ECOLOGICAL CHEMISTRY AND ENGINEERING A

Vol. 16, No. 10 2009

Monika BOJANOWSKA[1] and Jerzy TYS[2]

DETERMINATION OF THE LEVEL OF B[a]P CONTENT IN RAPE SEEDS SUBJECTED TO VARIOUS POST-HARVEST TREATMENTS

OKREŚLENIE POZIOMU ZAWARTOŚCI B[a]P W NASIONACH RZEPAKU PODDANYCH ZRÓŻNICOWANEJ OBRÓBCE POZBIOROWEJ

Abstract: Polycyclic aromatic hydrocarbons (PAH) constitute one of the largest and most varied groups of organic compounds with known toxic, mutagenic and carcinogenic properties characteristic of many representatives of the group. Food contamination with PAH may result not only from environmental pollution but also from certain technological processes used in processing of raw materials and in storage of agricultural food products. The objective of the presented study was to determine the benzo[a]pyrene content in rape seeds subjected to various post-harvest treatments and processing.

The study showed that rape seed contamination with B[a]P is dependent primarily on the temperature of drying, but also on the regions of cultivation and on the weather conditions in particular years.

Keywords: benzo[a]pyrene, rape seeds

The occurrence of polycyclic aromatic hydrocarbons in agricultural food products is caused by their common presence in the environment and penetration into plants during their vegetation or as a result of technological processes of food preservation [1]. In recent years, in numerous countries, requirements have been published concerning the content of PAH in vegetable fats. And thus, in Germany it is recommended that the content of total PAH should not exceed 25 $\mu g \cdot kg^{-1}$, according to the British requirements the content of benzo[a]pyrene (B[a]P) should not exceed 2 $\mu g \cdot kg^{-1}$, and acc. to the Spanish ones – 5 $\mu g \cdot kg^{-1}$ [2]. Observed in Poland level of contamination of agricultural materials (rapeseed, among other things) and food products with polycyclic aromatic hydrocarbons does not differ from that observed in other countries (and accepted by the requirements of the world standards). The highest share in the uptake of

[1] Department of Chemistry, University of Life Sciences in Lublin, ul. Akademicka 15, 20–950 Lublin, Poland, phone 81 445 6640, email: monika.bojanowska@up.lublin.pl

[2] Institute of Agrophysics Polish Academy of Sciences, ul. Doświadczalna 4, 20–290 Lublin, Poland, phone 81 744 5061, email: jtys@demeter.ipan.lublin.pl

PAH is that of agricultural products, and especially products of plant origin, which PAH content is low, but the level of their consumption is very high [3, 4].

The degree of rapeseed contamination with PAH depends on the region of cultivation, level of contamination of the environment, and contamination resulting from drying and supplementary drying of seeds. Frequently, rape seed is dried using dryers that do not meet technical and operational requirements, eg such in which air circulation is forced without the use of heat exchangers or with damaged exchangers, and additionally without control of quality of the drying medium [5].

Monitoring of threats related with the occurrence of PAH appears to be strongly recommended due to the presence of B[a]P in samples that were not subjected to the processes of postharvest treatment. This indicates the common occurrence of the compound in the human environment [6].

The objective of the presented study was determination of the content of benzo[a]pyrene in rape seeds subjected to various post-harvest treatments.

Material and methods

The material for the study consisted of samples of rape seed obtained from suppliers of the raw material from the regions of the north, south and west of Poland.

Determinations of benzo[a]pyrene were made with a method based on high--efficiency liquid column chromatography (HPLC) using an US-made Waters liquid chromatograph equipped with Controller 600, Waters 600E Multisolvent Delivery System pump and Waters 996 Photodiode Array Detector with resolution of 1.2 nm. Operation of the chromatograph and data acquisition and processing were made with the use of the Millennium Version 3.05 software package.

The studied solutions, obtained after ultrasonic extraction of benzo[a]pyrene from rape seed samples by means of acetonitrile, were concentrated, purified and extracted using the "BAKER spe 12G" system with spe filtration columns with two 20 μm PE sinters and 0.45 μm filters and with Oktyl C_8, 500 mg separation columns, and then sprayed onto a Nova-Pak®, C18, 60 Å, 4 μm, 3.9×150 mm column. Deaeration (deoxygenation) of eluents was conducted with the use of helium at the rate of 30 $cm^3 \cdot min^{-1}$.

Remaining conditions of chromatographic analysis were: elution: gradient – 95 % acetonitrile – 5 % water, mobile phase flow rate: 1 $cm^3 \cdot min^{-1}$, injection: 20 mm^3, wavelength: λ = 254 nm, limit pressure above which flow stops: 3600 PSI, measurement temperature: 25 ^oC. Recovery, limit of detection and coefficient of variation for determinations of benzo[a]pyrene were 91.23 %, 0.12 $\mu g \cdot kg^{-1}$ and 4.26 %, respectively.

Reagents used for the analyses were BAKER ANALYZED® HPLC-reagent, while the standards were prepared from benzo[a]pyrene produced by Fluka.

Results and discussion

The obtained results describing the content of benzo[a]pyrene indicate that the compound occurs in greater amounts in samples of seeds subjected to the process of

drying. This demonstrates that the treatment is the most hazardous in the process of postharvest processing.

Drying temperature proved to be a factor significantly affecting the content of B[a]P in rape seeds (Fig. 1).

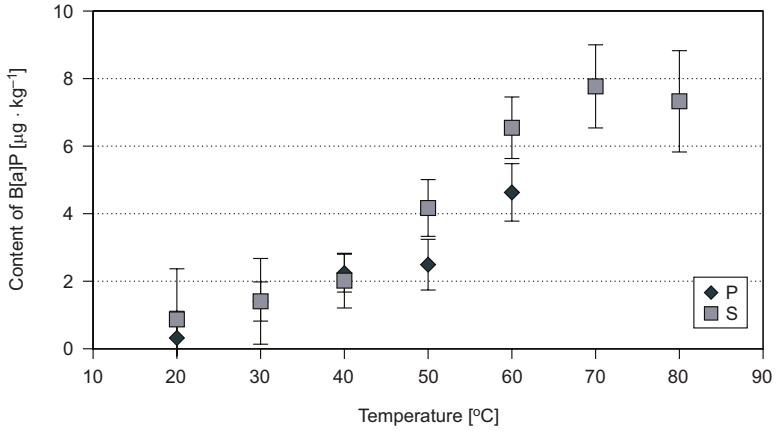

Fig. 1. Effect of drying temperature on the content of benzo[a]pyrene in rape seeds: S – dried seeds, P – seeds before drying

Within the temperature range of 20–40 °C there occurred the lowest level of contamination with B[a]P, at the level from 0.32 to 2.24 μg · kg^{-1}, both for samples subjected to the process of drying and for those immediately after the harvest. For the drying temperature of 50 °C, the content of benzo[a]pyrene increased two-fold, and at temperatures of 60 °C and 70 °C increase by 70 and 75 % in the level of B[a]P, respectively, was recorded, which clearly demonstrates the growing hazard of seed contamination with increase in the temperature of drying. A slight decrease in the content of benzo[a]pyrene at the temperature of 80 °C may be attributed to partial decomposition of the compound at high temperature, which is supported by data available [7, 8]. Decreasing content of benzo[a]pyrene in rape seeds subjected to the effect of high temperature creates the risk of their contamination with the products of its decomposition that often prove to be more toxic due to the better solubility of lighter PAH in water [9].

In rape seed delivered to oil producing companies in the regions of southern and western Poland, in a great majority of samples the values did not exceed the level of 2 μg · kg^{-1} (Fig. 2).

The lack of very high amounts of B[a]P (individual cases at the level of 3–4 μg · kg^{-1}) and the use of relatively low drying temperatures (mostly within the range of up to 50–60 °C) indicate very good condition of drying plants in those regions and observance of principles of safe food production by the producers. In isolated cases a relatively high content of benzo[a]pyrene was observed in spite of the use of low drying

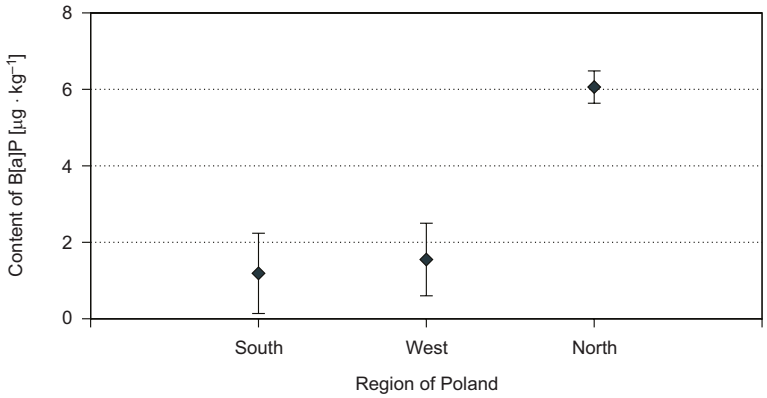

Fig. 2. Effect of region of cultivation on the content of benzo[a]pyrene in rape seeds

temperature (30–40 ^{o}C). This may be a result of drying rape seed with air without heat exchangers (a measure applied by unreliable producers for reasons of economy).

Results of analysis of samples obtained in the particular years of the study indicate that also different weather conditions may cause variation in that feature of seeds, so important for health (Fig. 3).

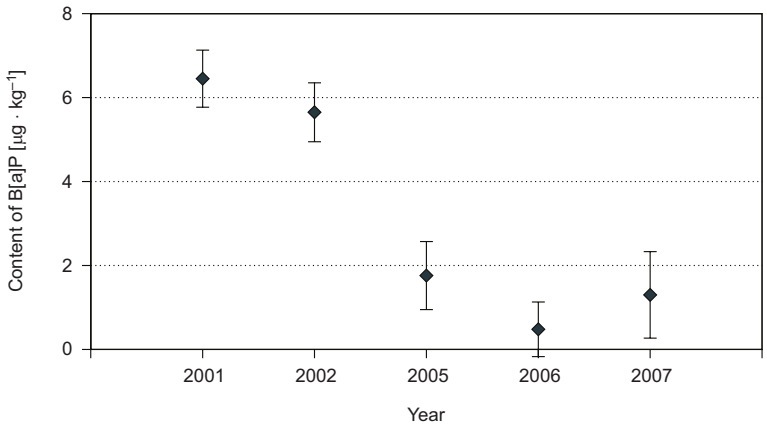

Fig. 3. Effect of year of cultivation on the content of benzo[a]pyrene in rape seeds

Worse weather conditions during harvest in 2001 had an effect on the conditions of rape seed drying (samples with high moisture content required longer drying). Seeds produced under such conditions displayed notably higher level of contamination with B[a]P compared with seeds from 2002 which was a year with much more favourable weather conditions. Another cause of contamination is the age and technical condition of dryers used by rape seed producers.

Most of the samples tested in 2001–2002 came from producers from the north of Poland. A study by Rybacki et al [10] showed that more than a half of the dryers in use

in that region are older than 15 years, and 24 % of them were made before the year 1980. Most of the dryers are operated after considerable modifications and upgrades that not always resulted in sealing of the heating elements that would preclude exhaust fumes penetration to the material dried. For these reasons, the highest amounts of benzo[a]pyrene were recorded in the region of suppliers from the north of Poland. The year 2006 was characterised by high temperature and low amount of rainfall during the vegetation and harvest of rapeseed, hence the lowest level of B[a]P in the seed that mostly did not require supplementary drying. In 2007, on the other hand, in spite of not really favourable weather conditions, relatively low levels of benzo[a]pyrene were found in the seed, which may have been a result of increased awareness of the producers with respect to food safety and observance of regimes in the process of rape seed drying. Lower content of that compound in seeds obtained in the years 2005–2007 was also due to the activity of agricultural services that eliminate from the list of suppliers those producers who provide seed that is the worst in this respect.

Rapeseed is one of the major crop plants grown in Poland for many years, and is the fundamental raw material for the production of vegetable oil. The results of the presented study show that rape seed contamination with benzo[a]pyrene is at a level acceptable in terms of the relevant world standards. However, the occurrence of individual samples of dried seed in which the content of B[a]P exceeds the level of 8 $\mu g \cdot kg^{-1}$ (from the region of northern Poland) indicates that the problem of rape seed contamination with PAH exists, and control of raw material for oil production is a necessity. In some European countries (Czech Republic, Germany) actions are undertaken to reduce the level of benzo[a]pyrene when food product contamination occurs at the level of 2 $\mu g \cdot kg^{-1}$ [11, 12]. Also significant is the fact that rape seeds are only the raw material that is then subjected to complex processes of refinement and purification, in the course of which a notable part of noxious compounds can be removed.

Conclusions

1. Generally, the content of benzo[a]pyrene in rape seeds does not exceed the standards in force in the EU countries.

2. The process of rape seed drying is one of the major sources of contamination with B[a]P. This creates the necessity of continuous control of dryers, aimed at elimination of unreliable producers from the approved list of suppliers of the material.

3. Temperature of drying is the most important factor determining the content of benzo[a]pyrene in rape seeds. Firstly, application of high temperature increases the level of the compound, and secondly – the products of its decomposition may cause a decrease in the health value of the seeds.

References

[1] Bojanowska M., Czerwiński J. and Tys J.: Polish J. Environ. Stud. 2008, **17**(1B), 207–212.
[2] Oleszczuk P.: Arch. Ochr. Środow. 2002, **28**(1), 107–118.
[3] Kazerouni N., Sinha R., Hsu C.H., Greenberg A. and Rothman N.: Food Chem. Tox. 2001, **39**, 423–436.

[4] Phillips P.H.: Mutat. Res. 1999, **44**3, 139–147.
[5] Tys J. and Rybacki R.: Acta Agrophys. 2001, **44**, 33–44.
[6] Jankowski P.S. and Obiedziński M.W.: Tłuszcze Jadalne 2000, **35**(3–4), 112–125.
[7] Tys J., Rybacki R. and Malczyk P.: Rośl. Oleis. 2003, **XXIV**, 617–626.
[8] Gworek B. and Klimczak K.: Ochr. Środow. Zasob. Natur. 2000, **20**, 5–20.
[9] Reyes C.A., Medina M., Crespo-Hernandez C., Cedeno M.Z., Arce R., Rosario O., Steffenson D.M., Ivanov I.N., Sigman M.E. and Dabestani R.: Sci. Technol. 2000, **34**(3), 415–421.
[10] Rybacki R., Skawiński P. and Lampkowski M.: Rośl. Oleis. 2001, **XXII**, 539–549.
[11] Moret S. and Conte L.S.: J. Chromatogr. A 2000, **882**, 245–253.
[12] Malczyk P.: [in:] Konferencja "Strategia pozyskiwania nasion rzepaku w roku 2002 i latach następnych o wysokiej jakości", Stegna 11–12.04.2002.

OKREŚLENIE POZIOMU ZAWARTOŚCI B[a]P W NASIONACH RZEPAKU PODDANYCH ZRÓŻNICOWANEJ OBRÓBCE POZBIOROWEJ

[1] Katedra Chemii, Uniwersytet Przyrodniczy w Lublinie
[2] Instytut Agrofizyki PAN w Lublinie

Abstrakt: Wielopierścieniowe węglowodory aromatyczne (WWA, PAH) stanowią jedną z największych i zróżnicowanych grup związków organicznych o znanych właściwościach toksycznych, mutagennych i kancerogennych, którymi cechuje się wielu przedstawicieli tej grupy. Skażenie żywności nimi jest wynikiem nie tylko skażenia środowiska, ale może być również rezultatem niektórych procesów technologicznych stosowanych w przetwórstwie surowców i przechowalnictwie produktów rolno-spożywczych. Celem podjętych badań było określenie poziomu zawartości benzo[a]pirenu w nasionach rzepaku poddanych zróżnicowanej obróbce pozbiorowej. Przeprowadzone badania wykazały, że zanieczyszczenie nasion rzepaku B[a]P jest uzależnione przede wszystkim od temperatury suszenia, ale także rejonu uprawy, jak również od przebiegu pogody w poszczególnych latach.

Słowa kluczowe: benzo[a]piren, nasiona rzepaku