

Contaminants in the paper-based food packaging materials used in the Czech Republic

LUKÁŠ VÁPENKA – ADAM VAVROUŠ – LENKA VOTAVOVÁ –
KRISTINA KEJLOVÁ – JAROSLAV DOBIÁŠ – JITKA SOSNOVCOVÁ

Summary

A set of 132 packaging materials based on paper, commonly used in the Czech Republic for food products packaging, was tested as regards the occurrence of contaminants. A number of 101 extractible substances were identified and the levels of 68 compounds, including residues from paper pulp processing (e.g. processing aids), substances originating from printing inks or adhesives (photoinitiators, plasticizers, solvents), impregnation and coating (solvents, hydrocarbons) in all the tested materials were quantified using gas and liquid chromatography coupled with tandem mass spectrometry techniques. The results indicated that phthalate plasticizers, anthraquinone, aromatic hydrocarbons and photoinitiators formed the most frequent group of xenobiotics in paper. The highest content in tested papers was determined for dibutyl phthalate (628 mg·kg⁻¹), benzophenone (369 mg·kg⁻¹) and diisobutyl phthalate (108 mg·kg⁻¹). Most of the contaminants in paper packaging materials originated from materials used for modification of functional properties (water-proof or fat-proof adjustment, coating, lamination with polymer films, etc.) and/or residues from recycled pulp.

Keywords

paper packaging; food contact materials; contaminants; migration; recycled pulp

Paper is an important material used for manufacturing of food packages. It is utilized (1) plain, (2) impregnated or coated with polymer materials, (3) laminated by polymer and/or metallic films and (4) decorated by printed inks. Paper materials can come into contact with food also in other cases, e.g. during filtration of liquid food through paper materials or baking on “baking” paper. Components of packaging materials in contact with food can migrate into foodstuffs and thus increase the xenobiotic load of the consumer organism.

Concerning the contaminants from paper packaging, migration of residues from the recycled pulp is of main importance [1–3]. There is a significant worldwide pressure on utilization of packaging waste. Systems of paper waste collection are becoming better organized in consequence of ever stricter legislative requirements. Due to this situation, paper and paperboard containing the re-

cycled pulp are more frequently offered for application in packaging materials intended for direct contact with food.

The level of migration from polymeric parts of paper-based packaging materials is controlled by European legislation [4].

Printing inks may contain substances with a so far incomplete toxicological profile, as printed surfaces are not intended to come into direct contact with food. However, it has been already proven that these substances may be transferred into food either by penetration through the food contact layer or by the so called “set-off” transfer, when contaminants from printing inks are dissolved in the food contact layer during storage of packaging materials in a roll. Printing inks are complex mixtures of colorants (pigments and dyes), vehicles or binders (various types of resins), solvents and additives (plasticizers, desiccants,

Lukáš Vápenka, Lenka Votavová, Jaroslav Dobiáš, Department of Food Preservation, University of Chemistry and Technology Prague, Technická 5, 166 28 Praha 6, Czech Republic.

Adam Vavrouš, Centre for Toxicology and Health Safety, National Institute of Public Health, Šrobárova 48, 100 00 Praha 10, Czech Republic; Department of Analytical Chemistry, Faculty of Science, Charles University in Prague, Albertov 6, 128 43 Praha 2, Czech Republic.

Kristina Kejlová, Jitka Sosnovcová, Centre for Toxicology and Health Safety, National Institute of Public Health, Šrobárova 48, 100 00 Praha 10, Czech Republic.

Correspondence address:

Lukáš Vápenka, e-mail: lukas.vapenka@vscht.cz

photoinitiators, adhesion promoters or wetting agents, biocides, etc.). They can be formed by systems dissolved in organic solvents, by water dispersions, by UV-cured inks or others. In the final form, the printing consists of a thin, dried or cured film, which forms the outside layer or interlayer of the packaging material [5].

At present, there is no EU-harmonized legislation on (1) paper-based packaging materials intended for direct contact with food, (2) control of application of paper containing recycled pulp in food packages similarly to that for recycled polymer materials [6, 7] and (3) quality of printing inks for food packages. Therefore, national regulations are utilized for these purposes. Generally, the Federal Institute for Risk Assessment Recommendations for paper and board for food contact (Berlin, Germany) [8, 9] provides the most widely accepted rules in Europe concerning paper packages, and Swiss Ordinance of the Federal Department of Home Affairs on Materials and Articles (Bern, Switzerland) [10] is regarded as the most reputable regulation for the quality of printing inks.

Studies on paper-based food packaging materials published in the last decade identified a wide range of substances including phenols [11, 12], 3-chloro-1,2-propanediol [13], methylnaphthalene [14], mineral oil hydrocarbons [15–20], perfluorinated compounds (PFC) [21–24], photoinitiators [25–27], phthalic acid esters [28, 29], solvent residues [30, 31] and others. Due to the great extent of use of packaging materials based on paper, it is important to search the ways how to reduce the occurrence of potentially dangerous contaminants and minimize their transfer to the packaged food products [32].

The aim of this research was, therefore, to investigate the presence of potentially dangerous substances in a large set of packaging materials based on paper used in the Czech Republic.

MATERIALS AND METHODS

Packaging materials

A set of 132 samples of paper-based food packaging materials and completed packages (boxes, trays, cups, sachets, etc.) used in the Czech Republic for food products was obtained from their producers or distributors. This collection included 69 samples of unprinted paper and paperboard (8 of them with polyethylene or polypropylene coating), 12 samples of unprinted baking papers, 10 oil-proof printed papers, 31 samples of printed paper without polymeric coating and

10 samples of printed paper with polyethylene or polypropylene coating. The content of recycled pulp was known for 42 tested samples and the set included mainly papers produced with a low content of recycled pulp ($\leq 10\%$, w/w) and samples containing more than 90% w/w of recycled fibres.

Chemicals

The standards of the investigated substances had a purity of $\geq 95\%$ w/w and were purchased from Dr. Ehrenstorfer (Augsburg, Germany), Sigma-Aldrich Chemie (St. Louis, Missouri, USA) or Tokyo Chemical Industry (Tokyo, Japan). Standard mixture solution ($100\ \mu\text{g}\cdot\text{ml}^{-1}$) of 16 polycyclic aromatic hydrocarbons (PAH) was obtained from Sigma-Aldrich. Selected perfluorinated compounds (PFC) were purchased from Wellington Laboratories (Guelph, Canada) in the form of solutions ($50\ \mu\text{g}\cdot\text{ml}^{-1}$). Isotopically labelled anthracene (D_{10}), benzophenone (D_{10}), bisphenol A (D_{14}) and di-2-ethylhexyl phthalate (D_4) were obtained from Sigma-Aldrich. Perfluorooctanoic acid (PFOA, $^{13}\text{C}_2$) was purchased from Wellington Laboratories. All quantified compounds are listed in Tab. 1.

All solvents used were of high purity grade and obtained from Sigma-Aldrich. Eluent additives ammonium acetate, ammonium formate and monobasic sodium phosphate monohydrate were purchased from Sigma-Aldrich. Water was purified by Purelab Classic system (ELGA LabWater, Wycombe, United Kingdom). Anhydrous magnesium sulfate (MgSO_4) and sodium chloride (NaCl) were purchased from Merck (Darmstadt, Germany). NaCl and MgSO_4 were treated by baking at $400\ ^\circ\text{C}$ for at least 4 h.

Standards were dissolved to form stock solutions ($1\ \text{mg}\cdot\text{ml}^{-1}$) in ethylacetate (PAH) or acetonitrile (other compounds), respectively. Calibration solutions ($0.1, 0.3, 1, 3, 10, 30, 100, 200$ and $300\ \text{ng}\cdot\text{ml}^{-1}$) were prepared by dilution of working mixtures ($1\ \mu\text{g}\cdot\text{ml}^{-1}$), which were diluted from stock or obtained solutions in acetonitrile.

Procedure of non-targeted screening

Solvent extraction

Tested paper packaging materials were cut into pieces of $5\ \text{mm} \times 5\ \text{mm}$ and $0.5\ \text{g}$ of the sample was extracted by $10\ \text{ml}$ of methanol in an ultrasonic bath (Ultrasonic UC 006 DMI, Bandelin Electronic, Berlin, Germany) for 30 min at laboratory temperature. The extract was evaporated to dryness at $40\ ^\circ\text{C}$ using a rotary vacuum evaporator and re-dissolved in $2\ \text{ml}$ of methanol. A volume of $1\ \mu\text{l}$ of this solution was injected into a gas chromatograph coupled to a mass spectrometric detec-

tor and analysed at following conditions: gas chromatograph Agilent 6890N (Agilent Technologies, Santa Clara, California, USA); detector Agilent 5973N mass selective detector, electron impact ionization 70 eV, temperature 280 °C; capillary column DB-5ms (30 m × 0.25 mm × 0.25 µm, Agilent Technologies); mobile phase He, flow rate 1.0 ml·min⁻¹, linear speed 36.0 cm·s⁻¹; injection 1 µl using split 1:1, temperature 250 °C; oven temperature 40 °C for 1 min, increase 10 °C·min⁻¹ to 325 °C, 325 °C for 15 min. Identification of separated substances was firstly based on comparison of the obtained mass spectra with the spectrum library of the chromatography software NIST MS Search 2.0, Standard Reference Data Program (National Institute of Standards and Technology, Gaithersburg, Maryland, USA). The identification was then confirmed using standard chemicals.

Solid phase extraction

An amount of 0.5 g of cut paper was placed in a vial for solid phase microextraction (SPME). Volatiles in headspace were trapped by SPME fibre type divinylbenzene/carboxen/polydimethylsiloxane (Supelco, Bellefonte, Pennsylvania, USA) at 40 °C for 30 min. The fibre with adsorbed volatiles was transferred into the desorption port of a gas chromatograph Agilent 7890 coupled to a mass selective detector Agilent 5975C and analysed in the same conditions as mentioned above for solvent extraction.

Procedure of contaminants quantification

Quantification of 68 selected contaminants was performed using techniques of gas chromatography coupled to tandem mass spectrometry (GC-MS/MS) and high-performance liquid chromatography coupled to tandem mass spectrometry (HPLC-MS/MS) after solvent extraction as described in our previous study [33].

Expression of results

Each packaging material was tested in two replicates and the results were averaged. Content of each contaminant in paper was expressed as amount of contaminant per dry matter weight of the paper material.

Statistical analysis

At least two parallel tests were performed for all experiments mentioned above. The mean value (\bar{x}) and the standard deviation (SD) were calculated for each xenobiotic content in twenty tested packaging materials with the content of recycled pulp below 10% w/w and above 90% w/w. The difference between results of determination of

contaminant content in papers with and without recycled fibres was evaluated statistically using Student's t-test ($\alpha = 0.05$).

RESULTS AND DISCUSSION

The first aim of this study was to evaluate the occurrence of contaminants in a relatively large set of packaging materials based on paper, which are used in the Czech Republic for packaging food products. This was achieved by a non-targeted screening by GC-MS technique providing identification of a maximum number of extractable contaminants. At this stage, 132 samples of paper-based food packaging materials were analysed and 101 extractable contaminants, including residues from paper pulp processing (e.g. processing aids, products of wood degradation), the substances originating from printing inks or adhesives (photoinitiators, plasticizers, solvents), impregnation and coating (solvents, hydrocarbons), etc. were identified.

A set of 68 substances was selected, on the basis of the preliminary experiments and literature data, and their levels in 132 packaging materials were quantified by GC-MS/MS and HPLC-MS/MS techniques. The results are summarized in Tab. 1. The identified xenobiotics were arranged into groups with regard to their probable origin: (1) eight residues from paper pulp processing, (2) ten phthalate plasticizers, (3) five non-phthalate plasticizers, (4) twenty seven aromatic hydrocarbons, with the highest levels of isopropyl-naphthalene isomers, (5) nine photoinitiators, (6) three bisphenols, (7) twenty PFC, (8) five lubricants, and (9) fourteen other contaminants.

Residues from paper pulp processing

Anthraquinone was the most frequent contaminant originating from pulp processing [34]. It was found in 91 of the tested packaging materials at levels from 0.015 mg·kg⁻¹ to 26.5 mg·kg⁻¹. Considering the grammage of paper sheets in the range of 50–250 g·m⁻² and the highest found content of anthraquinone, the amount of this contaminant in the packaging material could have been in the range of 0.013–0.066 mg·dm⁻². If the layer of such paper was not separated from the packaged food with an efficient barrier, the level of anthraquinone migration could easily exceed the specific migration limit of 0.0017 mg·dm⁻² (0.01 mg·kg⁻¹) given by Regulation (EC) No. 10/2011 [4].

Phthalate plasticizers

The obtained data on the occurrence of

Tab. 1. Identified and quantified compounds found in 132 examined samples of paper and paperboard packaging materials.

Compound	CAS No.	Toxicological data	Occurrence in real samples [mg·kg ⁻¹]		N	Origin/function	Legislation restriction for food contact materials
			Min.	Max.			
Residues from pulp processing							
Anthraquinone	84-65-1	Acute oral median <i>LD</i> ₅₀ in rats > 5000 mg·kg ⁻¹ , very low acute toxicity, possible carcinogen for humans	0.015	26.5	91	Catalyst, pesticide ingredient	SO-IVB
Apocynin	498-02-2	Acute oral <i>LD</i> ₅₀ in rats 9 g·kg ⁻¹ , very low acute toxicity, investigated as a mutagen and reproductive effector	not quantified		2	Results from lignin sulphonic acid	–
Octadecyl palmitate	100231-75-2	Toxicological data not available	not quantified		6	Natural compound of wood	–
Eicosyl palmitate	22413-01-0	Toxicological data not available	not quantified		2	Natural component of wood	–
3-Hydroxy-4-methoxy benzaldehyde	621-59-0	Toxicological data not available	not quantified		26	Component of paper pulp	–
Coniferyl aldehyde	458-36-6	Toxicological data not available	not quantified		3	Results from apocynin	–
4-((1 <i>E</i>)-3-Hydroxy-1-propenyl)-2-methoxyphenol	1000297-95-5	Toxicological data not available	not quantified		1	Product of heat decomposition of lignin	–
γ-Sitosterol	83-47-6	Toxicological data not available	not quantified		31	Natural compound of wood	–
Phthalic acid esters							
Dimethyl phthalate	131-11-3	<i>LD</i> ₅₀ for rats 6.8 g·kg ⁻¹ , not classifiable as to human carcinogenicity	0.005	1.54	89	Plasticisers for cellulose esters, fragrance ingredient in cosmetic)	SO-IVA: <i>SML</i> = 0.5 mg·kg ⁻¹
Diethyl phthalate	84-66-2	Intraperitoneal <i>LD</i> ₅₀ in the range from 2 830 mg·kg ⁻¹ in mice; not classifiable as to its carcinogenicity to humans	0.024	1.56	99	Plasticizer, ingredient in cosmetic formulations	SO-IVB
Dibutyl phthalate	84-74-2	Oral <i>LD</i> ₅₀ in rats between 8 000 and 20 000 mg·kg ⁻¹ , potential risk to human health, moderately toxic by ingestion and skin contact; experimental teratogen; reproductive effects	0.124	628	98	Plasticizer, paint solvent, vehicles for pigment dispersion	PL: <i>SML</i> = 0.3 mg·kg ⁻¹ PU: <i>SML</i> = 0.3 mg·kg ⁻¹ SO-IVA: <i>SML</i> = 0.3 mg·kg ⁻¹
Diisobutyl phthalate	84-69-5	<i>LD</i> ₅₀ for mice 12.8 g·kg ⁻¹ , reproductive toxicity	0.077	108	109	Plasticizer in the flexible vinyl industry	PU: <i>SML</i> = 0.3 mg·kg ⁻¹ SO-IVB
Dipentyl phthalate	131-18-0	<i>LD</i> ₅₀ for rats 29.6 g·kg ⁻¹ , reproductive toxicity	0.001	0.075	26	Plasticizer in the flexible vinyl industry	–
Diheptyl phthalate	3648-21-3	No data on <i>LD</i> ₅₀ values; lowest observed-adverse effect level for rat developmental toxicity 0.25 g·kg ⁻¹ ·d ⁻¹	0.001	0.075	70	Plasticizer in the flexible vinyl industry	SO-IVB
Dioctyl phthalate	117-84-0	<i>LD</i> ₅₀ for rats 53.7 g·kg ⁻¹ , reproductive toxicity – Category 1B, no risk for human health	0.006	0.643	85	Plasticizer in the flexible vinyl industry, dye carrier in plastics production	SO-IVB
Di-2-ethylhexyl phthalate	117-81-7	Oral <i>LD</i> ₅₀ in rats between 26 g·kg ⁻¹ and 33 g·kg ⁻¹ , low toxicity from acute (short-term) and chronic (long-term) exposures, possible carcinogen for humans	0.133	22.1	75	Plasticizer in the flexible vinyl industry; lubricating oils and defoaming agents in paper and paperboard manufacture	PL: <i>SML</i> = 1.5 mg·kg ⁻¹ PU: <i>SML</i> = 1.5 mg·kg ⁻¹ SO-IVA: <i>SML</i> = 1.5 mg·kg ⁻¹
Diisononyl phthalate	28553-12-0	Oral <i>LD</i> ₅₀ values of diisopropylnaphthalene in rats from > 9 800 mg·kg ⁻¹ to > 50 000 mg·kg ⁻¹ , low degree of acute toxicity, not classified or labelled for human health effects	0.141	25.1	79	Plasticizer in the flexible vinyl industry	PL: <i>SML</i> (T) = 9 mg·kg ⁻¹ for sum of aliphatic esters with C8–C10

Tab. 1. continued

Compound	CAS No.	Toxicological data	Occurrence in real samples [mg·kg ⁻¹]		N	Origin/function	Legislation restriction for food contact materials
			Min.	Max.			
Diisodecyl phthalate	26761-40-0	LD ₅₀ for rats 29.1 g·kg ⁻¹ , developmental toxicity	0.102	7.59	78	Plasticizer in the flexible vinyl industry	PL: SML(T) = 9 mg·kg ⁻¹ for sum of aliphatic esters with C9–C11
Non phthalate plasticizers							
Di-2-ethylhexyl adipate	103-23-1	Oral LD ₅₀ in rats 45 g·kg ⁻¹ , very low acute toxicity	0.133	22.1	75	Plasticizer in the flexible vinyl industry; additive in processing of nitrocellulose and synthetic rubber	PL: SML = 18 mg·kg ⁻¹ SO-IVA: SML = 18 mg·kg ⁻¹
Tributyl phosphate	126-73-8	Acute oral toxicity values from 1.39 g·kg ⁻¹ to 3.35 g·kg ⁻¹ in rats and from 0.4 g·kg ⁻¹ to 1.2 g·kg ⁻¹ in mice	not quantified		7	Plasticizer for cellulose esters, printing ink solvent	SO-IVA: SML = 0.05 mg·kg ⁻¹
Dibutyl phenyl phosphate	2528-36-1	Oral LD ₅₀ for adult hen 1.5 g·kg ⁻¹ , further toxicological data not available	not quantified		1	Polyvinyl chloride plasticizer	–
Diethylene glycol dibenzoate	120-55-8	Oral LD ₅₀ for rats 2.83 g·kg ⁻¹ , life-threatening acute toxicity at large, deliberate ingestions	not quantified		46	Plasticizer for polyvinyl chloride acetate, component of adhesives	SO-IVB
Methyl n-hexadecanoate	112-39-0	Toxicological data not available	not quantified		1	Plasticizer, printing ink solvent, lubricant	–
Polycyclic aromatic hydrocarbons							
1,1,2-Dimethylnaphthalene	573-98-8	Median LC ₅₀ for <i>Paracartia grani</i> 161 µg·l ⁻¹ , further toxicological data not available	0.003	0.100	28	Precursor to produce dyes and resins, AAHs	–
1,4-Dimethylnaphthalene	571-58-4	Oral LD ₅₀ in rats 2730 mg·kg ⁻¹ , no adverse effects to humans	0.002	0.075	30	Sprout inhibitor, PAHs	–
1,6-Dimethylnaphthalene	575-43-9	Toxicological data not available	0.003	0.369	79	PAHs, liquid scintillators	–
1-Methylfluorene	1730-37-6	Toxicological data not available	0.002	1.10	101	Product of decomposition, AAHs	–
1-Methylnaphthalene	90-12-0	Oral LD ₅₀ values in rats 1840 mg·kg ⁻¹ , no toxicological risk assessment	0.004	0.160	39	Precursor to produce dyes and resins, AAHs	–
2,6-Diisopropylnaphthalene	24157-81-1	Oral LD ₅₀ values in rats 5.1 g·kg ⁻¹ , may cause irritation to eyes, skin and mucous membranes	0.008	4.04	107	Dye solvent for carbonless copy paper, sprout inhibitor	PU: as low as technically feasible
2,6-Dimethylnaphthalene	581-42-0	Toxicological data not available	0.002	0.244	77	Material for high performance polyester fibres and films, AAHs	–
2,7-Diisopropylnaphthalene	40458-98-8	Oral LD ₅₀ values in rats 4.1 g·kg ⁻¹	0.007	3.72	105	Dye solvent for carbonless copy paper, sprout inhibitor	PU: as low as technically feasible
2-Methylantracene	613-12-7	Toxicological data not available	0.004	0.209	77	Pollutant, combustion product, AAHs	–
2-Methylnaphthalene	91-57-6	Oral LD ₅₀ values in rats 4.2 g·kg ⁻¹ , may cause irritation to skin, eyes, mucous membranes and upper respiratory tract	0.005	0.188	33	Solvent, dye carrier, combustion product, mineral oil aromatic hydrocarbon	–
9-Methylantracene	779-02-2	Mouse Toxic Dose Low (intraperitoneal) 11 mg·kg ⁻¹ , equivocal carcinogenic agent by Registry of Toxic Effects of Chemical Substances criteria	0.030	0.148	6	Product of decomposition and combustion, AAHs	–

Tab. 1. continued

Compound	CAS No.	Toxicological data	Occurrence in real samples [mg·kg ⁻¹]		N	Origin/function	Legislation restriction for food contact materials
			Min.	Max.			
Acenaphthene	83-32-9	Oral LD ₅₀ values in rats 1.7 g·kg ⁻¹ , may cause irritation to skin and mucous membranes, not classifiable as to carcinogenicity to humans	0.013	0.014	2	Precursor to produce dyes and resins, product of decomposition and combustion, PAHs	–
Acenaphthylene	208-96-8	Oral LD ₅₀ values in mice 1.7 g·kg ⁻¹ , not enough information to classify as a carcinogen	0.002	0.031	9	Used to produce dyes, plastics and pesticides, PAHs	–
Anthracene	120-12-7	Oral LD ₅₀ values in mice 4.9 g·kg ⁻¹ , not classifiable as to carcinogenicity to humans	0.003	0.675	54	Component of coal tar, precursor to produce dyes, anthraquinone, PAHs	–
Benzo(a)anthracene	56-55-3	Intravenous LD ₅₀ values in rats > 200 mg·kg ⁻¹ , possibly carcinogenic to humans	0.002	0.039	72	Product of decomposition and combustion, PAHs	–
Benzo(a)pyrene	50-32-8	Intraperitoneal LD ₅₀ in mice 232 mg·kg ⁻¹ , limit in food products from 1 µg·kg ⁻¹ to 10 µg·kg ⁻¹ , carcinogenic to humans	0.006	0.007	3	Product of combustion, component of coal tar, pollutant, PAHs	–
Benzo(b)fluoranthene	205-99-2	Causes skin and eye irritation, produced skin tumours in mice following repeated skin paintings, possibly carcinogenic to humans	0.003	0.035	63	Product of combustion, pollutant, PAHs	–
Benzo(g,h)perylene	191-24-2	Not classifiable as to carcinogenicity to humans	0.007	0.080	65	Product of combustion, pollutant, PAHs	–
Benzo(k)fluoranthene	207-08-9	Causes skin and eye irritation, skin application on mice produced tumours, possibly carcinogenic to humans	0.003	0.017	33	Product of combustion, pollutant, PAHs	–
Dibenzo(a,h)anthracene	53-70-3	May irritate skin and eyes. B2 – probable human carcinogen, probably carcinogenic to humans	0.012		1	Product of combustion, pollutant, PAHs	–
Fluorene	86-73-7	Causes skin, eye and respiratory irritation, low order of acute toxicity in humans, not classifiable as to carcinogenicity to humans	0.004	1.21	81	Component of coal tar, precursor to produce dyes, resins and polymers, pollutant, PAHs	–
Fluoranthene	206-44-0	Dermal LD ₅₀ values in rabbits 3.1 g·kg ⁻¹ ·d ⁻¹ , causes skin, eye and respiratory irritation, low order of acute toxicity in humans, not classifiable as to carcinogenicity to humans	0.002	0.119	88	Component of coal tar, product of combustion, pollutant, PAHs	–
Chrysene	218-01-9	Oral LD ₅₀ values in mice > 320 mg·kg ⁻¹ , causes skin, eye and respiratory irritation, low order of acute toxicity in humans, possibly carcinogenic to humans	0.003	0.137	82	Component of coal tar and creosote, precursor to produce dyes, pollutant, PAHs	–
Indeno(1,23-cd)pyrene	193-39-5	Causes skin, eye and respiratory irritation, low order of acute toxicity in humans, possibly carcinogenic to humans	0.004	0.022	32	Component of coal tar, cigarette smoke, pollutant, PAHs	–
Naphthalene	91-20-3	May cause irritation to eyes, skin, and mucous membranes, oral LD ₅₀ in mice 533 mg·kg ⁻¹ , possibly carcinogenic to humans	0.013	0.338	28	Household fumigant, precursor to other chemicals used as plasticizers, precursor to produce dyes, component of creosote, mineral oil aromatic hydrocarbon	–
Phenanthrene	85-01-8	Oral and intravenous LD ₅₀ values in mice 700 mg·kg ⁻¹ and 56 mg·kg ⁻¹ , respectively, causes skin, eye and respiratory irritation, not classifiable as to carcinogenicity to humans	0.004	0.408	90	Precursor to produce dyes, plastics and pesticides, explosives and drugs, component, cigarette smoke, pollutant, PAHs	–
Pyrene	129-00-0	Oral LD ₅₀ value in rats 2.7 g·kg ⁻¹ , causes skin and eye irritation, not classifiable as to carcinogenicity to humans	0.004	0.120	86	Precursor to produce dyes, plastics and pesticides, pollutant, PAHs	–

Tab. 1. continued

Compound	CAS No.	Toxicological data	Occurrence in real samples [mg·kg ⁻¹]		N	Origin/function	Legislation restriction for food contact materials
			Min.	Max.			
Photoinitiators							
2-Isopropylthioxanthone	5495-84-1	Available in vivo studies do not indicate a genotoxic potential	0.005	1.86	72	Photoinitiator	SO-VA: <i>SML</i> = 0.05 mg·kg ⁻¹ G-1C: <i>SML</i> = 0.05 mg·kg ⁻¹
4-Isopropylthioxanthone	83846-86-0	Toxicological data not available	0.013	0.230	68	Photoinitiator	SO-VA: <i>SML</i> = 0.05 mg·kg ⁻¹ G-1C: <i>SML</i> = 0.05 mg·kg ⁻¹
4-Methylbenzophenone	134-84-9	Oral <i>LD</i> ₅₀ value in mice > 2 g·kg ⁻¹ , intraperitoneal <i>LD</i> ₅₀ in mouse 250 mg·kg ⁻¹	0.006	2.38	102	Photoinitiator	SO-VA: <i>SML</i> = 0.05 mg·kg ⁻¹ G-1C: <i>SML</i> * = 0.6 mg·kg ⁻¹
Benzophenone	119-61-9	Oral <i>LD</i> ₅₀ value in mice 2.9 g·kg ⁻¹ , possibly carcinogenic to humans	0.015	369	112	Flavour ingredient, manufacture of insecticides, agricultural chemicals, hypnotic drugs, antihistamines and other pharmaceuticals, photoinitiator	PU: <i>SML</i> = 0.6 mg·kg ⁻¹ SO-VA: <i>SML</i> (T) = 0.6 mg·kg ⁻¹ G-1C: <i>SML</i> * = 0.6 mg·kg ⁻¹
Ethyl-4-dimethylamino benzoate	10287-53-3	Toxicological data not available	0.003	0.598	83	Photoinitiator	SO-VA: <i>SML</i> = 0.05 mg·kg ⁻¹ (under re-evaluation) G-1C: <i>SML</i> = 0.05 mg·kg ⁻¹
2-Ethylhexyl-4-dimethylamino benzoate	21245-02-3	Low acute toxicity, no observed adverse effect level for pigmentation of the spleen in rats 100 mg·kg ⁻¹ ·day ⁻¹ , causes skin and serious eye irritation	0.002	53.5	75	Photoinitiator	SO-VA: <i>SML</i> = 2.4 mg·kg ⁻¹ G-1A: <i>SML</i> = 2.4 mg·kg ⁻¹
2,2-Dimethoxy-2-phenylacetophenone	24650-42-8	Oral <i>LD</i> ₅₀ for rats > 6 g·kg ⁻¹ , low oral toxicity, ingestion may cause irritation of the gastrointestinal tract	not quantified		2	Photoinitiator	SO-VB, G-2
Methyl 2-benzoylbenzoate	606-28-0	Toxicological data not available	not quantified		2	Photoinitiator	SO-VB G-1C: <i>SML</i> = 0.05 mg·kg ⁻¹
4-Phenylbenzophenone	2128-93-0	Intraperitoneal <i>LD</i> ₅₀ for mice 2 g·kg ⁻¹	not quantified		13	Photoinitiator	SO-VB, G-2
Bisphenols							
Bisphenol A	80-05-7	Acute intraperitoneal <i>LD</i> ₅₀ in rats 841 mg·kg ⁻¹ intraperitoneal, acute intravenous <i>LD</i> ₅₀ in rats 35.3 mg·kg ⁻¹ , acceptable daily intake 50 µg·kg ⁻¹ ·d ⁻¹ , not carcinogenic to humans	0.052	25.4	74	Intermediate in the production of polycarbonate, resins and modified polyamides	PL: <i>SML</i> = 0.6 mg·kg ⁻¹ PU: <i>SML</i> = 0.6 mg·kg ⁻¹ SO-IA: <i>SML</i> = 0.6 mg·kg ⁻¹ SO-IB
Bisphenol F	620-92-8	Toxicological data not available	0.039	0.873	27	Production of epoxy resins lacquers, varnishes, liners, adhesives plastics	
Bisphenol S	80-09-1	Acute oral <i>LD</i> ₅₀ in rats > 5 000 mg·kg ⁻¹ , very low acute toxicity	0.003	8.41	71	Substitute of bisphenol A, anticorrosive agent	PL: <i>SML</i> = 0.05 mg·kg ⁻¹
Perfluorinated compounds							
Sodium bis(1H,1H,2H,2H-perfluorooctyl) phosphate	–	Toxicological data not available	0.004	13.9	64	Fluorochemical-treated paper for food, grease-proofing agents for food-contact paper, surfactant and surface protection products, pollutant	–
Sodium 1H,1H,2H,2H-perfluorooctyl phosphate	–	Toxicological data not available, covalent binding to plasma, liver and kidney proteins in rats	0.123	27.2	6	–	–

Tab. 1. continued

Compound	CAS No.	Toxicological data	Occurrence in real samples [mg·kg ⁻¹]		N	Origin/function	Legislation restriction for food contact materials
			Min.	Max.			
Sodium bis(1H,1H,2H,2H-perfluorodecyl) phosphate	–	Toxicological data not available, effects on steroidogenesis in H295R human adrenal corticocarcinoma cells	0.013	4.75	8	–	–
Sodium 1H,1H,2H,2H-perfluorodecyl phosphate	–		0.072	23.5	26	–	–
Perfluorooctylsulfonamide	754-91-6	Toxicological data not available	0.004	0.005	2	Fluorochemical-treated paper for food, grease-proofing agents for food-contact paper, pollutant	–
Perfluorobutanoic acid	375-22-4	Drinking water criteria (Health Risk Limit) 7 µg·l ⁻¹	0.005	0.022	8	Fluorochemical-surfactant, grease-proofing agents, pollutant	–
Perfluorobutanesulfonic acid	375-73-5	Oral LD ₅₀ values in rats 430 mg·kg ⁻¹ , causes severe skin burns and eye damage	< 0.0013 **		0	Fluorochemical-surfactant, grease-proofing agents, pollutant	–
Perfluorodecanoic acid	335-76-2	Oral LD ₅₀ values in rats 57 mg·kg ⁻¹	0.026		1	Fluorochemical-surfactant, grease-proofing agents, pollutant	–
Perfluorododecanoic acid	307-55-1	Causes skin and serious eye irritation	0.014		1	Fluorochemical-surfactant, grease-proofing agents, pollutant	–
Perfluorodecane-phosphonic acid	–	Toxicological data not available	0.023	0.070	18	Levelling and wetting agents in waxes and coatings, dampening agents	–
Perfluorooheptanoic acid	375-85-9	LC ₅₀ for <i>Daphnia magna</i> 10 g·l ⁻¹ , causes severe skin burns and eye damage, further toxicological data not available	0.007	0.021	2	Fluorochemical-surfactant, grease-proofing agents, pollutant	–
Perfluorohexanoic acid	307-24-4	No evidence of carcinogenicity in rats when administered orally daily for 7 days per week for 104 weeks, pathologic changes restricted to kidney at 200 mg·kg ⁻¹ ·d ⁻¹	0.001	0.018	28	Fluorochemical-surfactant, grease-proofing agents, pollutant	–
Perfluorohexane-phosphonic acid	–	Toxicological data not available	0.014	0.038	4	Levelling and wetting agents in waxes and coatings, dampening agents	–
Perfluorohexane-sulphonic acid	355-46-5	Increases blood lipid levels, further toxicological data not available	< 0.030 **		0	Fluorochemical-surfactant, grease-proofing agents, pollutant	–
Perfluorononanoic acid	375-95-1	Immunotoxic effects from a single dose, including lymphoid organ atrophy, splenic and thymic cellularity, and altered ratios of leukocyte populations	0.036		1	Fluorochemical-surfactant for the production of the fluoropolymers, grease-proofing agents	–
Perfluorooctanoic acid	335-67-1	Oral LD ₅₀ values in rats from 430 mg·kg ⁻¹ to 680 mg·kg ⁻¹ , no observed adverse effect level for male rats 0.06 mg·kg ⁻¹ ·d ⁻¹ , chronic toxicity and carcinogenicity recently evaluated by U.S. EPA	0.006	0.028	2	Fluorochemical-surfactant for the production of the fluoropolymers, grease-proofing agents, pollutant	–
Perfluorooctane-phosphonic acid	–	Causes skin and serious eye irritation, lack of hazard data, potential persistence and toxicity	0.017	0.044	3	Levelling and wetting agents in waxes and coatings, dampening agents	–
Perfluorooctane-sulphonic acid	1763-23-1	Oral LD ₅₀ values in rats from 199 mg·kg ⁻¹ to 318 mg·kg ⁻¹ , no observed adverse effect level for monkeys 0.3 mg·kg ⁻¹ ·d ⁻¹ , chronic toxicity and carcinogenicity recently evaluated by U.S. EPA	0.007		1	Fluorochemical-surfactant, impregnation agents for textiles, paper, and leather, pollutant	–

Tab. 1. continued

Compound	CAS No.	Toxicological data	Occurrence in real samples [mg·kg ⁻¹]		N	Origin/function	Legislation restriction for food contact materials
			Min.	Max.			
Perfluoropentanoic acid	2706-90-3	Causes severe skin burns and eye damage, further toxicological data not available	< 0.052**		0	Fluorochemical-surfactant, grease-proofing agents, pollutant	–
Perfluoroundecanoic acid	2058-94-8	Causes skin and serious eye irritation, possible effects on reproduction and development as well as possible general toxic effects in rats	0.022		1	Fluorochemical-surfactant, grease-proofing agents, pollutant	–
Lubricants							
Methyl eicosanoate	1120-28-1	Not classifiable as a human carcinogen	not quantified		32	Lubricant	–
Methyl laurate	10233-13-3	Not classifiable as a human carcinogen	not quantified		22	Lubricant	–
Methyl linoleate	112-63-0	Not classifiable as a human carcinogen	not quantified		13	Lubricant	–
Methyl stearate	112-61-8	Not classifiable as a human carcinogen	not quantified		2	Lubricant	–
Methyl linoleate	112-63-0	Oral LD ₅₀ for rabbits 3.2 g·kg ⁻¹ , further toxicological data not available	not quantified		7	Plasticizer, solvent of printing inks, lubricant	–
Other contaminants							
4,4a,9,10-Tetrahydro-4a-methyl-2(3H)-phenanthrene	6606-34-4	Toxicological data not available			1	–	–
2,2',5,5'-Tetramethyl-1,1'-biphenyl	3075-84-1	Toxicological data not available			1	–	–
Methyl dehydroabietate	1235-74-1	Oral LD ₅₀ for mice 300 mg·kg ⁻¹ , further toxicological data not available			32	Cellulose derivative, component of varnishes, printing inks and adhesives	–
2,5-Dichloranilin	95-82-9	Oral LD ₅₀ for mice 1.6 g·kg ⁻¹ , intraperitoneal LD ₅₀ for mice 0.4 g·kg ⁻¹			2	Semiproduct in pigment production	–
Aliphatic hydrocarbons C17-C24	–	Not specified for the whole group			42	Hydrocarbon residues from polyolefins or mineral oil saturated hydrocarbon contaminants	–
Dibutyl phenyl phosphate	2528-36-1	Oral LD ₅₀ for mice 1.5 g·kg ⁻¹			2	Component of hydraulic fluid	–
Di-2-ethylhexyl fumarate	141-02-6	Oral LD ₅₀ for mice 29.2 g·kg ⁻¹			3	Forming agent for polyester resins, plasticizer	SO-IB

N – number of occurrences, AaHs – alkylated aromatic hydrocarbons, LC₅₀ – median lethal concentration, LD₅₀ – median lethal dose, PAHs – polycyclic aromatic hydrocarbons, SML – specific migration limit, SML(T) – total specific migration limit* means the maximum permitted sum of particular substances released in food or food simulants, * – sum of four benzophenone photoinitiators, ** – below limit of quantification of used method, the substance was not identified in any of tested packaging materials

Legislation: G – included in positive list of EuPIA Suitability list of photoinitiators for low migration UV printing inks and varnishes [35] (explanations: numerals 1, 2 mean group of photoinitiators, A – photo-initiators have both low migration potential and are supported by toxicological data, B – photo-initiators have low migration potential and/or have high molecular weight, they should not migrate into the food above 10 mg·kg⁻¹, C – photo-initiators have been evaluated and have a migration limit); PL – included in the positive list of Commission Regulation (EU) No. 10/2011 [3]; PU – included in preconditions for the use of recycled fibres as raw materials for the production of paper of BFR Recommendation XXXVI [7]; SO – included in positive list of Swiss Ordinance SR 817.023.21 [9] (explanations: Roman numerals I, IV, V mean number of positive list for additives group, A – evaluated substances, B – have not been subjected to any officially recognised scientific testing), U.S. EPA – United States Environmental Protection Agency.

phthalic acid esters in paper packaging materials confirmed that phthalates represent one of the most common contaminants in packaging materials [28, 29]. Ten phthalic acid esters were identified and quantified in almost all tested materials. The frequency of occurrence of each phthalate exceeded 70 packaging materials from 132 tested, with the only exception of dipentyl phthalate (26 findings). Phthalates in tested paper materials are used mainly as plasticizers in printing inks or they originate as contaminants in recycled fibres and/or pollutants from the environment [2, 28, 29, 35]. The most frequent esters were diisobutyl phthalate (DIBP): 109 findings, dibutyl phthalate (DBP): 98 findings and diethyl phthalate (DEP): 99 findings. The highest content was found for DBP ($628 \text{ mg}\cdot\text{kg}^{-1}$) and DIBP ($108 \text{ mg}\cdot\text{kg}^{-1}$). Considering the above mentioned conditions, the legislative limits could be exceeded during the application of the tested packaging materials for four phthalic acid esters, i.e. dimethyl phthalate (DMP), DEP, DBP and DIBP.

Non-phthalate plasticizers

Concerning the identified non-phthalate plasticizers, only di-2-ethylhexyl adipate contents in the tested materials were quantified. Due to a quite high specific migration limit (*SML*) for polymeric materials ($18 \text{ mg}\cdot\text{kg}^{-1}$), the levels found should not have posed a hazard for consumers. The evaluation of the danger related to the occurrence of the rest of identified and not quantified plasticizers, i.e. tributyl phosphate, dibutyl phenyl phosphate, diethylene glycol dibenzoate (DEGDB), methyl *n*-hexadecanoate, dibutyl phenyl phosphate and di-2-ethylhexyl fumarate, could not have been performed. As there are no official limits for their migration into food, even their low contents in packaging materials could cause a problem, in particular in case of DEGDB with 46 findings.

Aromatic hydrocarbons

Contamination of paper materials with mineral oil hydrocarbons (MOH) poses one of the topical problems of paper-based packaging materials intended for direct contact with food. Besides paraffins and naphthenes, MOHs are constituted by aromatics, i.e. alkyl-substituted polyaromatic hydrocarbons (PAH). Some of them are regarded as potentially genotoxic and carcinogenic to humans [2, 16, 36]. A number of 27 aromatic hydrocarbons were identified and quantified in packaging materials tested in this study. They could originate as residues of dyes and/or solvents from printing inks, pollutants (MOH residues, products of decomposition and

combustion processes, components of coal tar) from recycled fibres. The occurrence of aromatic hydrocarbons in the tested samples was recorded in more than 50% of the tested materials, e.g. 2,7-diisopropyl naphthalene was found in 105 of 132 tested packaging materials. The highest contents were quantified for diisopropylnaphthalenes ($4.044 \text{ mg}\cdot\text{kg}^{-1}$) and fluorene ($1.212 \text{ mg}\cdot\text{kg}^{-1}$). Considering the transfer of individual PAH from package into food is limited at the level of $0.0017 \text{ mg}\cdot\text{dm}^{-2}$, the contents of two quantified PAH (namely, 1-methylfluorene and fluorene) could cause migration exceeding this level. Considering the toxicity of a majority of PAH, their frequent occurrence in a quite large set of packaging materials used in practice gives rise to concern.

Photoinitiators

The growing extent of the use of UV-cured printing inks for the decoration of food packaging materials has caused the possibility of transfer of photoinitiators from printed packaging into packaged food product [37]. Nine photoinitiators were identified and six of them quantified in packaging materials tested in this study. Photoinitiators were found practically in all printed materials, e.g. benzophenone was identified in 112 packages, 4-methylbenzophenone in 102 packages. There are no official migration limits established in the EU legislation, but the European Printing Inks Association (EuPIA) stated migration limits for photoinitiators suitable for low-migration printing inks for food packages. The only substance, which could overpass *SMLs* given by EuPIA, was benzophenone with a maximum content in tested materials of $369 \text{ mg}\cdot\text{kg}^{-1}$ (EuPIA *SML* is $0.1 \text{ mg}\cdot\text{dm}^{-2}$), which corresponds to a release from $0.18 \text{ mg}\cdot\text{dm}^{-2}$ to $0.92 \text{ mg}\cdot\text{dm}^{-2}$ for packaging materials with grammage of $50\text{--}250 \text{ g}\cdot\text{m}^{-2}$ [38].

Bisphenols

The occurrence of three identified and quantified bisphenols, namely, bisphenol A (BPA), bisphenol F (BPF) and bisphenol S (BPS), was also quite frequent. BPA and BPS, which are allowed for manufacturing of polymeric food contact materials, were found in 74 and 71 cases, respectively. The determined contents of BPA (up to $26.4 \text{ mg}\cdot\text{kg}^{-1}$) were relatively low related to the *SML* given by Regulation (EC) No. 10/2011 [4] for food contact polymers ($0.1 \text{ mg}\cdot\text{dm}^{-2}$), e.g. papers with grammage of $250 \text{ g}\cdot\text{m}^{-2}$ could contain BPA maximally at a level of $0.066 \text{ mg}\cdot\text{dm}^{-2}$. In case of BPS (maximum content found in packaging material was $8.4 \text{ mg}\cdot\text{kg}^{-1}$, *SML* for polymers is $0.0083 \text{ mg}\cdot\text{dm}^{-2}$), the packaging materials of more

than $100 \text{ g}\cdot\text{m}^{-2}$ could have contained enough BPS ($0.0084 \text{ mg}\cdot\text{dm}^{-2}$) to exceed *SML* in certain conditions. In case of BPF, the use of which is not allowed in food contact polymers, the packaging material could contain enough BPF to exceed *SML* ($0.0017 \text{ mg}\cdot\text{dm}^{-2}$) even at the low quantified content (a maximum of $0.87 \text{ mg}\cdot\text{kg}^{-1}$), if the grammage of tested papers was above $195 \text{ g}\cdot\text{m}^{-2}$. The obtained results are in good agreement with data published by SUCIU et al. [35] and PIVNENKO et al. [2, 3, 12].

Perfluorinated compounds

PFC are used mainly in oil-proof papers [23, 24]. In this study, 17 PFC were identified and quantified. The frequency of occurrence of PFC in the tested packaging materials was quite low (i.e. in papers for baking purposes, pastry boxes or oil-proof pouches for grilled meat) with the exception of sodium bis(1H,1H,2H,2H-perfluorooctyl)phosphate (detected in 64 packaging materials), sodium 1H,1H,2H,2H-perfluorodecyl phosphate (26 findings), perfluorodecanephosphonic acid (18 findings) and perfluorohexanoic acid (28 findings), which were also detected in other paper materials, probably as residues from recycled pulp. The found quantities of PFC in the tested packaging materials were also quite low, only perfluorooctyl phosphate and perfluorodecyl phosphate expressed as sodium salts were found at maximum contents of $4.8 \text{ mg}\cdot\text{kg}^{-1}$ and $27.2 \text{ mg}\cdot\text{kg}^{-1}$, respectively. These contents of PFC could easily exceed *SML* at the level of $0.0017 \text{ mg}\cdot\text{dm}^{-2}$.

Lubricants and other contaminants

The rest of identified substances, i.e. five lubricants on the base of methyl esters of fatty acids, methyl dehydroabietate, aliphatic hydrocarbons of the number of carbon atoms from C17 to C24, 2,5-dichloranilin, 4,4a,9,10-tetrahydro-4a-methyl-2(3H)-phenanthrenone and 2,2',5,5'-tetramethyl-1,1'-biphenyl, were not quantified. The occurrence of the last three substances was quite low. Methyl dehydroabietate is a cellulose derivative, which is used as a component of varnishes, printing inks and adhesives. The aliphatic hydrocarbons C17–C24 were probably residues from polyolefin components of tested packages or residues of mineral oil.

The results in Tab. 1 indicate that plasticizers were the most frequent group of xenobiotics identified in packaging materials based on paper, in particular phthalic acid esters of lower molecular weight (DMP, DEP, DBP, DIBP). The most frequent contaminants included anthraqui-

none, several aromatic hydrocarbons (1-methyl fluorene, diisopropyl naphthalene isomers, phenanthrene) and photoinitiators (4-methyl benzophenone, benzophenone). The contaminants of the highest content in tested papers comprised DBP ($628 \text{ mg}\cdot\text{kg}^{-1}$), benzophenone ($369 \text{ mg}\cdot\text{kg}^{-1}$), DIBP ($108 \text{ mg}\cdot\text{kg}^{-1}$) and 2-ethylhexyl-4-dimethyl-amino benzoate ($53.5 \text{ mg}\cdot\text{kg}^{-1}$). No difference in the content of contaminants was found between papers with various grammage. The results proved a higher occurrence of contaminants in printed packaging materials as well as in papers with higher contents of recycled fibres. The negative effect of the use of recycled pulp, resulting in an increase of the content of extractable contaminants, was reported in several previous studies [1, 2, 11, 16, 17, 39] and the results of our experiments confirmed those published results. In Fig. 1, the average contents of ten important contaminants in plain papers with low (less than 10 % w/w) and high (above 90 % w/w) contents of recycled pulp are compared. Eight samples with low and twelve samples with high contents of recycled fibres were included in this comparison. It can be seen that, with the exception of anthraquinone, which is a residue from pulp processing, the contents of all other analysed contaminants were significantly higher in samples containing recycled pulp ($\alpha = 0.05$).

The obtained results show that a number of the tested substances occur in packaging materials in quantities that could exceed the migration limits laid down by valid legislation.

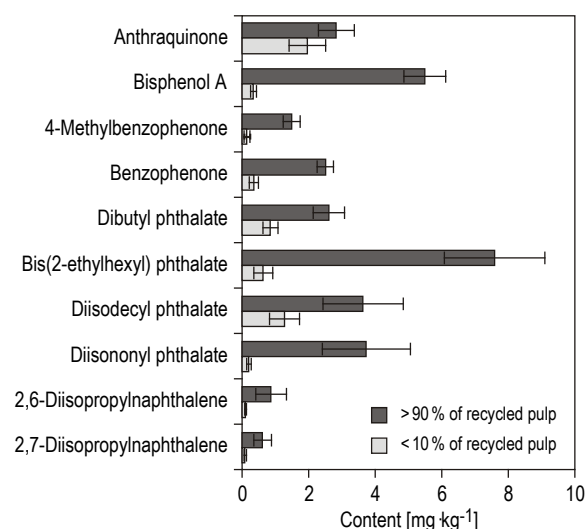


Fig. 1. Comparison of average contents of typical contaminants in plain papers with recycled fibres content below 10 % w/w and above 90 % w/w.

CONCLUSIONS

The range of contaminants with possible occurrence in paper packaging materials intended for food contact is very wide, including residues from paper pulp processing (e.g. processing aids, products of wood degradation), substances originating from printing inks or adhesives (photoinitiators, plasticizers, solvents) and impregnation and coating (solvents, hydrocarbons). DBP, DIBP and benzophenone were found as the most frequent contaminants of paper materials, being also present at the highest contents. Most of the contaminants in paper packaging materials originate from materials used for modification of functional properties (water-proof or fat-proof adjustment, coating, printing, lamination with polymer films, etc.) or are residues from recycled pulp.

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Supplementary data

Supplementary data related to this article can be found at <http://www.vup.sk/download.php?bulID=1915>.

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