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Secondary poisoning of cadmium, copper and mercury: implications for the Maximum Permissible Concentrations and Negligible Concentrations in water, sediment and soil

C.E. Smit, A.P. van Wezel, T. Jager and T.P. Traas

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RIVM, P.O. Box 1, 3720 BA Bilthoven, telephone: 31 - 30 - 274 91 11; telefax: 31 - 30 - 274 29 71

Samenvatting

De betekenis van doorvergiftiging voor de Maximum Toelaatbaar Risiconiveau's (MTRs) en Verwaarloosbaar Risiconiveau's (VRs) van cadmium, koper en kwik in water, sediment en bodem is geëvalueerd. Veldgegevens met betrekking tot de accumulatie van deze elementen door vissen, mosselen en regenwormen zijn gebruikt om MTRs en VRs af te leiden voor vogels en zoogdieren die deze organismen als voedselbron gebruiken. Accumulatie door water- en bodemorganismen lijken negatief gecorreleerd te zijn met externe concentraties, maar de correlaties zijn niet sterk. Voor vissen en mosselen zijn er te weinig gegevens beschikbaar om conclusies te trekken en de wetenschappelijke rechtvaardiging voor het gebruik van locatie-specifieke BCFs bij het afleiden van risicogrenzen ontbreekt dan ook. Doorvergiftiging bij vogels en zoogdieren via het eten van vis of mosselen kan bijdragen aan het risico van cadmium en kwik voor het aquatische ecosysteem. Voor koper zijn de MTRs voor water vergelijkbaar; voor dit element waren echter alleen veldgegevens voor mosselen beschikbaar. De invloed van doorvergiftiging op de MTRs van cadmium en koper voor de bodem is gering. Het is niet mogelijk conclusies te trekken voor kwik, aangezien er nauwelijks bodemtoxiciteitsgegevens beschikbaar zijn. Nader onderzoek naar de accumulatie van cadmium, koper en kwik door waterorganismen wordt aanbevolen, waarbij dieren en water van dezelfde locatie moeten worden geanalyseerd. Bij de bepaling van de veld-BCFs voor kwik moet tevens onderzoek worden gedaan naar de relatieve bijdrage van methyl-kwik aan de totale concentratie kwik in bodem, water en sediment en de dieren die in deze compartimenten leven.

Abstract

The impact of secondary poisoning on the Maximum Permissible Concentrations (MPCs) and Negligible Concentrations (NCs) of cadmium, copper and mercury in water, sediment and soil have been evaluated. Field data on accumulation of these elements by fish, mussels and earthworms were used to derive MPCs and NCs for birds and mammals for which these organisms are a food source. Accumulation by aquatic and terrestrial biota seems to be negatively correlated with external concentrations. The correlations lacked in strength and too few data on external concentrations for fish and mussels were available to draw conclusions. The scientific justification for using location-specific BCFs in the estimation of risk limits therefore still has to be established. Secondary poisoning of birds and mammals via fish or mussels may contribute to the risks of cadmium and mercury for the aquatic ecosystem. MPCs for copper in water derived with or without the inclusion of secondary poisoning are similar, although this conclusion is based on field data for mussels only. For the terrestrial compartment, inclusion of secondary poisoning does not lead to major changes in the MPCs for cadmium and copper. As toxicity data on soil organisms are hardly available, conclusions for mercury cannot be drawn. Further research into the accumulation of cadmium, copper and mercury by aquatic organisms is recommended. Data collection should include measurements in animals and water from the same location. For mercury, the determination of field BCFs should also include investigations into the relative contribution of methyl-mercury to the total mercury concentration in soil, water, sediment and animals living in these compartments.

Preface

This report was written within the framework of the project 'Setting Integrated Environmental Quality Standards'. The results as presented in this report have been discussed by members of the ‘Setting Integrated Environmental Quality Standards Advisory Group’, who are acknowledged for their contribution. These members are: dr. C. van de Guchte (National Institute of Inland Water Management), dr. K. den Haan (Shell International Chemical BV), Ir. J. Lijzen (National Institute of Public Health and the Environment), dr. D. Sijm (National Institute of Public Health and the Environment), dr. E. Sneller (National Institute of Inland Water Management), dr. W. van Tilborg (VTBC), dr. M. van der Weiden (Ministry of Housing, Spatial Planning and the Environment), and dr. J. van Wensem (Technical Soil Protection Committee). The results of the study do no necessarily reflect the opinion of each individual member of the advisory group.
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Contents

Uitgebreide samenvatting

In dit rapport worden de risico's van doorvergiftiging van cadmium, koper en kwik voor het aquatische en terrestrische milieu geëvalueerd. No Observed Effect Concentraties (NOECs) voor vogels en zoogdieren worden gebruikt als uitgangspunt voor de berekeningen. De NOECs, die zijn uitgedrukt in mg/kg voer, zijn omgerekend naar concentraties in het milieu met behulp van accumulatiegegevens voor vissen, mosselen en regenwormen die zijn bepaald in veldstudies. Op basis van deze NOECs, alleen of in combinatie met NOECs voor rechtstreeks blootgestelde water- en bodemorganismen, zijn Maximum Toelaatbaar Risiconiveau's (MTRs) en Verwaarloosbaar Risiconiveau's (VRs) afgeleid. De afleiding van MTRs en VRs is gebaseerd op de toegevoegd risico-benadering. Met deze methode wordt een Maximaal Toelaatbare Toevoeging (MTT) bepaald, die is gedefinieerd als de concentratie die mag worden toegevoegd aan de achtergrondconcentratie (C_b) zonder dat ontoelaatbare schade aan het ecosysteem wordt veroorzaakt. Toepassen van een veiligheidsfactor van 100 leidt tot de Verwaarloosbare Toevoeging (VT), die wordt beschouwd als een veilige ondergrens. Onder de aanname dat de achtergrondconcentratie niet bijdraagt aan nadelige effecten op het ecosysteem, wordt het MTR gedefinieerd als de som van MTT en C_b. Op vergelijkbare wijze wordt het VR afgeleid als de som van VT en C_b.
De accumulatie van cadmium, koper en kwik door organismen is afhankelijk van de externe concentratie. Dit betekent dat, afhankelijk van de locatie, verschillende concentratiefactoren zouden kunnen worden gebruikt voor het afleiden van het MTR en VR. Op basis van de nu beschikbare accumulatiegegevens is een dergelijke differentiatie in de MTR-afleiding echter nog niet mogelijk. De berekeningen zijn daarom uitgevoerd met de geometrische gemiddelden van de beschikbare BCFs, en er wordt aangenomen dat deze waarden representatief zijn voor de gemiddelde Nederlandse situatie.
De MTRs en VRs voor het aquatische milieu die in dit rapport zijn afgeleid zijn weergegeven in Tabel I en II. De in deze tabellen weergegeven waarden voor rechtstreekse blootstelling (MTR/VR_{direct}) worden momenteel als MTR en VR gehanteerd. De lagere waarden van het MTR voor cadmium en anorganisch kwik op basis van doorvergiftiging (MTR/VR_{SP}), geven aan dat blootstelling van vogels en zoogdieren via het eten van vis of mosselen kan bijdragen aan het risico voor het aquatische ecosysteem. Voor koper zijn de MTRs vergelijkbaar en is de overdracht via de voedselketen even belangrijk als directe blootstelling. De VRs worden voornamelijk bepaald door de achtergrondconcentratie.

*Tabel I In dit rapport afgeleide MTRs en VRs voor **water**, gebaseerd op gegevens voor doorvergiftiging (SP), rechtstreekse blootstelling (direct) en beide routes gecombineerd (direct+SP). De waarden voor directe blootstelling worden momenteel als MTR en VR gehanteerd.*

	$MTR_{water, SP}$	$MTR_{water, direct}$	$MTR_{water, direct+SP}$	$VR_{water, SP}$	$VR_{water, direct}$	$VR_{water, direct+SP}$
	[µg/l]	[µg/l]	[µg/l]	[µg/l]	[µg/l]	[µg/l]
cadmium	0.10	0.42	0.24	0.08	0.08	0.08
koper	1.44	1.5	1.5	0.5	0.4	0.4
anorganisch kwik	0.02-0.06	0.24	0.08-0.15	0.01	0.01	0.01
methyl-kwik	0.01	0.02	0.01	0.01	0.01	0.01

*Tabel II In dit rapport afgeleide MTRs en VRs voor **sediment**, gebaseerd op gegevens voor doorvergiftiging (SP), rechtstreekse blootstelling (direct) en beide routes gecombineerd (direct+SP). De waarden voor directe blootstelling worden momenteel als MTR en VR gehanteerd.*

	$MTR_{sed, SP}$	$MTR_{sed, direct}$	$MTR_{sed, direct+SP}$	$VR_{sed, SP}$	$VR_{sed, direct}$	$VR_{sed, direct+SP}$
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
cadmium	2.1	30	15	0.8	1.1	0.9
koper	70	73	73	36	36	36
anorganisch kwik	1.1-5.9	26	8.5-16	0.4	0.6	0.4-0.5
methyl-kwik	0.6-0.7	1.4	0.5	0.3	0.3	0.3

*Tabel III In dit rapport afgeleide MTRs en VRs voor de **bodem**, gebaseerd op gegevens voor doorvergiftiging (SP), rechtstreekse blootstelling van bodemorganismen (direct) en beide routes gecombineerd (direct+SP).*

	$MTR_{bodem, SP}$	$MTR_{bodem, direct}$	$MTR_{bodem, direct+SP}$	$VR_{bodem, SP}$	$VR_{odem, direct}$	$VR_{bodem, direct+SP}$
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
cadmium	0.84	1.6	0.90	0.8	0.8	0.8
koper	51	60	61	36	36	36
anorganisch kwik	0.86	-	0.86	0.3	-	0.3
methyl-kwik	0.44	0.67	0.44	0.3	0.3	0.3

De in dit rapport afgeleide MTRs en VRs voor het terrestrische milieu zijn samengevat in Tabel III. De momenteel gebruikte MTRs en VRs voor de bodem zijn samengevat in Tabel IV. Voor cadmium en koper leidt het meenemen van doorvergiftiging in de berekening niet tot grote veranderingen in het MTR. Het hier afgeleide MTR voor koper is bovendien hoger dan het momenteel gehanteerde MTR_{bodem}, dat is gebaseerd op het effect van koper op microbiële processen en enzymactiviteit.

Tabel IV Huidige MTRs en VRs voor het terrestrische milieu.

	MTR_{bodem}	VR_{bodem}
	[mg/kg]	[mg/kg]
cadmium	1.6	0.8
koper	40[a]	36
anorganisch kwik	2.2[a]	0.3
methyl-kwik	0.67	0.3

[a]: gebaseerd op effect op microbiële processen en enzym activiteit

Omdat er nauwelijks toxiciteitsgegevens beschikbaar zijn voor kwik, kunnen er geen conclusies worden getrokken omtrent de bijdrage van doorvergiftiging aan het risico van dit metaal. De NOECs voor doorvergiftiging zijn vergelijkbaar met de NOEC voor regenwormen. Wanneer andere bodemorganismen even gevoelig zijn, zal het MTR voor rechtstreekse blootstelling de achtergrondconcentratie benaderen en zal het betrekken van doorvergiftiging in de afleiding van het MTR dan waarschijnlijk ook niet leiden tot een substantiële verlaging van het MTR. Ook voor het terrestrische milieu worden de VRs bepaald door de achtergrondconcentratie.

De hier gepresenteerde berekeningen voor het aquatische milieu zijn gebaseerd op een beperkte set aan accumulatiegegevens. Bovendien moesten de bioconcentratiefactoren worden berekend op basis van concentraties in dieren en zwevend slib die op verschillende locaties bemonsterd waren. De afgeleide MTRs moeten daarom als indicatief worden beschouwd. Verder onderzoek naar de accumulatie van cadmium, koper en kwik door waterorganismen wordt dan ook aanbevolen. Hierbij moeten dieren en water van dezelfde locatie worden bemonsterd. Bovendien zou ook de bijdrage van methyl-kwik aan de totale concentratie in bodem, sediment, water en dieren moeten worden onderzocht. Tenslotte zou het beschikbaar komen van meer chronische toxiciteitsgegevens voor vogels en zoogdieren, uit toetsen met relevante soorten en blootstellingscondities, kunnen bijdragen aan een betere beoordeling van het risico van doorvergiftiging.

Summary

In this report, the risks of secondary poisoning of cadmium, copper and mercury for the aquatic and terrestrial ecosystem have been evaluated. No Observed Effect Concentrations (NOECs) for birds and mammals were used as starting point for the calculations. The NOECs that are expressed in mg/kg food were recalculated into concentrations in the environment using bioconcentration factors (BCFs) for fish or mussels and biota-to-soil accumulation factors (BSAFs) for earthworms that were obtained from field studies. Maximum Permissible Concentrations (MPCs) and Negligible Concentrations (NCs) have been derived on the basis of the resulting NOECs, using them either separately or in combination with NOECs for directly exposed aquatic and terrestrial species. MPCs and NCs have been derived according to the added risk approach. This method results in a Maximum Permissible Addition (MPA) that is defined as the concentration that may be added on top of the background concentration (C_b) without causing impermissible damage to the ecosystem. Application of a safety factor of 100 to the MPA leads to the Negligible Addition (NA), that is regarded as a lower risk threshold. Assuming that the background concentration does not lead to any deleterious effects on the ecosystem, the MPC is defined as the sum of MPA and C_b. In the same way, the NC is given as the sum of NA and C_b.
BCFs and BSAFs of cadmium, copper and mercury seem to be dependent on the external concentration. This implies that depending on the location under consideration, different BCFs and BSAFs may be used for the estimation of MPCs. However, on the basis of the currently available accumulation data, it is not yet possible to make such a differentiation in MPCs. Therefore, geometric mean BCFs have been used in the calculations, assuming that these values are representative for the average Dutch situation.
The MPCs and NCs for the aquatic compartment derived in the present report are presented in Table I and II. The values for direct exposure (MPC/NC_{direct}) are currently used as MPC and NC. The lower values for the MPCs of cadmium and inorganic mercury based on secondary poisoning (MPC/NC_{SP}), indicate that exposure of birds and mammals via fish or mussels may contribute to the risks for the aquatic ecosystem. For copper, MPCs for water derived with or without inclusion of secondary poisoning are similar and food chain transfer of copper is considered to be of equal importance compared to direct exposure. NCs are determined mainly by the background concentrations for the respective elements.

*Table I MPCs and NCs for **water** derived in this report, based on data on secondary poisoning (SP), direct exposure (direct) and both routes combined (direct+SP). The values for direct exposure are currently used as MPC and NC.*

	$MPC_{water, SP}$ [µg/l]	$MPC_{water, direct}$ [µg/l]	$MPC_{water, direct+SP}$ [µg/l]	$NC_{water, SP}$ [µg/l]	$NC_{water, direct}$ [µg/l]	$NC_{water, direct+SP}$ [µg/l]
cadmium	0.10	0.42	0.24	0.08	0.08	0.08
copper	1.44	1.5	1.5	0.5	0.4	0.4
inorganic mercury	0.02-0.06	0.24	0.08-0.15	0.01	0.01	0.01
methyl-mercury	0.01	0.02	0.01	0.01	0.01	0.01

*Table II MPCs and NCs for **sediment** derived in this report, based on data on secondary poisoning (SP), direct exposure (direct) and both routes combined (direct+SP). The values for direct exposure are currently used as MPC and NC.*

	$MPC_{sed, SP}$ [mg/kg]	$MPC_{sed, direct}$ [mg/kg]	$MPC_{sed, direct+SP}$ [mg/kg]	$NC_{sed, SP}$ [mg/kg]	$NC_{sed, direct}$ [mg/kg]	$NC_{sed, direct+SP}$ [mg/kg]
cadmium	2.1	30	15	0.8	1.1	0.9
copper	70	73	73	36	36	36
inorganic mercury	1.1-5.9	26	8.5-16	0.4	0.6	0.4-0.5
methyl-mercury	0.6-0.7	1.4	0.5	0.3	0.3	0.3

*Table III MPCs for **soil** derived in this report, based on data on secondary poisoning (SP), direct exposure of soil organisms (direct) and both routes combined (direct+SP).*

	$MPC_{soil, SP}$ [mg/kg]	$MPC_{soil, direct}$ [mg/kg]	$MPC_{soil, direct+SP}$ [mg/kg]	$NC_{soil, SP}$ [mg/kg]	$NC_{soil, direct}$ [mg/kg]	$NC_{soil, direct+SP}$ [mg/kg]
cadmium	0.84	1.6	0.90	0.8	0.8	0.8
copper	51	60	61	36	36	36
inorganic Mercury	0.86	-	0.86	0.3	-	0.3
methyl-Mercury	0.44	0.67	0.44	0.3	0.3	0.3

MPCs for the terrestrial compartment that are derived in this report are summarised in Table III. The currently used MPCs and NCs for soil are given in Table IV. For the terrestrial compartment, inclusion of secondary poisoning does not lead to major changes in the MPCs of cadmium and copper. The newly derived MPC_{soil} for copper is higher than the currently used MPC for soil that is based on the effects on microbial processes and enzyme activity.

Table IV Currently used MPCs and NCs for soil.

	MPC_{soil} [mg/kg]	NC_{soil} [mg/kg]
cadmium	1.6	0.8
copper	40[a]	36
inorganic mercury	2.2[a]	0.3
methyl-mercury	0.67	0.3

[a]: based on effect on microbial processes and enzyme activity

No conclusions can be drawn with respect to the impact of secondary poisoning on the risks of mercury, as toxicity data on soil organisms are hardly available. The NOECs for secondary poisoning are comparable to the NOEC for earthworms. If other soil organisms are equally sensitive, the MPC for direct exposed organisms will aproach the background concentration and the inclusion of secondary poisoning will not lead to a substantial reduction of the MPC. As for the aquatic compartment, the NCs are determined by the background concentration.
The present calculations for the aquatic compartment are based on a limited set of field accumulation data and BCFs had to be calculated using concentrations in animals and suspended solids that were sampled at different locations. The resulting MPCs must therefore be regarded as indicative. It is recommended to perform further research into the accumulation of cadmium, copper and mercury by aquatic organisms. Data collection should include measurements in animals and in water from the same location. For mercury, the determination of field BCFs should also include investigations into the relative contribution of methyl-mercury to the total mercury concentration in soil, sediment, water and animals living in those compartments. The availability of more chronic toxicity data for birds and mammals from tests that are conducted with relevant species and exposure routes, may also contribute to a better assessment of the impact of secondary poisoning.

1. Introduction

1.1 Environmental Quality Standards

From 1989, the project 'Setting Integrated Environmental Quality Standards' has been carried out by the National Institute of Public Health and the Environment. Goal of the project is to set environmental quality standards (EQSs) for water, sediment, air, soil, and groundwater in line with the risk philosophy of the Dutch Ministry of Housing, Spatial Planning and the Environment (VROM, 1988-1989). The EQSs are based on Maximum Permissible Concentrations (MPCs) and Negligible Concentrations (NCs), which are risk limits that are derived using data on (eco)toxicology and environmental chemistry[1]. The derivation of these MPCs and NCs has been delegated by the Ministry of VROM to the National Institute of Public Health and the Environment (RIVM). An expert group with members of governmental research institutes, industry and non-governmental organisations is involved in the derivation process. By now, integrated EQSs have been set for a large number of substances, including metals, pesticides, PCBs, polycyclic aromatic hydrocarbons (PAHs), anilines and chlorophenols. An overview of risk limits for about 200 substances is presented in a recently published RIVM report, together with the procedures and data used for their derivation (De Bruijn et al., 1999). This report also contains the official memorandum of the Interdepartmental Working Party on Setting Integrated Environmental Quality Standards for Substances (IWINS), in which the currently valid environmental quality standards for 150 substances are presented (IWINS, 1999).

1.2 Bioconcentration and secondary poisoning

Part of the substances for which risk limits have been derived have a potential for bioconcentration or bioaccumulation. These substances involve both highly lipophilic organic compounds and heavy metals. Bioconcentration means that direct uptake by organisms of a certain substance exclusively from the surrounding environment, i.e. not via food, leads to a higher concentration in the organism compared to the environmental concentration. The term bioaccumulation is used for the same phenomenon in case of combined uptake from food and the surrounding environment (Moriarty, 1983)[2]. Accumulated substances may lead to secondary poisoning and therefore impose a risk on organisms at a higher level in the food chain.

For cadmium and mercury, literature data indicate that food chain transfer of these metals to higher organisms occurs. For copper, such information is scarce. In terrestrial foodchains, high cadmium concentrations are found in some organisms, such as earthworms (Ma et al., 1983) and woodlice (Donker, 1992). In habitats with high cadmium concentrations such as river floodplains and near metal smelters, earthworms can accumulate cadmium to such levels as to be of concern for mammals feeding on earthworms (Hendriks et al., 1995b, Ma et

[1] The term Environmental Quality Standards (EQSs) is the general term used for all legally and non-legally binding standards that are used in the Dutch environmental protection policy; MPCs and NCs are non-legally binding standards. MPCs and NCs are scientifically based toxicological limits and do not take account of economic considerations or realisability (IWINS, 1999).

[2] When these definitions are applied in a strict sense, it is not possible to determine a field BCF because in the field no distinction can be made between uptake from the surrounding medium and uptake from food. In this report, the term BCF is used in a somewhat broader sense and refers to the ratio between the concentration in the organism and the concentration in the corresponding medium.

al., 1991). The toxicological endpoint which is used to assess the risk of cadmium is generally a critical kidney concentration between 120 and 200 mg/kg (Balk et al., 1993; Ma, 1987). This value is exceeded for moles, badges and shrews on several locations in The Netherlands (Ma 1987; Ma et al., 1991; Ma and Broekhuizen, 1989). Cadmium concentrations in the kidney and liver of the mole (*Talpa europea*) were elevated on sites near metal smelters compared to a control site (Ma et al., 1987). The same was found for the shrew *Sorex araneus* (Ma et al., 1991) where cadmium was about four-fold higher in kidney and seven-fold higher in liver than at the control site. Badgers (*Meles meles*) foraging in river floodplains had about four-fold elevated cadmium in kidney, compared to badgers foraging outside floodplains (Ma and Broekhuizen, 1989). In aquatic foodchains, benthic species accumulate cadmium readily from food sources (Van Hattum et al., 1989; Timmermans et al., 1992, Munger and Hare 1997). High cadmium concentrations can be found in shellfish (*Dreissena, Corbicula*) which may pose a threat to shellfish consuming fish and waterfowl (Van Hattum et al., 1996). Organ analysis of birds that that were found dead or moribund in the field, indicates that mercury levels of about 70 to 120 mg/kg in the kidney are lethal to birds. Evidence of accumulation of mercury in the aquatic food chain was found by Van Hattum et al. (1993; 1998a), who observed that levels of mercury in roach and eel increased with age or size and found elevated levels of mercury in cormorant eggs. Elevated mercury levels were also found in livers of spoonbill chicks, but concentrations were below the reported effect level of 5 mg/kg for a sensitive bird species (Van Hattum et al., 1998b). For mammals, field data indicate that kidney levels of 20 to 60 mg/kg are lethal, liver levels of dead or moribund field animals are in the same range (Slooff et al., 1995).

1.3 Risk assessment of secondary poisoning

From the above, it is clear that for the risk assessment of accumulating substances, not only toxicity data on directly exposed aquatic and terrestrial organisms have to be taken into account, but effects on species that use these organisms as a food source have to be considered as well. Several risk assessment models exist to predict the risks for animals with a high proportion of earthworms and or insects in their diet and predators that prey on carnivorous small birds and mammals. A general method to include secondary poisnoning in the derivation of environmental risk limits has been developed by Romijn et al. (1991ab) and Van de Plassche (1994). Information on the bioconcentration potential in terms of bioconcentration factors (BCFs) is essential in these methods.

As already explained, BCFs are defined as the ratio between the concentration in the organism and the corresponding concentration in the environment. In case of metals, many organisms are able to keep the internal concentrations constant, when external concentrations are at a sub-lethal level. This is especially the case for essential metals, but may also apply to other metals for which efficient excretory mechanisms have evolved. As the BCF is calculated from the internal concentration divided by the external concentration, a constant internal level at increasing external concentrations will result in decreasing BCFs, whereas low external concentration will result in relatively high BCFs. This concentration dependency was observed in laboratory studies on accumulation of copper and cadmium in fish (Seim et al., 1984; Pascoe and Mattey, 1977; Rombough and Garside, 1982). The same was found in a field survey on water organisms by Hendriks (1995a).

Van de Plassche (1994) used laboratory BCFs for the derivation of MPCs of cadmium, copper and mercury in water. One of the reasons for this is that the quality and reliability of these studies can be evaluated. However, the external concentrations of metals used in laboratory tests exceed by far the actual concentrations in the field and this may lead to an underestimation of the bioconcentration potential. This was observed for copper in bivalves

where the geometric mean of the laboratory BCFs was more than a factor of 60 lower than field values (Van de Plassche, 1994). Monitoring data indicate that the same is true for cadmium (Hendriks, 1995a). The use of a fixed value obtained from laboratory studies that are performed at high concentrations, may result in an underestimation of the risk at the relatively low environmental concentrations encountered in the field. A similar situation exists for risk assessment of heavy metals in soil. In most cases, however, risk assessment of secondary poisoning in the terrestrial food chain has already been based on field bioconcentration data and are thus based on representative environmental concentrations (Romijn et al., 1991a; Van de Plassche, 1994).

1.4 Aim of the present report, readers guide

The currently used MPCs and NCs for cadmium, copper and mercury are solely based on direct exposure. The risk of secondary poisoning was not included in the derivation, mainly because of limited data and uncertainty about the representativity of laboratory BCFs for the field situation (Crommentuijn et al., 1997). As was mentioned in the previous section, field BCFs may exceed the laboratory values by far. Therefore, the aim of the present report is to investigate the risks of secondary poisoning on the basis of field bioconcentration data. The concentration dependency of bioconcentration is evaluated and implications for setting environmental quality standards are discussed. Results are compared with previously derived MPCs and NCs and recommendations are made with respect to possible adjustments of the environmental quality standards.

The derivation of MPCs and NCs is a dynamic process that depends on advancing scientific views and ongoing research, and therefore MPCs and NCs have to be updated from time to time. As a result, the values and methods that are presented may differ from previous reports. It was therefore decided to include an overview of the previously derived MPCs for cadmium, copper and mercury. This overview of methods and data is given in **Chapter 2**. The next chapter (**Chapter 3**) focuses on the methods for collection of toxicity and accumulation data and the derivation of MPCs and NCs that are used in the present report. The results are presented and discussed in **Chapter 4**, followed by conclusions and recommendations in **Chapter 5**.

2. Overview of previously derived MPCs and NCs: methods and data

2.1 Methods to include secondary poisoning

The first RIVM reports on the risks of secondary poisoning were published in 1991 when a method was presented to include food chain transfer of persistent chemicals in environmental risk assessment (Romijn et al., 1991ab). They proposed the following formula to calculate MPCs based on secondary poisoning:

$$MPC_{water} = \frac{NOEC_{bird,mammal}}{BCF_{fish}} \quad (2.1)$$

and

$$MPC_{soil} = \frac{NOEC_{bird,mammal}}{BCF_{worm}}, \quad (2.2)$$

In these formulas, the $NOEC_{bird,mammal}$ is for the whole group of fish or worm eating birds or mammals. This $NOEC_{bird,mammal}$ is derived from individual toxicity data using assessment factors or a statistical approach (e.g. the method of Aldenberg and Slob). It has to be noted that the test species used in toxicity tests almost never involve the fish or worm eating mammals and birds under concern. It has therefore been assumed that the standard test species are representative for field species to be protected. The BCF_{fish} is defined as the ratio between the concentration in the fish and the corresponding concentration in the water. The BCF_{worm} in the latter formula refers to the ratio between the concentration in the organism and the concentration in soil. In recent years, it has become common practice to indicate this ratio as the Biota-to-Soil-Accumulation-Factor (BSAF), and this term will be used in the present report. Van de Plassche (1994) elaborated further on the work of these authors and presented a method in which MPCs based on secondary poisoning and MPCs based on direct effects are combined, to give a MPC for the whole ecosystem. He used mussels next to fish as a second route of exposure in the aquatic food chain.

The work of Romijn et al (1991ab) raised a lot of discussion concerning whether or not correction factors should be used (see Van de Plassche, 1994). The main reasons for applying correction factors involve:

- differences in metabolic rate between laboratory and field animals
- differences in caloric content between laboratory food (cereals) and field prey (fish, mussels and earthworms)
- differences in food assimilation efficiency
- differences in bioavailability of the toxic compound
- differences in relative sensitivity between laboratory species and field organisms
- differences in metabolic rate in specific periods of the life cycle

Most aspects could not be addressed due to lack of sufficient data. It was decided to apply a correction factor for the second aspect only, and to use conversion factors of 0.32 for fish, 0.20 for mussels and 0.23 for worms. The conversion factors for fish and mussels were

derived by Ruys and Pijnenburg (1991) on the basis of a broad literature search. The conversion factor for worms is based on Westerterp et al. (1982). The resulting formulas as used by Van de Plassche (1994) are:

$$MPC_{water} = \frac{NOEC_{bird,mammal}}{BCF_{fish}} \times 0.32, \quad (2.3)$$

$$MPC_{water} = \frac{NOEC_{bird,mammal}}{BCF_{mussel}} \times 0.20, \quad (2.4)$$

and

$$MPC_{soil} \frac{NOEC_{bird,mammal}}{BCF_{worm}} \times 0.23 \quad (2.5)$$

After calculating MPCs based on secondary poisoning in the above mentioned way, the resulting values are compared with the MPCs based on direct exposure, and the lower value of the two is used as the MPC for the whole ecosystem. This method, further referred to as Method I, is shown schematically on the left hand side in Figure 1. In an alternative method, NOECs for predators (in mg/kg food) are first converted to NOECs for the compartment (in mg/kg food or mg/l water), using accumulation data. The resulting NOECs are combined with data on lower organisms and used together in an appropriate extrapolation method (Figure 1).

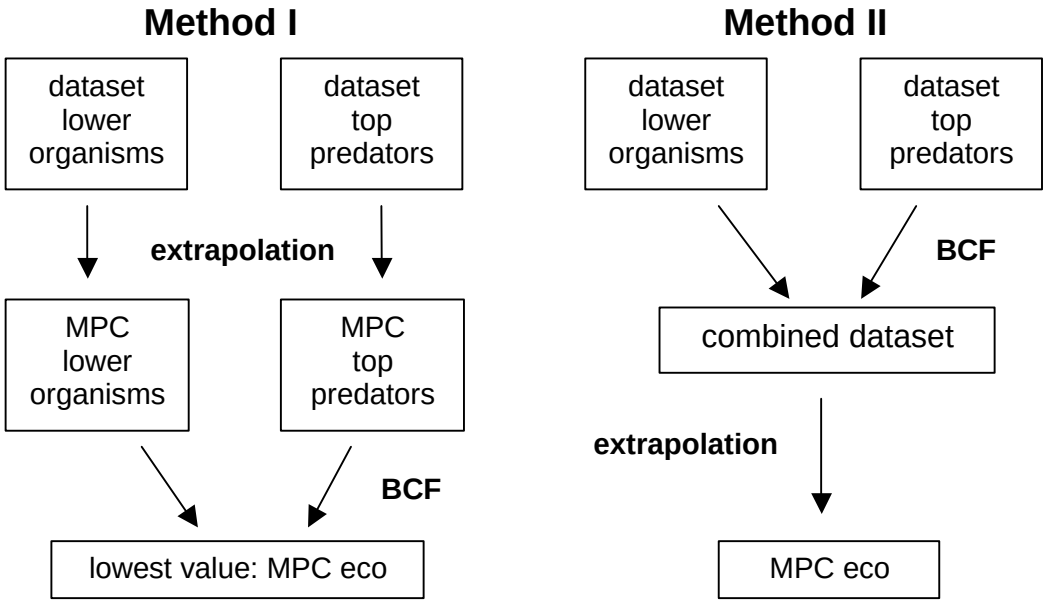

Figure 1 Methods to include secondary poisoning in MPCs. Method I: direct exposure and secondary poisoning are treated separately. Method II: data on direct exposure and secondary poisoning are combined.

Van de Plassche (1994) used both approaches to derive MPCs, but decided to base the definite MPCs on Method I because Method II yielded relatively low as well as high MPCs. In the meanwhile, however, it was decided on theoretical grounds that Method II is to be preferred for the derivation of MPCs (Kalf et al., 1999). The main reason for this is that Method II is more in line with the original assumptions of the statistical extrapolation method, in which the distribution of species sensitivities for the whole ecosystem is

considered, rather than the NOECs for a limited part of the ecosystem. A major drawback of Method II is that the contribution of secondary poisoning may be biased as in most cases the data set for top predators is very small compared to the data set for directly exposed organisms.

2.2 Overview of existing data

2.2.1 Toxicity data

For cadmium, copper and mercury, the most recent compilation of *aquatic* and *terrestrial* toxicity data is given by Crommentuijn et al. (1997). For cadmium, the most recent compilation of data on toxicity for *birds and mammals* can be found in reports by Romijn et al. (1991ab), Jongbloed et al. (1994) and Romijn et al. (1991b); data for copper in Van de Plassche (1994) and for mercury in the Integrated Criteria Document by Slooff et al. (1995).

2.2.2 Data on accumulation

The risks of secondary poisoning of cadmium, copper and mercury have been addressed in several RIVM reports (Romijn et al., 1991ab; Van de Plassche, 1994). The risks of secondary poisoning were also addressed in the Integrated Criteria Document on mercury (Slooff et al., 1995). At some points, the methods used in the latter report differ from the methods that are adopted within the framework of the INS-project, e.g. in not including conversion factors for differences in caloric content of food. The reason for this is that discussion on correction factors was still going on at the time the Integrated Criteria Document was written.
For all reports, accumulation data have been collected for earthworms, fish and bivalves and used as input for the terrestrial food chain model (*soil => earthworm => worm eating bird or mammal*), and for the aquatic food chain model (*water and/or sediment => fish or mussel =>fish- or mussel-eating bird or mammal*). Some authors used data of previously published reports, in some cases combining these with newly collected data.
The accumulation data that are most recently used for the derivation of MPCs based on secondary poisoning are given in the tables below for aquatic organisms and earthworms (Table 1). Although the latest report on mercury is that of Slooff et al. (1995), data used by Van de Plassche (1994) are presented as well, since the latter report was written within the framework of the INS-project. The BCF of methyl mercury for bivalves as used by Van de Plassche (1994) and Slooff et al. (1995) originates from the same study, the difference is due to rounding off.

Table 1 Geometric means and maximum BCFs/BSAFs (in bold) for fish, bivalves and worms previously used for derivation of MPCs. BCFs are given in l/kg wwt, BSAFs in kg dwt/kg wwt. Origin of data (lab or field) is indicated by L and F, n=number of data.

	BCF fish	max	lab/ field	n=	**BCF bivalves**	max	lab/ field	n=	**BSAF worm**	max	lab/ field	n=	Ref
Cd	**38**	540	L	7	**1400**[a]	2900	F	?	**2.7**[b]	39.5	L/F	71[c]	1
Cu	**120**[d]	-	L	5	**8.1**	79	L	3	**1**[e]	10[e]	L/F	?	1
inorg. Hg	**300**	5700	L	6	**2500**	5300	L	2	**0.36**	0.39[Field]	F	2	1
inorg. Hg	**3030**	5670	L	4	**2540**	5333	L	5	**0.7**	8.31[Lab]	L/F	19[f]	2
methyl-Hg	**14000**	35000	L	5	**13000**	-	L	1	**8.3**[g]	83[h]	L	2	1
methyl-Hg	**21700**	100000	F	18	**13300**	-	L	1					2

[a]: not used by Van de Plassche (1994), since only field data are available; [b]: data of Romijn et al. (1991); values were standardised to pH 6.5 according to Ma (1982); [c]: 3 laboratory values used; [d]: geometric mean of 5 values, range 50-300; [e]: mean and maximum set to 1 and 10 by Van de Plassche (1994), based on data of Slooff et al. (1989); f: 6 laboratory values used; [g]: data of Romijn et al. (1991), Slooff et al. (1995) consider this value to be valid for inorganic mercury and give 8.31 as the maximum BCF for earthworms; [h]: maximum set to 83 by Van de Plassche (1994); References: 1 Van de Plassche (1994); 2 Slooff et al. (1995)

2.3 Current Environmental Quality Standards

2.3.1 MPCs and NCs: direct route

MPCs and NCs for cadmium, copper and mercury for water, sediment and soil based on direct exposure of organisms have been derived by Crommentuijn et al. (1997). Secondary poinsoning was not included in this derivation. These authors used the so called 'added risk approach' (Struijs et al., 1997). This method results in a Maximum Permissible Addition (MPA) that is defined as the concentration that may be added on top of the background concentration (C_b) without causing impermissible damage to the ecosystem. Application of a safety factor of 100 to the MPA leads to the Negligible Addition (NA), that is regarded as a lower risk threshold (IWINS, 1999). Assuming that the background concentration does not lead to any deleterious effects on the ecosystem, the MPC is defined as the sum of MPA and C_b. In the same way, the NC is given as the sum of NA and C_b. Background concentrations for surface water are based the upper limits of concentrations measured in relatively unpolluted areas, the origin of the values can be found in Crommentuijn et al. (1997). The MPAs, NAs, C_bs and resulting MPCs and NCs as derived by Crommentuijn et al. (1997) are included in the overview of Dutch environmental quality standards (IWINS, 1999). Data for cadmium, copper and mercury are summarised below:

Table 2 Current MPAs and C_bs and MPCs for freshwater, sediment and soil based on direct exposure. Values for freshwater refer to dissolved concentrations. Values for sediment and soil refer to standard soil and sediment with 10% o.m. and 25% clay. (Crommentuijn et al., 1997; IWINS, 1999).

	MPA_{water} [µg/l]	$C_{b\ water}$ [µg/l]	MPC_{water} [µg/l]	MPA_{sed}[a] [mg/kg]	$C_{b\ sed}$ [mg/kg]	MPC_{sed} [mg/kg]	MPA_{soil} [mg/kg]	$C_{b\ soil}$ [mg/kg]	MPC_{soil} [mg/kg]
Cd	0.34	0.08	0.4	29	0.8	30[b]	0.76	0.8	1.6
Cu	1.1	0.4	1.5	37	36	73	3.5[d]	36	40[d]
inorganic Hg	0.23	0.01	0.2	26	0.3	26[c]	1.9[d]	0.3	2.2[d]
methyl Hg	0.01	0.01	0.02	1.1	0.3	1.4	0.37	0.3	0.67

[a]: all MPAs for sediment are based on the Equilibrium Partitioning Method; [b]: MPC refers to the ecotoxicological risk limit, the EQS is set at the current Intervention Value of 12 mg/kg; [c]: MPC refers to the ecotoxicological risk limit, the EQS is set at the current Intervention Value of 10 mg/kg; [d]: MPC is based on effects on microbial processes and enzymatic activity.

Table 3 Current NAs, C_bs and NCs for freshwater, sediment and soil based on direct exposure. Values for freshwater refer to dissolved concentrations. Values for sediment and soil refer to standard soil and sediment with 10% o.m. and 25% clay. (Crommentuijn et al., 1997; IWINS, 1999).

	NA_{water} [µg/l]	$C_{b\ water}$ [µg/l]	NC_{water} [µg/l]	NA_{sed}[a] [mg/kg]	$C_{b\ sed}$ [mg/kg]	NC_{sed}[b] [mg/kg]	NA_{soil} [mg/kg]	$C_{b\ soil}$ [mg/kg]	NC_{soil} [mg/kg]
Cd	0.0034	0.08	0.08	0.29	0.8	0.8	0.0076	0.8	0.81
Cu	0.011	0.44	0.5	0.37	36	36	0.035	36	36
inorganic Hg	0.0023	0.01	0.012	0.26	0.3	0.32	0.019	0.3	0.32
methyl Hg	0.0001	0.01	0.01	0.011	0.3	0.30	0.0037	0.3	0.30

[a]: all NAs for sediment are based on the Equilibrium Partitioning Method; [b]: all NCs for sediment are set at the NC for soil

2.3.2 Secondary poisoning

The added risk approach was not yet developed at the time that MPCs for secondary poisoning were first derived. Therefore, the MPCs calculated previously, are considered as MPAs, and will be referred to as such in the following.

Van de Plassche (1994) derived MPAs based on secondary poisoning according to Method I (see § 1.1.2). This was done for birds and mammals separately and using the combined toxicity data for birds and mammals. Resulting MPAs are summarised in the tables below for the route *water => fish => fish-eating bird or mammal* (Table 4), for the route *water => mussel => mussel-eating bird or mammal* (Table 5) and for the route *soil => earthworm => worm-eating bird or mammal* (Table 6). MPAs for mercury derived by Slooff et al. (1995)

are also presented. The latter values are also calculated using Method I on the combined toxicity data for birds and mammals.

*Table 4 MPAs based on secondary poisoning via **fish**.*

	MPA_{bird} via *fish* [µg/l]	MPA_{mammal} via *fish* [µg/l]	$MPA_{bird,mammal}$ via fish [µg/l]	BCF used		Reference
Cd	0.35	20	2.9	38	lab	1
Cu	-	6.4	6.4	120	lab	1
inorganic Hg	0.43	2.1	0.43	300	lab	1
inorganic Hg	-	-	0.23	3030	lab	2
methyl Hg	0.0021	0.0022	0.0027	14000	lab	1
methyl Hg	-	-	0.007	21700	field	2

Ref 1: Van de Plassche (1994)
Ref 2: Slooff et al. (1995)

*Table 5 MPAs based on secondary poisoning via **mussels**.*

	MPA_{bird} via *mussels* [µg/l]	MPA_{mammal} via *mussels* [µg/l]	$MPA_{bird,mammal}$ via mussels [µg/l]	BCF used		Reference
Cd	-	-	-	-*		1
Cu	-	59	59	8.1	lab	1
inorganic Hg	0.032	0.16	0.032	2500	lab	1
inorganic Hg	-	-	0.27	2540	lab	2
methyl Hg	0.0014	0.0015	0.0019	13000	lab	1
methyl Hg	-	-	0.011	13300	lab	2

*: only field data available
Ref 1: Van de Plassche (1994)
Ref 2: Slooff et al. (1995)

*Table 6 MPAs based on secondary poisoning via **earthworms**.*

	MPA_{bird} via *worms* [mg/kg]	MPA_{mammal} via *worms* [mg/kg]	$MPA_{bird,mammal}$ via worms [mg/kg]	BCF used		Reference
Cd	0.0035	0.20	0.03	2.7	lab/field	1
Cu	-	0.55	0.55	1	set value	1
inorganic Hg	0.26	1.3	0.26	0.36	field	1
inorganic Hg	-	-	1	0.7	lab and field	2
methyl Hg	0.0026	0.0027	0.0033	8.3	lab	1
methyl Hg	-	-	-	-	-	2

Ref 1: Van de Plassche (1994)
Ref 2: Slooff et al. (1995)

3. Methods used in the present report

3.1 Data collection and treatment

3.1.1 Toxicity data for birds and mammals

It was decided to rely on readily available sources for toxicity data on birds and mammals, since the performance of an extensive literature search and the evaluation of resulting literature would be too time consuming. Furthermore, it was not expected that one of the shortcomings of the present data, namely the use of standard laboratory species, would be different in recent publications. This means that for cadmium, data from Romijn et al. (1991a) and Jongbloed et al. (1994) were used. For mercury, data of Slooff et al. (1995) were used. Data on copper toxicity for mammals were taken from Van de Plassche (1994), supplemented with information from the recently published Environmental Health Criteria Copper (WHO/IPCS, 1998). Recent CSR-advisory reports on several copper compounds were used to find data on copper toxicity for birds (Montforts and Smit, 1998).

3.1.2 Accumulation data

As was outlined in the Introduction, the main reason to perform the present re-evaluation of MPCs was the observed discrepancy between laboratory and field accumulation data, and it was decided to solely use field data. A literature search was performed to retrieve field accumulation data for fish, bivalves and earthworms. The resulting references for aquatic organisms were very small in number and in some cases large differences with Dutch field values were observed. This may be the result of differences in external concentrations or other environmental conditions. For instance, some studies were performed in relatively heavily polluted stagnant water (Lithner et al., 1995) which may not be comparable to Dutch rivers. Therefore, Dutch monitoring data on fish and bivalves were used first. These data are published in Hendriks (1995) and Hendriks et al. (1998), raw data were provided by the authors. For earthworms, Dutch field accumulation data from previous reports were taken from Romijn et al. (1991a), supplemented with monitoring data provided by the Province of Zuid-Holland (PIMM, 1987ab; 1988; 1989; 1990; 1992; 1993;) and data from the former Institute for Forestry and Nature Research IBN-DLO (Ma et al., 1998). Dutch field data available from previous RIVM reports were included in the database.

In some cases, BSAFs were reported instead of BCFs, with BSAFs based on concentrations in suspended matter. If no monitoring data on corresponding dissolved concentrations in water were available, BSAFs were converted to BCFs using the equilibrium partitioning method, either by first calculating concentrations in the water and using this value to calculate the BCF:

$$C_{water} = \frac{C_{susp}}{K_{p,susp}} \qquad (3.1)$$

and

$$BCF = \frac{C_{organism}}{C_{water}} \tag{3.2}$$

or, if concentrations in the organisms were not available, by directly converting BSAFs into BCFs:

$$BCF = BSAF \times K_{p,susp} \tag{3.3}$$

All BCFs and BSAFs are to be expressed on a wet weight basis, because toxicity data are also given on the basis of moist food. If no information on the wet to dry weight ratio of the organisms was available, the following dry to wet weight ratio's were used: crustaceans: 9%; bivalves: 12%; chironomids: 5%; roach: 24%; eel: 38 % (Hendriks, 1995b) and for earthworms: 16% (Jager, 1998).

3.2 Derivation of MPAs and NAs

In view of the advice of the Technical Soil Protection Committee (Technische Comissie Bodembescherming; TCB, 1994) and following guidance of the 'Stuurgroep INS', Method II (see § 2.1) was adopted in the guidance documents on derivation of MPCs (Kalf, 1996; Kalf et al., 1999). It was therefore decided to use this method in the present report. The following steps were applied:

1. NOECs for birds and mammals, which were given in mg/kg food, were converted to values in mg/l water or mg/kg soil on the basis of the formulas in § 2.1:

$$NOEC_{water,\,fish-to-bird} = \frac{NOEC_{bird}}{BCF_{fish}} \times 0.32, \tag{3.4}$$

$$NOEC_{water,mussel-to-bird} = \frac{NOEC_{bird}}{BCF_{mussel}} \times 0.20, \tag{3.5}$$

and

$$NOEC_{soil,worm-to-bird} = \frac{NOEC_{bird}}{BSAF_{worm}} \times 0.23 \tag{3.6}$$

For mammals, similar formulas were used:

$$NOEC_{water,\,fish-to-mammal} = \frac{NOEC_{mammal}}{BCF_{fish}} \times 0.32, \tag{3.7}$$

$$NOEC_{water,mussel-to-mammal} = \frac{NOEC_{mammal}}{BCF_{mussel}} \times 0.20 \tag{3.8}$$

and

$$NOEC_{soil,worm-to-mammal} = \frac{NOEC_{mammal}}{BSAF_{worm}} \times 0.23 \qquad (3.9)$$

2. If, for a certain species, more than one NOEC was available for the same parameter, the geometric mean of the NOECs was calculated.
3. For the aquatic compartment, the lowest of the two NOEC-values (via fish or via mussel) per test species was then selected. This value was combined with data on aquatic species and these data were used as input for the appropriate extrapolation method[3]. NAs were calculated by applying a factor of 100 to the MPAs.
   For the terrestrial compartment, the NOECs for worm eating birds or mammals were added to the data on terrestrial species and the combined data set was used for the estimation of MPAs and NAs.
4. To gain insight into the relative contribution of secondary poisoning to the overall environmental risk, MPAs and NAs based on secondary poisoning alone were also calculated. To this end, MPAs were estimated from the NOECs for birds and mammals after conversion of these values to concentration in water and soil according to formula 3.4-3.9. NAs were calculated by applying a factor of 100 to the MPAs.
5. The results were compared with the MPAs and NAs for water, sediment and soil derived by Crommentuijn et al. (1997) based on direct exposure of aquatic and terrestrial organisms, and the relevance of the newly derived MPAs and NAs is discussed (Chapter 4).

[3] The choice of the extrapolation method depends on the availability of data. When data of four or more species are available, the statistical extrapolation method according to Aldenberg & Slob is applied. When less data are available, assessment factors are applied according to the EU-Technical Guidance Document (ECB, 1996) or according to the so-called modified EPA assessment factors. For detailed guidance, see Kalf et al. (1999).

4. Results and discussion

4.1 Toxicity data for birds and mammals

In Appendix 2, an overview of toxicity data for birds and mammals is presented. These data are summarised in Table 7.

Table 7 Availability of toxicity data for birds and mammals

	birds			mammals		
	number of studies	number of species	lowest value*	number of studies	number of species	lowest value*
Cd	5	5	0.2	9	5	3
Cu	1	1	285	14	4	7
inorganic Hg	3	3	1	2	2	7
methyl Hg	8	7	0.25	6	4	0.22

*: in mg/kg food

Cadmium

The distribution of toxicity values for cadmium is shown in Figure 2. For cadmium, NOECs for birds range from 0.2 to 38 mg/kg food. The lowest value is found for the turkey. Data indicate that mammals may be less sensitive than birds, with NOECs ranging from 3 to 50 mg/kg food. The difference, however, is not significant (T-test, $P<0.05$). There is no indication for differences in sensitivity between small mammals and domestic animals, the variation in NOECs within one species is similar to the variation between species. The relatively low value of 3 mg/kg food for the rhesus monkey may result from the fact that this was a very long term study (3 years).

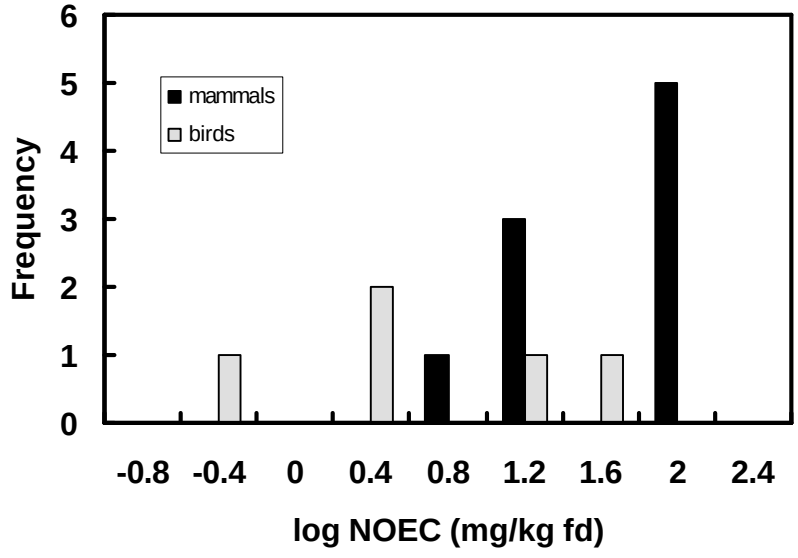

Figure 2 The distribution of cadmium toxicity values for birds and mammals.

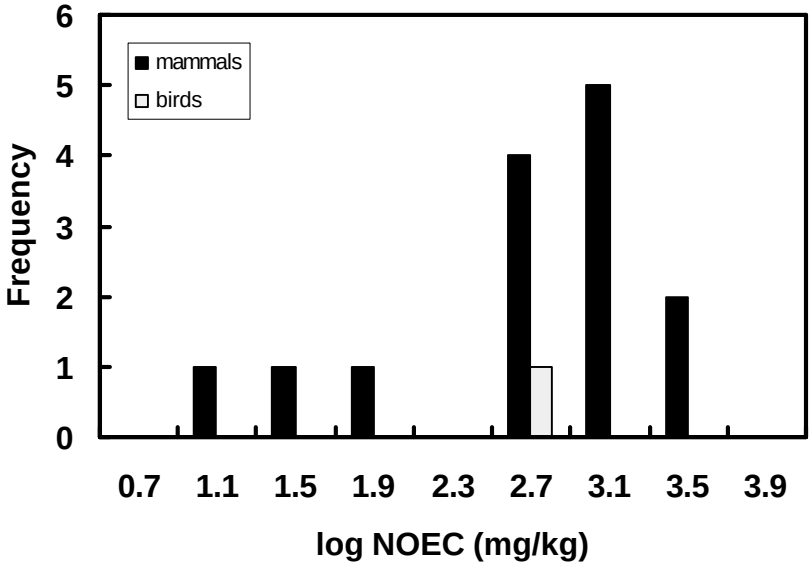

Figure 3 The distribution of copper toxicity values for birds and mammals.

Copper
The distribution of NOEC-values for copper is given in Figure 3. For copper, no bird toxicity data were found by Van de Plassche (1994). One NOEC for reproduction of the duck *Anas platyrhynchos* was available from a recent CSR-advisory report on several copper compounds (Montforts and Smit, 1998). This bird is equally sensitive to copper compared to most of the mammals. Relatively low values were found for sheep compared to other mammals, with NOECs being a factor of 3 to 6 lower than the lowest value for the mouse. This is consistent with the fact that sheep are known to be sensitive to copper. In an extensive overview on copper toxicity to livestock, Janus et al. (1989) give a safe level of 15 mg/kg for copper in sheep food whereas for pigs, the optimum copper content in food is about 200 mg/kg. Based on these figures, the scatter in sensitivity data for copper is at least a factor of 13.

Mercury
For inorganic mercury, only few toxicity data are available. The frequency distribution of NOEC values is shown in Figure 4. NOECs range from 1 to 20 mg/kg food, but conclusions about differences in sensitivity between birds and mammals, or between species within one group, cannot be drawn. From figure 4, it can be seen that methyl-mercury is more toxic than inorganic mercury, with NOECs for small mammals ranging from 0.22 to 2.25 mg/kg and values for birds between 0.25 and 4.3 mg/kg (expressed as mercury). As for cadmium, the lowest NOEC resulted from a long term study with the rhesus monkey.

It may be questioned whether or not data for proven sensitive species have to be included in the data set. The starting point of risk assessment procedures in The Netherlands, is that the functioning of ecosystems should be protected. It is assumed that this goal is reached when less than 5% of all species and/or processes has a chance to be exposed to concentrations above the NOEC. Since the 95% protection level refers to all species regardless of sensitivity, no beforehand selection is made on the basis of sensitivity for a certain compound. On the contrary, it may be argued that sensitive species should be included in risk assessment to

assure that the protection level is properly set. This is in line with the assumption that the data set is a random sample from all species and may therefore also contain sensitive species.

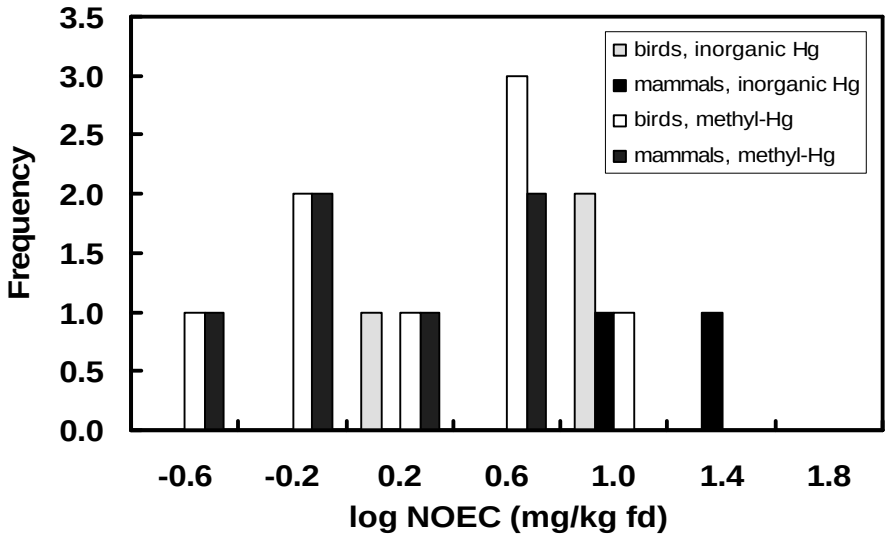

Figure 4 The distribution of mercury toxicity values for birds and mammals.

As was stated before, there are almost no toxicity data that reflect the predator-prey relationships under investigation in this report. In principle, one would like to rely on experiments in which only birds and/or mammals are used for which either fish and mussels or earthworms are the primary food source, and in which the test organisms are exposed to the contaminants via that particular food. The aspect of differences in food source between test species and predators in the field is partly solved by introducing a correction factor to correct for the difference in caloric content of the experimental food (mostly cereals) and the prey (fish, mussels or worms). The question remains whether 'birds' and 'mammals' may be regarded as groups, regardless of feeding behaviour, habitat and other species specific characteristics or that a selection of data must be made depending on the purpose. Such a selection may be made when clear patterns in sensitivity exist, for instance, when the NOECs for domestic livestock are always lower than those for small mammals. On the basis of the available data, however, such a conclusion cannot be drawn. There is also no scientific data to draw the conclusion that some test species are *not* representative for the field species to be protected.

In view of the above, it is realised that the use of toxicity data obtained with common test species may bias the results. As there is no indication that results are biased in one direction and thus lead to non realistically low or high risk limits, it is decided to use all available toxicity data for further calculations. If the outcomes indicate a serious contribution of secondary poisoning to the environmental risks, a decision has to be made on the significance of the value. Where possible, observations on field inhabiting species must be included in such an evaluation.

4.2 Accumulation in fish

The available Dutch field data on accumulation of cadmium and mercury in fish are presented in Appendix 3 and summarised in Table 8, BCFs are based on raw data underlying Hendriks and Pieters (1993). According to Slob (1987) and Seiler and Alvarez (1996), there are strong theoretical and empirical considerations to assume a log-normal distribution *a priori* for many physical entities. This implies that the geometric mean represents a better

Table 8 Field BCFs for fish in l/kg wwt

	number of data	Average BCF	SD	CV [%]	min	max	geometric mean
Cd	8	143	141	98	16	451	91
Cu	-						
Hg	8	27961	37706	135	3728	114631	13576

estimate than the arithmic mean and therefore, geometric mean values are also presented in the table. No data were available for copper. Fish samples consisted of two species, *Rutilus rutilus* (roach) and *Anguilla anguilla* (eel) that originate from 4 different locations in the Haringvliet, Hollands Diep, Ketelmeer, and Rhine (Lobith). Measured dry to wet weight ratios were used to recalculate concentrations in fish on a wet weight basis. Concentrations in suspended solids were reported, but these values originate all from the same nearest monitoring station upstream (Lobith), which means that fish and suspended solids were sampled at considerable distance. As a result, the possible concentration dependency of BCFs as observed by Hendriks (1995) could not be evaluated. Since corresponding dissolved concentrations in water were not available, BCFs had to be calculated using the suspended solids concentrations. The K_ps for suspended matter are derived from Crommentuijn et al. (1995), log K_ps are 5.11 for cadmium, 4.70 for copper and 5.23 for mercury. These values, based on measurement in water and particulate matter at four locations in The Netherlands between 1983 and 1986, are considered as average values as shown by Crommentuijn et al. (1997). When using data on fish and suspended solids that originate from different locations, and applying partitioning coefficients to calculate BCFs, an uncertainty is introduced. However, data from monitoring programmes show that these concentrations can be regarded as representative for Dutch rivers. In view of this, the resulting accumulation data can be considered as indicative for the average Dutch field situation.

Cadmium

Calculated BCF-values ranged from 16 to 451 l/kg wwt (average ± SD: 143 ± 141; geometric mean: 91 l/kg wwt). In Figure 5, the frequency of log BCF-values is shown together with the curve for a normal distribution of data. The log-transformed BCF-data fit reasonably well to a normal distribution (Kolmogorov-Smirnov, $P<0.01$), which justifies the use of the geometric mean BCF for further calculations. It has to be noted that statistical tests are not very powerful at this low number of data.

When comparing the geometric mean field BCF with the BCFs for fish used in previous reports (see Table 1 in § 2.2), it can be concluded that the field BCF for cadmium is higher than the laboratory based value of 38 l/kg wwt used by Van de Plassche (1994). A similar conclusion can be drawn when comparing the field BCFs with whole body BCFs obtained in laboratory studies with the atlantic salmon *Salmo salar* and the three spined stickleback *Gasterosteus aculeatus* (Rombough and Garside, 1982; Pascoe and Mattey, 1977; cited in the draft risk assessment on cadmium oxide, prepared within the framework of the existing chemicals program of the European Union (EU, 1999)). At external concentrations of 0.13 to 300 µg/l, BCFs for the salmon ranged from 1 to 277 l/kg wwt (recalculated assuming 20% dry weight). BCFs for the stickleback were 0.51 to 511 l/kg wwt at corresponding concentrations in the water of 0.8 µg/l to 97.5 mg/l. Geometric mean BCFs were 41 and 16 l/kg wwt for salmon and stickleback, respectively. For both species, BCFs were negatively correlated with concentrations in the water, the following relationships were obtained (with BCF in l/kg wwt and C_w in µg/l):

salmon: $\log BCF_{ww} = 2.86 - 0.69 \log C_w$ (r^2=0.91; n=8)

stickleback: $\log BCF_{ww} = 2.53 - 0.60 \log C_w$ (r^2=0.98; n=13)

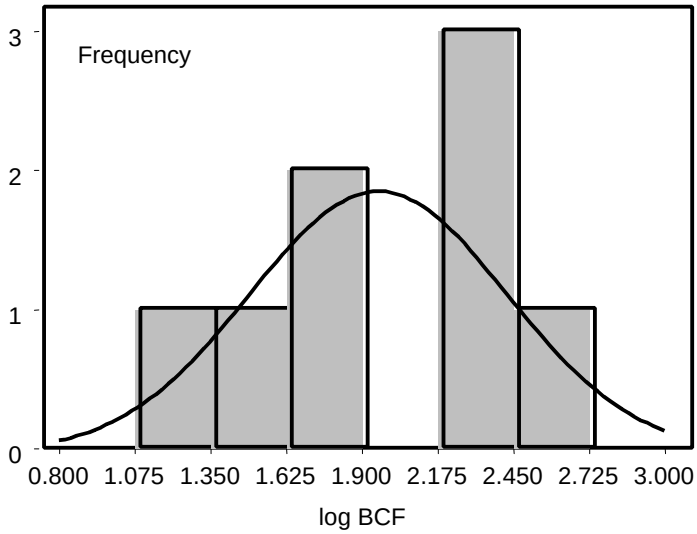

Figure 5 Distribution of log BCFs in fish for cadmium: bars represent absolute frequencies, the line represents the curve for the normal distribution.

As was said before, the concentration dependency of the present field BCFs could not be evaluated, since corresponding external concentrations in water were not available. The fact that the average BCFs for *A. anguilla* of 242 l/kg wwt is higher than for *R. rutilus* (44 l/kg wwt), can therefore not be attributed to differences in the external concentrations. Since for both species there was also no relationship between BCFs and organism size, it may be concluded that the absolute accumulation of cadmium by eel is higher than by roach. This may be attributed to differences in feeding behaviour or habitat. The geometric mean BCF of **91 l/kg wwt** is used to calculate the MPA for water based on exposure via fish.

Copper

No field data from Dutch freshwater fish were available, and only one less reliable reference was found in the open literature (Lithner et al., 1995). In this study, BCFs were determined in fish liver on a dry weight basis. Liver BCFs of 31000 and 12000 l/kg dwt were derived for *Esox lucius* and *Perca fluviatilis* by fitting a model on experimental field BCFs. Since information to recalculate whole body BCFs is not available, the estimation of a reliable field BCF for fish is not possible. It is decided to use the geometric mean laboratory value of **120 l/kg wwt** used by Van de Plassche (1994) in further calculations.

Mercury

Calculated BCFs for mercury ranged from 3728 to 114631 l/kg wwt (average ± SD: 27961 ± 37706; geometric mean: 13576 l/kg wwt). The distribution of accumulation data is shown in Figure 6, where the frequency of log BCF-values is shown together with the curve for the normal distribution (Kolmogorov-Smirnov, $P<0.01$).

As for cadmium, BCFs for eel were higher than for roach: the average BCFs were 51301 l/kg wwt for eel and 4620 l/kg wwt for roach. The difference between the two species is larger than for cadmium, but the data for eel are more variable in this case. The geometric mean BCF of 13567 l/kg wwt is lower than reported by Slooff et al. (1995), who used a BCF of 21700 l/kg wwt. The latter value was based on monitoring data from 1988-1989 reported in Romijn et al. (1991b). In this monitoring programme, fish and water were sampled at 18 locations, and BCFs were calculated on the basis of *measured* dissolved concentrations of mercury.

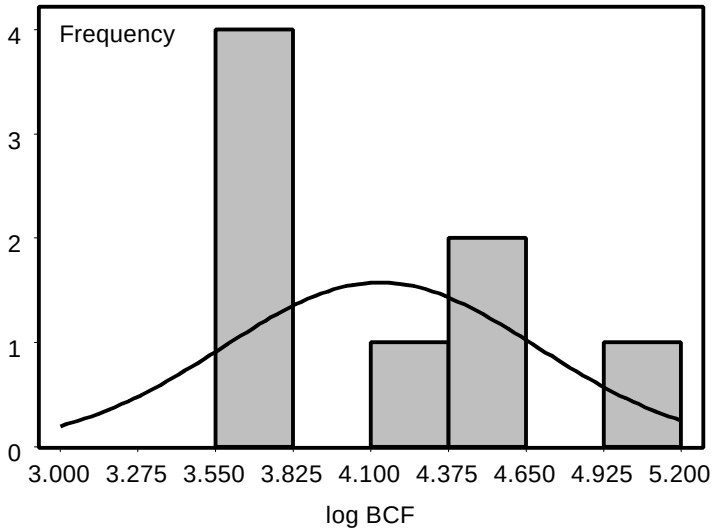

Figure 6 Distribution of log BCFs in fish for mercury: bars represent absolute frequencies, the line represents the curve for the normal distribution.

On the contrary, the BCFs in Table 8 had to be calculated using equilibrium partitioning, because only data on mercury concentrations in particulate matter were available.
In water, mercury occurs mainly in metallic and inorganic forms and about 1-10% is present as methyl-mercury. In fish, 80-99% is present in the methylated form due to uptake of considerable amounts of methyl-mercury via the food and because fish are able to methylate inorganic mercury externally and internally (Slooff et al., 1995). Therefore, it was concluded by Slooff et al. (1995) that the field BCF for mercury, although based on total mercury (inorganic and methylated), should be used for the accumulation of *methyl*-mercury by fish.
The question remains what value should be used for inorganic mercury. For the proper estimation of a BCF, the amount of inorganic mercury taken up by fish has to be known. Assuming that the minimum amount of inorganic mercury in fish is 20% of the total, and that at least 90% of the mercury in water is present in the inorganic form, it can be argued that the BCF is at least 0.20/0.90=0.22 times the observed field value, and amounts to >4774 l/kg wwt. Since part of the inorganic mercury is methylated internally after uptake, it may be assumed that the actual amount of inorganic mercury taken up by fish is considerably higher, leading to a higher value for the BCF. The laboratory BCFs for inorganic mercury are 3030 and 300 l/kg wwt (Slooff et al. 1995; Van de Plassche, 1994). Comparing these values with the estimated BCF of >4774 l/kg wwt, it seems that the laboratory BCFs give an under-estimation of the true bioaccumulation potential.
The same calculation can be made for methyl-mercury, assuming that at most 10% of the total mercury in water is present in the methylated form and that the maximum amount taken up by fish as methyl-mercury is 80-99% of the total concentration observed in the animals. This would lead to a BCF for methyl-mercury that is at most 0.80-0.99/0.1 = 8-9.9 times higher than the observed field value and amounts to <173600-214830 l/kg wwt. Considering the available laboratory values for methyl-mercury (8100 and 14000 l/kg wwt), the thus calculated values seem to be a gross overestimation of the true BCF. The main reason for this may be that a considerable part of the methyl-mercury content in fish results from internal methylation by the organism.
In view of the above, the field-BCF of **21700 l/kg wwt** is used in further calculations for methyl-mercury. For inorganic mercury, the field BCF of **21700 l/kg wwt** is used for a *worst case* calculation, the estimated value of **4774 l/kg wwt** is used as an indication for the minimum risk.

To conclude this section, the BCFs for fish that are selected in this report report are given in bold figures in the table below, together with the data that are used previously.

Table 9 Summary of BCFs (in l/kg wwt) for fish

	BCFs used previously	**BCFs selected in the present report**	log BCFs used previously	log BCFs selected in the present report
Cd	38	**91**	1.58	1.96
Cu	120	**120**	2.08	2.08
inorganic Hg	300 and 3030	**4774 and 21700**	2.48 and 3.48	3.68 and 4.34
methyl Hg	14000 and 21700	**21700**	4.15 and 4.34	4.34

4.3 Accumulation in bivalves

The available Dutch field data on accumulation in bivalves are given in Appendix 3 and are summarised in Table 10. For cadmium and mercury, raw data of Hendriks and Pieters (1993), Hendriks (1995b) and Hendriks et al. (1998) were used, for copper these were supplemented with 3 BCFs of Van de Plassche (1994). Except for the latter, all BCFs were calculated from concentrations in mussels and suspended solids, using the equilibrium partitioning method according to Formula 3.1 and 3.2. As was the case for fish, suspended solids were sampled at different and less locations than mussels, and as a consequence, the calculated BCFs have to be used with the same care as fish BCFs. An average dry to wet weight ratio of 12% was used to re-calculate concentrations in mussels on a wet weight basis. As for fish data, the resulting BCFs are used to evaluate the potential influence on the derivation of MPAs.

Table 10 BCFs for bivalves l/kg wwt

	number of data	Average BCF	SD	CV [%]	min	max	Geometric mean
Cd	9	6018	4321	72	1780	15845	4945
Cu	11	1188	704	59	447	2405	1017
Hg	12	4026	5730	142	1034	22077	2728

Cadmium

A total of 9 BCF values was available for bivalves, ranging from 1780 to 15848 l/kg wwt (average ± SD: 6018 ± 4321; geometric mean: 4945 l/kg wwt). The distribution of log-transformed accumulation data is shown in Figure 7. Data are normally distributed (Kolmogorov-Smirnov, P<0.01).

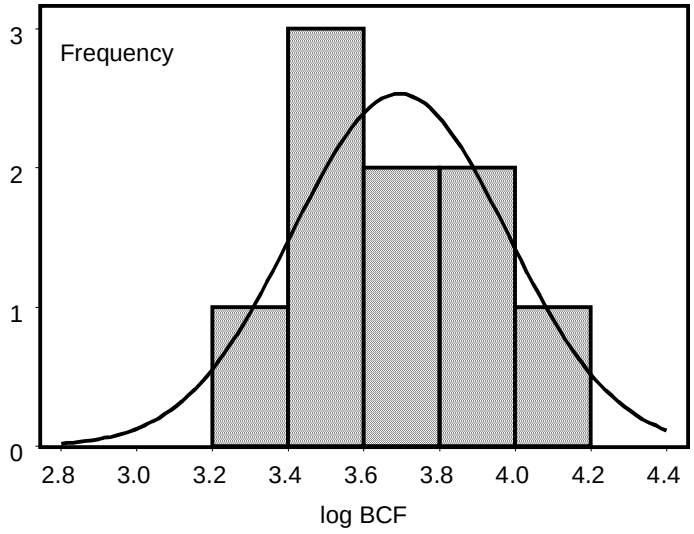

Figure 7 Distribution of log BCFs (l/kg wwt) in bivalves for cadmium: bars represent absolute frequencies, the line represents the curve for the normal distribution.

There is no straightforward relationship between BCFs and concentrations in water: linear regression coefficients r^2 are 0.03 and 0.05 for BCFs based on wet and dry weight, respectively. A geometric mean field BCF of 1400 l/kg wwt (maximum 2900) was given by Van de Plassche (1994). The data underlying this value were not available and could not be included in the database. Lim et al. (1998) determined BCFs of 2600, 3300 and 4100 l/kg wwt for saltwater oysters *Crassostrea iredalei* and *C. belcheri* after incubation in a tropical river estuary. Although these values fit in the range of Dutch field BCFs, data are not used as equilibrium was not reached. The value of **4945 l/kg wwt** is used to estimate the contribution of eating bivalves to the MPA for water.

Copper

For copper, 11 BCFs were available, ranging from 447 to 2405 (average ± SD: 1188 ± 704 l/kg wwt; geometric mean: 1017 l/kg wwt). The frequency distribution of log BCF-values is given in Figure 8, together with the curve for a normal distribution (Kolmogorov-Smirnov, $P<0.01$). Van de Plassche (1994) gives a field BCF of 610 l/kg wwt (geometric mean) based on 2 values for *Mytilus edulis* and 1 for *Dreissena polymorpha*. These data are combined with the new field data, resulting in a geometric mean of **1017 l/kg wwt**.

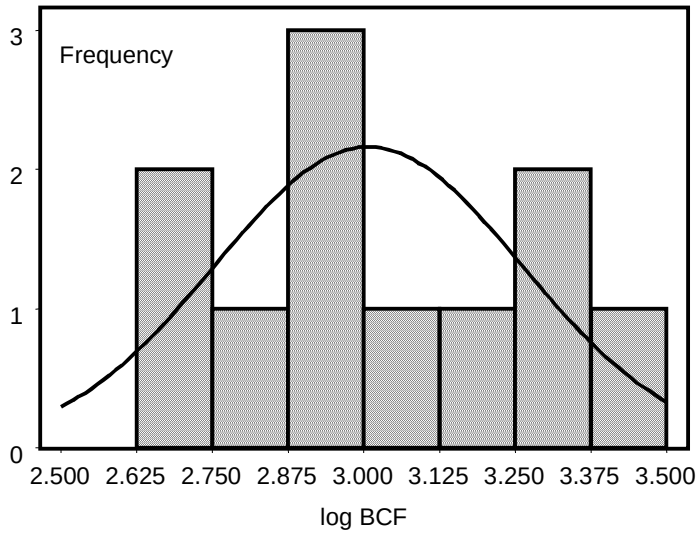

Figure 8 Distribution of log BCFs in bivalves for copper: bars represent absolute frequencies, the line represents the curve for the normal distribution.

Lim et al. (1995, 1998) report BCFs of 4000 to 8100 l/kg wwt for the saltwater oysters *Crassostrea iredalei* and *C. belcheri* after caged incubation in a Malaysian river estuary. These values are higher than the Dutch field BCFs, which may be due to a lower external copper concentration (ca. 1 µg/l) and the different environmental conditions. The distribution pattern of BCF-values is less clear than for cadmium or mercury (see below), which may be explained by the fact that copper is an essential metal. To a certain extent, organisms are able to keep their internal copper level constant (homeostasis), irrespective of the external concentration. Copper concentrations within bivalves differed by only a factor of about 3 to 4 and ranged from 11 to 36 mg/kg dwt (1.1 to 4.4 mg/kg wwt), while the corresponding concentrations in the water differed by a factor of 6 (0.5 to 3 µg/l). As was explained in the introduction, observed differences in BCFs may depend on the external concentration and characteristics of the organism. Regression analysis showed that BCFs were negatively related to concentrations in water. Figure 9 shows the dry weight based BCFs as a function of

the external concentration. Resulting equations, with wet and dry weight based BCFs in l/kg and water concentrations (C_w) in µg/l, were:

$$BCF_{ww} = 2.5\times10^{3} - 0.5\times10^{3} C_w \qquad (r^2=0.44;\ n=8)$$

$$BCF_{dw} = 30\times10^{3} - 8.3\times10^{3} C_w \qquad (r^2=0.64;\ n=8)$$

This implies that at higher external concentrations, accumulation may be lower than expected. It should be kept in mind that BCFs were calculated using data on suspended matter that originate from different, and less locations than the organism samples. A more extensive survey of accumulation in relation to environmental concentrations may shed more light on the relationship. Once such a relationship between BCFs and concentrations is established, it may be considered in the future to differentiate between locations and to use different BCFs for different concentration ranges.

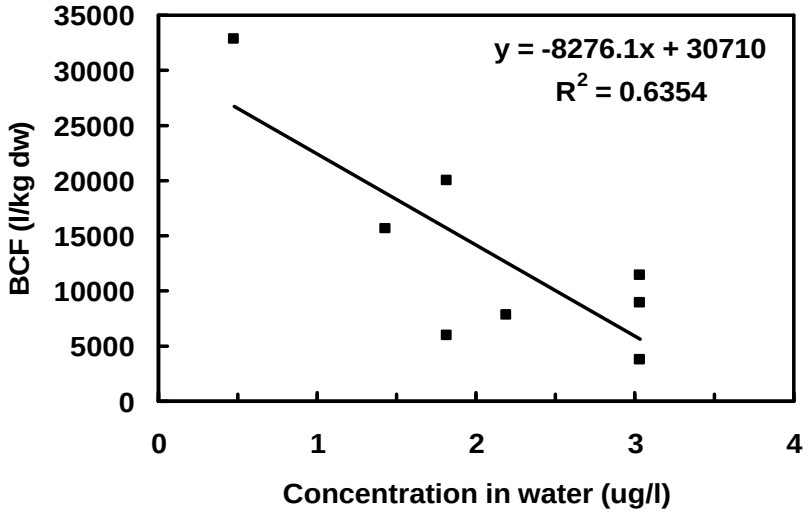

Figure 9 BCFs for copper as a function of the concentration in surface water

Mercury

Twelve BCFs were available for mercury, with a minimum of 1034 and a maximum of 22077 l/kg wwt (average ± SD: 4026 ± 5730; geometric mean: 2728 l/kg wwt). The distribution of log-transformed accumulation data is shown in Figure 10, data fit the normal distribution ($P<0.01$). As for copper, a negative relationship between wet and dry weight based BCFs (in l/kg) and concentrations in water (C_{water}, in µg/l) was found:

$$BCF_{ww} = 14\times10^{3} - 1\times10^{6} C_{water} \qquad (r^2=0.51;\ n=8)$$

$$BCF_{dw} = 1.8\times10^{5} - 2\times10^{7} C_{water} \qquad (r^2=0.48;\ n=8)$$

Relationships, however, were strongly determined by one data point at the lower extreme of the concentration range (see Figure 11 for the dry weight based BCF). The other points were clustered in the center.

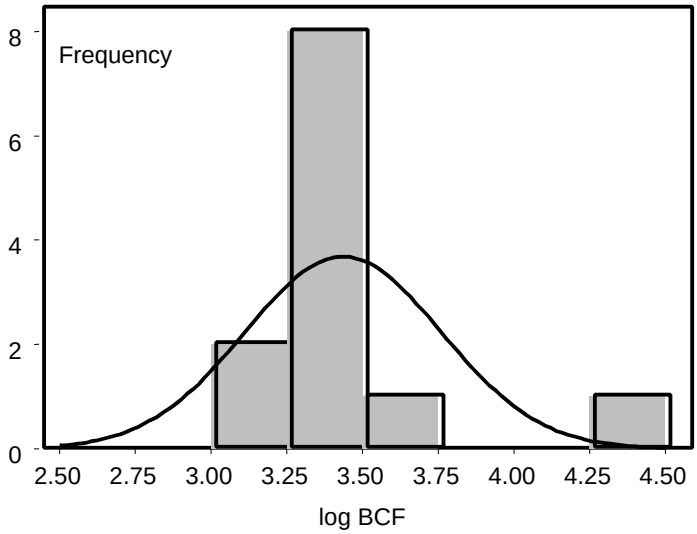

Figure 10 Distribution of log BCFs in bivalves for mercury: bars represent absolute frequencies, the line represents the curve for the normal distribution.

As for fish, field BCFs for mercury are related to total mercury. According to Pieters (1993) (cited in *Slooff et al., 1995*), methyl-mercury accounts for 20-50% of the total mercury in invertebrates. For water this figure is 1-10%. Assuming that the minimum amount of inorganic mercury in bivalves is 80% of the total, and that at least 90% of the mercury in water is present in the inorganic form, it can be argued that the BCF is at least 0.80/0.90=0.56 times the observed field value, and amounts to >1528 l/kg wwt. The same calculation can be made for methyl-mercury, assuming that at most 10% of the total mercury in water is present in the methylated form and that the maximum amount taken up by bivalves is 50% of the total concentration observed. This would lead to a BCF that is at most 0.50/0.10=5 times higher than the observed field value and amounts to < 13640 l/kg wwt. The thus estimated values are in good agreement with the geometric means of laboratory BCFs for inorganic mercury (2500-2540 l/kg wwt) and the value for methyl-mercury (13300 l/kg wwt) used by Van de Plassche (1994) and Slooff et al. (1995).

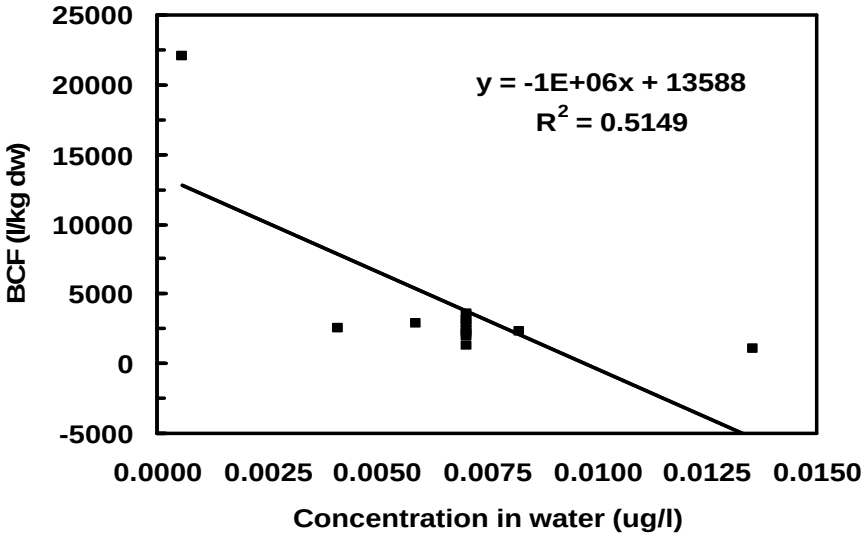

Figure 11 BCFs for mercury as a function of the concentration in surface water

Considering the available data, the field-BCF of **2728 l/kg wwt** is used in further calculations for methyl-mercury, and the laboratory value of **13300 l/kg wwt** is considered as a *worst-case* situation. For inorganic mercury, the field BCF of **2728 l/kg wwt** is used for a *worst case* calculation, the estimated value of **1528 l/kg wwt** is used as an indication for the minimum risk.

To conclude this section, the BCFs for bivalves that are selected in this report are given in bold figures in the table below, together with the data that are used previously.

Table 11 Summary of BCFs (in l/kg wwt) for bivalves

	BCFs used previously	**BCFs selected in the present report**	log BCFs used previously	log BCFs selected in the present report
Cd	1400[#]	**4945**	3.15[#]	3.69
Cu	8.1	**1017**	0.91	3.01
inorganic Hg	2500 and 2540	**1528 and 2728**	3.40	3.18 and 3.44
methyl Hg	13000 and 13300	**2728 and 13300**	4.11 and 4.12	3.44 and 4.12

[#]: reported by Van de Plassche (1994), but not used

4.4 Accumulation in earthworms

Earthworm accumulation data were obtained from the PIMM-monitoring programme of the Province of Zuid-Holland (PIMM, 1987ab; 1988; 1989; 1990; 1992; 1993;) and from the former Institute for Forestry and Nature Research IBN-DLO (Ma et al., 1998). Dutch field data from previous RIVM reports were included in the database. Combining all available Dutch field data, the results on earthworm BSAFs can be summarised as follows:

Table 12 BSAFs for earthworms (kg dry soil/kg wet worm) used for MPC derivation

	number of data	Average BSAF	SD	CV [%]	min	max	Geometric mean
Cd	147	3.79	6.79	179	0.27	42.2	2.10
Cu	170	0.14	0.26	186	0.02	2.67	0.09
Hg	91	0.45	0.48	107	0.03	2.50	0.28

The log transformed BSAFs (in kg dwt/kg wwt) are shown in Figures 12 to 14, together with the curve for a normal distribution. Accumulation data were fitted to a log-normal distribution. The geometric means compare very well to the data used before (see Table 1 in § 2.2), except for copper. Van de Plassche (1994) set the BSAF for this element to 1, based on fact that BSAFs compiled in Slooff et al. (1989) were almost all smaller than 1. No distinction can be made for earthworm BSAFs with respect to the chemical form of mercury. Since mercury in soils is mainly present in the inorganic form (Slooff et al., 1995), the BSAFs are assumed to be valid for inorganic mercury and the significance of secondary poisoning of methyl-mercury may be small. Methylation of mercury in the soil pore water and by earthworms can, however, not be excluded. Therefore, the BSAF for mercury is also combined with toxicity data for methyl-mercury. Geometric mean BSAFs of **2.10**, **0.09** and **0.28** kg dwt/kg wwt for cadmium, copper and mercury, respectively, are used in further calculations.

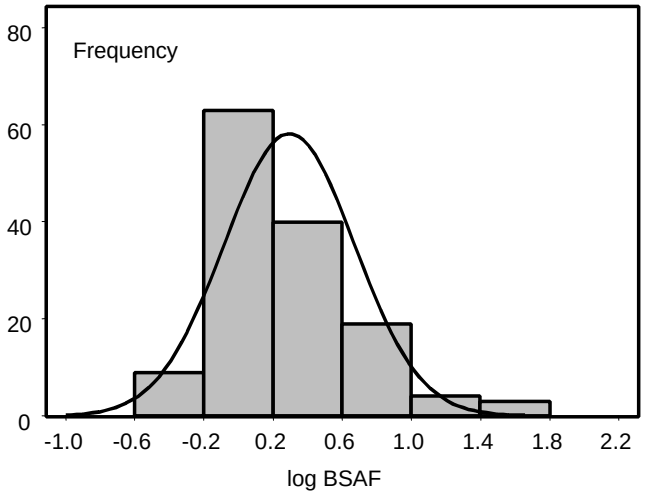

Figure 12 Distribution of log BSAFs in earthworms for cadmium: bars represent absolute frequencies, the line represents the curve for the normal distribution.

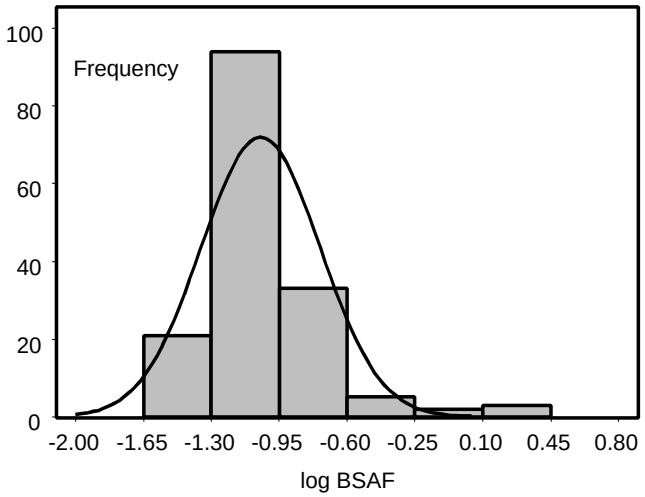

Figure 13 Distribution of log BSAFs in earthworms for copper: bars represent absolute frequencies, the line represents the curve for the normal distribution.

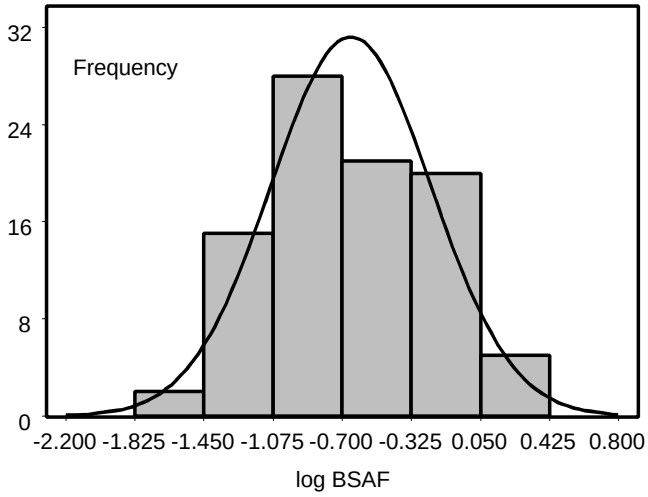

Figure 14 Distribution of log BSAFs in earthworms for mercury: bars represent absolute frequencies, the line represents the curve for the normal distribution.

4.4.1 Accumulation as a function of soil characteristics

The uptake and accumulation of contaminants by organisms depends on the supply of a substance from the environment at one side and the biological demand of an organism at the other side. In this way, bioavailability can be regarded as a dynamic process, comprising environmental availability and biological availability as two distinct phases (Posthuma et al., 1998; Peijnenburg et al., 1999). In the aquatic environment, both the environmental and biological availability of metals are usually strongly related to total concentrations in the water. The situation is far more complex for the terrestrial compartment. Soil organisms potentially have different uptake routes, depending on their morphological, physiological and behavioural properties. At the same time, the distribution of metals over the various soil phases is dependent on a number of soil characteristics that differ from site to site and that interact with each other in a complex way. From this, it can be concluded that even when the same species is regarded and differences at the biological side may be considered marginal, the differences at the soil chemical side will lead to differences in uptake, accumulation and potential effects between sites. The use of total concentrations without taking the variation in bioavailability into account, may thus lead to soil quality criteria that are not accurate for the prediction of (no) effects (Peijnenburg et al., 1999). A pragmatic approach towards the inclusion of bioavailability into risk assessment for soils can be found in the identification of those soil properties that are critical for uptake and accumulation by biota (Janssen et al., 1997ab; Sample et al., 1999). Once a relationship between soil properties and accumulation is established, soil quality standards may be differentiated between soil types or locations.

To detect which soil characteristics are determining uptake of cadmium, copper and mercury by earthworms in the present set of accumulation data, a multiple linear regression analysis was performed using the STATISTIX©-program (©Sigma Research Company). Since pH-H_2O was reported in some cases instead of pH-KCl, first a linear regression analysis between the two parameters was performed using the cases in which both were measured. The resulting relationship:

$pH_{KCl} = -2.18 + 1.20 \times pH_{H_2O}$ (r^2=0.82; n=57) was used to fill data gaps.

A stepwise regression analysis was performed using log based BSAFs (kg/kg wwt) as dependent variables and the log of soil metal concentrations (log[ME_{soil}]), organic carbon (logOC) and clay content (logCL), and pH-KCl as independent variables. The fit of models with three or two variables in all possible combinations was determined. The resulting best fitting equations were as follows:

$$\log BSAF_{Cd} = 0.75 - 0.42 \times \log[Cd_{soil}] - 0.50 \times \log OC \qquad (r^2=0.45;\ n=133)$$

$$\log BSAF_{Cu} = 0.13 - 0.53 \times \log[Cu_{soil}] - 0.32 \times \log OC \qquad (r^2=0.56;\ n=153)$$

$$\log BSAF_{Hg} = -1.76 - 0.71 \times \log[Hg_{soil}] + 0.12 \times pH_{KCl} \qquad (r^2=0.39;\ n=87)$$

In all cases, the soil metal concentration was significantly contributing to the model fit. The modelled BSAFs are plotted against the experimental values in the following figures.

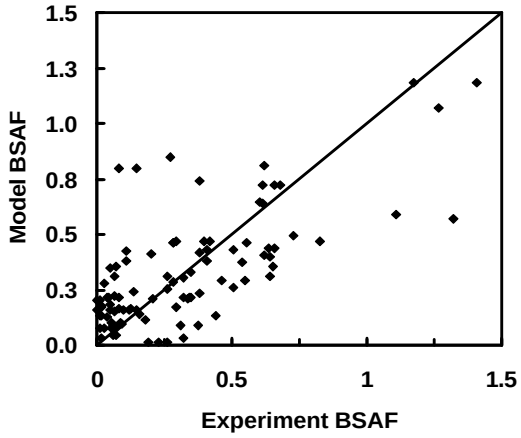

*Figure 15 Predicted log BSAFs (kg/kg wwt) as a function of experimental values for **cadmium**. Solid line represents the 1:1 situation.*

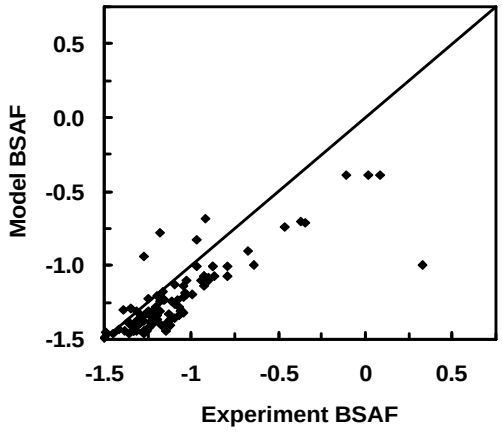

*Figure 16 Predicted log BSAFs (kg/kg wwt) as a function of experimental values for **copper**. Solid line represents the 1:1 situation.*

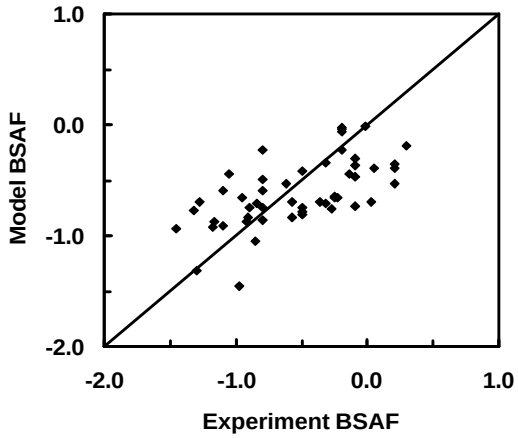

*Figure 17 Predicted log BSAFs (kg/kg wwt) as a function of experimental values for **mercury**. Solid line represents the 1:1 situation.*

From these figures it is clear that the descriptive power of the models is rather limited. The negative correlation of earthworm BSAF with soil metal concentration indicates that at higher concentrations, accumulation in earthworms may be less than expected. This concentration dependency was also observed by Romijn et al. (1991a), who found the following relationship for cadmium, based on field data:

$$\log BSAF_{Cd} = 0.54 - 0.55 \times \log[Cd_{soil}] \qquad \text{(BSAF in kg/kg wwt; } r^2=0.57\text{; n=76)}$$

Results, however, are not comparable with the present analysis because Romijn et al. (1991) did not perform multiple linear regressions.
For mercury, the same authors give the following equation:

$$\log BSAF_{Hg} = -0.17 - 0.007 \times [Hg_{soil}] \qquad (r^2=0.38\text{; n=10; inorganic mercury})$$

This relationship is partly based on laboratory studies, which may explain the difference between this equation and the relationship found on the basis of the present field data. In contrast with Ma (1982), who found that BSAFs for cadmium were highly correlated with soil pH, pH-KCl was not a determining factor in the present analysis.
Data of 26 field studies on uptake of contaminants by earthworms were used recently by Sample et al. (1998; 1999) to develop bioaccumulation models. Data from 6 other studies were used for model validation. It was found that simple log-log regression of concentrations in earthworms and soil (both in mg/kg dwt) gave the best fit for all compounds tested, including cadmium, copper and mercury. The following relationships were obtained:

$$\ln[Cd_{worm}] = 2.11 + 0.79 \times \ln[Cd_{soil}] \qquad (r^2=0.67\text{; n=226})$$

$$\ln[Cu_{worm}] = 1.67 + 0.26 \times \ln[Cu_{soil}] \qquad (r^2=0.18\text{; n=197})$$

$$\ln[Hg_{worm}] = -0.68 + 0.12 \times \ln[Hg_{soil}] \qquad (r^2=0.06\text{; n=30})$$

Using the relationship $\ln[BSAF_{Me}] = \ln[Me_{worm}] - \ln[Me_{soil}]$, this leads to the following relationships for the dry weight based BSAFs:

$$\ln[BSAF_{Cd}] = 2.11 - 0.21 \times \ln[Cd_{soil}]$$

$$\ln[BSAF_{Cu}] = 1.67 - 0.74 \times \ln[Cu_{soil}]$$

$$\ln[BSAF_{Hg}] = -0.68 - 0.88 \times \ln[Hg_{soil}]$$

Inclusion of additional parameters such as pH and/or calcium content improved the models only marginally, but definite conclusions regarding this could not be drawn because these parameters were not determined in all cases. In another study, Abdul Rada and Bouche (1995) analysed metal content in earthworms and soil from 186 location over France. They concluded that despite correlations between levels in soil and worms, the metal content in the earthworms could not be predicted from the concentrations in soil. According to Sample et al. (1999), this could be due to the relatively narrow range of soil concentrations included in the survey.
To check the validity of Sample's equations for the Dutch field data, the observed dry weight BSAFs are plotted against the metal concentration in soil, toghether with the BSAFs that are calculated using Sample's formulas (Figures 18-20).

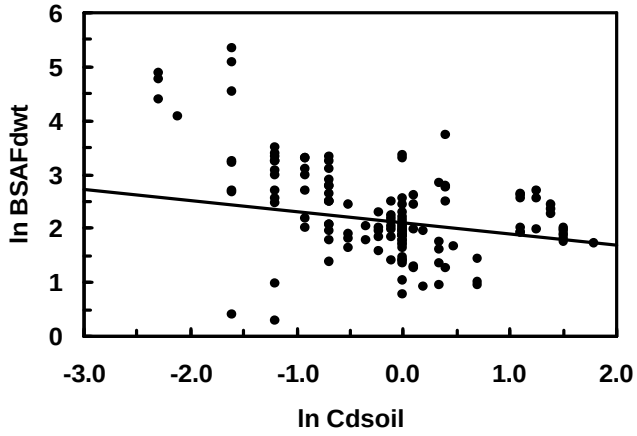

Figure 18 Observed earthworm BSAFs for cadmium as a function of the concentration in soil. The solid line represents the modelled values according to Sample et al. (1998, 1999).

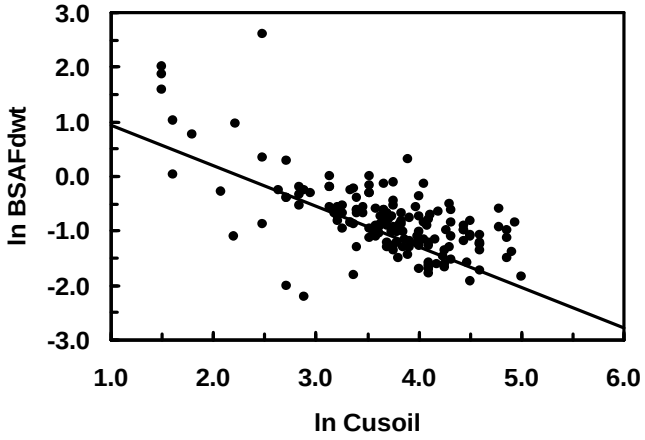

Figure 19 Observed earthworm BSAFs for copper as a function of the concentration in soil. The solid line represents the modelled values according to Sample et al. (1998, 1999).

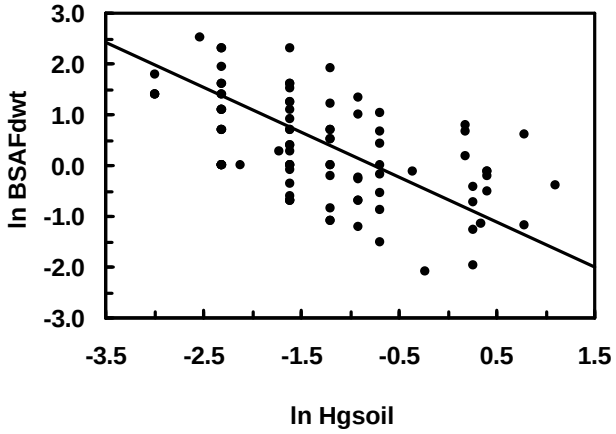

Figure 20 Observed earthworm BSAFs for mercury as a function of the concentration in soil. The solid line represents the modelled values according to Sample et al. (1998, 1999).

From the figures it appears that for cadmium and copper, Sample's models tend to underestimate the BSAF, for mercury the picture is less clear (note that both BSAFs and soil metal concentrations are given as natural logarithms). The reason for this may be that the soil concentrations in the Dutch field data set represent an equally narrow concentration range as the French study.
In conclusion, it may be stated that the available data confirm that bioaccumulation of metals by earthworms is non-linear and that single BSAF-values are therefore not fully suitable for risk assessment at specific locations. However, the regression models obtained in this study and by other authors are highly dependent on the choice of the parameters included in the models. Regression coefficients are not very high and it seems premature to use any of the equations for a soil-type correction of BSAFs, especially where generic risk assessment is concerned. This justifies the use of a geometric mean BSAF-value for the derivation of MPAs for soil. In case site-specific risk assessment has to be carried out, the use of locally determined accumulation factors may, however, be considered.

4.5 Derivation of MPCs and NCs

4.5.1 NOECs based on secondary poisoning

The NOECs for the respective compartments, calculated according to the formulas in Section 3.1 are given in Appendix 3. According to the protocol used for MPC-derivation (Kalf et al., 1999), no correction of earthworm BSAFs to pH or other soil characteristics are made, because no clear correlation between the respective parameters was observed. It is assumed that the resulting NOECs for soil are valid for all soils, including the 'standard soil' with 10% organic matter and 25% clay. Therefore, the values are used as such as input for the extrapolation method.

4.5.2 Extrapolation

4.5.2.1 Aquatic route

Based on the data in Tables 1-4 of Appendix 3, the NOECs that are selected to be used as input in the extrapolation method are given below (Table 13-16). These data are combined with the aquatic toxicity data of Crommentuijn et al. (1997). The lowest NOECs were selected for the derivation of MPAs and NAs, these were:

- cadmium: NOECs via mussels
- copper: NOECs via mussels
- inorganic mercury: NOECs via fish, using the *worst-case* BCF of 21700 l/kg wwt and the calculated minimum BCF of 4774 l/kg wwt.
- methyl-mercury: NOECs via fish with BCF 21700 l/kg wwt and NOECs via mussel using the *worst-case* BCF of 13300 l/kg wwt. The resulting NOECs are very similar, because the difference between the BCFs is practically the same as the difference between the correction factors for caloric content.

For copper, the decision to use the route via mussels may be biased because no field accumulation data for fish are available.

*Table 13 NOECs for mammals and birds to be used in the extrapolation method: **cadmium**.*

species	common name	NOEC in water, based on BCF mussel [µg/l]	Note
mammals			
Rattus norvegicus	Norwegian rat	0.83	geometric mean of 0.4 and 1.7 for most sensitive parameter (growth)
Macaca mulatta	rhesus monkey	0.12	
Ovis amon aries	sheep	0.61	
Bos primigenius taurus	cow	1.62	
Sus scrofa domesticus	pig	1.81	geometric mean of 1.6 and 2.0
birds			
Meleagris galopavo	turkey	0.01	
Anas platyrhynchos	mallard duck	0.06	
Gallus domesticus	chicken	0.49	
Coturnix c. japonica	Japanese quail	1.54	
Streptopelia risoria	ring dove	0.08	

*Table 14 NOECs for mammals and birds to be used in the extrapolation method: **copper**.*

species	common name	NOEC in water, based on BCF mussel [µg/l]	Note
mammals			
Rattus norvegicus	Norwegian rat	52	most sensitive parameter (reproduction)
Mus musculus	domestic mouse	8	most sensitive parameter (reproduction)
Ovis amon aries	sheep	1.7	geometric mean of 3 and 1
Sus scrofa domesticus	pig	49	
birds			
Anas platyrhynchos	mallard duck	56	

*Table 15 NOECs for mammals and birds to be used in the extrapolation method: **inorganic mercury**. Both the worst-case and minimum BCF for fish are used.*

species	common name	NOEC in water, based on worst-case BCF fish [µg/l]	NOEC in water, based on minimum BCF fish [µg/l]
mammals			
Mustela vison	mink	0.10	0.47
Mus musculus	domestic mouse	0.29	1.34
birds			
Sturnus vilgaris	European starling	0.01	0.07
Gallus domesticus	chicken	0.15	0.67
Coturnix c. japonica	Japanese quail	0.06	0.27

*Table 16 NOECs for mammals and birds to be used in the extrapolation method: **methyl-mercury**.*

species	common name	NOEC in water, based on BCF fish [µg/l]	Note	NOEC in water, based on worst-case BCF mussel [µg/l]	Note
mammals					
Rattus norvegicus	Norwegian rat	0.006		0.006	
Mustela vison	mink	0.017	geomean: 0.017, 0.018, 0.037	0.017	geomean of 0.017, 0.08, 0.038
Mus musculus	domestic mouse	0.033		0.034	
Macaca spec.	rhesus monkey	0.003		0.003	
birds					
Anas platyrhynchos	mallard duck	0.004		0.004	
Phasianus colchicus	pheasant	0.008		0.008	
Gallus domesticus	chicken	0.008	geomean of 0.005, 0.013	0.008	geomean of 0.005, 0.013
Coturnix c. japonica	Japanese quail	0.025		0.026	
Poephila guttata		0.040		0.041	
Buteo jamaicensis	red-tailed hawk	0.041		0.042	
Colinus virginianus	bobwhite quail	0.063		0.065	

Cadmium

The resulting data set for **cadmium** involves 97 data in total, 87 of which are toxicity values for directly exposed fresh- and saltwater species as reported by Crommentuijn et al. (1997). The data set for birds and mammals follows a log-logistic distribution. The data on species are not log-logistically or normally distributed, nor is the combined data set for aquatic species, birds and mammals. However, in line with Crommentuijn et al. (1997), the MPAs are calculated for the combined data set according to the method of Aldenberg and Slob. The following MPAs for the aquatic compartment are obtained, based on data on secondary poisoning ($MPA_{water,SP}$), direct exposure ($MPA_{water,direct}$) and both routes combined ($MPA_{water, direct+SP}$):

- $MPA_{water,SP}$, solely based on the NOECs for birds and mammals: **0.015 µg/l**.
- $MPA_{water,direct}$, based on data of directly exposed species and assuming a log-logistic distribution: **0.34 µg/l**.
- $MPA_{water, direct+SP}$, based on all available data: **0.16 µg/l**.

The corresponding NAs (in ng/l) are:

- $NA_{water,SP}$: **0.15 ng/l**.
- $NA_{water,direct}$: **3.4 ng/l**.
- $NA_{water, direct+SP}$: **1.6 ng/l**.

Copper

The combined data set for **copper** consists of 92 values, 87 of which are of fresh- and saltwater species as reported by Crommentuijn et al. (1997). The NOECs for birds and mammals are log-logistically distributed, The data on aquatic species are not log-logistically distributed, the conditions of the normal distribution are met. The combined data set for aquatic species, birds and mammals is also normally distributed. The following MPAs are obtained:

- $MPA_{water,SP}$, solely based on the NOECs for birds and mammals: **1.00 µg/l**.
- $MPA_{water,direct}$, based on data of directly exposed species: **1.1 µg/l**.
- $MPA_{water,direct+SP}$, based on all available data: **1.1 µg/l**.

The corresponding NAs (in ng/l) are:

- $NA_{water,SP}$: **10 ng/l**.
- $NA_{water,direct}$: **11 ng/l**.
- $NA_{water, direct+SP}$: **11 ng/l**.

Inorganic mercury

The combined data set for **inorganic mercury** consists of 43 values, 38 of which are of fresh- and saltwater species (Slooff et al., 1995; data also reported by Crommentuin et al., 1997). The NOECs for birds and mammals, the NOECs for aquatic species and the combined data are all log-logistically distributed. The following MPAs are obtained:

- $MPA_{water,SP}$, solely based on the NOECs for birds and mammals using the *worst-case* BCF for fish: **0.0072 µg/l**.
- $MPA_{water,SP}$, solely based on the NOECs for birds and mammals using the minimum BCF for fish: **0.05 µg/l**.
- $MPA_{water,direct}$, based on data of directly exposed species: **0.23 µg/l**.
- $MPA_{water,direct+SP}$, based on all available data and using the *worst-case* BCF: **0.073 µg/l**
- $MPA_{water,direct+SP}$, based on all available data and using the minimum BCF: **0.14 µg/l**

The corresponding NAs (in ng/l) are:
- $NA_{water,SP}$ (using the *worst-case* BCF for fish): **0.72 ng/l**.
- $NA_{water,SP}$ (using the minimum BCF for fish): **5 ng/l**.
- $NA_{water,direct}$: **2.3 ng/l**.
- $NA_{water,direct+SP}$ (using the *worst-case* BCF): **0.73 ng/l**
- $NA_{water,direct+SP}$ (using the minimum BCF): **1.4 ng/l**

Methyl-mercury
The resulting data set for **methyl mercury** involves 22 data in total, 11 of which are toxicity values for directly exposed fresh- and saltwater species as reported by Slooff et al. (1995; data also reported by Crommentuin et al., 1997). The NOECs for birds and mammals, the NOECs for aquatic species and the combined data are all log-logistically distributed. The following MPAs are obtained:
- $MPA_{water,SP}$, solely based on the NOECs for birds and mammals using the BCF for fish: **0.0022 µg/l**.
- $MPA_{water,SP}$, solely based on the NOECs for birds and mammals using the *worst-case* BCF for mussels: **0.0036 µg/l**.
- $MPA_{water,direct}$, based on data of directly exposed species: **0.01 µg/l**.
- $MPA_{water,direct+SP}$, based on all available data and using the BCF for fish: **0.0015 µg/l**.
- $MPA_{water,direct+SP}$, based on all available data and using the *worst-case* BCF for mussels: **0.0016 µg/l**.

The corresponding NAs (in ng/l) are:
- $NA_{water,SP}$ (using the BCF for fish): **0.022 ng/l**.
- $NA_{water,SP}$ (using the *worst-case* BCF for mussels): **0.036 ng/l**.
- $NA_{water,direct}$: **0.1 ng/l**.
- $NA_{water,direct+SP}$ (using the BCF for fish): **0.015 ng/l**.
- $NA_{water,direct+SP}$ (using the *worst-case* BCF for mussels): **0.016 ng/l**.

The results for the aquatic compartment are summarised in Table 17:

*Table 17 Overview of MPAs and NAs for **water** based on data on secondary poisoning (SP), direct exposure (direct) and both routes combined (direct+SP). Note that MPAs are given in µg/l, NAs are given in ng/l.*

		$MPA_{water, SP}$ [µg/l]	$MPA_{water, direct}$ [µg/l]	$MPA_{water, direct+SP}$ [µg/l]	$NA_{water, SP}$ [ng/l]	$NA_{water, direct}$ [ng/l]	$NA_{water, direct+SP}$ [ng/l]
Cd		0.015	0.34	0.16	0.15	3.4	1.6
Cu		1.00	1.1	1.1	10	11	11
inorganic Hg	*worst case*	0.0072	0.23	0.073	0.72	2.3	0.73
	minimum	0.05	0.23	0.14	0.5	2.3	1.4
methyl-Hg		0.0022	0.01	0.0015	0.022	0.1	0.015
	worst case	0.0036	0.01	0.0016	0.036	0.1	0.016

From these data, values for sediment are derived applying the Equilibrium Partitioning method using the K_ps for sediment of Crommentuijn et al. (1995). Log K_ps are 4.93 for cadmium, 4.53 for copper and 5.05 for mercury. Values for sediment are given in Table 18.

*Table 18 Overview of MPAs and NAs for **sediment** based on data on secondary poisoning (SP), direct exposure (direct) and both routes combined (direct+SP). Note that MPAs are given in mg/kg, NAs are given in µg/kg.*

		$MPA_{sed, SP}$ [mg/kg]	$MPA_{sed, direct}$ [mg/kg]	$MPA_{sed, direct+SP}$ [mg/kg]	$NA_{sed, SP}$ [µg/kg]	$NA_{sed, direct}$ [µg/kg]	$NA_{sed, direct+SP}$ [µg/kg]
Cd		1.3	29	14	13	290	136
Cu		34	37	37	339	373	373
inorganic Hg	*worst case*	0.81	26	8.2	81	258	82
	minimum	5.6	26	16	56	258	157
methyl-Hg		0.25	1.1	0.17	2.5	11	1.7
	worst case	0.4	1.1	0.18	4.0	11	1.8

The MPCs and NCs for water and sediment are derived by addition of the background concentration to the MPA and NA, respectively. Background concentrations for cadmium, copper and mercury are given in Table 2, based on IWINS (1999). Using these figures, the following MPCs and NCs are derived for water (Table 19) and sediment (Table 20):

*Table 19 Overview of MPCs and NCs for **water** based on data on secondary poisoning, direct exposure and both routes combined. All concentration are given in µg/l. The current quality standards are equal to the $MPC_{water,direct}$*

		$C_{b\ water}$ [µg/l]	MPC water, SP [µg/l]	MPC water, direct [µg/l]	MPC water, direct+SP [µg/l]	NC water, SP [µg/l]	NC water, direct [µg/l]	NC water, direct+SP [µg/l]
Cd		0.08	0.10	0.42	0.24	0.08	0.08	0.08
Cu		0.44	1.44	1.5	1.5	0.5	0.4	0.4
inorganic Hg	*worst case*	0.01	0.02	0.24	0.08	0.01	0.01	0.01
	minimum	0.01	0.06	0.24	0.15	0.01	0.01	0.01
methyl-Hg		0.01	0.01	0.02	0.01	0.01	0.01	0.01
	worst case	0.01	0.01	0.02	0.01	0.01	0.01	0.01

*Table 20 Overview of MPCs and NCs for **sediment** based on data on secondary poisoning, direct exposure and both routes combined. All concentration are given in mg/kg. The current quality standards are equal to the $MPC_{sed,direct}$*

		$C_{b\ sed}$ [mg/kg]	MPC sed, SP [mg/kg]	MPC sed, direct [mg/kg]	MPC sed, direct+SP [mg/kg]	NC sed, SP [mg/kg]	NC sed, direct [mg/kg]	NC sed, direct+SP [mg/kg]
Cd		0.8	2.1	30	15	0.8	1.1	0.9
Cu		36	70	73	73	36	36	36
inorganic Hg	*worst case*	0.3	1.1	26	8.5	0.4	0.6	0.4
	minimum	0.3	5.9	26	16	0.4	0.6	0.5
methyl-Hg		0.3	0.6	1.4	0.5	0.3	0.3	0.3
	worst case	0.3	0.7	1.4	0.5	0.3	0.3	0.3

The inclusion of secondary poisoning as a route of exposure of cadmium and mercury yields lower risk limits than the current standards that are derived on the basis of directly exposed species alone. For copper, there is no difference between the two values, but field data for fish are not available for this metal. For mercury, the MPAs based on secondary poisoning alone are very close to or even lower than the background concentrations. As a result, newly derived MPCs for the combined route approach the background concentration or are equal to this value. In this case, it may be considered to set the MPC at the background concentration for mercury. It must be realised, however, that the calculations for mercury are based on assumptions about the distribution of inorganic mercury and methyl-mercury in water and organisms. Since considerable uncertainty exists on the extent to which inorganic mercury is methylated internally by organisms, these calculations have to be regarded as indicative. Furthermore, the present calculations for all three elements are based on a small data set, and the inclusion of more bioaccumulation data may lead to different results.
In view of this, a beforehand adjustment of the MPCs is considered premature. It is recommended to perform further research into the accumulation of cadmium, copper and

mercury by aquatic organisms. For cadmium, data should be collected primarily for mussels; for copper both mussels and fish should be included. For mercury, efforts should be made to determine field BCFs for inorganic mercury and methyl-mercury by determining the relative contribution of methyl-mercury to the total mercury concentration in animals and water. Data collection should include measurements in animals and in water from the same location. The availability of bioaccumulation data from a broad range of locations will allow for the evaluation of the relationship between external concentrations and accumulation. In this way it may be possible to differentiate between locations with respect to the risk assessment of secondary poisoning. It should be kept in mind, however, that the measured accumulation is not solely determined by the external concentration, but that specific characteristics of the location and biota under concern are also important.

4.5.2.2 Terrestrial route

Based on the data presented in Tables 1-4 of Appendix 3, the NOECs that are selected to be used as input in the extrapolation method are given below in Table 21-23. These data are combined with the toxicity data of Crommentuijn et al. (1997) for cadmium and copper and with data of Slooff et al. (1995) for mercury. It has to be noted that since mercury in soil is mainly present in its inorganic form, it may be assumed that BSAFs may not be representative for methyl-mercury. Calculations for this form of mercury are therefore indicative only.

Table 21 NOECs for mammals and birds to be used in the extrapolation method: ***cadmium****.*

species	common name	NOEC [mg/kg]	Note
mammals			
Rattus norvegicus	Norwegian rat	2.25	geometric mean of 1.1 and 4.6 for most sensitive parameter (growth)
Macaca mulatta	rhesus monkey	0.33	
Ovis amon aries	sheep	1.64	
Bos primigenius taurus	cow	4.38	
Sus scrofa domesticus	pig	4.90	geometric mean of 4.38 and 5.48
birds			
Meleagris galopavo	turkey	0.02	
Anas platyrhynchos	mallard duck	0.18	
Gallus domesticus	chicken	1.31	
Coturnix c. japonica	Japanese quail	4.16	
Streptopelia risoria	ring dove	0.21	

Table 22 NOECs for mammals and birds to be used in the extrapolation method: ***copper****.*

species	common name	NOEC [mg/kg]	Note
mammals			
Rattus norvegicus	Norwegian rat	677	
Mus musculus	domestic mouse	102	
Ovis amon aries	sheep	26	geometric mean of 38 and 18
Sus scrofa domesticus	pig	639	
birds			
Anas platyrhynchos	mallard duck	728	

Table 23 NOECs for mammals and birds to be used in the extrapolation method: ***inorganic mercury****.*

species	common name	NOEC [mg/kg]
mammals		
Mustela vison	mink	5.8
Mus musculus	domestic mouse	16.4
birds		
Sturnus vilgaris	European starling	0.8
Gallus domesticus	chicken	8.2
Coturnix c. japonica	Japanese quail	3.3

Table 24 NOECs for mammals and birds to be used in the extrapolation method: ***methyl-mercury****.*

species	common name	NOEC [mg/kg]	Note
mammals			
Macaca spec.	Norwegian rat	0.2	
Rattus norvegicus	mink	0.4	
Mustela vison	domestic mouse	0.94	geometric mean of 0.4, 1 and 2.1
Mus musculus	rhesus monkey	1.8	
birds			
Anas platyrhynchos	mallard duck	0.21	
Phasianus colchicus	ring-necked pheasant	0.30	
Gallus domesticus	chicken	0.46	geometric mean of 0.30 and 0.71
Coturnix c. japonica	Japanese quail	1.40	
Poephila guttata		2.22	
Buteo jamaicensis	red-tailed hawk	2.30	
Colinus virginianus	bobwhite quail	3.53	

Cadmium

The resulting data set for **cadmium** involves 23 data in total, 13 of which are toxicity values for directly exposed soil inhabiting species as reported by Crommentuijn et al. (1997). The data set for birds and mammals, for soil species and the combined data set follow a log-logistic distribution. The following MPAs for the terrestrial compartment are obtained, based on data on secondary poisoning ($MPA_{soil,SP}$), direct exposure ($MPA_{soil,direct}$) and both routes combined ($MPA_{soil,direct+SP}$):

- $MPA_{soil,SP}$, solely based on the NOECs for birds and mammals: **0.036 mg/kg**
- $MPA_{soil,direct}$, based on the data for directly exposed species: **0.76 mg/kg**.
- $MPA_{soil,direct+SP}$, based on all available data: **0.10 mg/kg**.

Corresponding NAs are:

- $NA_{soil,SP}$: **0.00036 mg/kg**
- $NA_{soil,direct}$: **0.0076 mg/kg**.
- $NA_{soil,direct+SP}$: **0.001 mg/kg**.

Copper

The combined data set for **copper** consists of 17 values, 12 of which are of soil inhabiting species. The NOECs for birds and mammals, the data on soil species and the combined data are log-logistically distributed. The following MPAs are obtained:

- $MPA_{soil,SP}$, solely based on the NOECs for birds and mammals: **15 mg/kg**.
- $MPA_{soil,direct}$, based on the data for directly exposed species: **24 mg/kg**.
- $MPA_{soil,direct+SP}$, based on all available data: **25 mg/kg**.

Corresponding NAs are:
- $NA_{soil,SP}$: **0.15 mg/kg**
- $NA_{soil,direct}$: **0.24 mg/kg**.
- $NA_{soil,direct+SP}$: **0.25 mg/kg**.

Mercury
There is only one value for mercury toxicity to soil species, this concerns a NOEC of 3.7 mg/kg for reproduction of *Eisenia fetida* in a potting soil contaminated with methyl-mercury. Considering the length of the test (84 days) and assuming that most of the added methyl mercury had been converted to inorganic mercury, Slooff et al. (1995) considered this value to be valid for inorganic mercury. Crommentuijn et al. (1997), however, interpreted this value as a NOEC for methyl-mercury since hardly any data is available on mercury speciation in soils. In the present report, the NOEC is used in line with Crommentuijn et al. (1997) and is added to the data set for methyl-mercury. Thus, the data set for **inorganic mercury** involves only data on birds and mammals. The NOECs are log-logistically distributed and the following MPA is obtained:
- $MPA_{soil,SP}$, solely based on the NOECs for birds and mammals: **0.56 mg/kg**.
- The corresponding $NA_{soil,SP}$ is **5.6 µg/kg**.

Since no data on soil species are available, the $MPA_{soil,direct}$ and $MPA_{soil,direct+SP}$ and corresponding NAs cannot be calculated.

For **methyl-mercury**, the NOECs for birds and mammals and the combined data are log-logistically distributed. The following MPAs are obtained:
- $MPA_{soil,SP}$, based on the NOECs for birds and mammals: **0.14 mg/kg**
- $MPA_{soil,direct}$, applying a factor of 10 on the NOEC for *E. fetida*: **0.37 mg/kg**.
- $MPA_{soil,direct+SP}$, based on the combined data set for birds, mammals and the earthworm: **0.14 mg/kg**.

Corresponding NAs (in mg/kg) are:
- $NA_{soil,SP}$: **0.0014 mg/kg**
- $NA_{soil,direct}$: **0.0037 mg/kg**.
- $NA_{soil,direct+SP}$: **0.0014 mg/kg**.

The results for the terrestrial compartment are summarised in Tables 25:

Table 25 Overview of MPAs and NAs for the terrestrial compartment based on data on secondary poisoning, direct exposure of soil inhabiting species and both routes combined.

	$MPA_{soil, SP}$ [mg/kg]	$MPA_{soil, direct}$ [mg/kg]	$MPA_{soil, direct+SP}$ [mg/kg]	$NA_{soil, SP}$ [mg/kg]	$NA_{soil, direct}$ [mg/kg]	$NA_{soil, direct+SP}$ [mg/kg]
Cd	0.036	0.76	0.10	0.00036	0.0076	0.001
Cu	15	24	25	0.15	0.24	0.25
inorganic Hg	0.56	-	0.56	0.0056	-	0.0056
methyl-Hg	0.14	0.37	0.14	0.0014	0.0037	0.0014

The MPCs and NCs for soil are derived by addition of the background concentration to the MPA and NA, respectively. Background concentrations for cadmium, copper and mercury are given in Table 2, based on IWINS (1999). Using these figures, the following MPCs and NCs are derived for soil (Table 26):

Table 26 Overview of MPCs and NCs for the terrestrial compartment based on data on secondary poisoning, direct exposure of soil inhabiting species and both routes combined.

	$C_{b\ soil}$	$MPC_{soil,\ SP}$	$MPC_{soil,\ direct}$	$MPC_{soil,\ direct+SP}$	$NC_{soil,\ SP}$	$NC_{soil,\ direct}$	$NC_{soil,\ direct+SP}$
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
Cd	0.8	0.84	1.6	0.90	0.8	0.8	0.8
Cu	36	51	60	61	36	36	36
inorganic Hg	0.3	0.86	-	0.86	0.3	-	0.3
methyl-Hg	0.3*	0.44	0.67	0.44	0.3	0.3	0.3

*background concentration is set at the value for inorganic mercury

For cadmium and methyl-mercury, the current MPCs are equal to the $MPC_{soil,direct}$ in the above table. The current $MPCs_{soil}$ for copper and inorganic mercury are based on the effects on microbial processes and enzyme activity. These $MPCs_{soil,processes}$ are **40** and **2.2 mg/kg**, respectively. For cadmium and methyl-mercury, inclusion of data on secondary poisoning results in a lower MPC than the value based on soil inhabiting species alone. The differences, however, are rather limited. For copper, the difference between the calculated $MPC_{soil,direct}$ and $MPC_{soil,direct+SP}$ is negligible.
Since no information is available on the significance of methylation processes in soil pore water and biota, the estimated MPCs for mercury should be regarded as indicative. The available NOEC of methyl-mercury for earthworms is low compared to the NOECs for cadmium and copper. If this is also true for other soil organisms, it may be expected that the MPA based on direct exposure of soil species will be lower than the current value of 0.37 mg/kg. In this case, the MPC may approach the background concentration. In any case it is expected that for this element direct exposure of soil organisms is the determining factor in the derivation of the MPC. It has to be noted that the background concentration for methyl-mercury in soil is set at the same value as for inorganic mercury.
Given the uncertainties in the derivation procedure and the relatively small differences between the current risk limits and the newly derived values, it is regarded as premature to adjust the MPCs for cadmium and mercury to the newly derived values.

4.5.2.3 Comparison with field effects

Preferably, MPCs should be compared with field data to validate the predicted safe levels for the environment. As was outlined in the introduction, ample data exist on the accumulation of cadmium and mercury in higher organisms. These data involve measured concentrations in whole animals or organs and a direct link with the environmental concentrations in water or soil to which the animals may have been exposed is not made. A way to evaluate the standards, may be the analysis of higher organisms captured at sites that a regarded as unpolluted according to the current environmental quality criteria. If these analyses show that internal levels of the elements under investigation are indeed below the levels that are considered toxic, this is an argument to consider the current standards as appropriate. If, on the other hand, analyses indicate elevated levels or even toxicity, this may be regarded as an indication that the standards are underprotective. It will be clear that interpretation of such data is strongly hampered by the fact that higher organisms may have a considerable home range and that the observed internal concentrations thus result from exposure at different sites. A link between local concentrations in water and soil and effects due to secondary poisoning will therefore be hard to prove.

5. Conclusions and recommendations

MPAs and NAs for cadmium, copper and mercury in water and soil are derived taking secondary poisoning into account by using field bioaccumulation data.

- The following conclusions are drawn with respect to the **aquatic ecosystem**:
  - Secondary poisoning of birds and mammals via fish or mussels may contribute to the risks of **cadmium** and **mercury**. Inclusion of secondary poisoning leads to MPCs that are ca. 2 to 3 times lower than the values based on directly exposed species alone.
  - For **copper**, field accumulation data for fish are not available. Secondary poisoning via mussels does not lead to changes in the MPA.
- The following conclusions can be drawn with respect to the **terrestrial ecosystem**:
  - For **cadmium**, inclusion of secondary poisoning of birds and mammals via earthworms does not have a major impact on the derived risk limit for soil.
  - For **copper**, inclusion of secondary poisoning results in a similar MPC_{soil} as was derived on the basis of species toxicity data alone. Both values are higher than the current MPC that is based on the effect on processes and enzyme activity.
  - For **mercury**, no conclusions on the impact of secondary poisoning can be drawn, since toxicity data for terrestrial species are not available and information on speciation in both soil and biota are lacking. It may be possible that availability of more toxicity data for soil inhabiting species will lead to an estimated MPC that is close to the background concentration in soil. In this case, it may be considered to set the MPC at the background concentration, inclusion of secondary poisoning is then not relevant anymore. Data on BCFs for mussels indicate that accumulation of cadmium, copper and mercury may be higher under field conditions than in laboratory experiments. The same was found for fish with respect to cadmium and mercury, data for copper are not available.
- Accumulation by biota, both aquatic and terrestrial, seems to be negatively correlated with external concentrations. Correlations are not very strong, and for fish and mussels too few data on external concentrations are available to draw conclusions. Implications for the validity of the use of one value for the BCF or BSAF remain therefore to be established.

- The following comments can be made with respect to methods and data:
  - A number of assumptions are underlying the current methods for the inclusion of secondary poisoning in the derivation of risk limits. The main uncertainties are connected with the use of standard laboratory species to assess the toxicity for predatory birds and mammals in the field.
  - Data on the chronic toxicity of cadmium, copper and mercury for birds and mammals are scarcely available, especially when the relevance of the way of exposure for the aquatic or terrestrial food chain is taken into account. To reduce the uncertainties in the derivation of MPCs, more toxicity data for birds and mammals should become available. Special attention should be given to the choice of test species and way of exposure. However, since the number of data for directly exposed organisms will exceed the number of data on secondary poisoning by far, the impact of new toxicity data for birds and mammals may be rather small when data are used in for a combined dataset in the derivation of MPCs. It is therefore questioned whether it is ethically justified to promote this research.

- No data are available on the toxicity of inorganic mercury to soil species, only one toxicity study is available for methyl-mercury.

- The following recommendations are made:
  - Given the uncertainties in the derivation procedure and the relatively small differences between the current risk limits and the newly derived values, it is regarded as premature to adjust the MPCs to the newly derived values.
  - Further research into the accumulation of cadmium, copper and mercury by aquatic organisms should be performed. Data collection should include measurements in animals and in water from the same location.
  - For mercury, the determination of field BCFs should also include investigations into the relative contribution of methyl-mercury to the total mercury concentration in soil, water and animals living in those compartments.

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Appendix 1: Mailing list

1-10. mw. dr. M. van der Weiden
11. dr. ir. B.C.J. Zoeteman
12. Hoofd afdeling stoffen, DGM-SVS
13. mw. dr. W. Tas (DGM-SVS)
14. mw. dr. S. Boekhold (DGM/Bo)
15. dr. T. Crommentuijn (DGM/Bo)
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40. dr. J.W. Wegener (IVM-VU)
41. R. Mes (Provincie Zuid-Holland)
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Appendix 2: toxicity data for birds and mammals

*Table 1 Chronic toxicity of **cadmium** to mammals*

species	english	animal characteristics	application route	exposure time	criterion	type of effect	result	unit	NOEC mg/kg fd	reference	original source
Rattus norvegicus	rat	90d	diet	2y	NOEC	growth	10	mg/kg fd	10	Van de Plassche, 1994	Jongbloed et al., 1994
Rattus norvegicus	rat	28d	diet	90d	NOEC	growth	42	mg/kg fd	42	Van de Plassche, 1994	Jongbloed et al., 1994
Rattus norvegicus	rat	28d	diet	6m	NOEC	mortality	45	mg/kg fd	45	Van de Plassche, 1994	Jongbloed et al., 1994
Rattus norvegicus	rat	28d	diet	41w	NOEC	mortality	10	mg/kg fd	10	Van de Plassche, 1994	Jongbloed et al., 1994
Macaca mulatta	rhesus monkey		diet	3y	NOEC	growth	3	mg/kg fd	3	Van de Plassche, 1994	Jongbloed et al., 1994
Ovis amon aries	sheep		diet	191d	NOEC	growth	15	mg/kg fd	15	Van de Plassche, 1994	Jongbloed et al., 1994
Bos primigenius taurus	cow		diet	12w	NOEC	growth	40	mg/kg fd	40	Van de Plassche, 1994	Jongbloed et al., 1994
Sus scrofa domesticus	pig		diet	5m	NOEC	growth	40	mg/kg fd	40	Van de Plassche, 1994	Jongbloed et al., 1994
Sus scrofa domesticus	pig		diet	6w	NOEC	growth	50	mg/kg fd	50	Van de Plassche, 1994	Jongbloed et al., 1994

*Table 2 Chronic toxicity of **cadmium** to birds*

species	english	application route	exposure time	criterion	type of effect	result	unit	NOEC mg/kg fd	note	reference	original source
Meleagris galopavo	turkey	diet	2w	NOEC	growth	2	mg/kg fd	0.2	1	Van de Plassche, 1994	Jongbloed et al., 1994
Anas platyrhynchos	duck	diet	90d	NOEC	reproduction	1.6	mg/kg fd	1.6		Van de Plassche, 1994	Jongbloed et al., 1994
Gallus domesticus	chicken	diet	48w	NOEC	mortality, reproduction	12	mg/kg fd	12		Van de Plassche, 1994	Jongbloed et al., 1994
Coturnix c. japonica	J. quail	diet	6w	NOEC	growth	75	mg/kg fd	38	2	Van de Plassche, 1994	Jongbloed et al., 1994
Streptopelia risoria	pigeon	diet	5m	NOEC	reproduction	1.7	mg/kg fd	1.9	3		Jongbloed et al., 1994

1: NOEC/10 because test duration is <4 weeks
2: <20% effect at lowest conc. Tested, NOEC as LOEC/2
3: reported value based on ww food

*Table 3 Chronic toxicity of **copper** to mammals*

species	english	animal characteristics	application route	exposure time	criterion	type of effect	result	unit	NOEC mg/kg fd	note	reference	original source
Rattus norvegicus	rat	90d	gavage	20d	LOEL	growth	25.4	mg/kg bw	508	1	Van de Plassche, 1994	USEPA
Rattus norvegicus	rat	28d	diet	4w	NOEC	mortality	2000	mg/kg fd	2000		Van de Plassche, 1994	USEPA
Rattus norvegicus	rat	28d	diet	4w	LOEC	growth	500	mg/kg fd	500		Van de Plassche, 1994	USEPA
Rattus norvegicus	rat	28d	diet	44w	NOEC	growth, mortality	530	mg/kg fd	530		Van de Plassche, 1994	USEPA
Rattus norvegicus	rat	28d	diet	44w	LOEC	reproduction	530	mg/kg fd	265	1	Van de Plassche, 1994	USEPA
Rattus norvegicus	rat		diet	92d	NOEC	growth	509	mg/kg fd	509	2	WHO/ICPS, 1998	Hébert et al., 1993
Rattus norvegicus	rat		diet	15w	LOEC	growth	3000	mg/kg fd	3000	3	WHO/ICPS, 1998	Haywood, 1985; Haywood & Loughran, 1985
Rattus norvegicus	rat		diet	21w	LOEC	growth	2600	mg/kg fd	867	4	WHO/ICPS, 1998	Llewellyn et al., 1985
Mus musculus	mouse		diet	4w	NOEC	reproduction	398	mg/kg fd	40	5	Van de Plassche, 1994	USEPA
Mus musculus	mouse		water	15d	LOEL	mortality	100	mg/kg bw	830	6	Van de Plassche, 1994	FAO/WHO
Mus musculus	mouse		diet	92d	NOEC	growth	254	mg/kg fd	254		WHO/ICPS, 1998	Hébert et al., 1993
Sus scrofa domesticus	pig		diet	61-88d	NOEC	growth	250	mg/kg fd	250		Van de Plassche, 1994	USEPA/Janus
Ovis amon aries	sheep		diet	88d	LOEC	mortality	15	mg/kg fd	15		Van de Plassche, 1994	Janus
Ovis amon aries	sheep	6-12m	diet	37w	NOEC	mortality	7	mg/kg fd	7		Van de Plassche, 1994	FAO/WHO

1: NOEC as 20*LOEL
2: result 2000 mg/kg fd as copper sulfate pentahydrate
3: lowest concentration tested, as copper sulfate
4: one concentration tested, 23% effect; NOEC as LOEC/3
5: NOEC/10 because test duration is <4 weeks
6: NOEC as 8.3*LOEL (100 mg/kg bw)
7: result 1000 mg/kg fd as copper sulfate pentahydrate

*Table 4 Chronic toxicity of **copper** to birds*

species	english	animal characteristics	application route	exposure time	criterion	type of effect	result	unit	NOEC mg/kg fd	notes	reference
Anas platyrhynchos	duck	7m	diet	23w	NOEC	reproduction	285	mg/kg fd	285	1	Montforts & Smit, 1998

1: tested as copper hydroxide

*Table 5 Chronic toxicity of **inorganic mercury** to mammals*

species	english	application route	exposure time	criterion	type of effect	result	unit	NOEC mg/kg fd	notes	reference	original source
Mustela vison	mink	diet	135d	NOEC	repro	7	mg/kg fd	10		Slooff et al., 1995	Aulerich et al., 1974
Mus musculus	mouse	diet	560d	NOEC	growth	20	mg/kg fd	20		Slooff et al., 1995	Ganser & Kirchner, 1985

*Table 6 Chronic toxicity of **inorganic mercury** to birds*

species	english	application route	exposure time	criterion	type of effect	result	unit	NOEC mg/kg fd	notes	reference	original source
Sturnus vilgaris	starling	diet	56d	NOEC	mortality	1	mg/kg fd	1		Slooff et al., 1995	Nicholson & Osborn, 1984
Gallus domesticus	chicken	diet	21d	NOEC	hatching	100	mg/kg fd	10	1	Slooff et al., 1995	Romijn et al., 1991; Scott, 1977
Coturnix c. japonica	J. quail	diet	365d	NOEC	egg fertility	4	mg/kg fd	4		Slooff et al., 1995	Hill & Schafner, 1975

1: NOEC/10 because test duration is <4 weeks

*Table 7 Chronic toxicity of **methyl mercury** to mammals*

species	english	application route	exposure time	criterion	type of effect	result	unit	NOEC mg/kg fd	notes	reference	original source
Macaca spec.	monkey	diet	365d	NOEL	growth	0.01	mg/kg bw	0.22	1	Slooff et al., 1995	Kawasaki et al., 1986
Rattus norvegicus	rat	diet	3 gen	NOEC	repro	0.43	mg/kg fd	0.43		Slooff et al., 1995	Verschuuren et al., 1976
Mustela vison	mink	diet	60d	NOEC	mortality	0.5	mg/kg fd	0.5		Slooff et al., 1995	Wren, 1987
Mustela vison	mink	diet	93d	NOEC	mortality	1.2	mg/kg fd	1.2		Slooff et al., 1995	Wobeser et al., 1976
Mustela vison	mink	diet	100d	NOEC	mortality	2.5	mg/kg fd	2.5		Slooff et al., 1995	Jernelöv et al., 1976
Mus musculus	mouse	diet	60d	NOEL	growth	0.27	mg/kg bw	2.25	2	Slooff et al., 1995	Berthoud et al., 1976

1: NOEC as 20*NOEL
2: NOEC as 8.3*NOEL

*Table 8 Chronic toxicity of **methyl mercury** to birds*

species	english	application route	exposure time	criterion	type of effect	result	unit	NOEC mg/kg fd	notes	reference	original source
Anas platyrhynchos	duck	diet	3 gen.	EC	egg production	0.5	mg/kg fd	0.25	1	Slooff et al., 1995	Heinz, 1979
Phasianus colchicus	pheasant	diet	20d	NOEC	mortality	3.6	mg/kg fd	0.36	2	Slooff et al., 1995	Gardiner, 1972
Gallus domesticus	chicken	diet	20d	NOEC	mortality	3.6	mg/kg fd	0.36	2	Slooff et al., 1995	Gardiner, 1972
Gallus domesticus	chicken	diet	20d	NOEC	mortality	8.6	mg/kg fd	0.86		Slooff et al., 1995	Fimreite, 1970
Coturnix c. japonica	J. quail	diet	63d	NOEC	mortality	1.7	mg/kg fd	1.7		Slooff et al., 1995	Hill & Soares, 1984
Poephila guttata	zebra finch	diet	67d	NOEC	mortality	2.7	mg/kg fd	2.7		Slooff et al., 1995	Scheuhamer, 1988
Buteo jamaicensis	red-tailed hawk	diet	84d	NOEC	mortality, growth	2.8	mg/kg fd	2.8		Slooff et al., 1995	Fimreite & Karstad, 1971
Colinus virginianus	bobwhite quail	diet	54d	NOEC	mortality	4.3	mg/kg fd	4.3		Slooff et al., 1995	Spann et al., 1986

1 NOEC as EC/2, <20% effect
2: NOEC/10 because test duration is <4 weeks

Appendix 3: Field BCFs for fish and bivalves

*Table 1 BCFs for fish: **cadmium**. Numbers in italics refer to measured data, other data are calculated from these figures.*

species	fraction dwt	$C_{suspended\ solids}$ [µg/kg]	C_{water} [µg/l]	$C_{organism}$ [µg/kg dwt]	$C_{organism}$ [µg/kg wwt]	**BCF [l/kg wwt]**	reference#
A.anguilla	*0.3671*	*4000*	0.031	*16*	6	**193**	Hendriks and Pieters 1993
A.anguilla	*0.3663*	*4000*	0.031	*14*	5	**161**	Hendriks and Pieters 1993
A.anguilla	*0.4464*	*4000*	0.031	*11*	5	**161**	Hendriks and Pieters 1993
A.anguilla	*0.3135*	*4000*	0.031	*45*	14	**451**	Hendriks and Pieters 1993
R.rutilus	*0.2395*	*4000*	0.031	*2*	1	**16**	Hendriks and Pieters 1993
R.rutilus	*0.2420*	*4000*	0.031	*8*	2	**64**	Hendriks and Pieters 1993
R.rutilus	*0.2251*	*4000*	0.031	*4*	1	**32**	Hendriks and Pieters 1993
R.rutilus	*0.2493*	*4000*	0.031	*8*	2	**64**	Hendriks and Pieters 1993

#: original references, data are compiled in Hendriks, 1995b

*Table 2 BCFs for fish: **mercury**. Numbers in italics refer to measured data, other data are calculated from these figures.*

species	fraction dwt	$C_{suspended\ solids}$ [µg/kg]	C_{water} [µg/l]	$C_{organism}$ [µg/kg dwt]	$C_{organism}$ [µg/kg wwt]	**BCF [l/kg wwt]**	reference#
A.anguilla	*0.3671*	*1200*	0.007	2206	810	**114631**	Hendriks and Pieters 1993
A.anguilla	*0.3663*	*1200*	0.007	805	295	**41748**	Hendriks and Pieters 1993
A.anguilla	*0.4464*	*1200*	0.007	314	140	**19813**	Hendriks and Pieters 1993
A.anguilla	*0.3135*	*1200*	0.007	654	205	**29012**	Hendriks and Pieters 1993
R.rutilus	*0.2395*	*1200*	0.007	147	35	**4982**	Hendriks and Pieters 1993
R.rutilus	*0.2420*	*1200*	0.007	176	43	**6020**	Hendriks and Pieters 1993
R.rutilus	*0.2251*	*1200*	0.007	117	26	**3728**	Hendriks and Pieters 1993
R.rutilus	*0.2493*	*1200*	0.007	106	27	**3752**	Hendriks and Pieters 1993

#: original references, data are compiled in Hendriks, 1995b

*Table 3 BCFs for bivalves: **cadmium**. Numbers in italics refer to measured data, other data are calculated from these figures.*

species	fraction dwt	$C_{suspended\ solids}$ [µg/kg]	C_{water} [µg/l]	$C_{organism}$ [µg/kg dwt]	$C_{organism}$ [µg/kg wwt]	**BCF [l/kg wwt]**	reference#
not specified	0.12	*5000*	0.039	*1780*	214	**5503**	Anonymous, 1990
Dreissena polymorfa	0.12	*4000*	0.031	*460*	55	**1780**	Hendriks and Pieters, 1993
Dreissena polymorfa	0.12	*5000*	0.039	*2600*	312	**8038**	Hendriks and Pieters, 1993
not specified	0.12	*4000*	0.031	*4100*	492	**15845**	Anonymous, 1990
not specified	0.12	*4000*	0.031	*821*	99	**3174**	Anonymous, 1990
Dreissena polymorfa	0.12	*4000*	0.031	*858*	103	**3315**	Hendriks and Pieters, 1993
Dreissena polymorfa	*0.12*	*2400*	0.019	1333	*160*	**8588**	Hendriks and Pieters, 1993
Dreissena polymorfa	*0.11*	*14000*	0.109	3818	*420*	**3865**	Hendriks and Pieters, 1993
Dreissena polymorfa	*0.07*	*2000*	0.016	900	*63*	**4058**	Hendriks and Pieters, 1993

#: original references, data are compiled in Hendriks, 1995b

*Table 4 BCFs for bivalves: **copper**. Numbers in italics refer to measured data, other data are calculated from these figures.*

species	fraction dwt	$C_{suspended\ solids}$ [µg/kg]	C_{water} [µg/l]	$C_{organism}$ [µg/kg dwt]	$C_{organism}$ [µg/kg wwt]	**BCF [l/kg wwt]**	reference
not specified	0.12	*91000*	1.82	*10800*	1296	**714**	Anonymous, 1990#
Dreissena polymorfa	0.12	*152000*	3.03	*34536*	4144	**1366**	Hendriks and Pieters, 1993#
Dreissena polymorfa	0.12	*91000*	1.82	*36395*	4367	**2405**	Hendriks and Pieters, 1993#
not specified	0.12	*152000*	3.03	*11300*	1356	**447**	Anonymous, 1990#
not specified	0.12	*152000*	3.03	*26857*	3223	**1063**	Anonymous, 1990#
Dreissena polymorfa	*0.12*	*72000*	1.44	22500	*2700*	**1879**	Hendriks and Pieters, 1993#
Dreissena polymorfa	*0.11*	*110000*	2.19	17273	*1900*	**866**	Hendriks and Pieters, 1993#
Dreissena polymorfa	*0.07*	*24000*	0.48	15714	*1100*	**2297**	Hendriks and Pieters, 1993#
Dreissena polymorfa						**480**	Van de Plassche, 1994
Mytilus edulis						**800**	Van de Plassche, 1994
Mytilus edulis						**754**	Van de Plassche, 1994

#: original references, data are compiled in Hendriks, 1995b

*Table 5 BCFs for bivalves: **mercury**. Numbers in italics refer to measured data, other data are calculated from these figures.*

species	fraction dwt	$C_{suspended\ solids}$ [µg/kg]	C_{water} [µg/l]	$C_{organism}$ [µg/kg dwt]	$C_{organism}$ [µg/kg wwt]	**BCF [l/kg wwt]**	reference
Dreissena polymorfa	0.12	*1200*	0.007	*169*	20	**2867**	Hendriks and Pieters, 1993#
Dreissena polymorfa	0.12	*1400*	0.008	*156*	19	**2270**	Hendriks and Pieters, 1993#
Anodonta	0.12	*1200*	0.007	*128*	15	**2173**	Hendriks and Pieters, 1993#
Anodonta	0.12	*1200*	0.007	*115*	14	**1956**	Hendriks and Pieters, 1993#
Dreissena polymorfa	0.12	*1200*	0.007	*185*	22	**3145**	Hendriks and Pieters, 1993#
Dreissena polymorfa	0.12	*1200*	0.007	*210*	25	**3573**	Hendriks and Pieters, 1993#
Dreissena polymorfa	0.12	*1200*	0.007	*145*	17	**2465**	Hendriks and Pieters, 1993#
Dreissena polymorfa	0.12	*700*	0.004	*87*	10	**2540**	Hendriks and Pieters, 1993#
Dreissena polymorfa	0.12	*1200*	0.007	*78*	9	**1324**	Hendriks and Pieters, 1993#
Dreissena polymorfa	*0.12*	*1000*	0.006	142	*17*	**2887**	Hendriks and Pieters, 1993#
Dreissena polymorfa	*0.11*	*2300*	0.014	127	*14*	**1034**	Hendriks and Pieters, 1993#
Dreissena polymorfa	*0.07*	*100*	0.001	186	*13*	**22077**	Hendriks and Pieters, 1993#

#: original reference, data are compiled in Hendriks, 1995b

Appendix 4: NOECs for birds and mammals recalculated to concentrations in water and soil, based on secondary poisoning

Table 1 NOECs for mammals and birds: ***cadmium***.

species	common name	parameter	NOEC direct mg/kg fd	NOECaq via fish **µg/l**	NOECaq via mussel **µg/l**	NOECsoil via worm **mg/kg**
			BCF/BSAF:	91	4945	2.10
mammals						
Rattus norvegicus	Norwegian rat	growth	10	35.2	0.40	1.10
Rattus norvegicus		growth	42	148	1.70	4.60
Rattus norvegicus		mortality	45	158	1.82	4.93
Rattus norvegicus		mortality	10	35.2	0.40	1.10
Macaca mulatta	rhesus monkey	growth	3	10.5	0.12	0.33
Ovis amon aries	sheep	growth	15	52.7	0.61	1.64
Bos primigenius taurus	cow	growth	40	141	1.62	4.38
Sus scrofa domesticus	pig	growth	40	141	1.62	4.38
Sus scrofa domesticus		growth	50	176	2.02	5.48
birds						
Meleagris galopavo	turkey	growth	0.2	0.7	0.01	0.02
Anas platyrhynchos	mallard duck	reproduction	1.6	5.6	0.06	0.18
Gallus domesticus	chicken	mortality, reproduction	12	42.2	0.49	1.31
Coturnix c. japonica	Japanese quail	growth	38	134	1.54	4.16
Streptopelia risoria	ring dove	reproduction	1.9	6.7	0.08	0.21

Table 2 NOECs for mammals and birds: ***copper***.

species	common name	parameter	NOEC direct mg/kg fd	NOECaq via fish **µg/l**	NOECaq via mussel **µg/l**	NOECsoil via worm **mg/kg**
			BCF/BSAF:	120	1017	0.09
mammals						
Rattus norvegicus	Norwegian rat	growth	508	1355	100	1298
Rattus norvegicus		mortality	2000	5333	393	5111
Rattus norvegicus		growth	500	1333	98	1278
Rattus norvegicus		growth, mortality	530	1413	104	1354
Rattus norvegicus		reproduction	265	707	52	677
Rattus norvegicus		growth	509	1357	100	1301
Rattus norvegicus		growth	3000	8000	590	7667
Rattus norvegicus		growth	867	2312	171	2216
Mus musculus	domestic mouse	reproduction	40	107	8	102
Mus musculus		mortality	830	2213	163	2121
Mus musculus		growth	254	677	50	649
Ovis amon aries	sheep	mortality	15	40	3	38
Ovis amon aries		mortality	7	19	1	18
Sus scrofa domesticus	pig	growth	250	667	49	639
birds						
Anas platyrhynchos	mallard duck	reproduction	285	760	56	728

Table 3 NOECs for mammals and birds: ***inorganic mercury****.*

species	common name	parameter	NOEC direct mg/kg fd	BCF/BSAF:	NOECaq via fish **µg/l** 21700 worst-case	NOECaq via fish **µg/l** 4774 minimum	NOECaq via mussel **µg/l** 2728 worst-case	NOECaq via mussel **µg/l** 1528 minimum	NOECsoil via worm **mg/kg** 0.28
mammals									
Mustela vison	mink	repro, mortality, growth	7		0.10	0.47	0.51	0.92	5.8
Mus musculus	domestic mouse	growth	20		0.29	1.34	1.47	2.62	16.4
birds									
Sturnus vulgaris	European starling	mortality	1		0.01	0.07	0.07	0.13	0.8
Gallus domesticus	chicken	hatching	10		0.15	0.67	0.73	1.31	8.2
Coturnix c. japonica	Japanese quail	egg fertility	4		0.06	0.27	0.29	0.52	3.3

Table 4 NOECs for mammals and birds: ***methyl-mercury****.*

species	common name	parameter	NOEC direct mg/kg fd	BCF/BSAF:	NOECaq via fish **µg/l** 21700	NOECaq via mussel **µg/l** 13300 worst-case	NOECaq via mussel **µg/l** 2728 minimum	NOECsoil via worm **mg/kg** 0.28
mammals								
Rattus norvegicus	Norwegian rat	repro	0.43		0.006	0.003	0.03	0.4
Mustela vison		mortality	0.5		0.007	0.006	0.04	0.4
Mustela vison		mortality	1.2		0.018	0.008	0.09	1.0
Mustela vison		mortality	2.5		0.037	0.018	0.18	2.1
Mus musculus		growth	2.25		0.033	0.038	0.16	1.8
Macaca spec.	rhesus monkey	growth	0.22		0.003	0.034	0.02	0.2
birds								
Anas platyrhynchos	mallard duck	egg production	0.25		0.004	0.004	0.02	0.2
Phasianus colchicus	ring-necked pheasant	mortality	0.36		0.005	0.005	0.03	0.3
Gallus domesticus	chicken	mortality	0.36		0.005	0.005	0.03	0.3
Gallus domesticus		mortality	0.86		0.013	0.013	0.06	0.7
Coturnix c. japonica	Japanese quail	mortality	1.7		0.025	0.026	0.12	1.4
Poephila guttata		mortality	2.7		0.040	0.041	0.20	2.2
Buteo jamaicensis	red-tailed hawk	mortality, growth	2.8		0.041	0.042	0.21	2.3
Colinus virginianus	bobwhite quail	mortality	4.3		0.063	0.065	0.32	3.5