].

The most frequent source for the PAH in soil are the saturated (wet) and dry atmospheric precipitations, and the application of wastes and waste residues and industrial decline in fertilisation of agricultural surface and green lands [1,9,17]. The contamination of land with polynuclear aromatic hydrocarbons (PAH) in Poland is mainly regional. Most of the WWA are gathered around industrial lands and main centres of the emission. Research in the area of Puławy

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demonstrates that a purely agricultural land has a lower content of PAH than the land under the harmful influence of industrial operators and the city of Puławy – with average density values to be respectively 191 and 217 $\mu\text{g kg}^{-1}$ [3,9].

As a hydrophobic pollutant, the polynuclear aromatic hydrocarbons (PAH) are being filtered mainly at the level of decayed soil (land), where they are being actively sorbed. Noticeable is the significant influence of land acidity on the content of the PAH in the soil, while this correlation is especially clear for decayed land structures [4,9,11,12,18].

The polynuclear aromatic hydrocarbons (PAH), if present in the soil in sufficiently high concentration, may be absorbed by the root structures of plants along with other conveying components such as xylem for leaves and fruits [11,15,17]. The PAH can also be absorbed by the leaves themselves directly from the air and further transferred by the phloem down to the roots [6,15]. PAH found in the leaves is much more through the polluted air, than through the soil, as plants seem to absorb more PAH through the leaves than the roots [18].

Food contamination is not only a consequence of environment pollution but it also originates from some technological processes of treating raw materials and storing agricultural and food products.

Rapeseed drying is one of the most important elements in the chain of activities referred to as the post-harvest processing. In the case of rapeseed, it is often true that the drying facilities do not comply with technical standards, for instance some having systems with air as the drying medium, some without heat exchangers or – if damaged – without additional control over the drying factor [16]. As a result of this, the dried seeds may become contaminated with some substances of the PAH group, including benzopyrene.

Results of examinations on contamination of grain and rapeseeds with the PAH clearly indicate that the pollution has been unchanged for several years in the past. In 1998, the total content of PAH in the seeds and rape and rye was varying from 5.3 to 73.9 $\mu\text{g kg}^{-1}$, while concentration of benzo(a)pyrene was not more than 1.8 $\mu\text{g kg}^{-1}$. Concentration of the latter in the food products should not exceed (according to the FAO/WHO directives) the level of 10 $\mu\text{g kg}^{-1}$ [7].

The research has pointed out a strict correlation between the level of rapeseed contamination by the PAH and the region where the seeds were cultivated, the pollution of the environment and contamination derived under drying or complementary drying of seeds [10]. The aim of the research was to determine the content of benzo(a)pyrene, the most outstanding representative of the PAH, in the seeds of rape treated under the different post-crop stages.

MATERIAL AND METHODS

Material for the research were the samples of rapeseed gathered from producers in the area of northern Poland

(Kujawsko-Pomorskie, Wielkopolskie, Zachodnio-Pomorskie, Lubuskie, Warmińsko-Mazurskie), where the seeds are planted in the greatest concentration. The samples of seeds were collected from the producers directly after harvesting and then after drying. The structure of suppliers was the same in each of the regions, and different types of drying facilities were also applied (the Araj, Drzewicz, Pedriotti, Rogoźno and other types – Kusbas, Riela and those without the heat exchangers, which are rare nowadays in the market). Each unit type was checked for the year of production and drying temperature. All the examinations were carried on the seeds from harvest 2001 and 2002. Overall, there were 120 rapeseed samples to be checked for the presence of benzo(a)pyrene (B(a)P).

The test was made with the use of high-end liquid column chromatography (the HPLC), liquid chromatograph: 'the Waters' made in the US and equipped with 'the Controller 600', the 'Waters 600E Multisolvant Delivery System' pump and the PDA 'Waters 996 Photodiode Array Detector' detector of 1.2 nm accuracy. The 'Millennium³² Version 3.05' software was used to enable chromatography and gather and process the data.

The examined solutions, after the ultrasound extraction of benzo(a)pyrene from the samples of rapeseed and with the support of acetonitrile, were further condensed, purified and extracted by means of 'the BAKER spe 12G', using the spe filtration columns with two 20 μm monoliths of the PE and 0.45 μm filters and some dividing columns of Octyl C₈, 500 mg. They were later syringed on the column of Nova-Pak[®], C18, 60 · 10⁻¹⁰ m, 4 · 10⁻⁶ m, 3.9x150 · 10⁻³ m. The de-oxidation of eluents was then done with helium at the speed of 30 cm³ min⁻¹.

All the remaining conditions of the chromatograph analysis were: the gradient elution – 95 % of acetonitrile, 5% water, intensity of flow at the moving phase: 1 cm³ min⁻¹, injection: 20 ml, wavelength: 254 nm, bordering pressure, above which the flow is stopped: 3600 PSI, measuring temperature: 25°C. The recuperation, detection limit and alteration coefficient for marking the benzo(a)pyrene were respectively: 91.23%, 0.12 $\mu\text{g kg}^{-1}$ and 4.26%. BAKER ANALYZED[®] HPLC-reagent was used for the analysis, while specimen samples were made of benzo(a)pyrene produced by the Fluka.

The analysis of all the rapeseed samples was made in three repetitions. If the relative variance versus the standard was more than 5%, the analysis was restarted.

All the results were further analysed statistically to determine the median (dividing the result of generated numbers into half), the lower quartile (below which there are 25% of the numbers) and the upper quartile (above which there are 75% of the numbers) while the full range of generated figures was defined in terms of their maximum and minimum values.

RESULTS

All the generated results of the research, defining the content of benzo(a)pyrene B(a)P, have shown that this substance is much more present, and in greater amounts, in the samples of seeds treated with the drying process (Fig. 1–4). This clearly contributes to the fact that this process is the most dangerous one in the range of all the post-cropping treatments. There are several factors supporting this argumentation.

One of the reasons for the increased presence of B(a)P in some of the analysed samples is (luckily enough there being not many of them) the existence of drying facilities without heat exchangers. Another significant problem is the lack of responsibility and discipline from the rapeseed producers who, in order to make some ‘savings’, dry the seeds directly with fumes. Such cases, though marginal, are still to be spotted (and were listed under the ‘other’ group of drying facilities).

Another reason is the age and condition of the drying facilities used by the rapeseed producers. The research conducted by Rybacki *et al.* [14] has proven that more than half of the facilities operating in the seed area of ZT Kruszwica S.A. have above 15 years of use, while 24% of them were produced before 1980. Most of the facilities were re-engineered and modified, which results in their sealing of the heating elements (the heat exchangers) to allow for the penetration of fumes in the dried seeds. It was therefore, more and more frequent, greater or lower in extent, that the fumes were in direct contact with the seeds.

The results presented in Fig. 1, where B(a)P seed contamination is shown in respect to the usage of equipment,

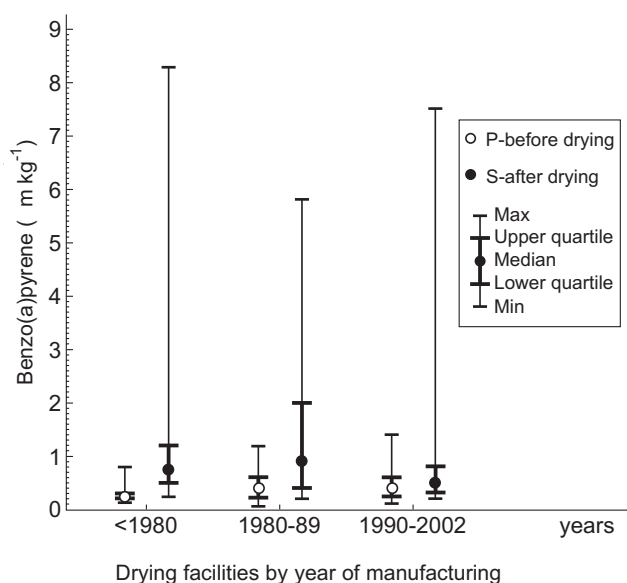


Fig. 1. Influence of drying facilities by year of manufacturing on the contamination of benzo(a)pyrene in rapeseeds.

demonstrate how important this problem is. They also show that any drying facilities produced before 1980 (whose share in the total number of the examined facilities was above 24%) are much more harmful (pollutant) for the dried rapeseeds than the units produced after 1990. So both, the inter-quartile spread, which for the drying facilities before 1980 was from 0.40 to 2.00 $\mu\text{g kg}^{-1}$, and the maximum number (value) – 8.30 $\mu\text{g kg}^{-1}$ are clear evidence of this. On the other hand, the same indications applied for the seeds dried in facilities produced between 1990 and 2002 were respectively: the inter-quartile spread – from 0.30 to 0.81 $\mu\text{g kg}^{-1}$, the maximum value – 5.8 $\mu\text{g kg}^{-1}$. The narrowing of the inter-quartile spread with the new drying facilities introduced to the market is noticeable. This means that most of the new units operate properly and only a few of them pollute the seeds with substantial amounts of B(a)P, which could be an effect of the ‘potential savings’ introduced in them by the producers. It also speaks for the good quality of the seeds but also, through incidental cases, shows that the quality of the process should continue to be carefully monitored while unreliable producers should be excluded from the range of the suppliers.

Also noticeable is a very low content (0.08–1.40 $\mu\text{g kg}^{-1}$) and stable amount of the B(a)P in the seeds of rape just after the harvest. The amounts present in the seeds are mainly of anthropogenic origin and arise through the pollution of soil and atmosphere.

The conducted research has also proven that the type of drying facilities has significant influence on the content of the benzo(a)pyrene in the seeds of rape (Fig. 2). The greatest concentration of it was noticed in the samples of seeds from

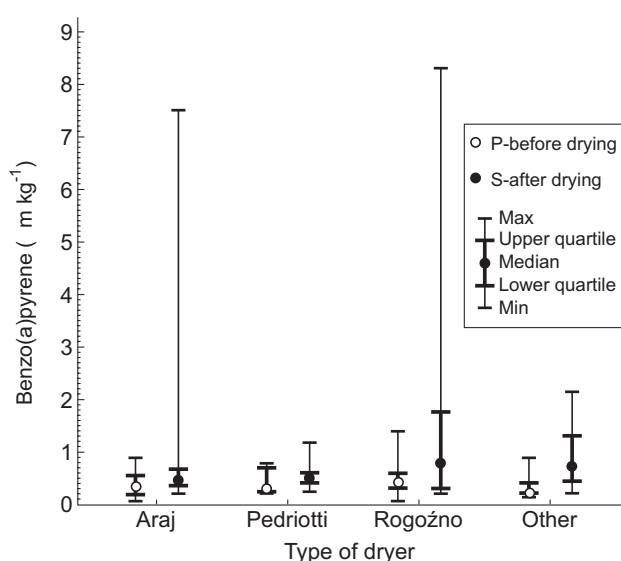


Fig. 2. Influence of type of dryer on the contamination of benzo(a)pyrene in rapeseeds.

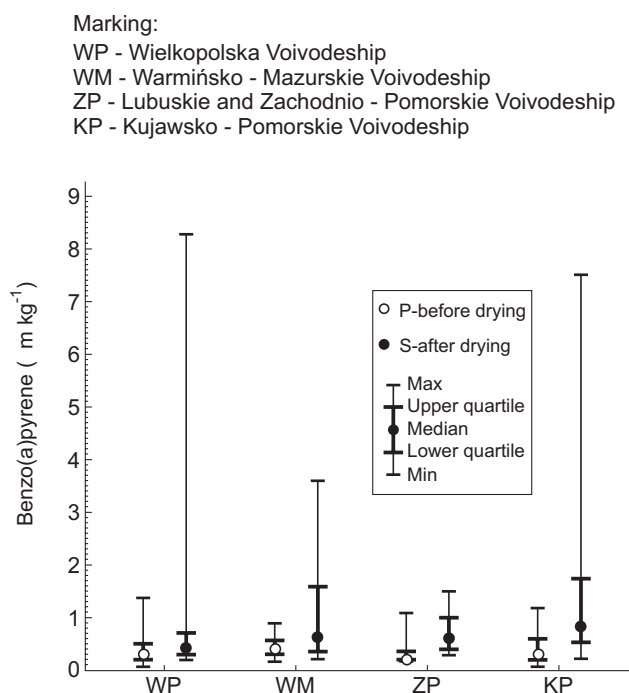


Fig. 3. Influence of regions cultivation on the contamination of benzo(a)pyrene in rapeseeds.

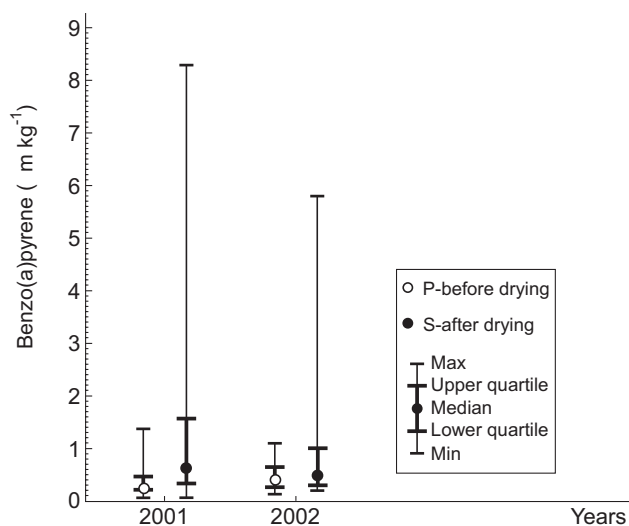


Fig. 4. Contamination of benzo(a)pyrene in rapeseeds in different years.

the Rogoźno drying units, showing wide inter-quartile spread ranging from 0.31 to 1.83 $\mu\text{g kg}^{-1}$ and the maximum value equal to 8.30 $\mu\text{g kg}^{-1}$. At the same time, the 'Pedriotti' unit parameters were much lower (the spread from 0.48 to 0.63 and maximum value of 1.21 $\mu\text{g kg}^{-1}$). The marginal spread and low deviation compared to the seeds procured

after the harvest (0.37 $\mu\text{g kg}^{-1}$) seems to add to the proper performance of the operating drying units.

Evaluation of respective regions (voivodeships) has exposed significant diversity in the level of B(a)P environmental pollution. It is expressly shown in the results of samples taken after the harvest, which for different voivodeships represented different values. The greatest amount of B(a)P in the non-treated samples was noticed in the areas of Wielkopolska and Kujawsko-Pomorskie while the lowest was in Warmińsko-Mazurskie voivodeship (Fig. 3).

The analysis of dried samples has demonstrated that the lowest level of B(a)P in the seeds (the best drying units and best producers) is gathered around the Wielkopolskie voivodeship. There are, however, some suppliers in the region using facilities below the standards of safe food production. The worst, in this sense, were the Kujawsko-Pomorskie and Warmińsko-Mazurskie regions. The observed wide spread of values has proven that there are suppliers in the regions who deliver seeds with very high B(a)P content.

The analysis of samples from harvest 2001 and 2002 has proven that even particular years can vary in delivering seeds with different nutritional value (Fig. 4). The main reason for this is different weather conditions. Year 2001 was mostly of frequent and heavy rainfalls during the harvest, hence the high humidity in the harvested seeds. This apparently affected the drying conditions, the time and level of temperature in particular. These were the reasons for the increased content of B(a)P in the seeds of that period compared to the seeds of 2002, which was much friendlier on this account.

SUMMARY

In our climate zone, rapeseed is the base raw material for the production of vegetable fats. The conducted research has demonstrated, that the general rapeseed contamination with benzo(a)pyrene, as the main representative of the PAH family, is at the level of permitted world standards. One should also account for the fact that seeds are just a raw material which is further submitted to the complex process of refining (deacidification, bleaching, deodorization, etc.), during which significant amounts of the substance are extracted. However, individual cases of dried samples where the B(a)P content was high enough to reach 8.30 $\mu\text{g kg}^{-1}$ of seeds, show that the problem of seed pollution by the polynuclear aroma hydrocarbons is still unsolved and the raw material for further processing should be carefully monitored. It should also be noted that in certain European countries (the Czech Republic, Germany) in any cases where B(a)P contamination of food raw materials is equal to 2 $\mu\text{g kg}^{-1}$, immediate measures are taken to reduce the content.

Monitoring the PAH risks seems most appropriate given the presence of B(a)P in the samples without any post-crop treatment. It demonstrates how common the occurrence of the substance is in the human environment.

Sources can be found in both the anthropogenic and the environmental factors such as polluted rains and dusts.

Significant variance between the samples taken directly after the harvest and those after the drying, shows how important the process of drying is on the content of B(a)P. The increased level of the substance in the seeds from the year of adverse weather conditions demonstrates that the drying time and applied temperature affect the quality of the seeds to a great extent. It should also be noticed that B(a)P represents only a fractional part of all the substances incorporated in and comprising the PAH.

CONCLUSIONS

1. The conducted research has demonstrated that the content of B(a)P in the seeds of rape is generally below the norm of the EU. Only individual cases point out the need for carefully monitoring the danger.

2. The increased amounts of B(a)P in the seeds under the drying process show that this is one of the major sources for the seed contamination. It shows how important the control of drying units is, especially those obsolete in technology. Severe measures should also be taken to exclude the producers without a strict regime of food production.

3. The conducted research demonstrates that the pollution of rapeseed with B(a)P depends on the type of drying facilities, the regions under analysis and the weather conditions in respective years of harvest.

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