Ministerie van Verkeer en Waterstaat

Directoraat-Generaal Rijkswaterstaat

Rijksinstituut voor Kust en Zee/RIKZ

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An analysis of possible problems in the aquatic environment

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Inhoudsopgave

Preface

The Directorate of Water Management (RWS) has commissioned the RIZA and the RIKZ to prepare risk assessment reports for a number of contaminants. The aim is to identify the most important contaminants in the North Sea together with the gaps in knowledge, management and policy.

The present study is focuses on toxaphene. This study is co-ordinated by Prof. R.W.P.M. Laane of the RIKZ, and executed by TNO-MEP.

The authors thank Mr. J. De Boer and Mr. P. Leonards of the RIVO-DLO for helpful discussions.

Summary

This report reviews the most recent information on toxaphene. The presence, fate and effects in the aquatic environment will be analysed, and the (international) policy goals will be discussed.

Toxaphene is a mixture of more than 180 congeners, consisting mainly of chlorinated bornanes (ca. 75%), bornenes, bornadienes, camphenes and dihydrocamphenes. Several nomenclature systems for toxaphene are used in practice, but there is a need for uniformity in order to avoid confusion.
Toxaphene is non-systemic contact pesticide introduced in 1949, and used in cotton and other cultures. Toxaphene has never been registered as a pesticide for use in the Netherlands. In Europe, it has been used in Germany and to a smaller extent Italy and Spain; the use in Central and Eastern Europe is less transparent.
Toxaphene is generally recognised as a global pollutant. Atmospheric transport and subsequent deposition is an important dispersion process. It is detected all over the world, including the Arctic regions and the Netherlands. Residues are detected in biota like fish and molluscs.

Emissions of toxaphene to the aquatic environment
The main emissions of toxaphene result from the use as contact-insecticide and acaricide in agriculture: cotton growing industry, production of crops such as cerials, grains, fruits, soybeans, nuts and vegetables, the control of ticks and mites in livestock, and application as a piscicide. In the Netherlands, it has never been used and is banned officially since 1968. Because of its persistence and potential for long-range atmospheric transport, global emissions are important to consider. The global use is estimated at 1.330.000 tonnes (1950-1993). Regions with the highest use are the southern USA, the former Soviet Union and Central America. In Europe, the heaviest use was in Germany (new *Länder*), Italy, Spain, Poland and other Central- and Eastern European countries. Its major legal use took place in the seventies. Currently, the heaviest use is in Africa. Compared to the 1970s current use can be described as ''residual''.

Environmental characteristics
Toxaphene is poorly soluble in water and moderately volatile. It has a log K_{ow} of 3.2 - 6.6, and adsorbs strongly to (suspended) sediments, with a log K_{oc} of 3.2 - 5.3. Toxaphene has a high bioaccumulation potential, with an experimental BCF of 3100 to 2000000. Toxaphene is persistent: degradation by hydrolysis and photolysis is negligible, and biodegradation is slow. Only in soils, under anaerobic conditions, significant biodegradation may occur. The persistent character combined with a moderate volatility and poor water solubility result in long-range atmospheric transport being a major dispersion mechanism for toxaphene. Volatilisation in warmer regions and deposition in colder regions may occur. For The Netherlands, atmospheric deposition is thought to be the major source of toxaphene in water systems. It is not possible yet to reliably quantify the loading of pesticides, including toxaphene, on the Dutch water systems. It should be kept in mind that toxaphene is a mixture of congeners, and environmental characteristics and environmental fate differ strongly between congeners. It is important to determine solubility, vapour pressure and evaporation of major toxaphene congeners, for instance the numbers 26, 50, and 62 according to the Parlar nomenclature system.

Toxicity in aquatic systems
Ecotoxicity data have been collected for a large number of organisms. Acute as well as chronic toxicity is high to all tested organisms. In the freshwater environment, toxaphene is very toxic for algae, molluscs, crustaceans, fish, amphibians and (benthic) insect larvae. In the marine environment, toxaphene was found to be very toxic for molluscs, fish and (benthic) crustaceans. For other groups of species, no information was found. Chronic ecotoxicity data were only available for fish, crustaceans and insects. Crustaceans and fish appear to be the most sensitive taxonomic groups. It is important to conduct chronic studies with freshwater fish, marine fish, marine crustaceans, and marine algae in order to determine toxicological endpoints for toxaphene in these taxonomic groups.
No information is available on the toxicity of individual toxaphene congeners for aquatic organisms. Both acute and chronic effects of indicator congeners should be determined for the standard organism groups (algae, crustaceans and fish). Attention can be focused on the three indicator congeners with Parlar numbers 26, 50 and 62.

Occurrence in aquatic systems
No efforts have been made to measure toxaphene in surface waters and sediments in the Netherlands. However, toxaphene has been detected in marine molluscs, fish and mammals of the North Sea. The composition of congeners in samples from biota and sediment can differ considerably from the composition of the applied mixture. This is due to different degradation rates and other physico-chemical properties as well as the rates of metabolism inside the organisms. Toxaphene congeners Parlar no. 26, 50, and 62 can be regarded as indicator congeners because they generally comprise a major part of the toxaphene residues found in aquatic biota.
In other countries (US, Canada) toxaphene has been measured in watersystems. The situation in the US and Canada can be considered a "worst case" estimation for the Netherlands situation.

Risk
In the current study indicative MTRs (iMTRs) for toxaphene are derived. An iMTRs of 3.9 ng/l for surface water and 200 μg/g for sediment (DW) is proposed. It is not possible to compare these criteria with measured environmental concentrations of toxaphene in surface water and sediment in The Netherlands because of the lack of data. However, based on data for environmental concentrations in the USA and Canada it can be assumed that there is no serious ecological risk resulting from toxaphene contamination in Dutch freshwater systems and coastal marine systems. For definitive conclusions it is necessary to improve the reliability of quality criteria for toxaphene by conducting more toxicity studies, as well as to determine environmental concentrations in Dutch surface waters and sediments in both freshwater and marine systems. It was not possible to derive iMTR's for toxaphene congeners due to the lack of toxicity data. It is important to notice that while environmental concentrations of toxaphene congeners can be measured, toxicity tests are conducted generally with the technical toxaphene mixture. This limits the possibilities for risk assessment.
A risk of exposure of the Dutch human population to occasionally high residues of toxaphene in fish and sea food can not be ruled out. However, toxaphene residues in samples from fish originating from Dutch freshwater and North Sea are probably below the German MRL, which is set at 0.1 mg/kg based on the 3 indicator congeners.
A human toxicologic based advisory (HTBA) value could not be calculated due to the absence of an ADI.

Policy
Toxaphene is banned officially in the Netherlands, since 1968. Internationally, toxaphene is (practically) banned in the European Union. Toxaphene is a PIC chemical (listed in the Rotterdam convention) and is included in the UN/ECE Persistent Organic Chemicals programme. It is mentioned in the OSPARCOM list of substances with endocrine activity, and on the EPA list of priority substances.

Prognosis
The presence of toxaphene in Dutch surface waters is not measured, but from the fact that toxaphene has been detected in biota from the North Sea, its presence in water systems can be deduced. The most important source is thought to be atmospheric deposition. This means that solutions to (further) reduce concentrations must be sought in international policy.

Recommendations
The presence of toxaphene in Dutch surface waters is suspected but cannot be confirmed due to the absence of measurements. It is recommended to execute indicative measurements aimed at estimating the concentration range in surface waters, including sediments. Atmospheric deposition measurements are useful as this is the major source of toxaphene. Furthermore, it is recommended to decide upon a standard identification scheme for toxaphene congeners. The German approach, with three indicator congeners, seems useful.

Samenvatting

Dit rapport bevat een overzicht van de meest recente informatie over toxafeen. Het beschrijft het voorkomen, het lot en de effecten van toxafeen in het aquatische milieu, evenals een overzicht van het beleid ten aanzien van toxafeen.

Toxafeen is een mengsel van meer dan 180 congeneren. De voornaamste bestanddelen zijn gechloreerde bornanen (ca. 75%), bornenen, bornadienen, kamfenen en dihydrokamfenen. In de praktijk worden verschillende naamgevingsystemen voor toxafeen gebruikt, maar er is behoefte aan uniformiteit om verwarring te voorkomen.
Toxafeen is een niet-systemisch pesticide, dat sinds 1949 in gebruik is in met name de katoenteelt. Het pesticide is nooit geregisteerd geweest in Nederland. Binnen Europa is het gebruikt in Duitsland en (in mindere mate) Italië en Spanje. Over het gebruik in Centraal - en Oost-Europa bestaat weinig duidelijkheid. Toxafeen wordt algemeen beschouwd als globale verontreiniging. Atmosferisch transport en (vervolgens) atmosferische depositie is een belangrijk verspreidingsproces. Toxafeen wordt over de gehele wereld aangetroffen, waaronder de poolstreken en Nederland. In Nederland worden residuen aangetroffen in organismen zoals vis en weekdieren.

Emissies naar het aquatisch milieu
De belangrijkste toxafeen-emissies treden op bij de toepassing als pesticide in de katoen-industrie, bij de produktie van granen, fruit, sojabonen, noten en groenten, bij de bestrijding van teken en mijten in de veehouderij, bij de bestrijding van de tsetse-vlieg in de tropen, en bij toepassing als piscicide. Toxafeen is in Nederland nooit toegelaten geweest, en is in 1968 officieel uitgebannen. Door zijn persistentie en potentie voor atmosferisch transport over lange afstanden is het belangrijk om naar de globale emissies te kijken. Het totale wereldgebruik wordt geschat op 1.330.000 ton (periode 1950-1993). De regio's waar toxafeen het meest werd toegepast zijn de zuidelijke VS, de vroegere Soviet Unie, en Centraal Amerika. De belangrijkste toepassing in Europa was in Duitsland, Italië, Spanje, Polen en Centraal- en Oost-Europa. Het belangrijkste (legale) gebruik vond plaats in de jaren '70. Op dit moment is Afrika het gebied waar toxafeen het meest wordt toegepast. Echter, vergeleken met het gebruik in de zeventiger jaren kan het huidige gebruik als ''residuaal'' worden omschreven.

Milieueigenschappen
Toxafeen is slecht oplosbaar in water, en redelijk vluchtig. De log K_{ow} is 3,2 - 6,6; toxafeen adsorbeert sterk aan (gesuspendeerde) sedimentdeeltjes, met een log K_{oc} van 3,2 - 5,3. Toxafeen is sterk bioaccumulerend, met een BCF van 3100 tot 2000000. Toxafeen is persistent; de afbraak ten gevolge van hydrolyse en fotolyse is verwaarloosbaar, en de biologische afbraaksnelheid is gering. De afbraak wordt echter gestimuleerd door anaerobe omstandigheden, en alleen in anaerobe bodems treed noemenswaardige afbraak op.
Atmosferisch transport over lange afstanden is een belangrijk verspreidingsproces voor toxafeen, door de combinatie van persistentie, matige vluchtigheid en slechte wateroplosbaarheid. In warmere streken kan vervluchtiging optreden, gevolgd door depositie in koudere streken. Vermoedelijk is atmosferische depositie de belangrijkste bron van toxafeen in watersystemen. Het is nog niet goed mogelijk de opname van toxafeen in

Nederlandse watersystemen op betrouwbare wijze in te kwantificeren. Er moet rekening mee worden gehouden dat toxafeen een mengsel van verschillende congeneren is, en dat de milieukarakteristieken en het lot verschillen per congeneer. Het is belangrijk de wateroplosbaarheid, dampdruk en vervluchtiging van de belangrijkste toxafeencongeneren te bepalen, bijvoorbeeld die van de nummers 26, 50, en 62 van het Parlar naamgevingssysteem.

Toxiciteit in het aquatisch milieu.
Voor een groot aantal organismen zijn toxiciteitsgegevens verzameld. De acute en chronische toxiciteit van toxafeen is zeer hoog in alle geteste groepen van organismen. In zoet water blijkt toxafeen zeer giftig te zijn voor alle soorten waarvoor gegevens zijn gevonden: algen, weekdieren, kreeftachtigen, vissen, amfibieën, en (bodembewonende) insecten-larven. In zout water blijkt toxafeen zeer toxisch te zijn voor weekdieren, vissen en (bodembewonende) kreeftachtigen. Over andere groepen is geen informatie gevonden. Alleen voor vis, kreeftachtigen en insecten zijn gegevens gevonden over de chronische toxiciteit.. Kreeftachtigen en vissen blijken de meest gevoelige groepen van organismen te zijn. Het is belangrijk dat er chronische studies worden uitgevoerd met zoetwatervissen, mariene vissen, mariene kreeftachtigen en mariene algen om voor deze taxonomische groepen toxicologische eindpunten vast te stellen.
Informatie over de giftigheid van individuele toxafeencongeneren voor waterorganismen is niet beschikbaar. De acute en chronische toxiciteit van individuele congeneren moet worden bepaald voor de standaard groepen van organismen (algen, kreeftachtigen, vissen). Hierbij kan de meeste aandacht worden gegeven aan de drie indicator congeneren met de Parlar nummers 26, 50 en 62.

Voorkomen in watersystemen
Er zijn geen pogingen gedaan toxafeen te meten in oppervlaktewater en sedimenten in Nederland. Toxafeen is echter wel aangetoond in weekdieren, vis en zoogdieren uit de Noordzee. De samenstelling van congeneren in biota en sedimenten kan sterk verschillen van de (oorspronkelijke) samenstelling van toxafeen. Dit komt door verschillen in degradatie-snelheid, en andere fysisch-chemische eigenschappen en metabolisatie-snelheden in organismen. Toxafeencongeneren Parlar nummers 26, 50, 62 kunnen worden beschouwd als indicatorcongneren omdat deze over het algemeen een belangrijk deel vormen van de toxafeenresiduen in biota. In andere landen (VS, Canada) is toxafeen wel gemeten in watersystemen. De situatie in Canada en de VS kan beschouwd worden als een "worst-case" situatie om de Nederlandse situatie te beoordelen.

Risico
In het onderhavige rapport zijn indicatieve iMTR afgeleid. Een iMTR voor oppervlaktewater van 0,0039 µg/l, en een iMTR voor waterbodems van 200 µg/kg DS zijn berekend. Het is niet mogelijk deze criteria te vergelijken met gemeten waarden voor toxafeenresiduen in oppervlaktewater en sediment in Nederland, omdat gegevens hiervoor ontbreken. Op basis van het niveau van gemeten toxafeenresiduen in VS en Canada, kan worden verondersteld dat er in Nederlandse zoetwatersystemen en zoutwatersystemen waarschijnlijk geen sprake is van een groot ecologisch risico. Om definitieve conclusies te trekken is het noodzakelijk de betrouwbaarheid van de waterkwaliteitsnormen te verbeteren door meer toxiciteitsstudies uit te voeren, tevens moeten toxafeenconcentraties in Nederlandse oppervlaktewateren en sedimenten, zowel zoetwater als zoutwater, worden gemeten. Er konden geen iMTR's voor

individuele congeneren worden berekend, door afwezigheid van ecotoxiciteitsgegevens. Het is belangrijk zich te realiseren dat vaak concentraties van individuele congeneren in het milieu worden gemeten, terwijl de giftigheid van deze congeneren niet bekend is. Toxiciteitstesten worden over het algemeen uitgevoerd met technische mengsels van toxafeen..Dit beperkt de mogelijkheden voor een risicoschatting.
Een risico voor de Nederlandse bevolking via de consumptie van vis en schelpdieren met hoge toxafeenresiduen kan niet worden uitgesloten. Toxafeen gehaltes in monsters van vis afkomstig uit Nederlandse binnenwateren en Noordzee, zijn echter waarschijnlijk beneden de door Duitsland voorgestelde MRL van 0,1 mg/kg, gebaseerd op 3 indicator congeneren.
Er kon geen humaan toxicologisch onderbouwde advieswaarde (HTOA) worden berekend, door het ontbreken een ADI.

Beleid
In Nederland is toxafeen officieel uitgebannen in 1968. Ook in de EU is toxafeen (praktisch) uitgebannen. Toxafeen is verder een PIC-stof (opgenomen in de Rotterdam conventie) en is opgenomen in de UN/ECE Persistent Organical Chemicals programma. Verder is toxafeen opgenomen in de OSPARCOM-lijst van stoffen met endocriene eigenschappen, en op de EPA-lijst van prioritaire stoffen.

Prognose
Het is niet bekend of toxafeen in Nederlands oppervlaktewater aanwezig is, maar aangezien toxafeen in biota in de Noordzee is aangetoond, mag aangenomen worden dat toxafeen ook in het water voorkomt. De belangrijkste bron is atmosferische depositie. Dit betekent dat oplossingen voor (verdere) reductie van concentraties gezocht moet worden in internationaal beleid.

Aanbevelingen
De aanwezigheid van toxafeen in oppervlaktewater wordt vermoed, maar is niet aangetoond in het Nederlandse oppervlaktewater door de afwezigheid van metingen. Aanbevolen wordt om indicatieve metingen uit te voeren die erop gericht zijn om de concentratie-range in het Nederlandse water te bepalen. Hierbij zijn metingen aan atmosferische depositie belangrijk, omdat dit een belangrijke bron van toxafeen is. Er wordt aanbevolen om te besluiten over een standaard identificatie-methode (naamgeving) voor toxafeen congeneren. De Duitse benadering met drie indicator-congeneren is hierbij mogelijk bruikbaar.

1 Introduction

1.1 Background

Toxaphene is a non-systemic contact insecticide, which was introduced in 1949 and has been widely used since, especially on cotton. In the Netherlands, it has never been registered. However, toxaphene, being persistent and semi-volatile, can be regarded as a "global pollutant", and has been detected e.g. in European marine fish. It is subject to international initiatives regarding Persistent Organic Pollutants (POP's).
Toxaphene is a mixture of many chlorinated terpenes, mainly bornanes. Differences among toxaphene congeners in biotic and abiotic degradation potentials may occur but is only scarcely investigated. This complicates the environmental risk assessment of toxaphene in a way analogous to PCBs.

1.2 Objectives

The objective of this study is to assess the presence of toxaphene in the aquatic environment: emission, occurrence, environmental fate and effects, including an assessment whether toxaphene will affect the aquatic ecosystem functioning.
This study represents the most recent information on toxaphene. Despite the international interest for toxaphene, only limited information is available. When relevant, recommendations regarding research are made, or on-going research projects are mentioned.
This study has a wide scope. The following aspects will be addressed:

1. Physico-chemical properties;
2. Sources and emissions to surface water;
3. Environmental fate in surface water;
4. Presence in surface water;
5. Aquatic ecotoxicity;
6. Policy review.

1.3 Scope

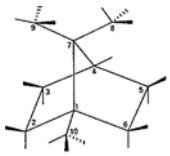
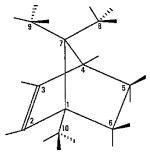
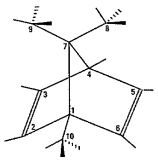
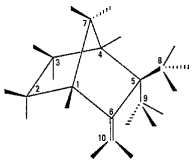
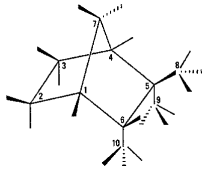
The scope of this study is limited to aquatic systems in the Netherlands, including the North Sea. When relevant, other systems in the close geographical proximity are mentioned, such as the Atlantic or the Rhine, Scheldt and Meuse catchment basins. The study is a synoptic review; for further information the reader is referred to the original publications.

2 Physico-chemical properties

2.1 Identification

Toxaphene is a reproducible mixture of polychlorinated camphenes and comprises more than 180 components. The major part of technical toxaphene consists of chlorinated bornanes (ca. 75%). The formula of the toxaphene components is $C_{10}H_{18-n}Cl_n$ or $C_{10}H_{16-n}Cl_n$ with n is 6 to 10.
The molecular structures of the main components of toxaphene are shown in Table 2.1.

Table 2.1
The main components of toxaphene, molecular formulas and structural formulas (De Geus et al., 1999)

Component	Molecular formula	Number of congeners	Structure formula
chlorinated bornanes	$C_{10}H_{18-x}Cl_x$	32767	
chlorinated bornenes	$C_{10}H_{16-x}Cl_x$	8191	
chlorinated bornadienes	$C_{10}H_{14}Cl_x$	2047	
chlorinated camphenes	$C_{10}H_{16}Cl_x$	16383	
chlorinated dihydrocamphenes	$C_{10}H_{18}Cl_x$	65534	

Trade names of formulations with toxaphene are shown in Table 2.2, together with CAS number and CAS name. Toxaphene was never registered in The Netherlands for use in agriculture.

Table 2.2
CAS number and chemical names of toxaphene and trade names of formulations with toxaphene (Ritter et al., 1995; Saleh, 1991)

Component	CAS number chemical name	Common names	Synonyms and Trade names (partial list)
toxaphene	8001-35-2	Toxaphene, Camphechlor, Chlorinated camphene, Octachlorocamphene, Polychlorocamphene, Polychloroterpenes	Alltex, Alltox, Attac 4-2, Attac 4-4, Attac 6, Attac 6-3, Attac 8, Camphechlor, Camphochlor, Camphoclor, Chemphene M5055, chlorinated camphene, Chloro-camphene, Clor chem T-590, Compound 3956, Chloroter, Cristoxo-90, Dark, Delicia Fribal, Estonox, Fasco Terpene, Geniphene, Gy-phene, Hercules 3956, Huilex, Kamfochlor, Melipax, Motox, Octachlorocamphene, Penphene, Phenacide, Phenatox, Phenphane, Polychlorocamphene, Strobane-T, Strobane T-90, Synthetic 3956, Toxadust, Toxadust 10, Toxakil, Texadust, Toxakil, Toxon 63, Toxyphen, Vapotone, Vertac 90%.

Several nomenclature systems have been developed for toxaphene compounds. However, it is difficult to combine completeness, transparency, and simplicity in one single system. De Geus *et al.* (1999) suggest that an international body such as the International Union of Pure and Applied Chemistry should make an attempt to obtain uniformity in the literature. For a recent comprehensive overview of the five main nomenclature systems for toxaphene reference is made to De Geus *et al.* (1999). Table 2.3 lists the names for three indicator toxaphene congeners according to the main nomenclature. In the sections 5.3 and 5.4 it is described that these congeners are the main toxaphene congeners found in samples from fish in European coastal waters.

Table 2.3
Systemic names and nomenclature codes of three indicator compounds present in toxaphene (cited from De Geus et al., 1999)

Systemic name	Parlar nos. (1993, 1995)	Nikiforov *et al.* (1995)	Oehme & Kallenborn (1995)	Andrews & Vetter (1995)	Wester *et al.* (1997)
2-endo,3-exo,5-endo,6-xo, 8,8,10,10-octachlorobornane	26	OCB-4921	198-605	B8-1413	B[12012]-(202)
2-endo,3-exo,5-endo,6-exo, 8,8,9,10,10-nonachlorobornane5	50	NCB-4925	198-643	B9-1679	B[12012]-(212)
2,2,5,5,8,9,9,10,10-nonachlorobornane	62	NCB-6551	99-133	B9-1025	B[30030]-(122)

2.2 Physico-chemical characterisation

Table 2.4 lists a number of important physical-chemical properties of toxaphene. Water solubility, vapour pressure and octanol-water partition coefficient are dealt with in chapter 4 (behaviour in the aquatic environment). Sometimes different values are found for a physical-chemical property and it is chosen to show them all.

Table 2.4
Physical-chemical properties of toxaphene (De Geus et al., 1999; Ritter et al., 1995; PIC, 1999; Richardson & Gangolli, 1993; Saleh, 1991)

Component	molecular mass	appearance	melting point (°C)	boiling point (°C)	density (g/cm^3)
toxaphene	413.82[#]	yellow (amber) waxy solid	65-90, 65-95 (softens)	>120, 155 (decom-poses)	1.63, 1.65

[#] on average

2.3 Comparable chemical compounds

Some compounds have chemical properties quite comparable to those of toxaphene for instance other organochlorines like DDT, hexachlorobenzene (HCB) and PCBs. The octanol-water partitioning coefficient (log K_{ow}) of toxaphene is comparable to HCB and somewhat lower than that of technical PCBs but higher than those of pp-DDT and its metabolites (De Geus *et al.*, 1999). Furthermore, these compounds are also very persistent and residues are found on a global scale. Like the organochlorines DDT, HCB and lindane, toxaphene was and still is used as insecticide. These pesticides can all be regarded as so-called PBT pollutants (persistent, bioaccumulative, and toxic pollutants).

The occurrence, behaviour and effects of some other organochlorine pesticides were described in a previous Water System Evaluation report (Teunissen-Ordelman *et al.*, 1995). Dicofol, dienochlor, endosulfan, lindane and methoxychlor were considered in that document. In contrast with toxaphene, these pesticides have been registered in the Netherlands for agricultural pest control.

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3 Sources and emissions to the aquatic environment

3.1 Sources and emissions during industrial processes

The preparation of toxaphene is described in Appendix 1. In short, the process of producing toxaphene firstly involves the preparation of the raw camphene feed which is subsequently chlorinated with or without using UV light to produce toxaphene (De Geus *et al.*, 1999). Chlorination of technical camphene purchased from commercial sources also takes place and other synthesis routes are used as well. Toxaphene has never been produced in the Netherlands according to available information and in the EU production is now discouraged by EU regulations (see chapter 7). Information on emissions from production in the United States indicates heavily contaminated water systems adjacent to chemical plants that produced toxaphene for a sustained period. Chlorobornanes found in unmodified toxaphene were reported in fish, several miles from the contaminated site. However, it can be assumed that this type of contamination remains restricted to a local scale. Although no quantitative data such as emission factors are available, it is probably safe to say that the amounts released through application will by far outweigh emissions from production. The larger part of the emission to water systems due to production of the substance most likely results from storage and handling activities on site which are difficult to quantify in general.

Chlorine bleaching of wood pulp in the paper and pulp industry produces chlorinated camphenes similar to toxaphene. However no evidence has been found of compounds identical to the main congeners in commercial toxaphene (De Geus *et al.,* 1999). Toxaphene serves no purpose as an intermediate technical chemical according to available information. Its sole purpose is therefore application as a pesticide.

3.2 Sources and emissions during application as a pesticide

Toxaphene is a non-systemic contact and stomach insecticide with some acaricidal action and belongs to the first generation organochlorine insecticides such as
dieldrin, DDT and chlordane. At this moment for almost all purposes at least equally effective alternatives are available. It has often been used in combination with other pesticides. Its primary applications include:

- the cotton growing industry (more than 80%)
- the production of:
  - cereals
  - fruits
  - soybeans
  - nuts
  - vegetables
- the control of ticks and mites in livestock
- the control of tsetse-flies in tropical regions
- application as a piscicide

In general, emission of pesticides takes place during and after application. For a given pesticide emission to water systems can be calculated based on among others application rate, soil properties, tillage practise, the way in which the pesticide is applied, physical and chemical properties of the pesticide and meteorological conditions. The pathways by which pesticides enter the environment during and after application are discussed in more detail in (Teunissen-Ordelman *et al.,* 1995). However, since use does not take place in the Netherlands nor in its direct surroundings, these emission mechanisms are not considered relevant for toxaphene in the Netherlands water systems.

As will be further discussed in the following section, toxaphene is a typically semi-volatile compound, a characteristic that favours the long range transport of this substance. It can be transported over great distances through the atmosphere. Volatilisation may occur from plant and soil surfaces following application as pesticide. Atmospheric long range transboundary transport is probably the dominant imission pathway for toxaphene in the Netherlands (see below). Other sources may include ocean currents and rivers (Voldner & Li, 1995) (see section 3.3).

3.3 Long range transboundary transport

As mentioned above, one important property of toxaphene is that of semi-volatility. This property confers a mobility through the atmosphere that allows relatively great amounts to enter the atmosphere and be transported over long distances. On the other hand this moderate volatility does not result in the substance remaining permanently in the atmosphere. Moreover, due to its persistence toxaphene is continually deposited and re-evaporated. It may volatilise from hot regions but will condense and tend to remain in colder regions. This has far-reaching implications for the global environment because volatilised residues disperse through the global atmosphere. This results in the compound being found almost everywhere, including in the Netherlands, but also in the most remote areas (e.g. polar regions) far from any source of use.

The importance of atmospheric transport of toxaphene has been demonstrated by many studies on the presence of toxaphene in the US Great Lakes area. Toxaphene detected in marine and fresh waters in and around the Netherlands is most likely almost entirely the result of atmospheric deposition. Though other mechanisms should not a priori be disregarded. Concentrations are low in the Dutch waters and discrete exposure may appear limited, however, the tendency of toxaphene to bioaccumulate can result in toxicologically relevant concentrations in for instance fish.

Current use of toxaphene

In order to assess the origin of toxaphene present in water systems in the Netherlands, one might focus on countries where it still finds use. In the Netherlands toxaphene has never been used at all and it was officially banned in 1968. Within the European Union, only Germany and to a smaller extent Italy and Spain have reported historic use. Germany (former FRG) totally banned the substance in 1981, while European Union legislation, which became effective in 1984, "prohibits to use or place on the market all plant protection products containing toxaphene with no remaining uses allowed". In Norway and Switzerland toxaphene is neither used at present.

The situation in Central and Eastern Europe may be more complicated. At present, national laws ban toxaphene from (principal) use in Estonia, Lithuania, Romania and the Slovak Republic. Its use is according to national law restricted in the Czech Republic, The Former Yugoslav Republic Of Macedonia and the Russian Federation. The Ukrainian Ministry of Agriculture states that toxaphene is not in use. In Latvia import and usage is not permitted since 1994 but there are stockpiles of obsolete toxaphene. International reportings on emissions (e.g. EMEP) by Hungary suggest that there is no use of toxaphene. Almost no information is available for the present situation in Poland, Belarus, Bulgaria, Slovenia, Moldova, Croatia, Bosnia Herzegovina and Yugoslavia. In 1991, Saleh (1991) reported use for Romania, Hungary, Poland and the former Soviet Union. Use in these regions was also expected by other authors at the end of the 1980s (e.g. Voldner & Schroeder 1989). Considering the historic use patterns for these countries it is estimated that if any use occurs it will be low, for instance in the order of 10 to 100 tonnes annually.

A global inventory of the registration status of toxaphene, under the United Nations Environmental Programme (UNEP) indicates that by June 1999 toxaphene was banned by 58 countries while in 12 countries use is (severely) restricted. 37 Countries stated that there were inconclusive data to determine the status and in 8 countries legislation was lacking. 33% of all countries failed to respond.

However, it should be kept in mind that the official registration status of a pesticide is never a 100% accurate indication for the actual use since it might not be fully clear whether for instance 'restricted use' is significant, or whether illegal or otherwise not administered amounts are used. Also old stocks of obsolete pesticides might still be used. The FAO administers obsolete stocks of dangerous pesticides. Results are now available for Africa and other regions are expected to follow (UNEP, 1996).

Within the framework of the global negotiations on Persistent Organic Pollutants (POPs) by the INC several attempts have been undertaken to establish a complete inventory of imports, exports, production, stocks and usage of toxaphene. The most recent study has been performed for the Global Environment Facility (GEF) by the Worldbank (Jorgenson, 1999) the results of which are, however, still considered as internal. Another attempt concerns a trade survey on POPs held by UNEP Chemicals in 1996 (UNEP, 1996). In the period 1991 to 1994, production of toxaphene was at least 1200 tonnes in Africa. Production was also reported during this period for Central America while in South America import of the substance took place. At least 131 tonnes were exported from Europe (including Central and Eastern Europe) in 1991. In another work, which was undertaken by Sweden (KEMI, 1996), an inventory has been prepared of companies reporting to be producing or marketing POP pesticides. The study performed by the Worldbank (Jorgensen, 1999) expands upon this work. The FAO also keeps records of trade in pesticides. Their work however only comprises a pastiche trade of total organo-chlorine pesticides.

In conclusion, it can be stated that toxaphene is not used in Western Europe, but there might be minor use in Central and Eastern Europe and Russia for certain crops. Outside Europe, toxaphene is not used anymore in the USA and Canada, but does still take place in Central and South America. Currently, the heaviest current use seems to occur in certain African countries. In literature, Ethiopia, Sudan, Tanzania and Uganda are mentioned more than once. No significant uses are reported for Asia although for many Asian countries recent data and legislation are lacking. It should be noted that these conclusions

remain partly speculative since there are no central registers for this substance and available information is scarce. Compared to the use as it was in the 1960s, 1970s and 1980s, the current use can be described as 'residual". In this report usage will not be further discussed, as producing an exact global overview of toxaphene use falls outside the scope of this document.

Historic use

Due to its low volatility', toxaphene migrates relatively slowly in the atmosphere. The above described process of deposition and re-evaporation may continue after the pesticide's initial application. Furthermore, toxaphene is very persistent. It is therefore also relevant to consider its historic use. In Voldner & Li (1995), an attempt was made to quantify the total global use of this chemical. The total cumulative global usage accounted for 450,000 tonnes. The interpolated usage came to 1,330,000 tonnes for 1950 to 1993 and 670,000 tonnes during 1970 to 1993. These are enormous quantities (compare 2,600,000 tonnes for DDT during 1950-1993). The regions for which the highest usage is recorded seem to be the (Southern) USA, the former Soviet Union and Central America. But also in Europe, at least 10.000 tonnes has been used in Germany (in the former GDR, during 1960-1980, heaviest use in the 1970s) and there was also some usage in Italy, Spain (both minor), Poland and other Central and Eastern European countries.

Transboundary aerial transport

Atmospheric transport of toxaphene after volatilisation into the atmosphere is probably the major environmental pathway to most of the oceans and surface waters of the world. Reported losses of toxaphene a few months after application range from 50 to 80% (Majewski & Capel, 1999). Current atmospheric concentrations are also partly caused by volatilisation of persistent residues, although this can not be quantified at present. Atmospheric deposition is not a once-only process and toxaphene can be re-introduced into the atmosphere for further dispersal again and again (Majewski & Capel, 1999). Voldner & Schroeder (1989) estimated that 70-80% of the toxaphene load to the US-Great Lakes area was caused by long range transport and wet deposition. Similar phenomena were also observed in Europe. Air masses which had passed over Eastern Europe have been shown to deposit organochlorine pesticides such as toxaphene during the 1980's (Majewski & Capel, 1999).

Pollutant transport time into the troposphere above the surface boundary layer is generally in the order of a few weeks to months. Once in the atmosphere the global wind circulation patterns control long-range transport. Although the mixing time is in the order of 1 or 2 years, limited transport between hemispheres does occur (Majewski & Capel, 1999).

Based on the currently available information it is not possible to go beyond the qualitative description of atmospheric deposition which is given here. The importance of atmospheric transport of pesticides into surface waters is only beginning to be understood and so far no models have been developed which can reliably quantify the toxaphene loading on the Dutch water systems. Also it is not clear to which degree the re-introduction of persistent residues affect currently observed concentrations.

Contribution by foreign rivers
Since there is no use or production reported in the catchment areas of the main rivers in the Netherlands it is unlikely that these make a significant contribution to water systems. Although the magnitude of atmospheric deposition in the catchment areas is basically not known, toxaphene compounds have not been measured in the main Dutch rivers (see chapter 5). There might be a contribution to the North Sea by ocean currents but this has so far never been quantified.

3.4 An outlook to the situation in Europe

Within Europe, other countries might have the same concerns about toxaphene present in water sytems while there is no use of the substance. European policy in this respect focuses on elimination of use resulting in several European initiatives that ban toxaphene. Use and marketing within the EU is prohibited as plant protection product (directive 83/181/EEC of 14/31983-OJ L91 p35). Furthermore, toxaphene is now a PIC chemical (listed in the Rotterdam Convention) and is listed in ANNEX 1 of REG 2455/92 and is therefore subject to the Export Notification Procedure.

Toxaphene is also addressed by the UN/ECE Protocol on Persistent Organic Pollutants. This Protocol focuses on a list of 16 substances that have been singled out according to risk criteria. The Protocol bans the production and use of toxaphene outright and has been signed by the majority of the countries in Europe. Full implementation of this Protocol will eliminate all remaining uses, trade, stockpiles and production of toxaphene in UN/ECE-Europe. At present (November 1999) The Russian Federation, Belarus, Turkey, Bosnia-Herzegovina, The former Yugoslav Republic of Macedonia and Yugoslavia have not yet signed this Protocol for various reasons. Toxaphene is currently not addressed by OSPARCOM-HELCOM reporting obligations.

3.5 Conclusions and recommendations

Toxaphene can be classified as a "global pollutant". Use during the last decade has not taken place in the Netherlands nor in other parts of Western Europe. Atmospheric transport of toxaphene after volatilisation into the atmosphere elsewhere is probably the major environmental pathway to most of the oceans and surface waters of the world.

Beyond Western Europe, toxaphene is either banned or its use is severely restricted in many countries. Nevertheless, use and production is still reported in some areas of the world. Currently the heaviest use of toxaphene seems to be in Africa. There is however very little reliable information available about the specific application and usage in each country. Based on the scarce quantitative data available, the annual global use can roughly be estimated to be at least a few hundred tonnes. But this could well be a significant underestimation.

Toxaphene found in the Dutch water systems partly originates from recent use as a pesticide but possibly also from the re-introduction of persistent residues. The atmospheric deposition of toxaphene in and around the Netherlands has not yet been quantified at this moment and basically the loading of the Dutch water systems is still unknown.

Policy aimed at a reduction of toxaphene levels will only be effective at an international level.

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4 Behaviour in the aquatic environment

4.1 Introduction

The behaviour of organic compounds in the aquatic environment is determined by the physical-chemical properties as solubility, sorption, volatility, and by the characteristics of the water system of concern (residence time of the water, sedimentation area, etc.). The properties also determine to which extent a compound will accumulate in organisms.

4.2 Solubility and volatilisation

The water solubility of a compound is a good indication of the extent to which this compound will be transported with water. In general, poorly soluble compounds have a high affinity for the organic matrix of silt particles in a water system. For this reason that these compounds will sedimentate together with the silt particles and as a result the transport along with the water stream will be slowed down. Poorly soluble compounds will also accumulate in organisms more easily. Solubility and vapour pressure together determine whether a compound will evaporate out of the water. The extent of evaporation is denoted with a single parameter, the Henry constant (H).

In case of the absence of a Henry constant, it is possible to calculate a value for the Henry constant from the values for solubility and vapour pressure (Van Leeuwen & Hermens, 1995). Different values and ranges are found in the literature, probably due to application different measuring techniques and different technical mixtures of toxaphene. The selected value for the Henry constant is an experimental value for a technical mixture of toxaphene congeners reported by De Geus *et al.* (1999). This value is listed in Table 4.1.

Table 4.1
Solubility (S), vapour pressure (P_{vp}) and Henry constant (H) of toxaphene (Sources: De Geus et al., 1999; Ritter et al., 1995; Saleh, 1991; Richardson & Gangolli, 1993).

Component	S ($g.m^{-3}$)	P_{vp} (Pa)	H ($Pa.m^3.mol^{-1}$)
toxaphene	0.4-3.3 (20-25 °C)	26.3-52.6 (25 °C)	0.62 (20 °C)

According to the scheme in Appendix 2 toxaphene has a low water solubility and is volatile. The evaporation of toxaphene out of the water is an important process also due to the rather slow degradation rate in water-sediment systems (see section 4.4.3).

4.3 Sorption

The extent of sorption strongly depends on the presence of the amount of organic matter in the sediment layer or suspended particles. Therefore sorption is often indicated relative to the amount of organic matter content (K_{om}) or the organic carbon content (K_{oc}). Both values are found in the literature. In Table 4.2 values for K_{oc} are presented.

For some toxaphene congeners octanol-water partitioning coefficients (K_{ow}) have been derived (see table 4.2). K_{oc} values are not available for toxaphene congeners but can be predicted using the K_{ow} (Brown & Flagg, 1981). This equation is applicable for neutral organic compounds. Alternatively, also the solubility can be used to predict the K_{oc} value (Kenaga, 1980).

Available K_{ow} and K_{oc} values are reported in Table 4.2.

Table 4.2
Octanol-water-partition coefficient K_{ow} and sorption coefficient K_{oc} of toxaphene.

Component	$logK_{ow}$	$logK_{oc}$	Reference
toxaphene mixture	3.23-6.60 6.44	3.18; 5.32 5.0	Ritter (1995) De Geus (1999)
hexachloronorbornadiene heptachloronorbornene	5.28 5.28		Veith *et al.* (1979)
7 persistent polychlorinated bornanes with a high bioconcentration potential in fish	5.80-7.85		Geyer *et al.* (1999)

4.4 Transformations in freshwater and marine environments

4.4.1 Hydrolysis
The rate of hydrolysis of toxaphene is negligible.

4.4.2 Photolysis
Toxaphene formulations are relatively stable in water and soil but may be degraded by losing HCl or Cl_2 after prolonged exposure to sunlight, alkali or temperatures above 100 ℃. According to Saleh (1991), technical toxaphene does not undergo a serious change when exposed to sunlight. The stability with respect to UV light, and acid and alkaline treatment differs among toxaphene congeners (De Geus *et al.*, 1999). It is suggested that dechlorination of toxaphene occurs during photolysis and the dechlorination rate is nonachlorobornanes > octachlorobornanes > heptachlorobornanes.

4.4.3 Biodegradation and mineralisation
The half-life of toxaphene in soil ranges from 100 days up to 12 years, depending on the soil type and climate (Ritter *et al.,* 1995). Microbial degradation in soil and sediment is enhanced by anaerobic conditions. Half-lives of 3 weeks (Richardson & Gangolli, 1993) and 6 weeks (EPA, 1999) were reported for degradation of toxaphene in anaerobic soils. For (partly) aerobic soils half-lives between 0.8 and 14 yr were reported. Toxaphene will adsorb strongly to soil and sediment with a K_{oc} of $2.1x10^5$ (EPA, 1999). Despite its strong adsorption, toxaphene will gradually evaporate from soil to the air. Based on the (above-mentioned) physical-chemical properties it is not expected that toxaphene will leach to groundwater (EPA, 1999; PIC, 1999). In general, groundwater toxaphene concentration exceeding 1 ng/l have not been observed (PIC, 1999).

Boon *et al.* (1996) studied the biotransformation of toxaphene with bioassays. They concluded that the *in-vitro* biotransformation capacity differed among taxonomic groups, with an increase in activity in the order sperm whale < seebirds & dolphins << seals. Residue patterns of toxaphene in these animals in

the field situation confirmed these findings.

Fingerling *et al.* (1997) studied the degradation of toxaphene components in UV irradiated air and flooded soil. They concluded that the contribution of abiotic processes is more important in atmosphere, water, and perhaps part of the aquatic biota, whereas the contribution of microbial pathways is probably more important in soil. Angerhöfer *et al.* (1999) found that residue patterns of UV irradiated toxaphene and toxaphene in fish samples are quite similar. Fish seem to be able to metabolise some toxaphene congeners like Parlar 44 and 62 in contrast with the Parlar 26 and 50 congeners.

4.4.4 Summary

In Table 4.3 the half-life values from the preceding sections are summarised.

Table 4.3
Half-life values for degradation of toxaphene

component	DT50 hydrolysis	DT50 photolysis	DT50 biodegradation
toxaphene	not significant (> 10^5 year)	not significant	aerobic: not significant ananaerobic: slow (3-6 weeks)

4.5 Bioconcentration

Bioconcentration is the process in which compounds are taken up by organisms. When an organism is not able to metabolise the compound, higher internal concentrations are reached compared to situation where metabolism does occur. Bioconcentration is considered to be an equilibrium partition process between water and organisms which iscomparable to sorption to soil and octanol-water partitioning.

Bioconcentration of compounds in aquatic organisms can occur via uptake of compounds directly from the water (bioaccumulation) or via food (biomagnification). Bioaccumulation can be measured in different ways. Organisms can be exposed to water with contaminants until equilibrium is attained (internal contents do not increase anymore). The bioconcentration factor (BCF) can be calculated from the ratio between the content in organisms and water: BCF = $C_{organism}$ / C_{water}. The BCF can be expressed on lipid basis as well as on fresh weight basis. A second method is based on the kinetics of the process. First, an organism is exposed to water with the compound of concern and the uptake rate (k_1) is measured. Subsequently the organisms are transferred to clean water and the elimination rate (k_2) is determined. The BCF is calculated with the formula: BCF = k_1 / k_2.

Problems or inaccuracies with BCF values often can be ascribed to the fact that equilibrium is not reached. Confusion about the BCF values for a compound can also occur in case it is not clear whether the BCFs are based on lipid weight or on total fresh weight of organisms.

For toxaphene, bioconcentration factors of 400-1200 for shrimp, 6920 for algae, 8000 for oyster, and 9600 for aquatic snails have been reported (Richardson & Gangolli, 1993). In fathead minnows and channel catfish, maximum bioconcentration factors were 69000 and 50000, respectively (Richardson & Gangolli, 1993). Toxaphene BCF's for freshwater fish species are 10000-69000. Excretion was very slow: 56 days for 36% elimination. In general, the bioconcentration factor for total toxaphene in fish varies from

3100 to 33300 (PIC, 1999). However occasionally much higher BCFs can be found. For instance, for the arctic cod a high BCF value of 2 x 10^6 has been reported (De Geus *et al.*, 1999). Swackhammer *et al.* (1998) presented the most recent data for toxaphene in the Great lakes of North America for water, sediment and the foodweb. It was shown that toxaphene significantly biomagnifies in the foodweb. Mean lipid normalised log bioaccumulation factors (BAFs) for phytoplankton, zooplankton, Mysid shrimps, sculpin and lake trout amounted to 5.82, 6.53, 6.29, 6.58, and 6.96.

In Table 4.4, experimental and calculated BCF values are presented for toxaphene (mixture) and some toxaphene congeners.

Table 4.4
Bioconcentration factors (BCFs) of 3 selected toxaphene congeners in mg/kg fresh weight.

Toxaphene congener	Experimental BCF zooplankton	Experimental BCF fish	Calculated BCF fish #	Reference
Parlar 26	163000	133000-5660000	48000-65000	Geyer *et al.* (1999)
Parlar 50	290000	100000-680000	85000-115000	Geyer *et al.* (1999)
Parlar 62	n.d.	n.d.	2630000-3500000	Geyer *et al.* (1999)

n.d not determined
assuming a lipid content of 5%

It can be concluded that toxaphene is highly accumulating. The bioconcentration potential can be expected to differ considerably among toxaphene mixtures of different composition. Experimental BCF values for toxaphene congeners are still scarce.

4.6 Distribution in water systems

Transfer to and distribution within larger water systems can be expected and many data are available in literature, which confirm this. Due to slow degradation in surface water and sediment and the high adsorption to sediment, toxaphene concentrations in water and sediment will only slowly decrease in time.

4.7 Conclusions and recommendations

Environmental parameters
Toxaphene has a low solubility in water. The available information for volatility is very variable. It is assumed that toxaphene is volatile. Toxaphene has a high partition coefficient (log K_{ow}). Sorption of toxaphene to soil and sediment is high. Toxaphene is mainly present in the sediment and biota. Hydrolysis, photolysis and microbial/total degradation are very slow. Only in anaerobic sediments, significant biodegradation is reported (DT_{50} 3-6 weeks). The accumulation potential of toxaphene in biota is high.

Reliability of the data
For individual toxaphene congeners there are insufficient data available concerning the physical-chemical properties like solubility, volatility and octanol-water partitioning.

Distribution behaviour
Distribution in large water systems has been demonstrated. Toxaphene is found in marine waters but also in large freshwater systems (lakes) far away from the sites of main applications. Toxaphene was shown to be relatively persistent, highly mobile and bioaccumulating in biota. Furthermore toxaphene is volatile, and relatively easily washed out by rain, allowing long distance transport in the atmosphere. This all explains its widespread presence in the biosphere.

Recommendations
Further efforts should be made to determine the physical-chemical properties of the key congeners of toxaphene ($\log K_{ow}$, water solubility, volatility). For this purpose at least the 3 key congeners listed in table 2.3, section 2.1, should be selected.

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5 Occurrence in the aquatic environment (environmental concentrations)

5.1 Analytical techniques

In the 1980's, much progress has been achieved in the selectivity, accuracy and sensitivity of detection techniques (Saleh, 1991). This made it possible to demonstrate the presence of toxaphene on pbb level in human populations, fish and wildlife, soil, water, groundwater and food. Only then, it became fully clear that toxaphene was a global pollutant like PCBs, DDT and some other persistent organochlorines (POP's).

The state-of-the-art analytical techniques are comprehensively described by De Geus *et al.* (1999). The major steps in analysis for toxaphene are extraction, pre-separation and clean-up, gas chromatographic separation, and detection. Negative chemical ionisation (NCI) is the most widely used MS detection method but has the disadvantage that it is insensitive to lower chlorinated toxaphene congeners. The electron impact (EI) mode is more sensitive to these congeners, but will lead to false positive results as well. The electron capture detector (ECD) is an alternative detector but is less sensitive than MS detection. NCI/MS gave generally higher results than ECD.

Measured concentrations of total toxaphene and individual toxaphene congeners can be expressed on a wet weight basis or on a lipid weight basis.

The following limits of detection are reported for toxaphene (Leonards, pers. com.):

- GC-NCIMS: between 0.002 and 0.02 μg/kg wet weight.
- GC-ECD: between 0.01 and 0.1 μg/kg wet weight.

New developments in mass spectrometric detection using NCI or EI modes, as well as in multidimensional gas chromatography recently have led researchers to suggest congener-specific approaches. The methods predominantly used for determination of toxaphene are based on ECNI-MS measurements using technical toxaphene as standard. Individual congeners can be determined by GC/ECD (Alder & Vieth, 1996). A number of toxaphene congeners were numbered by Parlar (Burhenne *et al.*, 1993), based on gas chromatographic retention and are not structure related. Other systems provide structural information, but are either incomplete, or complex to handle. Wester *et al.* (1997) introduced a new system which seems suitable to meet the most important criteria. De Boer (1997) recommended that an authoritative international body should take a decision on the choice of the nomenclature system for toxaphene.

5.2 Measurements in freshwater systems

Data for European freshwater systems (surface water, ground water, rain water) are not available to our knowledge. Information is available for the North American continent because of the regional heavy use of toxaphene in earlier decades. Swackhammer *et al.* (1998) reported recent toxaphene

concentrations in water from the North American Great Lakes ranging from 1.1 ng/l in Lake

Superior to 0.17 ng/l in Lake Ontario. Swackhammer *et al.* also recently determined suspended matter concentrations of toxaphene of 9.4 and 6.3 ng/l for Lake Michigan and Lake Ontario. Muir *et al.* (1997) determined toxaphene residues in water, sediment, zooplankton and fish in a Canadian lake. Residues of total toxaphene and individual toxaphene congeners increased with increasing trophic level within the foodweb. Water and sediment concentrations of total toxaphene amounted to 0.2 ng/l and 360 pg/g dw, respectively.

Toxaphene in rainwater is scarcely measured. Saleh (1991) reported an average toxaphene level of 28 ng/l in rainfall at pristine sites in South Carolina during July 1981. This was 80 times higher than any other orgnochlorine analysed in those samples.

5.3 Measurements in marine systems

Few data are available for toxaphene residues in European marine ecosystems. In general, toxaphene concentrations increase when moving in western and northern direction from the Netherlands (De Boer, personal communication). Alder *et al.* (1997) concluded that a relationship between toxaphene residue levels in fishing grounds and toxaphene contents in fish could not be established. On the other hand, accumulation of toxaphene was strongly related to age (length) of herring and sardines.

Muir *et al.* (1997) studied concentrations of 2 selected congeners (Parlar 26 and Parlar 50) and total toxaphene in sea water, zooplankton, fish and sea mammals in a Canadian arctic sea. In the investigated system the water concentration of toxaphene ranged from 35 to 100 pg/l. Biomagnification was demonstrated with much higher residue levels in Beluga (whale species) than in seals although both feed at the same trophic level. This corresponds with the findings of Boon *et al.* (1996) as discussed in section 4.4.3, that the biotransformation capacity of seals is better than that of dolphins and whales.

5.4 Measurements in organisms and sediments

Data for toxaphene residues in sediment are not available for Western Europe, but toxaphene has been measured in biota from both freshwater and marine systems (Table 5.1 and 5.2).

Table 5.1
Range of toxaphene residue levels in freshwater biota in the Netherlands measured in the period 1974-1995 (source: Hendriks et al., 1998; De Geus et al., 1999)

Species	Location/region	year	tissue	total toxaphene (μg/g WW)	total toxaphene (μg/g lipid)
Zebra mussel (*Dreissena polymorpha*)	Rhine Meuse Ysselmeer Rhine	1994	whole	0.0047 0.036 0.00074 0.012	
Eel (*Anguilla anguilla*)	Meuse Rhine Yssel	1994 1989	fillet muscle	0.020	 0.3 0.09

Table 5.2
Range of toxaphene residue levels in marine biota in North and Western Europe measured in the period 1974-1995 (source: De Geus et al., 1999)

Species	Location/ region	year	tissue	total toxaphene µg/g WW	total toxaphene µg/g lipid
Atlantic cod	Gulf of Finland	1988	liver		0.64
(*Boreogadus saida*)	Vester Tana	1989	liver		0.54
	Southern North sea	1989	liver		0.4
	Central North sea	1989	liver		0.6
	Northern North Sea	1989	liver		1
	Germany	1993	liver		2.45
	Germany	1993	liver		2.73
	North sea	?	liver	0.3	
	Galway, Ireland	1979	spawn	0.26	3.5
Atlantic salmon	Norway	1993	oil		1.1
(*Salmo salar*)	Norway	1993	oil		0.54
Hake (*Merluccius merluccius*)	Ireland	?	liver	0.9	
Herring	Baltic	1978	muscle		13
(*Clupea harengus*)	Southern North Sea	1989	muscle		0.4
	Skagerrak	?	muscle	0.04	
Plaice	German Bight	1989	liver		0.1
(*Pleuronectes platessa*)	Skagerrak	1989	muscle	0.013	
Twait shad (*Alosa fallax*)	North sea	?	muscle		0.02
White-beaked dolphin	North Sea	?	blubber	19	

Toxaphene residues are demonstrated in fish from the North Sea, with an increasing trend from the southern to the northern North Sea (De Geus *et al.*, 1999). The measured toxaphene residues in herring and mackerel from the North Sea and remote waters West and Northwest from Ireland and the Shetland Islands exceeded the German tolerance level of 0.1 mg/kg on fat basis. Marine fish from Danish water had concentrations in the range 5 to 50 ng/g fat.

Toxaphene production, in quantities similar to those of polychlorinated biphenyls, has resulted in high toxaphene levels in fish from the Great Lakes and in Arctic marine mammals (up to 10 and 16 µg/g lipid). Toxaphene concentrations in North Sea fish are at least 10-fold lower than in fish from Arctic and Canadian waters and vary from 1 to 600 µg/kg wet weight (De Boer, 1997). Similarly, toxaphene concentrations in seals living near Norway were much lower than in animals originating from the Canadian Arctic (Wolkers *et al.*, 1998). However, because of the large variability in total toxaphene concentrations reported, few reliable conclusions can be drawn about trends or geographic differences in toxaphene concentrations.

Profiles for toxaphene congeners may vary between those for technical mixture, sediment, invertebrates, fish, mammals. Toxaphene profiles found in trout, shrimp and sediment in toxaphene treated lakes were complex and comparable. However mammals like seals are known to rapidly metabolise most chlorobornanes. Toxaphene profiles in fish vary considerable depending on source characteristic, geographic location, species and age.

The composition of toxaphene residues in environmental samples can differ widely. However, Angerhöfer *et al.* (1999) noted that in samples of fish species or fish products from North Atlantic and North Sea toxaphene peak patterns are remarkably similar with only 20-25 dominant congeners. The main mass of these residues is represented by 6 compounds. Three indicator congeners for toxaphene were more often selected for analysis in fish caught in several European coastal waters. These congeners are B[12012]-(202), B[12012]-(212) and B[30030]-(122), which can also be indicated as Parlar 26, 50, 62, respectively (see Table 2-3 in section 2.1). These 3 congeners comprised a major portion of the toxaphene residues in cod liver oil (25-30%) and fresh fish (8-12%) from Northern and Western European coastal waters. Highest residues were found in marine fish with moderate and high fat content (Wells & De Boer, 1997). In the German legislation the Maximum Risk Level for toxaphene is based on the residue level of the sum of these three toxaphene congeners.
In control laboratories the 3 above-mentioned indicator congeners, can be determined for fish samples, whereas a fourth chlorobornane (Parlar 44) which does not persist in the environment may serve as indicator of recent contamination (Alder & Vieth, 1996).

According to a field study by Kidd *et al.* (1998) biomagnification of toxaphene in long food chains can result in concentrations in fish which are hazardous to human health. The extent of biomagnification is expected to be higher at arctic and subarctic latitudes.

5.5 Water quality in relation to quality criteria and iMTR

It is not possible to compare measured environmental concentrations of toxaphene in water and sediment with quality criteria set for the Dutch environment. Neither residue levels, nor official quality criteria (MTR's) in water and sediment have been determined (V&W, 1998). In the current study, indicative MTRs (iMTRs) for toxaphene of 3.9 ng/l water and 200 µg/g sediment (DW) have been calculated (see section 6.3). These iMTR values are higher than the concentrations measured in the US Great Lakes (0.03-1.1 ng/l). Environmental residue levels of toxaphene in the Netherlands may be expected to be lower than the ones reported for the Great Lakes district in the USA because the Netherlands are situated at lower latitude, and in contrast to the US, toxaphene has never been used in the Netherlands. Thus a serious ecological risk resulting from toxaphene contamination of water and sediment in Dutch freshwater systems and coastal marine systems is not expected. However, it should be noted that the iMTR for toxaphene in surface water is lower than the concentration in the Canadian rain water (28 ng/l) reported by Saleh (1991).

A risk of exposure of the Dutch human population to occasionally high residues of toxaphene in fish and sea food can not be ruled out. However, toxaphene residues in samples from fish originating from Dutch freshwater and North Sea are probably below the German Maximum Risk Level which is set at 0.1 mg/kg based on the 3 indicator congeners.

5.6 Conclusions and recommendations

In Europe, risk evaluations for exposure to toxaphene are focused more on selected congeners than on total toxaphene. This requires analysis of indicator congeners, for which methods are available, but still can be improved. There is a need for certified reference materials and isotopically labelled toxaphene congeners (De Boer, 1997). Furthermore, it is recommended to perform indicative measurements of toxaphene in Dutch surface waters and rain water. Exposure of the general population is most likely through food. Recent food surveys have generally not included toxaphene and recent monitoring data are not available due to its being banned in many countries. Therefore toxaphene residues should be measured in environmental compartments as well as in biota with emphasis on certain indicator (key) congeners, such as the three congeners of Table 2.3 in section 2.1.

5.7 References

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6 Toxicity in the aquatic environment

6.1 Mechanism of action

Toxaphene is an insecticide with stomach and contact action. The mechanism of action is relatively unknown. At low temperatures less effect on pest organisms can be expected because of lower feeding activities (PIC, 1999). Toxaphene can be absorbed by ingestion, by inhalation and through the skin.

Exposure to toxaphene in fish resulted in several effects, namely on backbone collagen and hydroxyproline concentration, backbone anomalies, skin effects and growth. Toxaphene can reduce the vitamin C content of the backbone which may be the cause of a reduction of colagen formation and subsequently abnormal growth of the backbone. It has been experimentally demonstrated that addition of vitamin C reduces the effects of toxaphene on skin, growth and vertebrate development (Saleh, 1991).

After absorption toxaphene is rapidly distributed to all organs of the body, but especially concentrated in fatty tissues and muscle from which the release is slow. Toxaphene is metabolised by hepatic mixed function oxidases. Metabolites are formed via hydroxylation and dechlorination. Toxaphene and metabolites are excreted in faeces and urine (PIC, 1999). Boon *et al.* (1996) demonstrated the ability of marine top predators to biotransform toxaphene using *in-vitro* bioassays. This capacity increased in the order sperm whale < sea birds & dolphins << seal which was also reflected in the residue patterns in the adipose tissue of these animals. Furthermore it was shown that technical toxaphene is probably directly mutagenic and biotransformation does not induce a stronger effect.

6.2 Toxicity in the aquatic environment

General
This section presents the data for toxicity for unicellular organisms, algae, molluscs, crustaceans, worms, fish, amphibians, and insect larvae which result from a literature search. Separate data are presented for the freshwater and marine environment. A distinction is made between acute and chronic toxicity data. Furthermore pelagic (water) organisms and benthic (sediment) organisms are separately treated. It is not possible to make distinctions between pelagic and benthic organisms on the basis of larger taxonomic groups. Representatives for typical benthic occurrence as well as typical pelagic occurrence can be found within all groups. Furthermore also within species, a shift from one compartment to the other often takes place during the development from the larval stage to the adult stage.

6.2.1 Toxicity in freshwater environment

Cladocerans and copepods are classified as pelagic organisms. The remaining crustaceans are regarded as benthic organisms. In the freshwater environment algae, molluscs, fish and amphibians are classified as pelagic. In general, insect larvae and worms are classified as benthic organisms. For this purpose, organisms tested in sediment are also considered benthic organisms. In this report tests with an exposure time < 96 hours are classified as acute studies. The other studies are considered to be chronic. The results are summarised in Table 6.1.

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Table 6.1
Survey of the toxicity of toxaphene in freshwater; 0 = very slightly toxic; * slightly toxic; **= moderately toxic; *** =very toxic; see classification system in appendix 3. - = no data available. Based on the data in Table 6.2 and 6.3

Component	water organisms							
	algae		mollucs		crustaceans		fish	
	acute	chron	acute	chron	acute	chron	acute	chron
toxaphene	***	-	***	-	***	***	***	***

Component	benthic organisms					
	amphibians		worms		insects	
	acute	chron	acute	chron	acute	chron
toxaphene	***	-	-	-	***	***

Pelagic organisms
The lowest acute and chronic toxicity data of toxaphene are listed in Table 6-2 and 6-3, respectively. No data are available for macrophytes. Toxaphene has a high acute toxicity for all organisms tested (crustaceans, fish, amphibians, molluscs and insects).

The chronic toxicity is high for crustaceans and fish. The highest observed chronic toxicity is found for fish (< 0.039 µg/l). Information on the chronic toxicity is much more restricted than on acute toxicity. However, the risk of chronic exposure is probably more relevant in the case of toxaphene, being a persistent and widely dispersed insecticide. Therefore, details from these and other chronic toxicity studies with toxaphene are dealt with in more detail below.

Brook trout exposed to toxaphene for 90 days experienced a 46% reduction in weight at 0.039 µg/l, the lowest concentration tested. Egg viability in female trout was significantly reduced upon exposure to a concentration of 0.075 µg/l or more. Long term exposure to 0.5 µg/l reduced egg viability to zero.

The viability of eggs of the brook trout (*Salvelinus fontinals*) was reduced by exposure to 0.068 µg/l toxaphene. Sanders (1980) conducted flow-through studies with experiments with daphnids, scuds (*Gammarus pseudolimnaeus*) and midges. It was found that reproduction of daphnids was a more sensitive indicator for chronic exposure of an invertebrate species to toxaphene than the emergence of midges and growth of scuds. The maximum acceptable concentration was estimated at 0.07-3.2 µg/l.

Some species of marine and freshwater fish may be more sensitive to toxaphene. Water concentrations of 0.054-0.299 µg/l caused effects on backbone, histopathology and reproductive success. Stickel & Hickley (1977) showed a difference in sensitivity among three species of freshwater fish.

Toxaphene concentrations of 0.6 and 3.4 µg/l reduced bone development and growth, respectively, in the most tolerant species the channel catfish. The water quality may influence the effects of toxaphene considerable. An indication comes from a study on the effects of toxaphene on larvae of the striped bass (*Morone saxatilis*) which were more sensitive towards a mixture of organic

micro pollutants including toxaphene in freshwater with a hardness of 280 mg/l $CaCO_3$ than in saltwater (Mehrle *et al.*, 1987).

Benthic organisms

The acute toxicity of toxaphene for benthic crustaceans and insect larvae is high and chronic (see Table 6.2 and 6.3).

Table 6.2

Lowest acute effect concentration (LC_{50} and/orEC_{50}) (µg/l) of toxaphene for groups of species of the freshwater environ-ment.The number between brackets refers to the number of available data from which the lowest is selected (see appendix 4)

Class	conc. (µg/l)	time (h)	effect type	organism	reference
Pelagic organisms					
algae	380	-	EC_{50}	*Selenastrum sp.*	US-EPA (1980)
molluscs	740	48	LC_{50}	*Anodonta imbecilis*	Keller (1993)
crustaceans	1.4	48	LC_{50} (4)	*Bosmina longirostris*	Saleh (1991)
fish	2.0	96	LC_{50} (15)	*Micropterus salmoides*	Saleh (1991)
amphibians (larvae)	34	96	LC_{50} (7)	*Bufo americanus, Ambystoma maculatum*	Hall & Swineford (1981)
Benthic organisms					
crustaceans	6	48	LC_{50} (2)	*Gammarus fasciatus*	Saleh (1991)
insects (larvae)	1.3	96	LC_{50} (6)	*Claassenia sabulosa*	Sanders & Cope (1968)

Table 6.3 Lowest chronic no observed effect concentration (NOEC) (µg/l) of toxaphene for groups of species of the freshwater environment

Class	conc. (µg/l)	time (d)	effect type	organism	reference
Pelagic organisms					
crustaceans	0.07	21	reproduc-tion	*Daphnia magna*	Sanders (1980)
fish	< 0.039	90	growth	*Salvelinus fontinalis*	Mayer *et al.* (1975)
Benthic organisms					
crustaceans	0.13	30	grouth	*Gammarus pseudolimnaeus*	Sanders (1980)
insects	1.0	30	emer-gence	*Chironomus plumosus*	Sanders (1980)

Field effects
Miskimmin and Schindler (1994) monitored the response of aquatic organisms in small North American lakes during 30 years after toxaphene applications in 1961 and 1962. Populations of planktonic cladocerans were affected by toxaphene. Abundance was reduced and a shift from small body types to large body types took place. Populations of invertebrate predators increased probably due to the poor survival of fish. The authors assume that the observed long term effects of toxaphene are primarily caused by manipulation on fish populations and not by residual toxicity of toxaphene.

Saleh (1991) referred to a study of Cushing & Olive (1957) in which it was mentioned that toxaphene caused mortality and residual effect on macroscopic bottom fauna in freshwater reservoirs, however, *oligochaeta* were not affected.

Delorme *et al.* (1999) conducted a study on the potential long term (5 years) effects of toxaphene on fish in a Canadian lake. Individuals of lake trout *(Salvelinus namaycush*) and white sucker (*Catastomus commersoni*) were treated with intra-peritoneal injections of toxaphene (7 µg/g or 3.5 µg/g). Toxaphene reduced the survival of both fish species, but did not affect growth. Reproductive success was unaffected in the treated fish but reduced in the following two generations. Depuration rates of toxaphene were slow in lake trout and white sucker (314 and 793 days respectively).

6.2.2 Toxicity in marine environments
The lowest acute and chronic toxicity data of toxaphene for marine organisms are listed in the tables 6.5 and 6.6. The data are classified for the groups: crustaceans, molluscs and fish.

Table 6.6 presents an overview of the toxicity range classified according to the scheme in appendix 3.

Pelagic organisms
Acute and chronic toxicity data is presented in Table 6.4 and 6.5. Acute toxicity is highest for crustaceans. Information on chronic toxicity was found for only one fish species (LOEC of 0.3 µg/l).

Benthic organisms
Few data are available for marine benthic organisms. Toxic effects of toxaphene are only determined for crustacean species.

Table 6.4
Lowest acute effect concentration (LC_{50} and/orEC_{50}) (µg/l) of toxaphene for groups of species of the salt water environment. The number between brackets refers to the number of available data from which the lowest is selected (see appendix 4)

Class	conc. (µg/l)	time (h)	effect type	organism	reference
Pelagic organisms					
molluscs	16	96	LC_{50} (2)	*Crassostrea virginica*	Saleh (1991)
crustaceans	0.11	?	LC_{50}	*Acartia tonsa*	Saleh (1991)
fish	0.5	96	LC_{50} (4)	*Lagodon rhomboides*	Saleh (1991)
Benthic organisms					
crustaceans	0.05	96	LC_{50} (6)	*Sesarma cinereum*	Saleh (1991)

Table 6.5
Lowest chronic no observed effect concentrations (NOEC) (μg/l) of toxaphene for groups of species of the salt water environment

Class	conc. (μg/l)	time (d)	effect type	organism	reference
Pelagic organisms					
fish	< 0.3	28	NOEC	*Fundulus similis-*	*Schimmel et al.* (1977)-

6.2.3 Comparison of sensitivity of freshwater organisms and marine organisms

Comparison of the available toxicity data for freshwater and marine species reveals that the marine species seem more sensitive than freshwater species based on short-term effects. Chronic data for toxaphene are too scarce to come to conclusions. According to Saleh (1991) marine fish are generally more sensitive to toxaphene than freshwater fish (mean acute toxicity values of 0.07 and 1.6 μg/l). This difference is not confirmed by the information gathered in this document. Saleh (1991) concluded from the available information for toxaphene for saltwater organisms that in the marine environment 0.07 μg/l should never be exceeded. However, it may be assumed from the collected data in the current literature that the critical value for freshwater has to be set even lower. For brook trout a LOEC of 0.039 μg/l is found. It seems reasonable to assume that this also applies to marine fish. At this stage it can be preferred to combine the available toxicity data for freshwater and marine organisms in order to derive critical environmental values of toxaphene in aquatic environments. Before drawing definitive conclusions the chronic effects of toxaphene on marine species especially fish and crustaceans should be investigated.

Table 6.6
Survey of the toxicity of toxaphene in salt water; 0 = very slightly toxic; * slightly toxic; **= moderately toxic; *** =very toxic; see classification system in appendix 3. - = no data available. Based on the results in table 6.5 and 6.6

Component	Pelagic organisms							
	algae		mollucs		crustaceans		fish	
	acute	chron	acute	chron	acute	chron	acute	chron
toxaphene	-	-	***	-	***		***	***

Component	benthic organisms					
	molluscs		crustaceans		worms	
	acute	chron	acute	chron	acute	chron
toxaphene	-	-	***	-	-	-

6.3 Environmental quality criteria and derivation of iMTRs

Within the framework of the Dutch INS project, integrated environmental quality standards for various environmental compartments have been derived in MilBoWa (VROM, 1991) for a number of substances including plant protection products. The objective of MilBoWa is to operationalise a system of limiting- and target values ("grenswaarden" and "streefwaarden") for soil and

surface

water. An overview of the quality standards for water and sediment has been published in V&W (1994), and the most recent version is published in V&W (1998). No value for toxaphene is included. In V&W (1998), the limiting values have been replaced by MTR's.

The MTR is the quality level that should be reached or maintained. Starting point for the MTR (Maximum Tolerable Risk level) is the concentration at which at least 95% of the species in an ecosystem is protected (method Van Straalen & Denneman, 1989, modified by Aldenberg & Slob, 1991; 1993). The target value is based on the VR, which is equivalent to 1% of the (concentration that corresponds with the) MTR. The 95% protection level (MTR) can be calculated for any individual substance when NOEC values are present for at least for four different groups of organisms (for example, fish, molluscs, crustaceans and algae). When sufficient data are not available, arbitrary safety factors (assessment factors) are applied (modified EPA method). In Table 6.7, the safety factors according to the modified EPA-method are presented in relation to the number of available toxicity data.

Table 6.7
Safety factors for derivation of iMTR's in surface water (modified EPA-method)

Available information	Safety factor
lowest acute L(E)C_{50} or QSAR estimate for acute toxicity	1000
lowest acute L(E)C_{50} or QSAR estimate for acute toxicity for at least algae, crustaceans and fish	100
lowest NOEC or QSAR estimate for chronic toxicity	10*
lowest NOEC or QSAR estimate for chronic toxicity for at least algae, crustaceans and fish	10

* This value has to be compared to the value based on acute L(E)C_{50}-values. The lowest value is selected.

The MTR in this report is called iMTR ("indicative" MTR), to stress the difference with the MTR's and target values of V&W (1998). The iMTR's have an indicator-functions, indicating the level of pollution. They do not have an official policy status.

iMTR's have been calculated on the basis of the toxicity data gathered in this report, according to the procedure described by Slooff (1992) and Beek (1993). Data for fresh water and marine species have been pooled. Food chain poisoning is not accounted for in this approach. An overview of all toxicity data used for the iMTR calculation is presented in Annex 4.

As discussed in the previous section, there are no clear indications from the available toxaphene toxicity data set that the sensitivity of freshwater species differs from the sensitivity of marine species (see Appendix 4). Therefore the data sets are combined.

Acute toxicity data for toxaphene are available for 6 taxonomic groups. The lowest L(E)C_{50} value is found for insects, namely 1.3 µg/l. A safety factor of 100 has to be applied to this value, resulting in a value of 0.013 µg/l.

Chronic toxicity data are available for only 2 taxonomic groups: crustaceans and fish. The most critical value is a LOEC for fish amounting to 0.039 µg/l. Two NOECs are available, which exceed this LOEC. Therefore it is chosen to select this LOEC for the derivation of an iMTR. A safety factor of 10 has to be

applied, resulting in a value of 0.0039 µg/l. Comparison of the acute toxicity with the chronic toxicity reveals that the iMTR should be based upon the chronic data. The iMTR is only indicative and is < 0.0039 µg/l. In fact the iMTR is lower than this value because it is based on a LOEC instead of a NOEC.

An iMTR for toxaphene (mixture) in sediment can be calculated from the iMTR for toxaphene in water. The soil-water partitioning coefficient (Kp) is calculated form the K_{oc} (see table 4.2). The following formulas are applied:

MTRsed = MTRwater x Kp

$Kp = K_{oc} \times f_{oc}$ (l/kg)

A $\log K_{oc}$ amounting to 5 is selected together with a fraction organic matter (f_{oc}) of 5% (standard sediment). This results in an iMTR in sediment of 200 µg/kg dry matter. It is also possible to propose environmental quality criteria for the 3 indicator congeners in analogy with the German approach for the MRLs in fish. We assume that the 3 congeners comprise 10% of total toxaphene. In that case the MTRs in water and sediment are a factor 10 lower than the ones for total toxaphene (see table 6.8).

Table 6.8
Safety factors for derivation of iMTR's in surface water (modified EPA-method). Indicative MTRs for toxaphene in water and in sediment

Component	iMTR (ng/l)	iMTR (µg/kg dry matter)
Toxaphene, total	3.9	200
Toxaphene, sum of 3 indicator congeners	0.39	20

Environmental protection criteria for toxaphene are proposed by Saleh (1991) and Braune *et al.* (1999). Saleh (1991) recommended to consider 0.013 µg/l as an average 24 hour exposure criterion for freshwater aquatic life. Furthermore, toxaphene concentration should never exceed 1.6 and 0.07 µg/l at any time for freshwater and marine life, respectively.

In Braune *et al.* (1999) environmental and health criteria values are presented for toxaphene (Table 6.9). These are US EPA and Canadian EQG values based on an evaluation of all available toxicological data related to establishing a NOAEL in the most sensitive species. These criteria can be useful for toxaphene risk assessment in the Netherlands. In the Netherlands environmental and health criteria for toxaphene are not established yet.

Table 6.9
Regulatory, environmental quality guideline (EQG), no-observable adverse effects levels (NOAELs) and critical levels used for assessment of effects of toxaphene in Canadian Arctic biota (all concentrations are in ng on a wet weight basis) (Source: Braune et al., 1999)

Criteria	Notes	Value (ng/g)
USFDA level for fish	a	5
Canadian EQG	b	6.3
Dietary (i.e. fish) NOAEL for reproductive effects in mink food	c d	4000
Critical levels in bird tissues	e f	40000
Canadian ADI		0.2 µg/kg BW

notes:
a USFDA regulation/guideline levels in edible portions of fish for human consumption and export.
b Canadian Environmental Quality Guidelines for protection of wildlife that consume aquatic biota (CCME, 1999)
c Dietary no adverse effects concentrations in mink food (Giesy *et al.*, 1994b)
d Toxaphene dietary no adverse effects concentration for rat and dog (Chu *et al.*, 1986)
e Critical kidney concentration in wild mammals (Cooke and Johnson, 1996)
f Carcass levels associated with reduced duckling growth (Wiemeyer, 1996)

Table 6.10
Regulatory critical levels for toxaphene within Europe (Source: De Geus et al., 1999)

Criteria	Notes	Value (ng/g)
German MRL for fish and fish products	a b	0.1 mg/kg
German MRL all other food of animal origin	b	0.1 mg/kg

notes:
a On the basis of three toxaphene indicator congeners
b This is comparable with 100 ng/g on lipid basis.

The EPA has not established a reference concentration or reference dose for toxaphene. The EPA has classified toxaphene as a Group B2, probable human carcinogen of medium carcinogenic hazard.

Alder *et al.* (1997) estimated the daily intake of total toxaphene in Germany at 2.8-5.6 ng/kg BW. This is based on the assumptions that the 3 indicator compounds represent 25-50% of total chlorobornanes together with a fish consumption in Germany of ca. 20 g per person each day.

6.4 Toxicity for higher organisms

Birds
Toxaphene is moderately to slightly toxic to birds with oral LD_{50} values ranging between 20 and 581 mg/kg (Saleh, 1991). After application for pest control, toxaphene appeared to be toxic to birds under certain conditions.

Female ring-necked pheasants exposed to 300 mg toxaphene/kg in their diet experienced reductions in egg laying and hatchability (De Geus *et al.*, 1999). Some birds species were affected by 10 or 50 ppm toxaphene in their diets, whereas others were not. Therefore, 10 ppm toxaphene/mg feed can be regarded as a LOEC for long-term exposure (by feeding) of birds.

Mammals
The acute oral toxicity of toxaphene is in the range of 49 mg/kg body weight in dogs to 365 mg/kg in guinea pigs. Chronic oral exposure of mammals has resulted in effects on liver, kidney, adrenal and thyroid glands, central nervous system, and the immune systems. The incidence of tumors in thyroid gland an liver was increased in laboratory mammal studies (EPA, 1999).

In a 13 week study, rats were fed diets containing toxaphene. Liver/body weight ratio and hepatic microsomal enzyme activities were increased in rats fed 500 ppm. Dose dependent histological changes were observed in the kidney, thyroid and liver. The NOAEL was determined to be 4.0 ppm

(0.35 mg/kg). In another study, beagle dogs were fed toxaphene for 13 weeks. The liver/body weight ratio and serum alkaline phosphatase were increased in dogs fed 5.0 mg/kg. Mild to moderate dose dependent histological changes were observed in the liver and thyroid. The NOAEL for dogs was determined to be 0.2 mg/kg. IARC has concluded that while there is inadequate evidence for the carcinogenicity of toxaphene in humans, there is sufficient evidence in experimental animals. IARC has classified toxaphene as a possible human carcinogen (Group 2B).

Toxaphene is demonstrated to be highly carcinogenic in rats and mice (Saleh, 1991). Toxaphene is mutagenic in the Ames Salmonella test. However, the most easily extracted major toxic component heptachlorobornane-1 was not mutagenic (in Saleh, 1991). There is no evidence for genotoxicity and teratogenicity of toxaphene (Saleh, 1991).

Adverse effects of toxaphene on learning and behaviour have been observed in several studies with rats (Saleh, 1991).

Toxaphene is one of the compounds preliminary classified as endocrine disruptor by the Dutch Health Board (Gezondheidsraad, 1999). Several endocrine disruption effects in wildlife have been attributed to toxaphene (EPA, 1999). These effects comprise growth reduction in adult birds, shortened egg-laying period and reduced hatchability in birds, growth reduction in fish, and vertebrate anomalies. Up to now there is no convincing evidence for endocrine effects in vivo. Weak estrogenic effects of toxaphene in vitro are also reported (Soto *et al.*, 1994). However, it is not known which congeners are responsible for the estrogenic effect.

It is more relevant to know the toxicity of toxaphene mixtures which occur in the environment than the toxicity of manufactured toxaphene mixtures. Therefore, a laboratory study was initiated aimed at determining the effect of food spiked with an environmentally relevant toxaphene mixture on rats. The toxaphene was extracted from fish caught in the North Sea. The outcome of this study is not yet known (De Boer, personal communication).

6.5 Human toxicity

Exposure routes

Contamination of the aquatic environment (surface water and sediment) can pose a threat to public health. The hazards can be caused by direct and/or indirect contact with the contaminants. In principle, uptake of contaminants by humans can take place via ingestion (oral), via skin contact (dermal) and via the lungs (inhalation). Inhalation exposure is most probably not important because the Henry coefficients are low. Dermal exposure is more important when log K_{ow} values are high (> 5). The main uptake route for toxaphene by humans is most likely through fish consumption, although recently considerable toxaphene residues have also been found in some fruit and vegetables from certain countries (Wells and De Boer, 1997). In the Netherlands, it is expected that the most of the toxaphene enters the water via aerial transport and deposition. Toxaphene is relatively easily bioconcentrated in biota due to its high K_{ow}. Alder *et al.* (1997) measured toxaphene residues in samples from various fish species from (amongst others) the North Sea. Residue levels were very variable. High levels were found in marine as well as freshwater species and in high-fat, medium-fat and low-fat species.Generalisation is not possible (see section 5.3).

Effects
Toxicological information on individual chlorobornanes is scarce, but some reports have recently appeared. Neurotoxic effects of toxaphene exposure such as those on behaviour and learning have been reported. Technical toxaphene and some individual congeners were found to be weakly estrogenic in in vitro test systems; no evidence for endocrine effects in vivo has been reported. In vitro studies show technical toxaphene and toxaphene congeners to be mutagenic. However, in vivo studies have not shown genotoxicity; therefore, a nongenotoxic mechanism is proposed. Nevertheless, toxaphene is believed to present a potential carcinogenic risk to humans. Until now, only Germany has established a legal tolerance level for toxaphene of 0.1 mg kg^{-1} wet weight for fish.

Current hazard classifications are:

USEPA	B2: probable carcinogen
EU	Toxic, carcinogen Cat. 3
IARC	Group 2B (possibly carcinogenic to humans)

6.6 Summary and conclusions

Toxaphene is acutely and chronically highly toxic for all tested groups, freshwater as well as marine organisms. Crustaceans, insects and fish are the most sensitive organisms. In the current report indicative MTRs (iMTRs) are derived for toxaphene mixture. For this purpose no distinction is made between freshwater and marine ecosystems. The iMTR for surface water amounts to 0.0039 µg/l. This value is used to derived an iMTR for sediment amounting to 200 µg/kg DW.
For a reliable derivation of MTRs it is necessary to conduct the following studies on the toxicity of toxaphene: chronic studies with freshwater fish; chronic study with marine fish; chronic study with marine crustaceans; study with marine algae.
The toxicity of individual toxaphene congeners is not investigated yet. Both acute and chronic effects of indicator congeners should be determined for the standard organism groups (algae, crustaceans and fish).

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7 Policy

7.1 National environmental policy

Toxaphene has never been used in the Netherlands, and was banned officially in 1968. No environmental quality standards for toxaphene are available.

7.2 International environmental policy

European policy focuses on elimination of use resulting in several European initiatives to ban toxaphene. At the level of the European Union, use and marketing within the EU is forbidden as plant protection product (directive 83/181/EEC of 14/31983-OJ L91 p35). The control actions consist of prohibition to use or place on the market all plant protection products containing toxaphene (camphechlor) as an active ingredient. No remaining uses are allowed. Furthermore, toxaphene is now a PIC chemical (listed in the Rotterdam Convention) and is listed in Annex 1 of REG 2455/92 and is therefore subject to the Export Notification Procedure.
Also, toxaphene is addressed by the UN/ECE Protocol on Persistent Organic Pollutants. This Protocol focuses on a list of 16 substances that have been singled out according to risk criteria. The Protocol bans the production and use of toxaphene outright and has been signed by the majority of the countries in Europe. Full implementation of this Protocol will eliminate all remaining uses, trade, stockpiles and production of toxaphene in UN/ECE-Europe. At present (November 1999) The Russian Federation, Belarus, Turkey, Bosnia-Herzegovina, The former Yugoslav Republic of Macedonia and Yugoslavia have not yet signed this Protocol for various reasons.

Toxaphene is mentioned on the OSPARCOM list of substances with endocrine-disrupting activity and is a candidate for the list of chemicals for priority action of the hazardous substance strategy.

Globally, toxaphene is one of the persistent organic pollutants (POPs) addressed by the global POP negotiations by the Intergovernmental Negotiating Committee (INC). The INC has been convened by the Executive Director of the United Nations Environmental Programme (UNEP) with the aim of preparing an international legally binding instrument for implementing international action on twelve specific POPs. Regarding toxaphene the ultimate goal of the negotiations is to come the world wide elimination of this chemical. Toxaphene is on the EPA list of priority substances.

7.3 Legislative framework

The legislative framework for pesticides is the bestrijdingsmiddelenwet (1962) on the Netherlands national level, and the EC Plant Protection Products Directive 91/414/EC. However, toxaphene is banned in both the Netherlands and the EC.

7.4 Policy evaluation

Toxaphene has never been used in the Netherlands and has been banned officially since 1968. Therefore, policy evaluation on national level is not relevant. International policy tends to a ban of toxaphene in the whole of Europe (see 7.2).

7.5 Effects of policy to water systems

Although toxaphene has not been used in the Netherlands, its absence in the Dutch surface waters is not self-evident. As described in chapter 4, the persistent and semi-volatile character of toxaphene results in a global dispersion, and toxaphene may have entered the surface water by atmospheric deposition after long-range atmospheric transport. Toxaphene concentrations in surface water or sediments however are not available. The fact that toxaphene congeners have been detected in marine biota from the North Sea (chapter 5) indicates its presence in, at least, the North Sea.

7.6 Conclusions and recommendations

Toxaphene is banned in the Netherlands since 1968, and has never been used. International policy is aimed at banning toxaphene from use. As toxaphene may enter Dutch surface waters by atmospheric deposition after long-range atmospheric transport, international policy is also of relevance for the Netherlands. However, the absence of measurements in Netherlands surface waters makes it impossible to assess the necessity for additional international policy.

List of appendices

Appendix 1 Production/manufacturing of toxaphene

Toxaphene has been manufactured in the U.S., Europe, South Africa, USSR and Israel. Varying procedures were applied. The manufacturing procedure according to the main producer of toxaphene in the US was as follows.

The principal raw material is pine stumps. The stumps were washed, ground into chips and extracted with methyl isobutyl ketone under heat and pressure. The crude resin was obtained by destillation and further refined to crude pinene.

The crude camphene was then chlorinated using liquid chlorine in carbontetrachloride until chlorine, by weight reached 70% using UV light as a catalyst (7 moles of chlorine are required per mole of camphene to produce 1 mole of toxaphene and 6 moles of HCl).

Toxaphene was also manufactured by a batch process in which chlorine gas reacted with molten camphene to form a waxy solid with chlorine content of 67-69% by weight. Xylene was added in a blending process to produce a 90% active ingredient.

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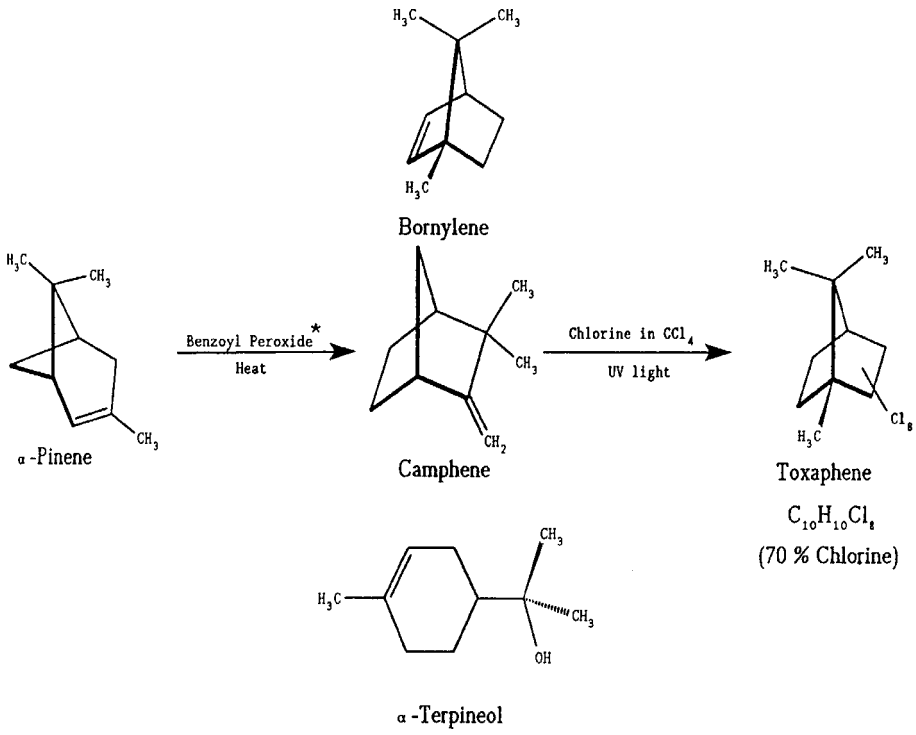
Figure 1
Industrial manufacturing of toxaphene



Appendix 2 Classification system for environmental chemistry parameters

Vapour pressure (P), Pa

Class	P (Pa)
Not volatile	$P < 10^{-4}$
Somewhat volatile	$10^{-4} < P < 10^{-2}$
Moderately volatile	$10^{-2} < P < 1$
Volatile	$1 < P < 100$
Very volatile	$P > 100$

Solubility (S), mg/l

Class	S (mg/l)
Very low solubility	$S < 0,1$
Low solubility	$0,1 < S < 10$
Moderate solubility	$10 < S < 1000$
Good solubility	$S > 1000$

Persistence in water (DT_{50}), days

Class	DT_{50} (days)
Low persistence	$DT_{50} < 7$
Moderate persistence	$7 < DT_{50} < 30$
High persistence	$DT_{50} > 30$

Bioconcentration factor (BCF)

Class	BCF
Low bioconcentration potential	$BCF < 100$
Moderate bioconcentration potential	$100 < BCF < 1000$
High bioconcentration potential	$BCF > 1000$

Appendix 3 Classification system for aquatic toxicity

Toxicity to algae (96-h, EC_{50}), crustaceans (48-h, LC_{50}) and fish (96-h, LC_{50}):

Class	$E(L)C_{50}$ (mg/l)		
very toxic	< 1		
moderately toxic	1	-	10
slightly toxic	10	-	100
very slightly toxic			> 100

Toxicity to aquatic organisms: chronic tests:

Class	NOEC (mg/l)		
very toxic	< 0.01		
moderately toxic	0.01	-	0.1
slightly toxic	0.1	-	1
very slightly toxic			> 1

Toxicity to birds: acute oral LD_{50} (mg/kg body weight)

Class	LD_{50} (mg/kg)		
very toxic	< 5		
moderately toxic	5	-	50
slightly toxic	50	-	500
very slightly toxic			> 500

Appendix 4 Overview of the toxicity data per group of organisms (freshwater and marine)

The bold printed value is used for the calculation of iMTRs in surface water / sediment

Table A4.1
Acute toxicity data (L(E)C50 in µg/l)

taxonomic group	freshwater	marine
algae	380	
crustaceans	1.4; 10; 10; 14.2; 15; 19	0.05; 0.4; 1.4; 4.4
fish	2.0; 2.4-29.0; 3.1; 3.7; 4.2-13.1; 5.8; 7.0; 8.0; 10.6; 12.0; 13.0; 13.0; 14.0; 18.0; 20.0	0.5; 1.1; 4.4; 8.6
molluscs	740	16
worms		
insects	1.3; 2.3; 3.0; 18.0; 30.0; 40.0	
amphibians	34; 34; 76; 99; 130; 195; 342	

Table A4.2
Chronic toxicity data (NOEC and LOEC in µg/l)

Taxonomic group	Freshwater		Marine	
	NOEC	LOEC	NOEC (µg/l)	LOEC (µg/l)
algae				
crustaceans	0.07; 0.13; 32			
insects	1.0			
fish	0.068	**0.039**; 0.055; 0.068	0.5	0.3
molluscs				
worms				

Appendix 5 Human health risk assessment evaluation method

Human health risk may occur by direct contact of recreating people with contaminants in the aquatic environment (water, sediment). Playing children (1.5 - 4.5 years old with a body weight of 14 kg) are seen as the most vulnerable groups based on age-bound factors. The relevant exposure routes are through oral intake and dermal contact. The intake (in mg/day) can be calculated for the separate exposure routes for 1 day of playing at the waterside in a worst-case scenario (for a detailed description see BKH, 1991):

Oral intake through sediment

The oral intake through sediment is:

$S_1 * 10^{-6} * B$

in which:

S_1	sediment intake in mg dw/day
10^{-6}	conversion factor for units in the given dimensions
B	level of contamination in soil material in mg/kg dw

Oral intake through suspended matter

The oral intake through suspended matter is:

$I * S_2 * 2 * 10^{-9} * B$

I	intake surface water (50 ml/day)
S_2	concentration in suspended matter (300 mg dw/l)
2	correction factor for higher concentrations in suspended matter
10^{-9}	conversion factor for units in the given dimensions
B	level of contamination in soil material in mg/kg dw

Oral intake through surface water

The oral intake through surface water is:

$W_i * 10^{-3} * (10^{0.21}/f_{oc}*K_{ow}) * B$

W_i	intake of surface water (50 ml/day)
10^{-3}	conversion factor for units in the given dimensions
f_{oc}	organic carbon fraction in sediment (0.05)
K_{ow}	partition coefficient octanol/water
B	level of contamination in soil material in mg/kg dw

Dermal contact with sediment

The dermal contact with sediment is:

$O_{skin} * B_{b,skin} * A * M * 10^{-6} * B$

O_{skin} surface of skin exposured (2800 cm^2)
$B_{b, skin}$ area of skin covered with sediment parts (0.5 mg dw/cm^2)
A absorption coefficient (0.12/day)
M matrix effect: the effect of the binding of contaminants to soil particles on body intake (0.15)
10^{-6} conversion factors for units in the given dimensions
B level of contamination in soil material in mg/kg dw

Dermal contact with suspended matter

Dermal contact with suspended matter is negligible compared to dermal contact with sediment:

Dermal contact with sediment

Dermal contact with water is:

$O_{skin} * t * A'' * B_{w,skin} * 10^{-9} * C_w$

O_{skin} exposed skin surface (4560 cm^2)
t exposure time (3 hours/day)
A'' absorption coefficient (0.01/hour)
$B_{w, skin}$ area of skin covered with water (0.5 µg/cm^2)
10^{-9} conversion factors for units in the given dimensions
C_w concentration in water; this is:

$(10^{0.21})/(f_{oc} * K_{ow}) * 10^3 * B$

with:
f_{oc} organic carbon fraction in sediment (0.05)
K_{ow} partition coefficient octanol/water
10^3 conversion factor for units in the given dimensions
B level of contamination in soil material in mg/kg dw

For the calculation of the yearly-averaged daily intake, the reflected formulas should be multiplied with a factor 30/365; the number of playing days at the water side is estimated at 30 per year.
For the calculation of concentrations of individual contaminants in sediment, the yearly-averaged daily total intake through the above-mentioned exposures routes are compared to a human health guidance value, at which there is a maximal tolerable risk (MTR, ADI). In this way HTBA-values may be derived.

In the report of BKH (1991) the level at which there is a maximal tolerable risk (MTR) is linked to the intervention-value-level, an environmental quality level that is established in view of direct measures and at which there is a "serious risk for human health". For the derivation of the HTBA-values for sediment, above which there is a "serious risk", the total contribution of exposure to sediment is set at a maximum of 5% of the MTR. Using this percentage, it is expected that other sources as well as the contribution of other substances, which comparable effects, are sufficiently encountered for.

Appendix 6 List of abbreviations

ADI	Acceptable Daily Intake
BCF	BioConcentration Factor
BKH	Bongaerts, Kuyper and Huiswaard Consulting Engineers
BW	Body Weight
CAS	Chemical Abstract Service
DNZ	North Sea Directorate
DT_{50}	Disappearance Time for 50% of the substance
DW	Dry Weight
EC	European Commission
EC_{50}	Effect Concentration for 50% of the organisms
ECD	Electron Capture Detection
EI	Electron Impact
ENEP	United Nations Environmental Programme
EPA	Environmental Proctection Agency
EQG	Environmental Quality Guideline
EU	European Union
FAO	Food and Agriculture Organisation
foc	fraction organic carbon
FRG	Federal Republic of Germany
GC	Gas Chromatography
GC-ECD	Gas Chromatography with Electron Capture Detection
GDR	German Democratic Republic
GEF	Global Environment Facility
H	Henry-constant
HCB	HexaChloroBenzene
HTBA	Human Toxicologic Based Advisory value
HTOA	Humaan-Toxicologisch Onderbouwde Advieswaarde
iMTR	indicative Maximum Tolerable Risk level
INC	Intergovernmental Negotiating Committee
K_{oc}	Partition coefficient organic carbon - water
K_{om}	Partition coefficient organic matter - water
K_{ow}	Partition coefficient octanol - water
Kp	Partition coefficient
LC_{50}	Lethal concentration for 50% of the organisms
LD_{50}	Lethal dose for 50% of the organisms
LOEC	Lowest Observed Effect Concentration
MilBoWa	Milieukwaliteitsdoelstellingen Bodem en Water
MRL	Maximum Risk Level
MS	Mass-Spectroscopy
MTR	Maximum Tolerable Risk Level
NCI-MS	Negative Chemical Ionisation - Mass-Spectroscopy
NCI	Negative Chemical Ionisation
NOAEL	No-Observed Adverse Effect Level
NOEC	No-Observed Effect Concentration
OSPARCOM	Oslo and Paris Commission
PCB	PolyChlorinated Biphenyls
PIC	Prior Informed Consent
POP	Persistent Organic Pollutant
P_{vp}	Vapour Pressure
RIVO-DLO	DLO-Netherlands Institute for Fisheries Research
RIKZ	National Institute for Coastal and Marine Management
RIZA	National Institute for Inland Water Management and Waste Water Treatment

QSAR	Quantitative Structure - Activity Relationship
S	Solubility
TNO	Netherlands Organisation for Applied Scientific Research
UNEP	United Nations Environmental Programme
US	United States
UV	UltraViolet
VR	Verwaarloosbaar Risiconiveau (Negligible Risk Level)
WW	Wet Weight