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ARTICLE

Analysis and Migration of Phthalates in Infant Food Packed in Recycled Paperboard

Sonja Gärtner, Matthias Balski, Matthias Koch,* and Irene Nehls

BAM Federal Institute for Materials Research and Testing, Richard-Willstaetter-Strasse 11, D-12489 Berlin, Germany

The contamination of infant food with substances from its packaging due to migration processes is still a problem. Most recently, great attention was paid to the migration of epoxidized soybean oil (ESBO) and phthalates from twist-off closures into baby food packed in glass jars. Besides, packaging made of recycled fiber materials such as paper and paperboard were found to be the source of contaminants in dry and powdery foodstuffs such as sugar, rice, and maize flour. In this study 20 infant food samples packed in recycled paperboard containers were tested for phthalates and diisopropyl naphthalenes (DIPN), known incorporated substances in recycled paper. Furthermore, the barrier function of different secondary packaging materials (paper and aluminum-coated foil) was investigated. The highest contents of phthalates (mainly diisobutyl phthalate, DiBP) and DIPN in infant food samples were found for those foods packed in inner bags made of paper. Migration experiments were performed under authentic conditions to evaluate possible transfer mechanism (gas phase, direct contact) of phthalate esters into foodstuff. It is shown that paper does not provide an appropriate barrier against migration of semipolar compounds such as phthalates. The air space itself otherwise effectively prevents migration of the less volatile phthalates under the applied conditions.

INTRODUCTION

The contamination of foodstuffs with substances from the packaging material is a well-known issue. The presence of such contaminants can arise either from the packaging process itself (for example, via overprinting labels) or from migration processes. Primarily wrappings mainly made of polyvinyl chloride (PVC) or other plastic material are currently being discussed as potential sources of plasticizers or polymeric degradation products such as bisphenol A in food (*1*, *2*). In addition, components from UV inks such as benzophenone or isopropylthioxanthone (ITX) possess a pronounced migration potential (*3*, *4*). Migration of undesirable substances [phthalate esters, epoxidized soybean oil (ESBO)] in infant and baby food packed in glass jars with twist-off closures (*5*) received most recently great public attention. Another large group of packaging includes recycled paper and paperboards. Because recovered paper is the most important raw material for the production of this kind of packaging, migration of incorporated substances into foodstuffs is possible. Herewith also occurs the possibility of migration of phthalates (deriving from dispersion adhesives) or isopropyl naphthalenes (DIPN, originating from recycled carbonless copy paper) into dry foods such as rice, pasta, sugar, maize flour, and others (*6*, *7*) as recently reported. Whereas DIPN is to date classified as a toxicologically

harmless substance (*8*), phthalates are considered to react as endocrine disrupters (*9*, *10*). A more detailed survey concerning toxicological effects of different phthalate esters is given by the European Food Safety Authority (EFSA) (*11*).

Legislation concerning food contact materials is based on the relevant EC framework regulation 1935/2004 (*12*). According to article 3 of this regulation, food contact materials should be processed in such a way that they should not release their constituents into food in quantities which could endanger human health. More detailed, specific migration limits (SML) for food contaminants are listed in different directives mainly implemented on plastic materials and articles (*13*). However, until now the application of food packaging made of recycled fibers has been insufficiently regulated. Furthermore, because infants are more sensitive to a variety of chemicals than adults, special attention must be paid to such aspects in context to their nutrition. Therefore, on the basis of the published tolerable daily intake (TDI) values of phthalate esters, a national recommendation gives a SML of 0.5 mg kg^{-1} (DiBP) in infant food (*14*).

Contrary to plastic materials, there exist no official guidelines defining migration experimental parameters such as temperature, contact time, or food simulant for food contact materials made of paper/paperboard. In the literature, migration studies concerning solid foodstuffs packed in paper and paperboard usually address the use of common simulants such as Porapak, Tenax (also referred to as MPPO, modified polyphenylene oxide), or a mixture of Celite with olive oil and water under different conditions (*6*, *15*).

*Author to whom correspondence should be addressed (telephone +49-30-8104-1123; fax +49-30-8104-1127; e-mail matthias.koch@bam.de).

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DiBP and DnBP were found in these tests to migrate about 20−74%, strongly depending on the food type and the migration conditions such as contact time and temperature. Data including the kinetics of migration of phthalates are until now limited. Nérin et al. investigated the migration of phthalates into Porapak and postulated a mass transfer involving evaporation and adsorption processes, but without appropriate differentiation in the experimental design (*16*). Another work studied the migration of different organic pollutants from fluting paper into food powder under terms of accelerated conditions. The results show a rapid uptake of DnBP into the food, approaching equilibrium after 4 h at 70 °C (*17*). The poor barrier function of paper to the transfer of different substances from carton board was reported by Jickells et al. (*18*). However, no migration of the only phthalate investigated in this study (diheptyl phthalate) could be detected.

The aim of this work was to determine different contaminants present in recycled paper and paperboard, namely, phthalates and DIPN (**Figure 1**), as well as in dry infant food also packed in recycled packaging. Because such kinds of foods are additionally packed in inner bags (in the following referred to as secondary packaging), the dependency of the degree of contamination on the material used was also included in the investigations. Additionally, different migration experiments were performed by means of realistic samples to examine possible transfer mechanisms of phthalates into the food matrix. Two main migration pathways were thereby evaluated: migration via direct contact and via gas phase transfer. Furthermore, the barrier function of different secondary materials (paper, aluminum-coated foil) was investigated over a period of 2 months at 40 °C. The applied
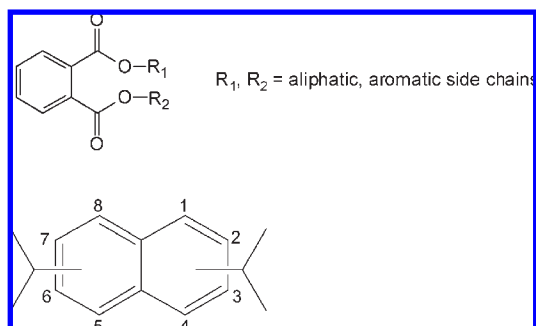
conditions were chosen with regard to the real-life storage time of these products under an enhanced temperature representing a "worst case" scenario.

MATERIALS AND METHODS

Reagents and Chemicals. Isooctane (HPLC grade) and ethyl acetate (HPLC grade) were obtained from Merck (Darmstadt, Germany). Di-isobutyl phthalate (DiBP), bis(2-ethylhexyl) phthalate (DEHP), di-*n*-octyl phthalate (DOP), and benzylbutyl phthalate (BBP) were purchased from Fluka (Steinheim, Germany), and di-*n*-butyl phthalate (DnBP) was from Supelco (Bellefonte, PA). All standards were pure substances (>99%). The corresponding [^{2}H$_4$]-phthalates (purity 98%) (internal standard) were obtained from Cambridge Isotope Laboratories (Andover, MA) with the exception of di-isobutyl phthalate-3,4,5,6-d_4 (100 μg mL^{-1}), which was purchased from Chiron AS (Trondheim, Norway). 2,6-Di-isopropyl naphthalene (2,6-DIPN) (purity = 99%) was from Acros Organics (Fair Lawn, NJ).

Sample Collection. Twenty samples of infant foods (4 milk powders, 7 cereal flakes, 9 semolina powders), packed in recycled paperboard containers, were purchased from retail stores located in Berlin, Germany. They represented typical domestic brands. Two types of packaging samples were collected depending on the material of the secondary packaging, which was either aluminum-coated foil (13 samples) or coated paper (7 samples). The food samples were of dry and powdery consistency and differed in their fat contents. An interesting observation was that only infant food with a low fat content (<3%) was packed in paper-coated bags (see **Table 2**). Samples were stored at room temperature (23 °C) in the dark and analyzed after 2−3 months.

Sample Preparation and Extraction Conditions. Before the analysis of the paperboard samples, the printing of the containers was deliberately removed with the aid of a scalpel. Parts with adhesive residues were discarded. The remaining carton was cut into small equal pieces (about 5 × 5 mm), which were then mixed. Two grams of the cut pieces was used in the analysis. For the powdery food samples, 2−4 g of homogenized material was used for the accelerated solvent extraction (ASE): 11 mL ASE extraction cells with two inserted cellulose filters were filled with the sample and spiked with the internal standard solution (mix of deuterated phthalates). Five blank controls (equally treated extraction cells without paperboard or food material) were prepared for each sampling sequence. Prebaked silica sand was not used because of irreversible adsorption of the phthalates. All extractions were carried out using an ASE 200 from Dionex (Idstein, Germany) equipped with a solvent controller, using a 120% flush volume with a 60 s purge. The extraction conditions were as follows: 100 °C, 140 bar, preheat for 0 min, heat for 5 min, static for 10 min, two cycles per vial, respectively. The extracts were each filled with the extraction solvent iso-octane to a final weight of 21 g and analyzed with GC-MS. Analyses were done in triplicate.

Figure 1. Typical structures of contaminants present in recycled paper: phthalate esters (phthalates) and diisopropyl naphthalenes (DIPN).

Scheme 1. Experimental Setup of the Migration Tests Performed at 40 °C in Closed Petri Dishes

Article

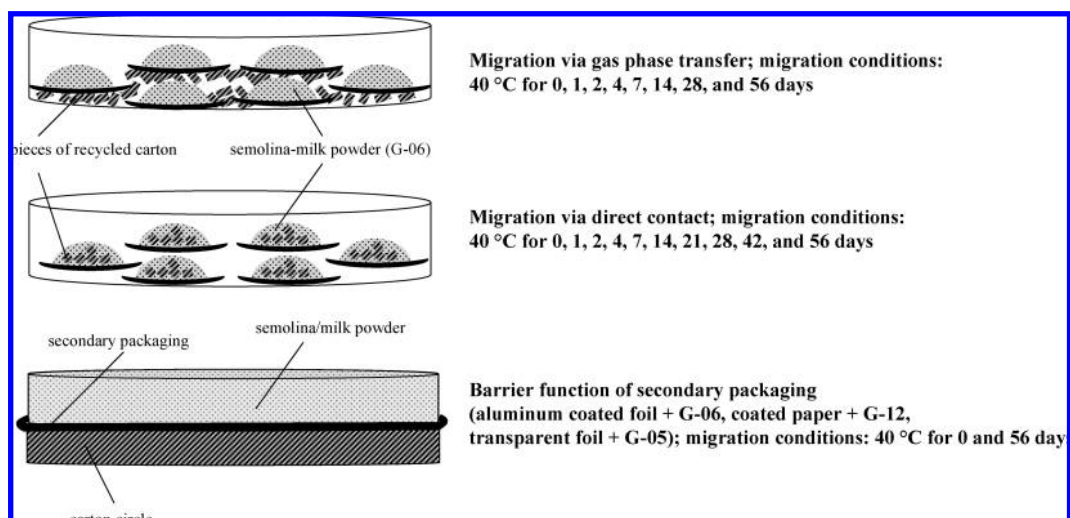*J. Agric. Food Chem.,* Vol. 57, No. 22, 2009 **10677**

Table 1. Method Parameters: Retention Time (t_R) of the Quantifier Ions *m/z* 149 (Native Phthalates) and *m/z* 153 (Deuterated Phthalates), Qualifier Ions of the Native Phthalates, Recovery, Limit of Detection (LOD), and Limit of Quantification (LOQ) of Five Phthalates

compd	t_R (min) *m/z* 149	*m/z* 153	qualifier ions *m/z* (intensity [a])	% recovery [b]	LOD ($\mu g\ g^{-1}$)	LOQ ($\mu g\ g^{-1}$)
DiBP	8.22	8.22	57 (11%)	94.1 ± 0.7 [c]	0.005 [e]	0.016 [e]
			223 (9%)	97.7 ± 7.4 [d]	0.010 [f]	0.030 [f]
DnBP	8.47	8.47	205 (5%)	102.4 ± 0.5	0.016 [e]	0.048 [e]
			223 (6%)	101.4 ± 3.8 [d]	0.030 [f]	0.091 [f]
BBP	9.72	9.71	91 (53%)	88.7 ± 0.5 [c]	0.007 [e]	0.021 [e]
			206 (29%)	97.4 ± 4.6 [d]	0.014 [f]	0.039 [f]
DEHP	10.49	10.48	167 (35%)	90.9 ± 0.1 [c]	0.050 [e]	0.156 [e]
			279 (14%)	105.2 ± 8.2 [d]	0.095 [f]	0.295 [f]
DOP	11.63	11.62	150 (10%)	92.6 ± 0.3 [c]	0.011 [e]	0.031 [e]
			279 (11%)	104.8 ± 6.8 [d]	0.021 [f]	0.059 [f]

[a] Relative to the quantifier ion *m/z* 149. [b] Mean ± SD (*n* = 3). [c] Recovery in paperboard. [d] Recovery in food. [e] LOD/LOQ in food. [f] LOD/LOQ in paperboard.

Table 2. Overview on the Phthalate Content of 20 Investigated Paperboards and Food Samples with Details on the Sample Composition

sample/product	fat (%)	secondary packaging	code	paperboard [a] ($\mu g\ g^{-1}$) DiBP	DnBP	BBP	DEHP	infant food [a] ($ng\ g^{-1}$) DiBP	DnBP	DEHP
milk powder	27.2	aluminum	M-01	28.4 ± 1.6	21.7 ± 1.4	0.15 ± 0.02	16.6 ± 0.3	<LOQ	<LOQ	nd
milk powder	25.8	aluminum	M-02	27.9 ± 1.6	3.8 ± 0.1	0.36 ± 0.03	8.5 ± 0.1	18.9 ± 1.2	<LOQ	<LOQ
milk powder	24.1	aluminum	M-05	18.0 ± 1.0	4.2 ± 0.2	0.22 ± 0.01	7.1 ± 0.6	<LOQ	<LOQ	<LOQ
milk powder	23.2	aluminum	M-06	13.9 ± 1.3	3.0 ± 0.5	0.07 ± 0.01	8.8 ± 0.4	64.8 ± 5	53.0 ± 3.4	<LOQ
semolina/milk powder	15.0	aluminum	G-01	20.6 ± 1.1	3.4 ± 0.2	0.24 ± 0.01	7.4 ± 0.2	nd	nd	nd
semolina/milk powder	15.0	aluminum	G-03	22.3 ± 1.4	3.5 ± 0.2	0.28 ± 0.02	8.2 ± 0.3	<LOQ	<LOQ	nd
semolina/milk powder	12.4	plastic foil	G-05	19.2 ± 1.0	3.6 ± 0.1	0.36 ± 0.07	6.3 ± 0.1	<LOQ	<LOQ	<LOQ
semolina/milk powder	10.0	aluminum	G-06	24.1 ± 2.6	3.9 ± 0.4	0.34 ± 0.04	7.3 ± 0.1	<LOQ	<LOQ	<LOQ
semolina/milk powder	9.0	aluminum	G-08	19.1 ± 1.2	4.3 ± 0.4	0.36 ± 0.01	6.4 ± 0.1	19.5 ± 1	<LOQ	<LOQ
semolina/milk powder	5.7	aluminum	G-09	46.1 ± 0.8	5.5 ± 0.1	0.87 ± 0.12	8.7 ± 0.2	21.1 ± 1.3	nd	<LOQ
semolina powder	2.5	paper [b]	G-10	30.1 ± 1.7	4.5 ± 0.4	0.52 ± 0.18	6.7 ± 0.1	**1796 ± 33**	99 ± 3	nd
semolina powder	1.2	paper [b]	G-11	14.6 ± 1.3	2.3 ± 0.2	0.17 ± 0.03	7.9 ± 0.1	**444 ± 39**	<LOQ	nd
semolina powder	2.2	paper [b]	G-12	14.2 ± 0.7	3.9 ± 0.7	0.39 ± 0.02	9.0 ± 0.2	**778 ± 8**	86.6 ± 9.8	<LOQ
oat flakes	7.2	aluminum	F-01	38.5 ± 1.9	10.6 ± 0.3	0.37 ± 0.05	8.0 ± 0.1	96.7 ± 11.1	65.7 ± 4.4	<LOQ
oat flakes	6.9	paper [c]	F-02 [d]	1.5 ± 0.1	nd	1.28 ± 0.02	0.7 ± 0.1	34.6 ± 2	<LOQ	nd
oat flakes	6.8	aluminum	F-03	23.3 ± 1.2	4.2 ± 0.1	0.45 ± 0.02	9.1 ± 0.2	<LOQ	nd	<LOQ
spelt flakes	2.8	paper [b]	F-05	8.5 ± 0.5	2.5 ± 0.1	0.15 ± 0.01	6.9 ± 0.2	294 ± 18	49.7 ± 7.8	nd
baby rice cereal	2.4	paper [b]	F-06	16.1 ± 1.2	3.4 ± 0.1	0.37 ± 0.01	8.7 ± 0.1	**944 ± 2**	100 ± 9	nd
baby rice cereal	1.0	paper [b]	F-07 [d]	1.9 ± 0.2	nd	nd	0.54 ± 0.08	67.7 ± 0.5	<LOQ	nd
baby rice cereal	0.7	aluminum	F-08	59.7 ± 3.2	3.3 ± 0.2	0.13 ± 0.03	6.4 ± 0.1	<LOQ	nd	<LOQ

[a] Mean ± SD (*n* = 3). [b] White paper, coated. [c] Transparent, brown paper, coated. [d] No recycled material.

Precautions during Handling Due to Blank Problems. Due to the ubiquitous presence of phthalates in the environment, the analysis of these compounds is complicated by the lack of appropriate blanks. Therefore, special precaution was taken regarding the experimental proceeding: solvents were primarily tested for phthalate contamination and covered with aluminum foil when kept in beaker glasses. Laboratory glassware and ASE extraction cells were consecutively rinsed before use with ethyl acetate, ethyl acetate/iso-octane (1:1, v/v), and iso-octane, two times, respectively. ASE cellulose filters were cleaned according to the ASE extraction procedure. Samples were handled wearing latex gloves. Each sampling sequence was started with two solvent injections to check the cleanliness of the GC-MS system.

Migration Tests. Three migration tests were performed over a period of 2 months at 40 °C by means of authentic samples to provide representative migration information (**Scheme 1**). Because the commercial samples were of unknown storage time, paperboard was spiked with phthalates in 10-fold amounts of the average phthalate content measured in 20 analyzed paperboard samples. The sampling was carried out isochronously, and each test was done in triplicate.

The objective of the first two tests was to study the gas phase transfer and the direct migration of phthalates from the recycled paperboard into

infant food. Semolina powder (3 g for the gas phase transfer, 1.25 g for the direct contact) was weighed in a watch glass dish according to the number of sampling points, which in turn were arranged in closed Petri dishes. Pieces of chopped carton were either placed evenly on the bottom of the Petri dishes (3 g for the gas phase transfer) or mixed with the foodstuffs (0.2 g for the direct contact).

The third experimental setup was designed to estimate the barrier function of three different secondary packaging materials: coated paper, aluminum-coated foil, and plastic foil. Thereby, each secondary packaging was in contact with the corresponding food material, because the type of secondary packaging depended obviously on the fat content of the infant food. Thirteen grams of the respective food sample and 45 cm² paperboard circles were used, which was in accordance with the original ratio of food amount to surface area of the carton. Finally, the Petri dishes were weighed down to ensure closeness of the system.

Quantification and Quality Parameters. Identification of the compounds was done by comparing the retention times against those of known standards. Additionally, two qualifier ions were selected for each native phthalate to confirm their presence in sample matrices (**Table 1**).

All standard and calibration solutions were prepared gravimetrically in brown glass vials and stored at 4 °C. Phthalates were quantified using
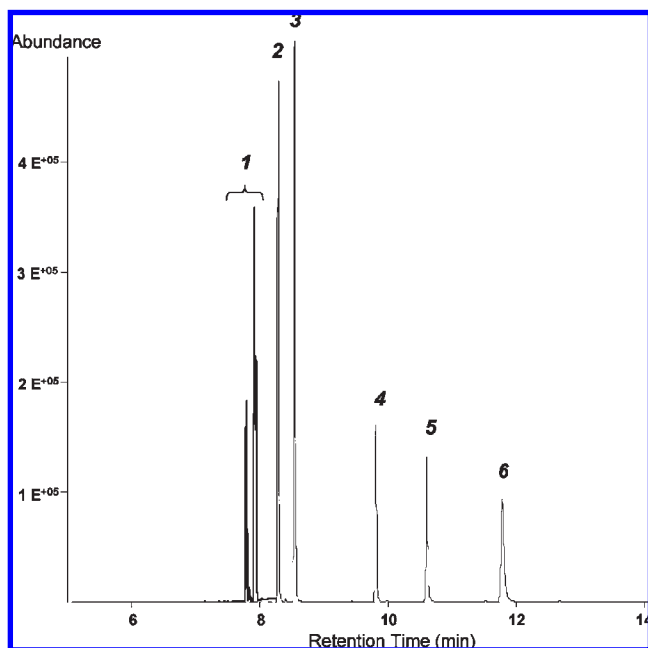
Figure 2. GC-MS chromatogram of standard compounds: 1 = DIPN (seven peaks corresponding to its isomeric forms), 2 = DiBP, 3 = DnBP, 4 = BBP, 5 = DEHP, and 6 = DOP.

deuterated standards. The retention times of the deuterated forms were therefore nearly identical to those of the native phthalates (**Table 1**). Calibration was performed from 0.06 to 10 $\mu g\ g^{-1}$ with regression coefficients of the calibration curves amounting to $R^2 > 0.999$. The phthalate content in the paperboards and food samples (each $n = 3$) was determined after subtraction of the arithmetic mean of the measured phthalate level in the corresponding blank controls. The sum of DIPN isomers was quantified in selected samples via standard addition using 2,6-DIPN.

Recovery tests were performed by spiking paperboard ($n = 3$) and food samples (milk powder, $n = 2$ and cereal flakes, $n = 1$) with target compounds in three different concentrations in each case. According to DIN 32645, the limit of detection (LOD) and the limit of quantification (LOQ) were determined for DiBP, DnBP, and DEHP on the basis of the standard deviation of 25 blank samples and for BBP and DOP on the basis of the calibration line method (**Table 1**).

GC-MS Analysis. Samples were analyzed with a gas chromatography system consisting of a 6890N series gas chromatograph (GC) with a 5975B series mass selective detector (MSD), both from Agilent Technologies (Waldbronn, Germany), equipped with a retention gap of 1 m × 0.25 mm i.d., deactivated fused silica (Agilent Technologies), and a 30 m × 0.25 mm i.d., 0.25 μm, HP-5 MS fused silica capillary column (J&W Scientific, Berlin, Germany). The column temperature was programmed as follows: the initial temperature was 70 °C for 3 min and increased to 280 °C at 40 °C min^{-1}, then held for 20 min. Helium was used as carrier gas at a flow rate of 1 mL min^{-1}. The injector temperature was maintained at 250 °C, and the injection volume was 1.0 μL in the splitless mode. The MSD operation conditions were the following: the electron impact ionization mode (70 eV) was operated in scan mode (50−400 amu) for compound confirmation and in time-scheduled selected ion monitoring mode (SIM) for quantification. Selected quantifier ions for the phthalates were m/z 149 (native forms) and m/z 153 (deuterated standards) and for DIPN m/z 197 and 212 with a dwell time of 100 ms, respectively (**Figure 2**). Temperatures for the MSD were 280 °C (transfer line), 230 °C (ion source), and 150 °C (quadrupole).

RESULTS AND DISCUSSION

Analytical Aspects. A known phenomenon regarding GC-MS analysis is the matrix-induced response enhancement, which is predominantly observed for the determination of semipolar compounds in food matrices (*19*). There already exist many publications describing such matrix effects during pesticide
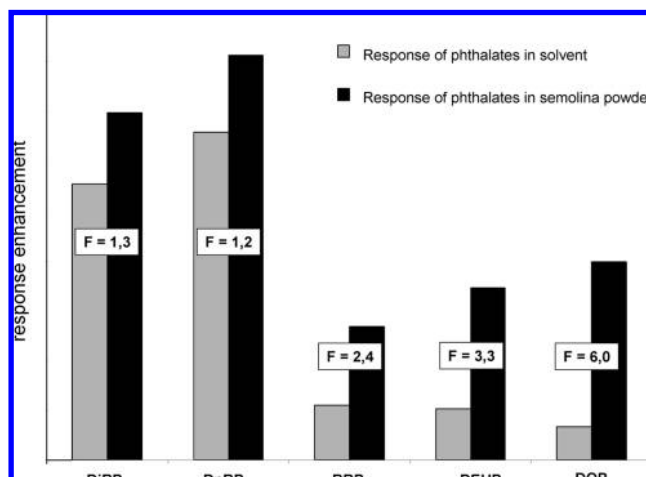

Figure 3. Matrix-induced response enhancement effect of phthalates in semolina powder.
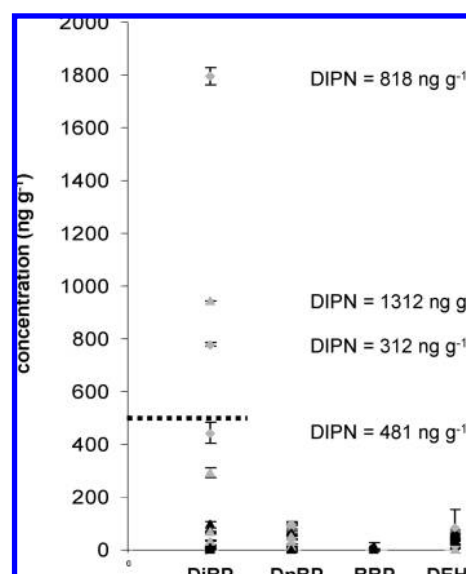

Figure 4. Content of phthalates and DIPN (ng g^{-1}) in infant food depending on the secondary packaging material applied: paper, gray; aluminum, black color; dashed line, SML (DiBP).

residue analysis with GC-MS in different matrices (*19−21*). Apart from that, De Carlo et al. observed an increase of the sensitivity up to 300% for the analysis of phthalates carried out in matrix extracts (*22*). This effect is commonly attributed to protecting effects of the matrix in the injection system of the GC (where matrix molecules are supposed to cover active sides in the liner or column and therefore prevent adsorption or decomposition of analytes) and/or in the detection system of the MS, where the matrix "guards" the phthalate ion against loss of its charge.

Likewise, preliminary experiments in this work also indicated matrix enhancement effects up to 600% for the analysis of phthalates in infant food samples (**Figure 3**). The extent of this increased sensitivity varied strongly for each phthalate depending on the lipophilic character and the space-filling properties of the molecular structure of the corresponding phthalate. Therefore, the application of deuterated standards for each phthalate to be quantified is absolutely necessary to achieve accurate results.

Analysis of Contaminants. In the present work 20 samples of infant foods (milk powder, cereal flakes, and semolina powder) were analyzed with GC-MS after ASE. Besides the food sample
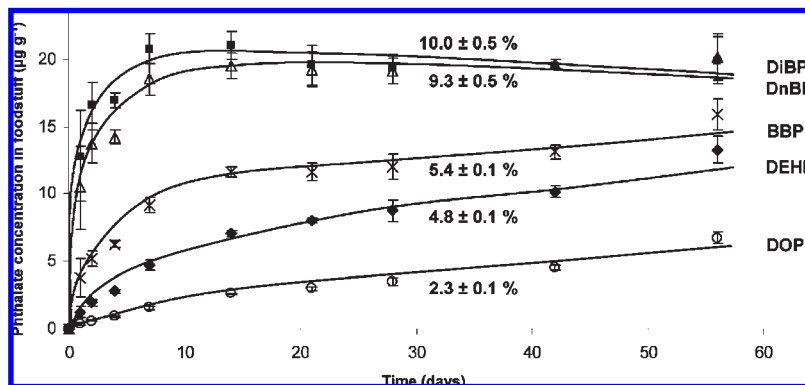
Figure 5. Migration of phthalates into semolina powder via direct contact at 40 °C with maximal migration values in percent.
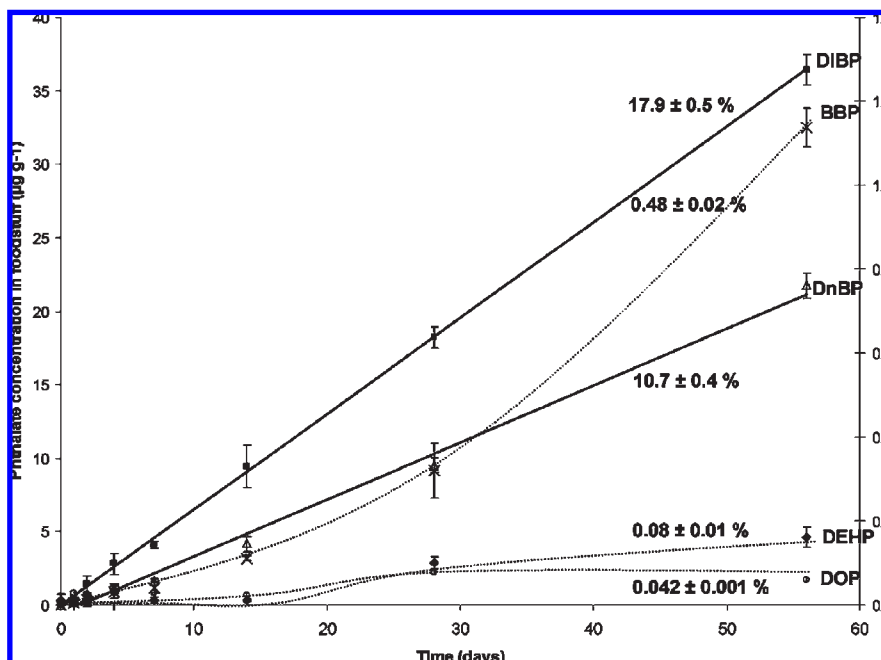

Figure 6. Migration of phthalates into semolina powder via gas phase transfer at 40 °C with maximal migration values in percent; BBP, DEHP, DOP are displayed on the secondary axis.

itself, the corresponding packaging, composed of recycled paperboard, was also tested for phthalate esters and DIPN, both known to be present as contaminants in recycled fiber materials. In almost all paperboards, the phthalate esters DiBP (x_{median} = 19.2 μg g^{-1}), DnBP (x_{median} = 3.7 μg g^{-1}), BBP (x_{median} = 0.3 μg g^{-1}), and DEHP (x_{median} = 7.9 μg g^{-1}) as well as DIPN (x_{median} = 7.5 μg g^{-1}) could be detected and quantified. However, the phthalate esters DiBP, DnBP, and DEHP were also detected in nearly all food samples with the exception of one (G-01). Furthermore, 40% of the food samples were contaminated with DIPN (data not shown). A detailed overview of the results is given in **Table 2**.

The main contaminant in infant foods was DiBP (x_{median} = 20.3 ng g^{-1}). In this context, three samples exceeded the appropriate SML of 500 ng g^{-1} clearly, with a maximal value of 1796 $\pm$ 33 ng g^{-1} (**Table 2**). These samples also showed a very high content of DIPN (x_{max} = 1312 ng g^{-1}). It is noteworthy that the topmost concentrations of phthalates and DIPN were detected in food samples, which were packed in secondary packaging made of paper (**Figure 4**). The contamination of the corresponding paperboards was in contrast not that conspicuous. In conclusion, it can be derived from these results that paper may be an insufficient barrier to the migration of nonpolar contaminants

such as phthalates and DIPN from paperboard into foodstuff independent of its fat content.

Migration Tests. For our migration experiments, we chose the food itself as a test medium to ensure an authentic migration process relevant to this kind of food matrix in particular. Migration conditions were also selected by means of the predictable storage time (2 months) and a slightly increased temperature (40 °C) to simulate a worst case scenario.

Figure 5 shows the results of the migration experiment via direct contact in the two-phase system paperboard/semolina powder. The maximal migration is expressed as percentage of the initial phthalate concentration in the paperboard according to eq 1.

$$migration \ (\%) = \frac{c_{food}}{c_{paper,initial}} \times 100 \qquad (eq1)$$

It is shown that the migration process of the phthalates occurs rather quickly. The phthalates DiBP and DnBP reached an equilibrium corresponding to a saturation of the food phase already after 1 week. One should note that in this case the migration potential of the phthalates into the foodstuff depends not mainly on their lipophilic character represented by the octanol–water coefficients K_{ow}. DiBP and DnBP show maximal

Table 3. Overview on Physicochemical Parameters of Phthalates

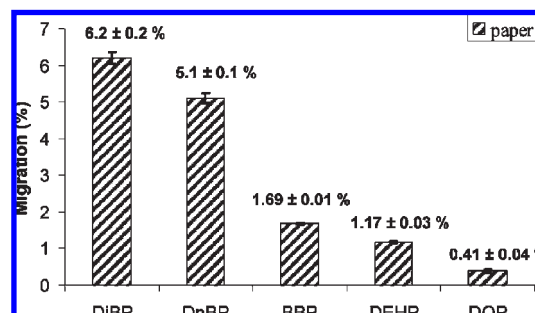| compd	MW (g mol^{-1})	bp (°C)	$V_p{}^a$ (Pa)	log $K_{ow}{}^a$
DiBP	278.35	327	4.73×10^{-3}	4.27
DnBP	278.35	340	4.73×10^{-3}	4.27
BBP	312.37	370	2.49×10^{-3}	4.7
DEHP	390.56	386	2.52×10^{-5}	7.73
DOP	390.56	385	2.52×10^{-5}	7.73

^{a} According to ref *23*

Scheme 2. Migration Process of Phthalates into Semolina Powder via Gas Phase Transfer^a
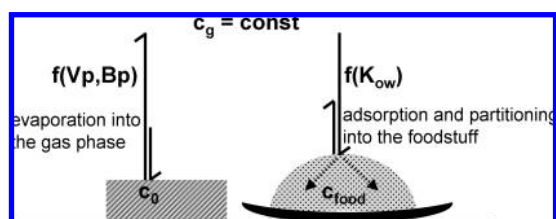
^{a} c_0 = initial phthalate concentration (paperboard), c_g = phthalate concentration (gas phase), and c_{food} = phthalate concentration (food).

Figure 7. Migration of phthalates through different secondary packaging materials at 40 °C with migration values in percent after 2 months. The migration values for the aluminum-coated and plastic foils are below 0.1% and therefore not illustrated.

migration values of about 10% (log K_{ow} = 4.27) in descending order to DOP with a maximal migration value of 2.3% (log K_{ow} = 7.73). The mass transfer in the two-phase system (board/food) could be better described including diffusion as well as distribution processes. Therewith the migration progress rather depends on diffusion coefficients (D_p − paperboard) and partition coefficients ($K_{p,f}$ − paperboard/food), which take material-specific parameters such as the porosity of the packaging and the dimension of the phthalate molecule into account. Our results are in accordance with those of Nerín et al., who investigated the migration behavior of phthalates from paper and board into Porapak as solid food simulant (*16*).

The results of the migration experiment via gas phase transfer in the three-phase system paperboard/gas phase/semolina powder are shown in **Figure 6**. Only DiBP and DnBP showed considerable migration potency, with maximal migration values of 17.9% (DiBP) and 10.7% (DnBP). The corresponding migration values for the phthalates BBP, DEHP, and DOP were below 1% over a period of 2 months. Given that mainly the vapor pressure (V_p) and accordingly the boiling point of a substance influence their transfer into the gas phase, the results are in good accordance with the relevant physicochemical data reported in the literature (**Table 3**). Therefore, the gas phase itself could function as a migration barrier when the less volatile phthalates are considered. The volatility cutoff threshold would be therefore between those of BBP and DEHP.

It should also be noted that the migration process in the three-phase system is quite different from the first experiment. For the phthalates DiBP (R^2 = 0.9996) and DnBP (R^2 = 0.9942) the migration proceeds linearly without reaching equilibrium, following the kinetics of a zero-order reaction (**Scheme 2**): The phthalates DiBP and DnBP vaporize continually into the gas phase, where their concentrations could be regarded as constant over the period of 2 months. However, their concentrations in the foodstuff increase with storage time due to adsorption and partitioning into the foodstuff. The corresponding reaction rate constants (k), derived from the slope of the regression line of the phthalate concentration depending on time, were calculated as k = 650 μg kg^1 day^{-1} (DiBP) and k = 390 μg kg^{-1} day^{-1} (DnBP).

The results of the investigation of the barrier function of different secondary packaging materials are shown in **Figure 7**. It is obvious that paper is not a suitable barrier for the transfer of phthalates from paperboard into foodstuff. The migration values of DiBP and DnBP are about 6 and 5% for the paper packaging and largely below 0.1% as determined for the other materials tested. Again, migration of BBP, DEHP, and DOP occurs only to a smaller extent.

These results confirm our data from the analysis of 20 infant food samples, where only the foodstuff packed in paper bags was highly contaminated with DiBP, DnBP, and DIPN. It can be concluded that paper does not provide an appropriate barrier to the transfer of nonpolar and volatile substances incorporated in paperboard into dry and even nonfatty food. The application of appropriate secondary packaging (for example, aluminum-coated foil) could rather prevent the contamination of foodstuff with migration active substances from recycled paperboard.

LITERATURE CITED

(1) Bosnir, J.; Puntaric, D.; Galic, A.; Skes, I.; Dijanic, T.; Klaric, M.; Grgic, M.; Curkovic, M.; Smit, Z. Migration of phthalates from plastic containers into soft drinks and mineral water. *Food Technol. Biotechnol.* **2007**, *45* (1), 91–95.

(2) Lopez-Cervantes, J.; Paseiro-Losada, P. Determination of bisphenol A in, and its migration from, PVC stretch film used for food packaging. *Food Addit. Contam.* **2003**, *20* (6), 596–606.

(3) Papilloud, S.; Baudraz, D. Analysis of food packaging UV inks for chemicals with potential to migrate into food simulants. *Food Addit. Contam.* **2002**, *19* (2), 168–175.

(4) Pastorelli, S.; Sanches-Silva, A.; Cruz, J. M.; Simoneau, C.; Losada, P. P. Study of the migration of benzophenone from printed paperboard packages to cakes through different plastic films. *Eur. Food Res. Technol.* **2008**, *227*, 1585–1590.

(5) Pedersen, G. A.; Jensen, L. K.; Fankhauser, A.; Biedermann, S.; Petersen, J. H.; Fabech, B. Migration of epoxidized soybean oil (ESBO) and phthalates from twist closures into food and enforcement of the overall migration limit. *Food Addit. Contam.* **2008**, *25* (4), 503–510.

(6) Aurela, B.; Kulmala, H.; Soderhjelm, L. Phthalates in paper and board packaging and their migration into Tenax and sugar. *Food Addit. Contam.* **1999**, *16* (12), 571–577.

(7) Mariani, M. B.; Chiacchierini, E.; Gesumundo, C. Potential migration of diisopropyl naphthalenes from recycled paperboard packaging into dry foods. *Food Addit. Contam.* **1999**, *16* (5), 207–213.

(8) Hoke, H.; Zellerhoff, R. Metabolism and toxicity of diisopropyl-naphthalene as compared to naphthalene and monoalkyl naphthalenes: a minireview. *Toxicology* **1998**, *126* (1), 1–7.

(9) Colon, I.; Caro, D.; Bourdony, C. J.; Rosario, O. Identification of phthalate esters in the serum of young Puerto Rican girls with premature breast development. *Environ. Health Perspect.* **2000**, *108* (9), 895–900.

(10) Lovekamp-Swan, T.; Davis, B. J. Mechanisms of phthalate ester toxicity in the female reproductive system. *Environ Health Perspect.* **2003**, *111* (2), 139–45.

Article

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(11) EFSA. Statement of the Scientific Panel on Food Additives, Flavourings, Processing Aids and Materials in Contact with Food (AFC) on a request from the Commission on the possibility of allocating a group - TDI for Butylbenzylphthalate (BBP), di-Butylphthalate (DBP), Bis(2-ethylhexyl) phthalate (DEHP), di-Isononylphthalate (DINP) and di-Isodecylphthalate (DIDP); **2005**; pp 1−5.

(12) EC Regulation 1935/2004 of the European Parliament and the Council of 27 October 2004 on materials and articles intended to come into contact with food and repealing directives 80/590/EEC and 89/109/EEC. *Off. J. Eur. Union* **2004**, *L 338*, 4−17.

(13) ECCommission Directive 2002/72/EC (with amendments) relating to plastic materials and articles intended to come into contact with foodstuff. *Off. J. Eur. Union* **2002**, *L 39*, 1−42.

(14) BfR. Di-isobutylphthalat in Papieren und Kartons für den Kontakt mit Lebensmitteln. *Kurzprotokoll einer ausserordentlichen Sitzung der Arbeitsgruppe "Papier, Karton und Pappe*; **2007**; pp 1−2.

(15) Summerfield, W.; Cooper, I. Investigation of migration from paper and board into food − development of methods for rapid testing. *Food Addit. Contam.* **2001**, *18* (1), 77−88.

(16) Nerin, C.; Contin, E.; Asensio, E. Kinetic migration studies using Porapak as solid-food simulant to assess the safety of paper and board as food-packaging materials. *Anal. Bioanal. Chem.* **2007**, *387* (6), 2283−2288.

(17) Triantafyllou, V. I.; Akrida-Demertzi, K.; Demertzis, P. G. A study on the migration of organic pollutants from recycled paperboard packaging materials to solid food matrices. *Food Chem.* **2007**, *101*, 1759−1768.

(18) Jickells, S. M.; Poulin, J.; Mountfort, K. A.; Fernandez-ocana, M. Migration of contaminants by gas phase transfer from carton board and corrugated board box secondary packaging into foods. *Food Addit. Contam.* **2005**, *22* (8), 768−782.

(19) Kirchner, M.; Matisova, E.; Otrekal, R.; Hercegova, A.; de Zeeuw, J. Search on ruggedness of fast gas chromatography−mass spectrometry in pesticide residues analysis. *J. Chromatogr., A* **2005**, *1084* (1−2), 63−70.

(20) Anastassiades, M.; Mastovska, K.; Lehotay, S. J. Evaluation of analyte protectants to improve gas chromatographic analysis of pesticides. *J. Chromatogr., A* **2003**, *1015* (1−2), 163−184.

(21) Schmeck, T.; Wenclawiak, B. Sediment matrix induced response enhancement in the gas chromatographic-mass spectrometric quantification of insecticides in four different solvent extracts from ultrasonic and Soxhlet extraction. *Chromatographia* **2005**, *62* (3−4), 159−165.

(22) Del Carlo, M.; Pepe, A.; Sacchetti, G.; Compagnone, D.; Mastrocola, D.; Cichelli, A. Determination of phthalate esters in wine using solid-phase extraction and gas chromatography−mass spectrometry. *Food Chem.* **2008**, *111* (3), 771−777.

(23) Cousins, I.; Mackay, D. Correlating the physical−chemical properties of phthalate esters using the 'three solubility' approach. *Chemosphere* **2000**, *41* (9), 1389−1399.