**SATURATED AND AROMATIC MINERAL OIL HYDROCARBONS
FROM PAPERBOARD FOOD PACKAGING: ESTIMATION OF
LONG-TERM MIGRATION FROM CONTENTS IN THE
PAPERBOARD & DATA ON BOXES FROM THE MARKET**

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**SATURATED AND AROMATIC MINERAL OIL HYDROCARBONS FROM
PAPERBOARD FOOD PACKAGING: ESTIMATION OF LONG-TERM MIGRATION
FROM CONTENTS IN THE PAPERBOARD & DATA ON BOXES FROM THE MARKET**

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Abstract

In the absence of a functional barrier, mineral oil hydrocarbons from printing inks and recycled fibers tend to migrate from paper-based food packaging materials through the gas phase into dry food. Concentrations easily far exceed the limit derived from the Acceptable Daily Intake (ADI) of the Joint FAO/WHO Expert Committee on Food Additives (JECFA). Since estimation of long-term migration into the food by testing at 40°C for 10 days is difficult, it seems preferable (and easier) to use the mineral oil content in the paperboard. Evaporation experiments showed that hydrocarbons eluted up to about n-C₂₄ are sufficiently volatile for relevant migration into dry food: in worst case situations about 80% migrate into the packed food. The extraction of the paperboard was optimized to give good recovery of the relevant hydrocarbons, but discriminate against those of high molecular mass which tend to disturb gas chromatographic analysis in on-line coupled normal phase HPLC-GC-FID. Even though some of the relevant hydrocarbons had already evaporated, the average concentration of <C₂₄ mineral oil saturated hydrocarbons (MOSH) in the paperboard boxes of 102 products from the Swiss and Italian market was 626 mg/kg. Nearly 15% of investigated boxes still contained more than 1000 mg kg⁻¹ <C₂₄ MOSH up to over 3000 mg kg⁻¹ (maximum, 3500 mg kg⁻¹). This amount of MOSH in the board have the potential of contaminating the packed food at a level exceeding the limit, derived from the JECFA ADI, hundreds of times.

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Keywords: mineral oil saturated hydrocarbons (MOSH); mineral oil aromatic hydrocarbons (MOAH); recycled paperboard; printing inks; migration from food packaging; on-line HPLC-GC-FID analysis.

Introduction

Paper-based food packaging materials tend to contain contaminants (e.g. Binderup et al. 2002, Ozaki et al. 2004, Sturaro et al. 2006, de Fátima Poças and Hogg 2007, EU Biosafepaper project), among them mineral oils. Here mineral oil saturated hydrocarbons (MOSH), including paraffins (straight chain and branched alkanes) and cyclic naphthenes are distinguished from mineral oil aromatic hydrocarbons (MOAH). In contrast to the polyaromatic hydrocarbons (PAH) commonly analyzed, the MOAH are largely alkylated (Grob et al. 1991a, Biedermann and Grob 2009, Biedermann et al. 2009).

No European legal limits for MOSH and MOAH have been established. For plastics (EU Directive 2002/72), the use of mineral oil products free of MOAH and with a high molecular mass (average of at least 480 Da, i.e. n-C₃₄, and a carbon number at the 5% distillation point of at least 25) is authorized without a specific migration limit. The mineral oils which are subject of this paper are of smaller molecular mass (Biedermann and Grob 2010) and fall into the categories for which JECFA specified a “temporary” ADI of 0-0.01 mg kg⁻¹ body weight (JECFA 2002). Assuming generally applied conventions, i.e. 60 kg body weight and 1 kg of food contaminated with the given substance being daily consumed, the Specific Migration Limit (SML) for these oils is calculated as 0.6 mg kg⁻¹ food. This JECFA evaluation was based on white mineral oils, refined to eliminate MOAH, whereas the mineral oils in recycled board and most printing inks are of technical grade, thus also contain MOAH.

The main sources of mineral oil in paperboard are offset printing inks, either directly applied for decorating the food packaging material or entering via recycling of fibers contaminated by mineral-oil-containing inks, primarily from newspaper (Biedermann et al. 2010). These mineral oils typically contain 15-20%, sometimes 50% MOAH (Biedermann and Grob 2010). For the transfer into dry food, direct contact is negligible. Migration is restricted to components of sufficient volatility to evaporate from the packaging material and recondense in the food (Shepherd 1982; Droz and Grob 1997; Jickells et al. 2005). The process depends on the vapor pressure (determining migration rate) and the partitioning between the packaging material and the food, but also on situational factors: from a box standing alone on a shelf, evaporated hydrocarbons are largely

removed into ambient air, whereas this is not possible for boxes packed into larger units and stacked on pallets. In the latter case, vapors are primarily transferred into the packed food unless there is an internal bag of a material stopping this migration.

For a worst case assumption, escape of vapors should be assumed to be negligible, i.e. the vapor pressure is likely to approach saturation in the air within the packs and between the packs.

Migration is driven towards equilibrium with the food. Triantafyllou and coworkers (2005) investigated this mechanism by determining the partitioning between paperboard and air and the uptake into model foods as a function of temperature. The partitioning coefficient depends on the properties of these materials. However, since the mass of the food exceeds that of the packaging material by a factor typically ranging from 5 to 25 (Fiselier et al. 2010), most of the hydrocarbons may end up in the food fairly independently of this partitioning coefficient.

For producers as well as enforcement authorities it is important to predict long-term migration from paperboard into foods (many products have shelf lives of 1-3 years). Migration from paper and board is often tested using modified polyphenylene oxide (MPPO – Tenax[®]) placed on the material during 10 d at 40°C (e.g. Aurela et al. 1999). MPPO may be considered as an adsorbent adequately simulating food, but the 10 d at 40°C do not reflect migration over up to several years at room temperature (RT). Such testing becomes even more equivocal if there is a barrier between the paperboard and the food - such as a plastic lamination on the paperboard or an internal bag acting as a weak functional barrier - slowing the transfer. In fact this type of barrier introduces a lag time with low migration until the migrant passed through this layer (Franz et al. 1996 and 1997; Piergiovanni et al. 1999; Feigenbaum et al. 2005). A low migration into MPPO after 10 d may then be misleading, as more substantial migration may only start later.

Here an alternative approach is proposed, based on the content in the paper or board. Prolonged storage under conditions preventing the escape of vapors to ambient atmosphere and the absence of an efficient barrier protecting the food causes a high proportion of the volatile hydrocarbons to be transferred to the food. The upper limit of molecular mass permitting relevant gas phase transfer is determined experimentally. This method is rapid and provides reliable worst case data.

In previous work, the upper limit of the mineral oil hydrocarbons migrating from paperboard into foods varied between C₂₀ and C₂₅ (partly published in Droz and Grob, 1997). Little was known about the age of the products. Since the more volatile components are transferred faster, the

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3 1 hydrocarbons found in young products range to lower carbon numbers than in aged packs, which
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5 2 was probably the main reason for the variation observed. Similar transfer was observed also in the
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7 3 hydrocarbons evaporation process from jute bags made with mineral batching oil (often used to
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9 4 contain raw foodstuff like nuts and beans). Comparing a new jute bag to an old one, the
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11 5 concentration of the hydrocarbons was diminished up to n-C₂₄ and the contaminants found in
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13 6 hazelnuts, chocolate, coffee and rice ranged to n-C₂₁, n-C₃₁, n-C₂₄ and n-C₂₁, respectively (Grob et
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15 7 al., 1991b). There was no certainty, however, that the migration from the jute bag was the only
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17 8 source of mineral oil contamination.
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20 10 Summerfield and Cooper (2001) investigated the migration of hydrocarbons and phthalates from
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22 11 paper products intended for food contact, using a mixture of dichloromethane and ethanol for the
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24 12 Soxhlet extraction of paperboard. Triantafyllou and coworkers (2002, 2005 and 2007) used ethanol
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26 13 at RT (5 min double extraction, 30 min, and 1 h, respectively). Schaefer et al. (2003) analyzed
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28 14 lubricants in food packaging materials, among which paraffins and wax esters, using *iso*-octane as
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33 17 This paper reports results with regard to the determination of the concentration of relevant MOSH
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35 18 and MOAH in paperboard. The range of hydrocarbons potentially migrating into dry food was
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37 19 investigated focusing on the first step of the transfer process, i.e. evaporation: the loss of
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39 20 hydrocarbons from paperboard was monitored during 180 d. The extraction of the paperboard was
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41 21 optimized to yield high recovery of these relevant hydrocarbons, but to discriminate against high
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43 22 molecular mass components tending to disturb GC analysis. The paperboard from 102 products
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45 23 sampled from the Italian and the Swiss market were analyzed for the potentially relevant MOSH
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47 24 and MOAH content.
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50 26 **Materials and Methods**

51 27 *Materials*

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53 28 Food samples packed in paperboard boxes were collected from the Italian and the Swiss retail
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55 29 market in spring and summer 2009. Only products without any kind of aluminum internal bag
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57 30 (aluminum foil or metalized plastic) were analyzed.
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60 32 Hexane (10 L) from Brenntag (Schweizerhall AG, Basel, Switzerland) was filtered through 400 g
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silica gel activated at 400°C (silica gel 60, 0.063-0.200 mm; Merck, Darmstadt, Germany) and

distilled before use. Technical grade methyl tert-butyl ether (MTBE) from Brenntag (Germany) was distilled before use. HPLC grade methanol, ethanol and dichloromethane were from J.T. Baker (Deventer, Holland). The dimethyl polysiloxane PS-255 was from Fluka (Buchs, Switzerland). White mineral oil centered on n-C₂₃, in the past used as release agent by a candy manufacturer, was used as external standard for recovery tests. MOSH and MOAH internal standard solutions were prepared as described by Biedermann et al. (2009).

Extraction of paper-based packaging

Chopped paperboard (1 g) was weighed into a 20 mL amber vial with PTFE-lined screw cap. After adding 10 µL of internal standard solution and 10 mL solvent, the vial was shaken on a vortex (Haidolph, Germany) and allowed to stand during various periods of time. Before injection, ethanol- if present - was removed from the extract by adding ca. 10 mL of water to 5 mL extract, vortexing and centrifuging. To prevent contamination, samples were handled without gloves; hand creams were avoided. Working up virgin fiber paperboard free of mineral oil verified the absence of sample contamination during manipulations.

Chromatographic analysis

MOSH and MOAH contents were analyzed by on-line coupled HPLC-GC-FID chromatography as described by Biedermann et al. (2009). Briefly, 20 or 50 µL extract (for MOSH and MOAH analysis, respectively) was injected onto a 25 cm x 2 mm i.d. HPLC silica gel column and chromatographed at 300 µL min⁻¹ using a gradient starting with hexane and reaching 30% dichloromethane. The column was backflushed with dichloromethane. HPLC-GC transfer occurred by the retention gap technique and partially concurrent eluent evaporation. A 10 m x 0.53 mm i.d. uncoated, deactivated pre-column was followed by a steel T-piece union connecting to the solvent vapor exit and a 15 m x 0.25 mm i.d. separation column coated in the laboratory with PS-255, a dimethyl polysiloxane. From HPLC, the MOSH were eluted between 2.0 and 3.5 min, the MOAH between 4.0 and 5.5 min. The oven temperature was programmed from 65°C (6 min) to 350°C at the rate of 20°C min⁻¹. White mineral paraffin oil served as external standard. The area representing the MOSH or MOAH were either integrated or determined manually by drawing one or several triangles into the chromatogram adjusted to the hump of the mineral oil hydrocarbons, as described by Concina et al. (2008) and Fiselier et al. (2009).

The detection limits were below 5 mg kg⁻¹. Results from repeated analyses of samples containing around 50 mg kg⁻¹ MOSH had a standard deviation below 10%. The uncertainty of the data was primarily from positioning the baseline and the upper contour of the hump and must be estimated

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for every chromatogram, but was below 25% for all except the lowest results presented here.
Concentrations given are averages of two or more independent analyses.

Results and discussion

Determination of the hydrocarbon fraction relevant for migration into dry foods

For the migration into dry foods, only the hydrocarbons of some volatility are relevant, since (wetting) direct contact is negligible and a minimum vapor pressure is required to support a transport through the gas phase. The minimum volatility could be determined by the hydrocarbons detected in food, but, as mentioned in the introduction, variations were noted, since the transfer also depends on other factors. Such influences can be avoided by observing the evaporation from the board into ambient air, i.e. by focusing on the first step of the migration process. A paperboard was hung up in the laboratory and sections were analyzed after various periods of time. The paperboard was exposed to air on all sides; there was neither air conditioning nor ventilation.

Figure 1 shows the MOSH and MOAH chromatograms from a 300 g m⁻² paperboard of recycled fibers before it was hung up as well as after 4 and 180 d. The vertical lines shown in the top chromatogram of the MOSH (extract of the paperboard before airing) indicate the integrated sections of a width corresponding to one carbon atom (every second section being labeled). The areas of these sections provided the data for Figures 2-4. In the early part of the chromatograms, the internal standards are eluted, assigned in italics in the middle MOSH and MOAH chromatograms. Before airing, a maximum concentration was found for the MOSH n-C₁₈/C₁₉ (top chromatogram). After 4 d, losses are visible in the early eluted part, being substantial up to about n-C₁₉. After 180 days, n-C₂₀ was largely evaporated and losses reached up to about n-C₂₄. Evaporation seemed to proceed by volatility, removing the hump of unresolved hydrocarbons from the left to the right. Vertical lines in the top MOAH chromatogram show the two fractions integrated and used for Figure 4, with retention times corresponding to the MOSH fractions n-C₁₈ and n-C₂₁. These retention windows do not mean that the MOAHs comprised a corresponding numbers of carbon atoms, but they reflect same volatilities in a nonpolar GC stationary phase. It is interesting to note that only about a third of the diisopropylnaphthalenes (DIPN) evaporated during 180 days, despite a volatility according to GC retention time which corresponded to MOAH evaporated to a large extent already after 4 days. This suggests that most of DIPN is still encapsulated.

Figure 2 was obtained from chromatograms as shown above, slicing the hump into sections of a width corresponding to a single carbon atom and cuts at a point immediately after the elution of the *n*-alkane designating the fraction. As most branched and cyclic hydrocarbons are eluted before the *n*-alkane of the same carbon number, the majority of the components in the MOSH fractions have this carbon number. However, the fractions are likely to include also hydrocarbons with one more or one less carbon atom.

For the C₁₇ section of the MOSH (b.p. *n*-C₁₇, 302°C) it is observed that 58% was evaporated during the first day and 80% within the first 4 days. Of the C₁₉ section, only 38% evaporated during the first 4 days, but 85% during two weeks. Some 44% of the C₂₃ evaporated in 180 days but rather little of the C₂₄ section. A small decrease was noticed for all hydrocarbons (up to about C₅₅), which was probably due to oxidation. It was concluded that *n*-C₂₄ is the upper end of the MOSH with a significant potential to evaporate and migrate into food.

Figure 3 shows the MOSH data before and after exposure of the paperboard to air at about 20°C (autumn/winter) during 14 and 180 days. During 2 weeks in summer, with an average temperature in the laboratory close to 30°C, the evaporation of the MOSH C₁₉ to C₂₃ was substantially faster (about a factor of 2 for C₁₉ and C₂₀), pointing out that temperature plays a significant role. The figure also includes data from a rice box made of the same paperboard and stored for about 6 months (described in Biedermann and Grob, 2010). Of the hydrocarbons C₁₆ to C₂₄ roughly 20% less material was lost than of the board exposed to air for 180 days. This might be due to the partitioning process with the rice: instead of being carried away by convection, the vapors were in stagnant air in contact with the rice and the transport was governed by the absorption into the rice. Since migration into the solid rice is slow, even after 6 months partitioning with the rice only involved a fraction of the rice particle. This confirms that the results observed for the board exposed to air correspond to a worst case of migration into foods readily absorbing hydrocarbons.

Figure 4 shows the results expressed in percent of the hydrocarbons present in the new board. It highlights the rapid loss of the C₁₈ fraction (87% in 20 days) and the far slower evaporation of the hydrocarbons with just 3 more carbon atoms. It also points out that the evaporation of MOAH (dashed lines) in segments eluted at the same retention window as the MOSH (solid lines) are similar: for MOAH C₁₈, the evaporation is somewhat slower, for the MOAH C₂₁ slightly faster (at least in the beginning) and for the sum of the MOSH and MOAH up to C₂₄ it is virtually identical (bold lines). This means that the retention time of the *n*-C₂₄ can also be considered as the upper end of the MOAH potentially being transferred to dry food to a significant extent.

Figure 4 shows that exposure to indoor air during 180 d caused 77% of the MOSH and MOAH $<C_{24}$ fraction to evaporate. It remains to be checked whether this is also an estimate for the worst case migration into food. The migration into rice packed during 6 months in the same type of board reached 86% of the MOSH $<C_{24}$. Despite the two evaporation percentages are similar, a direct comparison is not advisable because the two analyzed boards were from different batches. Although the variability in recycling row material composition can not be considered negligible, it is interesting to note that the two results are in the same order of magnitude.

Figure 5 shows the transfer of the mineral oil hydrocarbons for two products from the market: egg noodles and cocoa powder. On the left are the MOSH chromatograms of noodles (bottom) embedded in a paperboard tray of recycled fibers (top) and both wrapped into an outer plastic film. The example illustrates how the volatile components were largely transferred to the noodles (bottom left), whereas the high molecular mass hydrocarbons remained on the board (top left). For this rather fresh product (ca. 2 months on the market), the transfer of the C_{20} to C_{24} hydrocarbons was still modest. Transfer beyond $n-C_{24}$ (bold bar) was negligible.

The cocoa powder (right, MOSH and MOAH) was purchased packed in an internal polyethylene bag and an external paperboard largely consisting of recycled fibers. The paperboard (bottom, centre) contained a broad spectrum of MOSH with a strong maximum at $n-C_{24}$. Again the more volatile MOSH (from C_{13} to ca. C_{20}) were largely transferred to the cocoa powder (top centre), with a migration fraction reaching to about $n-C_{24}$. The n -alkanes C_{23} and C_{25} are from the cocoa powder. For this same product also the MOAH chromatograms are added (top and bottom, right). They also show migration for the hydrocarbons eluted up to the retention time of $n-C_{24}$. Again DIPN is transferred to a surprisingly small proportion compared to the MOAH of similar volatility.

Optimization of the extraction

The on-line HPLC-GC-FID analysis applied involved transfer by an on-column technique, which means that all material in the transferred HPLC fraction is deposited into the uncoated precolumn. Non-evaporating material may be a problem, since it accumulates there and builds up retention power. As a result, the reconcentration efficiency by the retention gap effect is reduced and peaks are broadened. Printed paper and board as well as recycled board often contain hydrocarbons of such a high molecular mass (e.g. from petroleum resins) that they cannot be eluted from GC. For instance, the use of MTBE for extracting paperboard, despite not being a particularly good solvent for high molecular mass compounds, resulted in a rapid deterioration of the chromatographic performance. Since these high molecular mass compounds are not of concern for migration into dry

food, extraction was optimized to be complete for hydrocarbons up to C₂₄, but discriminating against larger hydrocarbons.

Figure 6 shows MOSH and MOAH content from a printed recycled board extracted with hexane or ethanol for 2 h at RT. The chromatograms of the MOSH show a broad hump of unresolved hydrocarbons topped by some *n*- and *iso*-alkanes ranging from about C₁₄ to about C₅₀, with *n*-alkanes from about C₂₂ to C₄₅ representing paraffinic wax. The MOAH fraction comprised a hump of material corresponding to the early eluted MOSH, presumably representing the MOAH present in this mineral oil. It is topped by signals from diisopropyl naphthalene (DIPN) and components from wool oils. At higher elution temperature, a second hump is observed which is not accompanied by MOSH of similar molecular mass and which is assumed to represent petroleum resins, e.g. used as binder for printing inks. This hump grew with increasing extraction time (data not shown) and is assumed to extend into a range of molecular masses which are no longer eluted from GC. It is such material the extraction should discriminate against.

Ethanol and hexane showed complementary extraction properties: ethanol more efficiently extracted the low molecular mass hydrocarbons, which is probably due to its ability to swell cellulose polymeric chains. However, its extracting power is limited for the higher molecular weight hydrocarbons, particularly shown for the *n*-alkanes of the wax by the extracted segments of the upper chromatogram at the right. Hexane, on the other hand, because of chemical similarity, is the ideal solvent for hydrocarbons. Both properties (ability to swollen cellulose fibers and hydrocarbons extracting power) are needed for this application: the improved extraction of the hydrocarbons of interest as well as the discrimination against high molecular mass hydrocarbons, such as resins, waxes and hot melts.

Mixtures of ethanol and hexane combined the advantages of the two solvents. Different proportions were tested heading for high extraction efficiency up to at least C₂₄ and discrimination beyond this. Extraction during 2 h at RT was sufficient to quantitatively extract the MOSH and MOAH of interest; longer durations primarily increased the extraction of the high molecular mass hydrocarbons. Yields were tested by re-extraction of the paperboard at more drastic conditions (overnight at RT). The extraction performance of 50:50 (v/v) hexane/ethanol mixture was superior to 90:10, 80:20, 20:80 and 10:90. As shown in Figure 7 for a printed and an unprinted recycled paperboard, extraction of the *iso*-paraffins and the naphthenes (forming the unresolved hump) was quite complete up to beyond C₄₀, whereas the *n*-alkanes started to show up in the second extract

from C₂₃ in the upper and from C₂₄ in lower chromatogram. Extraction of the MOAH was quite complete up to a retention time of about n-C₄₀. For DIPN, however, immersion during 2 h was not sufficient, as shown by the large proportion of these compounds in the second extract. Recoveries were checked on four different printed paperboards made of recycled fibers; no relevant differences were noted. The discrimination against the high molecular mass material disturbing GC was confirmed by several hundred analyses which could be performed before the uncoated precolumn needed being exchanged (compared to hardly 10 when using hexane alone).

Data on paperboard boxes of products from the market

Totally 102 products were sampled from the Swiss and Italian market, 66 in paperboard mainly of recycled fibers and 36 in board of fresh fibers (chemical or mechanical pulp). The printed boards were analyzed for MOSH and MOAH up to the retention time of n-C₂₄. Figure 8 shows the results for the <C₂₄ MOSH fraction measured in the printed recycled paperboard. Concentrations ranged from 50 to 3800 mg kg⁻¹, with an average of 626 mg kg⁻¹ and a median of 350 mg kg⁻¹. MOAH concentrations (not reported in figure) related to the sum of MOSH and MOAH contained in mineral oil varied from 16 to 28% with mean value of 19%. For the interpretation of these results, two factors must be taken into consideration: firstly, the hydrocarbons of concern were already partly transferred to the packed food or evaporated into the atmosphere, with the effect that the concentrations were substantially reduced. Secondly, the boxes were printed and for a substantial proportion of the samples it must be assumed that still offset printing inks based on mineral oil were used, i.e. that the values measured represent the sum of the contributions from the recycled board and the printing ink. Since the MOSH concentrations below C₂₄ or C₂₈ in unprinted paperboard were usually below 1000 mg kg⁻¹ (Biedermann and Grob, 2010), it is assumed that the highest results were predominantly determined by the diluent in the printing inks. Conversely, there seems to be little room for contributions of mineral oil from printing inks for about half of the samples with a rather low <C₂₄ MOSH content.

Nine of the 36 printed paperboards (Figure 9) consisting fresh fibers contained less than 10 mg kg⁻¹ MOSH. However, the concentrations reached up to 1900 mg kg⁻¹ (median, 50 mg kg⁻¹). It is assumed that the printing inks were the major source of this contamination (with a molecular mass distribution indeed centered on C₁₈-C₂₁), but there were also samples containing higher molecular mass oils. Since such oils were also detected in unprinted fresh fiber board (Biedermann and Grob, 2010), printing inks are not the only source. MOAH concentrations ranged from 5 to 22% with an average of 15%.

To safely meet the 0.6 mg kg^{-1} limit for MOSH in food derived from the ADI of JECFA, the maximum concentration of the MOSH $<C_{24}$ in the paperboard is calculated as follows: if the mass ratio of the food to the paperboard is 5 (the average is around 10; Fiselier et al., 2010) and 70% of the MOSH $<C_{24}$ migrate into food, the limit is reached at 4.3 mg kg^{-1} in the paperboard. The data shown in Figures 7 and 8 do not enable to calculate the expected migration into food, since the process may already have progressed, but the data show that almost all paperboards still contained amounts of MOSH $<C_{24}$ far in excess of 4.3 mg kg^{-1} .

Conclusions

Mineral oil may migrate from printed paperboard into packed food at concentrations far exceeding the limit derived from the ADI specified by the WHO-JECFA (Droz and Grob, 1997; Biedermann and Grob, 2010). Both the design of migration tests and the analytical set-up for these contaminants and food packaging are often controversial. Reliable analytical tools are thus required to solve these difficulties.

This paper deals with two elements. Since standard testing with MPPO (Tenax®) at 40°C for 10 d does not reflect migration over several years, estimation of long term migration based on contents in the paperboard is proposed. To this end, the upper limit of the mass of the hydrocarbons capable of migrating through the gas phase was determined by focusing on the first step of the process, i.e. evaporation. Migration ends quite sharply at C_{24} both for MOSH and MOAH. It is estimated that 60-80% of the $<C_{24}$ MOSH and MOAH may end up being transferred into the packed food when there is no internal functional barrier (e.g. a bag with a layer of aluminum or PET) and the boxes are stored in such a way that evaporation into ambient air is hindered. This approach involves a rapid determination and provides a robust estimate of the potential migration. Some first applications validated the approach (Biedermann and Grob, 2010), but more work is on-going to compare real migration with such estimates.

On-column introduction into GC (in this case by on-line HPLC-GC) rules out distortion of the sample composition, but is sensitive to loading of the uncoated precolumn with non-evaporating material. The extraction of (printed or unprinted) paperboard with ethanol/hexane 1:1 was shown to provide virtually complete extraction of the hydrocarbons of interest, but to discriminate against those disturbing the analysis.

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7 3 been transferred, but they show a frightening remaining potential for migration: the highest
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Figure captions.

Figure 1. On-line HPLC-GC-FID analysis of MOSH and MOAH fractions from recycled paperboard before it was hung up in the laboratory air ("new") as well as 4 and 180 days later. Peaks of internal standards labeled in italics. DIPN: diisopropyl naphthalenes.

Figure 2. MOSH concentrations in recycled unprinted paperboard hung up in ambient air determined for fractions incremented by steps of one carbon atom at the time (x-axis).

Figure 3. MOSH concentrations in the board shown in Figure 2, including results for 14 days at about 30°C (substantially faster evaporation) and for the same type of board from 180 days old pack of rice (highest losses compared to other time and temperature conditions).

Figure 4. Evaporation of MOSH (solid lines) and MOAH (dashed lines) C₁₈ and C₂₁ fractions, diisopropyl naphthalenes (DIPN, dotted line) and the sum of MOSH and MOAH <C₂₄ (Σ, bold lines) from paperboard exposed to ambient indoor air during different periods of time.

Figure 5. Online HPLC-GC-FID analysis of MOSH and MOAH migrating from recycling paperboard (top chromatograms) into packed egg noodles and cocoa powder (bottom chromatograms). Migration beyond n-C₂₄ fraction is negligible. DIPN: diisopropyl naphthalenes.

Figure 6. Online HPLC-GC-FID chromatograms of MOSH and MOAH fractions obtained by extraction of recycled paperboard with different solvents during 2 h at RT: ethanol is the better solvent for the lower molecular mass hydrocarbons and discriminates against those of higher mass. DIPN: diisopropyl naphthalenes.

Figure 7. Online HPLC-GC-FID hydrocarbons recovery tests for extraction of printed and unprinted recycled paperboard with a 50:50 hexane/ethanol mixture during 2 h at RT. For each chromatogram, the overnight re-extraction is overlapped as the lower trace. DIPN: diisopropyl naphthalenes (high amount left in the board after 2 h at RT extraction).

Figure 8. MOSH n<C₂₄ concentrations in printed paperboard primarily consisting of recovered fibers from packed foods sampled on the market, sorted by increasing concentration.

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2
3 1 Figure 9. MOSH $n < C_{24}$ concentrations in printed fresh fiber paperboard from packed foods sampled
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5 2 on the market, sorted by increasing concentration.
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Figure 1.

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Figure 6.

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Figure 7.

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Figure 8.

Figure 9.