

Summary

A recent TNO project, studying the role of the atmosphere as a transport medium for persistent organic pollutants, showed the presence of a number of hazardous chemicals in the atmosphere and in precipitation. Exposure of living organisms to some particular hazardous chemicals can lead to hormone disrupting effects. At the moment, much attention is focused on the interaction of so-called xeno-estrogens, synthetic compounds with hormone receptors causing a number of reactions that eventually lead to reproduction and development related effects. The current study was initiated by Greenpeace to further investigate the presence of hazardous chemicals, in particular xeno-estrogens, in precipitation.

Precipitation samples were collected by Greenpeace at 47 locations in The Netherlands, 2 in Germany and 1 in Belgium, in a four-weekly period. The samples were analysed for bisphenol-A, alkylphenols and ethoxylates, phthalates, brominated flame retardants and synthetic musk compounds in the laboratory of the Department of Environmental Quality of TNO. A number of pesticides, also labelled as xeno-estrogens, were not analysed in these samples since they were already measured in a previous TNO study.

The results of the current study clearly show the presence of these compounds in precipitation. Apart from brominated flame retardants, several representatives of the compound groups were found in precipitation samples at most locations. The concentrations ranged from a low ng/l range for brominated flame retardants to several thousands of ng/l for the phthalates. Bisphenol-A was found in 32% of the locations in concentrations up to 357 ng/l while alkylphenols and ethoxylates were found at virtually every location in concentrations up to 924 ng/l for the individual compounds. Phthalates were by far the most abundant xeno-estrogens in the precipitation samples and present in every sample. At one location di-isodecyl phthalate was found in a surprisingly high concentration of almost 100,000 ng/l. Brominated flame retardants were identified in this study for the first time in precipitation and were found in a low ng/l range at 28% of the sampling locations. Noticeable was the finding of hexabromocyclododecane, a replacement for the polybrominated diphenyl ethers at one location in a concentration of nearly 2,000 ng/l. Finally, as expected, synthetic musk compounds could be found at almost every location. This is especially true for the polycyclic musks that were found in concentrations up to 147 ng/l. Nitro musks were found at about 30% of the locations.

Apart from measuring the concentrations of compounds, it was also possible to gain some insight into probable emission sources from these data. Kriging techniques were used to calculate deposition concentrations in between actual sampling locations and contour plots were prepared for a number of compounds. These plots clearly showed that a distinction can be made between on the one hand the sometimes high overall concentrations due to diffuse emissions, and on the other

hand located point emissions for a number of compounds, among which bisphenol-A, nonylphenol ethoxylate, phthalates (DEHP and DINP) and AHTN, a polycyclic musk.

Samenvatting

In een recent TNO onderzoek, met als primair doel het vaststellen van de rol van de atmosfeer bij het transport van persistente stoffen, werd de aanwezigheid van gevaarlijke chemicaliën in lucht en regen vastgesteld. De blootstelling aan bepaalde chemicaliën hebben hormonale effecten tot gevolg. Op het moment gaat veel aandacht uit naar de zogenaamde xeno-oestrogenen, synthetische verbindingen die interacties aangaan met hormonale receptoren wat op zijn beurt kan leiden tot beïnvloeding van de reproductie en de ontwikkeling. Het huidige onderzoek dat in opdracht van Greenpeace wordt uitgevoerd, is specifiek gericht op het vaststellen van de aanwezigheid en gehalten van persistente organische componenten in atmosferische depositie.

Monsters regenwater zijn verzameld door Greenpeace Nederland op 47 locaties in Nederland, 2 in Duitsland en 1 in België, in vierwekelijkse periodes. De monsters zijn geanalyseerd op bisfenol-A, alkylfenolen en ethoxylaten, ftalaten, brandvertragers en synthetische musk verbindingen, door het laboratorium van de Afdeling Milieukwaliteit en –analyse van TNO. Een aantal pesticiden, die aangemerkt worden als xeno-oestrogene stoffen, zijn niet geanalyseerd omdat deze reeds in de eerdere TNO studie zijn onderzocht.

De resultaten van deze studie tonen aan dat de onderzochte stoffen in regenwater aanwezig zijn. Met uitzondering van de gebromeerde brandvertragers komen de individuele stoffen van de overige stofgroepen zelfs veelvuldig voor en worden ze op de meeste locaties aangetroffen. De concentraties variëren daarbij van het lage ng/l gebied voor brandvertragers tot enkele duizenden ng/l voor ftalaten. Bisfenol-A werd in 32% van de monsters aangetroffen in gehalten tot 357 ng/l terwijl alkylfenolen en ethoxylaten op nagenoeg alle locaties werden aangetroffen in gehalten tot 924 ng/l voor de individuele componenten. Ftalaten waren veruit de meest voorkomende xeno-oestrogenen en werden in alle depositie monsters aangetroffen. Di-isodecylftalaat werd op één locatie zelfs aangetroffen met een verrassend hoog gehalte van bijna 100.000 ng/l. Gebromeerde brandvertragers, die in deze studie voor het eerst werden aangetoond in regenwater, werden in ca 28% van de monsters aangetoond in gehalten onder de 10 ng/l. Een opmerkelijke uitzondering was hexabroomcyclododecaan, een vervanger voor de polybroombifenylethers, die in één monster werd aangetroffen met een concentratie van bijna 2000 ng/l. Tenslotte, werden zoals verwacht ook een aantal, voornamelijk polycyclische musk verbindingen aangetroffen in bijna elk monster met een maximum gehalte van 147 ng/l. Nitro musk verbindingen werden nog in circa 30% van de gevallen aangetroffen.

Naast het vaststellen van de aanwezigheid en concentratie van deze stoffen bleek het ook mogelijk iets te zeggen over de aanwezigheid van emissiebronnen. Door gebruik te maken van Kriging technieken is het mogelijk gegevens te interpoleren en zodoende depositiegegevens ruimtelijk weer te geven in de vorm van contouren.

kaarten. Deze kaarten laten duidelijk zien dat er in het algemeen sprake is van min of meer uniforme, soms hoge concentraties op alle locaties, wat wijst op diffuse emissiebronnen, en een aantal lokale emissiebronnen, puntemissies, met name voor de stoffen bisfenol-A, nonylfenoethoxylaat, ftalaten (DEHP en DINP) en AHTN, een polycyclische musk.

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1. Introduction

1.1 Hazardous chemicals

The progress of the chemical industry in the past century supplied the world with a vast amount of chemicals. At present roughly 100,000 chemicals are used and over 500 new chemicals are introduced annually¹. From these, several are known to cause adverse effects to man and animal life. The best documented are probably the persistent organic pollutants (POPs), such as the polychlorinated biphenyls (PCB) and the pesticide DDT. In the fifties and sixties the DDT metabolite DDE caused eggshell thinning, resulting in the decline of the European bird population. In the eighties PCBs were suspected of causing a strong decline in the North Sea seal population by affecting their reproduction and increasing their susceptibility for infections^{2,3}. Although the use of chemicals like PCBs and DDT is prohibited some time ago, it is still possible to measure these compounds in the atmosphere worldwide. Meanwhile, new chemicals have replaced these compounds, and some chemicals, like phthalates and alkylphenol ethoxylates are produced and used in huge amounts. Since these compounds are found in sediments and surface waters, it is most likely that they can also be found in the atmosphere and atmospheric precipitation.

New evidence showed that substances such as PCBs and DDT disrupt the hormonal functioning of living organisms and are therefore called endocrine disruptors^{4,5,6}. Hormone disrupting effects of particular chemicals are caused by a wide variety of mechanisms. At the moment, most attention is focused on the so-called (xeno-)estrogens. (Xeno-)estrogens are natural or synthetic (“xeno”) compounds that mimic the feminizing effect of natural female sex hormone systems by binding to the cellular hormone receptor, thereby inducing a response. The interaction between an estrogenic hormone (or xeno-estrogenic compound) and its receptor causes a number of reactions that eventually lead to reproduction and development related effects.

¹ Jackson T. In: Material Concerns. Pollution, profit and quality of life. Routledge, London, ISBN 0-415-13248-7, 40, **1996**.

² Moriarty F. The Sci. Tot. Environ. 91, 267-268, **1983**.

³ Reijnders P.J.H. Nature 324, 456-457, **1986**.

⁴ Danzo J.B. Cell. Mol. Life Sci., 54, 1249-1264, **1998**.

⁵ Sumpter J.P. Toxicol. Letters 102-103, 337-342, **1998**.

⁶ Harrison P.T.C., Holmes P., Humfrey C.D.N. The Sci. Tot. Environ. 205, 97-106, **1997**.

1.2 Hazardous chemicals in air and in precipitation

The atmosphere is a major transport route for many POPs⁷. Pesticides, PCBs and polycyclic aromatic hydrocarbons (PAH) have been studied extensively in the atmosphere. Air samples from urban areas⁸, rural sites⁹, large ecosystems such as the Great Lakes¹⁰ and arctic regions¹¹ have been analysed. A global fractionation theory has been proposed, i.e. organic compounds become latitudinally fractionated according to their volatility, as they condense at different ambient air temperatures¹².

In a recent TNO study a large number of air and rainwater samples were analysed during a biennial period⁷. The results showed that many pesticides could be identified and quantified in the samples. They included several pesticides with hormone disrupting properties, PCBs and PAHs. A typical xeno-estrogen, also found in these samples, was tetrabromobisphenol-A (TBBA), a reactive flame retardant used in the production of epoxy based materials such as circuit boards for computers and television sets.

In the LOES-project (Landelijk Onderzoek oEstrogene Stoffen), initiated in 1997 by the Dutch Directorate-General for Public Works and Water Management, several typical estrogens and xeno-estrogens were determined in environmental matrices, in some cases including rainwater. Remarkable were the relatively high concentrations of phthalates in rainwater¹³.

Synthetic nitro-musk compounds, persistent compounds with toxic, potentially hormone disrupting properties, were found in Norwegian air samples and are therefore also expected to be present in deposition such as rainwater¹⁴.

⁷ Duyzer JH, Vonk AW. Atmosferische depositie van pesticiden, PAK en PCB's in Nederland. TNO report R2002/606, october 2002.

⁸ Halsall C.J., Lee R.G.M., Coleman P.J., Burnett V., Harding-Jones P., Jones K.C., *Environ. Sci. Technol.* **29**, 2368-2376, **1995**.

⁹ Lee R.G.M., Hung H., Mackay D., Jones K.C. *Environ. Sci. Technol.* **32**, 2172-2179, **1998**.

¹⁰ Eisenreich S.J., Looney B.B., Thornton J.D., *Environ. Sci. Technol.* **15**, 30-38, **1981**.

¹¹ Oehme M., Haugen J.E., Schlabach M. *Environ. Sci. Technol.* **30**, 2294-2304, **1996**.

¹² Wania F., Mackay D., *Ambio* **22**, 10-18, **1993**.

¹³ Vethaak A.D., Rijs G.B.J., Schrap S.M., Ruiter H., Gerritsen A., Lahr J. In: Estrogens and xeno-estrogens in the aquatic environment of the Netherlands. RIZA/RIKZ-report no. 2002.001, February **2002**.

¹⁴ Kallenborn R., Gaterman R., Planting S., Rimkus G.G., Lund M., Schlabach M., Burkow I.C. *J. Chromatogr. A*, **846**, 295-306, **1999**.

2. Study objective and approach

2.1 Objective of the Greenpeace study

The objective of this study is to gain insight into the presence of a number of POPs, especially xeno-estrogens in precipitation. In an earlier Greenpeace study it was shown that such compounds could be found in the dust in common houses in The Netherlands. Furthermore, the study of Duyzer et al gave evidence that POPs are present in air and in precipitation in The Netherlands⁷. The current study presents the results for the presence and concentrations of typical xeno-estrogens in precipitation.

2.2 Chemical parameters

In this study we concentrate on the determination of a number of compounds stated on the OSPAR and UN list and produced and used in The Netherlands. Since Duyzer et al already included results for a large number of pesticides, these were excluded from this study. The following compounds and compound groups were selected for this study:

- Bisphenol-A
- Alkylphenols and alkylphenol ethoxylates
- Phthalates
- Flame retardants
- Synthetic musk compounds.

The individual chemicals within each group are listed in table 1. Some additional information about the use of these compounds can be found in chapter 4.

2.3 Sampling and sampling locations

The sampling locations were chosen by Greenpeace Nederland. The choice was based on a representative distribution over The Netherlands, the presence of vulnerable receptors (schools), the presence of particular industries, and the availability of a suitable sampling site. In total 50 sample locations were selected, 47 in The Netherlands, 1 in Belgium and 2 in Germany. Because of the large number of sampling sites and the high costs of wet-only samplers it was decided to use open sample collectors. Therefore, it was not possible to differentiate between dry deposition and wet deposition, e.g. rain, and it should be kept in mind that the term “precipitation” used throughout this report should actually be read as “deposition”.

The samplers consisted of amber glass bottles of 2.5 litres fitted with a glass funnel with a diameter of approximately 30 cm. The flasks were placed in a metal holder

to ensure an upright position during sampling. A sampling protocol drawn up by TNO was used throughout this study. For the locations in The Netherlands sampling started in February and lasted four weeks. For the locations in Belgium and Germany sampling started at the end of March and also lasted about four weeks. Table 2 summarises the sampling locations while figure 1 shows a map of The Netherlands with the sampling locations.

Table 1 *Xeno-estrogens included in this study.*

Group	Specific compounds	Acronym
Bisphenol A	bisphenol A	BPA
Alkylphenols and ethoxylates	octylphenol	OP
	nonylphenol	NP
	octylphenol ethoxylates	OPEO
	nonylphenol ethoxylates	NPEO
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
	diphenyl phthalate	DPP
	di-n-octyl phthalate	DOP
	di-iso-nonyl phthalate	DINP
	di-iso-decyl phthalate	DIDP
Flame retardents	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	BDE 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
	octabromo diphenyl ether	BDE octa
	nonabromo diphenylether	BDE nona
	decabromo diphenylether	BDE 209
	hexabromo cyclododecane	HBCD
	tetrabromobisphenol A	TBBA
Synthetic musk compounds	cashmeron (6,7-dihydro-1,1,2,3,3-pentamethyl-4(5H)indanon)	DPMI
	celestolide (4-acetyl-1,1-dimethyl-6-t-butyl-dihydroindene)	ADBI
	galaxolide (1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-2-benzopyran)	HHCB
	phantolide (6-acetyl-1,1,2,3,3,5-hexamethyl-dihydroindene)	AHMI
	tonalide (7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene)	AHTN
	traseolide (5-acetyl-1,1,2,6-tetramethyl-3-isopropyl-dihydroinden)	ATTI
	musk ambrette (2,6-dinitro-3-methoxy-4-t-butyltoluene)	MA
	musk ketone (4,6-dinitro-2-acetyl-5-t-butylxylene)	MK
	musk moskene (4,6-dinitro-1,1,3,3,5-pentamethylindan)	MM
	musk tibetene (2,6-dinitro-3,4,5-trimethyl-1-t-butylbenzene)	MT
	musk xylene (2,4,6-trinitro-5-t-butylxylene)	MX

Table 2 Overview of sampling locations.

TNO sample number	City	Postal code	Country	Sample volume liters
52003067-01	Wageningen	6708 SG	The Netherlands	1.9
52003067-02	Hoorn	1625 PJ	The Netherlands	1.4
52003067-03	Weert	6065 SW	The Netherlands	2.2
52003067-04	Dongen	5102 DZ	The Netherlands	2.0
52003067-05	Nistelrode	5388 GB	The Netherlands	1.9
52003067-06	Enschede	7512 AD	The Netherlands	1.9
52003067-07	Zeewolde	3892 VJ	The Netherlands	1.8
52003067-08	Heerlen	6415 GJ	The Netherlands	2.0
52003067-09	Oostkapelle	4356 EH	The Netherlands	2.2
52003067-10	Pijnacker	2641 NC	The Netherlands	2.2
52003067-11	Burgh-Haamstede	4328 CA	The Netherlands	2.2
52003067-12	Den Hoorn, Texel	1797 RA	The Netherlands	1.7
52003067-13	Acquoy	4151 MK	The Netherlands	1.6
52003067-14	IJlst	8651 HB	The Netherlands	2.0
52003067-15	Lemmer	8531 RX	The Netherlands	2.1
52003067-16	Dwingeloo	7991 PR	The Netherlands	2.3
52003067-17	Borger	9531 MB	The Netherlands	1.3
52003067-18	Loosdrecht	1231 VP	The Netherlands	1.8
52003067-19	Winsum	9951 VG	The Netherlands	2.1
52003067-20	Delden	7491 GV	The Netherlands	1.8
52003067-21	Houten	3994 ZR	The Netherlands	2.1
52003067-22	Hellevoetsluis	3224 XG	The Netherlands	2.2
52003067-24	Krommenie	1561 KD	The Netherlands	1.6
52003067-25	Enkhuizen	1602 DK	The Netherlands	2.0
52003067-26	Vlaardingen	3197KS	The Netherlands	0.9
52003067-27	Coevorden	7741KC	The Netherlands	1.7
52003067-28	Den Haag	2555 XP	The Netherlands	1.7
52003067-29	Capelle a/d IJssel	2902 JD	The Netherlands	2.0
52003067-30	Utrecht	3511 XX	The Netherlands	1.7
52003067-31	Amersfoort	3818 TA	The Netherlands	2.1
52003067-32	Sleeuwijk	4254 XD	The Netherlands	2.1
52003067-33	Oostburg	4501 BE	The Netherlands	2.2
52003067-34	Terneuzen	4537 CD	The Netherlands	1.9
52003067-35	Eindhoven	5641 AG	The Netherlands	2.2
52003067-36	Horst	5961 BE	The Netherlands	2.0
52003067-37	Maastricht	6224 BW	The Netherlands	2.2
52003067-38	Arnhem	6828 WE	The Netherlands	2.2
52003067-39	Apeldoorn	7329 BZ	The Netherlands	2.2
52003067-40	Nijverdal	7441 BK	The Netherlands	1.9
52003067-41	Zwolle	8019 AD	The Netherlands	1.5
52003067-42	Buitenpost	9285 RV	The Netherlands	2.1
52003067-43	Heemstede	2102 LS	The Netherlands	1.5
52003067-44	Den Haag	2696 AK	The Netherlands	2.1
52003067-45	Veendam	9646 AA	The Netherlands	2.2
52003067-46	Coevorden	7742 AB	The Netherlands	2.1
52003067-48	Leidschendam	2266KA	The Netherlands	2.3
52003067-49	Vlaardingen	3197KA	The Netherlands	1.7
52003067-50	Antwerp		Belgium	1.6
52003067-51	Hamburg		Germany	0.8
52003067-52	Munich		Germany	1.6

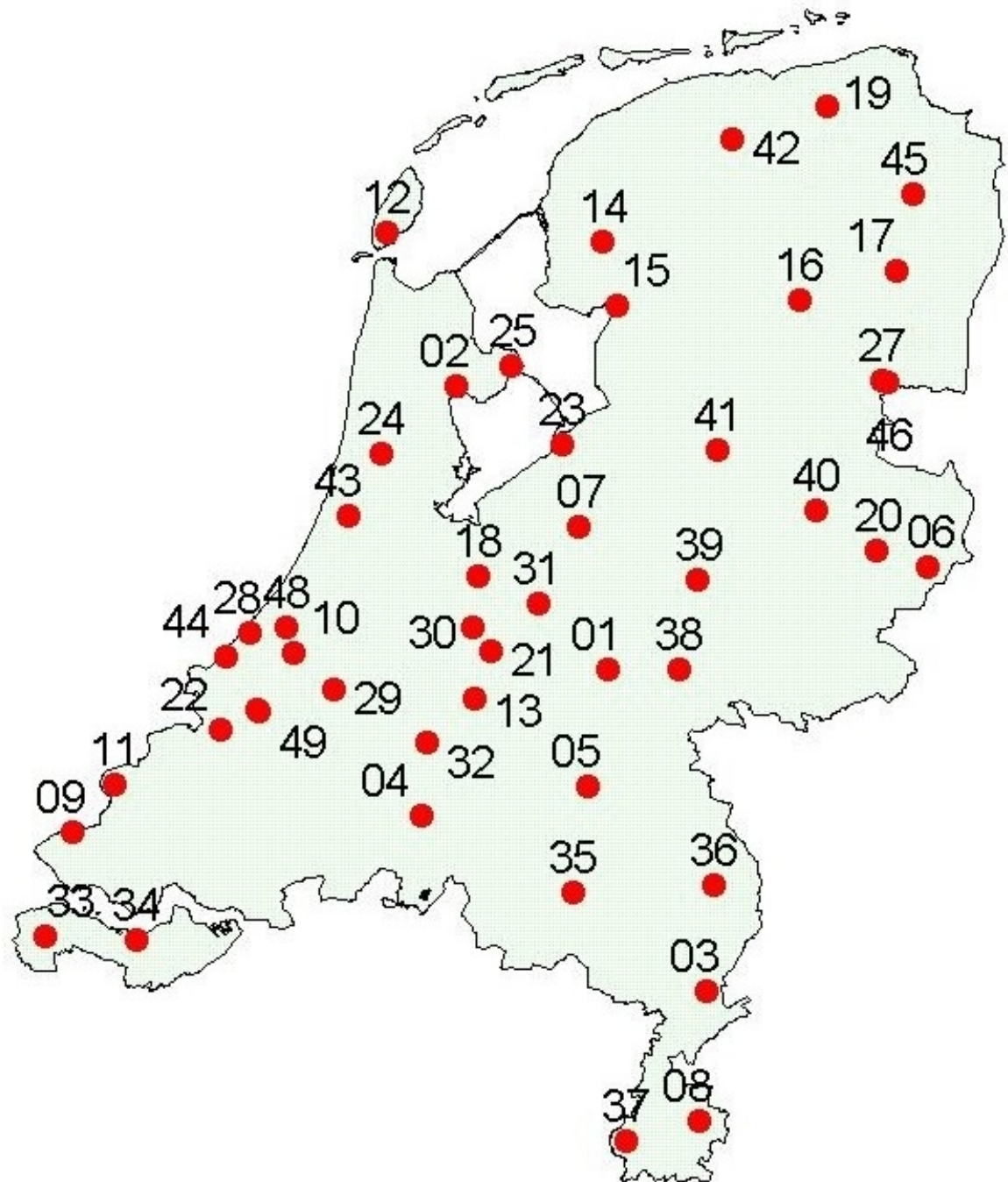


Figure 1 Overview of sampling locations in The Netherlands.

3. Methods and materials

3.1 Sampling

3.1.1 Sampling materials

New, amber glass bottles and white glass funnels were used. The bottles and funnels were cleaned in the TNO laboratory prior to sampling. All materials were rinsed with methanol followed by HPLC water, and baked in an oven at 260°C for 16 hours. About 10% of the materials were used as laboratory and field blanks.

3.1.2 Sample transport, storage and pre-treatment

At the end of the sampling period the funnel was rinsed with 100 ml HPLC water followed by 100 ml HPLC-grade methanol. The rinsing fluids were collected in the sample bottle. On the same day, the bottle was transported to the laboratory for analysis. Samples were stored at a temperature of 4°C until analysis. Apart from acidification of the samples to pH 5, no special pre-treatment was applied to the samples. Samples were extracted within one week after receipt. In general, sample extracts were analysed within two weeks after extraction.

3.2 Analytical procedures

3.2.1 Sample extraction

The sample bottle was shaken to homogenize the sample. The sample was transferred to a separatory funnel while iniquities, like small insects and leaves, were removed. To each sample 6-methylchryseen was added as an extraction standard and sodium chloride was added to facilitate extraction. The inside of the sample bottle was extracted with dichloromethane and subsequently added to the content in the separatory funnel. The sample was extracted by shaking for 3 minutes. The extraction was repeated once more with dichloromethane. The combined dichloromethane extracts were dried using sodium sulphate and carefully concentrated in a rotary evaporator to a volume of less than 10 ml. The extract was further concentrated under a stream of purified nitrogen gas to a final volume of 1.0 ml. Next 1,2,3,4-tetrachloronaphthalene was added as an injection standard and the extract was split in two equal portions of 0.5 ml each.

The first sub-extract was evaporated to dryness and the residue was re-dissolved in a 50/50 mixture of HPLC water and methanol. This extract was used for the deter-

mination of the BPA, APs and APEOs. To the second sub-extract 0.5 ml of a diethyl ether solution, saturated with diazomethane, was added for derivatization of TBBA. This extract was used to determine the flame retardants.

With each series of ten samples one blank sample was extracted. This blank sample consisted of a sample bottle and funnel, both pre-cleaned in the same way and together with all other sample materials. The funnel was rinsed with water and methanol and these rinsing fluids were collected in the sample bottle as was done in the field at the end of each sampling period. The blank sample was analysed together with the actual samples.

3.2.2 Instrumental analysis

BPA, APs and APEOs were analysed using liquid chromatography in combination with mass spectrometry (LC/MS). The LC/MS was a Hewlett Packard 1100 LC/ESI/MS system equipped with a guard column and a Waters Symmetry C₁₈ analytical column, length 15 cm, 3.9 mm i.d., 5 µm particle size. For BPA and APs negative ionisation was used, for APEOs positive ionisation. The mass spectrometer was used in the selected ion monitoring mode and typically three ions were monitored for BPA and APs. For APEOs fifteen ions (for n = 1 to n = 15, each separated by 44 mass units) were monitored.

All other compounds were analysed using gas chromatography in combination with mass spectrometry (GC/MS). The GC/MS was a Hewlett Packard 6890 gas chromatograph equipped with HP-5MS capillary column, length 30 m, 0.25 mm i.d., 0.25 µm film thickness, and interfaced to a Hewlett Packard 5973 mass spectrometer. The mass spectrometer was used in the selected ion monitoring mode and typically two or three ions were monitored for each compound.

3.2.3 Calculation of results

Identification of compounds was based on retention time and qualifier ion ratios. Quantification was based on external standards analysed within the same series as the sample extracts. The external standards were prepared from commercially available pure substances (phthalates, alkylphenols and ethoxylates, bisphenol-A, tetrabromobisphenol-A, hexabromocyclododecane) or compound mixtures (PBDEs, musks). The number of ethoxy units in the commercial alkylphenol ethoxylate standards ranged from n = 5 to n = 15 with a maximum around n = 8-9. In all cases peak areas were used for calculations. The recovery of the added extraction standard was calculated but none of the results were corrected for this recovery. For a number of compounds, especially some phthalates the results were corrected for a blank value.

For a number of compounds, contour plots over The Netherlands were prepared using the GIS-program Surfer. This program uses the measurement data and Kriging techniques to calculate deposition data for locations in between the actual sampling locations, resulting in contour plots. These calculations are made only if a compound is observed in at least 30% of the locations and only the data for locations in The Netherlands were included. These plots are useful for the identification of the presence of local emission sources, however, they should be interpreted carefully. The program does not take into account the wind directions during the sampling period, so, the actual location of an emission source is not shown by the contour plot.

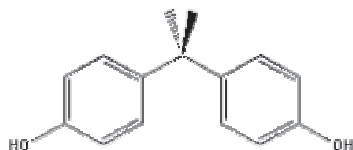
Furthermore, the concentrations shown in the plots were calculated based on a model and an algorithm in the Surfer program that does not take into account all aspects. As a consequence the concentrations in the plots can deviate to some extent from the actual concentrations measured on the sampling locations. Since method detection limits (MDL) can not be used in these calculations, and the true concentration of the compound can range between zero and the MDL, the MDL was replaced by one third of its value as an estimate of the actual concentration.

4. Results

4.1 Bisphenol-A

4.1.1 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. BPA may be released into the atmosphere during the production process, during the processing of intermediate products and from the final products that may still contain small amounts of not-reacted BPA. Research from a few years ago indicated that BPA has estrogenic potency and is therefore generally included as one of the suspected endocrine disruptors¹⁵. BPA is moderately water-soluble. The chemical structure of BPA is given in the figure below.



BPA was found in the LOES program in two out of five precipitation samples collected in the program for this compound. Both positive samples came from the same location and the BPA concentrations were 55 ng/l and 57 ng/l¹³.

4.1.2 Results for bisphenol-A in this study

Bisphenol-A (BPA) was detected in 32% of all samples in concentrations ranging from 6 to 357 ng/l. The highest concentration was found in the sample 3067-51 from location Hamburg, Germany. The highest concentration in The Netherlands, 130 ng/l, was found in sample 3067-26 from location Vlaardingeng. Other sample locations that also showed relatively high BPA concentrations were Pijnacker (3067-10) 64 ng/l, Hellevoetsluis (3067-22) 41 ng/l in The Netherlands and Antwerp in Belgium (3067-50) 80 ng/l. All other locations showed BPA concentrations below 15 ng/l deposition.

The results for BPA are summarised in table 3. This table also presents the average measured concentration, the standard deviation in the average measured concentra-

¹⁵ Toppari J. et al. Male reproductive health and environmental chemicals with estrogenic effects. Miljöprojekt no. 290. Danisch Environmental Protection Agency, Denmark, 1995.

tion and the median measured concentration. Note that “not detected” results are excluded from these calculations. If the median measured concentration is much lower than the average measured concentration this indicates that there are some locations for which the results are much higher than for most other locations. This is also indicated by a high standard deviation in the average measured concentration. One should of course take into account the number of samples in which the compound of interest was detected. This is indicated as a percentage of samples above the method detection limit (MDL). Since the actual number of samples is 50, dividing the percentage by two gives the absolute number of samples in which the compound was detected. The full results for BPA of all locations are given in the appendix.

Figure 2 presents a contour plot of BPA over The Netherlands, a spatial representation of the deposition data. These plots are useful to give an indication of the location of emission sources, but should be interpreted carefully. It was already mentioned that the highest concentrations in The Netherlands were found in samples 3067-26, -10 and -22. These locations are situated on a southwest line and are relatively close together. From the plot it becomes clear that the emission of BPA seems to be limited to one source only. If one takes into account that the predominant wind direction in The Netherlands is southwest, the actual source of the emissions will probably be somewhat southwest from the spot in the contour plot. It is likely that the industrial area of Rotterdam is the source of the BPA emissions.

Table 3 Bisphenol-A in precipitation expressed in ng/l.

Compound	BPA
method detection limit (MDL)	< 5
minimum measured concentration	6
maximum measured concentration	357
Average of measured concentration	48
standard of deviation in average	89
median of measured concentration	10
percentage of samples above MDL	32%

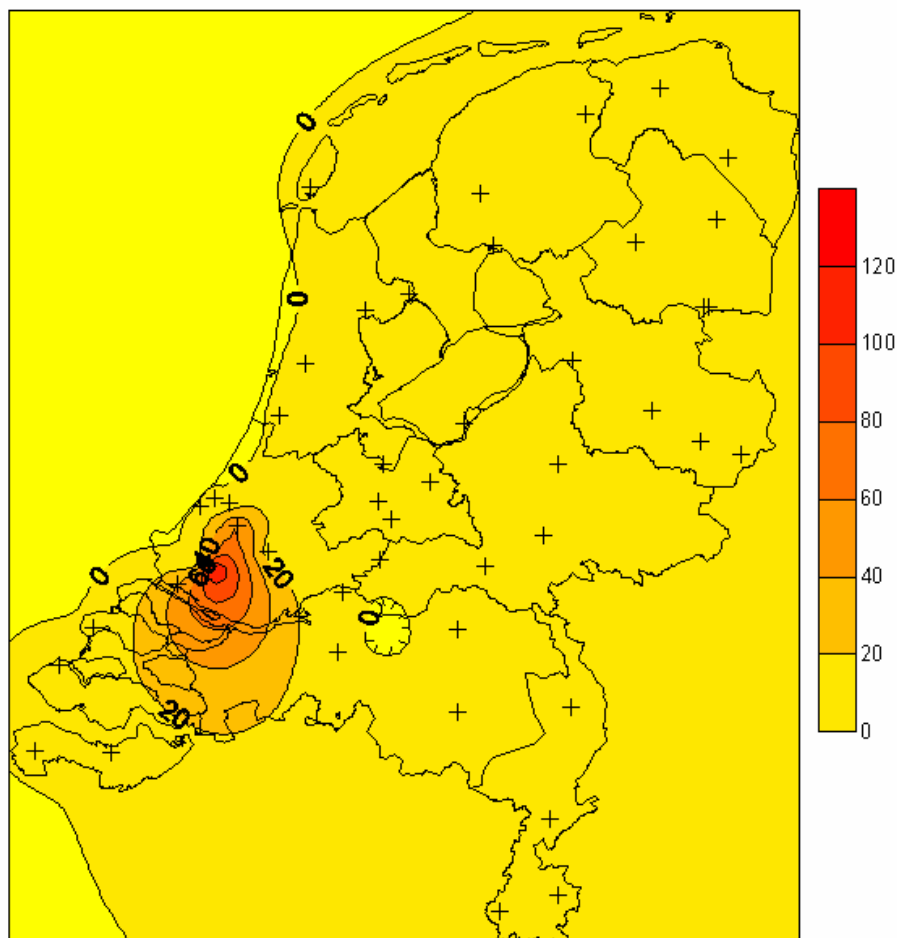


Figure 2 Contour plot of bisphenol-A concentrations in precipitation.

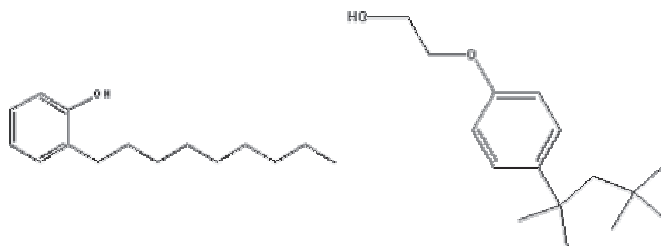
4.2 Alkylphenols and ethoxylates

4.2.1 General information

Alkylphenols (APs) and alkylphenol ethoxylates (APEOs) are used in plastics as additives and as surface-active ingredients in industrial detergents and emulsifiers. In industrial formulations of nonyl- and octylphenol isomers, the para-substituted isomers are the most common (> 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 tapestry cleaning, and as emulsifiers in solvents and agricultural pesticides¹⁶. APs are moderately soluble while the APEOs are generally more water-

¹⁶ Maguire R.J. Water Qual. Res. J. Canada 34, 37-78, 1999.

soluble than the parent APs themselves. The chemical structure of n-nonylphenol and octylphenol-mono-ethoxylate (better known as Triton X-100) are presented below.



Several studies mention the presence of APs and APEOs in the environment, especially in sediments. In a recent TNO study, NPs and NPEOs were found in sludge samples in concentrations up to 2000 mg/kg¹⁷. In the LOES program no detectable concentrations of APs or APEOs were found in precipitation¹³.

4.2.2 Results for alkylphenols and ethoxylates in this study

Nonylphenol (NP) was found in 34% of the locations, octylphenol (OP), however, in only 1 of the 50 locations despite the better method detection limit for OP. This is somewhat surprising even if we take into account that NP and NPEO are more frequently used than OP and OPEO. However, in the LOES study it was also observed that OP and OPEO were only found occasionally, while NP and NPEO were found in the majority of environmental samples¹³.

For NP the concentrations found ranged from 42 to 256 ng/l. The method detection limit for NP was higher than the one for OP due to some interference in the chromatograms that limited the quantification of NP. The OP concentration in the only sample in which it was detected was 8.4 ng/l. For the other locations the concentrations were below the method detection limit, < 5 ng/l. In the LOES study no detectable concentrations were found in precipitation samples but this may be due to the limited number of precipitation samples (5) and the method detection limit (< 100 to < 600 ng/l) which is above the median measured concentration that we found for NP and OP.

¹⁷ Peters RJB. Study of Toxic Substance Pollution in Hong Kong. TNO report R 2002/582, October 2002.

Table 4 Alkylphenols and ethoxylates in deposition expressed in ng/l.

Compound	NP	OP	NPEO	OPEO
method detection limit (MDL)	< 40	< 5	< 30	< 30
minimum measured concentration	42	8.4	31	30
maximum measured concentration	256	8.4	924	113
average of measured concentration	97	8.4	130	72
standard of deviation in average	65	-	140	18
median of measured concentration	82	8.4	91	69
percentage of samples above MDL	34%	2%	94%	78%

Nonyl- and octylphenol ethoxylates (NPEO and OPEO) were found in most samples with NPEO concentrations ranging from 31 to 924 ng/l, and OPEO concentrations ranging from 30 to 113 ng/l. The results for the alkylphenols and ethoxylates are summarised in table 4. The difference between the average and median measured concentration for NPEO suggest activities with this chemical at a limited number of locations. The highest NPEO concentrations were found at location 3067-49 (Vlaardingen) and location 3067-27 (Coevorden) both suggesting a production facility or an industry using vast amounts of this chemical. The results for all locations are presented in the appendix.

Although specific ethoxylates with a different number of ethoxy-units could not be distinguished chromatographically with this method, it was possible to determine the range of the ethoxy-units from the mass spectrum. For the ethoxylates found, the number of ethoxylate units generally ranged from $n = 1$ to $n = 12$. Ethoxylates found in sediments and waste water generally have a lower number of ethoxy-units due to degradation. This suggests that the ethoxylates found in the deposition were probably emitted from processes and not from other environmental compartments. Figure 3 gives an example of the mass spectrum of OPEO in the chromatogram of the sample of location 3067-49 (Vlaardingen).

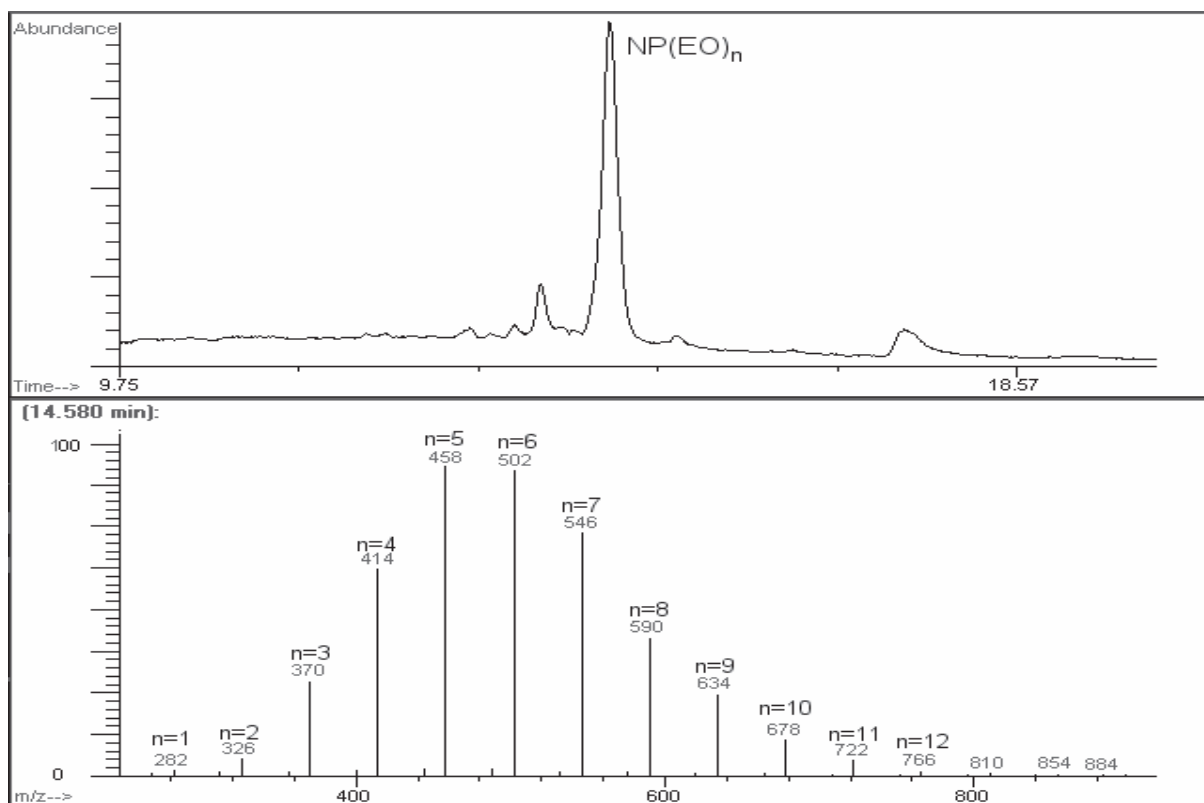


Figure 3 Nonylphenol ethoxylate in the sample from location 3067-49. The number of ethoxy units varies from $n = 1$ to $n = 12$ with a maximum around $n = 5-6$.

Figure 4 shows a spatial distribution of nonylphenol ethoxylate depositions over The Netherlands. From this one can conclude that two emission sources of this chemical can be identified, one in the industrial area of Rotterdam or, most likely, Vlaardingen and another close to the German border. The second source coincides more or less with the sampling location Coevorden.

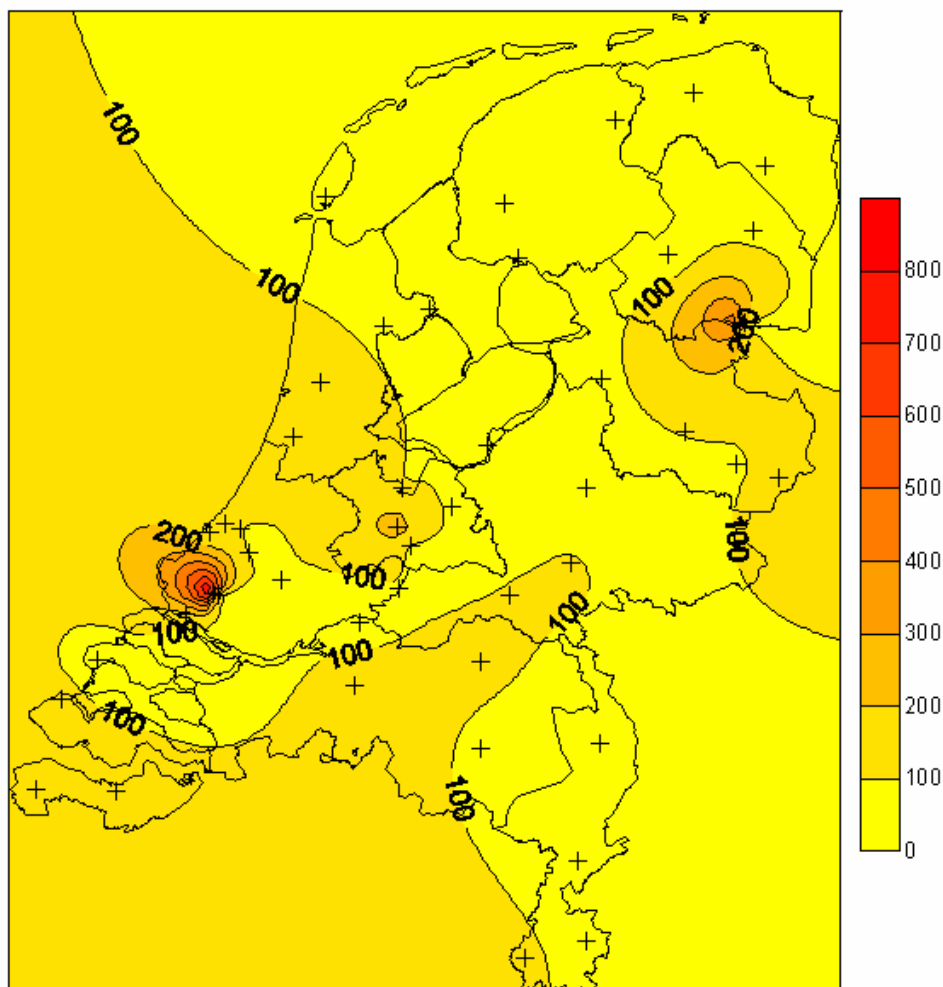


Figure 4 Contour plot of nonylphenol ethoxylate concentrations in precipitations.

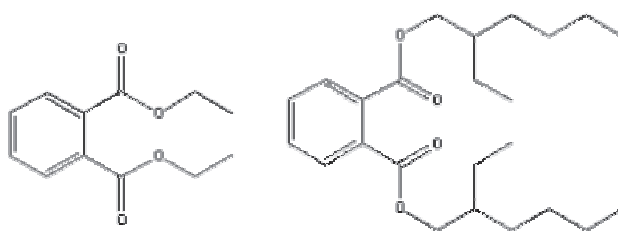
4.3 Phthalates

4.3.1 General information

The widespread use and manufacture of plastics have made the phthalate esters one of the most ubiquitous classes of compounds in our everyday environment. Phthalates are used as plasticizers to increase the flexibility of high molecular weight polymers. In some plastics, phthalates comprise up to 50% of the total weight. Di-(2-ethylhexyl) phthalate (DEHP) accounts for a quarter of the plasticizers produced. Phthalates are also used as heat-transfer fluids and carriers, and can be found in ink, paint, adhesives, pesticides and vinyl flooring¹³. Consequently, the potential for human exposure is very high. Scientists at the US Centers for Disease

Control have documented human exposure to phthalates by determinations of the monoester metabolites in human urine¹⁸.

Phthalates, and especially DEHP, dimethyl phthalate (DMP), diethyl phthalate (DEP) and dibutyl phthalate (DBP) are found in all environmental matrices. In recent years the use of some iso-alkyl phthalates like di-isononyl phthalate (DINP) is increasing. In general, phthalates are poorly water-soluble and adsorb quickly to suspended matter and sediment. The chemical structure of DEP and DEHP is presented below.



Phthalates were also found in precipitation in the LOES program¹³. The concentrations varied from non-detected to concentrations as high as 1700 ng/l for DEHP. In general the concentrations in precipitation were comparable to those encountered in surface water.

4.3.2 Results for phthalates in this study

Phthalates were found in all samples and in relatively high concentrations. The most prominent phthalates found in these precipitation samples were DINP and DEHP. Di-isodecyl phthalate (DIDP) was found in an extremely high concentration nearly 100,000 ng/l in sample 3067-49, location Vlaardingen, probably a location nearby a production facility for this chemical. Another location in Vlaardingen, location 3067-26, also showed elevated levels of DINP and DIDP. DINP and DIDP are technical formulations of iso-alkyl phthalates that do contain substantial amounts of the straight chain isomer as well as isomers that may be construed as originating from non-equivalent side chains. In a chromatogram these compounds form a more or less unresolved lump as shown in figure 5 for sample 3067-49. For this reason the method detection limit for iso-alkyl phthalates is generally higher than that for the other phthalates.

Diphenyl phthalate (DPP) was not found at all, while the concentrations of DMP, DEP, benzylbutyl phthalate (BBP), dicyclohexyl phthalate (DCHP) and di-n-octyl phthalate (DOP) were low compared to the other phthalates, although they were

¹⁸ Blount BC et al. Environmental Health Perspectives, 108, 979-982, **2000**.

found in most locations. The results for the phthalates are summarised in table 5. The difference between the average and median measured concentrations, notably for DMP, DEP, DINP and DIDP, suggests that these are used or produced in specific locations. The other phthalates show more or less comparable concentrations over all sampling locations.

Figure 6 shows a spatial distribution of DEHP depositions over The Netherlands, clearly highlighting one obvious source of DEHP emissions. Taking into account the predominant wind direction in The Netherlands the actual emission source is probably somewhere southwest of the location Hoorn.

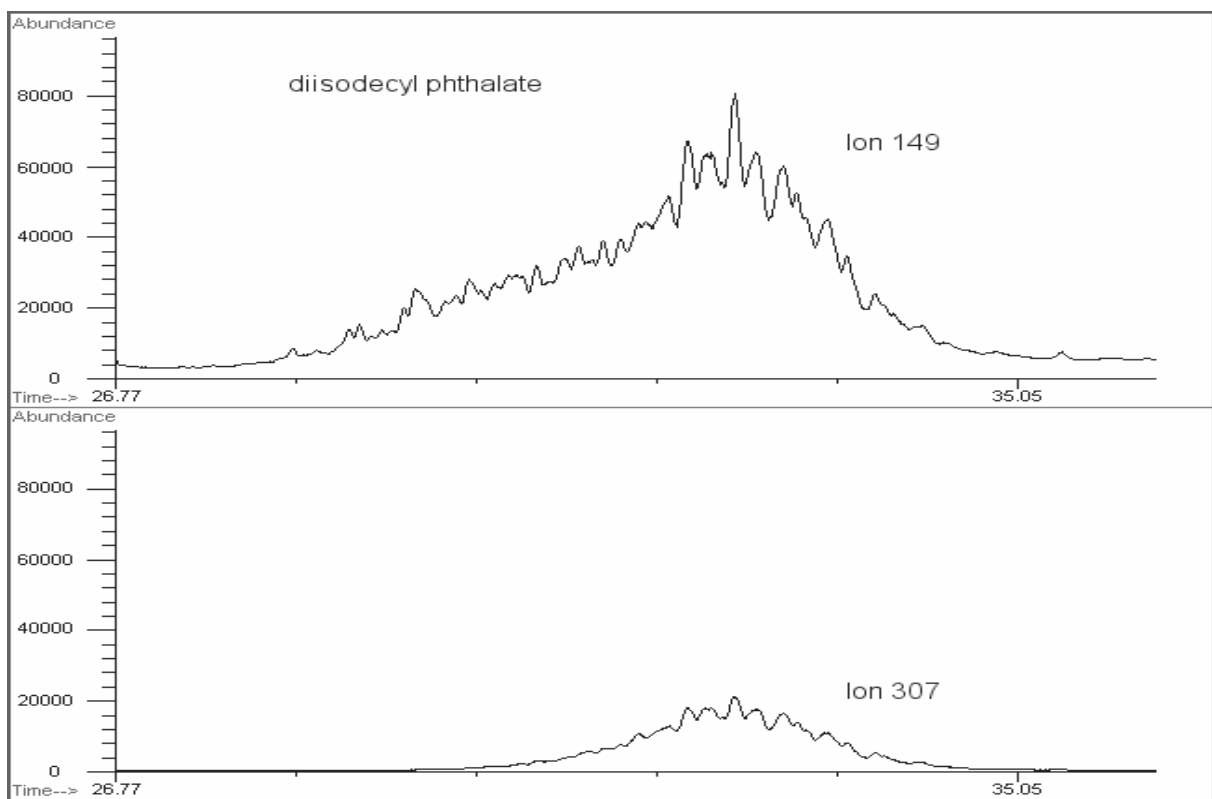


Figure 5 Part of the chromatogram of sample 3067-49 showing the response of di-isodecyl phthalate.

Table 5 *Phthalates in deposition expressed in ng/l.*

Compound	DMP	DEP	DIBP	DBP
method detection limit (MDL)	< 10	< 10	< 10	< 10
minimum measured concentration	22	14	77	139
maximum measured concentration	750	4050	3976	1173
average measured concentration	82	434	810	498
standard deviation in average	121	830	694	259
median measured concentration	47	192	713	425
percentage of samples above MDL	88%	94%	98%	100%

Compound	BBP	DCHP	DEHP	DPP
method detection limit (MDL)	< 10	< 10	< 10	< 10
minimum measured concentration	15	10	574	-
maximum measured concentration	896	196	30902	-
average measured concentration	189	38	4037	-
standard deviation in average	142	40	4697	-
median measured concentration	164	24	2370	-
percentage of samples above MDL	100%	92%	100%	0%

Compound	DOP	DINP	DIDP
method detection limit (MDL)	< 10	< 100	< 100
minimum measured concentration	39	285	1303
maximum measured concentration	437	48290	98429
average measured concentration	209	4214	36167
standard deviation in average	113	7108	54050
median measured concentration	204	2399	8768
percentage of samples above MDL	100%	98%	6%

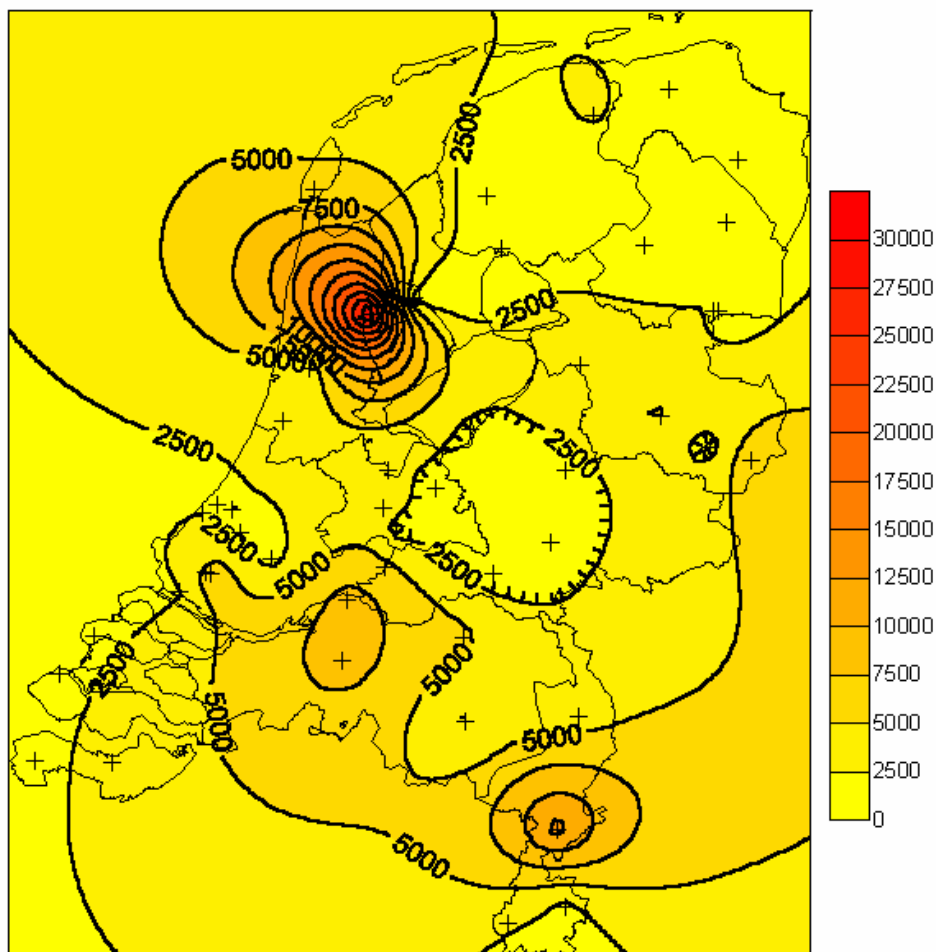


Figure 6 Contour plot of di-(2-ethylhexyl) phthalate concentrations in precipitation.

4.4 Flame retardants

4.4.1 General information

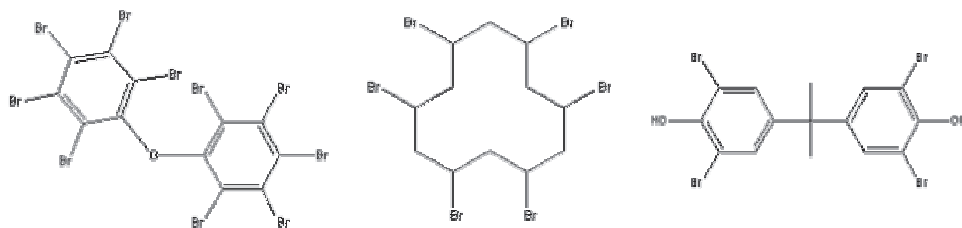
Flame retardants were already used 360 years BC when vinegar was employed to impregnate timber to protect it from fire. Halogenated flame retardants, and especially the brominated flame retardants (BFR) used nowadays, are of more recent make! The first BFRs that were used were polybrominated biphenyls (PBB), closely related to the well known PCBs. Due to negative environmental effects of PCBs, the PBBs were rapidly replaced by polybrominated diphenyl ethers (PBDEs).

PBDEs are so-called additive flame retardants. They are added to polymers used in a wide range of materials such as electric and electronic equipment, paint, textiles

and in vehicles and aircrafts. PBDEs are used as commercial mixtures such as Bromkal, with different degrees of bromination. The Deca-mix consists of 97% decaBDE and 3% nona- and octaBDE. The Octa-mix mainly consists of hepta- and octa-BDE, while the Penta-mix is a mixture of mainly penta- and tetra-BDE. The degree of bromination influences the PBDEs' individual physicochemical properties and subsequently their environmental fate. Because of their structural similarity with PCBs, the individual PBDEs follow the same numbering as the PCBs. Typically, PBDEs may comprise up to 5% to 20% of the total weight of a product to which they are added. Since these chemicals are not chemically bound they may "leak" from the polymer product, thus invade the environment.

Hexabromocyclododecane (HBCD) is a cyclo-aliphatic brominated chemical meant to partially replace PBDEs because of their known toxicity. HBCD is also an additive flame retardant as are the PBDEs and can enter the environment in much the same way. It is, however, less stable than PBDEs.

Tetrabromobisphenol-A (TBBA) is used as a flame retardant in epoxy polymers such as circuit boards in electronic equipment like computers and television sets. TBBA is a reactive flame retardant, e.g. it is added as a copolymer which means that it is chemically bound to the polymer material. However, small amounts of the TBBA monomer will not be polymerized and can "leak" into the environment. The chemical structure of decabromo diphenylether (BDE-209), HBCD and TBBA are presented below.



BFRs found in the environment are TBBA, BDE-209, BDE-47, BDE-99 and BDE-153. PBDEs were found in a recent TNO study in concentrations in the mg/kg range in sediments as well as in biota^{16,19}. In a recent TNO study of persistent organic pollutants in the atmosphere and in precipitation, TBBA was found in about 50% of the precipitation samples in concentrations ranging from 1 to 10 ng/l⁷. We do not know of any other studies in which BFRs were measured in precipitation.

¹⁹ Huisinga S, Peters RJB, Houtzager MMG. Surface water quality in the Walloon region. TNO report R2002/132, May 2002.

4.4.2 Results for brominated flame retardants in this study

A large number of BFRs were incorporated in this study, including the more “volatile”, though less used PBDEs. In addition, HBCD, a BFR meant to replace the PBDEs was determined in the samples. BFRs were found in 28% of the samples and in concentrations often below 10 ng/l. TBBA is the most often detected BFR and was found in 16% of the samples with a maximum concentration of 2.6 ng/l. This is only partly in agreement with earlier findings by Duyzer et al. who found TBBA in about 50% of the air and precipitation samples, for the latter in concentrations up to 4.1 ng/l⁷. The reason for this difference may be that in the latter study four-weekly samples were collected over a period of two years while in the present study four-weekly samples were collected in only one sampling campaign in February/March. The data of the study by Duyzer show that TBBA was found more frequently and in higher concentrations during the summer months. The lower findings in winter may be explained by lower passive venting from homes and factories. If the TBBA emissions are diffuse emissions mainly from consumer products, which probably is the case, lower passive venting would result in lower TBBA emissions, and thus lower TBBA concentrations in precipitation.

In general, when PBDEs were found in a sample several PBDEs congeners were found in that sample. Since commercially used PBDEs are mixtures, the so-called Penta-, Octa- and Deca-mix, this is what one would expect. In fact the PBDEs detected in sample 3067-11 and -24 from location Burgh-Heemstede and Krommenie, respectively, show a resemblance with the commercially available Penta-mix. In the same way the PBDEs found in sample 3067-34 from location Terneuzen show some resemblance with the commercial Octa-mix. The resemblance of the PBDE composition of both samples with the commercial mixtures is shown in figure 7 in the form of two bar graphs.

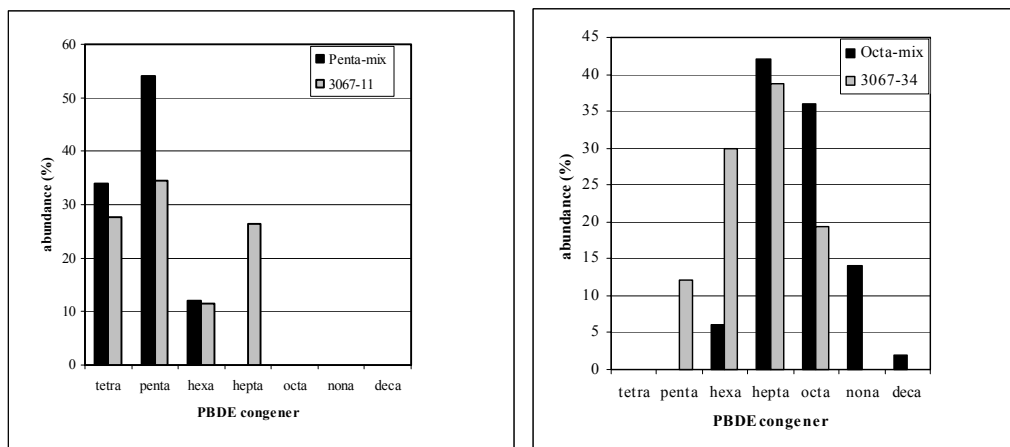


Figure 7 Comparison of PBDE composition in samples with commercial PBDE mixtures.

HBCD was found only in sample 3067-34 (location Terneuzen). The fact that the found concentration of nearly 2000 ng/l is more than two orders of magnitude higher than the concentration of any other BFR in this study, indicates the probable presence of a production facility at that location. The peak of HBCD in the chromatogram of sample 3067-34 is shown in figure 8. The results for the BFRs in this study are summarised in table 6. The full results for all locations are found in the appendix.

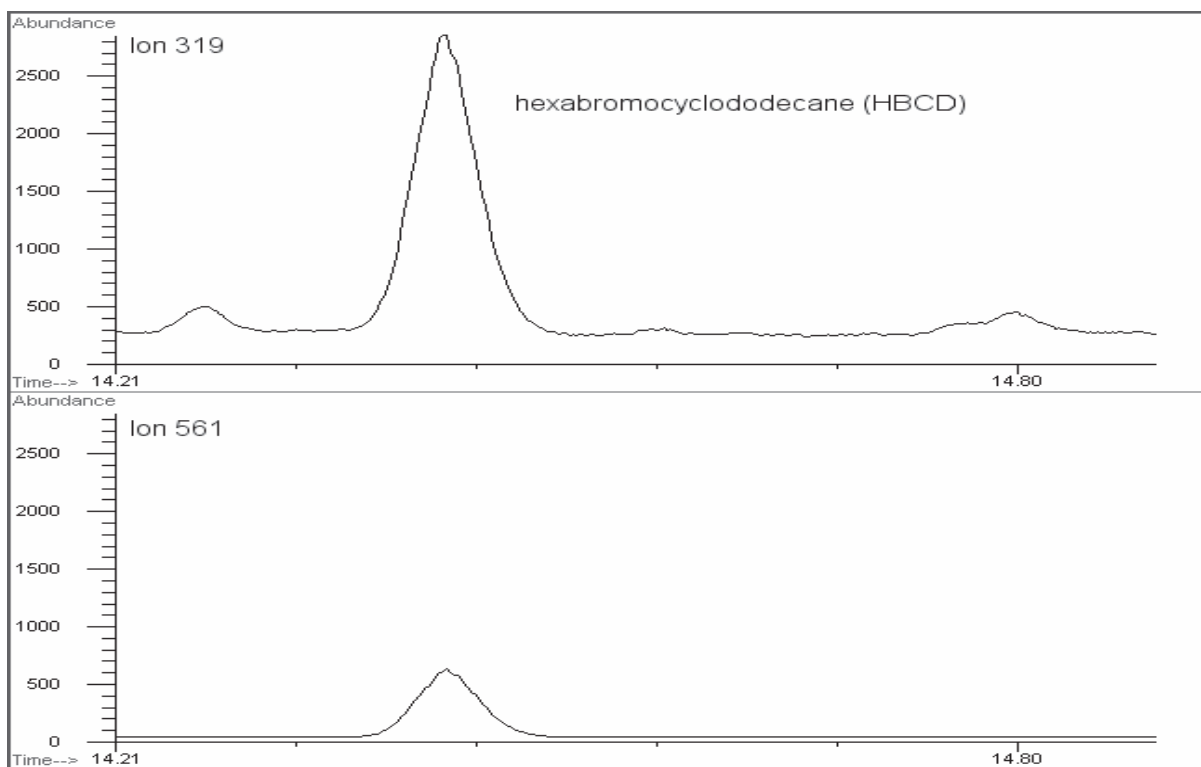


Figure 8 HBCD peak in the chromatogram of the sample 3067-34, location Terneuzen.

Table 6 Brominated flame retardants in deposition expressed in ng/l.

Compound	BDE 17	BDE 28	BDE 49	BDE 47
method detection limit (MDL)	< 0.5	< 0.5	< 0.5	< 1.0
minimum measured concentration	-	5.7	0.9	1.4
maximum measured concentration	-	17.1	0.9	8.0
average measured concentration	-	11.4	0.9	4.4
standard deviation in average	-	8.0	-	2.9
median measured concentration	-	11.4	0.9	3.6
percentage of samples above MDL	0%	4%	2%	12%

Compound	BDE 100	BDE 99	BDE 85	BDE 154
method detection limit (MDL)	< 1.0	< 1.0	< 1.0	< 0.5
minimum measured concentration	1.3	1.5	-	1.0
maximum measured concentration	2.9	8.8	-	1.0
average measured concentration	2.1	4.7	-	1.0
standard deviation in average	1.1	2.7	-	-
median measured concentration	2.1	4.9	-	1.0
percentage of samples above MDL	4%	10%	0%	2%

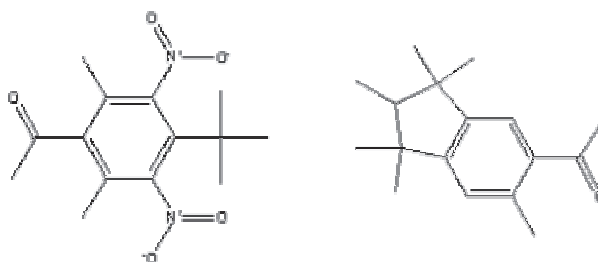
Compound	BDE 153	BDE 183	BDE-octa	BDE-nona
method detection limit (MDL)	< 0.5	< 1.0	< 2.0	< 5.0
minimum measured concentration	0.8	2.3	2.4	-
maximum measured concentration	3.9	9.5	2.4	-
average measured concentration	2.4	5.5	2.4	-
standard deviation in average	1.6	3.6	-	-
median measured concentration	2.4	4.8	2.4	-
percentage of samples above MDL	8%	6%	2%	0%

Compound	BDE 209	HBCD	TBBA
method detection limit (MDL)	< 25	< 15	< 0.5
minimum measured concentration	-	1835	0.6
maximum measured concentration	-	1835	2.6
average measured concentration	-	1835	1.1
standard deviation in average	-	-	0.7
median measured concentration	-	1835	0.9
percentage of samples above MDL	0%	2%	16%

4.5 Musk compounds

4.5.1 General information

Originally, musk is a male sexual scent signal and is since ancient times aspired to humans who used it in medicines and as a fixative in perfumes. The increasing demand resulted in the production of artificial musk fragrances. The most well known artificial musks are musk xylene (MX), musk ketone (MK), and the polycyclic musks tonalide (AHTN) and galaxolide (HHCB). Due to the toxicity and persistence of nitro musks, the production and use of Musk Ambrette (MA) is prohibited while MX and MK should be phased out in 2010. Nowadays the nitro musks in products are replaced by synthetic polycyclic musks²⁰. The structures of MK and AHTN are presented below.



Synthetic musks may enter the environment by disposal to sewer systems (both domestic and industrial). Another source can be the consumer himself. The application of perfumed products will result in a direct loss to the atmosphere¹⁴. Artificial musks have been found in the aquatic environment and biota in the ng/l, and the sub-ng/g range, respectively, and also in air in concentrations ranging from 45 to 223 pg/m³¹⁴. Although we are not aware of any studies involving artificial musks in precipitation, their presence in air suggests that they will also be present in precipitation

4.5.2 Results of musk compounds in this study

In total six polycyclic musks and the five nitro musks were analysed in the samples. The results for these compounds are summarised in table 7. It appeared that one polycyclic musk, AHMI and two nitro musks, MX and MM were not found at all. The nitro musks, MK and MT were found, but only at three locations with concentrations up to 10 ng/l. Another frequently found nitro musk is MA. This compound was found in 36% of the samples with concentrations ranging from 2.1 to

²⁰ Bester K, Hühnerfuss H, Lange W, Rinkus GG, Theobald N. *Water Res.* **32**, 1857-1858, **1998**.

14 ng/l. This result is remarkable since the production of MA was already banned before the prohibition of MK and MX.

The highest musk concentration is 147 ng/l found for the polycyclic musk DPMI in sample 3067-52, location Munich, Germany. The polycyclic musk HHCB was found in almost all samples with concentrations ranging from 2.3 to 25 ng/l. From the results in table 7 it is clear that, different from some other compounds, HHCB concentrations are fairly evenly spread over all sample locations. This suggests that there are no clear point emissions, but rather diffuse emissions of this compound. This again leads to the conclusion that consumers and domestic use are probably the main sources of emission of these compounds to the environment. The latter seems not to be the case for AHTN. The contour plot in figure 9 suggests an emission source of this chemical somewhere in the centre of The Netherlands.

Table 7 Musk compounds in deposition expressed in ng/l.

Compound	DPMI	ADBI	AHMI	MA
method detection limit (MDL)	< 2.0	< 2.0	< 2.0	< 2.0
minimum measured concentration	147	4.2	-	2.1
maximum measured concentration	147	4.2	-	14
average measured concentration	147	4.2	-	5.8
standard deviation in average	-	-	-	4.2
median measured concentration	147	4.2	-	3.7
percentage of samples above MDL	2%	2%	0%	36%

Compound	ATTI	HHCB	AHTN	MX
method detection limit (MDL)	< 2.0	< 2.0	< 2.0	< 2.0
minimum measured concentration	3.1	7.0	2.3	-
maximum measured concentration	4.5	25	19	-
average measured concentration	3.8	13	4.9	-
standard deviation in average	1.0	4.5	2.9	-
median measured concentration	3.8	13	4.1	-
percentage of samples above MDL	4%	100%	88%	0%

Compound	MM	MT	MK
method detection limit (MDL)	< 2.0	< 2.0	< 2.0
minimum measured concentration	-	10	3.0
maximum measured concentration	-	10	3.4
average measured concentration	-	10	3.2
standard deviation in average	-	-	0.2
median measured concentration	-	10	3.2
percentage of samples above MDL	0%	2%	4%

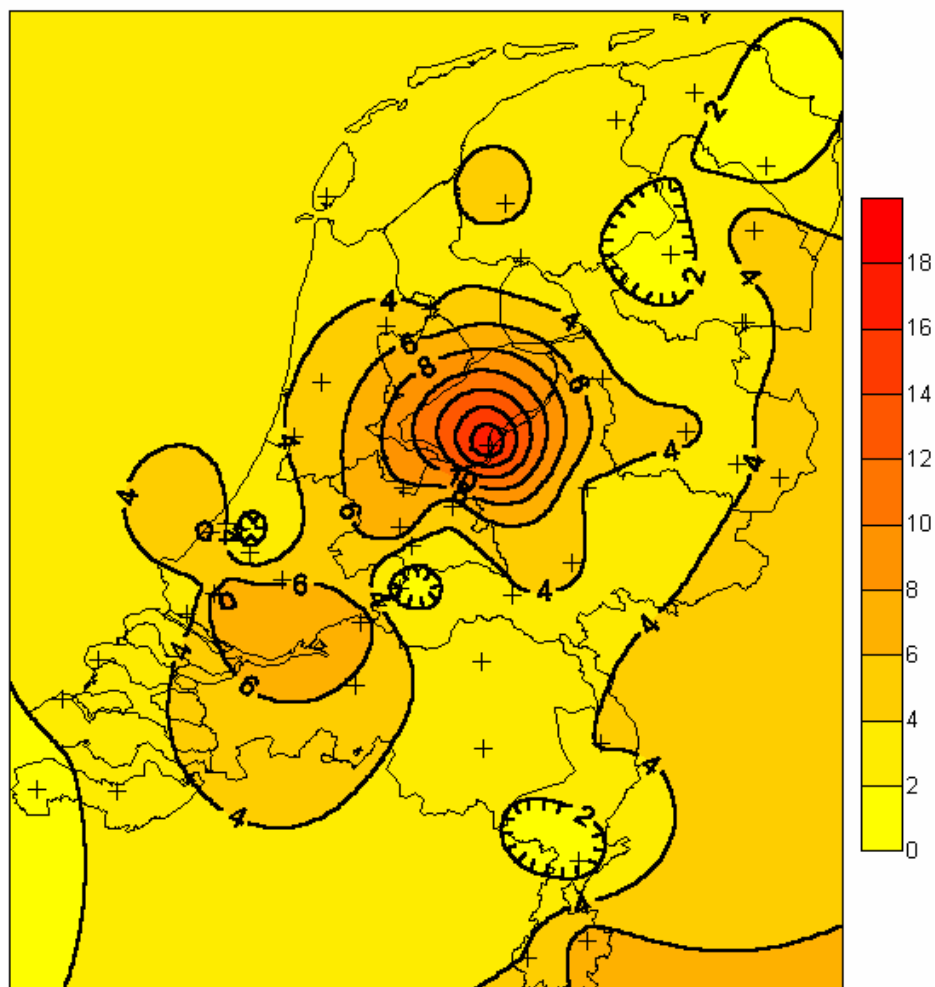


Figure 9 Contour plot for tonalide (AHTN) concentrations in precipitation.

4.6 Quality control measurements

4.6.1 Method validation parameters

All methods used were validated previous to the execution of this study. The parameters determined were linearity, repeatability, recovery from aqueous samples and the method detection limit (MDL). The latter parameter is already given in the tables in the previous sections for all individual compounds. All parameters are summarised for each group in table 8.

Table 8 Method validation parameters for each group.

Compound or group	Linearity ng/l	Repeatability %	Recovery %	MDL ng/l
bisfenol-A	5 – 800	8	65	5
alkylphenol and ethoxylates	40 – 500	8 – 18	87	5 – 40
phthalates	100 – 10000	3 – 9	60 – 100	10 – 100
brominated flame retardants	1 – 400	3 – 11	82 – 115	0.5 – 25
musk compounds	10 – 5000	5 – 10	80 – 125	2

4.6.2 Recovery of extraction standard

To all samples 100 ng of 6-methylchryseen was added as an extraction standard. The recovery of this standard in all samples ranged from 75% to 115% with an average recovery of $96 \pm 8\%$ which indicates a good overall recovery. The results are not corrected for the recovery of this extraction standard.

4.6.3 Blank samples

With each series of 10 samples a blank sample was included. This blank consisted of the sample bottle, the funnel and the rinsing fluids used to rinse the funnel at the end of the sampling period. For bisphenol-A, the alkylphenols and ethoxylates and the flame retardants no blank values were observed in any of the blank samples. For a number of phthalates and musk compounds blank results were observed. The blank result is listed in table 9. Because the blank results showed to be fairly repeatable (perhaps with the exception of DIBP) the results for these compounds were corrected for the blank value.

Table 9 Blank results for a number of compounds.

Compound	Blank result based on a 2 litre sample ng/l
phthalates:	
DIBP	50 ± 20
DBP	30 ± 3
DEHP	600 ± 70
DINP	90 ± 10
musk compounds:	
HHCB	2.2 ± 0.3

5. Conclusions

In this study the presence of a number of recognised xeno-estrogens in deposition was investigated. Precipitation samples were collected at 47 locations in The Netherlands, 2 in Germany and 1 in Belgium, using an open sampling system. The samples were analysed for bisphenol-A, alkylphenols and ethoxylates, phthalates, brominated flame retardants and synthetic musk compounds. From the results of the analysis the following conclusions can be drawn:

- BPA is found in 32% of the sampling locations with a median concentration of 10 ng/l (max. up to 357 ng/l). A contour plot calculated from the results clearly shows an emission source in the Rijnmond area.
- OPEO and NPEO are found in most samples with a median concentration of 91 ng/l (max. up to 924 ng/l) for NPEO. As with BPA there seems to exist an emission source in the Rijnmond area. NP is found as often as BPA but with a median concentration of 82 ng/l (max. up to 256 ng/l). OP is found in only one location.
- With the exception of DPP and DIDP, the other phthalates are found in virtually every location. DINP and DEHP are the most abundant with median concentrations around 2400 ng/l. Although DIDP is found only in a limited number of locations, extremely high concentrations of nearly 100,000 ng/l were measured for this chemical. For DEHP, DINP and DIDP it was possible to identify strong emission sources, probably production facilities of these compounds.
- Brominated flame retardants are identified in precipitation for the first time. These compounds are found in 28% of the samples, generally in concentrations below 10 ng/l. The most often encountered flame retardants are TBBA, BDE-47, -99 and -154. Where PBDEs are found the composition in the sample can be linked to commercial Penta- or Octa-mixes. HBCD is found at only one location (Terneuzen) in a concentration of 1835 ng/l, more than two orders of magnitude higher than that of any other brominated flame retardant in this study.
- The polycyclic musks HHCB and AHTN are found at almost all locations. While HHCB emissions seem mainly due to the use of consumer products, the results for AHTN clearly show an emission source in the centre of The Netherlands. The highest concentration found is 147 ng/l for DPMI, a polycyclic musk compound. Synthetic nitro musks are found in a few locations only.
- In general, the results of the study clearly indicate that the presence of xeno-estrogens in precipitation is a common feature. With the exception of BFRs, all

other groups of compounds in this study were found at 98% of the locations (100% in The Netherlands). This points to an overall presence, sometimes in high concentrations, of these compounds in the atmosphere. For many compounds these concentrations are caused by diffuse emissions from industries and consumer products. For some other compounds, however, the presence of located emission sources, probably point emissions from production facilities, could be established.

6. QA/QC statement

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

STERLAB is part of the Dutch Council for Accreditation (RvA) and is a member of the European co-operation for Accreditation (EA) and the International Laboratory Accreditation Co-operation (ILAC). TNO Environment, Energy and Process Innovation operates in compliance with the Quality System standard ISO 9001 (certificate no. 09381-2001-AQ-ROT-RvA).

7. Authentication

Name and address of the principal:

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1016 DW Amsterdam

Names and functions of the cooperators:

Dr. R.J.B. Peters	Project Leader
Ing. H. Beeltje	Technician
Drs. R.J. van Delft	Technician
Ing. J.A.D. van Renesse	Technician

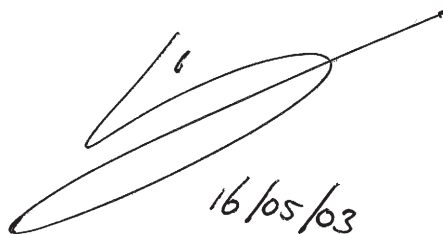
Names and establishments to which part of the research was put out to contract:

-

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

February 2003 – April 2003

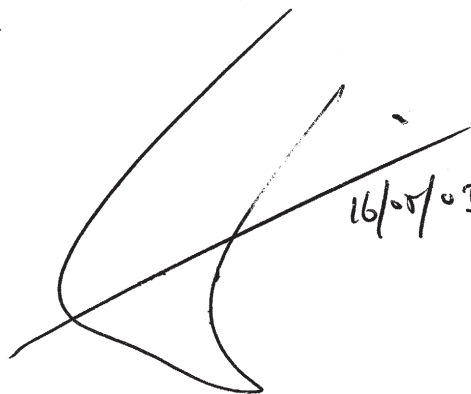
Signature:



16/05/03

R.J.B. Peters
Project leader MA

Approved by:



16/05/03

Dr. M.P. Keuken
Head of Department MA

Appendix 1 Full results of all locations

In the result tables the following acronyms are being used:

Group	Specific compounds	Acronym
Bisphenol A	bisphenol A	BPA
Alkylphenols and ethoxylates	octylphenol	OP
	nonylphenol	NP
	octylphenol ethoxylates	OPEO
	nonylphenol ethoxylates	NPEO
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
	diphenyl phthalate	DPP
	di-n-octyl phthalate	DOP
	di-iso-nonyl phthalate	DINP
	di-iso-decyl phthalate	DIDP
Flame retardents	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	BDE 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
	octabromo diphenyl ether	BDE octa
	nonabromo diphenylether	BDE nona
	decabromo diphenylether	BDE 209
	hexabromo cyclododecane	HBCD
	tetrabromobisphenol A	TBBA
Synthetic musk compounds	cashmeron (6,7-dihydro-1,1,2,3,3-pentamethyl-4(5H)indanon)	DPMI
	celestolide (4-acetyl-1,1-dimethyl-6-t.butyl-dihydroindene)	ADBI
	galaxolide (1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-2-benzopyran)	HHCB
	phantolide (6-acetyl-1,1,2,3,3,5-hexamethyl-dihydroindene)	AHMI
	tonalide (7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene)	AHTN
	traseolide (5-acetyl-1,1,2,6-tetramethyl-3-isopropyl-dihydroinden)	ATTI
	musk ambrette (2,6-dinitro-3-methoxy-4-t.butyltoluene)	MA
	musk ketone (4,6-dinitro-2-acetyl-5-t.butylxylene)	MK
	musk moskene (4,6-dinitro-1,1,3,3,5-pentamethylindan)	MM
	musk tibetene (2,6-dinitro-3,4,5-trimethyl-1-t.butylbenzene)	MT
	musk xylene (2,4,6-trinitro-5-t.butylxylene)	MX

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 uncertainty in the results (for instance the repeatability of the method given in 4.6.1.), the number of significant units is limited. This is especially true for the phthalates where concentrations of several thousands of ng/l are reported. In general no more than two significant numbers apply, so that for DEHP on location 3067-06 the result of 6940 ng/l should be read as 6900 ng/l.

Appendix 1

Sample code TNO Location (City) Unit	3067-01 Wageningen ng/l	3067-02 Hoorn ng/l	3067-03 Weert ng/l	3067-04 Dongen ng/l	3067-05 Nistelrode ng/l
Alkylphenols and ethoxylates					
BPA	<5.0	<5.0	13	<5.0	<5.0
OP	<5.0	<5.0	<5.0	<5.0	<5.0
NP	<40	<40	<40	74.3	<40
OPEO	103	< 30	68.2	90	98
NPEO	103	90	77	191	120
Phthalates					
DMP	39	87	37	72	50
DEP	214	354	298	299	310
DIBP	403	958	920	1158	1491
DBP	395	1018	801	669	711
BBP	173	192	154	257	245
DCHP	18	46	18	61	44
DEHP	1534	30902	13442	8542	5562
DPP	<10	<10	<10	<10	<10
DOP	85	258	167	93	119
DINP	2817	6508	7953	5328	4479
DIDP	<100	<100	<100	<100	<100
Flame retardants					
BDE-17	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-28	<0.5	5.7	<0.5	<0.5	<0.5
BDE-49	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-47	<1.0	<1.0	<1.0	<1.0	<1.0
BDE-100	<1.0	<1.0	<1.0	<1.0	<1.0
BDE-99	<1.0	<1.0	<1.0	<1.0	<1.0
BDE-85	<1.0	<1.0	<1.0	<1.0	<1.0
BDE-154	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-153	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-183	<1.0	<1.0	<1.0	<1.0	<1.0
BDE-octa	<2.0	<2.0	<2.0	<2.0	<2.0
BDE-nona	<5.0	<5.0	<5.0	<5.0	<5.0
BDE-209	<25	<25	<25	<25	<25
HBCD	<15	<15	<15	<15	<15
TBBA	<0.5	1.0	<0.5	0.8	0.7
Musk compounds					
DPMI	<2.0	<2.0	<2.0	<2.0	<2.0
ADBI	<2.0	<2.0	<2.0	<2.0	<2.0
AHMI	<2.0	<2.0	<2.0	<2.0	<2.0
MA	<2.0	3.7	<2.0	2.1	<2.0
ATTI	<2.0	<2.0	<2.0	3.1	<2.0
HHCB	12	16	7.0	14	9.6
AHTN	3.9	4.9	<2.0	5.7	3.2
MX	<2.0	<2.0	<2.0	<2.0	<2.0
MM	<2.0	<2.0	<2.0	<2.0	<2.0
MT	<2.0	<2.0	<2.0	<2.0	<2.0
MK	<2.0	<2.0	<2.0	<2.0	<2.0

Appendix 1

Sample code TNO Location (City) Unit	3067-06 Enschede ng/l	3067-07 Zeewolde ng/l	3067-08 Heerlen ng/l	3067-09 Oostkapelle ng/l	3067-10 Pijnacker ng/l
Alkylphenols and ethoxylates					
BPA	<5.0	9.5	<5.0	8.6	64
OP	<5.0	<5.0	<5.0	<5.0	<5.0
NP	47	<40	56	<40	<40
OPEO	68	89	69	50	62
NPEO	154	97	69	137	87
Phthalates					
DMP	162	86	57	25	60
DEP	679	769	284	192	159
DIBP	359	1379	1332	891	368
DBP	497	934	657	402	197
BBP	285	233	427	99	89
DCHP	51	30	15	15	18
DEHP	6940	1989	1761	1812	1819
DPP	<10	<10	<10	<10	<10
DOP	189	124	75	59	61
DINP	5052	4259	1935	2156	2684
DIDP	<100	<100	<100	<100	<100
Flame retardants					
BDE-17	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-28	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-49	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-47	4.8	<1.0	<1.0	<1.0	<1.0
BDE-100	1.3	<1.0	<1.0	<1.0	<1.0
BDE-99	5.4	<1.0	<1.0	<1.0	<1.0
BDE-85	<1.0	<1.0	<1.0	<1.0	<1.0
BDE-154	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-153	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-183	<1.0	<1.0	<1.0	<1.0	<1.0
BDE-octa	<2.0	<2.0	<2.0	<2.0	<2.0
BDE-nona	<5.0	<5.0	<5.0	<5.0	<5.0
BDE-209	<25	<25	<25	<25	<25
HBCD	<15	<15	<15	<15	<15
TBBA	<0.5	<0.5	<0.5	<0.5	<0.5
Musk compounds					
DPMI	<2.0	<2.0	<2.0	<2.0	<2.0
ADB1	<2.0	<2.0	<2.0	<2.0	<2.0
AHMI	<2.0	<2.0	<2.0	<2.0	<2.0
MA	3.1	<2.0	<2.0	<2.0	<2.0
ATTI	<2.0	<2.0	<2.0	<2.0	<2.0
HHCB	20	14	21	9.5	14
AHTN	5.9	19	7.0	2.8	2.4
MX	<2.0	<2.0	<2.0	<2.0	<2.0
MM	<2.0	<2.0	<2.0	<2.0	<2.0
MT	<2.0	<2.0	<2.0	<2.0	<2.0
MK	<2.0	<2.0	<2.0	<2.0	<2.0

Appendix 1

Sample code TNO	3067-11	3067-12	3067-13	3067-14	3067-15
Location (City)	Burgh-Haamstede	Den Hoorn (Texel)	Acquoy	IJlst	Lemmer
Unit	ng/l	ng/l	ng/l	ng/l	ng/l
Alkylphenols and ethoxylates					
BPA	<5.0	<5.0	<5.0	<5.0	<5.0
OP	<5.0	<5.0	<5.0	<5.0	8.4
NP	<40	<40	<40	<40	<40
OPEO	< 30	< 30	74.6	85	< 30
NPEO	42	69	98	90	< 30
Phthalates					
DMP	48	54	49	44	327
DEP	149	137	193	182	132
DIBP	633	479	715	3976	287
DBP	389	303	410	1173	457
BBP	53	114	119	275	41
DCHP	14	36	26	32	13
DEHP	2013	5849	5836	1519	2252
DPP	<10	<10	<10	<10	<10
DOP	58	91	72	77	176
DINP	3699	3654	4704	4412	2569
DIDP	<100	<100	<100	<100	<100
Flame retardants					
BDE-17	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-28	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-49	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-47	2.4	<1.0	<1.0	<1.0	<1.0
BDE-100	<1.0	<1.0	<1.0	<1.0	<1.0
BDE-99	3.0	<1.0	<1.0	<1.0	<1.0
BDE-85	<1.0	<1.0	<1.0	<1.0	<1.0
BDE-154	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-153	1.0	<0.5	<0.5	<0.5	<0.5
BDE-183	2.3	<1.0	<1.0	<1.0	<1.0
BDE-octa	<2.0	<2.0	<2.0	<2.0	<2.0
BDE-nona	<5.0	<5.0	<5.0	<5.0	<5.0
BDE-209	<25	<25	<25	<25	<25
HBCD	<15	<15	<15	<15	<15
TBBA	<0.5	<0.5	<0.5	<0.5	<0.5
Musk compounds					
DPMI	<2.0	<2.0	<2.0	<2.0	<2.0
ADBI	<2.0	<2.0	<2.0	<2.0	<2.0
AHMI	<2.0	<2.0	<2.0	<2.0	<2.0
MA	<2.0	<2.0	<2.0	2.1	7.2
ATTI	<2.0	<2.0	<2.0	<2.0	<2.0
HHCB	12	12	8.0	17	9.6
AHTN	2.6	2.7	<2.0	4.9	2.3
MX	<2.0	<2.0	<2.0	<2.0	<2.0
MM	<2.0	<2.0	<2.0	<2.0	<2.0
MT	<2.0	<2.0	<2.0	<2.0	<2.0
MK	<2.0	<2.0	<2.0	<2.0	<2.0

Appendix 1

Sample code TNO	3067-16	3067-17	3067-18	3067-19	3067-20
Location (City)	Dwingeloo	Borger	Loosdrecht	Winsum	Delden
Unit	ng/l	ng/l	ng/l	ng/l	ng/l
Alkylphenols and ethoxylates					
BPA	<5.0	14	<5.0	<5.0	<5.0
OP	<5.0	<5.0	<5.0	<5.0	<5.0
NP	244	107	<40	<40	<40
OPEO	< 30	< 30	95	43	72
NPEO	< 30	72	100	91	80
Phthalates					
DMP	58	140	48	32	59
DEP	237	2314	462	183	3726
DIBP	1011	1143	2398	795	963
DBP	319	710	1054	420	539
BBP	116	226	261	136	297
DCHP	52	176	34	24	15
DEHP	574	1670	2625	2139	1472
DPP	<10	<10	<10	<10	<10
DOP	39	292	335	228	222
DINP	2399	1682	3171	862	471
DIDP	<100	<100	<100	<100	<100
Flame retardants					
BDE-17	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-28	<0.5	<0.5	17.1	<0.5	<0.5
BDE-49	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-47	<1.0	<1.0	<1.0	<1.0	<1.0
BDE-100	<1.0	<1.0	<1.0	<1.0	<1.0
BDE-99	<1.0	<1.0	<1.0	<1.0	<1.0
BDE-85	<1.0	<1.0	<1.0	<1.0	<1.0
BDE-154	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-153	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-183	<1.0	<1.0	<1.0	<1.0	<1.0
BDE-octa	<2.0	<2.0	<2.0	<2.0	<2.0
BDE-nona	<5.0	<5.0	<5.0	<5.0	<5.0
BDE-209	<25	<25	<25	<25	<25
HBCD	<15	<15	<15	<15	<15
TBBA	<0.5	<0.5	<0.5	<0.5	<0.5
Musk compounds					
DPMI	<2.0	<2.0	<2.0	<2.0	<2.0
ADBI	<2.0	<2.0	<2.0	<2.0	<2.0
AHMI	<2.0	<2.0	<2.0	<2.0	<2.0
MA	<2.0	6.7	<2.0	<2.0	4.4
ATTI	<2.0	<2.0	<2.0	<2.0	<2.0
HHCB	7.6	21	21	7.9	13
AHTN	<2.0	5.6	7.8	2.5	2.8
MX	<2.0	<2.0	<2.0	<2.0	<2.0
MM	<2.0	<2.0	<2.0	<2.0	<2.0
MT	<2.0	<2.0	<2.0	<2.0	<2.0
MK	<2.0	<2.0	<2.0	<2.0	<2.0

Appendix 1

Sample code TNO	3067-21	3067-22	3067-24	3067-25	3067-26
Location (City)	Houten	Hellevoetsluis	Krommenie	Enkhuizen	Vlaardingen
Unit	ng/l	ng/l	ng/l	ng/l	ng/l
Alkylphenols and ethoxylates					
BPA	6.3	41	<5.0	8.5	130
OP	<5.0	<5.0	<5.0	<5.0	<5.0
NP	134	<40	51	83	59
OPEO	93	87	< 30	61	< 30
NPEO	83	146	123	74	56
Phthalates					
DMP	117	56	<10	159	750
DEP	148	235	34	202	4050
DIBP	297	570	367	537	846
DBP	142	399	289	170	837
BBP	37	219	84	15	503
DCHP	<10	15	22	26	50
DEHP	1506	2259	2827	1619	7037
DPP	<10	<10	<10	<10	<10
DOP	64	298	81	130	410
DINP	2635	400	4378	1246	6906
DIDP	<100	<100	<100	1303	8768
Flame retardants					
BDE-17	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-28	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-49	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-47	<1.0	<1.0	7.7	<1.0	<1.0
BDE-100	<1.0	<1.0	2.9	<1.0	<1.0
BDE-99	<1.0	<1.0	8.8	<1.0	<1.0
BDE-85	<1.0	<1.0	<1.0	<1.0	<1.0
BDE-154	<0.5	<0.5	1.0	<0.5	<0.5
BDE-153	<0.5	<0.5	3.9	<0.5	<0.5
BDE-183	<1.0	<1.0	9.5	<1.0	<1.0
BDE-octa	<2.0	<2.0	<2.0	<2.0	<2.0
BDE-nona	<5.0	<5.0	<5.0	<5.0	<5.0
BDE-209	<25	<25	<25	<25	<25
HBCD	<15	<15	<15	<15	<15
TBBA	0.6	<0.5	1.3	<0.5	<0.5
Musk compounds					
DPMI	<2.0	<2.0	<2.0	<2.0	<2.0
ADBI	<2.0	<2.0	<2.0	<2.0	<2.0
AHMI	<2.0	<2.0	<2.0	<2.0	<2.0
MA	2.4	<2.0	<2.0	3.7	12.0
ATTI	<2.0	<2.0	<2.0	<2.0	<2.0
HHCB	7.8	20	15	8.5	17
AHTN	3.3	3.2	4.5	4.0	9.1
MX	<2.0	<2.0	<2.0	<2.0	<2.0
MM	<2.0	<2.0	<2.0	<2.0	<2.0
MT	<2.0	<2.0	<2.0	<2.0	<2.0
MK	<2.0	<2.0	<2.0	<2.0	<2.0

Appendix 1

Sample code TNO	3067-27	3067-28	3067-29	3067-30	3067-31
Location (City)	Coevorden	Den Haag	Capelle a/d IJssel	Utrecht	Amersfoort
Unit	ng/l	ng/l	ng/l	ng/l	ng/l
Alkylphenols and ethoxylates					
BPA	10	<5.0	6.4	9.2	<5.0
OP	<5.0	<5.0	<5.0	<5.0	<5.0
NP	82	<40	<40	<40	49
OPEO	69	30	77	113	59
NPEO	475	47	96	260	90
Phthalates					
DMP	41	32	40	22	<10
DEP	27	39	61	55	28
DIBP	1193	713	910	907	102
DBP	471	804	684	522	323
BBP	165	201	294	221	163
DCHP	21	20	12	27	<10
DEHP	2530	2482	1698	4843	2079
DPP	<10	<10	<10	<10	<10
DOP	380	371	287	357	199
DINP	1746	599	638	5211	540
DIDP	<100	<100	<100	<100	<100
Flame retardants					
BDE-17	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-28	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-49	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-47	<1.0	<1.0	<1.0	<1.0	<1.0
BDE-100	<1.0	<1.0	<1.0	<1.0	<1.0
BDE-99	<1.0	<1.0	<1.0	<1.0	<1.0
BDE-85	<1.0	<1.0	<1.0	<1.0	<1.0
BDE-154	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-153	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-183	<1.0	<1.0	<1.0	<1.0	<1.0
BDE-octa	<2.0	<2.0	<2.0	<2.0	<2.0
BDE-nona	<5.0	<5.0	<5.0	<5.0	<5.0
BDE-209	<25	<25	<25	<25	<25
HBCD	<15	<15	<15	<15	<15
TBBA	<0.5	<0.5	<0.5	<0.5	<0.5
Musk compounds					
DPMI	<2.0	<2.0	<2.0	<2.0	<2.0
ADBI	<2.0	<2.0	<2.0	<2.0	<2.0
AHMI	<2.0	<2.0	<2.0	<2.0	<2.0
MA	<2.0	2.1	<2.0	<2.0	14
ATTI	<2.0	<2.0	<2.0	<2.0	<2.0
HHCB	9.9	20	25	19	12
AHTN	2.8	6.6	5.8	7.9	4.6
MX	<2.0	<2.0	<2.0	<2.0	<2.0
MM	<2.0	<2.0	<2.0	<2.0	<2.0
MT	<2.0	<2.0	<2.0	<2.0	<2.0
MK	<2.0	<2.0	3.4	<2.0	<2.0

Appendix 1

Sample code TNO	3067-32	3067-33	3067-34	3067-35	3067-36
Location (City)	Sleeuwijk	Oostburg	Terneuzen	Eindhoven	Horst
Unit	ng/l	ng/l	ng/l	ng/l	ng/l
Alkylphenols and ethoxylates					
BPA	<5.0	<5.0	<5.0	<5.0	<5.0
OP	<5.0	<5.0	<5.0	<5.0	<5.0
NP	<40	<40	<40	<40	<40
OPEO	< 30	72	71	60	64
NPEO	39	129	168	77	53
Phthalates					
DMP	25	37	24	23	38
DEP	36	29	50	34	44
DIBP	239	826	1254	517	373
DBP	370	791	554	427	221
BBP	60	148	326	117	58
DCHP	10	47	19	18	15
DEHP	8521	1656	3523	2254	3742
DPP	<10	<10	<10	<10	<10
DOP	257	248	330	231	224
DINP	2256	509	740	420	1837
DIDP	<100	<100	<100	<100	<100
Flame retardants					
BDE-17	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-28	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-49	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-47	<1.0	<1.0	<1.0	<1.0	<1.0
BDE-100	<1.0	<1.0	<1.0	<1.0	<1.0
BDE-99	<1.0	<1.0	1.5	<1.0	<1.0
BDE-85	<1.0	<1.0	<1.0	<1.0	<1.0
BDE-154	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-153	<0.5	<0.5	3.7	<0.5	<0.5
BDE-183	<1.0	<1.0	4.8	<1.0	<1.0
BDE-octa	<2.0	<2.0	2.4	<2.0	<2.0
BDE-nona	<5.0	<5.0	<5.0	<5.0	<5.0
BDE-209	<25	<25	<25	<25	<25
HBCD	<15	<15	1835	<15	<15
TBBA	0.7	<0.5	<0.5	<0.5	<0.5
Musk compounds					
DPMI	<2.0	<2.0	<2.0	<2.0	<2.0
ADBI	<2.0	<2.0	<2.0	<2.0	<2.0
AHMI	<2.0	<2.0	<2.0	<2.0	<2.0
MA	2.5	<2.0	<2.0	<2.0	2.5
ATTI	<2.0	<2.0	<2.0	<2.0	<2.0
HHCB	20	9.1	13	9.2	19
AHTN	7.3	<2.0	3.1	2.4	4.1
MX	<2.0	<2.0	<2.0	<2.0	<2.0
MM	<2.0	<2.0	<2.0	<2.0	<2.0
MT	<2.0	<2.0	<2.0	<2.0	<2.0
MK	<2.0	<2.0	<2.0	<2.0	<2.0

Appendix 1

Sample code TNO	3067-37	3067-38	3067-39	3067-40	3067-41
Location (City)	Maastricht	Arnhem	Apeldoorn	Nijverdal	Zwolle
Unit	ng/l	ng/l	ng/l	ng/l	ng/l
Alkylphenols and ethoxylates					
BPA	<5.0	<5.0	<5.0	<5.0	8.0
OP	<5.0	<5.0	<5.0	<5.0	<5.0
NP	<40	<40	<40	<40	<40
OPEO	70	58	41	56	47
NPEO	113	109	31	105	71
Phthalates					
DMP	<10	22	<10	26	23
DEP	230	531	216	598	843
DIBP	<10	178	636	680	205
DBP	232	335	610	538	239
BBP	129	205	135	182	182
DCHP	26	49	113	34	97
DEHP	2903	1820	1638	5202	4810
DPP	<10	<10	<10	<10	<10
DOP	221	191	123	437	424
DINP	629	480	1246	12630	8928
DIDP	<100	<100	<100	<100	<100
Flame retardants					
BDE-17	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-28	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-49	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-47	<1.0	<1.0	<1.0	<1.0	<1.0
BDE-100	<1.0	<1.0	<1.0	<1.0	<1.0
BDE-99	<1.0	<1.0	<1.0	<1.0	<1.0
BDE-85	<1.0	<1.0	<1.0	<1.0	<1.0
BDE-154	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-153	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-183	<1.0	<1.0	<1.0	<1.0	<1.0
BDE-octa	<2.0	<2.0	<2.0	<2.0	<2.0
BDE-nona	<5.0	<5.0	<5.0	<5.0	<5.0
BDE-209	<25	<25	<25	<25	<25
HBCD	<15	<15	<15	<15	<15
TBBA	<0.5	<0.5	1.1	<0.5	<0.5
Musk compounds					
DPMI	<2.0	<2.0	<2.0	<2.0	<2.0
ADBI	<2.0	<2.0	<2.0	<2.0	<2.0
AHMI	<2.0	<2.0	<2.0	<2.0	<2.0
MA	<2.0	<2.0	<2.0	<2.0	3.0
ATTI	<2.0	<2.0	<2.0	<2.0	<2.0
HHCB	14	15	14	9.9	14
AHTN	4.0	4.2	3.6	4.4	4.4
MX	<2.0	<2.0	<2.0	<2.0	<2.0
MM	<2.0	<2.0	<2.0	<2.0	<2.0
MT	<2.0	<2.0	10	<2.0	<2.0
MK	<2.0	<2.0	3.0	<2.0	<2.0

Appendix 1

Sample code TNO Location (City) Unit	3067-42 Buitenpost ng/l	3067-43 Heemstede ng/l	3067-44 Den Haag ng/l	3067-45 Veendam ng/l	3067-46 Coevorden ng/l
Alkylphenols and ethoxylates					
BPA	<5.0	<5.0	6.8	<5.0	<5.0
OP	<5.0	<5.0	<5.0	<5.0	<5.0
NP	<40	42	44	91	141
OPEO	65	< 30	63	69	75
NPEO	73	151	185	63	91
Phthalates					
DMP	27	39	46	<10	23
DEP	14	33	<10	25	36
DIBP	720	988	77	666	2621
DBP	341	714	177	422	881
BBP	71	110	170	127	314
DCHP	20	15	17	19	23
DEHP	2640	4029	1701	1038	1264
DPP	<10	<10	<10	<10	<10
DOP	246	357	173	178	209
DINP	7629	991	551	285	2294
DIDP	<100	<100	<100	<100	<100
Flame retardants					
BDE-17	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-28	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-49	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-47	<1.0	<1.0	<1.0	<1.0	<1.0
BDE-100	<1.0	<1.0	<1.0	<1.0	<1.0
BDE-99	<1.0	<1.0	<1.0	<1.0	<1.0
BDE-85	<1.0	<1.0	<1.0	<1.0	<1.0
BDE-154	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-153	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-183	<1.0	<1.0	<1.0	<1.0	<1.0
BDE-octa	<2.0	<2.0	<2.0	<2.0	<2.0
BDE-nona	<5.0	<5.0	<5.0	<5.0	<5.0
BDE-209	<25	<25	<25	<25	<25
HBCD	<15	<15	<15	<15	<15
TBBA	<0.5	<0.5	<0.5	<0.5	<0.5
Musk compounds					
DPMI	<2.0	<2.0	<2.0	<2.0	<2.0
ADBI	<2.0	<2.0	<2.0	<2.0	<2.0
AHMI	<2.0	<2.0	<2.0	<2.0	<2.0
MA	<2.0	<2.0	<2.0	<2.0	<2.0
ATTI	<2.0	<2.0	<2.0	<2.0	<2.0
HHCB	8.4	13	16	7.2	8.9
AHTN	2.8	4.1	4.8	<2.0	3.4
MX	<2.0	<2.0	<2.0	<2.0	<2.0
MM	<2.0	<2.0	<2.0	<2.0	<2.0
MT	<2.0	<2.0	<2.0	<2.0	<2.0
MK	<2.0	<2.0	<2.0	<2.0	<2.0

Appendix 1

Sample code TNO	3067-48	3067-49	3067-50	3067-51	3067-52
Location (City)	Leidschendam	Vlaardingen	Antwerp (Belgium)	Hamburg (Germany)	Munich (Germany)
Unit	ng/l	ng/l	ng/l	ng/l	ng/l
Alkylphenols and ethoxylates					
BPA	<5.0	<5.0	80	357	<5.0
OP	<5.0	<5.0	<5.0	<5.0	<5.0
NP	<40	<40	95	256	<40
OPEO	78	92	57	98	<30
NPEO	101	924	83	157	<30
Phthalates					
DMP	<10	23	131	99	266
DEP	<10	78	<10	389	1042
DIBP	331	98	206	269	718
DBP	169	182	139	542	337
BBP	133	186	75	896	108
DCHP	13	107	<10	196	<10
DEHP	2633	5035	6265	10530	1522
DPP	<10	<10	<10	<10	<10
DOP	171	388	223	323	105
DINP	521	48290	10903	10269	<100
DIDP	<100	98429	<100	<100	<100
Flame retardants					
BDE-17	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-28	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-49	0.9	<0.5	<0.5	<0.5	<0.5
BDE-47	1.9	1.4	<1.0	8.0	<1.0
BDE-100	<1.0	<1.0	<1.0	<1.0	<1.0
BDE-99	<1.0	<1.0	<1.0	4.9	<1.0
BDE-85	<1.0	<1.0	<1.0	<1.0	<1.0
BDE-154	<0.5	<0.5	<0.5	<0.5	<0.5
BDE-153	<0.5	0.8	<0.5	<0.5	<0.5
BDE-183	<1.0	<1.0	<1.0	<1.0	<1.0
BDE-octa	<2.0	<2.0	<2.0	<2.0	<2.0
BDE-nona	<5.0	<5.0	<5.0	<5.0	<5.0
BDE-209	<25	<25	<25	<25	<25
HBCD	<15	<15	<15	<15	<15
TBBA	2.6	<0.5	<0.5	<0.5	<0.5
Musk compounds					
DPMI	<2.0	<2.0	<2.0	<2.0	147
ADBI	<2.0	<2.0	<2.0	<2.0	4.2
AHMI	<2.0	<2.0	<2.0	<2.0	<2.0
MA	<2.0	9.5	<2.0	14	10
ATTI	<2.0	<2.0	<2.0	4.5	<2.0
HHCB	8.3	14	11	12	13
AHTN	<2.0	4.2	3.5	11	8.5
MX	<2.0	<2.0	<2.0	<2.0	<2.0
MM	<2.0	<2.0	<2.0	<2.0	<2.0
MT	<2.0	<2.0	<2.0	<2.0	<2.0
MK	<2.0	<2.0	<2.0	<2.0	<2.0