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Phthalate and adipate esters in Australian packaging materials

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Abstract

A total of 136 food packaging materials were analysed for the presence of six phthalate esters and one adipate ester. All of the sample materials were manufactured from either synthetic polymers or from wood pulp and most were in immediate contact with their food contents. The esters in the packaging materials were extracted into a 2:1 mixture of chloroform and methanol, and analysed by gas chromatography-mass spectrometry. All of the materials examined were found to contain two or more of these compounds above a detection limit of 0.01 μg/kg. Total phthalate concentrations ranged from 5 to 8160 μg/g and adipate concentrations ranged from not detected to 1728 μg/g. In general, materials with the most surface coverage of printing inks had the greatest concentrations of phthalates. Variations were noticed in the occurrence and concentrations of phthalate and adipate esters in the packaging materials over a 12 month period during 1996 and 1997.

1. Introduction

Plasticisers are used in the polymer industry to improve flexibility, workability and general handling properties. They are commonly used in films, in tubing, in liners or seals for bottle caps or lids, in liners of bulk liquid holding tanks or in conveyor belt material (Kirkpatrick, Ripley, & Pelletier, 1989). Di-2-ethylhexyl phthalate (DEHP) is the most common plasticiser used worldwide, with an estimated annual production rate of 2.7 million tonnes per year (Bradbury, 1996); DEHP and dibutyl phthalate (DBP) total about 80% of the total industrial production of phthalic acid esters in Japan (Morita, Nakaruma, & Mimura, 1973).

Phthalates are not bound chemically in the plastics and can consequently penetrate these materials, and migrate into food that comes into contact. The presence of phthalates in packaging materials and their migration into packaged foods have been confirmed by a number of authors (Castle, Mercer, Startin, & Gilbert, 1988; Page & Lacroix, 1992; Petersen, 1991; Nerin, Cacho, & Gancedo, 1993). The amount of phthalates in packaged foods depends on many factors including the concentration of phthalates in the packaging material or printing ink, the storage period, the storage temperature, the fat content in the food and the contact area.

Regulations governing the use of plasticisers in food-contact applications vary from country to country. Recently, the United Kingdom Ministry of Fisheries and Food (MAFF) released tolerable daily intakes (TDI) for some of the phthalate esters, including DEHP, DBP, benzyl butyl phthalate (BBP) and diethyl phthalate (DEP). Thus, in the United Kingdom, the acceptable concentrations (TDI) have been set for DEHP at 0.05 mg/kg body weight/day; BBP at 0.1 mg/kg body weight/day; DBP at 0.05 mg/kg body weight/day and DEP at 0.2 mg/kg body weight/day (MAFF, 1996). In Europe, the total tolerable daily intake (TTDI) per person of total phthalate esters has been estimated to be 0.3 mg/kg body weight (Petersen, Naamansen, & Nielsen, 1995). In Australia, acceptable limits for the presence of phthalate and adipate esters in foods and beverages have not been established. Consequently, foodstuffs containing such compounds could be regarded as adulterated. Following an extensive study of phthalates and di-2-ethyl hexyl adipate (DEHA) in packaging materials in the UK and Europe, the current study was undertaken to establish the concentrations of these compounds in a variety of packaging materials in use in Australia.

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2. Materials and methods

2.1. Packaging materials and chemicals

The reference materials DEP, DEHA and dioctyl phthalate (DOP) were purchased from Tokyo Kasei Kogyo Co., Nihobashi-Honcho, Japan. The reference materials DBP, dimethyl phthalate (DMP), BBP, DEHP and the internal standard (1-chlorotetradecane) were purchased from Sigma Aldrich Chemical Co., St. Louis, MO, USA.

Packaged food and beverages were obtained from supermarket outlets throughout various suburbs in Sydney during 1996–1997. A variety of packaging materials were selected for the analyses, including printed polyethylene (PPE), printed fibreboard (PFB), polystyrene (PS), Cellophane (CL), polyvinyl chloride (PVC) and laminated aluminium polyethylene (AL-PE).

Methanol (analytical reagent grade) and chloroform (Omnisolv CX1059-1) were purchased from Merck, Darmstadt, Germany. The solvents were analysed for phthalate and adipate ester contamination and, if necessary, were further purified by fractional distillation; the distillates were stored in all-glass containers.

2.2. Laboratory handling and sample preparation

All glassware used in these analyses was washed with Pyroneg (Diversey, Amsterdam, Luchthaven, Schiphol), rinsed with filtered water and ethanol and baked at 120°C overnight. A new extraction thimble (Whatman no. 2800258) was used for each sample extraction. Procedural blanks were performed on all solvents and equipment, including sample vials. These precautions were required to maintain low laboratory and reagent phthalate backgrounds. In addition, unprinted materials were extracted (controls) to reassure method efficiency and to confirm that no phthalate background was detected by gas chromatography–mass spectrometry (GC–MS). There was no indication of any targeted plasticisers at the specified retention times for these controls. Packaging materials were cut into 1 cm squares and thoroughly mixed to provide a representative sample.

2.3. Extraction of phthalate and adipate esters

All samples of packaging materials were analysed in duplicate. A sample of each material (1 g) was placed in an extraction thimble and transferred to a Soxhlet apparatus. Folch solution (chloroform:methanol 2:1, 50 ml) was added to the apparatus and the sample was extracted for 6 h. After such time, no further phthalates or adipate could be extracted. For all sample extractions, the condensers of the Soxhlet apparatus were connected to an iced water supply (temperature = 0°C), to ensure no loss of volatiles. After completion of the extraction, the extracts were transferred into 50 ml glass volumetric flasks and, after addition of the internal standard, 1-chlorotetradecane (1 mg), were made up to 50 ml with Folch solution. Samples of these solutions (1 ml) were transferred to Target DP 2 ml autosampler vials and analysed by GC–MS.

2.4. Analysis by gas chromatography–mass spectrometry (GC–MS)

A Hewlett–Packard (Palo Alto, CA) HP 5890 II gas chromatograph (GC) interfaced to a Hewlett–Packard HP 5972 mass selective detector, operated in the multiple ion detection (MID) mode was used for the analysis of the phthalate and adipate esters in all extracts. The GC was fitted with a 30 m×0.25 mm i.d. fused silica column coated with HP-5MS (0.25 μm film thickness). Aliquots (2 μl) of the sample extracts or calibration solutions were injected automatically using a Hewlett–Packard HP 7673 autosampler. For all analyses the injections were split 1:25. The GC oven was programmed as follows: the temperature was initially held at 70°C for 1 min, heated from 70 to 280°C at 20°C/min, then held at 280°C for 10 min. The helium flow was 0.7 ml/min. The introducer temperature was 250°C and the GC–MS transfer line was 280°C. The MS was operated in the electron ionisation mode with an energy of 70 eV. Quantitative analysis by MID was performed under software control by a Hewlett–Packard Vectra VL2 computer running a Hewlett–Packard MS ChemStation data system. The GC–MS was calibrated by the injection of three different concentrations of the phthalate and adipate esters (2, 10 and 20 μg/ml). The concentration of internal standard was constant in each of these solutions (20 μg/ml).

2.5. Extraction efficiency

The extraction efficiencies of the Soxhlet technique for the recovery of phthalate and adipate esters from polymeric materials and wood pulp products were determined as follows. Samples of polyethylene film (1 g) or fibreboard (1 g), previously shown to be free from the target compounds, were each inoculated with 100 μg each of the phthalate and adipate esters. The treated materials were then extracted, and the extracts were analysed by GC–MS as described above. Recoveries ranged from 95–131%.

3. Results and discussion

Packaging materials of dairy products, baked goods, breads, beverages, breakfast cereals, confectionery, pasta, and other miscellaneous food products were

analysed. The amounts of plasticisers varied from year to year; some compounds were higher in some samples in 1996 than in 1997 and others were lower. From the 136 samples analysed, all contained at least one of the targetted packaging additives. DMP was not present in any of the samples. DEP and DOP were only detected in trace quantities. The more predominant additives were DEHP, DBP, BBP and DEHA.

3.1. Dairy packaging

The GC–MS analyses of all 26 dairy packaging samples showed that they contained at least one of the targeted packaging additives (Table 1). The materials analysed during the 12 month period were either printed polyethylene (PPE), polystyrene (PS), printed fibreboard (PFB), polyethylene (PE), polyethylene terephthalate (PET) or high density polyethylene (HDPE). Total phthalate concentrations ranged from 15 to 8160 μg/g. DEP was only detected in one sample in trace amounts. This sample was the ice cream pack A (1997) with a concentration of 8 μg/g. DOP was present in trace quantities in eight samples with its concentration ranging from not detected to 30 μg/g. The shredded cheese pack A (1996) had the highest concentration of DOP. The predominant plasticisers in the dairy packaging were DEHP, followed by DBP, DEHA and BBP.

The concentrations of DEHP, DBP, DEHA and BBP during the 12 month period ranged from 5 to 6630 μg/g, not detected to 360 μg/g, not detected to 65 μg/g, and not detected to 2670 μg/g, respectively. Significant concentrations of DEHP were found in the ice cream wrappers A (1996: 2050 μg/g and 1997: 5976 μg/g) and the outer cheese pack A (1996: 5005 μg/g and 1997: 6630 μg/g). Higher concentrations of DEHP were detected in 1997 than in 1996 for both of these samples. The reverse trend was apparent in a number of other samples, where lower DEHP concentrations were detected in 1997 than 1996, including the shredded cheese pack A (1996: 3298 μg/g, 1997: 1352 μg/g) and the cheese wrapper A (1996: 1508 μg/g, 1997: 15 μg/g). Significant concentrations of DBP were found in the ice cream wrappers A in 1997 (360 μg/g) compared with 1996 (255 μg/g). Almost identical concentrations of DEHA were found in the milk carton B in 1996 and 1997 (65 and 64 μg/g, respectively). A significant amount of BBP was present

Table 1
Distribution of phthalate and adipate esters in dairy packaging (μg/g)[a]

Period analysed	Product[b]	Material[c]	DMP[d]	DEP	DBP	BBP	DEHP	DOP	TP	DEHA
1996	Milk carton A	Laminated PE-FB-PPE	0[e]	0	53	3	20	0	76	0
1997			0	0	7	0	28	0	35	0
1996	Milk carton B	Laminated PE-FB-PPE	0	0	10	0	5	0	15	65
1997			0	0	16	0	16	0	32	64
1996	Yoghurt tub A	PS	0	0	15	0	40	0	55	0
1997			0	0	0	0	84	0	84	0
1996	Ice cream wrappers A	PPE	0	0	255	2670	2050	5	4980	5
1997			0	0	360	1824	5976	0	8160	0
1996	Ice cream pack A	PFB	0	0	50	0	15	0	65	0
1997			0	8	80	0	880	0	968	0
1996	Shredded cheese pack A	PPE	0	0	0	0	3298	30	3328	8
1997			0	0	8	0	1352	0	1360	0
1996	Shredded cheese pack B	PPE	0	0	8	0	8	0	16	0
1997			0	0	5	5	15	0	25	0
1996	Cheese tray A	PS	0	0	0	0	110	5	115	5
1997			0	0	0	0	20	0	20	0
1996	Outer cheese pack A	PPE	0	0	10	0	5005	10	5025	10
1997			0	0	9	0	6630	0	6639	0
1996	Cheese wrapper A	PE	0	0	0	0	1508	25	1533	3
1997			0	0	10	0	15	0	25	0
1996	Cheese wrapper B	PE	0	0	0	0	145	15	160	10
1997			0	0	5	0	60	0	65	0
1996	Ice cream lid A	PET	0	0	15	10	10	5	40	0
1997			0	0	14	0	42	0	56	0
1996	Ice cream tub A	HDPE	0	0	10	0	10	5	25	0
1997			0	0	14	0	28	0	42	0

[a] Where samples were analysed in 1996–1997.
[b] A–B indicates different brand names.
[c] PE-FB-PPE, polyethylene-fibreboard-printed polyethylene; PS, polystyrene; PPE, printed polyethylene; PFB, printed fibreboard; PE, polyethylene; PET, polyethylene terephthalate; HDPE, high density polyethylene.
[d] DMP, dimethyl phthalate; DEP, diethyl phthalate; DBP, dibutyl phthalate; BBP, benzyl butyl phthalate; DEHP, di-2-ethyl hexyl phthalate; DOP, dioctyl phthalate; TP, total phthalates; DEHA, di-2-ethyl hexyl adipate.
[e] Not detected at a detection limit of 0.01 μg/kg.

in the ice cream wrappers A, with a higher concentration detected in 1996 (2670 μg/g) compared to 1997 (1824 μg/g).

3.2. Baked goods packaging

The 16 samples analysed were made of either printed polyethylene (PPE), laminated aluminium–polyethylene (AL-PE), polystyrene (PS), printed fibreboard (PFB) or Cellophane (CL) (Table 2). Total phthalate concentrations during the 12 month period ranged from 60 to 6950 μg/g with DBP and DEHP being the predominant phthalates, followed by BBP and the adipate DEHA. DMP was not present in any samples, while DEP and DOP were present in only five samples in trace amounts.

The concentrations of DBP and DEHP varied from 7 to 4750 μg/g and 15 to 1868 μg/g, respectively. Substantial DBP concentrations were found in the biscuit wrappers A (1996: 4750 μg/g and 1997: 2610 μg/g) and the chip bag B (1996: 1673 μg/g and 1997: 1722 μg/g). BBP was present in eight samples of the baked goods packaging. Substantial concentrations were found in the biscuit wrappers A (1996: 2150 μg/g and 1997: 1690 μg/g). DEHA was found in six samples of the baked goods packaging. Concentrations ranged from not detected to 95 μg/g, with the biscuit wrappers A (95 μg/g) having the highest amount in 1997.

3.3. Bread packaging

The GC–MS analyses of all 14 bread packaging samples showed that they contained at least two of the targetted packaging additives (Table 3). The material analysed during the 12 month period was all printed polyethylene (PPE). Total phthalate concentrations ranged from 27 to 295 μg/g. DMP, DEP and DOP were not present in any samples. BBP was present in only three samples (bread wrappers A, C and F) in identical trace amounts (5 μg/g) in 1996 only. The predominant plasticisers in the bread packaging were DEHA, followed by DEHP and DBP.

The concentrations of DEHP, DBP and DEHA during the 12 month period ranged from 7 to 120 μg/g, 5 to 265 μg/g and not detected to 1728 μg/g, respectively. Substantial concentrations of DEHP were found in the bread wrappers E (1997: 112 μg/g) and F (1997: 120 μg/g); and for DBP substantial concentrations were found in the bread wrappers F in 1996 (265 μg/g) compared with 1997 (30 μg/g). Large amounts of DEHA were found in the bread wrappers A (1996: 1463 μg/g), C (1996: 1708 μg/g), F (1996: 1618 μg/g and 1997: 878 μg/g) and G (1997: 1728 μg/g).

3.4. Beverage packaging

A total of 14 beverage packaging samples were analysed (Table 4). These materials consisted of polyethylene terephthalate (PET) and printed polyethylene (PPE). Total phthalate concentrations during the 12 months ranged from 10 to 3410 μg/g with the soft drink bottle A containing the highest phthalate concentrations (1996: 3410 μg/g). Predominant phthalates found were DEHP (2 to 3375 μg/g in 1996), DBP (not detected to 35 μg/g in 1996) and the adipate DEHA (not detected to

Table 2
Distribution of phthalate and adipate esters in baked goods packaging (μg/g)[a]

Period analysed	Product[b]	Material[c]	DMP[d]	DEP	DBP	BBP	DEHP	DOP	TP	DEHA
1996	Chip bag A	Laminated AL-PE	0[e]	0	10	5	1868	33	1916	0
1997			0	0	48	0	40	0	88	0
1996	Chip bag B	PPE	0	0	1673	5	708	13	2399	5
1997			0	0	1722	420	35	0	2177	0
1996	Chip bag C	PPE	0	0	30	0	365	0	395	0
1997			0	0	48	8	32	0	88	0
1996	Biscuit wrappers A	PPE	0	0	4750	2150	50	0	6950	0
1997			0	5	2610	1690	70	0	4375	95
1996	Biscuit inner tray A	PS	0	0	30	10	15	5	60	3
1997			0	0	7	0	63	0	70	7
1996	Biscuit outer pack A	PFB	0	0	45	0	50	0	95	0
1997			0	7	126	0	630	0	763	0
1996	Biscuit outer pack B	PFB	0	0	35	5	460	0	500	0
1997			0	0	25	0	135	0	160	5
1996	Biscuit contents pack A	CL	0	0	25	0	95	0	120	0
1997			0	0	20	0	125	0	145	5

[a] Where samples were analysed in 1996–1997.
[b] A–C indicates different brand names.
[c] AL-PE, aluminium polyethylene; PPE, printed polyethylene; PS, polystyrene; PFB, printed fibreboard; CL, Cellophane.
[d] DMP, dimethyl phthalate; DEP, diethyl phthalate; DBP, dibutyl phthalate; BBP, benzyl butyl phthalate; DEHP, di-2-ethyl hexyl phthalate; DOP, dioctyl phthalate; TP, total phthalates; DEHA, di-2-ethyl hexyl adipate.
[e] Not detected at a detection limit of 0.01 μg/kg.

Table 3
Distribution of phthalate and adipate esters in bread packaging (μg/g)[a]

Period analysed	Product[b]	Material[c]	DMP[d]	DEP	DBP	BBP	DEHP	DOP	TP	DEHA
1996	Bread wrappers A	PPE	0[e]	0	15	5	35	0	55	1463
1997			0	0	14	0	21	0	35	7
1996	Bread wrappers B	PPE	0	0	5	0	30	0	35	175
1997			0	0	20	0	7	0	27	397
1996	Bread wrappers C	PPE	0	0	20	5	35	0	60	1708
1997			0	0	14	0	49	0	63	0
1996	Bread wrappers D	PPE	0	0	10	0	55	0	65	5
1997			0	0	7	0	28	0	35	7
1996	Bread wrappers E	PPE	0	0	5	0	70	0	75	365
1997			0	0	21	0	112	0	133	203
1996	Bread wrappers F	PPE	0	0	265	5	25	0	295	1618
1997			0	0	30	0	120	0	150	878
1996	Bread wrappers G	PPE	0	0	18	0	24	0	42	0
1997			0	0	18	0	30	0	48	1728

[a] Where samples were analysed in 1996–1997.
[b] A–G indicates different brand names.
[c] PPE, printed polyethylene.
[d] DMP, dimethyl phthalate; DEP, diethyl phthalate; DBP, dibutyl phthalate; BBP, benzyl butyl phthalate; DEHP, di-2-ethyl hexyl phthalate; DOP, dioctyl phthalate; TP, total phthalates; DEHA, di-2-ethyl hexyl adipate.
[e] Not detected at a detection limit of 0.01 μg/kg.

Table 4
Distribution of phthalate and adipate esters in beverage packaging (μg/g)[a]

Period analysed	Product[b]	Material[c]	DMP[d]	DEP	DBP	BBP	DEHP	DOP	TP	DEHA
1996	Juice container A	PET	0[e]	0	0	0	338	5	343	1
1997			0	0	0	0	21	0	21	0
1996	Juice container B	PET	0	0	0	0	10	0	10	0
1997			0	0	0	0	15	0	15	0
1996	Juice container C	PET	0	0	10	0	20	0	30	0
1997			0	0	0	0	21	0	21	0
1996	Soft drink bottle A	PET	0	0	0	0	3375	35	3410	5
1997			0	0	7	0	35	0	42	0
1996	Milk shake cup A	PPE	0	0	0	5	15	5	45	0
1997			0	0	20	0	13	0	33	0
1996	Milk thick shake straw A	PPE	0	0	35	5	15	5	60	0
1997			0	0	21	0	2	0	23	0
1996	Soy milk tetra pack A	PPE	0	0	20	0	5	0	25	0
1997			0	0	7	0	35	0	42	0

[a] Where samples were analysed in 1996–1997.
[b] A–C indicates different brand names.
[c] PET, polyethylene terephthalate; PPE, printed polyethylene.
[d] DMP, dimethyl phthalate; DEP, diethyl phthalate; DBP, dibutyl phthalate; BBP, benzyl butyl phthalate; DEHP, di-2-ethyl hexyl phthalate; DOP, dioctyl phthalate; TP, total phthalates; DEHA, di-2-ethyl hexyl adipate.
[e] Not detected at a detection limit of 0.01 μg/kg.

5 μg/g in 1996). DEHP was detected in all seven samples, with substantial quantities found in the soft drink bottle A in 1996 (3375 μg/g).

3.5. Breakfast cereal packaging

The 18 samples analysed were made of either polyethylene (PE) or printed fibreboard (PFB) (Table 5). Total phthalate concentrations during the 12 month period ranged from 10 to 233 μg/g with DBP and DEHP being the predominant phthalate, followed by the adipate, DEHA. DMP was not present in any samples, while DEP, BBP and DOP in total were present in only six samples in trace amounts. The concentrations of DBP and DEHP varied from 5 to 113 μg/g and 5 to 170 μg/g, respectively. Substantial concentrations of DBP were found in the cereal contents pack A (1996: 113 μg/g) and the cereal outer pack A (1996: 110 μg/g).

Table 5
Distribution of phthalate and adipate esters in breakfast cereal packaging (μg/g)[a]

Period analysed	Product[b]	Material[c]	DMP[d]	DEP	DBP	BBP	DEHP	DOP	TP	DEHA
1996	Rolled oats pack A	PFB	0[e]	0	50	0	170	13	233	30
1997			0	0	24	0	8	0	32	0
1996	Cereal outer pack A	PFB	0	5	110	0	80	8	203	23
1997			0	0	45	8	23	0	76	0
1996	Cereal outer pack B	PFB	0	0	35	0	10	0	45	0
1997			0	0	28	0	49	0	77	0
1996	Cereal outer pack C	PFB	0	0	30	0	15	0	45	0
1997			0	0	15	0	30	0	45	0
1996	Cereal outer pack D	PFB	0	0	65	0	20	0	85	0
1997			0	0	56	0	14	0	70	0
1996	Cereal contents pack A	PE	0	0	113	10	73	8	204	20
1997			0	0	27	0	18	0	45	0
1996	Cereal contents pack B	PE	0	0	28	0	7	0	35	0
1997			0	0	21	0	35	0	56	0
1996	Cereal contents pack C	PE	0	0	5	0	5	0	10	0
1997			0	0	8	0	16	0	24	0
1996	Cereal contents pack D	PE	0	0	85	0	7	0	92	0
1997			0	0	81	0	9	0	90	0

[a] Where samples were analysed in 1996–1997.
[b] A–D indicates different brand names.
[c] PFB, printed fibreboard; PE, polyethylene.
[d] DMP, dimethyl phthalate; DEP, diethyl phthalate; DBP, dibutyl phthalate; BBP, benzyl butyl phthalate; DEHP, di-2-ethyl hexyl phthalate; DOP, dioctyl phthalate; TP, total phthalates; DEHA, di-2-ethyl hexyl adipate.
[e] Not detected at a detection limit of 0.01 μg/kg.

DEHP was present in all samples, with predominant concentrations apparent in the rolled oats pack A (1996: 170 μg/g) and the cereal outer pack A (1996: 80 μg/g). DEHA was found in three samples of the breakfast cereal packaging. Concentrations varied from not detected to 30 μg/g, with the rolled oats pack A having the highest amount in 1996.

Overall, the breakfast cereal packaging showed a decrease in the concentrations of plasticisers in 1997 compared to 1996, in particular levels of DBP, DEHP and DEHA were all reduced. This trend was prevalent in most of these materials analysed.

3.6. Confectionery packaging

Each of the 10 confectionery packaging samples contained at least two of the plasticisers under investigation (Table 6). Printed polyethylene (PPE) was the only material analysed in this sample category. Total phthalate concentrations ranged from 24 to 5401 μg/g with the chocolate bar wrapper A (1996) having the largest quantities. DBP and DEHP were the predominant plasticisers detected in all the samples, followed by BBP and DEHA, which were detected in seven samples. DBP concentrations ranged from 6 to 1580 μg/g with the lolly wrap A (1996) containing the largest amount. A concentration of 480 μg/g DBP was detected in the 1997 sample, which demonstrated a reduction in the use of this plasticiser over 1996. DEHP concentrations ranged from 18 to 2665 μg/g. Substantial amounts of DEHP were detected in 1996 in the chocolate bar wrapper A (2665 μg/g) and the carrot slice pack A (1555 μg/g). A significant drop of the use of DEHP was apparent in 1997 for these two samples, as for most of the other confectionery packaging samples analysed. Substantial BBP concentrations were observed in the chocolate bar wrappers A (1996: 2716 μg/g and 1997: 2618 μg/g) and the lolly wrap A (1997: 1775 μg/g). DEHA was detected in minor amounts in the carrot slice pack A in 1996 (20 μg/g), the lolly wrap A in 1997 (5 μg/g) and the lolly wrap B in 1997 (6 μg/g).

3.7. Pasta packaging

Among the eight pasta packaging samples analysed, printed polyethylene (PPE) was the only material sampled (Table 7). Total phthalate concentrations ranged from 17 to 1915 μg/g, with the pasta pack B having the largest concentration in 1996. In addition to the total phthalate amounts being high in this sample, the adipate DEHA was also detected in large concentrations (1996: 650 μg/g and 1997: 660 μg/g). Predominant phthalates apparent in the pasta packaging samples were DBP and DEHP. Substantial amounts of DBP were present in pasta pack A (1996: 1845 μg/g and 1997: 609 μg/g) and pasta pack B (1996: 1425 μg/g and 1997: 1045 μg/g), while high concentrations of DEHP were apparent in pasta pack B (1996: 490 μg/g and 1997: 650 μg/g).

Table 6
Distribution of phthalate and adipate esters in confectionery packaging (μg/g)[a]

Period analysed	Product[b]	Material[c]	DMP[d]	DEP	DBP	BBP	DEHP	DOP	TP	DEHA
1996	Carrot slice pack A	PPE	0[e]	0	145	0	1555	0	1700	20
1997			0	0	6	0	18	0	24	0
1996	Chocolate bar wrapper A	PPE	0	0	20	2716	2665	0	5401	0
1997			0	0	15	2618	173	0	2806	0
1996	Chocolate bar wrapper B	PPE	0	0	15	0	790	0	805	0
1997			0	0	100	0	110	0	210	0
1996	Lolly wrap A	PPE	0	0	1580	60	50	5	1695	0
1997			0	0	480	1775	60	0	2315	5
1996	Lolly wrap B	PPE	0	0	25	0	40	0	65	0
1997			0	0	12	0	18	0	30	6

[a] Where samples were analysed in 1996–1997.
[b] A–B indicates different brand names.
[c] PPE, printed polyethylene.
[d] DMP, dimethyl phthalate; DEP, diethyl phthalate; DBP, dibutyl phthalate; BBP, benzyl butyl phthalate; DEHP, di-2-ethyl hexyl phthalate; DOP, dioctyl phthalate; TP, total phthalates; DEHA, di-2-ethyl hexyl adipate.
[e] Not detected at a detection limit of 0.01 μg/kg.

Table 7
Distribution of phthalate and adipate esters in pasta packaging (μg/g)[a]

Period analysed	Product[b]	Material[c]	DMP[d]	DEP	DBP	BBP	DEHP	DOP	TP	DEHA
1996	Pasta pack A	PPE	0[e]	0	1845	5	25	0	1875	5
1997			0	0	609	7	98	0	714	0
1996	Pasta pack B	PPE	0	0	1425	0	490	0	1915	650
1997			0	0	1045	0	650	0	1695	660
1996	Pasta pack C	PPE	0	0	25	55	25	0	105	0
1997			0	0	42	28	35	0	105	0
1996	Noodles pack A	PPE	0	0	11	0	6	0	17	0
1997			0	0	13	0	7	0	20	0

[a] Where samples were analysed in 1996–1997.
[b] A–C indicates different brand names.
[c] PPE, printed polyethylene.
[d] DMP, dimethyl phthalate; DEP, diethyl phthalate; DBP, dibutyl phthalate; BBP, benzyl butyl phthalate; DEHP, di-2-ethyl hexyl phthalate; DOP, dioctyl phthalate; TP, total phthalates; DEHA, di-2-ethyl hexyl adipate.
[e] Not detected at a detection limit of 0.01 μg/kg.

3.8. Miscellaneous packaging

A total of 30 miscellaneous packaging samples were analysed (Table 8). These materials consisted of laminated aluminium polyethylene (AL-PE), printed fibreboard (PFB), printed polyethylene (PPE), Cellophane (CL), polyethylene terephthalate (PET) and polyvinyl chloride (PVC). Total phthalate concentrations over the 12 months ranged from 5 to 7088 μg/g with the lemon squeeze container A having of the highest phthalate concentrations (1996: 7088 μg/g). Predominant phthalates detected were DEHP (5 to 7058 μg/g in 1996), DBP (not detected to 555 μg/g in 1997) and BBP (not detected to 1620 μg/g in 1997). The adipate DEHA was apparent in seven samples, with the green beans pack A having the highest amount (1996: 260 μg/g). DEHP was detected in all the samples analysed, with substantial quantities found in the lemon squeeze container A in both years (7058 and 5803 μg/g), the raw cashews pack A in 1996 and 1997 (2180 and 1345 μg/g, respectively) and in the coffee pack A in 1996 and 1997 (2060 and 2176 μg/g, respectively). DEHP is widely used as a plasticiser for the production of PVC (National Toxicity Program, 1982), which probably explains the high concentrations detected in the lemon squeeze container. Moderate amounts of DBP were detected in both years of the raw cashews pack A (250 and 260 μg/g), the tea pack B in 1997 (555 μg/g) and in the cocoa outer pack A in 1996 (310 μg/g). BBP concentration was predominant in the outer jelly pack A in 1997 (1620 μg/g).

3.9. Comparison of the CSIRO survey with the MAFF Food Safety Directorate survey

A similar investigation with respect to phthalates and packaging material was undertaken by MAFF's Food

Table 8
Distribution of phthalate and adipate esters in miscellaneous packaging (μg/g)[a]

Period analysed	Product[b]	Material[c]	DMP[d]	DEP	DBP	BBP	DEHP	DOP	TP	DEHA
1996	Soup pack A	Laminated AL-PE	0[e]	0	18	0	88	0	106	0
1997			0	0	7	0	126	0	133	14
1996	Raw cashews pack A	PPE	0	0	250	60	2180	0	2490	0
1997			0	0	260	90	1345	0	1695	0
1996	Brown rice pack A	PPE	0	0	7	21	7	0	35	0
1997			0	0	35	0	413	0	448	5
1996	Green beans pack A	PPE	0	0	25	0	290	0	315	260
1997			0	0	21	0	931	0	952	14
1996	Lecithin pack A	PPE	0	0	15	10	20	5	50	0
1997			0	7	7	0	26	0	40	0
1996	Jelly outer pack A	PFB	0	0	60	5	20	5	90	0
1997			0	0	30	1620	20	0	1670	0
1996	Jelly inner pack A	CL	0	0	35	0	20	5	60	0
1997			0	0	24	720	24	0	768	0
1996	Lemon squeeze container A	PVC	0	0	30	0	7058	0	7088	8
1997			0	0	35	0	5803	0	5838	0
1996	Apricot pie pack A	PFB	0	0	8	3	490	8	509	0
1997			0	0	10	0	10	0	20	0
1996	Tea pack A	PFB	0	0	5	0	10	0	15	0
1997			0	0	17	0	85	0	102	0
1996	Tea pack B	PFB	0	0	5	0	1625	0	1630	0
1997			0	0	555	0	130	0	685	10
1996	Spring water bottle A	PET	0	0	30	0	103	5	138	5
1997			0	0	14	0	70	0	84	0
1996	Cocoa outer pack A	PFB	0	0	310	0	15	0	325	0
1997			0	0	182	0	35	0	217	0
1996	Cocoa inner pack A	CL	0	0	0	0	5	0	5	0
1997			0	0	16	0	48	0	64	0
1996	Coffee pack A	PPE	0	0	10	0	2060	0	2070	0
1997			0	0	8	0	2176	0	2184	0

[a] Where samples were analysed in 1996–1997.
[b] A–B indicates different brand names.
[c] AL-PE, aluminium polyethylene; PPE, printed polyethylene; PFB, printed fibreboard; CL, Cellophane; PVC, polyvinyl chloride; PET, polyethylene terephthalate.
[d] DMP, dimethyl phthalate; DEP, diethyl phthalate; DBP, dibutyl phthalate; BBP, benzyl butyl phthalate; DEHP, di-2-ethyl hexyl phthalate; DOP, dioctyl phthalate; TP, total phthalates; DEHA, di-2-ethyl hexyl adipate.
[e] Not detected at a detection limit of 0.01 μg/kg.

Safety Directorate. A survey of 100 retail samples of printed paper and board packaging were analysed for phthalates (MAFF, 1995). There were similar findings between the two studies (MAFF and CSIRO), in that DBP and DEHP were identified as the most common phthalates present in samples. In the MAFF study, DBP was present in 98% of the samples at concentrations from 5 to 5860 μg/g, and DEHP in 95% of samples from 5 to 3030 μg/g. In the CSIRO's study, DBP was present in 81% of samples from 5 to 4750 μg/g, and DEHP in 100% of samples from 2 to 7058 μg/g.

4. Conclusion

The results of this study provide information on the concentrations of DEHA, DEHP, BBP, DBP, DOP, DEP and DMP in a variety of packaging materials used by the Australian food industry during 1996–1997. Every material analysed contained a phthalate ester or DEHA. Total phthalate concentrations ranged from 5 to 8160 μg/g and demonstrated a large variation of the use of plasticisers in the packaging industry during a 12 month period. DEHP was the most common plasticiser detected in all samples (ranging from 2 to 7058 μg/g), followed by DBP (not detected to 4750 μg/g), DEHA (not detected to 1728 μg/g), BBP (not detected to 2716 μg/g), DOP (not detected to 35 μg/g), DEP (not detected to 8 μg/g), and DMP (not detected). These data suggest that DEHP and DBP have a more significant role in the food packaging industry than DOP, DEP or DMP. Overall, the highest concentrations of plasticisers were detected in the printed polyethylene materials; hence the ultimate source of the plasticisers may have been the printing inks. Other sources of these compounds could be processing line additives or contact

with other components during production and transportation.

Studies carried out since the completion of this work have shown that some of these Australian food manufacturers have reduced the phthalate and adipate esters in their packaging material to background levels. This demonstrates that the Australian food industry has reacted in a fast, positive and responsible manner.

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