THE MIGRATION OF POLYCHLORINATED DIBENZO-p-DIOXINS AND DIBENZOFURANS INTO MILKS AND CREAM FROM BLEACHED PAPERBOARD PACKAGING

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ABSTRACT

Samples of milks and cream packaged in glass, plastic and paperboard cartons have been analysed for PCDDs and PCDFs. PCDDs and PCDFs were not able to be detected in milk packaged in glass or plastic. The data confirms the source of TCDDs and TCDFs quantified in carton milks as coming from the paperboard packaging. TCDF isomers exhibit a greater ability to migrate than TCDD isomers. It has been found that the migration of these contaminants from the paperboard is *not* directly related to the fat content of the packaged dairy solution. Even though both brands of paperboard cartons investigated contained significant amounts of *PeCDDs, HxCDDs, HpCDDs* and *OCDD* these congeners were not detected in any of the milks analysed. Process and papermaking additives have been identified as sources of these higher congeners.

INTRODUCTION

In 1988, Ryan et al. (1) documented levels of TCDD and TCDFs in milk stored in bleached paperboard cartons and attributed their presence in the milk to migration from the paperboard packaging.

This paper reports the results of an extensive survey (2) of the New Zealand market place for the presence of PCDDs and PCDFs in both non-paperboard packaged (glass and plastic packaged) and paperboard packaged milks and cream. The significant features of these results are the non-detection of PCDDs and PCDFs in glass and plastic packaged milk, the time dependency and congener specificity of migration of PCDDs and PCDFs present in the paperboard and the importance of the fat content of the packaged dairy product. In addition the identification of paper making and process additives as sources of the higher chlorinated penta- to octa-congeners is described.

RESULTS AND DISCUSSION

PCDDs and PCDFs in New Zealand milk.

Levels of PCDDs and PCDFs determined in non-paperboard packaged standard (3.5% fat) homogenised milks are given in Table 1. The general absence of these contaminants is notable and is in contrast to the levels that have been reported for PCDDs and PCDFs in milk and related dairy products from Northern Europe (3,4,5) and elsewhere (6). Much of this contamination has been attributed to incinerator emissions, particularly from municipal waste incinerators (MWI). However with no MWI in New Zealand and a general sparsity of other combustion sources in rural districts, the levels of PCDDs and PCDFs observed in milks and other agricultural products (7) is not surprising.

Analysis of standard homogenised milk packaged in paperboard cartons showed elevated levels of TCDD and TCDF isomers compared to milk packaged at the same milk treatment stations in glass bottles and plastic containers, Table 1.

Table 1. PCDDs and PCDFs in non-paperboard and paperboard packaged standard homogenised milks, (ppt, whole product basis).

Congener	Glass	Plastic	Carton Brand A paperboard mean (n=8)	Carton Brand A paperboard (range)	Carton Brand B paperboard mean (n=5)	Carton Brand B paperboard (range)
2,3,7,8-TCDF	<0.002	<0.003	0.76	(0.41-1.21)	0.15	(<0.04-0.42)
1,2,7,8-TCDF	<0.001	<0.002	0.46	(0.25-0.664)	0.082	(<0.02-0.23)
non 2,3,7,8-TCDF	<0.001	<0.002	0.28	(0.13-0.49)	0.047	(<0.02-0.15)
2,3,7,8-TCDD	<0.003	<0.004	0.035	(0.030-0.091)	0.014	(<0.007-0.039)
non 2,3,7,8-TCDD	0.021	0.013	0.017	(<0.008-0.048)	0.009	(<0.02-0.018)
1,2,3,7,8-PeCDF	<0.001	<0.002	<0.006	(<0.003-<0.01)	<0.01	(<0.002-<0.04)
2,3,4,7,8-PeCDF	<0.001	<0.001	<0.006	(<0.003-<0.008)	<0.01	(<0.002-<0.03)
non 2,3,7,8-PeCDF	0.024	0.023	0.023	(<0.01-0.071)	0.017	(<0.004-0.044)
1,2,3,7,8-PeCDD	<0.004	<0.005	<0.008	(<0.004-<0.01)	<0.02	(<0.002-<0.05)
non 2,3,7,8-PeCDD	<0.001	0.009	0.009	(<0.01-0.016)	0.039	(<0.009-0.23)
1,2,3,4,7,8-/ 1,2,3,6,7,8-HxCDF	<0.009	<0.008	<0.005	(<0.004-<0.008)	<0.008	(<0.002-<0.02)
2,3,4,6,7,8-HxCDF	<0.005	<0.006	<0.005	(<0.004-<0.008)	<0.009	(<0.003-<0.02)
1,2,3,7,8,9-HxCDF	<0.007	<0.009	<0.007	(<0.002-<0.01)	<0.01	(<0.004-<0.03)
non 2,3,7,8-HxCDF	<0.007	<0.006	<0.01	(<0.004-<0.05)	<0.008	(<0.002-<0.01)
1,2,3,4,7,8-/ 1,2,3,6,7,8-HxCDD	<0.02	<0.02	<0.01	(<0.001-<0.02)	<0.03	(<0.008-<0.06)
1,2,3,7,8,9-HxCDD	<0.01	<0.01	<0.007	(<0.003-<0.01)	<0.01	(<0.004-<0.04)
non 2,3,7,8-HxCDD	<0.02	<0.02	<0.01	(<0.01-<0.03)	<0.03	(<0.008-<0.05)
1,2,3,4,6,7,8-HpCDF	<0.005	<0.006	<0.005	(<0.002-<0.006)	<0.005	(<0.002-<0.02)
1,2,3,4,7,8,9-HpCDF	<0.002	<0.004	<0.003	(<0.001-<0.006)	<0.005	(<0.002-<0.02)
non 2,3,7,8-HpCDF	<0.002	<0.005	<0.004	(<0.001-<0.006)	<0.006	(<0.002-<0.02)
1,2,3,4,6,7,8-HpCDD	0.016	0.014	0.019	(<0.02-0.033)	0.013	(<0.01-0.029)
non 2,3,7,8-HpCDD	<0.02	<0.009	<0.01	(<0.003-<0.02)	<0.02	(<0.007-<0.04)
OCDF	<0.02	<0.03	<0.02	(<0.02-<0.04)	<0.07	(<0.02-<0.2)
OCDD	0.049	0.10	0.074	(<0.04-0.18)	0.052	(<0.03-0.13)
TCDD TE (Nordic)	0.006	0.007	0.14	(0.097-0.22)	0.040	(0.012-0.093)

Interestingly, the penta- to octa- congeners in the paperboard packaged milks were at or near background levels as represented by the amounts determined for the glass and plastic packaged milks.

Time dependence of PCDD and PCDF migration.

To confirm the source of the contamination, a time trial study was undertaken whereby the levels of PCDDs and PCDFs were determined in standard homogenised milk packaged for 0 (non-paperboard packaged), 2, 4, 6 and 8 days in paperboard cartons. Again only tetrachlorinated congeners were quantifiable, with a progressive increase in the amounts determined in the milk with time, Figure 1.

Effect of fat content on PCDD and PCDF migration.

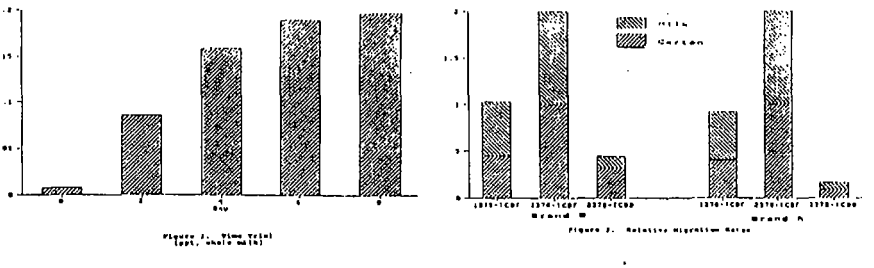
Given the lipophilicity of these chemicals it was believed that the degree of PCDD and PCDF migration from the paperboard would be related to the fat content of the material packaged. It was hoped to show this by analysing samples of low fat milk (< 0.5% fat) and cream (40% fat) packaged in paperboard cartons. Unexpectedly however, levels of TCDD and TCDFs quantified on a whole product basis for the low fat milk samples were comparable to the levels determined for the standard milks stored under identical conditions, Table 2. Similarly levels determined for the cream samples were not significantly different to those of the low fat and standard milks. It is apparent therefore that the migratory ability of PCDDs and PCDFs from the paperboard into dairy solutions is *not* directly related to the fat content of that solution.

Congener specificity of PCDD and PCDF migration.

The levels of PCDDs and PCDFs in the two brands of paperboard packaging are listed in Table 3. Generally the lower levels of TCDD and TCDFs in brand B paperboard are reflected in the levels of TCDD and TCDFs

Table 2. TCDDs and TCDFs in paperboard packaged (brand A) low fat milk and cream, (ppt, whole product basis).				
Congener	Low fat milk mean (n=4)	(range)	Cream mean (n=4)	(range)
2,3,7,8-TCDF	1.48	(0.89-2.11)	1.10	(0.26-2.49)
1,2,7,8-TCDF	0.97	(0.53-1.45)	0.59	(0.16-1.35)
non 2,3,7,8-TCDF	0.51	(0.32-0.74)	0.14	(<0.07-0.37)
2,3,7,8-TCDD	0.056	(0.039-0.076)	<0.2	(<0.1-<0.2)
non 2,3,7,8-TCDD	0.004	(0.002-0.006)	<0.3	(<0.2-<0.5)

in the milk packaged in these cartons. By normalising the levels of TCDD and TCDF isomers determined in the paperboard and 3.5% fat milk samples to 2,3,7,8-TCDF, there would appear to be, for both brands of paperboard, a preferential rate of migration of TCDF isomers > TCDD, Figure 2. Interestingly while all samples showed the characteristic 1,2,7,8-, 2,3,7,8-, 1,2,8,9-TCDF bleaching profile, 4 of the 8 samples examined also showed significant amounts of PeCDD, HxCDD, HpCDD and OCDD congeners. It was somewhat surprising therefore, that, particularly, no HxCDDs having a profile similar to that observed in the paperboard were determined in any of the milk or cream samples examined and levels of HpCDD and OCDD in the products packaged in paperboard cartons were only slightly elevated compared to the levels determined for the non-paperboard packaged milks. In addition, the time trial experiment did not show any increase in the amounts of these higher chlorinated congeners in the milk with time.



This indicates a preferential migration of the tetra- chlorinated congeners from the paperboard into the milk products. Several factors may contribute to this phenomenon; molecular size and mass, lipophilicity (as reflected in log $k_{o/w}$ values) and the manner in which these isomers are present in the finished product (see below).

Sources of PCDDs and PCDFs in finished paper products.

The sources of PeCDDs, HxCDDs, HpCDDs and OCDD in finished paper products will be shown to be different to, and independent of, the sources of TCDDs and TCDFs. The tetrachlorinated congeners have been shown to arise from the chlorine bleaching of kraft pulp (8). We have identified a number of additives used in papermaking processes that contribute these higher chlorinated congeners to the finished product (9). The tetrachlorinated congeners are intimately associated with the pulp while the higher chlorinated congeners may have quite different associations with the pulp and with other additive preparations. The availability of these

for migration may be controlled by different factors than those that control the tetrachlorinated congeners.

The extent to which any or all of these factors may influence migratory ability of the congeners into milk is not yet apparent.

Table 3. PCDDs and PCDFs in paperboard cartons, (ppt).

Congener	Brand A paperboard		Brand B paperboard	
	Mean (n=4)	(range)	mean (n=4)	(range)
2,3,7,8-TCDF	261	(30.8-444)	28.2	(5.82-81.3)
1,2,7,8-TCDF	105	(14.2-213)	12.8	(5.82-36.4)
non 2,3,7,8-TCDF	50.4	(4.27-105)	7.50	(1.79-36.4)
2,3,7,8-TCDD	24.9	(1.72-42.9)	9.02	(2.63-23.1)
non 2,3,7,8-TCDD	7.46	(<0.6-26.1)	0.18	(<0.07-0.57)
1,2,3,7,8-PeCDF	1.67	(0.41-3.70)	0.47	(0.20-1.08)
2,3,4,7,8-PeCDF	<0.08	(<0.04-<0.1)	<0.08	(<0.03-<0.1)
non 2,3,7,8-PeCDF	4.82	(<0.2-8.46)	2.46	(1.19-4.13)
1,2,3,7,8-PeCDD	0.76	(<0.01-1.16)	2.13	(<0.3-0.63)
non 2,3,7,8-PeCDD	18.0	(0.75-68.9)	1.02	(0.73-1.81)
1,2,3,4,7,8-HxCDF	0.07	(<0.03-0.17)	0.14	(<0.1-0.19)
1,2,3,6,7,8-HxCDF	0.09	(<0.05-0.23)	0.39	(<0.2-1.18)
2,3,4,6,7,8-HxCDF	0.54	(<0.06-0.87)	1.84	(0.15-6.73)
1,2,3,7,8,9-HxCDF	<0.05	(<0.04-0.07)	<0.06	(<0.04-<0.07)
non 2,3,7,8-HxCDF	0.12	(<0.03-0.25)	0.46	(<0.07-2.41)
1,2,3,4,7,8-/1,2,3,6,7,8-HxCDD	15.4	(0.48-59.5)	5.46	(0.46-8.37)
1,2,3,7,8,9-HxCDD	9.22	(<0.5-28.9)	2.78	(0.36-4.30)
non 2,3,7,8-HxCDD	55.7	(1.61-232)	23.9	(1.76-38.5)
1,2,3,4,6,7,8-HpCDF	0.94	(0.14-2.29)	20.1	(1.26-68.9)
1,2,3,4,7,8,9-HpCDF	<0.08	(<0.04-<0.11)	<0.1	(<0.09-<0.2)
non 2,3,7,8-HpCDF	0.19	(<0.04-0.53)	1.87	(<0.09-6.86)
1,2,3,4,6,7,8-HpCDD	9.10	(<2-18.7)	13.9	(20.5-5.14)
non 2,3,7,8-HpCDD	9.24	(1.16-22.6)	12.0	(3.97-18.2)
OCDF	0.47	(0.29-0.72)	9.33	(0.28-34.8)
OCDD	21.0	(10.3-36.5)	170	(20.9-576)
TCDD TE (Nordic)	54.1	(14.6-86.0)	13.7	(4.41-31.6)

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