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**TOWARDS INTEGRATED ENVIRONMENTAL
QUALITY OBJECTIVES FOR SEVERAL
COMPOUNDS WITH A POTENTIAL FOR
SECONDARY POISONING**

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This research was carried out on behalf of the Directorate for Environmental Protection, Directorate for Chemicals, External Safety, and Radiation Protection, in the frame of the project "Setting integrated environmental quality objectives" (Quality objectives and risks, project no. 679101).

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PREFACE

This report contains results of research carried out in the framework of the project 'Setting integrated environmental quality objectives'. The results have been discussed in the 'Setting integrated environmental quality objectives advisory group'. Members thereof are C.W.M. Bodar (Health Council of The Netherlands), J.H.M. de Bruijn (Ministry of Housing, Physical Planning and Environment), J.H. Canton (National Institute of Public Health and Environmental Protection), C.A.J. Denneman (Ministry of Housing, Physical Planning and Environment), J.W. Everts (National Institute for Coastal and Marine Management), C. v.d. Guchte (National Institute of Inland Water Management), M.P.M. Janssen (National Institute of Public Health and Environmental Protection), W. Ma (Institute for Forestry and Nature Research), P. Leeuwangh (Winand Staring Centre for Integrated Land, Soil and Water Research), E.J. van de Plassche (National Institute of Public Health and Environmental Protection), J. Struijs (National Institute of Public Health and Environmental Protection), M. Vossen (National Institute of Inland Water Management), and J. van Wensem (Technical Soil Protection Committee).

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SUMMARY

In the present report Maximum Permissible Concentrations (MPCs) are derived for 25 compounds with a potential for secondary poisoning. First, MPCs are calculated based on direct effects on aquatic and soil organisms using extrapolation methods. Secondly, possible adverse effects due to secondary poisoning are incorporated. Two foodchains are taken into account: an aquatic route (water → fish or mussel → fish- or mussel-eating bird or mammal), and a terrestrial route (soil → earthworm → worm-eating bird or mammal). Starting-point in the method applied is that a NOEC is derived for birds and mammals which is divided by the BCF for mussels or fish for the aquatic route and by the BCF for earthworms for the terrestrial route.

With respect to the aquatic route the most critical one, i.e. via fish or mussels, is determined and used for further calculations. MPCs are derived by comparing the one based on direct effects with the one based on effects due to secondary poisoning.

For sediment no toxicity data are available. Therefore MPCs are calculated from the MPCs for surface water using the equilibrium partitioning method.

MPCs for soil are harmonized using the equilibrium partitioning method. For deriving the 'final' MPC for soil a choice had to be made between the MPC based on (in)direct effects and the MPC based on equilibrium partitioning. This choice is based on data availability: if chronic data are available for 4 or more different taxonomic groups, while data for soil are scarce the MPC based on equilibrium partitioning is given greater weight.

Secondary poisoning may be critical via the aquatic route for the following compounds: aldrin, cadmium, DDT and derivatives, dieldrin, endrin, all HCH isomers, penta- and hexachlorobenzene and methyl-mercury. For heptachlor, heptachlor epoxide and quintozene toxicity data for aquatic organisms as well as birds and mammals are too scarce to draw conclusions. Via the terrestrial route secondary poisoning may be critical for cadmium, copper, penta- and hexachlorobenzene and methyl-mercury. Due to scarcity of data (effects on soil organisms as well as toxicity data for birds and mammals) these results should be treated with caution. Also, the method for assessing effects due to secondary poisoning via the terrestrial food-chain has several important limitations.

The method applied in the present report to incorporate effects due to secondary poisoning is considered a first screening. For those compounds for which these effects may be critical more research is necessary, of which obtaining local and species specific information from field studies is most important.

Comparison of MPCs and NCs derived for the different compartments with actual concentrations is not possible for many compounds because the detection limit is higher than the NC, or even the MPC. Compounds for which the MPC is exceeded on a relatively large scale in surface water, particulate matter and sediment are copper, DDT and derivatives, α -endosulfan, heptachlor, hexachlorobenzene, mercury. For soil and groundwater data are scarce. In soil the MPC_{soil} for endrin and especially DDT and DDE is exceeded.

In the subjoined table values are presented which can be used to set environmental quality objectives (limit and target values).

Maximum Permissible Concentrations (MPC) and Negligible Concentrations (NC). Values for water in ng/l; for sediment and soil in µg/kg (derived for a standard soil containing 25% clay and 10% organic matter).

compound	water		sediment		soil	
	MPC ng/l	NC ^d ng/l	MPC µg/kg	NC ^d µg/kg	MPC µg/kg	NC ^d µg/kg
aldrin	18	0.18	120 ^b	1.2 ^b	50 ^a	0.50 ^a
cadmium	350 ^c	3.5 ^c	29,000 ^{b,c}	290 ^{b,c}	3.5 ^c	0.035 ^c
carbofuran	15 ^a	0.15 ^a	0.032 ^b	0.00032 ^b	4.7 ^a	0.047 ^a
chlordane	1.5 ^a	0.015 ^a	2.4 ^b	0.024 ^b	4.3 ^a	0.043 ^a
chlorpyrifos	2.8	0.028	1.1 ^b	0.011 ^b	1.1 ^b	0.011 ^b
copper	4,100 ^c	41 ^c	142,000 ^{b,c}	1,420 ^{b,c}	550 ^c	5.5 ^c
DDD	0.44	0.0044	1.8 ^b	0.018 ^b	10 ^a	0.10 ^a
DDE	0.44	0.0044	1.5 ^b	0.015 ^b	10 ^a	0.10 ^a
DDT	0.44	0.0044	9.4 ^b	0.094 ^b	10 ^a	0.10 ^a
dieldrin	18	0.18	670 ^b	6.7 ^b	50 ^a	0.50 ^a
endosulfan	0.40	0.0040	0.026 ^b	0.00026 ^b	50 ^a	0.50 ^a
endrin	3.0	0.030	2.9 ^b	0.029 ^b	2.9 ^b	0.029 ^b
fenthion	3.1	0.031	0.35 ^b	0.0035 ^b	0.35 ^b	0.0035 ^b
α-HCH	2,500 ^a	25 ^a	220 ^b	2.2 ^b	220 ^b	2.2 ^b
β-HCH	80 ^a	0.80 ^a	92 ^b	0.92 ^b	92 ^b	0.92 ^b
γ-HCH	770	7.7	190 ^b	1.9 ^b	5.0 ^a	0.050 ^a
heptachlor	0.46 ^a	0.0046 ^a	0.65 ^b	0.0065 ^b	0.70 ^a	0.0070 ^a
heptachlor epoxide	0.46 ^a	0.0046 ^a	0.020 ^b	0.00020 ^b	0.70 ^a	0.0070 ^a
hexachlorobenzene	2.1	0.021	1.2 ^b	0.012 ^b	28	0.28
mercury	1.9 ^c	0.019 ^c	210 ^{b,c}	2.1 ^{b,c}	200 ^c	2.0 ^c
methyl-mercury	1.9 ^c	0.019 ^c	210 ^{b,c}	2.1 ^{b,c}	3.3 ^c	0.033 ^c
pentachlorobenzene	30 ^a	0.30 ^a	12 ^b	0.12 ^b	120 ^a	1.2 ^a
pentachlorophenol	3,500	35	310 ^b	3.1 ^b	170 ^a	1.7 ^a
quintozene	290 ^a	2.9 ^a	330 ^b	3.3 ^b	330 ^b	3.3 ^b
thiram	32 ^a	0.32 ^a	0.79 ^b	0.0079 ^b	38 ^a	0.38 ^a

^a indicative value

^b based on equilibrium partitioning

^c for setting of environmental quality objectives these MPC/NC values must be compared with natural background concentrations

^d based on a factor 100 between MPC and NC

SAMENVATTING

In dit rapport zijn voor 25 stoffen met een potentieel risico voor doorvergiftiging Maximaal Toelaatbare Risiconivo's (MTRs) afgeleid. Ten eerste zijn MTRs voor directe effecten op aquatische en bodemorganismen bepaald door het toepassen van extrapolatiemethoden. Vervolgens zijn MTRs afgeleid rekening houdend met doorvergiftiging in de voedselketen. Hiertoe zijn twee voedselketens beschouwd: een aquatische (water → vis of mossel → vis- of mossel-etende vogel of zoogdier) en een terrestrische (bodem → regenworm → worm-etende vogel of zoogdier). Uitgangspunt bij de gevolgde methode is dat een NOEC wordt afgeleid voor vogels of zoogdieren die voor de aquatische route gedeeld wordt door de bioconcentratie factor (BCF) voor mossel of vis en door de BCF voor regenwormen voor de terrestrische route.

Voor de aquatische route is telkens uitgegaan van de meest kritische: via vis of via mosselen. MTRs zijn vervolgens afgeleid door de waarde gebaseerd op directe effecten te vergelijken met de MTR gebaseerd op effecten via de voedselketen.

Er zijn geen toxiciteitsgegevens gevonden voor sediment organismen. MTRs zijn dan ook afgeleid uit die voor water met behulp van de evenwichtspartitiemethode.

MTRs voor bodem zijn afgestemd met die voor water met behulp van de evenwichtspartitiemethode. Bij het bepalen van de 'definitieve' MTR is een keuze gemaakt tussen de MTR gebaseerd op (in)directe effecten en de MTR afgeleid met de evenwichtspartitiemethode. Deze keuze is gebaseerd op data beschikbaarheid: wanneer 4 of meer NOECs voor aquatische organismen voor verschillende taxonomische groepen aanwezig zijn, terwijl voor bodem weinig gegevens beschikbaar zijn is de voorkeur gegeven aan de MTR afgeleid met evenwichtspartitie.

Voor aldrin/dieldrin, cadmium, DDT en derivaten, endrin, alle HCH isomeren, penta- en hexachloorbenzeen en methyl-kwik is doorvergiftiging via de aquatische route waarschijnlijk kritisch. Voor heptachloor, heptachloor epoxide en quintozeen zijn zowel voor aquatische organismen als voor vogels en zoogdieren te weinig data beschikbaar. Via de terrestrische route is doorvergiftiging waarschijnlijk kritisch voor cadmium, koper, penta- en hexachloorbenzeen en methyl-kwik. De resultaten voor bodem dienen als voorlopig beschouwd te worden gezien het grote gebrek aan gegevens voor met name bodemorganismen maar ook voor vogels en zoogdieren. Daarnaast is de terrestrische voedselketen waarschijnlijk te beperkt om het risico van effecten door middel van doorvergiftiging te kunnen beoordelen.

De hier gehanteerde methode om rekening te houden met voedselketen effecten moet gezien worden als een eerste screening. Voor die stoffen waarvoor deze effecten kritisch zijn is nader onderzoek noodzakelijk. In dit onderzoek is het verzamelen van lokale en soortspecifieke informatie essentieel.

Voor veel stoffen is het niet mogelijk om actuele concentraties te vergelijken met MTR's en VR's omdat de detectielimiet hoger is dan het VR, of zelfs het MTR. Voor de volgende stoffen wordt het MTR in oppervlaktewater, zwevend stof of sediment regelmatig overschreden: koper, DDT en derivaten, α -endosulfan, heptachloor, hexachloorbenzeen en kwik. Voor de compartimenten bodem en grondwater zijn slechts voor een aantal stoffen gegevens beschikbaar. In bodem wordt het MTR_{bodem} voor endrin en met name DDT en DDE overschreden.

In onderstaande tabel zijn waarden gepresenteerd die gebruikt kunnen worden voor het opstellen van grens- en streefwaarden.

Maximaal Toelaatbare Risiconivo's (MTR) en Verwaarloosbare Risiconivo's (VR). De waarden voor water zijn weergegeven in ng/l; voor sediment en bodem in µg/kg (voor standaard bodem met 25% klei en 10% organisch stof).

stof	water		sediment		bodem	
	MTR	VR ^d	MTR	VR ^d	MTR	VR ^d
	ng/l	ng/l	µg/kg	µg/kg	µg/kg	µg/kg
aldrin	18	0.18	120 ^b	1.2 ^b	50 ^a	0.50 ^a
cadmium	350 ^c	3.5 ^c	29,000 ^{b,c}	290 ^{b,c}	3.5 ^c	0.035 ^c
carbofuran	15 ^a	0.15 ^a	0.032 ^b	0.00032 ^b	4.7 ^a	0.047 ^a
chloordaan	1.5 ^a	0.015 ^a	2.4 ^b	0.024 ^b	4.3 ^a	0.043 ^a
chloorpyrifos	2.8	0.028	1.1 ^b	0.011 ^b	1.1 ^b	0.011 ^b
koper	4,100 ^c	41 ^c	142,000 ^{b,c}	1,420 ^{b,c}	550 ^c	5.5 ^c
DDD	0.44	0.0044	1.8 ^b	0.018 ^b	10 ^a	0.10 ^a
DDE	0.44	0.0044	1.5 ^b	0.015 ^b	10 ^a	0.10 ^a
DDT	0.44	0.0044	9.4 ^b	0.094 ^b	10 ^a	0.10 ^a
dieldrin	18	0.18	670 ^b	6.7 ^b	50 ^a	0.50 ^a
endosulfan	0.40	0.0040	0.026 ^b	0.00026 ^b	50 ^a	0.50 ^a
endrin	3.0	0.030	2.9 ^b	0.029 ^b	2.9 ^b	0.029 ^b
fenthion	3.1	0.031	0.35 ^b	0.0035 ^b	0.35 ^b	0.0035 ^b
α-HCH	2,500 ^a	25 ^a	220 ^b	2.2 ^b	220 ^b	2.2 ^b
β-HCH	80 ^a	0.80 ^a	92 ^b	0.92 ^b	92 ^b	0.92 ^b
γ-HCH	770	7.7	190 ^b	1.9 ^b	5.0 ^a	0.050 ^a
heptachloor	0.46 ^a	0.0046 ^a	0.65 ^b	0.0065 ^b	0.70 ^a	0.0070 ^a
heptachloor epoxide	0.46 ^a	0.0046 ^a	0.020 ^b	0.00020 ^b	0.70 ^a	0.0070 ^a
hexachloorbenzeen	2.1	0.021	1.2 ^b	0.012 ^b	28	0.28
kwik	1.9 ^c	0.019 ^c	210 ^{b,c}	2.1 ^{b,c}	200 ^c	2.0 ^c
methyl-kwik	1.9 ^c	0.019 ^c	210 ^{b,c}	2.1 ^{b,c}	3.3 ^c	0.033 ^c
pentachloorbenzeen	30 ^a	0.30 ^a	12 ^b	0.12 ^b	120 ^a	1.2 ^a
pentachloorfenol	3,500	35	310 ^b	3.1 ^b	170 ^a	1.7 ^a
quintozeen	290 ^a	2.9 ^a	330 ^b	3.3 ^b	330 ^b	3.3 ^b
thiram	32 ^a	0.32 ^a	0.79 ^b	0.0079 ^b	38 ^a	0.38 ^a

^a indicatieve waarde

^b gebaseerd op de evenwichtspartitiemethode

^c voor het opstellen van grens- en streefwaarden moeten deze MTRs en VRs nog vergeleken worden met de natuurlijke achtergrondgehalten

^d uitgaande van een factor 100 tussen MTR en VR

1. INTRODUCTION

In 1989 the Directorate-General for Environmental Protection started the project "Setting integrated environmental quality objectives". In this project action A-35 of the National Environmental Policy Plan is worked out [1]. Goal is to derive integrated environmental quality objectives for air, ground and surface water, sediment and soil for a large number of compounds, based on the risk philosophy of the Ministry of Housing, Physical Planning and Environment [2]. The project is carried out by the National Institute for Public Health and Environmental Protection. The first project (a) "MILBOWA"¹ resulted in the report "Desire for levels" [3]. In this report a methodology was proposed for deriving Maximum Permissible Concentrations for several compounds like heavy metals, chlorophenols, pesticides and polycyclic aromatic hydrocarbons. Based on "Desire for levels" integrated environmental quality objectives for water, sediment and soil were proposed by the Minister of the Environment from The Netherlands [4].

The second project (b) is divided into three sub-projects: 'Exotic Metals' (b-1), 'Volatile Compounds' (b-2) and 'Secondary Poisoning' (b-3). In project b-1 for nine trace metals, i.e. antimony, barium, beryllium, cobalt, molybdenum, selenium, thallium, tin, and vanadium, values have been derived which can be used to set integrated environmental quality objectives for ground and surface water, sediment and soil [5]. In project b-2 values have been proposed for 46 volatile substances for water, sediment, soil and air [6].

The method applied within the sub-projects b-1, b-2 and b-3 is based on the one described in "Desire for levels" [3]. First, Maximum Permissible Concentrations (MPC) and Negligible Concentrations (NC) are determined for all compartments based on ecotoxicological data. Subsequently these MPCs and NCs are harmonized. Reason for harmonization is that the concentration at MPC (or NC) level in one compartment may not lead to exceeding of the MPC (or NC) in other compartments due to transport of the chemical. For the trace elements of project b-1 the equilibrium partitioning method was used for harmonization [7, 8, 9]. In project b-2 a harmonization procedure was used applying computed steady state concentration ratios rather than equilibrium partitioning [6].

A flow diagram of the different steps leading to integrated environmental quality objectives is given in Figure 1.

Several compounds of the ones for which integrated environmental quality objectives had to be derived, are considered to have a bioaccumulation potential based on the high value of their n-octanol/water partition coefficient (K_{ow}). Uptake of accumulated substances by higher members of the food chain, either living in the aquatic or terrestrial environment, may lead to secondary poisoning. This means that when quality objectives are set for such compounds, not only direct but also indirect effects have to be taken into account. How this should be done has been subject of much discussion in The Netherlands recently [10]. It was therefore decided to deal with these compounds in a separate project (b-3). The present report contains the results thereof.

¹ Abbreviation in Dutch for 'Environmental quality objectives for water and soil'.

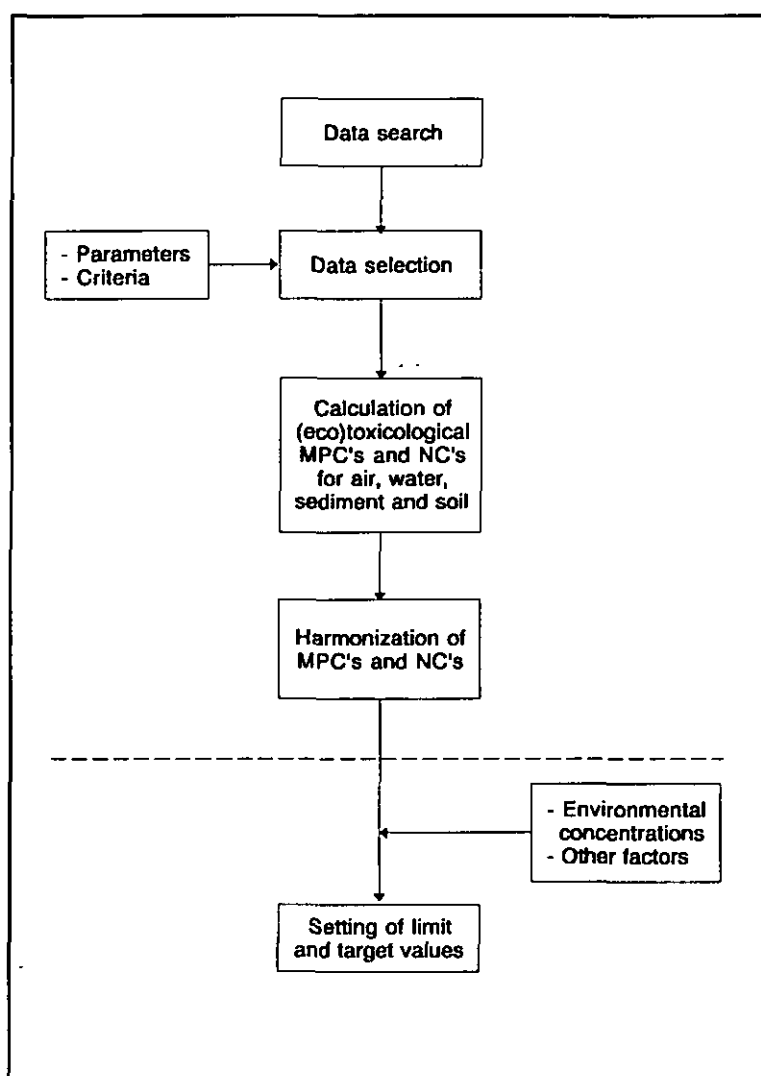


Figure 1. Process of setting integrated environmental quality objectives

Summarizing, the following activities had to be carried out within the project "Secondary Poisoning":

1. deriving MPCs for water, sediment and soil based on ecotoxicological data taking also secondary poisoning into account,
2. gathering sediment-water and soil-pore water partition coefficients in order to apply the equilibrium partitioning method,
3. harmonization of the MPCs and NCs for water, soil and sediment using the equilibrium partitioning method,
4. setting integrated environmental quality objectives (limit and target values).

It was decided by the National Institute of Public Health and Environmental Protection and the Ministry of Housing, Physical Planning and Environment to publish separate reports about several of these activities. Sediment-water and soil-pore water partition coefficients are reported in Bockting et al. [11]. The present report deals with activities 1 and 3, mentioned above. Values derived here can be used to set integrated environmental quality objectives. The last step, setting

limit and target values, will be the subject of a separate policy document that will include also integrated environmental quality objectives for the nine trace metals and 46 volatile compounds (sub-projects b-1 and b3, respectively).

2. METHODOLOGY

2.1 Selected compounds

The following compounds are selected: aldrin, carbofuran, chlordane, chlorpyrifos, DDD, DDE, DDT, endosulfan, endrin, fenthion, α -HCH, β -HCH, heptachlor, heptachlor epoxide, hexachlorobenzene, pentachlorobenzene, quintozone and thiram. Most compounds, e.g. organochlor pesticides, are selected because of their bioaccumulating potential. Carbofuran, chlorpyrifos, fenthion and thiram are selected to investigate whether pesticides belonging to other groups also pose a risk via secondary poisoning. Additionally several compounds, already reviewed in other projects, are added in order to extend the data set: cadmium, copper, dieldrin, γ -HCH, mercury, methyl-mercury and pentachlorophenol.

In Table 2.1 all compounds are presented. Also an overview is given of the origin of the data used to calculate MPCs. Data for many compounds are taken from other reports. Hence, these data are not presented in detail here.

2.2 Literature search

Several sources are used for the collection of single species toxicity data and bioconcentration factors for fish and bivalves:

- literature present at the Toxicology Advisory Centre of the National Institute of Public Health and the Environment,
- on-line search carried out in TOXLINE, AQUIRE and BIOSIS for aquatic and terrestrial organisms. On-line search was performed either updating from the publication of the most reliable review, or over a longer period when no reliable review was available. The retrieved references that seemed relevant were collected and evaluated.
- retrospective literature search using public literature and reviews as a basis.

For the collection of single species toxicity data for mammals and birds only reviews present at the Toxicology Advisory Centre of the National Institute of Public Health and the Environment are used.

2.3 Deriving toxicity data from literature

2.3.1 Quality criteria for studies

First of all a study must meet several requirements with respect to the experimental design. Most of these requirements are stated in test-guidelines like the ones of the Organisation for Economic Co-operation and Development (OECD).

Table 2.1 Selected compounds and origin of data used to calculate MPCs.

compound	freshwater organisms	saltwater organisms	terrestrial organisms	birds	mammals	BCFs fish	bivalves
aldrin	1	1	1	1	1	1	2
cadmium	3	4	5	6	6	6	4
carbofuran	1	1	1	1	1	1	2
chlordane	1	1	1	1	1	1	2
chlorpyrifos	1	1	1	1	1	1	2
copper	3	4	1	1	1	1	2
p,p'-DDD	1	1	1	7	1	7	7
p,p'-DDE	1	1	1	7	1	7	7
p,p'-DDT	1	1	1	9	9	7	7
o,p'-DDT	1	1	1	7	1	7	7
endosulfan	1	1	1	1	1	1	2
endrin	1	1	1	1	1	1	2
dieldrin	3	4	5	6	6	6	4
fenthion	1	1	1	1	1	1	2
α -HCH	1	1	1	7	1	7	7
β -HCH	1	1	1	1	1	1	1
γ -HCH	3	4	5	6	6	6	4
heptachlor	1	1	1	1	1	1	2
heptachlor epoxide	1	1	1	1	1	1	2
hexachlorobenzene	8	8	8	7	1	7	7
mercury	5	4	5	6	6	6	4
methyl-mercury	5	4	5	6	6	6	4
pentachlorobenzene	8	8	8	7	1	7	7
pentachlorophenol	3	4	5	9	9	1	2
quintozene	1	1	1	1	1	1	2
thiram	1	1	1	1	1	1	2

- 1 present study (see annex to present report)
- 2 Eys, Y.A. (1992). Bioconcentratiefactoren van tweekeppigen. AIDEnvironment. Amsterdam (in Dutch).
- 3 Emans, H.J.B., P.C. Okkerman, E.J. van de Plassche, P.M. Sparenburg and J.H. Canton (1992). Validation of some extrapolation methods with toxicity data derived from multiple species experiments on organic and metals in aquatic ecosystems. RIVM report No. 679102 014.
- 4 Seaworthy. Derivation of micropollutant risk levels for the North Sea and Wadden Sea. Ministry of Housing, Physical Planning and the Environment and Ministry of Transport, Public Works and Water Management. Publikatiereeks gebiedsgericht beleid, No. 1992/3.
- 5 Van de Meent, D., T. Aldenberg, J.H. Canton, C.A.M. van Gestel and W. Slooff (1990). Desire for levels. Background study for the policy document "Setting environmental quality standards for water and soil". RIVM report No. 679101 002.
- 6 Romijn, C.F.A.M., R. Luttik, D. v.d. Meent, W. Slooff and J.H. Canton (1993). Presentation of a general algorithm to include effect assessment on secondary poisoning in the derivation of environmental quality criteria. Part 1. Aquatic food chains. Ecotox. Environ. Saf. 26, 61-85.
- 7 Van de Plassche, E.J., J. Lahr, H.J. van der Valk, J.W. Everts en J.H. Canton (1991). Afleiding van het maximaal toelaatbaar risico met betrekking tot doorvergiftiging voor een aantal stoffen in het kader van het vaststellen van bijzondere milieukwaliteitsdoelstellingen voor de Noordzee en Waddenzee. RIVM report No. 679101 001 (in Dutch).
- 8 Van de Plassche, E.J. and G.J.M. Bockting (1993). Towards environmental quality objectives for several volatile compounds. RIVM report No. 679101 011.
- 9 Romijn, C.F.A.M., R. Luttik and J.H. Canton (1994). Presentation of a general algorithm to include effect assessment on secondary poisoning in the derivation of environmental quality criteria. Part 2. Terrestrial food chains. Ecotox. Environ. Saf. 27, 107-127.

Due to the low water solubility of most compounds special attention was paid to the preparation and characterization of test media in aquatic toxicity tests. Aspects like the way in which the test solutions are prepared, nominal versus measured concentrations, presence of dissolved organic material, temperature, solvent usage, feeding and sorption to glass were considered. With respect to solvent usage according to OECD guidelines the amount of solvent should not exceed 0.1 ml per liter medium. As a rule both a control and a solvent control must have been tested while the solvent control should contain as much solvent as the highest tested concentration. While evaluating the obtained literature it was concluded that these criteria are too stringent. Therefore, deviating from the OECD guidelines, a maximum of 1 ml solvent per liter medium is accepted.

Often results are reported above the water solubility. A discussion about the interpretation of observed effects above the water solubility is still ongoing in aquatic toxicology [12]. Effects may be caused by a contribution of undissolved particles to the apparant toxicity due to physical damage to e.g. the respiratory apparatus of invertebrates or the gills of fish. It should be stated that reported water solubilities of highly lipophilic compounds in physico-chemical handbooks and reviews are often variable because the determination of the water solubility of compounds with a water solubility below e.g. 1 mg/l depends more on the analytical method applied or the conditions of measurement compared to compounds with a higher water solubility. Next to this, in most cases the analytical method used is not reported. Therefore, according to Vaal et al. toxicity data up to 10 times above the water solubility may be accepted [12].

2.3.2 Parameters

For environmental effect assessment principally only those parameters are taken into account that exclusively affect species on the level of population [8]. In general the parameter in acute studies is mortality. In (semi)chronic studies next to mortality other parameters like growth and reproduction are studied. With respect to chronic tests with birds and mammals, reproduction studies are selected which reported on effects on spermatogenesis, fertility, pregnancy rate, number of live fetuses, pup mortality, eggshell thinning, egg production, egg fertility, hatchability and chick survival [8, 13].

Also other parameters are studied however, e.g. behaviour. Results of such studies are used only if the parameter is considered ecologically relevant, e.g. immobility in tests with daphnids or lying on the bottom of the test-vessel in experiments with fish.

All results from experiments with soil organisms are converted to a standard soil, which is a soil with a clay and organic matter content of 25 and 10%, respectively. For organic compounds this normalisation is based only on the organic matter content of the soil. This means that test results are corrected according to the following formula [8]:

$$NOEC_{ss} ; L(E)C50_{ss} = NOEC_{exp} ; L(E)C50_{exp} \times \frac{f_{om}(ss)}{f_{om}(exp)} \quad (1)$$

where:

ss = standard soil,

exp = data from experiment,
 $f_{om}(ss)$ = fraction organic matter in standard soil, i.e. 10%,
 $f_{om}(exp)$ = fraction organic matter in soil from experiment.

If tests are carried out with an organic matter content of <2% or >30%, these contents are set equal to 2 and 30%, respectively for conversion to standard soil. If tests are carried out with a clay content of <5% or >50%, these contents are set equal to 5 and 50%, respectively for conversion to standard soil.

2.3.3 Procedures for deriving L(E)C50 values

L(E)C50 values are gathered for aquatic and terrestrial organisms and birds. In principle a distinct concentration-effects relationship must be present. In most cases however, the raw data are not presented in literature. In general these studies are considered reliable, because acute studies have been carried out already for a long time and standardized to a great extent, especially in aquatic ecotoxicology. Only when strong indications are present about the unreliability of a study or when the results are given as a very short summary only, these data are not accepted. If only raw data are available the L(E)C50 is calculated according to the method of Spearman and Karber [14].

2.3.4 Procedures for deriving NOEC values

The following procedures are used for deriving NOEC (No Observed Effect Concentration) values for aquatic and terrestrial organisms:

- If the NOEC value is based on a statistical method these results are used: the highest concentration tested not differing from the control at $P < 0.05$ is regarded as the NOEC,
- If no statistical method is applied or could be used in principle the concentration showing less than 10% effect is considered as the NOEC. There must be a distinct concentration-effects relationship, however.
- If there are not enough NOEC values available to apply refined effects assessment or when there is a LOEC (Lowest Observed Effect Concentration) which is lower than the available reliable NOEC value(s) the following procedures are applied:
 - 1) $LOEC > 10$ to 20% effect: the $NOEC = LOEC/2$,
 - 2) $LOEC \geq 20\%$ effect and a distinct concentration-effects relationship: the EC_{10} is calculated or extrapolated and regarded as the NOEC,
 - 3) $LOEC \geq 20\%$ with no distinct concentration-effects relationship:
 - $LOEC$ 20 to 50% effect: $NOEC = LOEC/3$,
 - $LOEC \geq 50\%$ effect: $NOEC = LOEC/10$.

If other test-results are available within the same taxonomical group with distinct concentration-effects relationships, these are used to verify the above mentioned factors. If for instance an acute-chronic ratio is available within the same taxonomical group this ratio is used instead of one of the factors mentioned above.

In terrestrial ecotoxicology also microbial processes are studied. With pesticides often two concentrations are tested in such studies: one equal to and another one 10 times the application

rate in the field. If a test resulted in two effect concentrations an EC10 is calculated using a logistic response model [15, 16]. Prerequisite is that these ECs differ by more than 15% and are lower than the EC70, or that they lay around the EC10.

In aquatic ecotoxicology often the Maximum Acceptable Toxicant Concentration (MATC) is calculated instead of the NOEC. In order to derive a NOEC from a MATC, the latter is divided by 2 if the MATC is presented as a single value, while the lowest value is used if the MATC is presented as a range of 2 values:

From collected reviews NOEC values for mammals and birds are derived as follows:

- the highest test dose causing no adverse effects is selected as the NOEC,
- NOECs are calculated from LOECs as described above; if the percentage effect is not reported NOECs are calculated as LOEC/2,
- from chronic tests with mammals no NOEC values for mortality are derived because more than 20% mortality occurs in many tests in the second year; mortality which cannot be ascribed to the test substance,
- if no adverse effects are observed at any of the doses tested no NOEC is recorded,
- according to Romijn et al. an uncertainty factor of 10 is applied to NOEC values from studies on short-term exposure (< 1 month) [13].
- if NOECs are reported in mg/kg bw these values are converted to mg/kg food using the following BW/DFI (BW: body weight; DFI: daily food intake) factors: *Canis domesticus* (dog): 40; *Macaca spec.* (rhesus monkey): 20; *Microtus spec.* (hamster): 8.3; *Mus musculus* (mouse): 8.3; *Oryctolagus cuniculus* (rabbit): 33; *Rattus norvegicus* (rat): 20 and *Mustela vison* (mink): 10 [8, 13].

2.5 Bioconcentration factors for fish and bivalves and earthworms

In aquatic ecosystems the bioconcentration factor (BCF) is defined as the ratio of the concentration in a target organism to that in water at steady state. For organic compounds BCFs are determined either in laboratory tests or predicted from physico-chemical properties using quantitative structure-activity relationships (QSARs); in most cases the octanol-water partition coefficient (K_{ow}) is used. According to Romijn et al. and Slooff, in the present report preference is given to experimentally obtained BCFs [8, 13]. However, these BCFs are compared with the ones calculated using the following equations [17, 18]:

$$\text{fish : } BCF = 0.048 K_{ow} \quad [l.kg^{-1}] \quad (2)$$

$$\text{mussel : } BCF = 0.013 K_{ow} \quad [l.kg^{-1}] \quad (3)$$

Most K_{ow} values are taken from Bockting et al. [11]. They preferred experimental values obtained by the slow-stirring method [19]. So called 'star values' from the MEDCHEM database are used for compounds for which no slow-stirring values are available [20]. The MEDCHEM database is considered the most extensive and reliable source for K_{ow} s available. The value that is considered most reliable in the data-base is indicated with a star. Besides a large number of K_{ow} values from the literature the MEDCHEM database contains a routine for estimation of K_{ow} s based

on structural properties of the compound (ClogP method). A description of the database and the ClogP method is given by Leo et al. [21]. Log K_{ow} values used for the different compounds are presented in Table 2.2.

Table 2.2 Selected organic compounds and their log K_{ow}

compound	log K_{ow}	compound	log K_{ow}
aldrin	6.50	fenthion	4.09
carbofuran	2.32	α -HCH	3.78
chlordane	5.80	β -HCH	3.84
chlorpyrifos	5.27	γ -HCH	3.69
p,p'-DDD	6.22	heptachlor	5.58
p,p'-DDE	6.50	heptachlor epoxide	3.49
p,p'-DDT	6.91	hexachlorobenzene	5.73
o,p'-DDT	6.61	pentachlorobenzene	5.18
dieldrin	6.20	pentachlorophenol	4.74
endosulfan	3.83	quintozone	5.50
endrin	5.20	thiram	1.76

dieldrin and pentachlorophenol: from Van de Meent et al. [3]

penta- and hexachlorobenzene: from Van de Plassche and Bocking [6]

other compounds: from Bocking et al. [11]

For the selected compounds literature was screened on BCFs measured in laboratory studies with fresh- and saltwater fish and bivalves. The following quality criteria are used for selecting BCFs:

1. the experimental duration had to be sufficiently long in order to establish or approach a steady state between concentrations in water and the test species. However, in many studies it is not clear whether steady state is reached. Therefore, an estimate was made of the duration of the uptake phase to reach 80% of the steady state (T80) based on the log K_{ow} according to OECD guidelines [22]. Only studies with an exposure time longer than the estimated T80 are included.
2. no signs of overt toxicity should have been observed. According to the OECD guidelines the highest concentration should be less than 0.1 of the incipient LC50 for the test species and at least 10 times higher than the detection limit in water [22]. While evaluating the obtained literature it was concluded that these criteria are too stringent. Therefore it was decided to deviate from OECD guidelines in the following way: if mortality occurred the test concentration is excluded, while if nothing is reported on mortality by the author(s) all test concentrations higher than 0.20 times the 96 h LC50 of the test species are excluded.
3. only studies reporting BCFs for whole body based on wet weight are selected. For bivalves BCFs for whole body are based on the soft parts, i.e. without the shell.

A geometric mean BCF is calculated from the values selected from literature. If more than one value was determined on a single species, a geometric mean value is calculated first on this species, before an overall geometric mean value is calculated.

BCFs for earthworms can also be obtained experimentally or estimated using QSARs. Romijn et al. showed that for dieldrin, DDT and pentachlorophenol geometric mean BCFs obtained from laboratory tests are < 1 [23]. Also, these BCFs were in good agreement with results reported by Connell and Markwell, who derived the following regression equation [24]:

$$BCF = \left(\frac{Y_L}{x \times f_{oc}} \right) \times K_{ow}^{b-a} \quad (4)$$

where:

- Y_L = lipid fraction of earthworms. According to Romijn et al. Y_L is equal to circa 1% [23].
- x = a constant, estimated to be 0.66 by Rao and Davidson [25].
- f_{oc} = organic carbon fraction of the soil.
- K_{ow} = octanol-water partition coefficient,
- $b-a$ = *b and a are both non-linearity constants: a for the soil to pore water partitioning and b for porewater to earthworm partitioning.* Markwell et al. estimated $b-a$ equal to 0.07 for earthworms [26].

Romijn et al. showed that the BCF is probably only dependent on soil characteristics and the lipid content of the organism and independent of the K_{ow} , and hence physico-chemical properties [23]. Therefore Slooff proposed to use a mean and maximum BCF of 1 and 10, respectively for all organic compounds [8]. In the present report this approach is followed. This means that no literature search was carried out on BCFs for earthworms. For cadmium and mercury the BCFs derived by Romijn et al. are used [23]. For copper BCFs were searched for in reviews.

2.6 Soil - pore water and sediment - water partition coefficients

Soil-water partition coefficients (K_p s) describe the equilibrium distribution of a chemical over a solid phase (soil, sediment or suspended matter) and water.

$$K_p = \frac{C_{soil}}{C_{water}} \quad [l.kg^{-1}] \quad (5)$$

where:

- C_{soil} = equilibrium concentration in soil (mg/kg),
- C_{water} = equilibrium concentration in water (mg/dm³).

K_p values are taken from Bockting et al. [11]. They evaluated and complemented a large number of experimental organic carbon normalized soil-water partition coefficients (K_{oc} values) compiled by Gerstl [27].

Bockting et al. preferably based K_p s on experimental values and calculated K_p s from K_{oc} s according to:

$$K_p = K_{oc} \times f_{oc} \quad [l.kg^{-1}] \quad (6)$$

where f_{oc} is the fraction organic carbon of the soil or sediment. According to Slooff f_{oc} is fixed at 5% and 10% for soil/sediment and particulate matter, respectively [8].

When no experimental K_{oc} values were found, K_{oc} s (and K_p s) were derived from K_{ow} values according to an empirical regression equation [8, 9, 28]:

$$K_{oc} = K_{ow} \quad [l.kg^{-1}] \quad (7)$$

2.7 Extrapolation methods

In the Netherlands two extrapolation methods are used for deriving environmental quality objectives:

1. preliminary effects assessment: modified EPA method,
2. refined effects assessment: a modification of the method of van Straalen and Denneman as developed by Aldenberg and Slob [29, 30].

These methods are described in detail by Slooff, Romijn et al. and by Aldenberg and Slob [8, 13, 30, 31]. A short description of both methods is given below:

2.7.1 Preliminary effects assessment

In the modified EPA method assessment factors are applied on toxicity data. The size of this factor depends on the number and kind of toxicity data. In Tables 2.3, 2.4 and 2.5 the method is summarized for aquatic organisms, terrestrial organisms and birds and mammals, respectively. It should be reminded that for birds and mammals a subdivision in taxonomic groups is not possible because data sets are almost always too limited [13]. The outcome of the method is called an indicative MPC.

In the modified EPA method chronic as well as acute toxicity data are weighted over the species as follows [8]:

- if for a single species several L(E)C50 or NOEC values are derived for different effect parameters the lowest is selected,
- if for a single species several L(E)C50 or NOEC values are derived for the same effect parameter a geometric mean value is calculated.

In addition also acute/chronic ratios are used to derive NOEC values. These ratios are applied only within a taxonomical group.

Table 2.3. Modified EPA method for aquatic organisms

available information	Assessment factor
lowest acute L(E)C50 or QSAR estimate for acute toxicity	1,000
lowest acute L(E)C50 or QSAR estimate for acute toxicity for minimal algae/crustaceans/fish	100
lowest chronic NOEC or QSAR estimate for chronic toxicity	10*
lowest chronic NOEC or QSAR estimate for chronic toxicity for minimal algae/crustaceans/fish	10

* this value is subsequently compared to the extrapolated value based on acute L(E)C50 toxicity values. The lowest one is selected

Table 2.4. Modified EPA method for terrestrial organisms

available information	Assessment factor
lowest acute L(E)C50 or QSAR estimate for acute toxicity	1,000
lowest acute L(E)C50 or QSAR estimate for minimal three representatives of microbe-mediated processes, earthworms or arthropods and plants	100
lowest chronic NOEC or QSAR estimate for chronic toxicity	10*
lowest chronic NOEC or QSAR estimate for chronic toxicity for minimal three representatives of microbe-mediated processes, earthworms or arthropods and plants	10

* this value is subsequently compared to the extrapolated value based on acute L(E)C50 toxicity values. The lowest one is selected

Table 2.5. Modified EPA method for birds and mammals

available information	Assessment factor
less than 3 acute LC50 values and no chronic NOECs	1,000
at least 3 acute LC50 values and no chronic NOECs	100
less than 3 chronic NOECs	10*
3 chronic NOECs	10

* this value is subsequently compared to the extrapolated value based on acute LC50 toxicity values. The lowest one is selected

2.7.2 Refined effects assessment

The aim of environmental quality objectives is that the MPC is set at a level that protects all species in an ecosystem. However, in order to be able to use extrapolation methods like the one of Aldenberg and Slob, in effect assessment a 95% protection level is chosen as a sort of cut-off value. This 95% protection level can be calculated with a 50% and 95% confidence level. In The Netherlands the former value is called the MPC [8]. To indicate the uncertainty in the estimation of

the MPC the 95% protection level with both 50 and 95% confidence is calculated. The method uses the lowest NOEC per species as input data and is applied when at least 4 NOEC values for different taxonomic groups are available for aquatic and terrestrial organisms, while for mammals and birds NOECs should be available for 4 different species. In the method of Aldenberg and Slob NOEC values used as input data are weighted over the species in the same way as described above in paragraph 2.5.1 for the modified EPA method.

The method of Aldenberg and Slob assumes that the NOEC values used for calculation fit the log-logistic distribution. For checking this assumption the data available are tested statistically with the so called empirical distribution function (EDF); Kolmogorov-Smirnov $D \cdot \sqrt{n}$ test. Only if the NOEC values are not log-logistically distributed at a significance level of 1% and there are no reasons for leaving out outliers the modified EPA method is applied [8].

2.8 Secondary poisoning

2.8.1 How to include secondary poisoning in effect assessment?

In order to develop a method on incorporating secondary poisoning in effect assessment Romijn et al. analyzed two simple food chains: water → fish → fish-eating bird or mammal and soil → worm → worm-eating bird or mammal [13, 23, 32]. They proposed the following algorithm to calculate a MPC for secondary poisoning:

$$MPC_{\text{water ; soil}} = \frac{NOEC_{\text{bird ; mammal}}}{BCF_{\text{fish ; worm}}} \quad (8)$$

where:

$NOEC_{\text{bird ; mammal}}$ is calculated using extrapolation methods (modified EPA method as presented in Table 2.5 or the method according to Aldenberg and Slob).

This MPC can then be compared with the MPC for direct effects on aquatic or terrestrial organisms. Romijn et al. applied the algorithm to lindane, dieldrin, cadmium and mercury (both in water and soil), PCB153 (only in water) and DDT and pentachlorophenol (only in soil). Based on the work of Romijn et al. a discussion started in The Netherlands whether so called correction factors should be applied for the following aspects which influence secondary poisoning [33, 34]:

- laboratory - field conversion: differences in metabolic rate between animals in laboratory (toxicity tests) and the field,
- caloric conversion: differences in caloric content of the different types of food: cereals versus fish or mussels,
- normal versus extreme conditions: differences in metabolic rate under normal field conditions and more extreme ones, e.g. breeding period, migration, winter,
- food assimilation efficiency: differences in use of different types of food,
- pollutant assimilation efficiency: differences in bioavailability in test animals (surface application of a test compound) and in the field (compound incorporated in food),
- relative sensitivity: differences in biotransformation of certain compounds between taxonomic groups of birds or mammals.

Based on a broad literature search Ruys and Pijnenburg calculated correction factors of 0.36 for birds for the first aspect and 0.32 (fish) and 0.20 (mussel) for the second one [35]. Everts et al. applied these correction factors to derive quality objectives for the marine environment for the foodchain water → fish or mussel → fish- or mussel-eating seabird for cadmium, mercury, DDT and derivatives, lindane, dieldrin, hexachlorobenzene and PCB153 [18, 36]. As a follow-up of the work of Romijn et al. and Ruys and Pijnenburg a project has started carried out by the National Institute of Public Health and Environmental Protection in collaboration with the National Institute for Coastal and Marine Management. Aim of this project is to develop a general algorithm for effect assessment of effects from secondary poisoning in a more complex terrestrial foodweb: soil via plants and invertebrates to small birds and mammals to birds and beast of prey. [34]. The above mentioned factors influencing secondary poisoning will be investigated in this project in detail. This may lead to adjusted correction factors compared to the ones calculated by Ruys and Pijnenburg.

2.8.2 Method applied

Much discussion has been going on within the project 'Setting environmental quality objectives' about how to deal with secondary poisoning. Main issues in these discussions are the following [37]:

- which method must be used to derive a MPC? Two options were developed which are depicted schematically in Figure 2.

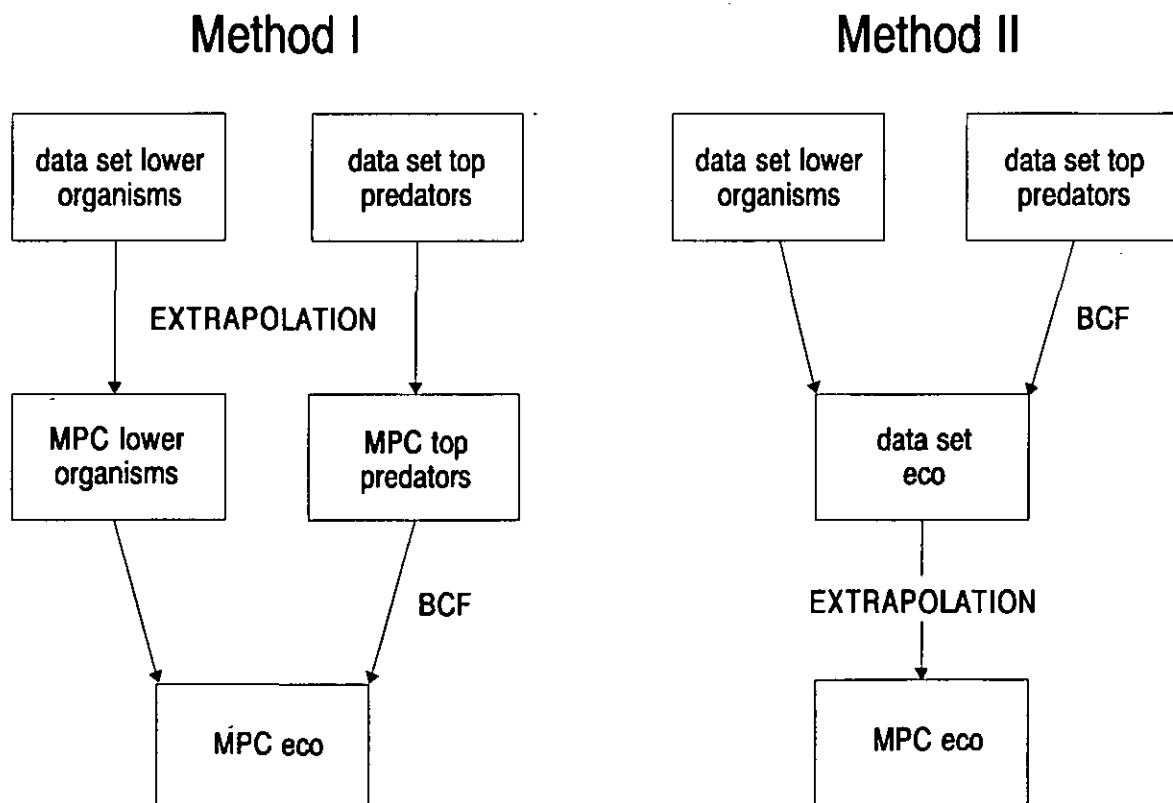


Figure 2. Methods to incorporate secondary poisoning in effect assessment. Method I: MPC based on separate data sets for aquatic or soil organisms and top predators (birds or mammals).

Method II: MPC based on combined data sets.

In method I data sets for lower organisms (i.e. fresh- and saltwater organisms for the aquatic food chain and soil organisms for the terrestrial food chain) and top predators (i.e. birds and mammals) are treated separately. Two MPCs are calculated from which one is selected. In method II both data sets are combined: first all individual NOEC values for birds and mammals are divided by the BCF to obtain a concentration in water or soil. These values are used as input data for the modified EPA method or the extrapolation method of Aldenberg and Slob together with the L(E)C50 or NOEC values for aquatic or soil organisms.

An advantage of method I is that in the whole process toxicity data for aquatic organisms (direct effects) are kept separate from the data for birds and mammals as long as possible. Such a method is more suitable to use in phase 1, which is a screening phase where it is decided whether effects due to secondary poisoning are critical for setting environmental quality objectives.

An advantage of method II is that it is more in agreement with the original design of the statistical extrapolation method as proposed by Van Straalen and Denneman: the distribution of NOEC values of species within a large community, rather than for a relatively limited group of species, can be described by a log-logistic function [29]. However, most toxicity data are available for 'terrestrial' mammals and birds whereas only some for 'aquatic birds', e.g. *Anas platyrhynchos*. Next to this, the larger data set used as input for the method of Aldenberg and Slob leads to a more reliable estimation of the MPC (95% protection level). On the other hand, dividing all NOECs for birds and mammals by the BCF creates another source of uncertainty. However, a more or less arbitrary choice for one of the MPC_{sps} or the $MPC_{direct\ aq.}$ is not needed.

- must the correction factors developed by Everts et al. be applied and if so: all factors or only some of them? Correction factors are available for only two of the aspects mentioned in paragraph 2.8.1. Besides, correction factors derived are based on a global literatures search.
- do these methods provide sufficient protection to top predators? It is still uncertainty whether MPC values derived can be regarded as 'safe' values as a validation with results from field studies has not been carried out yet.

In May 1992 the Dutch minister of Housing, Physical Planning and Environment asked the Health Council of The Netherlands for advice about the methods developed by Romijn et al. and the modification thereof by Everts et al. Conclusions of the Health Council on the method of Romijn et al. are as follows: "The committee regards the RIVM-method as a pragmatic approach for obtaining a rough initial indication of the potential for secondary poisoning on the basis of existing (limited) data. In view of the major uncertainties and the limited number of (simple) food chains considered, the recommended values derived by means of the RIVM-method do not guarantee higher species of animals sufficient protection. To clarify this matter, extensive follow-up research is required in which detailed local and species-specific information is gathered" [10]. Furthermore the Health Council concluded that the method of Romijn et al. for the terrestrial route has several important limitations. Firstly, the BCF is probably not a suitable parameter to predict accumulation of xenobiotics in soil organisms via uptake from soil. Secondly, the Health Council doubted whether the route via earthworms is the most critical one with respect to secondary poisoning in terrestrial ecosystems. This is also concluded by Romijn et al. themselves who state that "considering the dependence of BCF_{worm} on soil properties, it can be concluded that the algorithm can only be used in defined situations" [23].

About the modifications by Everts et al. the Health Council states: "The committee believes that the use of certain general energy correction factors, as proposed in the DGW's modification, is an

effective addition to the original model. Despite this modification, however, there still remains a large number of uncertainties in the extrapolation from laboratory to the field and, in the committee's view, the modified method is still only suitable for an initial evaluation of the possible effects of toxic substances in the food chain". About the several correction factors the Health Council concluded that the one for differences in caloric content of the different types of food (e.g. cereals versus worms) has a firmer scientific basis than the other ones. With respect to the combining of data sets for calculating a MPC the Health Council has a slight preference to keeping the data for lower organisms and top predators separate (method I in Figure 2). According to the Health Council method I is more in agreement with one of the purposes of environmental policy in The Netherlands: a separate conservation strategy for top predators.

Based on the discussion within the project and on the advice of the Health Council it has been decided to use the following approach:

1. As method I and II have advantages as well as disadvantages MPCs will be calculated using both methods. Based on these results it will be decided which method must be preferred (see Chapter 4).

If less than 4 NOECs are available the EPA method is applied in method II. As data for certain taxonomic groups are not required in contrast to the method for aquatic and terrestrial organisms (see Tables 2.3 and 2.4, respectively), the EPA method has to be slightly modified. This is presented in Table 2.6. Birds and mammals are both considered as one taxonomic group.

Table 2.6. Modified EPA method used in method II.

available information	Assessment factor
less than 3 acute LC50 values from different taxonomic groups and no chronic NOECs	1,000
at least 3 acute LC50 values from different taxonomic groups and no chronic NOECs	100
less than 3 chronic NOECs from different taxonomic groups	10*
3 chronic NOECs from different taxonomic groups	10

* this value is subsequently compared to the extrapolated value based on acute LC50 toxicity values. The lowest one is selected

2. Only the correction factor for differences in caloric content of food (cereals versus fish or mussels) will be applied. Ruys and Pijnenburg derived their correction factors for differences between caloric content of laboratory food and fish or mussels for birds only. Based on preliminary results of the project mentioned in paragraph 2.8.1 of the National Institute of Public Health and Environmental Protection in collaboration with the National Institute for Coastal and Marine Management it is decided to use these correction factors also for mammals because the caloric content of fodder for laboratory birds and mammals is almost the same: 14.8 and 16.8 kJ/g based on fresh weight for birds and mammals, respectively [38].

Summarizing, the following formulas are used to calculate a MPC for secondary poisoning for the aquatic route:

$$MPC_{water} = \frac{NOEC_{bird ; mammal} \times 0.32}{BCF_{fish}} \quad (9)$$

$$MPC_{water} = \frac{NOEC_{bird ; mammal} \times 0.20}{BCF_{mussel}} \quad (10)$$

The most critical route will be selected as the MPC for water for secondary poisoning. Although it can be assumed that for organic compounds the BCF for fish is higher than the one for mussels, due to the higher lipid content of fish, the critical route may not always be via fish. Because mussels have a lower caloric value leading to a higher correction factor, birds or mammals must consume more mussels compared to fish for the same amount of energy needed, leading to a higher body burden of the pollutant.

Experimentally determined BCFs for fish and mussels are used. The geometric mean value will be used to calculate MPCs while the maximum BCF will be used in an evaluative sense: if there is no risk for secondary poisoning using the maximum BCF also, this conclusion can be drawn more firmly. If no experimental data are available calculated BCFs are used.

In the same project as mentioned above a correction factor of 0.23 is derived for earthworms based on Westerterp et al. [39]. It should be stated that this correction factor is based on a limited data-set compared to the one for mussels and fish.

$$MPC_{soil} = \frac{NOEC_{bird ; mammal} \times 0.23}{BCF_{worm}} \quad (11)$$

For organic compounds a mean and maximum BCF for worms of 1 and 10 is used, respectively. For metals experimentally determined BCFs for earthworms are used. The maximum BCF will be used in the same sense as for the aquatic route.

3. 'attention species': In The Netherlands a number of species have been selected as deserving priority in environmental policy [1]. Examples are seals, porpoises, bottle-nose dolphins and sandwich terns [33]. Environmental quality objectives should be set at such a level that no adverse effects will occur for these species. Experimental data, either laboratory or from field investigations, for such species are obviously very scarce. It is decided to do no extensive literature search in 'phase 1' to obtain effect data for these species but to compare the derived MPC with the lowest toxicity data for birds and mammals. This comparison is used as an indication for the risk for 'attention species'. In 'phase 2' more detailed data will be gathered.
4. this method is regarded as a first assessment of the potential for secondary poisoning, and can be regarded as 'phase 1 research'. If the method indicates that there is a risk for secondary poisoning, more research is needed in a sense described as 'phase 2 research' in the report of the Health Council. Therefore, in the present report toxicological data for birds and mammals tested in the laboratory are obtained from review articles and monographs, only. In 'phase 2' an extensive literature search will be carried out, next to obtaining local and species-specific information (field studies).

3. RESULTS

Toxicity data for freshwater organisms, saltwater organisms, soil organisms, birds and mammals and BCFs for fish and bivalves are presented in the annex to this report. In the following paragraphs several manipulations of these data will be presented. Several MPCs are calculated in these paragraphs. The following terminology is used:

MPC_{direct} :	MPC based on direct effects (aquatic and terrestrial organisms),
MPC_{sp} :	MPC based on secondary poisoning,
$MPC_{aq.}$:	MPC for surface water,
MPC_{soil} :	MPC for soil,
MPC_{sed} :	MPC for sediment,
MPC_{bird} :	MPC based on direct effects on birds,
MPC_{mammal} :	MPC based on direct effects on mammals.

3.1 Bioconcentration factors

3.1.1 BCFs for fish

Geometric mean and maximum BCFs are presented in table 3.1, with the number of data in parenthesis. Some comments have to be made with respect to several compounds.

No data are available for aldrin. Aldrin is rapidly converted into dieldrin in water, however [40]. After 33 days in a model ecosystem study only 0.5% of the original applied radioactive aldrin was detected by Metcalf et al. in the mosquitofish (*Gambusia affinis*), which was the organism at the top of this model food chain [41]. Therefore it is assumed that the BCF for aldrin is equal to the one for dieldrin.

For carbofuran no reliable BCF was found. A value of 2.6 l/kg is presented in a limited test, in which ^{14}C -carbofuran is added to a sediment-water system. This value supports remarks found in literature that carbofuran has no bioaccumulating potency.

For copper Janus et al. give ranges of 150-700 l/kg for saltwater fish and 1-450 l/kg for freshwater fish [42]. In a study of Seim et al. whole body concentrations are determined. After 78 days exposure to 3 (control), 6, 9, 16 and 31 $\mu g/l$, whole body concentrations of approximately 0.45, 0.53, 0.54, 0.57 and 0.78 $\mu g/g$ based on dry weight, respectively are found [43]. If it is assumed that dry weight is 20% of wet weight, corresponding BCFs of 300, 176, 120, 72, and 50 l/kg, respectively can be calculated. From this study it can be concluded that with increasing water concentrations the content in fish hardly increases. This conclusion is supported by a study in which BCFs are determined for several tissues and a short-term bioaccumulation study [44, 45]. It can be suggested that fish have an effective excretory mechanism for copper which enables them to maintain a constant body concentration when water concentrations are at sublethal concentrations. Because in the present report a first assessment of the potential for secondary poisoning is carried out, it is decided to use the geometric mean value of the BCFs measured by Seim et al [43].

For fenthion only one experimental BCF is available from a study with exposure to a mixture of seven compounds.

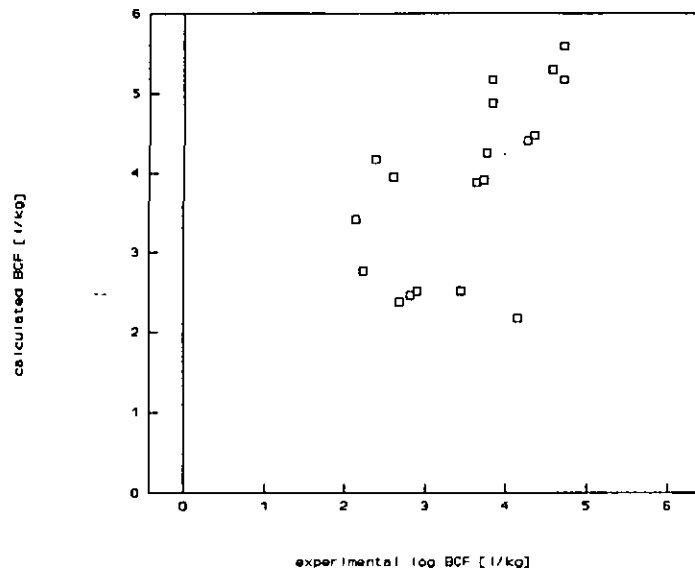


Figure 3. Laboratory derived BCFs and calculated BCFs for fish using $BCF = 0.048 K_{ow}$.

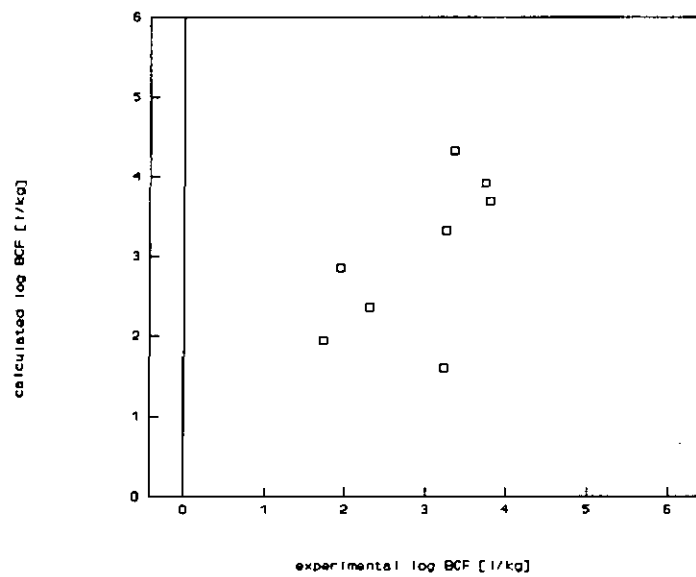


Figure 4. Laboratory derived BCFs and calculated BCFs for mussels using $BCF = 0.013 K_{ow}$.

The low BCF values of pentachlorophenol for saltwater fish might be explained by the high ionic strength of saltwater causing dissociation to the phenolate anion. In freshwater pH levels above 5-6 have a similar effect.

For thiram no BCF data are available.

As can be seen from Figure 3 for most compounds the calculated BCFs are comparable with the geometric mean BCFs obtained from laboratory experiments. For endosulfan and especially for heptachlor epoxide the experimental BCFs are much higher than the calculated ones. For aldrin, chlorpyrifos, DDD, DDE, DDT, dieldrin, pentachlorophenol and quitozene the calculated BCFs are higher than the experimental ones. The low BCFs for pentachlorophenol have already been discussed above. For chlorpyrifos and quitozene the difference between calculated and experimental BCFs is probably caused by biotransformation [46, 47]. For the other compounds this may also be the case, although most are relatively stable compounds.

Table 3.1 Whole body bioconcentration factors for fish (l/kg): geometric mean BCFs for saltwater, freshwater and fresh- and saltwater fish together are presented as well as the maximum BCFs and calculated BCFs based on K_{ow} (see paragraph 2.5).

compound	saltwater fish BCF (n)	freshwater fish BCF (n)	salt- and freshwater fish BCF (n)	maximum BCF	calculated BCF
aldrin	-	-	6,700 ^a	13,000 ^a	150,000
cadmium	-	-	38 (7)	540	
carbofuran	-	-	-	-	10
chlordane	12,000 (4)	38,000 (1)	22,000 (5)	38,000	30,000
chlorpyrifos	270 (4)	1,700 (1)	400 (5)	1,700	8,900
copper	120	-	120	-	
p,p'-DDD	-	-	-	-	80,000
p,p'-DDE	-	-	51,000 (1)	-	150,000
p,p'-DDT	-	-	52,000 (3)	93,000	390,000
o,p'-DDT	-	-	37,000 (1)	-	200,000
dieldrin	-	-	6,700 (9)	13,000	76,000
endosulfan	2,800 (1)	-	2,800 (1)	-	330
endrin	2,300 (2)	8,200 (2)	4,300 (4)	12,000	7,600
fenthion	-	170 (1)	170 (1)	-	590
α -HCH	-	-	650 (8)	1,200	290
β -HCH	-	800 (6)	800 (6)	1,500	330
γ -HCH	-	-	480 (14)	1,600	240
heptachlor	4,900 (3)	9,500 (1)	5,800 (4)	9,500	18,000
heptachlor epoxide	-	14,000 (1)	14,000 (1)	-	150
hexachlorobenzene	-	-	18,000 (3)	22,000	26,000

compound	saltwater fish BCF (n)	freshwater fish BCF (n)	salt- and freshwater fish BCF (n)	maximum BCF	calculated BCF
mercury	-	-	300 (6)	5,700	
methyl-mercury	-	-	14,000 (5)	35,000	
pentachlorobenzene	-	5,300 (2)	5,300 (2)	8,100	7,300
pentachlorophenol	38 (2)	340 (3)	140 (5)	770	2,600
quintozone	-	240 (1)	240 (1)	-	15,000
thiram	-	-	-	-	2.8

^a assumed equal to dieldrin

3.1.2 BCFs for bivalves

A summary of the BCFs for bivalves obtained from a literature search by Eys are presented in the annex to the present report [48]. For many compounds no data could be retrieved from literature. Also, for several compounds only field data are available. Geometric mean and maximum BCFs are presented in table 3.2, with the number of values in parenthesis.

For copper field BCFs are much lower than BCFs derived from laboratory experiments. The explanation may be the same as for fish resulting in low BCFs for bivalves tested in laboratory experiments (high exposure concentrations) and high BCFs for bivalves measured in the field (low exposure concentrations).

Table 3.2 Whole body bioconcentration factors for bivalves (l/kg): geometric mean BCFs for saltwater, freshwater, fresh- and saltwater bivalves together are presented as well as the maximum BCFs and calculated BCFs.

compound	saltwater bivalves BCF (n)	freshwater bivalves BCF (n)	salt and fresh- water bivalves BCF (n)	maximum BCF	calculated BCF
aldrin	-	-	2,200 ^a	-	41,000
cadmium	-	-	1,400 ^b (1)	2,900 ^b	
carbofuran	-	-	-	-	3
chlordane	5,400	140 ^b	5,400 (1)	-	8,200
chlorpyrifos	-	-	-	-	2,400
copper	480 ^b (1)	780 ^b (2)	610 ^b (3)	800 ^b	
copper	8.1 (3)	-	8.1 (3)	79	

compound	saltwater bivalves BCF (n)	freshwater bivalves BCF (n)	salt and fresh- water bivalves BCF (n)	maximum BCF	calculated BCF
p,p'-DDD	-	-	-	-	22,000
p,p'-DDE	-	-	118,000 ^b	310,000 ^b	41,000
p,p'-DDT	-	-	151,000 ^b	690,000 ^b	110,000
o,p'-DDT	-	-	-	-	53,000
dieldrin	-	-	2,200 (2)	3,100	21,000
endosulfan	53 (3)	-	53 (3)	600	88
endrin	1,800 (2)	-	1,800 (2)	1,900	2,100
fenthion	-	-	-	-	160
α -HCH	-	-	-	-	78
β -HCH	-	-	-	-	90
γ -HCH	-	-	200 (1)	-	64
heptachlor	6,300 (1)	-	6,300 (1)	-	4,900
heptachlor epoxide	1,700 (1)	-	1,700 (1)	-	40
hexachlorobenzene	-	-	-	-	7,000
mercury	-	-	2,500 (2)	5,300	
methyl-mercury	-	-	13,000 (1)	-	
pentachlorobenzene	-	-	-	-	2,000
pentachlorophenol	60 (1)	130 (1)	88 (2)	130	710
quintozone	-	-	-	-	4,100
thiram	-	-	-	-	0.7

^a assumed equal to dieldrin.

^b based on field data

As can be seen from Figure 4 also for bivalves experimental BCFs are comparable with calculated ones. Again heptachlor epoxide and pentachlorophenol are exceptions.

3.1.3 Comparison of BCFs for fish and bivalves

Comparing BCFs for fish and bivalves it can be concluded that for most compounds BCFs for fish are higher than the ones for bivalves. For organic compounds this is expected because fish have a higher lipid content than bivalves (it is well known that organic compounds accumulate in lipid). Only for p,p'-DDE and p,p'-DDT BCFs for bivalves measured in the field are much higher than the ones for fish from laboratory experiments.

For metals the situation may be different. Only for mercury and methyl-mercury reliable laboratory tests for bivalves are available resulting in comparable BCFs to the ones for fish for methyl-mercury and much higher BCFs for mercury. Field BCFs for copper and cadmium are considerably higher than the experimental BCFs for fish. Based on these scarce data it cannot be excluded that bivalves accumulate these metals to a higher extent than fish.

As already stated in paragraphs 2.5 and 2.8.2 the geometric mean and maximum BCF for fish and mussels will be used for assessing effects due to secondary poisoning. These are derived from the values from laboratory experiments presented in Tables 3.1 and 3.2. If no experimental data are available calculated BCFs are used. Field BCFs for mussels are regarded as a kind of 'phase 2 research' as described in paragraph 2.8.2.

The geometric mean value will be used to calculate MPCs while the maximum BCF will be used in an evaluative sense: if there is no risk for secondary poisoning using the maximum BCF also, this conclusion can be drawn more firmly.

3.1.4 BCFs for earthworms

As already stated in paragraphs 2.5 and 2.8.2 for all organic compounds a mean and maximum BCF of 1 and 10, respectively will be used.

For cadmium Romijn et al. derived a geometric mean and maximum BCF of 2.70 and 39.5, respectively from reliable laboratory and field studies. These BCFs are standardized to a soil with a pH of 6.5 based on the following relation using a QSAR from Ma [49]:

$$BCF_{\text{standardized}} = BCF_{\text{experiment}} \times e^{-4.89+0.752 \times pH} \quad (12)$$

For mercury and methyl-mercury almost no data on BCFs were found by Romijn et al. For both compounds only one reliable study was available. For inorganic mercury a geometric mean and maximum BCF was derived of 0.36 and 0.39, respectively. For methyl-mercury these values were 8.28 and 8.31, respectively. No standardization was carried out by Romijn et al. because of the lack of information on the relation between BCF and soil parameters. It is decided to use a geometric mean and maximum BCF of 0.36 and 3.6, respectively for inorganic mercury and 8.3 and 83, respectively for methyl-mercury. These maximum BCFs are used to be consisted with the approach used for organic compounds and because in the experiments mentioned above with mercury and methyl-mercury two concentrations were tested using one earthworms species in one type of soil.

In an extensive review on copper Slooff et al. concluded that the concentration in worms increases with increasing concentration in soil, but BCFs are usually less than 1 [50]. Therefore a mean and maximum BCF of 1 and 10, respectively is assumed.

3.2 Maximum permissible concentrations for surface water based on direct effects

Toxicity data for aquatic organisms are presented in the annex to this report (sensitivity plots of chronic toxicity data are presented in paragraph 4.3). Using data for freshwater organisms, saltwater organisms and the combined data sets $MPC_{\text{direct; aq.}}$ s are calculated. These are presented in Table 3.3. Toxicity data used as input for the modified EPA or Aldenberg and Slob method are given in appendix A.

The $MPC_{\text{direct; aq.}}$ based on freshwater toxicity data is for most compounds almost equal to the one based on saltwater toxicity data. Differences are mainly caused by the use of different extrapolation methods as the modified EPA method normally leads to lower extrapolated values than the method of Aldenberg and Slob. An extreme example is γ -HCH

Table 3.3 Maximum permissible concentrations ($\mu\text{g/l}$) for freshwater, saltwater and combined data sets.

compound	MPC _{direct; eq.} freshwater ($\mu\text{g/l}$)	MPC _{direct; eq.} saltwater ($\mu\text{g/l}$)	MPC _{direct; eq.} combined ($\mu\text{g/l}$)	lowest NOEC ($\mu\text{g/l}$)	lowest L(E)C50 ($\mu\text{g/l}$)
aldrin	-	-	0.029 ^a	3.3	0.32
cadmium	0.16 (5.5 ^b)	6.1 (5.9)	0.38 (3.7)	0.085	
carbofuran	0.016 ^c	0.015 ^c	0.015 ^c	0.5	1.5
chlordane	0.03 ^c	0.0015 ^c	0.0015 ^c	0.015	0.4
chlorpyrifos	0.00011 (9.1 10 ⁶)	0.00035 ^c	0.0028 (113)	0.012	0.035
copper	3.9 (1.8)	6.4 (7.4)	4.1 (1.7)	4.0	
p,p'-DDD	-	-	0.005 ^d	-	2.4
p,p'-DDE	-	-	0.005 ^d	0.1	2.5
p,p'-DDT	-	-	0.005 ^d	0.05	0.36
o,p'-DDT	-	-	0.005 ^d		
endosulfan	0.013 (4.6 10 ⁵)	0.0004 ^c	0.0004 ^c	0.2	0.04
endrin	0.00089 ^c	0.0031 (155)	0.003 ^{c,*}	0.03	0.037
dieldrin	0.083 (75)	0.01 ^c	0.029 (31)	0.12	
fenthion	0.00062 ^c	0.0002 ^c	0.0031 (6.1 10 ⁶)	0.037	0.024
α -HCH	2.2 (110)	5 ^c	3.5 (41)	9	500
β -HCH	17 (20)	1 ^c	6.1 (24)	10	-
γ -HCH	0.86 (14)	0.00017 ^c	1.0 (14)	2.2	
heptachlor	0.0009 ^c	0.00046 ^c	0.00046 ^c	0.86	0.046
heptachlor epoxide			0.00046 ^f	-	0.04
hexachlorobenzene	-	-	2.4 ^g		
mercury	0.02 (22)	0.22 (14)	0.056 (6.4)	0.02	
methyl-mercury	-	-	0.056 ^h		
pentachlorobenzene	-	-	7.5 ^g		
pentachlorophenol	3.2 (6.1)	2.6 (62)	3.5 (4.5)	3.2	
quintozone	0.29 ^c	-	0.29 ^c	-	290
thiram	0.032 ^c	-	0.032 ^c	0.32	30

^a set equal to the MPC_{direct; eq.} for dieldrin

^b between brackets: ratio between MPC_{50% confidence} and MPC_{95% confidence} calculated with method of Aldenberg and Slob

^c indicative MPC_{direct; eq.} calculated using the modified EPA method

^d set equal to 0.005 $\mu\text{g/l}$ based on total information on DDT and derivatives

^e MPC using EPA method because logistic distribution of NOEC values is rejected at 1% (see paragraph 2.7.2). MPC based on method of Aldenberg and Slob is 0.0045 $\mu\text{g/l}$

^f MPC set equal to the one for heptachlor

^g MPC calculated by Van de Plassche et al. using QSARs [6, 51]

^h MPC_{direct; eq.} for mercury and methyl-mercury set equal (in Van de Meent et al. no distinction is made between mercury and methyl-mercury [3])

(see also sensitivity plot on page). For mercury and cadmium freshwater organisms seem to be more sensitive than saltwater organisms (both $MPC_{direct; aq.}$ s are calculated using the method of Aldenberg and Slob).

With respect to the $MPC_{direct; aq.}$ values derived in Table 3.3 a number of specific remarks can be made for several compounds:

As with the BCF for aldrin, the $MPC_{direct; aq.}$ for this compound is set equal to the one for dieldrin because aldrin is rapidly epoxidized into dieldrin in surface waters. The $MPC_{aq.}$ based on the toxicity data for aldrin as presented in the annex is $0.0032 \mu\text{g/l}$ for the combined data set using an assessment factor of 100 on the lowest LC50. This value is lower than the one for dieldrin due to the use of different extrapolation methods. Only two chronic studies are available for aldrin, compared to six for dieldrin. Subsequently, the method of Aldenberg and Slob could be applied for dieldrin while the modified EPA method had to be applied for aldrin.

For carbofuran and chlordane the modified EPA method is used. If the EPA method as presented in Table 2.3 is applied strictly a factor of 1,000 on the lowest L(E)C50 had to be applied because for both compounds no toxicity data are available for algae. However, for carbofuran and chlordan a considerable amount of NOECs and L(E)C50s are available for a.o. fish, crustaceans and insects. Because chlordan is an insecticide and carbofuran an insecticide/acaricide/nematicide it can be expected that toxicity tests with algae will not result in lower NOECs or EC50s compared to the ones already available. It is therefore considered acceptable to apply a lower factor instead of 1,000 on the lowest L(E)C50.

An overall $MPC_{direct; aq.}$ is derived for DDT and its degradation products DDE and DDD. For none of these compounds sufficient chronic information is available to apply the method of Aldenberg and Slob. Based on the modified EPA method $MPC_{direct; aq.}$ s are 0.0024 , 0.0025 and $0.005 \mu\text{g/l}$ for DDD, DDE, and DDT, respectively using data for salt- as well as freshwater organisms. The lower values for DDD and DDE compared to DDT are caused by the use of higher assessment factors because these compounds have been studied less. However, the available data show that DDT is the most toxic to aquatic organisms as has also been concluded by others [52]. It is therefore decided to use the $MPC_{direct; aq.}$ derived for DDT also for DDE and DDD.

The $MPC_{direct; aq.}$ for endosulfan based on the combined data sets is calculated using the EPA method although enough chronic data are available to apply the method of Aldenberg and Slob. The $MPC_{direct; aq.}$ of $0.12 \mu\text{g/l}$ based on the latter method is higher than several LC50 values, e.g. 0.04 for *Peneaus duorarum*, $0.1 \mu\text{g/l}$ for *Morone saxatilis* and $0.09 \mu\text{g/l}$ for *Leiostomus xanthurus*. Obviously, chronic data are available for relatively insensitive species only. This is also the case for the only chronic NOEC for fish available, i.e. $0.2 \mu\text{g/l}$ for *Sarotherodon mossambicus*. It is well known that endosulfan, especially the α -isomer, is highly toxic to fish [53].

Although for fenthion the variation in chronic data available is large (see sensitivity plot on page) the $MPC_{direct; aq.}$ presented in Table 3.3 seems a reasonable value considering the lowest NOEC present of $0.037 \mu\text{g/l}$. One saltwater crustacean, *Penaeus spec.*, is extremely sensitive for fenthion: the lowest L(E)C50 value is $0.024 \mu\text{g/l}$ (no chronic data available). Acute L(E)C50 values for all other crustaceans, 10 species in total, are more than a factor 10 higher. Using the acute-chronic ratio of c. 7 for *Mysidopsis bahia* (for the other crustaceans no chronic data are available) a NOEC of $0.0034 \mu\text{g/l}$ for *Penaeus spec.* can be derived. Although this NOEC value must be considered as an indicative one, it can be concluded that the $MPC_{direct; aq.}$ seems reasonable.

The same accounts for endrin for which also a LC50 for *Penaeus duorarum* can be

considered as a test-result for an extremely sensitive species. For endrin enough NOECs are available to apply the method of Aldenberg and Slob. However, the Kolmogorov-Smirnov $D \cdot \sqrt{n}$ test rejected the distribution of NOECs as being log-logistic at a significance level of 1% (see paragraph 2.5.2). Looking at the chronic toxicity data this can be expected: the distribution seems bimodal (see sensitivity plot on page). On the other hand it is remarkable that also algae are sensitive species: based on the working-mechanism of endrin no values can be left out. Therefore, the modified EPA method is applied, using a factor 10 on the lowest NOEC for *Palaemonetes pugio*, a saltwater crustacean. It must be stated that the $MPC_{direct; aq.}$ based on the modified EPA method doesn't differ much from the one using the method of Aldenberg and Slob: 0.003 versus 0.0045 $\mu\text{g/l}$, respectively.

The value for heptachlor epoxide, being a persistent degradation product of heptachlor, is set equal to the one for heptachlor. The $MPC_{direct; aq.}$ for heptachlor epoxide based on aquatic toxicity data presented in the annex is 0.00004 $\mu\text{g/l}$. This value is lower than the one for heptachlor because only a few toxicity data are available for heptachlor epoxide leading to the use of high assessment factors in the modified EPA method.

Emans et al. compared NOEC values derived from field studies with results from extrapolations method, a.o. the modified EPA method and the method of Aldenberg and Slob [54]. They report a NOEC for the most sensitive species tested in the experiment, called the multiple species NOEC (MS NOEC). For cadmium, copper, dieldrin, γ -HCH, mercury and pentachlorophenol MS NOECs of 0.07-2.3, 0.3-4.0, 2.6, 0.1- ≥ 0.5 and 20 $\mu\text{g/l}$ are presented. Stephenson et al. tested γ -HCH in outdoor artificial streams and derived a NOEC of 0.22 $\mu\text{g/l}$ [55]. Although differences occur, it can be concluded that the $MPC_{direct; aq.}$ agree reasonably well with these NOECs derived from field tests.

3.3 Maximum permissible concentrations for soil based on direct effects

Toxicity data for soil organisms are presented in the annex to this report (sensitivity plots of chronic toxicity data for cadmium and copper are presented in paragraph 6.4). Using these data $MPC_{direct; soil}$ s are calculated and presented in Table 3.3. Toxicity data used as input for the modified EPA or Aldenberg and Slob method are given in appendix B. For p,p'-DDD, p,p'-DDE, o,p'-DDT, fenthion, α -HCH, β -HCH and quintozone no toxicity data for soil organisms are available so no $MPC_{direct; soil}$ can be calculated for these compounds. For these compounds the equilibrium partitioning method can be used to derive MPC_{soil} s (see Chapter 6).

Toxicity data are very scarce for soil organisms. Only for cadmium and copper the method of Aldenberg and Slob can be applied. For all other compound the modified EPA method is used to derive a $MPC_{direct; soil}$. For several compounds this leads to relatively low values, e.g. for carbofuran, chlordane, chlorpyrifos, endrin, heptachlor and heptachlor epoxide. The $MPC_{direct; soil}$ for these compounds are based on experiments with insects and collembola. It can be assumed that these organisms belong to relatively sensitive taxonomic groups for as all are insecticides.

With respect to the $MPC_{direct; aq.}$ values derived in Table 3.4 a number of specific remarks can be made for several compounds:

One single $MPC_{direct; soil}$ is derived for aldrin and dieldrin because epoxidation of aldrin takes place rapidly in soil [40]. Considering the whole data-set for both compounds the $MPC_{direct; soil}$ of 0.05 mg/kg as has been derived by Van de Meent et al. for dieldrin seems a

reasonable value [3].

The value for carbofuran is calculated using the modified EPA method as presented in Table 2.4. If the method is applied strictly a factor of 1,000 on the lowest L(E)C50 has to be applied because no toxicity data are available for plants. As acute data are present for at least 4 taxonomic groups it is considered acceptable to lower this factor to 100.

The $MPC_{direct; soil}$ for heptachlor epoxide is set equal to the one for heptachlor, calculated with the modified EPA method. The lowest L(E)C50 of 0.1 mg/kg for *Folsomia candida* for heptachlor epoxide leads to a lower $MPC_{direct; soil}$. For almost all compounds this organism appears to be very sensitive. For heptachlor epoxide the other L(E)C50 values are at least a factor 100 higher, although it must be stated that only for three organisms data are available. It is considered acceptable to set the $MPC_{direct; soil}$ for heptachlor epoxide at 0.0007 mg/kg.

Table 3.4 Maximum permissible concentrations (mg/kg) for soil in standard soil

compound	$MPC_{direct; soil}$ (mg/kg)	lowest NOEC (mg/kg)	lowest L(E)C50 (mg/kg)
aldrin	0.05 ^{a, b}	1.5	0.55
cadmium	0.27 (17) ^c	0.75	185
carbofuran	0.0047 ^b	0.5	0.47
chlordane	0.0043 ^b	1.7	4.3
chlorpyrifos	0.00036 ^b	0.46	0.36
copper	6.2 (33) ^c	13	140
p,p'-DDT	0.01 ^b	-	10
dieldrin	0.05 ^b	0.5	1.1
endosulfan	0.05 ^b	170	5.0
endrin	0.00095 ^b	-	0.95
γ -HCH	0.005 ^b	0.05	0.95
heptachlor	0.0007 ^b	-	0.7
heptachlor epoxide	0.0007 ^{b, d}	-	0.1
hexachlorobenzene	1.3 ^e		
mercury	0.2 ^b	2	-
methyl-mercury	0.2 ^{b, f}		
pentachlorobenzene	0.3 ^{b, e}		
pentachlorophenol	0.17 ^b	1.7	30
thiram	0.038 ^b	0.38	-

^a set equal to the $MPC_{direct; soil}$ for dieldrin

^b indicative $MPC_{direct; soil}$ based on the modified EPA method

^c between brackets: ratio between $MPC_{50\% confidence}$ and $MPC_{95\% confidence}$ calculated with the method of Aldenberg and Slob

^d set equal to $MPC_{direct; soil}$ for heptachlor

^e indicative $MPC_{direct; soil}$ calculated by Van de Plassche and Bockting [6] (the value for hexachlorobenzene is based on equilibrium partitioning while the one for pentachlorobenzene is based on toxicity data for soil organisms)

^f set equal to $MPC_{direct; soil}$ for mercury (in Van de Meent et al. no distinction is made between mercury and methyl-mercury [3])

3.4 Maximum permissible concentrations for birds and mammals

Toxicity data for birds and mammals are given in Appendix C (sensitivity plots of chronic toxicity data are presented in paragraph 4.3). In Table 3.5 MPCs are presented using these toxicity data as input for extrapolation methods. MPCs are calculated based on data for birds and mammals separately and based on data for birds as well as mammals. For copper, α -HCH and pentachlorobenzene no toxicity data for birds are available while for p,p'-DDD, p,p'-DDE and o,p'-DDT no toxicity data for mammals could be found.

For birds chronic data are scarce. Often NOECs had to be derived applying high factors because severe effects were observed at the lowest test concentration; e.g. aldrin, chlorpyrifos, endrin and thiram. With respect to the MPC values derived in Table 4.3 a number of specific remarks can be made for several compounds:

The lowest NOECs available, and consequently also the MPC_{birds} for heptachlor and heptachlor epoxide differ considerably, while the data for mammals show an almost equal toxicity for these two compounds. For both compounds only one NOEC is available for birds: for heptachlor 50 mg/kg food for Japanese quail (*Coturnix c. japonica*) and for heptachlor epoxide 0.02 mg/kg food for chickens (*Gallus domesticus*), respectively. The low value for chickens might be an overestimation of toxicity, however. First of all it is known from studies with mammals that heptachlor is rapidly metabolized to the epoxide which is similar in toxicity to heptachlor [56]. Secondly, it is stated in a review from IPCS that hatchability was only slightly decreased in eggs from the chickens fed 0.1 and 0.2 mg/kg (the latter being the highest dose tested), while the viability of hatched chickens was not affected [56]. The original study could not be obtained, however.

The data on the HCH isomers show that β -HCH may be more toxic to mammals than the other isomers. This is possibly caused by an effect on the endocrine organs: an estrogenic potency of β -HCH has been shown [57].

Romijn et al. state one should be careful when combining data sets for birds and mammals because there are indications that birds and mammals are not equally sensitive to xenobiotics [13, 58]. However, comparison of the sensitivity of birds and mammals for the compounds discussed in the present report is hampered by the lack of toxicity data. Only for a few compounds enough NOEC values are available to allow such a comparison. The following conclusions can be drawn (see sensitivity graphs on pages):

- aldrin and dieldrin: birds seem to be more sensitive than mammals for aldrin although it must be stated that for birds only LOECs are available. This difference in sensitivity is remarkable because for dieldrin birds seem only slightly more sensitive and because it is known from metabolism studies in mammals that aldrin is rapidly transformed to dieldrin by mixed-function mono-oxygenases in the liver [40].
- cadmium: one NOEC value for birds for *Meleagris gallopavo* is much lower than all the other ones: 8 and 15 times lower than the next NOEC for birds and the lowest NOEC for mammals, respectively. Based on these data it cannot be excluded that birds are more sensitive than mammals.
- γ -HCH: one NOEC value for birds for *Gallus domesticus* is much lower than all the other ones: 63 and 16 times lower than the next NOEC for birds and the lowest NOEC for mammals, respectively. However, for birds only two NOECs are present. Based on these data it cannot be excluded that birds are more sensitive than mammals.

Table 3.5 MPC (mg/kg food) for birds, mammals and combined data sets.

compound	MPC _{bird} (mg/kg food)	lowest 5 d LC50 (n ^a) (mg/kg food)	lowest NOEC (n ^a) (mg/kg food)	MPC _{mammal} (mg/kg food)	lowest NOEC (n ^a) (mg/kg food)	MPC _{bird + mammal} (mg/kg food)
aldrin	0.005 ^b	34 (4)	0.05 (2)	0.34 (200)	1.25 (4)	0.16 (89)
cadmium	0.041 (3,700)	562 (3)	0.2 (4)	2.3 ^b (17)	3 (5)	0.35 (14)
carbofuran	0.26 ^b	23 (4)	2.6 (3)	1.7 ^b	17 (3)	2.0 (14)
chlordane	3.3 ^b	330 (4)	-	3 ^b	30 (1)	3 ^b
chlorpyrifos	4.9 (9.1 ^c)	190 (3)	12.5 (4)	0.6 ^b	6 (1)	3.7 (6.3)
copper	-	-	-	2.4 (490)	7 (4)	2.4 (490)
p,p'-DDD	0.11 ^b	445 (4)	1.1 (1)	-	-	0.11 ^b
p,p'-DDE	0.15 (20)	825 (4)	0.3 (7)	-	-	0.15 (20)
p,p'-DDT	0.21 (22)	311 (8)	0.5 (7)	7.4 (14)	20 (6)	0.47 (22)
o,p'-DDT	5 ^b	-	50 (1)	-	-	5 ^b
dieldrin	0.29 (8.1)	107 (5)	0.5 (7)	0.35 (12)	1.0 (6)	0.38 (3.2)
endosulfan	8.1 ^b	805 (4)	-	0.68 (140)	3.3 (4)	0.68 (140)
endrin	0.13 (20)	14 (4)	0.25 (4)	0.074 (14)	0.62 (4)	0.085 (990)
fenthion	0.03 ^b	3 (5)	-	0.013 ^b	0.13 (1)	0.013 ^b
α-HCH	-	-	-	5 ^b	50 (1)	5 ^b
β-HCH	63 ^b	-	≥630 (1)	0.2 ^b	2 (1)	0.2 ^b
γ-HCH	0.16 ^b	425 (4)	1.6 (2)	2.5 ^b	25 (3)	1.2 (83)
heptachlor	0.9 ^b	92 (4)	50 (1)	0.6 ^b	6 (1)	0.6 ^b
heptachlor epoxide	0.002 ^b	-	0.02 (1)	0.7 ^b	7 (1)	0.002 ^b
hexachlorobenzene	0.5 ^b	617 (1)	5 (1)	0.07 (720)	0.5 (5)	0.12 (120)
mercury	0.4 ^b	2,805 (3)	4 (2)	2 ^b	20 (1)	0.4 ^b
methyl-mercury	0.093 (22)	40 (1)	0.25 (5)	0.097 (40)	0.22 (4)	0.12 (4.4)
pentachlorobenzene	-	-	-	0.5 ^b	5 (2)	0.5 ^b
pentachlorophenol	25 ^b	3,400 (4)	245 (1)	5.5 ^b	55 (2)	5.5 ^b
quintozene	10 ^b	-	100 (1)	2.5 ^b	25 (1)	2.5 ^b
thiram	0.29 ^b	5,000 (4)	2.9 (2)	0.5 ^b	5 (1)	0.29 ^b

^a number of species for which LC50 or NOEC values are available^b indicative MPC based on modified EPA method^c between brackets: ratio between MPC_{50% confidence} and MPC_{95% confidence} calculated with method of Aldenberg and Slob

- p,p'-DDT: a substantial amount of chronic data are present for birds as well as mammals. Based on these data it can be concluded that birds are more sensitive: mean NOECs are 130 and 12 mg/kg food for mammals and birds, respectively.
- endrin and methyl-mercury: birds and mammals seem to be equally sensitive.
- carbofuran: birds may be slightly more sensitive, although only 3 NOECs are available for each group.

Combining data sets for birds and mammals leads for cadmium and aldrin to MPCs higher than the lowest NOEC available. For carbofuran, chlorpyrifos, p,p'-DDE, p,p'-DDT, dieldrin, γ -HCH and methyl-mercury the lowest NOEC is less than a factor 2 higher than the MPC based on the combined data sets. For aldrin, cadmium, carbofuran, chlorpyrifos, p,p'-DDT, dieldrin, endrin, hexachlorobenzene and methyl-mercury the MPC based on the combined data set is higher than the MPC_{bird} or MPC_{mammal} . Exceeding factors vary from 1.1 to 32 for endrin and aldrin, respectively. For the latter compound and cadmium, carbofuran and chlorpyrifos these factors are relatively high, i.e. > 6.

3.5 K_p s for soil and sediment

In Table 3.6 K_{oc} s and K_p s are presented that are used for application of the equilibrium partitioning method in Chapter 6. An organic carbon content of 5% is used for soil and sediment to calculate K_p s.

Table 3.6 log K_{oc} and log K_p (l/kg)

compound	log K_{oc}	log K_p soil/sediment
aldrin	5.11	3.81
cadmium		4.92
carbofuran	1.63	0.33
chlordane	4.60	3.30
chlorpyrifos	3.88	2.58
copper		4.54
p,p'-DDD	4.91	3.61
p,p'-DDE	4.82	3.52
p,p'-DDT	5.63	4.33
o,p'-DDT	5.63	4.33
dieldrin		4.57
endosulfan	3.11	1.81
endrin	4.29	2.99
fenthion	3.35	2.05
α -HCH	3.25	1.95
β -HCH	3.36	3.06
γ -HCH		2.40
heptachlor	4.45	3.15
heptachlor epoxide	2.94	1.64

compound	log K_{oc}	log K_p soil/sediment
hexachlorobenzene		2.74
mercury		5.04
pentachlorobenzene		2.60
pentachlorophenol		1.94
quintozone	4.36	3.06
thiram	2.69	1.39

cadmium, copper, dieldrin, γ -HCH, mercury, pentachlorophenol: from Van de Meent et al. [3]

penta- and hexachlorobenzene: from Van de Plassche and Bockting [6]

other compounds: from Bockting et al. [11]

4. SECONDARY POISONING: AQUATIC FOOD CHAIN

4.1 Critical route: via fish or mussel?

In Table 4.1 MPC_{sp}s are presented based on effects on birds and mammals separately, or on the combined data set using the BCF for fish or mussels. For carbofuran, p,p'-DDD, o,p'-DDT, and thiram no laboratory BCFs are available for fish as well as mussels so calculated BCFs are used. For p,p'-DDE, DDT, fenthion, β - and γ -HCH, hexa- and pentachlorobenzene and quintozone only the MPC_{sp} via mussels is based on a calculated BCF. For chlorpyrifos and quintozone no calculated BCF for mussels is used because this leads to an overestimation of the BCF (see paragraph 3.1.1.).

Table 4.1 MPC_{sp} ($\mu\text{g/l}$) for birds, mammals and the combined data set using the geometric mean BCF for fish and mussels.

compound	MPC _{sp} birds		MPC _{sp} mammals		MPC _{sp} combined	
	BCF _{fish}	BCF _{mussel}	BCF _{fish}	BCF _{mussel}	BCF _{fish}	BCF _{mussel}
aldrin	0.00024	0.00045	0.016	0.031	0.0076	0.015
cadmium	0.35	-	20	-	2.9	-
carbofuran	8.3	17	54	110	64	130
chlordane	0.048	0.12	0.044	0.11	0.044	0.11
chlorpyrifos	3.9	-	0.48	-	3.0	-
copper	-	-	6.4	59	6.4	59
p,p'-DDD	0.00044	0.0010	-	-	0.00044	0.0010
p,p'-DDE	0.00094	0.00073	-	-	0.00094	0.00073
p,p'-DDT	0.0013	0.00038	0.045	0.013	0.0029	0.00085
o,p'-DDT	0.043	0.019	-	-	0.043	0.019
dieldrin	0.014	0.026	0.017	0.032	0.018	0.035
endosulfan	0.93	31	0.078	2.6	0.078	2.6
endrin	0.0097	0.014	0.0055	0.0082	0.0063	0.0094
fenthion	0.057	0.038	0.025	0.016	0.025	0.016
α -HCH	-	-	2.5	13	2.5	13
β -HCH	25	140	0.080	0.44	0.080	0.44
γ -HCH	0.11	0.16	1.7	2.5	0.77	1.2
heptachlor	0.044	0.025	0.033	0.019	0.033	0.019
heptachlor epoxide	0.000045	0.00024	0.016	0.082	0.000045	0.00024
hexachlorobenzene	0.0089	0.014	0.0012	0.0020	0.0021	0.0034
mercury	0.43	0.032	2.1	0.16	0.43	0.032
methyl-mercury	0.0021	0.0014	0.0022	0.0015	0.0027	0.0019
pentachlorobenzene	-	-	0.030	0.050	0.030	0.050
pentachlorophenol	57	57	13	13	13	13
quintozone	13	-	3.3	-	3.3	-
thiram	33	83	57	140	33	83

MPC_{sp} using BCFs for mussels and fish are almost equal to each other (difference is less than a factor 2-3): the higher BCF for fish is compensated by the higher correction factor for mussels. Exceptions are endosulfan and mercury caused by the difference in geometric mean BCFs: 2,800 l/kg for fish versus 53 l/kg for mussels for endosulfan and 300 l/kg for fish versus 2,500 l/kg for mussels for mercury. It is unlikely that for endosulfan the difference between both routes is that large, because no indications were found in literature for a specific metabolism route for mussels.

4.2 MPCs for secondary poisoning

In Table 4.2 MPCs incorporating effects due to secondary poisoning are calculated using the two methods described in paragraph 2.6.2:

- method I: the MPC based on direct effects on aquatic organisms ($MPC_{direct\ aq.}$) is compared with the one based on effects on top predators due to secondary poisoning using the BCF for the most critical route (MPC_{sp}). The MPC_{sp} is based on effects on birds and mammals separately, or on the combined data set. In order to decide which route is most critical preference is given to experimentally determined BCFs. For fenthion, heptachlor, mercury and methyl-mercury the critical route is via mussels, while for the other compounds this is the one via fish (see Table 4.1).
- method II in which a MPC is calculated using effect data for aquatic organisms as well as for top predators in one data-set: NOEC values for birds and mammals are divided by the BCF for fish or mussels, depending on the critical route, and used as input data for the modified EPA method or the statistical extrapolation method of Aldenberg and Slob together with $L(E)C50$ and NOEC values for aquatic organisms.

Table 4.2: MPCs using method I based on aquatic organisms ($MPC_{direct\ aq.}$), birds ($MPC_{sp; birds}$), mammals ($MPC_{sp; mammals}$) or data sets of birds and mammals ($MPC_{sp; combined}$) and method II (based on combined data sets for aquatic organisms, birds and mammals) using BCF_{mean} ($\mu g/l$).

compound	method I $MPC_{direct\ aq.}$	MPC_{sp} birds	MPC_{sp} mammals	MPC_{sp}	method II MPC combined	lowest NOEC/BCF for birds and mammals
aldrin	0.029	0.00024	0.016	0.0076	0.00087 (190 ^a)	0.0024
cadmium	0.38	0.35	20	2.9	0.57 (3)	1.7
carbofuran	0.015	8.3	54	64	0.91 (3.6)	83
chlordane	0.0015	0.048	0.044	0.044	0.019 (17)	0.44
chlorpyrifos	0.0028	3.9	0.48	3.0	0.016 (21)	4.8

compound	method I MPC _{direct; aq.}	MPC _{sp} birds	MPC _{sp} mammals	MPC _{sp}	method II MPC combined	lowest NOEC/BCF for birds and mammals
copper	4.1	-	6.4	6.4	3.3 (1.8)	19
p,p'-DDD	0.005	0.00044	-	0.00044	0.00044 ^b	0.0044
p,p'-DDE	0.005	0.00094	-	0.00094	0.0011 (11)	0.0019
p,p'-DDT	0.005	0.0013	0.045	0.0029	0.0047 (7.2)	0.0031
o,p'-DDT	0.005	0.043	-	0.043	0.043 ^b	0.43
dieldrin	0.029	0.014	0.017	0.018	0.012 (5.5)	0.024
endosulfan	0.0004	0.93	0.078	0.078	0.052 (47)	0.69
endrin	0.003	0.0097	0.0055	0.0063	0.0038 (8.8)	0.019
fenthion	0.0031	0.038	0.016	0.016	0.0027 (6.0 * 10 ⁴)	0.16
α-HCH	3.5	-	2.5	2.5	3.3 (24)	25
β-HCH	6.1	25	0.08	0.08	1.3 (34)	0.8
γ-HCH	1.0	0.11	1.7	0.77	0.91 (7.6)	1.1
heptachlor	0.00046	0.025	0.019	0.019	0.048 (490)	0.19
heptachlor epoxide	0.00046	0.000045	0.016	0.000045	0.000045 ^b	0.00045
hexachlorobenzene	2.4	0.0089	0.0012	0.0021	0.050 (13)	0.0089
mercury	0.056	0.032	0.16	0.032	0.057 (5.2)	0.32
methyl-mercury	0.056	0.0014	0.0015	0.0019	0.0036 (7.1)	0.0034
pentachlorobenzene	7.5	-	0.030	0.030	1.2 (8.6)	0.30
pentachlorophenol	3.5	57	13	13	4.6 (3.8)	130
quintozene	0.29	13	3.3	3.3	2.9 ^b	33
thiram	0.032	33	57	33	0.0061 (3.4 * 10 ⁶)	310

^a between brackets: ratio between MPC_{50% confidence} and MPC_{95% confidence} calculated with method of Aldenberg and Slob (for the MPC values based on method I this ratio is not given because they are already presented in Tables 3.3 and 3.5)

^b indicative MPC based on modified EPA method

Based on the calculations presented in Table 4.2 the following conclusions can be drawn:

- with respect to method I: for carbofuran, chlordane, chlorpyrifos, copper, o,p'-DDT, endrin, heptachlor, pentachlorophenol, quintozene and thiram the MPC_{direct; aq.} is lower than all MPC_{sp}s (bird, mammals and combined data sets). If the maximum BCF is used the opposite conclusion must be drawn for endrin and pentachlorophenol. For aldrin, p,p'-DDE, p,p'-DDE, dieldrin, α-HCH, hexachlorobenzene, methyl-mercury, and pentachlorobenzene all MPC_{sp}s are lower than the MPC_{direct; aq.}s using the geometric mean BCF. For the other compounds one or two of the MPC_{sp}s is lower than the MPC_{direct; aq.}
- comparing method I and II: for copper, dieldrin, endosulfan, endrin and thiram the MPC using method II is lower than the different MPCs calculated using method I. For dieldrin and endrin this is also the case if the maximum BCF is used. The difference between the lowest MPC based on method I and the MPC based on method II varies from 1.1 to 380 for

fenthion and carbofuran, respectively. Especially for carbofuran, chlordane, chlorpyrifos, β -HCH, heptachlor, hexachlorobenzene and pentachlorobenzene the difference is large being more than a factor 15. However, it should be stated that MPCs based on method I are sometimes calculated using the modified EPA method while all MPCs based on method II are calculated using the method of Aldenberg and Slob.

It is essential to know whether both methods can lead to different conclusions with respect to secondary poisoning. For most compounds this is not the case: If one or all of the MPC_{sp} s are lower than the $MPC_{direct; aq.}$, also the MPC based on method II is lower than the $MPC_{direct; aq.}$. Differences between both MPCs ($MPC_{direct; aq.}$ versus MPC_{sp} and MPC using method II) are in most cases larger if the MPC_{sp} is used of course, as many MPC_{sp} s are based on a relatively small data set leading to the use of the EPA-method.

However, method II can lead to unrealistic low MPCs because some NOEC values at the right side of the distribution are added to the ones already there for aquatic organisms, caused by a low bioaccumulation potential or a low toxicity towards birds and/or mammals, e.g. fenthion and thiram. Due to this increased variation in NOEC values the MPC becomes lower compared to the one based on data for aquatic organisms only, i.e. $MPC_{direct; aq.}$. On the other hand method II can also lead to unrealistic high MPCs because a relatively large amount of NOEC values for birds and/or mammals for a chemical with a low bioaccumulation potential or a low toxicity towards these organisms is added to some rather low NOECs for aquatic organisms, e.g. carbofuran.

In paragraph 2.8.2 it was concluded that on theoretical grounds both methods have disadvantages as well as advantages. However, based on the quantitative comparison between method I and II it can be concluded that the latter one may lead to relatively low as well as high MPCs. It is therefore decided to use method I in order to calculate MPCs for the aquatic environment ($MPC_{aq.}$). In the following paragraph the derivation of the MPCs will be described for each chemical.

4.3 MPCs for the aquatic environment

In the present paragraph $MPC_{aq.}$ s are determined based on the results presented in the previous paragraphs. Method I will be used to derive $MPC_{aq.}$ s. If secondary poisoning is critical for deriving the $MPC_{aq.}$ it has to be decided whether the MPC_{sp} based on toxicity data for *birds or mammals separately or combined* is chosen. As already concluded in paragraph 3.4, it is difficult to draw firm conclusions about differences in sensitivity of birds and mammals, due to lack of sufficient data. Therefore the following procedure is followed: as a rule the MPC_{sp} based on the combined data-set is used. However, if the lowest $NOEC/BCF_{max}$ is lower than this MPC_{sp} , the lowest value based on the separate data-set is used.

As an aid in the derivation of $MPC_{aq.}$ s sensitivity graphs are made for each compound for chronic toxicity data for aquatic organisms *divided into fresh- and saltwater species* and for chronic toxicity data for birds and mammals (see page 41 to 61). For several of the compounds discussed one of the graphs is not made while no data are available. E.g. for p,p'-DDE, heptachlor epoxide and quintozene no chronic data are present for aquatic organisms. For penta- and hexachlorobenzene no graphs are made for aquatic organisms because QSARs have been used to derive toxicity data.

Aldrin and dieldrin: it has been shown that aldrin is rapidly converted to dieldrin in surface water as well as mammals. Consequently toxicity of both chemicals is very similar. Only for birds low NOECs for aldrin are found, which are derived from LOECs using high application factors, however (see paragraph 3.4). These low NOECs lead to relatively low MPC_{sp} s compared to dieldrin; also because for aldrin the EPA method is used while for dieldrin this is the method of Aldenberg and Slob. It is therefore decided to derive a MPC_{aq} for both compounds based on the data for dieldrin for which a considerable amount of chronic data is available for aquatic organisms, birds and mammals.

Enough NOECs for aquatic organisms are present to apply the method of Aldenberg and Slob for dieldrin. Especially fish seem to be sensitive: the distribution of NOECs seems to be bimodal, which is possible for specifically acting chemicals like pesticides. The lowest NOEC is $0.12 \mu\text{g/l}$. Birds and mammals seem to be equally sensitive for dieldrin. Enough chronic data are available to apply the method of Aldenberg and Slob. $MPC_{direct; aq}$ and MPC_{sp} using method I and the MPC based on method II are all in the same range: 0.029, 0.018 (based on data for birds and mammals) and $0.012 \mu\text{g/l}$, respectively. Using the maximum BCF the latter two values are a factor 2-3 lower. All MPCs are higher than the lowest $NOEC/BCF_{mean}$ of $0.024 \mu\text{g/l}$ for birds and mammals.

Conclusion: MPC_{aq} is set at $0.018 \mu\text{g/l}$ (MPC_{sp} based on combined data-set).

Cadmium: based on an extensive data-set (46 NOECs are available) the $MPC_{direct; aq}$ is $0.38 \mu\text{g/l}$. Two NOEC values, one for fish and one for crustaceans, are much lower than the other ones, being 0.085 and $0.2 \mu\text{g/l}$. The other values are even distributed. The MPC using method II of $0.57 \mu\text{g/l}$ is almost equal to the $MPC_{direct; aq}$ because all $NOEC/BCF_{mean}$ values for birds and mammals (9 in total) fall within the range of NOECs for aquatic organisms. The MPC_{sp} s using method I show a large variation: 0.35, 20 and $2.9 \mu\text{g/l}$ based on toxicity data for birds, mammals and the combined data-set, respectively. All are calculated using the method of Aldenberg and Slob. Using the maximum BCF these values are a factor 14 lower. The lowest $NOEC/BCF_{mean}$ is $1.7 \mu\text{g/l}$. Birds may be more sensitive than mammals, although this conclusion is based on only one NOEC for birds being at least a factor 8 lower than the other NOECs for birds and mammals.

Conclusion: considering the results using the maximum BCF and the fact that there may be a risk for birds the MPC_{aq} is set at $0.35 \mu\text{g/l}$ (MPC_{sp} based on data for birds).

Carbofuran: the $MPC_{direct; aq}$ is $0.015 \mu\text{g/l}$ based on the EPA-method applying a factor 100 on the lowest $L(E)C50$. Chronic data are available for fish and crustaceans: the lowest NOEC is $0.5 \mu\text{g/l}$ for *Cancer magister* which is a factor 20-50 lower than the other ones. All MPCs based on method I or II are much higher than the $MPC_{direct; aq}$ caused by the low BCF for carbofuran. For birds and mammals 3 NOECs are available, so only the MPC_{sp} based on the combined data-set is calculated with the method of Aldenberg and Slob. The lowest $NOEC/BCF_{mean}$ is $83 \mu\text{g/l}$. It can be concluded that there is no risk for secondary poisoning at a concentration equal to the $MPC_{direct; aq}$.

Conclusion: MPC_{aq} is set at $0.015 \mu\text{g/l}$ (based on effects on aquatic organisms). This value must be considered as an indicative one.

Chlordane: the $MPC_{direct; aq}$ is $0.0015 \mu\text{g/l}$ based on the EPA-method applying a factor of 10 on the lowest NOEC. Chronic data are available for fish, insects and crustaceans; the lowest NOEC is $0.015 \mu\text{g/l}$. Distribution of NOECs seems unimodal and symmetrical although only

chronic data are available for organisms which can be regarded as target-species. All MPCs based on method I or II are much higher than the $MPC_{direct; aq.}$ using the geometric mean as well as the maximum BCF. However, for birds only acute data are present while for mammals only one NOEC for *Rattus norvegicus* is available (all MPC_{sp} s are based on the modified EPA method). The lowest $NOEC/BCF_{mean}$ is $0.44 \mu g/l$. Based on these data it can be concluded that there is no risk for secondary poisoning at a concentration equal to the $MPC_{direct; aq.}$

Conclusion: $MPC_{aq.}$ is set at $0.0015 \mu g/l$ (based on effects on aquatic organisms). This value must be considered as an indicative one.

Chlorpyrifos: the $MPC_{direct; aq.}$ is $0.0028 \mu g/l$ based on the Aldenberg and Slob method. The lowest NOEC is $0.012 \mu g/l$ for fish. Distribution of chronic data seems to be bimodal. All MPCs based on method I or II are higher than the $MPC_{direct; aq.}$ using the geometric mean as well as the maximum BCF. For birds enough chronic data are available to apply the method of Aldenberg and Slob, while for mammals only one NOEC is present being in the same range as the data for birds. The lowest $NOEC/BCF_{mean}$ is $4.8 \mu g/l$. Based on these data it can be concluded that there is no risk for secondary poisoning at a concentration equal to the $MPC_{direct; aq.}$

Conclusion: $MPC_{aq.}$ is set at $0.0028 \mu g/l$ (based on effects on aquatic organisms).

Copper: $MPC_{direct; aq.}$ is calculated using the method of Aldenberg and Slob based on 38 chronic data. Distribution of NOECs is unimodal and symmetrical, which is striking because copper is an essential element. The lowest NOEC is $4.0 \mu g/l$ for fish. $MPC_{direct; aq.}$, MPC_{sp} using method I and the MPC based on method II are all in the same range: 4.1, 6.4 (based on data for mammals, only) and $3.3 \mu g/l$, respectively. No toxicity data are available for birds, while enough chronic data are available for mammals to use the method of Aldenberg and Slob. The lowest $NOEC/BCF_{mean}$ is $.19 \mu g/l$. There are indications that copper is not accumulated at all by aquatic organisms.

Conclusion: considering the uncertainties about the accumulation potential the $MPC_{aq.}$ is set at $4.1 \mu g/l$ (based on effects on aquatic organisms).

DDT and derivatives: the $MPC_{direct; aq.}$ is $0.005 \mu g/l$ based on toxicity data for DDD, DDE and DDT. The lowest NOEC is $0.05 \mu g/l$ for p,p'-DDT for crustaceans. Available NOECs are even distributed. MPCs using method I and II are lower than the $MPC_{direct; aq.}$, except for the MPC_{sp} for o,p'- and p,p'-DDT based on toxicity data for birds and mammals only, respectively. DDT and DDE are considerably more toxic to birds than to mammals. For both groups enough chronic data are available to apply the method of Aldenberg and Slob. Using the maximum BCF the MPCs are a factor 2-3 lower. The lowest $NOEC/BCF_{mean}$ is $0.0019 \mu g/l$ for p,p'-DDE. Based on these data it can be concluded that there is a risk for secondary poisoning, especially for birds.

Conclusion: the $MPC_{aq.}$ is set at the lowest MPC_{sp} for birds of DDE, DDD and DDT using method I, i.e. $0.00044 \mu g/l$.

Endosulfan: the $MPC_{direct; aq.}$ is $0.0004 \mu g/l$ based on the EPA-method applying a factor 100 on the lowest LC50. Fish are extremely sensitive for endosulfan. This can also be concluded from the distribution of NOECs: the lowest value is one for fish. For birds only acute toxicity data are present while for mammals the method of Aldenberg and Slob can be used. All MPCs based on method I or II are much higher than the $MPC_{direct; aq.}$: the difference is a

factor 200 or more. Based on these data it can be concluded that there is no risk for secondary poisoning at a concentration equal to the $MPC_{direct; aq.}$.

Conclusion: $MPC_{aq.}$ is set at $0.0004 \mu\text{g/l}$ (based on effects on aquatic organisms).

Endrin: $MPC_{direct; aq.}$ is calculated using the EPA-method applying a factor 10 on the lowest NOEC. Distribution of NOECs is bimodal leading to a rejection of the log-logistic distribution. $MPC_{direct; aq.}$ and MPC_{sp} using method I and the MPC based on method II are all in the same range: 0.003, 0.0063 (based on data for birds and mammals) and $0.0038 \mu\text{g/l}$, respectively. Using the maximum BCF the latter two values are a factor 2-3 lower. Birds and mammals seem to be equally sensitive: for both groups enough chronic data are present to apply the method of Aldenberg and Slob. The lowest $NOEC/BCF_{mean}$ is $0.019 \mu\text{g/l}$.

Conclusion: $MPC_{aq.}$ is set at $0.003 \mu\text{g/l}$ (based on effects on aquatic organisms).

Fenthion: the $MPC_{direct; aq.}$ is $0.0031 \mu\text{g/l}$ based on the method of Aldenberg and Slob. The lowest NOEC is $0.037 \mu\text{g/l}$ for a saltwater crustaceans. Looking at the distribution of NOEC values it can be seen that this value is much lower than the other ones. Due to the specific mode of action of fenthion this can be expected. Although only acute data for birds and one NOEC for mammals is available it can be concluded that fenthion is rather toxic to these organisms. The MPC_{sp} using method I is considerably higher than the $MPC_{direct; aq.}$, while the one using method II is slightly lower. The reason for this difference has already been explained in the previous paragraph. The lowest $NOEC/BCF_{mean}$ is $0.16 \mu\text{g/l}$.

Conclusion: because there will probably be no risk for secondary poisoning due to the low bioaccumulation potential the $MPC_{aq.}$ is set at $0.0031 \mu\text{g/l}$ ($MPC_{direct; aq.}$ based on effects on aquatic organisms).

α -HCH: $MPC_{direct; aq.}$ is calculated using the method of Aldenberg and Slob. NOECs values are even distributed; the lowest one is $9 \mu\text{g/l}$. $MPC_{direct; aq.}$ and MPC_{sp} using method I and the MPC based on method II are all in the same range: 3.5, 2.5 and $3.3 \mu\text{g/l}$. Using the maximum BCF the latter two values are less than a factor 2 lower. No toxicity data are present for birds, while for mammals only one NOEC is available. The lowest $NOEC/BCF_{mean}$ is $25 \mu\text{g/l}$.

Conclusion: the $MPC_{aq.}$ is set at $2.5 \mu\text{g/l}$ (MPC_{sp} based on the combined data-set). This value must be considered as an indicative one.

β -HCH: the $MPC_{direct; aq.}$ is $6.1 \mu\text{g/l}$ using the method of Aldenberg and Slob. As for α -HCH chronic data are even distributed with a lowest NOEC of $10 \mu\text{g/l}$. Toxicity data for birds and mammals are scarce: for birds and mammals only one NOEC is available, being ≥ 625 and 2 mg/kg food , respectively. The low value for mammals leads to MPCs using method I and II being lower than the $MPC_{direct; aq.}$: 0.08 (based on the combined data-set) and $1.3 \mu\text{g/l}$, respectively. Using the maximum BCF these values are less than a factor 2 lower. As already stated in paragraph 3.4 the low NOEC for mammals for β -HCH compared to the other HCH-isomers can be explained by a possible endocrine effect.

Conclusion: the $MPC_{aq.}$ is set at $0.08 \mu\text{g/l}$ (MPC_{sp} based on combined data-set). This value must be considered as an indicative one.

γ -HCH: the $MPC_{direct; aq.}$ is $1.0 \mu\text{g/l}$ using the method of Aldenberg and Slob. Distribution of NOEC data seems bimodal with low values for crustaceans, insects and fish. The lowest NOEC is $2.2 \mu\text{g/l}$ for insects. Two and three NOECs are available for birds and mammals,

respectively. One value for birds is considerably lower than all the other ones: at least a factor 15. MPCs using method I and II are slightly lower than the $MPC_{direct; aq.}$, being 0.77 (based on the combined data-set using the method of Aldenberg and Slob) and $0.91 \mu\text{g/l}$, respectively. Using the maximum BCF these values are a factor 2-4 lower. The lowest $NOEC/BCF_{mean}$ is $1.1 \mu\text{g/l}$.

Conclusion: the $MPC_{aq.}$ is set at $0.77 \mu\text{g/l}$ (MPC_{sp} based on combined data-set).

Heptachlor and heptachlor epoxide: It has been shown that heptachlor is converted to heptachlor epoxide in surface water as well as mammals. For both compounds the $MPC_{direct; aq.}$ is $0.00046 \mu\text{g/l}$ using the EPA method applying a factor 100 on the lowest L(E)C50 for heptachlor. Only two NOECs are available: the lowest being $0.86 \mu\text{g/l}$. Toxicity data for birds and mammals are scarce: only one NOEC is available for both groups for heptachlor as well as heptachlor epoxide. One NOEC for birds for heptachlor epoxide is extremely low, although this value may be an overestimation of toxicity (see paragraph 3.4); the $NOEC/BCF_{mean}$ for this bird species is equal to the $MPC_{direct; aq.}$. Due to this low value for birds MPCs using method I (based on the combined data-set) and II are a factor 10 lower than the $MPC_{direct; aq.}$ for heptachlor epoxide while for heptachlor they are more than a factor 40 higher than the $MPC_{direct; aq.}$.

Conclusion: considering that the NOEC for the extremely sensitive bird species divided by the BCF_{mean} is already equal to the $MPC_{direct; aq.}$, which has been calculated using a high assessment factor, the $MPC_{aq.}$ is set at $0.00046 \mu\text{g/l}$ (based on effects on aquatic organisms for heptachlor). This value must be considered as an indicative one.

Hexachlorobenzene: the $MPC_{direct; aq.}$ is $2.4 \mu\text{g/l}$ using the QSAR-method as described in Van de Plassche et al. [6, 51]. MPCs using method I and II are considerably lower: more than a factor 50. Several NOECs are available for mammals, while only one is present for birds. The lowest $NOEC/BCF_{mean}$ is c. 4 times higher than the MPC_{sp} based on method I (combined data-set using the method of Aldenberg and Slob) and a factor 7 lower than the MPC based on method II.

Conclusion: the $MPC_{aq.}$ is set at $0.0021 \mu\text{g/l}$ (MPC_{sp} based on combined data-set).

Mercury: $MPC_{direct; aq.}$ is $0.056 \mu\text{g/l}$ using the method of Aldenberg and Slob based on a large data-set of 20 NOECs. Chronic toxicity data seem to be even distributed except for two extreme values of $0.020 \mu\text{g/l}$ for crustaceans. No distinction is made between mercury and methyl-mercury. MPCs using method I (based on the combined data-set using the modified EPA method) or II are in the same range as the $MPC_{direct; aq.}$, being 0.032 and $0.057 \mu\text{g/l}$, respectively. The lowest $NOEC/BCF_{mean}$ is $0.32 \mu\text{g/l}$.

According to Romijn et al. almost all mercury in fish and other water organisms is present as methyl-mercury, although in natural water the opposite situation occurs: only 1-10% of the total amount of mercury is present as methyl-mercury [13]. Consequently a $MPC_{aq.}$ based on the data for mercury may lead to a severe underestimation of the risk due to secondary poisoning as methyl-mercury is more toxic than mercury. Therefore it is decided to derive a $MPC_{aq.}$ for mercury based on the data for methyl-mercury.

Methyl-mercury: the same $MPC_{direct; aq.}$ of $0.056 \mu\text{g/l}$ is present for methyl-mercury. This compound is considerably more toxic to higher organisms than mercury. For birds and mammals chronic data are available for 5 and 4 species, respectively. They seem to be equally

sensitive towards methyl-mercury. MPCs based on method I and II are in the same range, being 0.0019 (combined data-set) and 0.0036 $\mu\text{g/l}$, respectively. Based on the maximum BCF these values are approximately a factor 2 lower. The lowest $\text{NOEC}/\text{BCF}_{\text{mean}}$ is 0.0034 $\mu\text{g/l}$. These values are much lower than the $\text{MPC}_{\text{direct; aq.}}$.

Conclusion: the $\text{MPC}_{\text{aq.}}$ is set at 0.0019 $\mu\text{g/l}$ (MPC_{sp} based on combined data-set).

Pentachlorobenzene: the $\text{MPC}_{\text{direct; aq.}}$ is 7.5 $\mu\text{g/l}$ using the QSAR-method as described in Van de Plassche et al. [6, 51]. MPCs using method I and II are lower: a factor 250 and 6, respectively. No toxicity data are available for birds, while only two, almost equal values, are present for mammals. Due to this scarcity in data for birds/mammals and the fact that 19 NOECs for different organisms are used in the QSAR-method, the MPC based on method I (based on the EPA-method) is much lower than the one using method II. The lowest $\text{NOEC}/\text{BCF}_{\text{mean}}$ is 0.30 $\mu\text{g/l}$. Based on the maximum BCF this value is 1.5 times lower.

Conclusion: the $\text{MPC}_{\text{aq.}}$ is set at 0.030 $\mu\text{g/l}$ (MPC_{sp} based on combined data-set). This value must be considered as an indicative one.

Pentachlorophenol: the $\text{MPC}_{\text{direct; aq.}}$ is calculated using the method of Aldenberg and Slob based on 23 NOECs. The distribution of these values seems unimodal and symmetrical with a lowest NOEC of 3.2 $\mu\text{g/l}$. $\text{MPC}_{\text{direct; aq.}}$ is somewhat lower than the MPCs using method I (calculated with the EPA-method). Using the maximum BCF all MPCs are comparable. Only one NOEC is available for birds, while 2 are present for mammals. The lowest $\text{NOEC}/\text{BCF}_{\text{mean}}$ is 130 $\mu\text{g/l}$.

Conclusion: $\text{MPC}_{\text{aq.}}$ is set at 3.5 $\mu\text{g/l}$ (based on effects on aquatic organisms).

Quintozene: the $\text{MPC}_{\text{direct; aq.}}$ is 0.29 $\mu\text{g/l}$ using the EPA-method applying a factor 1,000 on the lowest L(E)C_{50} . No chronic data are available for aquatic organisms. Only one NOEC is available for birds as well as mammals. The MPC_{sp} using method I is 3.3 $\mu\text{g/l}$ (using the EPA-method for the combined data-set), while the one using method II (using the EPA-method) is a factor 10 higher than the $\text{MPC}_{\text{direct; aq.}}$; the lowest $\text{NOEC}/\text{BCF}_{\text{mean}}$ is 33 $\mu\text{g/l}$. Based on these data it can be concluded that there is no risk for secondary poisoning at a concentration equal to the $\text{MPC}_{\text{direct; aq.}}$.

Conclusion: the $\text{MPC}_{\text{aq.}}$ is set at 0.29 $\mu\text{g/l}$ (based on effects on aquatic organisms). This value must be considered as an indicative one.

Thiram: the $\text{MPC}_{\text{direct; aq.}}$ is 0.032 $\mu\text{g/l}$ using the EPA-method applying a factor 10 on the lowest NOEC. Distribution of NOECs seems bimodal with low values for crustaceans and fish. Two NOECs are available for birds while only one is present for mammals, showing a comparable toxicity. The MPC_{sp} using method I (using the EPA-method) is considerably higher than the $\text{MPC}_{\text{direct; aq.}}$, while the one using method II is lower. The reason for this difference has already been explained in the previous paragraph. The lowest $\text{NOEC}/\text{BCF}_{\text{mean}}$ is 310 $\mu\text{g/l}$. Based on these data it can be concluded that there is no risk for secondary poisoning at a concentration equal to the $\text{MPC}_{\text{direct; aq.}}$.

Conclusion: the $\text{MPC}_{\text{aq.}}$ is set at 0.032 $\mu\text{g/l}$ (based on effects on aquatic organisms). This value must be considered as an indicative one.

Summarizing it can be concluded that secondary poisoning via the aquatic route may be critical for the following compounds: aldrin/dieldrin, cadmium, DDT and derivatives, all HCH

isomers, penta- and hexachlorobenzene and methyl-mercury. For endrin this may also be the case based on the results using the maximum BCF. For heptachlor, heptachlor epoxide and quintozone toxicity data are too scarce to draw conclusions, for aquatic organisms as well as birds and mammals. Especially for DDT and derivatives, β -HCH, penta- and hexa-chlorobenzene and methyl-mercury MPCs based on secondary poisoning are much lower than the ones based on direct effects on aquatic organisms, i.e. more than a factor 10. However, for β -HCH and pentachlorobenzene toxicity data for birds and mammals are scarce.

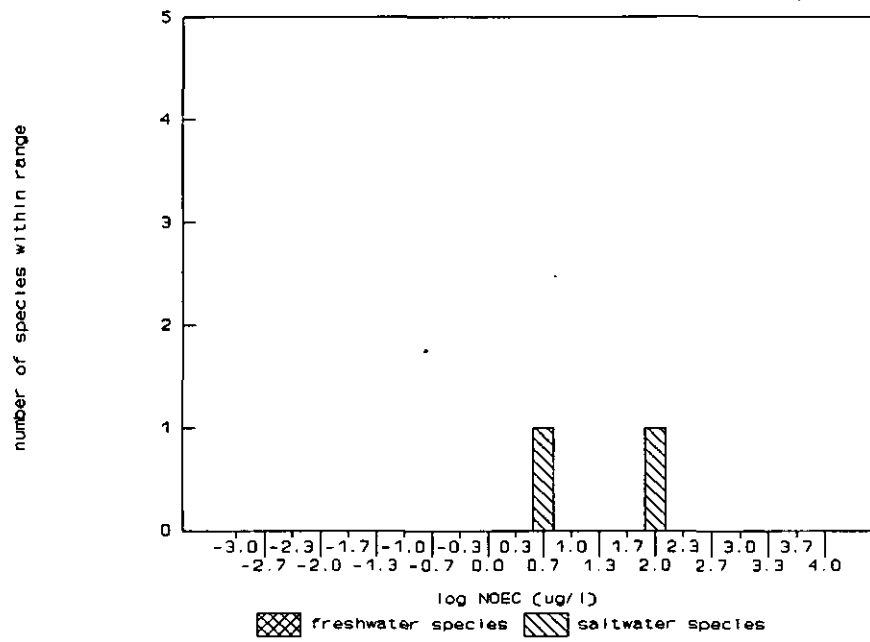
Table 4.3 gives an overview of the MPC_{aq} s derived in this paragraph.

Table 4.3 Maximum Permissible Concentrations for water ($\mu\text{g/l}$)

compound	MPC_{aq}	compound	MPC_{aq}
aldrin	0.018	fenthion	0.0031
carbofuran	0.015 ^a	α -HCH	2.5 ^a
cadmium	0.35	β -HCH	0.08 ^a
chlordane	0.0015 ^a	γ -HCH	0.77
chlorpyrifos	0.0028	heptachlor	0.00046 ^a
copper	4.1	heptachlor epoxide	0.00046 ^a
p,p'-DDD	0.00044	hexachlorobenzene	0.0021
p,p'-DDE	0.00044	mercury	0.0019
p,p'-DDT	0.00044	methyl-mercury	0.0019
o,p'-DDT	0.00044	pentachlorobenzene	0.030 ^a
dieldrin	0.018	pentachlorophenol	3.5
endosulfan	0.0004	quintozone	0.29 ^a
endrin	0.003	thiram	0.032 ^a

^a Indicative value

ALDRIN



ALDRIN

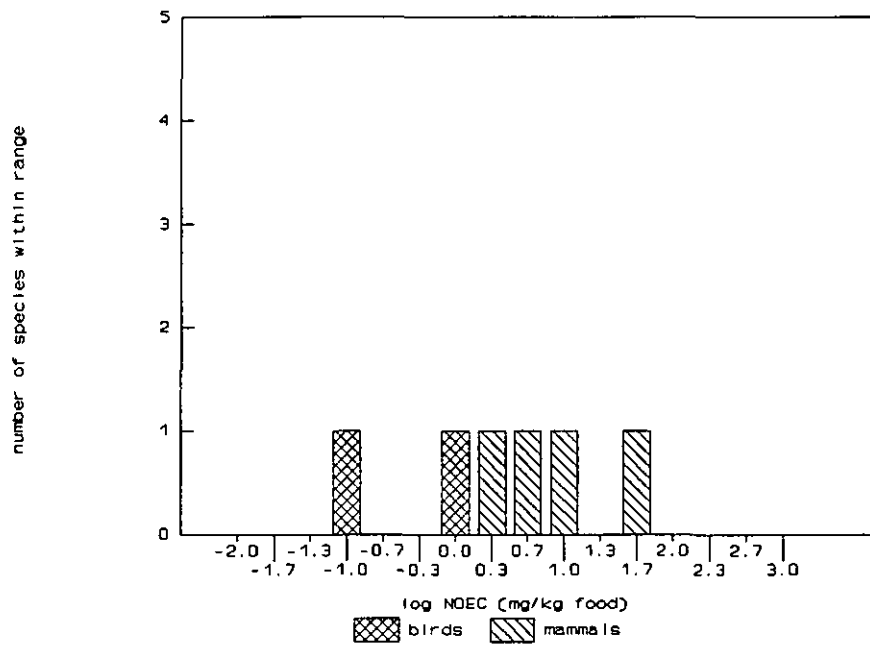
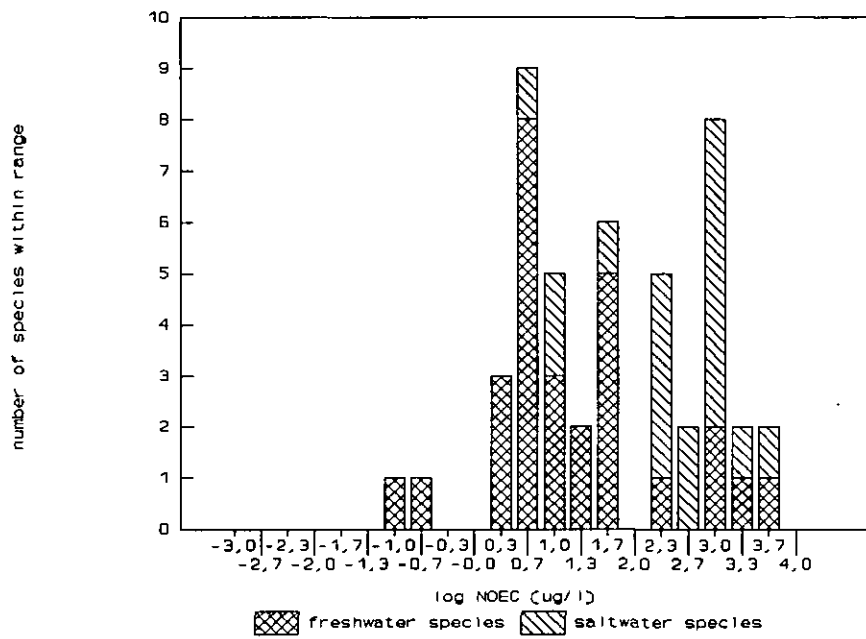


Figure 5. Sensitivity plots for aldrin.

CADMIUM



CADMIUM

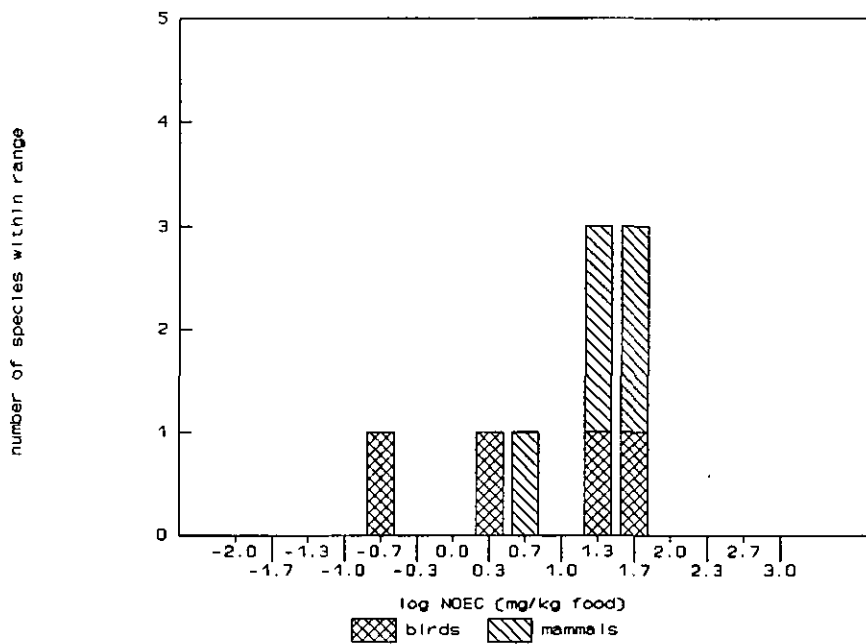
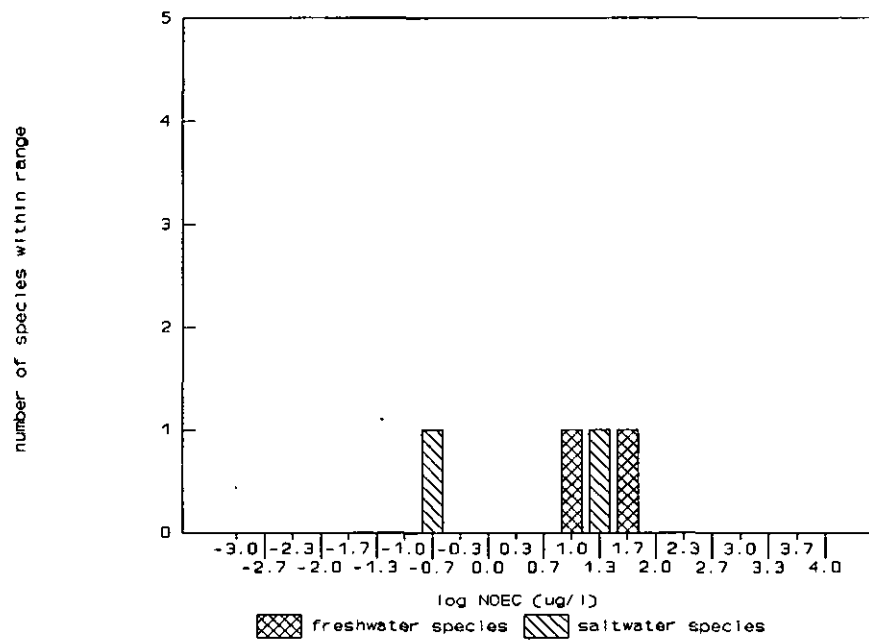


Figure 6. Sensitivity plots for cadmium.

CARBOFURAN



CARBOFURAN

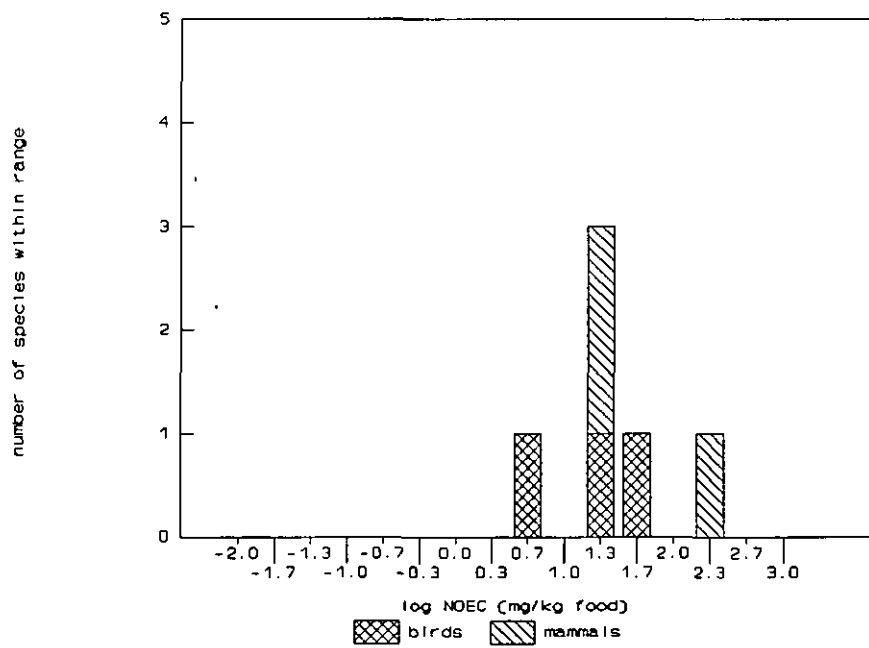
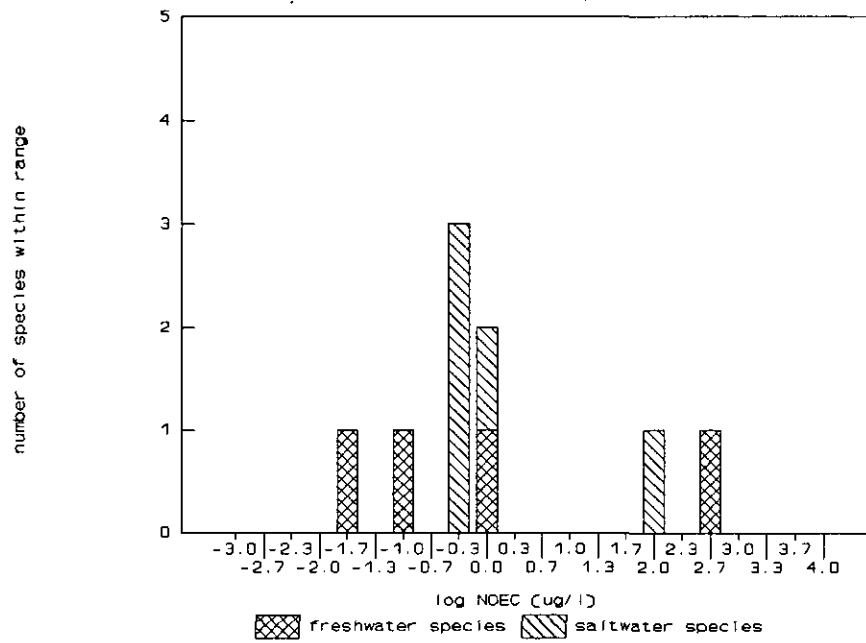


Figure 7. Sensitivity plots for carbofuran.

CHLORPYRIFOS



CHLORPYRIFOS

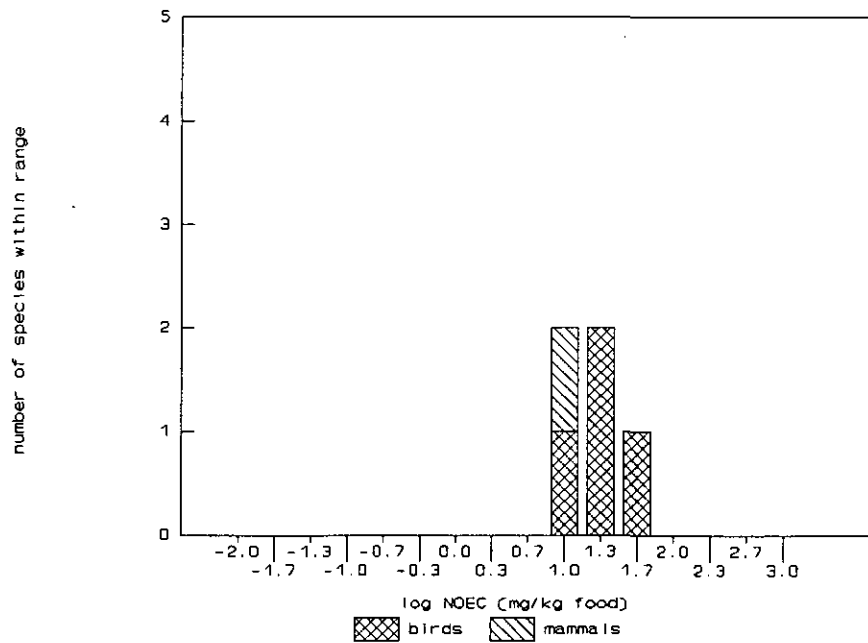
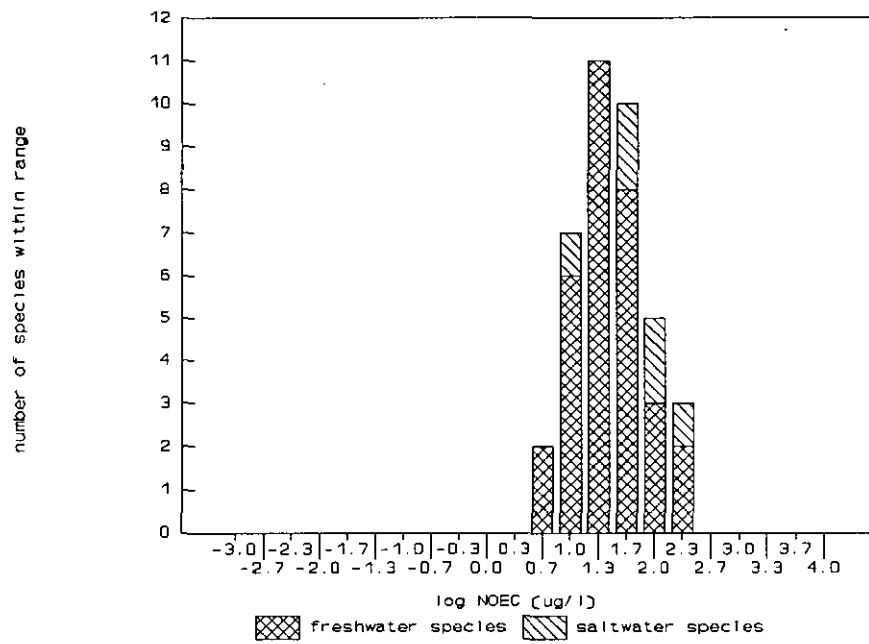


Figure 8. Sensitivity plots for chlorpyrifos.

COPPER



COPPER

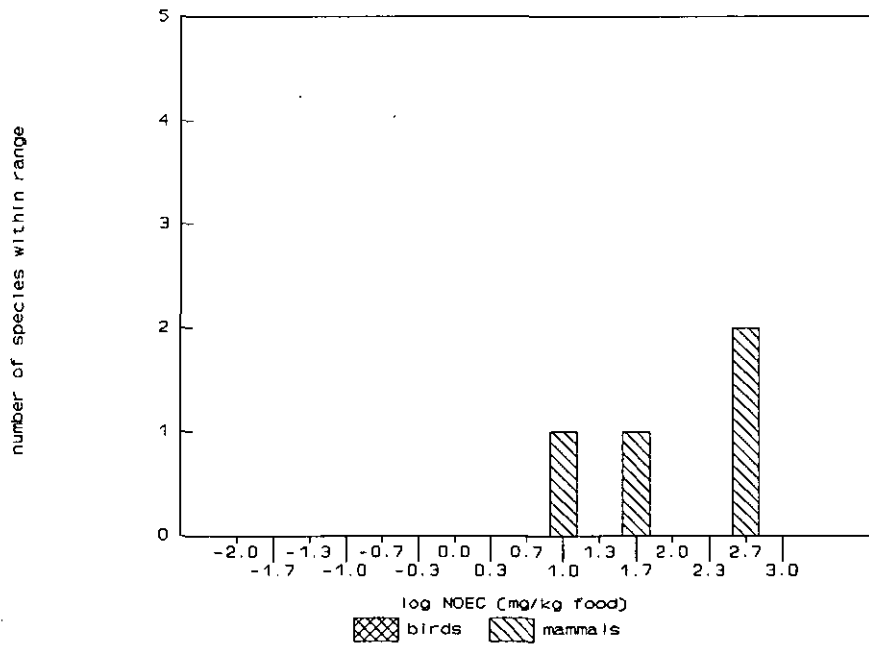
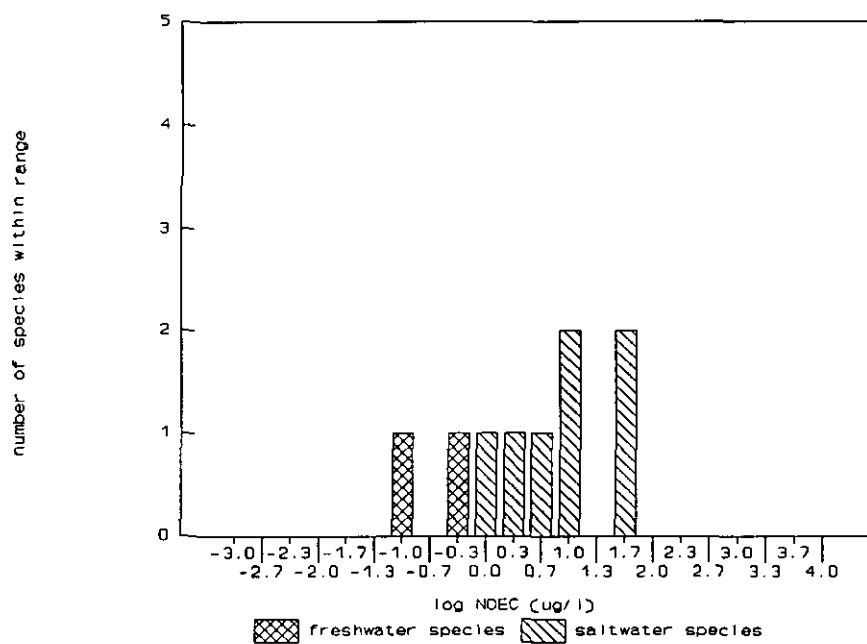


Figure 9. Sensitivity plots for copper.

DDT



p,p'-DDT

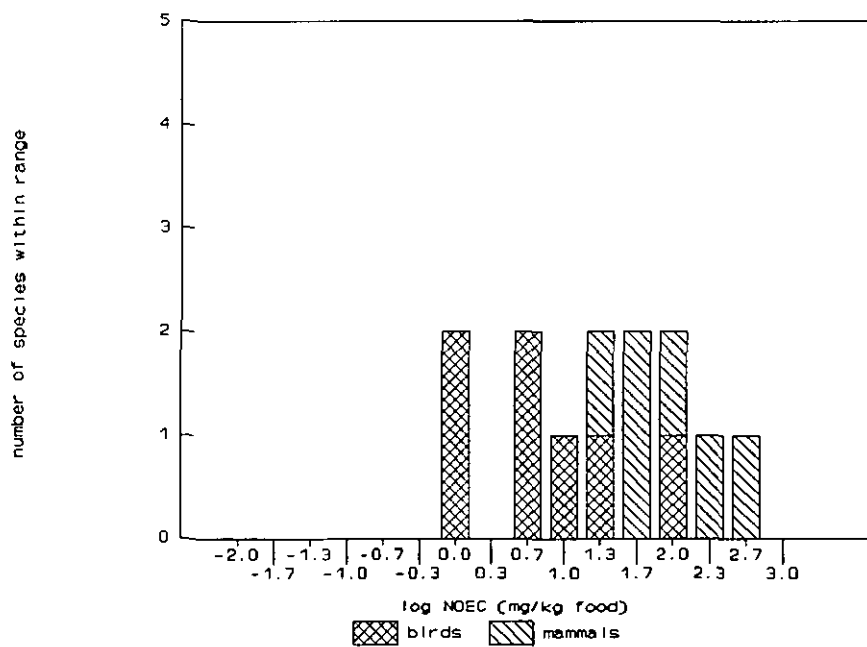
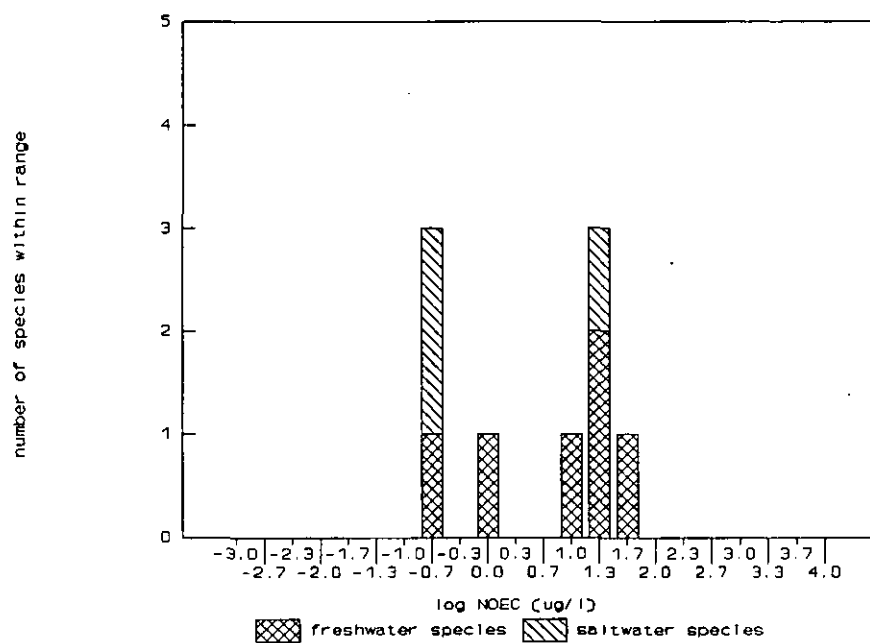


Figure 10. Sensitivity plots for DDT.

DIELDRIN



DIELDRIN

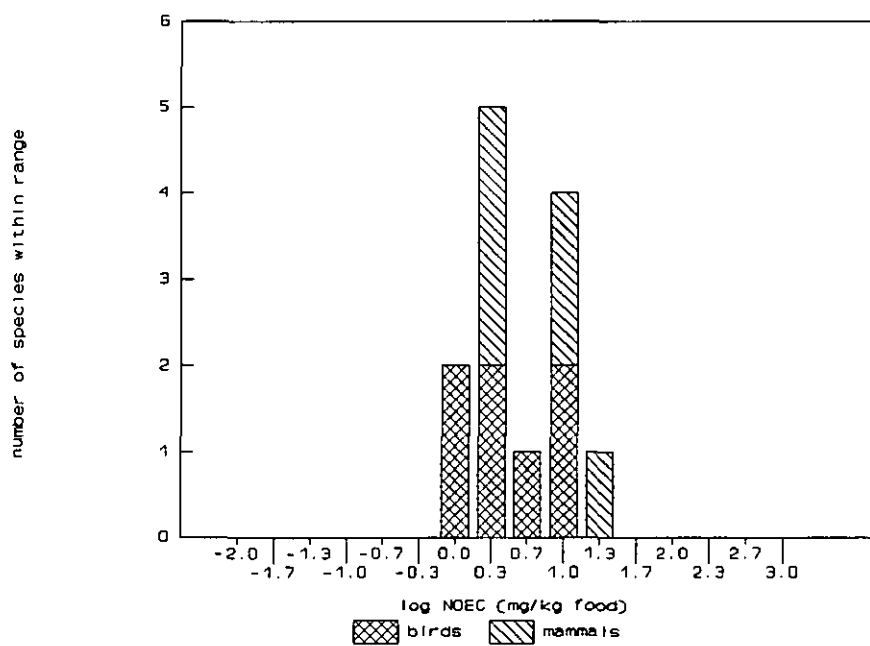
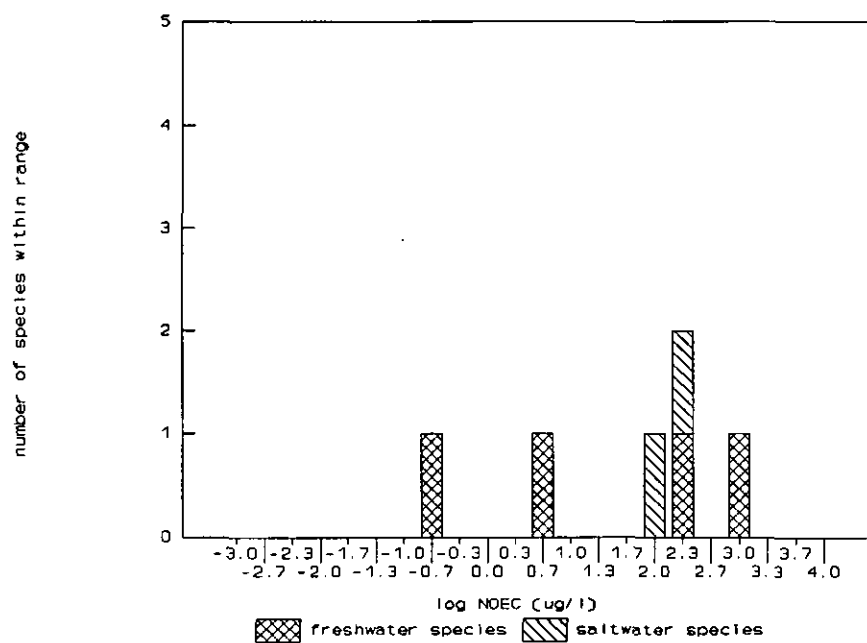


Figure 11. Sensitivity plots for dieldrin.

ENDOSULFAN



ENDOSULFAN

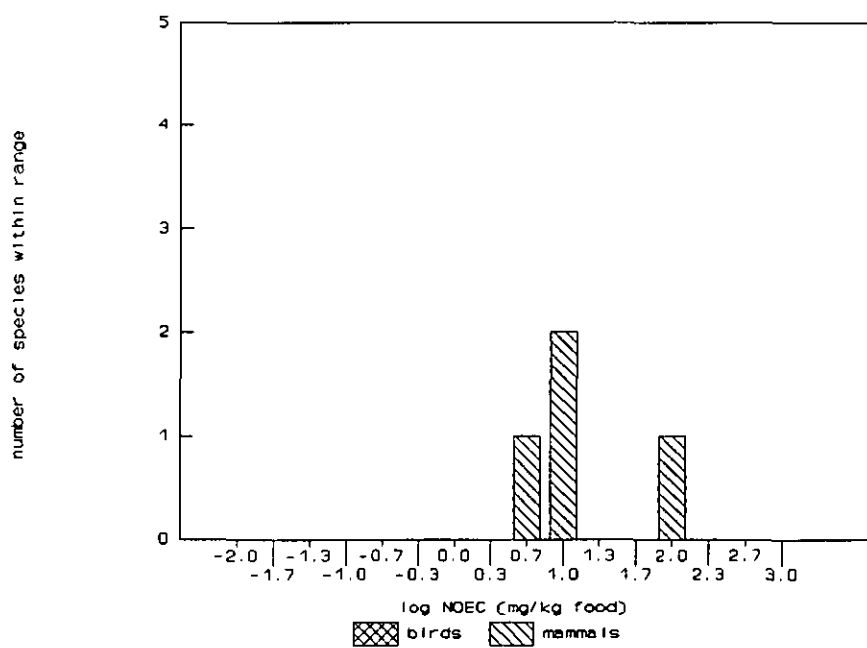
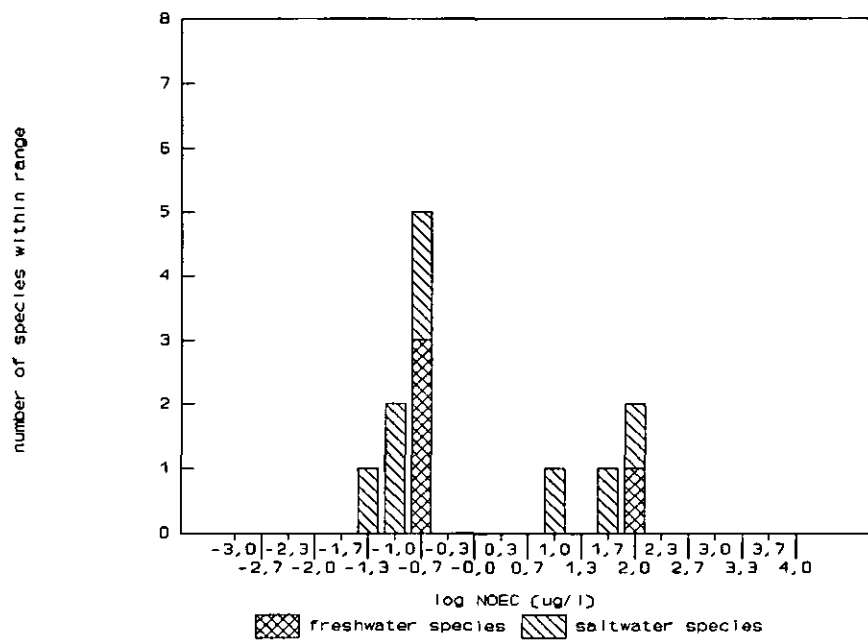


Figure 12. Sensitivity plots for endosulfan.

ENDRIN



ENDRIN

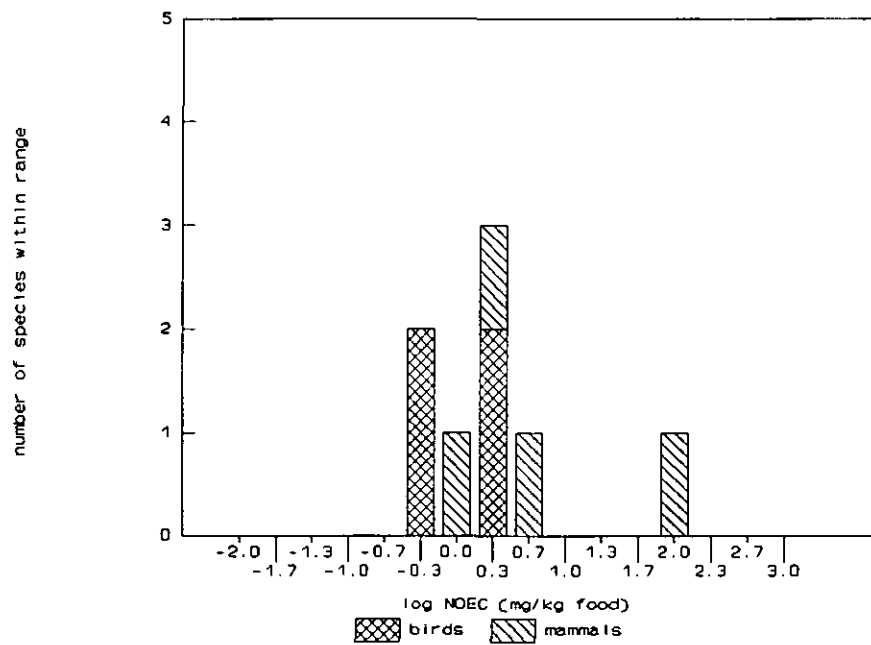
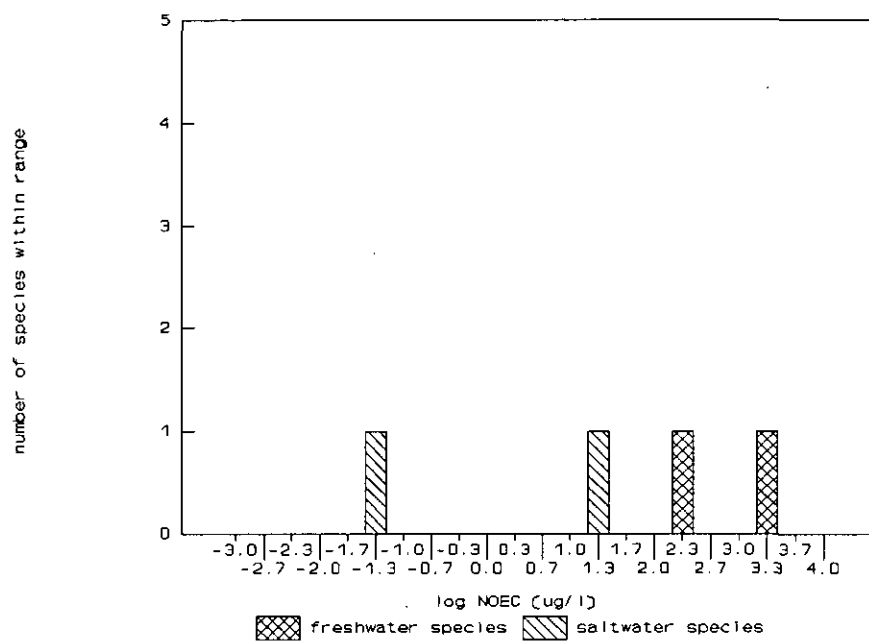


Figure 13. Sensitivity plots for endrin.

FENTHION



FENTHION

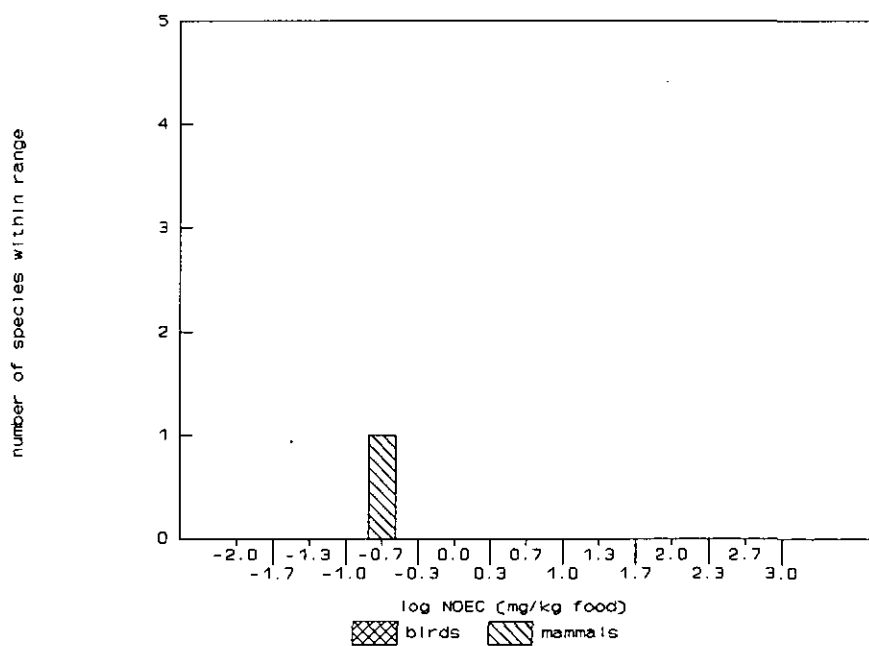
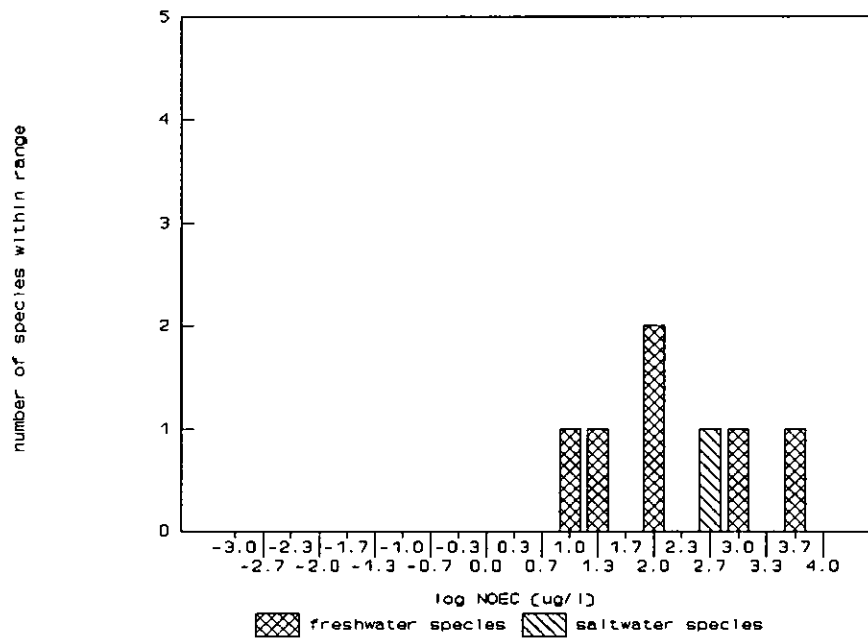
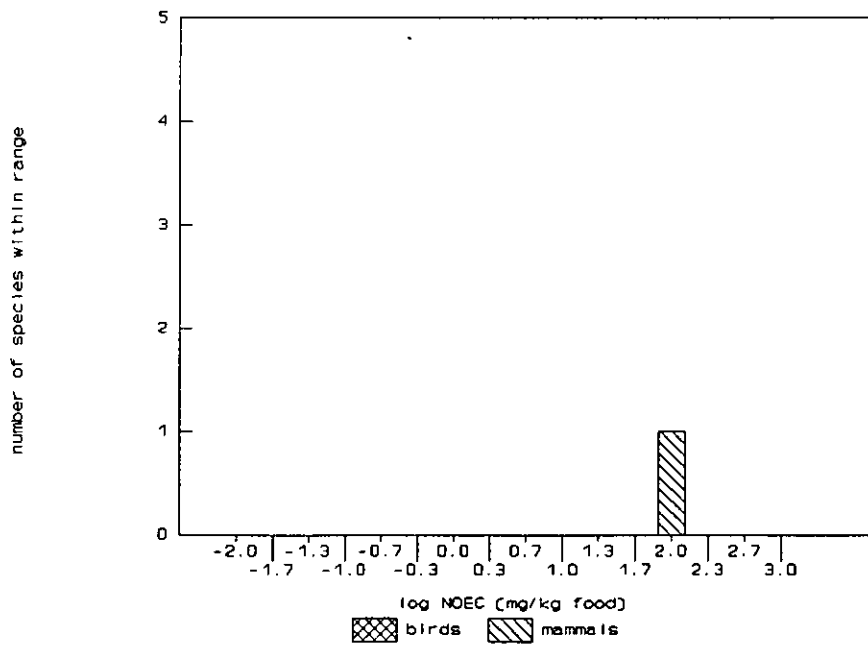
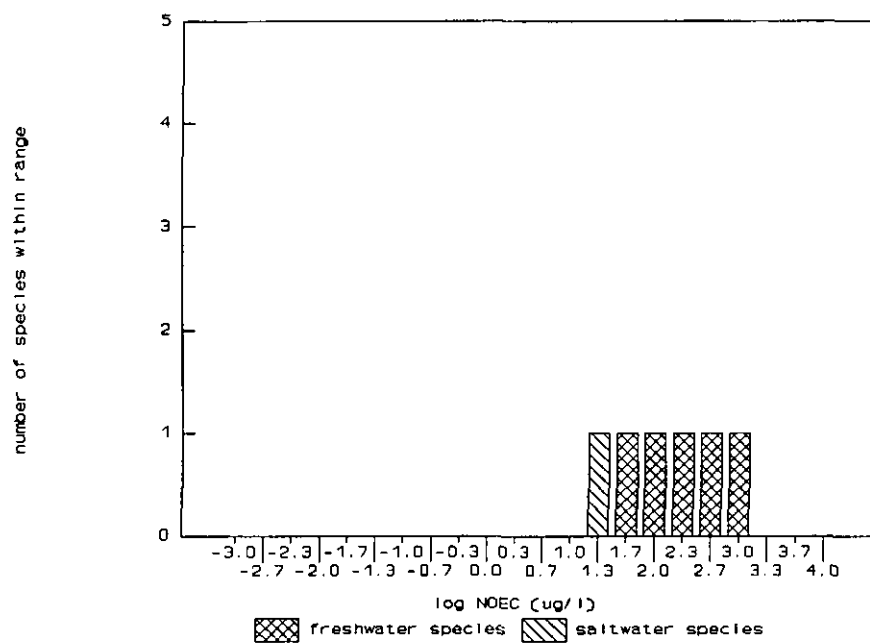


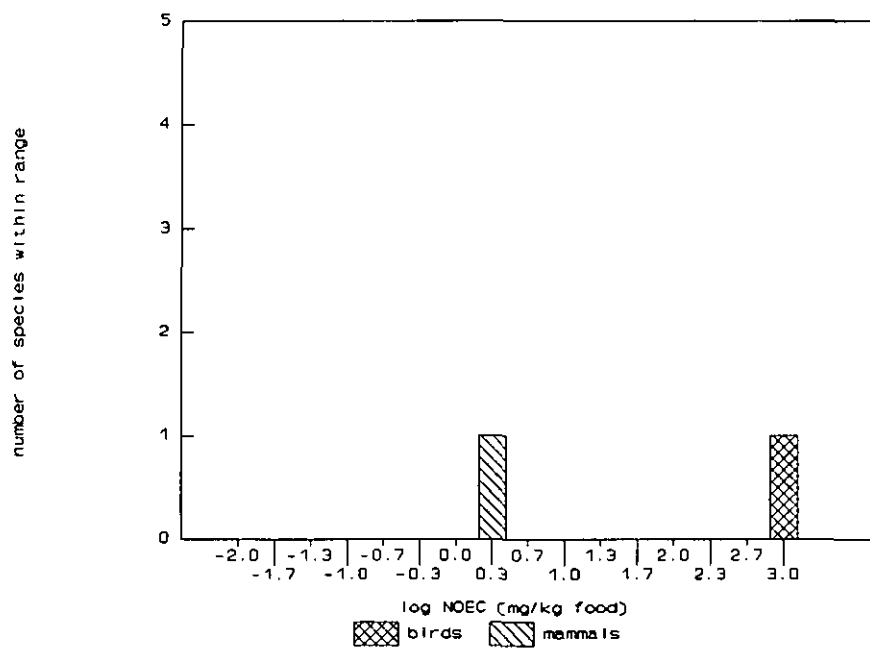
Figure 14. Sensitivity plots for fenthion.

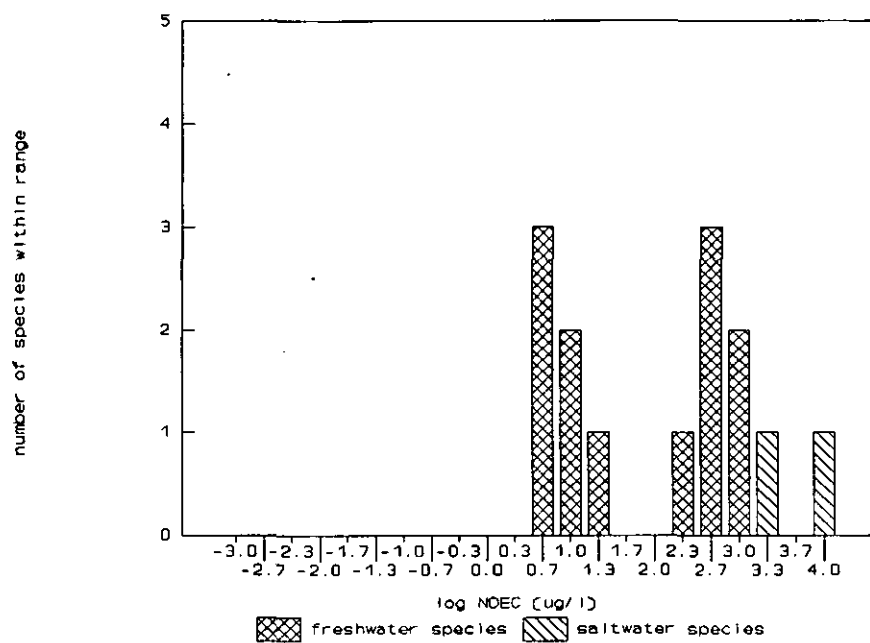
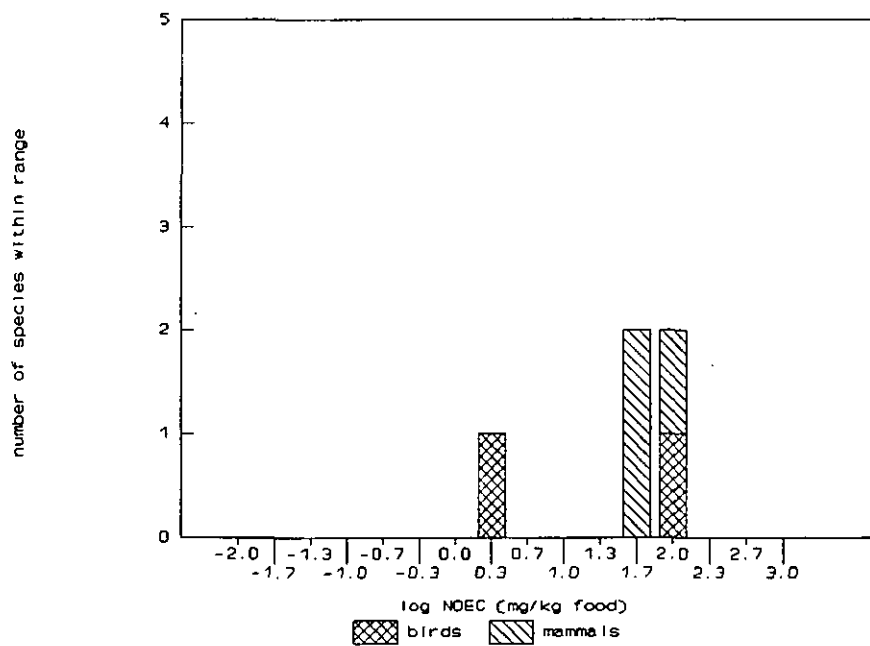
α -HCH α -HCHFigure 15. Sensitivity plots for α -HCH.

B-HCH

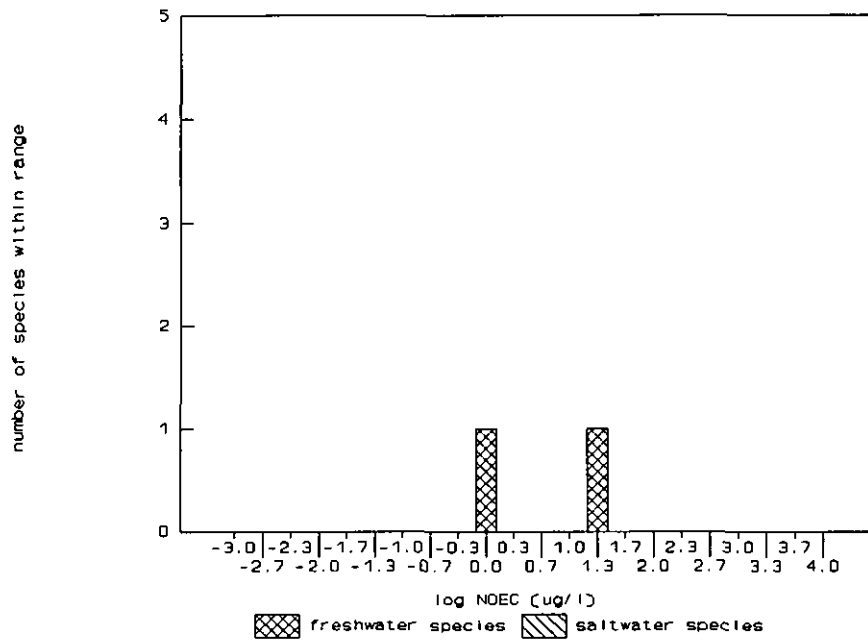


B-HCH

Figure 16. Sensitivity plots for β -HCH.

γ -HCH γ -HCHFigure 17. Sensitivity plots for γ -HCH.

HEPTACHLOR



HEPTACHLOR

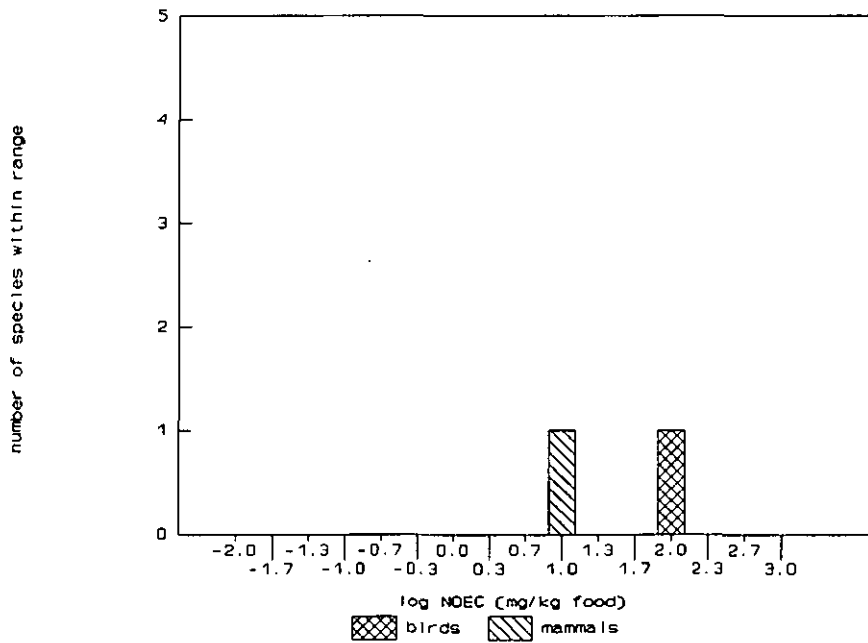
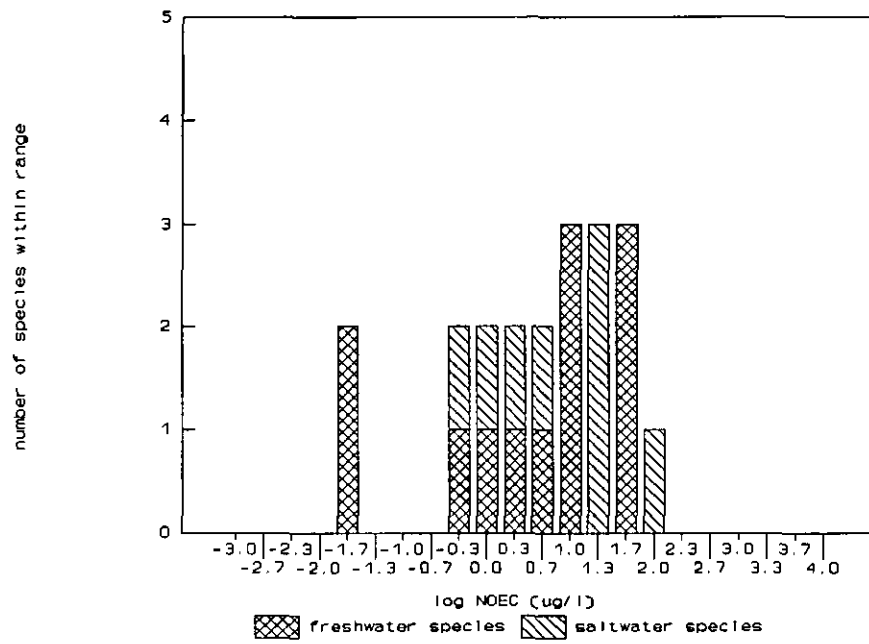


Figure 18. Sensitivity plots for heptachlor.

MERCURY



MERCURY

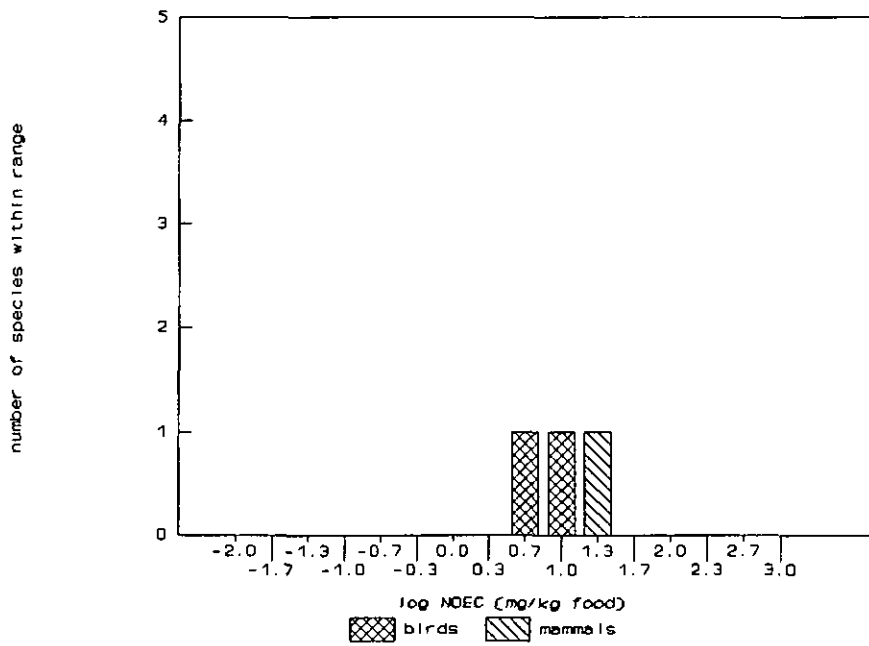
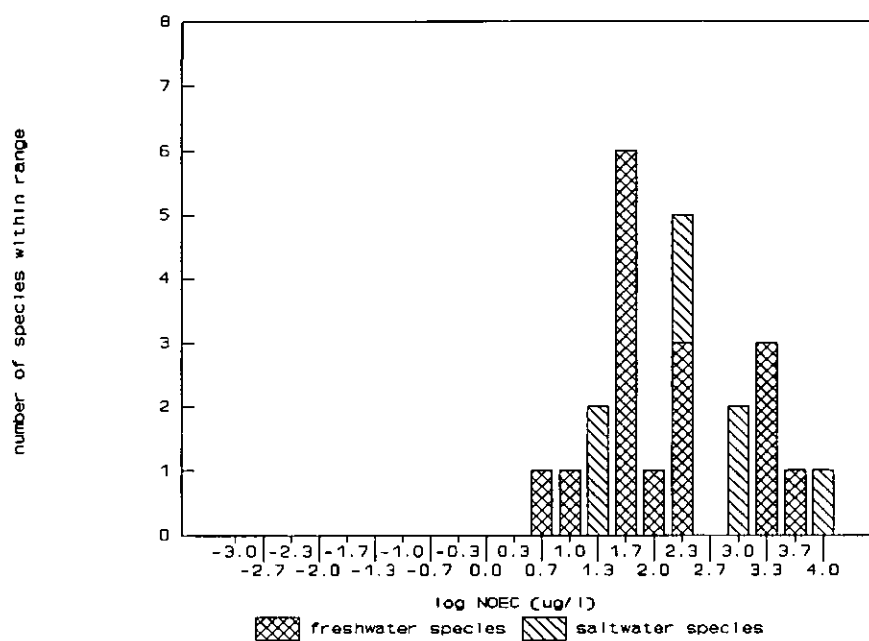


Figure 19. Sensitivity plots for mercury.

PENTACHLOROPHENOL



PENTACHLOROPHENOL

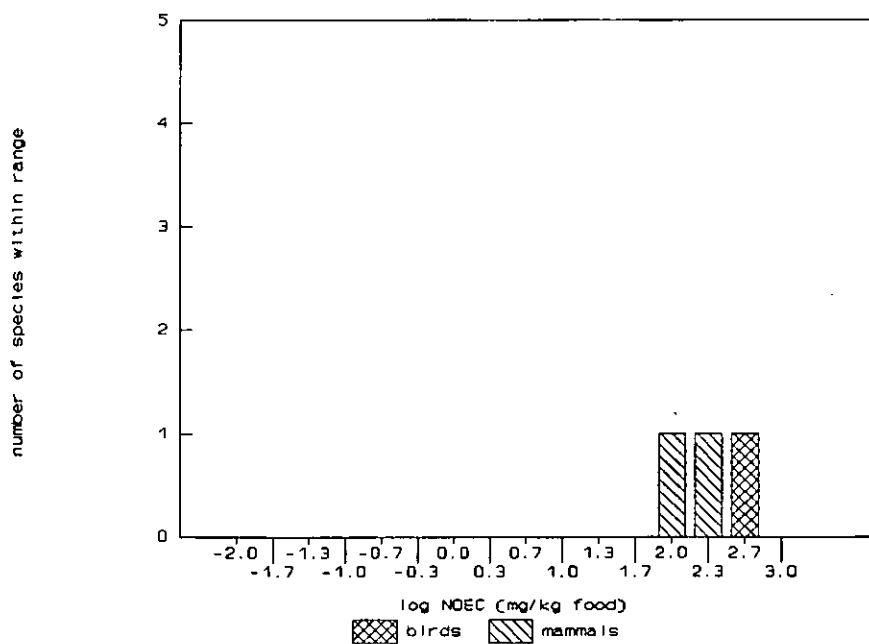
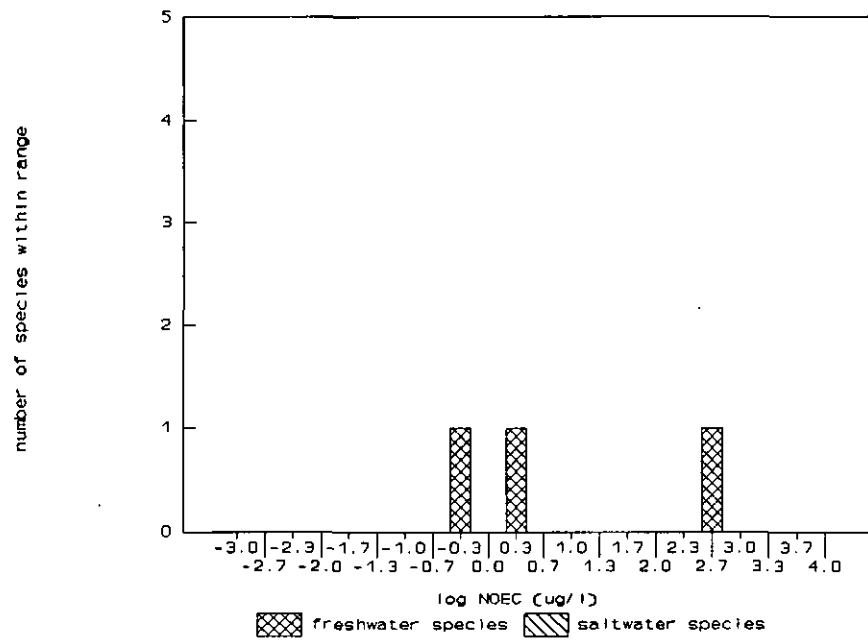


Figure 20. Sensitivity plots for pentachlorophenol.

THIRAM



THIRAM

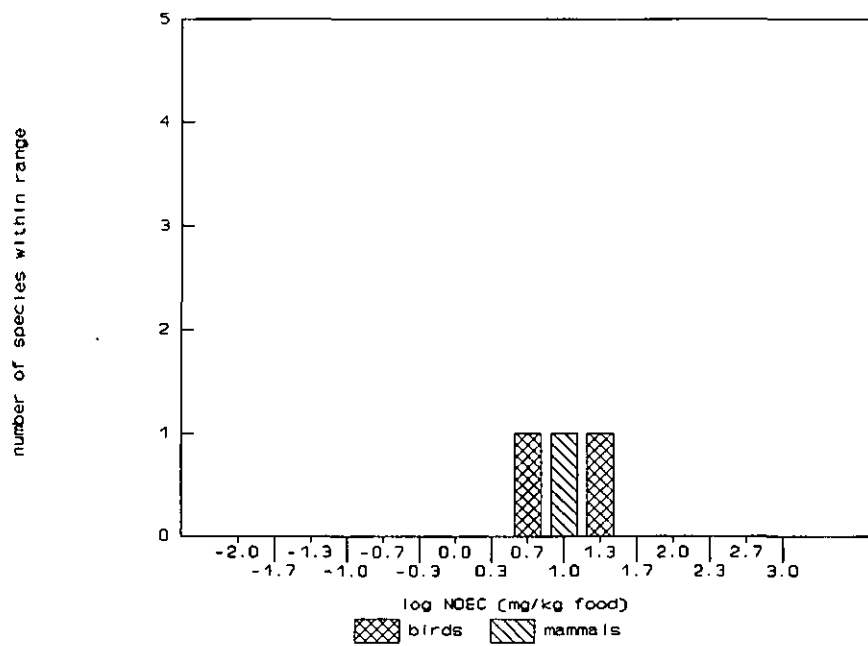


Figure 21. Sensitivity plots for thiram.

p,p'-DDD

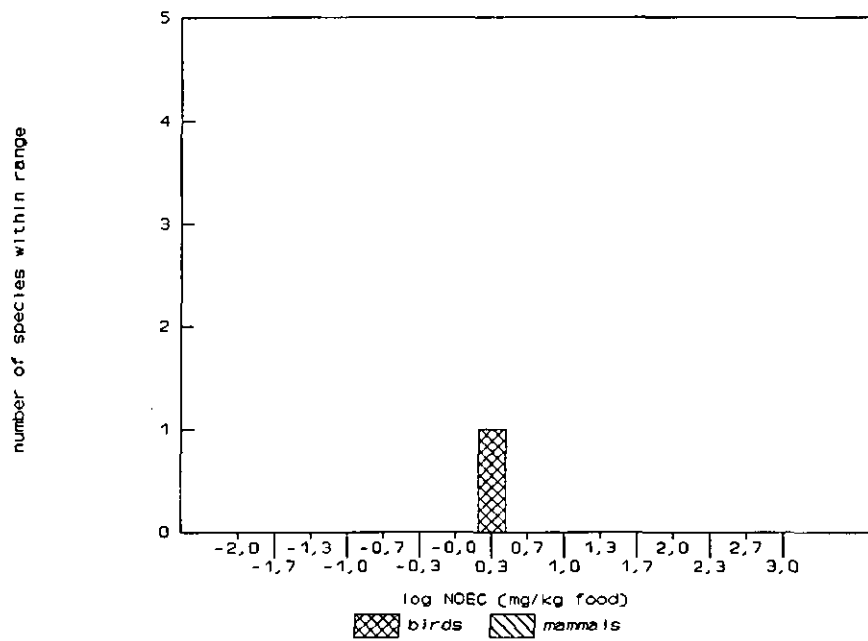


Figure 22. Sensitivity plot for chronic toxicity data for birds and mammals for p,p'-DDD.

p,p'-DDE

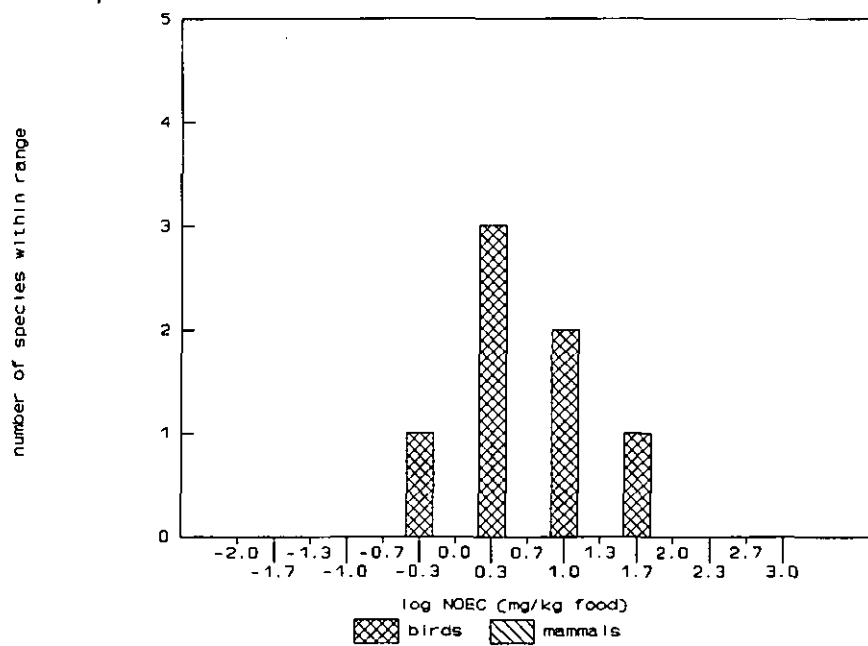


Figure 23. Sensitivity plot for chronic toxicity data for birds and mammals for p,p'-DDE.

o,p'-DDT

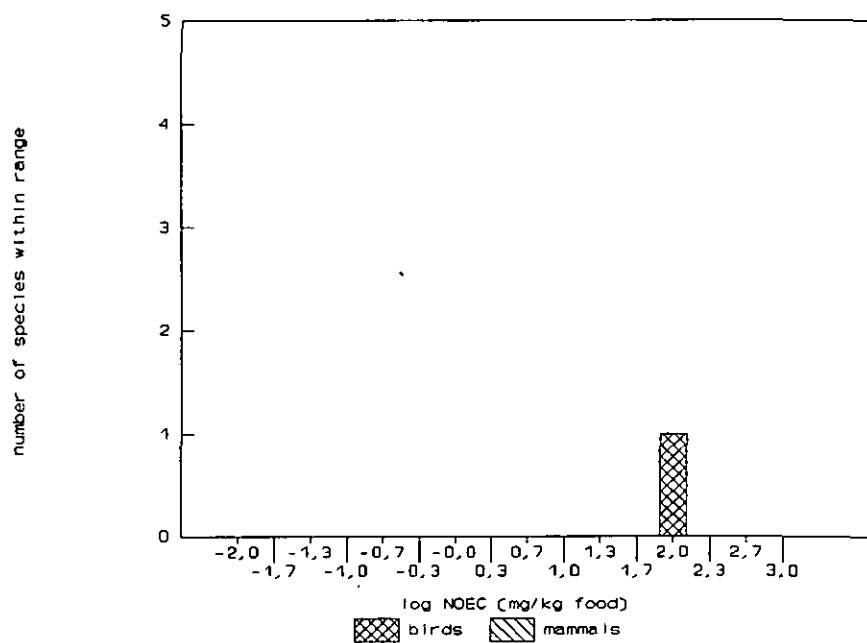


Figure 24. Sensitivity plot for chronic toxicity data for birds and mammals for o,p'-DDT.

HEPTACHLOR EPOXIDE

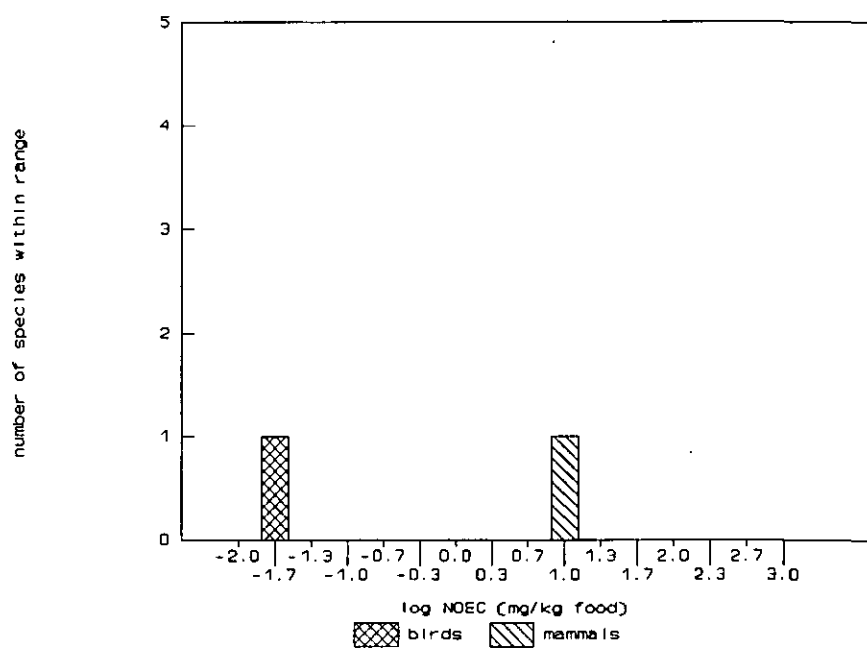


Figure 25. Sensitivity plot for chronic toxicity data for birds and mammals for heptachlor epoxide.

HEXACHLOROBENZENE

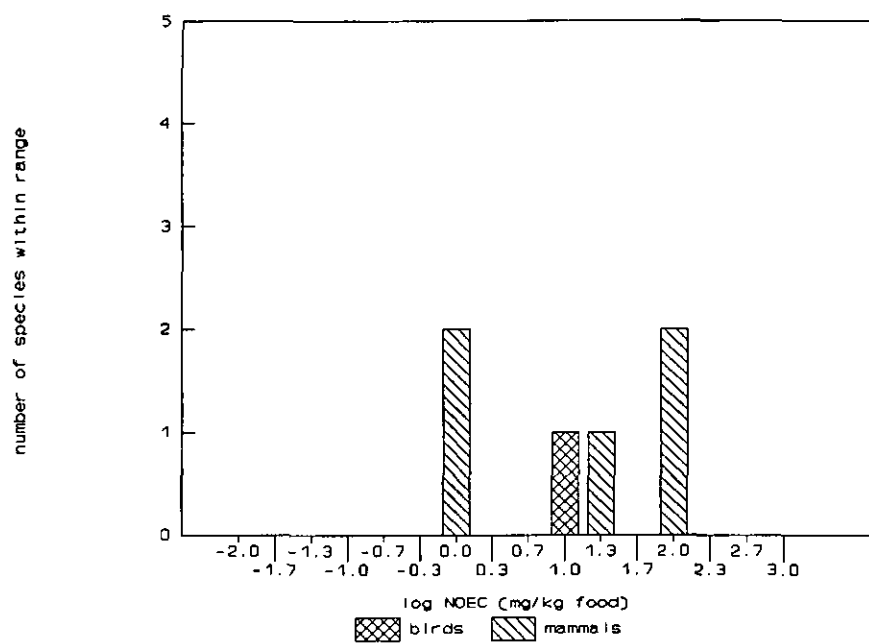


Figure 26. Sensitivity plot for chronic toxicity data for birds and mammals for hexachlorobenzene.

METHYL-MERCURY

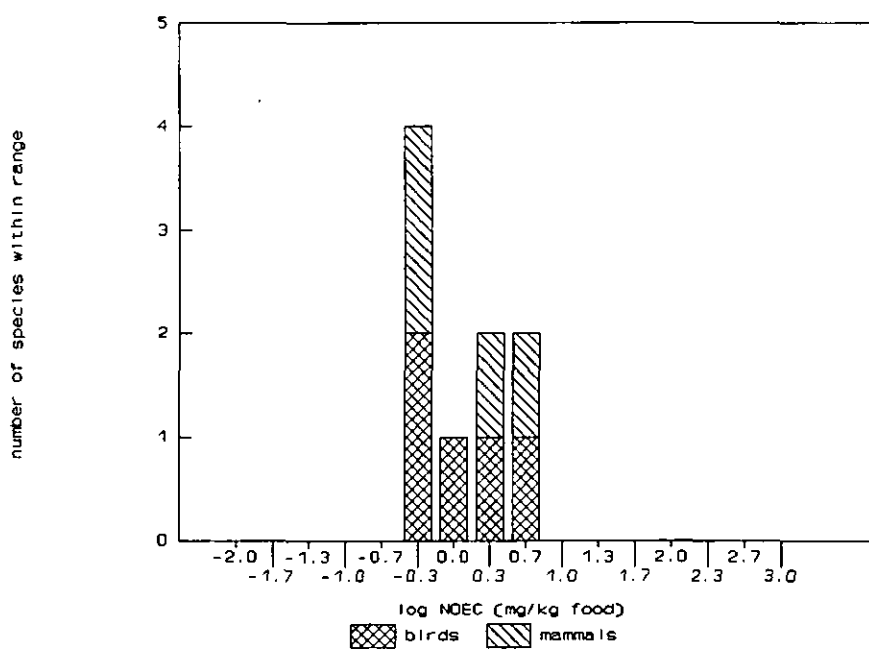


Figure 27. Sensitivity plot for chronic toxicity data for birds and mammals for methyl-mercury.

PENTACHLOROBENZENE

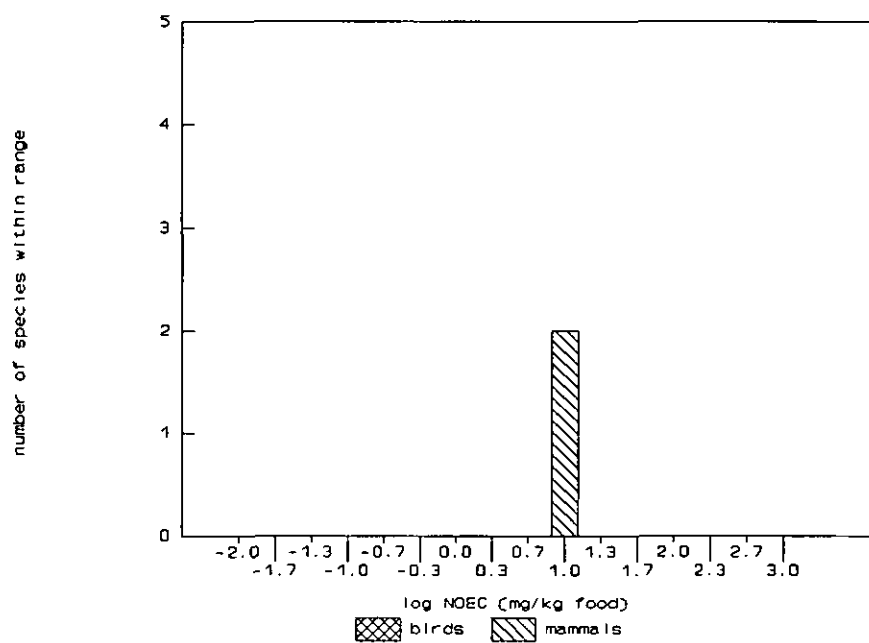


Figure 28. Sensitivity plot for chronic toxicity data for birds and mammals for pentachlorobenzene.

QUINTOZONE

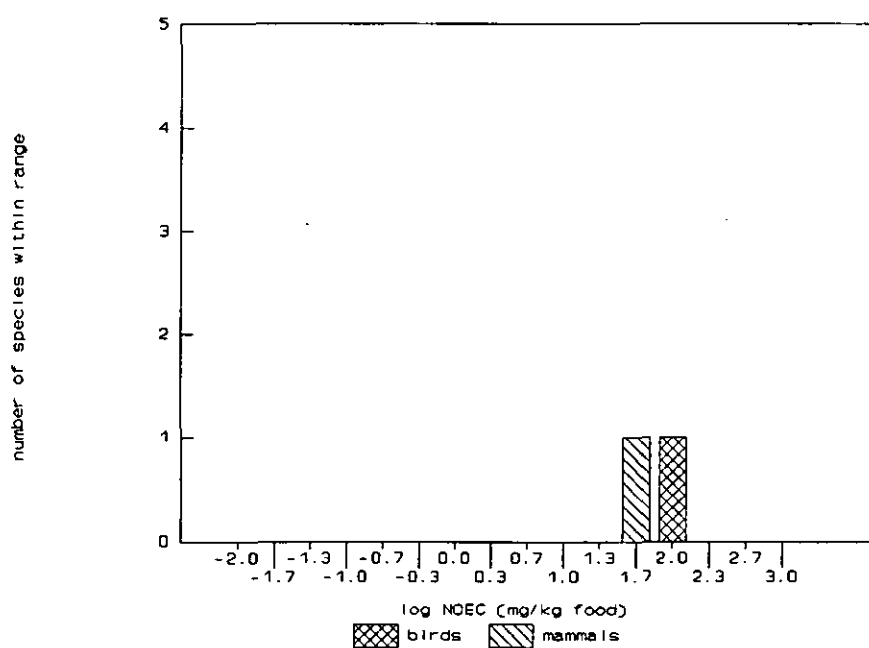


Figure 29. Sensitivity plot for chronic toxicity data for birds and mammals for quintozone.

5. SECONDARY POISONING: TERRESTRIAL FOOD CHAIN

5.1 MPCs for secondary poisoning

In Table 5.1 MPCs incorporating effects due to secondary poisoning are calculated using method I and II as described in paragraph 2.8.2. For p,p-DDD, p,p'-DDE, o,p'-DDT, fenthion, α -HCH, β -HCH and quitozene no results are presented because no $MPC_{direct; soil}$ is available as no ecotoxicological data are present for soil organisms. For these compounds the MPC based on equilibrium partitioning will be compared with the lowest $NOEC/BCF_{mean}$ in Chapter 6.

Table 5.1 MPCs using method I based on soil organisms ($MPC_{direct; soil}$), birds ($MPC_{sp; birds}$), mammals ($MPC_{sp; mammals}$), data sets of birds and mammals ($MPC_{sp; combined}$) and method II (based on combined data sets for soil organisms, birds and mammals) using BCF_{mean} for earthworms (mg/kg in standard soil).

compound	method I	method II lowest			MPC	NOEC/BCF for birds/ mammals
	$MPC_{direct; soil}$	$MPC_{sp; birds}$	$MPC_{sp; mammals}$	$MPC_{sp; combined}$		
aldrin	0.05	0.0012	0.078	0.0037	0.011 (50 ^a)	0.012
cadmium	0.27	0.0035	0.20	0.030	0.069 (5.8)	0.017
carbofuran	0.0047	0.060	0.39	0.46	0.27 (13)	0.60
chlordane	0.0043	0.76	0.69	0.69	0.69 ^b	6.9
chlorpyrifos	0.00036	1.1	0.14	0.85	0.42 (16)	1.4
copper	6.2	-	0.55	0.55	1.9 (13)	1.6
p,p'-DDT	0.01	0.048	1.7	0.11	0.01 ^b	0.12
dieldrin	0.05	0.067	0.081	0.087	0.052 (5.5)	0.12
endosulfan	0.05	1.9	0.16	0.16	0.019 (5,900)	1.4
endrin	0.00095	0.030	0.017	0.020	0.00095 ^b	0.058
γ -HCH	0.005	0.18	0.58	0.27	0.051 (82)	0.37
heptachlor	0.0007	0.18	0.14	0.14	0.0007 ^b	1.4
heptachlor epoxide	0.0007	0.00046	0.16	0.00046	0.0007 ^b	0.0046
hexachlorobenzene	1.3	0.12	0.016	0.028	0.018 (210)	0.12
mercury	0.2	0.26	1.3	0.26	0.19 ^b	2.6
methyl-mercury	0.2	0.0026	0.0027	0.0033	0.00061 ^b	0.0061
pentachlorobenzene	0.3	-	0.12	0.12	0.12 ^b	1.2
pentachlorophenol	0.17	5.8	1.3	1.3	1.2 (16)	13
thiram	0.038	0.067	0.12	0.067	0.038 ^b	0.67

^a between brackets: ratio between $MPC_{50\% confidence}$ and $MPC_{95\% confidence}$ calculated with method of Aldenberg and Slob (for the MPC values based on method I this ratio is not given because they are already presented in Tables 3.4 and 3.5)

^b indicative MPC based on modified EPA method

From the calculations presented in Table 5.1 it is clear that, based on the food chain soil → earthworm → birds/mammals for most compounds there is no risk for secondary poisoning. This is also the case if the maximum BCF is used. Only for aldrin, cadmium, copper, hexachlorobenzene, methyl-mercury and pentachlorobenzene the MPC_{sp} or the MPC using method II is lower than the $MPC_{direct; soil}$. This is in agreement with the results obtained by Romijn et al. [23]. It must be stated that the scarcity of ecotoxicological data for terrestrial organisms seriously hampers drawing conclusions.

5.2 MPCs for soil based on direct effects and secondary poisoning

The procedure used for deriving MPCs for soil is similar to the one used for deriving MPCs for the aquatic environment as described in paragraph 4.3: if secondary poisoning is critical, the MPC_{sp} based on the combined data-set is used. However, if the lowest $NOEC/BCF_{mean}$ is lower than this MPC_{sp} , the lowest value based on the separate data-set is used. This means that for cadmium, copper, hexachlorobenzene, methyl-mercury and pentachlorobenzene the MPC_{soil} is set at 0.0035 (based on data for birds only), 0.55 (based on data for mammals only), 0.028 (based on the combined data-set), 0.0033 (based on the combined data-set) and 0.12 mg/kg (based on data for mammals only), respectively. For the other compounds the MPC_{soil} is set at the one based on direct effects on terrestrial organisms. This is also done for aldrin although the $MPC_{direct; soil}$ of 0.05 mg/kg is higher than the lowest $NOEC/BCF_{mean}$ for birds/mammals being 0.012 mg/kg. As already explained in paragraph 3.4 the latter value is that low because high factors are used to convert LOECs to NOECs for birds. Therefore for aldrin and dieldrin the same $MPC_{direct; soil}$ is used.

In the following chapter $MPC_{direct; soil}$ s will be harmonized with the NOECs for the aquatic environment using the equilibrium partitioning method. This method is also used to derive MPCs for sediment and soil for those compounds for which no ecotoxicological data are available.

6. HARMONIZATION OF MAXIMUM PERMISSIBLE CONCENTRATIONS FOR WATER WITH SEDIMENT AND SOIL

6.1 Procedure

Toxicity data are scarce for soil organisms while no data at all are available for sediment dwelling organisms. In these cases a MPC for soil and sediment can be derived by means of the equilibrium partitioning method using the formula [5]:

$$MPC_{sed/soil} = MPC_{aq} \times K_p \quad (13)$$

where:

- K_p = partition coefficient between sediment or soil and water as presented in paragraph 3.5 (l/kg)
- MPC_{aq} = Maximum Permissible Concentration in water derived from toxicity data based on direct or indirect effects as presented in paragraph 4.3 (mg/l)
- $MPC_{sed./soil}$ = Maximum Permissible Concentration in soil or sediment (mg/kg dry sediment or soil)

This formula can also be used to harmonize independently derived MPCs for water and sediment or soil. However, if no toxicity data are available for soil and sediment dwelling organisms harmonization of MPCs for the different compartments is impossible. In that case the equilibrium partitioning method can be used only as an indirect method to derive MPCs based on ecotoxicological data. Results of these calculations are presented in paragraph 6.2.

Only for the compounds in Chapter 5 for which MPC_{soil} s are derived, harmonization is possible. Therefore MPC_{soil} s based on toxicity data based on direct or indirect effects and MPC_{soil} s calculated by means of the equilibrium partitioning method are compared. This will be presented in paragraph 6.3.

6.2 Calculation of Maximum Permissible Concentrations for sediment and soil using the equilibrium partitioning method

In Table 6.1 MPCs for soil and sediment are presented using MPC_{aq} s from Table 4.3 and partition coefficients from Table 3.6. Only for endosulfan toxicity results are available for sediment dwelling organisms exposed via contaminated sediment [59]. For two crustaceans no effects were observed on mortality and reproduction at 0.26-0.5 mg/kg, while the colonization rate of the polychaete *Streblospio benedicti* was reduced by 50-60% at 0.13 mg/kg. Comparing these values with the much lower $MPC_{sed.}$ of 2.6×10^{-5} mg/kg based on equilibrium partitioning it can be concluded that this $MPC_{sed.}$ is probably on the low side. An explanation for the low $MPC_{sed.}$ may also be the relatively low K_p used for endosulfan (log K_p is 1.81; see paragraph 3.5). Because more reliable toxicity studies are not available it is decided to maintain the $MPC_{sed.}$ as presented in Table 6.1, however.

Table 6.1. Maximum Permissible Concentrations ($MPC_{sed./soil}$) for sediment and soil based on equilibrium partitioning (mg/kg standard soil or sediment)

compound	$MPC_{eq.}$ ($\mu\text{g/l}$)	$\log K_p$ (l/kg)	$MPC_{sed./soil}$ (mg/kg)
aldrin	0.018	3.81	0.12
cadmium	0.35	4.92	29
carbofuran	0.015	0.33	0.000032
chlordane	0.0015	3.30	0.0024
chlorpyrifos	0.0028	2.58	0.0011
copper	4.1	4.54	142
p,p'-DDD	0.00044	3.61	0.0018
p,p'-DDE	0.00044	3.52	0.0015
o,p'-DDT	0.00044	4.33	0.0094
p,p'-DDT	0.00044	4.33	0.0094
dieldrin	0.018	4.57	0.67
endosulfan	0.0004	1.81	0.000026
endrin	0.003	2.99	0.0029
fenthion	0.0031	2.05	0.00035
α -HCH	2.5	1.95	0.22
β -HCH	0.08	3.06	0.092
γ -HCH	0.77	2.40	0.19
heptachlor	0.00046	3.15	0.00065
heptachlor epoxide	0.00046	1.64	0.00002
hexachlorobenzene	0.0021	2.74	0.0012
mercury	0.0019	5.04	0.21
methyl-mercury	0.0019	5.04	0.21
pentachlorobenzene	0.030	2.60	0.012
pentachlorophenol	3.5	1.94	0.31
quintozone	0.29	3.06	0.33
thiram	0.032	1.39	0.00079

6.3 Harmonization of $MPC_{eq.}$ with MPC_{soil}

In Table 6.2 MPC_{soil} s based on equilibrium partitioning and toxicity data are compared (based on equilibrium partitioning: from Table 6.1; based on toxicological data based on direct and indirect effects as derived in paragraph 5.2).

Table 6.2. Maximum Permissible Concentrations (MPC_{soil}) based on toxicological data and equilibrium partitioning (mg/kg standard soil).

compound	MPC_{soil} equilibrium partitioning (mg/kg)	MPC_{soil} ecotoxicological data (mg/kg)
aldrin	0.12	0.05
cadmium	29	0.0035
carbofuran	0.000032	0.0047
chlordane	0.0024	0.0043
chlorpyrifos	0.0011	0.00036
copper	142	0.55
p,p'-DDT	0.0094	0.01
dieldrin	0.67	0.05
endosulfan	0.000026	0.05
endrin	0.0029	0.00095
γ -HCH	0.19	0.005
heptachlor	0.00065	0.0007
heptachlor epoxide	0.00002	0.0007
hexachlorobenzene	0.0012	0.028
mercury	3.5	0.2
methyl-mercury	0.21	0.0033
pentachlorobenzene	0.012	0.12
pentachlorophenol	0.31	0.17
thiram	0.00079	0.038

For cadmium, copper, mercury and methyl-mercury the values obtained using equilibrium partitioning are much higher than the ones based on (in)direct effects. However, it is doubtful whether the partition coefficients used are representative for the distribution of metals between soil and porewater as they are derived from suspended particles - surface water distributions [3]. In addition the same value is used for mercury and methyl-mercury; which is not realistic.

Bockting et al. reviewed soil-water partition coefficients for several trace metals, e.g. cobalt and vanadium [60]. For comparison they also collected some K_p s derived from batch experiments for other metals. Average log K_p s are 2.30, 2.99 and 2.23 for cadmium, copper and mercury derived from experiments carried out by Buchter et al. [61]. The average log K_p for cadmium derived by Chardon is 2.47 [62]. These K_p s are a factor 40-650 lower than the ones used in Table 6.1. Consequently, application of the equilibrium partitioning method leads to lower MPC_{soil} s. Using K_p s from Buchter, MPC_{soil} s are 0.070, 4.0, 0.0054 and 0.00032 mg/kg for cadmium, copper, mercury and methyl-mercury, respectively. These values agree much better with the MPC_{soil} s based on effect data. It can be concluded that the K_p s used for metals must be critically reviewed first, before a meaningful comparison between MPCs based on effect data and equilibrium partitioning is possible. In addition natural background levels

must be taken into account if environmental quality objectives are set for metals. This falls outside the scope of the present report, however. In the present report the data for metals presented in Table 6.2 will therefore not be discussed further.

Noteworthy, MPC_{soil} s based on equilibrium partitioning and ecotoxicological data agree very well for many organic compounds; e.g. aldrin, chlordane, p,p'-DDT, endrin, heptachlor and pentachlorophenol. For the organic compounds for which both MPC_{soil} s differ significantly, one of the MPC_{soil} s is not consistently the lowest or the highest one. Differences may be caused by the use of different extrapolation methods or different assessment factors in calculating the MPC_{aq} s or MPC_{soil} s based on ecotoxicological data. Uncertainty is also introduced by converting the MPC_{aq} s using K_p s.

For determining the 'final' MPC_{soil} in general preference is given to the ones based on toxicological data for direct effects on soil organisms or indirect effects on birds and/or mammals via the terrestrial route. However, if the MPC_{aq} is based on a relatively large data-set containing chronic data for several taxonomic groups while the MPC_{soil} is based on a few data (e.g. acute data leading to the use of high assessment factors or only some data for birds and/or mammals) the MPC based on equilibrium partitioning may be given greater weight. As a criterium is used that enough chronic NOECs must be present for aquatic organisms to use the method of Aldenberg and Slob, i.e. at least 4 values for different taxonomic groups.

In the following paragraph the derivation of MPC_{soil} s is described per compound.

6.4 MPCs for soil

In this paragraph MPC_{soil} s are derived based on the results presented in the previous paragraphs of Chapter 6 and on the results presented in Chapter 5. The sensitivity graphs for birds and mammals on page 41-61 can again be used. Only for cadmium and copper graphs are made of chronic toxicity data for soil organisms (see page 73) as for the other compounds almost no NOECs are available. As already stated in the former paragraph, no comparison will be made for metals between the MPC based on (in)direct effects and the one based on equilibrium partitioning.

Aldrin and dieldrin: because also in soil aldrin is rapidly converted to dieldrin the same MPC_{soil} is set for both compounds. The $MPC_{direct; soil}$ of 0.05 mg/kg is calculated using the EPA-method applying a factor 10 on the lowest NOEC for dieldrin. Acute data are available for insects and collembola; chronic data for microbial processes, enzyme activity and microorganisms. For dieldrin the MPC_{sp} using method I and the MPC using method II (both calculated with the method of Aldenberg and Slob) are slightly higher than the $MPC_{direct; soil}$. If the maximum BCF is used the opposite occurs. The lowest $NOEC/BCF_{mean}$ is 0.12 mg/kg. For aldrin MPC s using method I or II are more than a factor 5 lower, which is caused by one extremely low NOEC value for birds, however (see also paragraph 4.3). It is therefore concluded that the value of 0.05 mg/kg doesn't need to be adjusted downwards.

The MPC s based on equilibrium partitioning are higher than the $MPC_{direct; soil}$, being 0.12 and 0.67 mg/kg for aldrin and dieldrin, respectively. The latter value is certainly too high being almost equal to the lowest L(E)C50. It is decided to set the MPC_{soil} equal to the one based on direct effects on soil organisms.

Conclusion: the MPC_{soil} is set at 0.05 mg/kg (based on effects on soil organisms). This value must be considered as an indicative one.

Cadmium: the $MPC_{direct; soil}$ is 0.27 mg/kg using the method of Aldenberg and Slob. Distribution of NOECs seems symmetrical with a lowest NOEC of 0.75 mg/kg. The MPC using method II is 0.069 mg/kg. MPC_{sp} s using method II differ much due to the possible greater sensitivity of birds (see also paragraph 4.3); the one based on data for birds only is 0.0035 mg/kg. The lowest $NOEC/BCF_{mean}$ is 0.017 mg/kg.

Conclusion: the MPC_{soil} is set at 0.0035 mg/kg (MPC_{sp} based on data for birds only). For setting of environmental quality objectives this value must be compared with natural background concentrations.

Carbofuran: the $MPC_{direct; soil}$ is 0.0047 mg/kg using the EPA-method applying a factor 100 on the lowest $L(E)C50$. Acute data are available for nematods, oligochaetes, collembola and insects; chronic data for microorganisms. The MPC_{sp} using method I and the one based on method II (both calculated with the method of Aldenberg and Slob) are more than a factor 10 higher than the $MPC_{direct; soil}$. Also if the BCF_{max} is used it can be concluded that there is no risk for secondary poisoning at a concentration equal to the $MPC_{direct; soil}$.

The MPC based on equilibrium partitioning of 0.000032 mg/kg is c. 150 times lower than the one based on direct effects. Several factors may be responsible for this large difference, e.g. the uncertainty in the relatively low K_p of 0.33 l/kg, or characteristics of tests with soil organisms (total concentrations versus bioavailable fraction). On the one hand it can be argued that concentrations in pore water above the MPC_{aq} may cause adverse effects. On the other hand terrestrial toxicity data are available for target organisms.

Conclusion: the MPC_{soil} is set at 0.0047 mg/kg (based on effects on soil organisms). This value must be considered as an indicative one.

Chlordane: the $MPC_{direct; soil}$ is 0.0043 mg/kg using the EPA-method applying a factor 1,000 on the lowest $L(E)C50$. Acute data are available for oligochaeta, insects and collembola; chronic data for microorganisms, microbial processes and enzyme activity. MPC_{sp} using method I and the MPC using method II are considerably higher than the $MPC_{direct; soil}$. This is also the case if the BCF_{max} is used. The lowest $NOEC/BCF_{mean}$ is 6.9 mg/kg. It can be concluded that there is no risk for secondary poisoning at a concentration equal to the $MPC_{direct; soil}$. The MPC based on equilibrium partitioning is 0.0024 mg/kg, being almost equal to the $MPC_{direct; soil}$.

Conclusion: the MPC_{soil} is set at 0.0043 mg/kg (based on effects on soil organisms). This value must be considered as an indicative one.

Chlorpyrifos: the $MPC_{direct; soil}$ is 0.00036 mg/kg using the EPA-method applying a factor 1,000 on the lowest $L(E)C50$. Acute data are available for oligochaeta and collembola; chronic data for microorganisms, microbial processes and enzyme activity. The MPC_{sp} using method I and the one using method II (both calculated using the method of Aldenberg and Slob) are much higher than the $MPC_{direct; soil}$, even if the BCF_{max} is used. The lowest $NOEC/BCF_{mean}$ is 1.4 mg/kg. It can be concluded that there is no risk for secondary poisoning at a concentration equal to the $MPC_{direct; soil}$.

The MPC based on equilibrium partitioning is 0.0011 mg/kg, being somewhat higher than the $MPC_{direct; soil}$. The former one is preferred because this value is based on a relatively large data-set for aquatic organisms (chronic data for 4 taxonomic groups) compared to soil organisms.

Conclusion: the MPC_{soil} is set at 0.0011 mg/kg (based on the equilibrium partitioning

method).

Copper: the $MPC_{direct; soil}$ is 6.2 mg/kg using the method of Aldenberg and Slob. NOECs are even distributed with a lowest NOEC of 13 mg/kg. The MPC_{sp} using method I (based on data for mammals only) and the MPC based on method II are lower, being 0.55 and 1.9 mg/kg.

Conclusion: the MPC_{soil} is set at 0.55 mg/kg (MPC_{sp} based on data for mammals only as data for birds are not available). For setting of environmental quality objectives this value must be compared with natural background concentrations.

DDT and derivatives: the $MPC_{direct; soil}$ for p,p'-DDT is 0.01 mg/kg using the EPA-method applying a factor 1,000. Only one acute study with *Gryllus pennsylvanicus* is available; no chronic data are present. No data are available for DDD, DDE and o,p'-DDT. For p,p'-DDT all MPC_{sp} s (calculated using the method of Aldenberg and Slob) are higher than the $MPC_{direct; soil}$, while the one based on method II (calculated using the EPA method) is equal to this value. Using BCF_{max} only the MPC_{sp} based on toxicity data for birds only is slightly lower than the $MPC_{direct; soil}$: 0.0048 versus 0.01 mg/kg, respectively. The MPC based on equilibrium partitioning is 0.0094 mg/kg, which is almost equal to the $MPC_{direct; soil}$.

It is remarkable that there seems to be no risk for secondary poisoning because adverse effects due to biomagnification have been reported in the past for DDT [52]. On the other hand the $MPC_{direct; soil}$ is calculated using a factor 1,000 on a LC50 for a target species. Especially in this case information from field studies should be compared with the MPCs presented here. This, phase 2 research, falls outside the scope of the present report, however. It can be mentioned that DDT is used as a model-compound in the research project of the National Institute of Public Health and Environmental Protection and National Institute for Coastal and Marine Management mentioned in paragraph 2.8.1.

Conclusion: the MPC_{soil} for DDT is set at 0.01 mg/kg (based on effects on soil organisms and equilibrium partitioning). For DDD and DDE it is proposed to use the same MPC_{soil} . This value must be considered as an indicative one.

Endosulfan: the $MPC_{direct; soil}$ is 0.05 mg/kg using the EPA-method applying a factor 100 on the lowest L(E)C50. Acute data are available for plants and oligochaetes; chronic data for microbial processes. MPC_{sp} using method I is higher than the $MPC_{direct; soil}$, while the one using method II is a factor 2.6 lower (both calculated using the method of Aldenberg and Slob). Using BCF_{max} the MPC_{sp} for the combined data-set is a factor 3.1 lower than the $MPC_{direct; soil}$.

The MPC based on equilibrium partitioning of 0.000026 mg/kg is much lower than the $MPC_{direct; soil}$. This is caused by the extreme sensitivity of fish for endosulfan and the low K_p . For the terrestrial environment the $MPC_{direct; soil}$ is therefore preferred.

Conclusion: the MPC_{soil} is set at 0.05 mg/kg (based on effects on soil organisms). This value must be considered as an indicative one.

Endrin: The $MPC_{direct; soil}$ is 0.00095 mg/kg using the EPA-method applying a factor 1,000 on the lowest L(E)C50. Only one acute study is available for *Folsomia candida*, while no chronic data have been found. MPC_{sp} using method I (calculated using the method of Aldenberg and Slob) is much higher than the $MPC_{direct; soil}$, also if the BCF_{max} is used. The MPC using method II and calculated using the EPA method is equal to the $MPC_{direct; soil}$.

The MPC based on equilibrium partitioning is 0.0029 mg/kg. This value is preferred because for aquatic organisms much more toxicity data are available (chronic data are available for 4 taxonomic groups) than for terrestrial organisms.

Conclusion: the MPC_{soil} is set at 0.0029 mg/kg (based on the equilibrium partitioning method).

Fenthion: no toxicity data are available for soil organisms. The MPC based on equilibrium partitioning is 0.00035 mg/kg. The lowest $NOEC/BCF_{mean}$ for birds and mammals of 0.030 mg/kg is considerably higher than this MPC_{soil} . This is also the case if the BCF_{max} is used. The value of 0.00035 mg/kg seems therefore reasonably 'safe' with respect to adverse effects due to secondary poisoning.

Conclusion: the MPC_{soil} is set at 0.00035 mg/kg (based on the equilibrium partitioning method).

α -HCH: no toxicity data are available for soil organisms. The MPC based on equilibrium partitioning is 0.22 mg/kg. The lowest $NOEC/BCF_{mean}$ for mammals is 1.2 mg/kg. No toxicity data are available for birds. Using the BCF_{max} the MPC based on equilibrium partitioning is somewhat higher. Based on these data it is decided that adjustment is not necessary.

Conclusion: the MPC_{soil} is set at 0.22 mg/kg (based on the equilibrium partitioning method).

β -HCH: no toxicity data are available for soil organisms. The MPC based on equilibrium partitioning is 0.092 mg/kg. The lowest $NOEC/BCF_{mean}$ for birds and mammals of 0.46 mg/kg is a factor 5 higher. If the BCF_{max} is used this value is a factor 2 lower. Based on these data it is decided that adjustment is not necessary.

Conclusion: the MPC_{soil} is set at 0.092 mg/kg (based on the equilibrium partitioning method).

γ -HCH: the $MPC_{direct; soil}$ is 0.005 mg/kg using the EPA-method applying a factor 10 on the lowest $NOEC$. Acute and chronic data are available for collembola and oligochaetes. MPC_{sp} using method I and the one using method II (both calculated with the method of Aldenberg and Slob) are higher than the $MPC_{direct; soil}$, also if the BCF_{max} is used.

The MPC based on equilibrium partitioning, being 0.19 mg/kg, is much higher than the $MPC_{direct; soil}$. This value is even considerably higher than the lowest $NOEC$ for soil organisms. Therefore the MPC based on direct effects on soil organisms is preferred.

Conclusion: the MPC_{soil} is set at 0.005 mg/kg (based on effects on soil organisms). This value must be considered as an indicative one.

Heptachlor and heptachlorepoxyde: the $MPC_{direct; soil}$ is 0.0007 mg/kg for both compounds using the EPA-method applying a factor 1,000 on the lowest $L(E)C50$ value for heptachlor. For heptachlor acute data are available for oligochaetes, collembola and insects, while for heptachlor epoxide only one study with collembola is present. For both compounds no chronic data are available. The MPC_{sp} using method I for heptachlor is much higher than the $MPC_{direct; soil}$, while the MPC_{sp} for heptachlor epoxide (both calculated using the EPA-method) is lower using BCF_{mean} or BCF_{max} . This is caused by an extremely low $NOEC$ for birds (see also paragraph 4.3). It is therefore concluded that the $MPC_{direct; soil}$ doesn't need to be adjusted downwards. The MPC using method II calculated with the EPA-method is equal to the

MPC_{direct; soil}

The MPC based on equilibrium partitioning is 0.00065 and 0.00002 mg/kg for heptachlor and heptachlor epoxide, respectively. The latter value is a factor 35 lower than the MPC_{direct; soil}. Based on the same considerations as for carbofuran it is decided that the MPC_{direct; soil} doesn't need to be adjusted downwards.

Conclusion: the MPC_{soil} is set at 0.0007 mg/kg for heptachlor and heptachlor epoxide (based on effects on soil organisms). This value must be considered as an indicative one.

Hexachlorobenzene: Van de Plassche and Bockting derived a MPC_{soil} of 1.3 mg/kg based on equilibrium partitioning [6]. However, secondary poisoning was not taken into account by them: the MPC_{aq} used was based on direct effects. If the MPC_{aq} of 0.0021 µg/l presented in Table 4.3 is used, in which secondary poisoning is incorporated, the MPC_{soil} is 0.0012 instead of 1.3 mg/kg.

The MPC_{sp} using method I and the one using method II (both calculated using the method of Aldenberg and Slob) are 0.028 and 0.018 mg/kg, respectively. The lowest NOEC/BCF_{mean} is 0.12 mg/kg. It can be concluded that because of possible adverse effects due to secondary poisoning the MPC of 1.3 mg/kg must be adjusted.

Conclusion: the MPC_{soil} is set at 0.028 mg/kg (MPC_{sp} based on the combined data-set).

Mercury: MPC_{direct; soil} is 0.20 mg/kg using the EPA-method applying a factor 10 on the lowest NOEC. Chronic data are available for microbial processes and molluscs. No acute data have been found. Data are taken from Van de Meent et al. who made no distinction between mercury and methyl-mercury. MPC_{sp} using method I and the one based on method II (both calculated using the EPA-method) are in the same range. The lowest NOEC/BCF_{mean} is 2.6 mg/kg.

It has been shown that methylation of inorganic mercury occurs in soils. However, the extent of methylation in terrestrial ecosystems is unclear. According to Romijn et al. therefore separate MPC_{soil}s are derived for mercury and methyl-mercury [23].

Conclusion: the MPC_{soil} is set at 0.20 mg/kg (based on effects on soil organisms). This value must be considered as an indicative one. For setting of environmental quality objectives this value must be compared with natural background concentrations.

Methyl-mercury: the MPC_{direct; soil} is equal to the one for mercury, i.e. 0.2 mg/kg. The MPC_{sp} using method I (using the method of Aldenberg and Slob) and the one using method II (using the EPA-method) are much lower: 0.0033 and 0.00061 mg/kg, respectively. The lowest NOEC/BCF_{mean} is 0.0061 mg/kg.

Conclusion: the MPC_{soil} is set at 0.0033 mg/kg (MPC_{sp} based on the combined data-set). For setting of environmental quality objectives this value must be compared with natural background concentrations.

Pentachlorobenzene: Van de Plassche and Bockting derived a MPC_{soil} of 0.30 mg/kg using the EPA-method applying a factor 1,000 on the lowest L(E)C50 [6]. This value is based on the only study available, being an acute one with plants. As for hexachlorobenzene secondary poisoning was not taken into account when deriving the MPC_{soil} of 0.30 mg/kg. The MPC_{soil} based on equilibrium partitioning using the MPC_{aq} of 0.030 µg/l from Table 4.3 (in which secondary poisoning is incorporated) is 0.012 mg/kg.

The MPC_{sp} using method I and the one using method II are slightly lower than the value

derived by Van de Plassche and Bockting, being both 0.12 mg/kg (both calculated with the EPA-method). The lowest NOEC/BCF_{mean} is 1.2 mg/kg. It is decided to adjust the value of 0.30 mg/kg, although it must be stated that there is a serious lack of data as only one study with plants and two with mammals are available.

Conclusion: the MPC_{soil} is set at 0.12 mg/kg (MPC_{sp} based on the combined data-set). This value must be considered as an indicative one.

Pentachlorophenol: the MPC_{direct; soil} is 0.17 mg/kg using the EPA-method applying a factor 10 on the lowest NOEC. Acute data are available for oligochaetes; chronic data for plants, oligochaetes and microbial processes. The MPC using method I and the one using method II (both calculated using the EPA-method) are higher than the MPC_{direct; soil}, even if the BCF_{max} is used. It can be concluded that there is no risk for secondary poisoning at a concentration equal to the MPC_{direct; soil}.

The MPC based on equilibrium partitioning is 0.31 mg/kg, which is in good agreement with the MPC_{direct; soil}.

Conclusion: the MPC_{soil} is set at 0.17 mg/kg (based on effects on soil organisms). This value must be considered as an indicative one.

Quintozene: no toxicity data are available for soil organisms. The MPC based on equilibrium partitioning is 0.33 mg/kg. The lowest NOEC/BCF_{mean} for birds and mammals is 5 mg/kg. The value of 0.33 mg/kg seems therefore reasonably 'safe' with respect to adverse effects due to secondary poisoning: this value is even somewhat lower than the NOEC/BCF_{max}.

Conclusion: the MPC_{soil} is set at 0.33 mg/kg (based on the equilibrium partition method).

Thiram: the MPC_{direct; soil} is 0.038 mg/kg using the EPA-method applying a factor 10 on the lowest NOEC. No acute data are available; chronic data are present for microorganisms, microbial processes and enzyme activity. The MPC_{sp} using method I (based on the combined data-set with the EPA method) is slightly higher, i.e. 0.067 mg/kg. The one using method II is equal to the MPC_{direct; soil}. If the BCF_{max} is used the opposite conclusion must be drawn. The lowest NOEC/BCF_{mean} is 0.67 mg/kg.

The MPC based on equilibrium partitioning of 0.00079 mg/kg is a factor 40 lower than the MPC_{direct; soil}. It must be stated that no terrestrial toxicity data are available for target species, while these data are present for aquatic organisms. On the other hand enzyme activity is a relative sensitive endpoint if data for thiram are compared with data for other compounds studied in the present report. Based on these considerations it is decided to use the MPC_{direct; soil}.

Conclusion: the MPC_{soil} is set at 0.038 mg/kg (based on effects on soil organisms). This value must be considered as an indicative one.

Summarizing it can be concluded that via the terrestrial route secondary poisoning may be critical for cadmium, copper, penta- and hexachlorobenzene and methyl-mecury. Due to scarcity of data for effects on soil organisms as well as toxicity data for birds and mammals, these results should be treated with caution. Also, as has already been stated in paragraph 2.8.2, the method used for assessing effects due to secondary poisoning via the terrestrial route soil → earthworm → worm-eating birds or mammals has several methodological drawbacks.

Table 6.3 gives an overview of the MPC_{soil}s derived in the present paragraph.

Table 6.3 Maximum Permissible Concentrations for a standard soil with 25% clay and 10% o.m. (mg/kg)

compound	MPC _{soil}	compound	MPC _{soil}
aldrin	0.05 ^a	fenthion	0.00035 ^b
cadmium	0.0035 ^c	α-HCH	0.22 ^b
carbofuran	0.0047 ^a	β-HCH	0.092 ^b
chlordane	0.0043 ^a	γ-HCH	0.005 ^a
chlorpyrifos	0.0011 ^b	heptachlor	0.0007 ^a
copper	0.55 ^c	heptachlor epoxide	0.0007 ^a
p,p'-DDD	0.01 ^a	hexachlorobenzene	0.028
p,p'-DDE	0.01 ^a	mercury	0.2 ^{a,c}
p,p'-DDT	0.01 ^a	methyl-mercury	0.0033 ^c
o,p'-DDT	0.01 ^a	pentachlorobenzene	0.12 ^a
dieldrin	0.05 ^a	pentachlorophenol	0.17 ^a
endrin	0.0029 ^b	quintozone	0.33 ^b
endosulfan	0.05 ^a	thiram	0.038 ^a

^a indicative value

^b based on equilibrium partitioning

^c must be compared with natural background concentrations for setting of environmental quality objectives

CADMIUM

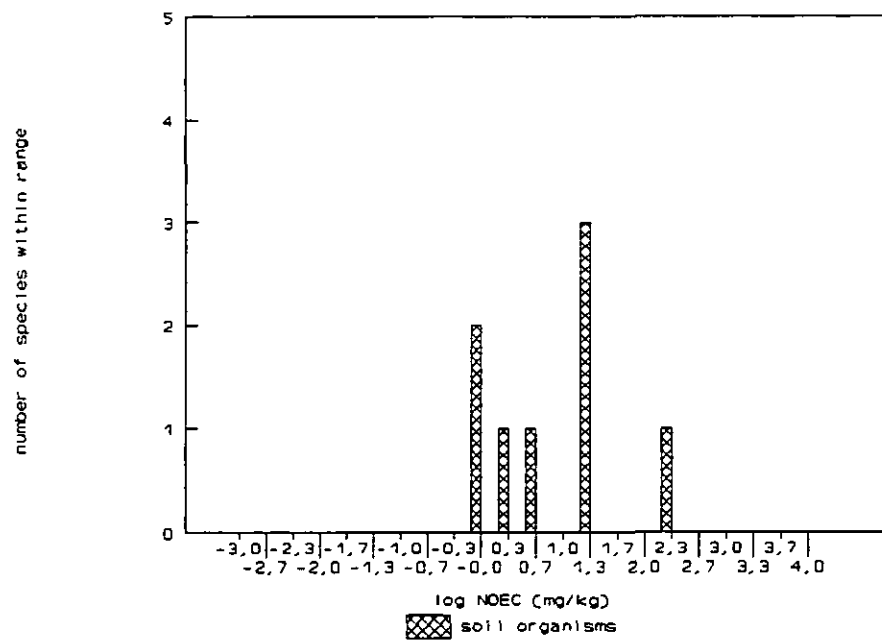


Figure 30. Sensitivity plot for cadmium for chronic toxicity data for soil organisms.

COPPER

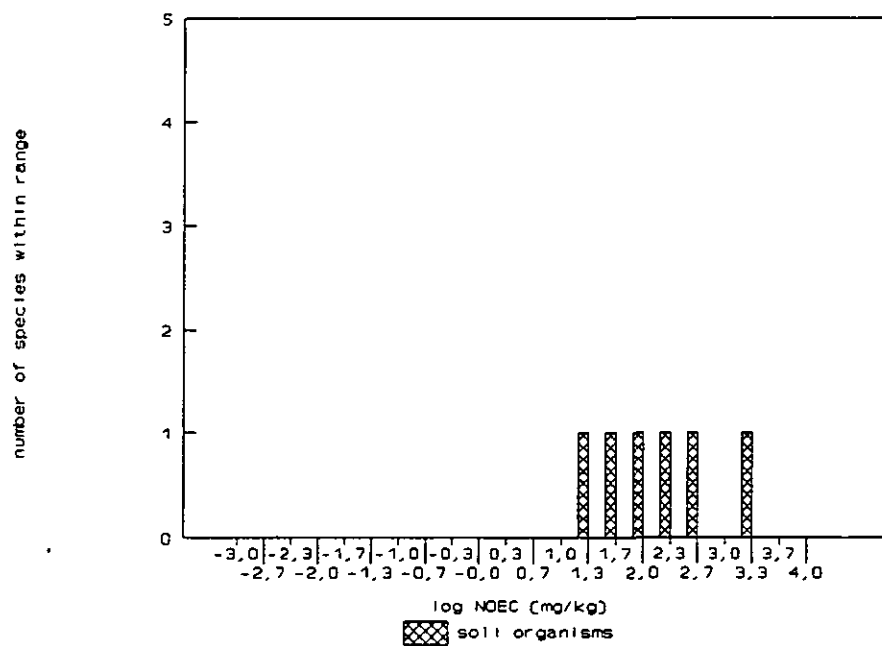


Figure 31. Sensitivity plot for copper for chronic toxicity data for soil organisms.

7. ENVIRONMENTAL CONCENTRATIONS MEASURED IN THE NETHERLANDS

Data on environmental concentrations in the Netherlands were collected for all compartments. In the following paragraphs these data are discussed and compared with the MPCs and NCs derived in Chapters 4, 5 and 6. Only the well-known data bases in the Netherlands have been consulted. Especially for the pesticides dealt with in the present report more data are probably available as these compounds are often also measured by local and regional institutes.

7.1 Environmental concentrations in surface water

The underlying data for surface water collected by the Cooperating Rhine and Meuse Waterworks in 1990 and 1991 are presented in Appendix D. Concentrations are measured at several locations, a.o. Rhine River (Lobith), Meuse River (Belfeld, Eysden and Keizersveer), Lek River (Hagestein), Lek Canal (Nieuwegein) and Lake IJssel (Andijk). For aldrin, p,p'-DDD, p,p'-DDE, o,p'-DDT, p,p'-DDT, endrin and α -endosulfan measurements are available. All concentrations are lower than the detection limit (0.01-0.02 $\mu\text{g/l}$), however.

Concentrations in surface water in The Netherlands are also measured by the National Institute of Inland Water Management. Because of the structure of their data base concentrations are not presented in the present report but the MPC_{aq} and NC_{aq} values as derived in Chapter 4 have been compared by the National Institute of Inland Water Management with the 90 percentiles for each location for state and non-state water bodies, respectively [63]. As the 90 percentiles are total concentrations the $\text{MPC}_{\text{aq},s}$ and $\text{NC}_{\text{aq},s}$, i.e. dissolved concentrations, are recalculated using the formula:

$$\text{MPC}_{\text{total}} = \text{MPC}_{\text{dissolved}} \times (1 + [K_p \times f_{\text{oc}} \times S]) \quad (14)$$

where:

$\text{MPC}_{\text{total}}$:	MPC_{aq} as total concentration (mg/l)
$\text{MPC}_{\text{dissolved}}$:	MPC_{aq} as dissolved concentration (mg/l)
K_p :	sediment - water partition coefficient (l/kg)
f_{oc} :	fraction organic carbon in particulate matter: 0.10
S :	particulate matter content of surface water: 30 mg/l

For state water bodies measurements from 1992 are used. Results are presented in Table 7.1. Only for 6 compounds data are available. For mercury the MPC_{aq} is exceeded at all locations. For the other compounds the NC_{aq} is exceeded at more than c. 65% of the locations. For dieldrin all 90 percentiles are equal to 'lower than the detection limit'. An overview of the detection limits for surface water, sediment and particulate matter is presented in Table 7.6.

Also for non-state water bodies measurements from 1992 are used. Results are presented in Table 7.2. Only for carbofuran, chlordane, pentachlorobenzene and quitozene no data are available. For thiram no data are present because no analytical method is available at the moment [64]. For mercury, DDT and derivatives the MPC_{aq} is exceeded at 70-90% of the

Table 7.1 Comparison of measurements in state water bodies in 1992 for surface water from National Institute of Waste Water Management with the $MPC_{aq.}$ and $NC_{aq.}$.

compound	number of locations	number of locations in %				
		$< NC_{aq.}$	$NC_{aq.} - MPC_{aq.}$	$(NC_{aq.} - MPC_{aq.})$	$> MPC_{aq.}$	$(> MPC_{aq.})$
cadmium	18	0	100	0	0	0
copper	39	0	92	0	8	0
dieldrin	5	0	100	100	0	0
γ -HCH	6	33	67	0	0	0
mercury	16	0	0	0	100	6
pentachlorophenol	20	30	70	0	0	0
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$< NC_{aq.}$:		number of locations lower than $NC_{aq.}$ (in %)				
$NC_{aq.} - MPC_{aq.}$:		number of locations between $NC_{aq.}$ and $MPC_{aq.}$ (in %)				
$(NC_{aq.} - MPC_{aq.})$:		fraction of $NC_{aq.} - MPC_{aq.}$ lower than the detection limit				
$< MPC_{aq.}$:		number of locations lower than $MPC_{aq.}$ (in %)				
$(> MPC_{aq.})$:		fraction of $> MPC_{aq.}$ lower than the detection limit				

Table 7.2 Comparison of measurements in non-state water bodies in 1992 for surface water from National Institute of Waste Water Management with the $MPC_{aq.}$ and $NC_{aq.}$.

compound	number of locations	number of locations in %				
		$< NC_{aq.}$	$NC_{aq.} - MPC_{aq.}$	$(NC_{aq.} - MPC_{aq.})$	$> MPC_{aq.}$	$(> MPC_{aq.})$
aldrin	118	0	95	88	5	1
cadmium	363	2	97	26	1	0

compound	number of locations	number of locations (in %)				
		<NC _{aq.}	NC _{aq.} -MPC _{aq.}	(NC _{aq.} -MPC _{aq.})	> MPC _{aq.}	(>MPC _{aq.})
chlorpyrifos	14	100	0	0	0	0
copper	485	0	89	1	11	0
DDD	74	0	0	0	100	9
DDE	75	0	0	0	100	28
DDT	98	0	4	4	96	28
dieldrin	159	8	91	73	1	1
α -endosulfan	177	21	7	5	72	60
endrin	116	0	28	19	72	70
fenthion	38	0	0	0	100	89
α -HCH	117	92	8	7	0	0
β -HCH	44	0	100	100	0	0
γ -HCH	194	22	78	27	0	0
heptachlor	99	0	0	0	100	92
heptachlor epoxide	113	0	0	0	100	90
hexachlorobenzene	133	0	10	9	90	81
mercury	308	0	5	2	95	23
pentachlorophenol	111	65	35	17	0	0

<NC_{aq.}: number of locations lower than NC_{aq.} (in %)
 NC_{aq.}-MPC_{aq.}: number of locations between NC_{aq.} and MPC_{aq.} (in %)
 (NC_{aq.}-MPC_{aq.}): fraction of NC_{aq.}-MPC_{aq.} lower than the detection limit
 <MPC_{aq.}: number of locations lower than MPC_{aq.} (in %)
 (<MPC_{aq.}): fraction of >MPC_{aq.} lower than the detection limit

Table 7.3 Comparison of measurements in state water bodies in 1992 for particulate matter from National Institute of Waste Water Management with the MPC and NC for particulate matter.

compound	number of locations	number of locations in %				
		$< NC_{aq.}$	$NC_{aq.} - MPC_{aq.}$	$(NC_{aq.} - MPC_{aq.})$	$> MPC_{aq.}$	$(> MPC_{aq.})$
aldrin	18	17	83	6	0	0
cadmium	19	0	100	0	0	0
copper	19	0	89	0	11	0
DDD	18	0	11	11	89	44
DDE	18	0	6	6	94	89
DDT	18	0	89	89	11	11
dieldrin	19	84	16	0	0	0
α -endosulfan	19	0	0	0	100	74
endrin	18	0	94	78	6	0
α -HCH	18	94	6	6	0	0
β -HCH	18	61	39	0	0	0
γ -HCH	19	74	26	0	0	0
heptachlor	18	0	22	6	78	11
heptachlor epoxide	18	0	0	0	100	100
hexachlorobenzene	19	0	16	5	84	5
mercury	19	0	0	0	100	0
pentachlorophenol	15	0	100	80	0	0
<hr/>						
$< NC_{aq.}$:	number of locations lower than $NC_{aq.}$ (in %)					
$NC_{aq.} - MPC_{aq.}$:	number of locations between $NC_{aq.}$ and $MPC_{aq.}$ (in %)					
$(NC_{aq.} - MPC_{aq.})$:	fraction of $NC_{aq.} - MPC_{aq.}$ lower than the detection limit					
$< MPC_{aq.}$:	number of locations lower than $MPC_{aq.}$ (in %)					
$(< MPC_{aq.})$:	fraction of $> MPC_{aq.}$ lower than the detection limit					

Table 7.4 Comparison of measurements in state water bodies up to 1992 for sediment from National Institute of Waste Water Management with the $MPC_{sed.}$ and $NC_{sed.}$.

compound	number of samples	number of samples in %				
		$< NC_{aq.}$	$NC_{aq.} - MPC_{aq.}$	$(NC_{aq.} - MPC_{aq.})$	$> MPC_{aq.}$	$(> MPC_{aq.})$
aldrin and dieldrin	3374	25	75	72	0	0
cadmium	5380	3	95	33	3	0
chlordane	30	27	3	3	70	70
copper	5427	0	88	7	11	0
DDT, DDD and DDE	1391	10	11	-	80	-
α -endosulfan	2364	0	4	4	96	89
endrin	3364	3	20	18	77	73
α -HCH	3320	31	69	66	0	0
β -HCH	3325	11	87	78	2	0
γ -HCH	3349	27	73	69	0	0
heptachlor and heptachlor epoxide	3370	0	6	5	94	92
hexachlorobenzene	3398	2	14	13	83	62
mercury	5300	0	26	-	74	-
pentachlorobenzene	294	12	63	35	25	18
<hr/>						
$< NC_{aq.}$:	number of locations lower than $NC_{aq.}$ (in %)					
$NC_{aq.} - MPC_{aq.}$:	number of locations between $NC_{aq.}$ and $MPC_{aq.}$ (in %)					
$(NC_{aq.} - MPC_{aq.})$:	fraction of $NC_{aq.} - MPC_{aq.}$ lower than the detection limit					
$< MPC_{aq.}$:	number of locations lower than $MPC_{aq.}$ (in %)					
$(< MPC_{aq.})$:	fraction of $> MPC_{aq.}$ lower than the detection limit					

Table 7.5 Comparison of measurements in non-state water bodies up to 1992 for sediment from National Institute of Waste Water Management with the $MPC_{sed.}$ and $NC_{sed.}$.

compound	number of samples	number of samples in %				
		$< NC_{aq.}$	$NC_{aq.} - MPC_{aq.}$	$(NC_{aq.} - MPC_{aq.})$	$> MPC_{aq.}$	$(> MPC_{aq.})$
aldrin and dieldrin	3506	50	50	47	0	0
cadmium	5361	21	78	18	0	0
chlordane	170	1	82	75	18	16
copper	5482	0	95	3	5	0
DDT, DDD and DDE	3536	2	24	-	74	-
α -endosulfan	3113	0	4	4	96	81
endrin	3474	4	34	26	61	55
α -HCH	3496	39	61	57	0	0
β -HCH	3485	19	81	72	0	0
γ -HCH	3415	34	66	58	0	0
heptachlor and heptachlor epoxide	3462	1	9	8	91	83
hexachlorobenzene	3460	1	21	12	78	64
mercury	5226	0	53	-	47	-
pentachlorobenzene	1235	1	72	46	27	27
pentachlorophenol	337	13	87	83	0	0
$< NC_{aq.}$:	number of locations lower than $NC_{aq.}$ (in %)					
$NC_{aq.} - MPC_{aq.}$:	number of locations between $NC_{aq.}$ and $MPC_{aq.}$ (in %)					
$(NC_{aq.} - MPC_{aq.})$:	fraction of $NC_{aq.} - MPC_{aq.}$ lower than the detection limit					
$< MPC_{aq.}$:	number of locations lower than $MPC_{aq.}$ (in %)					
$(< MPC_{aq.})$:	fraction of $> MPC_{aq.}$ lower than the detection limit					

Table 7.6 Detection limits for surface water, sediment and particulate matter for measurements of the National Institute of Inland Water Management.

compound	detection limit ^a	
	surface water ($\mu\text{g/l}$)	sediment/particulate matter ($\mu\text{g/kg}$)
aldrin	0.001	1.0
cadmium	0.04	400
chlordane	-	1.0
chlorpyrifos	0.01	-
copper	0.4	4000
DDD	0.001	1.0
DDE	0.001	1.0
DDT	0.001	1.0
dieldrin	0.001	1.0
endosulfan	0.001	1.0
endrin	0.001	1.0
fenthion	0.01	-
α -HCH	0.001	1.0
β -HCH	0.001	1.0
γ -HCH	0.001	1.0
heptachlor	0.005	1.0
heptachlor epoxide	0.005	1.0
hexachlorobenzene	0.001	1.0
mercury	0.01	30
pentachlorobenzene	-	1.0
pentachlorophenol	0.001	1.0

^a detection limits apply only to measurements in state water bodies. Measurements in non-state water bodies are carried out by several laboratories. According to the National Institute of Inland Water Management these detection limits are in most case 10 times and sometimes 100 times higher.

locations. For almost all compounds the NC_{aq} is exceeded at several locations. Only for α -HCH and chlorpyrifos the NC_{aq} is almost never exceeded, although chlorpyrifos has been measured at 14 locations only.

With respect to the comparison for metals it must be stated that 'background levels', as metals are naturally occurring compounds, have not been taken into account.

7.2 Environmental concentrations in particulate matter

Concentrations in particulate matter are measured by the National Institute of Inland Water Management in state water bodies [63]. According to the comparison for surface water 90 percentiles are compared with MPCs and NCs for particulate matter, which are recalculated from the MPC_{aq} s and NC_{aq} as presented in Chapter 4. For carbofuran, chlordane, chlorpyrifos, fenthion, pentachlorobenzene, quintozene and thiram no data are available. Results are presented in Table 7.3.

For DDD, heptachlor, hexachlorobenzene and mercury the MPC is exceeded for more than 50% of the locations. Also for DDT, DDE, α -endosulfan, heptachlorepoxyde the MPC is exceeded on many locations, but for these compounds many 90 percentiles are equal to 'less than the detection limit'.

The NC is exceeded on a relatively large scale for many compounds. Only for α -, β and γ -HCH and dieldrin the 90 percentiles are for most locations lower than the NC.

7.3 Environmental concentrations in sediment

Concentrations in sediment are measured by the National Institute of Inland Water Management for state and non-state water bodies [63]. 90 Percentiles are compared with MPC_{sed} s and NC_{sed} s as derived in Chapter 6 (see Table 6.1). Due to the requirements of the data base comparisons are carried out for the sum of aldrin and dieldrin, DDT and derivatives, heptachlor and heptachlorepoxyde.

For state water bodies no data are available for carbofuran, chlorpyrifos, fenthion, pentachlorophenol, quintozene and thiram. Results are presented in Table 7.4. For many compounds the MPC_{sed} is exceeded for a large percentage of the samples analyzed. However, for several compounds many 90 percentiles are equal to 'less than the detection limit': chlordane, α -endosulfan, endrin, heptachlor and heptachlorepoxyde, hexachlorobenzene. The same can be remarked for the comparison with the NC_{sed} , i.e. that for many compounds the NC_{sed} is lower than the detection limit.

For non-state water bodies no data are available for carbofuran, chlorpyrifos, fenthion, quintozene and thiram. Results are presented in Table 7.5. Also for non-state water bodies the comparison of 90 percentiles with MPC_{sed} s and NC_{sed} s is hampered by the high detection limits.

7.4 Environmental concentrations in soil

For aldrin, carbofuran, chlordane, chlorpyrifos, DDT and derivatives, endosulfan, endrin, fenthion, heptachlor, heptachlor epoxide and quintozene the data-base from the National Soil

Quality Monitoring Network has been consulted. Soil samples were taken at 40 locations in The Netherlands in 1987-1988 at 0-10 and 10-30 cm, representing 10 different combinations of land use/soil type. Only for aldrin, p,p'-DDE, DDT and endrin data are available. These are presented in detail in Appendix E.

For aldrin all concentrations are lower than the detection limit, i.e. $0.50 \mu\text{g/kg}$. Endrin has been found in orchards only. The indicative MPC_{soil} is exceeded in calcareous loam - clay loam by a factor 1.2 at 10-30 cm using the 90 percentile, and in thick earth soil by a factor of 2.9-3.6 and 7.9-10 using the average and 90 percentile, respectively.

The indicative MPC_{soil} s for DDE and DDT are exceeded in several combinations of land use/soil type at both depths. Especially in calcareous loam - clay loam in orchards, farmland and grassland and thick earth soil in orchards and farmland concentrations are high. Based on average concentrations exceeding factors in calcareous loam - clay loam are ≤ 12 , ≤ 55 and ≤ 17 for o,p'-DDT, p,p'-DDT and p,p'-DDE, respectively. For thick earth soil these factors are ≤ 5 , ≤ 49 and ≤ 32 , respectively. Using the 90 percentile exceeding factors are higher; up to 160.

7.5 Environmental concentrations in ground water

For aldrin, carbofuran, chlordane, chlorpyrifos, DDT and derivatives, endosulfan, endrin, fenthion, heptachlor, heptachlor epoxide and quintozone data-bases from the Provincial Groundwater Quality Monitoring Network and the National Groundwater Quality Monitoring Network have been consulted. For chlordane, carbofuran and quintozone no data have been found. For the other compounds measurements have been carried out in 1987 and 1990 for sand and clay at a depth of 5-15 meter. All concentrations are lower than the detection limit, however (see Appendix F).

8. DISCUSSION

8.1 Data availability

In the present report MPCs are derived for the aquatic and terrestrial environment based on direct effects on aquatic and terrestrial organisms as well as indirect effects due to secondary poisoning. With respect to the data availability it can be concluded that in many cases the appropriate data necessary for the calculation of the MPC are missing.

With respect to direct effects, most data are available for aquatic organisms, especially for freshwater organisms. It appears that for many compounds enough chronic data are present to apply the method of Aldenberg and Slob (refined effect assessment). However, it is striking that for pesticides which have been used in great amounts in the past, like DDT and heptachlor reliable chronic data are relatively scarce. For DDT NOECs are available for algae, crustaceans and fish only; for heptachlor only for crustaceans and fish. Probably additional tests have not been carried out because these persistent compounds were banned at a point of time when ecotoxicology was developing.

Toxicity data for soil organisms are rather scarce, while data for sediment dwelling organisms are fully lacking. Only for cadmium and copper enough chronic data for soil organisms are available to apply the method of Aldenberg and Slob. For 7 out of 25 compounds neither acute nor chronic data have been found. A special category of tests are studies on effects on microorganisms, microbial processes and enzyme activity. In these tests, in most cases performed with pesticides, often only two concentrations are tested: the normal application rate and 10 times this rate, so NOECs had to be derived from two effect concentrations. Consequently, clear concentration-effect relationships cannot be derived.

As for birds and mammals only reviews are consulted, it is likely that more data are available in literature. Especially for mammals the appropriate data with respect to secondary poisoning are often not presented in reviews, i.e. effect-data on mortality, growth and reproduction. These reviews are often aimed at effect or risk assessment for human health, e.g. for establishing an ADI. Other parameters like histopathology and biochemistry or effects on specific organs are described in greater detail. Especially effects on mortality and growth are often not reported because this is not the most critical effect with respect to human health. Hence, the original reference has to be consulted for extracting a NOEC on mortality or growth.

Chronic data for birds are scarce. Most data are relatively old whereas many data are obtained from two authors, i.e. DeWitt (1956 and 1963) and Hill et al. (1975) [65, 66, 67]. For aldrin and dieldrin severe effects were observed at the lowest test-concentration. NOECs had to be derived therefore applying high factors on LOECs.

In addition, terrestrial birds are used in most studies as test species, while the results are used for deriving a MPC for the route water → fish or mussel → fish- or mussel-eating bird or mammal.

Data on bioconcentration factors for fish are available for all compounds except carbofuran, p,p'-DDE and thiram. However, for 6 compounds only one single experimentally derived BCF has been found. For bivalves bioconcentration data are also scarce: for 11 compounds no BCFs are available while for 5 compounds only one BCF is present. Although reliable QSAR estimates are possible it must be concluded that there is a lack of reliable

bioconcentration data. Especially for compounds which may be transformed in the organism it is essential that experimentally derived BCFs are present, e.g. chlorpyrifos.

8.2 Secondary poisoning

In the present report MPCs have been derived for several compounds with a potential for secondary poisoning: 21 organic compounds and 4 metals including methyl-mercury. An aquatic and terrestrial route have been considered. With respect to the aquatic environment it can be concluded from the results presented in paragraph 4.3 that secondary poisoning may be a critical route for aldrin/dieldrin, cadmium, DDT and derivatives, all HCH isomers, penta- and hexachlorobenzene and methyl-mercury. Several compounds can be regarded as 'borderline cases': based on the geometric mean BCF MPCs based on direct and on indirect effects are in the same range but if the maximum BCF is used the MPC based on effects due to secondary poisoning is lower than the one based on direct effects. Examples are aldrin/dieldrin, endrin and α -HCH. For heptachlor, heptachlor epoxide and quintozone toxicity data for aquatic organisms as well as birds and mammals are too scarce to draw conclusions.

Based on the results for the terrestrial environment presented in paragraph 6.4, it can be concluded that secondary poisoning may be a critical route for cadmium, copper, penta- and hexachlorobenzene and methyl-mercury. However, these results should be treated with caution due to scarcity of data and because the terrestrial food-chain is probably too simple for investigating secondary poisoning. Besides, the correction factor for caloric content of food used for earthworms is based on a limited data-set, certainly if this data-set is compared to the one for fish and mussels. As already stated in paragraph 2.8.1 a model is being developed within a project carried out by the National Institute of Public Health and Environmental Protection in collaboration with the National Institute for Coastal and Marine Management. Results for cadmium, dieldrin, DDT, γ -HCH, mercury and pentachlorophenol, which are used as 'model-compounds', will be compared with the results obtained in the present report. In this model also other correction factors than the one for the energy content of food will be applied.

For mercury an 'Integrated Criteria Document' is being prepared at the moment, in which secondary poisoning for the aquatic as well as the terrestrial route will be dealt with also. Toxicity data for water- and soil organisms, which are taken from Van de Meent et al. in the present report, are updated in the 'Integrated Criteria Document' [3]. If integrated environmental quality objectives are set for mercury results presented in this document should be taken into account.

Based on the results showing that the MPC for indirect effects is lower than the MPC for direct effects it can be concluded that 'phase 2' research, as mentioned in paragraph 2.8.2 is necessary for the following compounds: aldrin/dieldrin, cadmium, DDT and derivatives, endrin, HCH isomers, penta- and hexachlorobenzene and methyl-mercury.

The above mentioned 'phase 2' research can include the following:

- extensive literature search, including on-line, for laboratory toxicity data for birds and mammals in order to obtain a more reliable of the MPC_{sp} . For several compounds extensive literature search may also be useful to extend the data set for birds and mammals, e.g. heptachlor, heptachlor epoxide and quintozone. In addition specific questions regarding certain data, such as the low value for heptachlor epoxide may be elucidated than.

- validate laboratory derived BCF values with monitoring data on concentrations in Dutch surface waters and fish and bivalves from these waters. Romijn et al. have already carried out such a validation for cadmium, dieldrin, γ -HCH and mercury [13]. They found a good fit between measured and calculated concentrations in fish using the geometric mean BCFs.
- gathering local and species specific information from field studies and comparing results from these studies with MPCs derived in the present report. It is realized that for several of the compounds mentioned above information from field studies will be scanty, e.g. α - or β -HCH or pentachlorobenzene.

8.3 Secondary poisoning: methodological aspects

In the present report MPCs are derived taking into account secondary poisoning via the aquatic route water \rightarrow fish/mussel \rightarrow fish/mussel-eating bird or mammal and the terrestrial route soil \rightarrow earthworm \rightarrow worm-eating bird or mammal according to a method originally developed by Romijn et al. [13, 23]. A correction factor for caloric content of food is applied (laboratory food, e.g. cereals versus food in the field, i.e. fish, mussels or worms). MPCs are calculated in two different ways: keeping the data sets for lower organisms and top predators separate (method I) and combining data sets of all organisms (method II). It appeared that method II can lead to unrealistic high or low values, so method I is preferred for deriving MPC values. Benefits and drawbacks of both methods are discussed in detail in paragraph 4.2.

As at the moment much work is ongoing with respect to secondary poisoning in which an attempt is made to give an answer to several methodological problems, these are not extensively discussed here. Reference is made to the project carried out by the National Institute of Public Health and Environmental Protection in collaboration with the National Institute for Coastal and Marine Management (see paragraph 2.8.1) and the report of the Dutch Health Council [11]. Results of the project mentioned above will be published in the near future.

The method applied in the present report is considered a 'screening method' for including secondary poisoning in effect assessment. Although the method is used for screening, a substantial amount of data is needed. However, for the aquatic route for organic compounds this can be slightly reduced by using calculated BCFs instead of measured ones. Considering this, it may be useful to study other methods. In the report of the Dutch Health Council two other methods are discussed: one from the EPA and another from Norstrom et al. [68, 69]. However, no time was available to study these methods in detail, while other methods were not discussed at all. It is recommended to include these methods in further discussions.

8.4 Harmonization of environmental quality objectives

For harmonization of MPCs for water with the ones for sediment and soil the equilibrium partitioning method is applied. For sediment no harmonization is possible as no toxicity data are available for sediment dwelling organisms. Hence, the method could only be used as an indirect method to calculate MPCs. Harmonization for soil is possible as MPCs are available

which are derived from toxicity data for soil organisms. Subsequently the problem arises which MPC must be preferred: the MPC based on the equilibrium partitioning method or the one based on ecotoxicological data for soil organisms? Terrestrial toxicity data are often scarce whereas the MPC for water is frequently based on a large data-set. Also the reliability of the partition coefficient must be taken into account. In the present report a strict criterium is applied: if the modified EPA method has to be used for deriving a MPC for soil organisms while it is possible to apply the statistical extrapolation method of Aldenberg and Slob for the aquatic environment (i.e. 4 or more chronic NOECs are available for different taxonomic groups) the MPC based on the equilibrium partitioning method is given greater weight; if this is not the case, the MPC based on toxicity data for soil organisms is preferred. A more thorough discussion on this 'selection problem' is needed. On the one hand there is a need for a set of general rules while on the other hand there must be room for expert judgement.

Many pitfalls are still associated with harmonization of MPCs for metals, and consequently setting of environmental quality objectives. With respect to soil and sediment there is a lack of reliable partition coefficients between water-sediment and especially pore water-soil. In addition, natural background concentrations are often decisive, but also here there is a need for more and better data. However, if environmental quality objectives are set at natural background concentrations the problem arises how to interpret actual concentrations in e.g. sediment or soil in terms of risk for the environment. Next to this, new developments like the AVS-method (Acid Volatile Sulfide) may be considered [70]. Within the National Institute of Public Health and Environmental Protection attention will be paid in the near future to setting environmental quality objectives for metals in a special project.

Harmonization of the MPCs for water, sediment and soil with air has not taken place, mainly because it is expected that for the compounds considered in the present report information on direct effects through inhalation is missing. However, it is recognized that transport via air can be an important contamination route for soil and water. Therefore, at a later stage limit concentrations in air that will not exceed the MPCs for the other compartments will be calculated using a similar approach as described by Van de Meent and de Bruijn [71].

9. CONCLUSION

In the present report MPCs are derived for several compounds with a potential for secondary poisoning: 21 organic compounds and 4 metals including methyl-mercury. MPCs are calculated in two different ways: keeping the data sets for aquatic/terrestrial organisms and top predators separate or combining data sets of all organisms. On theoretical grounds both methods have disadvantages as well as advantages. However, based on a quantitative comparison between both methods it is concluded that the latter one may lead to unrealistic low as well as high MPCs. Therefore the method in which data-sets are kept separate is used for deriving MPCs.

For deriving 'final' MPCs for surface water the following procedure is used: if secondary poisoning is critical, as a rule the MPC based on toxicity data for birds as well as mammals is used. However, if the lowest NOEC/BCF is lower than this MPC, the lowest value based on the separate data-set of birds or mammals is used. If secondary poisoning is not critical the MPC based on direct effects is used.

For sediment no toxicity data are available. Therefore MPCs are calculated from the MPCs for surface water using the equilibrium partitioning method.

For deriving the 'final' MPC for soil the procedure is basically the same as for surface water. Within the harmonization procedure the decision whether the MPC for (in)direct effects or the MPC calculated with the equilibrium partitioning method must be preferred, is made on the basis of data availability (see Chapter 6).

The method applied in the present report to incorporate effects due to secondary poisoning is considered as a first screening. Secondary poisoning may be critical via the aquatic route for the following compounds: aldrin/dieldrin, cadmium, DDT and derivatives, all HCH isomers, penta- and hexachlorobenzene and methyl-mercury. For endrin this may also be the case based on the results using the maximum BCF. For heptachlor, heptachlor epoxide and quintozone toxicity data for aquatic organisms as well as birds and mammals are too scarce to draw conclusions.

Via the terrestrial route secondary poisoning may be critical for cadmium, copper, penta- and hexachlorobenzene and methyl-mercury. Due to scarcity of data on effects on soil organisms as well as toxicity data for birds and mammals these results should be treated with caution: most values are indicative. In addition, the terrestrial route is probably too simple. However, at the moment a model for a more complex terrestrial foodweb is being developed. This model will be applied for several of the compounds studied in the present report.

For those compounds for which effects due to secondary poisoning may be critical, more research (called 'phase 2 research') is necessary of which obtaining local and species specific information from field studies is most important. Awaiting the outcome of this 'phase 2' research and taking into account that appropriate information is probably lacking, the MPCs derived in the present report can be used meanwhile.

Comparison of MPCs and NCs derived for the different compartments with actual concentrations is not possible for many compounds because the detection limit is higher than the NC, or even the MPC. Compounds for which the MPC is exceeded on a relatively large scale in surface water, particulate matter and sediment are copper, DDT and derivatives, α -endosulfan, heptachlor, hexachlorobenzene, mercury. For soil and groundwater data are scarce. In soil the MPC_{soil} for endrin and especially DDT and DDE is exceeded.

In Table 9.1 values are presented which can be used to set environmental quality objectives (limit and target values). Next to the MPCs, as derived in Chapters 4 and 6, Negligible Concentrations (NCs) are presented. The NC is defined in the policy document "Premises for risk management" as 1% of the MPC [2]. The safety factor of 100 is used because of the possibility of combined toxicity due to the presence of other chemicals in the environment. This factor may be changed in the near future taking into account the possible specific mode of action of certain compounds.

Table 9.1 Maximum Permissible Concentrations and Negligible Concentraions. Values for water in ng/l; for sediment and soil in $\mu\text{g/kg}$ (for a standard soil containing 25% clay and 10% organic matter).

compound	water		sediment		soil	
	MPC ng/l	NC ng/l	MPC $\mu\text{g/kg}$	NC $\mu\text{g/kg}$	MPC $\mu\text{g/kg}$	NC $\mu\text{g/kg}$
aldrin	18	0.18	120 ^b	1.2 ^b	50 ^a	0.50 ^a
cadmium	350 ^c	3.5 ^c	29,000 ^{b,c}	290 ^{b,c}	3.5 ^c	0.035 ^c
carbofuran	15 ^a	0.15 ^a	0.032 ^b	0.00032 ^b	4.7 ^a	0.047 ^a
chlordane	1.5 ^a	0.015 ^a	2.4 ^b	0.024 ^b	4.3 ^a	0.043 ^a
chlorpyrifos	2.8	0.028	1.1 ^b	0.011 ^b	1.1 ^b	0.011 ^b
copper	4,100	41	142,000 ^b	1,420 ^b	550 ^c	5.5 ^c
DDD	0.44	0.0044	1.8 ^b	0.018 ^b	10 ^a	0.10 ^a
DDE	0.44	0.0044	1.5 ^b	0.015 ^b	10 ^a	0.10 ^a
DDT	0.44	0.0044	9.4 ^b	0.094 ^b	10 ^a	0.10 ^a
dieldrin	18	0.18	670 ^b	6.7 ^b	50 ^a	0.50 ^a
endosulfan	0.40	0.0040	0.026 ^b	0.00026 ^b	50 ^a	0.50 ^a
endrin	3.0	0.030	2.9 ^b	0.029 ^b	2.9 ^b	0.029 ^b
fenthion	3.1	0.031	0.35 ^b	0.0035 ^b	0.35 ^b	0.0035 ^b
α -HCH	2,500	25	220 ^b	2.2 ^b	220 ^b	2.2 ^b
β -HCH	80 ^a	0.80 ^a	92 ^b	0.92 ^b	92 ^b	0.92 ^b
γ -HCH	770	7.7	190 ^b	1.9 ^b	5.0 ^a	0.050 ^a
heptachlor	0.46 ^a	0.0046 ^a	0.65 ^b	0.0065 ^b	0.70 ^a	0.0070 ^a
heptachlor epoxide	0.46 ^a	0.0046 ^a	0.020 ^b	0.00020 ^b	0.70 ^a	0.0070 ^a
hexachlorobenzene	2.1	0.021	1.2 ^b	0.012 ^b	28 ^b	0.28 ^b
mercury	1.9 ^c	0.019 ^c	210 ^{b,c}	2.1 ^{b,c}	200 ^{a,c}	2.0 ^c
methyl-mercury	1.9 ^c	0.019 ^c	210 ^{b,c}	2.1 ^{b,c}	3.3 ^c	0.033 ^c
pentachlorobenzene	30 ^a	0.30	12 ^b	0.12 ^b	120 ^a	1.2 ^a
pentachlorophenol	3,500	35	310 ^b	3.1 ^b	170 ^a	1.7 ^a
quintozone	290 ^a	2.9 ^a	330 ^b	3.3 ^b	330 ^b	3.3 ^b
thiram	32 ^a	0.32 ^a	0.79 ^b	0.0079 ^b	38 ^a	0.38 ^a

^a indicative value

^b based on equilibrium partitioning

^c for setting of environmental quality objectives these MPC/NC values must be compared with natural background concentrations

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APPENDIX A. TOXICITY DATA USED TO CALCULATE MPC_{eq}s BASED ON EFFECT DATA FOR AQUATIC ORGANISMS

Table 1. Toxicological data for freshwater organisms: chronic data ($\mu\text{g/l}$)

compound	taxonomic group	NOEC ($\mu\text{g/l}$)
cadmium	bacteria	40; 650
	green algae	3,100; 1,500; 120; 700
	blue algae	35
	protozoa	5.5
	worms	17
	molluscs	2.5
	crustaceans	0.085;
	fish	1.0; 4.2; 4.2; 11; 3.0; 31; 4.3; 1.3; 37; 4.4; 1.0; 3.8; 0.20; 9.0; 3.0; 31
	amphibians	9.0
carbofuran	crustaceans	9.8
	fish	25
chlordan	crustaceans	12; 5.3
	insects	0.7
	fish	0.54; 0.75; 0.11
chlorpyrifos	protozoans	330
	insects	0.5
	crustaceans	0.06
	fish	0.012
copper	green algae	50; 50; 10
	chrysophyta	10
	molluscs	8.0; 8.0
	crustaceans	12; 4.0; 5.0; 20; 40; 5.0; 15
	insects	34; 40; 8.0
	fish	13; 43; 50; 35; 12; 104; 21; 37; 120; 21; 8.0; 11; 22; 3.0; 22; 13
DDT	crustaceans	0.05
	fish	0.35

compound	taxonomic group	NOEC ($\mu\text{g/l}$)
dieldrin	blue algae	10
	molluscs	10
	crustaceans	32
	fish	5.0; 0.12; 0.75
endosulfan	green algae	700
	protozoa	100
	crustaceans	2.7
	fish	0.2
endrin	blue algae	95
	fish	0.21; 0.14; 0.15
fenthion	protozoa	100
	molluscs	1,000
α -HCH	green algae	3,300; 80
	protozoa	9
	molluscs	20
	crustaceans	90
	fish	800
β -HCH	green algae	500
	protozoa	83
	crustaceans	320
	fish	27; 180
γ -HCH	blue algae	150
	green algae	250; 950; 500
	protozoa	440
	molluscs	330
	crustaceans	11; 4.3
	insects	2.2
	fish	9.1; 2.9; 8.8
heptachlor	crustaceans	12.5
	fish	0.86
hexachlorobenzene		2,920; 570; 1,540; 1,090; 4,320; 810; 130; 10; 390; 30; 28; 70; 6.2; 7.1; 35; 13; 33; 55; 32
mercury	bacteria	5.0
	green algae	35
	blue algae	2.5

compound	taxonomic group	NOEC ($\mu\text{g/l}$)
mercury	protozoa	8.0; 9.0; 0.50; 39
	crustaceans	32; 1.1; 0.020; 0.020
	fish	0.31
pentachlorobenzene		7,260; 1,130; 3,040;
		2,270; 10,190; 1,770; 340;
		32; 940; 78; 73; 170; 20;
		25; 92; 35; 89; 19; 88
pentachlorophenol	bacteria	1,000
	blue algae	1,000
	green algae	100
	plants	1,000
	molluscs	32; 3.2; 50
	crustaceans	100; 23; 23
	insects	3,200
	fish	32; 45; 100; 8.9
	amphibians	32
thiram	algae	250
	crustaceans	1
	fish	0.32

Table 2. Toxicological data for freshwater organisms: acute data ($\mu\text{g/l}$)

compound	taxonomic group	L(E)C50 ($\mu\text{g/l}$)
aldrin	insects	0.8
carbofuran	crustaceans	1.6
chlordane	fish	0.8
DDD	crustaceans	3.2
DDE	fish	32
endrin	fish	0.089
fenthion	fish	0.62
heptachlor	insects	0.9
heptachlor epoxide	fish	5.3
quintozone	fish	290

Table 3. Toxicological data for saltwater organisms: chronic data ($\mu\text{g/l}$)

compound		NOEC ($\mu\text{g/l}$)
aldrin	molluscs	83
	fish	3.3
cadmium		5; 200; 320; 4.0; 109; 3000; 320; 560; 500; 200; 2000; 5.1; 112; 500; 1000; 1000; 584; 24.5
carbofuran	crustaceans	0.5
	fish	15
chlordan	crustaceans	0.015
	fish	0.5
chlorpyrifos	fish	0.3; 0.75; 0.28; 0.38; 93
copper		6.35; 50; 60; 38; 27.9; 100
dieldrin		0.1; 18; 0.1
DDE	crustaceans	0.1
DDT	algae	4.8; 3.2; 0.5; 8.0; 1.4; 25
	fish	33
endosulfan	algae	80
	molluscs	100
endrin	algae	0.067; 10; 0.1; 100
	crustaceans	0.03
	molluscs	25
	fish	0.12; 0.19
fenthion	algae	10
	crustaceans	0.037
α -HCH	fish	250
β -HCH	crustaceans	10

compound	NOEC ($\mu\text{g/l}$)
γ -HCH	5000; 1000
mercury	0.8; 2.0; 10; 50; 10; 2.7; 0.3; 10
pentachlorophenol	500; 125; 500; 10; 5800; 100; 10

Table 4. Toxicological data for saltwater organisms: acute data ($\mu\text{g/l}$)

compound	taxonomic group	L(E)C50 ($\mu\text{g/l}$)
aldrin	crustaceans	0.32
carbofuran	crustaceans	1.5
chlordane	crustaceans	0.4
chlorpyrifos	crustaceans	0.035
DDD	crustaceans	2.4
DDE	crustaceans	2.5
DDT	fish	0.3
endosulfan	crustaceans	0.04
fenthion	crustaceans	0.02
α -HCH	crustaceans	500
γ -HCH		0.17
heptachlor	crustaceans	0.046 ^a
heptachlorepoxyde	crustaceans	0.04
^a geometric mean of 0.03, 0.11 and 0.03 $\mu\text{g/l}$		

APPENDIX B. TOXICITY DATA USED TO CALCULATE MPC_{soils} BASED ON EFFECT DATA FOR SOIL ORGANISMS

Table 1. Toxicological data for soil organisms: chronic data (mg/kg)

compound	taxonomic group	NOEC (mg/kg)
aldrin	bacteria	125; 125
	fungi	57 ^a
	nematoda	1.5 ^b
cadmium	plants	19
	acari	0.97
	collembola	1.6
	isopoda	0.75
	oligochaeta	130; 14; 11
	molluscs	3.3
carbofuran	bacteria	24
	fungi	2.5 ^c
	oligochaeta	0.5
	enzym activity	12 ^d ; 1.7
chlordan	microbial processes	11 ^e
	enzym activity	1.7; 17; 1.7
	fungi	1.7 ^f
chlorpyrifos	fungi	17 ^g
	oligochaeta	100; 132; 9.2 ^g
	microbial processes	50; 16 ^h
	enzym activity	1.7; 0.46 ^a ; 8.5 ⁱ
copper	plants	370
	collembola	1,300
	oligochaeta	210; 68; 40
	molluscs	13
dieldrin	microbial processes	55; 100; 34; 34; 34
	insects	58
	collembola	0.5

compound	taxonomic group	NOEC (mg/kg)
endosulfan	microbial processes	170 ^j
	plants	2290
γ -HCH	collembola	0.05
	oligochaeta	29
hexachlorobenzene	plants	500
mercury	microbial processes	1.9; 47
	molluscs	8.3
pentachlorobenzene	plants	50
pentachlorophenol	microbial processes	6.5; 170; 17
	plants	1.7; 18
	oligochaeta	5.6
thiram	bacteria	3.8 ^k
	fungi	2.1 ^l
	microbial processes	120 ^a ; 24 ^m ; 15 ⁿ
	enzym activity	13 ^o ; 22; 0.38 ^a ; 0.6 ^p

^a extrapolated value using the model of Van Beelen

^b geometric mean of 2.4 (extrapolated value); 2.1 (extrapolated value) and 0.69 (calculated as EC82/10) mg/kg

^c geometric mean of 2.4 and 2.5 mg/kg

^d geometric mean of 25 and 5.7 (calculated as EC31/3) mg/kg

^e calculated as EC40/3

^f calculated as EC50/10

^g calculated as EC40/3

^h geometric mean of 50 and 5 (calculated as EC58/10) mg/kg

ⁱ calculated as EC28/2

^j geometric mean of 230 (calculated as geometric mean of EC50/10 values of 300 and 172 mg/kg) and 124 (calculated as geometric mean of EC50/10 values of 97, 209, 72 and 160 mg/kg)

^k geometric mean of 1.7 (calculated as EC52/10) and 8.3 (calculated as EC40/3) mg/kg

^l geometric mean of 1.7 (calculated as EC55/10) and 2.5 (calculated as EC50/10) mg/kg

^m geometric mean of 38 (extrapolated value) and 15 mg/kg

ⁿ geometric mean of 43 and 5 mg/kg

^o geometric mean of 12 and 15 mg/kg

^p calculated as EC38/3

^q geometric mean of 12 and 7.0 mg/kg

Table 2. Toxicological data for soil organisms: acute data (mg/kg)

compound	taxonomic group	L(E)C50 (mg/kg)
aldrin	insects	0.55
carbofuran	collembola	0.47 ^a
chlordane	insects	4.3
chlorpyrifos	collembola	0.36 ^b
dieldrin	collembola	1.1
DDT	insects	10 ^c
endosulfan	oligochaeta	5.0
endrin	collembola	0.95
heptachlor	insects	0.7 ^d
heptachlor epoxide	collembola	0.1
pentachlorophenol	oligochaeta	30

^a geometric mean of 0.75 and 0.3 mg/kg

^b geometric mean of 0.85 and 0.15 mg/kg

^c geometric mean of 22, 7.4, 12, 0.8, 35, 29.4, 17.3, 4.7, 7.4, 10.9, 11.4 and 12 mg/kg

^d geometric mean of 0.45, 0.46 and 1.4 mg/kg

APPENDIX C. TOXICITY DATA USED TO CALCULATE MPCs FOR BIRDS AND MAMMALS

Table 1. Toxicological data for mammals (mg/kg food)

compound	NOEC (mg/kg food)	species
aldrin	3	Mus musculus
	1.25 ^a	Rattus norvegicus
	40	Oryctolagus cuniculis
	8.7 ^b	Canis domesticus
cadmium	3	Macaca mulatta
	15	Ovis amon aries
	20	Rattus norvegicus
	40	Bos primigenius taurus
	45	Sus scrofa domesticus
carbofuran	17 ^c	Rattus norvegicus
	125	Mus musculus
	20 ^d	Canis domesticus
chlordane	30	Rattus norvegicus
chlorpyrifos	6 ^e	Rattus norvegicus
copper	265 ^e	Rattus norvegicus
	40 ^f	Mus musculus
	250	Susscrofa domesticus
	7	Ovis amon aries
DDT	20 ^g	Rattus norvegicus
	25	Mus musculus
	400 ^d	Canis domesticus
	200	Macaca mulatta
	28	Saimura sciureus
	100	Microtus pennsylvanicus
dieldrin	1.0	Mus musculus
	1.0	Macaca mulatta
	1.25	Rattus norvegicus
	5.0	Blerina brevicauda
	8.0	Canis domesticus

compound	NOEC (mg/kg food)	species
dieldrin	15	Damaliscus dorcas p.
endosulfan	75	Rattus norvegicus
	6	Mus musculus
	3.3 ^g	Oryctolagus cuniculus
	6	Canis domesticus
endrin	47	Mus musculus
	1	Rattus norvegicus
	0.62 ^h	Cricetus cricetus
	3	Canis domesticus
fenthion	0.13 ^a	Rattus norvegicus
α -HCH	50	Rattus norvegicus
β -HCH	2	Rattus norvegicus
γ -HCH	25	Mus musculus
	33	Oryctolagus cuniculus
	100	Rattus norvegicus
heptachlor	6	Rattus norvegicus
heptachlorepoxyde	7	Rattus norvegicus or Canis domesticus
hexachlorobenzene	18 ⁱ	Rattus norvegicus
	0.5 ^a	Mustela vision
	0.5 ^a	Mustela putorius
	52 ^d	Canis domesticus
	88	Felis domesticus
mercury	20	Mus musculus
methyl-mercury	0.22	Macaca spec.
	0.43	Rattus norvegicus
	1.2	Mustela vision
	2.25	Mus musculus
pentachlorobenzene	5	Mus musculus
	6.3	Rattus norvegicus

compound	NOEC (mg/kg food)	species
pentachlorophenol	55 ^a	Rattus norvegicus
	200	Mus musculus
quintozone	25	Rattus norvegicus
thiram	5 ^a	Rattus norvegicus

^a calculated as LOEC/2

^b geometric mean of 25 and 3 mg/kg food

^c geometric mean of 10, 20 and 25 mg/kg food

^d calculated as NOEC x 40 (BW/DFI factor)

^e calculated as NOEC x 20 (BW/DFI factor)

^f calculated as NOEC/10 because exposure time < 1 month

^g calculated as NOEC x 33 (BW/DFI factor)/10 because exposure time < 1 month

^h calculated as NOEC x 40 (BW/DFI factor)/10 because exposure time < 1 month

ⁱ geometric mean of 8 and 40 mg/kg food

Table 2. Toxicological data for birds: chronic data (mg/kg food)

compound	NOEC (mg/kg food)	species
aldrin	0.5 ^a	<i>Phasianus colchicus</i>
	0.05 ^a	<i>Coturnix c. japonica</i>
cadmium	0.2	<i>Meleagris gallopavo</i>
	1.6	<i>Anas platyrhynchos</i>
	12	<i>Gallus domesticus</i>
	38	<i>Coturnix c. japonica</i>
carbofuran	2.6 ^b	<i>Colinus virginianus</i>
	25	<i>Coturnix c. japonica</i>
	15 ^c	<i>Agelaius phoeniceus</i>
chlorpyrifos	40 ^c	<i>Anas platyrhynchos</i>
	10	<i>Coturnix c. japonica</i>
	12.5 ^c	<i>Gallus domesticus</i>
	13.5 ^c	<i>Passer domesticus</i>
p,p'-DDD	1.1	<i>Anas platyrhynchos</i>
p,p'-DDE	41	<i>Coturnix c. japonica</i>
	10	<i>Streptopelia resoria</i>
	1.3	<i>Anas platyrhynchos</i>
	6.3	Peking duck
	1	<i>Anas rubripes</i>
	1.4	<i>Otus asio</i>
	0.3	<i>Falco sparverius</i>
p,p'-DDT	0.5	<i>Streptopelia resoria</i>
	0.6	<i>Gallus domesticus</i>
	3.3	<i>Molothrus ater</i>
	3.3	<i>Anas platyrhynchos</i>
	10	<i>Coturnix c. japonica</i>
	17	<i>Colinus virginianus</i>
	50	<i>Phasianus colchicus</i>
o,p'-DDT	50	<i>Coturnix c. japonica</i>

compound	NOEC (mg/kg food)	species
dieldrin	0.5	quail
	0.8	Anas platyrhynchos
	1.5	Numida meleagris
	2.0	Phasianus colchius
	2.5	Colinus virginianus
	10	Gallus domesticus
	10	Coturnix c. japonica
endrin	1.5 ^c	Anas platyrhynchos
	0.25 ^c	Coturnix c. japonica
	0.40 ^c	Otis asio
	1 ^c	Phasianus colchicus
β-HCH	≥625	Gallus domesticus
γ-HCH	1.6	Gallus domesticus
	100	Anas platyrhynchos
heptachlor	50	Coturnix c. japonica
heptachlorepoxyde	0.02	Gallus domesticus
hexachlorobenzene	5	Coturnix c. japonica
mercury	4	Coturnix c. japonica
	10	Gallus domesticus
methyl-mercury	0.25	Anas platyrhynchos
	0.36	Phasianus colchius
	0.56	Gallus domesticus
	1.7	Coturnix c. japonica
	4.3	Colinus virginianus
pentachlorophenol	245	Gallus domesticus
quintozone	100	Gallus domesticus
thiram	2.9 ^d	Colinus virginianus
	18 ^a	Gallus domesticus

^a calculated as LOEC/10^b calculated as NOEC/10 because exposure time < 1 month^c calculated as LOEC/2^d calculated as LOEC/3

Table 3. Toxicological data for birds: acute data (mg/kg food)

compound	LC50 (mg/kg food)	species
chlordane	331	Colinus virginianus
endosulfan	805	Colinus virginianus
fenthion	3	Quiscalus quiscula
heptachlor	80	Coturnix c. japonica

APPENDIX D. CONCENTRATIONS IN SURFACE WATER MEASURED IN THE NETHERLANDS

Monitoring data from the Cooperating Rhine and Meuse Waterworks (In Dutch: RIWA) for 1990 and 1991. Data are presented per compound and per location. The following data selection was carried out:

- only one analysis result present for a location: this result is given,
- 2 analysis results present for a location: minimum and maximum is given,
- more than 2 and less than 10 analysis results present for a location: median is given,
- 10 or more analysis results present for a location: median, 10 and 90 percentile is given.

compound	location	concentration ($\mu\text{g/l}$)					
		one result	minimum	maximum	median	10 percentile	90 percentile
aldrin	IJsselmeer (Andijk)				<0.010	<0.010	<0.020
	Maas (Belfeld)				<0.010	<0.010	<0.010
	afgedamde Maas (Brakel)				<0.010	<0.010	<0.010
	Maas (Eysden)				<0.010	<0.005	<0.010
	Gat v/d Kerksloot (Inlaat de Gijster)				<0.010		
	Lek (Hagestein)				<0.010		
	Haringvliet (Stellendam)				<0.010	<0.010	<0.010
	Maas (Kelzersveer)				<0.010	<0.005	<0.010
	Rijn (Lobith)				<0.010	<0.010	<0.010
	Lekkanaal (Nieuwegein)				<0.010	<0.010	<0.010
p,p'-DDE	IJsselmeer (Andijk)				<0.010	<0.010	<0.020
	Maas (Belfeld)				<0.010	<0.010	<0.010
	afgedamde Maas (Brakel)				<0.010	<0.010	<0.010

compound	location	concentration ($\mu\text{g/l}$)					
		one result	minimum	maximum	median	10 percentile	90 percentile
p,p'-DDE	Haringvliet (Stellendam)	<0.010					
	Maas (Eysden)				<0.010	<0.005	<0.010
	Gat v/d Kersloot (Inlaat de Gijster)				<0.010		
	Lek (Hagestein)				<0.010		
	Maas (Keizersveer)				<0.010	<0.005	<0.010
	Rijn (Lobith)				<0.010	<0.010	<0.010
	Lekkanaal (Nieuwegein)				<0.010	<0.010	<0.010
p,p'-DDD	IJsselmeer (Andijk)				<0.010	<0.010	<0.020
	Maas (Belfeld)				<0.010		
	afgedamde Maas (Brakel)				<0.010		
	Maas (Eysden)				<0.010		
	Gat v/d Kersloot (Inlaat de Gijster)				<0.010		
	Lek (Hagestein)				<0.010		
	Haringvliet (Stellendam)	<0.010					
	Maas (Keizersveer)				<0.010		
	Rijn (Lobith)				<0.010	<0.010	<0.010
	Lekkanaal (Nieuwegein)				<0.010	<0.010	<0.010
o,p'-DDT	IJsselmeer (Andijk)				<0.010	<0.010	<0.020
	Maas (Belfeld)				<0.010	<0.010	<0.010
	afgedamde Maas (Brakel)				<0.010	<0.010	<0.010
	Maas (Eysden)				<0.010	<0.005	<0.010
	Gat v/d Kersloot (Inlaat de Gijster)				<0.010		
	Lek (Hagestein)				<0.010		
	Haringvliet (Stellendam)				<0.010	0.000	<0.010
	Maas (Keizersveer)				<0.010	<0.005	<0.010
	Rijn (Lobith)				<0.010	<0.010	<0.010

compound	location	concentration ($\mu\text{g/l}$)			10 percentile	90 percentile
		one result	minimum	maximum		
o,p'-DDT	Lekkanaal (Nieuwegein)				<0.010	<0.010
p,p'-DDT	IJsselmeer (Andijk)				<0.010	<0.010
	Maas (Belfeld)				<0.010	<0.010
	afgedamde Maas (Brakel)				<0.010	<0.010
	Maas (Eysden)				<0.010	<0.005
	Gat v/d Kerksloot (Inlaat de Gijster)				<0.010	
	Lek (Hagestein)				<0.010	
	Haringvliet (Stellendam)	<0.010				
	Maas (Keizersveer)				<0.010	<0.005
	Rijn (Lobith)				<0.010	<0.010
	Lekkanaal (Nieuwegein)				<0.010	<0.010
endrin	IJsselmeer (Andijk)				<0.010	<0.010
	Maas (Belfeld)				<0.010	<0.010
	afgedamde Maas (Brakel)				<0.010	<0.010
	Maas (Eysden)				<0.010	<0.005
	Gat v/d Kerksloot (Inlaat de Gijster)				<0.010	
	Haringvliet (Stellendam)	<0.010				
	Maas (Keizersveer)				<0.010	<0.005
α -endosulfan	IJsselmeer (Andijk)				<0.010	<0.010
	Maas (Belfeld)				<0.010	<0.010
	afgedamde Maas (Brakel)				<0.010	<0.010
	Maas (Eysden)				<0.010	<0.005
	Lek (Hagestein)				<0.010	
	Haringvliet (Stellendam)				0.010	<0.010

compound	location	concentration ($\mu\text{g/l}$)					
		one result	minimum	maximum	median	10 percentile	90 percentile
α -endosulfan	Maas (Keizersveer)				<0.010	<0.005	<0.010
	Rijn (Lobith)				<0.010	<0.010	<0.010
	Lekkanaal (Nieuwegein)				<0.010	<0.010	<0.010

APPENDIX E. CONCENTRATIONS IN SOIL MEASURED IN THE NETHERLANDS

For aldrin, carbofuran, chlordane, chlorpyrifos, DDT and derivatives, endosulfan, endrin, fenthion, heptachlor, heptachlor epoxide, quintozone the data-base from the National Soil Quality Monitoring Network has been consulted. Soil samples were taken in The Netherlands in 1987-1988 at 0-10 cm and 10-30 cm, representing 10 different combinations of land use/soil type. At each sample location four samples are taken from each depth. Only for aldrin, endrin, p,p'-DDE and DDT data are available.

land use	soil type	depth (below ground level)			
		0-10 cm	90 percentile	10-30 cm	90 percentile
		average ($\mu\text{g/kg}$)	($\mu\text{g/kg}$)	average ($\mu\text{g/kg}$)	($\mu\text{g/kg}$)
aldrin					
orchard	thick earth soil	0.50	0.50	0.50	0.50
	calcareous loam - clay loam	0.50	0.50	0.50	0.50
forest	ordinary hydropodzol	0.50	0.50	0.50	0.50
	sandy hydrovague soil	0.50	0.50	0.50	0.50
farmland	thick earth soil	0.50	0.50	0.50	0.50
	calcareous loam - clay loam	0.50	0.50	0.50	0.50
	ordinary hydropodzol	0.50	0.50	0.50	0.50
grassland	clay earthy peat soil	0.50	0.50	0.50	0.50
	ordinary hydropodzol	0.50	0.50	0.50	0.50
	thick earth soil	0.51	0.50	0.50	0.50

land use	soil type	depth (below ground level)			
		0-10 cm		10-30 cm	
		average (μg/kg)	90 percentile (μg/kg)	average (μg/kg)	90 percentile (μg/kg)
endrin					
orchard	thick earth soil	8.41	23.00	10.33	29.00
	calcareous loam - clay loam	1.16	2.80	1.29	3.50
forest	ordinary hydropodzol	0.50	0.50	0.50	0.50
	sandy hydrovague soil	0.50	0.50	0.50	0.50
farmland	thick earth soil	0.50	0.50	0.50	0.50
	calcareous loam - clay loam	0.50	0.50	0.50	0.50
	ordinary hydropodzol	0.50	0.50	0.50	0.50
grassland	clay earthy peat soil	0.54	0.50	0.59	0.50
	ordinary hydropodzol	0.50	0.50	0.50	0.50
	thick earth soil	0.50	0.50	0.50	0.50
o,p'-DDT					
orchard	thick earth soil	93.43	150.00	115.37	190.00
	calcareous loam - clay loam	50.88	170.00	32.81	100.00
forest	ordinary hydropodzol	0.50	0.50	0.50	0.50
	sandy hydrovague soil	0.50	0.50	0.50	0.50
farmland	thick earth soil	23.68	40.00	7.12	12.00
	calcareous loam - clay loam	2.36	3.80	1.80	4.00
	ordinary hydropodzol	1.13	2.70	0.69	1.00
grassland	clay earthy peat soil	0.54	0.50	0.76	0.50
	ordinary hydropodzol	0.78	1.50	0.69	1.30
	thick earth soil	10.62	28.00	11.89	29.00

land use	soil type	depth (below ground level)			
		0-10 cm		10-30 cm	
		average (μg/kg)	90 percentile (μg/kg)	average (μg/kg)	90 percentile (μg/kg)
pp-DDT					
orchard	thick earth soil	427.64	610.00	552.70	1000.00
	calcareous loam - clay loam	488.88	1600.00	313.33	700.00
forest	ordinary hydropodzol	0.54	0.50	0.50	0.50
	sandy hydrovague soil	0.83	1.20	0.51	0.50
farmland	thick earth soil	194.56	350.00	28.95	64.00
	calcareous loam - clay loam	28.63	44.00	14.19	31.00
	ordinary hydropodzol	5.10	13.00	1.59	4.40
grassland	clay earthy peat soil	1.44	1.50	1.34	1.60
	ordinary hydropodzol	2.73	8.00	2.13	6.50
	thick earth soil	86.43	230.00	88.04	210.00
p,p'-DDE					
orchard	thick earth soil	144.31	260.00	169.25	270.00
	calcareous loam - clay loam	321.57	880.00	210.91	460.00
forest	ordinary hydropodzol	0.50	0.50	0.50	0.50
	sandy hydrovague soil	0.50	0.50	0.50	0.50
farmland	thick earth soil	14.17	35.00	5.59	14.00
	calcareous loam - clay loam	5.08	10.00	2.16	3.30
	ordinary hydropodzol	1.36	2.00	1.04	1.20
grassland	clay earthy peat soil	3.53	5.70	2.49	2.90
	ordinary hydropodzol	0.94	1.30	0.88	1.40
	thick earth soil	13.90	34.00	15.94	34.00

APPENDIX F. CONCENTRATIONS IN GROUNDWATER MEASURED IN THE NETHERLANDS

For aldrin, carbofuran, chlordane, chlorpyrifos, DDT and derivatives, endosulfan, endrin, fenthion, heptachlor, heptachlor epoxide, quintozone data-bases from the Provincial Groundwater Quality Monitoring Network and the National Groundwater Quality Monitoring Network have been consulted. For chlordane, carbofuran and quintozone no data have been found. For the other compounds measurements have been carried out two periods: from 1987 and 1990; data are presented for each period separately. The mean, maximum and 90 percentile is presented for sand and clay for 5-15 meter. No data are available for peat and for 15-30 meter. Measurements lower than the detection limit are included for calculation of the mean, maximum and 90 percentile.

compound	soil type	depth (m)	concentration ($\mu\text{g/l}$)		
			mean	maximum	90 percentile
aldrin ^a	sand	5-15	0.01	0.01	0.01
	clay	5-15	0.01	0.01	0.01 (50)
chlorpyrifos ^b	sand	5-15	0.10	0.10	0.10 (50)
	clay	5-15	0.29	0.80	0.50 (80)
DDD (total) ^a	sand	5-15	0.01	0.01	0.01
	clay	5-15	0.01	0.01	0.01 (50)
DDE (total) ^a	sand	5-15	0.01	0.01	0.01
	clay	5-15	0.01	0.01	0.01 (50)
DDT (total) ^a	sand	5-15	0.01	0.01	0.01
	clay	5-15	0.01	0.01	0.01 (50)
p,p'-DDT ^b	sand	5-15	5,000	5,000	5,000
	clay	5-15	5,000	5,000	5,000 (50)
endosulfan ^a	sand	5-15	0.01	0.01	0.01
	clay	5-15	0.01	0.01	0.01 (50)
endrin ^a	sand	5-15	0.01	0.01	0.01
	clay	5-15	0.01	0.01	0.01 (50)
endrin ^b	sand	5-15	5,000	5,000	5,000
	clay	5-15	5,000	5,000	5,000 (50)

compound	soil type	depth (m)	concentration ($\mu\text{g/l}$)		
			mean	maximum	90 percentile
fenthion ^b	sand	5-15	0.30	0.30	0.30 (50)
	clay	5-15	0.30	0.30	0.30 (80)
heptachlor ^b	sand	5-15	5,000	5,000	5,000
	clay	5-15	5,000	5,000	5,000 (50)
heptachlor ^a	sand	5-15	0.01	0.01	0.01
	clay	5-15	0.01	0.01	0.01 (50)
heptachlor epoxide ^a	sand	5-15	0.01	0.01	0.01
	clay	5-15	0.01	0.01	0.01 (50)

^a measurements from 1987: National Groundwater Quality Monitoring Network

^b measurements from 1990: Provincial and National Groundwater Quality Monitoring Network