



EU-Project FAIR-CT98-4318 "Recyclability"

Project: "Programme on the Recyclability of Food Packaging Materials with Respect to Food Safety Considerations - Polyethylene Terephthalate (PET), Paper & Board and Plastics Covered by Functional Barriers".

Task: **Section 2. Paper & board**

Subject: **Consolidated project report for the period**
01-01-99 to 30-04-02

Contract type: Shared-cost research project
Total costs of project: 2,328.6 kEuro, EU contribution = 1,381 kEuro (59.3%)
Total costs of sections 1 & 2: 1,611 kEuro, EU contribution = 866 kEuro (53.8%)

Duration: 40 months (project start: 1 January 1999)

EC contact: Dr. Alkmini Katsada, DG Research
Project Coordinator: Roland Franz, Fraunhofer IVV, Freising, Germany
Section 2 leader: Laurence Castle
MAFF Central Science Laboratory,
York YO41 1LZ (UK)
tel 00-44-1904-462000
fax 00-44-1904-462133
l.castle@csl.gov.uk

Partners in Section 2

- P 01 Fraunhofer-Institut for Process Engineering and Packaging
Freising, DE. (CO & DC)
- P 02 Ministry of Agriculture, Fisheries and Food, Central Science Laboratory
York, UK. (DC)
- P 03 Swedish Pulp and Paper Research Institute
Stockholm, SE (AC to P02)
- P 04 VTT Biotechnology and Food Research
Espoo, FI (AC to P02)
- P 05 EC Joint Research Centre – IHCP
Ispra, I (DC1)
- P 06 University of Zaragoza. Dep. Quim. Anal. Centro Politécnico Superior
Zaragoza, E (AC to P01)
- P 07 University of Ioannina, Dep. Chemistry, Lab of Food Chemistry
Ioannina, GR (AC to P01)

Contents

	Page
1 Introduction to the work in Section 2, Paper and Board	
1.1 Background introduction	3
1.2 Project structure	5
1.3 Objectives of Section 2	5
1.4 Subtasks of Section 2 on paper and board	5
2 Summary of findings and conclusions	
Task 5 Literature review of contaminants on recycled fibres and limited experimental confirmation	6
Task 6 Definition of model contaminants and P&B test samples	7
Task 6.1 Selection of model contaminants	7
Task 6.2 Characterisation of the P&B test samples	9
Task 7 Systematic interaction studies	12
Tasks 7.1 & 7.2 Adsorption isotherms using plain P&B and coated P&B	12
Task 7.3 Mass transfer into foods and/or food simulants	13
Task 8 Development and verification of a physico-mathematical model	16
Task 9 Definition of criteria for the safe reuse of recycled fibres for food packaging	19
Task 10 Conclusions on test strategies for recycled P&B fibres intended for food contact	21
References	23
3 Individual consolidated reports from the Partners who participated in Section 2	
Partner 01	Annex 1
Partner 02	Annex 2
Partner 03	Annex 3
Partner 04	Annex 4
Partner 05	Annex 5
Partner 06	Annex 6
Partner 07	Annex 7

1 Introduction to the work in Section 2, Paper and Board

1.1 Background introduction

The scientific problem is that the factors that control the migration of contaminants from cellulosic fibres such as recycled paper and board, are poorly understood. The consequence of this is that although recycled P&B has been used for many years to package (especially) dry foods, there have been episodes when the use of chemicals ‘upstream’ of paper recyclers has caused unanticipated problems with consequent chemical migration to foods. The three most publicised examples are contamination by PCBs (polychlorinated biphenyls, from carbonless copypapers), by phthalates (from inks) and by DiPNs (diisopropylnaphthalenes, from inkjet inks and again carbonless copypapers). In a recent episode, even the presence of a ‘barrier layer’ of plastic as a coating or as a separate inner bag, unexpectedly failed to prevent migration of DiPNs to a variety of dry foods.

The economic and environmental benefits of paper recycling are considerable but for food packaging it is clearly problematical so long as the fundamental migration science is poorly understood. This project has addressed this issue.

Why recycled paper and board is so widely used to package dry foods

In Europe (as in the USA) food packages are assessed for chemical migration by considering the nature of the food that is to be packed. Foods are classified as aqueous, acidic, alcoholic or fatty since these characteristics are understood to control the migration process of organic and inorganic substances that may be present in the packaging material. Neither European [1] nor USA [2-3] regulations require the testing of packages used for dry foods that have no free fat or oil phase on the surface. The assumption is that with no intimate contact with a liquid food phase, the potential for migration is negligible.

The consequence of this rulemaking, applied to plastics in the EU and to packaging materials in general in the USA, is that packers and producers take the cue that dry foods are less demanding applications. Consequently, as paper and board made from recovered fibres has less reliable purity characteristics than virgin paper (because of residues that may not be removed completely) then recycled paper and board has found a ready outlet and is very widely used for packaging dry foods.

The mechanism of migration to dry foods

For migration to occur into dry foods, where there is only marginal point contact with the solid particles and no intimate contact of the packaging with a liquid food phase, it is generally accepted that a vaporisation step must occur whereby the substance ‘jumps’ [4-6] across the gap between the pack surface and the solid food surface. The migration process can be broken down into five steps and the nature of the chemicals that migrate and the extent of their migration, is controlled by a combination of all five steps.

Step 0. Composition of the packaging

The substance must (of course) be present (as a paper chemical or as a contaminant) in the packaging material. The propensity to migrate should be proportional to the concentration in the paper or board.

Step 1. Mobility in the packaging material

The substance must be mobile enough to diffuse through the packaging material to appear at the food contact surface. The rate of diffusion will determine how rapidly the surface is replenished with migrant. Paper and board are rather open and porous structures and this step is not likely to be rate-limiting.

Step 2. Volatilisation ('jumping the gap')

The substance must have a discernible vapour pressure under the conditions (temperature) of use of the pack. It must volatilise into the interspacial gap between the solid (rigid) food surface or food particles and the pack surface.

Step 3. Absorption onto the food surface

The substance must have an affinity for the food surface causing it to condense from the vapour phase, onto and into the food.

Step 4. Mobility in the food

The substance must be mobile enough in the food matrix to diffuse away from the surface into the bulk of the food. This is necessary to avoid a concentration build-up at the food surface which would slow subsequent migration.

A more detailed consideration of Step 2 - vaporisation

Of the controlling steps described above, steps 0, 1, 3 & 4 are not contentious because they apply to migration to any food or simulant and they are not special for dry foods. To the casual observer, step 2 might at first seem rather restrictive since there is the tendency to equate volatilisation with boiling point. Whilst they are of course related, it must be recognised that a substance can have an appreciable vapour pressure even at temperatures far below the boiling point. Further, the boiling point of a substance is defined as the temperature at which the vapour pressure equals one atmosphere above the pure liquid. The vapour pressure at any lower temperature can be predicted (e.g. from Henry's law or Raoult's law) but if the substance is in a matrix for which it has a lower affinity than for the pure liquid (e.g. as a contaminant on a wood fibre) then the vapour pressure will be higher. It should also be noted that diffusion in the gas phase is usually several orders of magnitude faster than diffusion in condensed phases meaning that diffusion across even millimetre gaps between the food and the packaging [14-15] could be faster than diffusion on the micrometer scale in the food or in the packaging itself [9-10].

This project has researched migration to dry foods, with special emphasis on step 2 in the mechanism outlined above.

Work Section 2 of this EU project involved a total of 7 project partners who had the task of investigating aspects of the recyclability of paper and board materials based on cellulosic fibres. In accordance with the objectives of the project overall, they aimed to provide the fundamental scientific understanding that will indicate where recycled paper materials can be used safely for food packaging. This understanding should help the many large and

small industries who want to make and use environmentally-friendly food packaging but who cannot at present operate in the uncertain legislative framework that exists. This project aim was achieved within Section 2 by gaining an understanding of cellulosic fibres with respect to their potential for the uptake of contaminating substances and their potential for subsequent release by migration to a food placed in contact.

1.2. Project structure

Section 2 work on paper and board fitted within the overall project organisation as follows. Each of the 3 task areas had a different sub-coordinator.

Section (LOGO)	Technical content of task (Sub-coordination)
1 (PET)	Criteria for PET recycling for direct food contact applications (Fraunhofer IVV, P01)
2 (P&B)	Usability of recycled paper & board for direct and/or indirect food contact (MAFF-CSL, P02)
3 (FB)	Usability of recycled plastics by protection with functional barriers for indirect food contact (INRA, P08)

The work on paper and board was supported by materials and technical endorsement from industrial platform members and benefited from their advisory function.

1.3. Objectives of Section 2

Objectives 1, 3 and 5 for the project overall, were pertinent to the activities of Section 2 members. *viz.*:-

- (1) To facilitate industrial innovation and to harmonise legislative enforcement of new environmental packaging requirements stemming from the Directive 94/62/EEC on packaging and packaging waste, by:
 - (2)(PET relevant only)
 - (3) Generating a scientific understanding of the physico-chemical behaviour of chemical contaminants on paper and board fibres as a basis for safety evaluation and definition of criteria for the appropriate reuse of recycled fibres for food packaging.
 - (4)(functional barrier studies, from Section 3, to feed into Section 2 considerations)
 - (5) Proposing practical recommendations for appropriate legislation on recycled paper and board, including predictive tools for the evaluation of recycled food packaging applications.

1.4. Subtasks of Section 2 on paper and board

Section 2 Paper & Board	
5	Literature review of contaminants on recycled fibres and limited experimental confirmation
6	Definition of model contaminants and P&B test samples
7	Systematic interaction studies
7.1	Adsorption isotherms using plain P&B
7.2	Adsorption isotherms and permeation tests using coated P&B
7.3	Mass transfer into foods and/or food simulants
8	Development and verification of a physico-mathematical model
9	Definition of criteria for the safe reuse of recycled fibres for food packaging
10	Conclusions on test strategies for recycled P&B fibres intended for food contact

2 Summary of findings and conclusions

Task 5. Literature review of contaminants on recycled fibres and limited experimental confirmation

Task 5 introduction and objectives

Taking the knowledge about chemical contaminants occurring in recycled fibres into account, the aim of this subtask was to establish the basis for selection of a representative set of model contaminants to be used in the interaction studies (see subtask 6). Based on the literature, a compilation of contaminants which have been found on recycled fibres was drawn-up. The compilation included a quantitative dimension to identify the major or more relevant contaminants. To verify the picture obtained, samples of recycled fibres from a small number of sources was analysed.

Task 5 findings

A large proportion of the feedstock for paper and board production in Europe, is recycled fibres. Figures available for the EU member states before the last enlargement, indicate between 25 and 75% use of recycled fibres [7]. The figures for direct and indirect contact with food are not known and they will be lower than these figures for all applications. Nevertheless, the volume of recycled fibres going into food packaging is very significant - as any examination of the things we buy as consumers will confirm.

Recycled fibres are generally categorised into four grades ranging from paper mill broke (Grade 1) to mixed used papers and boards (Grade 4). Waste paper from post-consumer domestic waste, hospital waste or non-food processing industrial waste, is not used. Before it is re-made into packaging, wastepaper is reduced to its constituent fibres and undergoes a basic washing process. In all cases, wastepaper is suspended in water and unwanted particulate components (e.g. stitches, clasps, adhesives, plastics, cord, wood or wet-strength paper and water-soluble components) are removed from the fibres by screening and de-watering. Un-wanted chemical components (e.g. printing inks, certain adhesives such as hot-melt and certain plastics such as varnishes) require special cleaning processes. These include: -fractionation by washing, de-inking by washing and floatation, bleaching with hydrogen peroxide or hydrosulphite, oxygen or ozone treatment, steam treatment and enzymatic treatment.

From the above it can be realised that the potential for the deliberate or adventitious introduction of chemicals into paper and board are numerous [16]. It is well known that pentachlorophenol and chloroanisoles can be a problem (from treated timber) and that polychlorinated biphenyls [13] can be contaminants from carbonless copy paper. More recently, there was a world-wide problem with the presence of diisopropyl-naphthalene (DiPN) isomer mixtures. DiPNs are widely used in ink for ink-jet printers and as solvents (as PCB substitutes) used in the preparation of special papers such as carbonless and thermal copy paper. DiPNs were detected in a range of food packaged in recycled cartonboard including even dry foods like rice and pasta [8].

A comprehensive literature review had been prepared in Year 1 and it was disseminated widely to more than 160 interested parties who were participants at the symposium '*Paper in Contact with Foodstuffs*' organised by Pira International (Edinburgh UK, December 1999). This was done with a request to conference participants to bring to our attention any studies or data that were not included in the review of the published literature. Just

two replies giving further information were received and this additional information was included in a revision of the review document. This suggested at the time that our understanding of the actual and likely contaminants of recycled paper and board materials was quite complete with no major omissions. A second literature search was conducted later in the project to update our knowledge. This update again revealed no significant new information. This information about the actual and likely contaminants of recycled paper and board materials was used to guide the selection of model substances and the concentration ranges used in the experimental work conducted in Section 2 by the project partners.

Limited experimental work was conducted to confirm the actual and likely contaminants. Thus, SFE (supercritical fluid extraction) as well as solvent extraction of the test samples (described below) was followed by GC-MS analysis, which detected diethylphthalate, diisopropylnaphthalenes, diisobutyl- and dibutyl phthalate, dioctyladipate, and di(2-ethylhexylphthalate) in the extracts.

Task 6. Definition of model contaminants and P&B test samples

Task 6 introduction and objectives

From subtask 5 it was evident that there are very many potential contaminants of recovered paper. On the other hand, there may be production stages in the treatment of recovered fibres where contaminants can be removed quite effectively. The contaminants most likely to resist washing and so may carry-through to packaging made from recycled fibres, are substances that are poorly water-soluble and are fibre-retentive - that is they have an attraction for the chemical groups on the surface of the paper fibres. From the list of actual contaminants obtained from subtask 5 a set of not more than 10 model contaminants was selected with the aim to cover the full range of chemical structure, polarity, molecular weight, volatility etc. This selection was made taking as far as possible model contaminants as proposed by the ILSI document as well as FDA guidelines into account. However, due to the P&B specific features and the different character compared to plastics, the choice of model contaminants for the interaction studies needed special care. As another criterion the ease of their analytical determination was taken into account - having in mind that numerous analyses were carried out within the work of subtask 7 and, more importantly, the fact that these model contaminants were ultimately to be widely used for testing P&B recycling processes. Along with this selection of model contaminants, a series of up to 10 market-typical P&B samples were selected including both uncoated as well as coated and plastic-laminated P&B. These are then the chemicals and the packaging materials that will be used for the interaction studies under subtask 7.

Task 6.1 results. Selection of model contaminants



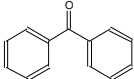
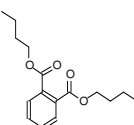
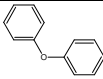
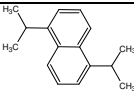
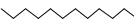
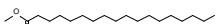

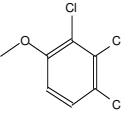
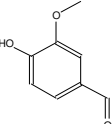
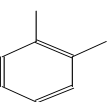
A large number of potential model contaminants were proposed initially and then an agreed list of model contaminants came from these discussions. The substances are tabled below.

It will be seen from inspection of the table that the model substances cover a range of chemical types and physical properties. Special care was taken to ensure that the selection was acceptable to the Section 3 members who have the task of studying and understanding functional barrier properties. The set is also in large agreement with the FDA list from a

chemical structure point of view but contains even more model contaminants of interest in the project's context.

Many of the substances selected, had the additional benefit that not only were they convenient model substances but they were also common contaminants of recycled paper and board packaging materials. Of special note are benzophenone, dibutylphthalate, diisopropylnaphthalenes and trichloroanisole, which have been reported in numerous publications and reports and being contaminants of recycled paper and board and having the potential to migrate to foods and food simulants.

Final selection of organic model contaminants for paper and board interaction studies

Nr	Substance	Formula	Structure	Mol. wgt.	Boiling point °C
1	Acetophenone	C ₈ H ₈ O		120	203
2	Benzoic acid	C ₇ H ₆ O ₂		122	249
3	Benzophenone	C ₁₃ H ₁₀ O		182	306
4	Dibutylphthalate	C ₁₆ H ₂₂ O ₄		278	340
5	Diphenyl ether	C ₁₂ H ₁₀ O		170	256
6	Diisopropyl-naphthalenes, isomeric mix	C ₁₆ H ₂₀		212	295
7	n-Dodecane	C ₁₂ H ₂₆		170	216
8	Methyl stearate	C ₁₉ H ₃₈ O ₂		298	450
9	Naphthalene	C ₁₀ H ₈		128	218
10	2,3,4-Trichloroanisole	C ₇ H ₅ Cl ₃ O		211	240-250
11	Vanillin	C ₈ H ₈ O ₃		152	285
12	<i>o</i> -Xylene	C ₈ H ₁₀		106	144

Task 6.2 results. Selection, procurement and characterisation of the P&B test samples

Selection and procurement

The industry members of the project were contacted and asked to identify suitable samples for the experimental part of the project. They were asked to nominate paper samples from new fibres as well as from recycled fibres, with and without surface coating.

From this consultation, a number of P&B test samples were proposed and were agreed by Section members. Care was taken to ensure that the set of paper and board materials were industrially relevant as potential food packaging materials and were economically important. Furthermore, care was taken to identify samples, which differ in those properties that may influence the adsorption behaviour of the fibre phase. Thus the samples include several different types of paper qualities e.g. liner, fluting, tissue, board and a thin mono-glazed paper (MG-paper). Further the samples cover a broad range of grammages from 33 to 522 g/m². Six of the samples contain mainly recycled fibres, four samples contain a smaller amount of recycled fibres and five samples were made from only new fibres. Since the pulp quality may also have an influence papers made from different types of pulp were represented e.g. unbleached kraft, bleached kraft, neutral sulphite (NSSC) and chemi-thermomechanical pulp (CTMP).

Four of the samples were plastic coated (PE, Al+PE, PET) one sample had a dispersion coating and two samples were clay coated. Only the samples with plastic coating were intended for liquid foodstuffs. In order to simplify the evaluation of the influence of the coating the same paper samples had, when possible, been collected before and after the coating process.

These samples were then procured from industry and set-aside in large quantities, stored in a freezer, sufficient for the duration of the project. Specimens were then distributed to Partners in Section 2 for their experimental studies.

P&B samples fused for the experimental studies

Sample code	Type	Pulp	Recycled %	Surface treatment	Chemicals added	Grammage (g/m ²)	Thickness (µm)	Density (kg/m ³)
R1	Testliner	Recycled	100	(none applied)	starch 7 % sizing 0,7 %	128	191	667
R2	Liner	Unbl kraft + recycled	10-30	(none applied)		178	234	761
R3	Liner	Unbl kraft + recycled	10-30	dispersion coating (SB latex + wax)		145	188	774
R4	Liner	Unbl kraft + recycled	10-30	LDPE 15 g/m ² + PET 17 g/m ²	sized	180	214	842
R5	Fluting	NSSC (birch)+ recycl.	30	(none applied)		107	209	511
R6	MG-Paper	Bleached kraft	0	(none applied)	sized	72	82	868
R7	Toilet Tissue	Recycled (deinked)	100	(none applied)		34	145	232
R8	Kitchen Towel	Recycled	100	(none applied)		47	188	248
R9	Liquid board triplex	Bl. kraft + CTMP	0	(none applied)	AKD	273	486	563
R10	Liquid board triplex (= R9)	Bl. kraft + CTMP	0	inside 25; outside 16 g/m ² LDPE	AKD	314	508	617
R11	Liquid board triplex	Bl. kraft + CTMP	0	(none applied)	AKD	267	478	559
R12	Liquid board triplex (= R11)	Bl. kraft + CTMP	0	inside PE 35/Al 17/ PE 26; outside PE 16 g/m ²	AKD	358	549	652
R13	White lined chipboard	Recycled (GD2)	100	clay coating 12-18 g/m ²	sized	497	719	691
R14	White lined chipboard (= R13)	Recycled (GD2)	100	clay coating 12-18 g/m ² + PE 25 g/m ²		522	739	707
R15	Chipboard	Recycled	100	(none applied)	sized	406	576	706

Characterisation of the P&B test samples

For further characterisation of the samples, the kappa number, indicating the lignin content, was determined by permanganate oxidation. This was done because it was considered possible that the lignin content may influence the interaction of the material with chemical substances.

Similarly, since the specific area of the samples may influence the adsorption of compounds to the fibres, the porosity was determined for some samples using mercury intrusion porosimetry. Also, some of the samples were studied by microscopy to show the porous structure of the paper.

All paper samples without a plastic coating, 10 in total, were extracted using ASE (accelerated solvent extraction). The extracts were analysed by GC-MS (gas chromatography coupled to mass spectrometry) and the molecular weight distribution of the extract was determined by SEC (size exclusion chromatography).

Task 7. Systematic interaction studies

Task 7 introduction and objectives

The sorption-desorption and the consequent migration behaviour of model contaminants interacting with P&B were especially interesting to measure and model. This task had therefore the aim to produce a full data set on the adsorption and mobility behaviour of the model contaminants in interaction with the P&B samples and this under different conditions such as temperature and moisture content. The data set obtained here formed the basis for the development of the mathematical model under subtask 8.

Tasks 7.1 and 7.2. Adsorption isotherms using plain P&B and coated P&B

Sub-task introduction and objectives

When leaching effects, i.e. direct contact of a liquid with paper and board, can be excluded (and this practically always the case in food packaging with plain P&B) then the vapour pressure p (in bar) of a contaminant in the gas phase over P&B and its corresponding concentration on the P&B, $c_{P\&B}$, can be considered to be crucial parameters for the transfer of the contaminant to a (dry) foodstuff. The aim of this subtask was therefore, to establish this relationship between p and $c_{P\&B}$ for the model contaminants and P/B test samples under a number of different test temperatures, covering the time-dependency of this partitioning process. These data along with the model to be established under subtask 8, would allow us to take measured $c_{P\&B}$ values in the future and feed directly the corresponding p value into the model and so to calculate the resulting migration to a food or food simulant. The contaminant's solubility in the foodstuff is the other decisive parameter that dictates its mass transfer. This was taken, as a worse-case consideration, to be always very high as a limiting case. This assumption was refined in subtask 7.3. The influence of a polymeric coating or plastic layer on the mass transfer of contaminants from P/B into food (simulant) was investigated also. For this, any partitioning effects between P/B and the polymer as well as the permeation process through the polymer, was considered.

Tasks 7.2 findings

An experimental design for determination of the adsorption isotherms between the selected model contaminants and plain and coated P/B samples was proposed and agreed by all Section 2 members as a working template. Since a large number of experiments were required for the determination of the physico-chemical parameters required within the project, the tasks were allocated to Partners 01, 03, 04, 05, 06 and 07. Agreement of the working template meant that all experimentation was conducted using agreed methodology and all experimental data were calculated and reported using an agreed format. This ensured consistency across the project and allowed a measure of cross-checking of the results and conclusions.

Adsorption isotherms were established for the range of model contaminant substances and for the 14 paper and board materials under study, by measuring the equilibrium partitioning of substance between the P/B phase and air, as a function of concentration and temperature. Results were calculated on a mass/volume concentration basis. Experiments were conducted at temperatures of 25, 50, 75, 100, 125 and 150°C (exact choice depended on the type of paper) using times of up to 120 minutes, to check that the equilibrium position was reached.

As expected, because the boiling point of many of the substances was above 200°C, they partitioned strongly into the condensed phase of the paper/board. The equilibrium concentration in the headspace gas phase depended on the boiling point of the substances and the test temperature. There were no significant differences noted between the different uncoated samples tested. That is, different compositions of the P/B samples made no significant difference in the distribution coefficients $K_{B/A}$ measured. This means that after allowing for the grammage of the samples (mass per unit area) they behaved essentially identically. In contrast, and as expected, board samples coated with a plastic layer – polyethylene or polyethyleneterephthalate - gave a reduction in the vapour phase concentration of substances compared to their uncoated counterparts tested under the same conditions.

The shape of the absorption isotherms was classical. A very important finding was that the linear range of the absorption isotherms covered the range of concentration of migrants in P/B that occur in practice,. In this linear range, the value of $K_{B/A}$ is approximately constant.

The distribution coefficients determined were fed-into the module on mathematical modelling (section 8 below).

Task 7.3. Mass transfer into foods and/or food simulants

Task 7.3 introduction and objectives

In this subtask, the time-dependency and the extent of the migration of model contaminants from uncoated and coated P&B samples into food (simulants) were measured under different test conditions. The aim was to verify the assumption of high solubility in the food (simulants) and to establish the scientific basis for the partition coefficient for the model contaminants between uncoated or coated P&B and food (simulant) as the other crucial mass transfer parameter as already mentioned above (see description of subtask 7.1) which contains the contaminant's solubility in the foodstuff. These experiments gave

evidence about the most suitable food simulant - that means a simulant which exhibits the most unfavourable partitioning compared to foodstuffs which in turn leads to inclusion of safety margins in the model to be established. Tenax® seems to be a very promising candidate for simulation of dry food behaviour.

Tests conducted

Migration tests were conducted using the impregnated paper/board materials placed in contact with the simulant Tenax (powdered polyphenylene oxide) and into the dry foods cookies, flour, milk powder, noodles, salt, semolina, soup powder, sugar and icing sugar. The test temperatures ranged from ambient temperature (ca. 23°C) up to 100°C. Sampling was conducted at different timepoints so that migration could be monitored until equilibrium was reached and so that kinetic migration curves could be constructed.

Calculation of results

Migration levels were calculated in two different ways. For the first, the mass of substance migrated to food/simulant was determined (using chemical analysis) and expressed as a percentage of the starting amount of substance in the impregnated paper/board. It was observed however, that especially for the more volatile substances at the higher test temperatures, there was not a mass balance found at the end of the exposure period. The amount of substance found migrated to the food/simulant plus the amount remaining in the paper/board, was less than the starting amount. The substances themselves were chemically inert under the conditions of the test. Consequently, it can be concluded that some fraction of the substance was lost from the test system. Of course, if this could occur during migration testing under carefully controlled conditions, then these fugitive losses could occur also with foods placed in contact with every-day packaging materials. Because the mathematical modelling would at first assume 100% efficient 'trapping' of substance migrating out of a paper/board sample, migration results were calculated in a second way too. In this calculation, the amount of substance remaining in the test specimen of paper/board after the exposure period was determined and the migration value was expressed as the fraction lost, as a percentage of the starting content. This would be the worst-case migration value.

Migration kinetics – general observations

What was immediately clear from all the migration tests was just how rapid migration is from the paper/board materials. There was efficient and rapid transfer with equilibration (max migration) established after a short period of time. As an example, under test conditions of 20°C even methyl stearate – which was the largest molecule studied and the slowest to migrate – had plateaued after 10 days, at 62% migration into Tenax and the highest migration was seen for acetophenone which plateaued-out at 93% migration.

The speed of migration to equilibrium can be summarised as:-

Test temperature	Equilibration time
20-25°C	2-10 days
40°C	1-3 days
50°C	1-2 days
60°C	5 hr

75°C	2-5 hours
100°C	ca. 1 hr

The kinetics depended on the grammage of the paper/board sample – tissue paper for example equilibrated very fast – and also on the nature (molecular size and volatility) of the substance.

Migration to Tenax compared with foodstuffs

The rate of migration into Tenax was nearly always greater than into the dry foodstuffs cookies, flour, milk powder, noodles, salt, semolina, soup powder, sugar and icing sugar, at the same test conditions. Similarly, the final equilibrium partitioning concentration between impregnated board and Tenax simulant, $K_{B/T}$ was always, at least one-order of magnitude less than the partitioning between board and foodstuff, $K_{B/F}$, indicating again that Tenax is a good simulant insofar as it is more severe than food. There were only a few exceptions to these general rules. For example, the extractive power of dry soup was apparently higher than Tenax at 100°C whereas it was comparable at 40°C. One interpretation of this observation is that some of the migrating chemicals are subsequently desorbing to some extent from the Tenax at the higher temperature. A more likely explanation is that the test condition of 100°C that was applied for experimental reasons, caused the texture of the dry soup powder to change. As a consequence, the comparison at this high temperature is not relevant because the dry soup is not a powder anymore.

Some technical difficulties were seen with the dry foods tested. The fat in the milk powder melted at high temperature and soaked into the paper/board samples. The reproducibility of analysis was relatively poor for soup powder. No migration was seen into salt - clearly, this inorganic solid has little or no affinity of the organic substances used in this work. There were analytical difficulties in extracting migrants out of sugar for analysis. Consequently, none of the dry foods tested can be recommended as an alternative to e.g. Tenax as general-purpose simulant of dry foods.

Effect of paper/board composition

There was no significant difference between the migration properties of paper/board samples with different compositions. So, for example, the rate and extent of migration from clay coated board was the same as from the uncoated board.

Effect of temperature on partition coefficients

The equilibrium partition coefficient $K_{B/T}$ was almost independent of temperature but there was evidence that it decreased slightly with increasing temperature e.g. at 60°C compared to 23°C. This means that the substances had a slightly greater affinity for the board relative to Tenax, at the higher temp. Two possible explanations are proposed for this.

- hemicellulose polymers pass their glass transition temp at 40-50°C and melt, so increasing the absorption affinity of the board,
- or, water absorbed on the fibre surface evaporates, changing the polarity of the surface and leading to an increase in absorption affinity.

The experimental evidence does not allow any firm decision between these two possibilities. Given that sorption isotherms and migration behaviour seemed to be

insensitive to the composition of the paper/board samples, the first explanation seems less likely. The second explanation is consistent with the general every-day observation that paper/board (especially 'brown' grades) release a faint smell when wetted – desorption due to wetting.

Effect of 'barrier' layers

The presence of a layer of aluminium foil laminated to the board, prevented all migration from the impregnated samples. Similarly, a PET layer prevented all migration, even at 100°C. These two materials, aluminium and PET, can be considered to be impermeable barriers to migration under the conditions of test employed here.

In contrast, a PE coating was not found to be a complete barrier. Rather, the PE coating caused the migration to be delayed and take longer to come to steady-state; but migration still occurred. The PE coating is rather permeable but reduces migration by providing a 'sink' or 'trap' for the organic substances. Thus, the substances partition strongly from the impregnated board into the PE layer. This reduces their chemical activity and so slows migration into food/simulant.

'Native' DiPN (i.e. that intrinsic to a recycled board) displayed kinetic behaviour that differed from DiPN that was incorporated into samples by solvent impregnation. This is interpreted as the 'native' DiPN being present as the encapsulated form, as microcapsules from the recycling of carbonless copy papers. The capsule wall impeded migration but did not prevent it.

The barrier properties of unimpregnated board were tested using a sandwich configuration of impregnated board // blank board // Tenax simulant. The test conditions were exposure at 23 to 50°C for between 1 to 3 days. Under these test conditions, the most fugitive substances – acetophenone, tridecane and naphthalene – migrated clear through the board and into the Tenax simulant with a high percentage transfer. Less fugitive substances – diisopropyl-naphthalene and trichloroanisole - partitioned into the middle board layer and only a modest fraction passed through into the simulant. Finally, the least fugitive substances – vanillin and dibutylphthalate - partitioned somewhat into the middle board layer but there was no measurable migration through the board and into the Tenax simulant. These findings are very relevant not only to the migration from recycled paper/board materials but also to a consideration of the behaviour of substances placed on the 'outside' non-contact surface of a paper/board material e.g. in printing inks, varnishes and adhesives.

A more detailed description of barrier behaviour is given by Section 3 ('Functional barrier') of this project.

Task 8. Development and verification of a physico-mathematical model

Task 8 introduction and objectives

Based on literature data and those produced under task 7 a mathematical model was developed from that already available for the migration prediction from polymers into food. The principle of this model will be such that, for a given initial concentration of a contaminant in P&B (which can relatively easily be measured) and under consideration of

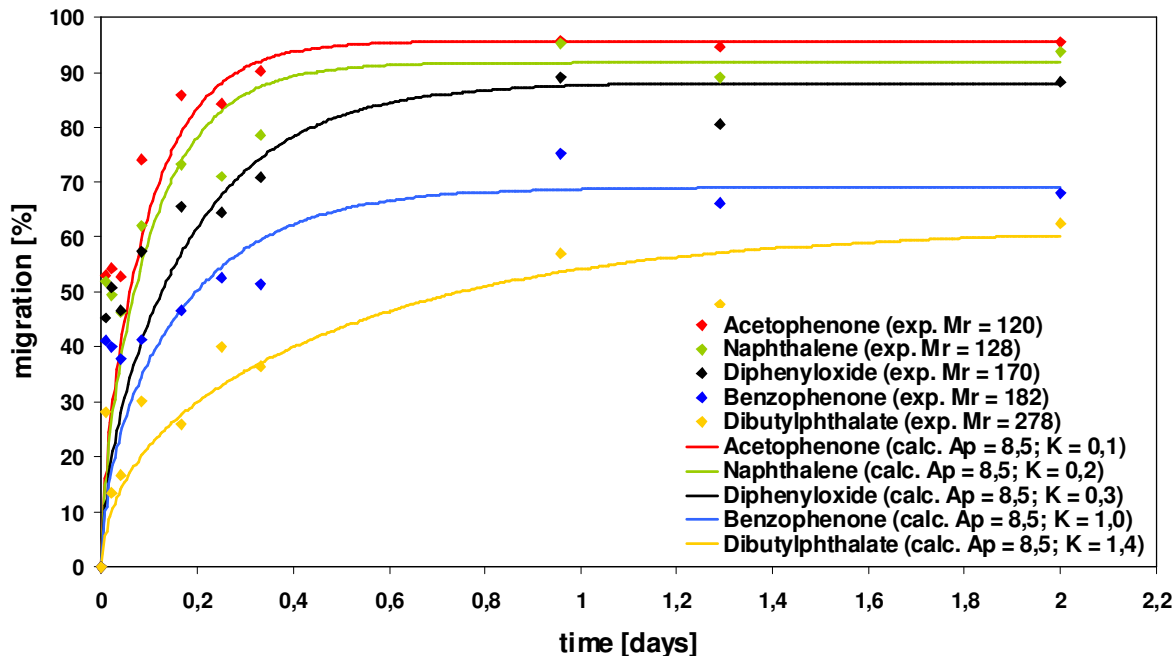
the respective food packaging application parameters, a corresponding maximum value for the migration into a foodstuff can be calculated (or *vice versa*). In this way a measured concentration in P&B will quickly allow an estimate whether a given regulatory migration limit in food could be exceeded or not.

Task 8 findings

A modelling procedure which had been validated for polyolefin plastics was applied to describing the migration behaviour from paper/board into food/simulants. The experimental kinetic migration data were ‘fitted’ by varying D_B , A_P and $K_{B/F}$ values to achieve the best fit, using MIGRATEST Lite 2000 software specifically developed for such calculations. D_B , is the substance-specific diffusion coefficient in the board. A_P is a pre-exponential term which describes the intrinsic resistance that the paper/board presents to migration. $K_{B/F}$ is the equilibrium partition coefficient of the substance between the paper/board and the food/simulant.

Using this mathematic model with numerical analysis, the experimental migration data could be fitted well. Estimated D_B , A_P and $K_{B/F}$ values were obtained by fitting the migration kinetic curves. This was done for Tenax, noodles, sugar and semolina, for 8 different P/B samples. The following figure gives an example of the fit that was obtained in these cases.

Migration of model contaminants from sample R2 (liner board containing unbleached kraft with a recycled content) into Tenax at 50°C (dots: experimental data and lines: calculated values).



As examples of the range of values of D_B , A_P and $K_{B/F}$ values needed to fit the migration data, the following table describes the situation for one substance, trichloroanisole, migrating from 8 paper/board samples into Tenax and into different foods, at a variety of temperatures.

Table. Fundamental physical constants (D_B , A_P , $K_{B,F}$ values) determined by fitting the experimental TCA migration data with the solution of the diffusion equation

Sample	Simulant <i>Food</i>	T [°C]	D_B [cm ² /s]	A_P	$K_{B,F}$	Comments
R1	Tenax	50 °C	5,16 E-8	10,5	1,0	Liner
	<i>Noodles</i>	50 °C	1,15 E-9	9,0	12,5	
R2	Tenax	50 °C	6,99 E-9	8,5	0,5	Liner
	<i>Noodles</i>	50 °C	4,24 E-9	8,0	15,5	
R5	Tenax	70 °C	1,03 E-8	7,0	0,5	Fluting
	<i>Semolina</i>	70 °C	1,03 E-8	7,0	45,0	
R6	Tenax	60 °C	1,84 E-8	8,5	2,0	MG-Paper
R7	Tenax	60 °C	1,36 E-7	10,5	3,0	Tissue
R8	Tenax	70 °C	2,79 E-8	8,0	6,0	Kitchen Towel
	<i>Semolina</i>	70 °C	2,79 E-8	8,0	85,0	
R9	Tenax	60 °C	6,11 E-7	12,0	0,2	Liquid board triplex
	<i>Sugar</i>	50 °C	5,16 E-8	10,5	3,5	
R13	Tenax	60 °C	6,11 E-7	12,0	0,01	Chipboard
	<i>Sugar</i>	50 °C	2,31 E-7	12,0	5,0	

When comparing the migration behaviour of different paper and board samples for one substance, it is clear from the parameters summarized in the table that there is a marked difference between the samples tested insofar as a range of D_B , A_P and $K_{B/F}$ values were required to fit the data, albeit that a variety of test temperatures were used.

Task 9. Definition of criteria for the safe reuse of recycled fibres for food packaging

Task 9 Introduction and objectives

With the relationships established in tasks 7 and 8 between concentrations in P/B and its resulting concentration in food, it should be possible to define maximum allowable concentrations on P/B (i.e. compositional limits, QM) if maximum admissible concentrations in foodstuffs (i.e. specific migration limits, SMLs) are prescribed by the legislator. For a given limit in food the corresponding maximum concentration on P/B depends on several parameters such as fill and storage conditions of the packed food as well as the type and thickness of any coating or plastic layer etc. This should be taken into account by the model.

Task 9 Findings

The 'no-migration' concept

As a general rule, migration is proportional to the starting concentration in the packaging. It has been suggested that for some combinations of substances and materials, a so-called threshold effect operates such that below a minimum concentration in the packaging then no migration occurs. This has been suggested for vinyl chloride monomer (VCM) migrating out of polyvinylchloride (PVC), for example. If such a threshold effect really does operate, it would require that a certain fraction of the substance is 'locked' into the packaging matrix and is immobilised so that it cannot migrate. Any substance above the critical concentration would, in contrast, exist in more accessible locations in the matrix and so be available for migration. It is difficult to explain such a postulate in terms of material structure and molecule-structure interactions. However, since paper/board materials are more heterogeneous at the microscopic level than plastics, the 'no-migration threshold of composition' was worthy of consideration.

There was, however, a linear migration behaviour for different levels of initial content of model substances in the paper/board. This means that, within the applied fortification concentrations, there was no evidence of a cut-off value, a so-called threshold content below which migration was zero.

Possibility to reduce migration by modifying the composition of paper/board

Paper consists mainly of fibres and fillers. The cellulose fibres have repeat units of glucose residues and are very hydrophilic but are largely non-ionic. The lignin component of paper, on the other hand, has aromatic phenolic repeat units with both hydrophilic and hydrophobic domains and both are anionic in character. This gives an overall negative charge to the surface of paper fibres due to the carboxy groups from the carbohydrates and the hydroxy groups of the lignins. In principle, positively charged species (i.e. cationic) and also electron-deficient substances (e.g. aromatics, halogenated) will experience a net attraction to the surface and will be fibre-retentive whereas anionics and electron-rich substances will suffer a net repulsion. It is pertinent that 10 of the 12 model substances selected as model contaminants, on the basis of known contaminants of recycled paper and board (Table, section 6.1) were aromatic substances. The fact that there were no significant differences noted between the different uncoated paper/board samples tested, in the distribution coefficients $K_{B/A}$ measured, means that there is no obvious way to moderate the migration properties of P/B samples by modifying the basic composition – other than to introduce a barrier layer by, for example, laminating to a plastic film.

Criteria for the reuse of recycled fibres for food packaging

Depending on the test temperature used (see table in 7.3) the migration was in general rapid and extensive. Since migration will occur when there is direct contact between the Migration was rapid and extensive. Since migration will occur when there is direct contact between the paper/board and a powdered (or small particle size) food/simulant, the following options are available (individually or in combination) to keep migration within acceptable limits:-

- keep the initial content of potential migrants in the P/B within limits
 - ⇒ source control
 - ⇒ sorting
 - ⇒ effective cleaning
 - ⇒ frequent testing of batches/lots
- use a barrier layer to prevent or slow migration
- use P/B only in indirect contact applications and/or at low temperature.

Relevant to this last bullet point, a recent study of benzophenone migration from cartonboard has assessed the relative migration levels seen under different contact conditions of retail foods [24]. For direct contact and room temperature storage, the average mass fraction migration was 16.1%. The average migration at room temperature storage but with indirect contact was 6-fold lower at 2.7%. The average migration with direct contact but with chilled or frozen storage was again 6-fold lower at 2.6%. Thus, the benefits of a lower storage temperature are the same as the benefits of making only indirect contact. Finally, the average migration with both indirect contact and with chilled or frozen storage was only 0.4% and this is 40-times lower than the room temperature/direct contact average. This shows that to a good approximation, the attenuation effects of indirect contact and of low temperature storage are cumulative; with a 6-fold reduction for indirect contact compared with direct contact, a 6-fold reduction for chilled/frozen storage compared with ambient storage, and a $6 \times 6 \approx 40$ -fold reduction for the two contact conditions combined [24].

An possible alternative to the frequent testing of batches/lots of recycled paper, is a one-off verification of the clean-up capabilities of the recycling process using a challenge-test as recommended for plastics (both by USA and Europe) and for paper by the US-FDA. At the 3rd plenary meeting the project partners received a presentation from Dr Christina Paquette from the US-FDA entitled 'Recycled paper in contact with food'. The presentation and the discussion that followed gave the project members a better understanding of the FDA requirements and thinking in this area. The FDA recommends a challenge test of a recycling operation using high levels of model contaminants. The intention is that this, coupled with effective source control, reduces greatly the need for testing the final product of recycled paper/board. However, during discussions with FDA it appeared that the challenge test is performed by very few US paper industries. This was substantiated by the European industry partners in this project who stated that challenge testing within a paper mill is extremely difficult or even impossible and the transferability of pilot plant challenge test results to a running industrial technology may be error-prone and misleading.

Task 10. Conclusions on test strategies for recycled P&B fibres intended for food contact

Task 10 introduction and objectives

The objective of this section of work was to use all the knowledge elaborated so far, to recommend if possible test strategies for recycled and for virgin fibres, that are economic whilst simultaneously safe-guarding consumers .

Task 10 recommendations

What is clear from all the results that have been obtained, is that the migration kinetics follow well-known laws. For all the paper/board test materials, for all the model substances, and for all the food and food simulants studied, and at temperatures of 40°C and above, migration is dominated by partitioning behaviour and diffusion constants are less important. On the other hand, at temperature around room temperature, diffusion constants play more of a role, especially for larger molecules. It can therefore be reasonably expected that at temperatures below room temperature migration is also diffusion controlled. This is consistent with the above discussion on the last bullet point in context with the options to minimise migration.

To fit the migration kinetics, applicable A_p values ranged from 7 to 12. However, in nearly every case migration equilibrium was reached rapidly, within 10 days at ambient temperature and within 2 days at higher temperatures. In determining the final (equilibrium) migration levels, the affinity of the different substances for the paper/board relative to the nature of the food, as expressed by the partition coefficient $K_{B/F}$ was found to be crucial. For Tenax the K values ranged between 0.01 and 6 whereas for foodstuffs a range between 3.5 and 85 was applicable. In comparison between Tenax and foodstuffs the partition coefficients between paper or board and Tenax are always approximate one order of magnitude smaller than the partition coefficients between paper or board and real foodstuffs. From these results one can conclude that Tenax is a suitable food simulant for testing migration from paper or board samples into foodstuffs - fulfilling the general safety requirement that the migration determined using Tenax is always higher than into foodstuffs.

At equilibrium, migration levels were typically in the range 50-100% (worst-case, migration losses from the P/B) or in the range 20-100% (measured in the food/simulant). Migration to Tenax was higher than to foods, with reduction factors of 1-5. However, migration was also simply a factor of 1-5 less than the initial content in the paper/board. Thus, for intimate contact with dry foods/simulants (e.g. powdered) at room temperature and above, there seems little point in determining migration to a simulant and then applying a reduction factor. Determining the initial content and applying a similar factor or modelling is both more straightforward and quicker, and does not introduce any more uncertainty in the validity of the test result. However, for temperatures at ca. 40°C and higher there is no strong need to apply kinetic migration models since the migration level is in the first place not determined by kinetics but by thermodynamics (at equilibrium). The kinetic model appears to be useful in describing short-term contact at ambient temperature and above – e.g. fast foods – and may be of even higher importance for contact temperatures below room temperature.

Future research needs

- analogous studies as carried out in this project but at lower spiking levels to investigate the no-migration possibility
- more intensive studies focusing on the migration of 'native' P&B constituents/contaminants to verify the migration model
- studies of the partitioning behaviour of substances into solid and dry foods, especially chilled and frozen
- extension of the kinetic migration modelling to include storage of food in paper/board packaging at refrigerated and freezer temperatures

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