

# PAHs, PCBs, PBDEs and Pesticides in Cold-Pressed Vegetable Oils

M. Roszko · A. Szterk · K. Szymczyk ·  
B. Waszkiewicz-Robak

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**Abstract** The aim of this study was to investigate levels of polychlorinated biphenyls (marker and dioxin-like congeners), polycyclic aromatic hydrocarbons (EPA 15 + 1), polybrominated diphenyl ethers (14 predominant congeners) and pesticides (74 compounds) in various cold-pressed vegetable oils. Poppy seed oil, rapeseed oil, sesame seed oil, pumpkinseed oil, hempseed oil, linseed oil, borage oil and evening star oil were investigated. Results of this study revealed that concentrations of PCBs, PBDEs and PAHs were low in majority of the investigated samples. However, high concentrations of organophosphorus insecticides were found. Chlorpyrifos methyl and pirimiphos methyl were the pesticide residues most commonly found in the studied oils. Concentration of 15 + 1 EPA PAHs was within the 17.85–37.16  $\mu\text{g kg}^{-1}$  range, concentration of (marker) PCBs varied from 127 to 24,882  $\text{pg g}^{-1}$ , dioxin-like TEQ values were below 0.1  $\text{pg TEQ g}^{-1}$ . Concentration of PBDEs was below LOQ in most cases.

**Keywords** Food contamination · PAH · PCB · PBDE · Pesticides · Vegetable oils

## Abbreviations

Ace	Acenaphthene
Acy	Acenaphthylene
Ant	Anthracene
B[a]A	Benzo(a)anthracene
B[a]P	Benzo(a)pyrene
B[b]F	Benzo(b)fluoranthene
B[ghi]P	Benzo[g,h,i]perylene
B[k]F	Benzo(k)fluoranthene
Chry	Chrysenes
DB[ah]A	Dibenz[a,h]anthracene
DMSO	Dimethylsulfoxide
EPA	Environmental protection agency
Flua	Fluoranthene
Fluo	Fluorene
IndP	Indeno[1,2,3-cd]pyrene
LDPE	Low density polyethylene
LOQ	Limit of quantification
Naf	Naphthalene
PAHs	Polycyclic aromatic hydrocarbon
PBDEs	Polybrominated diphenyl ether
PCB	Polychlorinated biphenyl
Phe	Phenanthrene
POPs	Persistent organic pollutants
Pyr	Pyrene
TEF	2,3,7,8-TCDD dioxin toxicity factor
TEQ	2,3,7,8-TCDD dioxin toxicity equivalency

M. Roszko (✉) · K. Szymczyk  
Department of Food Analysis, Institute of Agricultural and Food  
Biotechnology, Rakowiecka 36, 02-532 Warsaw, Poland  
e-mail: marek\_rozsko@sggw.pl

M. Roszko  
Department of Biotechnology, Microbiology and Food  
Evaluation, Warsaw University of Life Sciences,  
Nowoursynowska 166, 02-787 Warsaw, Poland

A. Szterk · B. Waszkiewicz-Robak  
Department of Functional Food and Commodities,  
Warsaw University of Life Sciences,  
Nowoursynowska 166, 02-787 Warsaw, Poland

## Introduction

Polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polybrominated biphenyl ethers (PBDEs) and pesticides are regarded as hazardous chemical

contaminants of food. These groups of substances are not uniform, they include numerous compounds differing in their chemical structure. PCBs and PBDEs each include 209 so-called congeners possessing different chlorination/bromination level and/or substituent position on the molecule [1, 2]. PAHs comprise a wide range of chemicals build of at least two connected aromatic rings [3]. Pesticides form a very diversified group of chemicals belonging to more than 100 different chemical classes.

Due to widespread use of pesticides in agriculture, their residues in food are practically unavoidable. It is estimated that more than 1,000 active substances are or were in the past used for plant/crop protection [4]. Residues of PAHs, PCBs and PBDEs in food are mainly related to the environment, into which these chemicals are brought mainly by some human activities. However, small amounts of PCBs and relatively high amounts of PAHs may originate as by-products of natural processes: PAHs are predominantly formed by incomplete combustion of organic materials [3], whereas small amounts of PCBs might be formed during combustion of materials containing carbon and chlorine.

Maximum permitted levels of selected food chemical contaminants including PAHs (B[a]P) and dioxin-like PCBs are specified in the 1881/2006 European Commission (EC) Regulation [5]. Maximum permitted levels of pesticide residues in food products are specified in the 299/2008 EC Regulation [6]. On the other hand, neither non-dioxin-like PCB nor PBDE maximum levels have been defined within the European Union (EU) food policy. However, according to the 2006/794 EU Recommendation [7], levels of non-dioxin-like PCBs should be monitored in foodstuffs in order to determine PCB back-ground levels.

Polybrominated biphenyl ethers are a relatively new group of food chemical contaminants. PBDEs are manufactured as flame retarding agents to be added to numerous consumer goods, including textiles, synthetic fibers, plastics [8]. Due to similarities between chemical structure/physical properties/chemical properties of PCBs and PBDEs, some concerns regarding circulation of these latter substances in the environment are still arising. Even if PCBs were banned from the industrial production in 1970s, they are still commonly found within the environment. Several studies indicate that PBDEs may also be widely distributed throughout the environment since residues of these substances have been found in vast majority of tested environmental/food samples [9, 10].

The aim of this study was to investigate concentrations of selected PAHs, PCBs, PBDEs and pesticides in several cold-pressed vegetable oils used as flavoring agents or regarded as possessing extraordinary nutritional value. Pumpkin seed oil, linseed oil, poppy-seed oil, hempseed oil, borage oil, sesame seed oil, evening star oil and rape seed oil were investigated. Literature data on presence of the

mentioned contaminants in the above listed oils are scarce. Concentrations of the following contaminants were determined:

- 12 dioxin-like PCBs listed in the 1881/2006 EC Regulation (congeners # 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169 and 189) and Benzo(a)-pyrene.
- 6 non-dioxin-like PCBs listed in the 2006/794 EC Recommendation (congeners # 28, 52, 101, 138, 153 and 180).
- 15 U.S. EPA Priority PAHs (Naf, Acy, Ace, Fluo, Phe, Ant, Flua, Pyr, B[a]A, Chry, B[b]F, B[k]F, DB[ah]A, B[ghi]P, IndP) [11].
- 14 PBDEs (congeners # 17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190 and 209).
- 74 pesticides belonging to various chemical classes (those that are most frequently identified in food products).

## Materials and Methods

### Vegetable Oil Samples

Cold-pressed oils available on the retail market were used. Poppy seed oil, rapeseed oil, sesame seed oil, pumpkinseed oil, hempseed oil, linseed oil, borage oil and evening star oil were taken into the investigation. Three samples of different oil brands were mixed up in equal proportions to prepare a composite (laboratory) oil sample of the given type. Only a single sample of hempseed oil was obtained and used for analyses. Due to high number of sophisticated and time consuming determinations composite samples were used to assess the presence of investigated compounds in studied types of cold pressed vegetable oils.

Laboratory made spiked samples used for the assessment of the analytical method performance were made by the addition of known amount of analytical standards to vegetable oil samples without detectable amounts of the studied compounds. PCB-, PBDE- and pesticide-spiked samples were prepared in the same manner as reported in our previous paper [12, 14]. PAH-spiked samples were prepared by the addition of the known amount of standard dissolved in cyclohexane. Spiking concentrations of the studied compounds are given in Tables 1, 1, 3.

### Chemicals

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

**Table 1** Recovery of the analyzed pesticides from oil samples spiked with known amount of pesticides (2.5–100 ppb)

Compound	Fortification level (mg kg <sup>-1</sup> )	Recovery (%) (n = 3)	RSD (%) (n = 3)	Compound	Fortification level (mg kg <sup>-1</sup> )	Recovery (%) (n = 3)	RSD (%) (n = 3)
Aldrin	0.04	70	11	Heptachlor	0.04	76	5
Azoxystrobin	0.1	85	9	Heptachlor epoxide	0.04	94	3
Bifenthrin	0.1	129	4	Kresoxim methyl	0.1	105	10
Bitertanol	0.1	113	7	l-Cyhalothrin	0.1	101	10
Bromopropylate	0.1	92	8	Malathion	0.1	105	9
Bupirimate	0.1	97	8	Mecarbam	0.1	102	10
Chlordane <sup>a</sup>	0.08	74	11	Metalaxyl	0.1	109	11
Captan	0.1	39	19	Methiocarb	0.1	14.8	27
Chlorothalonil	0.1	100	9	Methidathion	0.1	113	12
Chlorfenvinphos	0.1	94	8	Myclobutanil	0.1	96	11
Chlorpyrifos	0.1	86	6	Nitrofen	0.1	112	12
Chlorpyrifos methyl	0.1	102	9	Oxadixyl	0.1	93	5
Cyfluthrin	0.1	108	5	Parathion	0.1	105	9
Cypermethrin	0.1	111	3	Parathion methyl	0.1	97	15
Cyprodinil	0.1	91	7	Pendimethalin	0.1	84	9
DDVP	0.1	82	7	Permethrin	0.1	94	8
DDx <sup>b</sup>	0.4	79	5	Phosalone	0.1	110	10
Deltamethrin	0.1	136	9	Phosmet	0.1	108	1
Diazinon	0.1	96	8	Picoxystrobin	0.1	64	6
Dichlofluanid	0.1	102	14	Pyrimethanil	0.1	99	9
Dieldrin	0.04	82	14	Pirimicarb	0.1	79	8
Dimethoate	0.1	88	2	Procymidone	0.1	97	10
Diphenylamine	0.1	100	11	Propachlor	0.2	92	11
DMDT <sup>c</sup>	0.4	116	9	Propargite	0.1	92	9
Endosulfan a	0.1	96	13	Propoxur	0.1	103	6
Endosulfan b	0.1	87	9	Propyzamide	0.1	108	11
Endosulfan sulfate	0.1	100	8	Pirimiphos methyl	0.1	94	10
Endrin	0.04	91	10	Pyriproxyfen	0.1	106	4
Ethion	0.1	103	10	Simazine	0.1	119	6
Etrimfos	0.1	102	10	Tebuconazole	0.1	99	7
Fenarimol	0.1	97	10	Tetradifon	0.1	95	7
Fenitrothion	0.1	104	2	Tolyfluanid	0.1	96	12
Fenvalerate + Esfenvalerate <sup>d</sup>	0.4	123	5	Triadimenol	0.1	104	12
Flusilazole	0.1	103	9	Triazophos	0.1	98	15
Folpet	0.1	34	14	Trifloxystrobin	0.1	104	4
HCB	0.02	53	13	Trifluralin	0.1	92	10
HCH <sup>e</sup>	0.1	94	4	Vinclozoline	0.1	108	9

<sup>a</sup> Averaged for *cis* and *trans*-chlordane

<sup>b</sup> Averaged for o,p.-DDT, p,p.-DDT, DDD and DDE

<sup>c</sup> Averaged for o,p.-DMDT and p,p.-DMDT

<sup>d</sup> Averaged for fenvalerate and esfenvalerate

<sup>e</sup> Averaged for a-HCH, b-HCH, g-HCH, d-HCH

obtained from POCh (Gliwice, Poland). Silica gel 60 (0.063–200 mm) and Florisil 60 were obtained from Merck (Darmstadt, Germany). Florisil was heated at 500 °C for 4 h before use. Silver nitrate impregnated silica gel (10%)

was prepared by mixing silica gel with silver nitrate water solution and drying the obtained mixture at 130 °C in the dark. Silver nitrate impregnated silica gel was stored in the dark before use. Sulfuric acid impregnated silica gel was

**Table 2** Recovery (R), recovery relative standard deviation (RSD) and limit of quantification (LOQ) of individual PAHs from vegetable oil spiked samples ( $n = 3$ )

PAHs (Abbrev.)	R (%)	RSD (%)	LOQ (pg/ $\mu$ l)	$\lambda_{\text{ex}}$ (nm)	$\lambda_{\text{em}}$ (nm)	PAHs (Abbrev.)	R (%)	RSD (%)	LOQ (pg/ $\mu$ l)	$\lambda_{\text{ex}}$ (nm)	$\lambda_{\text{em}}$ (nm)
Naf	64.0	12	1	270	340	Chry	93.5	7	0.1	254	390
Acy&Ace	71.3	8	0.5	270	340	B[b]F	92.5	13	0.1	260	420
Fluo	84.2	6	0.5	270	340	B[k]F	87.8	11	0.1	260	420
Phe	95.7	8	0.1	274	375	B[a]P	94.2	8	0.1	260	420
Ant	92.2	10	0.1	260	420	DB[ah]A	98.9	6	0.3	260	420
Flua	78.6	9	0.1	260	420	B[ghi]P	92.8	11	0.1	260	420
Pyr	94.0	6	0.1	254	390	IndP	92.5	9	0.3	293	498
B[a]A	100.8	6	0.1	254	390						

Concentrations of the analyzed compounds in spiked samples were 25 pg g<sup>-1</sup>

**Table 3** Recovery (R), recovery relative standard deviation (RSD), limits of quantification (LOQ) and ionization parameters for the studied PBDE congeners

Congener	Precursor ion [ $m/z$ ]	Product ion [ $m/z$ ]	Excitation energy [V]	R ( $n = 9$ ) [%]	RSD ( $n = 9$ ) [%]	LOQ (S/N = 10) [pg g <sup>-1</sup> ]
17	246 ± 4	139 + 167	3.3	111.11	5.68	0.9
28				104.53	11.93	1.0
71	326 ± 4	217 + 219 + 245 + 247	3.8	84.56	13.33	0.6
47				93.54	13.26	0.8
66				78.72	12.87	0.6
100	404 ± 4	295 + 297 + 325 + 327	4.1	85.28	10.06	1.1
99				106.23	13.73	0.8
85				112.20	15.06	0.6
154	484 ± 4	375 + 377 + 403 + 405	4.3	70.61	13.55	2.1
153				79.20	12.08	1.2
138				75.11	5.57	2.3
183	565 ± 4	455 + 457	5.5	81.13	11.41	2.2
190				74.13	6.26	3.1
209 <sup>a</sup>	799 ± 8	638 + 640 + 642 + 718 + 720 + 722	6.9	63.52	12.15	120.0

<sup>a</sup> At 2.5 ml min<sup>-1</sup> dumping gas flow rate

R and RSD given as a mean value of three replicated at three concentration levels (3,60 and 240 pg g<sup>-1</sup> congener<sup>-1</sup>,  $n = 3 \times 3 = 9$ )

prepared by mixing concentrated sulfuric acid 96% with silica gel, while basic (KOH impregnated) silica gel was prepared by mixing a methanol solution of KOH with silica gel and drying the obtained mixture for 30 min at 130 °C. Sodium sulfate was heated for 4 h at 450 °C before use and stored in an desiccator over a silica-based moisture absorber. Laboratory-made semi-permeable membranes were prepared from a 80 mm thick low-density polyethylene (LDPE) walls of 250 × 25 mm lay flat tubing obtained from Artfolie (Bielsko-Biala, Poland). LDPE was extracted for 7 days with *n*-hexane before use. High purity (>97%) native PCB standards (IUPAC 28, 43, 52, 77, 81, 101, 105, 114, 118, 123, 126, 138, 146, 153, 156, 157, 167, 169, 180, 189, 194, and 209) and PAH standards (Naf, Acy, Ace, Fluo, Phe, Ant, Flua, Pyr, B[a]A, Chry, B[b]F, B[k]F,

B[a]P, DB[ah]A, B[ghi]P, IndP) were supplied by Dr Ehrenstorfer (Augsburg, Germany). <sup>13</sup>C<sup>12</sup>-labelled standards (IUPAC 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189) and native polybrominated biphenyl ethers standards (IUPAC 17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190, 209) were obtained from Cambridge Isotope Laboratories (Andover, MA, USA). Silica gel Discovery DSC-Si SPE cartridges (5 g) and Superclean Envicarb-PSA cartridges (1 g) were obtained from Supelco (Bellefonte, PA, USA).

#### Determination of Pesticides

Determinations were conducted on a Thermo-Finnigan Trace GC Ultra gas chromatograph (Austin, TX, USA)

connected via a heated transfer line with a Polaris Q low-resolution ion-trap mass spectrometer (Austin, TX, USA) was equipped with a Programmable Temperature Vaporizer (PTV)-based injector and TriPlus Autosampler (Austin, TX, USA). All separations were made on 60 m × 0.25 mm × 0.25 mm Zb-5 MS 5%-Phenyl-Arylene-fused-silica capillary column (Phenomenex, Torrance, CA, USA) connected via a Vu2 Union connector (Restek, Bellefonte, PA, USA) to a 5 m × 0.25 mm × 0.25 mm guard column/retention gap (Restek). Helium was used as a carrier gas at a constant flow rates of 1 ml min<sup>-1</sup>. The GC's oven program was as follows: initial 40 °C (1 min hold)—180 °C at 25 °C min<sup>-1</sup>—215 °C at 2 °C min<sup>-1</sup> (1 min hold)—255 °C at 5 °C min<sup>-1</sup> (0.5 min hold)—final 280 °C at 25 °C min<sup>-1</sup> (20 min hold). Spectrometer mass calibration was tuned against perfluorotributylamine (FC-43) in electron-impact positive ionization mode according to the manufacturer's recommendations. Pesticide residues in oil samples were determined using slightly modified method proposed in our previous study [12]. Briefly, 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. Neither recovery of pesticides from the analyzed spiked samples, relative recovery standard deviations, nor limits of quantification for individual pesticides were significantly different than those reported previously. Recovery of the analyzed pesticides from the fortified oil samples was within the 70–120% range, recovery relative standard deviation was below 20% in most cases. Pesticide recovery data are given in Table 1. Detailed analytical parameters including ionization and data acquisition methods used for pesticide determination were given previously [12].

#### Determination of PAHs

Determinations of PAHs were conducted on a Shimadzu (Duisburg, Germany) Prominence chromatographic system equipped with an auto injector, degasser and a FLD detector was used in this study. Analysis were performed on a Pinnacle II PAH (Restek), 4 μm, 150 mm × 3.2 mm column operated at a flow rate of 300 μl min<sup>-1</sup>. Following gradient mobile phase (A: Acetonitrile B: water) was used for separations: 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. Samples were introduced via a 10-μl loop type auto injector. PAHs were determined according to modified method proposed by Larsson et al. [13]. Briefly, 10 g of oil sample was placed in a separatory funnel, 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 with a 3 × 1 ml portions of cyclohexane on the SPE silica gel (5 g) cartridge, pre-conditioned with 20 ml of cyclohexane. 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 μl of acetonitrile and submitted to HPLC analysis.

#### Determination of PCBs and PBDEs

Determinations were performed on the same instrument/configuration as used for pesticide residue analysis. Helium was used as the carrier gas at a constant flow rate of 1 ml min<sup>-1</sup> in PCB analysis and programmed flow from 1.5 to 2.5 ml min<sup>-1</sup> for PBDE analysis. The GC's oven program in PCB analysis was as follows: initial 100 °C (3 min hold)—180 °C at 10 °C min<sup>-1</sup>—200 °C at 1.7 °C min<sup>-1</sup> (2 min hold)—240 °C at 1.8 °C min<sup>-1</sup> (8 min hold)—final 280 °C at 50 °C min<sup>-1</sup> (15 min hold), and for PBDE initial 80–180 °C at 3 °C min<sup>-1</sup> (20 min hold)—300 °C at 5 °C min<sup>-1</sup> (21 min hold)—310 °C at 10 °C min<sup>-1</sup> (41 min hold). To obtain the required sensitivity, the multiplier voltage was manually set to 1700 V, and automatic gain control to 15. Detailed analytical parameters including ionization and data acquisition methods used for PCB determination were given previously [14].

In the case of PBDE analysis the mass spectrometer was operated in the MS/MS mode. Helium was used as the ion-trap dumping gas (flow 1.7 ml min<sup>-1</sup> and 2.5 ml min<sup>-1</sup> for BDE 209) analysis were conducted at 31 eV electron energy and 250 mA emission current. [M-<sup>79</sup>Br<sup>81</sup>Br]<sup>+</sup> ions were used as an MS/MS precursor ion for all studied PBDEs. [M-(<sup>279</sup>Br)<sup>81</sup>Br]<sup>+</sup>, [M-<sup>79</sup>Br(<sup>281</sup>Br)]<sup>+</sup>, [M-(<sup>279</sup>Br)<sup>81</sup>Br-2CH<sub>2</sub>]<sup>+</sup> and [M-<sup>79</sup>Br(<sup>281</sup>Br)-2CH<sub>2</sub>]<sup>+</sup> peaks were monitored in MS/MS spectra for quantitative purposes. Determination of BDE 209 required separate ion optic lens optimization against *m/z* 614 of FC43 mass spectra. Ion source temperature was set to 300 °C, isolation time 20 ms, excitation time 30 ms. Excitation energies required for sufficient CID yield were in the 3.3–5.5 V range for tri- to deca- BDE. Xcalibur version 1.2 software was used for data acquisition and analysis.

Analytical method used to determine PCBs and PBDEs was based on procedures described in our previous study [13] with some major modifications based on results of Hanxia et al. [15]. Briefly, samples were spiked with <sup>13</sup>C<sub>12</sub> PCB recovery standards, dialyzed through LDPE semi-permeable membrane and cleaned with gel permeation chromatography as described previously. 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). First fraction contained PCBs and the second PBDEs. PCB fraction was subsequently fractionated using short (10 × 100 mm) Florisil column containing 2 g of activated Florisil. PCB fraction was evaporated to dryness and quantitatively transferred on the top of Florisil column with 2 × 1 ml portions of *n*-hexane. Florisil column was first eluted with 30 ml of dichloromethane:*n*-hexane mixture (0.5:99.5) (fraction containing *ortho*-substituted PCBs) and then with 25 ml of 50% dichloromethane : *n*-hexane mixture (fraction containing non-*ortho* substituted PCBs). PCB fractions were evaporated to dryness, spiked with injection standards, re-dissolved in 1 ml of *n*-hexane and submitted for GC/MS/MS analysis. GC/MS method used for PCB analysis was based on those reported previously [14] with modification of sample introduction technique. Injections were made into cold (60 °C) PTV injector baffle liner. A total of 40 µl of purified and concentrated extract was introduced into the PTV injector (10 µl s<sup>-1</sup>) working in the solvent split mode (with split valve set 200 ml min<sup>-1</sup>). After 1 min, the split valve was closed and the injector temperature was ramped to 280 °C and held for 2 min. Next, the injector temperature was increased to 320 °C (10 min hold) and the split valve was opened with flow rate set to 100 ml min<sup>-1</sup> to eliminate any residual high boiling contaminants out of the injector system.

The PBDE fraction was re-dissolved in *n*-hexane, spiked with injection standards and concentrated to an approximate volume of 100 µl under a gentle stream of nitrogen. The sample was introduced into GC/MS using the standard purged-splitless injection technique into a straight glass liner (2 mm ID). Injector was operated at 320 °C and helium pressure of 480 kPa was applied. A total of 6 µl of purified and concentrated extract was introduced into the PTV injector (10 µl s<sup>-1</sup>). Splitless time was set to 2 min. The carrier gas flow rate (not including initial ramp due to purged injection) was programmed starting from 1.5 ml min<sup>-1</sup> (50 min hold), to 2.5 ml min<sup>-1</sup> (40 min hold) and subsequently to 1.5 ml min<sup>-1</sup>.

#### Data Analysis

Results are given as a mean value of two parallel determinations (±one standard deviation, if given) of the composite laboratory sample (prepared from three different oils mixed at equal proportions). TEQs for individual PCBs were calculated using WHO 1998 published factors [16]. For each sample total TEQ value was calculated as the sum

of individual TEQs of all dl-PCBs. Lower-bound, medium-bound, and upper-bound results have been reported in line with Commission Regulation 1883/2006 [17]. Data in Table 8 were also calculated using the revised TEF 2005 values [18].

## Results and Discussion

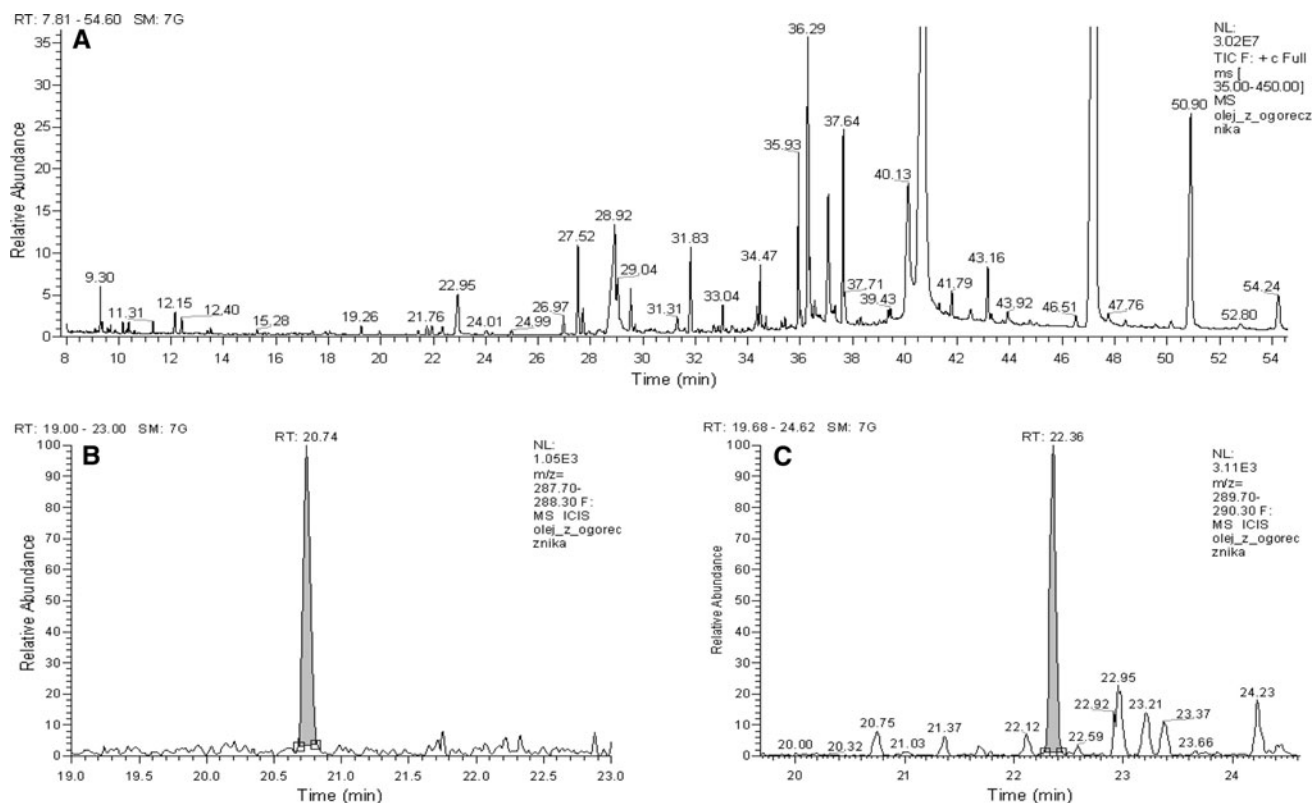
There is scarcely any literature data concerning the presence of chemical contaminants in cold-pressed vegetable oils. The present study revealed that pesticides, PAHs, PCBs and PBDEs were present in the cold pressed oils at varying concentration levels.

### Pesticides

Concentrations of pesticide residues found in the studied cold-pressed vegetable oil samples are given in Table 4. The results are quite surprising. Five out of 8 of the composite oil samples studied showed detectable amounts of pesticide residues. Mostly organophosphorus insecticide residues (Pirimiphos methyl, Chlorpyrifos methyl, DDVP) were found. DDT isomers and Trifluralin herbicide were determined in pumpkinseed oil. DDT is on the Stockholm persistent organic pollutant (POP) list and its presence in oil samples is most likely related to the environmental POPs background level. The highest total concentration of pesticides was found in the Linaire oil sample, with pirimiphos methyl concentration at the 1.170 mg kg<sup>-1</sup> level. European Union legislation does not recognize any maximum residue levels (MRLs) for the determined compound/ investigated oil combinations. Nevertheless, the concentrations are very high when compared to MRLs defined for oil seeds (0.05 mg kg<sup>-1</sup> for sum of DDT isomers, 0.05 mg kg<sup>-1</sup> for pirimiphos methyl, 0.01 mg kg<sup>-1</sup> for DDVP, 0.1 mg kg<sup>-1</sup> for trifluralin, 0.05 mg kg<sup>-1</sup> for chlorpyrifos methyl). Those MRLs were exceeded in the majority of the tested samples. A typical chromatogram of a vegetable oil sample is shown in Fig. 1. Pesticide residue levels found in the oil samples are probably among the most unexpected results. Organophosphorus (OPPs) insecticides are commonly used in agriculture for protection of oily plants. Most probably this fact is responsible for the presence of those compounds in cold-pressed vegetable oils. Most of OPPs are fat-soluble and might be easily stored in oil seeds. What's more, fats—as energy reserves for oil seeds—may be not subject to metabolic pathways that could affect OPPs. This hypothesis might also explain the very high concentrations of OPPs determined in the samples. Persistence of organophosphorus insecticides in vegetable oils was also reported previously [19]. Due to specific flavors and other characteristics of

**Table 4** Pesticide residues found in the studied vegetable oil samples (mean value of two parallel determinations for the composite oil sample)

Sample	Compound name	Concentration (mg kg <sup>-1</sup> )	Compound name	Concentration (mg kg <sup>-1</sup> )
Poppyseed oil	DDVP	0.032	Pirimiphos methyl	0.179
Pumpkinseed oil	DDT	0.02	Trifluralin	0.137
Linaire oil	Pirimiphos methyl	1.170		
Borage oil	Chlorpyrifos methyl	0.026	Pirimiphos methyl	0.054
Evening star oil	Pirimiphos methyl	0.059		

**Fig. 1** Full scan total ion current (a) 35–450 *m/z* chromatogram of a borage oil sample, and extracted ion current chromatograms showing peaks of chlorpyrifos methyl (b) and pirimiphos methyl (c)

cold-pressed vegetable oils, they are not as widely consumed as refined vegetable oils (except for virgin olive oil). Refined vegetable oils probably have significantly lower concentrations of various contaminants due to high temperature and/or pressure treatment. Those supposition is also confirmed by several literature data [20–22]. According to data reported by oil producers, organophosphorus insecticides are commonly found in vegetable oils at relatively high concentrations. Results of this study seem to confirm that data [21, 23].

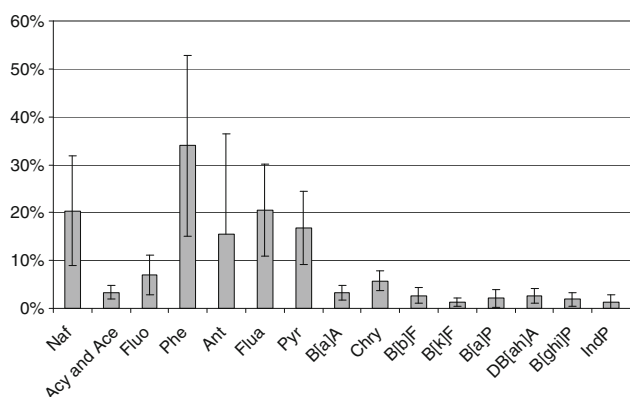
#### PAHs

Recovery of the studied PAHs, recovery relative standard deviation and operating parameters of the detector are given in Table 2. Data on PAHs contents found in the studied

cold-pressed vegetable oil samples are given in Table 5. Average concentration of all studied PAHs (15 + 1) was  $25.33 \pm 7.17 \mu\text{g kg}^{-1}$ . The highest concentration was found in cold-pressed pumpkinseed oil ( $37.16 \mu\text{g kg}^{-1}$ ) and the lowest one – in cold-pressed rapeseed oil samples ( $17.85 \mu\text{g kg}^{-1}$ ). Naphthalene, phenanthrene and pyrene were the most abundant PAHs among all studied ones. Average profile of PAHs in the studied samples is shown in Fig. 2. High concentrations of anthracene were also found in linaire seed and rapeseed oils. Maximum residue level of benzo[a]pyrene in vegetable oils according to the 1881/2006 EC Regulation is  $2 \mu\text{g kg}^{-1}$ . None of the samples exceeded that level: we found B[a]P concentrations within the  $0.02$ – $1.25 \mu\text{g kg}^{-1}$  range, the highest one in cold-pressed sesame oil, and the lowest one in cold-pressed rapeseed oil. Typical chromatogram showing the PAH vegetable oil PAH

**Table 5** Contents of PAHs determined in the studied vegetable oil samples (mean value of two parallel determinations for the composite oil sample)

PAHs (Abbrev.)	Sample							
	Poppy seed oil ( $\mu\text{g}/\text{kg}$ )	Hemp seed oil ( $\mu\text{g}/\text{kg}$ )	Pumpkin seed oil ( $\mu\text{g}/\text{kg}$ )	Linaira seed oil ( $\mu\text{g}/\text{kg}$ )	Borage oil ( $\mu\text{g}/\text{kg}$ )	Rapeseed oil ( $\mu\text{g}/\text{kg}$ )	Sesame seed oil ( $\mu\text{g}/\text{kg}$ )	Evening star oil ( $\mu\text{g}/\text{kg}$ )
Naf	2.26	<LOQ	3.98	8.87	1.46	3.86	4.19	2.97
Acy and Ace	0.41	0.15	0.88	0.73	0.78	1.06	0.45	0.63
Fluo	0.68	1.35	3.19	1.01	1.55	0.26	1.12	1.64
Phe	5.04	10.33	13.6	4.71	8.5	2.09	5.22	3.09
Ant	0.41	0.83	0.7	10.14	0.71	9.85	0.65	0.62
Flua	1.38	4.25	7.32	2.49	4.31	<LOQ	5.38	2.60
Pyr	4.66	2.52	3.91	2.44	3.65	0.64	5.74	2.49
B[a]A	0.81	0.27	0.44	0.27	0.78	<LOQ	1.08	0.78
Chry	1.52			0.41	0.97	<LOQ	1.39	1.29
B[b]F	0.67	0.19	0.67	0.23	0.88	0.02	0.77	0.75
B[k]F	0.28	0.06	0.28	0.12	0.49	0.01	0.42	0.37
B[a]P	0.27	0.12	0.42	0.19	0.39	0.02	1.25	0.58
DB[ah]A	0.33	0.1	0.35	<LOQ	0.57	<LOQ	1.09	0.59
B[ghi]P	0.4	0.16	0.4	0.12	0.32	0.03	0.96	0.52
IndP	0.22	0.11	0.06	0.14	0.09	0.02	1.03	0.35
Total PAHs ( $\mu\text{g}/\text{kg}$ )	19.35	20.95	37.16	31.87	25.46	17.85	30.76	19.26

**Fig. 2** Average profile of PAHs determined in the studied cold-pressed vegetable oil samples

fraction is shown in Fig. 3. The PAH contents found in the investigated samples were negligible as compared to the literature data. According to that data, a high concentration of polycyclic aromatic hydrocarbons in vegetable oils is mainly attributable to environment contamination, but may also be attributed to the process of oil production [24–26]. Oil seeds are subjected to a drying process prior to oil extraction. If some membrane-less drying technique based on combustion gases as the source of heat is used, a high contaminations of vegetable oils with PAHs may result. Drying methods commonly used nowadays are based rather on fluid beds that ensure a high quality of the final product.

PAH contents found in the samples do not differ significantly from literature data reported for common vegetable oils such as sesame oil, olive oil, or rapeseed oil [3, 26–30]. Low molecular PAHs are also reported as the most abundant compounds in vegetable oils.

#### PCBs and PBDEs

Recovery, recovery relative standard deviation, limits of quantification and ionization parameters for the PBDE congeners are given in Table 3.

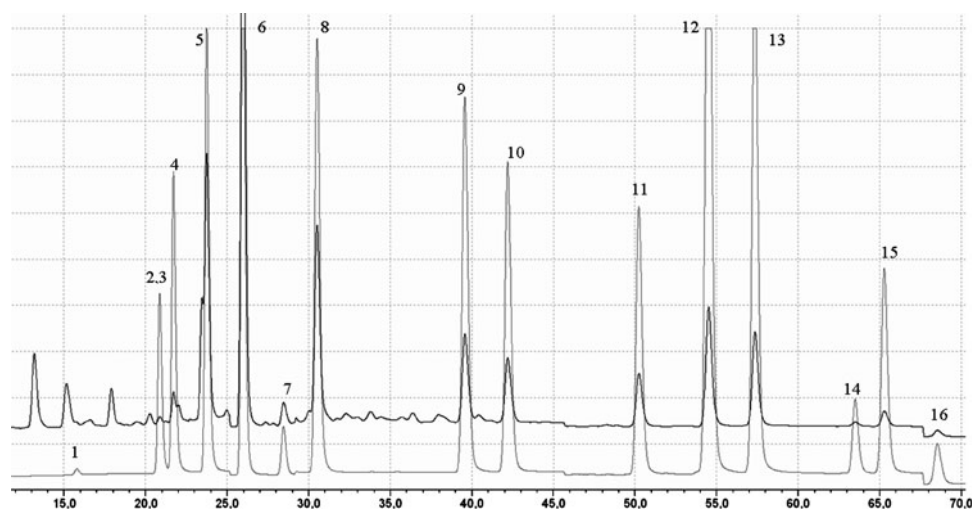
PCB and PBDE contents found in the studied cold-pressed vegetable oil samples are given in Tables 6 and 7.

Concentration of the marker PCBs (SUM6) in analyzed oil samples varied from 127 to 24,882  $\text{pg g}^{-1}$  (the pumpkinseed oil sample and the borage oil sample, respectively). Lower chlorinated congeners dominated the non-dioxin-like PCB fraction. PCB 28, 52 and 101 were the most abundant congeners.

Concentration of dioxin-like PCB congeners was generally low in the analyzed vegetable oil samples. The highest one was found for PCB 118 congener, while the most toxic PCB 126 congener was not found in majority of the analyzed samples at a concentration above LOQ (i.e.  $\geq 0.19 \text{ pg g}^{-1}$ ). The concentrations of twelve dioxin-like congeners were within the 9.7–128  $\text{pg g}^{-1}$  range (minimum for the hempseed oil sample, maximum for the borage oil sample).



**Fig. 3** HPLC-FLD chromatogram of a hemp seed oil fraction. Upper line shows the oil sample chromatogram, and the lower one chromatogram of the standard solution. (1 Naf, 2,3 Acy and Ace, 4 Fluo, 5 Phe, 6 Ant, 7 Flua, 8 Pyr, 9 B[a]A, 10 Chry, 11 B[b]F, 12 B[k]F, 13 B[a]P, 14 [DB[ah]A, 15 B[ghi]P, 16 IndP.)



**Table 6** Average contents of the studied PCB congeners in the analyzed oil samples (mean value of two parallel determinations for the composite oil sample)

PCB Congener	Concentration (pg g <sup>-1</sup> )							
	Poppy seed	Rapeseed	Sesame seed	Pumpkinseed	Hempseed	Linaire	Borage	Evening star
28	135.3	229.6	787.6	59.2	125.7	127.3	14935.3	624.7
52	104.7	187.8	664.2	25.9	72.3	56.4	9591.3	377.8
101	29.4	16.7	85.7	9.9	15.9	18.5	335.4	29.7
138	33.4	4.6	8.4	21.1	10.8	27.6	11.4	16.1
153	9.9	2.9	5.0	6.4	6.2	9.3	5.6	7.5
180	6.6	2.3	1.8	4.6	2.9	10.8	3.3	4.2
∑6	319.2	443.9	1552.7	127.2	233.7	250.0	24882.3	1060.0
77	2.0	1.8	8.4	1.0	<LOQ	1.0	19.0	2.8
81	<LOQ	<LOQ	<LOQ	<LOQ	0.7	<LOQ	0.7	<LOQ
105	8.6	4.2	21.3	<LOQ	2.4	2.9	28.6	6.1
114	1.1	2.0	2.2	<LOQ	1.8	2.9	23.9	3.5
118	14.2	7.2	33.0	<LOQ	4.8	6.2	54.3	13.6
123	0.2	0.2	1.0	<LOQ	0.0	0.0	1.4	0.3
126	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
156	1.0	<LOQ	<LOQ	<LOQ	<LOQ	1.9	<LOQ	<LOQ
157	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
167	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.7	<LOQ	<LOQ
169	0.2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
189	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

Typical chromatogram showing marker-PCB fraction extracted from an oil sample is shown in Fig. 4. Average profile of the PCB fraction within the oil samples is shown in Fig. 5.

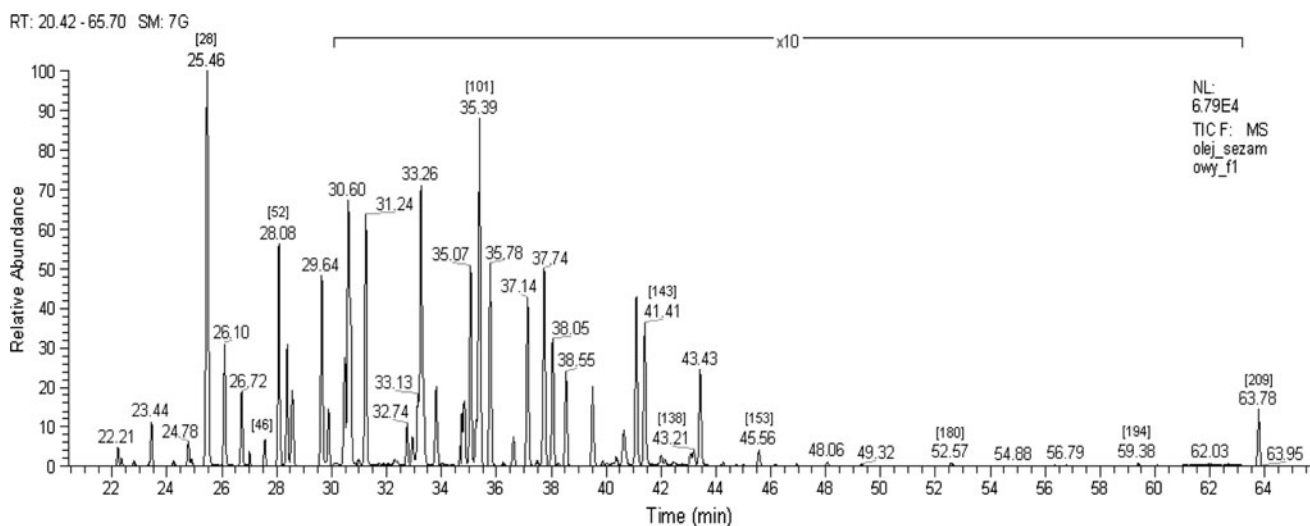
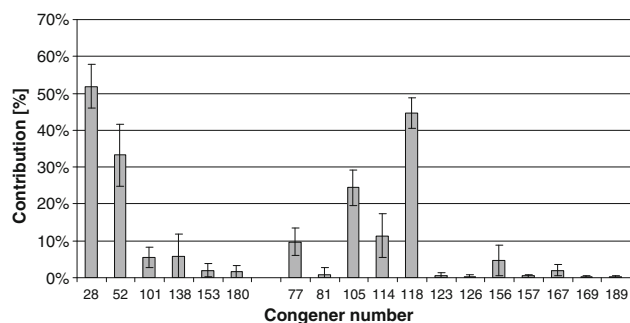
PCB TEQ values determined for the studied samples are shown in Table 8. PCBs 105, 114, 118 and 126 had the highest average contribution to PCB TEQ. Average total contribution of those four congeners accounted to more than 80% of the total PCB TEQ. TEQ results calculated for 2005 TEFs were generally lower than those calculated for

1998 TEFs. This is influenced mainly by decreased TEF values for mono-*ortho*-PCB in the 2005 TEF scheme.

Majority of the investigated PBDE congeners in the oil samples were below LOQ. BDE 47, 77 and 99 were the most abundant and subsequently the most frequently congeners found. The highest total concentration of 14 PBDEs was (19.3 pg g<sup>-1</sup>) found in the linaire oil sample. PCBs and PBDEs in oil may be attributable mainly to environmental contamination. However, such contaminants are typical for high-fat food products of animal origin

**Table 7** Average contents of the studied PBDE congeners in the analyzed oil samples (mean value of two parallel determinations for the composite oil sample)

PBDE Congener	Concentration (pg g <sup>-1</sup> )							
	Poppy seed	Rapeseed	Sesame seed	Pumpkin seed	Hempseed	Linaire	Borage	Evening star
17	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	3.7
28	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
47	2.8	2.1	<LOQ	<LOQ	<LOQ	19.3	<LOQ	<LOQ
66	<LOQ	1.6	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
71	1.3	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
85	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
99	2.3	6.2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
100	<LOQ	2.8	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
138	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
153	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	3.8	<LOQ
154	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
183	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
190	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
209	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
∑14	6.4	12.7			9.2	19.3		3.7

**Fig. 4** Total ion current MS/MS chromatogram of marker PCB sesame seed oil fraction. Numbers in brackets indicate PCB congener number**Fig. 5** Average contributions (±SD) of congeners to marker and dioxin-like PCB fractions

rather than for plant materials. Most of the studied PBDEs were generally not found in the investigated samples. Mostly lower brominated BDEs were found at very low concentrations. Those data are in concordance with data reported by other researchers [31–33]. However, Akutsu et al. reported high concentrations of decaBDE in vegetable oils. This study does not confirm those reports. Blanco et al. suggested that air concentrations of decaBDE could strongly affect analytical results and cause high values for procedural blanks [34].

Absolute concentration of PCBs in the samples were much higher than those found for PBDEs. Lower chlorinated PCBs were the most abundant, in concordance with

**Table 8** Average dioxin-like PCB contents expressed as dioxin toxicity equivalency determined in studied oil samples (mean value of two parallel determinations for the composite oil sample)

	Poppy seed oil	Rapeseed oil	Sesame seed oil	Pumpkin seed oil	Hempseed oil	Linaire oil	Borage oil	Evening star oil
TEQ 1998								
Lower bound	0.023	0.002	0.007	0.000	0.002	0.003	0.042	0.038
Medium bound	0.024	0.013	0.018	0.012	0.013	0.014	0.043	0.039
Upper bound	0.025	0.024	0.029	0.023	0.024	0.025	0.044	0.041
TEQ 2005								
Lower bound	0.020	0.001	0.003	0.000	0.000	0.001	0.024	0.035
Medium bound	0.023	0.013	0.015	0.013	0.013	0.013	0.027	0.038
Upper bound	0.026	0.025	0.027	0.025	0.025	0.025	0.030	0.041

results of Skribic et al. and Yagüe et al. [35] who reported high contribution of lower chlorinated biphenyls in vegetable oil samples. The profile of PCBs found in the analyzed samples shows a high contribution of low chlorinated congeners. Most probably such a profile is typical for products of plant origin. Concentrations of the most abundant 6 marker PCBs determined in this study were in the low  $\text{ng g}^{-1}$  range (except for one sample) and were similar to those reported by Skribic et al. and Marti et al.. An exceptionally high concentration was determined for the borage oil sample ( $\sim 25,000 \text{ pg g}^{-1}$ ). High differences in PCB concentration might be caused by regional PCB contamination, but in such a case, the PCB profile would differ, which was not the case in this study. The most probable cause of such a high variability are differences in atmospheric PCB absorption and/or mechanism of PCB deposition in plant fatty tissues. Different pathways of contaminations have already been reported for several plant varieties [36, 37]. Concentrations of dioxin-like PCBs in the studied samples expressed as dioxin toxicity equivalent were very low, significantly below  $0.1 \text{ pg TEQ g}^{-1}$  (even when expressed as the upper bound result). The difference between upper-bound and lower-bound results for many of the analyzed samples did not meet the requirements of the 1883/2006 EC Regulation [5] i.e. below 20% for  $\text{TEQ} \geq 1 \text{ pg g}^{-1}$  and within the 25–40% range for  $\text{TEQ} \leq 1 \text{ pg g}^{-1}$ . This is caused by very low TEQ concentrations determined in the analyzed samples. Concentration of the most toxic PCB 126 congener (with the highest assigned TEF value) was below LOQ.

The aim of this study was to investigate incidence of various groups of chemical food contaminants in cold-pressed vegetable oils. The environment was found to be the main source of contamination of cold-pressed oils with PCBs, PBDEs and also PAHs, whereas the presence of most of the pesticides may be traced back to agricultural practices. Results of this study indicate that various groups of chemical food contaminants may be found in

cold-pressed vegetable oils at relatively high concentrations. As it was mentioned earlier, literature data on presence of pesticides, PAHs, PCBs and PBDEs in cold-pressed oils are scarce, therefore it is impossible to assess health risk related to consumption of such oils. The main purpose of this study was to assess the necessity of monitoring residues of several classes of chemicals in cold-pressed vegetable oils. The presented data clearly expose the problem of cold-pressed oil chemical contamination (mainly by pesticides) rather than giving precise information on the levels of those substances in the studied group of products. Authors believe that further research on residues of various chemical compounds—especially pesticides—in cold-pressed vegetable oils is necessary.

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