# BEHAVIOUR OF ORGANIC POLLUTANTS IN PAPER AND BOARD SAMPLES INTENDED TO BE IN CONTACT WITH FOOD

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## ABSTRACT

This paper deals with the study of volatile compounds present in a set of 3 paper and board samples of different composition, surface treatment, grammage and thickness. The volatile compounds released by the packaging material (P&B) can be trapped on the food and may then affect the safety and health of consumers. To evaluate if the recycled P&B could be used as food packaging material, adsorption studies have been performed with a selection of chemical substances. The adsorption isotherms are provided. Partition coefficients between paper and air have been calculated for a series of volatile compounds used as model compounds to represent different families of contaminants commonly present in paper & board (P&B). Values from 4 to 3243 were obtained at different temperatures. The analysis of volatile compounds have been carried out by automatic headspace coupled on-line with GC/MS in SIM mode. The results obtained are shown and discussed.

## KEYWORDS

Adsorption isotherms, partition coefficients, pollutants, static headspace, food packaging, recycled paper.

## INTRODUCTION

The use of plastic materials for food contact is regulated in USA [1], Mercosur [2] and Europe [3], but with paper and board (P&B) the regulations have been delayed for several reasons. The main reason is that P&B are mainly used as secondary packaging material and then direct contact is restricted to some dry foodstuffs, such as flour, sugar, pasta or salt.

However, the increase of fast food, as well as the cooked or pre-cooked food ready to eat and to carry away has lead to an increase of paper and board as food contact materials. Pizza for instance is often in direct contact with a board box package.

On the other hand, the environmental pressure and the general tendency of recycling pose recycled P&B in the situation of being used as food contact material. Recycling of

P&B requires a chemical digestion, cleaning and deinking processes which produce a cleaner material. It cannot be excluded however that some pollutants may still remain in the paper matrix and could be transferred to the food [4-14]. For this reason, it is very important to establish the criteria to ensure that P&B containing recycled pulp are safe enough to be used as food contact materials.

One of the strongest arguments coming from the industrial sector is that the content of pollutants in the material is not enough to assure that such materials are safe food contact material. In fact, it is extremely important to know the transference capacity of these pollutants, which is the process called migration [15-20]. The comparison with plastics is a general and useless statement, and could find many exceptions [21-25].

Since paper is porous, diffusion inside the matrix occurs mainly through the gas phase. Consequently, the migration capacity of volatile chemicals can be estimated from their partition coefficients between paper and air [26-27].

This paper deals with the study of the behaviour of some organic pollutants, selected for being representatives of chemical families and likely contaminants commonly found in P&B samples. Three P&B samples were selected for the study, having different pulp, percentage of recycled matter, grammage and thickness.

Adsorption isotherms and partition coefficients are obtained.

## EXPERIMENTAL

### Apparatus and solutions

A headspace Perkin Elmer (Norwalk, CTO6859, USA) HS-40XL model equipped with autosampler and a capillary transfer line of fused silica of 0.25 µm (i.d.) heated at 280ºC was used. This transfer line was directly connected using an on column mode to the capillary GC column SGL-1710 (Sugelabor, Spain) of 60 m x 0.25 mm i.d. x 0.25 µm of film thickness, through a glass connector.

A Gas Chromatograph Hewlett-Packard Corp. HP 6890 (Delaware, USA) with electronic control of pressure and a Mass-Spectrometer detector HP-5973 was used, under the following conditions: oven temperature: 40ºC for 2 min, rate of 15ºC/min up to 250ºC and then held for 4 min.

Standards: *o*- xylene (> 99% purity, Probus), dodecane (99% purity, Aldrich), naphthalene (98% purity, Aldrich), diphenyl ether (99% purity, Aldrich) and 2,6-diisopropylnaphthalene (99% purity, Acros Organics).

**Samples**

Three different samples were studied. Table 1 describes their main characteristics.

*Table 1. Characteristics of the three samples studied.*

| Characteristics | Sample R1 | Sample R2 | Sample R3 |
|---|---|---|---|
| Type | Testliner | Fluting | Kitchen towel |
| Pulp | 100% recycled | NSSC[1]+30% recycled | 100% recycled |
| Surface treatment | No | No | No |
| Grammage ($g/m^2$) | 128 | 107 | 46.7 |
| Thickness (µm) | 191 | 209 | 188 |
| Volume air trapped ($cm^3$) | 0.0131 | 0.0092 | 0.0355 |

*[1] NSSC = neutral sulphite semi-chemical pulp*

**Procedure**

1 µL of diethyl ether solution containing *o*-xylene, dodecane, naphthalene, diphenyl ether and 2,6-diisopropylnaphthalene at the appropriate concentration each was added to a closed vial of 22.4 mL containing 200 mg of P&B sample cut in strips of 7 cm x 1 cm [28]. Seven different concentration values ranging from 0.2 to 200 mg/g (expressed on the paper base) were studied. A systematic study for the determination of partition coefficients was carried out with a group of semi-volatile model compounds (hydrocarbons, aromatics, ethers) with different polarity, structure and boiling points. In order to calculate correlation, different cardboard, temperature and times were tested [26-29]. These vials were placed in an oven under the following optimum kinetic conditions: 23ºC for 7 days, 40ºC for 5 days, 70ºC for 4 hours and 100ºC for 1 hour. The experiments were carried out by duplicated with each sample. The solution was carefully introduced on the walls of the cell, in order to avoid liquid droplets to come directly on the paper, and to favour a faster equilibrium. Then the vapour phase was analysed by HS-GC-MS under the conditions above described. The initial concentration of each compound in the paper was measured by the same HS-GC-MS procedure in blank vials without adding the surrogates.

In order to get the maximum sensitivity with the headspace used, the injection volume of the sample and the injection time were both independently and simultaneously varied from 1 to 2 µL and from 0.05 to 0.10 min respectively. No significant differences with respect to the conditions described in reference 26 were found (1µL and 0.05 min)

## RESULTS AND DISCUSSION

To calculate the partition coefficients between the paper and the air a series of volatile compounds commonly present in paper sample was selected. The same criteria as those used in FDA [1] and previous EU projects [3] were applied here and the following compounds were selected: acetophenone, benzoic acid, benzophenone, dibutyl phthalate, diphenyl ether, diisopropyl-naphthalenes isomeric mix, n-dodecane, methyl stearate, naphthalene, 2,3,4-trichloroanisole, vanillin and *o*-xylene. In this way, different chemical families as well as the likely contaminants from the misuse of paper and board which couldn't be eliminated with the recycling system, are represented. Among them, only diphenyl ether, 2,6-diisopropylnaphthalene, dodecane, naphthalene and *o*-xylene were volatile enough to permit the calculation of partition coefficients (paper/air). Although more polar compounds are present in the paper they are non volatile and consequently the release to the air is negligible.

To estimate the contamination of food the partitioning between packaging and air, air and food should be calculated. Partition coefficients between air and food or food simulants have been calculated by several authors [27-29] and for this reason, only the $K_{paper/air}$ will be studied here.

In any case, to evaluate the contamination of food, it could be assumed that the total concentration of the compounds in the gas phase would be trapped on the food. This situation would represent the worst case and provides a good approach for the estimation of food contamination

Partition coefficients of volatile compounds between air and paper are calculated using the following expression:

$$K_{paper,air} = \frac{C_{paper}}{C_{air}} = \frac{(V_0 \times C_0) - (V_{air} \times C_{air})}{V_{paper} \times C_{air}}$$

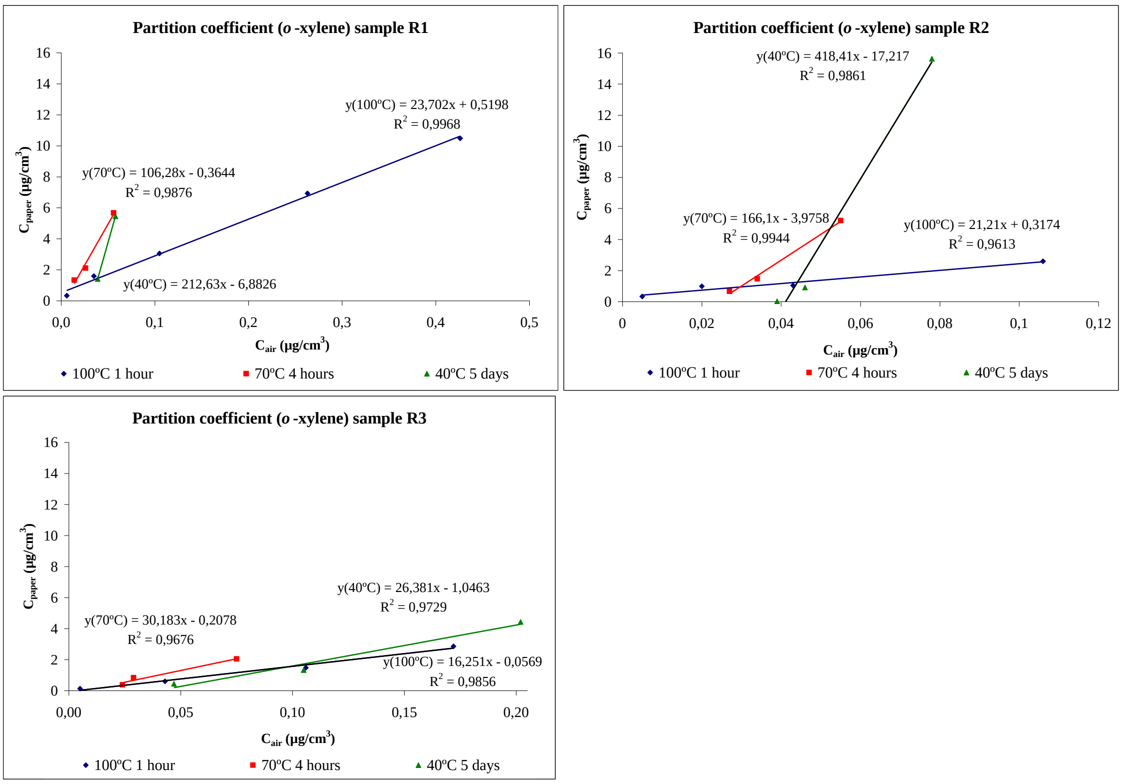
where: $C_{paper}$ is the concentration of each compound in the paper, expressed as µg/cm$^3$. $C_{air}$ is the concentration of each compound in the air after the test, expressed as µg/cm$^3$. $V_0$ is the volume of the empty vial in cm$^3$. $C_0$ is the concentration of each compound in the empty vial before the test, expressed as µg/cm$^3$, $V_{air}$ is the volume of the free air in the vial (volume of the empty vial – volume of the paper sample), in cm$^3$, and $V_{paper}$ is the volume of the paper sample in cm$^3$.

It is worth to point out that in all calculations the air trapped inside the paper sample was not considered. This volume of air could be calculated as the difference between the theoretical volume, that means, the number of paper strips multiplied by their length (cm), wideness (cm) and thickness (cm), and the real volume [(sample weight (g) divided by the grammage ($g/cm^2$)) x thickness (cm)]. The results obtained are shown in Table 1.

When the concentration of volatile substance in air ($C_{air}$) increases, its concentration also increases in the cardboard ($C_{paper}$). A plateau is then reached, corresponding to a saturation of the cardboard phase. When it is linear, the slope of the relationship [$C_{paper}$ = f ($C_{air}$)] in the initial part is the partition coefficient. The plateau is related to adsorption isotherms.

**Partition coefficients.**

Figures 1a, 1b and 1c show the plot obtained for *o*-xylene and the samples R1, R2 and R3 respectively, at 40ºC, 70ºC and 100ºC. Values at 23ºC were not obtained for all compounds as the concentration in vapour phase was closed to the detection limit.




*Figures 1a, 1b and 1c. Comparison of partition coefficient $K_{(board/air)}$ at three temperatures for the o-xylene.*

As can be seen the slope of the lines increases when the temperature diminishes which means that the partition coefficient between the vapour phase and the paper becomes lower. A similar behaviour was observed for all the compounds under study in the three paper samples.

Table 2 shows the average value for partition coefficient for each model pollutant in every paper sample. These values are also the slopes of the adsorption isotherms obtained as was above described.

*Table 2. Mean values of partition coefficients of surrogates between paper and air.*

| ***Compounds*** | ***Boiling point (ºC)*** | ***R1*** | ***R2*** | ***R3*** | ***R1*** | ***R2*** | ***R3*** |
|---|---|---|---|---|---|---|---|
| | | *100ºC, 1 hour* | | | *70ºC, 4 hours* | | |
| *o-xylene* | 143 | 24 ± 7.9 | 21 ± 2.5 | 16 ± 5.6 | 106 ± 11.6 | 166 ± 41.2 | 30 ± 8.2 |
| *dodecane* | 216.2 | 5 ± 1.5 | 7 ± 1.5 | 4 ± 0.8 | 3243 ± 122.9 | 22 ± 6.4 | 43 ± 5.9 |
| *naphthalene* | 217.7 | 190 ± 24.4 | 93 ± 16.8 | 48 ± 9.2 | 359 ± 89.6 | 235 ± 89.2 | 62 ± 12.1 |
| *diphenyl oxide* | 259 | 54 ± 1.9 | 189 ± 59.0 | 28 ± 10.6 | 78 ± 14.5 | 197 ± 50.3 | 80 ± 12.09 |
| *2,6-DiPN* | 279.3 | 20 ± 6.6 | 132 ± 24.3 | 46 ± 9.6 | - | 80 ± 5.6 | 18 ± 4.5 |
| | | ***R1*** | ***R2*** | ***R3*** | | | |
| ***Compounds*** | | *40ºC, 5 days* | | | | | |
| *o-xylene* | | 213 ± 56.6 | 418 ± 124.7 | 23 ± 7.4 | | | |
| ***o-xylene*** | ***R1*** | | ***R2*** | | ***R3*** | | |
| | $C_{paper}$[1] | $C_{air}$[2] | $C_{paper}$ | $C_{air}$ | $C_{paper}$ | $C_{air}$ | |
| *Point 1* | 0.33 | 0.006 | 0.33 | 0.005 | 0.13 | 0.005 | |
| *Point 2* | 1.67 | 0.011 | 0.99 | 0.200 | 0.62 | 0.020 | |
| *Point 3* | 1.59 | 0.035 | 1.04 | 0.043 | 0.60 | 0.043 | |
| *Point 4* | 3.06 | 0.105 | - | 0.106 | 1.48 | 0.106 | |
| *Point 5* | 6.93 | 0.263 | 10.82 | 0.172 | 2.86 | 0.172 | |
| *Point 6* | 10.48 | 0.426 | 12.69 | 0.351 | 3.50 | 0.351 | |
| *Point 7* | 27.78 | 0.661 | - | 0.560 | 6.67 | 0.559 | |

[1] $C_{paper}$ *and* [2] $C_{air}$ *expressed as* $\mu g/cm^3$.

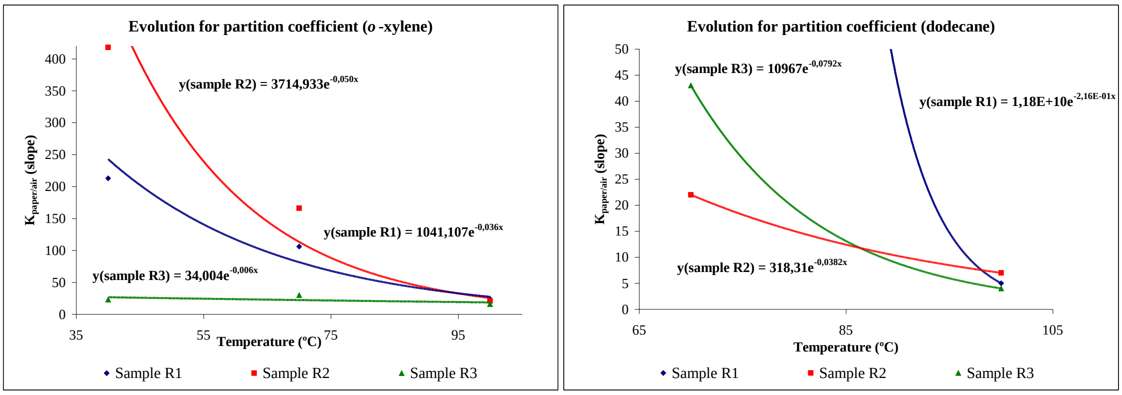
The partition coefficient values for DiPNs are lower than expected according to their boiling points. Taking into account their chemical structure, with a flat ring of naphthalene and two alkyl substitutions probably the activation energy to break the steric hindrance has been surpassed at high temperature, and consequently, the concentration in air is higher than expected.

When the volume of air trapped inside the paper sample is sum up to the free volume of the vial, the concentration values measured in air as well as the concentration values in the paper can be recalculated. With these new values, the partition coefficients were calculated again, but the differences found with respect to the previous values were negligible.

As can be seen in Table 2, R3 is the sample with the lowest partition coefficient and it has also the lowest thickness and grammage. This means that the compounds are easier released to the vapour phase. In other words, the migration of the volatile compounds to the vapour phase is higher in the case of thinner samples.

Not only the grammage and thickness but the paper composition and the chemical structure of the compounds play a role in the partition coefficients. Sample R2, for example, with only 30% of recycled pulp has the highest partition coefficient values for *o*-xylene ($C_8H_{10}$, boiling point = 143ºC), the most volatile compound, at both 70ºC and 40ºC and the same happen to diphenyl oxide ($C_{12}H_{10}O$, boiling point = 259ºC) and DiPNs ($C_{16}H_{20}$, boiling point = 279.3ºC) at 70ºC or 100ºC. These compounds have aromatic groups and some polarity which could have a stronger interaction with the paper matrix. On the other hand, dodecane ($C_{12}H_{26}$, boiling point = 216.2ºC) is a linear and non polar compound and the partition coefficient values are lower in the sample R2 (partially recycled pulp). In the case of naphthalene ($C_{10}H_8$, boiling point = 217.7ºC) with a flat structure, samples R1 and R2 (grammage > 100 $g/m^2$) presented similar partition coefficient values at both 70ºC and 100ºC. However, the sample R3 has the lowest values for naphthalene (grammage = 46.7 $g/m^2$).

When the partition coefficient values are plotted versus temperature, an exponential profile could be expected, according to the general relationship between equilibrium constants and temperature. When the temperature increases the partition coefficient should be lower which would mean that sorption is expected to follow an Arrhenius law, and this is observed indeed Figures 2a and 2b. These Figures show the evolution of partition coefficient values with temperature in each sample under study for *o*-xylene and dodecane, the most volatile compounds studied. This behaviour confirms the previous hypothesis.

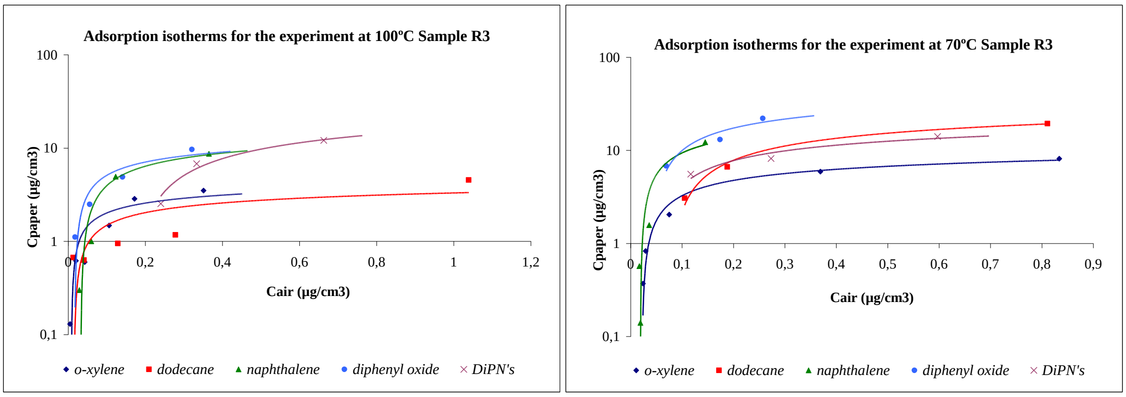



*Figures 2a and 2b. Evolution of partition coefficients values with temperature for the three paper samples.*

## Adsorption isotherms

As was above described, the adsorption isotherms represent the equilibrium, that means the limit in which the paper is saturated by the compound.

Figures 3a and 3b show the adsorption isotherms obtained at 100ºC and 70ºC for the five surrogates in the paper sample R3. As expected, the equilibrium is reached at lower concentration at the highest temperature (100ºC for 1 hour).




*Figures 3a and 3b. Adsorption isotherms for the five surrogates in the sample R3.*

## CONCLUSIONS

From the study carry out several conclusions can be emphasized:

1- The partition coefficients for the volatile compounds studied decrease when the temperature increases which means that paper samples are riskier as food packaging materials at high temperatures. The risk is higher when lower are the partition coefficient value.

2- Significant differences of the partition coefficients values were obtained with both the composition of the paper, the grammage and the thickness, being the partition coefficient values lower when lower are the grammage and thickness.

3- From the partition coefficients values, which range from 4 in the case of dodecane to 3243, it can be said that dodecane is the riskiest compound at high temperature in the series under study, followed by *o*-xylene, diphenyl ether and naphthalene.

4- Sorption behaviour of the compounds under study follows the Arrhenius law.

5- The partition coefficients not only depend on the boiling point of the compound but its chemical structure, being the chemical interaction with the pulp, and the stereochemistry important factors to explain the behaviour profile.

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