



Recycling of plastic waste: Presence of phthalates in plastics from households and industry



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ABSTRACT

Plastics recycling has the potential to substitute virgin plastics partially as a source of raw materials in plastic product manufacturing. Plastic as a material may contain a variety of chemicals, some potentially hazardous. Phthalates, for instance, are a group of chemicals produced in large volumes and are commonly used as plasticisers in plastics manufacturing. Potential impacts on human health require restricted use in selected applications and a need for the closer monitoring of potential sources of human exposure. Although the presence of phthalates in a variety of plastics has been recognised, the influence of plastic recycling on phthalate content has been hypothesised but not well documented. In the present work we analysed selected phthalates (DMP, DEP, DPP, DiBP, DBP, BBzP, DEHP, DCHP and DnOP) in samples of waste plastics as well as recycled and virgin plastics. DBP, DiBP and DEHP had the highest frequency of detection in the samples analysed, with 360 µg/g, 460 µg/g and 2700 µg/g as the maximum measured concentrations, respectively. Among other, statistical analysis of the analytical results suggested that phthalates were potentially added in the later stages of plastic product manufacturing (labelling, gluing, etc.) and were not removed following recycling of household waste plastics. Furthermore, DEHP was identified as a potential indicator for phthalate contamination of plastics. Close monitoring of plastics intended for phthalates-sensitive applications is recommended if recycled plastics are to be used as raw material in production.

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1. Introduction

Plastics are some of the most important materials for sustaining society and our current way of living (Andradý and Neal, 2009). Unfortunately, they are also associated with substantial environmental issues, as they are based primarily on non-renewable raw materials (e.g. oil), are commonly used in short-lived products (e.g. food packaging) and, once discarded, are predominantly landfilled or incinerated (Thompson et al., 2009). If not disposed

of properly, waste plastics can end up in the oceans, thereby creating another environmental issue of growing concern (Jambeck et al., 2015). To tackle some of these issues, plastics recycling has been promoted within the European Union (EU). Recently proposed amendments to the directives on waste (EC, 2015a) and packaging waste (EC, 2015b) require 65% of municipal and 75% of packaging waste, including plastics, to be recycled by 2030. Nevertheless, the recycling of waste plastic is challenging due to heterogeneity of the material (e.g. polyethylene (PE), high-density polyethylene (HDPE), and polystyrene (PS)) and its chemical composition (Ignatyev et al., 2014).

Chemical composition can vary based on the plastic type (e.g. PE) or the intended use of such a product. Moreover, many hazardous chemicals can be potentially present in plastics, including phthalic acid esters, polycyclic aromatic hydrocarbons (PAHs), potentially toxic metals, etc. (NEA, 2013). Phthalic acid esters, commonly known as 'phthalates', make up a group of industrial chemicals with high global production volumes. Phthalates are mostly used as plasticisers in plastics production, with polyvinyl chloride (PVC) incorporating the largest share of the market (Markarian, 2007). Although alternatives are available

Abbreviations: BBzP, butyl benzyl phthalate (CAS 85-68-7); DBP, dibutyl phthalate (CAS 84-74-2); DCHP, dicyclohexyl phthalate (CAS 84-61-7); DEHP, diethylhexyl phthalate (CAS 117-81-7); DEP, diethyl phthalate (CAS 84-66-2); DiBP, di-iso-butyl phthalate (CAS 84-69-5); DMP, dimethyl phthalate (CAS 131-11-3); DnOP, di-n-octylphthalate (CAS 117-84-0); DPP, dipropyl phthalate (CAS 131-16-8); HDPE, high-density polyethylene; HMW, high molecular weight; LOD, limit of detection; LWM, low molecular weight; MANOVA, multivariate analysis of variance; PE, polyethylene; PET, polyethylene terephthalate; PS, polystyrene; PVC, polyvinyl chloride; RHP, recycled household plastics; RIP, recycled industrial plastics; RWP, residual waste plastics; SSWP, source-segregated waste plastics; VP, virgin plastics.

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(Krauskopf, 2003; Markarian, 2007), phthalates still accounted for 70% of the plasticiser market in 2014, and they are forecast to account for 65% in 2019 (IHS, 2015). Phthalates can be divided into low molecular weight (LMW) and high molecular weight (HMW), whereby the former are used predominantly as solvents and in adhesives, waxes, inks, cosmetics, insecticides and pharmaceuticals, while HMW phthalates are produced in higher volumes and are used in construction materials, clothing, children's toys and household furnishing (BCERC, 2007). These two groups are commonly distinguished according to the alkyl group carbon chain length (R, Fig. 1). Examples of LMW (C_4 – C_8) phthalates are diethyl phthalate (DEP), dibutyl phthalate (DBP), di-*iso*-butyl phthalate (DiBP) and diethylhexyl phthalate (DEHP), whereas diisononyl phthalate (DINP), diisodecyl phthalate (DIDP), diundecyl phthalate (DUP) and dinitridecyl phthalate (DTDP) are commonly referred to as HMW (C_9 – C_{13}).

Growing concern about phthalates is related to their toxicity, in particular to their endocrine-disrupting activity (Matsumoto et al., 2008). Studies suggest that human exposure to e.g. DEHP may lead to serious effects on reproduction and development (Caldwell, 2012; Heudorf et al., 2007). Although adverse effects of high phthalate doses are relatively well documented (Martino-Andrade and Chahoud, 2010), epidemiological studies (Jurewicz and Hanke, 2011) and integrated approaches to toxicity (Kovacic, 2010) suggest potential adverse effects of even low-dose phthalate exposure and call for more data. Due to their low molecular weight, LMW phthalates are susceptible to migration from plastics, and hence they are more relevant to human toxicity (Heudorf et al., 2007). Thus, the majority of LMW phthalates are classified as substances of very high concern (SVHC) in Europe, and certain restrictions on their use and applications may apply (EC, 2007, 2005; EU, 2015). Similarly, US EPA issued an action plan to prioritise eight phthalates, the majority of which are LMW (USEPA, 2012).

The human population can be exposed to phthalates from a variety of sources, with medical devices, ingestion with food and dust constituting the major sources (Latini, 2005). As the most recent data on human exposure come from biomonitoring studies (a bottom-up approach reporting concentrations in, for example, human blood), there is still uncertainty in accounting for all the potential exposure routes and their importance to their total exposure to the population (Latini, 2005; Wittassek et al., 2011). From a risk assessment perspective, this calls for better data on the presence of phthalates in potential exposure sources.

Although phthalate plasticisers are predominantly used in PVC (Markarian, 2007), their potential use or contamination in a variety of polymers has been previously suggested (Jonas et al., 2014; Jaworek and Czaplicka, 2014; Shen, 2005). Shen (2005) looked into a variety of polymers, including PE, PS, PVC, as well as PE laminates and cellulose-based polymers, and identified phthalates in 24 out of the 25 plastics samples analysed. Polyethylene terephthalate

(PET) has been shown to leach endocrine-disrupting chemicals (EDCs), including phthalates, into water contained in PET bottles (Amiridou and Voutsas, 2011; Casajuana and Lacorte, 2003; Keresztes et al., 2013; Montuori et al., 2008; Sax, 2010; Wagner and Oehlmann, 2011). When compared to PET bottles made of virgin plastics, Keresztes et al. (2013) clearly showed higher concentrations of phthalates in water bottled in PET potentially containing 20–30% (w/w) of recycled PET, thus suggesting recycling of plastics as a source of phthalate contamination. The abundance of phthalates has also been identified in a number of foods coming from a variety of geographical areas (Fankhauser-Noti et al., 2006; Fierens et al., 2012; Poças et al., 2010; Schecter et al., 2013). Although packaging was identified as one source (Fankhauser-Noti et al., 2006; Wormuth et al., 2006), contamination during food preparation and packaging usually cannot be ruled out, either (Tsumura et al., 2001). Additionally, use of recycled plastics and paper for food packaging was connected to possible increase in childhood exposure to selected phthalates (Lee et al., 2014). Finally, only a few studies have discussed the potential impact of plastics recycling on phthalate content, and so whether or not recycling can lead to plastic contamination and the increased presence of phthalates remains unclear.

The aim of the present work was to quantify selected LMW phthalates (DMP, DEP, DPP, DiBP, DBP, BBzP, DEHP, DCHP and DnOP) in samples of household waste plastics, as well as recycled and virgin plastics. Based on a consistent and comprehensive statistical data analysis methodology, the aim was further to evaluate whether the source (i.e. waste, recycled or virgin plastics) had a significant influence on phthalate content in the collected samples. Finally, the importance of plastics recycling for phthalate contamination was discussed.

2. Materials and methods

2.1. Sample collection

Samples of residual (RWP) and source-segregated (SSWP) waste plastics were collected from a municipality in Southern Denmark in April 2013. The sampling campaign covered 100 single-family households for a period of two weeks. Further details of the residual waste sampling are available in an earlier publication (Edjabou et al., 2015), while the same temporal and geographical scopes were applicable to the source-segregated waste samples collected. Waste samples were sorted manually in accordance to polymer resin identification codes (e.g. 1 – PET, 2 – HDPE, etc.) provided on individual plastic items. Identification codes specify of what the main polymer plastic products are made, without taking into account the presence of other materials (e.g. plastic 'sleeves' or labels on packaging) or chemicals (e.g. glue) in the final product. To supplement the waste plastic samples obtained from households, samples of processed plastics were obtained from industry. Samples of recycled household (RHP) and industrial (RIP) as well as virgin (VP) plastics were collected directly from recyclers and producers. RHP, RIP and VP samples were obtained from China, Denmark, Germany and the Netherlands, in order to illustrate potential variations in the source and quality of the material, which could result in different phthalate contents. In total, 20 waste (13 for RWP and seven for SSWP) and 28 recycled (nine for RHP and 11 for RIP) and eight virgin plastic (VP) samples were collected and analysed. An overview of the samples used in the present study is provided in Table S1 (Supplementary material). In the case of recycled and virgin plastics samples, neither the precise source (apart from a general distinction between household (i.e. post-consumer) and industrial (i.e. pre-consumer)) nor the exact intended use of the final plastic product (packaging, transportation, food-contact materials, etc.)

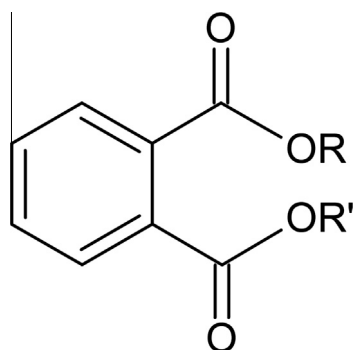


Fig. 1. Common structure of a phthalate molecule. R and R' denote alkyl (or aryl) group.

was known. The samples obtained (both waste and processed plastics) were not expected to represent the composition of plastics on the global market or in the respective countries but rather to provide a basis for evaluating the influence of plastic source on phthalate content and the potential for recycling.

2.2. Sample pre-treatment

Samples of waste plastics (i.e. RWP and SSWP) were treated by means of coarse shredding (ARP SC2000, Brovst, Denmark) followed by fine shredding (SM2000, Retsch, Germany) to a particle size <1 mm. Before being finely shredded, the samples were submerged in liquid nitrogen, in order to increase brittleness and avoid overheating and malfunctioning the equipment used. Samples of recycled and virgin plastics (RHP, RIP and VP) were obtained in the form of granules, flakes, granulate or pellets, and they did not undergo any additional treatment before being extracted and analysed. This did not apply to sample number 28 (RHP), which was obtained in the form of an extruded plastic block and which had to be ground down before extraction. The final samples were stored at room temperature in a dark and dry environment prior to extraction and chemical analysis.

2.3. Sample extraction and chemical analysis

The phthalates extraction procedure was a modified method based on selected scientific literature (Cano et al., 2002; Gawlik-Jędrzyński, 2013; Shen, 2005). For each of the samples 0.5 g of plastics were put into contact with 20 ml of dichloromethane (DCM), which was used as a solvent. Among potential alternative solvents for phthalates extraction, DCM has been shown to exhibit the highest recovery yields for plastics (Gawlik-Jędrzyński, 2013). An internal standard mix of DMP-d4 and DEHP-d4 was added to each of the samples to a final concentration of 2.5 mg/l. The extraction was performed in a microwave-assisted extraction setup (Multiwave 3000, Anton-Paar, Graz, Austria) at 120 °C for 20 min. Next, the extraction solvent was decanted, filtrated on a glass-fibre filter and evaporated to approximately 3 ml under a gentle stream of nitrogen. A solid-phase extraction (SPE) clean-up was performed on the evaporated extracts by passing extracts through a glass column containing activated Alumina-N, conditioned with DCM. The collected flow-through was analysed on a gas chromatograph coupled with a mass spectrometer (GC-MS). To avoid potential contamination of extracts and resulting blank problems with the phthalates analysis (Fankhauser-Noti and Grob, 2007), all glassware used in the extraction was rinsed in acetone and dried overnight at 200 °C before being used.

Chromatographic separation was achieved on an Agilent 6890 gas chromatograph (Agilent Technologies, Santa Clara, USA) equipped with a 60 m × 0.25 mm i.d. × 0.25 µm film thickness

ZB-5 ms 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 and 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. 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 achieved ranged from 0.036 µg/g (DPP) to 3.4 µg/g (DEP). Detailed detection limits for each of the phthalates are provided in Table 1.

In order to validate the analytical method and instruments used during the analysis, a standard reference material was used. A standard of three phthalates (DBP at 963 µg/g, BBP at 962 µg/g and DEHP at 1018 µg/g) in polypropylene (PP) resin pellets was accompanied by the reference material certificate from National Metrology Institute of Japan (NMIJ CRM 8151-a). Recoveries obtained for the three phthalates analysed in the standard were 141 ± 6%, 90 ± 5% and 99 ± 2% for DBP, BBP and DEHP, respectively. Additionally, each batch of samples (n = 15) was accompanied by a DCM blank, the response of which was subtracted from the results for the respective batch.

2.4. Statistical analysis

Statistical analysis of experimental data was performed in three steps, following the comprehensive methodology illustrated in Fig. 2. Data conversion and analysis were performed using freely available software for compositional data analysis (available at <http://www.compositionaldata.com>) and statistical computing and graphics (available at <https://www.r-project.org>). In order to apply the proposed statistical methodology, the evaluated dataset was transformed into isometric log-ratio (ilr) coordinates on an orthonormal basis (Egozcue et al., 2003). This approach avoids potential problems related to assuming normal distribution of the original experimental data (Limpert and Stahel, 2011). Importantly, the multivariate techniques applied in this study are invariant under change of basis (Martín-Fernández et al., 2015). For interpretation purposes, the log-ratio coordinates computed for a given data subset, comprising, for example, DiBP, DBP and DEHP, were as follows (the formulas are not simplified, in order to highlight the consistency of the expressions):

$$\begin{cases} ilr_1 = \sqrt{\frac{2-1}{2+1}} \cdot \log\left(\frac{\sqrt[3]{DiBP \cdot DBP}}{\sqrt[3]{DEHP}}\right) \\ ilr_2 = \frac{\sqrt{1-1}}{\sqrt{1+1}} \cdot \log\left(\frac{\sqrt[3]{DiBP}}{\sqrt[3]{DBP}}\right) \end{cases} \quad (1)$$

Normality of the log-ratio coordinates was assured through a Shapiro-Wilk test, assuming a 95% confidence interval when accepting or rejecting the null hypothesis. A multivariate analogy of the Shapiro-Wilk test was used to assess the multivariate normality

Table 1
Ranges of phthalate concentrations as measured in the samples of plastics and rounded to two significant figures [µg/g]. “<” indicates values lower than the respective limit of detection (LOD).

µg/g	DMP		DEP		DPP		DiBP		DBP		BBzP		DEHP		DCHP		DnOP	
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
LOD	0.077		3.4		0.036		0.20		0.094		0.022		0.43		0.16		0.20	
RWP	<	120	<	150	<	4.3	<	460	<	190	<	92	1.2	860	<	0.72	<	99
SSWP	<	0.54	<	5.5	<	0.36	<	23	0.56	360	<	1.1	<	2700	<	<	<	2.0
RHP	<	3.4	<	6.3	<	<	<	23	<	11	<	15	<	600	<	2.5	<	31
RIP	<	0.22	<	19	<	0.47	<	7.1	<	12	<	0.36	<	17	<	<	<	0.38
VP	<	<	<	5.3	<	0.44	<	4.8	<	15	<	0.21	<	21	<	0.34	<	0.75
FOD ^a	19		11		14		86		93		36		79		4		20	

^a FOD: Frequency of detection among 144 triplicates analysed (%).

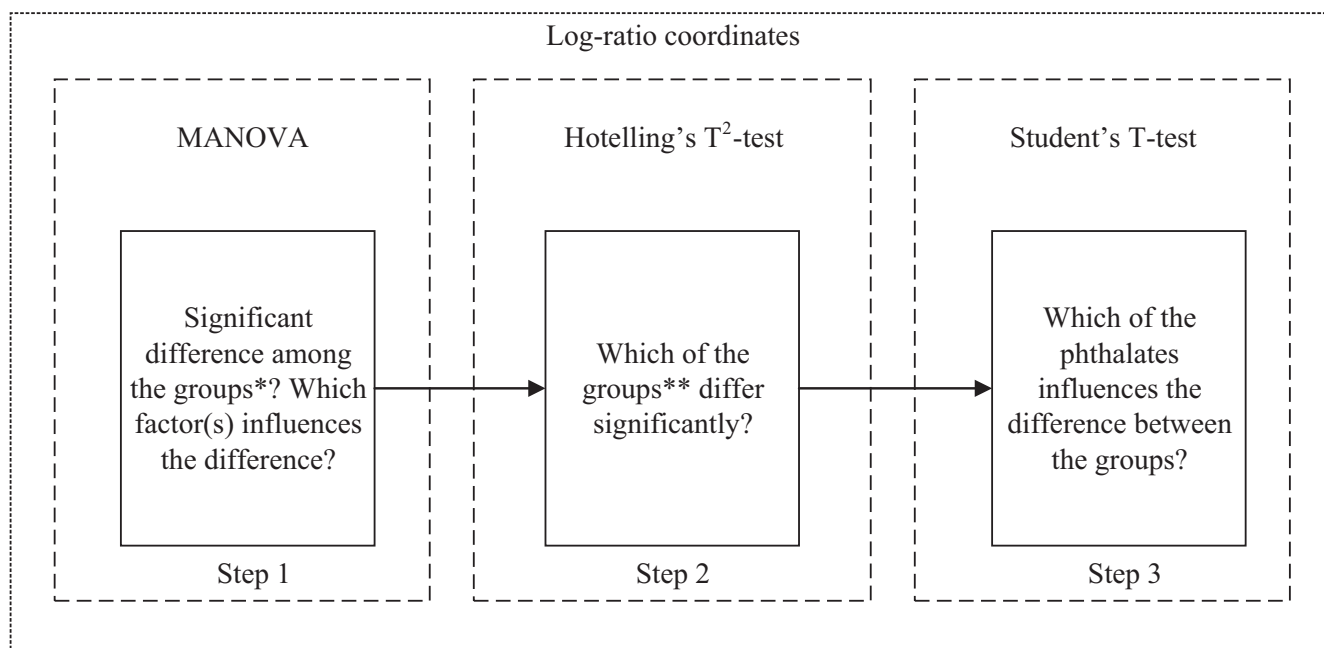


Fig. 2. Flowchart of the statistical methodology applied in experimental data analysis. Each of the steps (Step 1, 2 and 3) was designed to provide answers on the questions outlined in the respective boxes. *grouping according to the source of plastics (factor 1), plastic resin (factor 2) or the combination of two factors; **grouping according to the factor(s) with significant influence, as identified in Step 1.

of data distribution (Korkmaz et al., 2014). A two-way multivariate analysis of variance (MANOVA) for the log-ratio coordinates (Martín-Fernández et al., 2015) was performed, in order to evaluate the influence of two factors, namely the source of the plastic samples (waste plastics, recycled industrial plastics, etc.) and plastic resin (PET, PP, PS, etc.), on phthalate content (Fig. 2, Step 1). As the dataset was unbalanced (i.e. an unequal number of samples across RWP, SSWP, RHP, RIP and VP), MANOVA was based on the Type II sum of squares approach (Langsrud, 2003). In case significant differences were detected by the MANOVA test, a multivariate multiple comparison test (Hotelling's T^2 -test (Curran, 2013)) was performed (Fig. 2, Step 2). The test's results indicated which of the data groups (grouping was based on those factors with significant influence, as identified by MANOVA test) were significantly different. Finally, a pairwise t -test (Student's T -test (Winter, 2013)) was performed, in order to identify the phthalates responsible for the significance of differences between given groups (Fig. 2, Step 3). The results of the Hotelling's and Student's tests (p -values) were put in table format and are provided in the results and discussion section. For the purpose of statistical analysis, values under the detection limit in the used dataset were replaced with 65% of the respective detection limit, following an approach suggested by Palarea-Albaladejo and Martín-Fernández (2015).

3. Results and discussion

3.1. Analytical results

Detailed concentrations of all the phthalates analysed, including triplicates for each of the samples, are presented in Tables S2–S6 (Supplementary material). Concentration ranges (min and max) for each of the phthalates are presented in Table 1, together with the respective limits (LOD) and frequency (FOD) of detection.

Among the 144 replicates analysed (48 samples \times 3 replicates), DBP, DiBP and DEHP were quantified with the highest frequency. On the other hand, DCHP, DEP and DPP were only present in a few of the analysed samples. Iónas et al. (2014) also showed that

DPP and DnOP had the lowest frequency of detection among the plastic samples they analysed ($n = 50$). Limited use of DPP was also highlighted by not detecting it in any of the house dust samples analysed ($n = 29$) in the United Kingdom (Greenpeace, 2003). In our case, the highest concentrations measured were for DEHP (max 2700 $\mu\text{g/g}$ in SSWP), which was almost three times higher than the 0.1% or 1000 $\mu\text{g/g}$ limit for plastic articles intended to come into contact with food (EC, 2007) or be used in electric and electronic equipment (EU, 2015). DEHP is considered the most commonly used plasticiser, resulting in its relative abundance in the environment when compared to other monitored phthalates (Latini, 2005). Similarly, Shen (2005) identified DEHP in the majority of 25 samples analysed, with the highest concentration (1764 $\mu\text{g/g}$) found in a food packaging plastic bag. In accordance with Table 1, the second highest concentration was measured for DiBP (460 $\mu\text{g/g}$ in RWP), which may be used as a substitute for DEHP or DBP in plastics, and which has been related to an increasing trend in human exposure based on retrospective biomonitoring data (Wittassek et al., 2007). Phthalates found in the lowest concentrations were DPP and DCHP, with 4.3 $\mu\text{g/g}$ (RWP) and 2.5 $\mu\text{g/g}$ (RHP) being the highest concentrations measured, respectively. Correspondingly, the highest concentration of DPP found by Iónas et al. (2014) in plastics was 2 $\mu\text{g/g}$. DPP was also among the phthalates migrating into foods from plastic packaging in the lowest concentrations (Fan et al., 2012).

3.2. Statistical analysis

Fig. 3 summarises analytical data on the presence of phthalates in plastics. As evident from this figure and from Table 1, the majority of phthalates (six out of nine) were detected only in a few of the samples. In accordance with Helsel and Hirsch (1992), datasets with undetected values ($<\text{LOD}$) higher than 50% should be excluded from statistical data analysis, as they introduce considerable mathematical bias. Based on this assumption, only DiBP, DBP and DEHP were included in the statistical analysis, as these phthalates were identified at 86%, 93% and 79% frequency of detection,

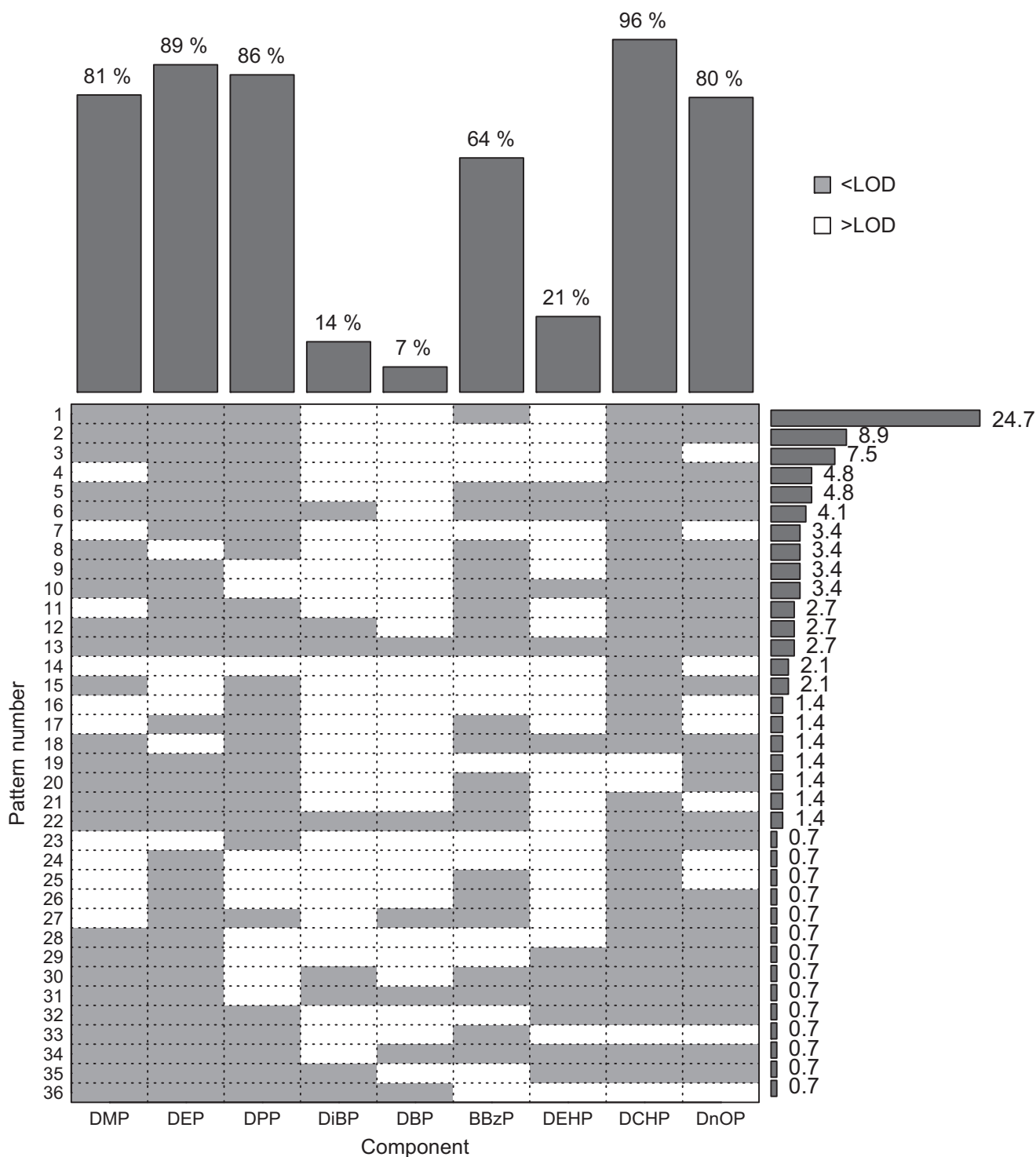


Fig. 3. Summary of detected (>LOD) vs undetected (<LOD) phthalates in the total of the dataset (Palarea-Albaladejo and Martín-Fernández, 2015). Bars on the top represent percentage distribution of undetected values to the total of a column. Bars on the right represent the percentage distribution of the patterns appearing in the table (e.g. top bar indicates that approximately 25% of all the samples analysed showed DMP, DEP, DPP, BBzP, DCHP and DnOP in values <LOD, while DiBP, DBP and DEHP were >LOD).

respectively. This corresponds to approximately 14% (DiBP), 7% (DBP) and 21% (DEHP) of samples under detection limit, as illustrated in Fig. 3.

Results of the MANOVA test (Fig. 2, Step 1) indicated that there was a significant difference (95% confidence interval) between plastics originating from the five sources (i.e. RWP, SSWP, RHP, RIP and VP). On the other hand, neither the plastic resin nor the combination of the sample source and plastic resin appeared to

have a significant influence on phthalate content. Based on this conclusion, only the source of plastic samples was evaluated as an influencing factor in the ensuing steps of the statistical analysis. A summary of the MANOVA test results is provided in Table S7 (Supplementary material).

The results of Hotelling's T^2 -test (Fig. 2, Step 2) are presented in Table 2. As evident from the table, waste plastics (RWP and SSWP) as well as RHP had no significant difference as to the phthalate

Table 2

Pairwise multivariate multiple comparison test. Values represent the p -values from Hotelling's T^2 -test. Values lower than 0.05 indicate statistically significant difference between the two groups being compared.

	Residual waste	Source-segregated waste	Recycled (Household)	Recycled (Industrial)
Source-segregated waste	0.41	1		
Recycled (Household)	0.48	0.66	1	
Recycled (Industrial)	<0.01	<0.01	0.01	1
Virgin	0.02	0.02	0.02	0.86

Table 3

Detailed pairwise comparison of log-ratio (ilr) coordinates (Eq. (1)). Values represent the p -values from Student's T -test. Values lower than 0.05 indicate statistically significant difference between the two groups being compared.

	ilr ₁		ilr ₂	
	Recycled (Industrial)	Virgin	Recycled (Industrial)	Virgin
Residual waste	<0.01	0.01	0.39	0.75
Source-segregated waste	<0.01	0.01	0.42	0.28
Recycled (Household)	<0.01	0.01	0.62	0.34

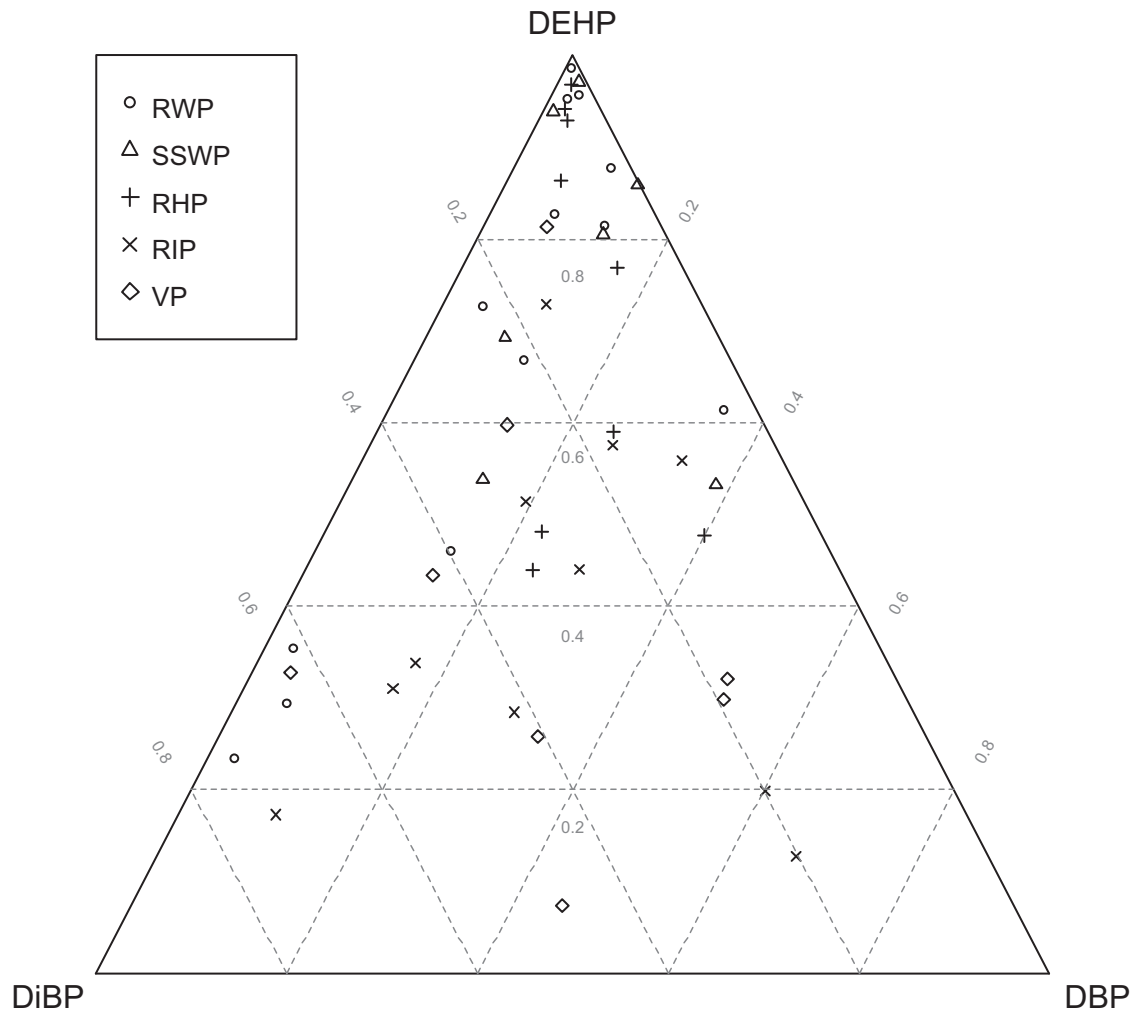


Fig. 4. Ternary plot of plastics composition with respect to DiBP, DEHP, and DBP for the samples of five plastic sources (RWP, SSWP, RHP, RIP and VP).

content (p -value > 0.05). On the other hand, all three groups of household plastics (RWP, SSWP and RHP) showed higher phthalate content and were significantly different (p -value < 0.05) from the recycled industrial (RIP) and virgin plastics (VP). Finally, recycled industrial and virgin plastics were similar in phthalate content (p -value > 0.05). Overall, and based on the analysed samples, these results may suggest that phthalates are not removed during the

recycling of household (i.e. post-consumer) plastics, which could lead to them spreading and accumulating despite the fact that some phthalate losses do occur in, for example, the mechanical re-processing of plastics (Huang et al., 2013). Furthermore, the similarity between RIP and VP indicates that the recycling of industrial or pre-consumer plastics does not lead to an increase in phthalate content.

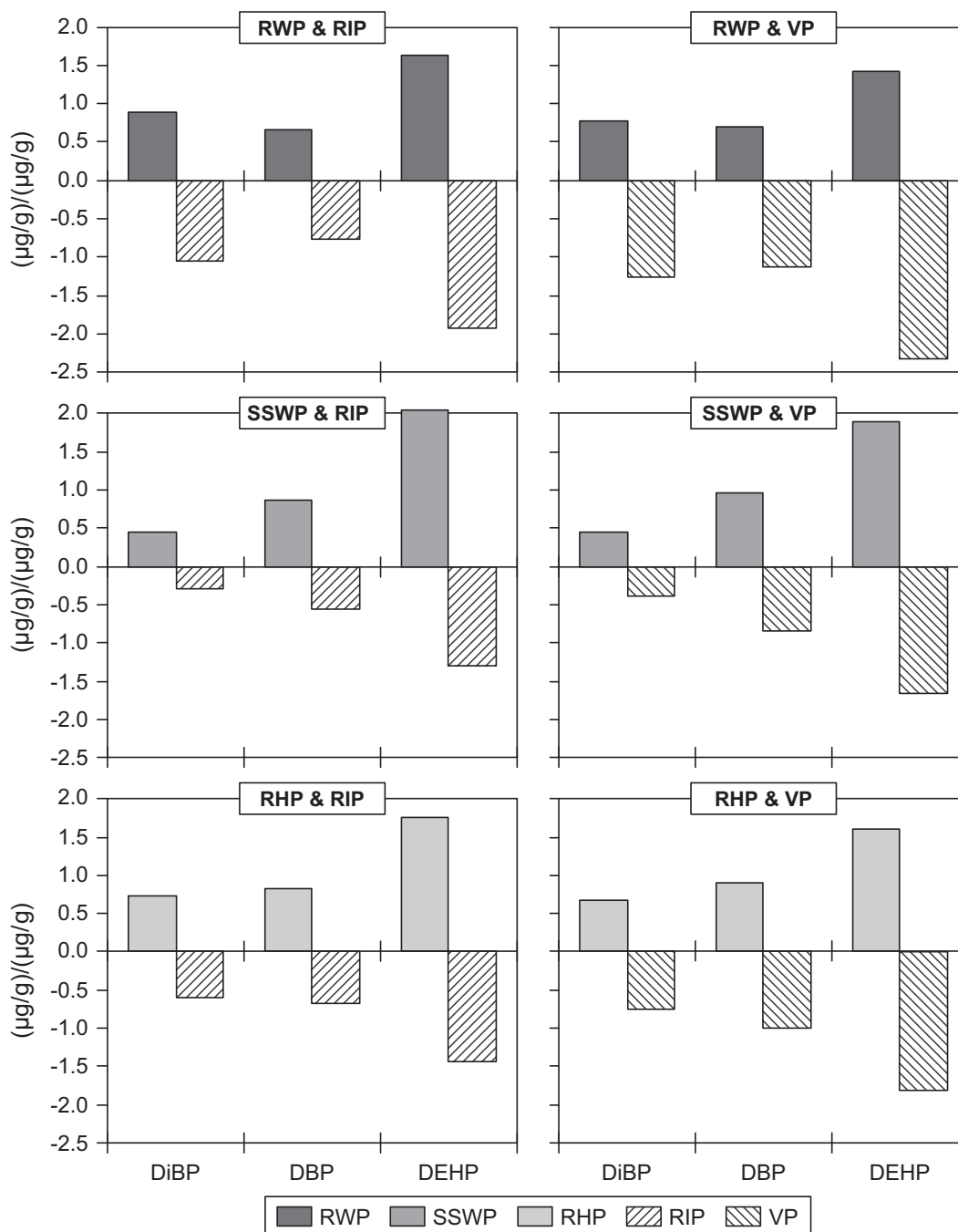


Fig. 5. Geometric mean barplots comparing the groups (i.e. sources of plastics) with statistically significant difference among them $[(\mu\text{g/g})/(\mu\text{g/g})]$. Each bar represents the ratio (logarithmic scale) between the geometric mean of an individual group and the combined geometric mean of the two groups being compared (Martín-Fernández et al., 2015).

Once significant differences between the groups were indicated by the Hotelling's T^2 -test (see Table 2 for details), one could interpret these differences in terms of phthalate content. The groups identified as being different in Step 2 were compared by means of a Student's T -test (Step 3). The results are provided in Table 3 and suggest consistently that waste or recycled household plastics were different to either recycled industrial or virgin plastics in ilr_1 (see Eq. (1)) coordinates, while differences in ilr_2 (see Eq. (1)) coordinates were consistently insignificant. This indicated that the ratio DiBP/DBP , on average, displayed the same behaviour in all of the groups. When combined with the results for ilr_1 coordinates, this suggested that DEHP had an important role in these differences. To illustrate which of the three phthalates dominated the

difference between the groups, the evaluated dataset is represented in a ternary diagram (Fig. 4).

It is evident from the ternary plot of the three phthalates (Fig. 4) that the results for the household plastic (i.e. RWP, SSWP and RHP) samples were dominated by DEHP, while data points for the last two groups (i.e. RIP and VP) were either scattered (with an increasing trend towards DEHP) or exhibited dominance favouring either DiBP or DBP. The significant difference in the ilr_1 (Table 3) suggested that among the three phthalates in focus (i.e. DiBP, DEHP and DBP) DEHP was the main one responsible for the differences between the groups. For further interpretation, data points in the ternary plot (Fig. 4) had to be projected from the DiBP vertex (or DBP vertex) towards the DEHP-DBP edge (or DEHP-DiBP edge).

This projection showed that samples in the first three groups (i.e. RWP, SSWP and RHP) had separated from the last two groups (i.e. RIP and VP). On the other hand, the non-significant difference in the ilr_2 (Table 3) suggested that all five groups (i.e. plastic sources) were not well separated in the sub-composition (DiBP, DBP), i.e. there were no significant differences in the DiBP/DBP ratio. Indeed, when the data from the DEHP vertex were projected to the DiBP-DBP edge, all the groups overlapped and did not separate clearly.

Finally, when the arithmetic mean of ilr coordinates of a group is transformed back, the geometric mean of the original data is obtained. The geometric mean barplot in Fig. 5 provides a further illustration of the differences between two individual groups (Martín-Fernández et al., 2015). For each plot (Fig. 5), each of the bars represents the ratio (logarithmic scale) between the geometric mean of an individual group and the combined geometric mean of the two groups being compared. As a consequence, positive (>0) bars for a group (e.g. RWP in Fig. 5) indicate higher phthalate content. Moreover, the larger the bar for a specific phthalate (e.g. DEHP in Fig. 5), the larger the difference between the two groups. The differences shown in Fig. 5 are on a logarithmic scale; for example, a bar larger than 1 (e.g. DEHP in Fig. 5) for a phthalate means that on average the samples in this group had almost double (172% or $\exp(1) = 2.72$) the phthalate content compared with the combined geometric mean of the two groups. Fig. 5 clearly illustrates higher phthalate content (i.e. positive bars) in RWP, SSWP and RHP when compared to RIP or VP (i.e. negative bars) as well as the clear dominance of DEHP (i.e. the largest differences in Fig. 5). Hence, the significant difference between the first three groups (RWP, SSWP and RHP) and recycled industrial and virgin plastics (as pointed out in the results for Step 2) was mainly due to differences in DEHP content. This conclusion was previously suggested by the Student's *T*-test for ilr coordinates (Table 3) and corroborated through the ternary diagram (Fig. 4).

3.3. Implications for plastics recycling

The statistical analysis of the experimental data for presence of phthalates in plastic samples highlighted several important issues: (i) the insignificant difference between the waste plastic (RWP and SSWP) samples indicated that the household plastics collection scheme had no influence on the presence of phthalates in waste plastics (i.e. phthalate content in plastic items disposed in residual or source-segregated waste was the same); (ii) the insignificant difference between household waste plastic samples (RWP and SSWP) and samples of recycled household plastics (RHP) suggested that phthalates were not removed following plastics recycling and could potentially persist in the recycling process, resulting in phthalate spreading and accumulating; (iii) as no difference was detected in pre-consumer plastic samples (RIP and VP), the recycling of industrial waste plastics does not appear to significantly increase phthalate content in plastics and (iv) finally, the significant difference between household plastic (RWP, SSWP, and RHP) samples and samples of pre-consumer plastics (RIP and VP) may indicate that phthalates were added in the later stages of manufacturing (labelling, gluing, etc.) or that samples of the household waste plastics were contaminated by other articles with higher phthalate content (e.g. PVC). This may lead to further contamination of recycled plastics, as achieving 100% purity when sorting household waste plastics is practically impossible (WRAP, 2010).

4. Conclusions

Samples of plastics from household waste, recycled waste and virgin plastics were obtained, and phthalates were identified in

most of the samples. DBP, DiBP and DEHP were the most abundant phthalates, with 460 $\mu\text{g/g}$, 360 $\mu\text{g/g}$ and 2700 $\mu\text{g/g}$ as the highest concentrations measured, respectively. Statistical data analysis showed that plastic resin (e.g. PET, HDPE, PS) could not explain the presence of phthalates, while the source of plastic material samples (e.g. waste plastics, recycled plastics, virgin plastics) was the single factor significantly influencing phthalate content. A comparison of the five sources of samples indicated that recycling could be a potential source of phthalates in recycled plastics. When recycled plastics are used in applications sensitive to phthalate content (e.g. children's toys and food-contact articles), the source of plastics and their chemical composition should be monitored closely. DEHP can serve as an indicator phthalate, as it was abundant in the analysed samples and was highlighted as the main factor influencing differences between the evaluated sources of plastics.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.wasman.2016.05.014>.

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