8(e) 151665

8EHQ-1002-15166

Great Lakes Chemical Corporation

MR 63117

Myra Karstadt
USEPA
Mail Stop 7403M
OPPT/RAD/SSB
1201 Constitution Avenue NW
Washington DC 20460-001

Contains No CBI

Dear Myra,

Enclosed is the September 2002 report prepared by RIVO (RIVO C033/02), the Dutch Institute for Fisheries Research. This work discussed in this report was the source of the 8(e) information that was reported by the Bromine Science and Environment Forum (BSEF).

Please feel free to contact BSEF or me if you have questions about the work that RIVO performed for BSEF.

Sincerely,

Contain NO CBI

Robert Campbell
Director, Corp. Regulatory Affairs
Great Lakes Chemical Corp.

RECEIVED
OPPT CBIC
02 OCT 24 PM 2:33

8EHQ-02-15166

89030000021

Responsible Care®
A Public Commitment

One Great Lakes Boulevard • P.O. Box 2200 • West Lafayette, IN 47996-2200 USA • Phone (765) 497-6100 • Fax (765) 497-6123
Email: http://www.greatlakeschem.com

C:\WINDOWS\TEMP\HBCD RIVO document

MR 63117

HBCD and TBBP-A in sewage sludge, sediments and biota, including interlaboratory study

J. de Boer, C. Allchin, B. Zegers, J.P. Boon, S.H. Brandsma, S. Morris, A.W. Kruijt, I. van der Veen, J.M. van Hesselingen, J.J.H. Haftka

RIVO rapport nr. C033/02
September 2002

RIVO - Netherlands Institute for Fisheries Research

WAGENINGEN UR

RIVO-Netherlands Institute for Fisheries Research

P.O. Box 68
NL 1970 AB Ymuiden
The Netherlands
Phone: +31 255 564646
Fax: +31 255 564644

P.O. Box 77
NL 4400 AB Yerseke
The Netherlands
Phone: +31 113 672300
Fax: +31 113 573477

Internet:postmaster@rivo.wag-ur.nl

RIVO report

Number: C033/02

HBCD and TBBP-A in sewage sludge, sediments and biota, including interlaboratory study

J. de Boer, C. Allchin, B. Zegers, J.P. Boon, S.H. Brandsma, S. Morris, A.W. Kruijt, I. van der Veen, J.M. van Hesselingen, J.J.H. Haftka

Commissioned by: Bromine Science Environmental Forum
Burson-Marsteller
Avenue de Corthenbergh 118
B-1000 Brussels
Belgium

Project number: 76001.91

Contract number: 01/060

Approved by: dr J. de Boer
Head Department Environment and Food Safety

Signature:

Date: 2 September 2002

Number of copies: 25
Number of pages: 40
Number of tables: 5
Number of figures: 8
Number of annexes: 6

Since the first of June 1999 the foundation DLO (Agricultural Research Department) is no longer part of the Ministry of Agriculture, Nature Management and Fisheries. We are registered in trade register of the Chamber of Commerce Centraal Amsterdam nr. 34135929 VAT nr. NL 808932184B09

The management of the RIVO-Netherlands Institute for Fisheries Research accepts no responsibility for the follow-up damage as well as detriment originating from the application of operational results, or other data acquired from the RIVO-Netherlands Institute for Fisheries Research from third party risks in connection with this application.

This report is drafted at the request of the commissioner indicated above and is his property. Nothing from this report may be reproduced and/or published by print, photoprint microfilm or any other means without the previous written consent from the commissioner of the study.

Table of Contents:

Table of Contents: 2

Executive summary 4

Conclusions 5

Recommendations 6

1. Introduction 7

2. Objectives 9

3. Methods and materials 10

3.1 Analytical methods 10

3.2 Materials 10

4. Work package 1 – Method development 11

4.1 HBCD and TBBP-A analysis by LC-MS at CEFAS 11

4.2 HBCD analysis by LC/MS at NIOZ 11

4.3 HBCD and TBBP-A analysis by LC/MS at RIVO. 12

4.4 Extraction and clean-up optimisation at CEFAS 13

4.5 Extraction and clean-up optimisation at NIOZ 13

4.5.1 Extraction 13

4.5.2 Determination of lipid content biota samples 14

4.5.3 Treatment with sulphuric acid 14

4.5.4 Silica column chromatography 14

4.5.5 Pre-treatment for TBBP-A analysis 14

4.6 Extraction and clean-up optimisation at RIVO 16

4.7 GC/MS analysis at NIOZ 17

4.8 GC/MS analysis at RIVO 18

4.9. Comparison of results 18

4.10 Discussion 19

5. Work package 2 - Scheldt Basin Study 21

5.1 Total HBCD in eel 21

5.2 Total HBCD in sediment 21

5.3 TBBP-A and MeTBBP-A in eel and sediment 22

5.4 HBCD isomer ratios 22

6. Work package 3 – Sewage Sludge and Landfill Study 25

6.1 Total HBCD, TBBP-A and PBDEs in Dutch STPs 25
6.2 Total HBCD and TBBP-A in UK and Irish STPs 25
6.3 HBCD ratios 26
6.4 Landfill study 26

7. Work package 4 –North Sea and river sediments and biota 28

7.1 North Sea food chain 28
7.1.1 Invertebrates and fish 28
7.1.2 Marine mammals 28
7.1.3 Discussion 29
7.1.4 HBCD isomer ratios 29
7.1.5 HBCD in relation to other contaminants 30

7.2 Tees food chain and other UK samples 32
7.2.1 Cormorant livers 32
7.2.2 Porpoise blubber 32
7.2.3 Sediment from UK rivers 33
7.2.3 Miscellaneous 34

7.3 Western Scheldt food chain and other Dutch samples 35
7.3.1 Western Scheldt food chain 35
7.3.2 Western Scheldt sediments 35
7.3.3 Dutch rivers: eel and sediment 36
7.3.4 Dublin Bay 36
7.3.5 Cod liver 36

8. Work Package 5 – Interlaboratory Study 38

9. Acknowledgements 39

10. References 40

Executive summary

Indicative studies had shown that relatively high levels of hexabromocylcododecane (HBCD) could be present in Dutch river sediments and biota. HBCD is used in upholstery textiles and polystyrene foams (e.g. for roof isolation). It was supposed that losses during the impregnation of the flame retardant in these materials would be the cause of environmentally detectable amounts of HBCD. A study on the occurrence of HBCD in sewage sludge, sediments and biota was carried out in order to trace possible sources of HBCD, to study the behaviour of HBCD in sewage treatment plants (STPs), and to study the distribution of HBCD in the aquatic environment. In addition to HBCD, tetrabromobisphenol-A (TBBP-A) and its dimethyl derivative (MeTBBP-A) were analysed as well. Occasionally, also polybrominated diphenyl ether (PBDE) concentrations were measured. The study consisted of four sub-projects: i) a method development part, ii) a study on the distribution of HBCD and TBBP-A in the river Scheldt basin in Belgium, iii) a study on the occurrence of HBCD and TBBP-A in sewage treatment plants and landfills, and iv) a study on the levels of HBCD and TBBP-A in various food chains and rivers and North Sea sediments. In addition to these parts and as a separate project, an interlaboratory study on HBCD, TBBP-A, MeTBBP-A and PBDEs was organised. The results of the first four parts are described in this report. The interlaboratory study will be reported separately.

As regards the sampling plan and the analyses, the project has been very successful. Almost all samples planned could be taken. This sampling process was facilitated through the kind collaboration with a number of colleague institutes throughout the world, for which we are very grateful. Some delay was encountered in the method development phase. At the start of the project, methods for HBCD and TBBP-A analysis in environmental samples were neither available in the group of research institutes in charge of this project, nor in the literature. HBCD consists of three different diastereomers (often just called, although not completely correct, isomers). At temperatures above 160-190°C thermal rearrangements can take place. That means that a gas chromatographic (GC) method may be prone to errors as regards the quantification of the total HBCD concentration. A GC separation of the three diastereomers is, at the current state-of-the-art not possible. As it was expected that certain industrial processes applied by the users of HBCD would result in a different isomer profile than that in the technical HBCD mixture, it was highly desirable for this project to develop an high performance liquid chromatographic (HPLC) method for the isomer-specific determination of HBCD. Consequently, a block of time was reserved for the development of methods, including an entire new method for the isomer specific analysis of HBCD. Because more difficulties than expected were met in this phase, the project was delayed by ca. 6 weeks. Apart from this delay, which seems very acceptable given the substantial risk factor of this part of the project, the progress was good and a large and consistent data set has been obtained, from which a lot can be learned about the occurrence and behaviour of HBCD and TBBP-A in the aquatic environment.

Conclusions

1. The analysis of a large set of various biota – invertebrates, fishes, birds, marine mammals – showed that HBCD can easily bioaccumualte and biomagnify through various food chains. Substantial HBCD concentrations were found in cormorants and harbour porpoises, as well as in seals and common tern eggs. HBCD concentrations were sometimes comparable to or even higher than those of polychlorinated biphenyls (PCBs). The predominant isomer in biota was α-HBCD.
2. A set of methods has been developed for the analysis of total HBCD, TBBP-A and MeTBBP-A by GC/MS and HBCD isomers by LC/MS. These methods are of sufficient quality to be used in studies on the environmental occurrence of these compounds. Further optimisation will be possible by further interlaboratory studies and use of certified reference materials of biota and sediments as soon as these would become available.
3. Total-HBCD patterns in eel and sediment from the Scheldt basin are in good agreement. At least two sources of HBCD have been identified: in the Scheldt near Oudenaarde and in the Leie near St. Martens. Furthermore, elevated HBCD concentrations were found in the Antwerp harbour.
4. In all sediment samples of the Scheldt basin analysed γ-HBCD is the highest in concentration. Often, none of the other isomers was found. However, at the two locations with the highest total HBCD concentrations, Scheldt, Oudenaarde and Leie, St. Martens also α-HBCD, and in the case of Oudenaarde, also β-HBCD was found in somewhat elevated amounts, ca. 25% of γ-HBCD, whereas otherwise the α-HBCD was less than 10% of γ-HBCD.
5. The Western Scheldt sediment analyses confirm the presence of HBCD in Antwerp harbour, but also reveal an input of HBCD around Terneuzen. This may include that the environmental presence of HBCD is caused by both the textile industry as well as by the manufacturers of HBCD.
6. The presence of α-HBCD and/or β-HBCD in eel does not give information on the presence of specific industries. That presence can be caused by a selective excretion of γ-HBCD. Metabolisation in the organism which would transfer α-HBCD into γ-HBCD is less likely, as no literature on such processes is available.
7. HBCD was found in substantial amounts in various sewage treatment plants (STPs) from The Netherlands, UK and Ireland. The HBCD concentrations in the samples from the UK and particularly in those from Ireland (up to 8.3 mg/kg d.w.) are considerably higher than in those from The Netherlands.
8. In case higher total HBCD concentrations were found in sewage treatment plants, α-HBCD is either the dominant isomer or it is present in substantial amounts, almost equal to those of γ-HBCD.
9. HBCD, TBBP-A and MeTBBP-A were absent in all landfill samples from the UK and Ireland. However, in Dutch landfill samples these compounds were found. Exceptionally high HBCD concentrations were found in two landfills, up to 68 mg/kg dry weight.
10. HBCD was found in all sediments of UK rivers. The highest concentrations were found in the river Skerne. γ-HBCD was normally the predominant isomer. However, in the river Mersey a deviating isomer profile was found with mainly β-HBCD, which possibly points to a specific application of HBCD.
11. HBCD is found in all Dutch river sediment and eel samples. The HBCD concentrations in the river Rhine basin are higher than those in the river Meuse.
12. HBCD is found in substantial concentrations in the Dublin Bay, Ireland. In addition to that, also substantial amounts of decaBDE were found. Also BDE183 was found, indicating the use of the octaBDE mix in Ireland.
13. HBCD was found in cod liver from the Central North Sea but not in southern North Sea cod liver and hake liver from the Atlantic. This may indicate a possible HBCD input from the UK East Coast. However, the sample numbers were too small for a more definitive conclusion.
14. TBBP-A was almost in all cases found in much lower concentrations than HBCD, as well as in biota as in sediments. In some cases it was found in the dissolved phase of the influent of some UK STPs. The lower TBBP-A concentrations in sediments may be explained by the

way TBBP-A is used as a flame retardant, i.e. as a reactive compound, whereas HBCD is used as an additive flame retardant. TBBP-A will therefore be stronger bound and less easily leave the matrix in which it has been used. The more polar character of TBBP-A limits its bioaccumulation potential. Also, easier excretion mechanisms in biota and possible degradation mechanisms may explain the lower TBBP-A concentrations in biota, since the phenolic group of TBBP-A allows conjugation to endogenous compounds (e.g. glucoronic acid and sulfate) without the necessity of any phase-I biotransfomation prior to it.

15. The MeTBBP-A concentrations were generally low, but its bioaccumulation potential is higher than that of TBBP-A.

Recommendations

Based on the results of this report, the following recommendations can be made.

1. This report contains the first substantial data set on HBCD. In relation with a possible further risk assessment of HBCD the HBCD in the aquatic environment, and in particularly in aquatic biota, should be followed closely. Given its high potential for bioaccumulation, it may be expected that HBCD will be qualified by authorities as an undesired chemical.
2. A further study on the uptake of HBCD diastereomers by biota and possible biotransformation mechanisms of HBCD in relation to the toxicity of the specific isomers will result in a better understanding of the risks of HBCD.
3. The isomeric profile of HBCD in various textiles should be analysed for a better understanding of the HBCD concentrations in sewage treatment plants.
4. A more detailed study of landfills may be helpful to understand possible losses of HBCD to the aquatic environment.
5. More information on temporal trends of HBCD (and its diastereomers) is needed, and could be obtained from sediment core studies and analyses of older biota samples.
6. A confirmation of the higher HBCD concentrations in Irish STPs is desirable.
7. A further study on the specific HBCD isomer profile found in sediment from the river Mersey could help to achieve a better understanding of the behaviour of HBCD in the environment.
8. Although MeTBBP-A concentrations found were relatively low compared to HBCD, further study of the behaviour of MeTBBP-A should also be considered as it may be possible that biotransformation would lead to a mono-methylated TBBP-A that could show a strong thyroid binding.

1. Introduction

The BSEF study on polybrominated diphenylethers (PBDEs) in the aquatic environment (de Boer et al., 2001) has resulted in the indicative observation of the environmental presence of hexabromocyclododecane (HBCD). It was shown that relatively high levels could be present in Dutch river sediments, among which the Western Scheldt, and in biota. HBCD is used in upholstery textiles and polystyrene foams (e.g. for roof isolation). It was supposed that losses during the impregnation of the flame retardant in these materials would be the cause of environmentally detectable amounts of HBCD. To trace the sources of this HBCD contamination, more samples from further upstream the Scheldt in Belgium, where a high density of textile industries is found, would be relevant to study. In the literature some indications have been found on the passage of PBDEs and possibly also of HBCD through sewage treatment plants (STPs). A further confirmation of these observations is required. Therefore, a sampling of a number of STPs in The Netherlands, UK and Ireland was proposed. Also, landfills may be a possible source of HBCD contamination. Therefore, leachates of landfills were proposed to study as well. For cost-effective reasons, tetrabromobisphenol-A (TBBP-A) and, if not measured already in the same samples, a number of PBDE congeners could also be included.

As a number of biological and sediment samples were still available at RIVO, NIOZ and CEFAS after use for PBDE analysis in the previous BSEF project on PBDEs in the aquatic environment (de Boer et al., 2001a), a selection of these samples could be analysed for a screening of HBCD and TBBP-A concentrations in the marine environment (mainly North Sea) and several freshwater locations in The Netherlands and the UK.

Finally, a project entitled "Study on HBCD and TBBP-A in sewage sludge, sediments and biota, including interlaboratory study" was proposed by The Netherlands Institute for Fisheries Research (RIVO) to the Bromine Science and Environmental Forum (BSEF) and accepted.

HBCD and tetrabromobisphenol-A (TBBP-A), including the dimethylated version of TBBP-A (MeTBBP-A), possibly a metabolite, can be analysed by GC/mass spectrometry (MS). The extraction and clean-up show similarities with the methods used for the analysis of polybrominated diphenylethers (PBDEs). However, given the higher polarity of TBBP-A, it is essential to adapt the clean-up and/or fractionation, most likely by increasing the elution volume in the last fraction from the silica columns. Other small modifications are also required. In addition, it seemed to be relevant to carry out an isomer-specific determination of HBCD, including the α,β, γ–isomers. HBCD consists of three different diastereomers (often just called, although not completely correct, isomers). Literature from the industry (Peled et al.) showed at high temperatures (above 160-190°C), thermal rearrangements of these diastereomers can occur. Consequently, a gas chromatographic (GC) method may be prone to errors as regards the quantification of the total HBCD concentration. A GC separation of the three diastereomers is, at the current state-of-the-art not possible. As it was expected that certain industrial processes applied by the users of HBCD would result in a different isomer profile than that in the technical HBCD mixture, it was highly desirable for this project to develop an high performance liquid chromatographic (HPLC) method for the isomer-specific determination of HBCD. LC/MS rather than GC/MS may be the method of choice for such a determination. Technical HBCD normally consists of mainly γ-HBCD. Due to high temperatures used in various impregnation processes, γ-HBCD may undergo rearrangement and be transformed into α-HBCD and/or β-HBCD. It was supposed by BSEF that identification of α or β-HBCD in the environment could possibly point to losses of HBCD caused by users rather than by producers.
Consequently, a method development part with emphasis on an isomer-specific HBCD determination was included in this study. Such an isomer-specific method could be helpful in the identification of sources.

A growing number of laboratories have started to work on environmental brominated flame retardant analysis. Initially, PBDEs were the main determinands. However, nowadays

laboratories are setting up analytical methods for HBCD and TBBP-A as well. Therefore, it was proposed to organise an interlaboratory study on these two compounds. Such a study could easily be combined with a follow-up of the successful interlaboratory study on PBDEs, which was held between November 1999 and April 2000. In the report on that study the advice was given to focus on the improvement of the BDE 99 and BDE 209 analysis in a second round. The analysis of these two BDEs, plus the BDEs 28, 47, 100, 153, 154, and 183 was combined with the analysis of HBCD and TBBP-A.

This project has been carried out by RIVO, and its partners NIOZ (Netherlands Institute for Sea Research), Texel, The Netherlands, and CEFAS (Center for Environment, Fisheries and Aquaculture Sciences), Burnham on Crouch, UK.

2. Objectives

The objectives of this study are the following:

To analyse concentrations of HBCD, TBBP-A, dimethyl TBBP-A, and some PBDE congeners in:

i) in eel and sediments from the Scheldt basin (Belgium),

ii) sewage sludges and landfill leachates from The Netherlands, the UK an Ireland,

iii) sediments and biota from The Netherlands, the UK an Ireland, including the North Sea,

in order to trace possible sources of HBCD, to study the behaviour of HBCD in sewage treatment plants (STPs), and to study the environmental distribution of HBCD, and

To organise an interlaboratory study on the analysis of HBCD, TBBP-A, and PBDEs with an aim to come to a standardisation of methods for HBCD and TBBP-A analysis.

3. Methods and materials

3.1 Analytical methods

Method development is a part of this project and is discussed under work package 1. Essentially, the available methods for PBDE analysis (de Boer et al., 2001b) have been adapted to enable the analysis of HBCD, TBBP-A and Me-TBBP-A. In addition, isomer-specific methods for the determination of HBCD have been developed. All methods are described under work package 1 (chapter 4).

3.2 Materials

Annexes 1.1 and 1.2 show maps of the Scheldt basin, including the sampling locations for eel and sediments, taken by the Institute for Forestry and Nature Management, Hoeilaart, Belgium. Annex 1.3 shows a map of The Netherlands, indicating the sampling locations samples of eel. Annex 1.4 show the same map, but with the sediment sampling locations. Annex 1.5 shows a map of Western Scheldt sampling locations. The rivers used for sampling have been indicated. These locations are identical to a selection of those sampled for the previous study on PBDEs (de Boer et al., 2001a). Annex 1.6 shows a map of the Dublin Bay. The result of the various sampling campaigns is very satisfying. Almost all samples that were planned for this project have been obtained. The STP and landfill samples from The Netherlands were sampled in the spring of 2002, which was later than originally planned. This was due to unexpected obligations of staff at the Institute for Inland Water Management and Waste Water Treatment. Annex 2 shows the rivers in the UK and Ireland, which have been used for sampling (in 1999). Relevant sample data for the samples analysed in work package 4 have been given in the previous PBDE report (de Boer et al., 2001a). Apart from the marine mammal samples and common tern eggs, all samples were pooled samples. Sediment samples were composed of 10 sub-samples of surface sediment taken by a Van Veen type of sampler and pooled at the location. Most fish samples consist of a pool of 25 individual fishes; equal parts from the back-side of the fish were collected and pooled. The eel samples from the river Scheldt were pooled samples of ca. 10 eels (tail-ends).

4. Work package 1 – Method development

Although HBCD and TBBP-A have been previously studied the literature is very sparse. The analytical methodology has been generally based on GC-ECD or GC-MS techniques. HBCD invariably has been determined without resolution of the individual isomers. HBCD has frequently been determined with PBDEs using GC/NCI-MS. Although this is a sensitive and demonstrably robust method for the determination of PBDEs, HBCD (as a mixture of isomers) is thermally labile and can undergo rearrangements within the injection port or the column oven at elevated temperatures, resulting to poor chromatographic performance. Co-elution, or partial co-elution, can also be a problem when HBCD and PBDEs are determined together especially if, as is commonly the case, only the bromine ion responses at m/z 79 & 81 are monitored. TBBP-A has only been determined by GC, sometimes after derivatisation to form a more stable compound than the parent compound at typical GC temperatures which is time consuming, and, once again co-elution can be a problem.

Consequently, it was decided to develop isomer-specific methods by LC/MS at all three institutes involved in this study: RIVO, CEFAS and NIOZ. Total HBCD and TBBP-A analysis by GC/NCI-MS were also carried out at RIVO and NIOZ. In addition, experiments were carried out at the three institutes to improve and optimise the extraction and clean-up for HBCD and TBBP-A analysis, starting from the existing methods for PBDEs (de Boer et al, 2001b). A final comparison of the developed methods took place during the interlaboratory study, which was part of this project.

4.1 HBCD and TBBP-A analysis by LC-MS at CEFAS

The developed LC-ESI-SIM-MS method at CEFAS uses gradient elution techniques to separate the HBCD isomers and determine the primary ion at m/z 640 $[M - H]^-$ and a useful, secondary confirmatory ion at m/z 676 $[M-H+2H_2O]^-$ or $[M+Cl]^-$. Under the same LC conditions TBBP-A at m/z 541 & 543 and dimethyl TBBP-A at m/z 573 & 571 can also be determined. Examples of standard chromatograms and sample extracts are shown in Annexes 2.1-2.3.

The absolute detection limit for both HBCD and TBBP-A on column is around 1 ng, which is considerably better than achieved using APCI at around 10 ng, although the sensitivity for DM-TBBP-A is currently less good. The use of advanced MS-MS techniques rather than the use of a single quadrupole instrument, may further enhance sensitivity.

This method was used to analyse the UK and Irish STP and landfill samples, the UK river sediment samples, and the UK river sediment and food chain samples.

4.2 HBCD analysis by LC/MS at NIOZ

It was possible to separate the isomers in a standard solution on a Hypersil C18 column. HPLC Conditions: Column: Column 150 * 2.1mm Zorbax Eclipse XDB-C18 3.5 µm; eluent: 0.3 ml/min gradient elution with methanol-water; inj. vol: 20 µl. The MS-settings (Hewlett-Packard) were optimised in order to monitor the parent ions (640.7 and 641.7 m/z). Therefore, very mild conditions had to be chosen, see Figure 4.1. (MSD settings: APCI Negative; Gas Temp: 250 C; Vaporiser: 300°C; Drying Gas: 6 L/min; Neb. pressure: 60 psig; V_{cap}: 3000 V; Corona: 40 µA; Fragmentator Ramp: *100,20; 1800,90* (*Mass, Value*)). The HBCD was quantified by using calibration lines of the different HBCD-isomers. The response of CB-112 (internal standard) was used to correct for recovery.

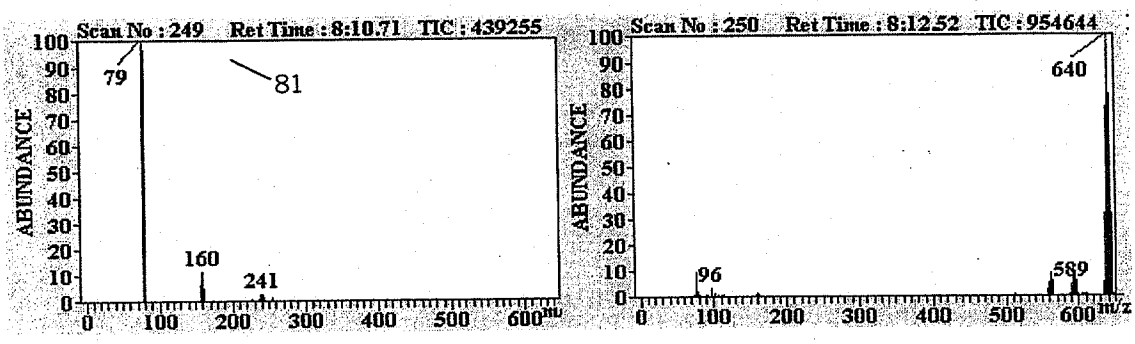


Figure 4.1: The effect of variation of the fragmentator ramp on the formation of ions in the mass-spectrometer. In the left spectrum only bromine and bromine clusters can be seen (fragmentor ramp 100,90; 1800,350) while on the right the parent ion cluster (M-1) and the (M-1-Br) cluster can clearly be seen (fragmentor ramp 100,20; 1800,90).

This method was used for the analysis of North Sea food chain samples, and the Scheldt sediment and eel samples.

4.3 HBCD and TBBP-A analysis by LC/MS at RIVO.

An LC-MS method was developed for the separation en determination of the HBCD isomers. It was possible to separate the HBCD isomers in a MeOH solution on a 2.1 x 150 mm Zorbax Eclipse XDB-C18 3.5 µm column. The injection volume was 20 µl. The gradient used is given in Table 4.1.

Table 4.1 LC gradient used at RIVO.

Time (min)	H_2O	MeOH	ACN	Flow (µl/min)
0	50	50	0	300
7	50	50	0	300
7.1	10	90	0	300
28	10	90	0	300
28.1	0	0	100	300
60	0	0	100	300
60.1	50	50	0	300
74	50	50	0	300

The mass-spectrometer used was an LCQ-advantage. The interface used was an ESI-interface because the detection limit with ESI is between 2-4 pg/µl as the detection limit for APCI is 10 ng. The α-HBCD en the γ-HBCD isomers give a strong signal at m/z 716.7 and a less strong signal at m/z 676.7 $[M-H + 2H_2O]^-$ or $[M+Cl]^-$. The β-HBCD isomer gives a strong signal at m/z 700.7 and a less strong signal at m/z 676.7 $[M-H + 2H_2O]^-$ or $[M+Cl]^-$ and m/z 716.7 The masses 700.7 and 716.7 are most likely Na and K adducts.

The optimised mass-spectrometer-settings for these m/z are:
ESI negative

Probe setting: A4
Sheath gas: 55
Auxiliary gas: 0
Source Voltage: 4.5 kV
Source Current 80 µA
Capillary Temperature: 135°C
Capillary Voltage: -4 V
Tube lens Offset Voltage: -60 V
Multipole 1 Offset Voltage: 4 V
Lens Voltage: 14 V
Multipole 2 Offset Voltage: 5.5 V
Scan Range: 630-1500
Number of Microscans: 3
Max Ion Injection Time: 200 ms

With every series of samples a complete calibration curve was injected because the area of the standards could vary by day. The relative standard deviation of the concentrations found in a reference sample measured at four different days is 6.6 %.

In some samples there were some other components co-eluting with β–HBCD which made it difficult to quantify β-HBCD. For this reason separation of the isomers at another column should be tried. Also, the effect of matrix on retention times should be tested, because retention times in some samples are shifted comparing to retention times in standards.

This method was used for the analysis of the Dutch STP and landfill samples, the Dutch river sediment and eel samples, the Western Scheldt food chain samples, some North Sea food chain samples and a number of Scheldt eel and sediment samples.

4.4 Extraction and clean-up optimisation at CEFAS

Both HBCD and TBBP-A are amenable to classic extraction techniques used for the routine measurement of other organohalogen compounds. Soxhlet extraction was used for it's simplicity and cheapness and used mixtures of solvents e.g. acetone/hexane to extract the samples.

Although HBCD can be recovered from adsorption columns utilising alumina and silica, the use of high solvent volumes and high polarity solvents to achieve this restricts it's usefulness. GPC is a viable option, but was not available for this work. Instead, a simple clean-up technique based on the use of sulphuric acid was utilised. The reported variable recoveries for TBBP-A using this technique were offset by the use of ^{13}C labelled TBBP-A surrogate standard. HBCD recoveries were quantitative.

4.5 Extraction and clean-up optimisation at NIOZ

4.5.1 Extraction

The method for biota samples is based on an Ultra Turrax extraction. Before extraction, the samples are homogenised and the brown 'amber' glassware is washed with hexane to remove impurities. Specifically, the amber glassware is employed to prevent breakdown of the more highly brominated BDEs by UV-light. The exact amount of sample to be weighed in has to be equal to about 100 mg of lipid and is therefore dependent on a predetermined lipid percentage. The sample is transferred to a centrifuge tube and internal standards (CB-112 and BB-209) are

added for quantification. One spatula of sodium chloride is added to facilitate phase separation. The sample is extracted with an automated device (Ultra Turrax, Model T25, IKA-Labortechnik, Germany) which adds the solvents and stirs for one minute at a speed of 13,000 rpm with an Ultra Turrax in between the additions. The solvents are consecutively added to the sample, in the order: acetone, pentane and bidistilled water. After the mixture is thoroughly mixed, the centrifugation tube is centrifuged for 15 minutes at 2500 rpm (Centaur 1, Abcoude, Holland). The upper pentane layer is subsequently removed and used for further treatment.

4.5.2 Determination of lipid content biota samples

The pentane layer is transferred via a capillary pipette with 2 cm of sodium sulphate (Na_2SO_4) onto a pre-weighed petri dish. Na_2SO_4 is used to remove residual water present in the sample. The Na_2SO_4 is washed with 2 ml of DCM to desorb any remaining molecules. The sample is evaporated on a water bath at a temperature of 70 °C and moved to a dry-oven (10 minutes at 60 °C). After cooling down the sample in an exsiccator, the lipid content is gravimetrically determined. The lipids are subsequently redissolved in pentane into amber tubes for further treatment.

4.5.3 Treatment with sulphuric acid

The tubes are cooled in ice and 2 ml of concentrated sulphuric acid (97%) is added. The tube is gently shaken and the sulphuric acid is allowed to react for about one hour at room temperature. The bottom layer (sulphuric acid) is removed, a new portion of 2 ml of sulphuric acid is added and the mixture is left to react overnight. After collecting the pentane layer in a test tube, the solution is neutralised with 5 ml of a $NaHCO_3$-buffer (pH 8). Finally, 500 µl of TMP is added and the pentane layer is removed and evaporated on a waterbath (70°C).

4.5.4 Silica column chromatography

The concentrated solution is transferred to a column with 2 grams of silica (deactivated with 6% water) with 2 cm of Na_2SO_4 on top. The column is eluted with 17 ml of pentane, which is sufficient to retrieve all the BDE-congeners up to BDE-209. After evaporation of the pentane on a waterbath (70°C), the sample is concentrated to 1 ml of TMP. The sample can be directly measured with GC-MS. The concentrations are quantified using external (BDE-congeners) and internal standards (CB-112 and BB-209).

4.5.5 Pre-treatment for TBBP-A analysis

The pre-treatment of the samples for the analysis of TBBP-A, MeTBBP-A and HBCD poses a few problems before final determination with GC-MS. The more polar TBBP-A can dissociate at a relatively high pH while the two other compounds show strong retention on the silica column. Also, the different stereoisomers (α, β and γ) of HBCD each show different properties. Therefore, the different steps in the pre-treatment were looked upon in a number of experiments to adequately measure these compounds with a sufficiently high recovery. Below, only the modifications implemented in the PBDE analysis for the correct analysis of TBBP-A, Me_2TBBP-A and HBCD in environmental samples will be given. The consecutive steps undertaken to reach a suitable method will be discussed in the results.

In the adjusted method, the pH of the water solution is controlled by using phosphate buffered solutions. After the sulphuric acid treatment, fractionation over a basic medium takes place that causes TBBP-A along with a ^{13}C-labelled internal standard of TBBP-A to ionise. The compounds are therefore able to fractionate in a basic water solution. After lowering the pH, the compounds can be redissolved in pentane. The volume and the solvent composition in the silica clean-up have been adjusted to resolve the β-isomer of HBCD completely from the silica.

The biota and sediment samples are weighed in a centrifugation tube and an Erlenmeyer, respectively. Internal standards are added, CB-112 for MeTBBP-A and HBCD, and a ^{13}C-labelled TBBP-A standard for the quantification of TBBP-A. The samples are extracted in the same way with the Ultra Turrax for the biota samples and the shake-flask method for the sediment samples. Control of the pH of the added water solution is achieved with the use of a 25 mM phosphate buffered solution of pH 6 to prevent losses of TBBP-A to the water phase when the pH gets too high. After transferring the pentane layer to a test tube, the pH is checked for neutrality with pH-paper. The lipid and water content was not determined in the samples as these data were already known from BDE-analyses with the same samples. After the sulphuric acid treatment, the pentane layer is mixed with 5 ml of a 100 mM phosphate buffered solution of pH 11 to fractionate the TBBP-A, which is ionised at high pH, quantitatively to the aqueous layer. Under these circumstances only TBBP-A partitions into the aqueous layer, whereas the other brominated flame retardants of interest (PBDEs, MeTBBP-A and HBCD isomers) still partition quantitatively into the organic layer.

The pentane layer is then transferred to a new test tube and after addition of 150 µl iso-octane, the pentane is evaporated on a water bath (70 °C). Subsequently, the concentrated solution is cleaned over a silica column with 2 cm of Na_2SO_4 on top. The column is eluted with 30 ml of a 85:15 pentane-diethylether mixture. After evaporation of the pentane on a waterbath, the solution is concentrated to 1 ml iso-octane and is analysed with GC-MS.

Next, the basic aqueous layer is mixed with 5 ml of pentane and 10 ml of 250 mM phosphate buffered solution of pH 6 to neutralise TBBP-A. After separation, the acidification of the aqueous layer makes it possible to back-extract the TBBP-A into the organic phase. The pH is again checked for neutrality with pH-paper. The pentane layer is subsequently transferred to a new test tube, 200 µl iso-octane is added and the pentane is evaporated on a waterbath (70°C). Finally, after concentrating the solution to 1 ml of iso-octane, the sample can be directly analysed with GC-MS without further clean-up.

In Figure 4.2. the different steps are shown for the pre-treatment of samples in the analysis of the different brominated compounds.

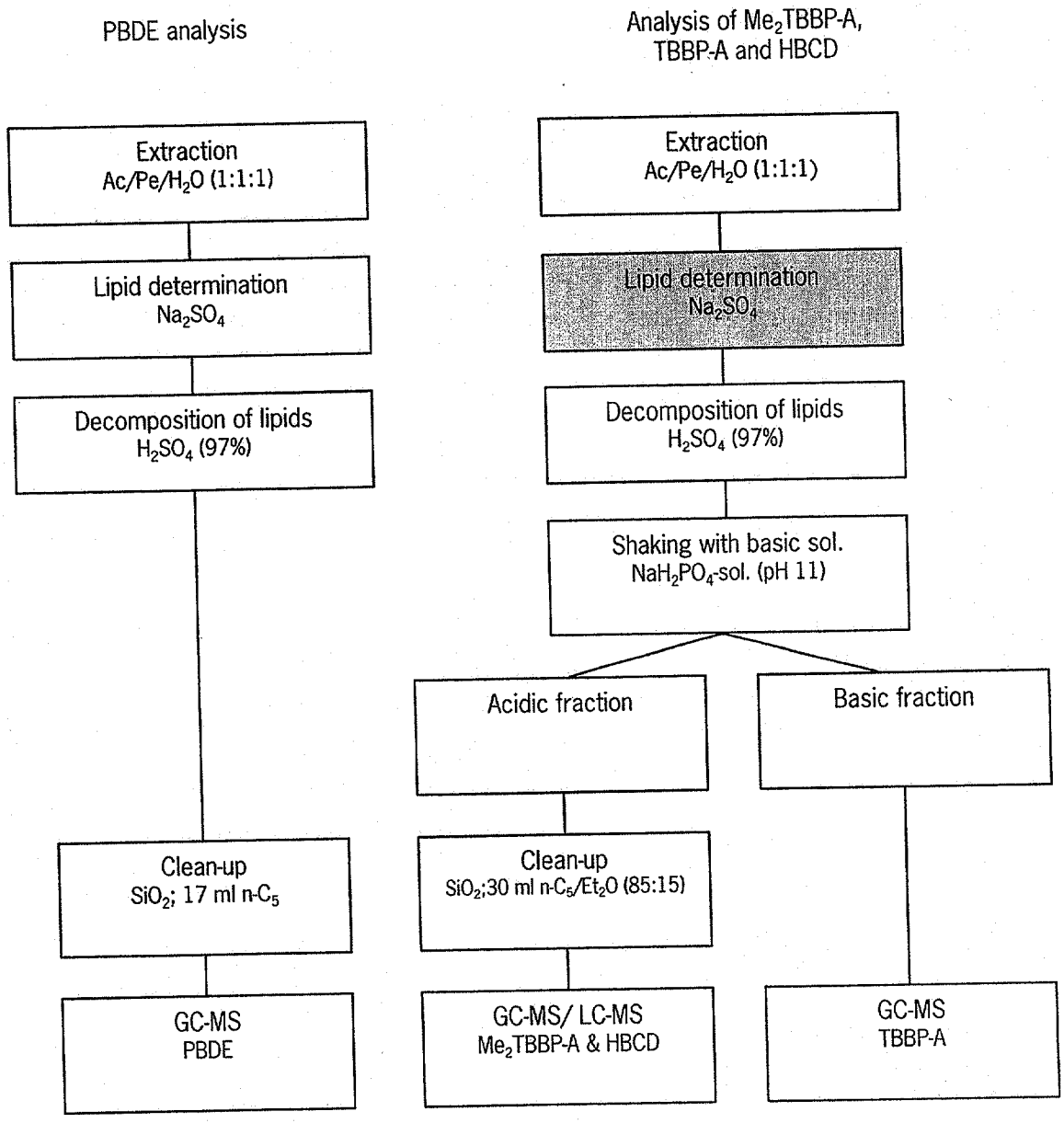


Figure 4.2: Procedures of the pre-treatment of samples for the analysis of PBDEs and for the modified analysis of TBBP-A, MeTBBP-A and HBCD. The lipid determination has not been performed in the adapted method (shaded part) as these data were already known.

4.6 Extraction and clean-up optimisation at RIVO

The RIVO method was based on a 6 – 12 h Soxhlet extraction (extraction time is dependent on the sample size and the volume of the equipment used). A combination of *n*-hexane and acetone (3:1 v/v) was chosen, as a 1:1 mixture yielded too much co-extracted water.
In the RIVO method, the extract is firstly shaken with sulphuric acid (pH=2) to prevent that TBBP-A is removed from the solution when dried with sodiumsulphate. After drying with sodiumsulphate, the extract is transferred to a GPC system with two PL gel columns in series in which the eluent is dichloromethane. The conditions used are as follows:

Piston pump: Gilson 305 and syringe pump: Gilson 402
Manometric module: Gilson 805 and sampling injector: Gilson 231 XL
Column cooler: Julabo FE-500 (water cooling at 18°C)
Fraction collector: ISCO Foxy-200
Automated switching valve: Waters ASV 003492
Degassing: helium (99.995%), 0.2 bar
Columns: Polymer Laboratories (PL gel) (crosslinked divinylbenzene)
Pore size: 50 Å, mesh: 10 µm
Injection volume: 0.5 – 2 ml, loop volume: 5 ml
Pressure: 2.5 MPa
Length: 300 mm, id: 25 mm (2 columns in series)
Flow: 10 ml/min (dichloromethane)
Target fraction: 17 – 24 min.

The dichloromethane is removed by evaporation on a rotary-film evaporator and the remaining solution is dissolved in 2 ml iso-octane. Because the collection of the target fraction starts one min earlier than in the case of PBDE analysis only, it may be possible that some is collected as well. Therefore, an additional clean-up step (sulphuric acid treatment) is added. One ml of sulphuric acid is added and the extract is mixed with the acid for ca. 10 sec using a Vortex* mixer. The extract is then left overnight to separate from the sulphuric acid. The top layer is then transferred to an amber coloured test tube and mixed on a Vortex mixer with 1 ml distilled water. The top layer is subsequently transferred to a second test tube together with a small quantity of sodium sulphate. Then, the extract is eluted over 1.8 g silica gel (Merck Kieselgel 60, 63-200 µm, no. 7754) in a glass column (id 0.6cm). The sample container is flushed with 1.5 ml *iso*-octane which is also transferred to the top of the column. The first fraction (11 ml *iso*-octane) and the second fraction (25 ml 15% (v/v) diethylether in *iso*-octane) are combined and concentrated to 1 ml. The silica elution was extended from 10 to 25 ml in the second fraction, in order to collect all of the HBCD including β-HBCD which is normally eluting rather late from silica. Finally, the cleaned extract is transferred to an injection vial.
The method obtained in this way was tested for repeatability. The coefficient of variation (CV) of the current quality chart for HBCD in eel is 22%. For HBCD in sediments a CV of 8% was obtained after analyis of six samples in different series. RIVO is accredited for the analysis of total HBCD by GC/MS (Sterlab L097).

4.7 GC/MS analysis at NIOZ

A HP6890 Gas Chromatograph (Hewlett Packard, Waldbronn, Germany) with a CP-Sil 8 fused silica capillary column (30 m × 0.25 mm ID, 0.25 µm film thickness, Varian, Bergen op Zoom, the Netherlands) was equipped with a HP 7683 automatic sampler and operated by Chemstation G1701BA (version B.01.00). The injector temperature was 275°C and samples of 1 µl were injected in pulsed splitless mode with a pulse pressure of 2.07 bar for 1.5 min. Helium was used as a carrier gas and separation was performed at a constant flow of 3.3 ml/min. The temperature program used for the BDE congeners, Me_2TBBP-A, TBBP-A and HBCD was as follows: injection temperature 90°C held for 1.5 min., followed by a increase in temperature (20°C/min.) up to 190°C. Thereafter, the temperature was increased to 270°C (4.5°C/min.). After 5 min., the temperature was increased to 320°C (10°C/min.) and held there for 10 min.

The GC was interfaced to a HP5973 quadrupole mass spectrometer (Hewlett Packard) measuring the negative ions formed at chemical ionisation (mass spectrometry-negative chemical ionisation [MS-NCI]) with methane as reagent gas. The temperatures of MS_{source} and MS_{quad} are 210 and 160°C, respectively. The mass fragments monitored were *m/z* -79 and -81 for all the brominated compounds, -324 and -326 for CB-112 (internal standard), -161 for Me_2TBBP-A, -542 and -544 for TBBP-A, -554 and –556 for ^{13}C-TBBP-A (internal standard) and -561 and -563 for HBCD. Quantification of the compounds Me_2TBBP-A, HBCD and BDEs was performed by monitoring the ion *m/z* –81. Confirmation of the compounds was performed using

the other mass fragments. The final quantification of the peak heights of Me_2TBBP-A and HBCD was made using a calibration line at three levels of external standards provided by RIVO (see section 3.1.). Quantification of TBBP-A was performed by calculating the ratio of the peak areas of TBBP-A (*m/z* –542 and -544) and an internal standard of ring-labelled ^{13}C-TBBP-A (*m/z* –554 and -556). The final quantification of TBBP-A was made using a calibration line of the ratios of the external standards of TBBP-A and ^{13}C-TBBP-A, which was added to the RIVO standard. The responses of the internal standards (CB-112 and ^{13}C-TBBP-A) were used to correct for recovery.

4.8 GC/MS analysis at RIVO

The final determination was carried out by GC/NCI-MS. The following conditions were used:

Table 4.2. GC/MS conditions used at RIVO.

Internal standard	CB112
GC column 1	CP Sil 8
Dimensions	50m-0.21mm-0.25µm
Injector temp. (°C)	275
Max. oven temp.(°C)	315
Injection technique	Pulsed splitless
GC col.2 (BDE209)	DB-5
Dimensions	15m-0.25mm-0.25µm
Injector temp. (°C)	275
Max. oven temp.(°C)	300
Detection technique	NCI-MS
Injection technique	Pulsed splitless
Quantification	Area
Scanned ions	79, 81; HBCD: 158, 160

4.9. Comparison of results

All laboratories participated in the BSEF/QUASIMEME interlaboratory study on brominated flame retardants, which was organised between November 2001 and March 2002. The results are given in Table 4.3.
The laboratories obtained good results for their standard solutions. Also, the analysis of the lake trout was satisfactory, in particular for HBCD. CEFAS and NIOZ could not determine TBBP-A, which was presumably due to the low level of TBBP-A in this test material. CEFAS did not produce a value for MeTBBP-A due to an initial lack of standards.
The sediment sample caused some problems. Both in the sediment itself as in the sediment extract CEFAS produced relatively high results for HBCD. This may be due to the fact that these data were only based on LC/MS, whereas RIVO and NIOZ produced GC/MS data. The comparability of LC/MS and GC/MS data at NIOZ and RIVO was generally good, but in case a deviation between the GC/MS and LC/MS result was found, this deviation could be relatively strong. This phenomenom needs further study. It could have played a role here. The TBBP-A data show that in general this determination is more difficult than that of HBCD. However, this picture is somewhat biased as the levels in the test materials were very low. As soon as higher levels would be found in environmental samples, the reliability of the method improves. Given the consistent results from this entire project, there is not much concern as regards possible differences per institute. An extra check on high HBCD concentrations in Irish STPs (chapter 6) is recommended as those data were determined by LC/MS only, and a GC/MS analysis would increase the reliability. The MeTBBP-A analysis could not be compared thoroughly, because the initial lack of commercial standards and low levels in the sediment test materials. The comparison between RIVO and NIOZ for lake trout was good (CV 17%).

Table 4.3. Results of the three institutes in the BSEF/QUASIMEME interlaboratory study on flame retardants.

Test material	Compound	RIVO	CEFAS	NIOZ	CV(%)
St. solution	HBCD	359	224	320	23
	TBBP-A	565	459	550	11
	MeTBBP-A	323		350	5.7
Lake trout	HBCD	2	1.2	2.4	33
	TBBP-A	<0.1			
	MeTBBP-A	2.8		2.2	17
Sediment	HBCD	140	372	68	82
	TBBP-A	1.1		0.19	
	MeTBBP-A				
Sediment extr.	HBCD	130	270	150	41
	TBBP-A	1.2		5	87
	MeTBBP-A				

4.10 Discussion

The adapted analytical methods that have been developed from the standard PBDE determination enabled the determination of MeTBBP-A, TBBP-A and HBCD in environmental samples. The validation of this method remains somewhat troublesome, as reference standards for MeTBBP-A were initally not commercially available.
The method developed for the analysis of MeTBBP-A, TBBP-A and HBCD is error-prone due to the many steps involved in sample pre-treatment. The addition of a basic fractionation step causes the sample extracts to be transferred frequently. These numerous transfers of volume accompanied with this method introduce a factor of uncertainty and are in general time-consuming. The correction made with the internal standard partially overcomes this problem, though. The critical steps involved in the method development are 1. the treatment of the sample extract with concentrated sulphuric acid, 2. the clean-up with silica and 3. the final determination by GC-MS.

In the treatment with sulphuric acid, vigorous mixing can cause the complete breakdown of lipids. Following the subsequent basic fractionation step, these breakdown products may initiate a saponification reaction. The products formed in this saponification remain on the interface of the organic and aqueous layers because of the polar and apolar ends of the formed organic molecules. This makes it rather difficult to separate the two layers effectively from each other. Therefore, the acid treatment had to be applied rather mildly and the amount of lipids to be extracted had to be minimised in order to prevent these unwanted reactions.

The silica clean-up of the extracts (NIOZ method) is assumed to be not very effective because of the rather polar eluent mixture (85:15 n-C_5/Et_2O) that has to be used. It is assumed that the extract will not be completely devoid of polar components above a percentage of 10% of diethylether in pentane. However, the complete recovery of the diastereomers of HBCD, in particular the β-isomer, makes it still necessary to use such a polar mixture with a concomitant increase of elution volume. In the method developed by RIVO for the analysis of HBCD, the β-isomer is eluted within 12,5 ml iso-octane and 23 ml of a mixture of iso-octane and diethylether (15%) (column of 1.8 g SiO_2*1.5% H_2O).

The addition of a basic fractionation step is an appropriate step in the procedure, because the more polar TBBP-A seems to be absorbed more strongly to the silica. Conveniently, this fractionation of TBBP-A also prevents its co-elution with BDE153 in the GC-separation. However, additional problems arise in the detection of TBBP-A as the GC-liner becomes rapidly activated by TBBP-A or co-extracted polar compounds. This results in a rapid decrease in response factor of TBBP-A- (and ^{13}C-TBBP-A) signal. Regular cleaning of the liner or even cutting the first piece of

the column is necessary before starting a new series of analyses. In other methods, TBBP-A is derivatised with acetic anhydride following basic fractionation over a basic aqueous medium (Sellström, 1995). Also, direct conversion of TBBP-A to the diethyl derivative by ethylation has been reported (Gustafsson and Wallen, 1988). These methods seem to be a suitable alternative. However, this method is not easily carried out quantitatively. Other problems encountered in the GC-MS analysis involve the co-elution of MeTBBP-A and BDE154, which makes the quantification of MeTBBP-A rather difficult.

5. Work package 2 - Scheldt Basin Study

Indications of high HBCD concentrations in biota and sediments from the Western Scheldt reported in the BSEF PBDE study (de Boer et al., 2001a) have initiated this project on HBCD in the Scheldt basin. The presence of HBCD in common tern eggs from a common tern colony near Terneuzen in particular has caused some concern with Dutch water authorities about HBCD. From the point of view of good product stewardship, BSEF would like to learn more on the environmental behaviour of HBCD in the Scheldt. It is known that in and upstream from Antwerp a high density of textile industry can be found. A substantial number of these industries may use HBCD as a flame retardant in their products. The processes in which HBCD is impregnated in the materials could lead to losses to the aquatic environment. In addition to that, a production plant of HBCD is situated at Terneuzen, at the border of the Western Scheldt. Also here, HBCD losses to the aquatic environment could take place. As outlined in the introduction, it was supposed that losses of the technical HBCD product during and immediately after production would mainly consist of γ-HBCD, whereas losses from the textile industry would mainly consist of α-HBCD. The aim of this study was to identify the possible sources of HBCD. In addition to that, TBBP-A and MeTBBP-A were analysed in the same samples, in order to obtain more information on possible sources of this compound.

5.1 Total HBCD in eel

In total 18 eel samples (yellow eel, *anguilla anguilla*) were received from the Institute of Forestry and Nature Management. These eels were taken during sampling campaigns in 2000. An overview of the locations is given in Annex 1.1. The samples are taken from the Scheldt basin, but also include three samples from reference sites: 2. Achelse Kluis, 15. Lo-Reninge and 18. Yzer, Nieuwpoort. Sediment samples were obtained through the same institute from the same locations, but sampled in 2001. Samples from 2000 were not available and new eel samples would only be sampled again in 2002. It was expected that differences in environmental conditions over a period of one year would be relatively small. However, the occurrence of incidental variations should be taken into account.

The highest HBCD concentrations were found in the Scheldt near Oudenaarde (33 mg/kg lipid weight), Leie St. Martens (7.1 mg/kg lipid w.), Leie Oeselgem (4.7 mg/kg l.w.), and Dender, Appels (1.3 mg/kg l.w.) (Annexes 3.1 and 3.3). The HBCD concentrations in and around Antwerp harbour are generally lower. It is noticeable that also in two of the three reference samples HBCD was found: 210 μg/kg l.w. in eel from the Yzer near Nieuwpoort and 32 μg/kg l.w. in eel from Achelse Kluis.
No HBCD was found in eel from the reference site Lo-Reninge. These results show that HBCD contamination is to some exten dependent of sources. However, with ongoing inputs into the aquatic environment, also more remote places are expected to be contaminated by HBCD in the future. HBCD sources can be expected to be present at the Scheldt near or upstream from Oudenaarde and at the Leie near St. Martens and Oeselgem. More upstream the Leie, near Wevelgem and Wervik, substantially lower HBCD concentrations were found.

5.2 Total HBCD in sediment

The high HBCD concentrations in eel are confirmed by high HBCD concentrations in sediments: Scheldt Oudenaarde (7.2 mg/kg org. C basis) and Leie St. Martens (5.4 mg/kg org. C) are the two highest HBCD levels found in the sediment samples. Another relatively high HBCD concentration was found near Antwerp harbour, in the Western Scheldt at the Dutch border: 2.5 mg/kg org. C. A measurable amount of HBCD was also found in the reference location Yzer, Nieuwpoort (94 μg/kg org. C). No measurable HBCD concentrations were found at the two other reference sites.

Summarizing, it can be concluded that the HBCD patterns found in eel and sediment are in good agreement, and that at least two clear sources have been found: in the Scheldt near Oudenaarde and in the Leie near St. Martens. Furthermore, a high HBCD concentration is found in sediment near Antwerp at the Dutch border, which is in agreement with the results of the previous study, in which a HBCD concentration of 780 μg/kg org C. was reported at this location (de Boer et al., 2001a). HBCD is also found in the river Yzer.

5.3 TBBP-A and MeTBBP-A in eel and sediment

The results of TBBP-A in eel and sediments (Annexes 3.1, 3.2, 3.5 and 3.6) show a less good correlation. The concentrations in eel are generally low. The highest concentration is found in eel from the reference location Yzer near Nieuwpoort (13 μg/kg l.w.). TBBP-A could not be detected in a large number of samples. In a few sediment samples TBBP-A was found in relatively high concentrations, up to 670 μg/kg in sediment from the Scheldt near Oudenaarde and 890 μg/kg in Beveren, Vrasenedok, near Antwerp). This shows that TBBP-A is in particular found close to point sources. Also, TBBP-A, because of its more polar character, shows a less bioaccumalative behaviour. A clear correlation between fat in an organism and organic carbon in sediment may therefore not be present. Also, TBBP-A may be easier excreted or degraded than HBCD.

The MeTBBP-A concentrations in eel and sediment (Annexes 3.1, 3.2, 3.7 and 3.8) are all relatively low. In sediment only one measurable concentration of 13 μg/kg org C. was found in the Leie near Wevelgem. A few more measurable concentrations were found in eel, up to 12 μg/kg org C. in eel from the Leie near Wervik.

5.4 HBCD isomer ratios

The HBCD ratios are given in Annex 3.9. For comparison, both the sum of the three HBCD isomer concentrations determined by LC/MS (LC-ESI-SIM-MS at RIVO) and the total HBCD concentration determined by GC/NCI-MS are given. The correspondence between both total HBCD concentrations is reasonably good. Deviations of a factor two, and in incidental cases more, occur, but it should be considered that the LC/MS method is one of the first methods for this purpose developed in the world, and just reflects the current state of the art. Given the relatively short period of time included for method development, the achieved comparability of the two methods is actually fairly good. On the other hand there is also doubt on the accuracy of the GC/MS method for total HBCD. This method is now much better under control. The mean coefficient of variation (CV) of the RIVO QC chart for eel is now 22% which is somewhat larger than that of e.g. BDE47, but considerably smaller than what is has been before. The sensitivity of HBCD for higher temperatures in the GC, however, always causes some peak broadening due to the presence of more than one isomer and the thermal rearrangements, which can take place. Therefore, the GC/MS determination of HBCD will never be as good as that of a tetra of penta-BDE. However, in this report the HBCD concentrations determined by GC/MS should, in case of doubt, be considered as superior to those determined by LC/MS, because the QA/QC documentation (such as the quality chart) on the GC/MS method is based on a longer period of experience, whereas the LC/MS was only recently developed. However, on the long term the LC/MS data are expected to be superior to the GC/MS data as the LC/MS method is in principle the better method. The ratios determined by LC/MS in this study should be considered as reliable.

The results show that in eel, apart from a number of non-detects, the α/γ-HBCD ratios are ca. 2.5-3.5. However, at the location Scheldt, Oudenaarde, a deviating pattern was found, with an α:β:γ ratio 21:21:1 (Figure 5.1). This is interesting, because this was the location with the highest total HBCD concentration in eel. At the other location with a relatively high total-HBCD, Leie, Oeselgem, also β-HBCD was found, ratio α:β:γ: 5:1:2.

In most other eel samples β-HBCD was not found. γ-HBCD was also found in eel from the Leie, St. Martens, and in eel from the Scheldt near Doel. In none of the samples was β-HBCD or γ-HBCD higher than α-HBCD.

In all sediment samples γ-HBCD is the highest in concentration. In most cases none of the other isomers was found. However, at the two locations with the highest total HBCD concentrations, Scheldt, Oudenaarde and Leie, St. Martens also α-HBCD, and in the case of Oudenaarde, also β-HBCD was found. In one other sediment sample, Antwerp Kruisschansstraat, a high γ-HBCD value is found together with β-HBCD and α-HBCD. However, in this sample, the total HBCD concentration determined by LC/MS differs considerably from that determined by GC/MS. A few examples of HBCD isomer ratios are shown in Figure 5.1.

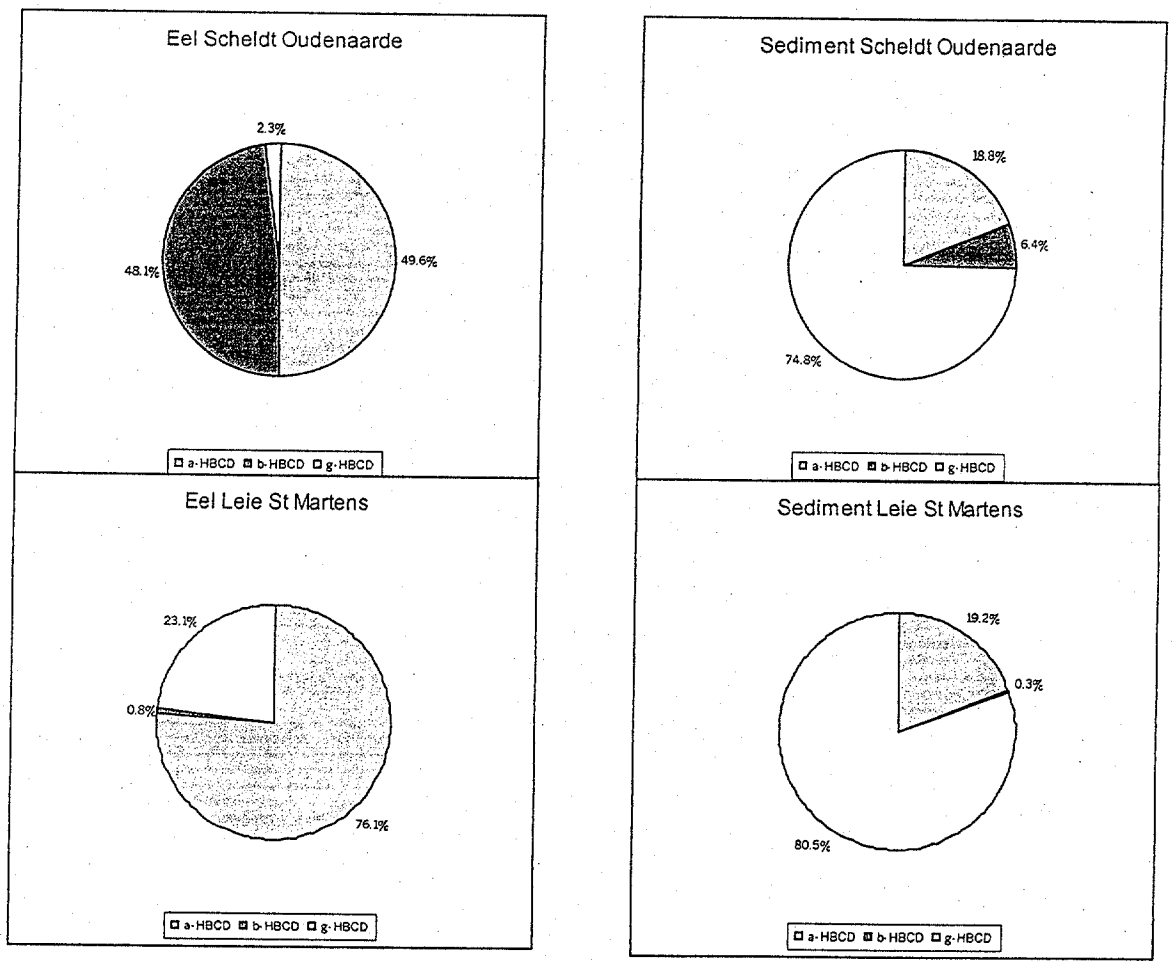


Figure 5.1. Isomer ratios of HBCD in a selection of eel and sediment samples.

The results found lead to the following tentative conclusions. HBCD is normally present in sediments as γ-HBCD (ca. 90%). In some cases, e.g. at Oudenaarde and St. Martens with high total HBCD concentrations, it seems as if somewhat elevated levels of α-HBCD and sometimes β-HBCD can be found together with γ-HBCD, with levels of α-HBCD at ca. 20% of those of γ-HBCD. Such a pattern may possibly be indicative for the presence of textile or plastic industry. The presence of α-HBCD and/or β-HBCD in eel does not give information on the presence of specific industries. That presence is most likely the result of a biotransformation process that takes place in eel. Other possibilities are a selective uptake of α-HBCD or a selective excretion of γ-HBCD by eel. However, when HBCD levels are high, γ-HBCD can also be found in eel, together with α- and β-HBCD.

It should be taken into account that the detection limits play an important role here. At lower levels one or two of the isomers disappear under the detection limit and it seems as if only the third isomer is present. However, most likely the ca. 10% of the other isomers will also be there but cannot be seen due to their low concentration.
When concentrations increase the other isomers are found at a certain level, and the suggestion is given that the mutual isomeric ratio has increased, which is not necessarily true. Nevertheless, we feel that, based on changing α/γ-HBCD ratios in sediments, some indications on the presence of textile/plastic industries have been found in this study.

6. Work package 3 – Sewage Sludge and Landfill Study

STP and landfill samples were taken in The Netherlands, UK and Ireland. At five STP's in The Netherlands, four with a high treatment capacity (200,000-750,000 population equivalents (pe)) (STP 1-4) and one small STP (100,000 pe) (STP 5), sewage sludge was sampled together with influent and effluent. At four other STP's, two small locations (150,000 pe) (STP 6 and 8) and two with a high treatment capacity STP 7 (750,000 pe) and STP 10 (400.000 pe) only sewage sludge was sampled. Besides these STP's also the sludge of the sewer from a residential area was sampled (location 9). The sampling was carried out by RIZA. The locations have been coded as the samples could only be obtained as long as the data would be kept confidential. Per influent sample, four litre was filtered in the laboratory. The residue was dried at 50°C and used for the analysis. The sewage sludge was centrifuged in the laboratory and dried at 50°C before analysis. The effluents were centrifuged at the location by means of a high throughput centrifuge. The residue was mixed with sodium sulphate and then Soxhlet extracted.

The samples in the UK and Ireland were taken by CEFAS. Sewage sludge, influent and effluent samples were taken from five locations in Essex: Burnham, Latchingdon, Wickford, S. Woodham Ferrers and Chelmsfords, varying in population from 4,750 (Latchingdon) to 143,000 (Chelmsford). In Ireland three STPs were samples for sewage sludge: Portlaoise, Clonmel and Cork. In addition, three sediment samples from downstream these STPs were analysed. Both the dissolved and the particulate phase of the influent and effluent samples were analysed. The particulate phase was obtained after filtration, over 0.45 μm PVDF filters

6.1 Total HBCD, TBBP-A and PBDEs in Dutch STPs

The results of the Dutch samples are shown in Annex 4.1. All results have been expressed in μg/kg on a dry weight basis. The highest HBCD concentrations were found in the samples of the STP 2: 570 μg/kg dw. in the influent residue, 93 μg/kg in the sludge and 140 μg/kg in the effluent. The other four influent samples, as well as the other four effluent samples, apart from that of STP5 (100 μg/kg), show non-detects for HBCD, but the sludge samples show detectable HBCD levels. Only in the STP1 sample HBCD is not found in any of the compartments. It should be considered that the analysis of the sludge is easier because more material can be taken for analysis. TBBP-A is found in most sludge samples and in all effluent samples, but not in any of the influent samples, normally in relatively low concentrations of a few μg/kg, but at higher levels in sludge from STP2 and STP6, and at one exceptional high concentration (600 μg/kg dw.) in the sludge from STP7. MeTBBP-A was occasionally found at low levels in some sludges.

As regards the PBDEs in these samples, in most cases only the congeners 47, 99, 100 and 209 were found. Occasionally, BDE183 and BDE 154 were reported in sludge samples. A high BDE209 concentration of 900 μg/kg d.w. was found in the influent of the STP4, which corresponds with earlier reports on high decaBDE concentrations in the same STP influent and effluent (Vethaak et al., 2002). In the sludge from a sewer of a residential area (location 9) the PBDE congeners 47, 99, 209 and also TBBP-A and HBCD were found in low concentrations.

6.2 Total HBCD and TBBP-A in UK and Irish STPs

The HBCD concentrations in the samples from the UK and particularly in those from Ireland are considerably higher than in those from The Netherlands (Annexes 4.2-4.3). The total HBCD concentrations in some UK sludges varied between 0.5 and 2.6 mg/kg d.w. In Irsih sludges the HBCD concentrations varied between 0.15 and 8.3 (Cork) mg/kg dw. The UK and Irish STP samples have not been analysed by GC/MS. A confirmation of these higher values is desired.

The influent and effluent samples from the UK and Ireland generally show low HBCD concentrations or non-detects, apart from the influent from Burnham (29 µg/kg d.w.). TBBP-A is found in sewage sludges from the UK and Ireland and, interestingly, also in the dissolved phase of four UK STP influents. The latter confirms the polar character of TBBP-A, which leads to a more balanced distribution over the water and lipid/carbon phases. MeTBBP-A could not be detected in the UK and Irish STP samples.

6.3 HBCD ratios

The HBCD isomer ratios generally show the presence of all three isomers in varying ratios (annexes 4.1a, 4.2, 4.3). Interestingly, also β-HBCD is found in substantial amounts. In case higher total HBCD concentrations were found such as in the STP2 in The Netherlands and in the Irish STPs, α-HBCD is either the dominant isomer or it is present in substantial amounts, almost equal to those of γ-HBCD (Figure 6.1). Most STPs studied were municipal STPs, some possibly with a mixed intake of industrial and municipal wastewater. The reported α- and β-HBCD concentrations in sewage sludge could maybe originate from textile, which is leached out during washing processes in households. This possibility should be studied more closely. Also, the isomeric composition of HBCD in various textiles should be analysed.
Finally, as regards the balance of the contaminants in the STPs, it should be taken into account that the sludge is the major compartment as regards volumes. In The Netherlands, the sludge is removed from the STP at regular intervals, on average every two weeks, to be burned in special waste incinerators. In the UK and Ireland, the sludge is also taken away at similar interval, but is then disposed on land. In that respect the landfill study is interesting, to see if some of the BFRs would enter the environment through leachate water.

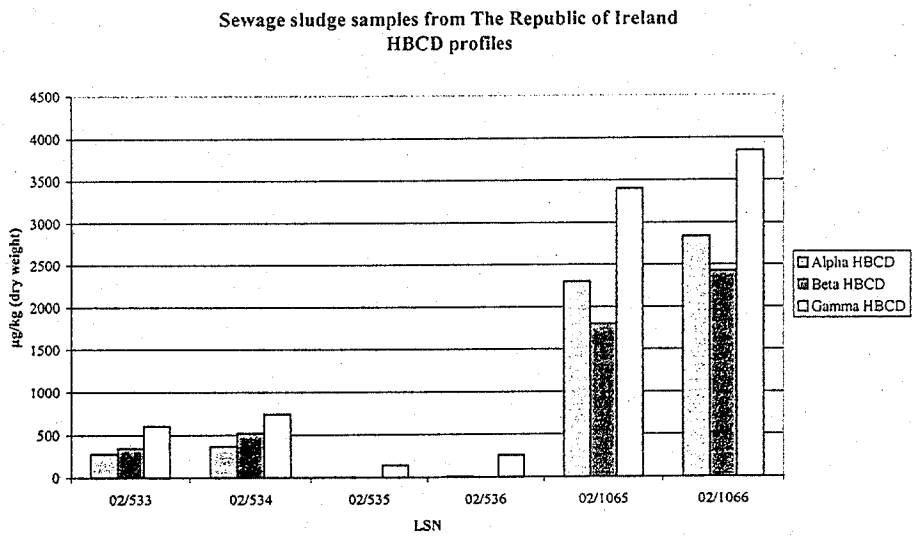


Figure 6.1. HBCD profile in Irish STP samples.

6.4 Landfill study

Dutch landfill samples were taken at nine locations. At two locations both sludge and leachate water was sampled. The leachate water that was sampled was not identical to the water that finally reaches the open environment. Prior to that this leachate water is purified to a final effluent. The Dutch landfills were sampled after a period of several weeks of dry weather, which means that the concentrations found, may be higher than those in the average situation with more rainfall. The leachates were filtered (1-2 L), the residue was dried at 50°C and analysed. For the same reason as in case of the STPs, the Dutch landfill samples have been coded. Three landfill leachate samples from the UK were taken at Rainham, Ockendon and Pitsea.

Three Irish landfill samples were taken at Kinsale road (near Cork), Kyletalesha and Dumore. All UK and Irish leachate water samples were split into a particulate part and a dissolved part. Both phases were analysed. However, in none of the samples HBCD was found. Also, no TBBP-A and MeTBBP-A was found (Annexes 4.3 and 4.6).

The Dutch samples showed HBCD concentrations between <29 and 660 µg/kg on a dry weight basis, with to extreme values of 22 and 68 **mg/kg** dw. (Annex 4.4). The median value for the leachate water was 110 µg/kg dw. The two sludge samples showed HBCD concentrations which were much lower than in the corresponding leachate water (2.1 and <0.3 µg/kg, respectively). The TBBP-A concentrations found varied between < 0.3 and 320 µg/kg dw. with a median of <25 µg/kg dw. in the leachate water. MeTBBP-A was not found at all in the Dutch landfill samples. The two extremely high HBCD concentrations in the two landfills are of concern. In these landfills a more detailed study, including an analysis of the effluent is recommended. Both α- and γ-HBCD are present in Dutch landfill samples. Normally γ-HBCD is somewhat higher in concentration, but α-HBCD is also present in substantial amounts

7. Work package 4 –North Sea and river sediments and biota

7.1 North Sea food chain

Samples of animals representing different trophic levels (invertebrates, fish and sea mammals) were analysed to determine the environmental occurrence of TBBP-A, MeTBBP-A and HBCD. The model of the North Sea food chain comprises benthic invertebrates (sea stars, whelks and hermit crabs), fish (whiting) and sea mammals (harbour porpoises and harbour seals). From every trophic level in the North Sea food chain, a small number of samples has been selected to investigate possible biomagnification. For the hermit crab, nine samples were analysed to investigate the geographical distribution of the studied compounds (Table 7.1).

Table 7.1. Selected biota and sediment samples with the number of samples analysed and locations

Sample	Species	n	Location
Hermit crab (abdomen)	*Pagurus bernhardus*	9	9-11-13-15-20-22-26-30-32
Common whelk (whole body)	*Buccinum undatum*	3	9-22-26
Sea star (pyloric caeca)	*Asterias rubens*	3	11-25-33A
Whiting (fillet)	*Merlangius merlangus*	3	9-21-31
Harbour porpoise (liver and blubber)	*Phocoena phocoena*	5	North Sea
Harbour seals (liver and blubber)	*Phoca vitulina*	5	Western Wadden Sea

7.1.1 Invertebrates and fish

The samples of invertebrates and fish were taken during cruise 64PE144 with the RV Pelagia in August-September 1999 (for locations see de Boer et al., 2001a). In this study, samples were already homogenised for the PBDE analysis. Specific tissues of the sea stars (*Asterias rubens*) and hermit crabs (*Pagurus bernhardus*) were selected as the hard parts were difficult to homogenise. Of the sea star, the parts of the digestive system (pyloric caeca) located pair-wise in each of the five arms of a starfish were chosen. The entire abdomen of six samples of the hermit crabs was taken and homogenised. This asymmetrical anterior part of the anomal holds the shell serving as the house of the crab. It contains muscle tissue, part of the digestive system (liver, gut) and gonads. No differentiation was made between the sexes during sampling. Of the whelks (*Buccinum undatum*), only males were used. They were taken out of their shell and the entire soft parts of the animals were used. Of the whiting (*Merlangius merlangus*), the fillet was taken out and homogenised for analysis. The advantage of invertebrates over higher organisms as fish and marine mammals, is that they are less migratory and are thus much more representative for the situation at the site of capture than fish and marine mammals (de Boer et al., 2001). The results obtained are summarised in Annex 5.1.

7.1.2 Marine mammals

The liver and blubber samples of the harbour porpoises (*Phocoena phocoena*) were obtained from Dr. Ch. Smeenk of the museum of natural history 'Naturalis' in Leiden, the Netherlands. The liver and blubber samples of the harbour seals (*Phoca vitulina*) were obtained from different sources and originated from the western Wadden Sea area. All animals were either beach-stranded or drowned in fishing nets. These migratory animals inhabit a larger area than invertebrates indicating that no geographical distribution of organohalogens can be inferred. They also differ from fish in the way of respiration. The respiration via lungs causes a decreased exchange with the water phase compared to the continuous gill-water exchange of fish.

The results of both invertebrates and fish, and marine mammals are summarised in Annex 5.1. Concentrations have been calculated as a weighted average of the duplicate samples and are normalised for lipid content. This normalisation has been done to compare the concentrations on a lipid weight basis as the magnitude of bioconcentration in different tissues largely depends on the hydrophobicity of the studied compounds. The values in table 1 represent the average values, the median (in brackets), and the minimum and maximum, respectively. The detection limit is expressed on a lipid weight basis and has been set to three times the noise level. Recoveries of MeTBBP-A and HBCD vary between 68 and 120% in relation to the internal standard used (CB-112).

7.1.3 Discussion

The presence of MeTBBP-A in biota was only detected at the higher trophic levels in a few samples of liver (harbour porpoise and cormorant) and blubber (harbour porpoise and harbour seal). The concentrations are relatively high in blubber tissues of marine mammals. This indicates that Me_2TBBP-A has the potential to bioaccumulate in fatty tissues and biomagnify through the food web. At lower trophic levels, the concentrations of MeTBBP-A were below the limit of detection.

High concentration levels of HBCD have mostly been found in the higher trophic levels, in tissues of liver (cormorant and harbour porpoise) and blubber (harbour porpoise and harbour seal). One individual harbour porpoise even contained 6.3 µg/g lipid in blubber tissue. In the invertebrates, HBCD has only been found in the sea star and the common whelk. HBCD was not found in muscle tissue of fish (whiting).

Concentrations of BDE-congeners have been measured to make a comparison with previously detected levels of these compounds. The results for the sum concentrations of BDEs are in good agreement with the concentrations analysed before.

The mean concentration levels of HBCD in the sea star, the common whelk and blubber tissue of the harbour porpoise are similar to the mean concentration of BDE congeners (sum of BDEs 28, 47, 99, 100, 153, 154). This may imply a similar behaviour of HBCD with regard to the observed biomagnification of BDEs. Although no significant calculation can be made from the available data, a similar biomagnifying effect can be deduced from the presence of HBCD in different trophic levels (Boon et al., in press).

7.1.4 HBCD isomer ratios

The concentrations of the different isomers of HBCD were determined by LC-MS. The results are shown in Annex 5.2. for the few samples analysed at this stage by this technique. In Figure 7.1, the distribution of HBCD-isomers is shown for a liver sample of a harbour porpoise and a sediment sample from the Western Scheldt. Only the α-isomer of HBCD was detected in the liver of a harbour porpoise and a cormorant, whereas the γ-isomer dominated in the sediment. In this case the total concentrations of HBCD determined by LC-MS did not agree very well with the GC-MS data. Possibly, this is due to the use of the APCI technique. The temperature during ionisation is around 250°C. Although the compounds are only exposed for a very short period, less than 1 second, this could have an effect on the thermal rearrangement process. In ESI ionisation takes place at ambient temperatures. In addition, APCI has a lower sensitivity for HBCD, compared to ESI. That may also have had a negative influence on the quality of the data.

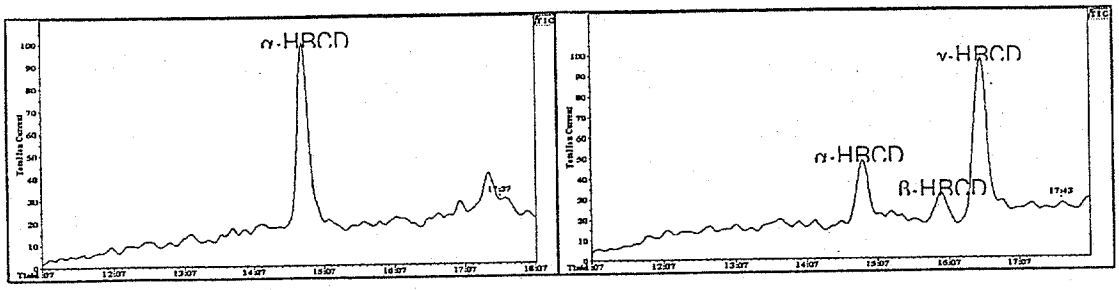


Figure 7.1: LC-chromatogram of a. liver of harbour porpoise (BSEF-4) and b. sediment from Western Scheldt.

7.1.5 HBCD in relation to other contaminants

In Table 7.2, the concentrations of HBCD in biota are compared with other halogenated contaminants by calculating the ratios between HBCD and the total concentrations PBDEs or PCBs. When values are above 1, the contribution of HBCD to the total environmental exposure exceeds that of the concentrations of PBDEs or PCBs, respectively. In two individuals of harbour porpoise, the relative contribution of HBCD is more than that of PBDEs or PCBs in tissues of blubber. One liver sample of a harbour porpoise shows an even higher exposure to HBCD than to PCBs (HBCD/PCB ratio of 4.2). The values shown indicate that the contribution of HBCD concentrations to the total environmental exposure of marine mammals to halogenated contaminants is relatively high.

Table 7.2: Concentrations of HBCD (GC-MS data) compared with total concentrations of HBCD and PBDEs (sum of BDEs 28, 47, 99, 100, 153, and 154) or PCBs (sum of CB28, CB101, CB153, CB138 and CB180) in sea stars, harbour porpoise and harbour seal

		Conc. (ng/g lipid weight)			Ratio HBCD/ PBDEs	Ratio HBCD/ PCBs
Species	Sample code	HBCD	Sum BDEs	Sum PCBs		
Sea star	AR11	84	143	164	0.59	0.51
	AR33	47	14	2303	3.4	0.006
Liver harbour porpoise	PP981024-4	3925	14160	930	0.28	4.2
Blubber harbour porpoise	PP990322-4	880	1952	2229	0.45	0.39
	PP981120-1	729	1382	3646	0.53	0.20
	PP990322-3	6275	4690	10163	1.3	0.62
	PP980325-2	3584	2475	10106	1.4	0.35
Blubber harbour seal	96PVc	63	558	13231	0.11	0.005
	96PVb	2055	15953	N.D.	0.13	-

Due to their physico-chemical properties, the investigated brominated flame retardants will be transported to the North Sea from direct sources in the countries around the North Sea through river run-off and by oceanic and atmospheric circulation. The latter will possibly occur at an earlier stage for the additive flame retardants like HBCD than for TBBP-A as a reactive flame retardant which is less likely to leach into the environment. Because of their low volatility and vapour pressures, TBBP-A and HBCD will primarily be transported by suspended particles. The highly lipophilic and persistent compounds are deposited in the sea, where they can accumulate in marine organisms and sediments. Uptake of these compounds in marine organisms takes

place directly from the sea (bio
bioaccumulation depends upor
compound's physicochemical pr
to the organism's metabolic ra
and further from fish to seabirds

The concentrations of MeTBBP
samples show a different beh
bioaccumulation. MeTBBP-A and
lipid tissues of marine mammals
undergo any phase-I biotransfor
absence of TBBP-A (preliminar
elimination of TBBP-A from org
sulphate (van Leeuwen and Herm
the pH dependency of TBBP-A c
resulting in a higher bioavailability

MeTBBP-A was only detected in
and the harbour seal (153 ng/g
indicating that this compound ha
the origin of the environmental p
section 2.2., MeTBBP-A is believe
1995). The presence of this comp
TBBP-A as part of an organism's
product in the production of TBBP-

HBCD appears to biomagnify in th
were found in some marine mamm
seem to be even comparable to th
HBCD in blubber tissue amounted
harbour seal and the harbour porp
much smaller concentrations of HB
the sea star (47 – 84 ng/g LW).
invertebrates possibly reflect their
the samples of the sea star and th
detected levels could also be due
contrast, the higher trophic levels c
with water is diminished by lung-re
energy requirement. The concentrat
the limit of detection, possibly ind
respiratory surfaces. Moreover, the
whiting is relatively low (31.1 mg lip
lipid for the other samples. The whi
species (e.g. the herring) use the mu
sample-extracts of the harbour seal
The concentrations of HBCD in these
limit of detection. From the few amo
could be calculated.

In order to identify a possible geogra
of the North Sea, nine samples of th
the North Sea. Since these invertebra
representatives for the site of captu
However, no concentrations of MeTBB
hermit crab. The selected samples
contained fairly low concentrations of
low amount of observations, the selec

production of HBCD takes place (Tees-estuary, loc. 11 and Western Scheldt, loc. 33A). The samples of the common whelk also contained low concentrations of HBCD near the English coast (loc. 9), in the German Bight (loc. 26) and in the Skagerrak (loc. 22). Still, no conclusions can be drawn regarding the dispersal of HBCD throughout the North Sea based on these low number of observations.

7.2 Tees food chain and other UK samples

7.2.1 Cormorant livers

Annex 5.3 shows the results for the cormorant samples. HBCD isomers were detected, but not all isomers in all samples. The sum of the three isomers (α, β, γ)

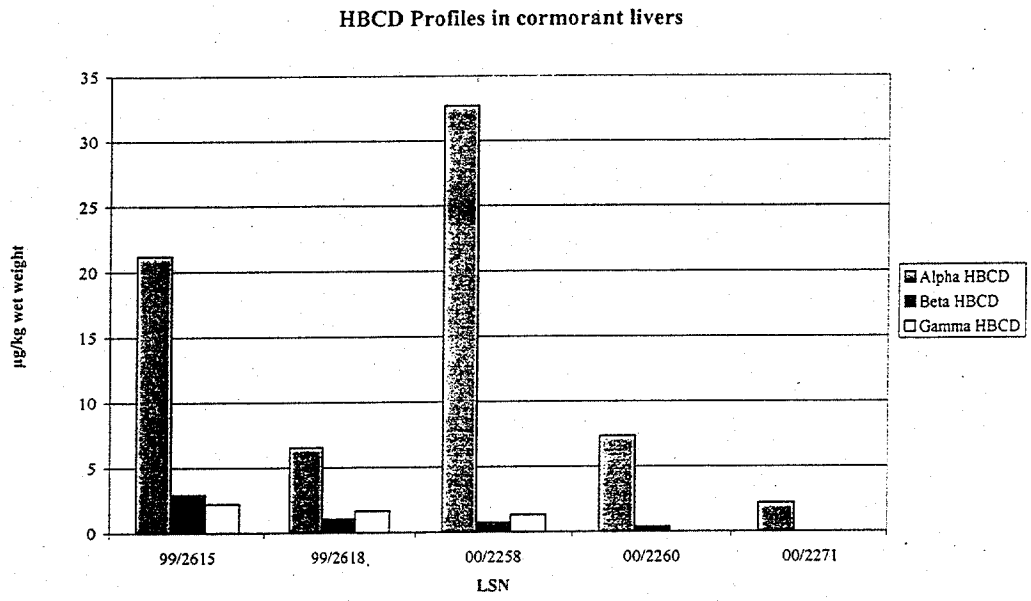


Figure 7.2. HBCD isomer profile in cormorant.

varied from 2.2 – 26.4 µg/kg wet weight with a mean of 16. The α isomer was dominant in all cases (Figure 7.2.). TBBP-A was detected in all samples (0.07 – 0.28 µg/kg wet weight, with a mean of 0.12). Me-TBBP-A was not detected.

7.2.2 Porpoise blubber

Annex 5.3 also shows the results for the porpoise samples. HBCD was commonly detected and at a generally higher concentration than that found in cormorant livers. However, HBCD was not detected in one sample, 98/7500, whereas another, 98/7479, had a high concentration of 917 µg/kg wet weight for the sum of the three isomers with an unusual isomer profile, in which each of the three isomers was present in approximately the same concentrations (Figure 7.3). It is difficult to draw any conclusions from such a small sample number, but clearly, and in agreement with the observations from the North Sea food chain, marine top predators have the potential to accumulate high levels of HBCD. TBBP-A was detected in all samples at a generally low level (0.05 – 0.26 µg/kg wet weight) although one sample, 98/7479, had a relatively high value of 376 µg/kg. MeTBBP-A was not detected.

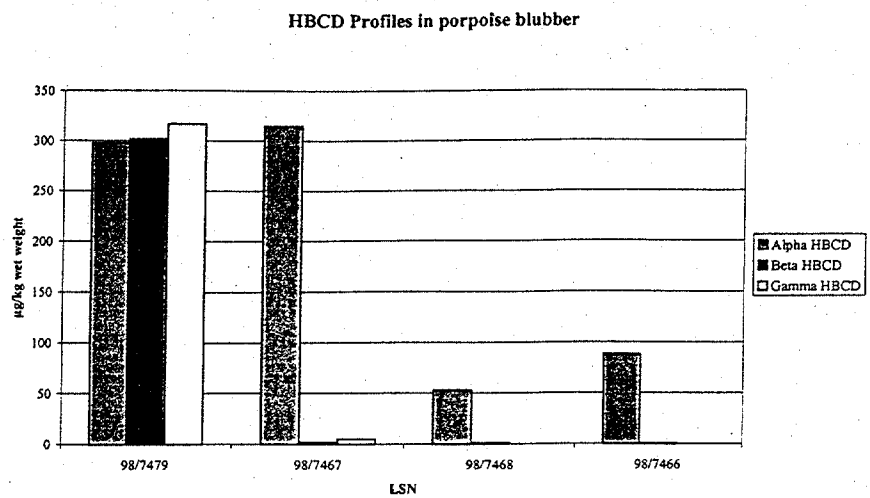


Figure 7.3. HBCD isomer profile in harbour porpoises.

7.2.3 Sediment from UK rivers

Annex 5.4 shows the results for the sediments from UK rivers.

7.2.3.1 River Tees

HBCD was commonly detected in river Tees sediment with values ranging from detection limits to 510 µg/kg dry weight with a mean of 192. In contrast to the biota samples, the γ isomer

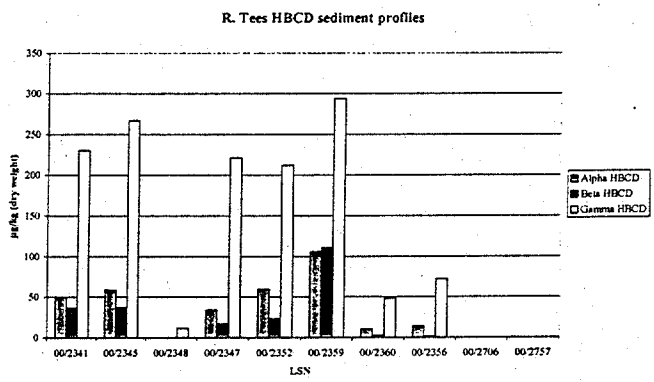


Figure 7.4. HBCD isomer profile in river Tees sediment

was dominant in the sediment samples (Figure 7.4). The two offshore samples did not contain detectable levels of either TBBP-A, Me-TBBP-A or HBCD. TBBP-A levels ranged from detection limits to 57.1 µg/kg dry weight with a mean of 24.6 µg/kg dry weight. MeTBBP-A was not detected.

7.2.3.2 River Tyne

The two samples from the river Tyne had low levels of TBBP-A (2 and 5 µg/kg dry weight) and values for the sum of the three HBCD isomers of 14.2 and 322. Again, with just two samples it is impossible to draw any conclusions, but the highest of the Tyne samples was comparable to and in many cases higher than the Tees samples. Again, the sediment profile was dominated by the gamma isomer.

7.2.3.3 River Skerne

The two samples from the river Skerne had two extreme values for TBBP-A. Sample 00/2586 was below the detection limit and the other 9750 µg/kg dry weight, which is the highest value recorded in this survey from any site. The reasons for two such disparate results is unclear. HBCD was present in both samples with values for the sum of the three isomers of 174 and 1,680 µg/kg dry weight

7.2.3.4 River Humber

For the single sediment sample from the river Humber only γ-HBCD at 6 µg/kg was detected. No TBBP-A and MeTBBP-A were found

7.2.3.5 River Mersey

TBBP-A and Me-TBBP-A were not detected in any of the five samples and only β-HBCD was detected in two samples at concentrations of 22 and 52 µg/kg dry weight. The absence of the normally dominant γ-HBCD isomer is unusual. It may also be an indication that the presence of HBCD in the Mersey is rather due to certain industries using HBCD than due to losses during production.

7.2.3.6 River Clyde

TBBP-A and Me-TBBP-A were both absent. Values for the sum of the three HBCD isomers were 7 and 187 µg/kg dry weight, with the γ isomer dominating the HBCD profile.

7.2.3 Miscellaneous

Annex 5.5 shows the results for the whiting muscle and starfish sample. TBBP-A was detected in one whiting sample at a value of 3.3 µg/kg wet weight. Me-TBBP-A was not detected. HBCD isomers were detected in two of the three samples with values for the sum of the three isomers of 291 and 1,040 µg/kg wet weight. In one sample, 01/1252, the α isomer was dominant and in the other, 01/1095, the γ isomer was dominant.

The single starfish sample had detectable concentrations of TBBP-A (4.5 µg/kg), and α and γ HBCD (10.2 and 6.7 µg/kg respectively).

7.3 Western Scheldt food chain and other Dutch samples

7.3.1 Western Scheldt food chain

A number of samples from a food chain sampled for the previous study on PBDEs (de Boer et al., 2001a), was analysed for total HBCD, TBBP-A and Me-TBBP-A, as well as for the HBCD isomers. The sample selection comprised common tern eggs, gudgeon, and mysid shrimp. In addition, a series of Western Scheldt sediment samples, also sampled for the previous PBDE study, was analysed.

Annex 6.1 shows the results of the gudgeon, mysid shrimp and common tern eggs. HBCD, TBBP-A and Me-TBBP-A were not found in mysid shrimp. The gudgeon has a total HBCD concentration of 49 µg/kg wet weight (230 µg/kg lipid weight). The HBCD concentrations in common tern eggs were roughly comparable to those reported as indicative concentrations by de Boer et al. (2001a). The concentrations varied between 35 and 640 µg/kg on a wet weight basis (median 87 µg/kg), and between 330 and 7200 µg/kg on a lipid weight basis (median 930 µg/kg). The data confirm the relatively strong bioaccumulative potential of HBCD. Also, biomagnification seems to occur from the mysid shrimp, via the gudgeon to the terns. The number of mysid shrimp and gudgeon samples analysed is too small to give reliable estimates of biomagnification factors. TBBP-A was not found in any of the eggs. It polar character apparently prevents a substantial bioaccumulation. Me-TBBP-A was found in relatively low concentrations: <0.2-0.8 µg/kg on a wet weight basis (median <0.6 µg/kg), and <2-7.6 µg/kg on a lipid weight basis (median <6 µg/kg).

The HBCD isomer ratios (Annex 6.1) show mainly γ-HBCD in gudgeon. In the common tern eggs α-HBCD is strongly dominating. In most samples the ratio α/γ-HBCD was substantially higher than 20. These data confirm the supposed mechanism of biotransformation of γ to α-HBCD in biota, which was already observed for eel (chapter 5). Still, a selective uptake or excretion of one of the isomers somewhere in the food chain cannot be excluded.

7.3.2 Western Scheldt sediments

Sediment samples from 19 locations in the Western Scheldt (The Netherlands) have been analysed for total HBCD and isomers, TBBP-A and Me-TBBP-A. The results are given in Annex 6.2 and are visualised in the Annexes 6.3-6.5. HBCD isomer ratios are given in Annex 6.6. The results show that the highest HBCD concentrations were found around Terneuzen and in Antwerp harbour, Dutch border (location 53, Annex 6.3). This is in agreement with the indicative values which were reported by de Boer et al. (2001a), in which a similar pattern of HBCD concentrations in the Western Scheldt was found. Also, sediment and eel samples analysed in work package 2 of this study (chapter 5) confirmed the earlier indicative values of de Boer et al. (2001a). Based on these observations, it is most likely that high HBCD concentrations in the Western Scheldt are caused by HBCD losses in industries furhter upstream the Scheldt as well as by an input of HBCD by the bromine industry in Terneuzen. All sediment samples show a dominant presence of γ-HBCD. α and β-HBCD are only occasionally found in relatively low levels. These results are evidently in contrast with those of the Western Scheldt biota, in which mainly α-HBCD was found. This confirms the hypothesis of a biotransformation process in the biota or a selective uptake or excretion of one of the isomers.

The TBBP-A concentrations are considerably lower than the HBCD concentrations. Only in the harbour of Vlissingen, a substantial amount of TBBP-A was found (130 µg/kg org C.). All MeTBBP-A concentrations are below or around the detection limits.

7.3.3 Dutch rivers: eel and sediment

The results of the Dutch sediment analyses are given in Annex 6.7 and those of the Dutch eel samples from the same locations in Annex 6.11. The Annexes 6.8-6.10 show maps of The Netherlands with the sediment results for HBCD, TBBP-A and MeTBBP-A. The Annexes 6.12-6.14 show maps for the eel results. Annex 6.15 shows a table with the HBCD isomer ratios in Dutch eel and sediment.

The sediment samples show total HBCD concentrations of 48-580 µg/kg on an org C. basis. The TBBP-A concentrations vary between 14 and 130 µg/kg org C., and the MeTBBP-A concentrations between <1 and 11 µg/kg org C. The HBCD values found at the location Lobith (German border) suggest that the HBCD found originated from Germany or further upstream the river Rhine. The HBCD concentrations in river Rhine sediment are higher than those in the river Meuse. This pattern is also found in the eel samples: the difference in HBCD concentrations between river Rhine and river Meuse eel is ca. 5-fold. River Roer eel shows the highest HBCD levels (850 µg/kg lipid weight), almost 2-fold higher than in river Rhine eel. Earlier high PCB, Ugilec and PBDE concentrations were found in this river. The supposed sources were hydraulic fluids used in a German mining area. It is unknown if HBCD could be used for a similar application. The TBBP-A and MeTBBP-A concentrations are all considerably lower than the HBCD concentrations. Interestingly, MeTBBP-A is found in higher concentrations than TBBP-A, which can be explained by the stronger non-polar character of MeTBBP-A, which makes it easier for this compound to bioaccumulate.

7.3.4 Dublin Bay

The results of the Dublin Bay sediment analyses are given in the Annexes 6.15 and 6.16. Annex 6.17 shows a map with the HBCD results. The difficulty of the Dublin Bay samples was the low TOC content. The samples were relatively sandy, which made it very difficult to measure detectable amounts of the target analytes. The TOC contents of the samples DB-1 – DB-4 were just high enough (0.55-4.35%) to find detectable amounts of HBCD (240-910 µg/kg org C.). In the other samples, the TOC contents were too low: (0.14-0.35%) to detect any of the target analytes. It is interesting to see that the HBCD concentrations in four of the Dublin Bay samples were considerably higher than those in the river Liffey, which was samples a year earlier. In contrast with that TBBP-A and MeTBBP-a were now lower than in the Liffey sample. This could suggest a certain temporal trend, but obviously, such conclusion cannot be based on only one sample. TBBP-A and Me-TBBP-A could not be found in any of the Dublin Bay samples. Apart from HBCD, relatively high concentrations of decaBDE have been found in the samples DB1-DB-4, and DB-5 and DB–6. The latter showed a decaBDE concetration of 7400 µg/kg org C. Interestingly, BDE 183, representative of the octa PBDE mix, was also found in a number of samples in concentrations of 16-250 µg/kg. This is an indication of the use of the octaBDE mix in Ireland. The penta-mix related congeners were all low in concentration. Only the BDEs100 and 153 have been found at low levels (0.9-23 µg/kg org C.).

7.3.5 Cod liver

Only in the cod liver sample from the Central North sea HBCD was found at a level of 50 µg/kg on a lipid weight basis (Annex 6.18). No HBCD was found in the southern North Sea sample. Also, in hake liver from the Atlantic, southwest from Ireland, HBCD could not be found. Similary, TBBP-A was only found in the Central North Sea cod liver (1.8 µg/kg l.w.). Me-TBBP-A was not found in any of the samples. Although only a few samples were studied, the result has some similarities with that of PBDEs, for which increasing PBDE concentrations were found in the Central North Sea, possibly explained by the presence of HBCD in river Tees dredge materials.

Paragraph 7.3.2.1 shows that HBCD was also found in the river Tees, in comparable concentrations to BDE47.
The isomeric profile of HBCD in cod liver from the Central North Sea only showed α-HBCD, in agreement with earlier observations in other biota.

8. Work Package 5 – Interlaboratory Study

An interlaboratory study on the analysis of HBCD, TBBP-A, MeTBBP-A and the PBDE congeners 28, 47, 99, 100, 153, 154, 183 and 209 has been organised in collaboration with the QUASIMEME programme (Aberdeen, UK). The materials, lake trout homogenate, mussels, sediment, human milk, a clean sediment extract and two unknown solutions, all tested for homogeneity, were dispatched at 1 November 2001. The number of participants, 42, was more than 2-fold higher than that of the first BSEF interlaboratory study on PBDEs. The statistical evaluation of the results took place in April 2002. Thirty-eight sets of results were received for the PBDEs. However, only six sets were received for HBCD, and only two sets for TBBP-A/MeTBBP-A. Apparently, the laboartories are still in the phase of setting up methods for HBCD and TBBP-A. The PBDE results were roughly comparable with those obtained in the first study. However, improvement was obtained for BDE99. The BDE209 analysis is still not under control by the participating laboratories. The results were even less good than those of the first study. Difficulties were also met in the analysis of the human milk sample. The low concentrations of the PBDEs caused apparently too many analytical difficulties in the laboratories.
The HBCD results that were returned showed a reasonably good comparability. Obviously, no conclusions could be drawn as regards the TBBP-A and MeTBBP-A analysis.
The participating laboratories will be informed on their performance before 15 June. The report of the interlaboratory study will be prepared separately and will be snet to the participants before 15 July. The results will be presented at the BFR session of the Dioxin2002 symposium in Barcelona (12-16 August).

9. Acknowledgements

We gratefully acknowledge the hard work of the CEFAS staff Lissaa Mead, Matthew Curtis, Moira Bennett and Philip Mellor, and RIVO staff Stefan van Leeuwen, Pim Leonards, Evert van Barneveld and Christiaan Kwadijk. Mr. Robin Law of CEFAS is gratefully acknowledged for his help in reviewing a part of this report.
The STP samples from the Republic of Ireland were supplied by mr. John Lucey of Kilkenny EPA and his hospitality and enthusiasm and that of his colleagues and associates are also gratefully acknowledged. Landfill leachates samples were kindly provided by Cleanaway Ltd. The co-operation of the Environment Agency and Anglia Water in the collection of sewage sludge samples is also acknowledged.
We thank Evin McGovern and Brendan McHugh of the Marine Institute for providing sediment samples from the Dublin Bay. We also thank mr. Gerard Rijs of RIZA for his co-ordination in obtaining the STP and landfill samples, and for the centrifugation of a number of STP samples.
We are grateful for the collaboration with dr. Claude Belpaire and mr. Geert Goemans of the Institute of Forestry and Nature Management, who provided eel and sediment samples from Belgium.
We are grateful for the collaboration with Cambridge Isotope Laboratories for the provision of standards for the interlaboratory study. Finally, we gratefully acknowledge the collaboration with dr. David Wells and Judith Scurfield of QUASIMEME for their assistance in the organisation and evaluation of the interlaboratory study.

10. References

de Boer, J., Aldridge, J., Allchin, C., Bennett, M., Boon, J.P., Brandsma, S.H., van Hesselingen, J.M., Law, R.J., Lewis, W., Morris, S., Tjoen-A-Choy, M.R., Zegers, B. (2001a). Polybrominated diphenylethers in the aquatic environment. RIVO report C023/01, IJmuiden, The Netherlands.

de Boer, J., Allchin, C., Law, R.J., Zegers, B., and Boon, J.P. (2001b). *Trends Anal. Chem.*, 20, 591-599.

Boon, J.P., Lewis, W.E., Tjoen-A-Choy, M.R., ten Hallers,-Tjabbes, C.C., Allchin, C.R., Law, R.J., de Boer, J., and Zegers, B.N. (in press). Polybrominated diphenyl ethers in the North Sea food web. *Environ. Sci. Technol.*

Borgå, K., Gabrielsen, G.W. and J.U. Skaare (2001). *Environ. Pollut.* 113, 187-198.

Gustafsson, K. and M. Wallen (1988) Status report on tetrabromobisphenol A (CAS no. 79-94-7) Clearing house Sweden, Solna, Sweden, National Chemicals Inspectorate.

Leeuwen, C.J. van and J.L.M. Hermens (1995) Risk assessment of chemicals: An introduction, Kluwer Academic Publishers, ISBN 0-7923-3740-9.

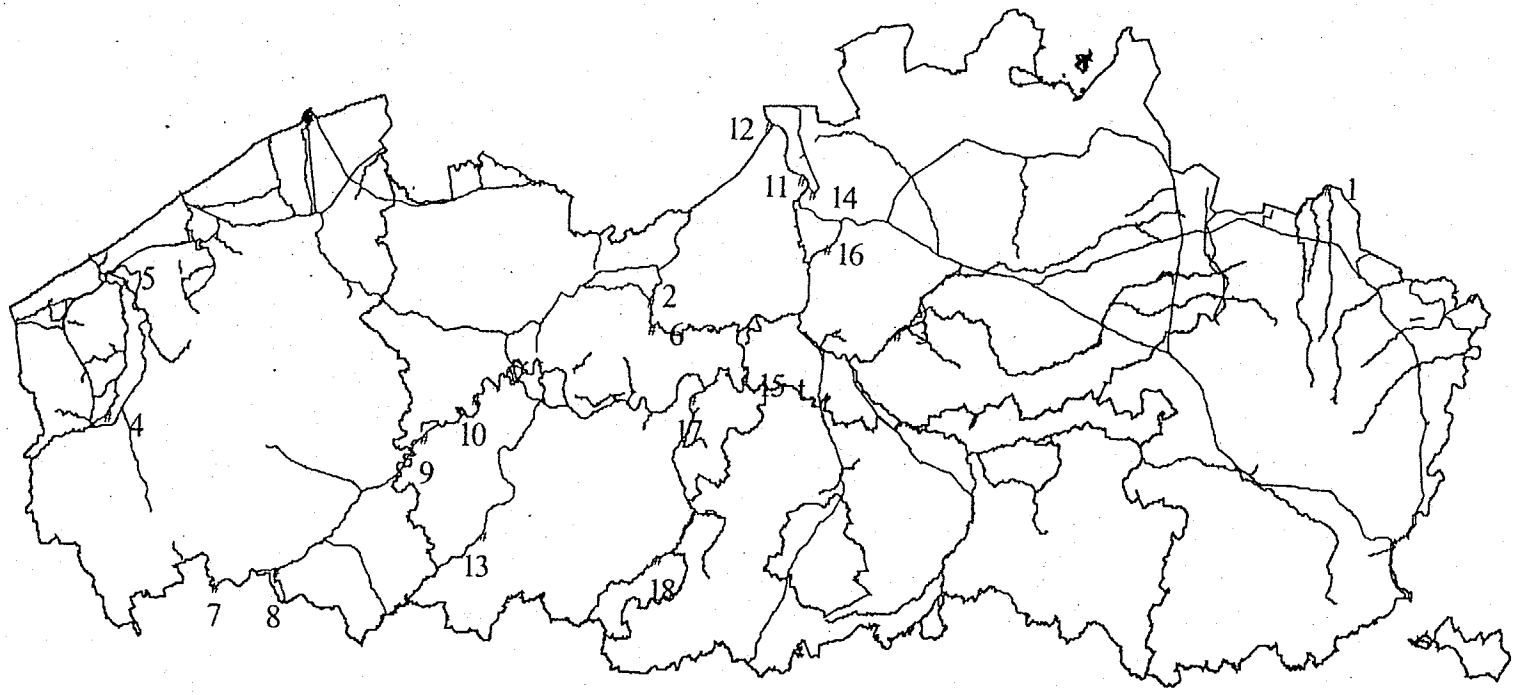
Peled, M., Scharia, R., Sondack, D. Thermal rearrangement of hexabromocyclododecane. Draft paper, Bromine Compounds, P.O. Box 180, Beer Sheva, 84101, Israel.

Sellström, U. and B. Jansson (1995) *Chemosphere* 31, 3085-3092.

Vethaak, A.D. et al. (2002). LOES report, RIKZ, RIZA, The Hague, The Netherlands.

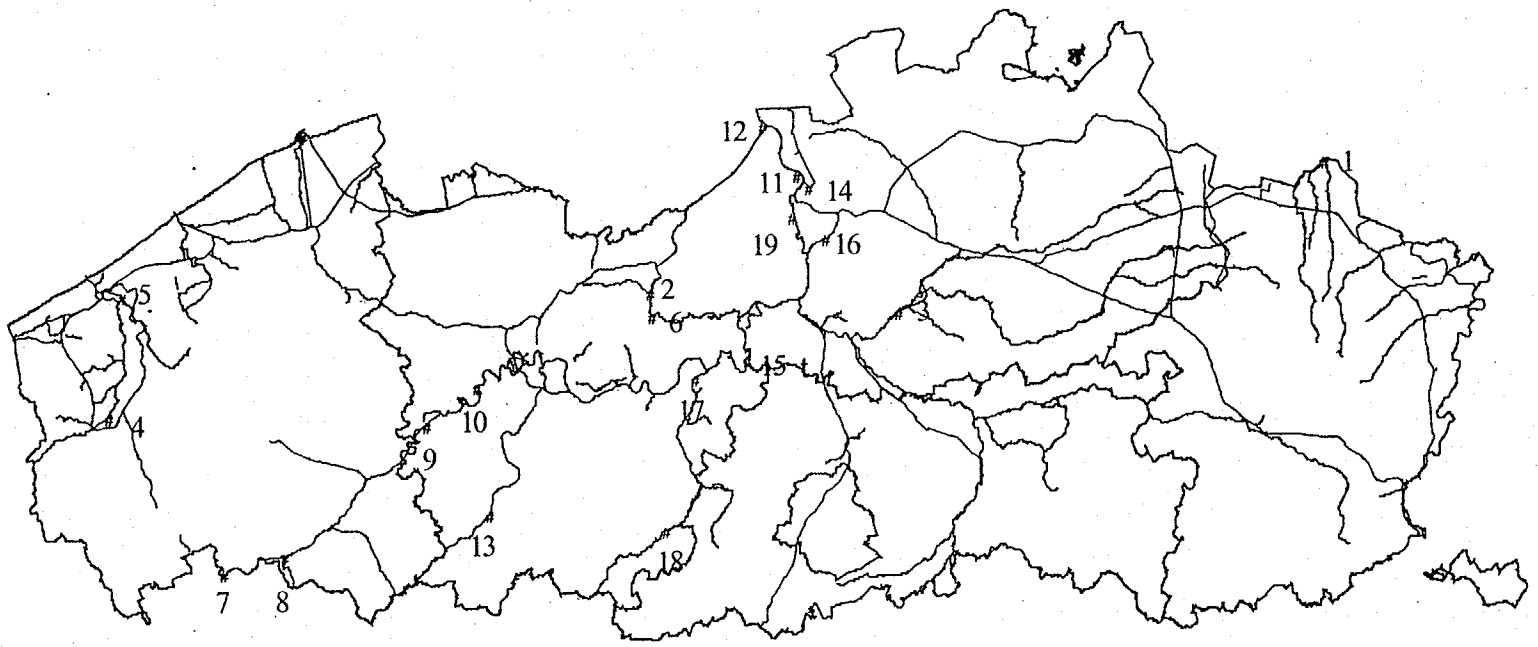
WHO (1995). IPCS, Environmental Health Criteria, Geneva, Switserland.

Annex 1.1 Scheldt basin sampling locations eel



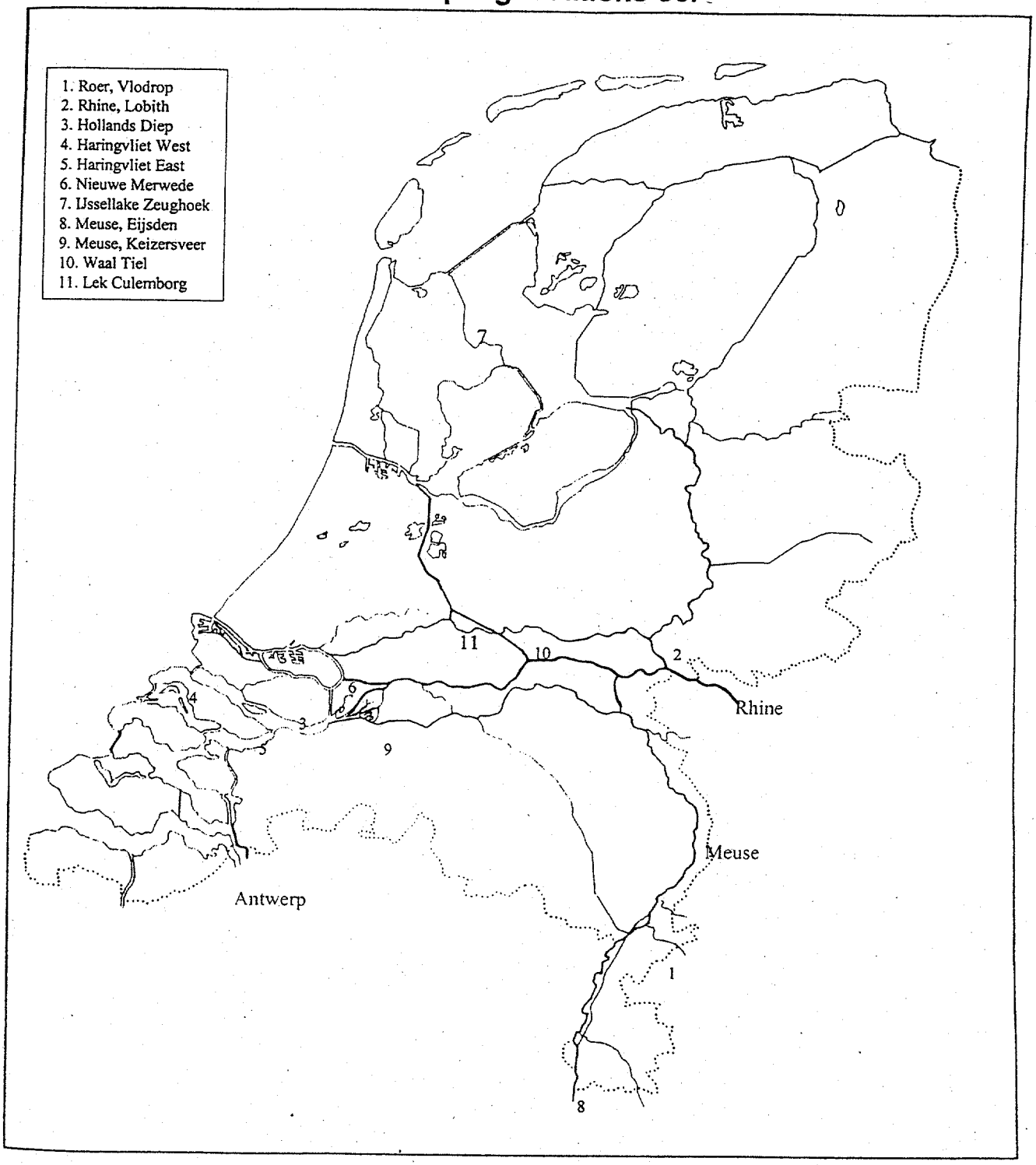
1. Warmebeek, Achel-Kluis
2. Moervaart, Daknam
10. Leie, St.Martens
11. Scheldt, Deal

Annex 1.2 Scheldt basin sampling locations sediment

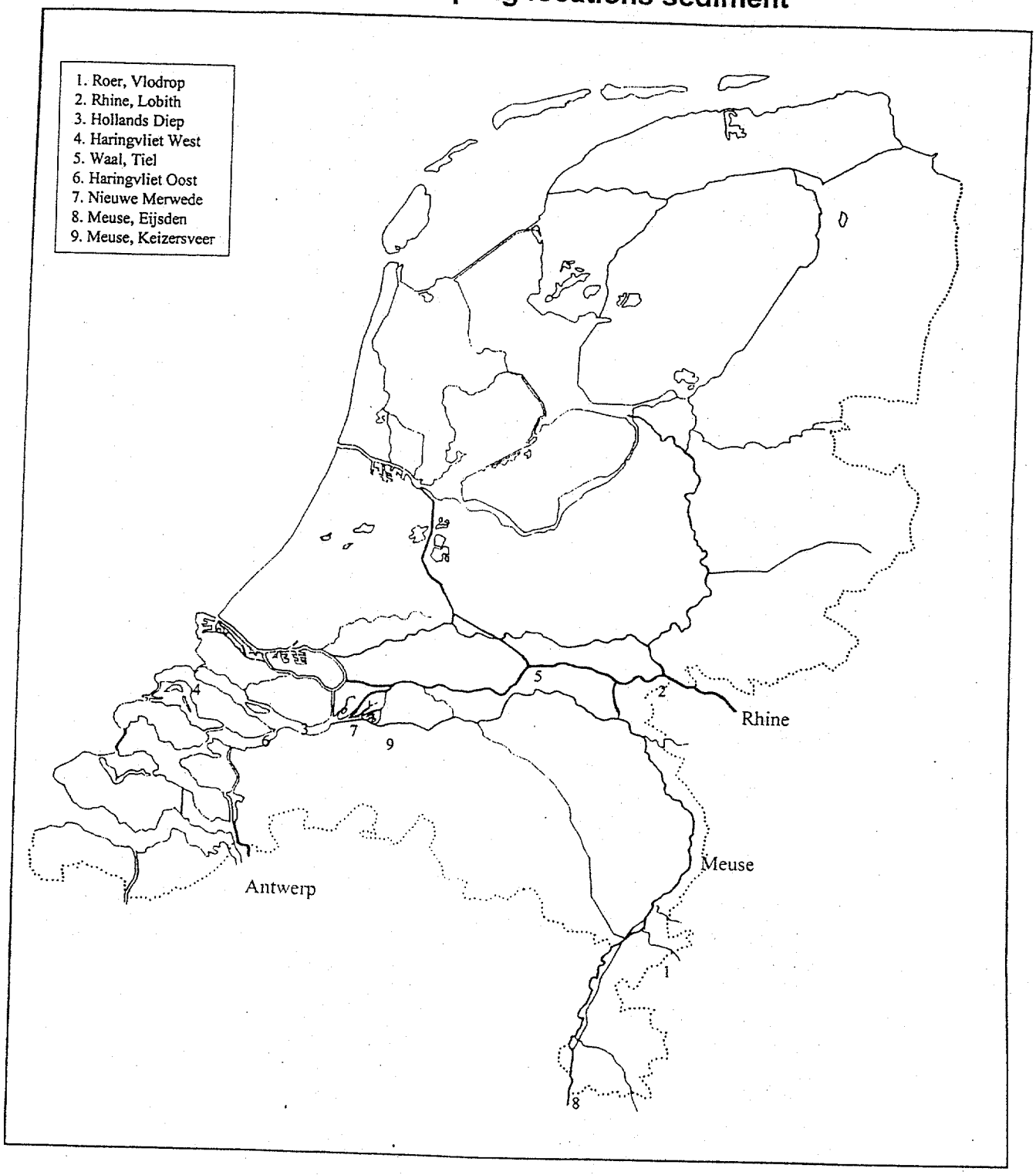


1. Warmebeek, Achel-Kluis
2. Moervaart, Daknam
3. Beneden Nete, Duffel
4. Grote Beverdijk, Lo-Reninge
5. IJzer, Nieuwpoort
6. Durne, Lokeren
7. Leie, Wervik
8. Leie, Wevelgem
9. Leie, Oeselgem
10. Leie, St.Martens
11. Scheldt, Doel
12. Scheldt, Grens
13. Scheldt, Oudenaarde
14. Antwerpen, Kruisschansbrug
15. Scheldt, Kastel
16. Scheldt, Kennedytunnel
17. Dender, Appels
18. Dender, Ninove
19. Vrasenedok, Beveren

Annex 1.3 - Dutch rivers sampling locations eel

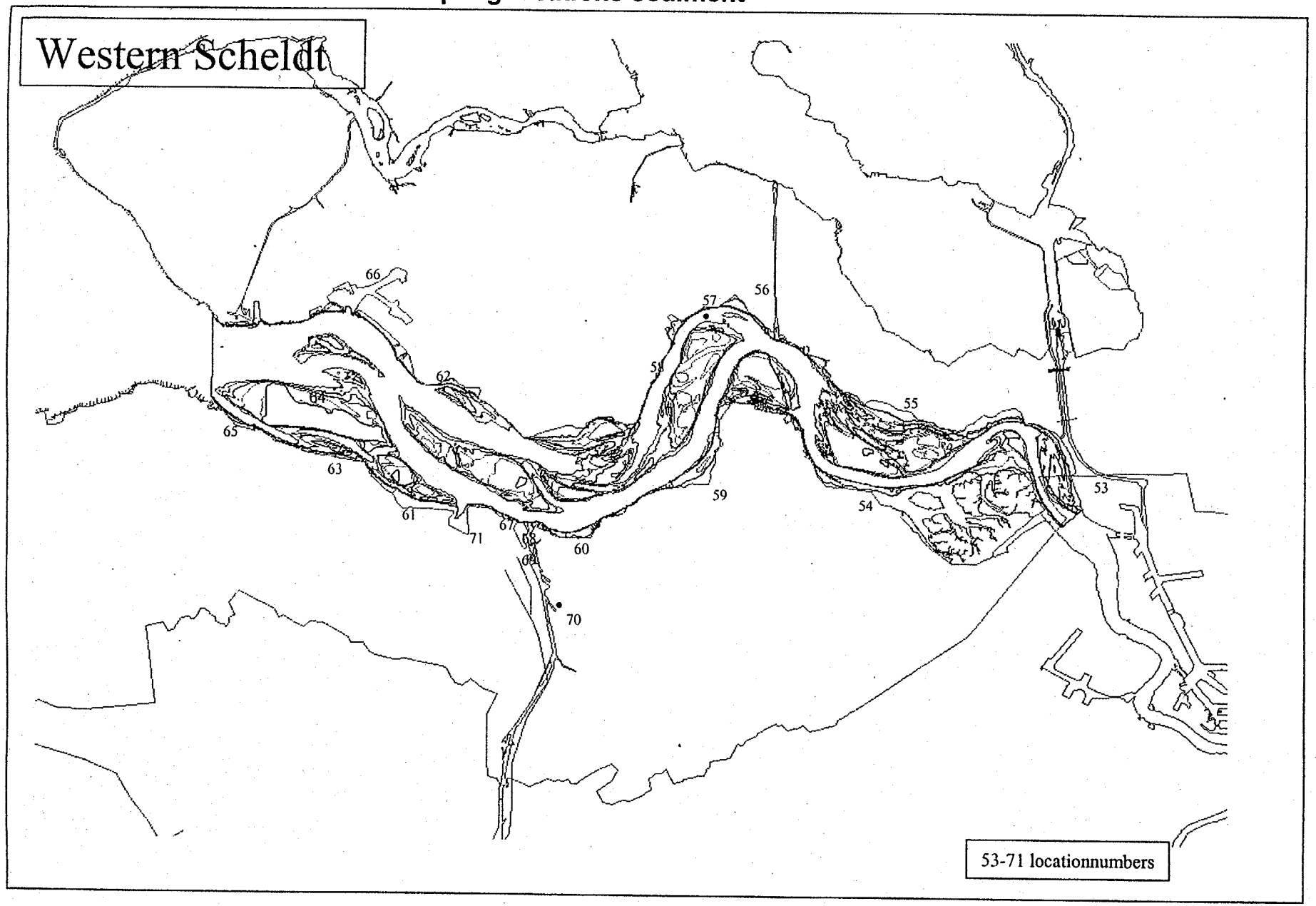


Annex 1.4 - Dutch rivers sampling locations sediment

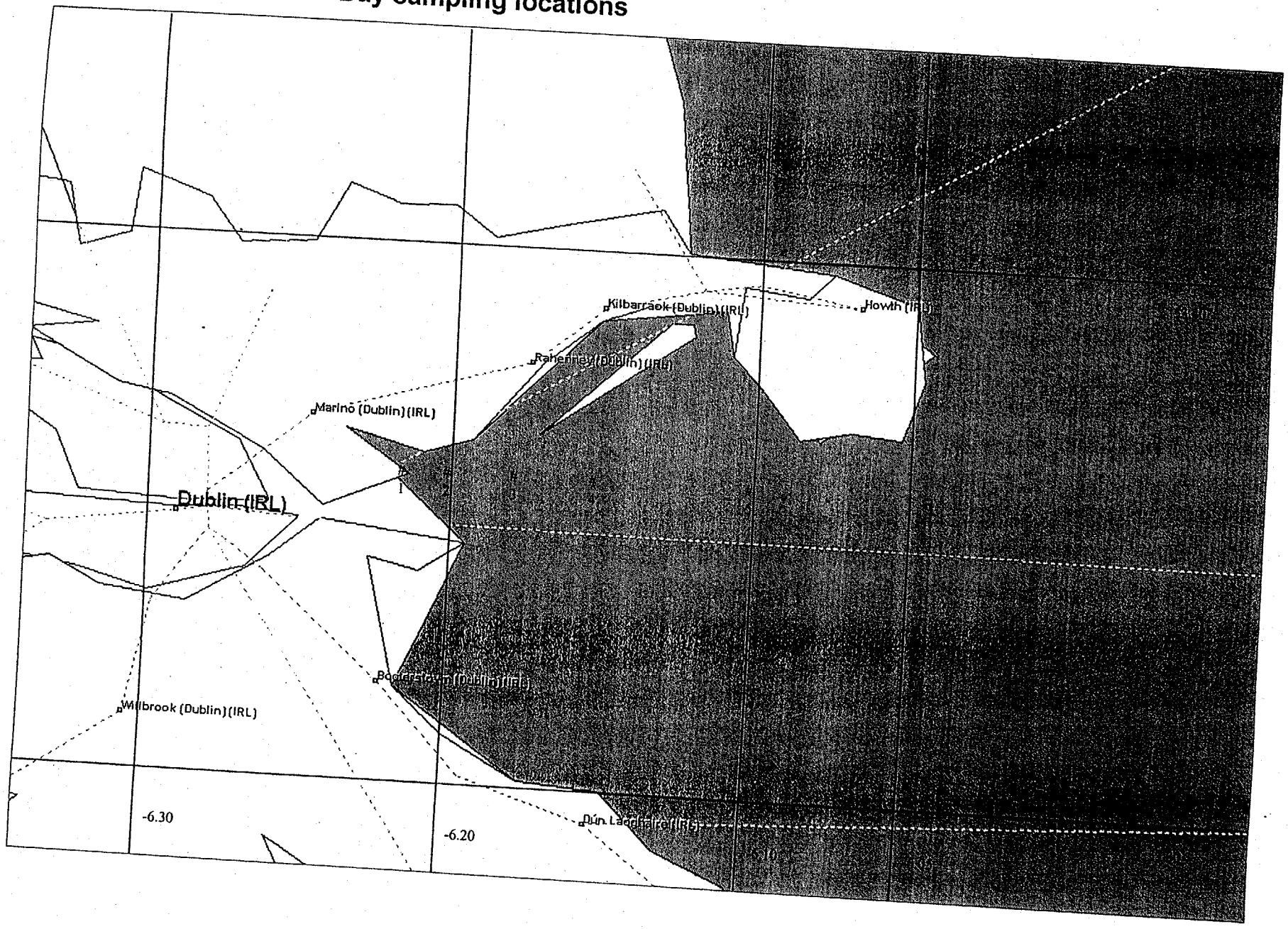


Annex 1.5 - Western Scheldt sampling locations sediment

Annex 1.5 - Western Scheldt sampling locations sediment

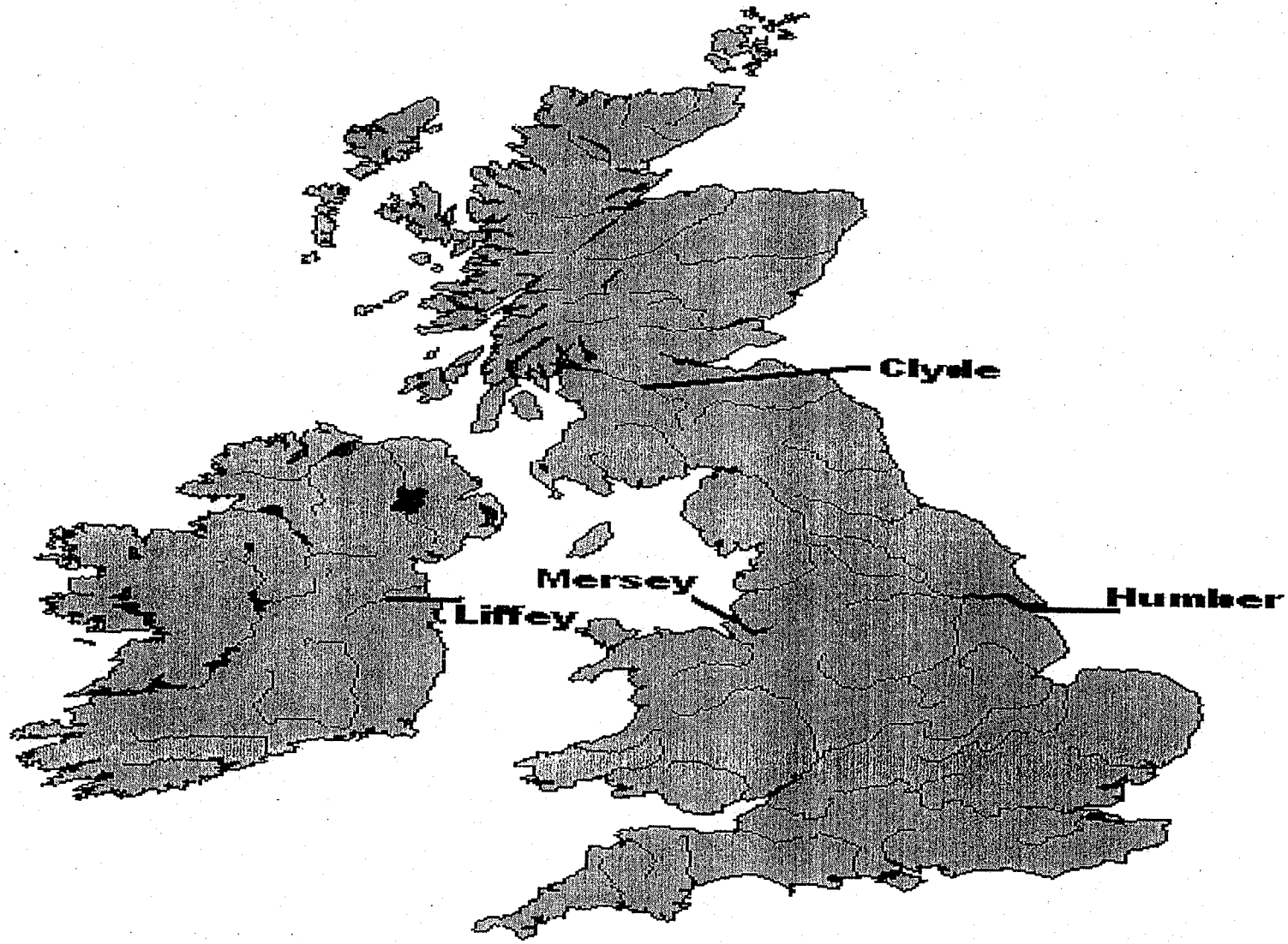


Annex 1.6 - Dublin Bay sampling locations

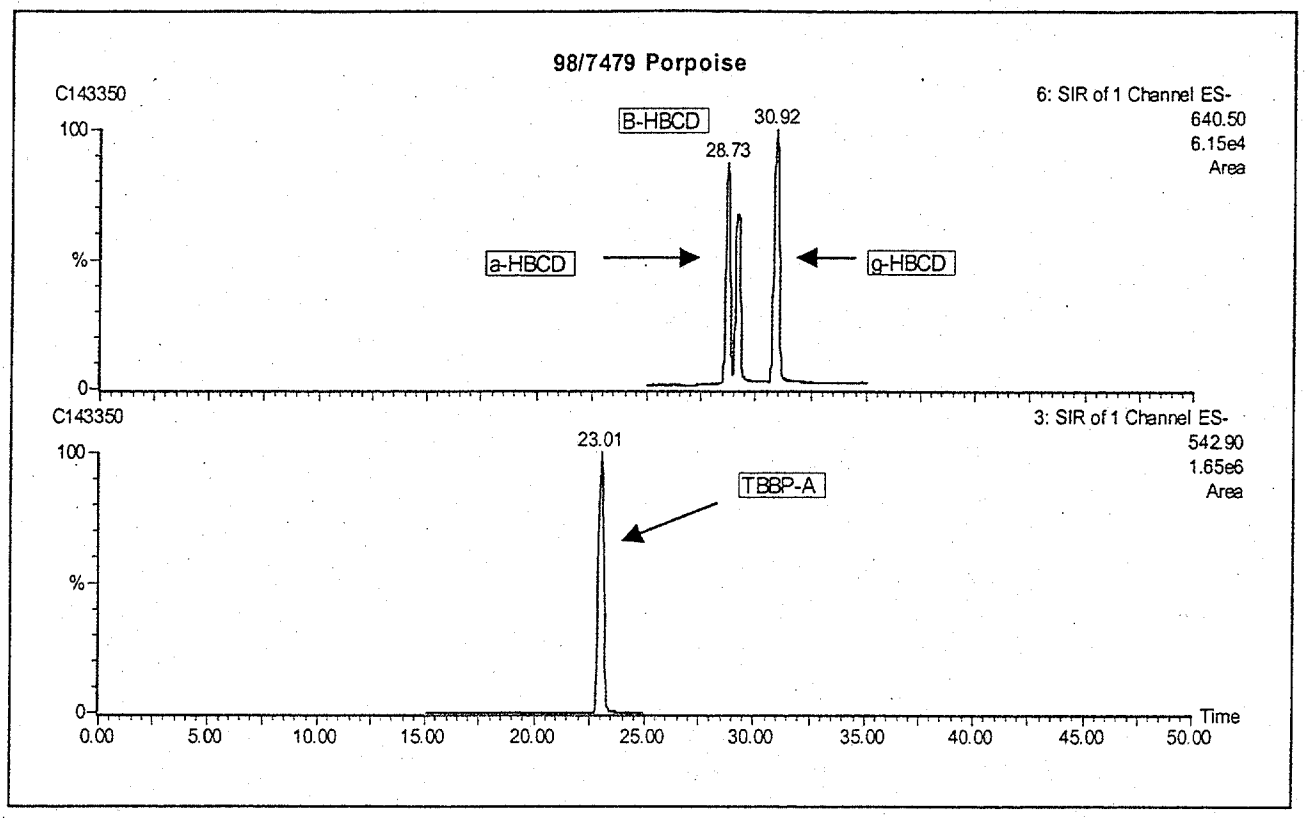


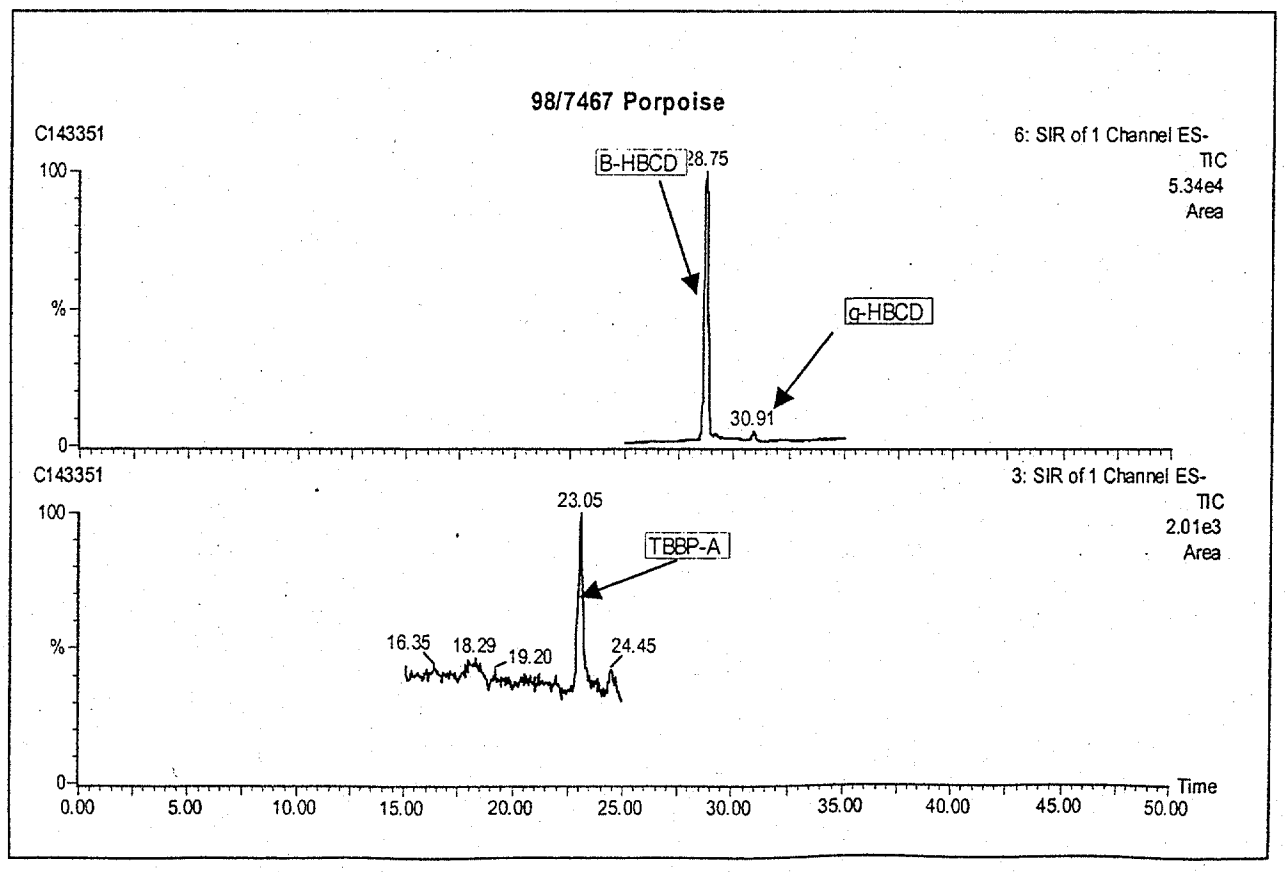
Annex 2

Annex 2

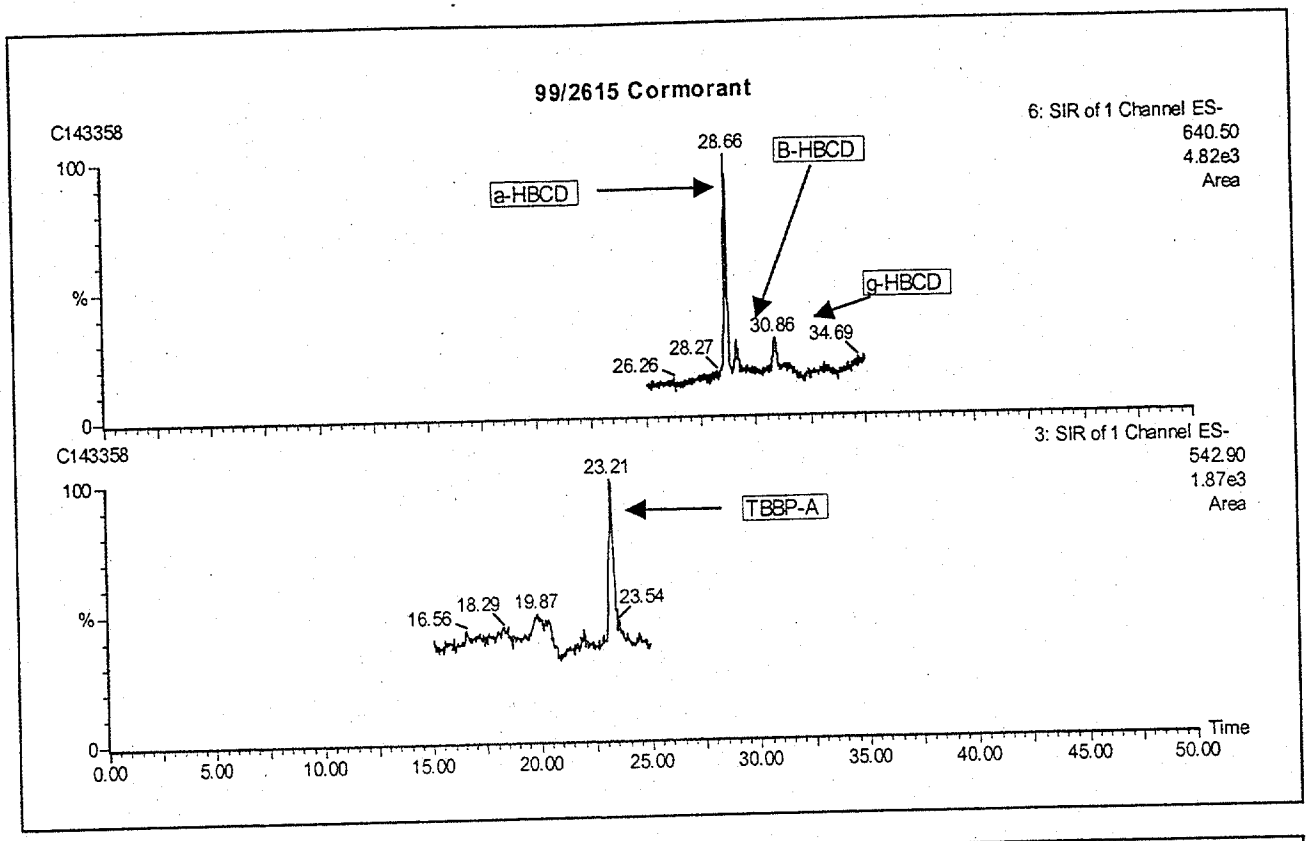


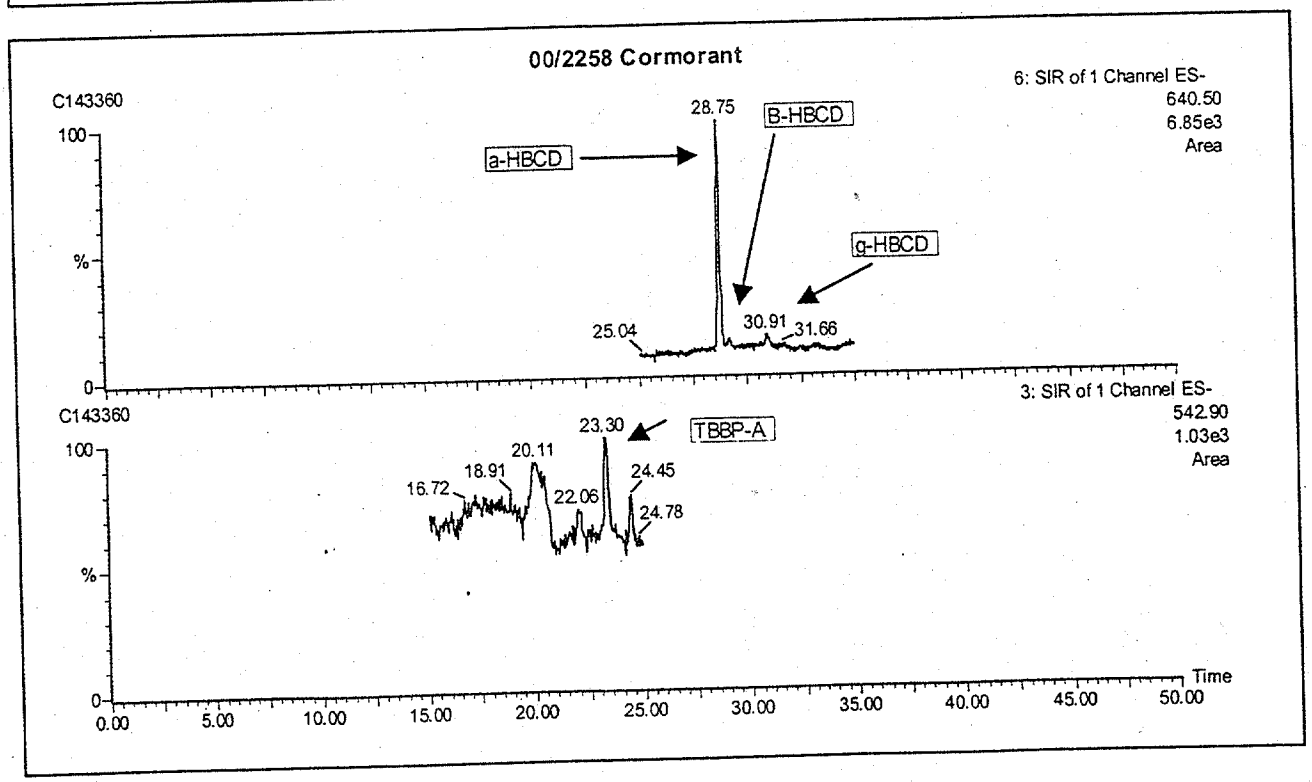
Annex 2.1. Chromatograms of porpoise blubber extracts

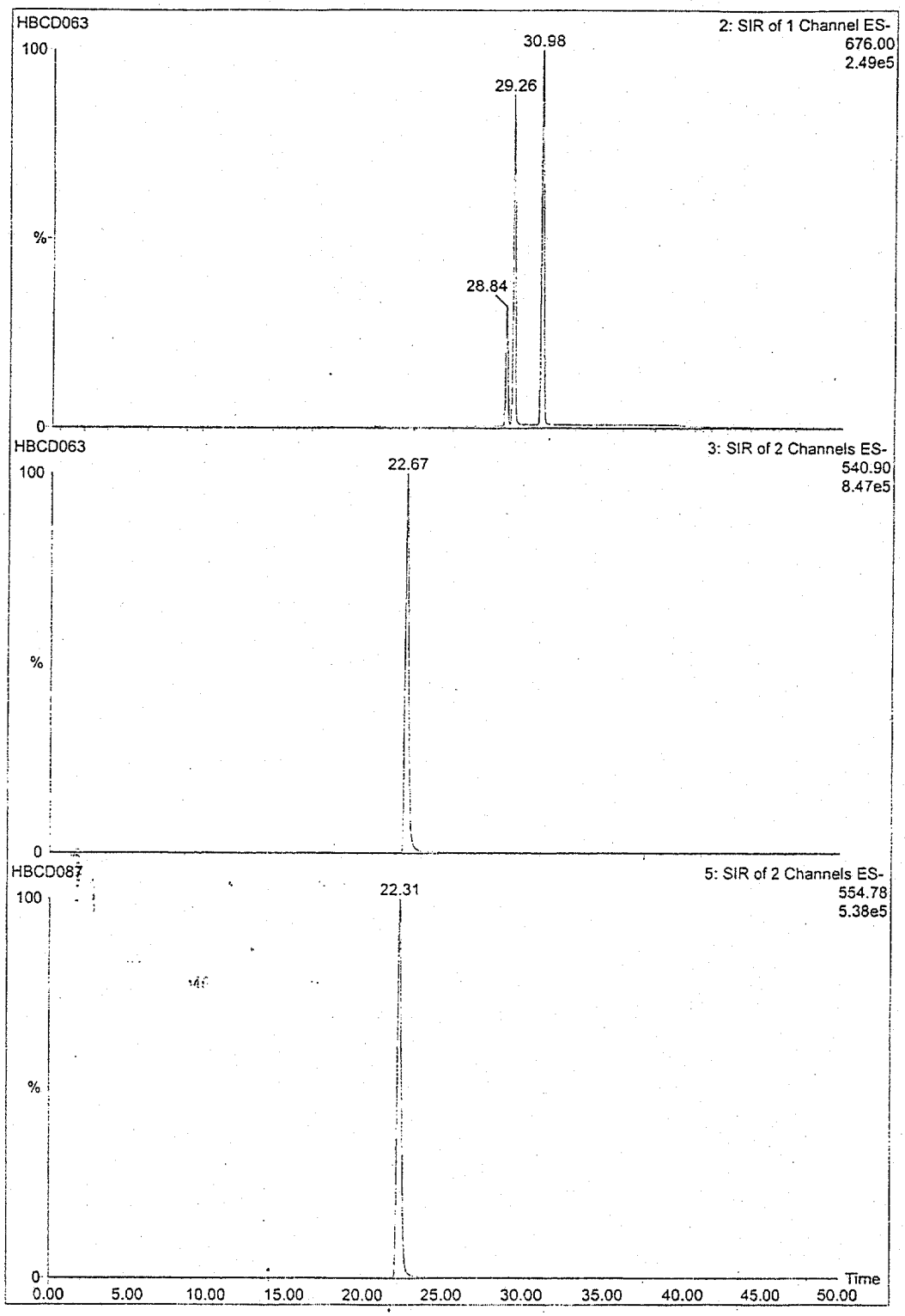




Annex 2.2. Selected chromatograms of cormorant liver extracts







Annex 2.3 LC/MS chormatogram of HBCD isomer standard and TBBP-A.

The top trace shows the three HBCD isomers at m/z 676. The middle trace shows the unlabelled TBBP-A at m/z 541. The bottom trace shows the ^{13}C labelled TBBP-A at m/z 555

Annex 3.1. - Total HBCD, TBBP-A, me-TBBP-A en PBDEs in eel from the Scheldt basin

results eel
ug/kg wet weight

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	20001/1477	2001/1478	2001/1479	2001/1480	2001/1481	2001/1482	2001/1483	2001/1484	2001/1485	2001/1486	2001/1487	2001/1488	2001/1489	2001/1491	2001/1492	2001/1493	2001/1494	2001/1495
	Warmebeek Achel-Kluis	Moervaart Daknam	Benede Nete Duffel	Grote Beverdijk Lo-Reninge	IJzer Nieuwpoort	Durne Lokeren	Leie Wervik	Leie Wevelgem.	Leie Oeselgem	Leie St Martens	Scheldt Doel	Scheldt Grens	Scheldt Oudenaarde	Antwerpen Kruisschansbr.	Scheldt Kastel	Scheldt Kennedyt.	Dender Appels	Dender Ninove
bde28	<0.1	0.2	0.4	<0.1	<0.1	<0.1	0.3	0.4	0.6	0.9	3.5	2.9	60	0.6	3.3	3.6	1.0	0.5
bde47	6.1	6.3	20	5.1	5.4	3.1	11	19	25	80	130	120	4800	29	230	100	72	29
bde66	<0.1	0.3	0.3	<0.1	<0.1	<0.1	<0.1	0.3	0.4	0.6	1.2	1.3	33	0.3	0.8	0.8	0.5	<0.1
bde71	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
bde75	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
bde77	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.4	<0.1	<0.1	<0.1	<0.1	<0.1
bde85	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.5	<0.1	<0.1	<0.1	<0.1	<0.1
bde99	0.4	0.2	2.1	0.3	0.4	<0.1	0.5	2.3	5.0	5.7	7.8	7.7	230	2.1	7.6	6.9	3.7	0.3
bde100	3.0	2.9	4.9	1.4	2.1	2.0	4.8	7.0	8.5	25	28	23	hoog	10	40	26	34	9.5
bde119	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.7	0.5	0.5	<0.1	<0.1	0.2	1.8	<0.1	0.1	<0.1	0.1	<0.1
bde138	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
bde153	0.4	0.7	1.6	0.5	0.6	0.3	13	8.6	7.5	4.3	5.2	5.8	89	1.8	9.7	7.0	6.3	1.7
bde154	0.4	0.6	1.0	0.4	0.4	0.3	15	10	6.5	4.1	3.3	3.3	69	1.1	5.1	3.7	3.4	0.8
bde183	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1.8	1.7	0.3	<0.1	<0.1	0.2	0.2	<0.1	<0.1	<0.1	<0.1	<0.1
bde190	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
bde209	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.4	<0.1	<0.1	0.5	0.5	<0.1	<0.1	0.5	<0.1	0.6	<0.1
me-TBBP-A	<0.1	0.2	1.3	<0.1	<0.1	<0.1	2.5	2.2	1.2	<0.1	<0.1	0.4	<0.1	0.2	<0.1	<0.1	<0.1	<0.1
TBBP-A	0.4	<0.1	<0.1	<0.1	2.6	0.7	<0.1	<0.1	<0.1	0.3	<0.1	<0.1	<0.1	1.0	0.1	<0.1	<0.1	<0.1
HBCD	5.5	31	22	<0.4	40	8.6	17	23	1300	890	72	49	5500	24	100	70	110	8.3

results eel
ug/kg lipid base

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	20001/1477	2001/1478	2001/1479	2001/1480	2001/1481	2001/1482	2001/1483	2001/1484	2001/1485	2001/1486	2001/1487	2001/1488	2001/1489	2001/1491	2001/1492	2001/1493	2001/1494	2001/1495
	Warmebeek Achel-Kluis	Moervaart Daknam	Benede Nete Duffel	Grote Beverdijk Lo-Reninge	IJzer Nieuwpoort	Durne Lokeren	Leie Wervik	Leie Wevelgem.	Leie Oeselgem	Leie St Martens	Scheldt Doel	Scheldt Grens	Scheldt Oudenaarde	Antwerpen Kruisschansbr.	Scheldt Kastel	Scheldt Kennedyt.	Dender Appels	Dender Ninove
Lipid (%)	17.3	17.78	11.84	23.32	19.27	16.92	21.3	29.13	26.89	12.49	20.26	16.42	16.57	20.21	26.31	12.31	7.93	23.44
BDE 28	0.5	1.2	3.4	<0.2	<0.2	<0.2	1.3	1.4	2.3	7	17	18	360	2.8	13	29	12	2
BDE 47	35	35	160	22	28	18	51	65	92	640	660	700	28700	140	870	830	920	120
BDE 66	<0.2	1.6	2.5	<0.2	<0.2	<0.2	<0.2	1.1	1.6	5.1	5.8	8	200	1.3	3	6.8	6.5	<0.2
BDE 71	<0.2	<0.2	<0.3	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.4	<0.2	<0.3	<0.3	<0.2	<0.2	<0.4	<0.7	<0.2
BDE 75	<0.2	<0.2	<0.3	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.4	<0.2	<0.3	<0.3	<0.2	<0.2	<0.4	<0.7	<0.2
BDE 77	<0.2	<0.2	<0.4	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.4	<0.2	<0.3	2.7	<0.2	<0.2	<0.4	<0.7	<0.2
BDE 85	<0.4	<0.3	<0.5	<0.2	<0.3	<0.3	<0.2	<0.1	<0.1	<0.3	<0.2	<0.2	3	<0.2	<0.2	<0.3	<0.5	<0.1
BDE 99	2.2	1.1	18	1.4	1.9	<0.2	2.3	8	19	46	38	47	1400	10	29	56	46	1.3
BDE 100	18	16	42	6.0	11	12	23	24	32	200	140	140	hoog	49	150	210	430	40
BDE 119	<0.2	<0.2	<0.3	<0.2	<0.2	<0.2	3.4	1.8	1.9	<0.1	<0.1	1.2	11	<0.2	0.5	1	1.5	0.4
BDE 138	<0.2	<0.2	<0.3	<0.2	<0.2	<0.2	<0.2	<0.1	<0.2	<0.4	<0.2	<0.3	<0.3	<0.2	<0.2	<0.4	<0.7	<0.2
BDE 153	2.2	4.0	13	2.1	2.9	1.6	61	30	28	34	26	35	540	8.9	37	57	80	7.4
BDE 154	2.5	3.5	8.4	1.5	2.0	1.7	71	35	24	33	16	20	420	5.6	19	30	44	3.6
BDE 183	<0.2	<0.2	<0.3	<0.1	<0.2	<0.2	8.4	5.7	1.2	<0.3	<0.2	1.4	1.4	<0.2	<0.2	<0.3	<0.6	<0.2
BDE 190	<0.5	<0.4	<0.7	<0.3	<0.4	<0.4	<0.2	<0.1	<0.2	<0.4	<0.2	<0.3	<0.3	<0.2	<0.2	<0.4	<0.7	<0.2
BDE 209	<0.4	<0.4	<0.6	<0.3	<0.3	<0.4	<0.4	1.5	<0.3	<0.6	2.4	2.8	<0.6	<0.4	1.9	<0.6	7.2	<0.4
me-TBBP-A	<0.2	0.9	11	<0.1	<0.2	<0.2	12	7.5	4.3	<0.1	<0.1	2.5	<0.1	0.9	<0.1	<0.1	<0.2	0.8
TBBP-A	2.6	0.4	<0.3	<0.2	13	4.0	<0.1	<0.1	<0.1	2.1	<0.1	0.4	<0.1	5.1	0.5	<0.1	<0.3	<0.1
HBCD	32	180	190	<1.7	210	51	78	80	4700	7100	360	300	33000	120	390	570	1300	35

Annex 3.2. - Total HBCD, TBBP-A, me-TBBP-A en PBDEs in sediments from the Scheldt basin

results ug/kg — sediment wet weight

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
	2001/1468	2001/1475	2001/1461	2001/1471	2001/1472	2001/1476	2001/1473	2001/1474	2001/1467	2001/1466	2001/1459	2001/1458	2001/1465	2001/1469	2001/1463	2001/1460	2001/1462	2001/1464	2001/1470
	Warmebeek Achel-Kluis	Moervaart Deknam	Benede Nete Duffel	Grote Beverdijk Lo-Reninge	IJzer Nieuwpoort	Durme Lokeren	Leie Wervik	Leie Wevelgem.	Leie Oeselgem.	Leie St Martens	Scheldt Doel	Scheldt Grens	Scheldt Oudeaarde	Antwerpen Kruisschansbr.	Scheldt Kastel	Scheldt Kennedyt.	Dender Appels	Dender Ninove	Vrasenedoc Beveren
BDE 28	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	0.6	1.0	1.6	0.4	0.1	<0.1	<0.1	<0.1	<0.1
BDE 47	<0.1	<0.1	0.3	<0.1	0.1	0.3	0.6	1.5	0.3	2.0	8.0	7.1	75	4.8	2.7	1.1	0.4	0.3	1.5
BDE 66	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.4	0.3	<0.1	0.2	<0.1	<0.1	<0.1	<0.1	<0.1
BDE 71	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
BDE 75	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
BDE 77	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
BDE 85	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	<0.1	0.2	0.6	0.5	6.5	0.4	0.2	<0.1	<0.1	<0.1	0.1
BDE 99	<0.1	<0.1	0.3	0.1	0.2	0.35	0.6	1.6	0.3	2.3	8.3	7.6	77	5.0	3.1	0.9	0.4	0.3	1.6
BDE 100	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	0.4	<0.1	0.7	2.6	2.5	<0.1	1.8	0.9	0.2	<0.1	<0.1	0.6
BDE 119	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
BDE 138	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	0.2	1.8	0.2	<0.1	<0.1	<0.1	<0.1	<0.1
BDE 153	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	0.2	0.4	<0.1	0.7	1.9	1.9	<0.1	1.7	0.6	0.1	<0.1	0.1	0.8
BDE 154	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	<0.1	0.4	1.5	1.5	<0.1	1.2	0.4	<0.1	<0.1	<0.1	0.4
BDE 183	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.4	0.6	<0.1	0.5	0.3	0.2	1.8	0.9	<0.1	<0.1	<0.1	<0.1	0.5
BDE 190	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
BDE 209	<0.1	5.1	7.6	0.4	10	4.4	380	91	93	400	65	130	440	310	100	6.7	7.4	<0.1	185
me-TBBP-A	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.3
TBBP-A	<0.1	0.1	<0.1	<0.1	<0.1	0.55	0.5	2.0	0.3	1.4	0.2	0.3	16	0.8	<0.1	<0.1	0.5	0.2	32
HBCD	<0.2	<0.2	1.1	<0.2	1.7	0.8	2.4	<0.2	<0.2	110	<0.2	36	180	5.8	3.6	1.4	0.7	<0.2	7.9

results ug/kg — sediment dry weight

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
	2001/1468	2001/1475	2001/1461	2001/1471	2001/1472	2001/1476	2001/1473	2001/1474	2001/1467	2001/1466	2001/1459	2001/1458	2001/1465	2001/1469	2001/1463	2001/1460	2001/1462	2001/1464	2001/1470
	Warmebeek Achel-Kluis	Moervaart Deknam	Benede Nete Duffel	Grote Beverdijk Lo-Reninge	IJzer Nieuwpoort	Durme Lokeren	Leie Wervik	Leie Wevelgem.	Leie Oeselgem.	Leie St Martens	Scheldt Doel	Scheldt Grens	Scheldt Oudeaarde	Antwerpen Kruisschansbr.	Scheldt Kastel	Scheldt Kennedyt.	Dender Appels	Dender Ninove	Vrasenedoc Beveren
dry weight (%)	70.9	69.9	74.6	56.7	53.3	65.8	58.2	64.6	81.9	61.5	57.9	57.4	68.9	43.8	72.3	76	82.6	82.7	47.9
BDE 28	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	1.3	1.8	2.2	1.0	0.2	<0.1	<0.1	<0.1	0.2
BDE 47	0.1	0.2	0.3	0.1	0.2	0.4	1.1	2.4	0.4	3.3	14	12	110	11	3.8	1.5	0.7	0.5	3.2
BDE 66	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	0.6	0.6	<0.1	0.4	<0.1	<0.1	<0.1	<0.1	0.2
BDE 71	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
BDE 75	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
BDE 77	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
BDE 85	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	<0.1	0.3	1.0	0.9	9.5	0.8	0.3	0.1	<0.1	<0.1	0.3
BDE 99	0.1	0.1	0.4	0.2	0.3	0.5	1.1	2.4	0.4	3.8	14	13	110	11	4.3	1.2	0.6	0.5	3.8
BDE 100	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	0.2	0.6	0.1	1.2	4.5	4.4	<0.1	4.2	1.3	0.3	0.2	0.1	1.2
BDE 119	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
BDE 138	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.4	0.3	2.6	0.4	<0.1	<0.1	<0.1	<0.1	<0.1
BDE 153	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	0.3	0.6	<0.1	1.2	3.3	3.3	<0.1	3.8	0.9	0.2	<0.1	0.2	1.7
BDE 154	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	0.3	<0.1	0.7	2.5	2.6	<0.1	2.8	0.6	0.1	<0.1	<0.1	0.8
BDE 183	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	0.8	0.8	<0.1	0.9	0.6	0.4	2.7	2.1	<0.1	<0.1	<0.1	<0.1	1.0
BDE 190	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
BDE 209	<0.1	8.6	10	0.7	19	6.65	650	140	110	640	110	220	640	700	150	8.8	12	<0.1	385
me-TBBP-A	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.3	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.5
TBBP-A	<0.1	0.2	0.1	0.1	<0.1	0.65	0.8	3.1	0.3	2.3	0.3	0.5	24	1.8	<0.1	<0.1	0.8	0.2	67
HBCD	<0.3	<0.3	1.4	<0.4	3.2	1.2	4.2	<0.3	<0.2	170	<0.4	63	260	13	5.0	1.9	1.0	<0.3	17

results ug/kg — sediment TOC base

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
	2001/1468	2001/1475	2001/1461	2001/1471	2001/1472	2001/1476	2001/1473	2001/1474	2001/1467	2001/1466	2001/1459	2001/1458	2001/1465	2001/1469	2001/1463	2001/1460	2001/1462	2001/1464	2001/1470
	Warmebeek Achel-Kluis	Moervaart Deknam	Benede Nete Duffel	Grote Beverdijk Lo-Reninge	IJzer Nieuwpoort	Durme Lokeren	Leie Wervik	Leie Wevelgem.	Leie Oeselgem.	Leie St Martens	Scheldt Doel	Scheldt Grens	Scheldt Oudeaarde	Antwerpen Kruisschansbr.	Scheldt Kastel	Scheldt Kennedyt.	Dender Appels	Dender Ninove	Vrasenedoc Beveren
TOC base (%)	0.63	2.38	1	2.4	1.81	1.46	1.46	1.39	0.23	1.98	1.59	1.43	2.45	4.09	0.36	1.43	2.3	1.58	3.57
BDE 28	<1.1	<0.7	2.2	<0.8	<1.0	<1.2	<1.2	2.2	<6.8	5.8	48	71	63	11	30	4.6	<0.3	<1.2	2.1
BDE 47	11	4.0	26	2.9	6.8	18.5	44	110	140	100	500	490	3100	120	750	79	20	20	43
BDE 66	<1.1	<0.8	<1.7	<0.8	<1.0	<1.2	<1.2	3.4	<6.9	4.5	22	22	<0.3	4.8	18	1.2	<0.3	<1.2	1.8
BDE 71	<1.1	<0.7	<1.7	<0.8	<1.0	<1.2	<1.2	<1.2	<6.8	<0.9	<0.5	<0.5	<0.3	<0.2	<1.9	<0.5	<0.3	<1.2	<0.2
BDE 75	<1.1	<0.8	<1.7	<0.8	<1.0	<1.2	<1.2	<1.3	<6.9	<0.9	4.8	<0.5	<0.3	<0.2	<1.9	<0.5	<0.3	<1.2	<0.2
BDE 77	<1.1	<0.8	<1.8	<0.8	<1.0	<1.3	<1.3	<1.3	<7.1	<1.0	<0.5	<0.6	<0.3	<0.2	<2.0	<0.5	0.6	<1.3	<0.2
BDE 85	<2.0	<1.1	<2.6	<1.2	<1.5	<1.8	<1.8	8.7	<10	9.0	37	38	270	8.6	67	5.9	0.1	<1.8	4.0
BDE 99	15	3.2	28	4.9	9.1	22.5	42	110	150	120	520	530	3100	120	860	63	17	21	50
BDE 100	1.0	1.2	5.9	<0.8	1.7	5.25	9.3	30	36	37	160	160	<0.3	45	260	17	4.1	4.8	17
BDE 119	<1.1	<0.7	<1.7	<0.8	<1.0	<1.2	2.8	1.7	<6.8	<0.9	<0.5	<0.5	<0.3	<0.2	<1.9	<0.5	<0.3	<1.2	<0.2
BDE 138	<5.3	<0.7	<1.7	<0.8	<1.0	<1.2	<1.2	<1.2	<6.8	2.5	14	11	74	4.0	10	<2.6	<1.6	<1.2	<1.0
BDE 153	0.6	1.0	3.0	<0.8	1.3	6.8	14	29	19	36	120	130	<0.3	41	180	9.1	2.1	6.9	23
BDE 154	<1.1	<0.8	<1.8	<0.8	<1.0	2.6	5.4	15	18	22	92	100	<0.3	30	120	6	0.9	2.4	11
BDE 183	<4.8	0.7	4.2	<0.7	0.8	6	30	38	<6.3	28	20	15	75	23	6.0	<2.3	<1.5	0.6	14
BDE 190	<5.4	<1.5	<3.4	<1.6	<2.0	<2.2	<2.4	<2.5	<14	<1.8	<2.4	<2.7	<1.5	<0.9	<9.5	<2.6	<1.7	<2.4	<1.0
BDE 209	<4.8	220	760	16	570	300	25900	6500	40600	20000	4100	8900	18000	7500	29200	470	320	<2.2	5150
me-TBBP-A	<0.8	<0.6	<1.3	<0.6	<0.8	<1.0	<0.9	13	<5.3	<0.7	<0.4	<0.4	<0.2	<0.1	<1.5	<0.4	<0.3	<0.9	8.6
TBBP-A	9.1	4.8	8.3	2.4	0.9	38.5	33	140	120	72	11	21	680	19	12	<0.5	22	10	890
HBCD	<29	<8.1	110	<8.6	94	54	170	<14	<74	5400	<13	2500	7200	140	1000	99	28	<13	230

Annex 3.2a - Comparison of eel and sediment results, Scheldt basin

results eel

ug/kg lipid base

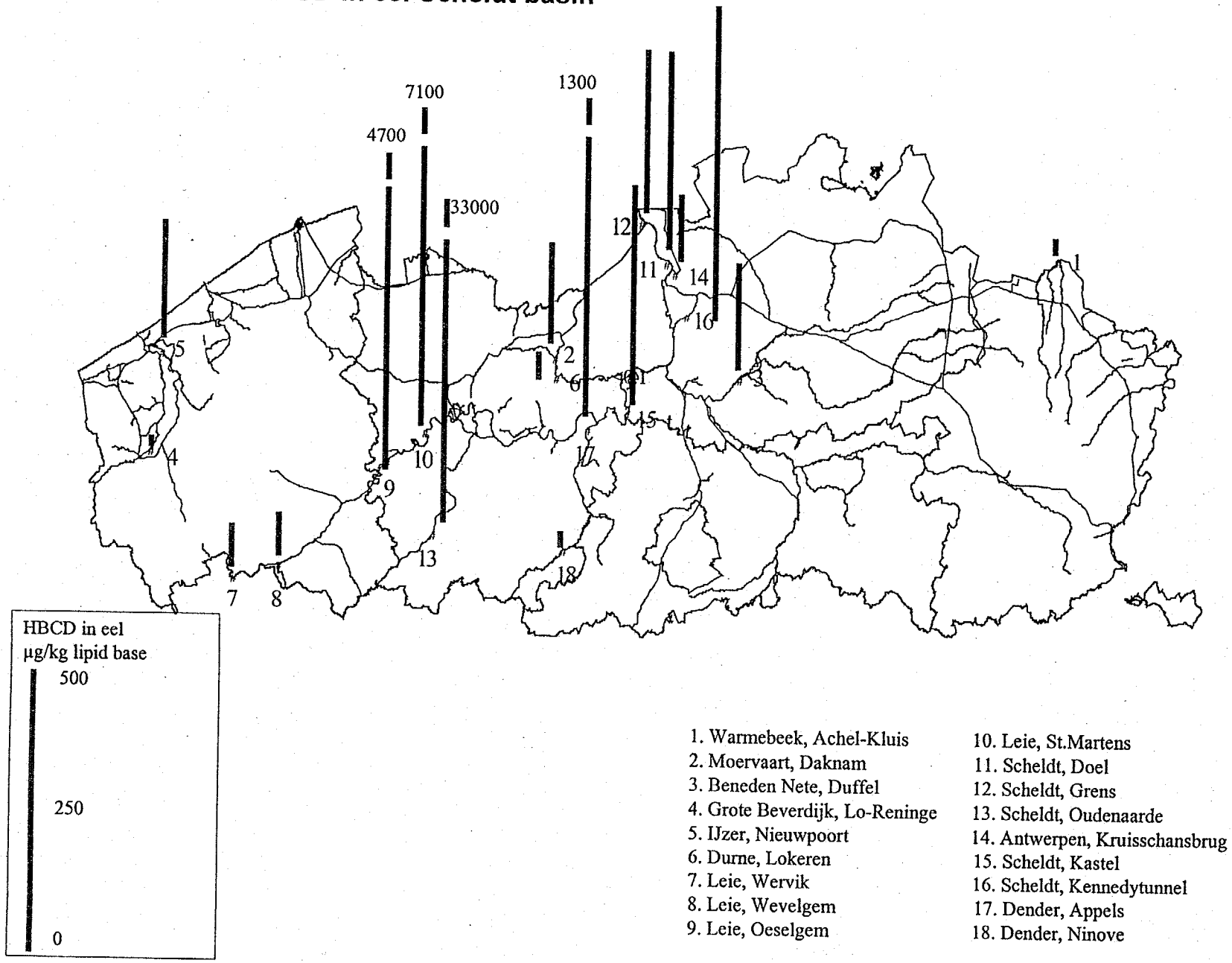
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	20001/1477	2001/1478	2001/1479	2001/1480	2001/1481	2001/1482	2001/1483	2001/1484	2001/1485	2001/1486	2001/1487	2001/1488	2001/1489	gemiddelde	2001/1492	2001/1493	2001/1494	2001/1495
	Warmebeek Achel-Kluis	Moervaart Daknam	Benede Nete Duffel	Grote Beverdijk Lo-Reninge	IJzer Nieuwpoort	Durne Lokeren	Lele Wervik	Lele Wevelgem.	Lele Oeselgem	Lele St Martens	Scheldt Doel	Scheldt Grens	Scheldt Oudenaarde	Antwerpen Kruisschansbr.	Scheldt Kastel	Scheldt Kennedyt.	Dender Appels	Dender Ninove
Lipid (%)	17.3	17.78	11.84	23.32	19.27	16.92	21.3	29.13	26.89	12.49	20.26	16.42	16.57	20.21	26.31	12.31	7.93	23.44
BDE 28	0.5	1.2	3.4	<0.2	<0.2	<0.2	1.3	1.4	2.3	7	17	18	360	2.8	13	29.0	12	2
BDE 47	35	35	160	22	28	18	51	65	92	640	660	700	28700	140	870	830	920	120
BDE 66	<0.2	1.6	2.5	<0.2	<0.2	<0.2	<0.2	1.1	1.6	5.1	5.8	8	200	1.3	3	6.8	6.5	<0.2
BDE 71	<0.2	<0.2	<0.3	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.4	<0.2	<0.3	<0.3	<0.2	<0.2	<0.4	<0.7	<0.2
BDE 75	<0.2	<0.2	<0.3	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.4	<0.2	<0.3	<0.3	<0.2	<0.2	<0.4	<0.7	<0.2
BDE 77	<0.2	<0.2	<0.4	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.4	<0.2	<0.3	2.7	<0.2	<0.2	<0.4	<0.7	<0.2
BDE 85	<0.4	<0.3	<0.5	<0.2	<0.3	<0.3	<0.2	<0.1	<0.1	<0.3	<0.2	<0.2	3	<0.2	<0.2	<0.3	<0.5	<0.1
BDE 99	2.2	1.1	18	1.4	1.9	<0.2	2.3	8	19	46	38	47	1400	9.8	29	56	46	1.3
BDE 100	18	16	42	6.0	11	12	23	24	32	200	140	140	hoog	49	150	210	430	40
BDE 119	<0.2	<0.2	<0.3	<0.2	<0.2	<0.2	3.4	1.8	1.9	<0.1	<0.1	1.2	11	<0.2	0.5	1	1.5	0.4
BDE 138	<0.2	<0.2	<0.3	<0.2	<0.2	<0.2	<0.2	<0.1	<0.2	<0.4	<0.2	<0.3	<0.3	<0.2	<0.2	<0.4	<0.7	<0.2
BDE 153	2.2	4.0	13	2.1	2.9	1.6	61	30	28	34	26	35	540	8.85	37	57.0	80	7.4
BDE 154	2.5	3.5	8.4	1.5	2.0	1.7	71	35	24	33	16	20	420	5.55	19	30.0	44	3.6
BDE 183	<0.2	<0.2	<0.3	<0.1	<0.2	<0.2	8.4	5.7	1.2	<0.3	<0.2	1.4	1.4	<0.2	<0.2	<0.3	<0.6	<0.2
BDE 190	<0.5	<0.4	<0.7	<0.3	<0.4	<0.4	<0.2	<0.1	<0.2	<0.4	<0.2	<0.3	<0.3	<0.2	<0.2	<0.4	<0.7	<0.2
BDE 209	<0.4	<0.4	<0.6	<0.3	<0.3	<0.4	<0.4	1.5	<0.3	<0.6	2.4	2.8	<0.6	<0.4	1.9	<0.6	7.2	<0.4
me-TBBP-A	<0.2	0.9	11	<0.1	<0.2	<0.2	12	7.5	4.3	<0.1	<0.1	2.5	<0.1	0.9	<0.1	<0.1	<0.2	0.8
TBBP-A	2.6	0.4	<0.3	<0.2	13	4.0	<0.1	<0.1	<0.1	2.1	<0.1	0.4	<0.1	5.1	0.5	<0.1	<0.3	<0.1
HBCD	32	180	190	<1.7	210	51	78	80	4700	7100	360	300	33000	120	390	570	1300	35

results sediment

ug/kg TOC base

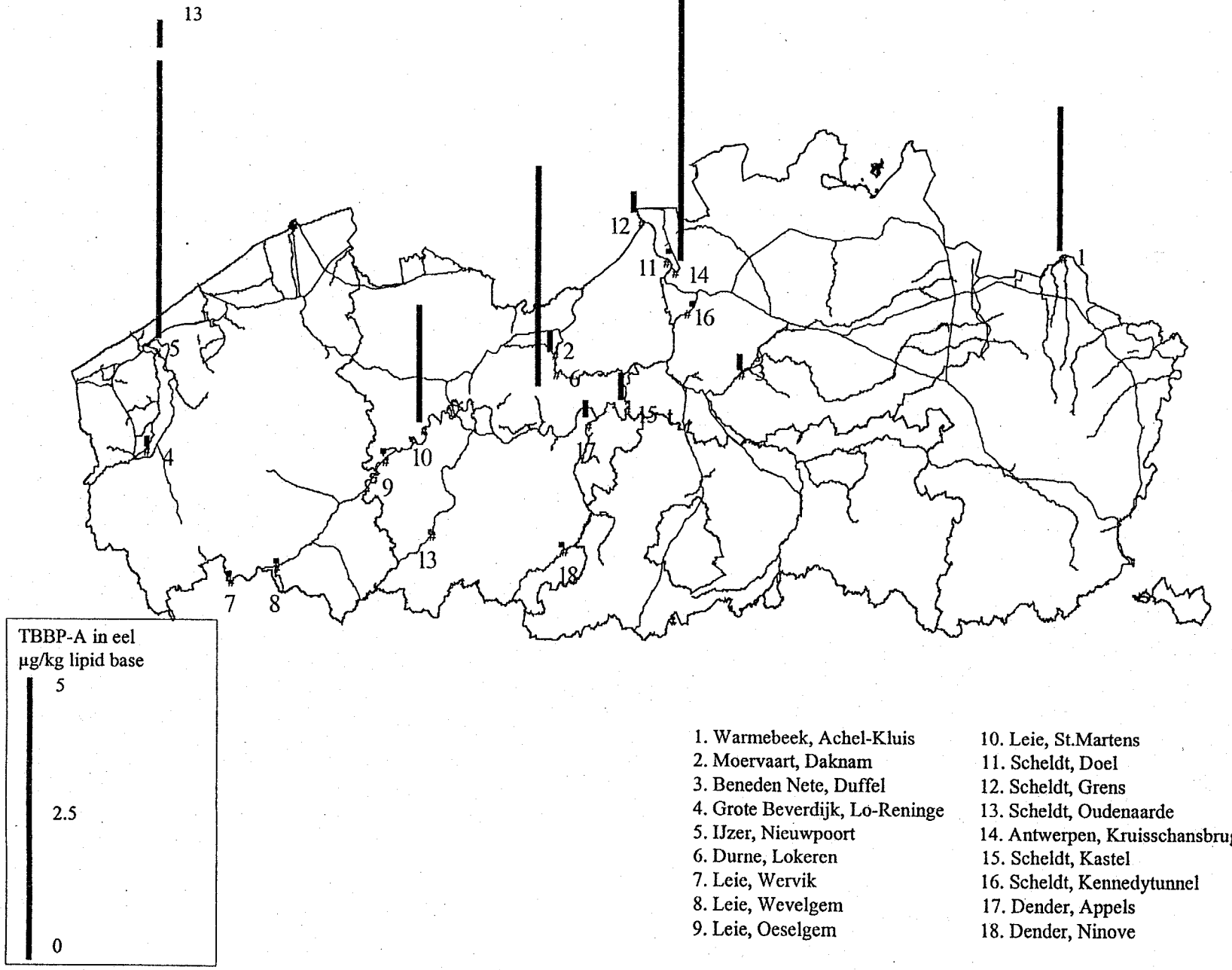
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	2001/1468	2001/1475	2001/1461	2001/1471	2001/1472	2001/1476.1	2001/1473	2001/1474	2001/1467	2001/1466	2001/1459	2001/1458	2001/1465	2001/1469	2001/1463	2001/1460	2001/1462	2001/1464
	Warmebeek Achel-Kluis	Moervaart Daknam	Benede Nete Duffel	Grote Beverdijk Lo-Reninge	IJzer Nieuwpoort	Durne Lokeren	Lele Wervik	Lele Wevelgem.	Lele Oeselgem.	Lele St Martens	Scheldt Doel	Scheldt Grens	Scheldt Oudeaarde	Antwerpen Kruisschansbr.	Scheldt Kastel	Scheldt Kennedyt.	Dender Appels	Dender Ninove
TOC base (%	0.63	2.38	1	2.4	1.81	1.46	1.46	1.39	0.23	1.98	1.59	1.43	2.45	4.09	0.36	1.43	2.3	1.58
BDE 28	<1.1	<0.7	2.2	<0.8	<1.0	<1.2	<1.2	2.2	<6.8	5.8	48	71	63	11	30	4.6	<0.3	<1.2
BDE 47	11	4.0	26	2.9	6.6	18	44	110	140	100	500	490	3100	120	750	79	20	20
BDE 66	<1.1	<0.8	<1.7	<0.8	<1.0	<1.2	<1.2	3.4	<6.9	4.5	22	22	<0.3	4.8	18	1.2	<0.3	<1.2
BDE 71	<1.1	<0.7	<1.7	<0.8	<1.0	<1.2	<1.2	<1.2	<6.8	<0.9	<0.5	<0.5	<0.3	<0.2	<1.9	<0.5	<0.3	<1.2
BDE 75	<1.1	<0.8	<1.7	<0.8	<1.0	<1.2	<1.2	<1.3	<6.9	<0.9	4.8	<0.5	<0.3	<0.2	<1.9	<0.5	<0.3	<1.2
BDE 77	<1.1	<0.8	<1.8	<0.8	<1.0	<1.3	<1.3	<1.3	<7.1	<1.0	<0.5	<0.6	<0.3	<0.2	<2.0	<0.5	0.6	<1.3
BDE 85	<2.0	<1.1	<2.6	<1.2	<1.5	<1.8	<1.8	8.7	<10	9.0	37	38	270	8.6	67	5.9	0.1	<1.8
BDE 99	15	3.2	28	4.9	9.1	21	42	110	150	120	520	530	3100	120	860	63	17	21
BDE 100	1.0	1.2	5.9	<0.8	1.7	4.7	9.3	30	36	37	160	180	<0.3	45	260	17	4.1	4.8
BDE 119	<1.1	<0.7	<1.7	<0.8	<1.0	<1.2	2.8	1.7	<6.8	<0.9	<0.5	<0.5	<0.3	<0.2	<1.9	<0.5	<0.3	<1.2
BDE 138	<5.3	<0.7	<1.7	<0.8	<1.0	<1.2	<1.2	<1.2	<6.8	2.5	14	11	74	4.0	10	<2.6	<1.6	<1.2
BDE 153	0.6	1.0	3.0	<0.8	1.3	6.6	14	29	19	36	120	130	<0.3	41	180	9.1	2.1	6.9
BDE 154	<1.1	<0.8	<1.8	<0.8	<1.0	2.2	5.4	15	16	22	92	100	<0.3	30	120	6	0.9	2.4
BDE 183	<4.8	0.7	4.2	<0.7	0.8	5.4	30	38	<6.3	28	20	15	75	23	6	<2.3	<1.5	0.6
BDE 190	<5.4	<1.5	<3.4	<1.6	<2.0	<2.5	<2.4	<2.5	<14	<1.8	<2.4	<2.7	<1.5	<0.9	<9.5	<2.6	<1.7	<2.4
BDE 209	<4.8	220	760	16	570	260	25900	6500	40600	20000	4100	8900	18000	7500	29200	470	320	<2.2
me-TBBP-A	<0.8	<0.6	<1.3	<0.6	<0.8	<1.0	<0.9	13	<5.3	<0.7	<0.4	<0.4	<0.2	<0.1	<1.5	<0.4	<0.3	<0.9
TBBP-A	9.1	4.8	9.3	2.4	0.9	28	33	140	120	72	11	21	680	19	12	<0.5	22	10
HBCD	<29	<8.1	110	<8.6	94	54	170	<14	<74	5400	<13	2500	7200	140	1000	99	28	<13

Annex 3.3 - Total HBCD in eel Scheldt basin



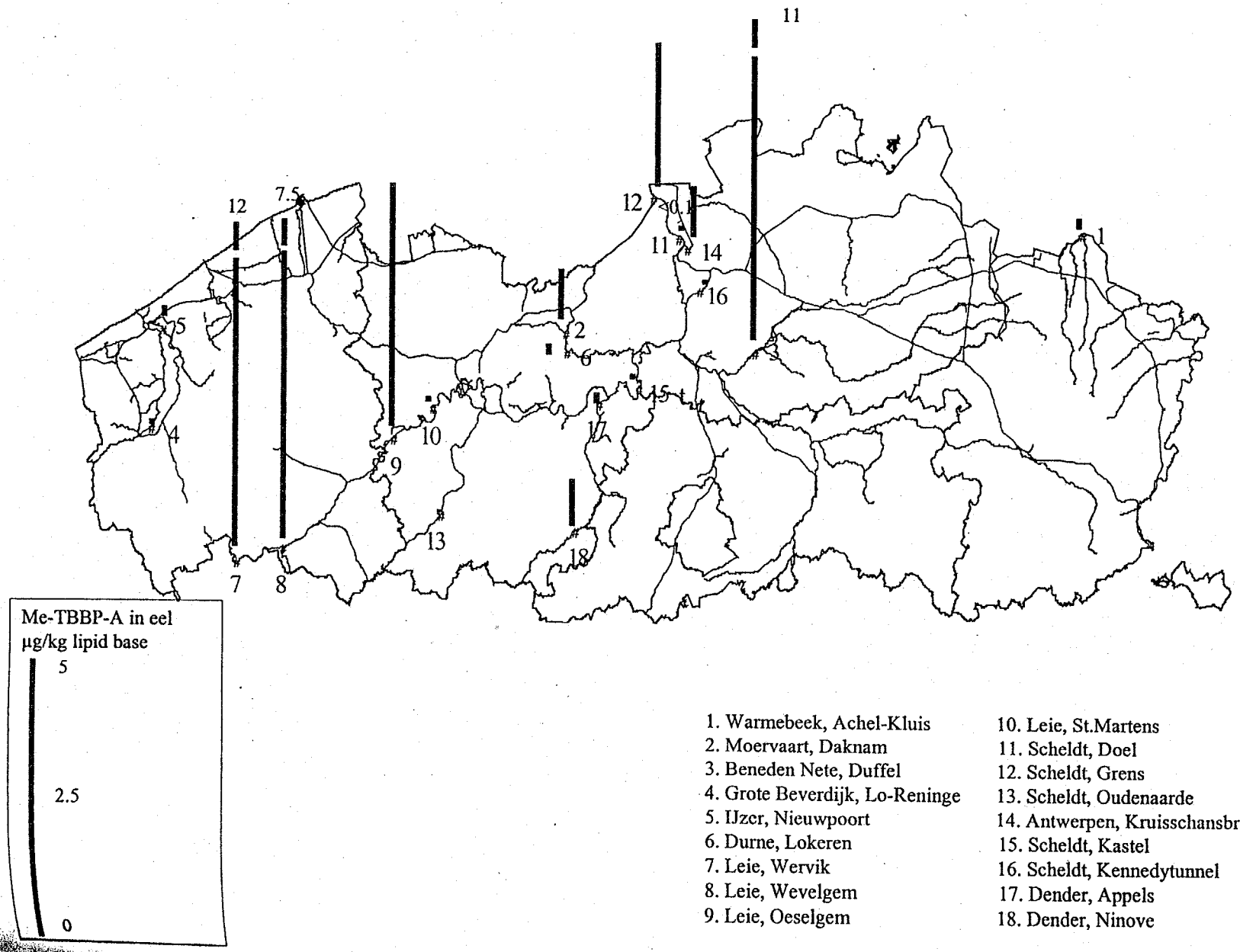
1. Warmebeek, Achel-Kluis
2. Moervaart, Daknam
3. Beneden Nete, Duffel
4. Grote Beverdijk, Lo-Reninge
5. IJzer, Nieuwpoort
6. Durne, Lokeren
7. Leie, Wervik
8. Leie, Wevelgem
9. Leie, Oeselgem
10. Leie, St.Martens
11. Scheldt, Doel
12. Scheldt, Grens
13. Scheldt, Oudenaarde
14. Antwerpen, Kruisschansbrug
15. Scheldt, Kastel
16. Scheldt, Kennedytunnel
17. Dender, Appels
18. Dender, Ninove

Annex 3.4 - Total TBBP-A in eel Scheldt basin



1. Warmebeek, Achel-Kluis
2. Moervaart, Daknam
3. Beneden Nete, Duffel
4. Grote Beverdijk, Lo-Reninge
5. IJzer, Nieuwpoort
6. Durne, Lokeren
7. Leie, Wervik
8. Leie, Wevelgem
9. Leie, Oeselgem
10. Leie, St.Martens
11. Scheldt, Doel
12. Scheldt, Grens
13. Scheldt, Oudenaarde
14. Antwerpen, Kruisschansbrug
15. Scheldt, Kastel
16. Scheldt, Kennedytunnel
17. Dender, Appels
18. Dender, Ninove

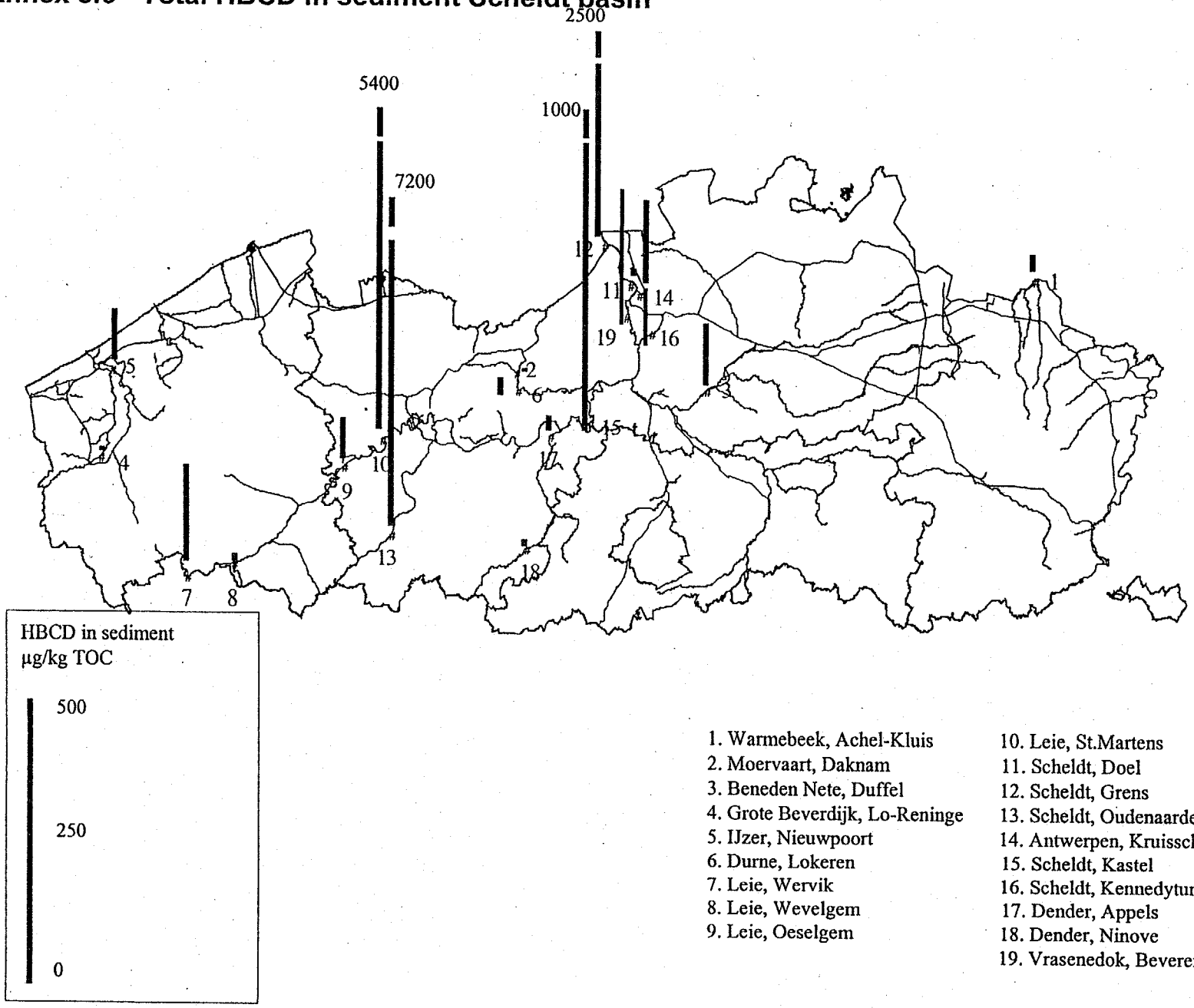
Annex 3.5 - MeTBBP-A in eel Scheldt basin



1. Warmebeek, Achel-Kluis
2. Moervaart, Daknam
3. Beneden Nete, Duffel
4. Grote Beverdijk, Lo-Reninge
5. IJzer, Nieuwpoort
6. Durne, Lokeren
7. Leie, Wervik
8. Leie, Wevelgem
9. Leie, Oeselgem
10. Leie, St.Martens
11. Scheldt, Doel
12. Scheldt, Grens
13. Scheldt, Oudenaarde
14. Antwerpen, Kruisschansbrug
15. Scheldt, Kastel
16. Scheldt, Kennedytunnel
17. Dender, Appels
18. Dender, Ninove

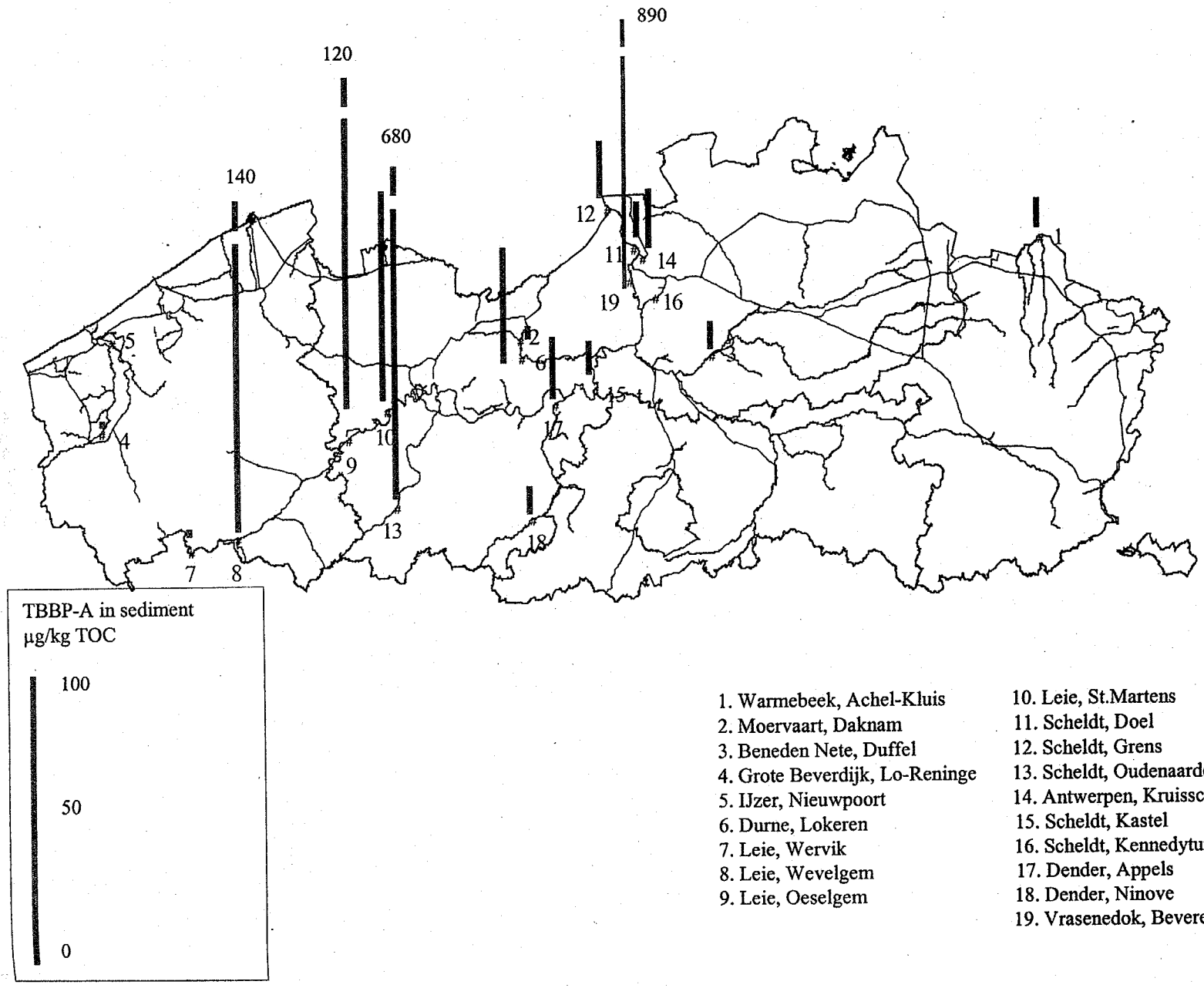
Annex 3.6 - Total HBCD in sediment Scheldt

Annex 3.6 - Total HBCD in sediment Scheldt basin



1. Warmebeek, Achel-Kluis
2. Moervaart, Daknam
3. Beneden Nete, Duffel
4. Grote Beverdijk, Lo-Reninge
5. IJzer, Nieuwpoort
6. Durne, Lokeren
7. Leie, Wervik
8. Leie, Wevelgem
9. Leie, Oeselgem
10. Leie, St.Martens
11. Scheldt, Doel
12. Scheldt, Grens
13. Scheldt, Oudenaarde
14. Antwerpen, Kruisschansbrug
15. Scheldt, Kastel
16. Scheldt, Kennedytunnel
17. Dender, Appels
18. Dender, Ninove
19. Vrasenedok, Beveren

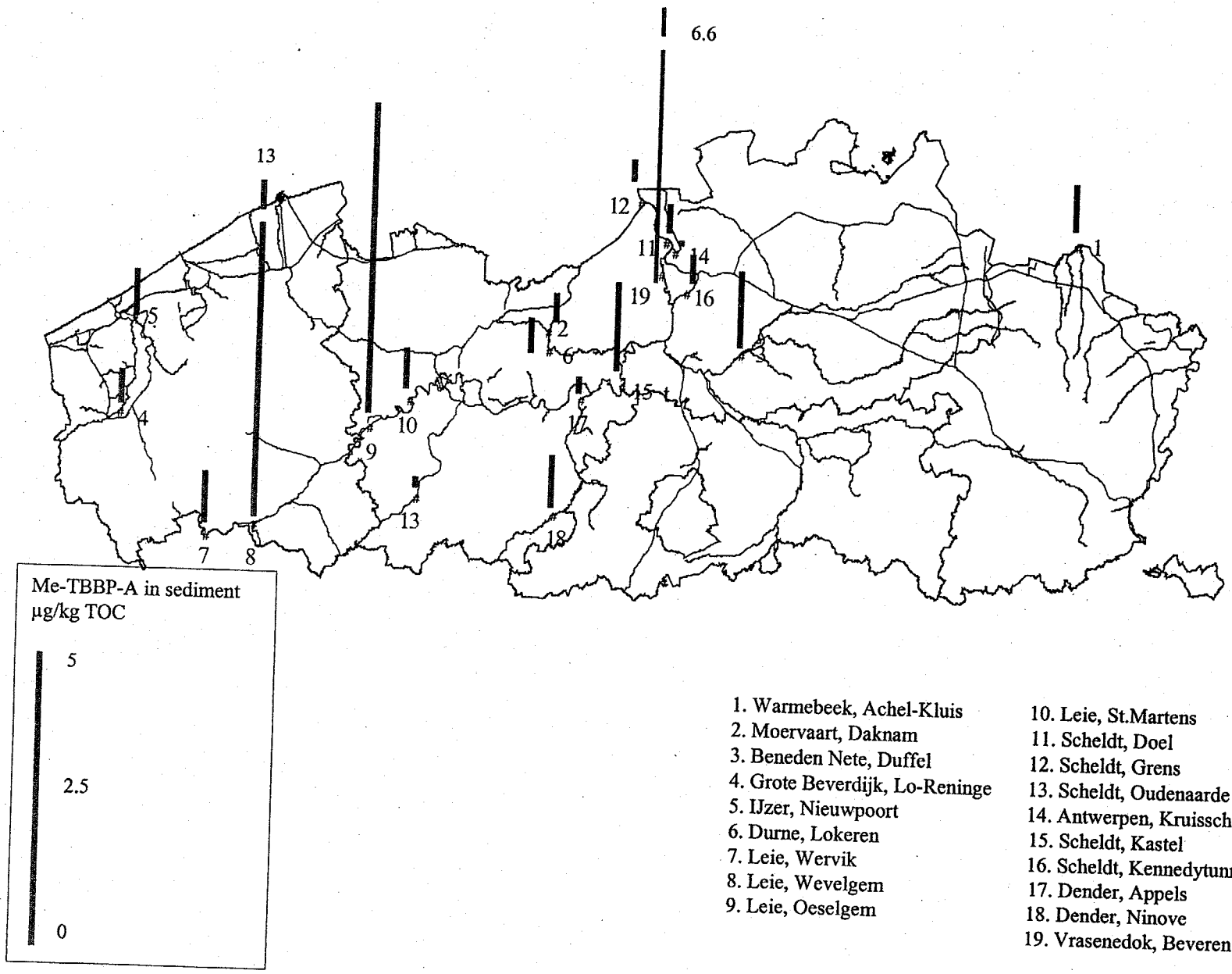
Annex 3.7 - Total TBBP-A in sediment Scheldt basin



1. Warmebeek, Achel-Kluis
2. Moervaart, Daknam
3. Beneden Nete, Duffel
4. Grote Beverdijk, Lo-Reninge
5. IJzer, Nieuwpoort
6. Durne, Lokeren
7. Leie, Wervik
8. Leie, Wevelgem
9. Leie, Oeselgem
10. Leie, St.Martens
11. Scheldt, Doel
12. Scheldt, Grens
13. Scheldt, Oudenaarde
14. Antwerpen, Kruisschansbrug
15. Scheldt, Kastel
16. Scheldt, Kennedytunnel
17. Dender, Appels
18. Dender, Ninove
19. Vrasenedok, Beveren

Annex 3.8 - MeTBBP-A in sedi

Annex 3.8 - MeTBBP-A in sediment Scheldt basin



1. Warmebeek, Achel-Kluis
2. Moervaart, Daknam
3. Beneden Nete, Duffel
4. Grote Beverdijk, Lo-Reninge
5. IJzer, Nieuwpoort
6. Durne, Lokeren
7. Leie, Wervik
8. Leie, Wevelgem
9. Leie, Oeselgem
10. Leie, St.Martens
11. Scheldt, Doel
12. Scheldt, Grens
13. Scheldt, Oudenaarde
14. Antwerpen, Kruisschansbrug
15. Scheldt, Kastel
16. Scheldt, Kennedytunnel
17. Dender, Appels
18. Dender, Ninove
19. Vrasenedok, Beveren

Annex 3.9. - HBCD ratios in eel and sediments from the Scheldt basin

				GC-MS	LC-MS Concentration (µg/kg)			
lims nr.	sample type	locationnr.	location	conc.(µg/kg)	α	β	γ	total
2001/1477	eel	1	Warmebeek Achel-kluis	5.5	<0.3	<0.3	<0.3	<0.9
2001/1478	eel	2	Moervaart Daknam	31	<0.2	<0.2	<0.2	<0.6
2001/1479	eel	3	Benede Nete Duffel	22	<0.2	<0.2	<0.2	<0.6
2001/1480	eel	4	Grote Beverdijk Lo-Reninge	<0.4	<0.2	<0.2	<0.2	<0.6
2001/1481	eel	5	IJzer Nieuwpoort	40	<0.2	<0.2	<0.2	<0.6
2001/1482	eel	6	Durne Lokeren	8.6	<0.2	<0.2	<0.2	<0.6
2001/1483	eel	7	Leie Wervik	17	<0.3	<0.3	<0.3	<0.9
2001/1484	eel	8	Leie Wevelgem	23	<0.3	<0.3	<0.3	<0.9
2001/1485	eel	9	Leie Oeselgem	1300	25	4.9	11	41
2001/1486	eel	10	Leie St Martens	890	25	<0.3	7.7	33
2001/1487	eel	11	Scheldt Doel	72	5.0	<0.3	0.7	5.7
2001/1488	eel	12	Scheldt Grens	49	<0.8	<0.8	<0.8	<2.4
2001/1489	eel	13	Scheldt Oudenaarde	5500	22	21	1.0	44
2001/1491	eel	14	Antwerp Kruisschansbr.	24	1.7	<0.3	<0.3	1.7
2001/1492	eel	15	Scheldt Kastel	100	4.6	<0.3	<0.3	4.6
2001/1493	eel	16	Scheldt Kennedyt.	70	3.4	<0.3	<0.3	3.4
2001/1494	eel	17	Dender Appels	110	<0.3	<0.3	<0.3	<0.9
2001/1495	eel	18	Dender Ninove	8.3	<0.7	<0.7	<0.7	<2.1
2001/1468	sediment	1	Warmebeek Achel-kluis	<0.2	<0.1	<0.1	<0.1	<0.3
2001/1475	sediment	2	Moervaart Daknam	<0.2	<0.1	<0.1	<0.1	<0.3
2001/1461	sediment	3	Benede Nete Duffel	1.1	<0.1	<0.1	0.5	0.5
2001/1471	sediment	4	Grote Beverdijk Lo-Reninge	<0.2	<0.1	<0.1	<0.1	<0.3
2001/1472	sediment	5	IJzer Nieuwpoort	1.7	<0.1	<0.1	0.9	0.9
2001/1476	sediment	6	Durne Lokeren	0.8	<0.1	<0.1	<0.1	<0.3
2001/1473	sediment	7	Leie Wervik	2.4	<0.1	<0.1	<0.1	<0.3
2001/1474	sediment	8	Leie Wevelgem	<0.2	<0.1	<0.1	<0.1	<0.3
2001/1466	sediment	10	Leie St Martens	110	7.4	<0.1	31	39
2001/1467	sediment	10	Leie Oeselgem	<0.2	<0.1	<0.1	<0.1	<0.3
2001/1459	sediment	11	Scheldt Doel	<0.2	<0.1	<0.1	<0.1	<0.3
2001/1458	sediment	12	Scheldt Grens	36	<0.2	<0.2	83	83
2001/1465	sediment	13	Scheldt Oudeaarde	180	180	60	710	950
2001/1469	sediment	14	Antwerpen Kruisschansbr.	5.8	<0.1	<0.1	<0.1	<0.3
2001/1463	sediment	15	Scheldt Kastel	3.6	<0.2	<0.2	3.6	3.6
2001/1460	sediment	16	Scheldt Kennedyt.	1.4	0.3	<0.1	<0.1	0.3
2001/1462	sediment	17	Dender Appels	0.7	0.3	<0.1	0.4	0.7
2001/1464	sediment	18	Dender Ninove	<0.2	<0.1	<0.1	0.2	0.2
2001/1470	sediment	19	Vrasenedoc Beveren	7.9				

Annex 3.9. - HBCD ratios in eel and sediments from the Scheldt basin

				GC-MS	LC-MS Concentration (µg/kg)			
lims nr.	sample type	locationnr.	location	conc.(µg/kg)	α	β	γ	total
2001/1477	eel	1	Warmebeek Achel-kluis	5.5	<0.3	<0.3	<0.3	<0.9
2001/1478	eel	2	Moervaart Daknam	31	<0.2	<0.2	<0.2	<0.6
2001/1479	eel	3	Benede Nete Duffel	22	<0.2	<0.2	<0.2	<0.6
2001/1480	eel	4	Grote Beverdijk Lo-Reninge	<0.4	<0.2	<0.2	<0.2	<0.6
2001/1481	eel	5	IJzer Nieuwpoort	40	<0.2	<0.2	<0.2	<0.6
2001/1482	eel	6	Durne Lokeren	8.6	<0.2	<0.2	<0.2	<0.6
2001/1483	eel	7	Leie Wervik	17	<0.3	<0.3	<0.3	<0.9
2001/1484	eel	8	Leie Wevelgem	23	<0.3	<0.3	<0.3	<0.9
2001/1485	eel	9	Leie Oeselgem	1300	25	4.9	11	41
2001/1486	eel	10	Leie St Martens	890	25	<0.3	7.7	33
2001/1487	eel	11	Scheldt Doel	72	5.0	<0.3	0.7	5.7
2001/1488	eel	12	Scheldt Grens	49	<0.8	<0.8	<0.8	<2.4
2001/1489	eel	13	Scheldt Oudenaarde	5500	22	21	1.0	44
2001/1491	eel	14	Antwerp Kruisschansbr.	24	1.7	<0.3	<0.3	1.7
2001/1492	eel	15	Scheldt Kastel	100	4.6	<0.3	<0.3	4.6
2001/1493	eel	16	Scheldt Kennedyt.	70	3.4	<0.3	<0.3	3.4
2001/1494	eel	17	Dender Appels	110	<0.3	<0.3	<0.3	<0.9
2001/1495	eel	18	Dender Ninove	8.3	<0.7	<0.7	<0.7	<2.1
2001/1468	sediment	1	Warmebeek Achel-kluis	<0.2	<0.1	<0.1	<0.1	<0.3
2001/1475	sediment	2	Moervaart Daknam	<0.2	<0.1	<0.1	<0.1	<0.3
2001/1461	sediment	3	Benede Nete Duffel	1.1	<0.1	<0.1	0.5	0.5
2001/1471	sediment	4	Grote Beverdijk Lo-Reninge	<0.2	<0.1	<0.1	<0.1	<0.3
2001/1472	sediment	5	IJzer Nieuwpoort	1.7	<0.1	<0.1	0.9	0.9
2001/1476	sediment	6	Durne Lokeren	0.8	<0.1	<0.1	<0.1	<0.3
2001/1473	sediment	7	Leie Wervik	2.4	<0.1	<0.1	<0.1	<0.3
2001/1474	sediment	8	Leie Wevelgem	<0.2	<0.1	<0.1	<0.1	<0.3
2001/1466	sediment	10	Leie St Martens	110	7.4	<0.1	31	39
2001/1467	sediment	10	Leie Oeselgem	<0.2	<0.1	<0.1	<0.1	<0.3
2001/1459	sediment	11	Scheldt Doel	<0.2	<0.1	<0.1	<0.1	<0.3
2001/1458	sediment	12	Scheldt Grens	36	<0.2	<0.2	83	83
2001/1465	sediment	13	Scheldt Oudeaarde	180	180	60	710	950
2001/1469	sediment	14	Antwerpen Kruisschansbr.	5.8	<0.1	<0.1	<0.1	<0.3
2001/1463	sediment	15	Scheldt Kastel	3.6	<0.2	<0.2	3.6	3.6
2001/1460	sediment	16	Scheldt Kennedyt.	1.4	0.3	<0.1	<0.1	0.3
2001/1462	sediment	17	Dender Appels	0.7	0.3	<0.1	0.4	0.7
2001/1464	sediment	18	Dender Ninove	<0.2	<0.1	<0.1	0.2	0.2
2001/1470	sediment	19	Vrasenedoc Beveren	7.9				

Annex 4.1. - Total HBCD, TBBP-A, me-TBBP-A en PBDEs in STP samples from The Netherlands (dry weight)

results	ug/kg	dry weight																		
	2001/1683	2001/1698	2001/1684	2001/1667	2001/1700	2001/1688	2001/1686	2001/1699	2001/1685	2001/1682	2001/1697	2001/1681	2001/1693	2001/1692	2001/1694	2001/1689	2001/1691	2001/1690	2001/1701	2001/1696
	STP1	STP1	STP1	STP2	STP2	STP2	STP3	STP3	STP3	STP4	STP4	STP4	STP5	STP5	STP5	STP6	STP7	STP8	STP9	STP10
	influent	effluent	sewage sludge	influent	effluent	sewage sludge	influent	effluent	sewage sludge	influent	effluent	sewage sludge	influent	effluent	sewage sludge	sewage sludge	sewage sludge	sewage sludge	sewer sludge	sewage sludge
BDE 28	<3.9	<0.1	<0.2	<3.1	0.9	0.2	<1.1	0.9	0.1	<2.0	1.0	0.2	<7.2	0.8	0.2	0.2	<0.1	<0.1	<0.1	0.2
BDE 47	25	67	5.0	22	45	9.9	16	43	5.1	27	57	8.5	43	33	6.1	17	17	2	0.4	6.9
BDE 66	<3.9	1.9	<0.2	<3.1	1.2	0.3	<1.1	1.2	0.2	<2.0	1.7	0.2	<7.3	1.1	0.3	0.5	0.6	<0.1	<0.1	0.3
BDE 71	<3.9	<0.1	<0.2	<3.1	<0.2	<0.1	<1.1	<0.1	<0.1	<2.0	<0.1	<0.1	<7.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
BDE 75	14	<0.1	<0.2	<3.1	<0.2	<0.1	<1.1	1.1	<0.1	<2.0	0.6	<0.1	<7.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
BDE 77	<4.1	<0.1	<0.2	<3.2	<0.2	<0.1	<1.1	<0.1	<0.1	<2.1	<0.1	<0.1	<7.5	<0.2	<0.1	<0.1	<0.1	<0.1	<0.1	0.2
BDE 85	<1.5	2.6	<0.1	<1.2	1.6	0.5	1.6	1.6	0.2	3.1	2.5	0.4	<2.8	1.3	0.3	1.2	0.7	<0.1	<0.1	6.3
BDE 99	25	75	5.6	19	39	9.8	12	40	4.5	27	59	8.5	39	36	6.9	22	19	2.4	0.4	1.5
BDE 100	13	28	1.7	10	7.8	2.2	5.0	8.8	1.4	10	16	2.0	24	7.2	1.6	6.7	3.1	0.4	0.1	<0.1
BDE 119	<3.9	<0.1	<0.2	<3.1	<0.2	<0.1	<1.0	<0.1	<0.1	<2.0	<0.1	<0.1	<7.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1
BDE 138	<3.9	0.8	<0.2	<3.1	<0.2	<0.1	<1.0	0.8	<0.1	<2.0	0.8	0.1	<7.1	0.6	0.1	0.3	0.6	<0.1	0.1	0.1
BDE 153	<4.1			<3.3			<1.1			<2.1			<7.6							
BDE 154	<4.0	6.7	0.8	<3.2	2.8	1.0	<1.1	3.3	0.4	<2.1	4.7	0.8	<7.4	2.9	0.6	3.2	1.4	0.2	0.2	0.7
BDE 183	<3.6	6.3	<0.1	<2.9	3.0	1.7	<1.0	3.0	0.4	<1.8	5.9	0.9	<6.7	3.0	1.4	1.0	2.6	0.2	<0.1	1.1
BDE 190	<9.9	<0.3	<0.4	<7.8	<0.4	<0.1	<2.7	<0.3	<0.1	<5.1	<0.3	<0.1	<18	<0.4	<0.1	<0.1	<0.3	<0.1	<0.1	<0.1
BDE 209	<18	130	97	180	130	110	110	160	33	900	130	240	<33	130	32	170	170	20	7.2	62
me-TBBP-A	<3.0	0.6	<0.1	<2.4	<0.1	0.2	<0.8	<0.1	<0.1	<1.5	0.5	<0.1	<5.6	0.4	<0.1	0.4	5.5	<0.1	<0.1	0.1
TBBP-A	<3.8	37	3.3	<3.0	62	31	<1.0	3.1	3.1	<1.9	63	2.1	<6.9	45	14	47	600	2.8	3.7	3.9
HBCD	<11	<0.4	<0.4	570	140	93	<3.0	<0.4	24	<5.6	<0.4	64	<20	100	29	28	42	11	5.3	27

Annex 4.1. - Total HBCD, TBBP-A, me-TBBP-A en PBDEs in STP samples from The Netherlands (dry weight)

results *ug/kg* *dry weight*

	2001/1683	2001/1698	2001/1684	2001/1687	2001/1700	2001/1688	2001/1686	2001/1699	2001/1685	2001/1682	2001/1697	2001/1681	2001/1693	2001/1692	2001/1694	2001/1689	2001/1691	2001/1690	2001/1701	2001/1696
	STP1	STP1	STP1	STP2	STP2	STP2	STP3	STP3	STP3	STP4	STP4	STP4	STP5	STP5	STP5	STP6	STP7	STP8	STP9	STP10
	influent	effluent	sewage sludge	influent	effluent	sewage sludge	influent	effluent	sewage sludge	influent	effluent	sewage sludge	influent	effluent	sewage sludge	sewage sludge	sewage sludge	sewage sludge	sewer sludge	sewage sludge
BDE 28	<3.9	<0.1	<0.2	<3.1	0.9	0.2	<1.1	0.9	0.1	<2.0	1.0	0.2	<7.2	0.8	0.2	0.2	<0.1	<0.1	<0.1	0.2
BDE 47	25	67	5.0	22	45	9.9	15	43	5.1	27	57	8.5	43	33	6.1	17	17	2	0.4	6.9
BDE 66	<3.9	1.9	<0.2	<3.1	1.2	0.3	<1.1	1.2	0.2	<2.0	1.7	0.2	<7.3	1.1	0.3	0.5	0.6	<0.1	<0.1	0.3
BDE 71	<3.9	<0.1	<0.2	<3.1	<0.2	<0.1	<1.1	<0.1	<0.1	<2.0	<0.1	<0.1	<7.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
BDE 75	14	<0.1	<0.2	<3.1	<0.2	<0.1	<1.1	1.1	<0.1	<2.0	0.6	<0.1	<7.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
BDE 77	<4.1	<0.1	<0.2	<3.2	<0.2	<0.1	<1.1	<0.1	<0.1	<2.1	<0.1	<0.1	<7.5	<0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
BDE 85	<1.5	2.6	<0.1	<1.2	1.6	0.5	1.6	1.6	0.2	3.1	2.5	0.4	<2.8	1.3	0.3	1.2	0.7	<0.1	<0.1	0.2
BDE 99	25	75	5.6	19	39	9.8	12	40	4.5	27	59	8.5	39	36	6.9	22	19	2.4	0.4	6.3
BDE 100	13	28	1.7	10	7.8	2.2	5.0	8.8	1.4	10	16	2.0	24	7.2	1.6	6.7	3.1	0.4	0.1	1.5
BDE 119	<3.9	<0.1	<0.2	<3.1	<0.2	<0.1	<1.0	<0.1	<0.1	<2.0	<0.1	<0.1	<7.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
BDE 138	<3.9	0.8	<0.2	<3.1	<0.2	<0.1	<1.0	0.8	<0.1	<2.0	0.8	0.1	<7.1	0.6	0.1	0.3	0.6	<0.1	0.1	0.1
BDE 153	<4.1			<3.3			<1.1			<2.1			<7.6							
BDE 154	<4.0	6.7	0.8	<3.2	2.8	1.0	<1.1	3.3	0.4	<2.1	4.7	0.8	<7.4	2.9	0.6	3.2	1.4	0.2	0.2	0.7
BDE 183	<3.6	6.3	<0.1	<2.9	3.0	1.7	<1.0	3.0	0.4	<1.8	5.9	0.9	<6.7	3.0	1.4	1.0	2.6	0.2	<0.1	1.1
BDE 190	<9.9	<0.3	<0.4	<7.8	<0.4	<0.1	<2.7	<0.3	<0.1	<5.1	<0.3	<0.1	<18	<0.4	<0.1	<0.1	<0.3	<0.1	<0.1	<0.1
BDE 209	<18	130	97	180	130	110	110	160	33	900	130	240	<33	130	32	170	170	20	7.2	62
me-TBBP-A	<3.0	0.6	<0.1	<2.4	<0.1	0.2	<0.8	<0.1	<0.1	<1.5	0.5	<0.1	<5.6	0.4	<0.1	0.4	5.5	<0.1	<0.1	0.1
TBBP-A	<3.8	37	3.3	<3.0	62	31	<1.0	3.1	3.1	<1.9	63	2.1	<6.9	45	14	47	600	2.8	3.7	3.9
HBCD	<11	<0.4	<0.4	570	140	93	<3.0	<0.4	24	<5.6	<0.4	64	<20	100	29	28	42	11	5.3	27

Annex 4.1a - HBCD ratios in STP samples from The Netherlands (dry weight)

			GC-MS	LC-MS Concentration (µg/kg)			
lims nr.	sample type	locationnr.	conc.(µg/kg)	α	β	γ	total
2001/1698	effluent	STP1	<0.4	<0.4	<0.4	<0.2	<1.0
2001/1683	influent	STP1	<11	670	<59	<59	670
2001/1684	sewage sludge	STP1	<0.4	<2.3	<2.3	<2.3	<6.9
2001/1700	effluent	STP2	140	9.0	<0.4	8.7	18
2001/1687	influent	STP2	570	3800	<47	<47	3800
2001/1688	sewage sludge	STP2	93	<1.2	<1.2	48	48
2001/1699	effluent	STP3	<0.4	<0.4	<0.4	5.1	5.1
2001/1686	influent	STP3	<3.0	40	<16	<16	40
2001/1685	sewage sludge	STP3	24	15	<0.4	5.4	20
2001/1697	effluent	STP4	<0.4	<0.4	<0.4	<0.2	<1.0
2001/1682	influent	STP4	<5.6	75	<30	180	260
2001/1681	sewage sludge	STP4	64	440	120	760	1300
2001/1692	effluent	STP5	100	1.4	<0.2	<0.2	1.4
2001/1693	influent	STP5	<20	<110	<110	<110	<330
2001/1694	sewage sludge	STP5	29				
2001/1689	sewage sludge	STP6	28	7.6	<0.4	20	28
2001/1691	sewage sludge	STP7	42	3.5	<1.6	3.6	7.1
2001/1690	sewage sludge	STP8	11	7.4	<0.6	13	20
2001/1701	sewer sludge	STP9	5.3	<0.2	<0.2	<0.2	<0.6
2001/1696	sewage sludge	STP10	27	<1.3	<1.3	<0.5	<3.1

Annex 4.1a - HBCD ratios in STP samples from The Netherlands (dry weight)

			GC-MS	LC-MS Concentration (µg/kg)			
lims nr.	sample type	locationnr.	conc.(µg/kg)	α	β	γ	total
2001/1698	effluent	STP1	<0.4	<0.4	<0.4	<0.2	<1.0
2001/1683	influent	STP1	<11	670	<59	<59	670
2001/1684	sewage sludge	STP1	<0.4	<2.3	<2.3	<2.3	<6.9
2001/1700	effluent	STP2	140	9.0	<0.4	8.7	18
2001/1687	influent	STP2	570	3800	<47	<47	3800
2001/1688	sewage sludge	STP2	93	<1.2	<1.2	48	48
2001/1699	effluent	STP3	<0.4	<0.4	<0.4	5.1	5.1
2001/1686	influent	STP3	<3.0	40	<16	<16	40
2001/1685	sewage sludge	STP3	24	15	<0.4	5.4	20
2001/1697	effluent	STP4	<0.4	<0.4	<0.4	<0.2	<1.0
2001/1682	influent	STP4	<5.6	75	<30	180	260
2001/1681	sewage sludge	STP4	64	440	120	760	1300
2001/1692	effluent	STP5	100	1.4	<0.2	<0.2	1.4
2001/1693	influent	STP5	<20	<110	<110	<110	<330
2001/1694	sewage sludge	STP5	29				
2001/1689	sewage sludge	STP6	28	7.6	<0.4	20	28
2001/1691	sewage sludge	STP7	42	3.5	<1.6	3.6	7.1
2001/1690	sewage sludge	STP8	11	7.4	<0.6	13	20
2001/1701	sewer sludge	STP9	5.3	<0.2	<0.2	<0.2	<0.6
2001/1696	sewage sludge	STP10	27	<1.3	<1.3	<0.5	<3.1

Annex 4.2. Sewage treatment works samples

Concentration: µg/kg dry weight for sludge & particulates, ng/L for dissolved phase

Lab No.	Location	Population	TBBP-A	MeTBBP-A	Alpha HBCD	Beta HBCD	Gamma HBCD	Total HBCD
Influent dissolved phase								
02/1045	Burnham	10,000	2.6	<15	7.9	12.5	3.2	23.6
02/1049	Latchingdon	4,750	42.3	<15	<15	<15	9.1	9.1
02/1053	Wickford	35,000	85.2	<15	<15	<15	4.6	4.6
02/1057	S. Woodham Ferrers	20,000	<15	<15	<15	<15	<15	0.0
02/1061	Chelmsford	143,000	17.6	<15	<15	<15	4.3	4.3
Influent particulate phase								
02/1046	Burnham		<3.9	<3.9	<3.9	29.4	<3.9	29.4
02/1050	Latchingdon		<3.9	<3.9	<3.9	<3.9	2.30	2.3
02/1054	Wickford		21.7	<3.9	<3.9	<3.9	<3.9	0.0
02/1058	S. Woodham Ferrers		<3.9	<3.9	<3.9	<3.9	<3.9	0.0
02/1062	Chelmsford		<3.9	<3.9	<3.9	<3.9	<3.9	0.0
Effluent dissolved phase								
02/1047	Burnham		<15	<15	<15	<15	<15	0.0
02/1051	Latchingdon		<15	<15	<15	<15	<15	0.0
02/1055	Wickford		<15	<15	<15	<15	<15	0.0
02/1059	S. Woodham Ferrers		<15	<15	<15	<15	<15	0.0
02/1063	Chelmsford		<15	<15	<15	<15	<15	0.0
Effluent particulate phase								
02/1048	Burnham		<3.9	<3.9	<3.9	<3.9	<3.9	0.0
02/1052	Latchingdon		<3.9	<3.9	<3.9	<3.9	<3.9	0.0
02/1056	Wickford		<3.9	<3.9	<3.9	<3.9	<3.9	0.0
02/1060	S. Woodham Ferrers		<3.9	<3.9	<3.9	<3.9	<3.9	0.0
02/1064	Chelmsford		<3.9	<3.9	<3.9	<3.9	<3.9	0.0
Sludges								
02/1017	Burnham		23.9	<2.4	132	458	666	1256
02/1018	Latchingdon		15.9	<2.4	205	321	432	958
02/1019	Wickford		54	<2.4	89.6	112	329	531
02/1020	S. Woodham Ferrers		112	<2.4	233	547	798	1578
02/1021	Chelmsford		87.9	<2.4	541	897	1245	2683
		Mean	58.74	<2.4	240.12	467	694	1401.1

Annex 4.3. HBCD , TBBP-A and MeTBBP-A in sewage sludge, sediments and landfills from Ireland

Concentration: µg/kg dry weight for sediment, sludge & particulates, dissolved phase : ng/L

Lab No.	Location	TBBP-A	MeTBBP-A	Alpha HBCD	Beta HBCD	Gamma HBCD	Total HBCD
Sewage sludge							
02/533	Portlaoise STW	83.40	<2.4	280	349	604	1233
02/534	Portlaoise STW	104.36	<2.4	372	523	750	1645
02/535	Clonmel STW	7.33	<2.4	3.9	<2.4	149	153
02/536	Clonmel STW	<2.4	<2.4	10.1	0.13	258	268
02/1065	Cork STW Replicate A	192.00	<2.4	2300	1800	3410	7510
02/1066	Cork STW Replicate B	185.00	<2.4	2840	2430	3850	9120
Sediments							
02/537	R. Nore (Kilkenny)	2.9	<2.4	0.29	<2.4	19.6	19.9
02/538	R. Nore (Kilkenny)	<2.4	<2.4	<2.4	<2.4	29.7	29.7
02/539	R. Bregagh (Kilkenny)	3.7	<2.4	<2.4	<2.4	<2.4	0.0
02/540	R. Bregagh (Kilkenny)	2.7	<2.4	<2.4	<2.4	13.3	13.3
02/541	R. Nore DS STW						
Landfill leachates	**Dissolved phase**						
02/1615/1	Kinsale Road #1	<15	<15	<15	<15	<15	0.00
02/1616/1	Kinsale Road #2	<15	<15	<15	<15	<15	0.00
02/1617/1	Kyletalesha #1	<15	<15	<15	<15	<15	0.00
02/1618/1	Kyletalesha #2	<15	<15	<15	<15	<15	0.00
02/625/1	Dumore #1	<15	<15	<15	<15	<15	0.00
02/625/2	Dumore #2	<15	<15	<15	<15	<15	0.00
Landfill leachates	**Particulate phase**						
02/1615/2	Kinsale Road#1	<3.9	<3.9	<3.9	<3.9	<3.9	0.00
02/1616/2	Kinsale Road#2	<3.9	<3.9	<3.9	<3.9	<3.9	0.00
02/1617/2	Kyletalesha#1	<3.9	<3.9	<3.9	<3.9	<3.9	0.00
02/1618/2	Kyletalesha#2	<3.9	<3.9	<3.9	<3.9	<3.9	0.00
02/625/3	Dumore #1	<3.9	<3.9	<3.9	<3.9	<3.9	0.00
02/625/4	Dumore #2	<3.9	<3.9	<3.9	<3.9	<3.9	0.00

Annex 4.4 HBCD, TBBP-A, MeTBBP-A and PBDEs in landfills: sewage sludge and leachate water

results *ug/kg* *dry weight*

	2002/262	2002/263	2002/264	2002-265	2002/266	2002/267	2002/268	2002/269	2002/270	2002/271	2002/291
Landfill code:	1	1	2	2	3	4	5	6	7	8	9
	Sewage sludge	Leachate water	Leachate water	Sewage sludge	Leachate water	Leachate water	Leachate water	Leachate water	Leachate water	Leachate water	Leachate water
BDE 28	<0.1	3.0	9.1	<0.1	0.9	12	<1.6	<4.1	<8.0	<5.4	<1.6
BDE 47	0.6	37	140	0.3	31	290	12	26	34	<6.2	180
BDE 66	<0.1	<1.2	13	<0.1	1.7	25	<1.6	<4.2	<8.1	<5.5	<1.6
BDE 71	<0.1	<1.2	<3.3	<0.1	<0.1	<3.4	<1.6	<4.1	<8.0	<5.4	<1.6
BDE 75	<0.1	<1.2	<3.3	<0.1	<0.1	<3.4	<1.6	<4.1	<8.1	<5.5	<1.6
BDE 77	<0.1	<1.2	<3.4	<0.1	0.2	<3.6	<1.7	<4.3	<8.4	<5.7	<1.6
BDE 85	<0.2	<2.2	<6.0	<0.1	1.4	22	<3.0	<7.5	<15	<10	<2.9
BDE 99	0.6	48	170	0.3	25	480	12	33	30	<6.1	290
BDE 100	<0.1	10	34	<0.1	5.9	87	<1.7	<4.3	<8.3	<5.6	62
BDE 119	<0.1	<1.2	<3.3	<0.1	<0.1	<3.4	<1.6	<4.1	<8.0	<5.4	<1.6
BDE 138	<0.1	<1.2	<3.3	<0.1	0.8	11	<1.6	<4.1	<8.0	<5.4	<1.6
BDE 153	0.2	17	43	<0.1	6.5	140	6.2	<4.3	<8.5	<5.7	59
BDE 154	<0.1	8.4	25	<0.1	3.7	56	<1.7	<4.3	<8.3	<5.6	33
BDE 183	0.3	10	36	<0.1	86	130	9.6	<3.8	<7.4	<5.0	23
BDE 190	<0.1	<1.2	<3.3	<0.1	<0.1	<3.4	<1.6	<4.1	<8.1	<5.5	<1.6
BDE 209	<0.4	<5.3	420	<0.2	230	<15	<7.3	<18	<36	<24	<7.0
me-TBBP-A	<0.1	<0.9	<2.5	<0.1	<0.1	<2.6	<1.2	<3.2	<6.2	<4.2	<1.2
TBBP-A	<0.4	<5.5	120	<0.3	320	<16	<7.6	<19	<37	<25	43
HBCD	2.1	120	70	<0.3	110	85	21	22000	660	<29	67700

Annex 4.5-HBCD ratios in leachate water and sewage sludge from landfills in The Netherlands

			GC-MS	LC-MS Concentration (µg/kg)			
lims nr.	sample type	location	conc.(µg/kg)	α	β	γ	total
2002/263	leachate water	LF1w	120	<18	<18	<18	<54
2002/264	leachate water	LF2w	70	<49	<49	58	58
2002/266	leachate water	LF3	110	48	13	52	110
2002/267	leachate water	LF4	85	<51	<51	<51	<150
2002/268	leachate water	LF5	21	<24	<24	<24	<72
2002/269	leachate water	LF6	22000	1500	<61	27000	28000
2002/270	leachate water	LF7	660	<120	<120	730	730
2002/271	leachate water	LF8	<29	<81	<81	<81	<240
2002/291	leachate water	LF9	67700	7000	<23	29000	36000
2002/262	sewage sludge	LF1s	2.1	<1.3	<1.3	2.5	2.5
2002/265	sewage sludge	LF2s	<0.3	14	<0.8	51	65

Annex 4.6. Landfill leachates

Concentration: particulate phase: μg/kg dry weight, dissolved phase: ng/L

Lab No.	Location	TBBP-A	MeTBBP-A	Alpha HBCD	Beta HBCD	Gamma HBCD	Total HBCD
Dissolved phase							
02/1069	Rainham	<15	<15	<15	<15	<15	0.00
02/1071	Ockendon	<15	<15	<15	<15	<15	0.00
02/1073	Pitsea	<15	<15	<15	<15	<15	0.00
Particulate phase							
02/1068	Rainham	<3.9	<3.9	<3.9	<3.9	<3.9	0.00
02/1070	Ockendon	<3.9	<3.9	<3.9	<3.9	<3.9	0.00
02/1072	Pitsea	<3.9	<3.9	<3.9	<3.9	<3.9	0.00

Annex 5.1. Concentrations of MeTBBP-A, TBBP-A, HBCD in biological samples (ng/g lipid weight) as measured by GC-MS.

Species	Sample code	Tissue	Lipid (%)	Conc. (ng/g lipid weight)		
				Me-TBBP-A	TBBPA	HBCD
Common whelk	BU09	Soft parts	2.4	<3	33	47
Common whelk	BU22	Soft parts	1.8	<3	5	30
Common whelk	BU26	Soft parts	1.5	<3	96	29
Sea star	AR11	Pyloric caeca	3.5	<3	10	84
Sea star	AR25	Pyloric caeca	7.5	<3	2	<30
Sea star	AR33	Pyloric caeca	7.6	<3	<1	47
Hermit crab	PB09	Abdomen	7.4	<3	<1	<30
Hermit crab	PB11	Abdomen	6.7	<3	29	<30
Hermit crab	PB13	Abdomen	8.5	<3	<1	<30
Hermit crab	PB15	Abdomen	10.6	<3	28	<30
Hermit crab	PB20	Abdomen	9	<3	<1	<30
Hermit crab	PB22	Abdomen	7.3	<3	35	<30
Hermit crab	PB26	Abdomen	9.5	<3	6	<30
Hermit crab	PB30	Abdomen	14.1	<3	5	<30
Hermit crab	PB32	Abdomen	9.8	<3	<1	<30
Whiting	MM09	Fillet	0.7	<9	245	<73
Whiting	MM21	Fillet	0.6	<9	<97	<73
Whiting	MM31	Fillet	0.5	<9	163	<73
Harbour Porpoise	PP981024-4	Liver	36.4	<11	<18	3925
Harbour Porpoise	PP980325-2	Blubber	93.8	223	<11	3584
Harbour Porpoise	PP981120-1	Blubber	91.6	<4	<11	729
Harbour Porpoise	PP990322-3	Blubber	89.5	<6	<11	6275
Harbour Porpoise	PP990322-4	Blubber	83.3	<4	<12	880
Harbour seal	01PVc	Liver	1.96	<3	<77	<36
Harbour seal	96PVd	Liver	0.65	<24	<231	<190
Harbour seal	01PVa	Liver	2.25	<5	<67	<42
Harbour seal	96PVb	Blubber	66.5	153	<15	2055
Harbour seal	96PVc	Blubber	73.8	<3	<14	63

Annex 5.2. Concentrations of HBCD in Biological Samples of the North Sea

Species	Code	LC (wet weight ng/g)				LC (lipid weight ng/g)				GC total HBCD	
		alfa	beta	gamma	total	alfa	beta	gamma	total	wet weight (ng/g)	lipid weight (ng/g)
Whelk	BU09	<2	<2	<2	<7	<103	<104	<104	<311	1.1	47
Whelk	BU22	<2	<2	<2	<5	<99	<99	<99	<296	0.5	30
Whelk	BU26	<2	<2	<2	<6	<123	<124	<124	<371	0.4	29
Sea star	AR11	<5	<5	<5	<14	<134	<135	<135	<404	3.1	84
Sea star	AR25	<12	<12	<12	<37	<165	<166	<166	<496	<2.3	<30
Sea star	AR33	<9	<9	<9	<28	<123	<123	<123	<370	2.5	47
Hermit crab	PB09	<9	<9	<9	<26	<115	<116	<116	<347	<2.2	<30
Hermit crab	PB11	<10	<10	<10	<30	<148	<149	<149	<446	<2.0	<30
Hermit crab	PB13	<9	<9	<9	<26	<103	<103	<103	<309	<2.6	<30
Hermit crab	PB15	<12	<12	<12	<36	<112	<112	<112	<336	<3.2	<30
Hermit crab	PB20	<9	<9	<9	<28	<103	<103	<103	<309	<2.7	<30
Hermit crab	PB22	<8	<8	<8	<24	<108	<109	<109	<326	<2.2	<30
Hermit crab	PB26	<10	<10	<10	<30	<106	<106	<106	<318	<2.9	<30
Hermit crab	PB30	<15	<15	<15	<46	<108	<109	<109	<325	<4.2	<30
Hermit crab	PB32	<10	<10	<10	<31	<105	<105	<105	<316	<2.9	<30
Whiting	MM09	<2	<2	<2	<5	<251	<252	<252	<754	<0.5	<73
Whiting	MM21	<2	<2	<2	<5	<246	<246	<246	<738	<0.5	<73
Whiting	MM31	<2	<2	<2	<5	<333	<334	<334	<1002	<0.4	<73
Harbour porpoise liver	PP981024-4	2400	<150	<150	2400	6500	<420	<420	6500	1600	3925
Harbour porpoise blubber	PP980325-2	3400	<420	<420	3400	3600	<450	<450	3600	3100	3584
Harbour porpoise blubber	PP981120-1	410	<80	<80	410	440	<80	<80	440	670	729
Harbour porpoise blubber	PP990322-3	6100	<320	<320	6100	6800	<360	<360	6800	5000	6275
Harbour porpoise blubber	PP990322-4	780	<80	<80	780	940	<90	<90	940	750	880
Harbour seal liver	01PVc	<3	<3	<3	<10	<169	<169	<169	<507	<0.7	<36
Harbour seal liver	96PVd	<7	<7	<7	<22	<1127	<1130	<1130	<3388	<1.2	<19
Harbour seal liver	01PVa	<3	<3	<3	<9	<137	<137	<137	<412	<0.9	0 <42
Harbour seal blubber	96PVb	1460	<70	<70	1460	2200	<110	<110	2200	1300	2055
Harbour seal blubber	96PVc	<61	<61	<61	<184	<83	<83	<83	<249	53	63

Annex 5.3. Cormorant livers & porpoise blubber

Cormorant Livers

Concentration (µg/kg wet weight)

Lab No.	Location	Age	Sex	TBBP-A	MeTBBP-A	Alpha HBCD	Beta HBCD	Gamma HBCD	Total HBCD
99/2615	Monmouthshire	Adult	Male	0.28	<5	21.2	2.93	2.24	26.4
99/2618	Hampshire	Adult	Male	0.11	<5	6.54	1.06	1.67	9.3
00/2258	Hampshire	Immature	Female	0.08	<5	32.7	0.73	1.31	34.7
00/2260	Surrey	Adult	Male	0.07	<5	7.37	0.38	<5	7.8
00/2271	Staffordshire	Immature	Male	0.07	<5	2.21	<5	<5	2.2
			Mean	0.12	<5	14.00	1.28	1.74	16.07

Porpoise Blubber

Lab No.	Location	Age	Sex	TBBP-A	MeTBBP-A	Alpha HBCD	Beta HBCD	Gamma HBCD	Total HBCD
98/7479	Humber	1	Female	376	<5	298	302	317	917.0
98/7467	Tyne/Tees	1	Female	0.26	<5	315	2.13	5.09	322.2
98/7468	Tyne/Tees	0	Female	0.11	<5	53.2	1.18	<5	54.4
98/7466	Humber	0	Female	0.06	<5	88.7	0.45	<5	89.2
98/7500	Southern Bight	-	Female	0.05	<5	<5	<5	<5	0.0
			Mean	75.30	<5	188.73	76.44	161.05	276.55

Annex 5.4. Sediment data

Concentration (µg/kg dry weight)

Lab No.	Location	TBBP-A	MeTBBP-A	Alpha HBCD	Beta HBCD	Gamma HBCD	Total HBCD
00/2341	Tees	54.53	<2.4	50	36.5	230	316.5
00/2345	Tees	57.07	<2.4	58.7	37.1	267	362.8
00/2348	Tees	<2.4	<2.4	<2.4	<2.4	11.8	11.8
00/2347	Tees	29.60	<2.4	34.4	17.3	221	272.7
00/2352	Tees	11.47	<2.4	59.6	23.1	212	294.7
00/2359	Tees	9.07	<2.4	106	111	294	511.0
00/2360	Tees	4.53	<2.4	10.7	2.8	48.1	61.6
00/2356	Tees	6.13	<2.4	14.1	1.5	72.3	87.9
00/2706	Tees	<2.4	<2.4	<2.4	<2.4	<2.4	0.0
00/2757	Tees	<2.4	<2.4	<2.4	<2.4	<2.4	0.0
	Mean	24.6	<2.4	47.6	32.8	169.5	191.9
00/2588	Tyne	2	<2.4	<2.4	<2.4	14.2	14.2
00/2589	Tyne	5.1	<2.4	32.00	15.7	274	321.7
00/2586	Skerne	<2.4	<2.4	745	396	537	1678.0
00/2584	Skerne	9753	<2.4	40.2	15.6	118	173.8
00/2758	Humber	<2.4	<2.4	<2.4	<2.4	6	6.0
02/986	Mersey	<2.4	<2.4	<2.4	<2.4	<2.4	0.0
02/987	Mersey	<2.4	<2.4	<2.4	<2.4	<2.4	0.0
02/989	Mersey	<2.4	<2.4	<2.4	22.3	<2.4	22.3
02/990	Mersey	<2.4	<2.4	<2.4	<2.4	<2.4	0.0
02/991	Mersey	<2.4	<2.4	<2.4	52.1	<2.4	52.1
00/3990	Clyde	<2.4	<2.4	<2.4	<2.4	7	7.0
00/3989	Clyde	<2.4	<2.4	64.1	31.2	92.1	187.4

Annex 5.5. Whiting and starfish samples

Concentration (µg/kg wet weight)

Lab No.	Location	Sample type	TBBP-A	MeTBBP-A	Alpha HBCD	Beta HBCD	Gamma HBCD	Total HBCD
01/1252	Tees	Whiting muscle	<4.8	<4.8	506	247	283	1036
01/1095	Tees	Whiting muscle	3.3	<4.8	80.8	61.1	149	290.9
01/1162	Tees	Whiting muscle		<4.8	<4.8	<4.8	<4.8	0
01/1236	Tees	Whole Starfish	4.5	<4.8	10.2	<4.8	6.72	16.92

Annex 6.1. - Total HBCD, TBBP-A, me-TBBP-A and BDE183 in Western Scheldt food chain

results common tern eggs Gudgeon en mysid shrimp from Terneuzen
ug/kg *wet weight*

	2001/0003	2001/0004	2001/0005	2001/0006	2001/0007	2001/0008	2001/0009	2001/0010	2001/0011	2001/0012	2000/1032	2000/1022
	tern eggs	tern eggs	tern eggs	tern eggs	tern eggs	tern eggs	tern eggs	tern eggs	tern eggs	tern eggs	Mysid shrimp	Gudgeon
BDE 183	2.0	5.3	1.2	<0.2	1.0	2.4	2.8	4.3	2.0	1.6	<0.1	<0.1
me-TBBP-A	<0.3	<0.4	<0.2	0.8	0.4	<0.2	<0.2	0.5	0.6	<0.6	<0.1	<0.1
TBBP-A	<0.1	<0.2	<0.1	<0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.3	<0.1	<0.1
HBCD	130	87	110	74	64	150	85	640	73	35	<0.1	49

results common tern eggs form Terneuzen
ug/kg lipide base

	2001/0003	2001/0004	2001/0005	2001/0006	2001/0007	2001/0008	2001/0009	2001/0010	2001/0011	2001/0012	2000/1032	2000/1022
	tern eggs	tern eggs	tern eggs	tern eggs	tern eggs	tern eggs	tern eggs	tern eggs	tern eggs	tern eggs	Mysid shrimp	Gudgeon
lipide (%)	10.4	9.4	9.4	10.8	10.9	10.2	10.5	9.1	10.8	10.8	10.5	20.8
BDE 183	19	56	13	<1.4	9.3	24	27	47	18	15	<0.3	<0.1
me-TBBP-A	<2.5	<3.9	<2.3	7.6	4.1	<2.3	<2.0	5.2	5.1	<5.9	<0.3	<0.1
TBBP-A	<1.2	<1.9	<1.1	<1.5	<0.9	<1.2	<1.0	<1.0	<1.0	<2.9	<0.4	<0.1
HBCD	1200	930	1200	680	590	1500	810	7100	670	330	<1.0	230

Annex 6.2. - Total HBCD, TBBP-A, me-TBBP-A and BDE183 in Western Scheldt sediment

results sediment
ug/kg wet weight

	2000/56	2000/57	2000/58	2000/59	2000/60	2000/61	2000/62	2000/63	2000/64	2000/65	2000/66	2000/67	2000/68	2000/69	2000/70	2000/0071	2000/0072	2000/0073	2000/0074
locationnr.	**66**	**62**	**58**	**57**	**56**	**55**	**64**	**68**	**53**	**54**	**59**	**60**	**67**	**69**	**70**	**71**	**61**	**63**	**65**
	Western Scheldt	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**
bde183	<0.1	0.3	0.4	0.6	0.2	0.2	0.3	1.5	0.4	<0.1	0.2	0.3	0.1	0.4	<0.1	<0.1	<0.1	0.2	<0.1
me-TBBP-A	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
TBBP-A	1.3	0.3	0.6	0.3	1.0	1.2	0.8	1.3	0.9	1.0	0.6	0.7	0.1	<0.1	<0.1	<0.1	<0.1	0.2	<0.1
HBCD	1.9	<0.3	4.4	3.5	<0.3	9.1	<0.3	9.4	127	<0.3	11	77	1.1	1.4	0.7	<0.1	<0.1	4.2	<0.1

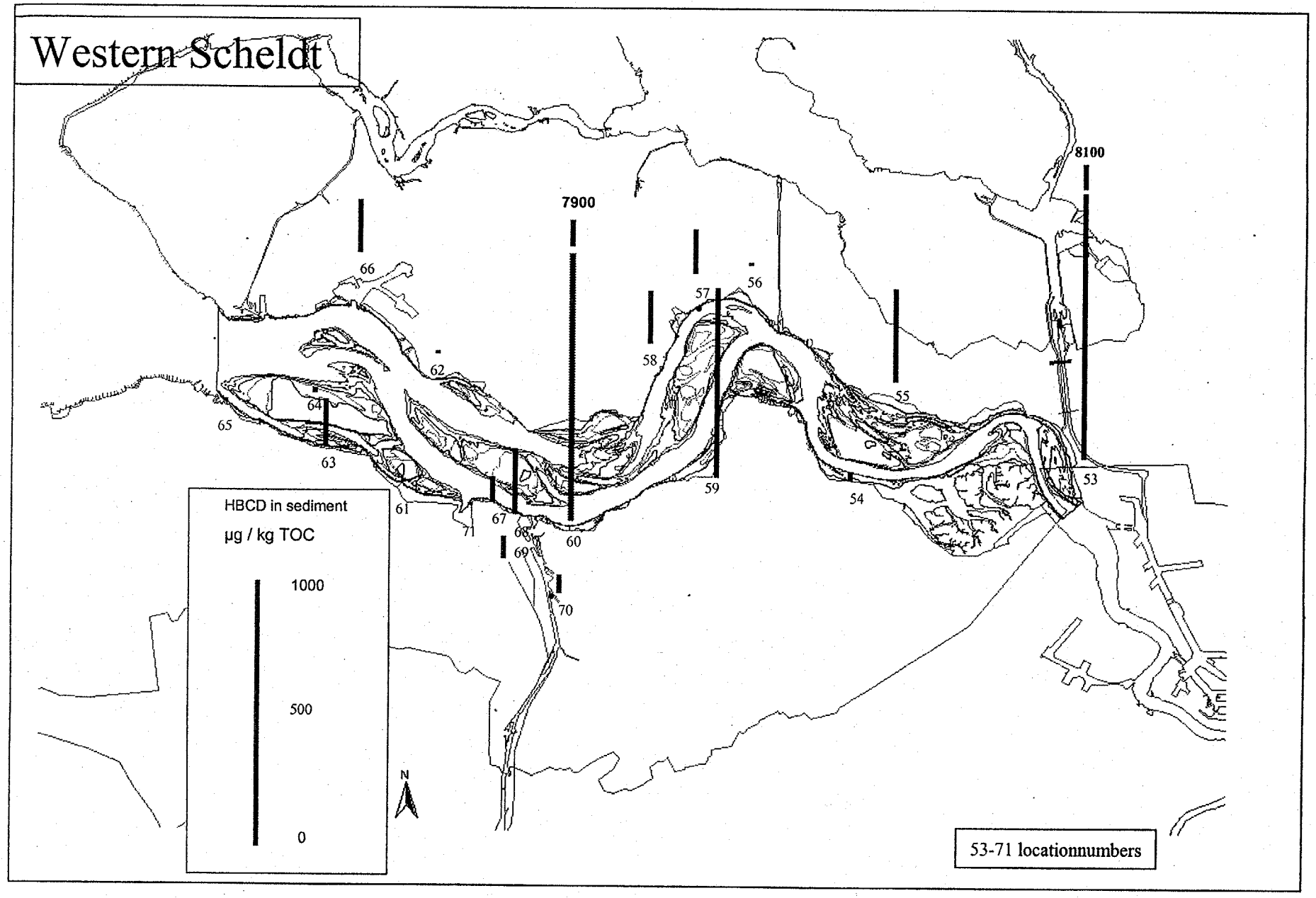
results
ug/kg dry weight

	2000/56	2000/57	2000/58	2000/59	2000/60	2000/61	2000/62	2000/63	2000/64	2000/65	2000/66	2000/67	2000/68	2000/69	2000/70	2000/0071	2000/0072	2000/0073	2000/0074
locationnr.	**66**	**62**	**58**	**57**	**56**	**55**	**64**	**68**	**53**	**54**	**59**	**60**	**67**	**69**	**70**	**71**	**61**	**63**	**65**
	Western Scheldt	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Westen Scheldt**	**Westen Scheldt**	**Westen Scheldt**	**Westen Scheldt**
dry weight (%)	**66**	**44.4**	**49.6**	**43.6**	**43.5**	**46.8**	**61.6**	**40.6**	**99.4**	**69.7**	**59.2**	**63.9**	**63.1**	**52.8**	**66.9**	**71.5**	**72.8**	**47.8**	**59.2**
BDE 183	0.1	0.7	0.8	1.4	0.5	0.5	0.5	3.8	1.2	<0.1	0.3	0.4	0.2	0.8	<0.1	<0.1	<0.1	0.5	<0.1
me-TBBP-A	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
TBBP-A	1.9	0.8	1.3	0.7	2.3	2.6	1.3	3.2	0.9	1.4	0.9	1	<0.1	<0.1	<0.1	<0.1	<0.1	0.3	<0.1
HBCD	2.9	<0.7	9	7.9	<0.7	20	<0.5	23	128	<0.5	18	120	1.8	2.8	1.1	<0.1	<0.1	8.8	<0.1

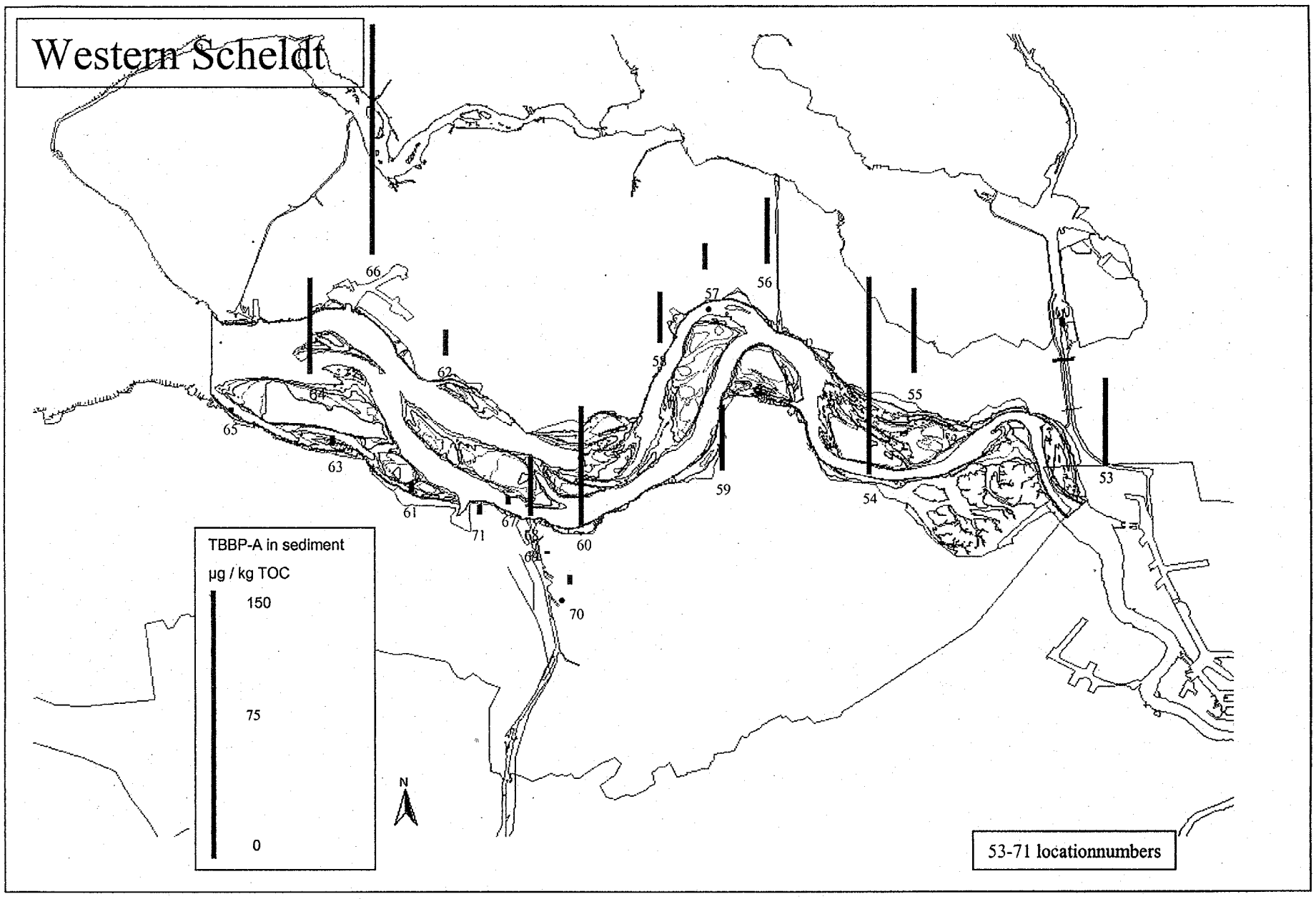
results
ug/kg TOC base

	2000/56	2000/57	2000/58	2000/59	2000/60	2000/61	2000/62	2000/63	2000/64	2000/65	2000/66	2000/67	2000/68	2000/69	2000/70	2000/0071	2000/0072	2000/0073	2000/0074
locationnr.	**66**	**62**	**58**	**57**	**56**	**55**	**64**	**68**	**53**	**54**	**59**	**60**	**67**	**69**	**70**	**71**	**61**	**63**	**65**
	Western Scheldt	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**	**Western Scheldt**
TOC base (%)	**0.98**	**2.34**	**2.2**	**1.98**	**2.71**	**2.61**	**1.42**	**3.95**	**1.58**	**0.87**	**1.51**	**0.98**	**1.18**	**1.7**	**0.75**	**0.54**	**0.52**	**2.33**	**1.4**
BDE 183	7.6	13	18	31	8.6	9.7	20	39	10	6.0	12	28	12	26	6.5	<2.0	<2.0	10	<0.8
me-TBBP-A	<2.3	<0.9	<1.0	<1.1	<0.8	<0.9	<1.6	0.8	0.8	<2.6	<1.5	<2.3	<1.9	<1.3	<3.0	<1.6	<1.7	<0.4	<0.6
TBBP-A	130	15	29	15	37	48	55	33	57	110	36	67	4.7	<1.7	<3.8	6.1	6.2	6.5	3
HBCD	200	<13	200	170	<12	350	<22	240	8100	<36	710	7900	96	85	99	<6.0	<6	180.4	<2.3

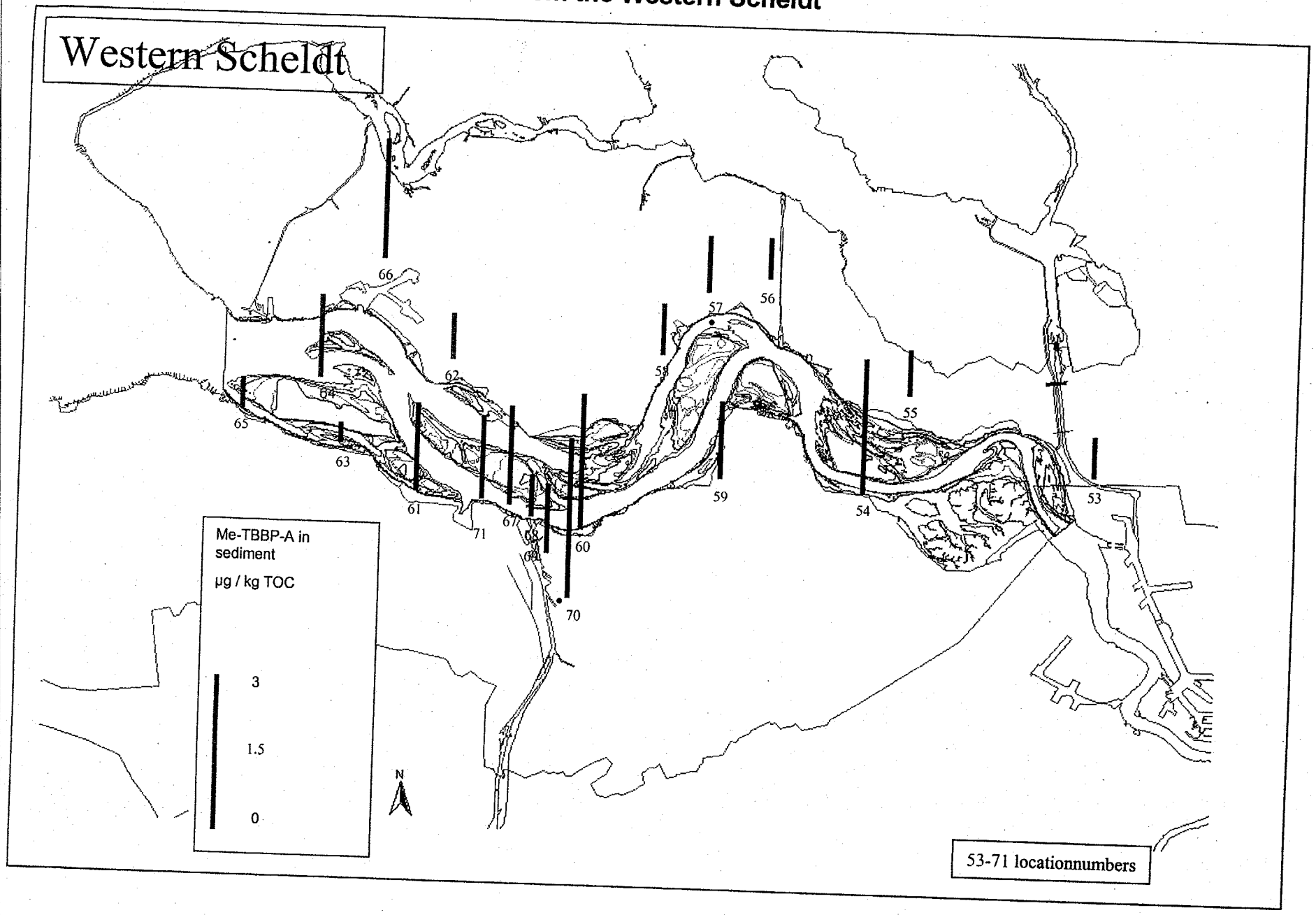
Annex 6.3 - Total HBCD in sediment from the Western Scheldt



Annex 6.4 - TBBP-A in sediment from the Western Scheldt



Annex 6.5 - MeTBBP-A in sediment from the Western Scheldt



Annex 6.6 - HBCD ratios in Western Scheldt sediments

				GC-MS	LC-MS Concentration (µg/kg)			
lims nr.	sample type	locationnr.	location	conc.(µg/kg)	α	β	γ	total
2000/64	sediment	53	Western Scheldt	130	2.6	<1.8	96	99
2000/65	sediment	54	Western Scheldt	<0.3	<0.4	<1.8	<0.5	<1.1
2000/61	sediment	55	Western Scheldt	9.1	<0.4	<0.2	7.3	7.3
2000/60	sediment	56	Western Scheldt	<0.3	<0.4	<0.2	<0.5	<1.1
2000/59	sediment	57	Western Scheldt	3.4	5.1	<0.5	<0.2	5.1
2000/58	sediment	58	Western Scheldt	4.4	<0.2	<0.5	7.7	7.7
2000/66	sediment	59	Western Scheldt	11	<0.5	<0.2	3.1	3.1
2000/67	sediment	60	Western Scheldt	77	2.1	0.3	57	59
2000/0072	sediment	61	Western Scheldt	<0.1	0.4	<0.2	3.6	4.0
2000/57	sediment	62	Western Scheldt	<0.3	<0.2	<0.4	<0.2	<0.8
2000/0073	sediment	63	Western Scheldt	4.2	<0.2	<0.2	0.7	0.7
2000/62	sediment	64	Western Scheldt	<0.3	<0.4	<0.2	<0.4	<1.0
2000/0074	sediment	65	Western Scheldt	<0.1	<0.2	<0.2	<0.2	<0.6
2000/56	sediment	66	Western Scheldt	1.9	<0.2	<0.4	1.8	1.8
2000/68	sediment	67	Western Scheldt	1.1	<0.4	<0.2	<0.4	<1.0
2000/63	sediment	68	Western Scheldt	9.4	<0.4	<0.2	4.8	4.8
2000/69	sediment	69	Western Scheldt	1.4	<0.4	<0.2	<0.5	<1.1
2000/70	sediment	70	Western Scheldt	0.7	<0.4	<0.2	<0.4	<1.0
2000/0071	sediment	71	Western Scheldt	<0.1	<0.2	<0.2	1.3	1.3

Annex 6.7. - Total HBCD, TBBP-A, me-TBBP-A and BDE183 in Dutch river sediments

results ug/kg sediment wet weight

	2000/1978	2000/1979	2000/1981	2000/1982	2000/35612	2000/35615	2000/35616	2000/35617	2000/35618
	Roer Vlodrop	Rhine Lobith	Hollands Diep	Haringsvliet West	Waal Tiel	Haringsvliet East	Nieuwe Merwede	Meuse Eijsden	Meuse Keizersveer
bde183	<0.2	<0.2	0.2	<0.2	0.2	0.4	0.4	0.2	1.3
me-TBBP-A	<0.1	<0.1	0.1	0.2	0.1	0.1	0.4	<0.1	<0.1
TBBP-A	<0.1	0.6	2	0.35	2	0.9	4.2	0.9	0.4
HBCD	<1.2	16	17	7.1	1.4	1.8	6.8	<0.3	3.7

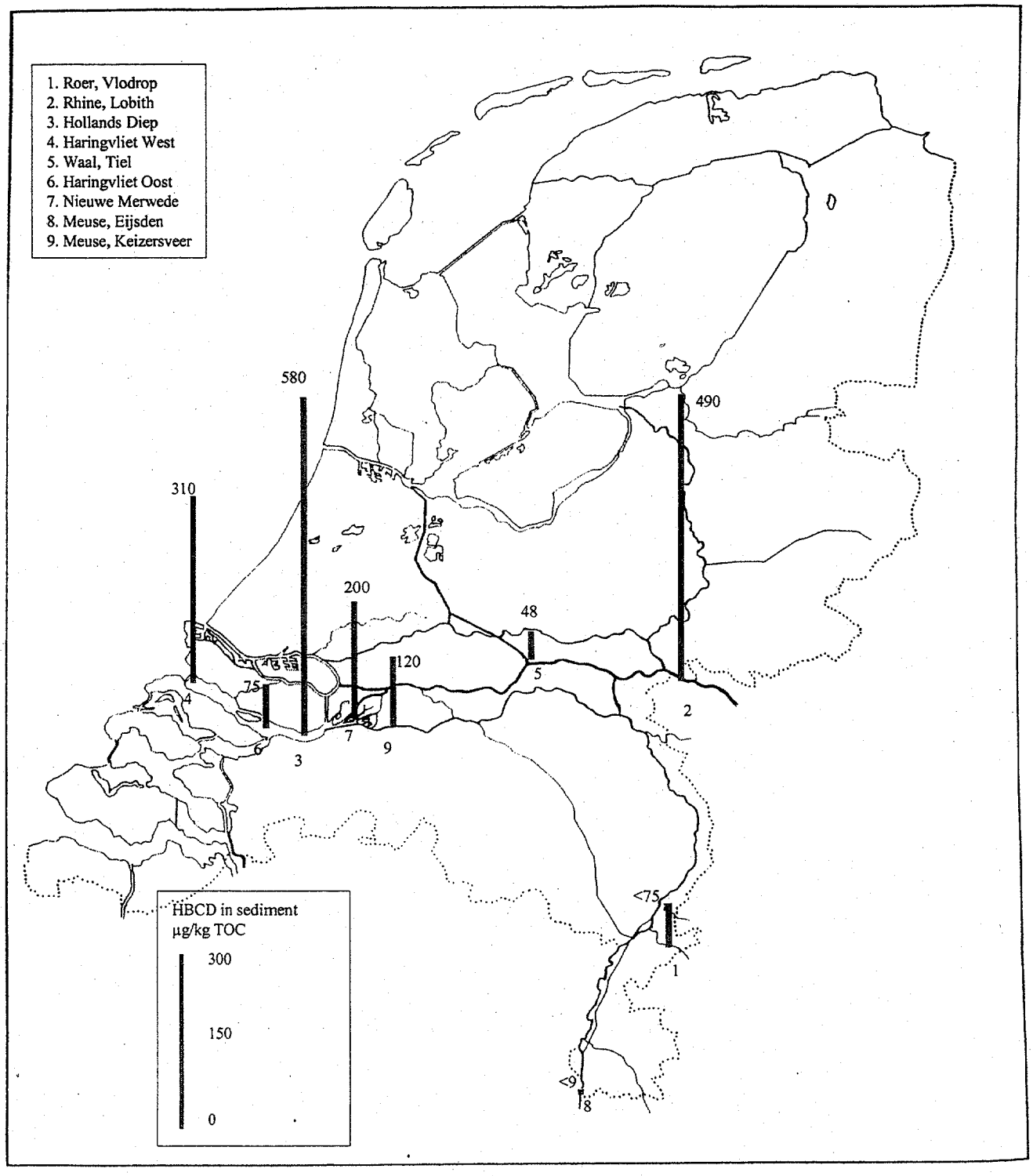
results ug/kg sedimeny dry weight

	2000/1978	2000/1979	2000/1981	2000/1982	2000/35612	2000/35615	2000/35616	2000/35617	2000/35618
	Roer Vlodrop	Rhine Lobith	Hollands Diep	Haringvliet West	Waal Tiel	Haringvliet East	Nieuwe Merwede	Meuse Eijsden	Meuse Keizersveer
dry weight (%)	67.4	51.9	50.4	50.9	61.5	52.5	61.3	58.4	54.3
BDE 183	<0.3	<0.4	0.4	<0.4	0.3	0.8	0.7	0.3	2.5
me-TBBP-A	<0.1	<0.1	0.3	0.3	0.2	0.3	0.6	<0.1	<0.1
TBBP-A	<0.1	1.2	4.0	0.65	3.2	1.8	6.9	1.6	0.8
HBCD	<1.8	30	34	14	2.3	3.4	11	<0.5	6.8

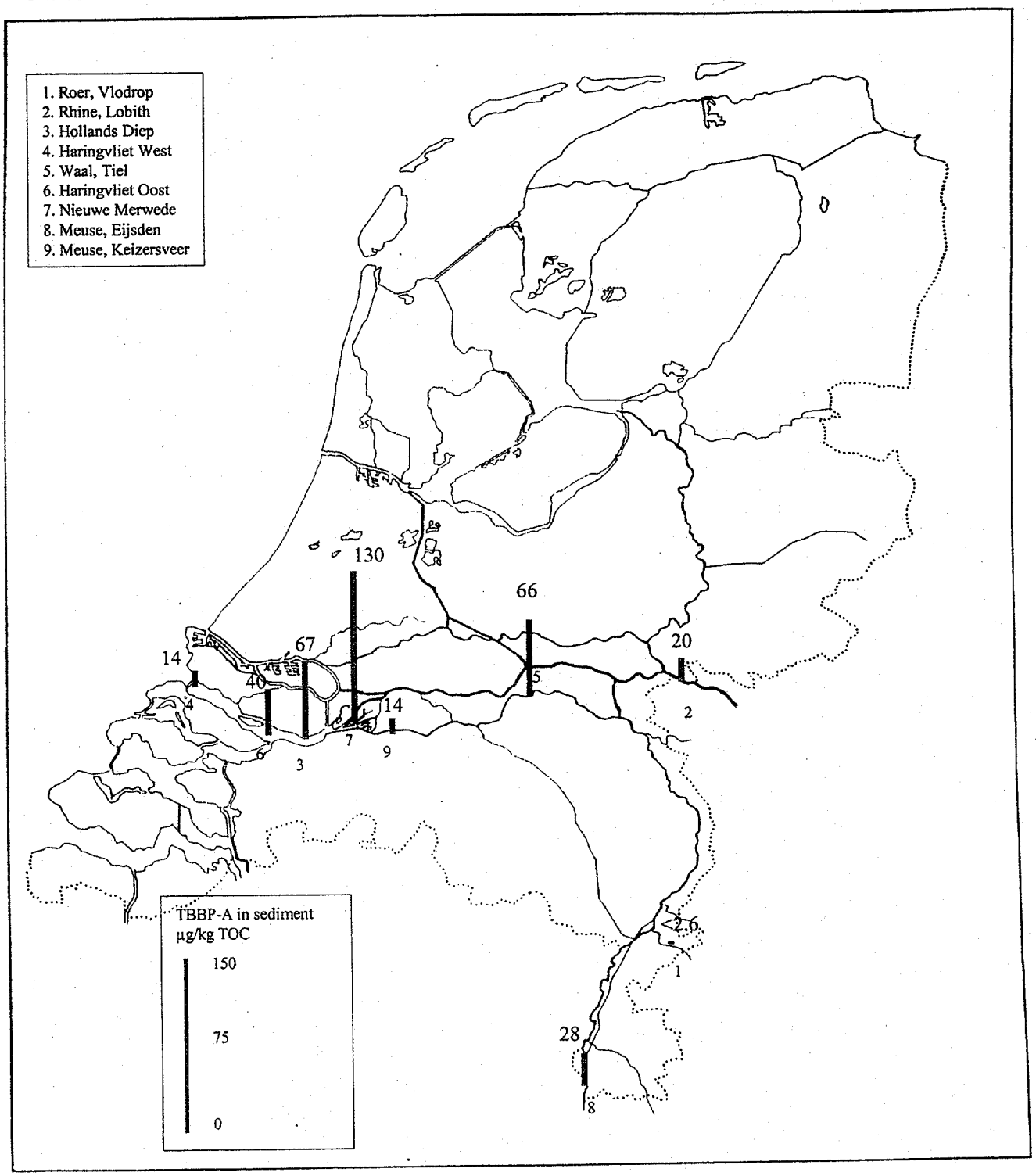
results *ug/kg* sediment *TOC base*

	2000/1978	2000/1979	2000/1981	2000/1982	2000/35612	2000/35615	2000/35616	2000/35617	2000/35618
	Roer Vlodrop	Rhine Lobith	Hollands Diep	Haringvliet West	Waal Tiel	Haringsvliet East	Nieuwe Merwede	Meuse Eijsden	Meuse Keizersveer
TOC base (%)	1.66	3.19	2.97	2.29	2.99	2.35	3.36	3.35	3.1
BDE 183	<12	<5.9	6.4	<9.0	6.7	17	14	4.5	43
me-TBBP-A	<2.1	<1.0	4.3	6.7	4.1	6.2	11	<0.6	1.7
TBBP-A	<2.6	20	67	14	66	40	130	28	14
HBCD	<75	490	580	310	48	75	200	<9	120

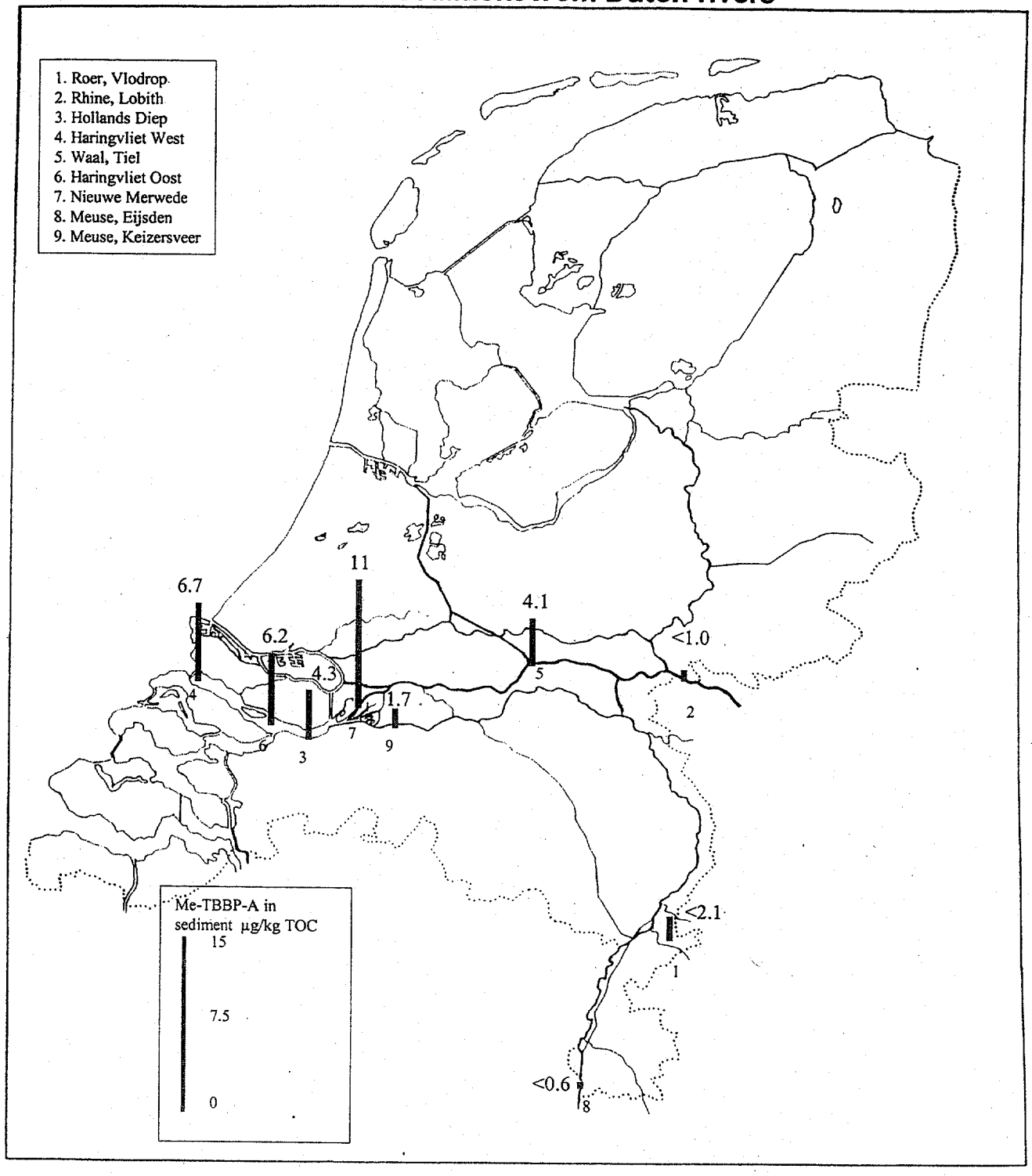
Annex 6.8 - Total HBCD in sediment from Dutch rivers



Annex 6.9 - TBBP-A in sediment from Dutch rivers



Annex 6.10 - MeTBBP-A in sediment from Dutch rivers



Annex 6.11. - Total HBCD, TBBP-A, me-TBBP-A and BDE183 in eel from the Dutch rivers

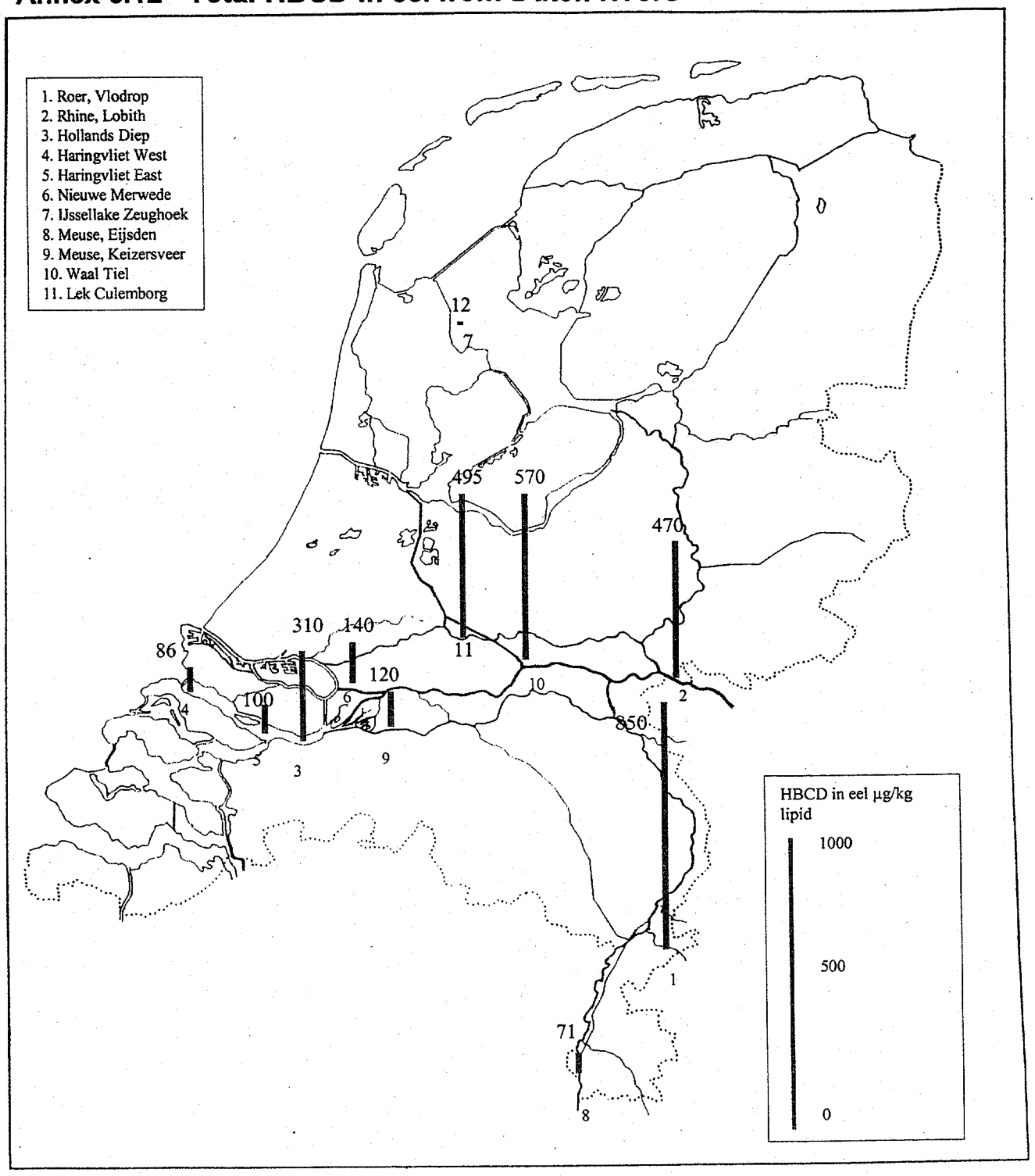
results ug/kg eel wet weight

	1999/4169	1999/4175	1999/4181	1999/4187	1999/4193	1999/4199	1999/4211	1999/4223	1999/4229	1999/4241	2001/829
	Waal Tiel	Rhine Lobith	Hollands Diep	Haringvliet West	Haringvliet East	Nieuwe Merwede	IJssel lake Zeughoek	Meuse Eijsden	Meuse Keizersveer	Roer Vlodrop	Lek Culemborg
BDE 183	0.2	0.1	0.1	0.1	0.3	0.1	<0.1	<0.1	0.2	0.2	<0.1
me-TBBP-A	0.5	0.6	0.8	1	0.8	1.3	0.3	0.2	0.6	<0.1	0.8
TBBP-A	0.2	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2
HBCD	100	73	48	19	19	28	2.3	6.2	19	110	71

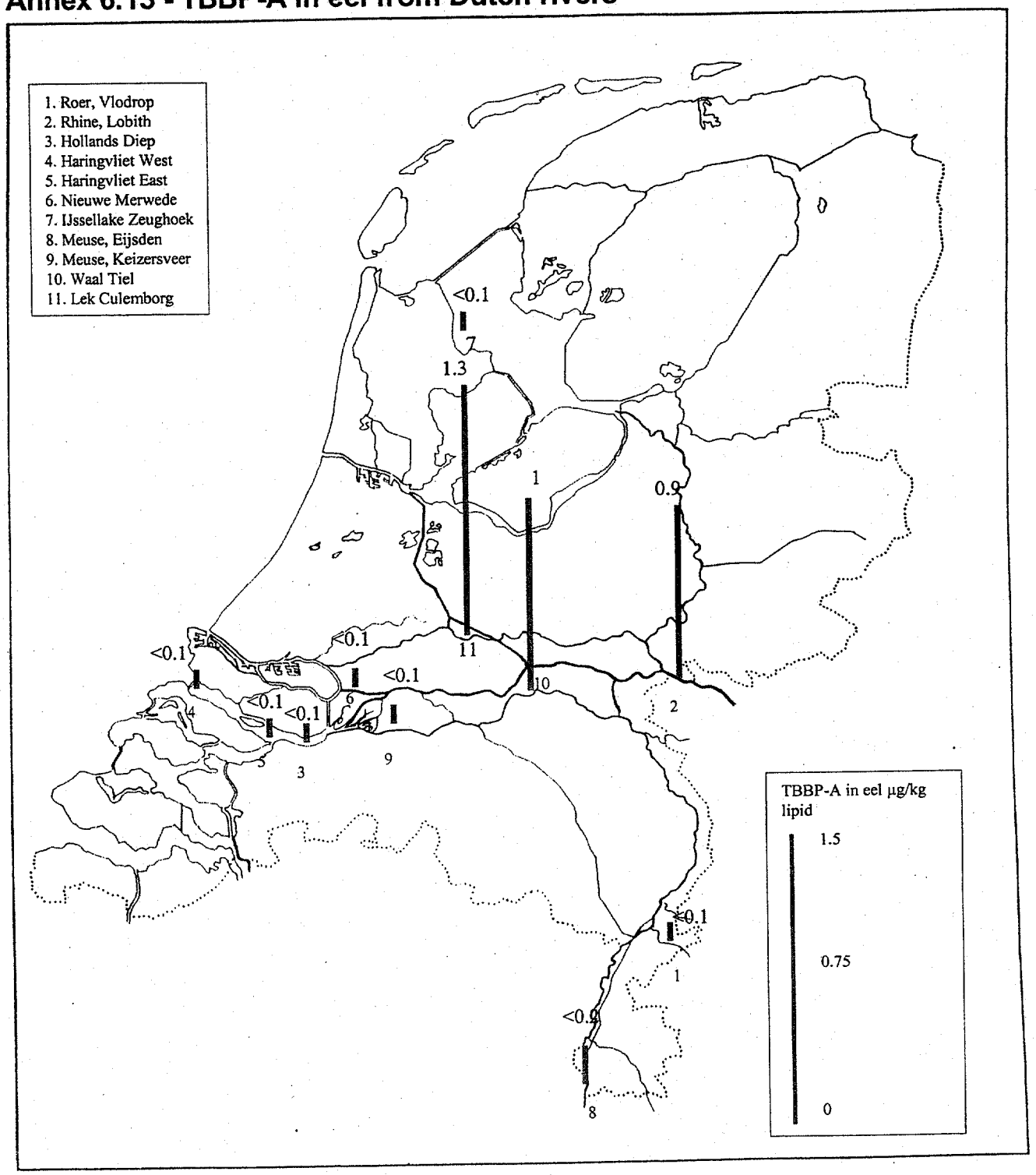
results ug/kg eel lipide base

	1999/4169	1999/4175	1999/4181	1999/4187	1999/4193	1999/4199	1999/4211	1999/4223	1999/4229	1999/4241	2001/829
	Waal Tiel	Rhine Lobith	Hollands Diep	Haringvliet West	Haringvliet East	Nieuwe Merwede	IJssel lake Zeughoek	Meuse Eijsden	Meuse Keizersveer	Roer Vlodrop	Lek Culemborg
lipide (%)	17.8	15.4	15.7	21.9	18.4	19.8	18.2	8.8	16.6	13.4	14.3
BDE 183	0.9	0.7	0.9	0.5	1.6	0.5	0.5	<0.2	1.3	1.3	0.6
me-TBBP-A	2.7	4.2	4.9	4.4	4.3	6.8	1.4	2	3.3	<0.3	5.8
TBBP-A	1	0.9	<0.1	<0.1	<0.1	<0.1	<0.1	<0.2	<0.1	<0.1	1.3
HBCD	570	470	310	86	100	140	12	71	120	850	495

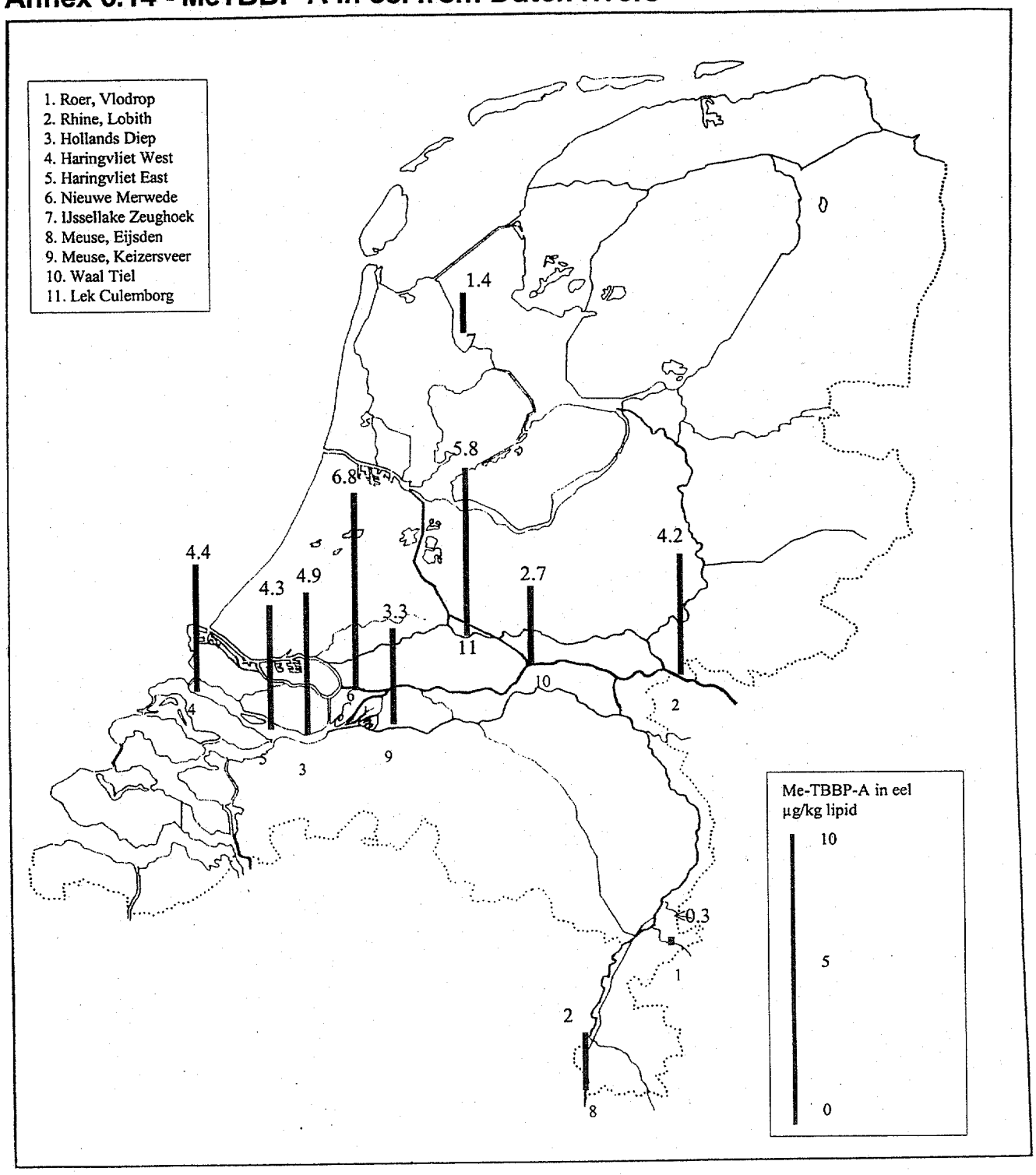
Annex 6.12 - Total HBCD in eel from Dutch rivers



Annex 6.13 - TBBP-A in eel from Dutch rivers



Annex 6.14 - MeTBBP-A in eel from Dutch rivers



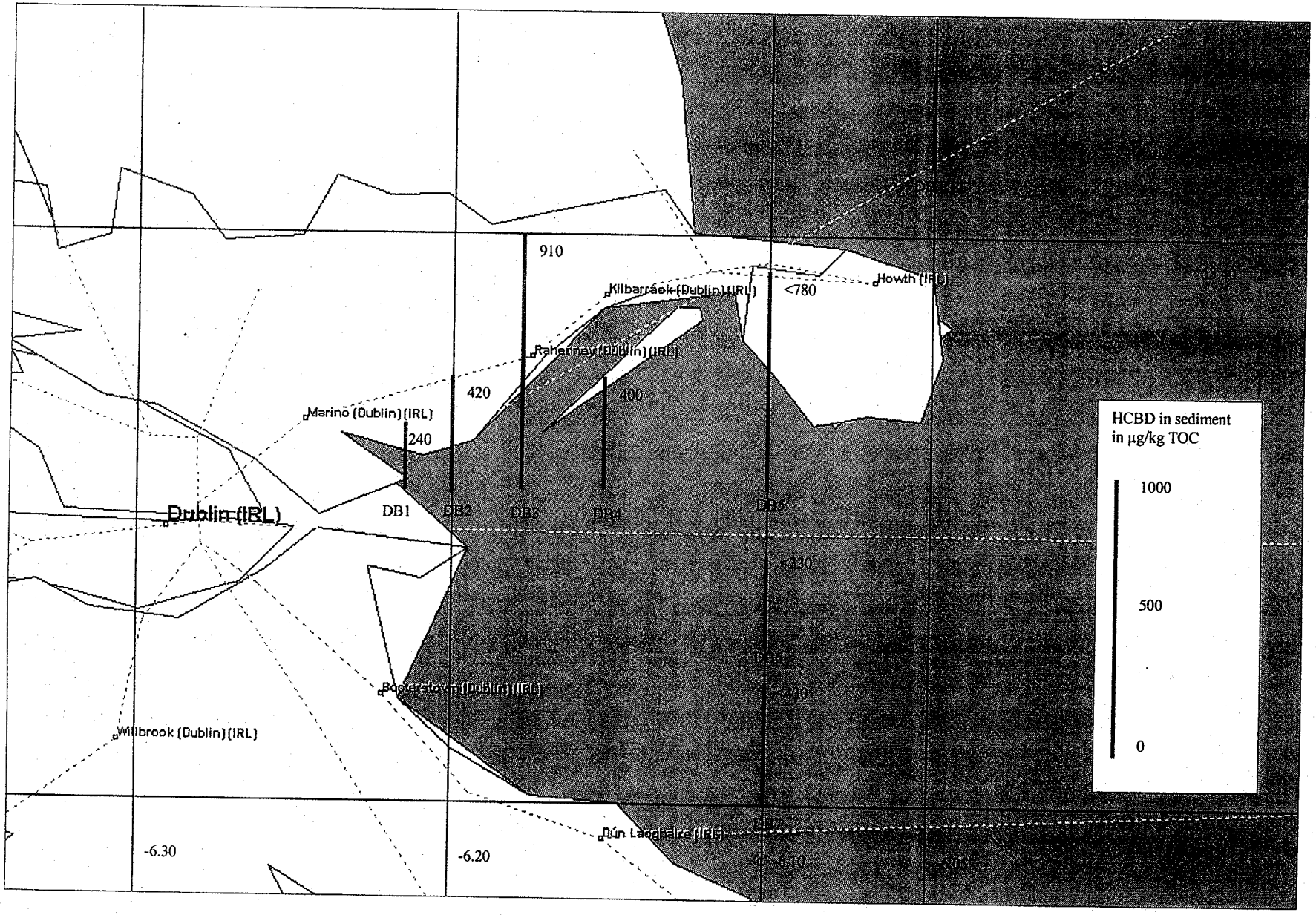
Annex 6.15 - HBCD ratios in eel and sediments from the Dutch rivers

			GC-MS	LC-MS Concentration (µg/kg)			
lims nr.	sample type	location	conc.(µg/kg)	α	β	γ	total
1999/4169	eel	Waal Tiel	100	52	<0.3	12	64
1999/4175	eel	Rhine Lobith	73	36	<0.3	7.5	44
1999/4181	eel	Hollans Diep	48	28	<0.3	7.2	35
1999/4187	eel	Haringvliet West	19	7.9	<0.3	<0.3	8
1999/4193	eel	Haringvliet East	19	14	<0.3	0.4	14
1999/4199	eel	Nieuwe Merwede	28	17	<0.3	15	32
1999/4211	eel	IJssel Lake Zeughoek	2.3	1.4	<0.3	<0.3	1
1999/4223	eel	Meuse Eijsden	6.2	2.0	<0.3	<0.3	2
1999/4229	eel	Meuse Keizersveer	19	4.2	<0.3	<0.3	4
1999/4241	eel	Roer Vlodrop	110	83	<0.3	9.7	93
2001/829	eel	Lek Culemborg	71	20	<0.3	<0.3	20
2000/1978	sediment	Roer Vlodrop	<1.2	<0.8	<1.0	<1.3	<3.1
2000/1979	sediment	Rhine Lobith	16	<0.6	3.9	4.2	8.1
2000/1981	sediment	Hollands Diep	17	<1.4	<1.4	9.9	9.9
2000/1982	sediment	Haringvliet West	7.1	<1.1	<1.2	5.9	5.9
2000/35612	sediment	Waal Tiel	1.4	<0.3	<0.9	<0.3	<1.5
2000/35615	sediment	Haringvliet	1.8	<0.2	<0.6	<0.2	<1.0
2000/35616	sediment	Nieuwe Merwede	6.8	2.1	<0.9	1.1	3.2
2000/35617	sediment	Meuse Eijsden	<0.3	<0.2	<0.4	<0.2	<0.8
2000/35618	sediment	Meuse Keizersveer	3.7	2.8	<0.4	<0.2	2.8

Annex 6.16 - HBCD ratios in sediments from the Dublin Bay

				GC-MS	LC-MS Concentration (µg/kg)			
lims nr.	sample type	locationnr.	location	conc.(µg/kg)	α	β	γ	total
2001/2074	sediment	DB-1	Dublin Bay	10	<1.4	1.1	11	12
2001/2075	sediment	DB-2	Dublin Bay	6.9	<1.4	<1.4	2.8	2.8
2001/2076	sediment	DB-3	Dublin Bay	13	<0.6	<0.6	11	11
2001/2077	sediment	DB-4	Dublin Bay	2.2	<1.3	<1.3	<1.3	<3.9
2001/2078	sediment	DB-5	Dublin Bay	<1.1	<0.4	<0.5	<0.8	<1.7
2001/2079	sediment	DB-6	Dublin Bay	<1.1	<1.3	<1.3	<1.3	<3.9
2001/2080	sediment	DB-7	Dublin Bay	<1.2	<0.6	<0.8	<1.1	<2.5
2001/2081	sediment	DB-REF	Dublin Bay	<1.2	<0.7	<0.9	<1.2	<2.8
2000/38979	sediment		Liffey Dublin	1.4	<0.9	<0.4	<0.9	<2.2

Annex 6.17 - Total HBCD in sediment from Dublin Bay



Annex 6.18. - Total HBCD, TBBP-A, me-TBBP-A and PBDEs in cod and hake liver from North and the Atlantic Sea

results *ug/kg* *wet weight*

	2000/2553	2000/2554	2001/0246
	cod liver North sea	cod liver North sea	hake liver S-Ireland
BDE 28	3	4.2	0.8
BDE 47	84	110	19
BDE 66	1.7	3.3	0.7
BDE 71	<0.1	<0.1	<0.1
BDE 75	<0.1	<0.1	<0.1
BDE 77	<0.1	<0.1	<0.1
BDE 85	<0.1	<0.1	<0.1
BDE 99	<0.1	1.6	1.7
BDE 100	<0.1	<0.1	3.4
BDE 119	0.6	0.8	0.4
BDE 138	1.3	1.2	<0.1
BDE 153			
BDE 154	3.1	5.6	2.4
BDE 183	<0.1	<0.1	<0.1
BDE 190	<0.3	<0.3	<0.3
BDE 209	<0.5	<0.5	<0.5
me-TBBP-A	<0.1	<0.1	<0.1
TBBP-A	<0.1	0.8	<0.1
HBCD	<0.3	22	<0.3

results *ug/kg* *lipid base*

	2000/2553	2000/2554	2001/0246
	Cod liver North sea	Cod liver North sea	Heek liver S-Ierland
lipide (%)	41.1	44.5	55.2
BDE 28	7.4	9.4	1.5
BDE 47	200	240	35
BDE 66	4.1	7.4	1.3
BDE 71	<0.3	<0.2	<0.2
BDE 75	<0.3	<0.3	<0.2
BDE 77	<0.3	<0.3	<0.2
BDE 85	<0.1	<0.1	<0.1
BDE 99	<0.3	3.7	3.1
BDE 100	<0.3	<0.3	6.1
BDE 119	1.5	1.7	0.8
BDE 138	3.1	2.6	<0.2
BDE 153			
BDE 154	7.6	13	4.2
BDE 183	<0.2	<0.2	<0.2
BDE 190	<0.7	<0.6	<0.5
BDE 209	<1.2	<1.2	<0.9
me-TBBP-A	<0.2	<0.2	<0.2
TBBP-A	<0.3	1.8	<0.2
HBCD	<0.7	50	<0.6

Annex 6.18 - HBCD ratios in cod liver and hake liver from the North Sea and the Atlantic

			GC-MS	LC-MS Concentration (µg/kg)			
lims nr.	sample type	location	conc.(µg/kg)	α	β	γ	total
2000/2553	Cod liver	North Sea	<0.3	11	<1.6	<1.6	11
2000/2554	Cod liver	North sea	22	<1.7	<1.7	<1.7	<5.1
2001/0246	Hake liver	South of Ireland	<0.3	<1.7	<1.7	<1.7	<5.1