Levels, temporal trends and risk of dioxins and related compounds in the Dutch aquatic environment

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1. Introduction

The presence of polychlorinated-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) in sediments of waterways located in industrialized and heavily populated areas in the Netherlands, is an environmental problem that has received considerable attention from Dutch regulatory agencies in recent years[1-4]. There is growing evidence that these compounds are extremely harmful to marine and freshwater ecosystems, especially when they bioaccumulate through aquatic foodwebs[5].

This study is part of the Dutch Aquatic Outlook project (WSV) which aims to describe the biological and chemical, physical and economic values in the past, present and future of Dutch water systems.
The objective of this study is to compare recent levels of dioxins in sedimentation areas (1993-1994) with "old" data (1985-1987[1,2], 1992[4]) and sediment core data[3]) and to relate them to sediment quality objectives. Also the riverine fluxes of dioxins into and out of the Netherlands are calculated. Another objective was to identify and quantify the relative contribution of different sources of dioxins in the Netherlands.

2. Methods

Sediment and suspended matter collection. At 27 locations (Fig. 1) samples were taken from surface sediments (upper 5 cm) with a stainless steel box corer in 1993. At 7 locations near the boundaries of the rivers suspended matter was collected by a continuous-flow centrifuge (15000 rpm) 4-6 times in 1994.
To compensate the effect of varying grain size, the marine sediment samples were sieved to isolate the <63 μm fraction[6]. Freshwater sediments were not sieved as nearly all material in sedimentation areas belongs to the $< 63\mu$ fraction.
The concentrations of the organic pollutants in both fresh and marine sediments were normalised to 10 % organic matter (OM) content (= 5.7 % organic carbon)[4].

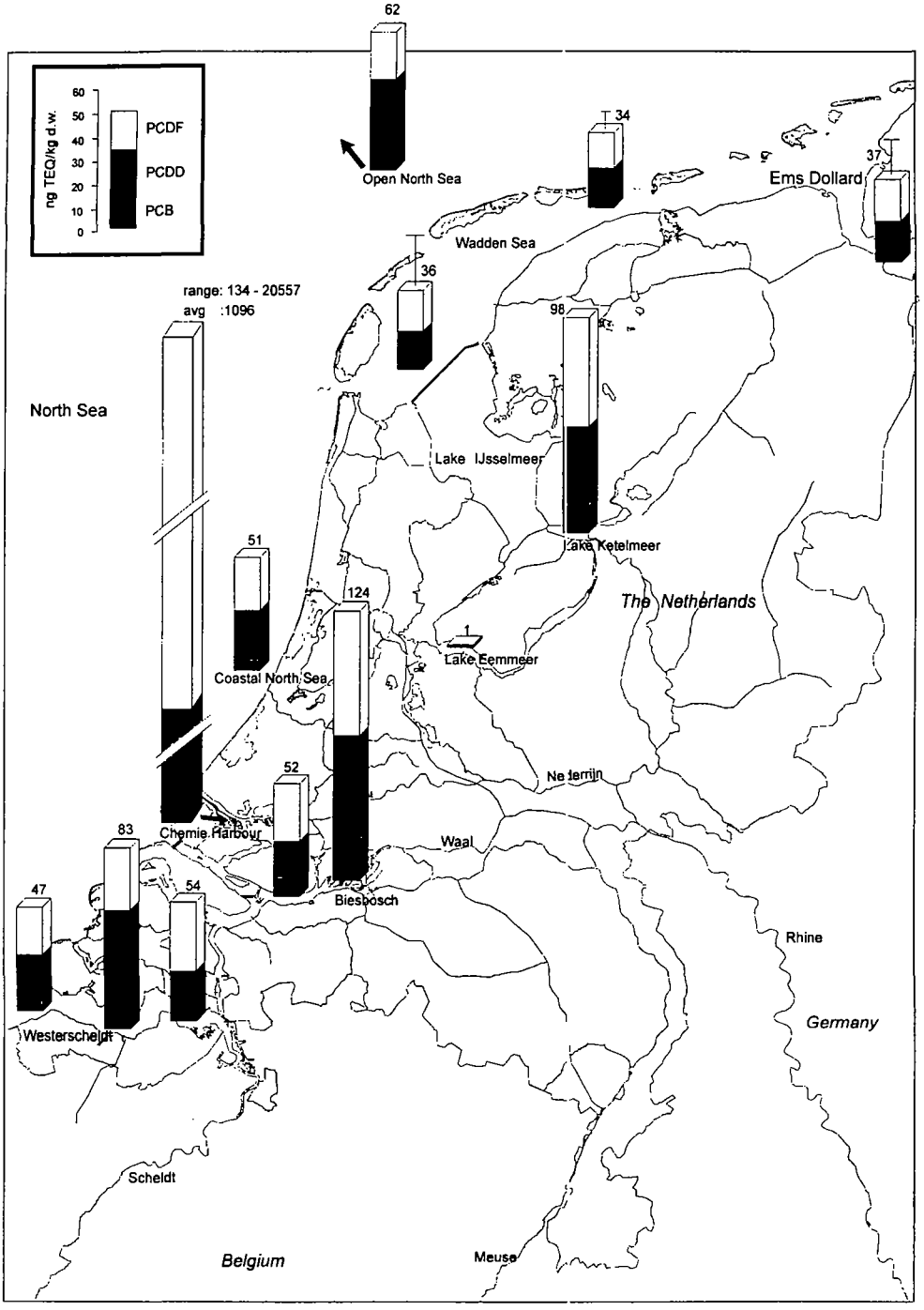

Fig. 1 Concentration of PCDD, PCDF and PCB in surface sediments (ng I-TEQ/kg dw, 10 % OM). Results from the Wadden Sea and the Ems-Dollard estuary have been grouped together; bars indicate the standard deviation of the averaged value.

Experimental
The quantification of PCDD and PCDF in the sediments has been described in detail elsewhere[4,7] and is summarized below. The clean-up procedure involved soxhlet extraction of freeze-dried sediment (spiked with all 17 2,3,7,8-substituted ^{13}C labelled PCDD/PCDF internal standards) with toluene, sample enrichment by sulphuric acid-, sodium hydroxide- and silver nitrate-coated silica gel and alumina adsorption column chromatography followed by reversed-phase HPLC. All measurements were made using a high resolution gas chromatography (HRGC)- high resolution mass spectrometry (Kratos Concept-HRMS) system. Additionally PCBs and non-ortho and mono-ortho substituted PCBs (no- and mo-PCBs) were analysed using the method described by Leonards[8].

Sources
Validated contaminant transport models of the coastal zone of the North Sea and the continental shelf[9,10] were used to determine the relative contributions of atmospheric deposition, fluvial input, inflow from the Strait of Dover and the Atlantic, emissions from ship traffic[11] and dredged sediments disposed of near the Dutch and Belgium coast.

Sediment quality objectives
From concurrently undertaken ecotoxicological studies on fish[12] and wildlife[13,14] sediment quality objectives for dioxins and related compounds could be derived which provide a means to assess the quality of freshwater and marine sediments. Among the eight approaches available to formulate sediment quality objectives[15], the equilibrium partitioning (EqP), the tissue residue-based (TRB) and the apparent effects threshold (AET) are commonly used. The TRB method that have we applied here, involves establishing a "safe" chemical concentration in sediment that is predicted (using the fugacity approach[16]) to result in an acceptable tissue residue in biota, such as fish and birds. Sediment, water and biotic phases will approach a common fugacity when left undisturbed for a long time (i.e., no processes such as resuspension, deposition, or bioturbation occur). According to the fugacity approach for hydrophobic compounds, chemical-specific parameters which describe the distribution properties at equilibrium (K_{ow}, H) in the biota to sediment ratio (BSAF) can be cancelled[16]. Therefore, a NOEC (No Observed effect Concentration) for fish-eating birds for the sum of the toxic equivalences of 200 ng TEQ/kg d.w. in sediment (10% O.M.) could be derived. When chronic toxicity data are scarce a safety factor of 10 is applied in the Netherlands (modified EPA-method[17]) which resulted in a safe sediment value of 20 ng TEQ/kg d.w.

3. Results and discussion

Sediments. The results of the sediment analysis are summarised in Figure 1: ranging from 1-20557 ng TEQ/kg dw, 10% OM. At deposition areas such as the Biesbosch, Hollandsch Diep, Nieuwe Merwede, Lake Ketelmeer and around point sources such as the Chemie harbour, sediment quality objectives are exceeded, sometimes by several orders of magnitude.
Non ortho-PCBs and mono-ortho PCBs contribute less than 20% to the total TEQ in the Biesbosch and Ketelmeer sediments. The CB-153 to ΣTEQ_{PCB} remains constant at around 0.00043 ($\pm$ $3x10^{-5}$) in freshwater sediments (Haringvliet, Oude Venen and the Biesbosch).

The congener patterns of PCDD and PCDF in the Rhine sediments revealed that the production vinylchloride monomer is still an important source of especially OCDF and other higher chlorinated congeners. In earlier days the production of 2,4,5-T was also an important sources of 2,3,7,8-TCDD in Rhine sediments[3], however this contribution diminished strongly. This has resulted in a reduction in TEQ of 70-80 percent in Rhine related sediments during the years

1975-1994.
Sediments from the Meuse and Scheldt river basins show different congener profiles, which originate from different sources such as sewage sludge and combustion related sources. Sediment core studies revealed that the maximum input of dioxins and PCBs occurs in between 1950-1980 in the Netherlands. In comparison to PCBs the sources of PCDDs and PCDFs are much more complex, which partly explains their varying profiles in different sedimentation areas.

Suspended matter and fluxes. Highest concentrations of PCDD and PCDF in suspended matter have been measured in the Scheldt and Rhine (Fig.2). The absolute concentrations of PCDD and PCDF did not changed much between 1985 and 1994. However, the relative contribution of OCDD in the Rhine and Scheldt (also OCDF) increased dramatically in 1994. In the river Meuse levels have decreased by twenty percent.
Riverine fluxes of PCDD and PCDF across the boundaries of Germany and Belgium into the Netherlands and from the rivers into the North Sea, together with the atmospheric deposition and direct discharges are presented in Table 1. The dioxin inflow into the North Sea appeared to be a factor 2 higher than the total inflow, discharges and deposition onto surface waters in the Netherlands.
The homolog profiles of the PCDD and PCDF in SPM at the outflow locations were similar to the profiles of sediments from inland deposition zones. This indicates that resuspension of sediments may contribute significantly to the total load of PCDDs and PCDFs into the North Sea.

Table 1. Fluxes of PCDD and PCDF into inland waters and the North Sea via Dutch rivers (g TEQ in 1994)[18]

Location	number of samples	TEQ (g in 1994)
Meuse at Eysden	4	15.3
Rhine at Lobith	5	65.7
Scheldt estuary at Schaar v. Doel	6	11.9
Total inflow into inland waters (excluding Scheldt)		81.0
Haringvliet sluices	1	10.8
Rhine outflow (Maassluis)	6	146.1
NZ channel at IJmuiden	2	1.1
Lake IJsselmeer	7	15.1
Total outflow into the North Sea		173.1
Atmospheric deposition to surface water[19]		15
Direct discharges to surface waters[19]		3

4. Conclusions

1. Relatively high TEQ (maximum 20557 ng/kg dw, 10%OM) are found in harbour sediments from Rotterdam, especially when these values are compared with a preliminary quality objective of 20ng/kg dw (10%OM).
2. A significant source of PCDD and PCDF in the sediments of the Rhine river in 1994 still is the vinylchlordide production. In earlier days the production of 2,4,5-T was also an important source of PCDD, which has stopped now.
3. Levels in suspended matter from the rivers Rhine and Scheldt have not declined significantly

between 1985 and 1993. In the river Meuse levels have decreased by twenty percent. Sediment core studies revealed that the maximum input of dioxins and PCBs occurs in between 1950-1980 in the Netherlands. Since 1975 TEQ levels in sedimentation areas have decreased by 70-80 percent.

4. A preliminary mass balance of PCDD and PCDF in Dutch surface waters indicate that about two times more of PCDD and PCDF are leaving the country to the North Sea than entering by rivers and atmosphere.

5. It is recommended to analyze the suspended matter for PCDD and PCDF at the borders of the Netherlands more frequently and in sedimentation areas once every five years.

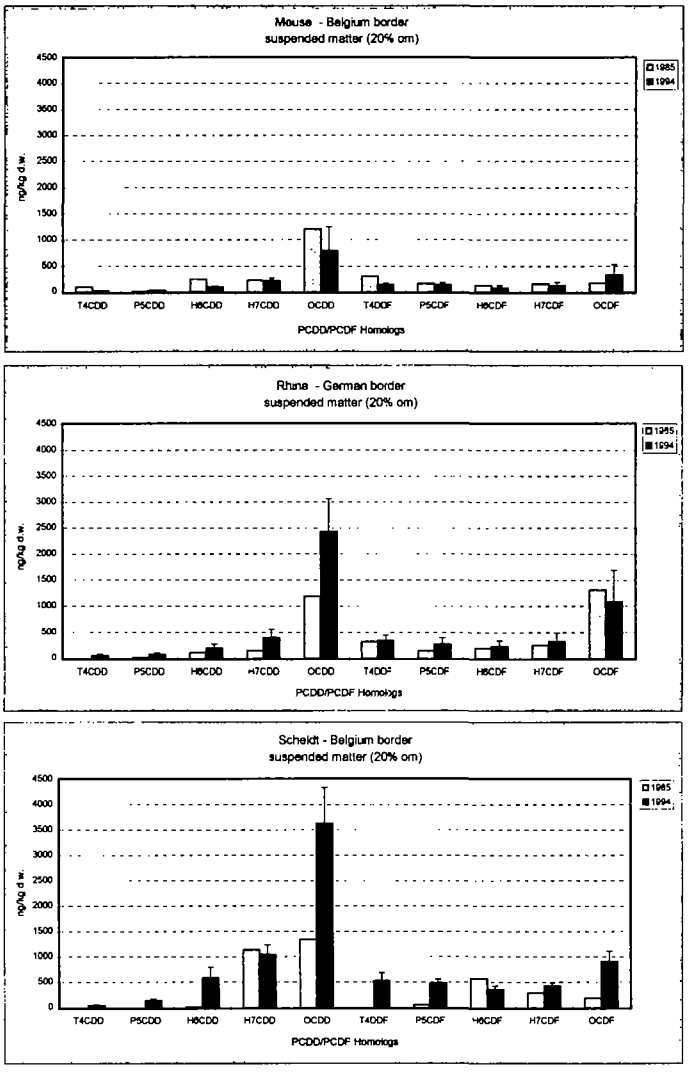

Fig. 2 Homolog profile of PCDD and PCDF in suspended matter at Dutch border crossing locations expressed as ng/kg d.w. (20 % O.M.).

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