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Food web transfer of dioxins and other organic contaminants in the Western Scheldt: implications for human and environmental health

Martine J. van den Heuvel-Greve[1], Pim E.G. Leonards[2] & A. Dick Vethaak[3]

[1]RWS - National Institute for Coastal and Marine Management (RIKZ), P.O. Box 8039, 4330 EA Middelburg, the Netherlands. Tel.: +31 118 622816; fax: +31 118 622999; email: M.J.vdHeuvel-Greve@rikz.rws.minvenw.nl.
[2]Vrije Universiteit - Institute for Environmental Studies (IVM), De Boelelaan 1085, 1081 HV, Amsterdam. Tel.: +31 20 5989 509; fax: +31-20-5989 553; email: pim.leonards@ivm.vu.nl.
[3]RWS - National Institute for Coastal and Marine Management (RIKZ), P.O. Box 20907, 2500 EX, The Hague, The Netherlands. Tel.: +31 70 3114219; fax: +31 70 3114321; email: A.D.Vethaak@rikz.rws.minvenw.nl.

Abstract
In 2005 a baseline study was conducted to assess the occurrence of dioxins (PCDD/Fs) and other organic contaminants (PCBs, PAHs, PBDEs, HBCD, PFOS/PFOA) in the estuarine environment of the Western Scheldt in the south-west of the Netherlands. Sediment was sampled along a transect and samples from two simple food chains were collected near Terneuzen. The samples were analysed for both food safety and environmental quality purposes. Dioxin concentrations in fish and fishery products did not exceed current EU standards, although concentrations in *A. anguilla* approached these limits. A new standard for both dioxins and dioxin-like PCBs will come into effect on November 4 2006 and will shine a new light on the outcomes of this study. Some contaminants showed a clear gradient with decreasing concentrations from the Belgian border towards the estuary mouth. Contaminants that accumulated in both the benthic and pelagic food chain were PCBs, lower brominated PBDEs and PFOS. Potential benefits and drawbacks of simultaneous sampling and combined use of data for food safety and environmental health purposes are briefly discussed.

Keywords: dioxins, organic contaminants, food web transfer, food safety, environmental health

1. Introduction

In 2005 the Provincial Executive of the Province of Zeeland, the Netherlands, received a question about the current status of dioxin pollution in the Western Scheldt environment. At the time little was known about the occurrence of dioxins in this estuary. Therefore, a baseline study was conducted in 2005 to obtain the required information. Here we report the results of dioxins and other priority and emerging organic contaminants. Results for organotin compounds and heavy metals (Cu, Se) have been published elsewhere (van den Heuvel-Greve et al, 2006).

The main questions of this baseline study were:

1) Do current dioxin concentrations in fish and fishery products of the Western Scheldt exceed international human health safety standards?
2) What is the dioxin status of the Western Scheldt environment?
3) Are other organic contaminants present in the Western Scheldt in concentrations that can possibly harm ecological health?

An additional aim was to combine monitoring activities for food safety and environmental purposes wherever possible in order to achieve cost-efficiency and to allow a more complete assessment.

2. Material & Methods

A variety of samples was taken in de Western Scheldt estuary, the Netherlands, in the summer of 2005 (see table 1). Sediment samples were collected at five locations along an east-to-west

Table 1. Sample collection in the Western Scheldt estuary in 2005.

Sample type	Latin name	English name	Sample	# sample locations
Fishery product	*Cerastoderma edule*	Common cockle	Tissue	1
	Crangon crangon	Brown shrimp	Peeled	1
	Solea solea	Sole (> 17 cm)	Fillet	1
	Sprattus sprattus	Sprat	Complete	1
	Anguilla anguilla	Eel	Fillet	
Simplified benthic food chain		Sediment	Total	5
		Unidentified benthic algae	Complete	1
	Arenicola marina	Lugworm	Complete	1
	Solea solea	Sole (< 17 cm)	Complete	1
	Sterna hirundo	Common tern	Egg	1
Simplified pelagic food chain		Suspended matter	Total	1
	Crangon crangon	Brown shrimp	Peeled	1
	Sprattus sprattus	Sprat	Complete	1
	Ammodytus marinus	Lesser sandeel	Complete	1
	Sterna hirundo	Common tern	Egg	1

Table 2. Chemical analysis of contaminants of samples.

Contaminant	Analysis	Reference
PCDD/Fs	GC-HRMS	RIKILT (2005a)
PCBs	GC-HRMS	RIKILT (2005b)
PAHs	HPLC	RIVO (2005a)
PBDEs	GC-MS, LC-MS	Morris et al (2006)
HBCD	GC-MS, LC-MS	Morris et al (2006)
PFOS/PFOA	LC-MS	Schrap et al (2004)

transect within the Western Scheldt. *Anguilla anguilla* samples were gathered at three locations. All other samples were taken in the Western Scheldt near Terneuzen (a port to both the Western Scheldt and the canal Gent-Terneuzen). Biota samples consisted of a mixture of individual organisms. One mixture sample was analysed per species per location. Contaminants concentrations were analysed in sediment and biota using standard procedures (see table 2).

3. Results & Discussion

PCDD and PCDF concentrations in fish and fishery products

The concentrations of ΣPCDDs and ΣPCDFs in fish and fishery products of the Western Scheldt are presented in figure 1. The results are expressed as pg TEQ Σ PCDDs+PCDFs/g product (wet weight) instead of on fat basis to reflect actual consumption concentrations. The highest concentrations were found in fillets samples from *A. anguilla*. This was not surprising as fillet of *A. anguilla* contains the highest fat percentages (avg 19.7%, stdev 4.6%) as compared to the other fish and fishery products presented in figure 1 (avg 2.2%, stdev 2.0%). No current EU standards were exceeded, although concentrations in *A. anguilla* approached these limits and two out of three samples exceeded the action threshold. Concentrations in eel were comparable to concentrations found in eel from other areas in the Netherlands, such as Volkerak, Lek, Lake IJssel and Haringvliet (van den Heuvel-Greve et al, 2006).

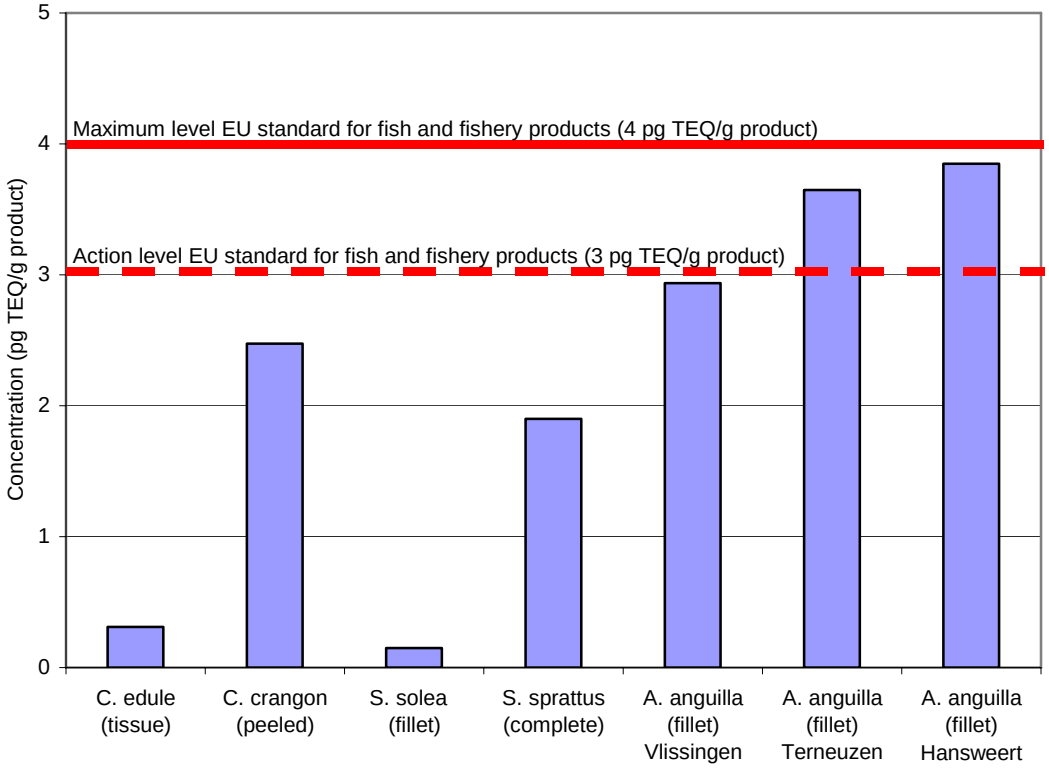

Figure 1. PCDD/Fs concentrations in fish and fishery products of the Western Scheldt including current EU standards for PCDD/Fs in food products.

Quality assessment of the Western Scheldt environment
A first assessment of diet quality of top predators in the Western Scheldt, such as the common tern (*S. Hirundo*) and the harbour seal (*Phoca vitulina*), was established with regard to dioxin-like compounds. Concentrations of dioxin-like compounds in food items of these top predators were compared to No Observed Effect Concentrations (NOECs) in their diet and in sediment of their habitat (figure 2). No effects on biochemical parameters were observed in chicks of *S. hirundo* at concentrations of 15 pg TEQ PCDDs+PCDFs+PCBs/g diet wet weight , whereas effects were noted at concentrations of 46 pg TEQ PCDDs+PCDFs+PCBs /g diet wet weight (Murk et al, 1994). Evers et al (1996) calculated a NOEC of 20 pg TEQ PCDDs+PCDFs+PCBs/g dry weight in sediment for *S. hirundo*. The examined fish of this study contained a sum PCDDs+PCDFs+PCBs TEQ of about a factor two below the NOEC of *S. hirundo* diet. The sediment PCDDs+PCDFs+PCBs TEQ was about a factor four below the established NOEC for *S. hirundo*.

The NOEC of a diet of *P. vitulina* was set at 7.8 pg TEQ/g wet weight based on a study by Leonards et al (2005). Flatfish (e.g. *S. solea*) and sandeel (*Ammodytus sp*.) together form about half of the diet of *P. vitulina* (Brasseur et al, 2004). The sum PCDDs+PCDFs+PCBs TEQ in *S. solea* is about a factor 2 lower than the assessed NOEC, whereas the sum PCDDs+PCDFs+PCBs TEQ in *A. marinus* is nearly equalling the NOEC.

Occurrence of contaminants in the Western Scheldt
Several of the analysed contaminants, i.e. PCBs and PBDEs, showed a decreasing trend in sediment of the Western Scheldt from upstream near the Belgian border towards the mouth of the estuary (figure 3). This indicates that transport of these compounds probably originates from the river Scheldt. The other contaminants such as PCDDs, PCDFs and PAHs did not show such a trend. PFOS and PFOA concentrations in sediment of the Western Scheldt were around the detection limit.

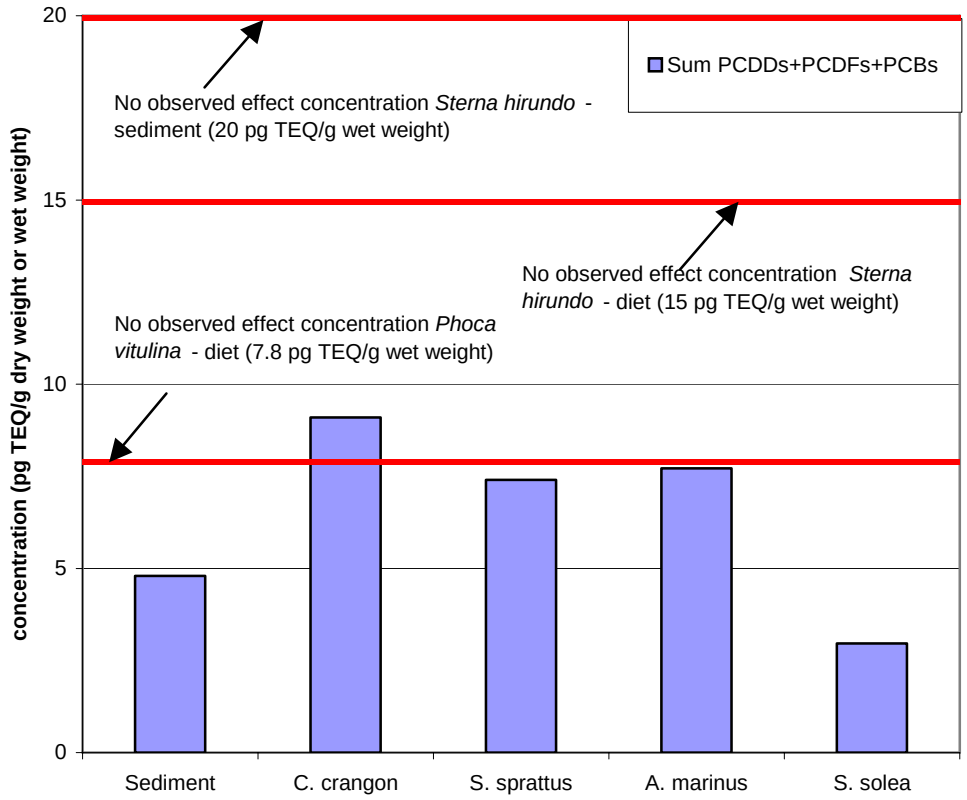

Figure 2. Concentration of PCDDs+PCDFs+PCBs in sediment and fish in the Western Scheldt and comparison to no observed effect concentrations as established for diet and sediment in relation to *S. hirundo* and *Phoca vitulina*.

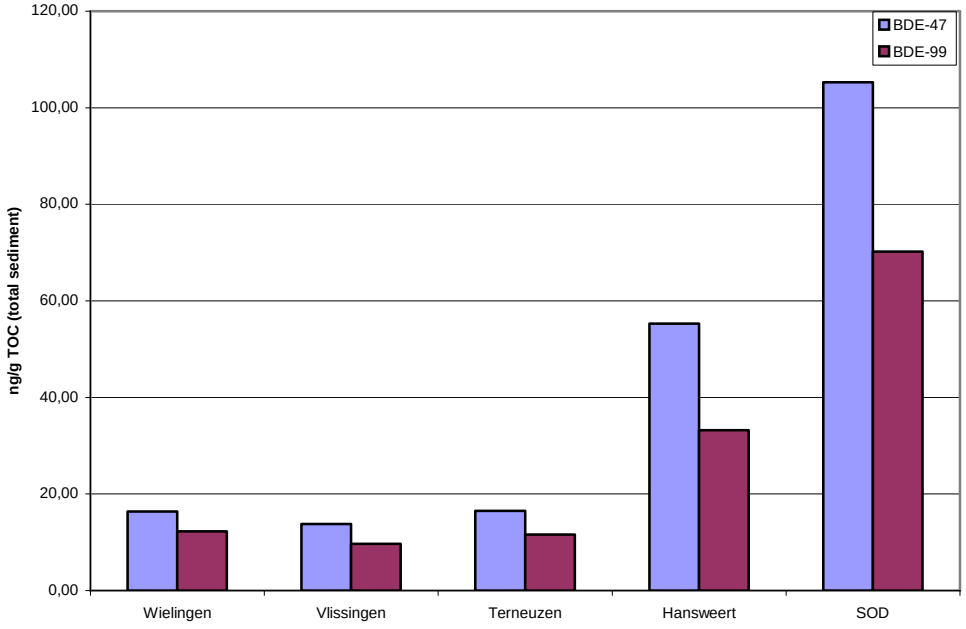

Figure 3. Occurrence of several PBDE congeners in sediment of the Western Scheldt estuary. Location Wielingen is located in the far west of the Western Scheldt, whereas location SOD is situated upstream near the Belgian border.

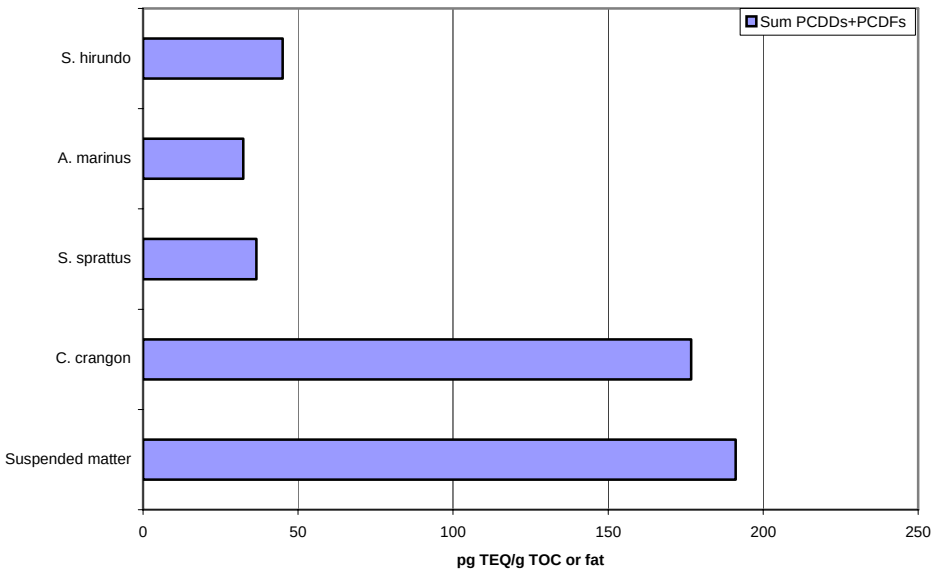

Figure 4. Sum TEQ of PCDDs and PCDFs in a simplified pelagic food chain of the Western Scheldt.

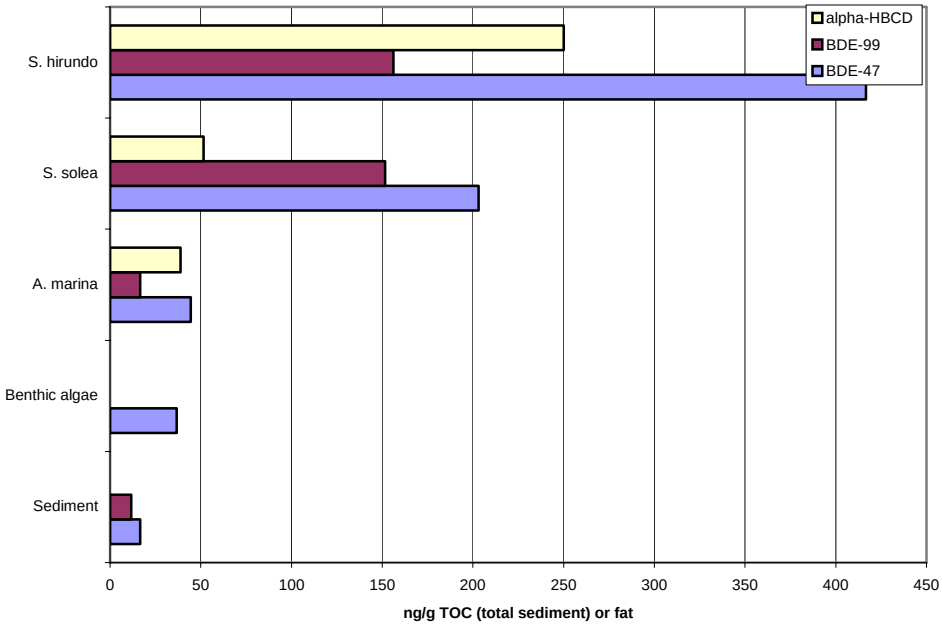

Figure 5. Concentrations of selected brominated flame retardants in a simplified benthic food chain of the Western Scheldt.

Food web transfer of contaminants in the Western Scheldt

Food web transfer of the contaminants was studied in the simplified pelagic and benthic food chain of the Western Scheldt. PCDDs and PCDFs showed no accumulation patterns in the Western Scheldt food chains (figure 4). The fact that these compounds are not entirely transported in aquatic food chains is also observed in other studies (e.g. Wan et al, 2005; Ruus et al, 2006). PAHs and heavy metals showed consistently decreasing concentrations when moving up the food chains. Contaminants that showed accumulation patterns in simplified food chains of the Western Scheldt were lower brominated PBDEs, HBCD (α-isomer)(figure 5), some PCBs and PFOS. These findings were in accordance with other studies (e.g. Veltman et al, 2005; Kannan et al, 2005).

4. Conclusions, final considerations and recommendations

The baseline study was conducted to get a first impression on the occurrence of these contaminants, not to obtain in depth information. The following preliminary conclusions were drawn:

1) Current PCDD and PCDF concentrations in fish and fishery products of the Western Scheldt did not exceed international human health safety standards. However, a new standard for both dioxins and dioxin-like PCBs will come into effect on November 4 2006 and shine a new light on the outcomes of this study. Therefore a follow-up study is recommended;
2) So far there were no indications that PCDDs, PCDFs and dioxin-like PCBs may have a negative effect on the environmental health status of the Western Scheldt estuary. However, it is recommended to measure contaminant concentrations in *P. vitulina* since the present study showed that concentrations in their diet were close to the established NOEC;
3) It is recommended to further study the fate (sources, spatial and temporal distribution) and potential effects of a selection of contaminants in the Western Scheldt estuary in relation to either human food safety and/or environmental health standards. These are brominated flame retardants (PBDEs and HBCD), PFOS and PCBs.

We largely succeeded in combining the sampling and use of obtained data for food safety and environmental health purposes. Benefits of simultaneous sampling for both monitoring purposes are 1) cost efficiency and cost effectivity of expensive sampling and chemical analyses including multiple use of research vessels and laboratory equipment; 2)allowing a completer picture and assessment of the status of a water body. A drawback is that sample types (e.g. fillet versus the complete organism) are not always suiting both purposes. In fishery products often samples consist of fillets or tissue samples, whereas in relation to food chains complete organisms must be analysed. Therefore, it is recommended to study ratios between tissue (fillet, liver, blood) and total organism concentrations for the most important contaminants. A particular problem was the timing to sample eels which highly depended on the ad hoc availability of local fyke fisheries. In these cases detailed information is crucial for environmental monitoring, e.g. representativeness of samples for sampling location.

5. Acknowledgements

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6. References

Brasseur, S., I. Tulp, P. Reijnders, C. Smit, E. Dijkman, J. Cremer, M. Kotterman, E. Meesters (2004). Food ecology of the harbour seal and grey seal in Dutch coastal waters (in Dutch). Alterra-report 905, Alterra, Wageningen, the Netherlands.

Evers, E.H., R.W.P.M. Laane, G.J.J. Groeneveld, K. Olie (1996). Levels, temporal trends and risks of dioxins and related compounds in the Dutch aquatic environment. Organohal. Comp. 28: 117-122.

Kannan,K., L. Tao, E. Sinclair, S.D. Pastva, D.J. Jude, J.P. Giesy (2005). Perfluorinated compounds in aquatic organisms at various trophic levels in a Great Lakes food chain. Arch. Environ. Contam. Toxicol. 48: 559-66.

Morris, S., Bersuder, P., Allchin, C. R., Zegers, B., Boon, J. P., Leonards, P. E. G., de Boer, J. (2006). Determination of the brominated flame retardant, hexabromocyclodocane, in sediments and biota by liquid chromatography-electrospray ionisation mass spectrometry. Trac-Trends in Analytical Chemistry 25(4): 343-349.

Murk, A.J., A.T.C. Bosveld, M. van den Berg, A. Brouwer (1994). Effects of polyhalogenated aromatic hydrocarbons (PHAHs) on biochemical parameters of the common tern (*Sterna hirundo*). Aquat.Toxicol. 30: 91-116.

RIKILT (2005a). Determination of dioxins and dibenzofurans by high resolution mass spectrometry, ISO 17025 accredited method, codes A0565, A0570, A0560-A0563 (www.RvA.nl, labcode L014).

RIKILT (2005b). Internal protocol similar to RIKILT (2005a).

RIVO (2005a). Determination of concentrations of polycyclic aromatic hydrocarbons by HPLC and fluorescence detection after saponification and hexane extraction, ISO 17025 accredited method, code A014 (www.RvA.nl, labcode L097).

Ruus, A., J.A. Berge, O.A. Bergstad, J.A. Knutsen, K. Hylland (2006). Disposition of polychlorinated dibenzofurans (PCDFs) in two Norwegian epibenthic marine food webs. Chemosphere 62: 1856-68.

Schrap, S. M., A.M.P.M. Pijnenburg, R.B Geerdink. (2004). Perfluorated compounds in Dutch surface water (in Dutch). RIZA-report 2004.0285/RIKZ-report 2004.037. Rijkswaterstaat, Lelystad.

Van den Heuvel-Greve, M.J., P.E.G. Leonards, A.D. Vethaak (2006). Dioxin survey Western Scheldt; analysis of concentrations of dioxins, dioxin-like compounds and other possible priority contaminants in fishery products, sediment and food chains of the Western Scheldt (in Dutch). RIKZ-report 2006.011. Rijkswaterstaat Rijksinstituut voor Kust en Zee, Middelburg, the Netherlands.

Veltman, K., J. Hendriks, M. Huijbregts, P. Leonards, M. van den Heuvel-Greve and D. Vethaak (2005). Accumulation of organochlorines and brominated flame retardants in estuarine and marine food chains: Field measurements and model calculations. Mar.Pollut.Bull. 50: 1085-1102.

Wan, Y., J. Hu, M. Yang, L. An, X. Jin, T. Hattori, M. Itoh (2005). Characterisation of trophic transfer for polychlorinated dibenzo-p-dioxins, dibenzofurans, non and mono-ortho polychlorinated biphenyls in the marine food web of Bohai Bay, north China. Environ. Sci. Technol. 39 : 2417-25.