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**Measurement and modelling of migration from paper and board into foodstuffs and dry food simulants**

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5 **Measurement and modelling of migration from paper and board into**  
6 **foodstuffs and dry food simulants**  
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## Abstract

In this study migration investigations with different spiked and non-spiked paper and board packaging materials in contact with foodstuffs and food simulants in the temperature range between  $-18^{\circ}\text{C}$  and  $40^{\circ}\text{C}$  were carried out. The aim was to deepen the understanding of the migration behaviour of target substances in paper and board fibres. Components and contaminants of paper and board with different molecular weight and chemical structure were selected as target migrants. From the kinetic migration studies diffusion and partition coefficients were derived by using software for modelling migration in multi-layer materials. On the basis of these results for the first time a model for the migration from paper and board into foods and simulants was developed by adapting the validated diffusion model for plastics. In contrast to the migration in plastic materials, where the migrants are solved and homogeneously distributed in the polymer matrix, mass transfer in paper and board is a more complex phenomenon, because the migrants can be adsorbed on the cellulose surface with different strength. The most important finding of the study was that for a correct modelling of the experimental results in many cases paper and board must be regarded as a 2-layer system: the main mass of paper and board (B1) defines the core layer with high diffusion rates and a thin second layer (B2) represents the surface region of the paper and board with decreased diffusion rates due to the slow desorption.

**Keywords:** food packaging; migration; modelling; diffusion coefficient; partition coefficient; paper; board

## Introduction

During the last two decades many studies on the migration from paper and board into foodstuffs and food simulants have been published. Some of these publications are cited as examples in the following. Castle *et al.* (1997a, 1997b) performed a comprehensive compositional analysis including migration tests with several paper and board samples. The results of migration investigations with phthalates and alkylbenzenes from paper and board packaging in contact with foodstuffs and the simulant Tenax<sup>®</sup> (modified polyphenylene oxide) were reported by Aurela *et al.* (1999, 2001). Boccacci Mariani *et al.* (1999) investigated the potential migration of diisopropyl naphthalenes from recycled paperboard packaging into dry foods and Summerfield and Cooper (2001) developed methods for rapid testing of mass transfer from paper and board packaging. Several studies demonstrate that Tenax<sup>®</sup> is a suitable food simulant for the migration from paper and board (Summerfield and Cooper 2001, Aurela *et al.* 1999, 2001, Castle 2004, Triantafyllou *et al.* 2007).

It was observed by Triantafyllou *et al.* (2007) that the migration from paper and board depends on the structure of the packaging samples, the chemical nature of the migrants and the time and temperature conditions of the migration tests.

Whereas in the last years diverse other migration investigations with paper and board in contact with foods or food simulants were described (Anderson and Castle 2003, Song *et al.* 2003, Jickells 2004, Sturaro *et al.* 2006, Nerin *et al.* 2007, Begley *et al.* 2008, Pastorelli *et al.* 2008), up to now only few authors reported on diffusion coefficients derived from kinetic migration investigations or partition coefficients for paper and board (Haack and Franz 2001, Aurela and Ketoja 2002, Triantafyllou *et al.* 2005).

The structure of paper can be described as a thin layer of mostly cellulosic plant fibres. With its polar hydroxyl groups natural cellulose is building hydrogen bonds between the individual fibres that account for the strength of the paper (Anders *et al.* 1995, Holik 2006).

Paper and board for food contact use is an inhomogeneous material and can be composed of virgin or recycled pulp (cellulose, hemicellulose and lignin), additives like fillers, sizes, starch, starch derivatives, wet strength sizing agents etc. and pigment or polymer coatings (Castle 2004).

Compared to plastic packaging materials, where the migrant is in general homogeneously distributed in the polymeric matrix, migrants in paper and board can be adsorbed on the cellulose fibres or other constituents employed for paper and board production. The mechanism of transport through the paper and board sample can be understood as a repeated process of desorption/evaporation and adsorption /condensation until thermodynamic equilibrium is reached in the system.

The overall aim of this study was to deepen the understanding of migration processes of migrants from paper and board into foodstuffs as well as dry food simulants and to explore migration modelling as a tool for compliance assessment of paper and board. The working strategy was to carry out migration investigations with different spiked and non-spiked paper and board food packaging materials in the temperature range

1  
2  
3 between -18°C and 40°C. The target migrants were components and contaminants  
4 determined in the non-spiked paper and board samples or model substances used for  
5 spiking the samples with a low initial concentration of migrants. From the kinetic  
6 migration studies diffusion and partition coefficients were derived by using the  
7 software MIGRATEST<sup>®</sup> Exp. for modelling migration in multi-layer materials. On  
8 the basis of these results for the first time a model for the migration from paper and  
9 board into foods and simulants was developed by adapting the validated diffusion  
10 model for plastics.  
11

## 12 **Materials and methods**

### 13 *Materials*

#### 14 *Paper and board*

15  
16 The paper and board samples used for the migration studies show a great variety of  
17 properties (Table 1). They were of food-grade quality, unprinted and supplied by  
18 members of the Confederation of European Paper Industries (CEPI) Food Contact  
19 group. An exception was the thermal fax paper which was purchased from the local  
20 market. According to their characteristics the samples were assigned to different  
21 foodstuffs as listed in Table 1.  
22  
23  
24  
25  
26

27 For the migration investigations with sample 10 at a temperature of 22°C and 40°C  
28 blotting paper was used as receptor material like a solid food simulant as given in  
29 Table 1. This blotting paper with a paper grade of 1600 according to ISO 5269-1:1998  
30 and a grammage of 250 g was purchased from Munktell Filter AB.  
31  
32

33 Insert Table 1.  
34

#### 35 *Foodstuffs*

36 For the migration studies with spiked paper and board samples the food (butter, ice  
37 cream and deep-frozen spinach) was purchased from the local market. Until the  
38 beginning of the migration investigations the food was removed from the original  
39 packaging, wrapped in aluminium foil or filled in glass containers and stored in the  
40 refrigerator or freezer.  
41  
42

43 For the migration studies with non-spiked paper and board samples one part of the  
44 food (rice, egg pasta, sponge finger biscuits and chocolate) was obtained from the  
45 food manufacture. The foods were sampled directly from the production line before  
46 packing and were placed in glass containers or wrapped in aluminium foil.  
47  
48

49 The other part (ice cream, wheat flour, tomatoes, deep-frozen puff pastry as well as  
50 deep-frozen straw berries and raspberries) was purchased in bulk packs from a local  
51 supermarket. To avoid contamination from the original packaging the food used for  
52 the migration experiments was preferably taken from the centre of the packaging and  
53 stored in glass containers until the beginning of the experimental studies.  
54  
55

#### 56 *Food simulant Tenax<sup>®</sup> and chemicals*

57 The model substances and solvents were of reagent grade or highest purity available  
58 purchased from Sigma Aldrich, Carl Roth, Fluka and VWR International Ltd.  
59  
60

1  
2  
3 Tenax<sup>®</sup> (60-80 mesh), a standard food simulant for dry fatty foods (Piringer *et al.*  
4 1993), was obtained from Grace Alltech Grom GmbH and cleaned up prior use by  
5 solvent extraction using acetone and ethanol.  
6

#### 7 *Selection of model migrants for spiking*

8  
9 Three different board samples were spiked with model migrants and typical  
10 contaminants of paper and board as shown in Table 2.

11 The target substances vary in their molecular weights (in the range of  
12 178 - 391 Dalton) as well as their chemical properties, especially in their polarity.  
13 Whereas diisobutyl phthalate (DiBP), di(2-ethylhexyl) phthalate (DEHP) and  
14 diisopropyl naphthalene (DIPN) represent the non-polar, hydrophobic compounds,  
15 benzophenone (BP) and triclosan (TRCL) are polar migrants.  
16  
17

18 Insert Table 2.  
19

#### 20 *Selection of components and contaminants in the non-spiked samples*

21  
22 For the migration investigations with non-spiked paper and board samples the initial  
23 concentration of potential migrants in 15 different samples was determined by means  
24 of solvent extraction in conjunction with semi-quantitative gas chromatographic  
25 screening. Six adequate substances in 10 of the 15 samples were identified in higher  
26 concentrations and employed as target migrants as listed in Table 3.  
27  
28

29 Insert Table 3.  
30

31 The assignment of the target migrants to the paper and board samples, the foods and  
32 the food simulants and the temperature conditions of the migration tests are given in  
33 Table 1.  
34

### 35 **Migration investigation**

#### 36 *Spiking procedure for the paper and board samples*

37  
38 For the migration tests with the spiked paper and board samples a special procedure  
39 for an interaction-free spiking was developed in order to avoid changes of the paper  
40 and board samples which might influence their migration behaviour.  
41

42 Blotting paper was spiked with a diethyl ether solution of the contaminants followed  
43 by the gentle evaporation of the solvent. The paper and board samples were  
44 sandwiched between two spiked blotting paper sheets and stored at a temperature of  
45 60°C to induce migration of the contaminants from the blotting paper into the paper  
46 and board samples. After three days a constant concentration of the surrogates in the  
47 samples was obtained.  
48  
49

#### 50 *Test design*

51  
52 Depending on the chosen foodstuffs the migration investigations were performed at  
53 -18°C, 5°C, 22°C as given in the Table 1.  
54

55 With sample 10 additional tests with blotting paper as receptor material at the  
56 elevated temperature of 40°C were carried out.  
57

58 Tenax<sup>®</sup> as food simulant for comparison with the migration into the foods was used  
59 for the migration investigations with the spiked sample 1, 2 and 3 as well as the non-  
60 spiked samples 9, 10 and 11.

1  
2  
3 In order to derive the migration parameters time dependent migration investigations  
4 with a minimum of five time points were carried out at the temperature of 5°C, 22°C  
5 and 40°C. The chosen time steps are listed in Tables 4 - 12.

6 Migration tests at a temperature of -18°C with one or two time points were not used  
7 for modelling migration.

8 The single-sided migration investigations were performed from the food contact side  
9 of the paper and board samples.

10  
11  
12 For the migration tests with sponge finger biscuits, chocolate and wheat flour, the  
13 following test design was applied.

14 Sponge finger biscuits and chocolate were exposed to a piece of paper or board  
15 sample with a defined area. In order to avoid losses through evaporation the samples  
16 in contact with the food were wrapped in aluminium foil. An intimate contact between  
17 sample and food was produced by covering the food exposed to the sample with an  
18 adequate weight.

19 For the migration test with paper sample 4 (Table 1) wheat flour was filled into the  
20 paper bag and stored at a temperature of 22°C.

21  
22  
23 The migration investigations with the other foodstuffs, Tenax<sup>®</sup> and blotting paper as  
24 well as wheat flour in contact with paper and board sample 10 and 11 were carried out  
25 using Petri dishes or with glass migration cells and stainless steel migration cells  
26 developed by FABES Forschungs-GmbH and Gaßner.

27  
28  
29  
30 *Glass migration cell.* The design and the application of the glass migration cell for  
31 migration tests are described by Franz and Störmer (2008). The paper and board  
32 sample was fixed in the migration cell and exposed to the food or the simulant  
33 Tenax<sup>®</sup>.

34  
35  
36 *Stainless steel migration cell.* For the migration tests with the stainless steel migration  
37 cell the paper and board sample was exposed to the receptor material blotting paper in  
38 a stack. This sandwich of two layers was fixed in the migration cell which was closed  
39 with a certain turning moment.

40  
41  
42 *Petri dishes.* The paper and board sample was placed in the Petri dish and exposed to  
43 the food or the simulant Tenax<sup>®</sup>. In order to avoid losses through evaporation the Petri  
44 dishes were sealed with Parafilm<sup>®</sup> M and wrapped in aluminium foil during the  
45 migration test.

46  
47  
48 After exposure the foodstuffs, Tenax<sup>®</sup> and blotting paper were worked up as  
49 described below.

## 50 51 52 **Analytical methods**

### 53 54 *Apparatus*

55  
56 The contaminant quantification from the migration investigations with the spiked  
57 paper and board samples was performed with a Thermo Electron Spectra System high  
58 performance liquid chromatograph equipped with a UV6000 series PDA diode array  
59 detector (HPLC-UV). The compounds were separated on a Phenomenex type Sphere  
60

Clone column (5 µm particle size ODS (2), 250 mm L × 4.6 mm ID) coupled with Security Guard Cartridges C18 (ODS, Octadecyl, 4 mm L × 3.0 mm ID).

The injections of 20 µl were performed by a Thermo Electron AS 3000 series auto sampler. The columns were thermostated at 40°C, the total flow was 1 ml min<sup>-1</sup> and the wave length was 230 nm. Water and methanol were used as eluents.

The contaminant quantification from migration investigations with the non-spiked paper and board samples was performed with a Shimadzu gas chromatograph equipped with a QP5000 or QP2010 series quadrupole mass spectrometer (GC-MS). The compounds were separated on a Phenomenex type ZB-50 capillary column (30 m L x 0.25 mm ID; 0.15 µm film thickness). Helium was used as carrier gas and the injections of 1 µl were performed by a Shimadzu AOC-20 i series auto sampler in splitless mode.

#### *Determination of the initial contaminant concentration in the paper and board samples*

1.0 g of each paper and board sample was cut into small pieces, placed in a septum glass vial and extracted with ethanol 95% for three days at a temperature of 60°C. To guarantee an optimal extraction the cut sample had to be fully immersed in the solvent. The extraction procedure was repeated twice. The extracts were combined and concentrated by rotary evaporation. The solutions were filtered with a 0.2 µm pore-size PTFE syringe filter and analysed by HPLC-UV (spiked paper and board samples) or GC-MS in the single-ion-monitoring (SIM) mode (non-spiked paper and board samples). The contaminants were quantified by external calibration.

#### *Determination of the contaminant concentration in the foodstuffs*

After exposure the foodstuffs were homogenized and an aliquot of 10.0 g was taken for analysis. The level of the contaminants was determined by solvent extraction according to well defined methods as described for instance in the final report of the EU Project "Foodmigrosure" (Paseiro *et al.* 2006, Franz and Simoneau 2008).

Depending on the matrix and the fat content the foods were extracted with acetonitrile (ice cream, spinach, chocolate), diethyl ether (rice, sponge finger biscuits), acetone (egg pasta), acetone/hexane (wheat flour), acetonitrile/hexane (butter, puff pastry) and ethanol 95%/diethyl ether (rasp berries, straw berries, tomatoes).

Anhydrous sodium sulphate was used to remove water from the extraction solutions.

Residues of fat were separated by solid phase extraction (SPE). After evaporation of the solvent the fatty residue was transferred into a SPE-column. The fat was adsorbed on the C18-matrix and the contaminants were eluted with acetonitrile.

The extraction solutions were concentrated by rotary evaporation and filtered using a 0.2 µm pore-size PTFE syringe filter if necessary.

The food extracts obtained from migration experiments with spiked paper and board samples were analysed by HPLC-UV. The contaminants were quantified by external calibration.

The food extracts obtained from migration experiments with non-spiked paper and board samples were analysed by GC-MS. The contaminants were quantified by external calibration in the SIM mode.

#### *Determination of the contaminant concentration in Tenax<sup>®</sup>*

After exposure Tenax<sup>®</sup> was extracted using diethyl ether. The extraction solution was concentrated by gentle evaporation under a nitrogen stream and analysed by GC-MS

1  
2  
3 in the SIM mode. For analysis of the contaminants by means of HPLC-UV the diethyl  
4 ether was evaporated and the extract was solved in ethanol 95%. The contaminants  
5 were quantified by external calibration.  
6

#### 7 *Determination of the contaminant concentration in the blotting paper*

8  
9 After exposure the blotting paper was cut into small pieces, placed in a septum glass  
10 vial and extracted with dichloromethane for two days at a temperature of 40°C. The  
11 solutions were filtered with a 0.2 µm pore-size PTFE syringe filter and analysed by  
12 GC-MS. The contaminants were quantified by external calibration in the SIM mode.  
13

### 14 **Experimental results**

#### 15 *Migration experiments with spiked paper and board samples*

16  
17 For the spiked samples the best kinetic results were obtained with sample 1 showing  
18 the smallest scatter of the experimental data points. Therefore, sample 1 was selected  
19 for the evaluation of the migration parameters (Table 1). Due to the great volume of  
20 data the results of the migration investigations with sample 2 and 3 are not presented.  
21 The experimental results with the spiked sample 1 are shown in the following  
22 Tables 4 - 9.  
23  
24  
25

26  
27 Insert Table 4 - 9.

#### 28 *Migration experiments with non-spiked paper and board samples*

29  
30 The migration of the target migrants from the non-spiked sample 1, 2, 5 and 8 into the  
31 foods was below the detection limit as well as the migration of the paper component  
32 abietic acid (Aa) from sample 6 into sponge finger biscuits (Table 1). The results of  
33 the migration experiments with the non-spiked samples 4, 6 and 7 are given in  
34 Table 10.  
35  
36

37  
38 Insert Table 10.

39  
40 The results of the migration of DiBP from the non-spiked samples 10 into dry and  
41 frozen foods, Tenax<sup>®</sup> and blotting paper at -18°C, 22°C and 40°C are given in  
42 Table 11 a) and b).  
43

44  
45 Insert Table 11 a)/b).

46  
47 The results of migration experiments with DiBP from the non-spiked samples 9 and  
48 with bisphenol A (BPA) and benzyl 2-naphthyl ether (NAP-2) from the non-spiked  
49 sample 11 are given in Table 12.  
50

51  
52 Insert Table 12.

### 53 **Modelling migration**

54  
55 The mass transfer (migration) from plastic materials into a contact medium is a  
56 predictable physical process. Mass transport is understood as the molecular diffusion  
57 in, out and through plastic materials. For the mathematical description many  
58 analytical and numerical solutions of the diffusion equation (1) are known (Crank  
59  
60

1  
2  
3 1975) where  $D$  is the diffusion coefficient and the concentration of the migrant  $c$  is a  
4 function of time  $t$  and position along the  $x$ -axis.

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2} \quad (1)$$

10 Modelling of potential migration based on these solutions is already used as an  
11 additional tool for quality assurance of food packaging materials (Directive  
12 2002/72/EC).

13 Whereas the migrant in a plastic material is distributed in the polymer matrix like in a  
14 liquid phase, the migration from paper and board is a more complex phenomenon, due  
15 to the adsorption/desorption process of the migrant on the fibre surface. Therefore, the  
16 specific behaviour of these materials must be taken into account in application of  
17 modelling. Nevertheless, the transfer process can also be treated as a diffusion  
18 phenomenon. Nevertheless, the transfer process can also be treated as a diffusion  
19 phenomenon.  
20 phenomenon.

21  
22 There are two different choices for a description of diffusion. The more fundamental  
23 is based on Fick's second law of diffusion (Equation 1). The second approach  
24 involves a mass transfer coefficient, that means a type of reversible rate constant  
25 (Cussler 1997). If, as an example, two reservoirs containing two different gases are  
26 connected with a long thin capillary, the change of concentration occurs direct  
27 proportional with time. This behaviour can be described easily by using a mass  
28 transfer coefficient. Nevertheless, the fundamental process is the molecular diffusion  
29 with a long period in a stationary state (Fick's first law), where the concentration  
30 changes proportional with time. With larger connecting tubes and smaller reservoirs  
31 the concentration in the second reservoir increases with the square route of time, as  
32 follows from the diffusion in the non-steady state regime.  
33 follows from the diffusion in the non-steady state regime.  
34 follows from the diffusion in the non-steady state regime.  
35 follows from the diffusion in the non-steady state regime.  
36 follows from the diffusion in the non-steady state regime.  
37 follows from the diffusion in the non-steady state regime.  
38 follows from the diffusion in the non-steady state regime.  
39 follows from the diffusion in the non-steady state regime.

40 Paper and board (B) can be compared formally with the first case, where two layers  
41 B1 and B2 with a thickness of  $d_{B1}$  and  $d_{B2}$  are responsible for the whole process of  
42 mass transfer. A large fraction of board B1 with the thickness  $d_{B1}$  contains the main  
43 part of the migrant which permeates through the thin layer B2 with the thickness  $d_{B2}$   
44 at the interface to the food (2-layer approach). The rate of transfer is determined by  
45 the desorption rate of the migrant from the surface. It is a function of the interaction  
46 strength between the board and migrant and can be characterized in principle with a  
47 mass transfer coefficient,  $k$ . As mentioned above, the mass transfer from the board  
48 sample as a whole into foodstuffs can be also described with the law of diffusion. But  
49 as will be shown later, due to the complexity of the occurring processes, transitions  
50 between direct proportionality with time (conform with Fick's first law) and  
51 proportionality with square root of time (conform with Fick's second law) are  
52 observed with different migrants and at different conditions.  
53 observed with different migrants and at different conditions.  
54 observed with different migrants and at different conditions.  
55 observed with different migrants and at different conditions.

56 In many cases the diffusion in B2 occurs much slower in comparison to B1. In such a  
57 situation the rate of mass transfer from paper and board into the food or food  
58 simulants is governed by the diffusion through the surface layer B2 and is  
59 proportional to the ratio  $D_{B2}/d_{B2} = k$  ( $\text{cm s}^{-1}$ ), between the diffusion coefficient  $D_{B2}$  in  
60 this layer and the thickness  $d_{B2}$ . The value of  $d_{B2}$  is an unknown parameter and is also  
a function of  $D_{B2}$ . The consequence of this is that within a certain range of  $d_{B2}$ -values

the ratio  $D_{B2}/d_{B2}$  remains constant, as can be observed experimentally. In order to obtain diffusion coefficients  $D_{B2}$  which are reproducible and comparable for different systems, a hypothetical thickness,  $d_{B2} = 10 \mu\text{m}$  has been defined which represents a value within the range, where the ratio  $D_{B2}/d_{B2}$  remains constant.

For migrants with a small molecular weight and polarity and for paper and board samples with high humidity a strong increase of the desorption rate occurs. The differentiation between the diffusion in B1 and B2 is then no longer necessary and  $D_{B1} = D_{B2} = D_B$  (1-layer approach).

With the above assumptions it is possible to use the modelling procedure as described for plastic materials also for modelling the mass transfer through paper and board into foodstuffs. By using the algorithms with numerical solutions for the diffusion equation the experimental results described in this publication were modelled with the FABES software MIGRATEST<sup>®</sup> Exp. for multilayer materials (Mercea *et al.* 2008). In order to characterize the migration behaviour in paper and board in a similar way as it was done for plastic materials, an equation for the estimation of the diffusion coefficient in paper and board  $D_B$  similar to that developed for polymers has been used. The semi-empirical formula for the estimation of the diffusion coefficient in plastics  $D_P$  (Piringer 1994, Begley *et al.* 2005) contains the relative molecular weight  $M_r$  of the migrant, the absolute temperature  $T$  and a polymer specific parameter  $A_P$ :

$$D_P = 10^4 \exp(A_P - 0.1351 M_r^{2/3} + 0.003 M_r - 10454/T) \quad (\text{cm}^2 \text{ s}^{-1}) \quad (2)$$

with  $A_P = A_P' - \tau/T$ .

$A_P'$  is an athermal dimensionless parameter and  $\tau$  a constant which together with the constant 10454 and the gas constant  $R$  give the activation energy of diffusion,  $E_A = (\tau + 10454) R$ .

A statistical evaluation of many experimentally obtained diffusion coefficients for different polymers used as food contact materials has shown that low density polyethylene (LDPE) gives the highest diffusion results and consequently the highest  $A_P$ -values (Begley *et al.* 2005). With the mean value of  $A_P = 10$  and  $\tau = 0$ , corresponding to a mean activation energy of  $E_A = 87 \text{ kJ mol}^{-1}$  in LDPE, Equation (2) is used as a reference for characterizing the diffusion in paper and board, with the following adaptation:

$$D_B = 10^4 \exp(10 + A_B - 0.1351 M_r^{2/3} + 0.003 M_r - 10454/T) \quad (\text{cm}^2 \text{ s}^{-1}) \quad (3)$$

where  $A_B$  is the board specific parameter, either as  $A_{B1}$  for layer B1 or  $A_{B2}$  for layer B2. Whereas the  $A_P$ -values in polymer matrices are more or less independent from the molecular weight and chemical nature of the migrant, the corresponding  $A_B$ -value for paper and board results from much more complex interactions between migrant and fibre and depends also on the polarity of the migrant. This is the reason why  $A_B$  is distinguished from the  $A_P$  for plastics and referred to the reference value of  $A_P = 10$  for LDPE.

For small  $A_{B2}$ -values, where the diffusion in B2 determines the whole migration rate in the board sample, more or less independently from  $A_{B1}$ , the value  $A_{B1} = 6$  for B1 is

used. This provides the maximum diffusion rates obtained in paper and board with the 1-layer approach.

If paper or board is selected as food simulant (blotting paper), also  $A_F = 6$  is used because the adsorption rate in the paper is much higher in comparison with the desorption rate from the board sample.

In Table 13 the results obtained with the multilayer modelling are summarized. With the  $A_{B2}$ -values and Equation (3) the diffusion coefficients,  $D_{B2}$  ( $\text{cm}^2 \text{s}^{-1}$ ) in the surface layer B2 are obtained and shown as their logarithmic values. In the last columns of Table 13 the partition coefficients,  $K_{B2/F}$ , of the migrants between the board layer B2 and food or food simulant (F) as well as the  $A_F$ -values of the foods or simulant are listed.

Insert Table 13.

Recently a full theoretical derivation of the diffusion coefficients in polymer matrices has been published (Piringer 2008). In the corresponding equation only the relative molecular weight,  $M_{r,p}$ , of the polymer and the melting temperature,  $T_{m,p}$ , or glass point,  $T_g$  of the polymer are used in addition to the molecular weight,  $M_r$ , of the migrant, without further empirical parameter values as in Equation (3):

$$D_{P,i} = D_u \exp\left(w_{i,e} - w_{p,e} \cdot 0.14(14j+2)^{2/3} - ww_{j,e}^{2/3} T_{m,p} R / RT\right) \quad (\text{cm}^2 \text{s}^{-1}) \quad (4)$$

with  $i = (M_r - 2)/14$ ,  $w_{i,e} = (1+2\pi/i)^{i/e}$ ,  $j = (i^{1/3})$ ,  $w_{j,e} = (1+2\pi/j)^{j/e}$ ,  $p = (M_{r,p}/14)^{1/3}$ ,  $w_{p,e} = (1+2\pi/p)^{p/e}$ ,  $w = e^{2\pi/e}$  and the unit  $D_u = 1 \text{ m}^2 \text{ s}^{-1}$ .

If LDPE with a mean relative molecular weight,  $M_{r,p} = 25000$  Dalton and  $T_{m,p} = 363 \text{ K}$  ( $90^\circ\text{C}$ ) is used as a reference polymer matrix for all polymers, than the following equation can be used for prediction of  $D_B$ -values in paper and board, which is equivalent to Equation (3):

$$D_{P,i} = 10^4 \exp\left(w_{i,e} + A_B - 0.9(14j+2)^{2/3} - 3662w_{j,e}^{2/3} / T\right) \quad (\text{cm}^2 \text{s}^{-1}) \quad (5)$$

with  $i = (M_r - 2)/14$ ,  $w_{i,e} = (1+2\pi/i)^{i/e}$ ,  $j = (i^{1/3})$ ,  $w_{j,e} = (1+2\pi/j)^{j/e}$

In Figure 1 the graph of Equation (3) (trace 1) for LDPE ( $A_B = 0$ ) is compared with the graph for Equation (5) (trace 5), also for LDPE ( $A_B = 0$ ) until relative migrant masses  $M_r = 400$  Dalton at  $25^\circ\text{C}$ . By using Equation (5) the only empirical parameter is  $A_B$  and for  $A_B = 0$  the diffusion in a defined type of LDPE as reference matrix results.

Insert Figure 1.

## Discussion

From the variety of the results obtained with different migrants, foodstuffs, simulants and different temperatures the following trends can be extracted.

With  $A_{B2} < -2$  the modelling of the migration kinetic can only be done correctly with the 2-layer approach. The diffusion coefficients in the large reservoir layer B1 are in these cases significantly higher than in the thin layer B2 and are modelled with a defined, constant value  $A_{B1} = 6$ . With  $A_{B2} \geq -2$  the modelling is done with the 1-layer approach, where  $A_{B2} = A_{B1} = A_B \leq 6$ .

The partition coefficients of the migrants between the two paper and board layers are in general considered  $K_{B1/B2} = 1$ , with the exceptions mentioned later in the conclusions.

For estimation of the diffusion in the foods or the food simulants (F), Equation (3) or Equation (5) can also be used. Instead of the  $A_B$ -value an  $A_F$ -value in the range of 3 – 7.5 is applied (except for egg pasta with an  $A_F$ -value of -2), which means that the diffusion in the foods or simulants is significant higher than in the B2 layer (Table 13).

The upper curve in Figure 1 (trace 2) is obtained with the 1-layer approach with  $A_B = 6$ . This represents the maximum diffusion values obtained for high humidity in the fibres, for volatile, non-polar migrants and at high temperatures. The typical migration behaviour in dry paper and board samples is obtained with the 2-layer approach between the lowest curve with  $A_{B2} = -11$  (trace 3) and the curve with  $A_{B2} = -2$  (trace 4), below the reference curve obtained with Equation (3) (trace 1) or with Equation (5) (trace 5), both with  $A_B = 0$ .

In the Figure 2 (a) and (b) for the migration of DiBP from the non-spiked sample 10 into Tenax<sup>®</sup> at 22°C the differences between the modelled migration curves obtained with the 2-layer approach and the 1-layer approach are compared.

The significant difference appears at the beginning of the migration where the concentration increases approximately linear with time. If one considers this initial stage of the kinetic it is not possible to model the whole process with a single layer, although a partition coefficient  $K_{B2/F} \ll 1$  is used, which means a high solubility of the migrant in the food or simulant (Figure 2 (b)).

The same behaviour was observed for the migration of diethylene glycol dibenzoate (DEGDB) from the non-spiked sample 7 into chocolate at 22°C shown in Figure 3 (a) and (b) and for the migration of DiBP from the non-spiked sample 10 into blotting paper at 22°C shown in Figure 4 (a) and (b).

In contrast the migration of DiBP from the non-spiked sample 10 into blotting paper at the elevated temperature of 40°C with  $A_{B2} = -2$  is best modelled with only one paper and board layer as shown in Figure 5 (b).

Insert Figure 2 - 5.

These different kinetic forms are the consequence of the complex phenomenon mentioned above, where both, the linear dependence resulting with the transport constant  $D_{B2}/d_{B2} = k$  and the square root dependence on a  $D_B$  for the whole paper and board, are occurring with different degrees.

1  
2  
3 A direct consequence of the rate determining desorption process at the paper surface  
4 is the dependency of the activation energy,  $E_A$ , of diffusion in the B2-layer from the  
5 humidity in the paper and board and from the polarity of the migrant. Similar as for  
6 plastics, the  $A_B$  for paper and board depends in general on the temperature:  
7  $A_B = A_B' - \tau/T$ . From the  $A_{B2}$ -values obtained at two different temperatures (Table 13)  
8 the athermal value  $A_{B2}'$  and  $\tau$  can be calculated and the corresponding  
9  $E_A = (\tau + 10454) R$  results. For DiBP in dry paper and board between 5°C and 40°C a  
10 value  $E_A = 145 \text{ kJ mol}^{-1}$  is obtained in the B2-layer. At 5°C and 22°C similar low  
11 diffusion coefficients in dry paper have been determined with the migrant  
12 phenanthrene (Ph). That means that dry paper and board is a relative good barrier for  
13 the diffusion of polar migrants at low temperatures.  
14

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16 With increasing humidity, as occurred during the contact with butter, a much higher  
17 diffusion rate and a lower activation energy of about  $87 \text{ kJ mol}^{-1}$  has been obtained  
18 between 5°C and 22°C for DiBP, DIPN, DEHP, TRCL and a much lower value of  
19  $31 \text{ kJ mol}^{-1}$  for BP.  
20

21  
22 In order to compare the migration behaviour between paper and board and the  
23 reference LDPE the following case study has been modelled: a 0.5 mm thick dry  
24 board sample with the density  $0.8 \text{ g cm}^{-3}$  has been compared with a 0.5 mm thick  
25 LDPE film. The initial concentration of a migrant with  $M_r = 300$  Dalton in both  
26 samples is assumed  $200 \text{ mg kg}^{-1}$ . A value  $A_{B2} = -5$  has been assumed and the same  
27 partition coefficient,  $K_{B2/F} = K_{LDPE/F} = 1$  between the packaging sample and the food  
28 simulant Tenax<sup>®</sup> with  $A_F = 6$ . With the 2-layer approach for board and by using the  
29 software MIGRATEST<sup>®</sup> Exp. for multilayers the following migration kinetic curves  
30 resulted at 40°C during 10 days (Figure 6). A significant difference between the two  
31 packaging materials can be observed. From the specific desorption behaviour of the  
32 board a more linear increase of the migration rate at the beginning occurs.  
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36 Insert Figure 6.  
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## 41 Conclusions

42 A general conclusion obtained from the systems studied is the principal possibility of  
43 modelling migration kinetics from paper and board. The matrix of paper and board  
44 behaves different than plastic materials due to the adsorption/desorption processes  
45 occurring at the fibres surface.  
46

47 A characteristic behaviour of the migration in paper and board systems is the  
48 dependency of the  $A_{B2}$ -values from the polarity of the migrant. This follows from the  
49 property of the fibres with their polar hydroxyl groups on the surface. Consequently  
50 low values of  $A_{B2}$  for polar substances result. In addition in some cases a partition  
51 coefficient  $K_{B1/B2} < 1$  was derived as for example for the migrants BP and Aa.  
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54 Like in plastic materials the diffusion rate decreases with increasing molecular weight  
55 of the migrants.  
56

57 With increasing humidity a rapid displacement of the polar migrants from the active  
58 sites on the fibre surface occurs, resulting in a high diffusion rate and higher  $A_{B2}$ -  
59 values (Table 13).  
60

Hence the  $A_{B2}$ -value is also influenced by the water activity  $a_w$  of the exposed foodstuff. The  $a_w$ -value is defined as the vapour pressure of water above the food divided by that of pure water at the same temperature. With an increasing  $a_w$ -value of the foods the migration rate and the  $A_{B2}$ -value in the paper and board are increasing as well. This could be observed for the migration of DiBP from sample 1 and 10 into foods with higher  $a_w$ -values like butter, wheat flour and chocolate at a temperature of 22°C (Table 13).

As shown in Figure 1 and Table 13 the typical values for  $A_{B2}$  in dry paper and board systems are  $< 0$  and consequently lower diffusion coefficients result than for the reference polymer LDPE. Dry paper and board are relative good barriers for polar migrants, especially at low temperature. As shown for example in Table 11 (a) a decrease of temperature from 22°C to -18°C leads to a drastic decrease of migration into the foods or simulants.

As given in Table 13 the migration rate of DiBP from the spiked sample 1 into Tenax<sup>®</sup> at a temperature of 22°C is higher ( $A_{B2} = -1.3$ ) than the migration from the non-spiked sample 10 ( $A_{B2} = -3.9$ ) under the same conditions of use. Both samples have a similar thickness and grammage (Table 3). Possibly there is a stronger retention of substances which remained in the paper and board matrix after the recycling process than of substances artificially spiked into the paper and board matrix.

For polar migrants higher values for the partition coefficients  $K_{B2/F}$  are observed in comparison to the non-polar compounds, as far as the paper and board matrix is dry.

In summary it can be concluded that the migration rates from paper and board into dry foods and simulants at a temperature below room temperature and under dry conditions are small compared to the migration rates from plastic materials. For a correct modelling the paper and board must be regarded as a 2-layer system.

Above room temperature and/or higher humidity diffusion increases. Therefore paper and board can be treated as a 1-layer system and the mass transfer can modelled in the same way as monolayer plastic packaging materials.

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#### 45 **Table captions**

46  
47 Table 1. Properties of paper and board samples, exposed foods and simulants, temperature of  
48 migration tests and modelling of experimental data.

49 Table 2. Model migrants and contaminants used for spiking of paper and board samples.

50 Table 3. Components and contaminants in the non-spiked paper and board samples.

51 Table 4. Results of migration experiments with benzophenone from the spiked sample 1.

52 Table 5. Results of migration experiments with diisobutyl phthalate from the spiked sample 1.

53 Table 6. Results of migration experiments with diisopropyl naphthalene from the spiked  
54 sample 1.

55 Table 7. Results of migration experiments with di(2-ethylhexyl) phthalate from the spiked  
56 sample 1.

57 Table 8. Results of migration experiments with phenanthrene from the spiked sample 1.

58 Table 9. Results of migration experiments with triclosan from the spiked sample 1.

59 Table 10. Results of migration experiments with abietic acid, diisobutyl phthalate, diethylene  
60 glycol dibenzoate and dipropylene glycol dibenzoate from the non-spiked samples  
4, 6 and 7.

Table 11 (a). Results of migration experiments with diisobutyl phthalate from the non-spiked sample 10 in contact with foodstuffs.

Table 11 (b). Results of migration experiments with diisobutyl phthalate from the non-spiked sample 10 in contact with Tenax<sup>®</sup> and blotting paper.

Table 12. Results of migration experiments with diisobutyl phthalate, bisphenol A and benzyl 2-naphthyl ether from the non-spiked samples 9 and 11.

Table 13. Results of modelling of the migration investigations.

### Figure captions

Figure 1. Diffusion coefficients,  $D_{B2}$  ( $\text{cm}^2 \text{s}^{-1}$ ), as function of the relative molecular weight  $M_r$ , calculated with Equation (3): trace 1 with  $A_{B2} = 0$ ; trace 2 with  $A_{B2} = 6$  (upper dots); trace 3 with  $A_{B2} = -11$  (lower dots); trace 4 with  $A_{B2} = -2$  and trace 5 with Equation (5) and  $A_{B2} = 0$ .

Figure 2. Comparison of (a) 2-layer approach ( $A_{B2} = -3.9$ ;  $A_{B1} = 6$ ) with (b) 1-layer approach ( $A_{B2} = A_{B1} = A_B = -2.7$ ) for paper and board: migration of DiBP from non-spiked sample 10 into Tenax<sup>®</sup> 60 days at 22°C (experimental data points and modelled data curve).

Figure 3. Comparison of (a) 2-layer approach ( $A_{B2} = -3.4$ ;  $A_{B1} = 6$ ) with (b) 1-layer approach ( $A_{B2} = A_{B1} = A_B = -3.3$ ) for paper and board: migration of DEGDB from non-spiked sample 7 into chocolate 60 days at 22°C (experimental data points and modelled data curve).

Figure 4. Comparison of (a) 2-layer approach ( $A_{B2} = -3.3$ ;  $A_{B1} = 6$ ) with (b) 1-layer approach ( $A_{B2} = A_{B1} = A_B = -2.4$ ) for paper and board: migration of DiBP from non-spiked sample 10 into blotting paper 13 days at 22°C (experimental data points and modelled data curve).

Figure 5. Comparison of (a) 2-layer approach ( $A_{B2} = -3.7$ ;  $A_{B1} = 6$ ) with (b) 1-layer approach ( $A_{B2} = A_{B1} = A_B = -2.0$ ) for paper and board: migration of DiBP from non-spiked sample 10 into blotting paper 10 days at 40°C (experimental data points and modelled data curve).

Figure 6. Migration kinetics: (a) from the reference LDPE and (b) from board into a food simulant at 40°C during 10 days. Same values for initial concentration, molecular weight, partition coefficients, film thickness and surface/volume ratio were used. Whereas LDPE is treated as single layer, the board is treated with the 2-layer approach, with  $A_{B1} = 16$  and  $A_{B2} = -5$ . This situation is typical for dry board samples and polar migrants.

Table 1. Properties of paper and board samples, exposed foods and simulants, temperature of migration tests and modelling of experimental data.

Properties of paper and board samples									
ID	Description	Grammage (g/m <sup>2</sup> )	Thickness (µm)	Percentage of virgin/recycled material	Spiking	Target migrants <sup>1</sup>	Exposed foods/simulant	Temp. (°C)	Modelling of data
1	Food board, one-side pigment coated	300	460	100% virgin	No	Aa, DiBP	Rice	22	No <sup>2</sup>
					Yes	BP, TRCL, DiBP, DIPN, DEHP, Ph	Butter Tenax <sup>®</sup>	-18/5/22 -18/5/22	-18°C: No <sup>3</sup> 5°C: Yes 22°C: Yes
2	Food board, one-side pigment coated	300	480	100% virgin	No	Aa	Ice cream	-18	No <sup>2</sup>
					Yes	BP, TRCL, DiBP, DIPN, DEHP, Ph	Ice cream Spinach Tenax <sup>®</sup>	-18/5/22 -18/5/22 -18/5/22	No
3	Virgin kraft liner	200	220	100% virgin	Yes	BP, TRCL, DiBP, DIPN, DEHP, Ph	Spinach Tenax <sup>®</sup>	-18/5/22 -18/5/22	No
4	MG paper bag	40	60	100% recycled	No	Aa	Wheat flour	22	Yes
5	Food board, one-side pigment coated	320	395	100% recycled	No	Aa, DiBP	Egg pasta	22	No <sup>2</sup>
6	Food board, one-side pigment coated	300	400	95% recycled	No	Aa, DiBP	Sponge finger biscuits	22	Aa: No <sup>2</sup> DiBP: Yes
7	Chocolate padding board	200	3300	approx. 20% recycled	No	DPGDB, DEGDB	Chocolate	22	Yes
8	White top corrugated board	950	6461	100% recycled	No	Aa, DiBP	Straw berries Tomatoes	5 5	No <sup>2</sup>
9	White top corrugated board	422	2882	n.s.	No	DiBP	Raspberries Tenax <sup>®</sup>	-18 -18	No <sup>3</sup>
10	Board, one-side pigment coated	350	448	n.s.	No	DiBP	Wheat flour Chocolate Egg pasta Sponge finger biscuits Puff pastry Tenax <sup>®</sup> Blotting paper	-18/22 -18/22 22 22 -18 -18/22 22/40	-18°C: No <sup>3</sup> 22°C: Yes 40°C: Yes
11	Thermal fax paper	52	64	n.s.	No	BPA, NAP-2	Wheat flour Chocolate Tenax <sup>®</sup>	-18 -18 -18	No <sup>3</sup>

1 Names and properties of the target migrants are listed in Table 2 and Table 3.

2 Migration of target migrants into foods was below the detection limit.

Because of interferences with the chromatographic fingerprint of the foodstuff a higher detection limit for DiBP between 30 µg/dm<sup>2</sup> and 90 µg/dm<sup>2</sup> was determined. The detection limit for Aa was between 1 µg/dm<sup>2</sup> and 7 µg/dm<sup>2</sup>.

3 Migration experiments at a temperature of -18°C with only one or two time points were not modelled.

n.s. not specified

Table 2. Model migrants and contaminants used for spiking of paper and board samples.

Substance	CAS Registry Number	Abbreviation	Category	Molecular weight (Dalton)
Benzophenone	119-61-9	BP	impurity from printing inks in recycled fibres	182
Diisobutyl phthalate	84-69-5	DiBP	impurity from adhesives in recycled fibres	278
Diisopropyl naphthalene	24157-81-1	DIPN	impurity from recycled fibres	212
Di(2-ethylhexyl) phthalate	117-81-7	DEHP	impurity from recycled fibres (plasticizer)	390
Phenanthrene	85-01-8	Ph	model migrant for polycyclic aromatic hydrocarbons	178
Triclosan; 5-Chloro-2-(2,4-dichlorophenoxy)phenol	3380-34-5	TRCL	model migrant for biocides	290

Table 3. Components and contaminants in the non-spiked paper and board samples.

Substance	CAS Registry Number	Abbreviation	Category	Molecular weight (Dalton)
Abietic acid	514-10-3	Aa	rosin component	303
Benzyl 2-naphthyl ether	613-62-7	NAP-2	component in fax paper	234
Bisphenol A	80-05-7	BPA	component in fax paper	228
Diisobutyl phthalate	84-69-5	DiBP	impurity from adhesives in recycled fibres	278
Diethylene glycol dibenzoate	120-55-8	DEGDB	impurity from adhesives	314
Dipropylene glycol dibenzoate	27138-31-4	DPGDB	impurity from adhesives	342

Table 4. Results of migration experiments with benzophenone from the spiked sample 1.

Food/Simulant	Temperature	Time point	Migration	Initial concentration after spiking	Quotient Migration/Initial concentration
	(°C)	(d)	(µg/dm <sup>2</sup> )	(µg/dm <sup>2</sup> )	(%)
Butter	-18°C	30	x	552	X
		30	x		X
		60	15		2.7
	5°C	0.33	x	552	X
		1	15		2.7
		2	28		5.1
		4	84		15.2
		10	212		38.4
		10	195		35.3
		22°C	0.33		x
	1		68	12.3	
	2		156	28.3	
	4		275	49.8	
	10		473	85.7	
	10		528	95.7	
Tenax <sup>®</sup>	-18°C		30	n.d.	552
		30	n.d.	<0.4	
		60	n.d.	<0.4	
	5°C	0.33	n.d.	552	<0.4
		1	n.d.		<0.4
		2	n.d.		<0.4
		4	n.d.		<0.4
		10	n.d.		<0.4
		10	n.d.		<0.4
		22°C	0.33		n.d.
	1		n.d.	<0.4	
	2		n.d.	<0.4	
	4		2.2	0.4	
	10		4.7	0.9	
	10		4.9	0.9	

x contaminant could not be detected because of interferences with the chromatographic fingerprint of the foodstuff (food blank)

n.d. not detectable (detection limit: 2,2 µg/dm<sup>2</sup>)

Table 5. Results of migration experiments with diisobutyl phthalate from the spiked sample 1.

Food/Simulant	Temperature	Time point	Migration	Initial concentration after spiking	Quotient Migration/Initial concentration
	(°C)	(d)	(µg/dm <sup>2</sup> )	(µg/dm <sup>2</sup> )	(%)
Butter	-18°C	30	83	422	19.7
		30	69		16.4
		60	111		26.3
	5°C	0.33	47	422	11.1
		1	69		16.3
		2	71		16.8
		4	69		16.4
		10	100		23.7
		10	115		27.3
	22°C	0.33	106	422	25.1
		1	87		20.6
		2	121		28.7
		4	178		42.2
		10	161		38.2
		10	187		44.3
Tenax <sup>®</sup>	-18°C	30	3.3	422	0.8
		30	2.5		0.6
	5°C	0.33	n.d.	422	<0.5
		1	5.3		1.3
		2	6.3		1.5
		4	16		3.8
		10	22		5.2
	22°C	10	23	5.5	
		0.33	17	422	4.0
		1	27		6.4
		2	35		8.3
		4	50		11.8
10	61	14.5			
10	52	12.3			

n.d. not detectable (detection limit: 2,2 µg/dm<sup>2</sup>)

Table 6. Results of migration experiments with diisopropyl naphthalene from the spiked sample 1.

Food/Simulant	Temperature	Time point	Migration	Initial concentration after spiking	Quotient Migration/Initial concentration
	(°C)	(d)	(µg/dm <sup>2</sup> )	(µg/dm <sup>2</sup> )	(%)
Butter	-18°C	30	34	438	7.8
		30	34		7.8
		60	36		8.2
	5°C	0.33	43	438	9.8
		1	64		14.6
		2	94		21.5
		4	133		30.4
		10	228		52.1
		10	237		54.1
	22°C	0.33	103	438	23.5
		1	137		31.3
		2	206		47.0
		4	211		48.2
		10	296		67.6
		10	326		74.4
Tenax <sup>®</sup>	-18°C	30	16	438	3.7
		30	41		9.4
	5°C	0.33	15	438	3.4
		1	25		5.7
		2	28		6.4
		4	51		11.6
		10	69		15.8
	10	80	18.3		
	22°C	0.33	42	438	9.6
		1	61		13.9
		2	94		21.5
		4	157		35.8
		10	196		44.7
		10	196		44.7

Table 7. Results of migration experiments with di(2-ethylhexyl) phthalate from the spiked sample 1.

Food/Simulant	Temperature	Time point	Migration	Initial concentration after spiking	Quotient Migration/Initial concentration
	(°C)	(d)	(µg/dm <sup>2</sup> )	(µg/dm <sup>2</sup> )	(%)
Butter	-18°C	30	12	214	5.6
		30	9.3		4.3
		60	5.8		2.7
	5°C	0.33	14	214	6.5
		1	18		8.4
		2	23		10.7
		4	19		8.9
		10	20		9.3
		10	23		10.7
	22°C	0.33	33	214	15.4
		1	23		10.7
		2	29		13.6
		4	26		12.1
		10	21		9.8
		10	29		13.6
Tenax <sup>®</sup>	-18°C	30	n.d.	214	<1.0
		30	n.d.		<1.0
	5°C	0.33	n.d.	214	<1.0
		1	n.d.		<1.0
		2	n.d.		<1.0
		4	n.d.		<1.0
		10	n.d.		<1.0
		10	n.d.		<1.0
	22°C	0.33	n.d.	214	<1.0
		1	n.d.		<1.0
		2	3.3		1.5
		4	8.1		3.8
10		15	7.0		
10		12	5.6		

n.d. not detectable (detection limit: 2,2 µg/dm<sup>2</sup>)

Table 8. Results of migration experiments with phenanthrene from the spiked sample 1.

Food/Simulant	Temperature	Time point	Migration	Initial concentration after spiking	Quotient Migration/Initial concentration
	(°C)	(d)	(µg/dm <sup>2</sup> )	(µg/dm <sup>2</sup> )	(%)
Butter	-18°C	30	23	515	4.5
		30	37		7.2
		60	21		4.1
	5°C	0.33	14	515	2.7
		1	28		5.4
		2	39		7.6
		4	79		15.3
		10	190		36.9
		10	183		35.5
	22°C	0.33	73	515	14.2
		1	133		25.8
		2	186		36.1
		4	270		52.4
		10	363		70.5
		10	394		76.5
Tenax <sup>®</sup>	-18°C	30	3.0	515	0.6
		30	10.6		2.1
	5°C	0.33	5.3	515	1.0
		1	8.0		1.6
		2	8.6		1.7
		4	13		2.5
		10	17		3.3
	10	17	3.3		
	22°C	0.33	10	515	1.9
		1	13		2.5
		2	24		4.7
		4	36		7.0
10		42	8.2		
10		42	8.2		

Table 9. Results of migration experiments with triclosan from the spiked sample 1.

Food/Simulant	Temperature	Time point	Migration	Initial concentration after spiking	Quotient Migration/Initial concentration
	(°C)	(d)	(µg/dm <sup>2</sup> )	(µg/dm <sup>2</sup> )	(%)
Butter	-18°C	30	38	571	6.7
		30	32		5.6
		60	29		5.1
	5°C	0.33	44	571	7.7
		1	56		9.8
		2	66		11.6
		4	57		10.0
		10	67		11.7
		10	70		12.3
	22°C	0.33	85	571	14.9
		1	92		16.1
		2	81		14.2
		4	84		14.7
		10	84		14.7
		10	95		16.6
Tenax <sup>®</sup>	-18°C	30	n.d.	571	<0.4
		30	n.d.		<0.4
	5°C	0.33	n.d.	571	<0.4
		1	n.d.		<0.4
		2	n.d.		<0.4
		4	n.d.		<0.4
		10	6.9		1.2
		10	5.3		0.9
	22°C	0.33	2.3	571	0.4
		1	7.3		1.3
		2	14		2.5
		4	29		5.1
		10	44		7.7
		10	33		5.8

n.d. not detectable (detection limit: 2,2 µg/dm<sup>2</sup>)

Table 10. Results of migration experiments with abietic acid, diisobutyl phthalate, diethylene glycol dibenzoate and dipropylene glycol dibenzoate from the non-spiked samples 4, 6 and 7.

Food/Simulant	Temperature	Time point	Migration	Initial concentration after spiking	Quotient Migration/Initial concentration
	(°C)	(d)	(µg/dm <sup>2</sup> )	(µg/dm <sup>2</sup> )	(%)
<b>Sample 4 (Abietic acid)</b>					
Wheat flour	22°C	1	2.9	437	0.7
		2	4.6		1.1
		4	5.8		1.3
		4	5.3		1.2
		15	14		3.2
		30	21		4.8
		30	22		5.0
		60	33		7.5
		60	27		6.2
<b>Sample 6 (Diisobutyl phthalate)</b>					
Sponge finger Biscuits	22°C	2	6.2	158	3.9
		4	11		7.0
		4	14		8.9
		15	28		17.7
		15	31		19.6
		30	36		22.8
		30	43		27.2
		60	55		34.7
		60	60		38.0
<b>Sample 7 (Diethylene glycol dibenzoate)</b>					
Chocolate	22°C	2	16	3359	0.5
		4	23		0.7
		4	24		0.7
		15	59		1.8
		15	63		1.9
		30	103		3.1
		30	107		3.2
		60	144		4.3
		60	148		4.4
<b>Sample 7 (Dipropylene glycol dibenzoate)</b>					
Chocolate	22°C	2	12	1709	0.7
		4	20		1.2
		4	20		1.2
		15	41		2.4
		15	42		2.5
		30	64		3.7
		30	66		3.9
		60	78		4.6
		60	83		4.9

Table 11 (a). Results of migration experiments with diisobutyl phthalate from the non-spiked sample 10 in contact with foodstuffs.

Food/Simulant	Temperature	Time point	Migration	Initial concentration after spiking	Quotient Migration/Initial concentration
	(°C)	(d)	(µg/dm <sup>2</sup> )	(µg/dm <sup>2</sup> )	(%)
<b>Sample 10 (Diisobutyl phthalate)</b>					
Wheat flour	-18°C	90	3.6	182	2.0
		90	3.6		2.0
	22°C	2	10.5	182	5.8
		6	20.6		11.3
		15	34.9		19.2
		30	44.2		24.3
		60	56.2		30.9
Chocolate	-18°C	90	2.2	182	1.2
		90	2.3		1.3
	22°C	2	13.8	182	7.6
		6	30.7		17.4
		15	55.8		30.7
		30	77.3		42.5
		60	108.5		59.6
Egg pasta	22°C	2	2.3	182	1.3
		6	11.6		6.4
		15	30.4		16.7
		30	51.5		28.3
		60	63.9		35.1
Sponge finger biscuits	22°C	2	2.3	182	1.3
		6	20.5		11.3
		15	31.6		17.4
		30	50.1		27.5
		60	56.8		31.2
Puff pastry	-18°C	90	2.9	182	1.6
		90	3.0		1.7

Table 11 (b). Results of migration experiments with diisobutyl phthalate from the non-spiked sample 10 in contact with Tenax<sup>®</sup> and blotting paper.

Food/Simulant	Temperature	Time point	Migration	Initial concentration after spiking	Quotient Migration/Initial concentration
	(°C)	(d)	(µg/dm <sup>2</sup> )	(µg/dm <sup>2</sup> )	(%)
<b>Sample 10 (Diisobutyl phthalate)</b>					
Tenax <sup>®</sup>	-18°C	90	7.2	182	4.0
		90	6.9		3.8
	22°C	2	13.6	182	7.5
		2	13.3		7.3
		6	23.7		13.0
		6	19.4		10.7
		15	47.0		25.8
		15	56.1		30.8
		30	67.7		37.2
		30	74.0		40.7
		60	79.5		43.7
		60	80.3		44.1
	Blotting paper	22°C	1	9.4	182
2			15.2	8.4	
2			15.1	8.3	
5			26.2	14.4	
6			35.6	19.6	
8			38.8	21.3	
10			40.5	22.3	
12			47.2	25.9	
12.9			48.9	26.9	
40°C			0.6	25.3	
		1	33.5	18.4	
		2	49.2	27.0	
		3	54.8	30.1	
		5	71.4	39.2	
	10	88.0	48.4		

Table 12. Results of migration experiments with diisobutyl phthalate, bisphenol A and benzyl 2-naphthyl ether from the non-spiked samples 9 and 11.

Food/Simulant	Temperature	Time point	Migration	Initial concentration after spiking	Quotient Migration/Initial concentration
	(°C)	(d)	(µg/dm <sup>2</sup> )	(µg/dm <sup>2</sup> )	(%)
<b>Sample 9 (Diisobutyl phthalate)</b>					
Raspberries	-18°C	90	n.d.	303	<0.9
		90	n.d.		<0.9
Tenax <sup>®</sup>	-18°C	90	6.3	303	2.1
		90	6.9		2.3
<b>Sample 11 (Bisphenol A)</b>					
Wheat flour	-18°C	90	1.1	2469	0.04
		90	1.1		0.04
Tenax <sup>®</sup>	-18°C	90	1.6	2469	0.07
		90	2.5		0.1
<b>Sample 11 (Benzyl 2-naphthyl ether)</b>					
Wheat flour	-18°C	90	15.9	5006	0.3
		90	15.6		0.3
Chocolate	-18°C	90	19.9	5006	0.4
		90	16.5		0.3
Tenax <sup>®</sup>	-18°C	90	24.9	5006	0.5
		90	20.3		0.4

n.d. not detectable (detection limit: 2,6 µg/dm<sup>2</sup>)

Table 13. Results of modelling of the migration investigations.

Migrants	$A_{B2}$	$\log D_{B2}$	$K_{B2/F}$	$A_F$
<b>Sample 1 (spiked) with Tenax®: 10days, 5°C</b>				
Benzophenone	-	-	-	6
Diisobutyl phthalate	-2.8	-11.3	29.0	
Triclosan	-	-	-	
Phenanthrene	-2.0	-10.5	95.0	
DIPN	-1.0	-10.2	1.0	
Di(2-ethylhexyl) phthalate	-	-	-	
<b>Sample 1 (spiked) with Tenax®: 10days, 22°C</b>				
Benzophenone	-10.2	-13.1	10.0	6
Diisobutyl phthalate	-1.3	-9.7	17.0	
Triclosan	-5.0	-11.4	10.0	
Phenanthrene	-4.6	-10.7	43.0	
DIPN	-1.0	-9.3	1.0	
Di(2-ethylhexyl) phthalate	-4.0	-11.4	15.0	
<b>Sample 1 (spiked) with butter: 10days, 5°C</b>				
Benzophenone	-4.8	-11.7	17.0	7.5
Diisobutyl phthalate	6.0	-7.9	20.0	
Triclosan	6.0	-7.6	55.0	
Phenanthrene	-2.2	-10.6	3.5	
DIPN	1.2	-9.1	0.01	
Di(2-ethylhexyl) phthalate	6.0	-8.0	65.0	
<b>Sample 1 (spiked) with butter: 10days, 22°C</b>				
Benzophenone	-6.2	-11.4	1.0	7.5
Diisobutyl phthalate	6.0	-6.6	11.0	
Triclosan	6.0	-6.6	40.0	
Phenanthrene	-0.45	-8.9	1.0	
DIPN	1.0	-8.4	3.0	
Di(2-ethylhexyl) phthalate	6.0	-7.1	50.0	
<b>Sample 4 (non-spiked) with wheat flour: 60days, 22°C</b>				
Abietic acid	-10.2	-13.7	100.0	6
<b>Sample 6 (non-spiked) with sponge finger biscuits: 60days, 22°C</b>				
Diisobutyl phthalate	-3.8	-10.8	18.5	4
<b>Sample 7 (non-spiked) with chocolate: 60days, 22°C</b>				
Diethylene glycol dibenzoate	-3.4	-10.8	13.8	3
Dipropylene glycol dibenzoate	-2.0	-10.3	1.5	
<b>Sample 10 (non-spiked) with Tenax®: 60days, 22°C</b>				
Diisobutyl phthalate	-3.9	-11.3	4.1	6
<b>Sample 10 (non-spiked) with blotting paper: 13days, 22°C</b>				
Diisobutyl phthalate	-3.3	-11.0	2.4	6
<b>Sample 10 (non-spiked) with blotting paper: 10days, 40°C</b>				
Diisobutyl phthalate	-2.0	-9.6	0.6	6
<b>Sample 10 (non-spiked) with wheat flour: 60days, 22°C</b>				
Diisobutyl phthalate	-2.0	-10.5	15.0	6
<b>Sample 10 (non-spiked) with egg pasta: 60days, 22°C</b>				
Diisobutyl phthalate	-4.5	-11.6	0.6	-2
<b>Sample 10 (non-spiked) with sponge finger biscuits: 60days, 22°C</b>				
Diisobutyl phthalate	-3.9	-11.3	33.0	6
<b>Sample 10 (non-spiked) with chocolate: 60days, 22°C</b>				
Diisobutyl phthalate	-3.3	-11.0	6.5	4

- Migration of target migrants was below the detection limit.

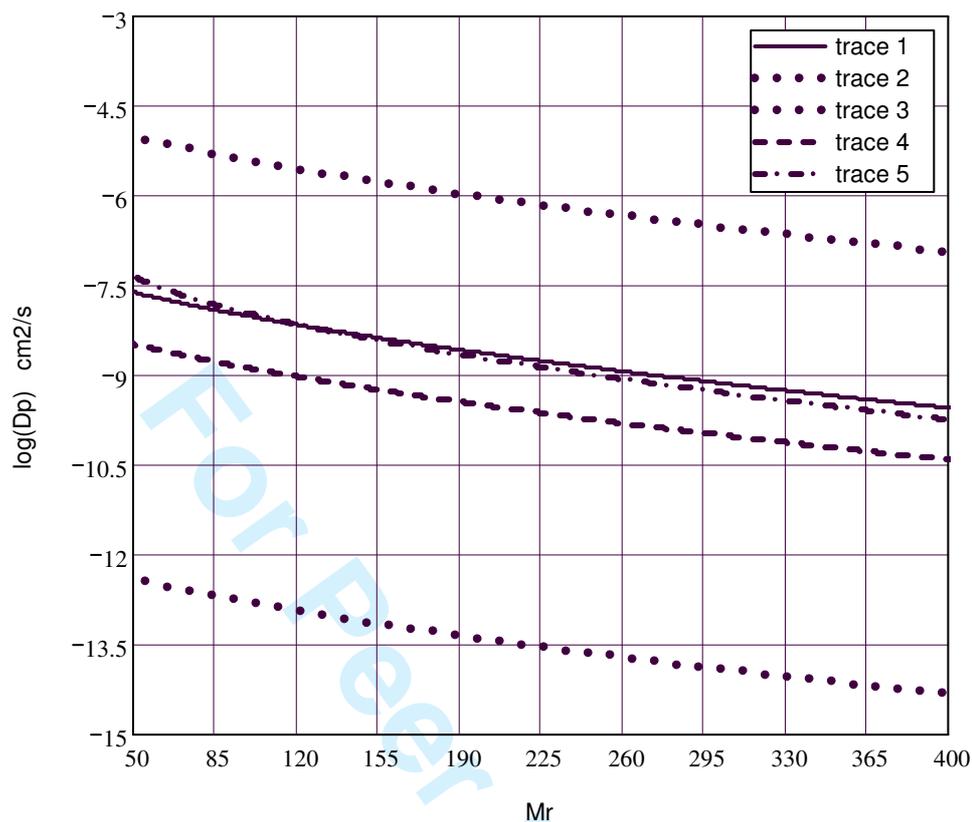


Figure 1. Diffusion coefficients,  $D_{B2}$  ( $\text{cm}^2 \text{s}^{-1}$ ), as function of the relative molecular weight  $M_r$ , calculated with Equation (3): trace 1 with  $A_{B2} = 0$ ; trace 2 with  $A_{B2} = 6$  (upper dots); trace 3 with  $A_{B2} = -11$  (lower dots); trace 4 with  $A_{B2} = -2$  and trace 5 with Equation (5) and  $A_{B2} = 0$ .

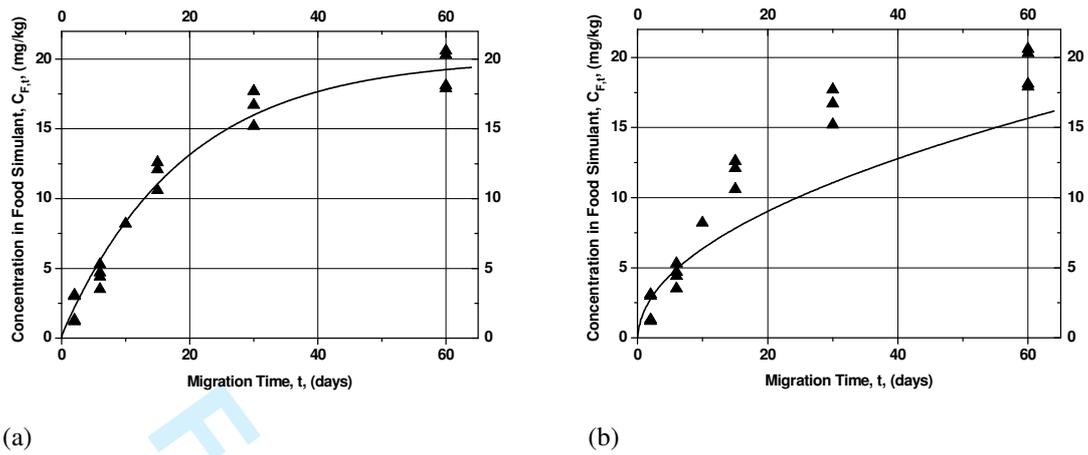


Figure 2. Comparison of (a) 2-layer approach ( $A_{B2} = -3.9$ ;  $A_{B1} = 6$ ) with (b) 1-layer approach ( $A_{B2} = A_{B1} = A_B = -2.7$ ) for paper and board: migration of DiBP from non-spiked sample 10 into Tenax<sup>®</sup> 60 days at 22°C (experimental data points and modelled data curve).

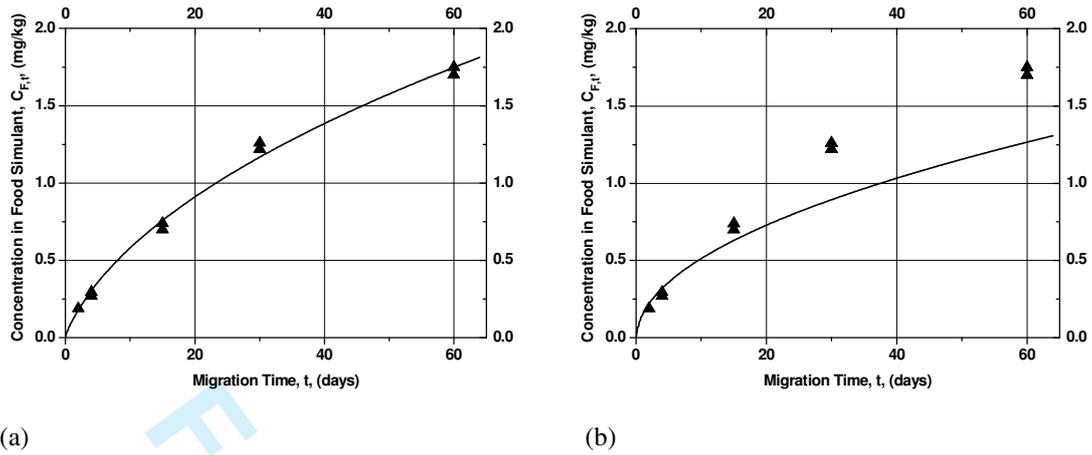


Figure 3. Comparison of (a) 2-layer approach ( $A_{B2} = -3.4$ ;  $A_{B1} = 6$ ) with (b) 1-layer approach ( $A_{B2} = A_{B1} = A_B = -3.3$ ) for paper and board: migration of DEGDB from non-spiked sample 7 into chocolate 60 days at 22°C (experimental data points and modelled data curve).

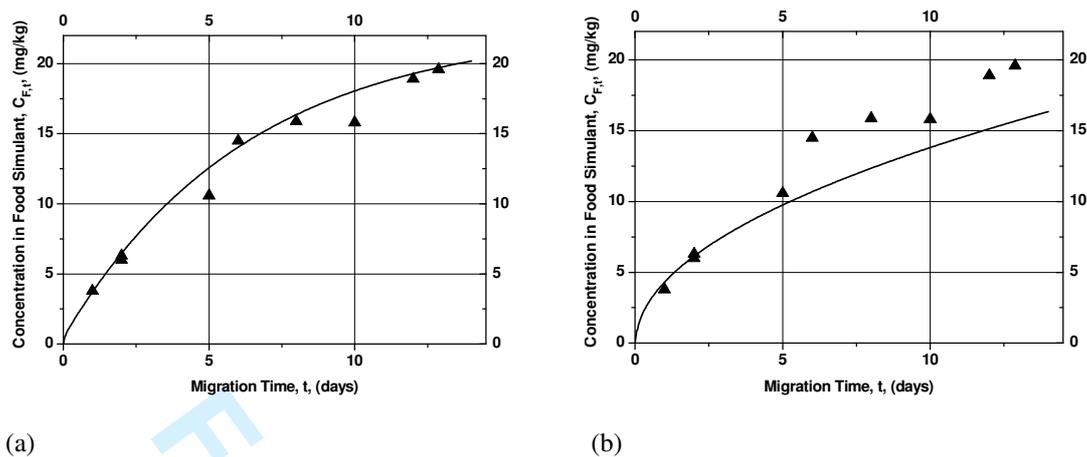


Figure 4. Comparison of (a) 2-layer approach ( $A_{B2} = -3.3$ ;  $A_{B1} = 6$ ) with (b) 1-layer approach ( $A_{B2} = A_{B1} = A_B = -2.4$ ) for paper and board: migration of DiBP from non-spiked sample 10 into blotting paper 13 days at 22°C (experimental data points and modelled data curve).

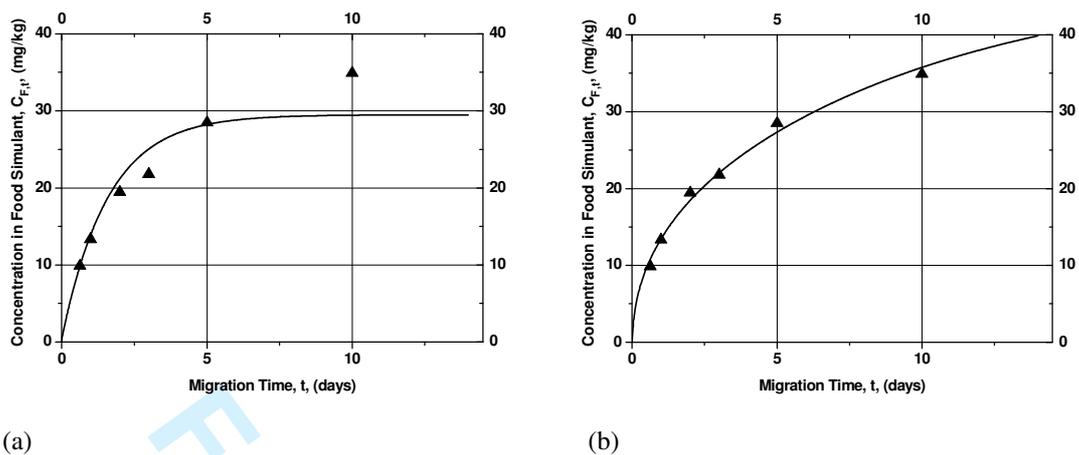


Figure 5. Comparison of (a) 2-layer approach ( $A_{B2} = -3.7$ ;  $A_{B1} = 6$ ) with (b) 1-layer approach ( $A_{B2} = A_{B1} = A_B = -2.0$ ) for paper and board: migration of DiBP from non-spiked sample 10 into blotting paper 10 days at 40°C (experimental data points and modelled data curve).

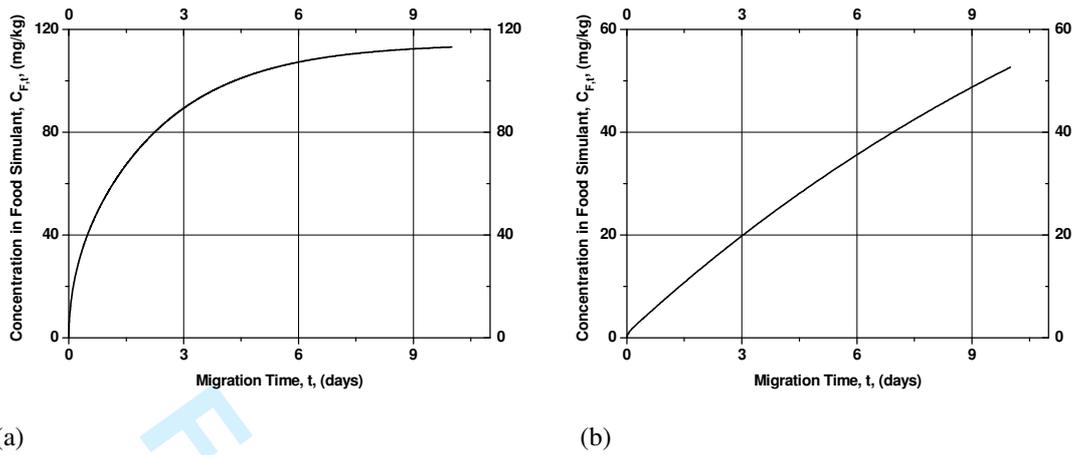


Figure 6. Migration kinetics: (a) from the reference LDPE and (b) from board into a food simulant at 40°C during 10 days. Same values for initial concentration, molecular weight, partition coefficients, film thickness and surface/volume ratio were used. Whereas LDPE is treated as single layer, the board is treated with the 2-layer approach, with  $A_{B1} = 6$  and  $A_{B2} = -5$ . This situation is typical for dry board samples and polar migrants.