DANISH MINISTRY
OF THE ENVIRONMENT
Environmental
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Phthalates in plastic sandals

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Preface

The project ”Phthalates in plastic sandals” was carried out from March 2010 till June 2010.

This report describes the project results, including a survey of products and chemical analyses of a number of selected products and a risk assessment.

As a starting point, it was examined which plastic sandals and foam clogs/foam shoes on the Danish market might contain phthalates. Subsequently, quantitative analyses and migration analyses were carried out on a number of selected products. Finally, a risk assessment was carried out with focus on phthalates.

The project was carried out by Danish Technological Institute with Kathe Tønning (MA) as project manager and Nils Nilsson (PhD), Eva Jacobsen (MSc), Eva Pedersen (laboratory technician) and Bjørn Malmgren-Hansen (PhD) as project co-workers.

The project was followed by a reference group consisting of the following persons:

- Shima Dobel, the Danish Environmental Protection Agency
- Maria Mostrup Scheel, the Danish Environmental Protection Agency
- Kathe Tønning, Danish Technological Institute
- Nils Nilsson, Danish Technological Institute
- Eva Pedersen, Danish Technological Institute.

The project was financed by the Danish Environmental Protection Agency.

Summary and conclusions

In the autumn of 2009, the Swedish Naturskyddsförening (the Swedish Society for Nature Conservation) published a study that demonstrated that many plastic sandals imported from the East contain phthalates.

In addition, a project carried out by the Danish Environmental Protection Agency concerning the exposure of 2-year-olds to chemical substances showed that a pair of foam clogs for children liberated very high concentrations of phthalates to artificial sweat and could constitute a health risk.

That is why plastic sandals available on the Danish market were investigated.

The objective of the investigation was to illustrate if phthalates in plastic sandals on the Danish market are problematic.

In the project, focus was on the four phthalates DEHP, BBP, DBP and DIBP that are classified as toxic for the reproduction.

Chapter 2 concerns the survey of plastic sandals and foam clogs/foam shoes on the Danish market that can be expected to contain phthalates. A wide range of the surveyed sandals and foam clogs/foam shoes will probably be used without socks and therefore there will be direct skin contact between the foot and the foam sandal or foam clog/foam shoe.

The survey comprises footwear for children as well as for adults but focus has mainly been on footwear for children.

Footwear for children was grouped in shoes for 2-year-olds and for 6/7-year-olds.

By plastic sandals is meant sandals where part of the product is made of foam and that part might be in contact with the skin i.e. sandals that consist of foam in the top side of the sole or that have a foam strap. The sandals come with or without a heel strap and other materials can form part of the product (e.g. textile and/or leather).

By foam clogs we mean a product similar to a wooden clog but made from a loosely cross-linked plastic material or vulcanised rubber.

The survey only comprises products that are marketed in Denmark or sold on Danish internet pages.

In addition to identifying plastic sandals and foam clogs/foam shoes, products for further analysis were selected and purchased. 60 sandals were selected and purchased for chemical analysis.

The sandals are distributed on 20 pairs of sandals for adults, 20 pairs of sandals for 2-year-olds and 20 pairs of sandals for 6/7-year-olds.

Chapter 3 shows the results of the quantitative analyses and the migration analyses that were carried out.

The 60 selected products from the survey were analysed quantitatively for four selected phthalates DIBP, DBP, BBP and DEHP. A sample amount of the products was extracted with dichloromethane and analysed by means of gas chromatography with mass spectrometric detection (GC-MS).

A content of the phthalates DIBP, DBP and DEHP was detected in several of the analysed plastic sandals and foam clogs/foam shoes and for all three age groups. More plastic sandals for children contain phthalates in the sole or strap in the order of magnitude of 10-46%. BBP was only detected in a few sandals and in low concentrations.

In the light of the quantitative analysis results, 19 products were selected for 22 migration analyses with artificial sweat to simulate the exposure of skin contact with the products. Furthermore, 5 additional tests were carried out to investigate if there is a difference between dynamic or static extraction and if exposure increases when using sun lotion.

Table 0.1 gives an outline of the selected products on which migration analyses were carried out. The results are stated as the average result of the single analysis for the quantitative and migration analysis, respectively.

Samples no. 1-20 are sandals for adults, samples no. 26-39 are sandals for 2-year-olds and samples no. 43-55 are sandals for 6/7-year-olds.

Table 0.1 Summary of selected results, mg/kg

Sample no.	Description	DIBP		DBP		BBP		DEHP	
		Quant.	Migr.	Quant.	Migr.	Quant.	Migr.	Quant.	Migr.
1.1	Sole	62650	13	228500	28	25	< L.O.D	22200	0.7
5.2	Strap	< L.O.D	< L.O.D	265500	53	< L.O.D	< L.O.D	24	0.4
6.1	Sole	51	< L.O.D	2190	< L.O.D	< L.O.D	< L.O.D	302000	0.8
8.1	Sole	212000	20	1	< L.O.D	< L.O.D	< L.O.D	148000	0.3
8.2	Strap	74000	23	82450	17	< L.O.D	< L.O.D	171000	0.4
12.1	Sole	115	< L.O.D	< L.O.D	< L.O.D	< L.O.D	< L.O.D	460500	1.3
13.2	Strap	< L.O.D	< L.O.D	345000	44	< L.O.D	< L.O.D	265	4.2
17.1	Sole	66250	7.6	8900	0.8	< L.O.D	< L.O.D	245000	0.3
18.1	Middle of sole	22050	122	1965	4.1	< L.O.D	< L.O.D	110500	8.3
18.2	Outer part of sole	116500	12	804	0.05	< L.O.D	< L.O.D	209500	0.2
20.2	Strap	53350	14	178000	29	< L.O.D	< L.O.D	10200	7.2
26.1	Sole	64	< L.O.D	0.01	< L.O.D	< L.O.D	< L.O.D	344500	0.4
29.2	Outer part of sole	15500	17	< L.O.D	< L.O.D	< L.O.D	< L.O.D	< L.O.D	0.3
37.2	Strap	121000	49	< L.O.D	< L.O.D	< L.O.D	< L.O.D	209000	2.3
38.2	Strap	121000	37	12250	2.6	< L.O.D	< L.O.D	138	< L.O.D
39.2	Strap	572	< L.O.D	< L.O.D	< L.O.D	< L.O.D	< L.O.D	258000	1.1
43.1	Sole	112	< L.O.D	< L.O.D	< L.O.D	< L.O.D	< L.O.D	327500	0.4
44.1	Sole	< L.O.D	< L.O.D	< L.O.D	< L.O.D	< L.O.D	< L.O.D	461500	1.0
46.1	Middle of sole	22300	38	2875	0.8	< L.O.D	< L.O.D	105000	21
46.2	Outer part of sole	38650	13	3080	0.3	< L.O.D	< L.O.D	154000	1.8
54.2	Strap	2860	< L.O.D	282500	51	< L.O.D	< L.O.D	3710	0.3
55.1	Sole	329000	393	33	< L.O.D	< L.O.D	< L.O.D	128	4.9

L.O.D: Detection limit

The detection limits were 10 mg/kg for the quantitative analyses and 0.02-0.2 mg/kg for the migration analyses.

The results of migration analyses of the phthalates DIBP, DBP and DEHP to the artificial sweat simulant is lower than the quantified content in the

products due to the low solubility of the phthalates in the stimulant, especially DEHP.

The highest concentrations were measured during the additional tests where sun lotion had been applied to the product before the migration analysis. Comparison tests were carried out between dynamic and static shaking and the result shows greater analysis uncertainty during dynamic shaking.

The results of the migration analyses were used for the risk assessment.

In the risk assessment the Risk Characterisation Ratios (RCR) were calculated for the static conditions in the 22 migration tests above.

No RCRs were larger than 1 but 4 RCR values were larger than 0.1.

Table 0.2 RCR values at static conditions (only RCR values >0.1 are shown)

Sample ID	RCR DIBP	RCR DBP	RCR DEHP	SUM of RCR 1)
1.1	0.0019	0.7459	0.0011	0.75
5.2	<0.0001	0.1373	<0.0001	0.14
13.2	<0.0001	0.1388	0.0009	0.14
54.2	<0.0001	0.1715	<0.0001	0.17

1) Only the values larger than detection limit has been added in SUM of RCR

A number of supplementary tests were performed to evaluate the influence of dynamic conditions and use of sun lotion.

In Table 0.3 is shown a significant effect of using sun lotion and dynamic conditions (corresponding to movement of the foot).

Table 0.3 Factor of increase in migration

Test	Factor of increase in migration of partly water soluble phthalates like DIBP	Factor of increase in migration low water soluble phthalate DEHP
Dynamic conditions	0.8-1.4 (1.1)	5-45 (25)
Sun lotion	0.8-3.9 (2.4)	5-23 (14)
Sun lotion and dynamic conditions	1.9-4.9 (3.4)	75-223 (149)

For partly water soluble phthalates like DBP and DIBP the increase from sun lotion and dynamic conditions is approximately a factor 3-4.

For DEHP which has a very low water solubility the increase is very large with a factor 150. The increase may be expected to be even larger when using oil based sun lotion.

The RCR values were recalculated at dynamic conditions and use of sun lotion as shown in Table 0.4 below. In this case no RCR values were larger than 1 but 9 out of 22 were larger than 0.1.

Table 0.4 RCR values at worst case-situation with dynamic conditions and use of sun lotion (only RCR values >0.1 are shown)

Product ID	Type 2)	RCR DIBP	RCR DBP	RCR DEHP	SUM of RCR [1)]
1.1	1	0.0021	0.8202	0.0573	**0.8796**
5.2	2	<0.0001	0.4644	<0.0103	**0.4644**
8.2	2	0.0009	0.1281	0.0177	**0.1468**
12.1	1	<0.0001	<0.0058	0.1185	**0.1185**
13.2	2	<0.0001	0.4695	0.2636	**0.7331**
20.2	2	0.0008	0.3028	0.4479	**0.7515**
37.2	2	0.0028	<0.0021	0.1441	**0.1469**
46.1	1	0.0006	0.0023	0.1825	**0.1854**
54.2	2	<0.0001	0.5801	<0.0133	**0.5801**

1) Only the values larger than detection limit have been added in SUM of RCR
2) 1: Part of soles (dynamic conditions), 2: Straps (dynamic conditions and sun lotion)

Of the RCR values above, 6 samples are from sandals for "grown ups", 2 samples from 6-7 year old children and one sample from 2–year old children.

Conclusions:

- Sandals for children seem to have a lower content of the four phthalates.
- The migrations of phthalates in plastic sandals present a significant contribution to the total phthalate exposure for consumers.

Sammenfatning og konklusioner

Den svenske Naturskyddsförening offentliggjorde i efteråret 2009 en undersøgelse, der viste, at mange plastsandaler, der var importeret fra Østen, indeholdt ftalater.

Endvidere Miljøstyrelsens projekt om 2-åriges udsættelse for kemiske stoffer, at et par gummitræsko til børn afgav så høje koncentrationer af ftalater til kunstig sved, at de kunne udgøre en risiko.

På denne baggrund er plastsandaler på det danske marked undersøgt.

Formålet med undersøgelsen er at få belyst, om ftalater i plastsandaler på det danske marked er problematisk.

Der er i projektet fokus på de fire ftalater DEHP, BBP, DBP og DIBP, der alle er klassificeret som reprotoksiske.

Af kapitel 2 fremgår kortlægningen af plastsandaler og gummitræsko/plastsko på det danske marked, der kan forventes at indeholde ftalater. For en lang række af de kortlagte sandaler og gummitræsko/plastsko kan det forventes, at der ikke anvendes en strømpe, og at der således er direkte hudkontakt mellem fod og plastsandal eller gummitræsko/plastsko.

Kortlægningen har omhandlet både børne- og voksenfodtøj, men med primært fokus på børnefodtøj.

Børnefodtøjet er grupperet i sko til 2-årige og til 6/7-årige.

Ved plastsandaler forstås sandaler, hvor en del af produktet er af plast, og hvor denne del kan have hudkontakt, dvs. sandaler hvor der er plast i oversiden af sålen, eller hvor remmen er af plast. Sandalerne kan være med og uden hælrem, og der kan indgå andre materialer i produkterne (fx tekstil og/eller læder).

Ved gummitræsko forstås et træskolignende produkt fremstillet af et løst tværbundet plastmateriale eller vulkaniseret gummi.

Kortlægningen omfatter kun produkter, der markedsføres i Danmark eller forhandles på danske internetsider.

Ud over at identificere plastsandaler og gummitræsko/plastsko er produkter til videre analyse udvalgt og indkøbt. Der er udvalgt og indkøbt 60 par sandaler til kemisk analyse.

Sandalerne fordeler sig med 20 par sandaler til voksne, 20 par sandaler til 2-årige børn og 20 par sandaler til 6/7-årige børn.

Af kapitel 3 fremgår resultaterne af de gennemførte kvantitative analyser og migrationsanalyser.

De udvalgte 60 produkter fra kortlægningen er analyseret kvantitativt for fire udvalgte ftalater DIBP, DBP, BBP og DEHP. En delprøve af produkterne er ekstraheret med dichlormethan og analyseret ved gaschromatografisk massespektrometri (GC-MS).

Der er påvist indhold af ftalaterne DIBP, DBP og DEHP i flere af de analyserede plastsandaler og gummitræsko/plastsko og til alle de tre aldersgrupper. Der er flere plastsandaler til børn, som i sål eller rem indeholder ftalater i størrelsesordenen 10-46 %. BBP er kun påvist i få sandaler og i lave koncentrationer.

Ud fra de kvantitative analyseresultater er der udvalgt 19 produkter til 22 migrationsanalyser med kunstigt sved for at simulere eksponeringen af hudkontakt med produkterne. Desuden er udført 5 supplerende forsøg for at undersøge, hvorvidt der er forskel på dynamisk eller statisk ekstraktion, og om eksponeringen øges ved anvendelse af solcreme.

I Table 0.1 ses en oversigt over de udvalgte produkter, hvor der er foretaget migrationsanalyser. Resultaterne er angivet som gennemsnitsresultatet af enkeltbestemmelserne for hhv. den kvantitative analyse og migrationsanalysen.

Prøve nr. 1-20 er sandaler til voksne, prøve nr. 26-39 er sandaler til 2-årige og prøve nr. 43-55 er sandaler til 6/7-årige.

Tabel 0.1 Sammenfatning af udvalgte resultater, mg/kg

Prøve nr.	Beskrivelse	DIBP		DBP		BBP		DEHP	
		Kvant.	Migr.	Kvant.	Migr.	Kvant.	Migr.	Kvant.	Migr.
1.1	Sål	62650	13	228500	28	25	< L.O.D	22200	0,7
5.2	Rem	< L.O.D	< L.O.D	265500	53	< L.O.D	< L.O.D	24	0,4
6.1	Sål	51	< L.O.D	2190	< L.O.D	< L.O.D	< L.O.D	302000	0,8
8.1	Sål	212000	20	1	< L.O.D	< L.O.D	< L.O.D	148000	0,3
8,2	Rem	74000	23	82450	17	< L.O.D	< L.O.D	171000	0,4
12.1	Sål	115	< L.O.D	< L.O.D	< L.O.D	< L.O.D	< L.O.D	460500	1,3
13.2	Rem	< L.O.D	< L.O.D	345000	44	< L.O.D	< L.O.D	265	4,2
17.1	Sål	66250	7,6	8900	0,8	< L.O.D	< L.O.D	245000	0,3
18.1	Midten af sål	22050	122	1965	4,1	< L.O.D	< L.O.D	110500	8,3
18.2	Yderste del af sål	116500	12	804	0,05	< L.O.D	< L.O.D	209500	0,2
20.2	Rem	53350	14	178000	29	< L.O.D	< L.O.D	10200	7,2
26.1	Sål	64	< L.O.D	0.01	< L.O.D	< L.O.D	< L.O.D	344500	0,4
29.2	Yderste del af sål	15500	17	< L.O.D	< L.O.D	< L.O.D	< L.O.D	< L.O.D	0,3
37.2	Rem	121000	49	< L.O.D	< L.O.D	< L.O.D	< L.O.D	209000	2,3
38.2	Rem	121000	37	12250	2,6	< L.O.D	< L.O.D	138	< L.O.D
39.2	Rem	572	< L.O.D	< L.O.D	< L.O.D	< L.O.D	< L.O.D	258000	1,1
43.1	Sål	112	< L.O.D	< L.O.D	< L.O.D	< L.O.D	< L.O.D	327500	0,4
44.1	Sål	< L.O.D	< L.O.D	< L.O.D	< L.O.D	< L.O.D	< L.O.D	461500	1,0
46.1	Midten af sål	22300	38	2875	0,8	< L.O.D	< L.O.D	105000	21
46.2	Yderste del af sål	38650	13	3080	0,3	< L.O.D	< L.O.D	154000	1,8
54.2	Rem	2860	< L.O.D	282500	51	< L.O.D	< L.O.D	3710	0,3
55.1	Sål	329000	393	33	< L.O.D	< L.O.D	< L.O.D	128	4,9

Detektionsgrænserne (L.O.D) er 10 mg/kg for kvantitative analyser og 0,02-0,2 mg/kg for migrationsanalyserne.

Analyseresultaterne viser, at migrationen af ftalaterne DIBP, DBP og DEHP til den kunstige sved-simulant er lavere end de kvantificerede indhold i produkterne. Dette skyldes den lave opløselighed af ftalaterne i simulanten, især DEHP.

Ved de supplerende forsøg er de højeste koncentrationer målt ved forsøgene, hvor der er påsmurt solcreme på produktet før migrationsanalysen. Der er

udført sammenligningsforsøg mellem dynamisk og statisk udrystning, og resultatet viser, at der er større analyseusikkerhed ved den dynamiske udrystning.

Resultaterne af migrationsanalyserne er anvendt til risikovurdering.

I risikoevalueringen er beregnet Risk Characterisation Ratios (RCR) under statiske betingelser for de 22 migrationstest vist ovenfor.

Ingen RCR værdier var større end 1 men 4 RCR-værdier var større end 0,1.

Tabel 0.2 RCR-værdier ved statiske betingelser (kun RCR-værdier >0,1 er vist)

Prøve ID	RCR DIBP	RCR DBP	RCR DEHP	Sum af RCR 1)
1.1	0,0019	0,7459	0,0011	0,75
5.2	<0,0001	0,1373	<0,0001	0,14
13.2	<0,0001	0,1388	0,0009	0,14
54.2	<0,0001	0,1715	<0,0001	0,17

1) Kun værdier større end detektionsgrænsen er adderet i Sum af RCR

Der er udført et antal supplerende tests for at undersøge betydningen af dynamiske migrationsbetingelser og betydning af brug af solcreme.

Af Tabel 0.3 ses, at der er en signifikant effekt ved brug af solcreme og dynamiske migrationsbetingelser (svarende til bevægelse af foden).

Tabel 0.3 Faktor for øget migration af ftalater

Test	Faktor for øget migration af delvis vandopløselige ftalater som DIBP	Faktor for øget migration af svært vandopløselige ftalater som DEHP
Dynamiske betingelser	0,8-1,4 (1,1)	5-45 (25)
Solcreme	0,8-3,9 (2,4)	5-23 (14)
Solcreme og dynamiske betingelser	1,9-4,9 (3,4)	75-223 (149)

For delvis vandopløselige ftalater som DBP og DIBP er fundet en stigning i migrationen på en faktor 3-4 ved brug af solcreme og dynamiske migrationsbetingelser.

For DEHP, som har meget lav vandopløselighed, er fundet en meget stor stigning i migrationen på en faktor 149 ved brug af solcreme og dynamiske migrationsbetingelser.

Stigningen i migration af DEHP og til dels DBP, DIBP forventes øget yderligere ved brug af oliebaseret solcreme.

RCR-værdierne er genberegnet for dynamiske migrationsbetingelser og brug af solcreme i Tabel 0.4. Der er nu 9 RCR-værdier over 0,1, men ingen over 1.

Tabel 0.4 RCR-værdier i worst case-situation med dynamiske migrationsbetingelser og brug af solcreme (kun RCR-værdier >0,1 er vist)

Prøve ID	Type [1)]	RCR DIBP	RCR DBP	RCR DEHP	SUM af RCR [2)]
1.1	1	0,0021	0,8202	0,0573	**0,8796**
5.2	2	<0,0001	0,4644	<0,0103	**0,4644**
8.2	2	0,0009	0,1281	0,0177	**0,1468**
12.1	1	<0,0001	<0,0058	0,1185	**0,1185**
13.2	2	<0,0001	0,4695	0,2636	**0,7331**
20.2	2	0,0008	0,3028	0,4479	**0,7515**
37.2	2	0,0028	<0,0021	0,1441	**0,1469**
46.1	1	0,0006	0,0023	0,1825	**0,1854**
54.2	2	<0,0001	0,5801	<0,0133	**0,5801**

1) 1: Del af sål (dynamisk betingelser), 2: Stropper (dynamiske betingelser og sollotion)
2) Kun værdier større end detektionsgrænsen er adderet i SUM af RCR

RCR værdier >0,1 fordeler sig på 6 prøver fra voksne, 2 prøver fra 6-7 årige børn og en prøve fra 2-årige børn.

Konklusion:

- Koncentrationen af de fire ftalater i sandaler til børn ser generelt ud til at være lavere end for voksen sandaler.
- Migrationen fra ftaltater i plastsandaler giver et væsentligt bidrag til den totale eksponering for ftalater for forbrugere

1 Introduction

In the autumn of 2009, the Swedish Naturskyddsförening (the Swedish Society for Nature Conservation) published a study that demonstrated that many plastic sandals imported from the East contain phthalates.

In addition, a project carried out by the Danish Environmental Protection Agency concerning the exposure of 2-year-olds to chemical substances showed that a pair of foam clogs for children liberated very high concentrations of phthalates to artificial sweat and could constitute a health risk.

That is why plastic sandals available on the Danish market have been investigated.

The objective of the investigation was to illustrate if phthalates in plastic sandals on the Danish market are problematic.

By plastic sandals is meant sandals where the top side of the sole (the side of the sole that is in touch with the skin) and the straps are made of foam and sandals where the top side of the sole is made of foam and the straps of another material (e.g. textile and/or leather). The sandals come with or without a heel strap.

By foam clogs is meant a product similar to a wooden clog but made from a loosely cross-linked plastic material or vulcanised rubber.

Plastic sandals and other lightweight foam shoes in the form of rubber/foam shoes are used by children and adults. The footwear is mainly used during summer and is used indoors as well as outdoors; however, the footwear can also be used during winter as a slipper.

2 Survey

2.1 Objective of the survey

The objective of the survey was to:

- Identify plastic sandals and foam clogs/shoes on the Danish market
- Procure products for chemical analyses.

2.2 Delimitation

The survey comprised plastic sandals and foam clogs/foam shoes on the Danish market that can be expected to contain phthalates. A wide range of the surveyed sandals and foam clogs/foam shoes will probably be used without socks and therefore there will be direct skin contact between the foot and the foam sandal or foam clog/foam shoe.

The survey comprised footwear for children as well as for adults but focus has mainly been on footwear for children.

Footwear for children was grouped in shoes for 2-year-olds and for 6/7-year-olds.

For the 2-year-olds, shoes in sizes 23-26 were investigated (as in the project of the Danish Environmental Protection Agency concerning the exposure of 2-year-olds to chemical substances /1/) and for the 6/7-year-olds shoes in sizes 29-32 were chosen (informed on the homepage of ”SKORINGEN”, a Danish shoe chain store, for that age group /2/).

The survey only comprised products that are marketed in Denmark or sold on Danish internet pages.

2.3 Procedure

The survey of sandals and foam clogs/foam shoes was carried out in March when plastic sandals and foam clogs/foam shoes had just started appearing in the shops.

Visits were paid to a number of retail shops in the Danish city of Aarhus and in that neighborhood. Mainly nation-wide shops were in question but local shops were also visited.

In addition, a wide range of internet shops dealing with sandals and foam clogs/foam shoes were visited.

2.3.1 Shop visits

Visits were paid to a wide range of shops, including:

- Shoe shops
- Department stores

- Sports shops
- Shops for children's wear
- Interior design shops with clothes/shoe department
- Supermarkets
- Drugstores
- Discount shops.

In addition, catalogues, advertising brochures etc. have been examined.

2.3.2 Internet visits

Searching took place on Google with different words and word combinations such as e.g. "plastic sandals, foam shoes, PVC", in order to find a number of internet shops that sell plastic sandals and foam clogs/foam shoes.

2.4 Result of survey

When the survey started, plastic sandals and foam clogs/foam shoes had just started appearing in the shops. The sandals and foam clogs/foam shoes were mainly registered in shoe shops, department stores and sports shops, while the selection was more modest in shops for children's wear and supermarkets.

Reduced goods (new products and products from the previous season) were nearly only registered in internet shops.

2.4.1 Result of shop visits

Especially for adults there was a large and varied supply of plastic sandals and they had many different product names.

Also for children a large supply of plastic sandals was registered. Unlike the supply of plastic sandals for adults the main impression was that as far as children's sandals were concerned there were less product names but to a greater extent there were many models within each individual product name/-brand.

One registered product name is very dominating on the market this year. Several shops informed that the product name also existed in 2009; but it should be expected to become very dominating in the summer of 2010. One department store had more than 20 different models for children of that specific product name.

2.4.2 Result of survey via internet pages

A number of the visited internet shops also sell many of the brands that were registered in the physical shops while other internet shops that were visited only have a limited supply of plastic sandals and foam clogs/foam shoes and either only sell known brands to a limited degree or not at all.

2.5 Selected products

Table 2.1, Table 2.2 and Table 2.3 show the products that were selected for analysis of content of the four classified phthalates DEHP, BBP, DBP and DIBP in cooperation with the Danish Environmental Protection Agency.

A total of 60 plastic sandals and foam clogs/foam shoes were selected, as follows:

- 20 pairs of plastic sandals and foam clogs/foam shoes for adults
- 20 pairs of plastic sandals and foam clogs/foam shoes for 2-year-olds
- 20 pairs of plastic sandals and foam clogs/foam shoes for 6/7-year-olds.

Mainly new goods from the 2010 season were purchased; however, a few models from last season were also included. They were mainly purchased in shops on the internet.

A total of 40 pairs of plastic sandals and foam clogs/foam shoes were purchased in physical shops and 20 pairs of plastic sandals and foam clogs/foam shoes were purchased from internet shops.

The criteria for the selection of plastic sandals and foam clogs/foam shoes for further analysis was that there was a strong probability that the footwear would be used without socks and therefore there would be direct skin contact between footwear and feet. Plastic sandals in the shape of so-called flip-flops and plastic sandals with a strap across the big toe therefore constitute a considerable amount of the footwear selected for further analysis as that type of footwear hinders the use of socks. Likewise, it must be expected that aqua sandals mainly are used without socks.

Another criterion for the selection of products was a wish for inexpensive as well as more expensive products.

The following plastic sandals and foam clogs/foam shoes were purchased.

Table 2.1 Purchased products – Plastic sandals and foam clogs/foam shoes for adults

No.	Type	Brief description	Remarks	Shop type
1	Aqua sandal	Foam sole and textile-lined foam upper part	Aqua sandal with ”acupressure nubs”	Shoe shop
2	Flip-flops	Foam sole and foam straps		Trade mark shop
3	Flip-flops	Foam sole and foam straps		Trade mark shop
4	Flip-flops	Foam sole and foam straps		Shop selling lingerie + sandals
5	Flip-flops	Foam sole and foam straps		Discount shop
6	Flip-flops	Foam sole and foam straps		Sports shop
7	Aqua sandal	Foam sole and textile-lined foam upper part		Sports shop
8	Flip-flops	Foam sole and foam straps		Shoe shop
9	Aqua sandal	Foam sole and textile-lined foam upper part		Shoe shop
10	Flip-flops	Foam sole and textile straps		Shoe shop
11	Sandal	Leather sole and foam straps	Sandal with big toe strap	Clothes shop
12	Aqua sandal	Foam sole and textile-lined foam upper part	Aqua sandal with ”acupressure nubs”	Internet shop
13	Flip-Flops	Foam sole and foam straps		Internet shop

No.	Type	Brief description	Remarks	Shop type
14	Flip-flops	Foam sole and textile straps		Internet shop
15	Flip-flops	Foam sole and foam straps	Sandal with heel strap	Internet shop
16	Flip-flops	Foam sole and textile straps	Outer side of straps made of plastics/leather	Internet shop
17	Closed foam shoe	Foam	Closed foam shoe with perforated pattern	Internet shop
18	Flip-flops	Foam sole and foam straps		Internet shop
19	Flip-flops	Foam sole and foam straps		Internet shop
20	Flip-flops	Foam sole and foam straps		Internet shop

Table 2.2 Purchased products – Plastic sandals and foam clogs/foam shoes for 2-year-olds

No.	Type	Brief description	Remarks	Shop type
21	Flip-flops	Foam sole and foam straps		Shop for children's wear
22	Flip-flops	Foam sole and textile straps		Interior design shop etc.
23	Flip-flops	Foam sole and textile straps	Sandal with heel strap	Clothes shop
24	Flip-flops	Foam sole and foam straps		Shop for children's wear and accessories
25	Foam shoes	Foam	Lightweight clog with heel strap	Discount shop
26	Aqua sandal	Foam	Closed aqua sandal	Shoe shop
27	Foam clog	Foam	Lightweight clog with heel strap	Shoe shop
28	Aqua sandal	Foam sole and textile straps	Sandal with heel strap	Shoe shop
29	Aqua sandal	Foam sole and textile-lined foam upper part		Department store
30	Closed foam shoe	Foam shoe with textile strap across instep and foam heel strap	Closed foam shoe with heel strap	Shoe shop
31	Foam clog	Foam	Lightweight clog with heel strap	Shoe shop
32	Sandal	Foam sole and textile straps	Sandal with heel strap	Sports shop
33	Closed foam shoe	Closed foam shoe with open toe		Shoe shop
34	Flip-flops	Foam sole and foam straps		Internet shop
35	Sandal	Foam sole with textile straps	Sandal with heel strap	Internet shop
36	Flip-flops	Foam sole with textile straps	Sandal with elastic heel strap	Internet shop
37	Flip-flops	Foam sole and foam straps	Sandal with elastic heel strap	Internet shop
38	Foam clog	Foam	Lightweight clog with heel strap	Internet shop
39	Sandal	Wooden sole and foam strap		Internet shop
40	Flip-flops	Textile sole and textile straps with plastic figures		Internet shop

Table 2.3 Purchased products – Plastic sandals and foam clogs/foam shoes for 6/7-year-olds

No.	Type	Brief description	Remarks	Shop type
41	Flip-flops	Foam sole and foam straps		Clothes shop
42	Flip-flops	Foam sole and foam straps		Shop for children's wear and accessories
43	Flip-flops	Foam sole and foam straps	Sandal with heel strap	
44	Aqua sandals	Foam	Closed aqua shoe	Sports shop
45	Sandal	Foam sole and textile straps	Sandal with heel strap	Clothes shop
46	Aqua sandal	Foam sole and textile-lined foam upper part		Shoe shop
47	Flip-flops	Foam sole and textile straps		Shoe shop
48	Sandal	Foam sole and textile straps	Sandal with heel strap	Shoe shop
49	Sandal	Foam sole and textile straps	Sandal with big toe strap	Shoe shop
50	Flip-flops	Foam sole and textile straps		Shoe shop
51	Foam clog	Foam	Lightweight clog with heel strap	Supermarket
52	Sandal	Foam sole and textile straps	Sandal with heel strap	Sports shop
53	Sandal	Foam sole and textile straps	Sandal with heel strap	Shoe shop
54	Flip-flops	Foam sole and foam straps		Shoe shop
55	Sandal	Foam sole and textile straps	Sandal with heel strap	Shoe shop
56	Sandal with closed toe	Foam sole and textile upper part and straps	Sandal with heel strap	Shoe shop
57	Sandal with closed toe	Foam sole and textile straps	Sandal with heel strap	Internet shop
58	Sandal	Foam sole and textile straps	Sandal with heel strap	Internet shop
59	Sandal	Foam sole and textile straps	Sandal with heel strap	Internet shop
60	Flip-flops	Foam sole and foam straps		Internet shop

The first part of the survey of plastic sandals and foam clogs/foam shoes took place by visiting physical shops.

The selection of the footwear took place by visual assessment and by smelling different parts of the footwear with which the skin is in direct contact.

In most cases, footwear of softened PVC has a characteristic and often unpleasant solvent smell. Footwear of foamed EVA often smell of acetophenone as this ketone is a degradation product from dicumyl peroxide which is the most frequently used cross-linking agent for EVA.

In a few cases, fragrance had been added to the footwear – possibly to disguise the unpleasant solvent odours and the nauseating acetophenone. Footwear to which fragrance had been added was also selected for the quantitative analysis.

To a great extent, the selection of footwear resulted from the visual assessment and from the odour of the footwear as they make it probable that

softened PVC is in direct contact with the skin or that footwear made of foam EVA is in question. The last-mentioned clog-like lightweight foam shoe is very popular and is available in a wide range of models and colours so it is considered important to include a segment of these foam shoes in order to ascertain if some of them are foam PVC with phthalates or if EVA footwear also can contain smaller or larger amounts of phthalates.

When selecting plastic sandals and foam clogs/foam shoes it was in general considered whether popular/trendy and/or branded goods were in question.

The selection of plastic sandals and lightweight foam shoes from internet shops was based on the experience obtained when visiting physical shops and on the basis of information about the footwear on the internet pages.

2.5.1 Product prices

During the survey, plastic sandals and foam clogs/foam shoes were registered in the price range from Euro 1.3/pair to Euro 73/pair.

3 Exposure scenarios

The main way of exposure for phthalates in plastic sandals is through dermal exposure of the foot.

The exposure of the foot is to either:

- the foot of the sole
- straps or top parts of the plastic sandals.

The chemical substances can get into contact with the foot through sweat but possibly also through skin care products, sun lotion etc.

Possible absorption through the skin can be estimated according to the formula ”Equation 15-8” from the REACH Guidance document, Chapter R.15 ”Consumer exposure estimation” (ECHA, april 2010). In the equation the factor F_{abs} has been added. F_{abs} is the fraction of substances that can be absorbed through the skin. Hereby the calculated D_{der} will amount to the real amount of substances that can be absorbed per kg bw per day, the internal exposure.

$$D_{der} = \frac{Q_{prod} \cdot Fc_{prod} \cdot Fc_{migr} \cdot F_{abs} \cdot F_{contact} \cdot T_{contact}}{BW} \cdot n \qquad (1)$$

$Fc_{prod} \bullet Fc_{migr}$ corresponds to the results of the migration analyses.

where

D_{der}	Dermal daily dose (amount of chemical substance that is absorbed)	µg/kg bw/day
Q_{prod}	Amount of product that is used	G
Fc_{prod}	Weight fraction of the substance in the product (decimal fraction between 0 and 1)	
Fc_{migr}	Fraction of substance that migrates per time unit out of the product	µg/g per hour
F_{abs}	Fraction of applied substance that is absorbed through the skin (decimal fraction between 0 and 1)	
$F_{contact}$	Fraction of contact area (to take into consideration that the product only partly is in touch with the skin)	m^2/m^2
$T_{contact}$	Duration of each exposure	Hours
N	Number of exposures (incidents)	per day
BW	Body weight (bw)	Kg

During migration tests from sandals the test are carried out on a smaller surface area A_{test} than the area that is exposed A_{exp}.

Intake per day per kg body weight can then be calculated on the basis of the following expression:

$$D_{der} = \frac{Q_{prod} \cdot M_{migr} \cdot A_{\exp} \cdot F_{abs} \cdot F_{contact} \cdot H_{\exp}}{A_{test} \cdot H_{test} \cdot BW} \quad \text{(µg/kg lgv/dag)} \qquad (2)$$

BW: Body weight (Body weight, kg)
M_{migr}: Migrated amount of substance = Fc_{prod} • Fc_{migr} (ug/g per hour of exposure, test)
A_{exp}: Area of exposure during use (cm^2)
A_{test}: Area of exposure in test (cm^2)
H_{test}: Exposure time in test (hours)
H_{exp}: Exposure time per day (hours) = Tcontact • n

Data for the fraction of phthalates that is absorbed through the skin are F_{abs} are shown later in chapter 5, Risk assessment.

In Table 3.1 are shown the weight and exposure time for the 3 groups that are in focus. The exposure time is chosen based on expected behaviour in a worst case scenario.

Table 3.1 weight and exposure time

Data	Children 2-year-olds	Children 6/7-year-olds	Adults
Weight kg	15.2	23.1 [1]	60
Exposure time (hours/day) worst case	10	12	16

1 from (WHO, 2007) 7 year old boy

Exposure areas will be estimated in chapter 5, Risk assessment.

Contact areas will be measured separately for each product depending on whether skin contact is with the sole of the foot, a strap or a larger surface, if the shoe is partly closed.

Adjustments will be made for differences in exposure time and area through tests in relation to use as stated in the formula (2).

3.1 Selecting of samples

22 samples of parts of plastic sandals are selected for migration analysis after evaluating the chemical analysis in chapter 4,

Chemical analyses. Furthermore, 5 supplementary migration tests are performed.

The selection is made on the basis of the following criteria:

- The shoes must contain one or more of the 4 selected phthalates in amounts of at least 0.05wt %.
- Focus is on phthalates with a high concentration.
- Focus is on a representative distribution on the different types of plastic sandals including manufacturing material and age groups.

When using the plastic sandals the conditions is dynamic part of the time in situations when persons are walking or placing weight on the sandals.

In summer time it is judged that especially kids will be using sun lotion.

It was previously ascertained that water-emulsion and oil-based lubricants can dramatically increase the washing out of phthalates compared to use without lubricants (Survey no. 77, 2006). Therefore an increase in amount of migrated phthalates is expected when using sun lotion.

Further from other studies (Survey no.100, 2008) dynamic migration conditions are known to increase the amounts which migrate.

In order to test the influence of dynamic conditions and the use of sun lotion 5 supplementary migration tests on a reference plastic sandal are carried out. The test matrix is shown in Table 3.2.

Table 3.2 Supplementary migration tests

No.	Second extraction step	Dynamic condition using shaker table	50% reduction in extraction time	Use of sun lotion
a (reference)				
b	X			
c			X	
d		X		
E				X
F		X		X

3.2 Test conditions for migration tests

- Test temperature is chosen to 37˚ C as the products are in direct contact with the body. Extraction medium for migration tests shall be artificial sweat simulant.
- The extraction time used in the migration tests has been set to 16 hours for all products corresponding to expected worst case exposure time for grownups. For products used by 2 year olds and 6-7 year olds correction for the shorter exposure time (see Table 3.1) is made using Equation 2.

4 Chemical analyses

The chemical analyses illustrate to which extent plastic sandals and lightweight clogs contain one or more of the four selected phthalates DIBP, DBP, BBP and DEHP. In addition, the migration analyses will illustrate to which extent there is a risk of exposure during use.

All the selected products were analysed quantitatively for the four phthalates DIBP, DBP, BBP and DEHP. In order to investigate the exposure when using the products with bare feet, migration analyses with artificial sweat were subsequently carried out on selected products with a quantified content of one or several phthalates.

4.1 Quantitative analyses

The selected analysis method for determination of the phthalates DIBP, DBP, BBP and DEHP in plastic sandals and lightweight clogs was extraction with dichloromethane which is judged to be the most suitable solvent for liberating the phthalates completely from the relevant polymer materials. PVC is for instance soluble in that solvent.

4.1.1 Sampling for quantitative analyses

In connection with the quantitative analyses, great importance was during sampling for the analyses placed on selecting sample amounts that will be in touch with the skin of the user meaning the sole and inner side of the strap if it is made of another material than the rest of the sandal/shoe and not covered with textile. In addition, decorations or plastic parts on straps were investigated as they might contain phthalates and might at the same time be in contact with the skin.

4.1.2 Initial analyses

Previous investigations have shown that PVC products sometimes do contain phthalates as additives. PVC contains chlorine, so in connection with the sample preparation the samples were tested for content of chlorine according to the Beilstein test. The test was carried out by heating a copper wire over a flame from a gas burner and subsequently, in cooled state, putting it into contact with the product. When the copper wire is reheated in the flame, a green flame will indicate a content of halogen, e.g. chlorine.

4.1.3 Method description of quantitative analyses

A weighed sample amount (app. 1 g) was extracted with 10 ml dichloromethane (DCM) with added deuterium marked internal standards (DBP-d_4 and DEHP-d_4) by ultrasound extraction. In connection with lightweight materials (foamed plastic), the sample amount can be smaller and a correspondingly smaller amount of extraction agent is used. Analysis in duplicate was carried out except for limited sample amounts (e.g. decorations on straps).

The extracts were analysed by means of gas chromatography with mass spectrometric detection (GC-MS). The concentration of phthalates was calculated quantitatively against standards of the respective phthalates DIBP, DBP, BBP and DEHP. Blank specimens and control tests were included in the analysis. If the analysis showed larger concentrations of other phthalates, they are stated as comments to the quantitative analyses, see chapter 4.2.4.

The detection limit was 10 mg/kg corresponding to 0.001 %(m/m) in the product.

The relative uncertainty of the method was estimated to 10-15%.

The uncertainty on the analyses in duplicate are stated as standard deviations (SD) in the result tables.

Table 4.1 states the complete name of the phthalates and the CAS no. besides the internal standards.

Table 4.1 Outline of the applied reference standards and internal standards

Phthalate abbreviation	Name	CAS no.	Application
DIBP	Diisobutyl phthalate	84-69-5	Reference standard
DBP	Dibutyl phthalate	84-74-2	Reference standard
BBP	Benzylbutyl phthalate	85-68-7	Reference standard
DEHP	Di(ethylhexyl) phthalate	117-81-7	Reference standard
DBP-d_4	Deuterium labelled Dibutyl phthalate		Internal standard
DEHP-d_4	Deuterium labelled Di(ethylhexyl) phthalate		Internal standard

Table 4.2 shows the chromatographic conditions.

Table 4.2 Parameters for GC-MS

GC/MS instrument	Agilent GC-MS
GC parameters	Column: Phenomex, ZB-5MS 30 m x 0.5 mm id., 0.25 µm film thickness Carrier gas: Helium, Constant flow at 1.8 ml/min. Oven program: 40 ºC for 0.5 min., 30 ºC/min. to 250 ºC, 20 ºC/min. to 320 ºC, 320 ºC for 8 min. Injection: 2 µl, 280 ºC, splitless
MS parameters	Scan mode: 40-450 m/z

Table 4.3, Table 4.4, Table 4.5, show the outlines of the sampling for quantitative analyses. Analyses in duplicate were carried out and their average weight is stated. In case of limited sample amount single analysis was carried out. Those samples are marked with '*' at each sample amount. In addition, the result of the initial test for halogens is stated where 'x' states the green flame, which can indicate content of chlorine and thus possible PVC based material to which phthalates could have been added as plasticisers.

Table 4.3 Outline of sampling for quantitative analyses, Adults

Product no.	Sample no.	Description	Chlorine test	Average weight (g)	Extraction volume (ml)
1	1.1	Sole	x	1.024	10
2	2.1	Sole		0.993	10
	2.2	Strap	x	1.007	10

Product no.	Sample no.	Description	Chlorine test	Average weight (g)	Extraction volume (ml)
3	3.1	Sole		1.004	10
	3.2	Strap	x	1.042	10
4	4.1	Sole		1.003	10
	4.2	Strap	x	0.997	10
5	5.1	Sole		0.999	10
	5.2	Strap	x	1.002	10
6	6.1	Sole	x	1.007	10
	6.2	Strap	x	1.009	10
7	7.1	Sole		1.006	10
8	8.1	Sole	x	0.999	10
	8.2	Strap	x	1.028	10
9	9.1	Sole		0.999	10
10	10.1	Sole		1.012	10
	10.2*	Mark	x	0.420	10
11	11.1	Sole		1.007	10
	11.2	Toe + shoe side	x	1.004	10
12	12.1	Sole	x	0.980	10
	12.2	Strap	x	0.527	10
	12.3	Pad	x	0.935	10
13	13.1	Sole		0.999	20
	13.2	Strap	x	0.967	10
14	14.1	Sole		0.507	10
15	15.1	Sole		0.986	10
	15.2*	Plastic near strap	x	0.579	10
16	16.1	Sole		0.522	10
17	17.1	Sole	x	0.960	10
	17.2*	Tag in sole	x	0.263	5
18	18.1	Middle of sole	x	0.506	10
	18.2	Outer part of sole	x	0.985	10
	18.3	Strap	x	0.992	10
19	19.1	Sole		0.544	10
	19.2	Strap		0.952	10
20	20.1	Sole		0.534	10
	20.2	Strap	x	0.858	10

'*' states single analysis

Table 4.4 Outline of sampling for quantitative analyses, 2-year-olds

Product no.	Sample no.	Description	Chlorine test	Average weight (g)	Extraction volume (ml)
21	21.1	Sole		1.009	10
	21.2	Strap	x	0.994	10
22	22.1	Sole		0.985	10
	22.2	Strap	x	1.003	10
	22.3*	Plastic between toes	x	0.295	5

Product no.	Sample no.	Description	Chlorine test	Average weight (g)	Extraction volume (ml)
23	23.1	Sole		0.994	10
	23.2*	Plastic between toes		0.110	10
24	24.1	Sole		0.994	10
	24.2	Strap	x	1.029	10
25	25.1	Sole		0.998	10
	25.2*	Button in strap	x	1.002	10
26	26.1	Sole		1.021	10
27	27.1	Sole		0.505	10
	27.2	Strap		0.534	10
28	28.1	Sole		0.554	10
29	29.1	Middle of sole	x	0.580	10
	29.2	Outer part of sole		0.608	10
	29.3	Strap	x	0.553	10
30	30.1	Sole		0.561	10
31	31.1	Sole		0.551	10
	31.2	Mark in sole	x	0.604	10
	31.3	Button in strap		0.360	10
32	32.1	Sole		0.521	10
33	33.1	Sole		0.522	10
34	34.1	Sole		1.020	10
	34.2	Strap	x	1.000	10
35	35.1	Sole		0.611	10
36	36.1	Sole		0.491	10
37	37.1	Sole		1.000	10
	37.2	Strap	x	1.007	10
	37.3	Plastic near elastic band		0.397	10
38	38.1	Sole		0.516	10
	38.2	Strap	x	0.888	10
39	39.1	Sole		0.549	10
	39.2	Plastic on strap	x	0.985	10
40	40.1	Sole, decoration in pad	x	0.627	10
	40.2	Sole		0.530	
	40.3*	Plastic between toes	x	0.385	5

'*' states single analysis

Table 4.5 Outline of sampling for quantitative analyses, 6/7-year-olds

Product no.	Sample no.	Description	Chlorine test	Average weight (g)	Extraction volume (ml)
41	41.1	Sole		0.987	10
	41.2	Strap		0.995	10
42	42.1*	Sole		1.025	10
	42.2	Strap	x	1.022	10

Product no.	Sample no.	Description	Chlorine test	Average weight (g)	Extraction volume (ml)
43	43.1	Sole	x	1.001	10
	43.2	Strap	x	1.010	10
44	44.1	Sole	x	1.028	10
45	45.1	Sole	x	0.989	10
46	46.1	Middle of sole	x	0.993	10
	46.2	Outer part of sole	x	1.040	10
	46.3*	Strap		0.765	10
	46.4*	Mark near heel		0.371	5
47	47.1	Sole		1.000	10
	47.2*	Plastic between toes		0.304	5
48	48.1*	Sole		1.034	20
	48.2*	Strap		0.810	10
	48.3*	Fancy rings near strap		0.355	5
49	49.1	Sole		1.007	10
50	50.1	Sole		1.016	10
51	51.1	Sole		0.523	10
	51.2	Button near strap		0.705	10
52	52.1	Sole		0.520	10
53	53.1	Sole		0.545	10
	53.2	Strap		0.359	10
54	54.1	Sole		0.518	10
	54.2	Strap	x	0.997	10
55	55.1	Sole		0.544	10
56	56.1	Sole		0.526	10
57	57.1	Sole		0.591	10
58	58.1	Sole		0.704	10
59	59.1	Sole		0.522	10
60	60.1	Sole		0.496	10
	60.2	Strap	x	0.959	10

'*' states single analysis

4.2 Results of quantitative analyses

The results are stated below and are organised according to the different age groups. They are stated in two tables with results calculated as mg/kg and in %(m/m), respectively, which is the weight percentage (mass/mass). The results (mg/kg) are reported with three significant figures except near the detection limit according to agreement with the Danish Environmental Protection Agency.

Analyses in duplicate were carried out for the quantitative analyses as far as the sample amount was sufficient. The results are stated as single analyses (a and b), the average of the analyses in duplicate and the calculated standard deviation of the analysis in duplicate. Sample amounts marked '*' were only

analysed as single analyses due to limited sample amount and therefore a standard deviation is not stated.

Results below the detection limit are stated as ”< L.O.D”, Limit of Detection.

The detection limits are 10 mg/kg equivalent to 0.001 %(m/m).

4.2.1 Quantitative analysis results for adults

Table 4.6 Results of quantitative analyses in mg/kg, adults

		DIBP				DBP				BBP				DEHP			
Product no.	Sample no.	a (mg/kg)	b (mg/kg)	Average (mg/kg)	SD (mg/kg)	a (mg/kg)	b (mg/kg)	Average (mg/kg)	SD (mg/kg)	a (mg/kg)	b (mg/kg)	Average (mg/kg)	SD (mg/kg)	a (mg/kg)	b (mg/kg)	Average (mg/kg)	SD (mg/kg)
1	1.1	60100	65200	62650	3606	222000	235000	228500	9192	26	24	25	1	22100	22300	22200	141
2	2.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
	2.2	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
3	3.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		13	11	12	1
	3.2	23	30	27	4	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
4	4.1	220	221	220	0.5	202	189	196	9	< L.O.D	< L.O.D	< L.O.D		11	11	11	0.1
	4.2	22500	24000	23250	1061	5840	6890	6365	742	< L.O.D	< L.O.D	< L.O.D		4230	6390	5310	1527
5	5.1	85	27	56	41	2350	2330	2340	14	< L.O.D	< L.O.D	< L.O.D		121	92	107	21
	5.2	< L.O.D	< L.O.D	< L.O.D		253000	278000	265500	17678	< L.O.D	< L.O.D	< L.O.D		29	18	24	8
6	6.1	47	54	51	5	1860	2520	2190	467	< L.O.D	< L.O.D	< L.O.D		302000	302000	302000	56
	6.2	32	29	30	3	113	130	121	12	< L.O.D	< L.O.D	< L.O.D		313000	248000	280500	45962
7	7.1	< L.O.D	< L.O.D	< L.O.D		15	15	15	0.3	< L.O.D	< L.O.D	< L.O.D		106	101	104	4
8	8.1	208000	216000	212000	5657	1	1	1	0.04	< L.O.D	< L.O.D	< L.O.D		151000	145000	148000	4243
	8.2	72000	76000	74000	2828	81100	83800	82450	1909	< L.O.D	< L.O.D	< L.O.D		168000	174000	171000	4243
9	9.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
10	10.1	12	12	12	0.3	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
	10.2*	13		13		15		15		< L.O.D		< L.O.D		17		17	
11	11.1	15	15	15	0.2	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		12	9	11	2
	11.2	1	4	3	2	4	3	3	0.4	< L.O.D	< L.O.D	< L.O.D		33	23	28	7
12	12.1	117	113	115	2	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		451000	470000	460500	13435
	12.2	108	82	95	18	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		112	77	95	25
	12.3	102	97	100	4	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		466000	456000	461000	7071

		DIBP				DBP				BBP				DEHP			
Product no.	Sample no.	a (mg/kg)	b (mg/kg)	Average (mg/kg)	SD (mg/kg)	a (mg/kg)	b (mg/kg)	Average (mg/kg)	SD (mg/kg)	a (mg/kg)	b (mg/kg)	Average (mg/kg)	SD (mg/kg)	a (mg/kg)	b (mg/kg)	Average (mg/kg)	SD (mg/kg)
13	13.1	< L.O.D	< L.O.D	< L.O.D		3580	1570	2575	1421	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
	13.2	< L.O.D	< L.O.D	< L.O.D		350000	340000	345000	7071	< L.O.D	< L.O.D	< L.O.D		280	250	265	21
14	14.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		30	32	31	1
15	15.1	10	11	10	0.3	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		212	63	138	105
	15.2*	99		99		107		107		< L.O.D		< L.O.D		334000		334000	
16	16.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
17	17.1	64700	67800	66250	2192	8400	9400	8900	707	< L.O.D	< L.O.D	< L.O.D		237000	253000	245000	11314
	17.2*	47100		47100		5890		5890		< L.O.D		< L.O.D		133000		133000	
18	18.1	22000	22100	22050	71	2100	1830	1965	191	< L.O.D	< L.O.D	< L.O.D		112000	109000	110500	2121
	18.2	119000	114000	116500	3536	538	1070	804	376	< L.O.D	< L.O.D	< L.O.D		213000	206000	209500	4950
	18.3	116000	112000	114000	2828	516	1050	783	378	< L.O.D	< L.O.D	< L.O.D		214000	204000	209000	7071
19	19.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
	19.2	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
20	20.1	22	114	68	65	48	296	172	175	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
	20.2	53500	53200	53350	212	176000	180000	178000	2828	< L.O.D	< L.O.D	< L.O.D		10100	10300	10200	141

'*' states single analyses

Table 4.7 Results of quantitative analyses in %(m/m), adults

		DIBP				DBP				BBP				DEHP			
Product no.	Sample no.	a (% v/v)	b (% v/v)	Average (% v/v)	SD (%)	a (% v/v)	b (% v/v)	Average (% v/v)	SD (%)	a (% v/v)	b (% v/v)	Average (% v/v)	SD (%)	a (% v/v)	b (% v/v)	Average (% v/v)	SD (%)
1	1.1	6.0	6.5	6.3	0.4	22.2	23.5	22.9	0.9	0.003	0.002	0.002	0.00014	2.2	2.2	2.2	0.01
2	2.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
	2.2	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
3	3.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.001	0.001	0.001	0.00009
	3.2	0.002	0.003	0.003	0.0004	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
4	4.1	0.022	0.022	0.022	0.00005	0.020	0.019	0.020	0.0009	< L.O.D	< L.O.D	< L.O.D		0.001	0.001	0.001	0.00001
	4.2	2.3	2.4	2.3	0.1	0.58	0.69	0.64	0.07	< L.O.D	< L.O.D	< L.O.D		0.42	0.64	0.53	0.15
5	5.1	0.008	0.003	0.006	0.004	0.24	0.23	0.23	0.001	< L.O.D	< L.O.D	< L.O.D		0.012	0.009	0.011	0.002
	5.2	< L.O.D	< L.O.D	< L.O.D		25.3	27.8	26.6	1.8	< L.O.D	< L.O.D	< L.O.D		0.003	0.002	0.002	0.0008
6	6.1	0.005	0.005	0.005	0.0005	0.19	0.25	0.22	0.05	< L.O.D	< L.O.D	< L.O.D		30.2	30.2	30.2	0.00
	6.2	0.003	0.003	0.003	0.0003	0.011	0.013	0.012	0.001	< L.O.D	< L.O.D	< L.O.D		31.3	24.8	28.1	4.6
7	7.1	< L.O.D	< L.O.D	< L.O.D		0.002	0.001	0.002	0.00003	< L.O.D	< L.O.D	< L.O.D		0.011	0.010	0.010	0.0004
8	8.1	20.8	21.6	21.2	0.6	0.0001	0.0001	0.0001	0.000004	< L.O.D	< L.O.D	< L.O.D		15.1	14.5	14.8	0.4
	8.2	7.2	7.6	7.4	0.3	8.1	8.4	8.2	0.2	< L.O.D	< L.O.D	< L.O.D		16.8	17.4	17.1	0.4
9	9.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
10	10.1	0.001	0.001	0.001	0.00003	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
	10.2*	0.001		0.001		0.002		0.002		< L.O.D		< L.O.D		0.002		0.002	
11	11.1	0.002	0.002	0.002	0.00002	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.001	0.001	0.001	0.0002
	11.2	0.0001	0.0004	0.0003	0.0002	0.0004	0.0003	0.0003	0.00004	< L.O.D	< L.O.D	< L.O.D		0.003	0.002	0.003	0.0007
12	12.1	0.012	0.011	0.011	0.0002	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		45.1	47.0	46.1	1.3
	12.2	0.011	0.008	0.009	0.002	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.011	0.008	0.009	0.002
	12.3	0.010	0.010	0.010	0.0004	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		46.6	45.6	46.1	0.7
13	13.1	< L.O.D	< L.O.D	< L.O.D		0.36	0.16	0.26	0.14	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
	13.2	< L.O.D	< L.O.D	< L.O.D		35.0	34.0	34.5	0.7	< L.O.D	< L.O.D	< L.O.D		0.028	0.025	0.027	0.002
14	14.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.003	0.003	0.003	0.0001

		DIBP				DBP				BBP				DEHP			
Product no.	Sample no.	a (% v/v)	b (% v/v)	Average (% v/v)	SD (%)	a (% v/v)	b (% v/v)	Average (% v/v)	SD (%)	a (% v/v)	b (% v/v)	Average (% v/v)	SD (%)	a (% v/v)	b (% v/v)	Average (% v/v)	SD (%)
15	15.1	0.001	0.001	0.001	0.00003	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.021	0.006	0.014	0.011
	15.2*	0.010		0.010		0.011		0.011		< L.O.D		< L.O.D		33.4		33.4	
16	16.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
17	17.1	6.5	6.8	6.6	0.2	0.84	0.94	0.89	0.07	< L.O.D	< L.O.D	< L.O.D		23.7	25.3	24.5	1.1
	17.2*	4.7		4.7		0.589		0.589		< L.O.D		< L.O.D		13.3		13.3	
18	18.1	2.2	2.2	2.2	0.01	0.21	0.18	0.20	0.02	< L.O.D	< L.O.D	< L.O.D		11.2	10.9	11.1	0.2
	18.2	11.9	11.4	11.7	0.4	0.05	0.11	0.08	0.04	< L.O.D	< L.O.D	< L.O.D		21.3	20.6	21.0	0.5
	18.3	11.6	11.2	11.4	0.3	0.05	0.11	0.08	0.04	< L.O.D	< L.O.D	< L.O.D		21.4	20.4	20.9	0.7
19	19.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
	19.2	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
20	20.1	0.002	0.011	0.007	0.007	0.005	0.030	0.017	0.018	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
	20.2	5.4	5.3	5.3	0.02	17.6	18.0	17.8	0.3	< L.O.D	< L.O.D	< L.O.D		1.0	1.0	1.0	0.01

'*' states single analyses

4.2.2 Quantitative analysis results for 2-year-olds

Table 4.8 Results of quantitative analyses in mg/kg, 2-year-olds

		DIBP				DBP				BBP				DEHP			
Product no.	Sample no.	a (mg/kg)	b (mg/kg)	Average (mg/kg)	SD (mg/kg)	a (mg/kg)	b (mg/kg)	Average (mg/kg)	SD (mg/kg)	a (mg/kg)	b (mg/kg)	Average (mg/kg)	SD (mg/kg)	a (mg/kg)	b (mg/kg)	Average (mg/kg)	SD (mg/kg)
21	21.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
	21.2	318	326	322	5	179	173	176	4	< L.O.D	< L.O.D	< L.O.D		835	845	840	7
22	22.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		10	11	11	1
	22.2	7	17	12	7	12	29	21	12	< L.O.D	< L.O.D	< L.O.D		18	32	25	10
	22.3*	49		49		54		54		< L.O.D		< L.O.D		191		191	
23	23.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		18	20	19	1
	23.2*	88		88		< L.O.D		< L.O.D		< L.O.D		< L.O.D		< L.O.D		< L.O.D	
24	24.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
	24.2	21	18	20	2	25	22	24	2	< L.O.D	< L.O.D	< L.O.D		87	62	74	18
25	25.1	< L.O.D	< L.O.D	< L.O.D		15	14	15	0	< L.O.D	< L.O.D	< L.O.D		29	134	81	74
	25.2*	< L.O.D		< L.O.D		< L.O.D		< L.O.D		< L.O.D		< L.O.D		< L.O.D		< L.O.D	
26	26.1	67	61	64	5	129	100	115	21	< L.O.D	< L.O.D	< L.O.D		335000	354000	344500	13435
27	27.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
	27.2	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
28	28.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
29	29.1	4600	5820	5210	863	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		238	140	189	70
	29.2	15000	16000	15500	707	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
	29.3	282	302	292	14	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		111	228	170	83
30	30.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
31	31.1	359	383	371	17	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		74	71	72	2
	31.2	66	65	66	1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		37	40	39	3
	31.3	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
32	32.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	

		DIBP				DBP				BBP				DEHP			
Product no.	Sample no.	a (mg/kg)	b (mg/kg)	Average (mg/kg)	SD (mg/kg)	a (mg/kg)	b (mg/kg)	Average (mg/kg)	SD (mg/kg)	a (mg/kg)	b (mg/kg)	Average (mg/kg)	SD (mg/kg)	a (mg/kg)	b (mg/kg)	Average (mg/kg)	SD (mg/kg)
33	33.1	383	279	331	73	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		17	19	18	2
34	34.1	3390	3630	3510	170	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		1650	2060	1855	290
	34.2	111000	95800	103400	10748	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		200000	176000	188000	16971
35	35.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
36	36.1	22	21	21	1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		19	25	22	4
37	37.1	1860	1810	1835	35	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		566	572	569	4
	37.2	121000	121000	121000	52	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		209000	209000	209000	582
	37.3	12	490	251	338	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		13	30	21	12
38	38.1	865	570	718	209	57	41	49	11	< L.O.D	< L.O.D	< L.O.D		115	191	153	54
	38.2	116000	126000	121000	7071	12400	12100	12250	212	< L.O.D	< L.O.D	< L.O.D		184	92	138	65
39	39.1	167	204	185	26	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		22	28	25	4
	39.2	760	384	572	266	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		250000	266000	258000	11314
40	40.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		1750	1650	1700	71
	40.2	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		134	151	143	12
	40.3*	103		103		254		254		< L.O.D		< L.O.D		185000		185000	

'*' states single analyses

Table 4.9 Results of quantitative analyses in %(m/m), 2-year-olds

		DIBP				DBP				BBP				DEHP			
Product no.	Sample no.	a (% v/v)	b (% v/v)	Average (% v/v)	SD (%)	a (% v/v)	b (% v/v)	Average (% v/v)	SD (%)	a (% v/v)	b (% v/v)	Average (% v/v)	SD (%)	a (% v/v)	b (% v/v)	Average (% v/v)	SD (%)
21	21.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
	21.2	0.032	0.033	0.032	0.0005	0.018	0.017	0.018	0.0004	< L.O.D	< L.O.D	< L.O.D		0.083	0.084	0.084	0.0007
22	22.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.001	0.001	0.001	0.00006
	22.2	0.001	0.002	0.001	0.0007	0.001	0.003	0.002	0.001	< L.O.D	< L.O.D	< L.O.D		0.002	0.003	0.002	0.001
	22.3*	0.005		0.005		0.005		0.005		< L.O.D		< L.O.D		0.019		0.019	
23	23.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.002	0.002	0.002	0.0001
	23.2*	0.009		0.009		< L.O.D		< L.O.D		< L.O.D		< L.O.D		< L.O.D		< L.O.D	
24	24.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
	24.2	0.002	0.002	0.002	0.0002	0.003	0.002	0.002	0.0002	< L.O.D	< L.O.D	< L.O.D		0.009	0.006	0.007	0.002
25	25.1	< L.O.D	< L.O.D	< L.O.D		0.001	0.001	0.001	0.00005	< L.O.D	< L.O.D	< L.O.D		0.003	0.013	0.008	0.007
	25.2*	< L.O.D		< L.O.D		< L.O.D		< L.O.D		< L.O.D		< L.O.D		< L.O.D		< L.O.D	
26	26.1	0.007	0.006	0.006	0.0005	0.013	0.010	0.011	0.002	< L.O.D	< L.O.D	< L.O.D		33.5	35.4	34.5	1.3
27	27.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
	27.2	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
28	28.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
29	29.1	0.46	0.58	0.52	0.09	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.024	0.014	0.019	0.007
	29.2	1.5	1.6	1.6	0.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
	29.3	0.028	0.030	0.029	0.001	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.011	0.023	0.017	0.008
30	30.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
31	31.1	0.036	0.038	0.037	0.002	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.007	0.007	0.007	0.0002
	31.2	0.007	0.007	0.007	0.0001	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.004	0.004	0.004	0.0003
	31.3	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
32	32.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
33	33.1	0.038	0.028	0.033	0.0073	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.002	0.002	0.002	0.0002

		DIBP				DBP				BBP				DEHP			
Product no.	Sample no.	a (% v/v)	b (% v/v)	Average (% v/v)	SD (%)	a (% v/v)	b (% v/v)	Average (% v/v)	SD (%)	a (% v/v)	b (% v/v)	Average (% v/v)	SD (%)	a (% v/v)	b (% v/v)	Average (% v/v)	SD (%)
34	34.1	0.34	0.36	0.35	0.02	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.17	0.21	0.19	0.03
	34.2	11.1	9.6	10.3	1.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		20.0	17.6	18.8	1.7
35	35.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
36	36.1	0.002	0.002	0.002	0.0001	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.002	0.003	0.002	0.0004
37	37.1	0.19	0.18	0.18	0.004	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.057	0.057	0.057	0.0004
	37.2	12.1	12.1	12.1	0.01	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		20.9	20.9	20.9	0.0
	37.3	0.001	0.049	0.025	0.034	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.001	0.003	0.002	0.0012
38	38.1	0.087	0.057	0.072	0.021	0.006	0.004	0.005	0.001	< L.O.D	< L.O.D	< L.O.D		0.012	0.019	0.015	0.005
	38.2	11.6	12.6	12.1	0.7	1.2	1.2	1.2	0.0	< L.O.D	< L.O.D	< L.O.D		0.018	0.009	0.014	0.007
39	39.1	0.017	0.020	0.019	0.003	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.002	0.003	0.003	0.0004
	39.2	0.076	0.038	0.057	0.027	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		25.0	26.6	25.8	1.1
40	40.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.18	0.17	0.17	0.01
	40.2	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.013	0.015	0.014	0.001
	40.3*	0.010		0.010		0.025		0.025		< L.O.D		< L.O.D		18.5		18.5	

4.2.3 Quantitative analyses results for 6/7-year-olds

Table 4.10 Results of quantitative analyses in mg/kg, 6/7-year-olds

		DIBP				DBP				BBP				DEHP			
Product no.	Sample no.	a (mg/kg)	b (mg/kg)	Average (mg/kg)	SD (mg/kg)	a (mg/kg)	b (mg/kg)	Average (mg/kg)	SD (mg/kg)	a (mg/kg)	b (mg/kg)	Average (mg/kg)	SD (mg/kg)	a (mg/kg)	b (mg/kg)	Average (mg/kg)	SD (mg/kg)
41	41.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		16	16	16	0.3
	41.2	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
42	42.1*	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
	42.2	< L.O.D	< L.O.D	< L.O.D		21	19	20	1	< L.O.D	< L.O.D	< L.O.D		34	39	36	3
43	43.1	42	182	112	99	20	50	35	21	< L.O.D	< L.O.D	< L.O.D		330000	325000	327500	3536
	43.2	102	19	60	58	29	11	20	13	< L.O.D	< L.O.D	< L.O.D		335000	335000	335000	153
44	44.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		445000	478000	461500	23335
45	45.1	25	47	36	16	9	9	9	1	< L.O.D	< L.O.D	< L.O.D		13	11	12	2
46	46.1	22200	22400	22300	141	2710	3040	2875	233	< L.O.D	< L.O.D	< L.O.D		108000	102000	105000	4243
	46.2	35000	42300	38650	5162	2920	3240	3080	226	< L.O.D	< L.O.D	< L.O.D		151000	157000	154000	4243
	46.3*	6430		6430		219		219		< L.O.D		< L.O.D		56200		56200	
	46.4*	21176		21176		2700		2700		79		79		100000		100000	
47	47.1	11	14	12	3	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		30	35	32	3
	47.2*	62		62		< L.O.D		< L.O.D		< L.O.D		< L.O.D		< L.O.D		< L.O.D	
48	48.1*	< L.O.D		< L.O.D		76		76		< L.O.D		< L.O.D		24		24	
	48.2*	< L.O.D		< L.O.D		< L.O.D		< L.O.D		< L.O.D		< L.O.D		26		26	
	48.3*	< L.O.D		< L.O.D						< L.O.D		< L.O.D		15		15	
49	49.1	19	18	18	0.2	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		61	37	49	17
50	50.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		9	12	10	2

		DIBP				DBP				BBP				DEHP			
Product no.	Sample no.	a (mg/kg)	b (mg/kg)	Average (mg/kg)	SD (mg/kg)	a (mg/kg)	b (mg/kg)	Average (mg/kg)	SD (mg/kg)	a (mg/kg)	b (mg/kg)	Average (mg/kg)	SD (mg/kg)	a (mg/kg)	b (mg/kg)	Average (mg/kg)	SD (mg/kg)
51	51.1	22	22	22	0.5	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
	51.2	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
52	52.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
53	53.1	36	47	41	8	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		69	71	70	1
	53.2	33	29	31	2	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
54	54.1	68	73	71	3	314	241	278	52	60	32	46	20	31	26	28	4
	54.2	2860	2860	2860	3	275000	290000	282500	10607	< L.O.D	< L.O.D	< L.O.D		3570	3850	3710	198
55	55.1	34200	31600	32900	1838	36	30	33	5	< L.O.D	< L.O.D	< L.O.D		150	105	128	32
56	56.1	21	25	23	3	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		57	65	61	6
57	57.1	23	16	19	5	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
58	58.1	14	15	14	1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		36	43	39	5
59	59.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		44	21	33	16
60	60.1	20	20	20	0.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
	60.2	64	33	49	22	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		1080	1130	1105	35

'*' states single analyses

Table 4.11 Results of quantitative analyses in %(m/m), 6/7-year-olds

		DIBP				DBP				BBP				DEHP			
Product no.	Sample no.	a (% v/v)	b (% v/v)	Average (% v/v)	SD (%)	a (% v/v)	b (% v/v)	Average (% v/v)	SD (%)	a (% v/v)	b (% v/v)	Average (% v/v)	SD (%)	a (% v/v)	b (% v/v)	Average (% v/v)	SD (%)
41	41.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.002	0.002	0.002	0.00003
	41.2	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
42	42.1*	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
	42.2	< L.O.D	< L.O.D	< L.O.D		0.002	0.002	0.002	0.0001	< L.O.D	< L.O.D	< L.O.D		0.003	0.004	0.004	0.0003
43	43.1	0.004	0.018	0.011	0.010	0.002	0.005	0.004	0.002	< L.O.D	< L.O.D	< L.O.D		33.0	32.5	32.8	0.4
	43.2	0.010	0.002	0.006	0.006	0.003	0.001	0.002	0.001	< L.O.D	< L.O.D	< L.O.D		33.5	33.5	33.5	0.02
44	44.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		44.5	47.8	46.2	2.3
45	45.1	0.002	0.005	0.004	0.002	0.001	0.001	0.001	0.00006	< L.O.D	< L.O.D	< L.O.D		0.001	0.001	0.001	0.0002
46	46.1	2.2	2.2	2.2	0.01	0.27	0.30	0.29	0.02	< L.O.D	< L.O.D	< L.O.D		10.8	10.2	10.5	0.4
	46.2	3.5	4.2	3.9	0.5	0.29	0.32	0.31	0.02	< L.O.D	< L.O.D	< L.O.D		15.1	15.7	15.4	0.4
	46.3*	0.643		0.643		0.022		0.022		< L.O.D		< L.O.D		5.6		5.6	
	46.4*	2.118		2.118		0.27		0.27		0.008		0.008		10.0		10.0	
47	47.1	0.001	0.001	0.001	0.0003	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.003	0.003	0.003	0.0003
	47.2*	0.006		0.006		< L.O.D		< L.O.D		< L.O.D		< L.O.D		< L.O.D		< L.O.D	
48	48.1*	< L.O.D		< L.O.D		0.008		0.008		< L.O.D		< L.O.D		0.002		0.002	
	48.2*	< L.O.D		< L.O.D		< L.O.D		< L.O.D		< L.O.D		< L.O.D		0.003		0.003	
	48.3*	< L.O.D		< L.O.D						< L.O.D		< L.O.D		0.001		0.001	
49	49.1	0.002	0.002	0.002	0.00002	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.006	0.004	0.005	0.002
50	50.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.001	0.001	0.001	0.0002
51	51.1	0.002	0.002	0.002	0.00005	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
	51.2	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
52	52.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
53	53.1	0.004	0.005	0.004	0.0008	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.007	0.007	0.007	0.0001
	53.2	0.003	0.003	0.003	0.0002	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	

		DIBP				DBP				BBP				DEHP			
Product no.	Sample no.	a (% v/v)	b (% v/v)	Average (% v/v)	SD (%)	a (% v/v)	b (% v/v)	Average (% v/v)	SD (%)	a (% v/v)	b (% v/v)	Average (% v/v)	SD (%)	a (% v/v)	b (% v/v)	Average (% v/v)	SD (%)
54	54.1	0.007	0.007	0.007	0.0003	0.031	0.024	0.028	0.005	0.006	0.003	0.005	0.002	0.003	0.003	0.003	0.0004
	54.2	0.29	0.29	0.29	0.0003	27.5	29.0	28.3	1.1	< L.O.D	< L.O.D	< L.O.D		0.36	0.39	0.37	0.02
55	55.1	3.4	3.2	3.3	0.2	0.004	0.003	0.003	0.0005	< L.O.D	< L.O.D	< L.O.D		0.015	0.010	0.013	0.003
56	56.1	0.002	0.003	0.002	0.0003	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.006	0.007	0.006	0.0006
57	57.1	0.002	0.002	0.002	0.0005	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
58	58.1	0.001	0.002	0.001	0.0001	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.004	0.004	0.004	0.0005
59	59.1	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.004	0.002	0.003	0.002
60	60.1	0.002	0.002	0.002	0.00001	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D	
	60.2	0.006	0.003	0.005	0.0022	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.11	0.11	0.11	0.004

'*' states single analyses

4.2.4 Comments to quantitative analyses

The phthalates DIBP, DBP, BBP and DEHP were detected in plastic sandals for all three age groups with content from the detection limit and way up to 46 %.

The main part of the products that during the flame test indicated chlorine have appeared to contain a large amount of phthalates but a number of other products also contain phthalates. Therefore, the Beilstein test should be accompanied by an extraction to prove phthalates in all types of materials that are used in plastic sandals as other plastics than the types with chlorine (e.g. PVC) might contain phthalates as well.

Several of the products showed a content of other phthalates, as stated in Table 4.12. It has not been investigated in this project whether the products contained other phthalates.

Table 4.12 Outline of other phthalates detected in plastic sandals

Phthalate abbreviation	Name	CAS no.	Product no.
Isophthalate	Di-(2-ethylhexyl) isophthalate	137-89-3	2, 3, 11, 24, 31, 42, 54, 60
DINP	Di-isononyl phthalate	28553-12-0	12, 22, 29, 43, 60
DEP	Diethyl phthalate	84-66-2	24, 27
DMP	Dimethyl phthalate	131-11-3	27
DiDeP	Di-isodecyl phthalate	26761-40-0	29

4.3 Migration analyses

The objective of the migration analyses was to investigate exposure when using sandals or lightweight plastic shoes whereas the quantitative analyses detected content of the four selected phthalates. During the migration analyses, the products were in contact with artificial sweat that subsequently was extracted and analysed for the phthalates DIBP, DBP, BBP and DEHP. The results are used for the risk assessment.

4.3.1 Selection for migration analyses

In co-operation with the Danish Environmental Protection Agency, 22 sandals/ lightweight plastic shoes were selected for migration analysis in the light of the results of the quantitative analyses. During the selection importance was attached to the following criteria:

- High concentrations of phthalates
- Large area of exposure (sole), but some straps were also included
- Representative selection of shoes for adults, 6/7-year-olds and 2-year-olds
- Representative selection of inexpensive and expensive (trademark) products
- Representative selection of the detected phthalates DBP/DIBP and DEHP.

One sandal contained several phthalates in high concentrations in the sole and was selected for additional tests as described in the following.

4.3.2 Applied artificial sweat simulant and exposure temperature and time

The applied artificial sweat simulant is described in DS/EN ISO 105-E04, used in connection with ØKO-TEX certification (Öko-Tex Standard 100). The simulant for the sweat migrations was previously used for comparable migration analyses for e.g. textiles and lightweight clogs (exposure of 2-year-olds to chemical substances, survey no. 103, 2009).

The sweat simulant in DS/EN ISO 105-E04 consists of 1-histidine-monohydrochlorid-1-hydrate, sodium chloride, sodium dihydrogen phosphate and sodium hydroxide for adjustment of pH to pH 5.5.

An analysis of the applied sweat simulant was carried out for the selected phthalates before exposure to ensure that it contains no phthalates.

The migration tests were carried out at 37 °C which is close to the body temperature and is used in DS/EN-71-3, DS/EN ISO 105-E04.

During the migration analysis, the simulant was pre-heated before being added to the sample amount of the footwear.

Additional test were carried out on a selected pair of sandals on which exposure took place two x 8 hours (with fresh artificial sweat in the second exposure). In addition, dynamic stress on a shaking table was investigated and so was the effect of sun lotion or corresponding fat cream on the migration of phthalates.

The results of the migration test and additional tests will be used in the risk assessment.

4.3.3 Method description for migration analyses

A weighed sample amount was extracted and the surface was estimated, Table 4.13, Table 4.14, Table 4.15. The sample amount was lowered in the pre-heated sweat simulant (20 ml). The samples were placed in a temperature controlled incubator (37 ± 3 °C) for 16 hours with static contact with the simulant. An analysis in duplicate was carried out, except when there was limited sample amount.

One pair of footwear was selected for exposure with sun lotion. A sample amount was weighed, Table 4.16, and a cloth was used to apply sun lotion across the surface of the product before exposure to the sweat simulant.

An analysis was carried out on the applied sun lotion for the selected phthalates before exposure to ensure that it contained no phthalates.

The sweat simulant was extracted by shaking it into a separatory funnel with dichloromethane (2x10 ml) added deuterium marked internal standards (DBP-d_4 and DEHP-d_4). The extracts were analysed by means of gas chromatography with mass spectrometric detection (GC-MS).

The amount of phthalates was quantified against standards of the respective phthalates DIBP, DBP, BBP and DEHP. Blank specimens and control tests were included in the analysis.

The detection limit was 0.02-0.2 mg/kg equivalent to 0.000002-0.00002 % (m/m).

The surface of the investigated sample amount was estimated in order to be able to calculate the entire exposure in the risk assessment.

Table 4.13 Outline of sampling for migration analyses, adults

Product type	Sample	Description	Area of sample cm^2 *	Weight** g
1	1.1	Sole	16	3.81
5	5.2	Strap	12	2.39
6	6.1	Sole	23	5.07
8	8.1a	Sole	22	5.13
	8.2	Strap	9,6	2.01
12	12.1	Sole	16	3.80
13	13.2	Strap	12	2.75
17	17.1	Sole	16	5.37
18	18.1	Middle of sole	16	0.29
	18.2	Outer part of sole	18	5.78
20	20.2	Strap	12	2.89

* The area of sample is the average for the area in duplicate.
** The weight is the average weight of the analysis in duplicate.

Table 4.14 Outline of sampling for migration analyses, 2-year-olds

Product type	Sample	Description	Area of sample cm^2 *	Weigt** g
26	26.1	Sole	20	4.74
29	29.2	Outer part of sole	23	2.75
37	37.2	Strap	9,6	1.48
38	38.2	Strap	10	1.80
39	39.2	Strap	20	1.39

*The area of sample is the average for the area in duplicate.
** The weight is the average weight of the analysis in duplicate.

Table 4.15 Outline of sampling for migration analyses, 6/7-year-olds

Product type	Sample	Description	Area of sample cm^2 *	Weight** g
43	43.1	Sole	23	4,61
44	44.1	Sole	16	3,16
46	46.1	Middle of sole	24	0,75
	46.2	Outer part of sole	19	2,28
54	54.2	Strap	12	2,37
55	55.1	Sole	24	0,48

*The area of sample is the average for the area in duplicate.
** The weight is the average weight of the analysis in duplicate.

Table 4.16 Outline of sampling for migration analyses, additional tests

Product type	Sample description	Test	Area of sample cm^2 *	Weight** g
8	8.1, sole	8.1b: Contact time 16 hours, replacement of sweat simulant after 8 hours	22	5.39
		8.1c: Contact time 8 hours	22	5.39
		8.1d: Dynamic	19	6.53
		8.1e: Sun lotion/static	21	6.96
		8.1f: Sun lotion/dynamic	17	4.56

*The area of sample is the average for the area in duplicate.
** The weight is the average weight of the analysis in duplicate.

In the additional tests a sun lotion without perfume factor 30 was used in test 8.1e and 8.1f.

The sun lotion was tested in a separate migration experiment and the migrated amount of phthalates was below the detection limit.
In the additional tests 8.1d and 8.1f dynamic conditions was used by performing the migration tests using a shaker table with a speed of 155 directional changes per minute.

The entire surface of the investigated products that are in touch with the skin was estimated for the calculation of the total exposure. The areas are stated in the chapter on Risk assessment.

4.4 Results of the migration analyses

The results are stated below in Table 4.17 and Table 4.18 with the results of the migration analyses calculated as mg/kg and in % (m/m, weight percentage), respectively. The results (mg/kg) are reported with three significant figures except near the detection limit according to agreement with the Danish Environmental Protection Agency.

In addition, there is a table with results of the additional tests with migration under dynamic conditions and with sun lotion, Table 4.19 and Table 4.20.

Analyses in duplicate were carried out for the migration analyses .The results are stated as single analyses (a and b), the average of the analyses in duplicate and the calculated standard deviation of the analysis in duplicate.

Results below the detection limit are stated as ”< L.O.D”.
The detection limits are 0.02-0.2 mg/kg equivalent to 0.000002-0.00002 %(m/m).

The relative uncertainty of the method is estimated to 10-15 %.
Uncertainties on the analyses in duplicate are stated as standard deviations (SD) in the result tables.

In cases were no average value could be calculated because phthalates were only detected in one of the two samples, the result of this sample is stated and no standard deviation is calculated.

BBP was not detected in any of the migration analyses.

The results of the migration analyses are used in the next chapter on Risk assessment.

4.4.1 Migration analysis results for adults

Table 4.17 Results of migration analyses, mg/kg

		DIBP				DBP				DEHP			
Sample no.	Sample, description	a (mg/kg)	b (mg/kg)	Average (mg/kg)	SD	a (mg/kg)	b (mg/kg)	Average (mg/kg)	SD	a (mg/kg)	b (mg/kg)	Average (mg/kg)	SD
1.1	Sole	14	13	13	0.4	29	28	28	1	0.80	0.50	0.7	0.2
5.2	Strap	< L.O.D	< L.O.D	< L.O.D		55	51	53	2	< L.O.D	0.4	0.4	
6.1	Sole	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		1.1	0.5	0.8	0.4
8.1	Sole	19	20	20	1	< L.O.D	0.33	0.3		0.33	0.33	0.3	0.001
8.2	Strap	24	22	23	1	17	16	17	1	0.5	0.3	0.4	0.1
12.1	Sole	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		1.1	1.5	1.3	0.3
13.2	Strap	< L.O.D	< L.O.D	< L.O.D		45	44	44	1	8.2	0.2	4.2	5.6
17.1	Sole	8.3	6.9	7.6	1.0	0.79	0.70	0.8	0.1	0.47	0.21	0.3	0.2
18.1	Middle of sole	121	123	122	1	3.5	4.8	4.1	0.9	7.7	8.9	8.3	0.8
18.2	Outer part of sole	13	12	12	0.8	0.03	0.07	0.05	0.02	0.41	0.17	0.3	0.2
20.2	Strap	13	15	14	1.1	30	27	29	2	< L.O.D	7.2	7.2	
26.1	Sole	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.55	0.30	0.4	0.2
29.2	Outer part of sole	19	15	17	2.5	< L.O.D	< L.O.D	< L.O.D		0.38	0.21	0.3	0.1
37.2	Strap	51	48	49	2.3	< L.O.D	< L.O.D	< L.O.D		4.2	0.4	2.3	2.7
38.2	Strap	41	32	37	6.3	2.9	2.4	2.6	0.4	< L.O.D	< L.O.D	< L.O.D	

		DIBP				DBP				DEHP			
Sample no.	Sample, description	a (mg/kg)	b (mg/kg)	Average (mg/kg)	SD	a (mg/kg)	b (mg/kg)	Average (mg/kg)	SD	a (mg/kg)	b (mg/kg)	Average (mg/kg)	SD
39.2	Strap	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		1.5	0.7	1.1	0.5
43.1	Sole	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.35	0.51	0.4	0.1
44.1	Sole	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.6	1.4	1.0	0.6
46.1	Middle of sole	40	36	38	3	0.5	1.1	0.8	0.4	30	12	21	13
46.2	Outer part of sole	16	11	13	3	0.19	0.33	0.26	0.10	1.5	2.1	1.8	0.4
54.2	Strap	< L.O.D	< L.O.D	< L.O.D		52	50	51	1	< L.O.D	0.26	0.3	
55.1	Sole	393	394	393	1	< L.O.D	< L.O.D	< L.O.D		8.1	1.7	4.9	4.5

Table 4.18 Results of migration analyses, %(m/m)

		DIBP				DBP				DEHP			
Sample no.	Sample, description	a %	b %	Average %	SD	a %	b %	Average %	SD	a %	b %	Average %	SD
1.1	Sole	0.001	0.001	0.001	0.00004	0.003	0.003	0.003	0.00010	0.0001	0.00005	0.0001	0.00002
5.2	Strap	< L.O.D	< L.O.D	< L.O.D		0.005	0.005	0.005	0.0002	< L.O.D	0.00004	0.00004	
6.1	Sole	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.0001	0.0001	0.0001	0.00004
8.1	Sole	0.002	0.002	0.002	0.0001	< L.O.D	0.00003	0.00003		0.00003	0.00003	0.00003	0.0000001
8.2	Strap	0.002	0.002	0.002	0.0001	0.002	0.002	0.002	0.00007	0.00005	0.00003	0.00004	0.00001
12.1	Sole	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.0001	0.0002	0.0001	0.00003
13.2	Strap	< L.O.D	< L.O.D	< L.O.D		0.004	0.004	0.004	0.00008	0.001	0.00002	0.0004	0.0006
17.1	Sole	0.001	0.001	0.001	0.0001	0.0001	0.0001	0.0001	0.00001	0.00005	0.00002	0.00003	0.00002
18.1	Middle of sole	0.012	0.012	0.012	0.0001	0.0003	0.0005	0.0004	0.00009	0.001	0.001	0.001	0.00008
18.2	Outer part of sole	0.001	0.001	0.001	0.0001	0.000003	0.00001	0.00001	0.000002	0.00004	0.00002	0.00003	0.00002
20.2	Strap	0.001	0.002	0.001	0.0001	0.003	0.003	0.003	0.0002	< L.O.D	0.001	0.001	
26.1	Sole	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.00005	0.00003	0.00004	0.00002
29.2	Outer part of sole	0.002	0.002	0.002	0.0002	< L.O.D	< L.O.D	< L.O.D		0.00004	0.00002	0.00003	0.00001
37.2	Strap	0.005	0.005	0.005	0.0002	< L.O.D	< L.O.D	< L.O.D		0.0004	0.0000	0.0002	0.0003
38.2	Strap	0.004	0.003	0.004	0.0006	0.0003	0.0002	0.0003	0.00004	< L.O.D	< L.O.D	< L.O.D	
39.2	Strap	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.00015	0.00007	0.00011	0.00005
43.1	Sole	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.00004	0.00005	0.00004	0.00001

		DIBP				DBP				DEHP			
Sample no.	Sample, description	a %	b %	Average %	SD	a %	b %	Average %	SD	a %	b %	Average %	SD
44.1	Sole	< L.O.D	< L.O.D	< L.O.D		< L.O.D	< L.O.D	< L.O.D		0.00006	0.00014	0.00010	0.00006
46.1	Middle of sole	0.004	0.004	0.004	0.0003	0.0001	0.0001	0.0001	0.00004	0.003	0.001	0.002	0.001
46.2	Outer part of sole	0.002	0.001	0.001	0.0003	0.00002	0.00003	0.00003	0.00001	0.0002	0.0002	0.0002	0.00004
54.2	Strap	< L.O.D	< L.O.D	< L.O.D		0.005	0.005	0.005	0.0001	< L.O.D	0.00003	0.00003	
55.1	Sole	0.039	0.039	0.039	0.0001	< L.O.D	< L.O.D	< L.O.D		0.001	0.0002	0.0005	0.0005

Table 4.19 Results of additional analyses, mg/kg (Plastic sandal 8.1)

Test	DIBP				DBP				DEHP			
	a (mg/kg)	b (mg/kg)	Average (mg/kg)	SD	a (mg/kg)	b (mg/kg)	Average (mg/kg)	SD	a (mg/kg)	b (mg/kg)	Average (mg/kg)	SD
Contact time 16 hours, static	19	20	20	1	< L.O.D	0.33	0.3		0.33	0.33	0.3	0.001
Contact time 16 hours, replacement of sweat simulant after 8 hours, static	26	16	21	7	0.55	0.69	0.6	0.1	12	0.3	6.4	8.6
Contact time 8 hours, static	15	17	16	2	0.48	0.61	0.5	0.1	< L.O.D	0.16	0.2	
Contact time 16 hours, Dynamic	28	16	22	8	1.4	0.5	1.0	0.7	15	1.5	8.3	9.6
Contact time 16 hours, sun lotion/static	77	17	47	43	0.9	0.4	0.7	0.3	7.6	1.7	4.6	4.2
Contact time 16 hours, sun lotion/dynamic	37	97	67	42	0.8	1.2	1.0	0.3	25	74	49	35

Table 4.20 Results of additional analyses, % (m/m)

Test	DIBP				DBP				DEHP			
	a %	b %	Average %	SD	a %	b %	Average %	SD	a %	b %	Average %	SD
Contact time 16 hours, static	0.002	0.002	0.002	0.0001	< L.O.D	0.00003	0.00003		0.00003	0.00003	0.00003	0.0000001
Contact time 16 hours, replacement of sweat simulant after 8 hours	0.003	0.002	0.002	0.0007	0.0001	0.0001	0.0001	0.00001	0.001	0.00003	0.001	0.0009
Contact time 8 hours	0.001	0.002	0.002	0.0002	0.0000	0.0001	0.0001	0.00001	< L.O.D	0.00002	0.00002	
Contact time 16 hours, Dynamic	0.003	0.002	0.002	0.0008	0.0001	0.0001	0.0001	0.00007	0.002	0.0002	0.001	0.001
Contact time 16 hours, sun lotion/static	0.008	0.002	0.005	0.004	0.0001	0.00004	0.0001	0.00003	0.001	0.0002	0.0005	0.0004
Contact time 16 hours, sun lotion/dynamic	0.004	0.010	0.007	0.004	0.0001	0.0001	0.0001	0.00003	0.002	0.007	0.005	0.003

4.5 Summary of analysis results

A content of the phthalates DIBP, DBP and DEHP was detected in several of the analysed plastic sandals and lightweight clogs and for all age groups. A majority of plastic sandals for children contain phthalates in the sole or strap in the order of magnitude of 10-46 %. BBP was only detected in a few sandals and in low concentrations.

Table 4.21 and Table 4.22 give an outline of the selected products on which migration analyses were carried out. The results are stated as the average result of the single analysis for the quantitative and migration analysis, respectively.

Test no. 1-20 are sandals for adults, test no. 26-39 are sandals for 2-year-olds and test no. 43-55 are sandals for 6/7-year-olds.

Table 4.21 Summary of selected results, mg/kg

Sample no.	Description	DIBP		DBP		BBP		DEHP	
		Quant.	Migr.	Quant.	Migr.	Quant.	Migr.	Quant.	Migr.
1.1	Sole	62650	13	228500	28	25	< L.O.D	22200	0.7
5.2	Strap	< L.O.D	< L.O.D	265500	53	< L.O.D	< L.O.D	24	0.4
6.1	Sole	51	< L.O.D	2190	< L.O.D	< L.O.D	< L.O.D	302000	0.8
8.1	Sole	212000	20	1	< L.O.D	< L.O.D	< L.O.D	148000	0.3
8.2	Strap	74000	23	82450	17	< L.O.D	< L.O.D	171000	0.4
12.1	Sole	115	< L.O.D	< L.O.D	< L.O.D	< L.O.D	< L.O.D	460500	1.3
13.2	Strap	< L.O.D	< L.O.D	345000	44	< L.O.D	< L.O.D	265	4.2
17.1	Sole	66250	7.6	8900	0.8	< L.O.D	< L.O.D	245000	0.3
18.1	Middle of sole	22050	122	1965	4.1	< L.O.D	< L.O.D	110500	8.3
18.2	Outer part of sole	116500	12	804	0.05	< L.O.D	< L.O.D	209500	0.2
20.2	Strap	53350	14	178000	29	< L.O.D	< L.O.D	10200	7.2
26.1	Sole	64	< L.O.D	0.01	< L.O.D	< L.O.D	< L.O.D	344500	0.4
29.2	Outer part of sole	15500	17	< L.O.D	< L.O.D	< L.O.D	< L.O.D	< L.O.D	0.3
37.2	Strap	121000	49	< L.O.D	< L.O.D	< L.O.D	< L.O.D	209000	2.3
38.2	Strap	121000	37	12250	2.6	< L.O.D	< L.O.D	138	< L.O.D
39.2	Strap	572	< L.O.D	< L.O.D	< L.O.D	< L.O.D	< L.O.D	258000	1.1
43.1	Sole	112	< L.O.D	< L.O.D	< L.O.D	< L.O.D	< L.O.D	327500	0.4
44.1	Sole	< L.O.D	< L.O.D	< L.O.D	< L.O.D	< L.O.D	< L.O.D	461500	1.0
46.1	Middle of sole	22300	38	2875	0.8	< L.O.D	< L.O.D	105000	21
46.2	Outer part of sole	38650	13	3080	0.3	< L.O.D	< L.O.D	154000	1.8
54.2	Strap	2860	< L.O.D	282500	51	< L.O.D	< L.O.D	3710	0.3
55.1	Sole	329000	393	33	< L.O.D	< L.O.D	< L.O.D	128	4.9

L.O.D: Detection limit

Table 4.22 Summary of selected results, %(m/m)

Test no.	Sample, description	DIBP		DBP		BBP		DEHP	
		Quant.	Migr.	Quant.	Migr.	Quant.	Migr.	Quant.	Migr.
1.1	Sole	6.3	0.001	23	0.003	0.002	< L.O.D	2.2	0.0001
5.2	Strap	< L.O.D	< L.O.D	27	0.005	< L.O.D	< L.O.D	0.002	0.00004
6.1	Sole	0.005	< L.O.D	0.22	< L.O.D	< L.O.D	< L.O.D	30	0.0001
8.1	Sole	21	0.002	0.0001	0.00003	< L.O.D	< L.O.D	15	0.00003
8,2	Strap	7.4	0.002	8.2	0.002	< L.O.D	< L.O.D	17	0.00004
12.1	Sole	0.01	< L.O.D	< L.O.D	< L.O.D	< L.O.D	< L.O.D	46	0.0001
13.2	Strap	< L.O.D	< L.O.D	35	0.004	< L.O.D	< L.O.D	0.003	0.000
17.1	Sole	6.6	0.001	0.89	0.0001	< L.O.D	< L.O.D	25	0.00003
18.1	Middle of sole	2.2	0.012	0.20	0.0004	< L.O.D	< L.O.D	11	0.001
18.2	Outer part of sole	12	0.001	0.08	0.00001	< L.O.D	< L.O.D	21	0.00003
20.2	Strap	5.3	0.001	18	0.003	< L.O.D	< L.O.D	1.0	0.001
26.1	Sole	0.006	< L.O.D	0.01	< L.O.D	< L.O.D	< L.O.D	35	0.00004
29.2	Outer part of sole	1.5	0.002	< L.O.D	< L.O.D	< L.O.D	< L.O.D	< L.O.D	0.00003
37.2	Strap	12	0.005	< L.O.D	< L.O.D	< L.O.D	< L.O.D	21	0.00023
38.2	Strap	12	0.004	1.2	0.0003	< L.O.D	< L.O.D	0.01	< L.O.D
39.2	Strap	0.06	< L.O.D	< L.O.D	< L.O.D	< L.O.D	< L.O.D	26	0.00011
43.1	Sole	0.06	< L.O.D	< L.O.D	< L.O.D	< L.O.D	< L.O.D	33	0.00004

Test no.	Sample, description	DIBP		DBP		BBP		DEHP	
		Quant.	Migr.	Quant.	Migr.	Quant.	Migr.	Quant.	Migr.
44.1	Sole	< L.O.D	< L.O.D	< L.O.D	< L.O.D	< L.O.D	< L.O.D	46	0.00010
46.1	Middle of sole	2.2	0.004	0.29	0.0001	< L.O.D	< L.O.D	11	0.002
46.2	Outer part of sole	3.9	0.001	0.31	0.00003	< L.O.D	< L.O.D	15	0.0002
54.2	Strap	0.29	< L.O.D	28	0.005	< L.O.D	< L.O.D	0.37	0.00003
55.1	Sole	3.3	0.039	0.003	< L.O.D	< L.O.D	< L.O.D	0.01	0.0005

The detection limits are 0.001% (m/m) for the quantitative analyses and 0.000002-0.00002% (m/m) for the migration analyses.

The results of migration analyses of the phthalates DIBP, DBP and DEHP to the artificial sweat simulant is lower than the quantified content in the products due to the low solubility of the phthalates in the stimulant, especially DEHP.

During the additional tests, the highest concentrations were measured during the tests where sun lotion was applied to the product before the migration analysis.

The analysis uncertainty on the results of the analyses in duplicate for the additional tests is much higher than on the other migration analyses. During the tests with sun lotion the reason might be that it was not possible to ensure that the sun lotion was homogenously applied on the sample before the migration analyses. Comparative tests were carried out between the dynamic and static migration and the result shows that the analysis uncertainty is larger for dynamic migration. Pattern in the material can also contribute to the variations in the analyses in duplicate. In addition, small concentrations will give higher analysis uncertainty.

The results from the migration tests are used in the following chapter on Risk assessment.

In 13 of the products, other phthalates were detected that have not been quantified. The detected phthalates are isophthalate, DINP, DEP, DMP and DiDeP.

5 Risk assessment

5.1 Calculation of risk – method

According to Reach Guidance Document on user exposure (ECHA April 2010 R.15) the different uptakes from exposure may be added to a total dosis $D_{total}=D_{inh}+D_{der}+D_{oral}$. In this study the only relevant route of exposure is dermal exposure and thus $D_{total}=D_{der}$.

The risk assessment is performed by calculating the Risk Characterisation Ratio (RCR) from the Derived No Effect Level (DNEL):

RCR = Exposure (D_{total})/DNEL

DNEL is calculated from NOAEL (No observed adverse effect level) or LOAEL(Lowest observed adverse effect level) which are test data of a given effect for animals like rats or mice. To calculate the level for humans an overall assessment factor (AF) is used to correct for a number of assessment factors:

- difference between species (interspecies)
- differences within species (intraspecies)
- the quality of studies (is it short term one generation study, or a several generations 2 year study) and
- dosis-response (if only data for LOAEL exist, an assessment factor is introduced to correct to a NOAEL level).

The overall assessment factor AF is the product of the individual assessment factors: AF = AF1 *AF2 *…AFn:

The correction to the derived No effect level (for humans) is then made by dividing NOAEL or LOAEL with the overall assessment factor AF:

DNEL = NOAEL/AF

If RCR>1 there is a health risk.

If more substances are present in the product combination effects may arise.

For phthalates an additive risk may be used as discussed and used for products with the phthalates of interest in this survey in (Survey, 2 year olds.., 2009).

$RCR(total)=RCR_1+RCR_2+\ldots RCR_n$

5.2 Risk assessment for DBP, DIBP, DEHP and BBP

Of the 4 substances only DBP, DIBP and DEHP was found in the migration tests.

5.2.1 Data for phthalates

The following data for phthales were used:

Table 5.1 Data for phthalates

Phthalate	CAS-no	Log KOW [1]	Internal DNEL [2] mg/kg/day	F abs [2]
DIBP	84-69-5	4.11	1.25	0.1
DBP	84-74-2	4.57	0.0067	0.1
DEHP	117-81-7	7.5	0.025 [3]	0.05

1 Data from (Echa 2008 DBP), (ECHA 2008 DEHP) and (ECHA 2009 DIBP)
2 Data from (Survey and Health assessment of the exposure of 2-year olds 2009)
3 Data for DEHP from unpublished report Danish Environmental Agency, (2010)

5.2.2 Contact areas

The areas in contact with the skin were measured for the individual parts/materials of the shoes.

Samples for migration tests were cut from either soles of the foot or from straps/top-parts of sandals.

The area of the sole was measured for the largest typical shoe size in the person groups as a worst case assumption. The contact area of the sole of the foot is estimated to be 90% of the sole area.

Table 5.2 Estimation of contact area of exposure

Group	Weight	Size	Measured sole of the foot of plastic sandal (cm^2)	Contact Area sole of the foot (cm^2)
2-years (1)	15.2	26	95	85
6/7-years (2)	23.1 (WHO)	32	127	114
Grownups (3)	60	44	244	222

Measured areas of straps and other subparts of plastic sandals were proportionally scaled up to the sizes in Table 5.2.

Example of scaling up. For a size 39 shoe the area facing the foot was measured to 38 cm^2. The area facing the foot of a size 44 is calculated to 44/39*38 = 42.8cm^2.

5.2.3 Calculation of uptake

The fraction of contact F_{cont} was set to 1 for soles of the foot as the complete area of the sole of a foot is in contact with the foot and to 0.5 for straps as these are expected to be in less close contact with the foot during the day (the body weight is resting on the foot of the sole but not on straps).

The results for calculated uptake are shown in Table 5.3.

Table 5.3 Calculated uptake of phthalates

Product ID	Weight test specimen	Test area	Contact area	Fcont	Group	Migr. DIBP	Migr. DBP	Migr. DEHP	Dder DIBP	Dder DBP	Dder DEHP
	g	Cm^2	cm^2			µg/g	µg/g	µg/g	µg/kg/day	µg/kg/day	µg/kg/day
1.1	3.81	16	222	1	3	13.47	28.35	0.65	2.3747	4.9974	0.0571
5.2	2.39	12	52.11	0.5	3	< L.O.D	53.13	< L.O.D	<0.0035	0.9202	<0.0017
6.1	5.07	23	222	1	3	< L.O.D	< L.O.D	0.82	<0.0326	<0.0326	0.0665

Product ID	Weight test specimen	Test area	Contact area	Fcont	Group	Migr. DIBP	Migr. DBP	Migr. DEHP	Dder DIBP	Dder DBP	Dder DEHP
8.1a	5.13	22	222	1	3	19.81	< L.O.D	0.33	3.4155	<0.0345	0.0286
8.1b	5.39	22	222	1	3	21.29	0.62	6.38	3.8620	0.1121	0.5789
8.1c	5.39	22	222	1	3	15.78	0.54	0.16	5.7230	0.1971	0.0290
8.1d	6.53	19	222	1	3	21.78	0.97	8.32	5.5371	0.2461	1.0575
8.1e	6.96	21	222	1	3	46.78	0.65	4.62	11.4720	0.1599	0.5671
8.1f	4.56	17	222	1	3	66.99	0.98	49.34	13.2988	0.1938	4.8973
8.2	2.01	9.6	42.87	0.5	3	22.84	16.93	0.40	0.3424	0.2538	0.0030
12.1	3.80	16	222	1	3	< L.O.D	< L.O.D	1.34	<0.0351	<0.0351	0.1181
13.2	2.75	12	55	0.5	3	< L.O.D	44.28	4.22	<0.0042	0.9302	0.0443
17.1	5.37	16	222	1	3	7.58	0.75	0.34	1.8831	0.1856	0.0426
18.1	0.29	16	107.3	1	3	121.67	4.13	8.27	0.7887	0.0268	0.0268
18.2	5.78	18	57.97	1	3	12.50	0.05	0.29	0.7750	0.0032	0.0091
20.2	2.89	12	52	0.5	3	14.26	28.69	7.20	0.2981	0.5998	0.0753
26.1	4.74	19.5	85	1	1	< L.O.D	< L.O.D	0.42	<0.0340	<0.0340	0.0358
29.2	2.75	22.5	47.2	1	1	16.78	< L.O.D	0.30	0.7964	<0.0095	0.0070
37.2	1.48	9.6	33.43	0.5	1	49.43	< L.O.D	2.29	1.0464	<0.0042	0.0242
38.2	1.80	10.4	17.68	0.5	1	36.64	2.63	< L.O.D	0.4616	0.0331	<0.0013
39.2	1.39	20	45	0.5	1	< L.O.D	< L.O.D	1.09	<0.0026	<0.0026	0.0070
43.1	4.61	22.6	114	1	2	< L.O.D	< L.O.D	0.43	<0.0302	<0.0302	0.0327
44.1	3.16	16	114	1	2	< L.O.D	< L.O.D	1.02	<0.0293	<0.0293	0.0745
46.1	0.75	24	86.61	1	2	38.16	0.80	20.70	0.6703	0.0140	0.1818
46.2	2.28	18.6	66.99	1	2	13.45	0.26	1.82	0.7177	0.0138	0.0485
54.2	2.37	12	35	0.5	2	< L.O.D	51.25	< L.O.D	<0.0045	1.1493	<0.0022
55.1	0.48	24	114	1	2	393.26	< L.O.D	4.94	5.7744	<0.0029	0.0363

In the table above the maximum value of the internal exposure has been calculated for the analyses where the migrated amount of phthalets< L.O.D. In these cases the migrated amount of phthalates was set to the maximum value of L.O.D = 0.2 mg/kg.

An example of calculation:

Sample 1.1 for DIBP:

$$D_{der} = \frac{Q_{prod} \cdot M_{migr} \cdot A_{\exp} \cdot F_{abs} \cdot F_{contact} \cdot H_{\exp}}{A_{test} \cdot H_{test} \cdot BW}$$

D_{der} = 2 sandals * 3.81 g*13.47 µg/g*222 cm^2/16 cm^2*0.1*1*16/16/60=2.375 µg/kg/day.

The risk characterisation ratios are shown in Table 5.4.

Example of calculation of RCR:

For sample 1.1 and DIBP RCR = 2.375/1250 = 0.0019.

Table 5.4 Risk characterisation ratios

Product ID	RCR DIBP	RCR DBP	RCR DEHP	SUM OF RCR 1)
1.1	0.0019	0.7459	0.0023	0.7501
5.2	<0.0001	0.1373	<0.0001	0.1373
6.1	<0.0001	<0.0049	0.0027	0.0027
8.1a	0.0027	<0.0051	0.0011	0.0039
8.1b	0.0031	0.0167	0.0232	0.0430
8.1c	0.0046	0.0294	<0.0012	0.0340
8.1d	0.0044	0.0367	0.0423	0.0835
8.1e	0.0092	0.0239	0.0227	0.0557
8.1f	0.0106	0.0289	0.1959	0.2355
8.2	0.0003	0.0379	0.0001	0.0383
12.1	<0.0001	<0.0052	0.0047	0.0047
13.2	<0.0001	0.1388	0.0018	0.1406
17.1	0.0015	0.0277	0.0017	0.0309
18.1	0.0006	0.0040	0.0011	0.0057
18.2	0.0006	0.0005	0.0004	0.0010
20.2	0.0002	0.0895	0.0030	0.0928
26.1	<0.0001	<0.0051	0.0014	0.0014
29.2	0.0006	<0.0014	0.0003	0.0009
37.2	0.0008	<0.0006	0.0010	0.0018
38.2	0.0004	0.0049	<0.0001	0.0053
39.2	<0.0001	<0.0004	0.0003	0.0003
43.1	<0.0001	<0.0045	0.0013	0.0013
44.1	<0.0001	<0.0044	0.0030	0.0030
46.1	0.0005	0.0021	0.0073	0.0099
46.2	0.0006	0.0021	0.0019	0.0046
54.2	<0.0001	0.1715	<0.0001	0.1715
55.1	0.0046	<0.0004	0.0015	0.0061

1) Only the values larger than detection limit has been added in SUM of RCR

The calculated RCR values are based on the static migration test used except some supplementary migration tests (8.1b to 8.1f).It is seen that no risk characterisation ratios are larger than 1 and 4 RCR value are larger than 0.1 (0.13 to 0.75 or up to 75 % of the value where there is possible risk of use). In the next chapter results from supplementary migration tests are discussed.

5.2.4 Supplementary migration tests

In the passive migration tests (Table 5.3) the following conditions was used:

- Extraction time: 16 hours
- No stirring.

For sample 8 which contains the partly water soluble DIBP (pKOW=4.11) and the very low water soluble DEHP (pKOW=7.5) a number of tests were performed to study the influence of extraction conditions based on the following:

- There is a an expected improved contact from walking which is suspected to increase migration of phthalates when compared to "static contact"
- In earlier migration tests (survey no.77, 2006) the influence of water based lubricant (which will have some content of an emulsifier) and an oil based lubricant was tested for migration of the phthalate DEHP from sextoys. An increase in migration of a factor 7 was observed with addition of water based lubricant and a factor of 1000 with oil based lubricant. As sun protecting agents (mostly water based with some emulsifier ingredients) may be used of kids and grownups during summer an increased migration is foreseen.

Test conditions for the experiments 8.1a-8.1f are shown in Table 5.5.

Table 5.5 Experimental condtions in supplementary migration tests

No	Second extraction step	Dynamic extraction conditions (Shaker table)	50% reduction in extraction time	Use of sun lotion
8.1a (reference)				
8.1b	X			
8.1c			X	
8.1d		X		
8.1e				X
8.1f		X		X

The results from Table 5.5 for test 8.1a-8.1f are shown in Figure 1 and Figure 2.

In the figures the relative migration is shown (migration values from the supplementary tests in µg/g divided by the migration for the reference 8.1a).

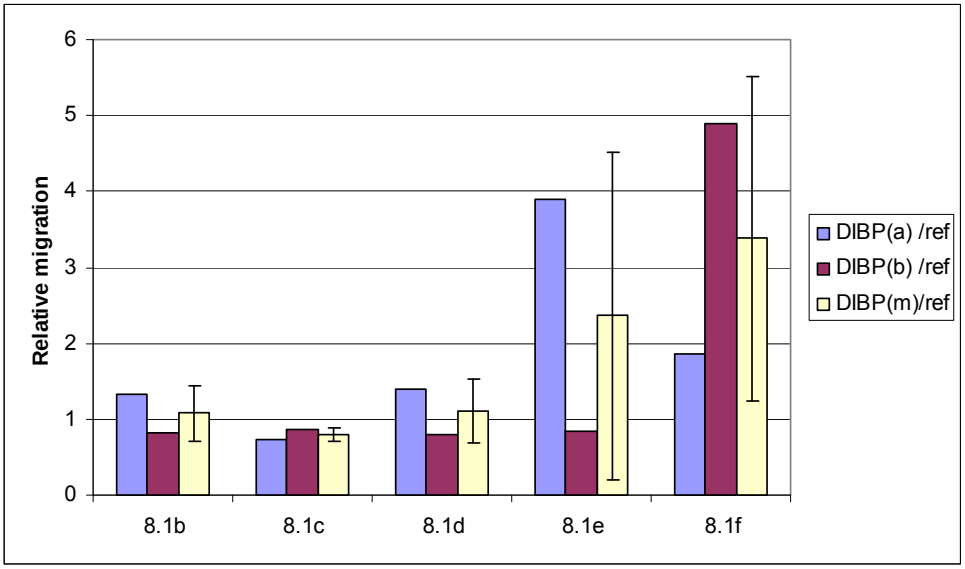

Figure 1 Relative migration for DIBP. DIBP (a)/ref: test no. 1 divided by reference DIBP (B)(Ref test no. 2 divided by reference, DIBP (m)/Ref average of the two tests divided by reference

For DIBP the figure shows:

8.1b Two extractions
The result for two sequential extractions shows approximately 10% increase in migration due to performing a second extraction. The standard deviation is considerable but the major part of phthalates seems to be extracted during the first extraction.

8.1c 50% Reduction in contact time
The result for a 50% reduction in contact time shows that the major part of DIBP (app 80%) is extracted during the first 8 hours.

8.1d Increased migration rate by dynamic migration conditions
The result from the migration using a shaker table shows a small increase in the extracted amount of phthalates (10% increase).

8.1e,f Use of sun lotion
The result from 8.1e (sun lotion) and 8.1f (sun lotion and shaker table) shows a relative increase in migration of up to a factor 3.4 in average (the individual tests give increases of a factor 1.9 and 4.9) at the worst case conditions. The analytical standard deviations are large but it is still judged that the use of sun protecting agents result in a considerable increase in the migration rate.

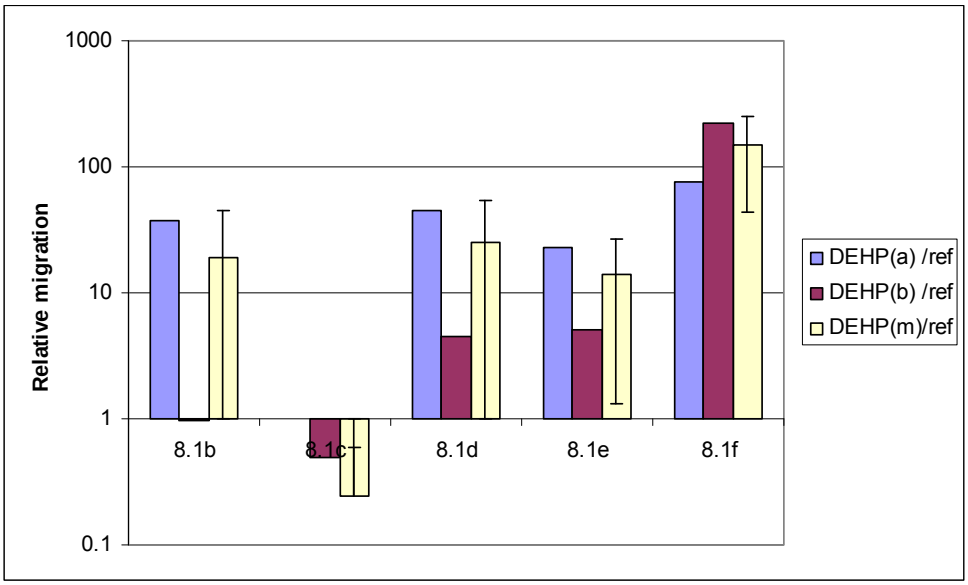

Figure 2 Relative migration for DEHP DEHP (a)/ref: test no. 1 divided by reference, DEHP (B)/Ref test no. 2 divided by reference, DEHP (m)/Ref average of the two tests divided by reference

For DEHP the results show:

8.1b Two extractions
The results for two sequential extractions are difficult to explain as the extracted amount in theory by two sequential extractions should be less than 2 times the extracted amount of one extraction.

8.1c 50% Reduction in contact time
The result for a 50% reduction in contact time shows 50% reduction for one test and a reduction below detection limit in the other test when the sample is extracted for only 8 hours. However the one test value above the detection

limit is close to the detection limit so the data seems reasonable. The result suggest as expected that DEHP is not easily extracted and that the extracted amount by using a double extraction time is doubled.

8.1d Increased migration rate by dynamic migration conditions

The result from the migration test using a shaker table shows a considerable increase in extracted amount of phthalates but with a high standard deviation. The relative increase is respectively a factor 46 and a factor 5 in the two tests with an average increase of a factor 25.

8.1e Use of sun lotion

The result from 8.1e (use of sun lotion) shows a considerable increase in extracted amount of phthalates but with a high standard deviation. The relative increase is respectively a factor 23 and a factor 5 in the two tests.

8.1f Use of sun lotion and shaker table

The result from 8.1f (worst case treatment) shows an even larger relative increase in migration of a factor 75 for one test and a factor 223 for the other test. The average is a 149 times increase. The standard deviations are large but there seems to be a high increase in migration rate.

5.2.5 Risk characterisation ratios for worst case scenarios with dynamic migration conditions and use of sun lotion

In Table 5.6 an estimation of Risk Characterisation Ratios for worst case scenarios with use of sun lotion and dynamic migration conditions are shown. In the calculation the following factors of increase in migration are used:

	DIBP	DBP	DEHP
Factor for straps (8.1f) dynamic condition and sun lotion	3.4	3.4	149.5
Factor for soles (8.1d) dynamic condition	1.1	1.1	25.1

The factors of increase in migration for DBP were assumed to be the same as for DIBP as pKOW for the two ftalates are similar with values of respectively 4.11 and 4.57.

Table 5.6 Revised calculation of RCR at worst case-situation with increased migration due to dynamic conditions and use of sun lotion

Product ID	Type[1)]	RCR DIBP	RCR DBP	RCR DEHP	SUM OF RCR[2)]
1.1	1	0.0021	0.8202	0.0573	**0.8796**
5.2	2	<0.0001	0.4644	<0.0103	**0.4644**
6.1	1	<0.0001	<0.0054	0.0667	0.0667
8.1a	1	0.0030	<0.0057	0.0287	0.0317
8.2	2	0.0009	0.1281	0.0177	**0.1468**
12.1	1	<0.0001	<0.0058	0.1185	**0.1185**
13.2	2	<0.0001	0.4695	0.2636	**0.7331**
17.1	1	0.0017	0.0305	0.0427	0.0748
18.1	1	0.0007	0.0044	0.0269	0.0320
18.2	1	0.0007	<0.0005	0.0092	0.0098
20.2	2	0.0008	0.3028	0.4479	**0.7515**
26.1	1	<0.0001	<0.0056	0.0360	0.0360
29.2	1	0.0007	<0.0016	0.0070	0.0077
37.2	2	0.0028	<0.0021	0.1441	**0.1469**

Product ID	Type[1)]	RCR DIBP	RCR DBP	RCR DEHP	SUM OF RCR[2)]
38.2	2	0.0012	0.0167	<0.0075	0.0180
39.2	2	<0.0001	<0.0013	0.0416	0.0416
43.1	1	<0.0001	<0.0050	0.0328	0.0328
44.1	1	<0.0001	<0.0048	0.0747	0.0747
46.1	1	0.0006	0.0023	0.1825	**0.1854**
46.2	1	0.0006	0.0023	0.0487	0.0516
54.2	2	<0.0001	0.5801	<0.0133	**0.5801**
55.1	1	0.0051	<0.0005	0.0364	0.0415

Values >0.1 are marked in bold writing

1) 1:Part of soles, 2: straps
2) Only the values larger than detection limit has been added in SUM of RCR

None of the calculated RCRs are higher than 1. However, 9 out of 22 tested samples showed RCR values larger than 0.1.

The highest RCR value is for product 1.1 with a RCR value of 0.88 and with a content of DBP which have the lowest DNEL but 5 samples with DEHP also contribute with RCR values from 0.1 to 0.45.

In some cases the migration may increase even further. If sun lotion accidentally is applied on the sole of the foot the migration will increase for all samples from soles (type 1) above.

It is also expected that use of other emulsions like moisturizing creams will increase the migration rate of phthalates.

For DEHP a very large increase in migration has earlier been seen when using oil based lubricants as mentioned in (survey no.77, 2006). Bearing this in mind the observed increase in the migration of a factor 150 may be even higher when using solely oil based sun lotion. In this case more of the products RCR values may well be higher than 1. However, a supplementary more in depth migration test program is needed to verify this judgement.

6 References

Danish Environmental Agency, Data for DEHP in unpublished report, communication with Shima Dobel 2010.

ECHA, April 2010. Guidance on information requirements and chemical safety assessment.
http://guidance.echa.europa.eu/docs/guidance_document/information_requirements_en.htm

ECHA, Oct. 2008 SVHC support document Dibutylftalate

ECHA, Oct. 2008 SVHC support document Bis(2-ethylhexyl)ftalate

ECHA, Nov. 2009 SVHC support document Diisosobutylftalate

Mapping of chemical substances in consumer products
no. 100 2008 N.H. Nilsson, B. Malmgren-Hansen, U. Thomsen, Mapping, emissions and environmental and health assessment of chemical substances in artificial turf, Danish EPA

WHO Growth reference 5-19 years 2007
http://www.who.int/growthref/wfa_boys_5_10years_z.pdf

Survey of chemical substances in consumer products no. 77, 2006, Danish EPA, K. Tønning et al.

Survey and Health assessment of the exposure of 2-year olds to chemical substances in Consumer Products Danish Environmental Agency no.102, 2009, K. Tønning et al.