Consumer exposure to phthalates from paper packaging - an integrated approach

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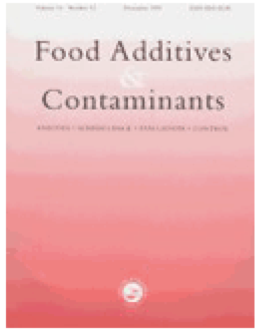

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Abstract

This paper presents an integrated approach to estimate exposure of Portuguese population to phthalates as a contaminant originating from paperboard packaging. The approach combined data of migrant concentration in the foods resulting from a stochastic simulation, with consumption data of food packaged in paperboard. The results from the exposure model were validated with experimental values actually found in the food. A short surveillance exercise was conducted with samples collection from the market shelves to identify and quantify the phthalates present in the packages and in the food. The distribution of values for the di-butyl phthalate concentration in the packages was used as input of the initial concentration in the Weibull model to estimate the concentration of this phthalate in the foods. This distribution of occurrence data was then combined with the packaging usage data in a probabilistic simulation with the Monte Carlo sampling method. Exposure values ranged between 0 and 8.95 μg/day.Kg_{bw}, a value close to the tolerable daily intake established by EFSA - 10 μg/day.Kg_{bw}. However, the 97.5th percentile and the average were, respectively, 1.82 and 0.44 μg/day.Kg_{bw}, indicating that further refinement of the estimates is not necessary. Other phthalates were also detected in the packaging samples: di-isobutyl phthalate and di-ethylhexyl phthalate. This latter was present in all packaging samples collected and was detected in a few food samples at values requiring further investigation.

Running head:- Probabilistic assessment of exposure to phthalates

Introduction

Phthalates are amongst the more commonly found organic contaminants in environment and consumer products. They are used as plasticizers in many plastics applications, including packaging and other food contact materials. Inks, lacquers, adhesives and recycled pulp are important sources of phthalates in paper and paperboard packaging (Aurela et al., 1999; Binderup et al., 2002; Bononi & Tateo, 2009; Mariani et al, 1999; Sturaro et al., 1995 and 2006). Some phthalates and their metabolites are known to present an endocrine disruptive action that as been associated with impairment of the development of male reproductive system in rodents. Although evidence in humans is still limited, data from human studies have explored possible associations between phthalates and men with altered semen quality, shortened gestation, reduced anogenital distance in baby boys, and premature breast development in young girls (Dickson-Spilmmann et al., 2009; Hauser & Calafat, 2005; Latini et al., 2003; Swan et al., 2005; Wittassek & Angerer, 2008). Consequently, exposure to phthalates has been a concern due to these potential health adverse effects.

The work reported here consisted on a surveillance exercise on the phthalates occurrence in paperboard packages and respective foods and on the estimation of Portuguese consumer's exposure to di-butyl phthalate (DBP) originating from paper and paperboard packaging. Exposure can be expressed as (Poças et al., 2007):

$$Exposure = Migration\ x\ Food\ \ Consumption \quad (1)$$

Where the *Migration* term represents the concentration of substance that, by transfer from the package, ends up in the food; and the term *Food Consumption* represents the daily intake of food packaged in the system from which the migrant originated, or the amount of packaging used to pack the food consumed, depending on the units used in the *Migration* term.

Mathematical models are important tools that have been used for compliance assessment of plastics materials, but rarely for paperboard packaging or for generating concentration data for exposure assessments. The generation of values for the distribution of the concentration of migrant in food from a stochastic analysis of the equations governing the migration process and its use in exposure assessments has been proposed (Vitrac & Leblanc, 2007; Poças, 2010). This approach was followed here using the Weibull kinetic model proposed to simulate concentration data of dibutyl-phthalate (DBP) in foods packaged in cellulosic materials (Poças, 2009). The Weibull kinetic model is a simple model that commonly describes complex processes with high variability (Cunha et al., 2001). Due to these characteristics, it has been used to describe different processes in food processing, quality and safety (Blasco et al., 2006; Freitas & Costa, 2006; Morales et al., 2004) and to describe the migration of substances from paperboard into solid simulants of food in spite of its empirical nature (Poças, 2009). The Weibull kinetic model may be written as:

$$\frac{C(t)-C_\infty}{C_o-C_\infty}=\exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right] \qquad (2)$$

Where *C(t)* is the concentration of migrant in food changing with time *t*, C_∞ is the concentration at equilibrium and C_o is the initial concentration. The model has two parameters: τ, the scale parameter, associated to the process rate, being the time required accomplish a one log cycle (63,8%) of the process; and β is the shape parameter, quantifying the pattern of curvature observed (Cunha et al., 2001). When applying this model to migration of a contaminant, its initial concentration in the food can be considered equal to zero. Normalising the migrant concentration in the food, *C(t)*, with the initial migrant concentration in the package C^P_o, gives:

$$\frac{C^F(t)}{C^P_o}=\frac{C^F_\infty}{C^P_o}\left[1-\exp\left(-\left(\frac{t}{\tau}\right)^{\beta}\right)\right] \qquad (3)$$

The model parameters (τ, β, C^F_∞/C^P_o) determined before (Poças, 2009) were used and the initial concentration of DBP (C^P_o) in the cellulosic packaging materials was determined experimentally from a short market survey. Samples of packages were collected from the shelves and screened for phthalates detection followed by quantification. Equation (3) was used to generate the C^F distribution of values required for the 1st term of the exposure equation (1).

The consumption of food that is in contact with paper or paperboard is the other term in the exposure equation (1). The packaging usage data of a Portuguese representative consumers sample gathered before was used (Poças et al., 2009). The exposure model can then be expressed as follows:

$$E\,(mg/day.Kg_{bw}) = C^{F}\,(mg/Kg_{food})\ \ x\ FW\,(Kg/day.Kg_{bw}) \qquad (4)$$

Where *FW* is the food weight packaged in paperboard consumed per day and per consumer body weight. Both terms of equation (4), for migrant concentration and for food consumption, are represented by distributions of values for a probabilistic analysis. The exposure to DBP is simulated through the propagation of the variables distribution through the model with the Monte Carlo (MC) sampling method. The results of the model were validated with DBP concentration data from the food samples collected in the market.

Materials and methods

Data of initial concentration of DBP in the packaging

A short survey of the local market was conducted: samples of paper and paperboard packages were collected and taken to the laboratory for screening analyses: phthalates present were identified and semi-quantified as described subsequently.

- Sample

Foods (21) packaged in cellulosic materials were purchased in one supermarket in Gaia, Portugal, in April 2009 (Table 1). Food products were mostly dried food such as cookies and biscuits, flour and sugar, cereals and dry pasta, but also butter, frozen ice cream and chocolate. The foods all had primary or secondary packages made of paper, paperboard or corrugated board. In most cases there was also an inner package in paper or in a different material and only a few products were in direct contact with the outer packaging.

- Sample preparation

Packaging materials (only the cellulose based) and food samples were extracted with hexane, followed by sonication for 30 min and filtration. Around 1 g of packaging material was cut into small pieces and extracted with 5 ml of hexane. For the food samples ca. 5 g were extracted with a varying amount of hexane from 5 ml to 15 ml, depending on the volume of the food. Powders and small solids like cereals were mixed up before sample collection. Solids such as chocolate and butter were sampled in small pieces from different areas at the product surface only. All foods were gross ground before extraction. The d-DHP was added as internal standard for semi-quantification. The extracts were analysed by GC-MS. This method was used before with average recovery values from paper samples of 97% and 106% respectively for DBP and DEHP; and from sugar samples of 77% and 51% respectively for DIBP and DBP (Aurela et al, 1999).

- Semi-quantification of phthalates

The amount of each phthalate in the packaging material was quantified in relation to the amount of d-DHP. This internal standard (100 mg/L) was added to the extract in the amount required to yield a concentration of 1 mg/l. This corresponded to a concentration of 5 mg/Kg of packaging materials and to concentrations in food between 1 and 3 mg/Kg. Because the purpose of the study was first to identify the type of phthalates present in market packages, the full scan mode was used in MS detection rather than the selected ions mode that would allow for a more accurate and sensitive quantification of known phthalates. Detection limits of 0.04 mg/L were found for DiBP, DEHP and DBP in hexane extracts that corresponded, for the extraction conditions observed, to 0.2 mg/Kg of packaging material and to 0.04 to 0.12 mg/Kg of foods. Precautions during sample and chemicals handling were taken to avoid blank problems with phthalate contamination: the system and all the material contacting samples were routinely run and rinsed for cleaning. Glassware was washed with acetone and non-volumetric material was left at 105-110 °C for at least 4 hours before use. Injections of blanks from solvents of extractions were accepted, as an indication of clean system, only with non detected phthalates (ratio signal/noise lower than 3).

- Chromatographic conditions for phthalates screening

Chromatograph Varian CP-3800 with detector Quadrupole MS 1200L (Ionisation mode: electronic impact 70 eV); Scan mode: full scan (m/z 90 to 300 m/z)

Column: Varian fused silica capillary VF-5MS (30 m x 0.25 mm, 0.25 µm)

Temperature of the injector: 300°C

Oven: 60°C during 1 min; 10°C /min. up to 320°C and 320°C during 5 min

Volume of injection: 1µl split:splitless (splitless time 0.5 min)

The chromatographic system used presents typically determination coefficients better than R^2>0.99 for all phthalates and the average variation between repeated injections was lower than 4%.

Packaging usage data: the database from MIGRAMODEL project (ESB, 2008) was used to provide data on the amount of food in contact with paper and paperboard packages; this database includes data collected at household level. The food weight consumed per day and per consumer body weight was derived. The average amount of paper and paperboard packaging usage for food eaten at home in the consumer sample was ca 2 dm^2/day.person. This value corresponded to 0.11 Kg of food packaged in cellulosic material consumed per day and per person. When the household bodyweight is taken into consideration, the average value is 0.002 Kg_{food}/day.Kg_{bw}(Poças et al. 2009). Figure 1 represents the distribution of values found that were best fitted to the lognormal probability distribution function (Table 2).

Weibull model parameters

The following Weibull model parameters were considered to describe the migration of DBP at 23°C: τ (hr) = 49.6±10.5, β = 1.35±0.32 and C^F_∞/C^P_o = 0.184±0.020. These parameters were derived from migration experiments from paper into Tenax® (Poças, 2009). These parameters were considered normally distributed and propagated in equation (3) to generate a distribution of values for the concentration of DBP in food.

Probabilistic analysis

The software Crystal Ball 7.2.2. (Decisioneering, Inc.) was used to fit the exposure model inputs (food consumption data and DBP concentration data) as well as the model output to probability distributions functions by the maximum likelihood method. The distributions were truncated to allow only positive values in the exposure model because there is no physical meaning for negative values of these inputs. The goodness-of-fit was assessed by the Anderson-Darling (A-D) test. MC simulation was used as sampling method with 10 000 iterations for each run. This sample size is suggested in principles of good practice for MC risk assessments (Burmester & Anderson, 1994). Descriptive statistics were calculated from the exposure estimates generated by the model.

Results and discussion

i. Phthalates concentration in packaging samples

All packaging samples collected and all corresponding foods were analysed. Phthalates were detected in all packaging samples but they were detected in only some of the food samples. Table 3 presents the concentration of each phthalate detected in the outer packaging materials collected and in the foods contained in each packaging system. Three phthalates were found in most of the packaging samples in concentrations typically lower than 20 mg/Kg: DEHP (Diethyl hexyl phthalate; CAS 117-81-7), DiBP (Diisobutyl phthalate; CAS 84-69-5) and DBP (Dibutyl phthalate; CAS 84-74-2). DEHP was present in all samples in concentrations ranging from 0.5 to 5 mg/Kg. DiBP presented the highest average concentration in the packaging samples: values ranged from 0.1 to 21 mg/kg; the highest value was found in sample P7. DBP concentration values ranged from 0.4 to 3 mg/Kg. DEP (Diethyl phthalate; CAS 84-66-2) was detected in one packaging sample (P4). In sample P7 DINP was additionally detected (Diisononyl Phthalate; CAS 28553-12-0) in a concentration of ca. 21 mg/kg.

The values found for DBP in the packaging samples can be compared with the values found in a recent USA survey, which showed values ranging from 0.14 to 55 mg/kg, with most of the individual values lower than 20 mg/kg (Zhang et al., 2008). DIBP was also found in Italian restaurants take-away pizza boxes (Bononi & Tateo, 2009). However, the values cannot be directly compared because the results were given per unit of box surface area and not for mass of board. Summerfiled & Cooper (2001) also found the same three phthalates in towels and napkins collected from UK market in concentrations of 12 to 21 mg DEHP/kg, 3 to 10 mg DiBP/kg and 2 to 3 mg DBP/kg. Aurela et al. (1999) found considerably higher values: 8 to 430 mg DEHP/kg, 30 to 450 mg DiBP/kg and 7 to 130 mg DBP/kg. This is not surprising because there has been a general effort in reducing the exposure levels of consumers to this group of chemicals in the past decade. Those authors had found at that time that most of the cases detected were associated to off-set printing and that DEHP was the more common phthalate. A few samples were flexo-printed and contained significant amount of DBP and DiBP (Aurela et al., 1999).

A survey in Australian market (1996-1997) to 136 food packaging materials including plastics, presented average values for the DBP and DEHP in printed fibre board packaging for baked foods, respectively 58 and 320 mg/kg, and in boxes for breakfast cereals average values of 45 and 42 mg/kg. these two phthalates were present and nearly all packaging samples. The values found in paper tea bags were considerably higher: 550 mg/Kg for DBP and 1625 mg/Kg for DEHP (Balafas et al., 1999).

In a recent analysis of phthalates in infant food (milk powders, cereal flakes and semolina powder) packaged in recycled paperboard collected in Germany, four phthalates were detected in all samples: DIBP, DBP, BBP and DEHP. Values found in this survey tend to be higher because the sampling targeted packages made of recycled board which did not necessarily happen in the present study. The average value found to DIBP was 23 mg/kg, the values to DEHP ranged from 0.5 to 17 mg/kg and the values for DBP were all lower than 6 mg/kg (Gärtner et al., 2009).

Although only 21 samples have been collected, the distribution of values found for the DBP detected in the packaging samples is shown in Figure 2. The samples presenting no-detectable DBP were attributed with a value equal to 0.01 mg/kg (a fraction of the quantification limit). This explains the high frequency of the lowest concentration bin in the histogram. Figures 3 and 4 show the distribution values of DEHP and DiBP concentration, respectively.

ii. DBP exposure estimates

Table 2 presents the results for the distribution functions fitting the input variables for the DBP exposure model according to equation (3): food weight packaged in cellulosic materials (FW) and the result of the market survey on DBP concentration in the packages that was used in the migration Weibull model to generate the data for the C^F term in the exposure equation (3).

The Weibull model was run to generate DBP concentration values after 1 month of contact between the package and the food. This period of time was selected taking into consideration the expected average shelf-life of the products. In fact, the Weibull model parameters used were derived from experiments where the packaging material was in direct contact with Tenax®. In those conditions, 1 month of migration time yields to the maximum (equilibrium) concentration of DBP as can be seen through a simple simulation using the model parameters given. In that range of concentration, considering different product shelf-life would not affect the exposure estimates (Poças et al., 2010). Furthermore, some of the food packaging systems used presented a primary package made of a better barrier material than paper. That layer acts as a "delaying" barrier, promoting a lag-phase in the migration curve. Therefore, at any time of contact, those foods present a DBP concentration lower than that predicted by the model for the same time of contact.

Figure 5(A) and (B) presents the output of MC simulation of the $C^F/C^P{}_o$ and C^F, respectively. Descriptive statistics for the DBP concentration in the food and for the exposure estimates are presented in Table 4. Estimates of concentration of DBP in food indicate a mean of ca. 0.21 mg/kg$_{food}$ with a maximum estimated value of ca. 0.6 mg/kg$_{food}$. The 97.5th percentile is at 0.46 mg/Kg$_{food}$ as indicated in Figure 5(B). If one takes as reference the limit for specific migration of DBP set in Directive 2007/19/CE for plastic, which is 0.3 mg/kg$_{food}$, the estimates indicate a 33% risk of finding higher values in the market samples.

The distribution of exposure values is presented in Figure 6. The curve presents a non-normal shape, exponential decreasing: the probability of exposure decreases as the exposure value increases. Exposure values ranged from 0 to 8.95 μg/day.kg$_{bw}$, thus presenting values close to the TDI established by EFSA in 2005, which is 10 μg/day.Kg$_{bw}$. However, the 97.5th percentile is 1.82 μg/day.kg$_{bw}$ and the mean is estimated as 0.44 μg/day.kg$_{bw}$, values considerably lower than TDI, indicating that probably no further refinement is required.

In order to validate the results of the exposure estimates, the actual values for the DBP phthalates in the food samples were also screened in order to verify that the phthalates concentration in the foods obtained by simulation are not lower then the values determined experimentally. The results for the food samples presenting detectable values of phthalates concentration are also presented in Table 3.

DiBP and DEHP were detected in 3 food samples and DBP, DINP or DEP were not detected under the conditions of test. DIBP was found at a concentration of 0.37 mg/kg in flour and at ca 0.15 mg/kg in a cake mix and tea. DIBP is not regulated yet by EFSA and it has been assigned to SCF List 8 (list of substances evaluated or under evaluated by EFSA), thus indicating that there is no adequate data for a scientifically sound decision on the safe use of this substance. Past evaluations by SCF indicated a group restriction of 0.05 mg/kg_{bw}.day for its use in plastics materials (EFSA, 2004). In the meanwhile, the German safety authority (BfR) has recommended a specific restriction of migration into foods of 1 mg/kg_{food} and suggested that German industry should agree on a common strategy to reduce and phase out the use of glues, printing inks and other products containing DIBP in order to reduce its levels in recycled paper (BfR, 2007). In 2009, FEFCO (European Federation of Corrugated Board Manufacturers) has also reached a voluntary agreement to phase out DiBP from corrugated products. The concentration values found in the food samples collected are around 1/3rd and 1/10th of the recommended by BfR, therefore a wider and precise survey is not necessarily required.

DEHP was found at a concentration of 0.06 mg/kg in a cake mix, 0.2 mg/kg in stocks and at a concentration of 2.2 mg/kg in butter. In this latter case, the Al/paper wrapping materials was in direct contact and the value exceeded the migration limit set in the Directive 2002/19/EC which is 1.5 mg/kg. This limit is applicable to all-plastic materials and therefore it is not applicable (in legal terms) to the present case. The sample analysed was collected from the surface of the butter piece, which represents a worst case. Nevertheless, this particularly high value found may indicate that a more refined survey is necessary.

Given the result for DBP (not detected in the food samples), the exposure estimates may be considered safe. As indicated in Table 1, many samples had a primary inner packaging that acts as a barrier between the outer cellulosic package and the food. The Weibull model parameters were derived for situations where paper is in direct contact, thus it could be anticipated that an overestimation of the DBP concentration of the food and hence of the exposure values would occur. The food samples with detected phthalates were in direct contact (F20), with inner paper packaging (F1, F8), and in the case of wrapping with aluminium (Al)/paper. In case of stocks (F2) the phthalates may originate from the printing ink applied in the paper wrap outer surface. However, since this material is commonly supplied in rolls, the set-off transfer into the inner material face during storage allows a ulterior migration into the food in spite of the excellent barrier that Al can provide.

Conclusions

The combination of mathematical models with food packaging usage data can be a practical and efficient tool to be considered in exposure assessments. The benefit of using these simulation tools is particularly interesting to avoid the analytical difficulties inherent to food matrices. Data of initial concentration in the packaging materials are still required but these are easier to obtain either through expert judgement or even by analytical means that, depending on the migrant, are typically simpler than those required to analyse food samples. The use of mathematical models requires the knowledge of the model parameters and for this study only the DBP parameters were available. The study should be extended to DiBP and DEHP when Weibull model parameters are available.

The parameters of the mathematical model used in the present study were derived with an experimental set up where the cellulosic material was in direct contact with the food simulant Tenax® (Poças, 2009). In those conditions migration is very fast because migrants do not need to cross a high barrier material. Furthermore, Tenax® is considered to be an adequate simulant of solids foods for compliance purposes as experience indicates that equilibrium concentration in this simulant is often higher than the equilibrium concentration found in actual foods, thus indicating that results obtained with the simulant have a safe margin. Therefore, using the model parameters obtained in the described conditions to simulate concentration values that occur in real food and non direct contact, yields simulated concentration values in the food that are higher and that are achieved faster than those that would be achieved in actual conditions of indirect contact with food. Consequently the exposure model yields overestimated exposure values.

Survey results indicate that DEHP is omni-present and that depending on the packaging system it may migrate into the food in quantities that become close to safety limits. This phthalate may justify a more specific study, first with the mathematical model as a source of concentration data and depending on the results a more extensive sample collection from the market could be made.

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Table 1. List of food samples and corresponding packaging system.

Code	Packaging	Food Contact	Inner packaging	Product
P1	Carton box	N	Paper pouch	Cake mix
P2	Carton box	N	Al/paper wrap	Stocks
P3	Carton box	N	Al/paper wrap	Chocolate
P4	Carton box	N	Plastic pouch/tea bag	Tea
P5	Carton box	N	Plastic pouch	Biscuits
P6	Carton box	N	Al/paper wrap	Stocks
P7	Carton box	N	Plastic pouch	Biscuits
P8	Carton box	N	Paper pouch	Flour
P9	Carton box	N	Plastic pouch	Biscuits
P10	Carton box	N	Metallized plastic pouch	Flour
P11	Carton box	N	Plastic pouch	Breakfast cereals
P12	Paper bag	Y	No	Sugar
P13	Paper bag	Y	No	Flour
P14	Carton box	N	Plastic pouch	Breakfast cereals
P15	Carton box	N	Al wrap	Chocolate
P16	Carton box	N	Metallized plastic pouch	Biscuits
P17	Carton box	Y	No	Dry pasta
P18	Composite can	Y	No	Snack
P19	Folding carton	N	HDPE bottle	Yogurt
P20	Flexible wrap	Y	Al/paper wrap	Butter
P21	Corrugated board box	N	Plastic pouch	Ice cream

Table 2. Parameters of functions describing the distribution of values of the exposure model inputs.

Variable	Distribution	A-D	Parameters
FW	Lognormal	0.1317	Mean=0.0021 Std. Dev.=0.00169 Location=-0.00022
C^{P}_{o} (DBP)	Beta	0.6098	Minimum=-0.07777 Maximum=2.29386 Alpha=0.42416 Beta=0.55836

Table 3. Concentration (mg/Kg) of phthalates found in the packaging samples and in the respective food samples.

Sample*	DiBP	DBP	DEHP	DEP	DINP
P1	2.3	0.68	1.2		
P2	3.9	1.3	1.8		
P3	0.15		0.46		
P4	12	0.79	1.9	0.28	
P5	8.3	0.88	5.1		
P6	4.0	2.1	3.5		
P7	21	1.6	3.9		21
P8	7.9	2.2	3.5		
P9	3.3	0.79	3.1		
P10	5.2	1.8	2.8		
P11	5.4	0.99	3.0		
P12	2.6	0.45	1.3		
P13	0.43		0.60		
P14	8.9	2.3	3.7		
P15	1.0		0.52		
P16	3.9		2.9		
P17	4.3		0.82		
P18	7.7	1.9	3.6		
P19			2.1		
P20			1.6		
P21	16	2.0	4.5		
F1	0.16		0.063		
F2			0.19		
F4	0.14				
F8	0.36				
F20			2.2		

* Pi packaging sample i and Fi corresponding food sample i.

Table 4. Descriptive statistics for the DBP concentration in food simulated with Weibull model and for the exposure model output.

Statistics	C^F, mg/Kgf_{ood}	E, $mg/day.Kg_{bw}$
Trials	10 000	10 000
Mean	0.211	0.000439
Standard Deviation	0.144	0.000522
Variance	0.021	0.000000
Skewness	0.127	3.27
Kurtosis	1.71	24.12
Coeff. of Variability	0.682	1.19
Minimum	0.000	0.000000
Maximum	0.579	0.008947
Range Width	0.579	0.008947
Mean Std. Error	0.0014	0.000005

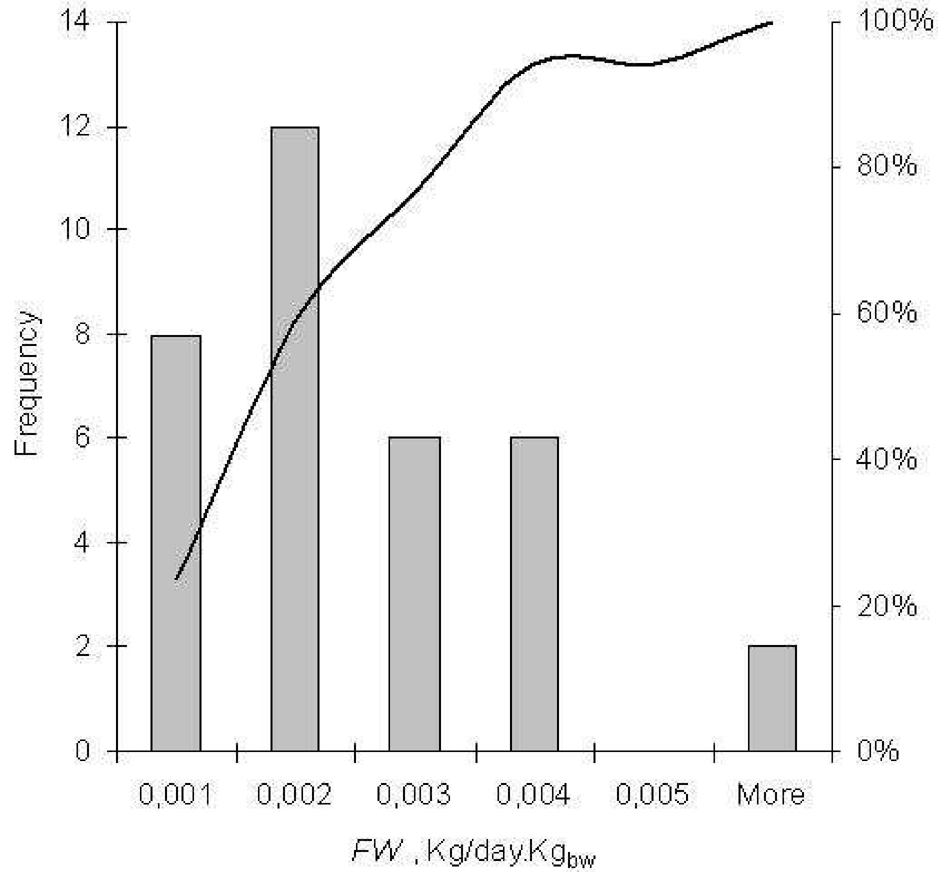

Figure 1. Food consumed packaged in paper and paperboard (Data from Poças et al., 2009).
145x138mm (96 x 96 DPI)

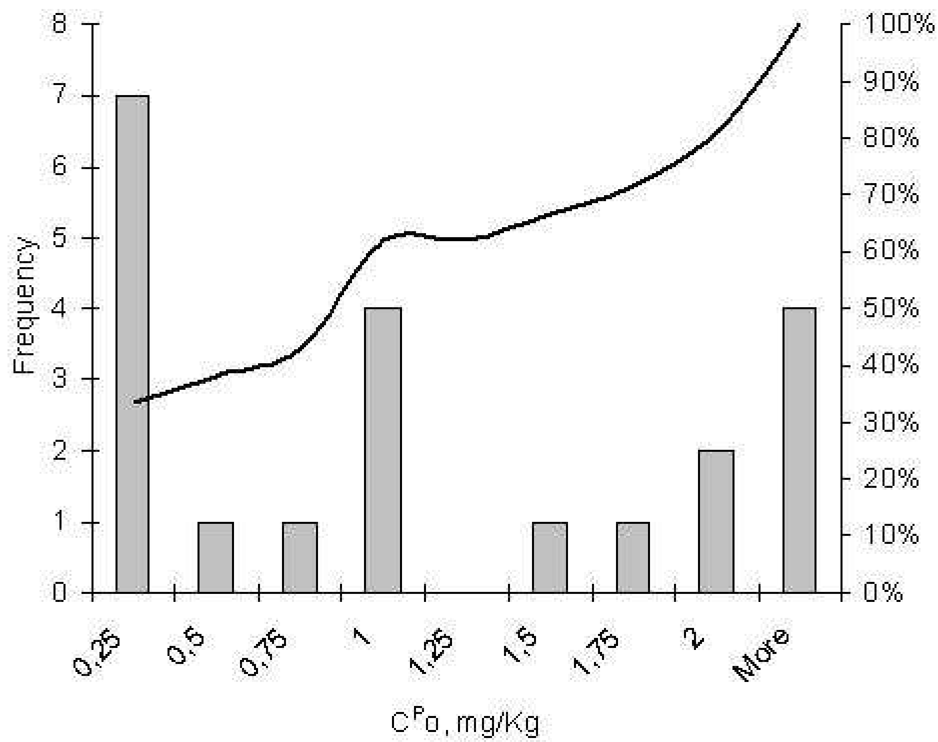

Figure 2. Concentration of DBP in packages collected from the market.
130x105mm (96 x 96 DPI)

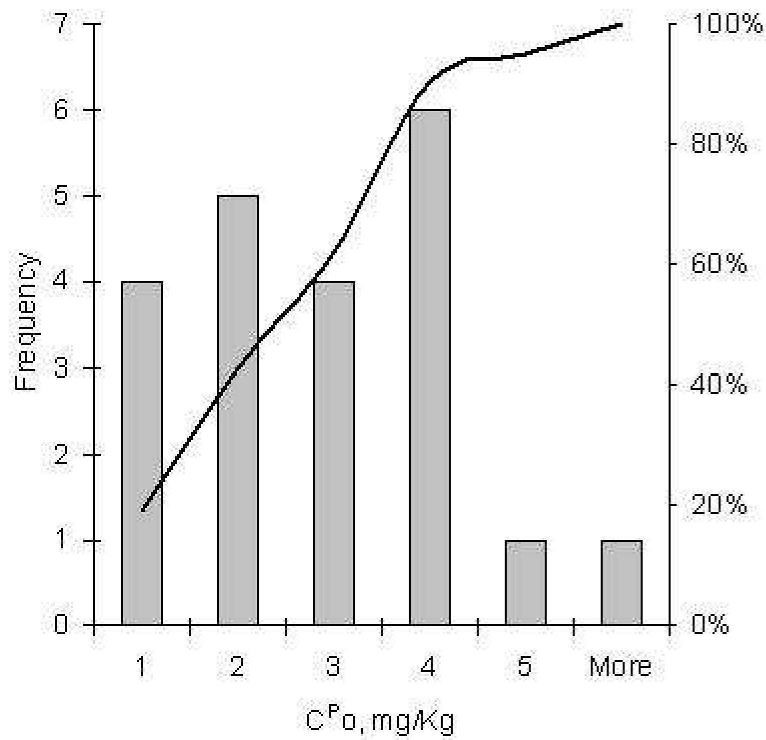

Figure 3. Concentration of DEHP in packages collected from the market.
107x104mm (96 x 96 DPI)

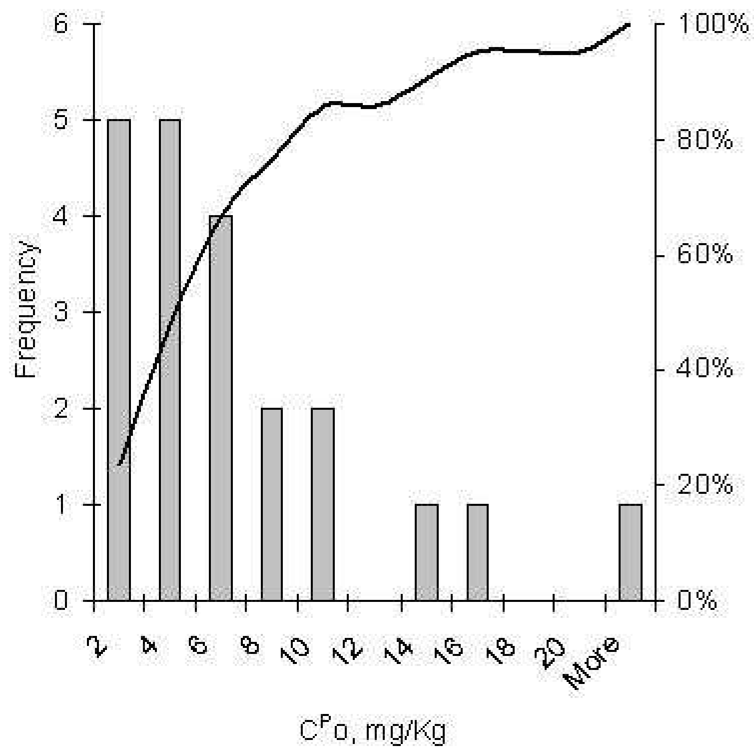

Figure 4. Concentration of DiBP in packages collected from the market.
107x106mm (96 x 96 DPI)

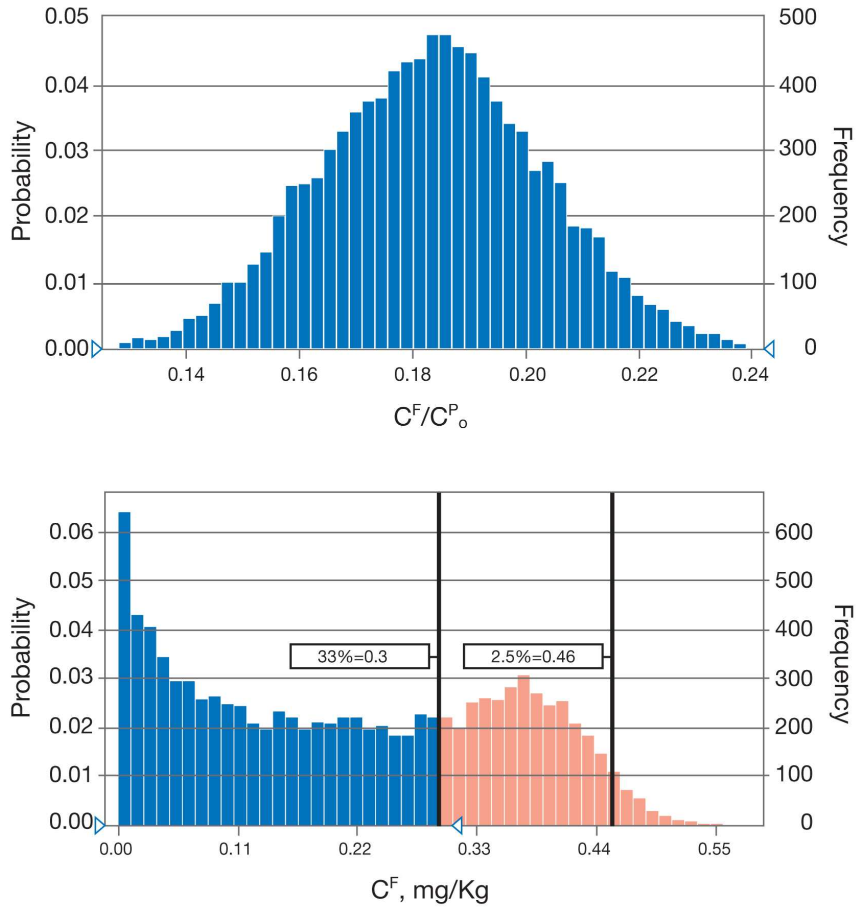

Figure 5. Weibull model output: (A) – ratio of DBP concentration in the food to the initial concentration in the paper; (B) – DBP concentration in the food.
165x168mm (300 x 300 DPI)

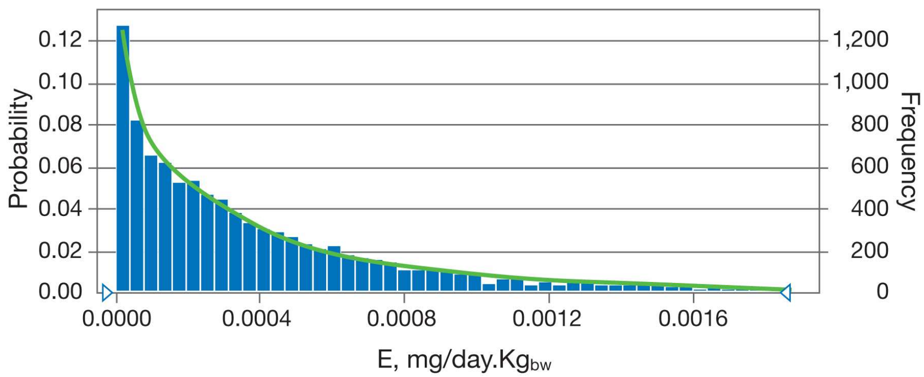

Figure 6. Estimates of exposure to DBP from food packaged in paper and board.
165x80mm (300 x 300 DPI)