A preliminary study of PCBs, PAHs, pesticides and trace metals contamination in cold-pressed rapeseed oils from conventional and ecological cultivations

Małgorzata Wroniak¹ · Agnieszka Rękas¹

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Abstract The purpose of this study was to investigate the levels of polycyclic aromatic hydrocarbons [benzo(a)anthracene, chrysene, benzo(b)fluoranthene, and benzo(a)pyrene], polychlorinated biphenyls (6 marker and 12 dioxin-like), pesticides (74 compounds) and heavy metals (Pb, Cd, As, Hg, Fe, Cu), in the cold-pressed rapeseed oils from conventional (RC) and ecological cultivations (RE). Similar level of PAHs, PCBs and heavy metals was found in the investigated cold-pressed oils; moreover, no effect of rapeseeds cultivation practice on the level of pesticide residues was found. Levels of PAHs, PCBs, and pesticides were within EU legislation limits. Concentration of 4 PAHs oscillated between 3.13 and 6.15 µg/kg, concentration of non-dioxin-like PCBs was within 2599.4–8380.8 pg/g range, dioxin-like PCSs levels varied from 310.2 to 819.4 pg/g (0.307–0.780 pg TEQ/g oil). Iron (Fe) and copper (Cu) were prevailing heavy metals found in the studied oils (0.236–1.690 mg/kg range, 0.036–0.062 mg/kg range, respectively). Measured lead (Pb) contents reached (RC1) or were nearly equal to the EU limit of 0.1 mg/kg (RE1 and RE2).

Keywords Ecological farming · Heavy metals · PAH · PCB · Pesticides

Abbreviations

B[a]A Benzo(a)anthracene
B[a]P Benzo(a)pyrene

B[b]F Benzo(b)fluoranthene
Chry Chrysene
PAH Polycyclic aromatic hydrocarbon
PCB Polychlorinated biphenyl
TEF 2,3,7,8-TCDD dioxin toxicity factor
TEQ 2,3,7,8-TCDD dioxin toxicity equivalency

Introduction

Since 1991, terms like “organic” and “ecological” have been protected by the European Union and may only be used for food items produced and certified in compliance with EU Regulation 834/2007 (European Commission 2007). The term “organically grown” refers to crops grown and processed using no synthetic fertilizers or pesticides, while utilization of pesticides derived from natural sources is allowed. Products derived from such raw materials are regulated by laws that mandate the framework and establish the production, labelling and control system standards. “Ecological” farming, a.k.a. “sustainable” agriculture is a much less defined description. “Ecological” farming uses a lot of organic practices, but it’s not strictly organic. “Ecological” agriculture follows principles that are based on the desire to maintain harmonious relationships between the food production and the environment. Central elements include: sensible and prudent use of natural resources, such as soil, water and livestock; respect for biological cycles and controls; long-term economic viability of farm operations as well as enhancement of life for farmers and society as a whole (Magdoff 2007).

The presence of chemical contaminants in cold-pressed oils may have different origins. Environment may induce contamination of oilseeds with crop protection implements chemicals like insecticides, fungicides or herbicides, heavy

✉ Agnieszka Rękas
agnieszka_rekas@sggw.pl

¹ Department of Food Technology, Faculty of Food Sciences,
Warsaw University of Life Sciences, Nowoursynowska St.
159c, 02-787 Warsaw, Poland

metals from industrial wastes, combustion of materials containing carbon and chlorine may lead to formation of dioxins and polychlorinated biphenyls (PCBs), while polycyclic aromatic hydrocarbons (PAHs) might be formed by incomplete combustion or pyrolysis of organic material (Lacoste 2014).

Polychlorinated biphenyls (PCBs) are environmentally stable, lipophilic chemicals that were widely manufactured for a range of industrial applications between the 1930s and 1970s. There are 209 theoretically possible PCB congeners, of which 12 non-*ortho* or mono-*ortho* compounds showing toxicological properties to polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), and are therefore referred to as dioxin-like PCBs (DL-PCBs) and non-dioxin-like PCBs (NDL-PCBs) which do not share the dioxin's toxic mechanism. Maximum permitted levels of dioxins, dioxin-like PCBs and non-dioxin-like PCBs in foodstuffs should be monitored in accordance with 1259/2011 EU Regulation (European Commission 2011b). The European Commission has fixed a limit for PAHs in vegetable oils (Commission Regulation No 835/2011), as well as maximum permitted levels of pesticide residues in food products (European Commission No 299/2008), while a limit values for Fe and Cu in vegetable oils have been established by Codex Alimentarius (CODEX STAN 2013).

The aim of this study was to investigate concentrations of selected PAHs, PCBs, heavy metals and pesticides in the cold-pressed rapeseed oils from conventional and ecological cultivations. To the best of our knowledge, there is no information in the literature on the effect of rapeseed cultivation practices on the concentration of mentioned contaminants in the cold-pressed rapeseed oil. Thus, the present work provides invaluable baseline data for future assessment.

Materials and methods

Material

Samples of rapeseed from conventional crops (RC1, RC2, RC3) were collected from grain elevators from various regions of Poland, namely Lubelskie, Mazowieckie, Śląskie, Opolskie and Wielkopolskie Provinces. Certified ecological seeds of rape (RE1, RE2, RE3) originated from different regions of Lubelskie Province.

Oil extraction by cold-pressing

Portions of particular batches of seeds were cold-pressed in a screw-press with a nozzle diameter of $\varnothing$ 8 mm (Farmer 10, Farmet, Czech Republic). The temperature inside the

press was 60 ± 10 °C, and the temperature of the out-flowing oil was 39 ± 1 °C. After pressing oil was collected, subjected to natural decantation under refrigerating conditions and analysed within 1 week since pressing.

Reagents

Only pestiscan-grade solvents were used in this study. Acetonitrile, dimethylsulfoxide, hexane, cyclohexane, dichloromethane, methanol, and ethyl acetate were supplied by Lab Scan (Dublin, Ireland). Analytical-grade anhydrous silver nitrate, sodium sulfate and sulfuric acid (96%) were obtained from POCh (Gliwice, Poland). Silica gel 60 and Florisil 60 were obtained from Merck (Darmstadt, Germany). High purity (>97%) native PCB standards (IUPAC 28, 52, 77, 81, 101, 105, 114, 118, 123, 126, 138, 153, 156, 157, 167, 169, 180, and 189) and PAH standards (B[a]A, Chry, B[b]F, and B[a]P) were supplied by Dr Ehrenstorfer (Augsburg, Germany).

Methods

Determination of polychlorinated biphenyls (PCBs)

Determinations were performed on the same instrument/configuration as used for pesticide residue analysis. The initial column temperature was started at 100 °C for (3 min hold), programmed at 10 °C min⁻¹ to 180 °C; 1.7 °C min⁻¹ to 200 °C (2 min hold); 1.8 °C min⁻¹ to 240 °C (8 min hold), and heated until 280 °C at 50 °C min⁻¹ (15 min hold). Helium was used as carrier gas with a constant flow-rate of 1.0 ml min⁻¹. Analytical method used to determine PCBs was based on procedures described by Roszko et al. (2012). Briefly, samples were spiked with ¹³C¹² PCB recovery standards, dialyzed through LDPE semipermeable membrane and cleaned with gel permeation chromatography. Subsequent cleanup was performed on a multilayer silica-gel-based chromatography column connected in series with short silver nitrate silica gel column (1 g 10% w/w). GPC-cleaned-up samples (after solvent exchange to *n*-hexane) were loaded on the columns and eluted with 30 ml of dichloromethane:*n*-hexane mixture (2:98 v/v). Subsequently only second silver nitrate column was eluted with 25 ml of a dichloromethane:*n*-hexane mixture (50:50 v/v). Detailed analytical parameters including sample fractionation and further introduction technique used for PCB analysis are described by Roszko et al. (2012).

Determination of pesticides

GC–MS was carried out using total ion monitoring mode on a Thermo-Finnigan Trace GC Ultra gas chromatograph

(Austin, TX, USA) interfaced to a Polaris Q low-resolution ion-trap mass spectrometer (Austin, TX, USA). The Zb-5 MS 5%-Phenyl-Arylene-fusedsilica capillary column (60 m $\times$ 0.25 mm $\times$ 0.25 μ m) was used (Phenomenex, Torrance, CA, USA). The initial column temperature was started at 40 °C for 1 min, programmed at 25 °C min⁻¹ to 180 °C; 2 °C min⁻¹ to 215 °C; 5 °C min⁻¹ to 255 °C and heated until 300 °C at 25 °C min⁻¹. Helium was used as carrier gas with a constant flow-rate of 1.0 ml min⁻¹. Spectrometer mass calibration was tuned against perfluorotributylamine (FC-43) in electron-impact positive ionization mode. Pesticide residues in oil samples were determined following method proposed by Roszko et al. (2012). In brief, oil samples were extracted with acetonitrile: water mixture (1:5), cleaned up on a double layer SPE cartridges, evaporated to dryness and analyzed with gas chromatography ion trap mass spectrometry. Recovery of the analyzed pesticides from the fortified oil samples was within the 70–120% range, recovery relative standard deviation was below 20%.

Determination of polycyclic aromatic hydrocarbons (PAHs)

The determination of PAHs was carried out using a Shimadzu HPLC chromatographic system (Duisburg, Germany) equipped with an auto injector, degasser and a FLD detector. A Pinnacle II PAH (Restek) column (250 $\times$ 4.6 mm, 5 μ m) operated at a flow rate of 300 μ l min⁻¹. The mobile phase consisted of acetonitrile (A) and water (B). The optimized elution conditions were: initial A:B 50:50 (5–20 min) A:B 75:25 (20–30 min) A:B 78:22 (30–60 min) A:B 100:0 (60–70 min) A:B 50:50. PAHs were determined following method proposed by Roszko et al. (2012). In brief, 10 g of oil sample was dissolved in 20 ml of cyclohexane and triple-extracted with 10-ml portions of dimethylsulfoxide (DMSO). Combined DMSO extracts were mixed with 60 ml of water and re-extracted with 50 ml of petroleum ether. Petroleum phase was evaporated to dryness with rotary evaporator operated at 30 °C. Subsequently dry residues were quantitatively transferred on the SPE cartridge. The cartridge was first washed with 15 ml of cyclohexane and with 10 ml of dichloromethane:cyclohexane mixture (5:95 v/v). PAHs were eluted with 15 ml of dichloromethane:cyclohexane mixture (50:50 v/v). The PAH fraction was rotary evaporated to dryness, re-dissolved in 500 μ l of acetonitrile and submitted to HPLC analysis.

Analysis of trace metal contents

For metals determination, the oil samples were wet-mineralized in Microwave Digestion System Milestone MLS-1200 (Milestone, Sorisole, Italy). 400 mg of oil sample was

digested with 5 ml of HNO₃ (65%) and 0.2 ml of H₂O₂ (30%). The microwave digestion program applied was: 3 min at 25% power (300 W), 1 min at 0 power, 5 min at 25% power (300 W) (Visinoni and Godman 1990). Quantification of trace metals was carried out with an atomic absorption spectrometer Perkin Elmer model 1100B (CA, USA). Cadmium (Cd), lead (Pb), arsenic (As), mercury (Hg), and copper (Cu) were determined by the graphite furnace atomic absorption spectrometry (GF-AAS), while flame atomic absorption spectrometry (F-AAS) was used for iron (Fe) determination. To provide quality control (QC), the elemental content in the oil samples was determined using certified reference materials (apple leaves) from the NIST–USA (National Bureau of Standards—No 1515). The accuracy of the analyzes was from 95 to 104%.

Statistical analysis

Statistical analysis was performed using Statgraphics 4.1. software. Results are expressed as mean value of two parallel determinations ($\pm$ SD, if given) of the sample. Variables were compared using one-way ANOVA, when the variables fulfilled parametric conditions, or by the Kruskal–Wallis test when these were non-parametric. Significant differences between means were determined through Tukey's Multiple Range Tests.

Results and discussion

PCBs

PCB contents found in the studied cold-pressed oil samples are given in Table 1. Concentration of the marker PCBs (SUM6) in the analysed oil samples varied from 2599.4 to 8380.8 pg/g (RE1 and RC2, respectively). The lower chlorinated congeners 28, 52, 101 were the prevailing non-dioxine-like PCBs (NDL-PCBs). Based on the results shown in Table 1, oils from conventional cultivations have higher NDL-PCBs, compared to ecological ones. Concentration of non-dioxin-like PCB congeners was up to tenfold higher than the level of dioxin-like PCBs. Contamination of studied oils by dioxin-like PCBs (a total of 12 congeners) was oscillating between 310.2 and 819.4 pg/g (minimum for the RE1, maximum for the RE3). Dioxin-like PCB 118, 105, 77 were the most abundant and subsequently the most frequently congeners found. Roszko et al. (2012) studies on various cold-pressed oils indicated the presence of twelve dioxin-like PCBs at a concentration between 9.7 and 128 pg/g range, for hemp seed oil and borage oil, respectively. Such differences in the level of PCBs concentration may have resulted from a regional differences in the PCB contamination. The most probable

Table 1 Average contents of the studied PCB congeners and average dioxin-like PCB contents expressed as dioxin toxicity equivalency (TEQ) determined in the analysed cold-pressed rapeseed oils

PCB congener	Concentration (pg/g)						
	RC1	RC2	RC3	RE1	RE2	RE3	
28	2576.2	6143.0	2983.6	1120.5	1179.1	1983.0	
52	1131.8	901.1	741.7	594.7	892.7	1437.5	
101	631.5	600.6	463.7	380.3	463.6	597.6	
138	263.1	266.2	223.9	181.2	211.4	201.3	
153	373.6	339.0	278.1	236.4	291.3	241.2	
180	119.1	130.9	97.0	86.3	101.7	90.1	
Σ 6	5095.3	8380.8	4788.0	2599.4	3139.8	4550.7	
77	111.5	75.7	93.2	65.9	89.0	144.3	
81	5.5	3.6	4.0	2.9	4.3	3.8	
105	91.0	78.6	66.7	52.9	75.0	220.0	
114	11.6	6.9	6.4	5.8	12.7	23.2	
118	217.9	178.0	175.9	141.8	156.8	375.5	
123	6.9	5.1	4.8	3.0	5.8	11.5	
126	6.3	2.2	2.6	2.4	5.4	2.3	
156	32.2	23.0	21.8	17.2	18.1	19.6	
157	5.1	5.6	5.2	3.8	4.5	3.9	
167	13.4	15.1	11.8	9.9	11.0	11.2	
169	4.2	2.3	1.5	2.5	6.4	1.9	
189	2.8	3.1	3.2	2.1	1.6	2.2	
Σ 12	508.4	399.2	397.1	310.2	390.6	819.4	
TEQ	Concentration (pg WHO-TEQ/g)						
	0.780		0.307	0.324	0.330	0.751	0.323

cause of such high variability are differences in atmospheric PCB absorption and/or mechanism of PCB deposition in plant fatty tissues (Roszko et al. 2012). TEQs were calculated using 2, 3, 7, 8-TCDD toxic equivalent factors reported by the World Health Organization (2005 WHO-TEF) (Table 1). Major contributors to the PCB TEQ were PCB-118, PCB-105 and PCB-77. TEQ values calculated for analysed oils meet requirements specified in EU legislation (European Commission 2011b). Although no major differences appeared among rapeseeds studied, one can however notice that in oil samples originating from conventional (RC1) and ecological cultivation (RE2) PCB-126 and PCB-169 were recorded at a level exceeding 5 pg/g oil. The TEQ values of dioxin-like PCBs calculated for oil produced from conventionally grown rapeseeds were 0.307 and 0.780 pg/g oil, whereas TEQ values recorded for rapeseed oils from ecological cultivations were within the range of 0.323 and 0.751 pg/g oil.

Pesticides

Concentrations of pesticide residues found in the surveyed rapeseed oils from conventional and ecological cultivations are presented in Table 2. Overall, all samples analysed for

target pesticides contained no detectable residues, only the sum of DDT isomers showed detectable amounts of pesticide residues, which was in agreement with previously published reports (Jankowski and Obiedziński 2000; Yagüe et al. 2005). Moreover, no effect of seeds cultivation method on the level of pesticide residues was found. The levels of DDT in rapeseed oil samples from conventional and ecological cultivations varied from 0.01 to 0.03 mg/kg. Maximum residues levels (MRLs) for the sum of DDT isomers in crude oils are not specifically set in EU legislation (European Commission 2008), however DDT isomers concentration in all analysed oil samples does not exceed the MRLs established for oilseeds (0.05 mg/kg). Despite the fact, that in the 1970s and 1980s agricultural use of DDT was banned in most developed countries, the presence of DDT may come from the soil contamination as this molecule soil half-life range from 22 days to even 30 years (Dimond and Owen 1996).

Polycyclic aromatic hydrocarbons (PAHs)

Data on PAHs contents found in the studied cold-pressed rapeseed oil samples are given in Table 3. The average concentration of 4 studied PAHs (B[a]A, Chry, B[b]F,

Table 2 Pesticide residues found in the studied cold-pressed rapeseed oils

Pesticide (common name)	Concentration (mg/kg)					
	RC1	RC2	RC3	RE1	RE2	RE3
Aldrin + dieldrin	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Azoxystrobin	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Bifenthrin	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Bitertanol	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Bromopropylate	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Bupirimate	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
<i>Cis</i> - + <i>trans</i> -chlordane	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Chlorfenvinphos	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Chlorpyrifos	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Chlorpyrifos methyl	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cyfluthrin	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Lambda-cyhalothrin	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Cypermethrin	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Cyprodinil	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Deltamethrin	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Diazinon	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Diphenylamine	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Sum of DDT	0.01	0.03	<0.01	0.02	0.01	0.01
Endosulfan*a + b + sulfate	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
Endrin	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ethion	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Fenitrothion	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Fenvalerate + esfenvalerate	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Flusilazole	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Phosalone	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Phosmet	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
α HCH + β HCH + δ HCH	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
HCB	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Heptachlor epoxide	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Kresoxim methyl	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Lindane (γ HCH)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Malathion	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Mecarbam	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Metalaxyl	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Methiocarb	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Methoxychlor	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Metribuzin	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Methidathion	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Myclobutanil	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Nitrofen	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Oxadixyl	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Parathion	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Parathion methyl	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Pendimethalin	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Permethrin	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Picoxystrobin	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Pirimiphos methyl	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Pirimikarb	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

Table 2 Pesticide residues found in the studied cold-pressed rapeseed oils

Pesticide (common name)	Concentration (mg/kg)					
	RC1	RC2	RC3	RE1	RE2	RE3
Pyrimethanil	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Procymidone	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Propachlor	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Propargite	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Propoxur	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Propyzamide	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Pyriproxyfen	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Simazine	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Tebuconazole	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Tetradifon	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Tolyfluanid	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Triazophos	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Trifluralin	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Vinclozoline	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

Table 3 Contents of PAHs ($\mu\text{g/kg}$) and heavy metals concentration (mg/kg) in the studied cold-pressed rapeseed oils

Oils	RC1	RC2	RC3	RE1	RE2	RE3
<i>PAHs ($\mu\text{g/kg}$)</i>						
B[a]A	0.49 ± 0.04^a	0.88 ± 0.05^c	0.93 ± 0.10^c	0.50 ± 0.13^a	0.58 ± 0.06^b	0.52 ± 0.19^a
Chry	1.25 ± 0.21^b	1.64 ± 0.11^d	2.37 ± 0.52^e	1.31 ± 0.03^b	1.52 ± 0.00^c	1.12 ± 0.32^a
B[b]F	0.91 ± 0.20^a	1.26 ± 0.05^c	1.92 ± 0.42^d	0.97 ± 0.06^a	1.05 ± 0.03^b	1.10 ± 0.18^b
B[a]P	0.48 ± 0.11^a	0.74 ± 0.13^c	0.94 ± 0.03^d	0.51 ± 0.01^a	0.66 ± 0.02^b	0.60 ± 0.08^b
Total PAHs	3.13 ± 0.56^a	4.51 ± 0.12^d	6.15 ± 0.81^e	3.29 ± 0.17^b	3.81 ± 0.06^c	3.33 ± 0.78^b
<i>Heavy metals (mg/kg)</i>						
Cd	0.001 ± 0.009^a	0.002 ± 0.001^a	0.001 ± 0.002^a	0.001 ± 0.000^a	0.007 ± 0.002^a	0.001 ± 0.000^a
Pb*	$0.100 \pm 0.001^{c,*}$	0.049 ± 0.003^b	0.012 ± 0.001^a	$0.099 \pm 0.004^{c,*}$	$0.098 \pm 0.006^{c,*}$	0.037 ± 0.005^b
As	0.002 ± 0.003^a	0.001 ± 0.002^a	0.010 ± 0.001^b	0.010 ± 0.002^b	0.002 ± 0.000^a	0.002 ± 0.000^a
Hg	0.010 ± 0.001^a	<0.005	<0.005	<0.005	<0.005	<0.005
Cu	0.055 ± 0.014^b	0.036 ± 0.008^a	0.037 ± 0.010^a	0.062 ± 0.008^c	0.037 ± 0.012^a	0.037 ± 0.009^a
Fe	0.329 ± 0.009^b	0.388 ± 0.005^c	1.320 ± 0.007^d	0.236 ± 0.013^a	0.360 ± 0.009^{bc}	1.690 ± 0.011^c

Different superscript letters within each column indicate significant differences ($p < 0.05$)

*Codex Alimentarius maximum permissible concentration of lead (Pb) is 0.1 mg/kg

B[a]P) was 4.59 and 3.47 $\mu\text{g/kg}$, for oil samples produced from conventionally and ecologically grown seeds, respectively. Recently maximum levels for the sum of 4 PAHs (benzo(a)anthracene, chrysene, benzo(b)fluoranthene, and benzo(a)pyrene) in vegetable oils according to the 853/2011 EC Commission Regulation is 10 $\mu\text{g/kg}$. None of the samples exceeded that limit: the highest concentration of 4 studied PAHs was found in RC3 (6.15 $\mu\text{g/kg}$), and the lowest one was found in RC1 (3.13 $\mu\text{g/kg}$).

Chrysene was the most abundant PAH among all studied ones, followed by considerably high concentrations of benzo(b)fluoranthene, their concentrations ranged from 1.12 to 2.37 $\mu\text{g/kg}$, and 0.91 to 1.92 $\mu\text{g/kg}$,

respectively. None of the oil samples exceeded the maximum level of 2 $\mu\text{g/kg}$ for benzo(a)pyrene specified by the European Union (European Commission 2011a). However, slightly higher level of benzo(a)pyrene was detected in the oil samples produced from conventionally grown seeds (0.48–0.94 $\mu\text{g/kg}$ range), than in the oils pressed from ecologically grown seeds (0.51–0.66 $\mu\text{g/kg}$ range). The PAH contents detected in the investigated oil samples are comparable to the results reported by Jankowski et al. (1998), Cozel and Obiedziński (2000), Jankowski and Obiedziński (2000), and Ciecierska and Obiedziński (2006), for cold-pressed oils from conventional cultivations.

Heavy metals

Heavy metal contents determined in cold-pressed oil samples are given in Table 3. Almost all oils studied showed detectable amounts of Cd, As, and Hg. The content of Pb in RE1 and RE2 oils was slightly below the regulation limit (0.099 and 0.098 mg/kg, respectively) or in the case of RC1 oil reached the EU limit value specified for cold-pressed oils (0.1 mg/kg). Limit value specified for Fe and Cu in cold-pressed oils according to Codex Alimentarius is 5.0 and 0.4 mg/kg, respectively. Cu and Fe have an essential influence on the stability of oils as they belong to strong pro-oxidants. Although none of the samples exceeded that limit, prooxidative metal contents in individual cold-pressed oils was varied and comparatively high, amounting to 0.036–0.062 mg/kg for Cu, and 0.236–1.690 mg/kg for Fe. The results obtained in the present study are in agreement with the findings of Shiers et al. (1999) study. These authors conducted a survey with respect to heavy metal contamination (Cd, Cu, Fe, Pb, and Hg), where 200 oils labelled as ‘cold-pressed’ were analysed. Similarly to our findings, most oils had either non-detectable or very low amounts of heavy metals present; however, many oils were found to have relatively high Fe content.

Conclusion

The environmental pollution was found to be the main source of contamination of cold-pressed oils with PCBs, and PAHs, whereas no correlation between the method of rapeseed cultivation (conventional vs. ecological) and the content of pesticides was found.

Maximum permitted levels of dioxin-like PCBs, PAHs and pesticides were within EU legislation limits.

Concentration of lead (Pb), a toxic metal, reached (RC1) or was nearly equal to the EU limit of 0.1 mg/kg for RE1 and RE2 oil samples (0.099 and 0.098 mg/kg).

The content of pro-oxidative metals (Fe, Cu) was within Codex limit; however it should be monitored due to its influence on the oils stability.

Further research on residues of various contaminants in a more representative number of cold-pressed rapeseed oils from conventional and ecological plantations is necessary in order to unequivocally determine differences in their contamination levels.

Compliance with ethical standards

Conflict of interest The authors have declared no conflict of interest.

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