TNO Environment, Energy and Process Innovation

Nederlandse Organisatie voor
toegepast-natuurwetenschappelijk
onderzoek / Netherlands Organisation
for Applied Scientific Research

Laan van Westenenk 501
Postbus 342
7300 AH Apeldoorn
The Netherlands

www.mep.tno.nl

T +31 55 549 34 93
F +31 55 541 98 37
info@mep.tno.nl

TNO-report

R 2004/493

Man-Made Chemicals in Human Blood

Date	November 2004
Authors	Ruud J.B. Peters
Order no.	35554
Dossier no.	52004045
Keywords	human blood bio-monitoring brominated flame retardants phthalates musks alkylphenols alkylphenol ethoxylates.
Intended for	Ms. M. Harthoorn Greenpeace Nederland Veemkade 18-20 1019 GZ Amsterdam

Summary

While the widespread presence of hazardous man-made chemicals in the environment is becoming increasingly well documented, there are now also studies that show the presence of such compounds in common house dust. Because many of these chemicals are used as additives in consumer products there is a potential for human exposure, and since many of them have a lipophilic nature they may be bio-accumulated, resulting in prolonged residence time in the human body.

The objective of this study is to determine the presence of a number of chemicals in blood samples from volunteers in The Netherlands. The chemicals considered in this study are; brominated flame retardants (polybrominated diphenyl ethers as well as hexabromocyclododecane and tetrabromobisphenol-A), phthalates, artificial musk compounds (nitro musks as well as polycyclic musks), organotin compounds, alkylphenols and alkylphenol ethoxylates and bisphenol-A. The results show that many of these compounds are present in human blood, sometimes in relatively high concentrations. Compounds like di-(2-ethylhexyl) phthalate, the brominated flame retardant BDE-153 and the artificial musks tonalide and galaxolide, are found in almost all samples.

PBDEs typically present in the commercially available penta-, octa- deca-mixtures were found in many samples, as well as TBBPA and the newer flame retardant HBCD. The highest concentration found was 1944 pg/g serum for decabromo diphenylether (BDE-209). Di-(2-ethylhexyl)-, dibutyl- and benzylbutyl phthalate are the major phthalates found in human blood serum with concentrations up to 5863 ng/g serum for di-(2-ethylhexyl) phthalate. Di-isononyl and di-isodecyl phthalate, found in two other studies, were not found in this study. Of the artificial musk compounds, the polycyclic musks tonalide and galaxolide were found in virtually every sample. Surprisingly, musk ambrette, a nitro-musk phased out years ago, was found in as many as 46 of the 88 samples. Organotin compounds, mostly mono- and dioctyltin are found in a limited number of the whole blood samples in concentrations up to 2.4 ng/g whole blood. Finally, bisphenol-A and nonylphenol are found in concentrations up to 16 ng/g serum. The alkylphenol ethoxylates are not found in human blood serum. In general, the results clearly indicate the presence of man-made chemicals in human blood, and therewith, in the human body.

Table of contents

1. Introduction

While the widespread presence of hazardous man-made chemicals in the environment is becoming increasingly well documented[1,2], there are now also studies that show the presence of such compounds in common house dust[3,4,5]. Since many of these chemicals are used as additives in consumer products such as carpets, curtains, toys and electronic equipment, their presence in house dust may be expected. This also implies that there is a potential for human exposure, and since many of these compounds have a lipophilic nature they may be bio-accumulated, resulting in prolonged residence time in the human body. That such compounds are indeed present in the human body was shown by recent studies in the UK and the US.

In the US the 2001 National Report on Human Exposure to Environmental Chemicals provides information about levels of 27 environmental chemicals measured in the US population. Chemicals included are metals, organophosphate pesticide metabolites, phthalate metabolites and cotinine, a marker of exposure to tobacco smoke[6]. In the second National Report on human Exposure to Environmental Chemicals, the study was extended with polycyclic aromatic hydrocarbons, polychlorinated dibenzo-p-dioxins and -furans, polychlorinated biphenyls, phyto-estrogens and pesticides to a total of 116 chemicals[7]. Chemicals and their metabolites were measured in blood and urine samples from selected participants.

The WWF-UK National Biomonitoring Survey presented results of blood sample analyses of 155 volunteers for 78 chemicals including organochlorine pesticides, polychlorinated biphenyls and polybrominated diphenyl ethers[8]. In a second WWF campaign blood samples from 47 volunteers from 17 European countries were analysed for 101 chemicals, predominantly persistent, bio-accumulative man-made chemicals including organochlorine pesticides, polychlorinated biphenyls,

---

1 Peters RJB. Hazardous Chemicals in Precipitation. TNO report R2003/198, May **2003**.

2 Vethaak AD, Rijs GBJ, Schrap SM, Ruiter H, Gerritsen A, Lahr J. Estrogens and xeno-estrogens in the aquatic environment of the Netherlands. RIZA/RIKZ-report 2002.001, February **2002**.

3 Santillo D, Labunska I, Davidson H, Johnston P, Strutt M, Knowles O. Consuming Chemicals, Greenpeace Research laboratories Technical Note 01/2003 (GRL-TN-01-2003) **2003**.

4 Peters RJB, The Determination of Hazardous Chemicals in House Dust from Belgium homes and offices. TNO report R2004/087, April **2004**.

5 Peters RJB, The Determination of Hazardous Chemicals in House Dust from Brazilian homes. TNO report R2004/159, April **2004**.

6 CDC report: National Report on Human Exposure to Environmental Chemicals. CDC, Atlanta, Georgia, March **2001**.

7 CDC report: National Report on Human Exposure to Environmental Chemicals. CDC, Atlanta, Georgia, January **2003**.

8 WWF-UK National Biomonitoring Survey, November **2003**.

brominated flame retardants, phthalates and perfluorinated chemicals[9]. The latter are chemicals used for there non-sticking properties in various applications.

The objective of this study is to determine the presence of a number of chemicals in blood samples from about 100 selected volunteers in The Netherlands. The chemicals considered in this study are; brominated flame retardants (polybrominated diphenyl ethers as well as hexabromocyclododecane and tetrabromobisphenol-A), phthalates, artificial musk compounds (nitro musks as well as polycyclic musks), organotin compounds, alkylphenols and alkylphenol ethoxylates and bisphenol-A.

[9] WWF Detox campaign: Chemical Check Up: An analysis of chemicals in the blood of Members of the European Parliament. April **2004** (Note that median concentrations in this report were calculated excluding results below the method detection limit).

2. Samples and Chemical Parameters

2.1 Samples

Blood samples were collected by Greenpeace in cooperation with The Academic Hospital of Groningen using a standard type BD-Vacutainer tube, closed with a rubber stopper, and a collection system consisting of two needles connected by a piece of polymer tubing. The samples were received by the TNO laboratory within 24 hours after collection and were kept cool (between 2 and 8°C) during transport. Samples were stored at 4°C until analysis. In total 91 samples were received.

2.2 Chemical parameters

The chemical parameters determined in this examination are listed below, including the abbreviations that are used in the text, tables and appendices.

Table 1 Overview of all individual parameters and their abbreviations used in the text, tables and appendices.

Brominated flame retardants	
2,2',4-tribromo diphenylether	BDE 17
2,4,4'-tribromo diphenylether	BDE 28
2,2',4,4'-tetrabromo diphenylether	BDE 47
2,2',4,5'-tetrabromo diphenylether	BDE 49
2,2',3,4,4'-pentabromo diphenylether	BDE 85
2,2',4,4',5-pentabromo diphenylether	BDE 99
2,2',4,4',6-pentabromo diphenylether	BBE 100
2,2',4,4',5,5'-hexabromo diphenylether	BDE 153
2,2',4,4',5,6'-hexabromo diphenylether	BDE 154
2,2',3,4,4',5',6-heptabromo diphenylether	BDE 183
decabromo diphenylether	BDE 209
hexabromo cyclododecane	HBCD
tetrabromodisphenol-A	TBBPA

Phthalates	
dimethyl phthalate	DMP
diethyl phthalate	DEP
di-iso-butyl phthalate	DIBP
di-n-butyl phthalate	DBP
butylbenzyl phthalate	BBP
dicyclohexyl phthalate	DCHP
di-(2-ethylhexyl) phthalate	DEHP
di-n-octyl phthalate	DOP
di-iso-nonyl phthalate	DINP
di-iso-decyl phthalate	DIDP

Musk compounds	
celestolide	ADBI
tonalide	AHTN
traseolide	ATTI
cashmeron	DPMI
galaxolide	HHCB
musk ambrette	MA
musk ketone	MK
musk moskene	MM
musk tibetene	MT
musk xylene	MX

Organotin compounds	
monobutyltin	MBT
dibutyltin	DBT
tributyltin	TBT
monooctyltin	MOT
dioctyltin	DOT
monophenyltin	MPT
diphenyltin	DPT
triphenyltin	TPT

Phenols and phenol ethoxylates	
bisphenol-A	BPA
nonylphenol	NP
octylphenol	OP
nonylphenol ethoxylates	NPEO
octylphenol ethoxylates	OPEO

3. Materials and methods

Before the start of the project, all methods used in this study were validated for the analytes listed in chapter 2. The validation experiments were carried out using fresh calf's blood as such and spiked with the analytes of interest. The validation study resulted in standard operation procedures that were tested on a limited number of human blood samples and subsequently used in this study.

3.1 Sample pre-treatment

Upon receipt a sub-sample of the whole blood sample is collected for the organotin analysis. The remaining part of the whole blood sample is allowed to clot at room temperature for 20 min and centrifuged at 4000 rpm for 15 min. The serum is transferred into PTFE-capped glass vials and stored at 4°C until further analysis.

3.2 Sample analysis

3.2.1 Extraction of serum samples

All glassware used in the analyses is cleaned, rinsed with demi-water and baked in oven for 16 hours at 280°C prior to use. All solvents are distilled prior to use to achieve low blank results. The latter is especially important for the determination of the phthalates.

The serum sample is weight into a clean glass 60 ml vial. Methanol, 0.1 M HCl and a set of internal standards (one or more for each group of chemicals) is added to the sample. The sample is extracted twice with a hexane-diethyl ether mixture and centrifuged after each extraction to separate the organic phase. The combined extracts are washed with a 1% KCl-solution and dried with anhydrous sodium sulphate. The extract is split into two equal parts, A and B.

3.2.2 Bisphenol-A, tetrabromo bisphenol-A, alkylphenols and alkylphenol ethoxylates

Part A of the extract is concentrated to a small volume without further purification. Methanol is added to the extract and the extract is concentrated further to remove all hexane-diethyl ether residues. The methanol extract is used for the determination of BPA, TBBPA, NP, OP, NPEO and OPEO. The final extracts are analysed with liquid chromatography coupled with mass spectrometry (LC/MS) in the selected ion monitoring mode (SIM).

3.2.3 Brominated flame retardants, phthalates and musk compounds

Part B of the extract is concentrated to a small volume. The extract is purified using a florisil clean-up procedure and separate fractions are collected containing the component groups. The purified extracts are concentrated to a small volume and an injection standard is added. The final extracts are analysed with gas chromatography coupled with mass spectrometry (GC/MS) in the selected ion monitoring mode (SIM).

3.2.4 Organotin compounds

The whole blood sample is weighed into a 60 ml vial and internal standards are added. After the addition of a sodium dithiocarbamate solution in ethanol, the sample is sonicated, left overnight, and sonicated once more. The residue is removed and an acetate buffer and a sodium tetraethylborate solution in ethanol are added. The mixture is extracted twice with hexane and the concentrated extract is purified using a silica clean-up procedure. The purified extract is concentrated and an injection standard is added. The final extracts are analysed with gas chromatography coupled with mass spectrometry (GC/MS) in the selected ion monitoring mode (SIM).

3.3 Identification, quantification and expression of results

The identification of analytes is based on correct retention times and qualifier ion ratios, compared to an external standard. The quantification was based on an external standard analysed together with the samples. The recovery of the added internal standards was used to determine the performance of the analysis, but not to correct the results of the target compounds with the exception of the organotin compounds. In the latter case the results were corrected for the recovery of the internal standard.

Blank values were determined with each series of samples. Only in the case of DEP and DEHP the results were corrected for the blank values.

The results in this report are expressed in pg/g serum (flame retardants) and ng/g serum (other analytes). Since there is evidence that in a body a relationship exists between the levels of lipophilic compounds in adipose tissue and blood serum, results in some scientific literature (referred to in this study) are sometimes expressed in pg/g lipid or ng/g lipid. Since the lipid content in blood serum is about 0.65%, results for lipophilic compounds in pg/g serum may be converted into pg/g lipid by multiplying the former with a factor 150.

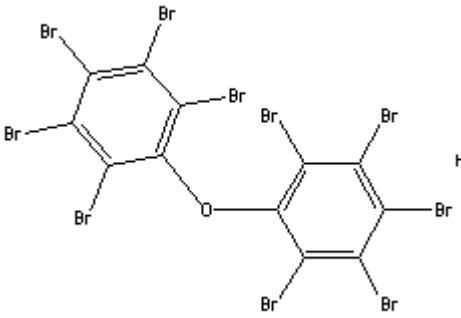
When reading the tables in section 4 and the appendix of this report please note that while results are rounded to the correct decimal number, they are not always rounded to the correct number of significant units. In general no more than two significant numbers apply. In the summary tables in section 4 percentiles (10^{th}, 25^{th}, 50^{th}, 75^{th}, 90^{th} and 95^{th}) are given to provide additional information about the shape of the distribution. The 50^{th} percentile is the median concentration. The percentiles are calculated on the results of all 91 participants. If the calculated percentile is smaller than the method detection limit, it is replaced by the method detection limit.

4. Results

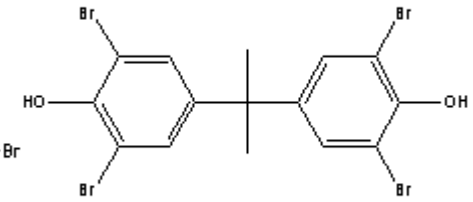
4.1 Brominated flame retardants

4.1.1 General information

Three types of brominated flame retardants are determined in this examination. The first are polybrominated diphenyl ethers (PBDEs), used as commercial mixtures with different degrees of bromination and used as additives to fireproof polymers. The second is hexabromocyclododecane (HBCD), a cyclo-aliphatic brominated chemical introduced as a replacement for the PBDEs and with the same applications. The third is tetrabromobisphenol-A (TBBPA) mainly used as a reactive (chemically bound) flame retardant in epoxy polymers such as printed circuit boards in electronic equipment. The structure of BDE-209 (better known as deca-BDE) and TBBPA is shown below.



decabromo diphenylether (BDE 209)



tetrabromo bisphenol-A (TBBA)

4.1.2 Brominated flame retardants in human blood

Brominated flame retardants have been found in human blood in several studies. Sjödin found that the total median PBDE concentrations in serum from workers with different occupations ranged from 5.4 to 37 pmol/g lipid with BDE-47 and BDE-183 being the most prominent PBDEs[10]. Mazdai studied the presence of PBDE in fetal and maternal blood and found comparable results with BDE-47 being the most prominent with an average concentration of 25 ng/g lipid[11]. The National Biomonitoring Survey 2003 of the WWF-UK showed that BDE-47, -99, -

[10] Sjödin A, Hagmar L, Klasson-Wehler E, Kronholm-Diab K, Jakobsson E, Bergman A. Environ. Health Perspec. 643-648, *107*, **1999**.

[11] Mazdai A, Dodder NG, Abernathy MP, Hites RA, Bigsby RM. Environ. Health Perspec. 1249-1252, *111*, **2003**.

100, -153, -154 and -183 were the most common PBDEs found in blood serum[12]. The highest median concentration was 1.7 ng/g lipid found for BDE-153. BDE-209 was found in less than 10% of the samples, but in high concentrations ranging from 35 to 240 ng/g lipid. The more recent WWF study showed similar results[9]. In addition to PBDEs the brominated flame retardants HBCD and TBBPA were determined. HBCD was found in one sample only, while TBBPA was found in about half of the samples in concentrations ranging from 2 to 330 pg/g serum.

4.1.3 Results for brominated flame retardants in this study

The results for the brominated flame retardants are summarised in table 2, expressed in pg/g serum. Of the PBDEs BDE-17 and -85 are not found in any of the samples while BDE-28 and -49 are found in one sample only. BDE-153 is found in 76 of the 91 samples (e.g. 84%) and is the most often found PBDE. The highest concentration found is 1944 pg/g serum for BDE-209, decabromo diphenylether. Apart from PBDEs, two newer types of brominated flame retardants, HBCD and TBBPA are determined in the serum samples. Both are found in respectively 11 and 32 of the 91 samples. The results for the PBDEs are comparable to those of other studies in the literature. The results for HBCD and TBBPA can only be compared to the recent WWF study[9]. HBCD is found more often in this study and the concentrations of HBCD, as well as TBBPA, appear to be higher in this study.

[12] Thomas GO, Hodson S, Jones KC. WWF-UK National Biomonitoring Survey 2003, Appendix 3: Lancaster University Analytical report, November **2003**.

Table 2 Summary of brominated flame retardants found in human blood serum (91 samples).

Parameter	BDE-17	BDE-28	BDE-47	BDE-49	BDE-85
	pg/g serum	pg/g serum	pg/g serum	pg/g serum	pg/g serum
number of samples above MDL	0	1	40	1	0
maximum measured value		2.0	226	3.0	
minimum measured value		2.0	2.3	3.0	
method detection limit (MDL)	< 1	< 1	< 2	< 1	< 3
10th percentile	<	<	<	<	<
25th percentile	<	<	<	<	<
50th percentile (median)	<	<	<	<	<
75th percentile	<	<	4.4	<	<
90th percentile	<	<	9.4	<	<
95th percentile	<	<	12	<	<

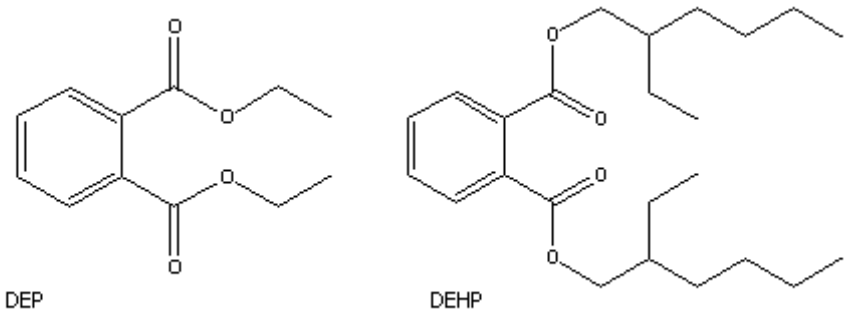
Parameter	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183
	pg/g serum	pg/g serum	pg/g serum	pg/g serum	pg/g serum
number of samples above MDL	23	21	76	19	10
maximum measured value	401	132	253	46	308
minimum measured value	3.6	2.4	1.9	1.2	2.2
method detection limit (MDL)	< 3	< 2	< 1	< 1	< 2
10th percentile	<	<	<	<	<
25th percentile	<	<	4.4	<	<
50th percentile (median)	<	<	7.5	<	<
75th percentile	1.8	<	9.9	<	<
90th percentile	6.8	5.8	22	3.1	2.2
95th percentile	8.2	12	35	7.2	5.6

Parameter	BDE-209	HBCD	TBBPA
	pg/g serum	pg/g serum	pg/g serum
number of samples above MDL	11	11	32
maximum measured value	1944	356	787
minimum measured value	151	96	56
method detection limit (MDL)	< 150	< 80	< 50
10th percentile	<	<	<
25th percentile	<	<	<
50th percentile (median)	<	<	<
75th percentile	<	<	85
90th percentile	174	114	170
95th percentile	312	217	339

4.2 Phthalates

4.2.1 General information

Phthalates are one of the most ubiquitous classes of compounds in our everyday environment. They are used as plasticizers to increase the flexibility of high molecular weight polymers (mainly in PVC), as heat-transfer fluids and as carriers, and can be found in ink, paint, adhesives, pesticides, vinyl flooring[2], but also in cosmetics and personal care products. Consequently, the potential for human exposure is very high. Di-(2-ethylhexyl) phthalate (DEHP) is the most commonly used plasticizers but is nowadays gradually replaced by iso-alkyl phthalate mixtures like di-isononyl phthalate (DINP). The chemical structure of di-ethyl phthalate (DEP) and DEHP is shown below.



4.2.2 Phthalates in human blood

Phthalates have been measured in blood, but more frequently as there metabolites in urine[6,7]. In a study of DEHP levels in blood samples from baby girls, the concentrations ranged from 70 to 450 ng/g serum[13]. In another study cord blood samples were analysed for DEHP and/or MEHP (the metabolite of DEHP). These compounds were found in 88% of the samples, with average concentrations of 1190 ng/g serum for DEHP and 520 ng/g serum for MEHP[14]. In the recent WWF study phthalates were determined in the human blood of 47 volunteers[9]. DEHP was found in most samples with a median concentration of 160 ng/g blood while DIBP was found in more than half of the samples with a median concentration of 7 ng/g blood. DINP and DIDP were found in 17 and 4 of the 47 samples in median concentrations of 31 and 95 ng/g blood. However, be aware that the median concentrations in the WWF study were calculated excluding results below the method detection limit. As a result the median concentration of 95 ng/g blood for

---

13 Colon I. Environ. Health Perspec. 895-900, *108*, **2000**.

14 Latini G, de Felice C, Presta G, del Vecchio A, Paris I, Ruggieri F, Mazzeo P. Environ. Health Perspec. On line 19 August **2003**.

DIDP is for the 4 out of 47 samples only, and the true median concentration of DIDP for all 47 samples will be much lower (in fact below the method detection limit). In the CDC study mono-isononyl phthalate in urine, measured as an indicator for exposure to DINP, was found only rarely and in concentrations close to the detection limit[7].

4.2.3 Results for phthalates in this study

The results for phthalates in this study are summarised in table 3, expressed in ng/g serum. As expected DEHP is the major phthalate, found in 84 of the 91 samples with a median concentration of 151 ng/g and a maximum concentration of 5863 ng/g serum. Somewhat surprising, DINP and DIDP, two newer di-isoalkyl phthalates increasingly found in products, are not found in any of the samples in this study.

Table 3 Summary of phthalates found in human blood serum (91 samples).

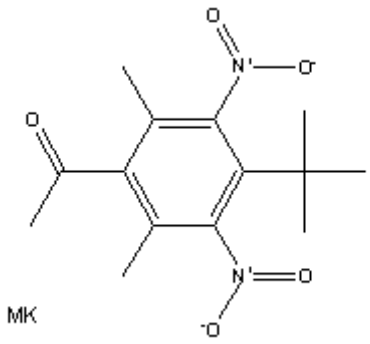
Parameter	DMP	DEP	DIBP	DBP	BzBP
	ng/g serum	ng/g serum	ng/g serum	ng/g serum	ng/g serum
number of samples above MDL	26	21	18	68	35
maximum measured value	10	14	93	136	305
minimum measured value	1.0	2.2	3.2	2.6	1.1
method detection limit (MDL)	< 1	< 2	< 2	< 2	< 1
10th percentile	<	<	<	<	<
25th percentile	<	<	<	1.3	<
50th percentile (median)	<	<	<	8.1	<
75th percentile	1.1	<	<	19	1.5
90th percentile	2.6	6.6	52	63	2.2
95th percentile	3.8	9.7	65	79	3.2

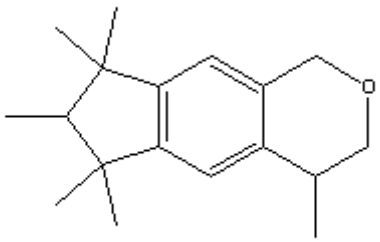
Parameter	DCHP	DEHP	DOP	DINP	DIDP
	ng/g serum	ng/g serum	ng/g serum	ng/g serum	ng/g serum
number of samples above MDL	4	84	2	0	0
maximum measured value	4	5863	17		
minimum measured value	1.0	28	2.0		
method detection limit (MDL)	< 1	< 25	< 1	< 10	< 10
10th percentile	<	31	<	<	<
25th percentile	<	48	<	<	<
50th percentile (median)	<	151	<	<	<
75th percentile	<	550	<	<	<
90th percentile	<	1680	<	<	<
95th percentile	<	3226	<	<	<

4.3 Musk compounds

4.3.1 General information

Originally, musk is a male sexual scent signal but the increasing demand resulted in the production of artificial musk compounds. The most well known are nitro musks like musk xylene (MX) and musk ketone (MK) that are nowadays replaced by polycyclic musks like tonalide (AHTN) and galaxolide (HHCB). Musks are used as additives for perfumes, in detergents and soaps, in body lotions and deodorizers. The structure of MK and HHCB is presented below.





4.3.2 Musk compounds in human blood

There is only little information about musk compounds in human blood, mainly about musk-ketone (MK) and musk-xylene (MX). In a study in1993, MX has been found in 92% of the serum samples with a median concentration of 24 ng/g lipid[15]. When this study was repeated in 1998, MX was found in only 12% of the samples with a median concentration < 10 ng/g lipid, suggesting a lower exposure to MX[16]. Another study reports median values of 6.5 ng/g lipid for MX and 5.5 ng/g lipid for MK[17]. For human adipose tissue samples maximum concentrations found for MX and HHCB were 288 ng/g lipid and 171 ng/g lipid, respectively[18].

4.3.3 Results for musks in this study

The results for artificial musk compounds, five nitro musks and five polycyclic musks, are summarised in table 4. As found in other matrices, HHCB and AHTN

---

15 Angere J, Kafferlein HU. J. Chromatogr. B Biomed. Sci. Appl. 71-78, *693*, **1997**.

16 Kafferlein HU, Angerer J. Int. Arch. Occup. Environ. Health. 470-476, *74*, **2001**.

17 Eisenhardt S, Runnebaum B, Bauer K, Gerhard I. Environ. Res. 123-130, *87*, **2001**.

18 Muller S, Schmid P, Schlatter C. Chemosphere. 17-28, *33*, **1996**.

are the most common musks found in median concentrations of 1.3 and 0.46 ng/g serum and maximum concentrations of 9.2 and 11 ng/g serum. Note that HHCB is found in every of the 91 samples. Surprisingly, MA that was phased out years ago, is found in 50% of the samples which is much more often than the other nitro musks. This result is comparable with that for MA in rainwater[1], were it was found in 40% of the rainwater samples. Additional analyses confirmed the identity of MA in these samples. The concentrations of MK and MX found in this study are much lower than those reported in the literature a few years ago, indicating that their use in products is apparently diminishing.

Table 4 Summary of musk compounds found in human blood serum (91 samples).

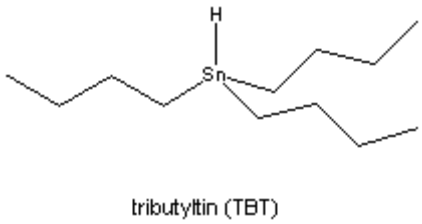
Parameter	ADBI	AHTN	ATTI	DPMI	HHCB
	ng/g serum	ng/g serum	ng/g serum	ng/g serum	ng/g serum
number of samples above MDL	1	88	4	1	91
maximum measured value	0.05	11	0.67	8.0	9.2
minimum measured value	0.05	0.1	0.29	8.0	0.2
method detection limit (MDL)	< 0.05	< 0.1	< 0.05	< 0.05	< 0.1
10th percentile	<	0.2	<	<	0.7
25th percentile	<	0.2	<	<	0.8
50th percentile (median)	<	0.4	<	<	1.3
75th percentile	<	0.7	<	<	2.0
90th percentile	<	1.0	<	<	2.8
95th percentile	<	1.3	<	<	3.6

Parameter	MA	MK	MM	MT	MX
	ng/g serum	ng/g serum	ng/g serum	ng/g serum	ng/g serum
number of samples above MDL	48	9	1	3	6
maximum measured value	4.0	1.47	0.15	0.20	0.27
minimum measured value	0.1	0.06	0.15	0.14	0.1
method detection limit (MDL)	< 0.1	< 0.05	< 0.05	< 0.05	< 0.05
10th percentile	<	<	<	<	<
25th percentile	<	<	<	<	<
50th percentile (median)	0.1	<	<	<	<
75th percentile	0.4	<	<	<	<
90th percentile	0.8	<	<	<	<
95th percentile	1.2	0.1	<	<	0.1

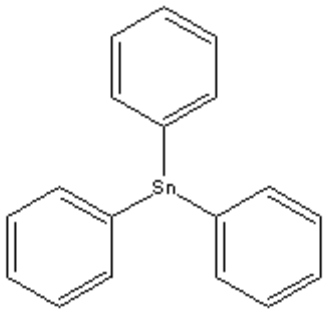
4.4 Organotin compounds

4.4.1 General information

There are three major applications for organotin compounds. Tributyltin (TBT) is used in anti-fouling paints for ships, triphenyltin (TPT) is used as a pesticide, and butyl- and octyltin compounds are used as stabilisers in polymers. Because of the latter application many textile products containing polymer parts, like T-shirts with prints, sanitary bandages, plasters and diapers, can contain organotin compounds[19]. Until a few years ago mainly TBT and its metabolites dibutyltin (DBT) and monobutyltin (MBT) were found. Nowadays, the concentrations found in products are declining and if organotins are found these are mainly di-octyltin (DOT) and mono-octyltin (MOT), and always in the polymer parts (foam, plastic or adhesives) of the earlier mentioned products[20]. The structures of TBT and TPT are presented below.



tributyltin (TBT)



triphenyltin (TPT)

4.4.2 Organotin compounds in human blood

The amount of information about organotin compounds (OT) in human blood is very limited. One study, concerned with the determination of methyl- and octyl-tin compounds in animal blood, reported low concentrations of trimethyltin[21]. Kannan et al reported for the first time the presence of mono-, di- and tributyltin in human blood[22]. Blood samples from 32 volunteers showed a total butyltin concentration ranging from 2.8 to 101 ng/ml with an overall mean concentration of 21 ng/ml. However, there has been some debate concerning these findings[23].

---

19 Gaikema F.J., Alberts P.J. Gaschromatografische bepaling van residuen van organotinverbindingen in textielproducten. De Ware(n)-Chemicus, 23-33, **1999**.

20 Observations of over four years of organotin determinations in materials by TNO

21 www.scienceinchina.com/yk/yb/0005/yb0531.pdf

22 Kannan K, Senthilkumar K, Giesy JP. Env. Sci. Technol. 1776-1779, *33*, **1999**.

23 Kannan K, Senthilkumar K, Giesy JP. Env. Sci. Technol. 1879-1880, *34*, **2000**.

4.4.3 Results for organotin in this study

The results for organotin in whole blood samples are summarised in table 5, expressed in ng/g blood. While the only literature study that was found reported relatively high concentrations of butyltins in human blood, in this study butyltins were only found in a few samples and at low concentrations. The octyltins MOT and DOT are the most frequently found organotin compounds with a maximum concentration of 2.4 ng/g for DOT.

Table 5 Summary of organotin compounds found in human whole blood (91 samples).

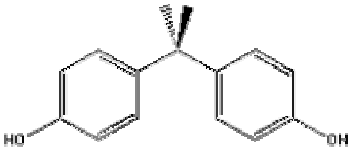
Parameter	MBT	DBT	TBT	MOT	DOT
	ng/g blood	ng/g blood	ng/g blood	ng/g blood	ng/g blood
number of samples above MDL	3	0	3	12	13
maximum measured value	0.1		0.1	0.5	2.4
minimum measured value	0.1		0.1	0.1	0.2
method detection limit (MDL)	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
10th percentile	<	<	<	<	<
25th percentile	<	<	<	<	<
50th percentile (median)	<	<	<	<	<
75th percentile	<	<	<	<	<
90th percentile	<	<	<	0.1	0.4
95th percentile	<	<	<	0.1	1.1

Parameter	MPT	DPT	TPT
	ng/g blood	ng/g blood	ng/g blood
number of samples above MDL	0	0	0
maximum measured value			
minimum measured value			
method detection limit (MDL)	< 0.2	< 0.2	< 0.4
10th percentile	<	<	<
25th percentile	<	<	<
50th percentile (median)	<	<	<
75th percentile	<	<	<
90th percentile	<	<	<
95th percentile	<	<	<

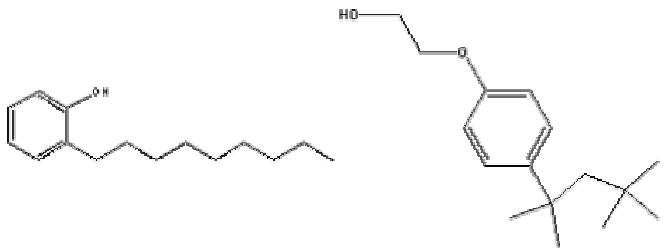
4.5 Bisphenol-A, alkylphenols and alkylphenol ethoxylates

4.5.1 General information

Bisphenol-A (BPA) is a widely used intermediate in the production of epoxy resins, polycarbonate plastics and flame retardants, e.g. a substance used in an extensive range of products. The most common monomer for polycarbonates intended for food contact is BPA[24]. Not polymerised BPA may be released from the polycarbonate and BPA was found in canned food in concentrations up to 7 µg/kg[25], probably due to migration of polymer material on the inside of the can to the food. The chemical structure of BPA is given in the figure below.



Alkylphenols (APs) and alkylphenol ethoxylates (APEOs) are used as additives in plastics and as surface-active ingredients in industrial detergents and emulsifiers. APs commonly used are nonylphenol (NP) and to a lesser extent octylphenol (OP), in both cases pre-dominantly the para-substituted isomers (> 90%). APEOs are produced by a condensation reaction of APs with ethylene oxide. While the lower condensates (number of ethoxylate units about 4) are used as emulsifiers, the higher ethoxylates are used in textile and carpet cleaning, and as emulsifiers in solvents and agricultural pesticides[26]. As with the APs nonylphenol ethoxylate (NPEO) is more used than octylphenol ethoxylate (OPEO). The chemical structure of n-nonylphenol and octylphenol-mono-ethoxylate (better known as Triton X-100) are presented below.



24 Mountfort KA, Kelly J, Jickels SM, Castle L. Food Additives and Contaminations, 56-63, *14*, **1997**.

25 Goodson A, Summerfield W, Cooper I. Food Additives and Contaminants. 1-12, *19*, **2002**.

26 Maguire R.J. Water Qual. Res. J. Canada 34, 37-78, **1999**.

4.5.2 Bisphenol-A, alkylphenols and ethoxylates in human blood

As with some other compounds in this report there is only limited information about the concentrations of such compounds in human blood. BPA is found in human blood serum in concentrations of 1-2 ng/g serum[27]. Nonylphenol (NP) was found in serum in concentrations ranging from 14 to 222 ng/g serum while octylphenol (OP) was found in only one sample in a concentration of 0.5 ng/g serum[28].

4.5.3 Results for bisphenol-A, alkylphenols and ethoxylates in this study

The results for BPA, the alkylphenols OP and NP and the alkylphenol ethoxylates OPEO and NPEO are summarized in table 6. BPA is found in 36 of the 91 samples (e.g. 40%) with a maximum concentration of 16 ng/g serum, comparable to what is published in the literature. For NP, found in 15% of the samples a similar maximum concentration is found. As expected, OP is found only incidentally. Both alkylphenol ethoxylates are not found at all.

Table 6 Summary of bisphenol-A, alkylphenols and ethoxylates found in human blood serum (91 samples).

Parameter	BPA	OP	NP	OPEO	NPEO
	ng/g serum	ng/g serum	ng/g serum	ng/g serum	ng/g serum
number of samples above MDL	36	2	16	0	0
maximum measured value	16	2.3	16		
minimum measured value	0.57	2,0	0.58		
method detection limit (MDL)	< 0.5	< 0.5	< 0.5	< 2.5	< 2.5
10th percentile	<	<	<	<	<
25th percentile	<	<	<	<	<
50th percentile (median)	<	<	<	<	<
75th percentile	1.1	<	<	<	<
90th percentile	2.5	<	1.2	<	<
95th percentile	5.2	<	2.2	<	<

[27] Ikezuki Y, Tsutsumi O, Kamei Y, Taketani Y. Hum. Reprod. 2839-2841, *11*, **2002**.

[28] Inoue K, Yoshimura Y, Makino T, Nakazawa H. Analyst. 1959-1961, *125*, **2000**.

4.6 Quality control measurements

4.6.1 Method validation parameters

Before the start of the project, all methods used in this study were validated for the analytes listed in chapter 2. The validation experiments were carried out using fresh calf's blood as such and spiked with the analytes of interest. The parameters determined were the repeatability, recovery and the method detection limit (MDL). The validation study resulted in standard operation procedures that were tested on a limited number of human blood samples and subsequently used in this study.

Table 7 Summary of method validation parameters and actual recoveries of added internal standards.

Compound or group	Average Recovery (n = 6)	Average repeatability (n = 6)	Method detection limit[A]	Actual recovery added internal standards (n = 91)
	%	%	ng/g serum	%
brominated flame retardants	86	12	0.001 - 0.15	86 ± 14
phthalates	90	13	1 - 25	81 ± 14
musk compounds	97	9	0.05 - 0.1	82 ± 13
organotin compounds	90	13	0.1 - 0.4	69 ± 12
bisphenol-A, alkylphenols	82	10	0.5 - 2.5	92 ± 21

[A]: See the summary tables in the text for the MDL's of the individual parameters.

4.6.2 Recovery of internal standards

For each group of compounds an internal standard was added before the analysis of the sample. The actual recovery of these internal standards in the 91 samples is given in table 7. As pointed out earlier the results are not corrected for the recovery of the internal standards with the exception of the organotin compounds.

4.6.3 Blank samples

With each series of samples a blank sample was included. For the blank analysis the complete analytical procedure was followed, including all chemicals and solvents, but no sample was added. Blank results were found for HHCB and AHTN, in both cases 0.1 ± 0.1 ng/g serum, for DEP, 1.2 ± 1.0 ng/g serum and for DEHP, 20 ± 5 ng/g serum. Only for the latter two phthalates a correction of the results for the blank value was applied, and the detection limit was raised to 2 and 25 ng/g serum respectively.

In addition to the blanks all parts of the blood collection system were tested for the presence of the analytes determined in this study. The glass of the tube and the needles (directly connected without a flexible tubing) did not contain any of the compounds of interest while the rubber stoppers of the BD-Vacutainer tubes did contain DEHP and a small amount of DEP. However, a static extraction experiment with salt water showed that no emissions of these phthalates from the materials to the salt water occur. Therefore, it is expected that no contamination of the blood samples by these materials took place.

5. Conclusions

In this study the presence of a large number of typical man-made chemicals in 91 samples of human blood is determined. The compound groups of interest are brominated flame retardants, phthalates, artificial musk compounds, organotin compounds, bisphenol-A, alkylphenols and alkylphenol ethoxylates. The results show that many of these compounds are present in human blood, sometimes in relatively high concentrations. Compounds like di-(2-ethylhexyl) phthalate, the brominated flame retardant BDE-153 and the artificial musks tonalide and galaxolide, are found in all or the majority of samples.

With exception of BDE-17, -28, -49 and -85, all other brominated flame retardants, including TBBPA and the newer flame retardant HBCD, are found in more than 10 of the 91 samples. The highest concentration, 1944 pg/g serum, is found for decabromo diphenylether (BDE-209). In general the findings are comparable with other recent studies, although HBCD is found more often and in higher concentrations in this study.

Di-(2-ethylhexyl) phthalate is the major phthalate found in human blood serum in this study. The median concentration for this phthalate is 151 ng/g serum with a maximum concentration of 5863 ng/g serum. Other phthalates that are frequently found are dibutyl- and benzylbutyl phthalate. Di-isononyl- and di-isodecyl phthalate are not found in this study, but were found in two other studies.

The fragrances tonalide and galaxolide are found in virtually every sample with median concentrations of 0.4 and 1.3 ng/g serum. The other polycyclic and nitro-musks are found only in a few samples with the exception of musk ambrette which, surprisingly, is found in as many as 48 of the 91 samples.

Organotin compounds are found in a limited number of the whole blood samples, mostly mono- and dioctyltin, with the latter in a maximum concentration of 2.4 ng/g in whole blood.

Bisphenol-A is found in 40% of the samples in this study in concentrations up to 16 ng/g serum. Of the alkylphenols, nonylphenol is found in 16 samples with a maximum concentration of 16 ng/g serum. The alkylphenol ethoxylates are not found in human blood serum.

In general, the results clearly indicate the presence of man-made chemicals in human blood, and thus, in the human body. Many of these chemicals are used as additives in consumer products and earlier studies showed their presence in house dust, rainwater and other environmental matrices. The latter studies indicated the potential for human exposure to these chemicals while the results of this study

confirm that potential and show that human exposure and uptake of these chemicals is a fact.

6. QA/QC Statement

The analytical determinations in this study are performed in compliance with NEN-EN-ISO/IEC 17025 and RvA accreditation no. 54, “The development and application of methods for the determination of organic contaminants in environmental matrices, wastes and materials”. TNO Environment, Energy and Process Innovation is listed in the RvA register under no. L 026.

RvA is the Dutch Council for Accreditation and is a member of the European co-operation for Accreditation (EA) and the International Laboratory Accreditation Co-operation (ILAC). In addition TNO Environment, Energy and Process Innovation operates in compliance with the Quality System standard ISO 9001 (certificate no. 07246-2003-AQ-ROT-RvA)

7. Authentication

Name and address of the principal:

Greenpeace Nederland
Veemkade 18-20
1019 GZ Amsterdam

Name and functions of the cooperators:

Dr. R.J.B. Peters	Project Leader
Drs. R.J. van Delft	Technician
Ing. H. Beeltje	Technician
Ing. M. Diks	Technician
Ing. R.F. Geenen	Technician
Ing. S. Walraven	Technician

Names and establishments to which part of the research was put out to contract:

-

Date upon which, or period in which, the research took place:

May 2004 – July 2004

Signature:

R.J.B. Peters
Project leader MO

Approved by:

Dr. M.P. Keuken
Coordinator MO

Appendix 1 Full results of all samples

In the result tables in this appendix the abbreviations given in table 1 in chapter 2 are used. When reading the tables in this appendix please note that while results are always rounded to the correct decimal number, they are not always rounded to the correct number of significant units. Due to the analytical uncertainty in the results the number of significant units is limited. This is especially true if concentrations of several hundreds or thousands of pg/g serum or ng/g serum are reported. In general no more than two significant numbers apply. As an example, the concentration of BDE-47 in sample 52004045-25 is given as 226 pg/g serum, but should be interpreted as 230 pg/g serum. The concentration of DEHP in sample 52004045-65 is given as 5863 ng/g serum, but should be interpreted as 5900 ng/g serum.

Table 1 Brominated flame retardants in human blood serum.

Sample code	BDE-17 pg/g serum	BDE-28 pg/g serum	BDE-47 pg/g serum	BDE-49 pg/g serum	BDE-85 pg/g serum	BDE-99 pg/g serum	BDE-100 pg/g serum	BDE-153 pg/g serum	BDE-154 pg/g serum	BDE-183 pg/g serum	BDE-209 pg/g serum	HBCD pg/g serum	TBBPA pg/g serum
4045-01	<	<	<	<	<	<	<	5.7	2.4	<	<	<	<
4045-02	<	<	<	<	<	<	<	12	1.7	<	<	<	<
4045-03	<	<	2.5	<	<	<	<	7.7	<	2.2	<	<	<
4045-04	<	<	2.5	<	<	<	3.1	5.4	<	<	<	<	<
4045-05	<	<	<	<	<	<	<	10	1.2	<	<	<	<
4045-06	<	<	9.4	<	<	5.9	5.6	8.1	<	2.6	307	<	<
4045-07	<	<	<	<	<	<	<	6.4	<	<	<	<	81
4045-08	<	<	<	<	<	<	<	6.4	<	<	<	<	<
4045-09	<	<	4.5	<	<	3.6	2.5	8.6	<	<	318	<	<
4045-10	<	<	2.7	<	<	<	3.3	37	4.8	<	<	<	<
4045-11	<	<	4.8	<	<	3.6	5.8	8.9	<	<	<	<	123
4045-12	<	<	2.4	<	<	<	<	7.5	<	<	<	<	68
4045-14	<	<	<	<	<	<	<	4.2	<	<	<	<	69
4045-15	<	<	2.6	<	<	<	2.4	6.3	<	<	<	<	<
4045-16	<	<	<	<	<	<	<	11	<	<	<	<	<
4045-17	<	<	<	<	<	<	<	6.4	<	<	<	<	<
4045-18	<	<	6.7	<	<	5.0	2.8	23	2.6	3.4	638	<	<
4045-19	<	<	<	<	<	<	<	8.2	<	<	<	<	<
4045-20	<	<	5.7	<	<	3.6	5.8	14	1.4	2.8	321	<	121
4045-23	<	<	<	<	<	<	<	6.0	<	<	<	<	<
4045-24	<	<	2.6	<	<	<	<	8.3	<	<	<	<	<
4045-25	<	2.0	226	<	<	401	132	206	38	308	174	<	120
4045-26	<	<	<	<	<	<	<	12	2.0	<	<	<	70
4045-28	<	<	<	<	<	<	<	34	2.7	<	<	<	<
4045-29	<	<	5.0	<	<	6.8	13.3	9.4	<	<	<	<	<
4045-30	<	<	<	<	<	<	<	7.8	<	<	<	<	<
4045-31	<	<	4.3	<	<	<	<	6.7	<	<	<	<	73
4045-35	<	<	<	<	<	<	<	14	<	<	<	<	<
4045-36	<	<	48	<	<	12	16.4	253	46	10	<	<	130
4045-37	<	<	9.9	<	<	5.0	8.6	9.2	3.2	<	<	<	<

Sample code	BDE-17 pg/g serum	BDE-28 pg/g serum	BDE-47 pg/g serum	BDE-49 pg/g serum	BDE-85 pg/g serum	BDE-99 pg/g serum	BDE-100 pg/g serum	BDE-153 pg/g serum	BDE-154 pg/g serum	BDE-183 pg/g serum	BDE-209 pg/g serum	HBCD pg/g serum	TBBPA pg/g serum
4045-38	<	<	26	<	<	6.8	9.2	<	<	<	<	<	76
4045-39	<	<	<	<	<	<	<	7.9	<	<	<	<	64
4045-40	<	<	18	<	<	6.3	<	<	<	7.8	<	<	<
4045-41	<	<	5.2	<	<	5.9	<	11	1.8	<	<	<	<
4045-42	<	<	<	<	<	<	<	11	<	<	<	<	<
4045-43	<	<	<	<	<	<	<	<	<	<	<	<	556
4045-44	<	<	7.6	<	<	<	<	4.6	<	<	<	<	136
4045-45	<	<	3.1	<	<	4.0	4.3	4.9	<	<	<	<	146
4045-46	<	<	3.3	<	<	<	<	8.9	<	<	<	147	<
4045-47	<	<	2.6	<	<	<	<	4.3	<	<	<	<	<
4045-48	<	<	8.5	<	<	<	<	7.2	<	<	<	356	<
4045-49	<	<	<	<	<	<	<	7.7	<	<	<	<	<
4045-50	<	<	9.9	<	<	8.0	<	3.6	<	<	<	114	<
4045-52	<	<	<	<	<	<	<	8.4	<	<	<	<	<
4045-53	<	<	<	<	<	<	<	8.3	<	<	<	123	391
4045-54	<	<	<	<	<	<	<	5.8	<	<	<	<	170
4045-55	<	<	<	<	<	<	<	3.0	<	<	<	<	<
4045-56	<	<	8.9	<	<	<	<	6.0	<	<	<	<	<
4045-57	<	<	<	<	<	<	<	<	<	<	<	<	<
4045-59	<	<	<	<	<	<	<	<	<	<	<	<	<
4045-60	<	<	<	<	<	<	<	11	<	<	<	<	<
4045-61	<	<	14	<	<	7.6	11.1	22	6.9	2.6	182	<	<
4045-62	<	<	11	<	<	<	<	7.9	<	<	<	<	<
4045-63	<	<	<	<	<	<	<	4.5	<	<	<	<	155
4045-64	<	<	<	<	<	<	<	16	3.6	<	<	<	<
4045-65	<	<	7.8	<	<	5.5	7.7	32	7.6	<	151	<	56
4045-66	<	<	<	<	<	<	<	10	<	<	<	246	<
4045-67	<	<	3.3	<	<	<	<	5.3	<	<	<	195	<
4045-68	<	<	<	<	<	<	<	9.3	<	<	<	<	67
4045-69	<	<	<	<	<	<	<	9.6	<	<	<	<	274
4045-70	<	<	<	<	<	<	<	<	<	<	<	<	<
4045-71	<	<	2.9	<	<	8.4	<	4.0	<	<	<	<	89

Sample	BDE-17	BDE-28	BDE-47	BDE-49	BDE-85	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209	HBCD	TBBPA
code	pg/g serum	pg/g serum	pg/g serum	pg/g serum	pg/g serum	pg/g serum	pg/g serum	pg/g serum	pg/g serum	pg/g serum	pg/g serum	pg/g serum	pg/g serum
4045-72	<	<	<	3.0	<	<	<	8.0	<	<	<	<	<
4045-73	<	<	<	<	<	<	<	35	7.5	27	266	<	<
4045-74	<	<	3.0	<	<	<	<	3.2	<	<	<	<	<
4045-75	<	<	<	<	<	<	<	5.9	<	<	<	254	169
4045-76	<	<	<	<	<	<	<	1.9	<	<	<	<	<
4045-77	<	<	<	<	<	<	<	4.8	<	<	<	<	<
4045-78	<	<	<	<	<	<	<	5.2	<	<	<	<	226
4045-79	<	<	2.8	<	<	5.4	2.8	4.4	<	<	<	<	<
4045-80	<	<	<	<	<	<	<	<	<	<	<	96	<
4045-81	<	<	4.1	<	<	<	<	<	<	<	<	<	<
4045-82	<	<	<	<	<	<	<	<	<	<	<	<	<
4045-83	<	<	<	<	<	<	<	<	<	<	1944	<	<
4045-84	<	<	<	<	<	<	<	<	<	<	<	<	<
4045-85	<	<	2.3	<	<	<	<	13	<	<	<	236	<
4045-86	<	<	<	<	<	6.2	<	7.5	<	<	<	<	93
4045-87	<	<	<	<	<	<	<	5.4	<	<	<	<	787
4045-88	<	<	<	<	<	54	13	95	19	145	446	<	127
4045-89	<	<	<	<	<	<	<	<	<	<	<	<	<
4045-90	<	<	8.7	<	<	7.4	15	22	<	<	<	312	<
4045-91	<	<	<	<	<	<	<	<	<	<	<	<	<
4045-92	<	<	<	<	<	<	<	<	<	<	<	<	<
4045-93	<	<	<	<	<	<	<	6.8	<	<	<	<	<
4045-94	<	<	10	<	<	14	3.2	7.7	1.3	<	<	<	286
4045-95	<	<	3.1	<	<	<	<	9.2	<	<	<	<	260
4045-96	<	<	<	<	<	<	<	2.5	<	<	<	<	129
4045-97	<	<	<	<	<	<	<	<	<	<	<	<	537
4045-98	<	<	<	<	<	<	<	9.3	<	<	<	<	428
4045-99	<	<	6.6	<	<	<	<	19	3.1	<	192	<	123
4045-100	<	<	5.9	<	<	6.6	4.6	7.4	<	<	<	197	<

Table 2 Phthalates flame retardants in human blood serum.

Sample code	DMP ng/g serum	DEP ng/g serum	DIBP ng/g serum	DBP ng/g serum	BzBP ng/g serum	DCHP ng/g serum	DEHP ng/g serum	DOP ng/g serum	DINP ng/g serum	DIDP ng/g serum
4045-01	<	<	<	5.1	<	<	272	<	<	<
4045-02	1.1	<	<	4.5	<	<	497	<	<	<
4045-03	7.5	<	<	6.1	1.1	<	115	<	<	<
4045-04	<	<	<	<	<	<	240	<	<	<
4045-05	<	<	<	34	<	<	30	<	<	<
4045-06	<	<	<	<	<	4.4	1347	<	<	<
4045-07	1.5	<	<	9.8	<	<	66	<	<	<
4045-08	<	<	<	53	1.8	<	74	<	<	<
4045-09	<	2.9	<	53	<	<	56	<	<	<
4045-10	<	<	<	58	<	<	48	<	<	<
4045-11	3.2	2.2	<	92	<	<	41	<	<	<
4045-12	<	<	<	56	<	<	43	<	<	<
4045-14	1.8	2.3	<	48	<	<	37	<	<	<
4045-15	1.2	6.6	<	136	<	<	428	<	<	<
4045-16	<	2.5	<	86	<	<	28	<	<	<
4045-17	<	<	<	114	<	<	34	<	<	<
4045-18	<	7.8	<	92	<	<	44	<	<	<
4045-19	1.1	9.6	<	72	<	<	33	<	<	<
4045-20	<	<	<	63	<	<	61	<	<	<
4045-23	<	<	<	72	1.5	<	<	<	<	<
4045-24	<	<	56	11	<	<	<	<	<	<
4045-25	3.7	<	80	25	2.4	<	46	<	<	<
4045-26	<	<	68	22	<	<	<	<	<	<
4045-28	2.1	<	58	15	1.2	<	65	<	<	<
4045-29	<	<	75	18	<	<	49	<	<	<
4045-30	<	<	51	15	<	<	48	<	<	<
4045-31	<	<	62	20	1.1	<	75	<	<	<
4045-35	<	<	52	14	<	<	<	<	<	<
4045-36	2.1	6.4	74	67	12	1.0	153	<	<	<
4045-37	<	<	55	17	<	<	<	<	<	<

Sample code	DMP ng/g serum	DEP ng/g serum	DIBP ng/g serum	DBP ng/g serum	BzBP ng/g serum	DCHP ng/g serum	DEHP ng/g serum	DOP ng/g serum	DINP ng/g serum	DIDP ng/g serum
4045-38	<	9.7	12	69	305	1.5	279	<	<	<
4045-39	<	<	<	<	<	<	31	<	<	<
4045-40	<	5.9	4.7	53	228	<	143	<	<	<
4045-41	<	<	<	18	<	<	32	<	<	<
4045-42	<	<	<	10	<	<	42	<	<	<
4045-43	1.5	<	<	28	1.2	<	41	<	<	<
4045-44	<	<	<	13	<	<	<	<	<	<
4045-45	<	<	<	10	<	<	32	<	<	<
4045-46	<	<	<	16	<	<	218	<	<	<
4045-47	<	<	<	14	<	<	1824	<	<	<
4045-48	9.9	2.8	<	7.0	3.0	<	101	<	<	<
4045-49	<	<	<	5.0	<	<	82	<	<	<
4045-50	<	<	<	9.9	<	<	307	<	<	<
4045-52	1.3	<	<	<	1.4	<	49	<	<	<
4045-53	<	<	<	10	2.0	<	231	<	<	<
4045-54	<	<	<	5.9	<	<	245	<	<	<
4045-55	<	<	<	2.6	1.5	<	4073	<	<	<
4045-56	<	<	<	7.2	1.3	<	1089	<	<	<
4045-57	<	<	<	5.2	2.0	<	157	<	<	<
4045-59	<	<	<	<	1.6	<	5322	<	<	<
4045-60	<	<	<	12	1.2	<	410	<	<	<
4045-61	<	<	<	3.1	1.5	<	1830	<	<	<
4045-62	3.3	<	<	23	<	<	<	<	<	<
4045-63	3.9	<	<	10	<	<	2035	<	<	<
4045-64	4.2	<	<	8.1	1.1	<	1680	<	<	<
4045-65	2.6	<	<	3.2	<	<	5863	<	<	<
4045-66	9.0	<	<	<	2.2	<	5003	17	<	<
4045-67	1.8	<	<	7.7	<	<	2378	<	<	<
4045-68	3.0	<	<	4.2	<	<	4764	<	<	<
4045-69	<	<	<	<	1.1	<	150	<	<	<
4045-70	<	<	<	<	<	<	797	<	<	<
4045-71	<	<	<	<	1.1	<	86	<	<	<

Sample code	DMP ng/g serum	DEP ng/g serum	DIBP ng/g serum	DBP ng/g serum	BzBP ng/g serum	DCHP ng/g serum	DEHP ng/g serum	DOP ng/g serum	DINP ng/g serum	DIDP ng/g serum
4045-72	<	<	4.3	<	<	<	309	<	<	<
4045-73	<	<	<	<	<	<	201	<	<	<
4045-74	<	<	<	<	<	<	416	<	<	<
4045-75	<	<	<	<	<	<	104	<	<	<
4045-76	<	<	<	<	<	<	76	<	<	<
4045-77	<	<	<	<	<	<	151	<	<	<
4045-78	<	<	<	<	1.1	<	76	<	<	<
4045-79	1.0	<	<	<	<	<	64	<	<	<
4045-80	<	<	<	<	<	<	123	<	<	<
4045-81	<	13	<	5.6	<	<	126	<	<	<
4045-82	1.0	8.9	<	4.9	1.5	<	150	<	<	<
4045-83	<	2.8	3.4	9.7	1.5	<	119	<	<	<
4045-84	<	2.5	<	6.3	1.7	<	866	<	<	<
4045-85	<	<	<	4.8	2.0	<	544	<	<	<
4045-86	1.5	<	8.7	12	4.2	<	709	<	<	<
4045-87	<	7.5	<	<	2.2	<	438	<	<	<
4045-88	2.4	10	3.2	5.0	3.4	<	963	<	<	<
4045-89	1.7	14	<	3.7	3.0	<	570	<	<	<
4045-90	<	5.3	13	<	1.9	<	478	1.5	<	<
4045-91	<	3.7	<	5.0	1.8	1.6	580	<	<	<
4045-92	<	<	<	5.9	1.7	<	602	<	<	<
4045-93	<	<	<	4.8	<	<	556	<	<	<
4045-94	<	<	<	<	<	<	223	<	<	<
4045-95	<	<	<	<	<	<	495	<	<	<
4045-96	<	<	<	10	<	<	584	<	<	<
4045-97	<	<	<	<	<	<	580	<	<	<
4045-98	<	<	93	30	<	<	809	<	<	<
4045-99	<	<	<	12	<	<	507	<	<	<
4045-100	1.4	10	<	8.7	<	<	472	<	<	<

Table 3 Artificial musk compounds in human blood serum.

Sample	ADBI	AHTN	ATTI	DPMI	HHCB	MA	MK	MM	MT	MX
code	ng/g serum	ng/g serum	ng/g serum	ng/g serum	ng/g serum	ng/g serum	ng/g serum	ng/g serum	ng/g serum	ng/g serum
4045-01	<	0.58	<	<	1.8	0.43	<	<	<	<
4045-02	<	0.77	<	<	1.4	<	<	<	<	<
4045-03	<	0.98	<	<	3.2	1.3	<	<	<	<
4045-04	<	0.42	<	<	1.2	0.19	<	<	<	0.13
4045-05	<	0.89	<	<	1.4	<	<	<	<	<
4045-06	<	0.75	<	<	2.5	<	<	<	<	<
4045-07	<	1.1	<	<	2.8	0.13	<	<	<	<
4045-08	<	0.95	<	<	2.5	0.12	<	<	<	<
4045-09	<	0.65	<	<	2.2	0.22	0.10	<	<	<
4045-10	<	0.61	<	<	2.2	0.19	<	<	<	<
4045-11	<	1.4	<	<	3.3	0.14	<	<	<	<
4045-12	<	0.99	<	<	1.2	<	<	<	<	<
4045-14	<	1.8	<	<	6.7	0.85	0.12	<	<	<
4045-15	<	0.68	<	<	1.8	<	<	<	<	0.27
4045-16	<	0.85	<	<	1.5	<	<	<	<	<
4045-17	<	0.86	<	<	2.1	<	<	<	<	<
4045-18	<	0.67	<	<	1.8	<	<	<	<	<
4045-19	<	1.2	<	<	2.2	0.14	<	<	<	<
4045-20	<	0.85	<	<	2.0	0.23	<	<	<	<
4045-23	<	0.52	<	<	1.5	<	<	<	<	<
4045-24	<	0.51	<	<	1.3	<	<	<	<	<
4045-25	<	0.59	0.29	<	1.2	0.36	0.36	0.15	<	0.17
4045-26	<	0.59	<	<	1.9	<	<	<	<	<
4045-28	<	0.80	<	<	2.0	<	<	<	<	<
4045-29	<	0.73	<	<	1.5	0.31	<	<	<	<
4045-30	<	0.46	<	<	1.2	<	0.34	<	<	<
4045-31	0.05	0.48	<	<	1.1	0.54	<	<	<	<
4045-35	<	0.35	<	<	0.78	0.31	<	<	<	<
4045-36	<	1.5	0.34	<	3.5	0.42	<	<	<	<
4045-37	<	0.36	<	<	0.74	0.73	<	<	<	<

Sample code	ADBI ng/g serum	AHTN ng/g serum	ATTI ng/g serum	DPMI ng/g serum	HHCB ng/g serum	MA ng/g serum	MK ng/g serum	MM ng/g serum	MT ng/g serum	MX ng/g serum
4045-38	<	11	0.67	<	8.7	0.81	1.5	<	<	0.11
4045-39	<	0.29	<	<	0.71	0.19	0.07	<	<	<
4045-40	<	0.91	0.29	<	2.1	0.71	0.32	<	0.20	<
4045-41	<	0.23	<	<	0.60	0.17	<	<	<	<
4045-42	<	0.34	<	<	1.0	0.46	<	<	<	<
4045-43	<	0.32	<	<	1.8	0.40	<	<	<	<
4045-44	<	0.81	<	<	0.71	1.4	<	<	<	<
4045-45	<	0.18	<	<	0.47	0.54	<	<	<	<
4045-46	<	0.48	<	<	1.5	3.4	<	<	<	<
4045-47	<	0.31	<	<	0.79	4.0	<	<	0.14	<
4045-48	<	0.58	<	<	2.4	<	<	<	<	0.13
4045-49	<	0.16	<	<	0.64	0.83	<	<	0.17	<
4045-50	<	0.17	<	<	0.80	<	<	<	<	<
4045-52	<	0.21	<	<	0.91	0.14	<	<	<	<
4045-53	<	0.24	<	<	1.3	0.24	<	<	<	<
4045-54	<	0.17	<	<	0.72	<	<	<	<	<
4045-55	<	0.15	<	<	0.66	<	<	<	<	<
4045-56	<	0.17	<	<	1.7	<	<	<	<	<
4045-57	<	0.17	<	<	0.55	<	<	<	<	<
4045-59	<	0.13	<	<	0.69	<	<	<	<	<
4045-60	<	0.15	<	<	0.65	<	<	<	<	<
4045-61	<	<	<	<	0.87	<	<	<	<	<
4045-62	<	0.24	<	<	1.3	<	<	<	<	<
4045-63	<	0.17	<	8.0	0.60	<	<	<	<	<
4045-64	<	0.23	<	<	0.69	1.0	<	<	<	<
4045-65	<	0.21	<	<	0.93	<	<	<	<	<
4045-66	<	0.24	<	<	1.0	0.56	<	<	<	<
4045-67	<	0.23	<	<	1.3	<	<	<	<	<
4045-68	<	0.20	<	<	1.1	<	0.17	<	<	<
4045-69	<	0.41	<	<	1.7	0.38	<	<	<	<
4045-70	<	0.17	<	<	0.70	0.17	<	<	<	<
4045-71	<	0.22	<	<	0.53	0.82	0.06	<	<	<

Sample code	ADBI ng/g serum	AHTN ng/g serum	ATTI ng/g serum	DPMI ng/g serum	HHCB ng/g serum	MA ng/g serum	MK ng/g serum	MM ng/g serum	MT ng/g serum	MX ng/g serum
4045-72	<	<	<	<	0.17	0.21	<	<	<	<
4045-73	<	0.16	<	<	0.71	<	<	<	<	<
4045-74	<	0.34	<	<	1.8	<	<	<	<	<
4045-75	<	0.19	<	<	0.52	<	<	<	<	<
4045-76	<	0.12	<	<	0.52	1.99	<	<	<	0.10
4045-77	<	0.21	<	<	0.94	0.10	<	<	<	<
4045-78	<	0.90	<	<	2.0	<	<	<	<	<
4045-79	<	0.69	<	<	2.5	<	<	<	<	<
4045-80	<	0.34	<	<	1.9	0.33	<	<	<	<
4045-81	<	0.72	<	<	4.2	0.95	<	<	<	<
4045-82	<	0.22	<	<	1.1	<	<	<	<	<
4045-83	<	0.27	<	<	0.91	<	<	<	<	<
4045-84	<	0.46	<	<	2.0	0.40	<	<	<	<
4045-85	<	1.2	<	<	9.2	<	<	<	<	<
4045-86	<	0.14	<	<	0.81	<	<	<	<	<
4045-87	<	0.53	<	<	2.3	1.1	<	<	<	<
4045-88	<	0.34	<	<	1.0	<	<	<	<	<
4045-89	<	0.46	<	<	1.5	0.50	<	<	<	<
4045-90	<	<	<	<	3.6	0.14	<	<	<	<
4045-91	<	0.19	<	<	0.84	<	<	<	<	<
4045-92	<	0.37	<	<	1.4	0.44	<	<	<	<
4045-93	<	0.49	<	<	1.6	0.31	<	<	<	<
4045-94	<	0.29	<	<	0.70	<	<	<	<	<
4045-95	<	0.50	<	<	1.5	0.88	<	<	<	<
4045-96	<	0.67	<	<	2.0	<	<	<	<	<
4045-97	<	0.51	<	<	1.5	<	<	<	<	<
4045-98	<	0.31	<	<	1.0	<	<	<	<	<
4045-99	<	0.22	<	<	0.97	0.28	<	<	<	<
4045-100	<	1.4	<	<	3.1	<	<	<	<	<

Table 4 Organotin compounds in human whole blood.

Sample code	MBT	DBT	TBT	MOT	DOT	MPT	DPT	TPT
	ng/g blood	ng/g blood	ng/g blood	ng/g blood	ng/g blood	ng/g blood	ng/g blood	ng/g blood
4045-01	<	<	<	0.3	2.4	<	<	<
4045-02	<	<	<	<	<	<	<	<
4045-03	<	<	<	<	<	<	<	<
4045-04	<	<	<	<	<	<	<	<
4045-05	<	<	<	0.3	1.9	<	<	<
4045-06	<	<	<	<	<	<	<	<
4045-07	<	<	<	<	<	<	<	<
4045-08	<	<	<	<	<	<	<	<
4045-09	<	<	<	<	<	<	<	<
4045-10	<	<	<	<	<	<	<	<
4045-11	<	<	<	<	<	<	<	<
4045-12	<	<	<	<	<	<	<	<
4045-14	<	<	<	<	<	<	<	<
4045-15	<	<	<	<	<	<	<	<
4045-16	<	<	<	<	<	<	<	<
4045-17	<	<	<	<	<	<	<	<
4045-18	<	<	<	<	<	<	<	<
4045-19	<	<	<	<	<	<	<	<
4045-20	<	<	<	<	<	<	<	<
4045-23	<	<	<	<	<	<	<	<
4045-24	<	<	<	0.5	1.9	<	<	<
4045-25	<	<	<	<	<	<	<	<
4045-26	<	<	<	<	<	<	<	<
4045-28	<	<	<	<	<	<	<	<
4045-29	<	<	<	<	<	<	<	<
4045-30	<	<	<	<	<	<	<	<
4045-31	<	<	<	<	<	<	<	<
4045-35	<	<	<	<	<	<	<	<
4045-36	<	<	<	<	<	<	<	<
4045-37	<	<	<	<	<	<	<	<
4045-38	<	<	<	<	<	<	<	<
4045-39	<	<	<	<	<	<	<	<
4045-40	<	<	<	<	<	<	<	<
4045-41	<	<	<	<	<	<	<	<
4045-42	<	<	<	<	<	<	<	<
4045-43	<	<	<	<	<	<	<	<
4045-44	<	<	<	<	<	<	<	<
4045-45	<	<	<	<	<	<	<	<
4045-46	<	<	<	<	<	<	<	<
4045-47	<	<	<	<	<	<	<	<
4045-48	<	<	<	<	<	<	<	<
4045-49	<	<	<	<	<	<	<	<
4045-50	0.1	<	<	<	<	<	<	<
4045-52	<	<	<	<	<	<	<	<
4045-53	<	<	<	<	<	<	<	<

Sample code	MBT	DBT	TBT	MOT	DOT	MPT	DPT	TPT
	ng/g blood	ng/g blood	ng/g blood	ng/g blood	ng/g blood	ng/g blood	ng/g blood	ng/g blood
4045-54	<	<	<	<	<	<	<	<
4045-55	<	<	<	<	<	<	<	<
4045-56	<	<	<	<	<	<	<	<
4045-57	<	<	<	<	<	<	<	<
4045-59	<	<	<	<	<	<	<	<
4045-60	<	<	<	<	<	<	<	<
4045-61	0.1	<	<	<	<	<	<	<
4045-62	0.1	<	<	0.1	1.1	<	<	<
4045-63	<	<	<	<	<	<	<	<
4045-64	<	<	<	<	<	<	<	<
4045-65	<	<	<	<	<	<	<	<
4045-66	<	<	<	<	<	<	<	<
4045-67	<	<	<	<	<	<	<	<
4045-68	<	<	<	0.1	0.7	<	<	<
4045-69	<	<	<	<	<	<	<	<
4045-70	<	<	<	<	<	<	<	<
4045-71	<	<	<	<	<	<	<	<
4045-72	<	<	<	0.22	1.6	<	<	<
4045-73	<	<	<	<	0.2	<	<	<
4045-74	<	<	0.1	0.1	0.5	<	<	<
4045-75	<	<	0.1	<	<	<	<	<
4045-76	<	<	<	<	<	<	<	<
4045-77	<	<	<	0.1	0.6	<	<	<
4045-78	<	<	<	0.1	1.0	<	<	<
4045-79	<	<	<	<	<	<	<	<
4045-80	<	<	<	<	<	<	<	<
4045-81	<	<	<	<	<	<	<	<
4045-82	<	<	<	<	<	<	<	<
4045-83	<	<	<	<	<	<	<	<
4045-84	<	<	<	<	<	<	<	<
4045-85	<	<	<	<	<	<	<	<
4045-86	<	<	<	<	<	<	<	<
4045-87	<	<	<	<	<	<	<	<
4045-88	<	<	<	0.1	0.4	<	<	<
4045-89	<	<	<	<	<	<	<	<
4045-90	<	<	<	0.1	0.2	<	<	<
4045-91	<	<	<	<	<	<	<	<
4045-92	<	<	<	<	<	<	<	<
4045-93	<	<	<	<	<	<	<	<
4045-94	<	<	<	<	<	<	<	<
4045-95	<	<	<	<	<	<	<	<
4045-96	<	<	0.1	<	<	<	<	<
4045-97	<	<	<	<	<	<	<	<
4045-98	<	<	<	<	<	<	<	<
4045-99	<	<	<	<	<	<	<	<
4045-100	<	<	<	0.1	0.4	<	<	<

Table 5 Bisphenol-A, alkylphenols and –ethoxylates in human blood serum.

Sample code	BPA	OP	NP	OPEO	NPEO
	ng/g serum	ng/g serum	ng/g serum	ng/g serum	ng/g serum
4045-01	<	<	<	<	<
4045-02	<	<	<	<	<
4045-03	<	<	<	<	<
4045-04	<	<	<	<	<
4045-05	<	<	<	<	<
4045-06	1.2	<	<	<	<
4045-07	<	<	<	<	<
4045-08	<	<	<	<	<
4045-09	1.9	<	<	<	<
4045-10	<	<	<	<	<
4045-11	<	<	<	<	<
4045-12	<	<	<	<	<
4045-14	<	<	<	<	<
4045-15	0.6	<	<	<	<
4045-16	<	<	<	<	<
4045-17	<	<	<	<	<
4045-18	<	<	<	<	<
4045-19	7.1	<	<	<	<
4045-20	<	<	<	<	<
4045-23	<	<	<	<	<
4045-24	<	<	<	<	<
4045-25	<	<	<	<	<
4045-26	<	<	2.1	<	<
4045-28	5.3	<	<	<	<
4045-29	<	<	<	<	<
4045-30	<	<	<	<	<
4045-31	<	<	<	<	<
4045-35	<	<	<	<	<
4045-36	1.1	<	6.6	<	<
4045-37	<	<	<	<	<
4045-38	2.5	<	16	<	<
4045-39	<	<	<	<	<
4045-40	1.4	<	12	<	<
4045-41	<	<	<	<	<
4045-42	<	<	<	<	<
4045-43	<	<	<	<	<
4045-44	<	<	<	<	<
4045-45	1.1	<	<	<	<
4045-46	<	<	<	<	<
4045-47	2.4	<	0.9	<	<
4045-48	16	<	2.3	<	<
4045-49	<	<	<	<	<
4045-50	<	<	<	<	<
4045-52	<	<	<	<	<
4045-53	<	<	<	<	<

Sample code	BPA	OP	NP	OPEO	NPEO
	ng/g serum	ng/g serum	ng/g serum	ng/g serum	ng/g serum
4045-54	<	<	<	<	<
4045-55	<	<	<	<	<
4045-56	0.7	<	<	<	<
4045-57	5.7	<	1.1	<	<
4045-59	2.4	<	<	<	<
4045-60	0.8	<	<	<	<
4045-61	0.7	<	<	<	<
4045-62	1.8	<	<	<	<
4045-63	1.3	<	<	<	<
4045-64	4.1	<	1.2	<	<
4045-65	<	<	<	<	<
4045-66	<	<	<	<	<
4045-67	1.4	<	<	<	<
4045-68	0.7	<	<	<	<
4045-69	<	<	<	<	<
4045-70	2.1	<	0.7	<	<
4045-71	<	<	<	<	<
4045-72	1.2	2.3	5.1	<	<
4045-73	<	<	<	<	<
4045-74	2.2	<	<	<	<
4045-75	1.1	<	<	<	<
4045-76	<	<	<	<	<
4045-77	0.8	<	<	<	<
4045-78	0.7	<	<	<	<
4045-79	<	<	<	<	<
4045-80	<	<	<	<	<
4045-81	<	<	<	<	<
4045-82	<	<	<	<	<
4045-83	<	<	<	<	<
4045-84	<	<	<	<	<
4045-85	3.4	2.0	<	<	<
4045-86	0.80	<	0.93	<	<
4045-87	4.0	<	0.6	<	<
4045-88	<	<	<	<	<
4045-89	<	<	<	<	<
4045-90	0.71	<	1.2	<	<
4045-91	<	<	<	<	<
4045-92	0.8	<	<	<	<
4045-93	6.8	<	1.6	<	<
4045-94	<	<	<	<	<
4045-95	2.2	<	0.9	<	<
4045-96	5.1	<	1.6	<	<
4045-97	<	<	<	<	<
4045-98	<	<	<	<	<
4045-99	0.8	<	<	<	<
4045-100	<	<	<	<	<