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QUANTIFICATION OF CHEMICAL CONTAMINANTS IN THE PAPER AND BOARD FRACTIONS OF MUNICIPAL SOLID WASTE

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Abstract

Chemicals are used in materials as additives in order to improve the performance of the material or the production process itself. The presence of these chemicals in recyclable waste materials may potentially affect the recyclability of the materials. The addition of chemicals may vary depending on the production technology or the potential end-use of the material. Paper has been previously shown to potentially contain a large variety of chemicals. Quantitative data on the presence of chemicals in paper are necessary for appropriate waste paper management, including the recycling and re-processing of paper. However, a lack of quantitative data on the presence of chemicals in paper is evident in the literature. The aim of the present work is to quantify the presence of selected chemicals in waste paper derived from households. Samples of paper and board were collected from Danish households, including both residual and source-segregated materials, which were disposed of (e.g., through incineration) and recycled, respectively. The concentration of selected chemicals was quantified for all of the samples. The quantified chemicals included mineral oil hydrocarbons, phthalates, phenols, polychlorinated biphenyls, and selected toxic metals (Cd, Co, Cr, Cu, Ni, and Pb). The results suggest large variations in the concentration of chemicals depending on the waste paper fraction analysed. Research on the fate of chemicals in waste recycling and potential problem mitigation measures should be focused on in further studies.

Keywords: additives, EDCs, MSW, organic pollutants, recycling, phthalates

1. Introduction

Material recycling and the substitution of virgin natural resources is generally considered to be beneficial for society. Recycling contributes to increasing resource efficiency in society, diverting waste from landfills, and minimizing the environmental impacts of waste management and the material turn-over of society (EC, 2015). Numerous studies have documented the environmental and economic benefits of recycling, from both technological and system-level perspectives (e.g., Björklund and Finnveden, 2005; Choi et al., 2004; Laurijssen et al., 2010; Thormark, 2001; Villanueva and Wenzel, 2007). Paper is one of the most prominent materials in municipal solid waste (The World Bank, 2012), as well as the waste material fraction with the highest recycling rates, reaching 72 % in Europe (CEPI, 2014) and 58 % at a global level (BIR, 2012). Paper recycling saves virgin fibres and consumes less energy compared with virgin-fibre-based production (Villanueva and Wenzel, 2007). Not all paper is recycled in the same amounts: corrugated and kraft grades, as well as newspapers and magazines, constitute just over 70 % of all the recovered paper in Europe (CEPI, 2014). These grades are mostly used in the production of packaging and graphic paper, which represent 68 % and 23 % of the total recovered paper utilization, respectively. Hence, the average recycled fibre content will range between 93 % and 95 % for case materials and newsprint to just over 12 % for other graphic paper (CEPI, 2014), which usually has high visual quality requirements. While paper recycling has been shown to be environmentally beneficial, it is not only the paper fibres that are reintroduced into the production cycle. Chemicals added during the original paper product manufacturing process (i.e. paper production, printing, and converting stages), and/or chemicals taken up by the paper during its use phase, will also be reintroduced into the recycling process. Recent studies have demonstrated that many of these chemicals are potentially hazardous and unwanted in the final products (Liao and

Kannan, 2011a; Pivnenko et al., 2015a). However, very few quantitative data exist documenting the levels of these chemicals in the waste paper materials collected for recycling.

Paper is a product with certain freedom in its physical appearance and chemical composition. Paper products may incorporate a significant number of chemicals, added mainly during the printing and converting processes (i.e. binding, gluing, laminating, labelling), before the product reaches the consumer (Pivnenko et al., 2015a). Such substances may include plasticizers, binders, strength-increasing agents, coatings, pigments, inks, solvents, etc. (Pivnenko et al., 2015a). The list of substances may increase even further during the use phase of the paper, in which chemicals may be added or taken up as a consequence of the paper products' use (e.g., use of adhesives or inks, contact with food, cleaning of surfaces, etc.). Once a paper product has become obsolete, the paper enters the waste management system: for example, it is collected either in the source-segregated or in the residual (mixed) flow of household waste. As the paper is co-disposed together with other paper and waste materials, substances may be transferred from another waste material to the paper fraction intended for recycling. Furthermore, paper as a commodity is traded on the international market, potentially posing additional challenges to the sustainable management of waste paper stream. As an example, 5.2 million tonnes of paper were imported to Europe for consumption in 2014, while almost 10 million tonnes (or 17 % of the total amount collected) of waste paper were exported for recycling (CEPI, 2014). This suggests that not all waste paper materials may be equally well suited to recycling (due to the presence of unwanted chemicals), but also that the collection system itself may affect the quality of paper as a secondary raw material (Miranda et al., 2013, 2010). Concerns about the presence of potentially hazardous chemicals in paper have been voiced in the literature, mainly in relation to food consumption (Binderup et al., 2002; Lorenzini et al., 2013; Pérez-Palacios et al., 2012; Triantafyllou et al., 2007). Food-contact materials are expected to be a significant source of exposure to the chemicals present in paper (Muncke, 2009).

This form of exposure may occur when chemicals present in packaging or other food-contact materials migrate onto the food, which is then ingested by humans (Parry and Aston, 2004; Triantafyllou et al., 2007). On the other hand, dermal exposure may also occur from handling paper contaminated with chemicals (Biedermann et al., 2010).

All food-contact materials in the European Union are subject to the general requirements set by the regulation framework (EC, 2004), which requires that materials do not: i) “release their constituents into food at levels harmful to human health”; ii) “change food composition, taste and odour in an unacceptable way”. Additionally, production of food-contact materials is covered by the EU regulations addressing “good manufacturing practices” (EC, 2006). Finally, European legislation has regulations for specific material groups coming into contact with food. Such materials include plastics (EU, 2011a), recycled plastic materials (EC, 2008), ceramics (EC, 1984), etc. Nevertheless, no specific regulations addressing paper (including recycled paper) as a food-contact material currently exist. Instead, in addition to the general food-contact regulations, food-contact paper materials are covered by the industry guidelines produced by the European paper and board food packaging chain (CEPI, 2012). A recent study (Pivnenko et al., 2015a) has outlined the chemicals of concern that could potentially be present in paper products and by extension in waste paper. It was suggested that around 10,000 different chemicals could potentially be present in paper. Of these, over 150 were identified as hazardous and requiring additional attention. Among the chemical groups identified as potentially critical for paper recycling were mineral oils, phenols, phthalates, and parabens. In order to further improve the quality of the waste paper collected for recycling, and avoid the potential re-circulation of unwanted hazardous chemicals, more detailed and quantitative information about the contents of these chemicals in actual waste paper samples is needed.

The aim of this paper is to provide compositional data concerning selected chemicals in individual fractions of waste paper collected from households, in order to provide an improved basis for evaluating the quality and recyclability of waste paper. The specific objectives are as follows: i) to provide data concerning the detailed fractional composition of paper and board materials in Danish household waste, based on a sampling campaign; ii) to quantify the solid concentrations of selected mineral oils, phenols, phthalates, polychlorinated biphenyls, and toxic metals (Cd, Co, Cr, Cu, Ni, and Pb); iii) to evaluate potential differences, in terms of the concentration levels of these potentially hazardous chemicals, between paper fractions collected as part of the residual waste and paper fractions collected after source-segregation in households, and finally; iv) to provide recommendations with respect to the inclusion or exclusion of individual fractions in source-segregation schemes for paper waste from households.

2. Materials and methods

2.1 Materials

Samples of waste paper and board were collected in April 2013 from a municipality in Southern Denmark, in accordance with standard methods for solid waste sampling (Nordtest, 1995). The municipality employs a separate collection scheme for the recyclable fractions of the waste, i.e., paper, metal, glass, etc. The samples collected represented both residual and source-segregated fractions of the waste generated by 100 single-family households within the period of two weeks. The details of the sampling campaign for residual waste are described in an earlier publication (Edjabou et al., 2015). The source-segregated waste paper was collected in parallel with the residual waste, sharing both geographical and temporal scopes. The source-segregated paper was sorted by the households and placed in a two-compartment waste bin (DuoFlex[®], Dansk Affald, Denmark). One compartment contained recyclable packaging (plastic, glass, and metal), while the other compartment was dedicated to paper, board, and light plastic foil. The sorting guidelines provided

by the municipality specified the individual paper and board items that should (e.g., newspapers, advertisements, magazines, folding boxes, tubes, etc.) or should not be included in the source-segregated flow (including paper and board packaging with food residues (e.g., pizza boxes), and milk, juice, and other beverage cartons, as well as books). The residual waste in the sample area was incinerated with energy recovery, whereas the source-segregated fractions were sent for further sorting and material recycling (outside the area). The total amount of residual and source-segregated paper samples collected was approx. 400 kg. The total waste paper collected (both residual and source-segregated) represents all the paper and board generated from the involved households in the study area, excluding the bulkier board items commonly collected as bulky waste at recycling stations.

2.2 Methods

2.2.1 Sample preparation

After collection, the residual waste paper was manually sorted from the remaining residual household waste. Subsequently, both waste paper flows (residual and source-segregated) were sorted into more detailed fractions of paper and board, according to the physical appearance of the paper items (e.g., advertisements, corrugated boxes) and their potential use (e.g., food packaging). In total, the waste paper from each flow was sorted into 17 paper fractions, and 13 board fractions. The separation between paper and board was qualitatively based on the material thickness (paper < ca. 0.3 mm $\leq$ board), since a quantitative distinction (e.g., based on mass of paper per unit of area (ISO 536:2012)) would not have been feasible for inhomogeneous samples in such large amounts. Each separate fraction was coarsely shredded (ARP SC2000, Brovst, Denmark), followed by one-dimension lot splitting (Petersen et al., 2005) for sample size reduction, and fine shredding down to a particle size of < 4 mm (SM2000, Retsch, Germany). The finely shredded samples were

lyophilized, placed in glass containers and stored at -20 °C before being analysed. Schematic representation of the sample preparation procedure is provided in Figure 1.

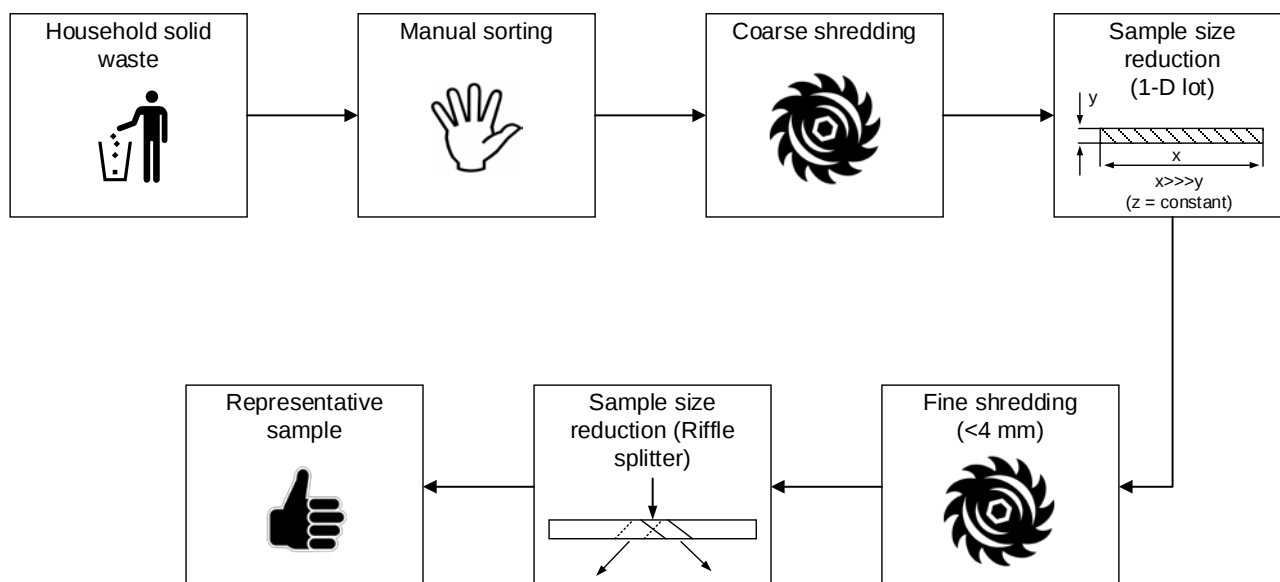


Figure 1. Schematic flowchart of sample preparation.

2.2.2 Chemical composition

Based on the overview of potentially critical chemicals in paper materials (Pivnenko et al., 2015a), selected groups of chemicals were analysed. These groups included mineral oils, phenols, phthalates, polychlorinated biphenyls (PCBs), and toxic metals. The overview of chemicals quantified in the study, as well as the equipment used, is presented in Table 1. Both the recoveries and the respective limits of detection (LOD) achieved for each of the chemicals, along with their CAS numbers, are provided in Tables S1–S10 (Supplementary Material). All the results presented are on a dry matter (dm) basis.

Table 1. Chemicals quantified in the present study and the equipment used.

#	Chemical group	Analytes	Equipment used*
1	Mineral oil hydrocarbons	nC_{10} - nC_{20} , nC_{20} - nC_{30} , nC_{30} - nC_{40}	GC-FID
2	Phenols	Nonylphenol (NP), 4-nonylphenol (4-NP), 4-chloro-3-methylphenol (4-C-3-MP), 4-octylphenol (4-OP), 4-tert-octylphenol (4-t-OP), 2-phenylphenol (2-	GC-MS

		PP), and bisphenol A (BPA)	
3	Phthalates	Bis (2-ethylhexyl)phthalate (DEHP), butyl benzyl phthalate (BBP), di (2-methoxyethyl) phthalate (DMEP), didecyl phthalate (DDP), dicyclohexyl phthalate (DCHP), dibutyl phthalate (DBP), di-iso-butyl phthalate (DiBP), didecyl phthalate (DPP), diethyl phthalate (DEP), and dimethyl phthalate (DMP)	GC-MS
4	Polychlorinated biphenyls	PCB-28, PCB-52, PCB-101, PCB-118, PCB-138, PCB-153, and PCB-180	GC-MS
5	Toxic metals	Cd, Co, Cr, Cu, Ni, Pb	ICP-MS

GC: gas chromatographer; FID: flame ionization detector; MS: mass spectrometer; ICP: inductively coupled plasma.

Mineral oil hydrocarbons (MOHs)

The mineral oils of interest were analysed as a sum parameter. Mineral oil or hydrocarbon oil index (HOI) is a parameter that quantifies the compounds extractable with an apolar hydrocarbon solvent (boiling point between 36 °C and 69 °C) and which may be chromatographed with retention times between those of n-decane ($C_{10}H_{22}$) and n-tetracontane ($C_{40}H_{82}$). The chemicals complying with the above definition are mainly long-chain or branched aliphatic, alicyclic or alkyl-substituted aromatic hydrocarbons. Some natural wood extractives present in paper (e.g., fatty acids) are too polar and would not be extracted, while others (e.g., esters of fatty acids or waxes) would be removed in the clean-up step. The results were split in three fractions: the first fraction (“light fraction”) included lighter MOHs with boiling points from 175 °C (nC_{10}) to 344 °C (nC_{20}); the second fraction (“intermediate fraction”) included heavier MOHs with boiling points from 344 °C (nC_{20}) to 450 °C (nC_{30}); and the final, “heavy fraction”, included MOHs with boiling points from 450 °C (nC_{30}) to 525 °C (nC_{40}). The MOH analysis was performed using a gas chromatograph (GC) coupled to a flame ionization detector (FID), in accordance with a standard method (ISO/FDIS 16703) applicable to the hydrocarbon content in a solid waste matrix between 0.1 and 10 g/kg dm.

Paper samples (1.5 g) were extracted using 50 ml n-hexane for 2 h. The n-hexane contained 1 mg/l n-decane and 2 mg/l n-tetracontane as GC retention time markers. Prior to the solid-phase extraction (SPE) clean-up, anhydrous Na_2SO_4 was added to the extracts. Commercially available cartridges containing 2 g of Florisil and 2 g of Na_2SO_4 were used for the clean-up. The columns

were equilibrated using 10 ml n-hexane before the extracts were passed through. The extracts were analysed using an Agilent 6980 GC-FID (Agilent Technologies, Santa Clara, USA). Chromatographic separation was achieved on a 30 m x 0.25 mm x 0.1 μ m Zebron ZB-5 capillary column (Phenomenex, Torrance, USA). The 1 μ l sample was injected in splitless mode at 280 °C. The initial temperature of 35 °C was held for 3 min and the oven was ramped at 20 °C/min from 35 to 350 °C and held for 5 min. Helium was used as a carrier gas at a 1 ml/min constant flow rate and the FID was operated at 380 °C. Certified oil mixture (diesel fuel/lubricating oil (1:1), BAM-K010e (BAM, Berlin, Germany)) was used for control and calibration purposes. The achieved LOD was 80 mg/kg dm, and replicates of a single sample resulted in a relative standard deviation (RSD) that ranged from 12 % (for the heavy fraction) to 32 % (for the light fraction).

Phenols

Selected phenols (see Table 1 for details) were extracted by microwave-assisted extraction (MAE). The MAE (Multiwave 3000, Anton-Paar, Graz, Austria), solid-phase extraction, derivatization and GC-MS analysis of selected phenols were based on methods described by Alonso et al. (1998) and Morales et al. (2005). Two grams of paper samples were extracted by MAE (Multiwave 3000, Anton-Paar, Graz, Austria) using 30 ml methanol/Milli-Q water/triethylamine (78:20:2) as a solvent, at 120 °C and approx. 4 bar for 40 min. Following this, 70 ml acidified Milli-Q water (pH < 2) was added to the extracts prior to filtration with a 0.45 μ m syringe filter. The samples were applied to an OASIS HLB SPE column (6 ml, 1 g, Waters Corp., Milford, USA), conditioned with 6 ml methanol and 6 ml acidified Milli-Q water. The columns were dried by lyophilization and eluted using 6 ml ethyl acetate. The samples were further subjected to SPE clean-up using LC-Florisil columns (Supelco, St. Louis, USA), conditioned with ethyl acetate, before being evaporated to dryness. Then, 50 μ l BSTFA:TMCS (99:1) and 10 μ l pyridine (anhydrous) were added and derivatization was achieved at 70 °C for 1 h, prior to GC-MS analysis. For this, 100 μ g/l Bisphenol

A-d16 and 4-tert-octylphenol-ring-13C6 were used as internal standards. Chromatographic separation was achieved on an Agilent 6890 gas chromatograph (Agilent Technologies, Santa Clara, USA) equipped with a 30 m x 0.25 mm i.d. x 1 µm film thickness HP-5ms column (Agilent Technologies, Santa Clara, USA), with the oven programmed to 80 °C for 1 min, then ramped at 10 °C/min to 300 °C and held for 2 min. Detection was achieved on an Agilent 5975C triple-axis mass-selective detector (Agilent Technologies, Santa Clara, USA), operated in selected ion monitoring (SIM) mode, with the MS source at 230 °C and the quadrupole at 150 °C. The detection limits ranged from 0.012 mg/kg to 0.79 mg/kg for 4-NP, 4-OP, 4-t-OP, and NP, respectively (see Tables S3 and S4 (Supplementary Material) for details). All samples were analysed in single, while replicates of a random sample resulted in an RSD that ranged between 1 % (4-t-OP) and 63 % (4-c-3-MP).

Phthalates

The phthalates covered in this study (see Table 1 for details) were extracted and analysed based on the CEN/TC 308 and EPA 8061A standard methods. In brief, 2 g samples were extracted in Erlenmeyer flasks using 20 ml ethyl acetate. The samples were shaken gently for 12 h at room temperature. The extracts were subjected to SPE clean-up using Alumina-N columns (Supelco, St. Louis, USA), conditioned with ethyl acetate, and evaporated to approx. 500 µl prior to GC-MS analysis. For this, 25 µg/l DMP-d4 and DEHP-d4 were used as internal standards. Chromatographic separation was achieved on an Agilent 6890 gas chromatograph (Agilent Technologies, Santa Clara, USA), equipped with a 60 m x 0.25 mm i.d. x 0.25 µm film thickness ZB-5ms column with a 5 m guard column (Phenomenex, Torrance, USA). The samples were injected in splitless mode with the sample inlet held at 300 °C. The oven was programmed to 70 °C for 3 min, then ramped at 13 °C/min to 270 °C, then at 50 °C/min to 300 °C and finally held for 12 min. Helium was used as a carrier gas with a 1 ml/min constant flow. The mass detector settings were as above. The detection

limits ranged from 0.012 to 2.5 mg/kg dm for DCHP and DEHP, respectively (see Tables S5 and S6 (Supplementary Material) for details). A single sample analysed in replicates resulted in an RSD that ranged from 4 % to 38 % for DBP and BBP, respectively.

Polychlorinated biphenyls (PCBs)

Analysing all the possible PCB congeners (209) would be technically challenging and time consuming. A commonly used list of six indicator PCBs (28, 52, 101, 138, 153 and 180), referred to as “PCB₆”, has been proposed by the German Institute for Standardization (DIN 51527-1). This list covers PCBs with high concentrations in technical mixtures and a wide range of chlorine atoms (from three to seven chlorine atoms per PCB molecule). The list, expanded to include the 118 congener (“PCB₇”), is generally used in the EU for the analysis of PCBs in environmental and food samples (Sundhedsstyrelsen, 2013). The extraction and analysis of the seven selected PCB congeners (see Table 1 for details) were performed in accordance with EPA 3546 standard method. Two grams of paper samples were extracted by MAE (Multiwave 3000, Anton-Paar, Graz, Austria) using 30 n-hexane at 120 °C and approx. 4 bar for 40 min. The extracts were subjected to SPE clean-up using LC-Florisil columns (Supelco, St. Louis, USA), conditioned with n-hexane, and evaporated to approx. 100 µl, prior to GC-MS analysis. For this, 10 µg/l 1,2,3,4-tetrachloronaphthalene was used as an internal standard and 2,2,4-trimethyl pentane as a keeper.

GC-MS analysis was performed as above but with the oven programmed to 80 °C for 1 min, then ramped at 5 °C/min to 170 °C, then 2 °C/min to 250 °C, then 10 °C/min to 280 °C, and finally held for 13 min. The mass detector settings were the same as in the phenols and phthalates analyses. The achieved LOD was 0.33 µg/kg dm for each of the PCB constituents. Replicates of a single sample showed RSDs ranging between 21 % for PCB-52 and PCB-101, and 31 % for PCB-153.

Toxic metals

The analysis of selected toxic metals (see Table 1 for details) was performed in accordance with the US EPA Method 3051a. In brief, 0.25 g of waste paper was digested by microwave-assisted digestion (Multiwave 3000, Anton-Paar, Graz, Austria) using 10 ml HNO₃. The temperature was ramped to 175 °C for 5.5 min and held for 4.4 min. The resulting digestates were diluted in Milli-Q water before analysis by ICP-MS (7700x, Agilent Technologies, Santa Clara, USA). The LODs achieved were between 0.039 and 0.38 mg/kg dm for Co and Cr, respectively (see Tables S9 and S10 (Supplementary Material) for details). Each digestate was analysed in triplicate, resulting in RSDs ranging from 6 % for Ni to 24 % for Cd.

2.2.3 Data handling and calculations

The limits of detection for each of the chemicals were calculated as an average of the analysed blanks plus three standard deviations of the blank. When no signal could be quantified in the blanks, the LOD was calculated as the lowest calibration standard plus three standard deviations of the standard. Blanks and standards were processed using the same extraction and clean-up steps as the samples. For the calculation of sum, mean, or median values, values below the limit of detection were substituted by 65 % of the respective limit of detection, as suggested by Martín-Fernández et al. (2003). The weighted concentrations (i.e., taking into account the fractional composition of waste paper) of chemicals in the residual and source-segregated waste paper flows were compared by means of the Student's *t*-test. The null hypothesis was that the true difference in mean values would be equal to zero, i.e. there is no difference in the concentration of chemicals between residual and source-segregated waste paper fractions. Assuming a 95 % confidence interval, the null hypothesis can be rejected for *p*-values < 0.05. The normality of data distribution was assured through log-transformation whenever necessary (Reimann et al., 2008). To visualize the difference between concentrations of chemicals in residual and source-segregated paper, box plots are provided in the results and discussion section. The box plots present data as a five-point summary:

the minimum, lower quartile (25th percentile), median (50th percentile), upper quartile (75th percentile), and maximum (Kabacoff, 2011).

3. Results and discussion

3.1 Fractional composition of waste paper

Table 2 presents the relative composition of paper and board in the residual and source-segregated waste flows, as well as in the combination of the two flows. Of the total waste paper and board collected, 21 % was from residual waste, while the remaining 79 % was recovered as source-segregated waste flow. The bulk of the total waste paper and board (72 %) came from advertisements, newspapers, and magazines. Most of these paper products were part of the source-segregated waste paper, as the municipality's sorting guide specifies newspaper, magazines, advertisements, phone books, office paper, and envelopes as the waste paper items intended for separate collection and recycling. These fractions are expected to account for the highest consumption of paper in an average household, since graphic paper represents 38 % of the total paper consumed in Europe (CEPI, 2014). Advertising material accounts for approx. 48 % of the total paper and board waste collected for this study, a figure significantly higher than the 23 % and 25 % reported in the literature (Riber et al., 2009; Salhofer et al., 2008). The difference is mainly the result of discrepancies in flow definitions between this study and the literature. The present study takes into account the waste paper generated at household level, but excludes bulky board items discarded at recycling stations. A recent study estimated that an average Danish household annually receives 55 kg of unsolicited mail, of which the majority is advertisements (Sanchez and Møller, 2011). On the other hand, the main fractions in the residual waste were office paper, beverage cartons, and newspapers. Fractions of waste board (F18–F30, Table 2) accounted for almost 13 % of the source-segregated paper flow. In contrast, board in the residual waste paper accounted for more than 43 % of the flow. Most board items not sorted into a separate waste stream

end up in the residual waste, either due to contamination from use (e.g., food packaging) or as a result of non-existent recycling schemes (e.g., beverage cartons).

Table 2. Composition of residual and source-segregated waste paper and board (% wet weight). Residual and source-segregated flows contributed with 21 % and 79 % of the total sample collected, respectively.

	#	Fractions	Residual [%]	Source-segregated [%]	Total [%]
Paper	F1	Advertisements (non-glued)	7.9	28.1	23.8
	F2	Advertisements (glued)	4.4	20.1	16.8
	F3	Newsprint advertisements (non-glued)	2.7	5.0	4.5
	F4	Newsprint advertisements (glued)	1.6	3.0	2.7
	F5	Newspapers	9.8	17.2	15.6
	F6	Magazines, Journals, TV guides (non-glued)	3.8	6.5	6.0
	F7	Magazines, Journals, TV guides (glued)	1.5	3.0	2.7
	F8	Office and administrative paper	12.9	3.0	5.1
	F9	Envelopes	2.5	0.4	0.9
	F10	Wrapping paper	0.9	0.1	0.3
	F11	Receipts	0.7	<0.1	0.1
	F12	Self adhesives	0.1	<0.1	<0.1
	F13	Books and booklets	2.0	0.7	1.0
	F14	Phonebooks	0.4	0.0	0.1
	F15	Tissue paper	0.9	<0.1	0.2
	F16	Kraft paper (brown and bleached)	2.1	0.2	0.6
	F17	Other paper ¹	2.2	0.1	0.5
		Total paper	56.6	87.3	80.8
Board	F18	Corrugated boxes - shipping	1.7	1.2	1.3
	F19	Corrugated boxes - sales (Food packaging)	4.1	4.1	4.1
	F20	Corrugated boxes - sales (Non-food packaging)	0.8	2.9	2.5
	F21	Folding boxes - shipping	0.0	0.0	0.0
	F22	Folding boxes - sales (Food packaging)	8.9	2.0	3.5
	F23	Folding boxes - sales (Non-food packaging)	5.7	0.9	1.9
	F24	Egg trays and alike	1.2	0.3	0.5
	F25	Tubes	4.5	0.2	1.1
	F26	Beverage cartons	11.9	0.2	2.7
	F27	Paper plates and cups	0.5	<0.1	0.1
	F28	Composites ²	0.5	0.1	0.2
	F29	Cards and labels	1.7	0.3	0.6
	F30	Other cardboard ¹	1.9	0.3	0.6
		Total board	43.4	12.7	19.2
		Total	100	100	100

¹ Includes articles of paper and board not covered by the fractions F1-F16 for paper, and F18-F29 for board (e.g., greaseproof and baking paper); ² Includes predominantly articles of board laminated with aluminum or plastics and not included in the remaining board fractions (e.g., Pringles® potato-based snack packaging).

3.2 Chemical composition

Figure 2 presents the concentration ranges (min–max) of the analysed chemicals. The figure covers concentration ranges in both residual and source-segregated waste paper, as well as the median values found. The results for each group of chemicals are discussed in detail in the following paragraphs (3.2.1–3.2.5), while Paragraph 3.2.6 addresses the differences in chemical content between the residual and source-segregated waste paper flows. Further details on the concentrations measured are provided in Figure 3 and the Supplementary Material (Tables S1–S10).

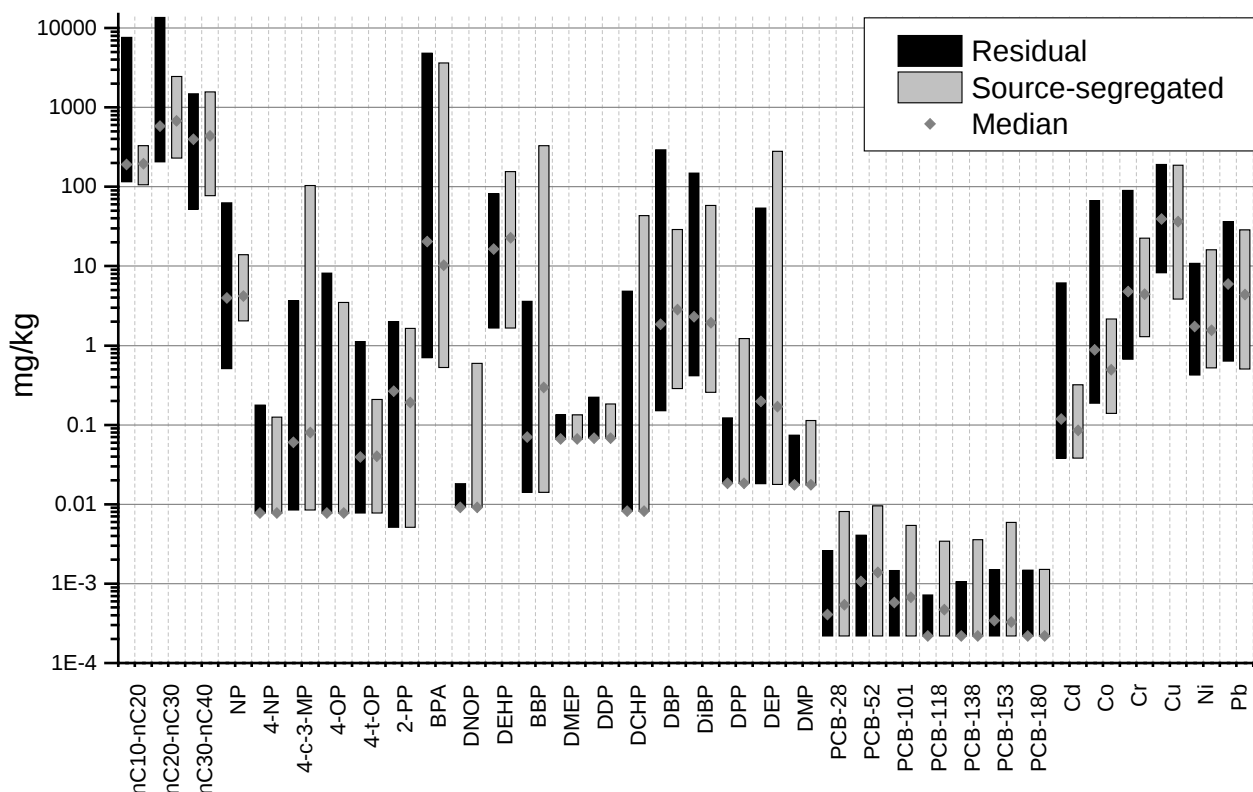


Figure 2. Concentration ranges (min-max) and median concentrations (logarithmic scale) of chemicals analysed in the present study in residual and source-segregated waste paper (mg/kg dm).

3.2.1 Mineral oil hydrocarbons (MOHs)

The presence of mineral oils in paper can be associated with a variety of sources, from solvents used in the paper printing and converting processes to lubricants and cleaning agents in the machinery employed (EFSA, 2012; Miljøstyrelsen, 2011). The mineral oil solvents used in paper printing mainly derive from inks, which can include between 20 % and 30 % mineral oil content (Droz and Grob, 1997). The concentrations of MOHs in the waste paper samples are presented in Figure 3(A) (detailed data are provided in Tables S1 and S2 (Supplementary Material)). On average, the intermediate mineral oils (nC_{20} – nC_{30}) were present in higher concentrations when compared to the lighter and heavier fractions, nC_{10} – nC_{20} and nC_{30} – nC_{40} , respectively (Tables S1 and S2 (Supplementary Material)). The mineral oils present in recycled board were shown to range from nC_{12} to nC_{50} , while the mineral oils from printing inks range between nC_{13} and nC_{30} (Biedermann and Grob, 2010) and centre at $nC_{18/19}$ (Lorenzini et al., 2010). Nevertheless, lighter mineral oils ($< nC_{24}$) are susceptible to volatilization (Lorenzini et al., 2010), explaining their relatively lower concentrations in the analysed samples. Previous studies have identified newspapers as the main potential source of mineral oils in the waste paper flows (Biedermann and Grob, 2010; BMELV, 2012). Newspapers contained MOHs at 2,300 and 1,700 mg/kg for residual and source-segregated waste paper, respectively. These values are comparable to the range, between 180 and 8,900 mg/kg, presented in the literature (Biedermann and Grob, 2010). Besides newspapers, high concentrations of mineral oils were also found in other paper, tissue paper, tubes, and self adhesives. Other paper from the residual waste paper flow contained a concentration almost an order of magnitude higher (22,000 mg/kg) when compared to the remaining fractions. The use of waxes and glues based on mineral oils (Biedermann and Grob, 2012) could potentially explain the mineral oil content in tubes and self adhesives, respectively. At the same time, presence of mineral oils in tissue paper and other paper may potentially be related to the use phases of these materials.

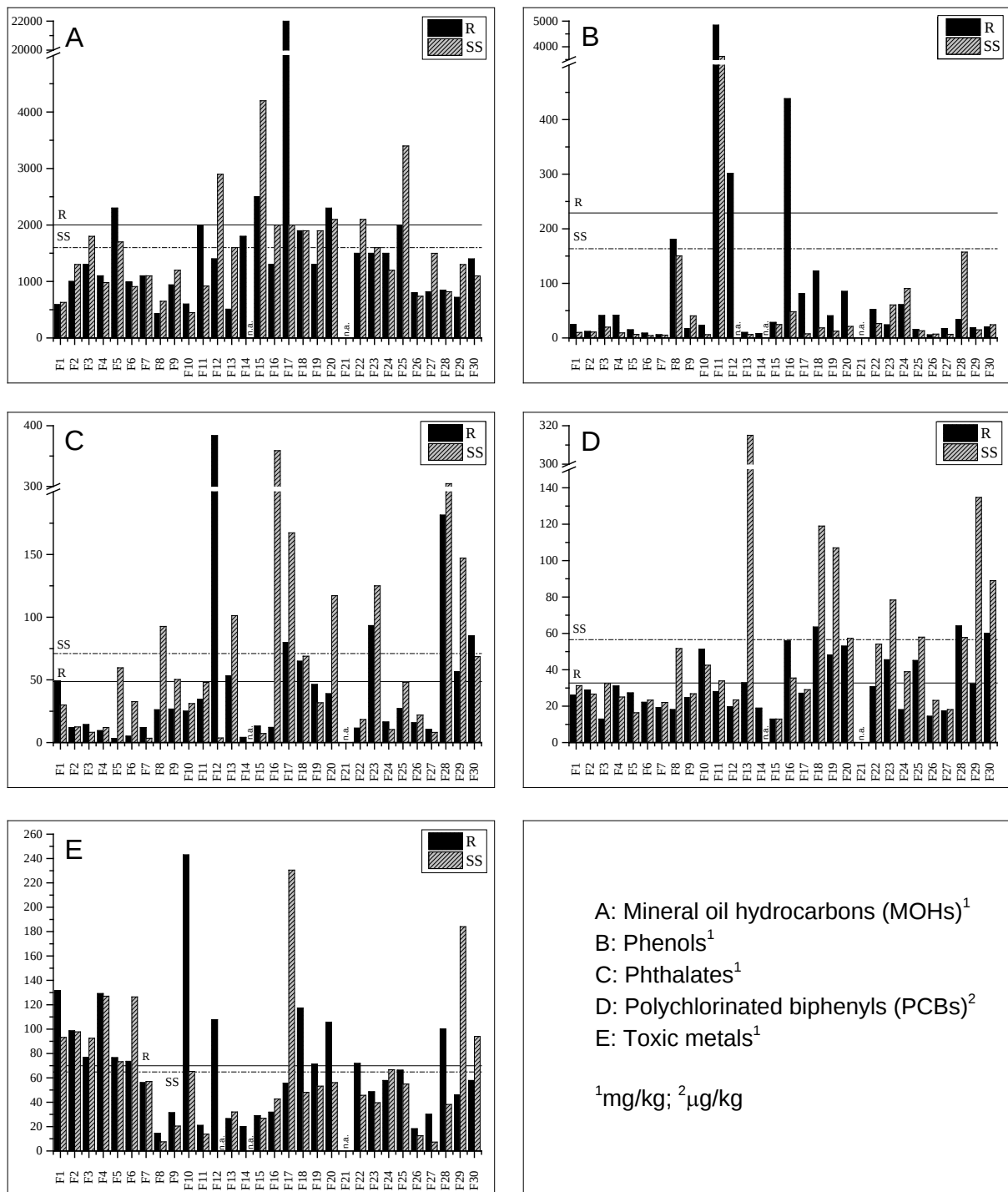


Figure 3. Total concentrations of chemicals in focus. Horizontal lines indicate the mean concentrations. R: residual waste paper; SS: source-segregated waste paper.

3.2.2 Phenols

Phenols have a variety of applications in paper product manufacturing. They can be used as additives in thermal paper, as polymeric resin components, as surfactants in printing, etc. (Pivnenko et al., 2015a). All the analysed phenols showed endocrine-disrupting properties (Pivnenko et al., 2015a). By far the most significant application of phenolic compounds is in thermal paper production, where phenol-based chemicals are commonly employed as colour developers. Thermal paper is largely used in point-of-sale cashier receipts in concentrations of up to 3.2 % of the paper weight (Östberg and Noaksson, 2010). Not surprisingly, the receipts fraction contained the highest amount of phenols. This was largely associated with the presence of BPA (Tables S3 and S4 (Supplementary Material)): a developer commonly employed in thermal paper (Pivnenko et al., 2015b). Further details on the presence of BPA and its structural analogues, in thermal paper receipts and in a subset of the waste paper fractions analysed in this study, can be found in an earlier publication (Pivnenko et al., 2015b). BPA was the only phenol-based chemical detected in all the samples, in concentrations ranging between 0.53 and 4,800 mg/kg. Since in paper industry BPA is only used in specialty paper, its presence in all the analysed waste paper samples could indicate the spreading of this chemical through paper recycling. Similarly, earlier studies have pointed to the potential spreading of BPA between paper products as a result of paper recycling (Liao and Kannan, 2011a, 2011b).

Although the marketing and use of NP and its ethoxylates in pulp and paper production have been banned in the EU from 2005 (EC, 2003), NP was identified in almost all the samples analysed (ranging from < 0.79 to 63 mg/kg). This could be the result of the presence of residual NP potentially used in surfactant formulations in the printing industry (Miljøstyrelsen, 2011). Both NP and octylphenol are common pollutants detected in process wastewater from paper recycling (Latorre et al., 2005). The median concentrations of NP in both residual and source-segregated

waste paper in our study (3.9 and 4.2 mg/kg) were lower than the concentrations found in toilet paper (between 14.3 and 68.9 mg/kg), but higher than the concentrations found in German waste paper, which ranged between 0.40 and 1.01 mg/kg (Gehring et al., 2004). However, although 4-NP has been identified as the main constituent of the technical NP mixtures (Eganhouse et al., 2009), relatively low concentrations of 4-NP (up to 0.18 mg/kg) were quantified in 38 % and 19 % of the residual and source-segregated waste paper fractions, respectively.

3.2.3 Phthalates

Phthalates are mainly used as plasticizers in a variety of materials and applications. Although phthalates have repeatedly been reported to have negative health impact — mainly related to their being endocrine disrupting agents — they still dominate the plasticizers market (Schossler et al., 2011). Concerns have been expressed especially regarding the lightest phthalate molecules (the most common being DEHP, BBP, DBP, and DiBP), as they have a greater potential to be released and to migrate from the host materials. These so-called “low” phthalates have been banned in the EU in toys and childcare items (EC, 2005). They were also phased out for the remainder of applications in February 2015, unless authorization had been granted for a specific use (EU, 2011b).

Gärtner et al. (2009) found that paperboard food packaging contained DiBP, DBP, BBP and DEHP. Selected phthalates, namely DiBP, DBP, and DEHP, were found in almost all the samples analysed in the present study. DiBP and DEHP were found in relatively high concentrations ranging from < 0.26 to 160 mg/kg, with DEHP quantified in the highest median concentrations: 15 and 23 mg/kg for residual and source-segregated waste paper, respectively. Similarly, a study conducted by Poças et al. (2010) found phthalates in all paper samples used for food packaging, with DiBP in the highest concentrations (up to 21 mg/kg).

The highest total phthalate concentrations were found in self adhesives (380 mg/kg), kraft paper (360 mg/kg) and composites (300 mg/kg) (Tables S5 and S6 (Supplementary Material)). Relatively highest concentrations were found for DBP, DIBP, and DEP, which are all commonly used as additives in adhesives (National Research Council, 2008; US EPA, 2010). On the other hand, use of BBP-rich inks (Pivnenko et al., 2015a) or high-strength label printing (involving more than 0.1 % w/w of BBP (e.g., MACTac, 2013)) can be done on kraft paper..

DMEP was not detected in any of the samples analysed, while several other phthalates (DDP, DCHP, DPP, and DNOP) were only detected in a few fractions (less than 30 % of the samples). Comparison of total phthalate content (Figure 3(C)) between food (F19 and F22) and non-food packaging board (F20 and F23) revealed higher concentrations in the latter, suggesting limited use of phthalates or recycled fibre in food–packaging board. Migration from packaging onto food represents an important source for human exposure to phthalates (Fromme, 2011). This is mostly due to the presence of DEHP, DBP, and BBP, with the latter being found in concentrations of up to 330 mg/kg (Table S6 (Supplementary Material)). Phthalates have been shown to migrate rapidly from paper packaging onto food, with 20 % to 40 % of the initial concentration of some phthalates being transferred (Summerfield and Cooper, 2001).

3.2.4 Polychlorinated biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) were previously used in a variety of applications. In view of potential human contact and release potential, the uses of PCBs are commonly differentiated in terms of closed and open applications. The main bulk of PCBs produced were used in closed applications, e.g., in electrical transformers, as hydraulic liquid, lubricants, etc. (US EPA, 1976). Although the USA, the largest producer of PCBs at a global level, banned their production in 1977 (Breivik et al., 2007) — followed by the rest of the world by 1993 (Breivik et al., 2007) — their

extreme physical and chemical inertness (thermal stability, non-flammability, low water solubility, etc.) (Hutzinger et al., 1974) has allowed them to persist in the environment and to be detected even today in a variety of environmental matrices (Dömötörövá et al., 2012; Hermanson and Johnson, 2007; Kassa and Bisesi, 2001). The main open application for PCBs was in carbonless copy paper, as a carrier for the ink in the ink capsules (US EPA, 1977). Such paper contained between 2 % and 6 % PCBs by weight (Voogt et al., 1984), and accounted for 20,000 tonnes or 3 % of the total PCBs produced in the USA between 1930 and 1975 (Erickson and Kaley, 2011). Upon recycling, the ink capsules would burst and the PCBs would be released; once the fibres were processed, the PCBs could then be transferred into the newly manufactured paper products (US EPA, 1977).

Aroclor (formerly manufactured by Monsanto Co., St Luis, MO, USA) is one of the most commonly known commercial names for PCB mixtures. Aroclor name is accompanied by a four-digit suffix, denoting the number of carbon atoms in the phenyl rings (first two digits) and mass-based chlorine content (last two digits). The mixture of PCBs most commonly used in carbonless copy paper was Aroclor 1242, which included a 42 % chlorine content (Albro and Parker, 1979; US EPA, 1976). Other minor applications of PCBs in paper included the use of Aroclor 1254 in paper inks and other additives (US EPA, 1976). Aroclor 1242 contained 11.9 % PCB₇ (Frame et al., 1996), resulting in a correction factor of 8.4 when extrapolating from PCB₇ to PCB_{total} concentration. This factor is close to the range of 2.5 to 8.1 commonly used when estimating the total PCB concentration based on the PCB₇ indicator (Sundhedsstyrelsen, 2013).

Of the seven target PCBs, the congeners that were identified in almost all samples were PCB-52 and PCB-101 (Tables S7 and S8 (Supplementary Material)), while the heaviest congener (PCB-180) was only identified in one and four samples of residual and source-segregated paper, respectively. This congener distribution can be related to the composition of Aroclor 1242, the bulk of which is represented by lighter congeners, i.e., approx. below PCB-75 (Frame et al., 1996). On

the other hand, the relatively high frequency of detection (> 50 % of the samples) for PCB-153 can potentially be attributed to the presence of Aroclor 1254, of which PCB-153 is an important constituent. The fraction with by far the highest concentrations of PCBs was F13 (books and booklets) from the source-segregated paper flow, which contained up to 320 µg/kg (Table S8 (Supplementary Material)). This was related to the fact that, in the source-segregated flow, the fraction contained mainly books, while the residual fraction contained mainly booklets. The lifespan of books is expected to be significantly longer than that of booklets (Cote et al., 2014), resulting in a greater potential for PCBs to be present. Additionally, board fractions (F18–F30) presented higher concentrations of PCBs than paper fractions (F1–F17). The PCB₇ median values of 3.3 and 4.1 µg/kg correspond well to the range (1.5–5.0 µg/kg) presented by Binderup et al. (2002) for 16 congeners analysed in paper samples obtained from the paper industry; nevertheless, the authors characterized these levels as low and insignificantly different from the background concentrations. Values for PCB₆ were in the range of 1.3–7.3 µg/kg and 1.3–34 µg/kg for residual and source-segregated flows, respectively. For comparison, European legislation allows concentrations of PCB₆ in selected foodstuffs to be as high as 300 µg/kg, while food fed to young children should not contain more than 1 µg/kg of PCB₆ (EC, 2011).

3.2.5 Toxic metals

The presence of metals in paper can be attributed to the natural presence of metals in wood (Algreen et al., 2012), metals added as part of inks, pigment preparation, and coatings or impurities (Pivnenko et al., 2015a). Concentration of metals naturally occurring in wood may vary depending on plant species, part of plant used in paper making, and local soil conditions (McLaughlin et al., 2011). Presence of metals in some of the analysed samples could be explained by metals contained in wood, as typical concentration ranges are 0.05 – 0.5 mg/kg, 0.03 - 10 mg/kg, 1.6 – 14 mg/kg, and 0.3 – 5.3 mg/kg for Cd, Cr, Cu, and Ni, respectively (Algreen et al., 2013, 2012). Among the

potentially toxic metals analysed in this study, Cu showed the highest median and maximum concentrations in both residual and source-segregated waste paper. In both flows, the highest concentration was 190 mg/kg in wrapping and other paper, respectively. Interestingly, fractions of printed periodicals (F1-F5, see Table 2 for details), showed elevated Cu concentrations (> 50 mg/kg) suggesting printing inks as potential source of Cu. An earlier study on chemicals in paper handkerchiefs and toilet paper also observed higher concentrations of Cu in articles with colour decorations (Miljøstyrelsen, 2003). Additionally, Cr and Pb were found in high median concentrations (Tables S9 and S10 (Supplementary Material)). The self adhesives fraction of the residual waste paper contained Cr concentrations (90 mg/kg) well above the median value of all the fractions (4.8 mg/kg), potentially due to the attachment of fine particles of materials containing Cr to the adhesive part of the paper. Nevertheless, the values were still within the concentration ranges found in the literature (Pivnenko et al., 2015a). In both residual and source-segregated waste paper, Pb was found in slightly higher concentrations (from < 0.056 to 36 mg/kg) when compared to older studies from Denmark (from 0.65 to 12 mg/kg) (Riber et al., 2009), or when compared to Rotter et al. (2004), in which Pb amounted to 23 ± 9 mg/kg in paper and board from German household waste. These values can be higher than the limit of 3.0 mg/kg for Pb in food-contact paper and board as set by the European paper industry guideline (CEPI, 2012).

Among the remaining toxic metals, the highest concentrations for Cd, Co, and Ni were found in board composites (6.1 mg/kg), shipping corrugated boxes (67 mg/kg), and other paper (16 mg/kg), respectively. Presence of Co in corrugated boxes can be result of packaging ink raw material that can potentially contain cobalt acetate, carbonate, or sulphate (Pivnenko et al., 2015a). In case recycled board composites are to be used in food-contact material production, content of Cd may be of concern as it was more than tenfold higher than the established limit of 0.5 mg/kg (CEPI, 2012).

3.2.6 Residual versus source-segregated waste paper

Box plots of the total concentrations of the abovementioned groups of chemicals in residual and source-segregated waste paper and board flows are presented in Figure 4. Each point represents cumulated concentrations of the chemical groups discussed above for each of the fractions in residual and source-segregated waste paper. The cumulated concentrations were multiplied by the respective shares of residual or source-segregated waste paper composition, in order to derive weighted concentrations. As evident from Figure 4, the concentrations of chemicals in the source-segregated flow show larger variations and are skewed towards lower values when compared to

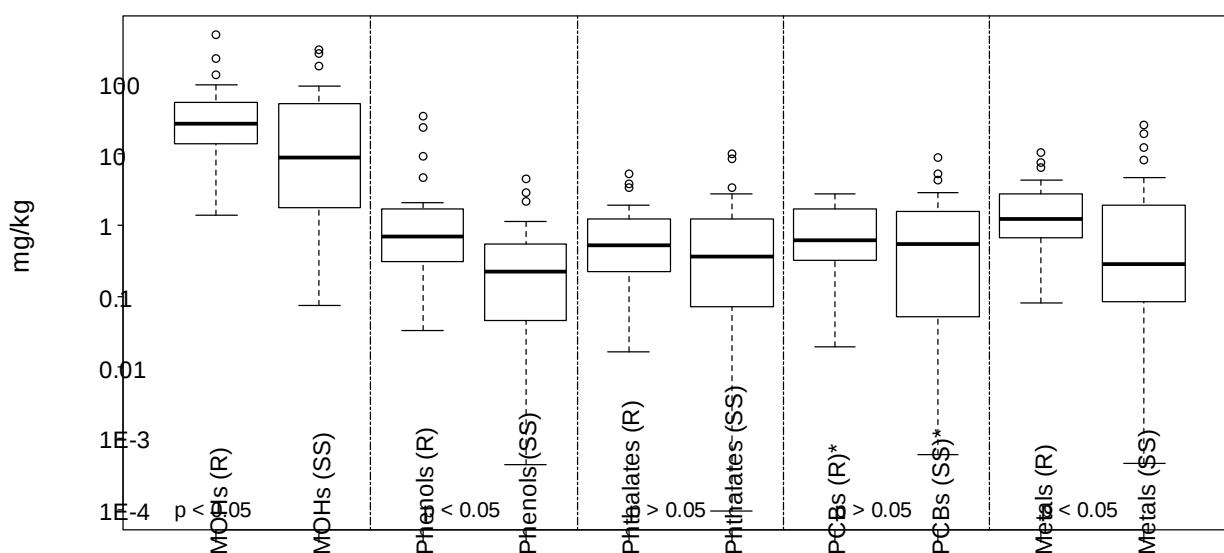


Figure 4. Box plots of chemicals analysed in the present study (logarithmic scale). R: residual waste paper; SS: source-segregated waste paper (mg/kg dm). The p – values indicate significant ($p < 0.05$) or non-significant ($p > 0.05$) difference between residual and source-segregated waste paper. * Values for PCBs are in $\mu\text{g/kg dm}$.

those in the residual flow. When the log-transformed concentrations for both flows were compared using the Student's t -test, only phthalates and PCBs showed no significant difference (p -value > 0.05), while MOHs, phenols, and metals were all significantly different from one flow to the other. This could indicate that potential cross-contamination during collection, and potential differences in

the use or disposal patterns for the individual paper and board items in the two waste flows, have a significant influence on the total content of MOHs, phenols, and metals in the paper matrices. For the three chemical groups mentioned, the median concentrations found in the residual flow were higher than those found in the source-segregated flow.

3.3 Implications of the results

The presence of chemicals in waste paper has the potential to result in the persistence or spreading of chemicals through the paper recycling processes and the re-introduction of unwanted chemicals into newly manufactured products. Although paper is treated in order to remove certain contaminants (including chemicals) during the recycling process (e.g., pulping, de-inking, cleaning, bleaching), the efficiency of these removal processes with respect to chemical contamination remains questionable (BMELV, 2012; Jamnicki et al., 2012). For example, we cannot expect mineral oils, as hydrophobic chemicals, to be sufficiently removed in a conventional paper recycling process. Previously reported flotation de-inking experiments have shown a removal rate of less than 50 % for semi-volatile organic compounds (including mineral oil components) (Schabel, 2011). The fact that up to 2,200 mg/kg of mineral oils have been observed in pulp from recycling and paper products containing recycled fibres may be a result of this (Biedermann and Grob, 2010; BMELV, 2012). Additionally, number or steps employed in paper recycling and specific conditions for each of these steps (e.g., pH, temperature, residence time, type of chemicals used, etc.) will influence the final efficiency of contaminant removal. For example, removal efficiency of BPA decreased from 95 % to 10 % for paper recycling sites with and without de-inking stage, respectively (JRC-IHCP, 2008). Where the paper industry has recognized the issues concerning chemicals, some measures against the spreading of contaminants into food-contact materials have already been taken. The existing industry guidelines on the compliance of paper and board articles for food-contact applications specify, among other things, limit values for polycyclic

aromatic hydrocarbons, selected phenols, phthalates and toxic metals in final food-contact paper and board articles (CEPI, 2012). Nevertheless, effects of selected chemicals with endocrine-disrupting potential (e.g., NP, OP, BPA, BBP, DBP, DEHP, etc.) is an area of active scientific research, and the currently used limit-values might be misleading. As an example, recent significant reduction (from 50 $\mu\text{g}/\text{kg}_{\text{bw}}/\text{d}$ to 4 $\mu\text{g}/\text{kg}_{\text{bw}}/\text{d}$) in safe levels of BPA (EFSA, 2015), has not been reflected in industry's guidelines. Additionally, the results of our study clearly indicate that the list of chemicals potentially present in recycled paper might be longer than the selected chemicals already regulated. Take the example of PCBs: although they have been banned in most of the world for decades, the PCB measurements in this study indicate a relatively slow process of contaminant removal from the paper cycle, as a result of the long lifespan of certain paper items and the potential persistence of chemicals in the recycling process. The results show that board fractions had higher PCBs levels than paper, potentially as a result of material recycling (since board recycling rates are generally higher than paper recycling rates) (CEPI, 2014). Older studies have shown the presence of PCBs only in recycled paper (Storr-Hansen and Rastogi, 1988). The concentrations found in our study (between 13 and 320 $\mu\text{g}/\text{kg}$), although comparable to the results of other recent studies (Binderup et al., 2002), are substantially lower than the concentrations found in paper three decades ago (between 100 and 12,400 $\mu\text{g}/\text{kg}$) (Voogt et al., 1984). This may indicate the gradual removal of PCBs from the paper cycle, as a result of the ban.

To ensure a high quality of paper and board for recycling, the chemicals of concern can be substituted by alternatives of reduced hazard. For example, vegetable oils can be used in place of mineral oils in printing process (Roy et al., 2007), while variety of phenol-based and phenol-free alternatives to BPA can be used in thermal paper (US EPA, 2014). Alternatively, fractions with high levels of problematic chemicals could potentially be removed from the source-segregated flows sent to recycling. Based on data such as those reported in this study, updated sorting guides

for waste paper and board could be developed. Excluding fractions containing high concentrations of chemicals from source segregation, and instead routing these materials, e.g., to incineration, could contribute to the phasing out of specific chemicals. Based on our results, the fractions most relevant for exclusion from source-segregation are i) thermal paper receipts (due to their phenol content), ii) kraft paper and board composites (due to their phthalate content), and iii) books (due to their high PCB content). When considering potential control measures for mitigation of chemical contamination in paper cycle, both concentration of hazardous chemicals in a waste paper fraction and mass of a fraction in the total paper should be considered.

4 Conclusions

Waste paper and board contains measurable levels of MOHs, phenols, phthalates, PCBs, and selected toxic metals. Although the chemicals present in paper and board are not uniformly distributed among paper and board fractions, a detailed fractionation of paper and board in household waste offered in-depth data for chemical contents in individual fractions collected as part of the residual and source-segregated waste flows, respectively. The results indicate that paper fractions differ in terms of the chemicals concentrations in the two waste paper flows considered. The significant differences found in the concentrations of MOHs, phenols, and metals between residual and source-segregated flows should receive specific attention when planning waste collection and management activities. The fate of chemicals in paper recycling processes is not sufficiently well documented to allow a specific evaluation of the potential implications of the presence of these chemicals on recyclability. However, the results provided by this study clearly indicate that certain paper and board fractions (i.e. thermal paper receipts, kraft paper, composites, and books) contain relatively high concentrations of problematic chemicals. Both the paper industry and the waste management authorities should be aware of the presence of chemicals in paper

materials destined for recycling, in order to help maintain the high paper recycling rates without compromising the quality of the products manufactured.

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Supplementary material

Supplementary data containing the detailed results of chemical composition of residual and source-segregated waste paper fractions (Tables S1–S10) can be found, in the online version, at <http://dx.doi.org/10.1016/j.wasman.2016.03.008>.

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