DISTRIBUTION OF PCDDS/PCDFS IN BLEACHED PAPERBOARD AN EXPLANATION FOR THE MIGRATION OF PCDDS/PCDFS FROM PAPER AND BOARD PRODUCTS

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ABSTRACT

The distribution of polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in uncoated and polyethylene (PE) coated paperboards was studied. The results of the analysis of different layers of boards (PE-films, surface and body of the board) revealed the presence of PCDDs/PCDFs in the PE-film detached from the coated board, whenever PCDD/PCDF congeners were found in the board. Amount of PCDD/PCDF congeners in the PE-film varied from 5 to 50% of the total. The analysis of uncoated board showed an even distribution of the PCDDs/PCDFs between the surface and the body of the board. The results show that PCDDs/PCDFs migrated from the board into the PE coat already during the manufacture. The presence PCDDs/PCDFs in the PE-layer explains easy migration into food observed in other studies.

INTRODUCTION

The use of chlorine in chemical pulping has since the late 1980' been known to be a source of PCDDs/PCDFs. PCDDs/PCDFs formed in pulp bleaching have been found both from the pulping products and the effluents (Rappe et al., 1987, Swanson et al., 1988, Swanson, 1988, Amendola et al., 1989, Clement et al., 1989). Because of low solubility in water PCDDs/PCDFs adsorbed to the cellulose fibers. 20 to 50% (Amendola et al., 1989) of all PCDDs/PCDFs produced may be found in the cellulose and consequently also in the products. The migration of PCDDs/PCDFs from paper and paperboard into food during storage or use has been raported (Ryan et al., 1988, Beck et al., 1989a, Beck et al., 1989b, Startin et al., 1989). We searched for the explanation of easy migration of PCDDs/PCDFs by analysing PE-coated and uncoated boards, the possible barrier function of PE-films and the different layers of boards separately.

MATERIALS AND METHODS

Both unused and used paperboards or paperboard packagings produced in US, Canada and Finland during the years 1987 to 1990 were sampled. The packaging boards used as an example of this paper weighed roughly 300g/m^2 containing 14g/m^2 PE at one side and 26g/m^2 PE at the other side (double side coated).

30 to 200g of pulperized (Kitunen and Salkinoja-Salonen, 1989) paperboard or PE-film was extracted 48 for hours with a soxhlett extractor with 1 to 1.5 l with acetone, ethanol (99%) or toluene. Pieces of the board (1cm x 1cm and 10cm x 10cm, leach test) were refluxed with acetone/hexane (2/1) 1 hour at 55 ^{0}C. Before extraction all board samples were spiked with the 13C-labelled surrogates purchased from Wellington Laboratories (Guelph, Canada): 2378-TCDD, 12378-PeCDD, 123678-HxCDD, 1234678-HpCDD, OCDD, 12378-PeCDF, 1234678-HpCDF or Cambridge Isotope Laboratories (Woburn, MA): 2378-TCDF, 23478-PeCDF and 123678-HxCDF. 13C-labelled 1234-TCDD (Wellington) was used as an injection standard. Quantitative mixture containing all the unlabelled 2378-substituted standards was from Cambridge Isotope Laboratories. All solvents except ethanol were of HPLC grade (Rathburn, Walkerburn, UK). Ethanol (99%) used for the extraction and also washing of the glassware was purchased from OY Alko AB, Finland.

Sample clean-up was carried out as described earlier (Kitunen and Salkinoja-Salonen, 1989) or, when automated chromatografic clean-up system (Fluid Management Systems, Watertown, MA) was used, according Lapeza et al. (1986) with minor modifications.

GC-MS analysis was carried out by Hewlett-Packard 5890 / Hewlett-Packard 5970 B GC-MSD-system operating with SIM-detection. Injection was splitless injection with all glass solid injector (Chrompack, Middelburg, Netherlands) at 270°C or 280°C. SP-2331 (60m x 0.25mm x 0.2um, Supelco, Inc., Bellefonte, Switzerland). NB-9C (50m x 0.2mm x 0.2um, HNU-Nordion OY Ltd, Espoo, Finland) or HP-5 (25m x 0.2mm x 0.3um, Hewlwtt-Packard, Avondale, PA, USA) fused silica capillary columns were used for the GC.

RESULTS

Leaching of PCDDs/PCDFs from PE-coated and uncoated board

Pieces of board (1cm x 1cm and 10cm x 10cm) were refluxed 1h with acetone/hexane (2:1). The solvent was evaporated with rotating evaporator. Further protocol was as described earlier (Kitunen and Salkinoja-Salonen, 1989). Results in Table 1 show that the yield of PCDDs/PCDFs leaching from the board cut to pieces was only slightly lower than that from board pulperized to slurry. Good extractability of PCDDs/PCDFs from large pieces of PE-coated board shown in Table 1, is also rather surprising. Table 1. further shows that the extraction yield of PCDDs/PCDFs was only slightly, if at all (within analysis variation limits), higher from uncoated board compared to fully PE-coated board. Microscopic examination revealed that the PE-films studied here were undamaged and that the PE covered the pulp matrix well. Cracking, micropores or uncoated areas were not seen.

Equally high leaching yield from uncoated and PE-coated board strongly indicates that access of the solvent to the PCDDs/PCDFs was little limited by the PE-film. To investigate this more closely the distribution of PCDDs/PCDFs in PE-coated and the uncoated paperboard was examined.

Table 1. Leachability of PCDDs and PCDFs from board. Results are given as pg/g of dry weight.

PCDD/PCDF congener	Board A[a] 1cm x 1cm	Board B[a] 1cm x 1cm	Board A[b] 1cm x 1cm	Board A[c] 10cm x 10cm	Board B[c] 10cm x 10cm	Board A[d] pulperized	Board B[d] pulperized
OCDD	<5	<5	<2	<5	<5	<5	<5
1234678-HpCDD	<2	<2	<1	<2	<2	<2	<2
1234679-HpCDD	<2	<2	<1	<2	<2	<2	<2
123478-HxCDD	<1	<1	<0.3	<1	<1	<1	<1
123678-HxCDD	5.8	3.5	0.77	7.5	7.3	5.9	4.8
123789-HxCDD	3.9	3.4	0.59	3.7	3.7	3.8	2.1
HxCDDs other	27	24	3.7	26	24	22	31
12378-PeCDD	<1	<1	<0.2	<1	<1	<1	<1
PeCDDs other	7.9	6.8	1.2	9.5	9.7	8.7	11
2378-TCDD	1.0	1.1	0.39	1.6	1.2	1.9	2.2
TCDDs other	2.1	2.8	0.35	4.4	2.9	5.1	4.1
2378-TCDF	12	12	2.5	17	12	18	18
TCDFs other	14	10	1.9	17	10	18	14

a) board A (uncoated), board B (same board after coating) b) leaching procedure was repeated (extracted 1 hour with asetone/hexane and analysed as described before) with board A[a] (1cm x 1cm), c) 10cmx10cm board pieces: board A (uncoated) and board B (PE-coated). d) pulperized and soxhlett extracted boards; board A (uncoated) and board B (PE-coated)

Distribution of PCDDs/PCDFs in PE-coated and uncoated board

PE is extrudet on the board base as a hot liquid. To obtain better attachment of PE, an open flame may have used to produce eg. carbonyl groups on the cellulose matrix. During the sizing the surface temperature of the board can reach 100 or 200°C. The PE coating operation itself did not generate PCDDs and PCDFs (results not shown here).

To establish the distribution of PCDDs/PCDFs in PE-coated board, the PE-films were peeled off and analysed separately. A portion of the separated PE-films was cleaned with cold water until translucent and practically cellulose-free. Results of these analyses in Table 2. show that the PE layers contained roughly a half of all PCDD and PCDF of the fully coated board. Analysis of the PE granulate used by the same mill showed that PE raw material itself did not contain any measureable (<1 pg/g) amounts of PCDDs and PCDFs.

Table 2. Distribution of PCDDs/PCDFs in fully coated and uncoated packaging board. Results are given as pg/g of dry board.

	Board B (fully coated)					Board A (uncoated)	
PCDD/PCDF congeners	Body of board	Thick film[a] (inside)	Thin film[b] (outside)	Cleaned film	PE raw material	Surface[c] layer	Body[d] of board
OCDD	<5	<5	<5	<5	<5	<5	<5
1234678-HpCDD	<2	2.8	7.2	8.7	<2	<2	<2
1234679-HpCDD	<2	<2	3.6	2.7	<2	<2	<2
123478-HxCDD	<1	<1	<1	<1	<1	<1	<1
123678-HxCDD	3.4	7.9	9.3	12	<1	5.2	4.6
123789-HxCDD	0.71	7.5	11	6.4	<1	2.4	2.4
HxCDDs other	13	29	32	28	<1	24	26
12378-PeCDD	<1	<1	<1	<1	<1	<1	<1
PeCDDs other	8.2	23	20	22	<1	24	26
2378-TCDD	0.79	2.3	2.6	2.4	<1	2.4	2.4
TCDD	3.3	7.0	6.1	9.1	<1	7.3	6.7
2378-TCDF	5.9	12	12	11	<1	17	21
TCDF	8.4	14	13	17	<1	13	17

a) inside surface of package board, b) outside surface of package board, c) 0.1mm of the surface of uncoated board was peeled for the sample, d) roughly 0.3mm of the body of the board

Uncoated board was also peeled to reveal the distribution of PCDDs/PCDFs before the coating operation. Results (Table 2) show that the congeners of PCDDs/PCDFs were evenly distributed in the uncoated board.

DISCUSSION

From the results as those shown above we conclude that PCDDs/PCDFs migrated into the PE-coating during the sizing operation where the hot PE melt was spread on the paperboard. Vaporization of PCDD/PCDF compounds inside of cellulose matrix and then dissolution into the liquid PE would explain their precence in the PE-film. Diffusion of these compounds into the PE-layer after the board cooled down, or during the use of the packaging material is less likely. We verified that the heating of board (<150°C) did not increasce the PCDD/PCDF content of PE-film (results not presented here).

The PE layer is in direct contact with the packaged food. According to our present results, the PE-film, usually assumed to function as a migration barrier, in fact acted like a sorbent for the PCDDs/PCDFs. Situations like heating-up or long term storage at room temperature may cause the migration of PCDDs/PCDFs from the package into the packaged material. In fact, such migration of PCDDs/PCDFs from the package into food has already been reported (Ryan et al., 1988, Beck et al., 1989b, Startin et al., 1989).

Decreasing the sizing temperature or the use of aluminum foil as barrier may decrease migration of PCDDs/PCDFs from the board into the PE (and food). These procedures, however, add to the costs and may lead to inferior package stability. The best way to prevent PCDD and PCDF contamination of the packaged material is to use packaging board which does not contain these compounds. This has in fact already been achived by the industries during the course of the present study.

CONCLUSIONS

PCDDs/PCDFs migrated from the body of the board into the PE film during the coating operation. PE-film, assumed as a barrier between the package board the food, acted actully like a sorbent for PCDD/PCDF-type contaminats of the board. The PCDD/PCDF content of analysed paperboard PE films varied between 5 to 50% of total PCDDs/PCDFs. Relatively high PCDD/PCDF contents may explain why the PCDDs/PCDFs are sometimes found from the packaged product.

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