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Application of CATS models for regional risk-assessment of toxicants

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ABSTRACT

Application of CATS models for regional assessment of bioaccumulation risks proved feasible. Case studies on heavy metals and organotin showed that initial concentrations, toxicant loading of the system and sorption coefficients strongly influence the prediction of bioaccumulation risks. Consistent quality objectives for soil, water and sediment allow a comparison between different ecosystems or regions. The evaluation of foodweb bioaccumulation for different toxicants is much less consistent since critical concentrations, NOECs etc. are not always available for the same organisms within food webs. Exceedance of quality objectives for food webs can be calculated routinely by simplification of the procedure presented here.

SUMMARY

Application of CATS models for regional assessment of bioaccumulation risks proved feasible. The study showed that a coherent framework for evaluation of bioaccumulation risks is missing, since critical concentrations, NOECs etc. usually are available for a limited number of organisms from ecosystems. A more unifying concept could be found if instead of bioaccumulation, population effects could be studied for all toxicants. This requires a high degree of definition of the ecosystem studied, availability of specific dose-response functions and adequate description of population effects. Although effect modelling on an ecosystem level might be preferable for ecological risk analysis, exceedance of quality objectives, NOECs or critical concentrations seems to be the most realistic goal for mapping of ecosystem risks of toxicants.

As an example of aquatic regional risk assessment, the fate and bioaccumulation of TBT in lake Westeinder was modelled. The Dutch ban on anti-fouling paints containing TBT was simulated with a load reduction scenario. Model predictions indicate a fast decrease of concentrations in water, suspended matter and the zebra mussel *Dreissena polymorpha*. TBT concentrations in sediment, chironomids, amphipods and benthivorous fish are predicted to decrease at a much slower rate. The relative proportion of sediment uptake increases for (partly) benthivorous fish after TBT load reduction. Substantial risks of TBT are calculated for fish and zooplankton in marinas, both before and during load reduction.

As an example of terrestrial regional risk assessment, the accumulation of Cd, Cu and Pb was modelled and risks predicted for the year 2000 and 2015. Target Values for Cd are not exceeded for any soil type in 2000. In 2015 however, ongoing accumulation leads to a small risk of 0.44% on sandy soil, and 5.4% on peat. Target Values for Cu are exceeded most for peat and sandy soil, but increase fast between 2000 and 2015 on clay from 8.2 to 43.1%. For Target Values of Pb, the situation is more favourable since only on peat, a slight increase in risk from 12.3 to 22.7% from 2000 to 2015 is expected. Bioaccumulation of Cd in the food web of grassland was evaluated with a Maximum Permissible Concentration (MPC) for food. Meadow birds and moles but risks are absent or very low for herbivorous mice and their predators. Predicted copper accumulation in soils leads to risks for birds, as evaluated with an MPC. Due to the high toxicity of Cu to sheep, a substantial risk of 37% is predicted for Cu on sandy soils. Cu accumulation in earthworms is already a problem in the year 2000. Due to the ongoing, but slow Pb accumulation in soils and earthworms, risks for moles are expected to increase slowly but steadily for all soil types.

SAMENVATTING

De toepassing van CATS modellen voor regionale risk assessment van bioaccumulatie bleek goed mogelijk. De studie toont echter aan dat een samenhangende set van milieukwaliteitsnormen voor bioaccumulatie in ecosystemen nog niet aanwezig is. Dit heeft voornamelijk te maken met het gebrek aan NOEC's of dosis-effect relaties van voldoende organismen, verspreid over de soorten in een ecosysteem. Een eenduidig raamwerk kan gevonden worden als populatie-effekten van stoffen bestudeerd worden, maar daarvoor geldt eveneens dat nog onvoldoende kennis is voor een routinematige toepassing. Er is namelijk veel specifieke ecosysteemkennis nodig, naast dosis-effekt relaties voor organismen uit het ecosysteem en voldoende studies ter validatie van de voorspelde ecosysteemeffekten. Voorlopig is de overschrijding van normen, NOEC's of kritieke concentraties het meest realistische beoordelingskader bij het karteren van ecologische risico's van stoffen voor ecosystemen.

Een voorbeeld van regionale risico-analyse voor een aquatisch ecosysteem is de studie van het aangroeiwerende middel TBT in de Westeinder plassen. Het verbod op TBT voor kleine schepen werd gesimuleerd met een reductiescenario. Modelvoorspellingen laten zien dat de waterkwaliteit snel verbetert, wat ook gunstig is voor de zebramossel. TBT concentraties in sediment, dansmuggen, vlokreeften en benthivore vis dalen echter veel minder snel. Het relatieve aandeel van TBT opname via het voedsel in de totale TBT opname (via water, sediment en voedsel) stijgt als de TBT concentratie in het water daalt door het verbod op TBT. De risico's van TBT in jachthavens zijn vooral hoog voor vissen en zooplankton, ook nog jaren nadat TBT verboden is. De risico's in het meer zijn laag.

Een voorbeeld van terrestrische risico-analyse is de accumulatie van de zware metalen Cd, Cu en Pb in weilanden op de bodemtypes veen, klei en zand. De belasting van het systeem met metalen zoals vastgesteld in 1985 werd gebruikt als het standaard scenario. Streefwaarden voor Cd worden op geen enkel bodemtype overschreden in 2000, maar in 2015 is er een klein risico voor zand- en veenbodem. Het risico dat streefwaarden voor Cu worden overschreden is groot voor zand- en veenbodem. Voor Pb is overschrijding van streefwaarden vooral te verwachten op veenbodem, met een risico van 22.7 % in 2015. Bioaccumulatie van Cd in het voedselweb is vooral een probleem voor wormen en wormeneters. Cu is vooral een probleem op zandbodems, waar risico's vooral optreden voor regenwormen, vogels en schapen. Pb accumulatie blijft langzaam doorgaan op alle bodems bij het 1985 scenario en leidt tot een kans op chronische nierschade bij mollen.

ACKNOWLEDGEMENTS

This report documents the methodology of adapting functional, dynamic ecosystem models for specific regions or ecosystems. It serves as a background document for a study on bioaccumulation of Tributyltin in a freshwater lake, in cooperation with the Institute for Environmental Studies Amsterdam[1] (IVM), co-authored by J.A. Stäb and W. Cofino (IVM) and P.R.G. Kramer (RIVM).
It also documents the methodology for RIVM report nr 719102038 (' Ecosysteemgerichte beoordeling van stoffen'), in cooperation with the Centre of Environmental Science Leiden[2] (CML), co-authored by F. Klijn (CML). Both institutes are acknowledged for support and cooperation.

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1. INTRODUCTION

1.1 Background and goal

Persistent chemicals and heavy metals are found in Dutch rivers, sediments and soils. Due to local differences in emission history and sorption characteristics of soils and sediments, the degree of contamination can vary considerably between locations. The availability of toxicants to organisms (bio-availability) is believed to be influenced by both the abiotic characteristics of the exposure medium (57) and properties of the organisms (58). A regional risk assessment of toxicants for ecosystems should therefore take into account the characteristics of both the abiotic and biotic components of ecosystems.

A family of dynamic multicompartments models was designed to study bioaccumulation and effects of Contaminants in Aquatic and Terrestrial ecoSystems (CATS). Emphasis has been placed on bioaccumulation in foodwebs (11,12) and propagation of secondary effects of toxicants in foodwebs (59). This report is a documentation of the methodology used to produce risk predictions for bioaccumulation in specific regions.

In CATS models, the fate of the toxicant in the abiotic compartments of the ecosystem is integrated with uptake of the toxicant in the biotic components of the ecosystem. This makes it possible to study the relations between toxicant load, partitioning of the toxicant over water, soil or sediment and uptake of toxicant by organisms. The actual bioavailability of the toxicant is determined mainly by the degree of contamination and loading, sorption characteristics of water, soil or sediment and characteristics of the organisms itself. From experience with existing CATS models, it has become clear that characteristics of the exposure media such as organic matter content, pH, clay content etc. can influence bioaccumulation and effects considerably (11-13).

The goal of this report is to make regional predictions of bioaccumulation in foodwebs with CATS models and evaluate the methodology. This was done by feeding the models with regional input, such as loading history, geological and hydrological properties of soil, water and sediment of selected ecosystems (60). Bioaccumulation of cadmium, copper, lead and TBT was calculated for several ecosystems and soiltypes and risks were calculated and compared between different regions or locations.

1.2 Report organization

Building on the information already available about CATS models, chapter 2 is a brief outline of the method how to adapt the models for different regions. In Chapter 3, an example is given for the antifouling Tributyltin (TBT) in lake Westeinder. In Chapter 4, examples are presented for cadmium, copper and lead in a meadow ecosystem on different soils. In Chapter 5, conclusions are presented.

2. MATERIALS AND METHODS

2.1 Elements of regional risk assessment

The risk assessment method presented in this report is developed to calculate bioaccumulation and risks of toxicant loading on different ecosystems or ecosystem units. First, three main elements of regional risk assessment of toxicants were discerned (Figure 1):

- Ecosystem classification. A system for determining which ecosystems to take into account and where they are located. The definition of ecosystem units is closely linked to the next two elements, and should lead to realistic geographical units that can be used for mapping with Geographical Information Systems (GIS).
- Environmental chemistry. Determination of toxicant retention and loss for a particular ecosystem and calculation of (bio-available) exposure concentrations.
- Ecosystem structure and function. Species in ecosystems are lumped in functional groups, connected by trophic interactions to form a food web model.

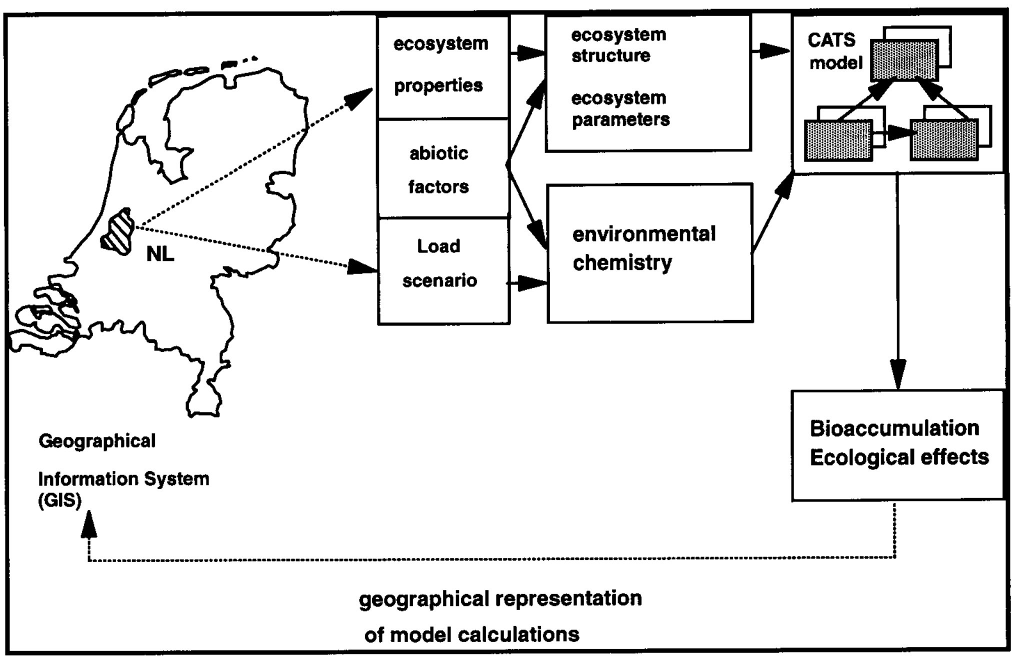

Figure 1: diagram of information flow in ecological risk assessment

It is expected that different ecosystems have a different sensitivity for a toxic chemical. This is hypothesized to be caused by a number of factors:

- The degree of retention (by sorption and bioaccumulation) and loss (by percolation or run-off, harvesting etc.).

- The bioavailability of a toxicant, influenced by properties of water, soil or sediment, and of specific organisms
- The degree of bioaccumulation in food webs with different structures, containing species with differences in sensitivity
- The direct and indirect effects of a toxicant, influenced by the persistence and dose of the toxicant, the structure of the foodweb and the trophic interactions within the foodweb.

These factors are seen as essential for regional risk prediction and are integrated in the model structure.

2.1.1 Ecosystem classification

Ecosystems can be classified according to different principles. A review of ecosystem classification based on ecotopes, developed to work in conjunction with CATS models was given in Traas et al. (60). Different classifying principles lead to other ecosystem classifications such as the Ecological Infrastructure (61). The type of ecosystem for which we calculate bioaccumulation and risks of toxicants determines the food web structure, the species composition but also the abiotic conditions that govern fate and bioavailability of the toxicant (Figure 1). Therefore, the ecosystem classification should provide the modeller with parameters for these aspects, such as pH, organic matter content of soils, food web structure etc, to make a general model structure specific for a certain location by using specific parameter values.

2.1.2 Environmental chemistry

Previous studies with CATS models have shown that properties of the toxicant and soil, sediment and suspended matter determine partitioning and availability of a toxicant to a great extent (11-13). Any regional risk assessment starts with a description of toxicant loading, description of exposure media (water, soil, sediment), retention and loss of toxicant. The definition of the bioavailable fraction is intimately linked to the description of partitioning of the toxicant.

2.1.3 Ecosystem structure

Model structure is derived from the structure of the ecosystem; this process requires abstraction and reduction of ecosystem complexity into a 'manageable' model. As for now, model structure is not automatically deduced from ecosystem characteristics (such as species lists). In CATS models, a choice was made for an intermediate level of complexity (Figure 2), based on physico-geographical regions (61) or main water body structures (62). These main model structures can be made specific for regions or locations by feeding the model with specific parameters from the ecosystem units (Figure 1), soilmaps, databases or other geograhical data sources.

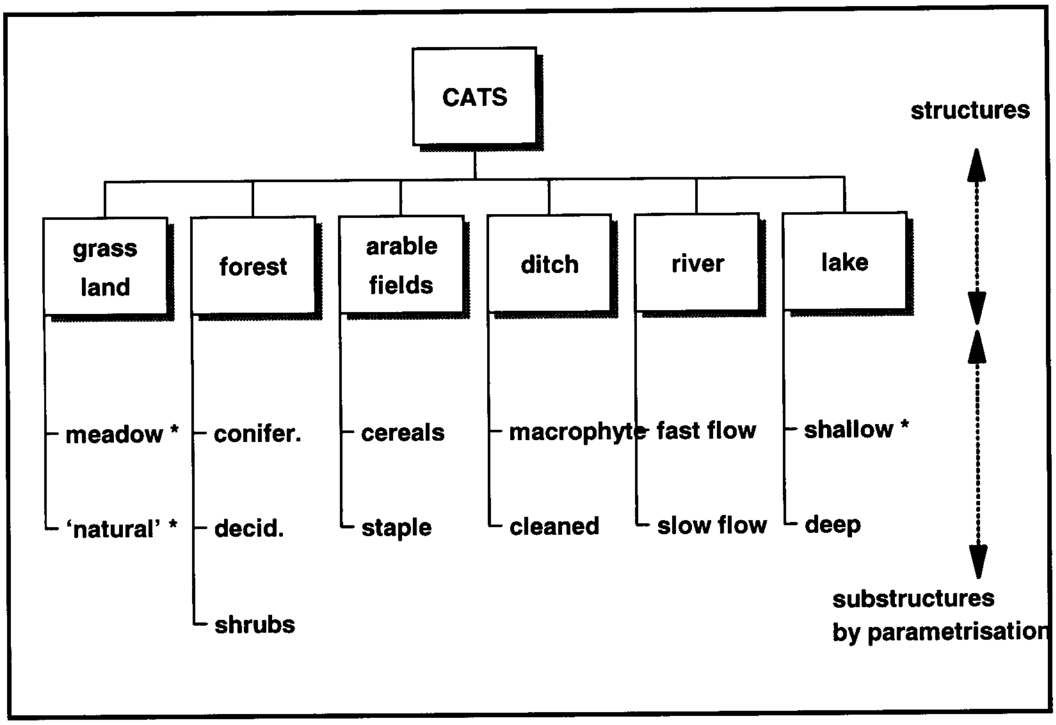

Figure 2: model structures and parametrization. Case studies are indicated with an asterisk.

2.2 Definition of model and input

In order to make regional risk predictions for toxicants in ecosystems, different steps must be taken to define the ecosystem, the food web model and model input. To facilitate comparison of the method between different studies, model input categories are defined (Figure 3).

The choice for the type of ecosystem is the first and most essential; it also defines the species composition, the food web structure, abiotic conditions etc. In an ideal case, the different categories parameters are deduced from the ecosystem type (except physico-chemical properties of the toxicant). In practice, many ecological parameters are known for specific locations and or species or must be estimated. Scaling relationships based on body size can provide estimates for physiological parameters (24). For each case study, collection of model input is evaluated for the different categories. It may be difficult to evaluate the importance of certain model parameters for regional risk prediction. Where possible, an uncertainty analysis will show which parameters are most important for regional predictions.

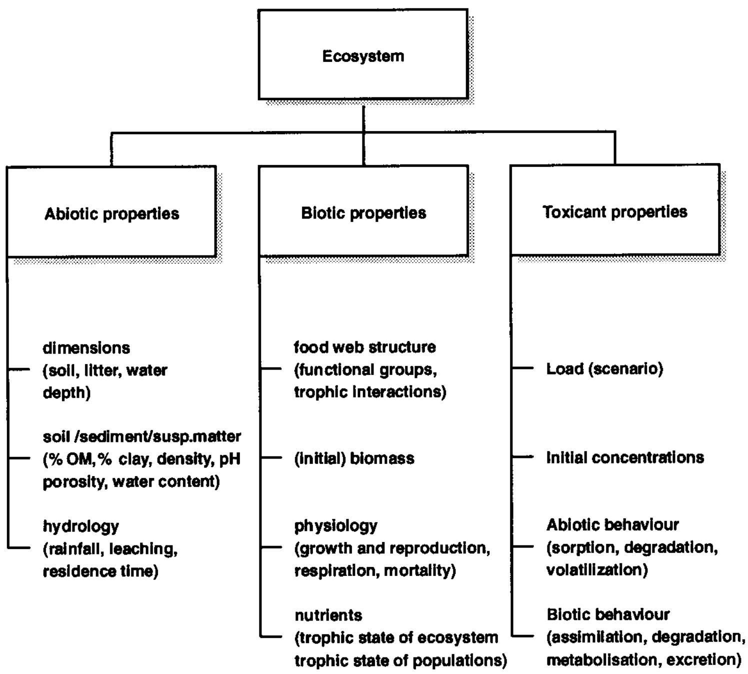

Figure 3: categories of parameters for regional risk assessment of toxicants

2.3 Model implementation

Models are implemented in the simulation language ACSL (40). All additional model code is written in portable FORTRAN 77 (63) and calculations were performed on a HP 9000-735 system. Uncertainty analysis was performed with UNCSAM (64). Special file handling was required for regional risk analysis. This procedure is explained in Appendix A. Specification of model uncertainty for toxicant properties is documented in Appendix B.

3. MODELLING AND RISK ASSESSMENT OF TBT ACCUMULATION IN THE FOOD WEB OF LAKE WESTEINDER[3].

3.1 Introduction

Organotin compounds have attracted much attention because of their detrimental effects on marine organisms, especially bivalves (1) and gastropods (2). Tributyltin compounds are present in anti fouling paints as active ingredients. Recently, a number of studies showed that organotins (OT) in freshwater could be a matter of concern. High concentrations of TBT have been found in water, sediment and zebra mussels (3,4), indicating a substantial use of TBT-containing anti-fouling paints in freshwater marinas. A survey of TBT in zebra mussels in the Netherlands showed high concentrations of TBT near locations with high yachting activity (5). This prompted an investigation of OT compounds in the food web of the freshwater lake 'Westeinder', a lake with many marinas (6).

In this study, a model for *Contaminants in Aquatic and Terrestrial ecoSystems* (CATS) is used (11-13). A comprehensive field sampling programme was designed attuned to the needs of the model. Time constraints allowed only a single sampling campaign, therefore no information is available about temporal phenomena. In addition, the contaminant load is not known and needs to be estimated. Information is available on the variability of inter- and intraspecific concentrations arising from the natural variability of the bioaccumulation process, environmental heterogeneity, etc. Consequently, substantial data uncertainty and therefore model uncertainty exists which should be analysed in order to indicate the reliability of model predictions.

The major aim of the present study is to gain insight into TBT accumulation and associated risks in freshwater food webs. This was accomplished by:

(1) a study of the mechanisms for accumulation of TBT in sediments and biota and for food chain transfer;

(2) a comparison of model predictions with the concentrations in the survey and calibration of the model;

(3) the development of a reduction scenario for TBT emission taking into account the Dutch ban since 1990 on TBT in anti-fouling paints for vessels smaller than 25 m.;

(4) a risk assessment of TBT in lake Westeinder and in a typical marina.

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[3] Modified from Traas, Stäb, Kramer, Cofino and Aldenberg, in: Stäb 1995 (65); submitted to Env. Sci. Technol.

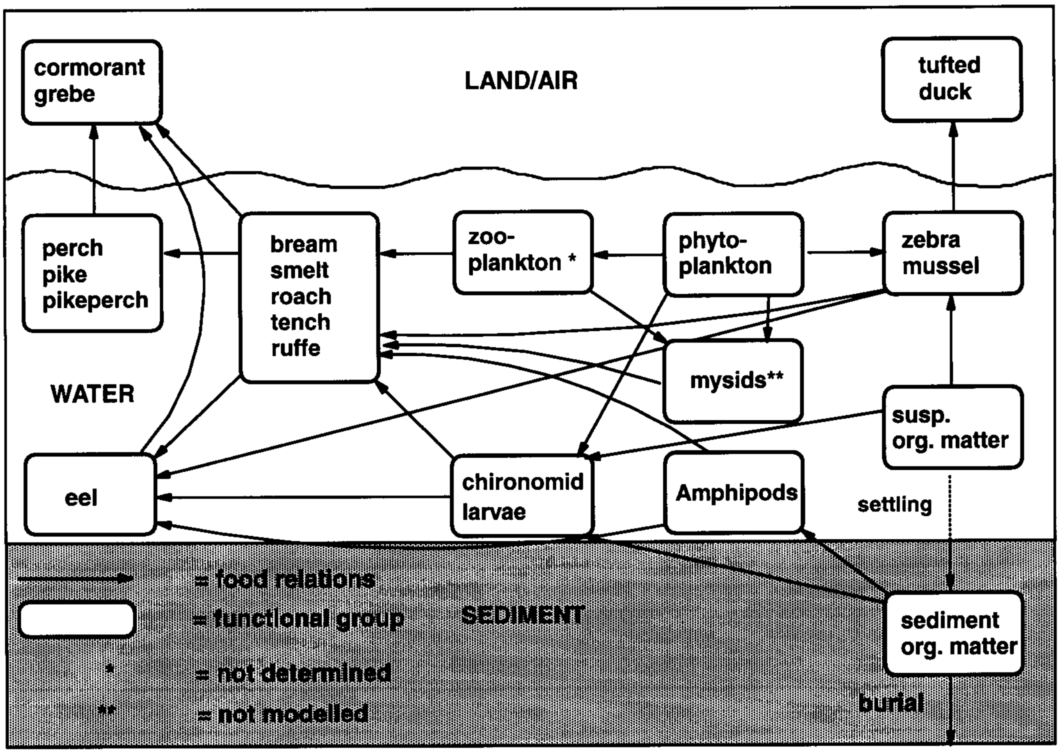

Figure 4: Food web of lake Westeinder

3.2 Materials and methods

3.2.1 Model structure

CATS-TBT (version 1.9) is a model to predict bioaccumulation in lakes without macrophytes. CATS-TBT is an application of CATS-2 (12). Principles of CATS models have been described previously (11-13).

Abiotic properties

Hydrological properties are incorporated in the model by inflow of water, including suspended matter and associated toxicant, and outflow of suspended matter, dissolved and sorbed toxicant. Physical dimensions, water residence time and suspended matter content were provided by the regional water authorities 'Rijnland'. Sedimentation of suspended matter was modelled as a net yearly flux. The deposited suspended matter is assumed to be instantaneously mixed with the upper sediment layer. The highest TBT concentrations in lake sediment are found in the upper 5-10 cm (4). Since biological activity of benthic invertebrates also takes place in this layer, a sediment depth of 10 cm was used in the model. Burial of the mixed sediment layer is a function of the net deposit flux of suspended matter and the density of the sediment.

Biotic properties

The field sampling strategy (6) was aimed at a comprehensive sampling of organisms from the food web. Regrettably, reliable measurements for algae and zooplankton were not obtained so bioaccumulation of these organisms could not be determined in lake Westeinder. Modelling of bioaccumulation of algae and zooplankton is however necessary for food chain transfer, so these groups were included in the model. Species were combined into the following functional groups with similar food preferences and with similar roles in nutrient cycling (12) (Figure 4):

(1) phytoplankton as the first biotic carrier for TBT;
(2) zooplankton, grazing on algae;
(3) benthic invertebrate detrivores, feeding on organic matter deposited on the sediment. In general, oligochaete worms are present in large numbers. However, measurements were only available for amphipods (*Gammarus spec.*);
(4) benthic invertebrate omnivores feeding on organic matter, suspended organic matter and phytoplankton. Within the chironomid family, species display different feeding strategies with varying degrees of omnivory (29). They were combined into one group because sampled chironomids were not determined at the species level;
(5) bivalves, feeding on phytoplankton and suspended organic matter. Only zebra mussels (*Dreissena polymorpha*) were sampled;
(6) benthivorous fish, mainly eel (*Anguilla anguilla*) feeding on benthic invertebrates such as amphipods and chironomids;
(7) omnivorous fish, feeding on benthic invertebrates, zooplankton and bivalves. This group consists of roach (*Rutilus rutilus*), bream (*Abramis brama*), silver bream (*Blicca bjoerkna*), smelt (*Osmerus eperlanus*), tench (*Tinca tinca*) and ruffe (*Acerina cernua*);
(8) predatory fish, such as pike (*Esox lucius*), pike perch (*Stizostedion lucioperca*) and perch (*Perca fluviatilis*);
(9) ducks feeding on bivalves such as tufted duck(*Aythya fuligula*);
(10) fish-eating birds consisting of cormorants (*Phalocrocorax carbo*) and great-crested grebes (*Podiceps cristatus*).

Toxicant properties

No information is available on the temporal trends in TBT concentrations in lake Westeinder. In order to calculate concentrations in water, sediment and the food web, TBT emission was estimated for the entire lake and for an average-sized marina, based on the anti-fouling module of the Uniform System for the Evaluation of Substances (USES) (30). In the present study, the emission of TBT for the entire lake has been estimated from the total number of pleasure craft, the fraction of ships treated with anti-fouling and emission fluxes per vessel (Appendix D).

To simulate a realistic period of TBT emission to the lake, it was assumed that widespread use of TBT started after 1975. Most states of the European Union have recently banned organotin compounds for vessels smaller than 25 m. The restriction on TBT use in the Netherlands is taken into account by using a logistic reduction scenario, for both the lake and the marina to arrive at half the estimated TBT load in 1992.

Toxicant states and output variables of TBT are expressed in units of g Sn in accordance with measurements (6). TBT sorption to organic carbon is based on equilibrium partitioning (18) and the sorption coefficient (K_{oc}) is estimated from the octanol-water partition coefficient, P (or K_{ow}) (19). The estimated K_{oc} is used for both suspended organic carbon and organic carbon in sediment. The sorption constant of TBT to dissolved organic matter (DOM) is related to K_{oc} (20). Degradation of TBT in the water phase, consisting of biodegradation, hydrolysis and photolysis was described as a first-order process. Hydrolysis and photolysis were considered negligible compared to biodegradation (21). Volatilization was described according to the two-layer volatilization model (22).

3.2.2 Quantification of parameter uncertainty

Uncertainty in prediction of TBT accumulation arises from many sources, many of which are the result of imperfect knowledge of TBT emission, fate and bioaccumulation throughout the food web. The foodweb is built from functional groups consisting of several species which implies that rates for growth, respiration, metabolic biotransformation, etc. are inherently variable and should be treated as such. Much information about these processes has been obtained from a recent study about TBT uptake by fish (10) and a recent compilation of TBT literature (31). Monte Carlo simulation (32,33) was used for analyzing uncertainty in calculated TBT concentrations by Latin Hypercube sampling of model parameter distributions and regression analysis of model uncertainty (15). The Standardized Regression Coefficient (SRC) was used as a relative measure for uncertainty (15,35). The SRC is especially suited when model components are uncorrelated (15). After calibration, parameters are no longer uncorrelated. Correlations between parameters were within reasonable bounds as judged by the Variance Inflation Factor (VIF, (35,36)), so the SRC could still be used. A preliminary sensitivity analysis (e.g. (34)) was performed to reduce the number of uncertain parameters by eliminating those parameters to which calculated concentrations were relatively insensitive.

Table 1: Ranges of acceptable model output as used for calibration of lake Westeinder

Variable	Low bound	High bound	Reference
Biomass variables			
% org. matter in sediment ((g dw/g dw) * 100)	0.1	14	[6]
phytoplankton (g dw/m2)	1.0	20	[48]
zooplankton (g dw/m2)	0.1	2.0	[29]
dreissena (g dw/m2)	0.1	6.0	[49]
chironomids (g dw/m2)	0.005	10	[50]
amphipods (g dw/m2)	0.5	20	[51,52]
cyprinids (g dw/m2)	1.0	12.5	[51]
eel (g dw/m2)	0.05	2.5	[51]
perch (g dw/m2)	0.05	2.5	[51]
ducks (g dw/m2)	0.001	0.25	[51]
cormorant (g dw/m2)	0.0005	0.125	[51]
susp. matter (g dw/m3)	1.0	20	[6]
TBT variables (expressed on Sn basis)			
TBT dissolved in water phase (ng/l)	0.0	50	[6]
TBT in suspended matter (ng/g dw)	1.0	660	[6]
TBT in total sediment (ng/g dw)	0.1	520	[6]
Bioconcentration Factor phytoplankton (kg dw/l)	175	100 000	[53]
TBT in dreissena (ng/g dw)	1.5	2520	[6]
TBT in chironomids (ng/g dw)	0.01	300	[6]
TBT in amphipods (ng/g dw)	0.01	400	[6]
TBT in cyprinids (ng/g dw)	0.01	2000	[6]
TBT in eel (ng/g dw)	0.01	500	[6]
(TABLE 3, Cont)			
TBT in perch (ng/g dw)	0.01	440	[6]
TBT in ducks (ng/g dw)	0.01	60	[6]
TBT in cormorant (ng/g dw)	0.01	60	[6]
apparent K_d (log kg dry sediment / l water)	1.0	4.9	[10]

3.2.3 Calibration

Calibration of CATS models is based on random generation of parameter combinations. Calculated biomass in the food web had to conform to realistic values as determined in similar freshwater lakes in the Netherlands since regrettably no reliable biomass estimates could be obtained for lake Westeinder. Simulated apparent values for the sediment-water partition coefficient ($K_{d,app}$), suspended matter concentration and sediment organic matter content had to conform to field ranges. Model output in the year 1993 from every model simulation was compared with field and literature data ranges (Table 1) to assess the validity of parameter combinations (32). Table 2 provides an overview of the accepted parameter ranges and associated uncertainty after calibration. Rejected parameter combinations are those that lead to calculated quantities outside one or more of the specified ranges. This acceptation/rejection step is adapted from the 'uncertain but bounded' concept of Hornberger & Spear (37). Initial parameter ranges were adjusted until an acceptable number of model simulations remained (more than 5 times the number of uncertain parameters as a rule of thumb (34), in this case 668 out of 2000). With the set of accepted parameter combinations, a separate simulation was performed for an average sized marina using a TBT load as estimated in Appendix D. No restrictions were imposed on the concentrations in the food web of the marina because no organisms were sampled in marinas.

3.2.4 Risk assessment

Model output distributions were used to calculate the risk of exceeding certain No Observed Effect Concentrations (NOEC) (38), lethal body concentrations (LBC) (10) or environmental quality standards (39). Risks are expressed as the right tail probability of model output exceeding a certain NOEC, LBC or quality standard. Risk calculations were performed for both the lake and the marina scenario. Risks calculated for the marina could be seen as the risks for organisms that could be present in the marina if pollution were absent.

Table 2: Specification of uncertainty in (eco)toxicological parameters after calibration. Parameter uncertainty is specified by the 50th percentile (median), mean, minimum and maximum values. Parameter uncertainty for the biomass cycle was described for the CATS-2 model (11).

Parameter	50 perc.	Mean	Minimum	Maximum	References for initial specification
Environmental chemistry					
log K_{ow} [a]	4.43	4.42	3.86	4.6	[9]
log K_{oc} [b]	4.18	4.15	3.69	4.36	calc. from log P acc. to [18]
fast sorption rate k_{SORP} (d^{-1})	0.76	0.75	0.5	1	[12]
degr. in water[3] k_{DW} (d^{-1})	0.028	0.027	0.013	0.038	[54]
degr. in pore water[3] k_{DS} (d^{-1})	0.0034	0.0034	0.0014	0.0055	[6]
Load L (mg Sn/m^2 d)	7.6	7.78	3.28	15.03	Appendix A (Westeinder)
Assimilation efficiency from food *f*XAss (%)					
zooplankton	12.5	12.5	5	20	[42,55]
dreissena	45	45	30	60	[42,55], calibration
chironomids	6.5	6.5	5	8	calibration
amphipods	7.6	7.6	5	10	calibration
cyprinids	70	70	50	90	[44,55]
eel	70	70	50	90	[44,55]
perch	69	70	50	90	[44,55]
duck	12	13	5	20	calibration
cormorant	18	19	5	30	calibration
Assimilation efficiency over gills *f*XUp (%)					
zooplankton	5.0%	5.0%	1.0%	10.0%	passive calibration
dreissena	5.0%	5.0%	1.0%	10.0%	calibration
Uptake rate from water *k*XUp (d^{-1})					
phytoplankton	5.50E-04	5.55E-04	1.42E-04	6.84E-04	calibrate on [53]
chironomids	6.78E-06	6.95E-06	3.50E-07	1.37E-05	calibration
amphipods	1.39E-05	1.39E-05	2.85E-07	2.74E-05	calibration
cyprinids	8.21E-06	8.20E-06	2.85E-07	1.64E-05	[56]
eel	1.10E-06	1.10E-06	1.09E-06	2.18E-06	estimate from [56]
perch	1.37E-05	1.35E-05	2.85E-07	2.74E-05	estimate from [56]
Half-saturation constants *h*XUp (mg/l)					
phytoplankton	3.00	3.00	1.0	5.00	calibrate on [53]
chironomids	2.50	2.50	1.0	4.00	calibration
amphipods	0.551	0.55	0.1	1.0	calibration
cyprinids	0.40	0.51	0.01	1.0	calibration
eel	0.105	0.105	0.10	0.11	calibration
perch	0.54	0.54	0.1	1.0	calibration
Biotransformation rates[c] *k*XMeta (d^{-1})					
zooplankton	0.068	0.068	0.027	0.11	passive calibration
chironomids	0.48	0.48	0.41	0.55	calibration
amphipods	0.48	0.48	0.41	0.55	calibration
dreissena	0.015	0.016	0.0027	0.027	[9]
cyprinids	0.023	0.023	0.014	0.033	estimated from [10]
eel	0.029	0.030	0.014	0.046	estimated from [10]
perch	0.021	0.021	0.014	0.027	estimated from [10]
duck	0.45	0.45	0.36	0.55	calibration
cormorant	0.26	0.26	0.19	0.33	calibration

[a] K_{ow} has been drawn uniformly. Basic statistics are log transformed

[b] K_{ow} is used to predict K_{oc} which determines sorption to suspended matter and sediment

[c] DT_{50} (or $t_{1/2}$) values can be calculated from these rates: DT_{50} = ln 2 / rate constant

3.2.5 Model implementation.

The model is implemented in ACSL (40). The full model consists of 12 state variables for the biomass cycle (including detritus), 15 state variables for the toxicant cycle, 4 state variables to check mass balance and 143 model parameters. TBT accumulation in the food web and the environment was calculated from 1975 to the year 2025. Results are presented starting from 1977 to allow the biomass cycle to reach steady state. Evolution of uncertainty in TBT accumulation is demonstrated by plotting the 5th percentile, median and 95th percentile of the lake Westeinder simulations together with data.

3.3 Results and discussion

3.3.1 Calibration and uncertainty analysis

Environmental chemistry. TBT concentrations in the water phase were below detection limits (20 ng Sn/l). Because of difficulties with calibration, TBT concentrations up to 50 ng Sn/l in 1993 were accepted (). Uncertainty in abiotic concentrations is mainly determined by the TBT emission rate (Load) and to a lesser extent by K_{ow} (Table 3). Since K_{oc} is estimated from K_{ow}, the uncertainty in K_{ow} greatly influences partitioning over water, suspended matter and sediment. High log K_{ow} values were selected with median log $K_{ow}$of 4.43 (Table 2), indicating that strong sorption is preferred. High values for log K_{ow} have been reported (10), but are generally not confirmed (10,31). Sorption of OT to clay minerals (41) could be the cause for sorption that is higher than expected from K_{ow} alone.

Another important source of uncertainty is the degradation rate of TBT in water (kXDegrDiss). Quite a wide range of rates was reported (21). A comparison of selected and rejected parameter ranges showed a preference for high biodegradation rates with a DT50 between18 and 50 days (Table 2). After load reduction, the parameter determining the residence time of the lake and the background TBT influx (cInFlow), starts to contribute to model uncertainty. High settling rates (cDSetSusOM) reduce the residence time of suspended organic matter, and thus show a negative influence on TBT concentrations in suspended matter.

Parameters from the biomass cycle contribute to uncertainty in water and sediment concentrations, such as the carrying capacity of phytoplankton (cDCarrPhyt). It influences the absolute phytoplankton biomass, and thereby the amount of sorbed TBT. The organic matter content of the sediment and thus total sorption capacity is influenced by partitioning of dead phytoplankton to detritus (fDAutoPhyt), which becomes progressively more important with time. On the other hand, parameters determining the abiotic facte of TBT contribute to uncertainty of food web accumulation. Uncertainty in bioaccumulation of chironomids and *Gammarus spec.* is influenced most by log K_{ow}, the degradation rate of TBT in water (kXDegrDiss), and TBT load. Simple monitoring of water, suspended matter and sediment in risk areas could reduce uncertainty about load and abiotic behaviour and increase the influence of (eco)toxicological parameters on model outcome.

Food assimilation efficiency. Food chain transfer of toxicants is caused by the assimilation of toxicants from food through several trophic levels. In general, high food assimilation efficiencies of 70-90% are found for lipophilic compounds (42), but TBT uptake may differ because of its organometallic nature. Little information is available so we assumed ranges of food assimilation efficiencies between 50-90% for vertebrates. In several cases, low assimilation efficiencies had to be chosen to ensure successful calibration.Sediment-dwelling organisms that are (partly) detritivorous, are exposed to high concentrations of TBT. Low assimilation efficiencies ranging from 5 to 10% for chironomids (fXAssChiro) and amphipods (fXAmph) had to be chosen to guarantee successful calibration. This parameter uncertainty still contributes significantly to uncertainty in TBT concentrations in invertebrates (Table 3). The same holds true for both ducks and fish-eating birds where calibration was only successful for food assimilation efficiencies ranging between 5 and 30% (Table 2) with high associated uncertainty. Recently, an assimilation efficiency of 9.5-12.7 % was determined for the red sea bream (43). Uncertainty in TBT concentrations in eel is influenced by the assimilation efficiency of mussels (fXUpDreiss,) indicating the importance of assimilation efficiencies in food chain transfer.

Rates and half-saturation constants for water uptake. TBT uptake from water was assumed to be important for all species. For zebra mussels and all fish groups, water uptake was substantial because TBT levels in the samples could not be calibrated on food chain transfer alone. For chironomids and tubificids, the importance of water uptake was even harder to assess, since exposure to TBT by way of sediment was extremely high. TBT uptake rates for phytoplankton and zooplankton could not be calibrated on measured concentrations. TBT in phytoplankton was calibrated on the range of allowed bioconcentration factors (Table 1).

TBT uptake of zooplankton and mussels from water was modelled by a filter-feeding mechanism and subsequent assimilation over the gills (12). gill assimilation efficiencies for metals in fish are estimated to be around 10%, and about 75% for highly lipophilic toxicants (44). Low assimilation efficiencies were assumed for zooplankton and mussels because of the organometallic nature of TBT and its relatively low K_{ow}. In the case of Dreissena, calibration showed a preference for low assimilation efficiencies (Table 2). An uncertain parameter for *Dreissena* is uptake efficiency over the gills (fXUpDreiss), which leads to additional prediction uncertainty.

It has been observed that bioaccumulation factors decrease as concentrations in the environment increase (25,26). All filtering and uptake processes were implemented as saturating processes, to prevent a linear increase of bioaccumulation at high environmental concentrations (12). In this case, the data probably did not warrant this detail (45). Uncertainty in the value of half-saturation constants is generally high and contributes significantly to prediction uncertainty for fish, zebra mussels and their predators.

Parameters controlling uptake of TBT are important for all fish (Table 3). When concentrations start to fall due to load reduction, the uptake rate from water (kXUpPerch, kXUpCypr) becomes less important while the uncertainty in the TBT load becomes more dominant (results not shown).

Table 3: Ranking of the five parameters contributing most to uncertainty in TBT concentrations, according to the value of the SRC (between brackets) in 1992.

	Parameters contributing most to uncertainty in TBT concentrations				
Compartment	First	Second	Third	Fourth	Fifth
Dissolved	Load(1.06)	kXDegrDiss(-0.43)	Kow(-0.33)	cOutFlow(-0.11)	cDCarrPhyt(-0.11)
Susp.Matter	Load(0.83)	Kow(0.51)	kXDegrDiss(0.34)	cInFlow(0.21)	cDSetSusIM(0.11)
Sediment	Load(0.60)	Kow(0.36)	cDCarrPhyt(0.30)	fDAutoPhyt(-0.26)	kXDegrDiss(-0.24)
Chironomids	Load(0.75)	Kow(0.53)	kDRespChiro(0.38)	kXDegrDiss(-0.30)	fXAssChiro(0.25)
Amphipods	Load(0.71)	Kow(0.48)	kDRespAmph(0.36)	fXAssTubi(0.33)	kXDegrDiss(-0.29)
Bivalves	fXUpDreiss(0.63)	Load(0.62)	kXMetaDreiss(-0.31)	kXDegrDiss(-0.26)	hDFiltDreiss(-0.18)
Eel	Load(0.60)	kXMetaEel(-0.59)	fXUpDreiss(0.27)	kXUpEel(0.27)	kXDegrDiss(0.25)
Cyprinids	hXUpCypr(-0.48)	Load(0.39)	kXUpCypr(0.35)	kXMetaCypr(-0.28)	kXDegrDiss(-0.19)
Perch	kXUpPerch(0.60)	hXUpPerch(-0.43)	Load(0.41)	kXMetaPerch(-0.19)	hXUpCypr(-0.15)
Duck	fXAssDuck(0.53)	fXUpDreiss(0.49)	Load(0.46)	kXMetaDreiss(-0.24)	kXDegrDiss(-0.20)
Corm	fXAssCorm(0.49)	Load(0.36)	hXUpCypr(-0.33)	kXUpCypr(0.23)	kXMetaCorm(-0.21)

Biotransformation rates. In the model, rate constants for biotransformation were not separated from elimination. Biotransformation rates were obtained for zebra mussels and fish (Table 2). Due to computing constraints, dibutyltin (DBT) and monobutyltin (MBT) concentrations could not be modelled simultaneously. We can however, compare the biotransformation rates after calibration of the model with observed DBT/TBT ratios (6). High DBT/TBT ratios point to substantial transformation which should correspond to high transformation rates in the model. Low DBT/TBT ratios were found for mussels and most fish (6). Low biotransformation rates of TBT in mussels and fish (Table 2) proved successful in calibration. The DBT/TBT ratio in pike liver (predatory fish) was higher than in other fish livers (6), but high biotransformation rates were not needed to calibrate TBT in predatory fish. Successful calibration for chironomids, amphipods and birds could only be achieved by assuming a combination of low assimilation efficiencies, and high biotransformation rates corresponding to median biological halflives ($t_{½}$) of 1.5 days for chironomids, 2.7 days for fish-eating birds and 1.5 days for ducks (Table 2). High biotransformation rates for birds are plausible, since very high DBT/TBT ratios were found in duck and grebe organs. The low DBT/TBT ratio found in the cormorant, however, does not indicate substantial biotransformation. Parameters controlling elimination of TBT are important sources of uncertainty for all fish and birds (Table 3).

3.3.2 TBT accumulation

Water, suspended matter and sediment. TBT concentration in water (Figure 5A) closely follows the logistic TBT emission scenario. The calculated concentrations are the result of TBT partitioning between water, suspended matter, the food web and the sediment. The median concentration in 1993 for the entire lake is 21 ng/l which conforms to the upper range of clean sites and the lower range of polluted freshwater sites in the Netherlands (3).

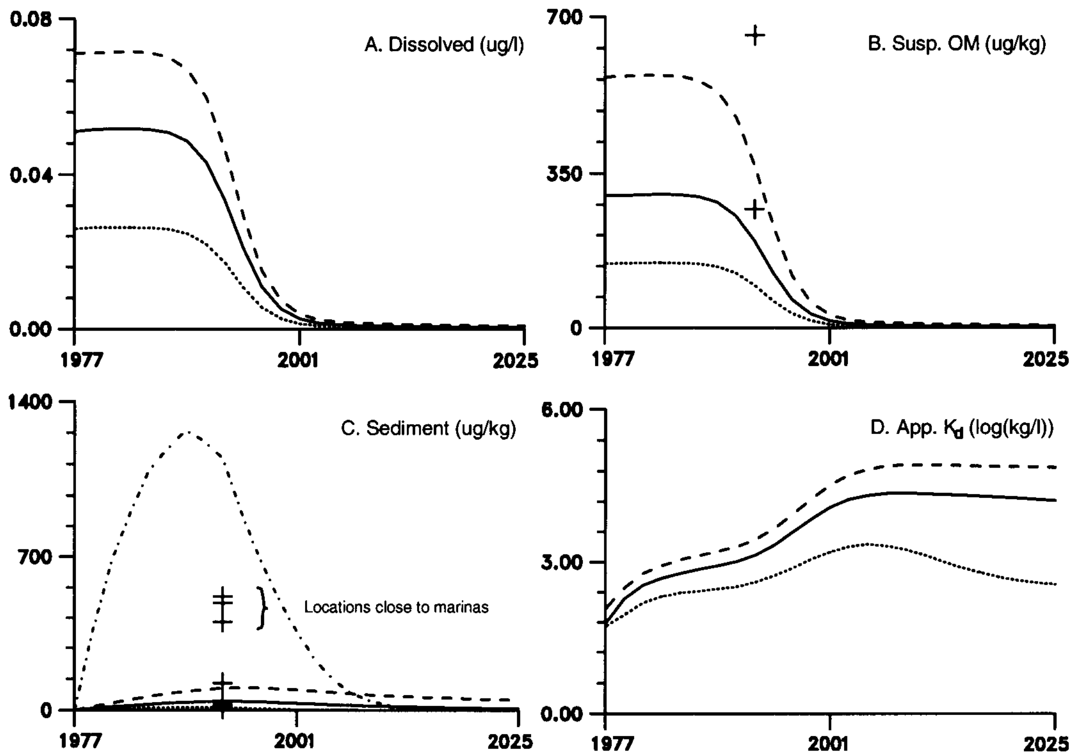

Figure 5: Calculated distributions (for the period 1977-2025) of TBT in abiotic compartments of lake Westeinder. Crosses are data, drawn lines median values, dotted lines 5th percentile and dashed line 95th percentile of the distribution. Fig C also shows the 5th percentile of the marina simulation (dash-dotted line)

TBT sorption to suspended matter was predicted to be in the range of 200 - 600 ng/g dw in 1993 (Figure 5B) which slightly underestimates the measured range, but only two measurements are available. The sediment was presumed to be clean at the start of the simulation. A slow but steady increase in the lake up to levels of 150 ng Sn/g dw is calculated (Figure 5C), corresponding quite well to values found in fresh water sediments elsewhere in the Netherlands (46). The lower range of sediment measurements in lake Westeinder is covered adequately by the model output distribution for the whole lake. The highest sediment concentrations measured are close to 5th (lower) percentile of the marina simulation. The highest sediment concentrations were measured closer to marinas (6), which is in accordance with a gradient from the marinas towards the lake. Most spatial heterogeneity of TBT concentrations could be included in the lake simulation but apparently not in close proximity of marinas.

Apparent K_d values for water-sediment partitioning are used as a check on sediment-water partitioning and had to conform to the range known from literature (Table 1), as part of model calibration. The range of $K_{d,app}$ values calculated from model results is shown (Figure 5D). It can be seen that between 1990 and 2010, K_d values will rise and, then, fall much more slowly afterwards. This is probably due to the faster clean-up of the water in relation to the sediment, illustrating the dependence of $K_{d,app}$ on loading conditions. The use of single $K_{d,app}$ values for model calibration of sediment-water partitioning should therefore be disencouraged.

Invertebrates. Chironomids and *Gammarus spec.* live in close contact with the sediment and therefore are expected to be exposed by uptake from sediment pore water, but also by ingestion of organic matter from water or sediment. Accumulation of TBT in chironomids and *Gammarus spec.* (Figure 6A,B) shows a steady increase with time, closely resembling the sediment accumulation pattern (Figure 5C). Most of the data range is covered adequately for both groups. TBT accumulation by mussels (Figure 6C) follows the temporal trend of the TBT concentration in water and suspended matter (Figure 6B,C). TBT accumulation in zebra mussels decreases as soon as the water quality improves in the scenario, because no direct sediment exposure was assumed. Recently, it was found that exposure of zebra mussels to sediment-bound TBT is probably low (9). An improvement in water quality in Swiss lakes was found after a ban on TBT for small ships. However, a decrease in TBT concentrations in zebra mussels in marinas was not found (47). High resuspension rates of sediment in marinas could be the cause for prolonged exposure of mussels as compared to less turbulent situations.

High TBT accumulation was observed on a location close to marinas (Figure 6C). These data are not covered by the model output distribution for the entire lake. Apparently, spatial heterogeneity of TBT concentrations from the marina to the lake is significant for TBT exposure of zebra mussels.

Fish. Calibration of TBT accumulation by fish covers most of the data but some high values lie outside the predicted range (Figure 6D-F). Some very high concentrations were measured in roach, tench and bream (6). It proved very difficult to calibrate TBT in whitefish (Figure 6E) such that the entire range of concentrations in this functional group was covered (high concentrations of roach not shown). The accumulation pattern in fish also follows the water concentrations. Some influence of the increasing sediment accumulation can be detected for whitefish and eel.

Birds. In spite of high TBT contamination in their food,(Figure 6C-F). TBT accumulation by birds is low (Figure 6G,H) . TBT accumulation of fish-eating birds shows a less strong reduction after the TBT ban than for ducks. This is probably due to the importance of sediment concentrations in the transfer of TBT to fish.

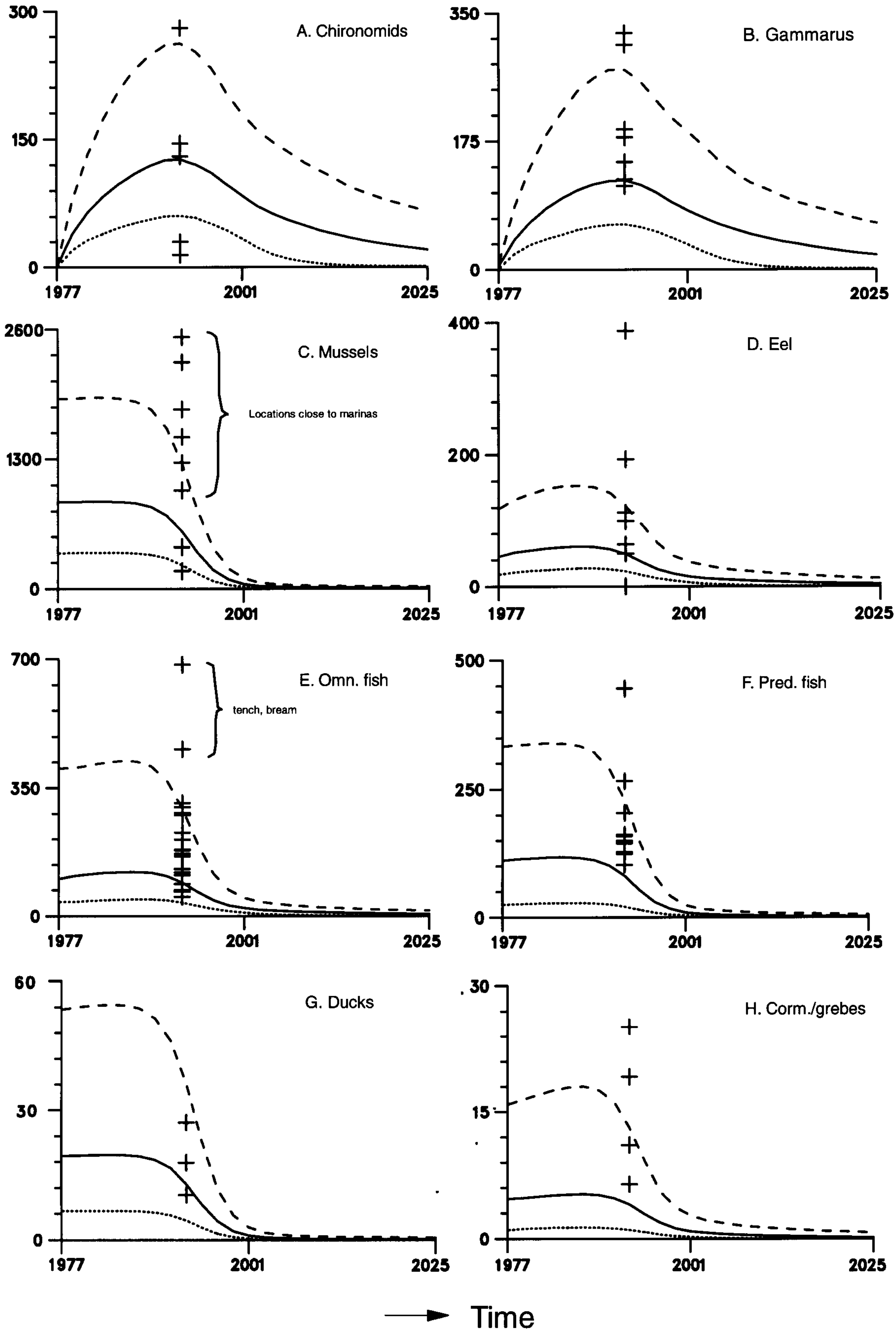

Figure 6: Calculated distributions (for the period 1977-2025) of TBT in functional groups in lake Westeinder. Crosses are data, drawn lines median values, dotted lines 5th percentile and dashed line 95th percentile of the distribution

Food/water uptake ratio. The ratio of uptake of TBT from food including suspended matter, and from water (FWU ratio) was calculated for several species, and is shown for mussels and predatory fish (Figure 7A,B). A ratio larger than 1 indicates dominance of toxicant uptake from food, a ratio smaller than 1 indicates dominance of toxicant uptake from water. The median FWU ratio for mussels is about 0.7, indicating that water uptake is the major pathway. Due to uncertainty in assimilation efficiencies from water and or food, the FWU ratio is not known precisely, but described by a distribution. The 5th-95th percentile of the FWU ratios varies from 0.2-5. The median FWU ratio for predatory fish is also below 1, but when loading is reduced, the food uptake starts to dominate bioaccumulation rising to median values of 2 before decreasing again. The median FWU ratio for whitefish and eel is never below 1 (results not shown), indicating that food is the dominant exposure route for TBT in lake Westeinder.

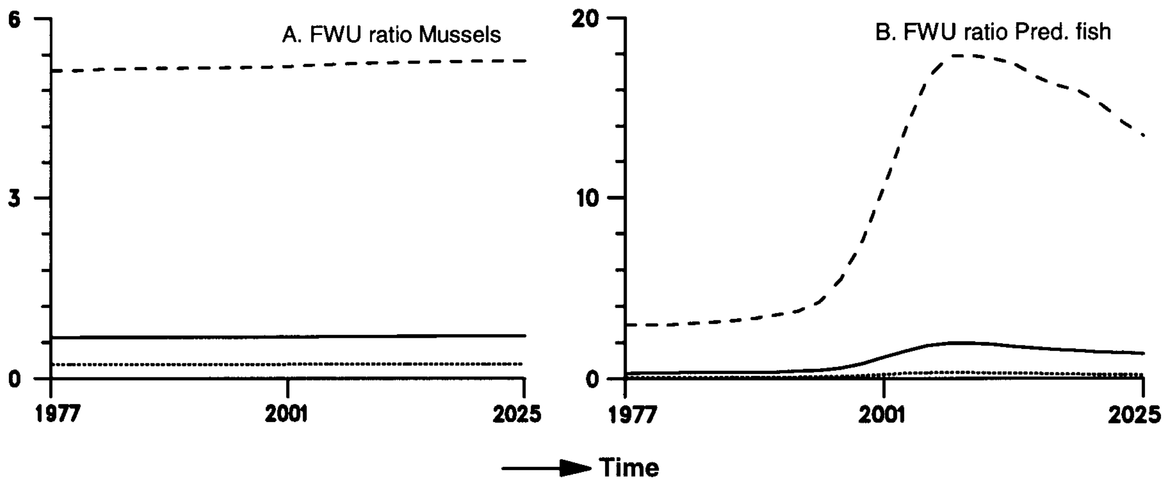

Figure 7: Calculated food-water uptake ratio (for the period 1977-2025) for mussels and predatory fish. Drawn lines are median values, dotted lines 5th percentile and dashed line 95th percentile of the distribution.

It seems that the more a species feeds on benthic invertebrates, the higher the FWU ratio. It has been shown that food uptake can be a significant portion of total TBT uptake for fish (43). This study shows that in situations with very low TBT concentrations in the water over contaminated sediment, food is a major exposure pathway for benthic or benthivorous organisms.

3.3.3 Risk assessment

Prediction uncertainty for the whole lake and the marina was used for risk assessment by calculating the right-tail exceedance of:

1) a lethal body concentration (LBC);
2) no observed effect concentrations (NOECs) derived from laboratory tests (38);
3) Dutch environmental quality standards (39).

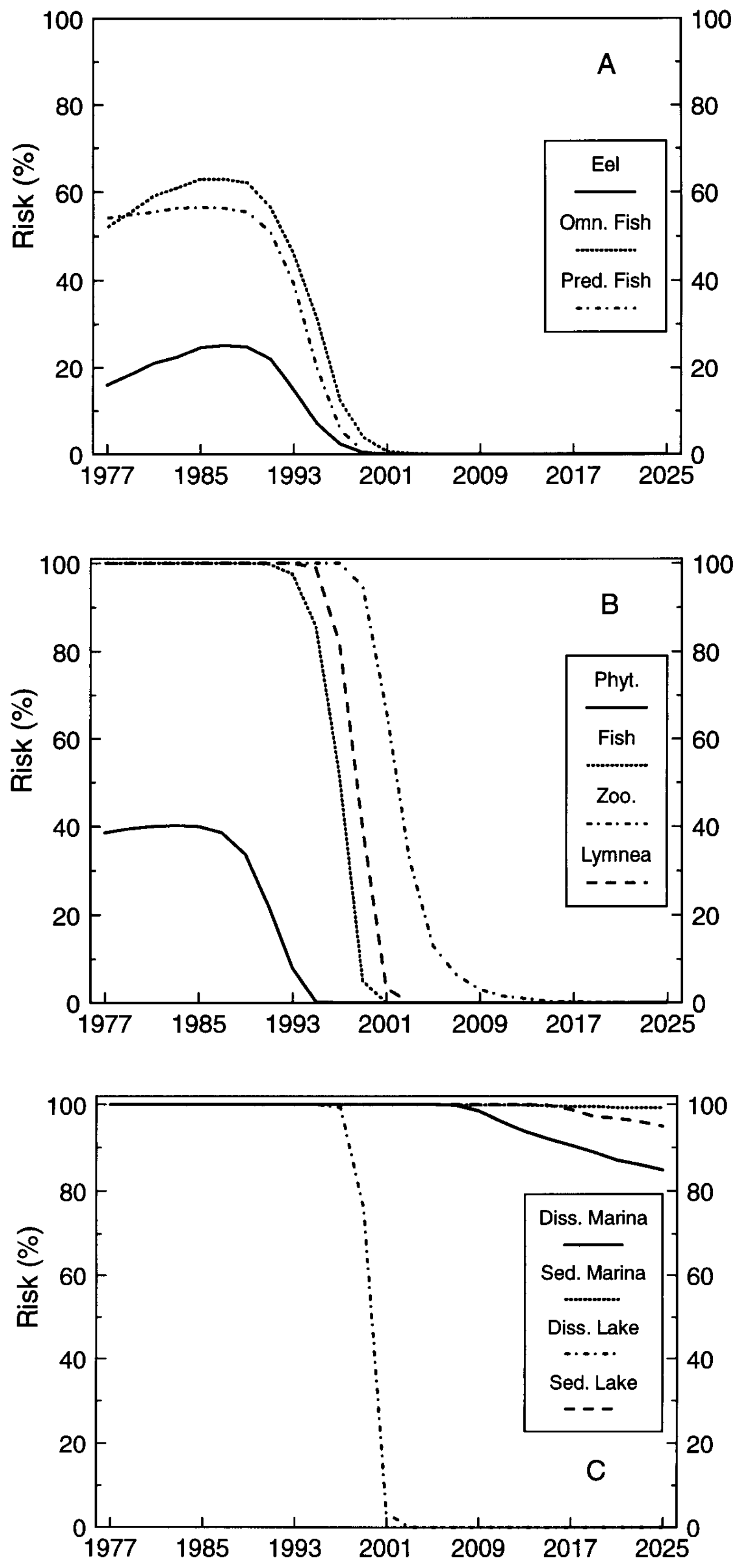

Figure 8: Calculated probabilities (expressed as % risk) of (a) exceeding a lethal body concentration for fish, (b) exceeding no-observed effect concentrations, or (c) quality standards for lake Westeinder and an average marina for the years 1977-2025.

Tas (10) determined a lethal body concentration for small fish and found values between 13 and 30 nmol TBT/g ww. Because of lack of data on larger fish, a LBC of 100 nmol TBT/g dw was used and recalculated to 11.8 mg Sn/g dw. Risks in marinas as judged by the LBC are predicted to be substantial for most fish especially whitefish and predatory fish (Figure *8*A). When the ban is as effective as we presume in our scenario, risks can be reduced to very low levels on a timescale of approximately 10 years. Concentrations in eel are lower than in other fish in the year of sampling. Therefore, levels below the LBC are reached sooner for eel than for omnivorous fish and predatory fish. Risk assessment for fish in the lake did not show any risk during the simulation period (results not shown) since output distributions of TBT concentrations in fish were all below the LBC.

NOECs for phytoplankton (*Chlorella pyrenoïdosa*), zooplankton (*Daphnia magna*), snails (*Lymnea stagnalis*) and fish (*Gasterosteus aculeatus*) were compared with calculated dissolved concentrations for both the lake and the marina scenario. In the case of the marina a significant risk at exceeding NOECs could be shown for fish, snails and zooplankton (Figure 8B). After the ban on TBT, risks are reduced on a time scale of 10 years but risks for zooplankton extend for a longer period.

Dutch quality standards based on ecotoxicity testing, i.e. maximum permissible concentrations (MPC,(39)) were compared with concentrations calculated in water and newly formed sediment. MPCs for dissolved TBT were exceeded in the whole lake (Figure 8C), indicating the necessity of the ban on TBT. After the ban, the quality standard for dissolved TBT is reached reasonably fast in the lake but not so in the marina. TBT accumulation in new sediment takes much longer to arrive at acceptable levels since risk levels do not fall below 80% for the lake simulation. Sediment quality standards are exceeded for both the lake and the marina and a time span of 50 years could be needed to arrive at levels conforming to quality standards in the Netherlands.

3.4 Conclusions

Successful modelcalibration on field data and general knowledge about the system (e.g. Table 1) improves the coherence of model predictions, taking into account nonlinearities of toxicant uptake, biological and spatial variability etc. The model was calibrated on a 'snapshot of ecological TBT distribution' in one particular year. Because of the lack of time series, the possibilities for calibration and reduction of model uncertainty is limited. The remaining uncertainty however, was used to calculate risk probabilities which is not possible when uncertainty is not taken into account.

The risk assessment of the marina indicates serious risks for fish and invertebrates. Risks of exposure to TBT by water and by food were calculated for fish, by checking the internal concentration against the Lethal Body Concentration (9). In the case of the other organisms, TBT toxicity was assessed with tests using only water exposure. Thus, risks of exposure by food are not incorporated in such tests. Uncertainty analysis showed that for many organisms, uptake of toxicant from the sediment or food contributes significantly to total TBT exposure.

Therefore, risks as judged by customary LC50 or NOEC tests could be seriously underestimated. Sediment toxicity testing (36) could lead to better toxicity estimates if the issue of bio-availability in the laboratory versus the field can be addressed.

Integration of existing ecotoxicological knowledge was best achieved for fish (9) and bivalves (8). However, substantial uncertainty about uptake of TBT remains as the relative importance of exposure routes (Fig. 6) demonstrates. Uncertainty analysis subsequently showed that half-saturation constants for TBT uptake contributed to additional model uncertainty. In this case, the data probably did not warrant such detail (37). Uptake efficiencies from food are important sources of uncertainty if the food is highly contaminated such as for chironomids and ducks, yet had to be estimated.

In this study integration of knowledge from environmental chemistry and ecotoxicology was attempted. Uncertainty analysis showed that loading and sorption (as determined by K_{OW}) and to a lesser extent degradation in water dominated model uncertainty. Uncertainty of ecotoxicological processes tended to be overshadowed by this. Simple monitoring of water, suspended matter and sediment in risk areas could reduce uncertainty about abiotic behaviour and increase the influence of (eco)toxicological parameters on model outcome. True biological variability could then be separated better from uncertainty of essentially abiotic behaviour of TBT.

4. RISK ASSESSMENT OF BIOACCUMULATION OF CD, CU AND PB IN MEADOWS ON DIFFERENT SOIL TYPES

4.1 Introduction

The first regional risk assessment was performed for meadows on moist, nutrient-rich soil. This type of grassland (66) is one of the most abundant ecotope types in the Netherlands because it encompasses almost all grassland for agricultural use. Bioaccumulation of heavy metals in grassland food webs is measured in several local and regional monitoring programs (57, 67). The model CATS-1 (11) was used for a prediction of bioaccumulation risks.

The goal of this analysis was to test the hypothesis that differences in soil type can cause major differences in risk predictions. This expectation is based on the knowledge that the speciation and bioavailability of heavy metals is determined primarily by properties of the soil. Three different soil types were chosen, based on an ecological soil classification (68,69). Since different heavy metals can differ significantly in abiotic and biotic behaviour, risks were calculated for cadmium, lead and copper.

4.2 Materials and methods

4.2.1 Model structure

General model structure, parameters and initial conditions were taken from the CATS-1 model, version 2_31, as described and calibrated previously (11,13). Specific changes and additions are described below.

Abiotic properties. Ecoseries (66) were used to parametrize the CATS-1 model for different soil types:

- 'PEAT': V08/V09/Z03 peaty soils with a clay layer, dominant in the ecodistrict 'laagveen'.
- 'CLAY': K01/K02 light clay and 'zavel', frequent occurrence in the ecodistrict 'rivierengebied'
- 'SAND': Z12 (humic sand, frequent in ecoregion 'Pleistoceen Nederland'

Sorption, leaching and uptake of toxicant by organisms are influenced by a number of soil properties such as soil density, soil porosity, soil water content, organic matter content, clay content, CEC and pH. The range of these soil parameters has been determined for the three soil types chosen, by combining the ecological soil classification with soil maps in a GIS system (70).

Biotic properties. Food web structure, range of biomass density in the field and physiology were determined previously and were kept the same for the different heavy metals. Since no feedback exists between bioaccumulation and effects, a steady state biomass is calculated for each consecutive run in the Monte Carlo analysis.

Toxicant properties. Total load of heavy metals was calculated for 1985 (71). No GIS analysis could be made of the map for the ecosystem map and for total load, therefore toxicant load could only be estimated by roughly comparing both maps. Since the presence of the three different soil types is scattered of the Netherlands, the range of total load was estimated for each soil type.

The load scenario used for all three metals was 'Business As Usual', i.e. no change in future load, which is probably a worst case scenario.

For each metal, a different relation between the sorption coeffficient K_d and soil properties was used; For Cd the regression equation by Chardon (72) and for Cu and Pb, the eqations as used by Vissenberg & van Grinsven (73).

4.2.2 Quantification of parameter uncertainty and calibration

The uncertainty in the biomass cycle of the ecosystem was defined before(11) and uncertainty in soil parameters was determined by Sinnige et al. (69). Uncertainty in inital soil concentration and total load was determined by RIVM from monitoring programmes (71). Calibration of CATS models is based on random generation of parameter combinations. Calculated biomass in the food web had to conform to realistic field values. For Cd, the model was calibrated on bioaccumulation in peat soils (11). For Cu and Pb, the model was calibrated on bioaccumulation in sandy soils (Appendix B). After calibration, the model was applied to different soil types by parametrization of soil properties (Appendix A,B).

4.2.3 Risk assessment

Model output distributions were used to calculate the risk of exceeding certain No Observed Effect Concentrations (NOEC) or environmental quality standards (Appendix C). Risks are expressed as the right tail probability of model output exceeding a certain NOEC, LBC or quality objective (11).

4.3 Results

4.3.1 Calibration

Environmental chemistry. Sorption coefficients of the metals (K_d) , as influenced by the naturally occuring variation of soil properties as % organic matter, clay content etc., varied between ranges (Appendix B). Total metal content was used to specify the range of initial metal concentrations. Since no concentration time series were available, calibration of soil sorption or leaching was not performed.

Toxicant assimilation efficiency. Assimilation efficiencies (*fXAss*) for heavy metals have been determined for vertebrates, mainly rodents, and some species from the soil fauna. Calibration of *fXAss* is only possible together with metal excretion rate (*kXExcr*), since both together determine retention of metals. These two parameters were calibrated on Bioconcentration Factors for specific soils. Assimilation efficiencies for Pb and Cd are lower than for Cu. Since Cu is an essential metal, animals may vary their Cu assimilation efficiency according to their needs. All efficiencies are sampled from uniform distributions of *fXAss*.

Excretion rates. Excretion rates for Pb and Cd are comparable with half times between 12 and 500 days for most small animals. For Cu, half times between 8 and 25 days were used for most animals, except for cattle, where uncertainty in excretion rates is large due to a lack of bioaccumulation data.

Uptake from pore water. Uptake of heavy metals from pore water by grasses and earthworms was calibrated by 'filling up' to concentrations or bioconcentration factors as reported in literature (cf ref. 11). Uptake rates for all metals are in the same order of magnitude, but differ between organisms.

4.3.2 Heavy metal accumulation

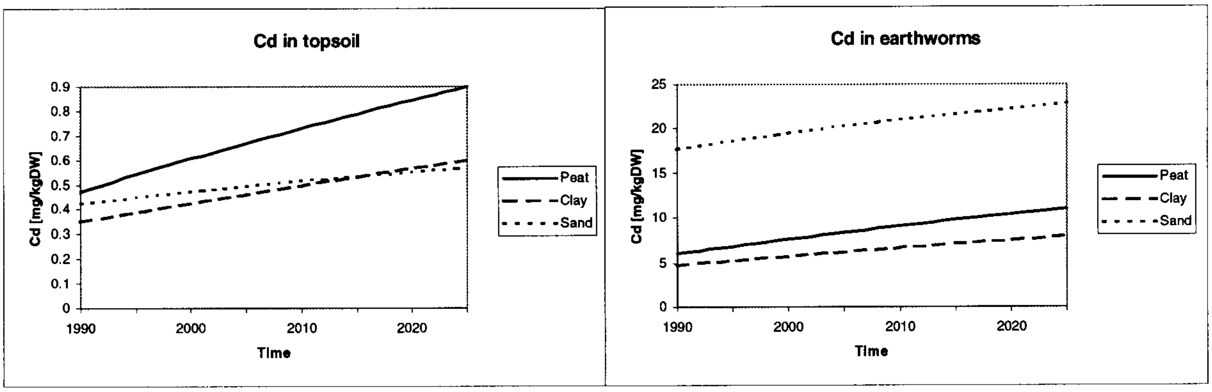

Figure 9: Cd accumulation in top soil and earthworms.

The average Cd accumulation, as judged from the median value of all parameters after calibration, is plotted to study general accumulation behaviour in different soils.

Cd accumulation continues for all soils considered (Figure 9a), least for sandy soils due to low sorption and high leaching, and most for peat soils with high sorption and low leaching. Cd accumulation in earthworms (Figure 9b) shows that the bioavailability of Cd in these soils differs a great deal. In meadows on sandy loam, accumulation is three times higher than on peat soils. Cu accumulation on peat and clay soils also continues for all soils considered (Figure 10a), but increases much faster for sand, due to a higher Cu input, mainly from manure (71). For Cu too, bioavailability for earthworms is higher for sand than for peat and clay soils (Figure 10b). Cu concentrations in sand already start to level off in 2025 with the 1985 scenario.

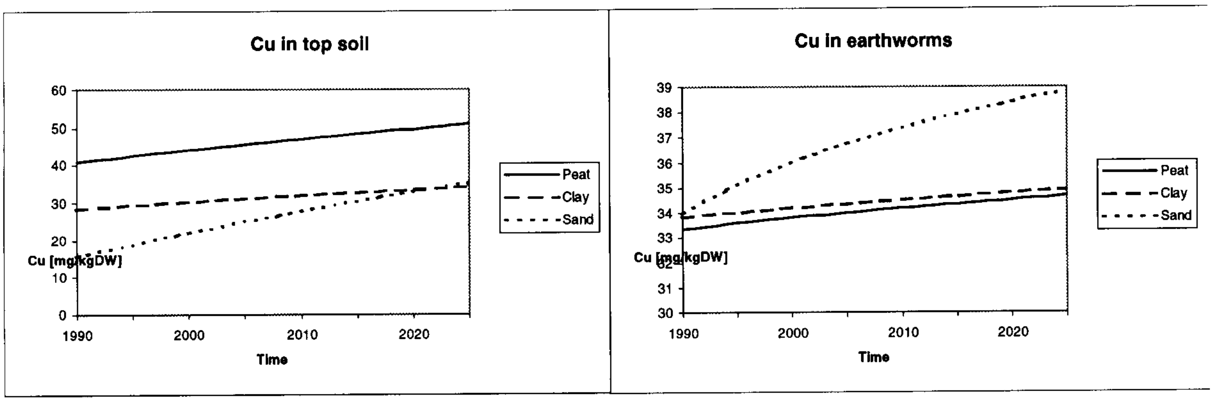

Figure 10: Cu accumulation in top soil and earthworms.

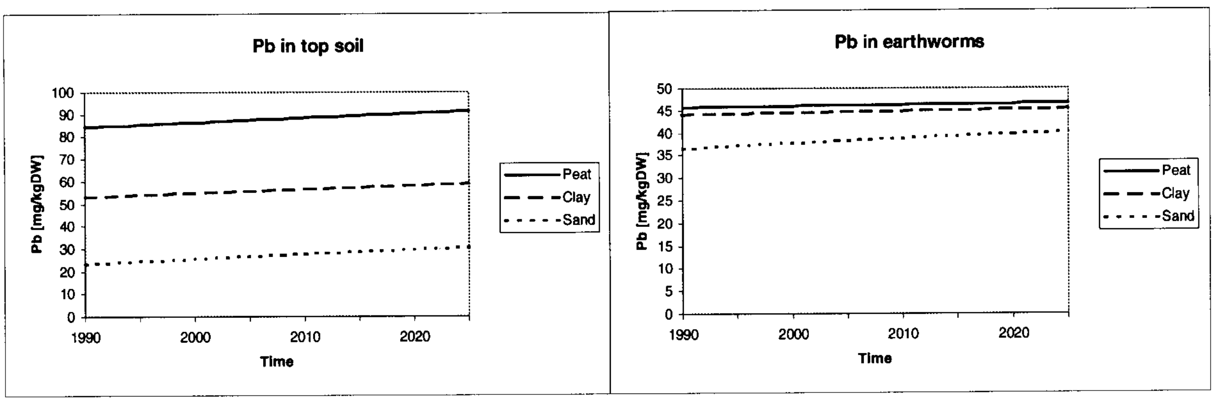

Figure 11: Pb accumulation in top soil and earthworms.

Pb accumulation is very slow at the 1985 emission scenario (Figure 11a), suggesting that a steady state for Pb accumulation is almost reached for all soils given the already high Pb concentrations in all soils. The same pattern is shown for Pb accumulation in earthworms, where Pb concentrations do not differ very much between different soil types (Figure 11b).

A Monte Carlo analysis was performed to asssess uncertainties in the calculated concentrations, depending on variation in soil properties, toxicant loading, biological variability and parameter uncertainty. Model calculations are presented as cumulative distributions to enable comparison for different soil types. The dissolved Cu concentration is calculated to be highest in sandy soils, followed by peat and clay (Figure 12a). The BCF of Cu in earthworms (Figure 12b) calculated for the different soil types does not show a dependence on the dissolved concentration, but on the bioavailability of Cu in relation to soil parameters.

The same phenomenon seems to take place with the BCF for Pb in earthworms (Figure 13b), even though the dissolved Pb concentrations (Figure 13a) are in reverse order of BCFs for differrent soil types.

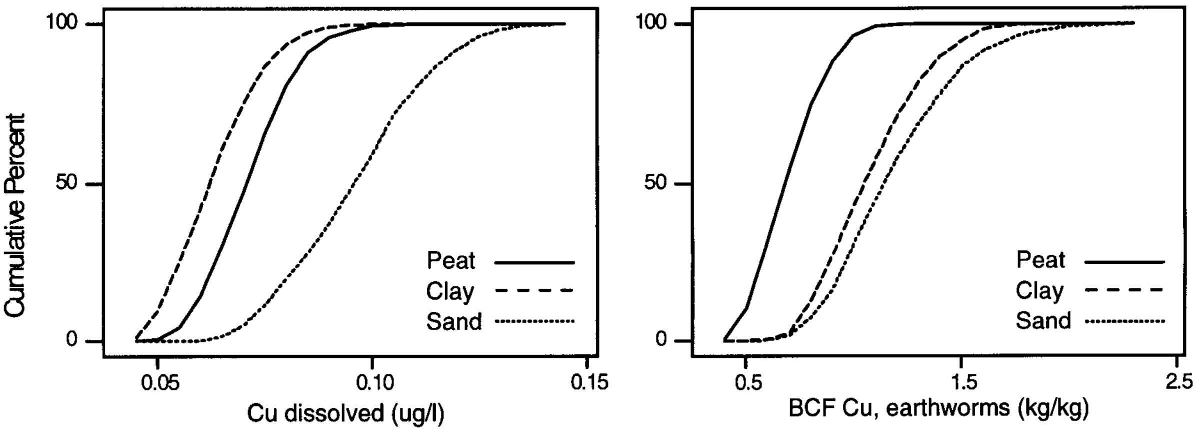

Figure 12: Cumulative distributions of dissolved Cu concentrations and BCF of earthworms in 2015 for different soil types.

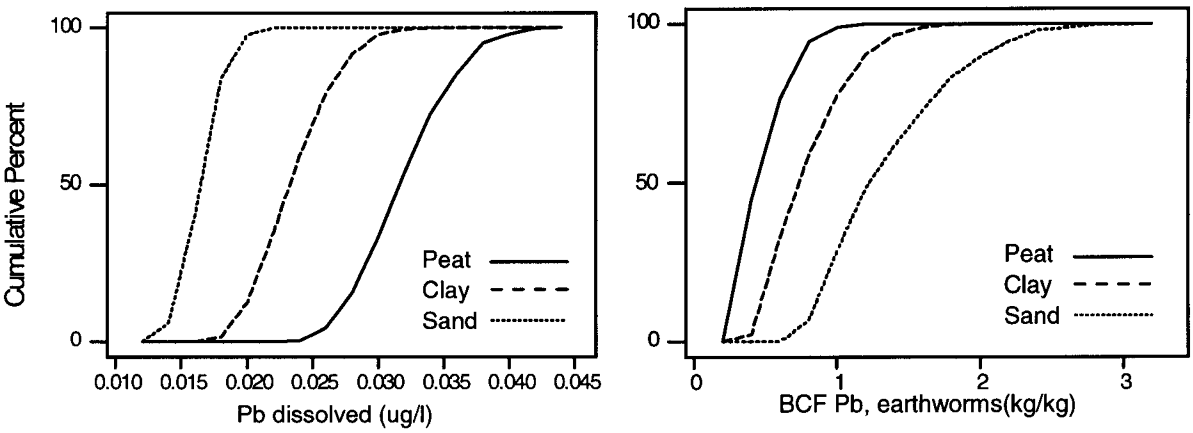

Figure 13: Cumulative distributions of dissolved Pb concentrations and BCF of earthworms in 2015 for different soil types

Cu accumulation in earthworms is not much different for all soil types as judged from Figure 2b, but uncertainty ranges between approx. 20 and 60 mg/kg dm (Figure 14a). Ma (1982) derived a relation between internal concentration of Cu and growth inhibition of *Lumbricus rubellus*. At 30 mg/kg DW, growth was inhibited by almost 40 %. Risk of growth inhibition of Cu in earthworms can be judged from the cumulative frequency distributions by determining the percentage of calculations above the risk limit of 30 mg/kg.

Chronic Pb exposure of small mammals can lead to Pb accumulation in kidney (Ma 1987) where levels of 25 mg/kg dm are associated with histopathological lesions. On comparison of calculated Pb concentrations in mole kidney with this critical tissue concentration, risks can be expected: a substantial part of the distributions lies above the critical concentration (Figure 14b).

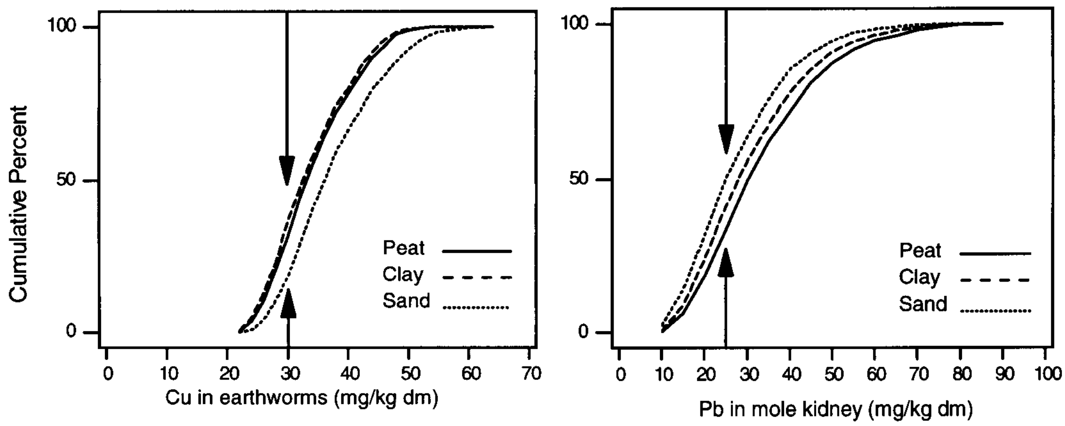

Figure 14: Cumulative distributions of metal concentrations in earthworms and moles in 2015. Critical concentrations indicated with arrows.

4.3.3 Risk assessment

The probability distributions of concentrations in the environment and the food web were used for risk assessment by calculating the right-tail probability of exceeding:

- environmental quality objectives
- no-observed effect concentrations (NOECs) or critical levels derived from laboratory tests
- Acceptable Daily Intake (ADI) derived from laboratory of field tests.

Calculated distributions of total heavy metal content of the three different soil types were used to calculate the risk that quality objectives used in the Netherlands are exceeded in the year 2000 and 2015 (Figure 15). Target Values for Cd (0.8 mg/kg dm for a standardized soil) are not exceeded for any soil type in 2000. In 2015 however, ongoing accumulation leads to a very small risk of 0.44% on sandy soil, and 5.4% on peat. The Maximum Permissible Concentration (MPC), based on extrapolation of laboratory toxicity tests (74), is calculated at 0.26 mg/kg dm (75) and is exceeded in 2000 and 2015 for all soil types except clay with 57% exceedance in 2000.

Target Values for Cu (36 mg/kg dm for a standardized soil) are exceeded most for peat and sandy soil, but increase fast between 2000 and 2015 on clay from 8.2 to 43.1% (Figure 16). For Target Values of Pb (85 mg/kg dm), the situation is more favourable since only on peat, a slight increase in risk from 12.3 to 22.7% is expected.

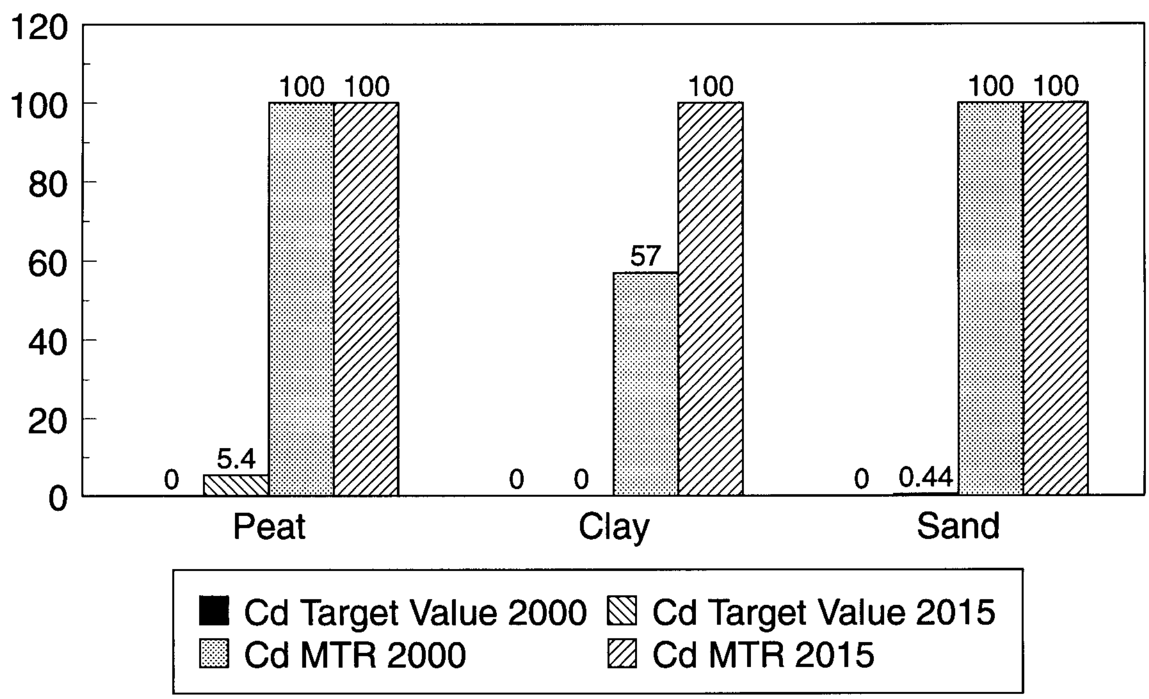

Figure 15: Risk at exceeding quality objectives for Cd in soil, for different soil types.

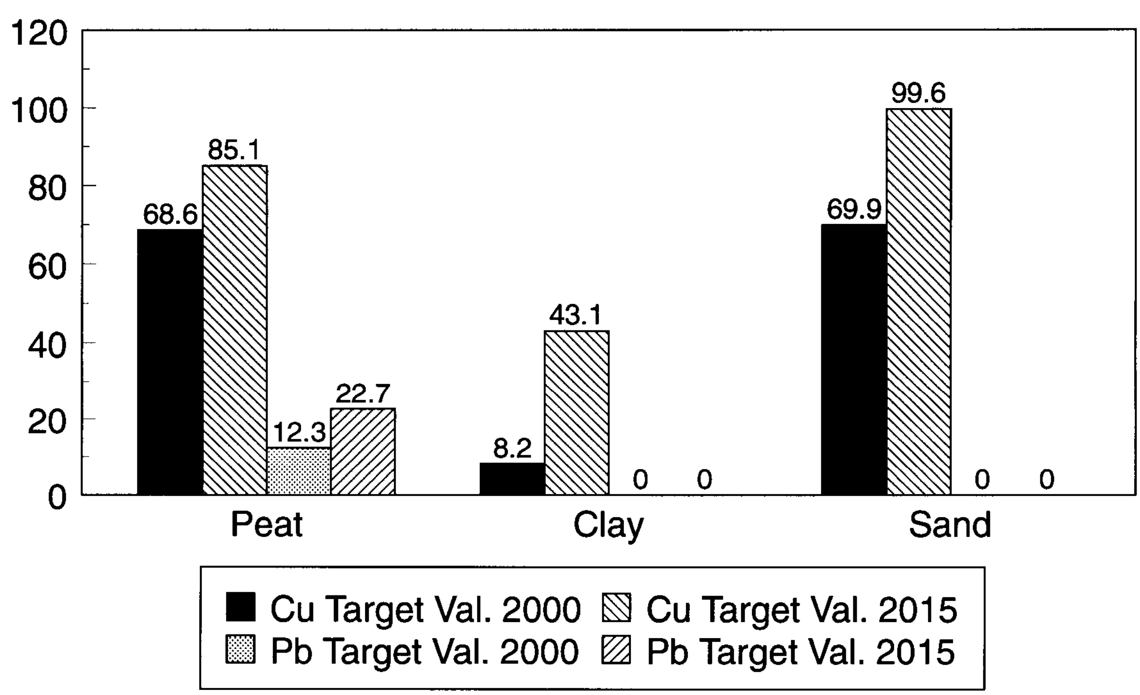

Figure 16: Risk at exceeding quality objectives for Cu and Pb in soil, for different soil types.

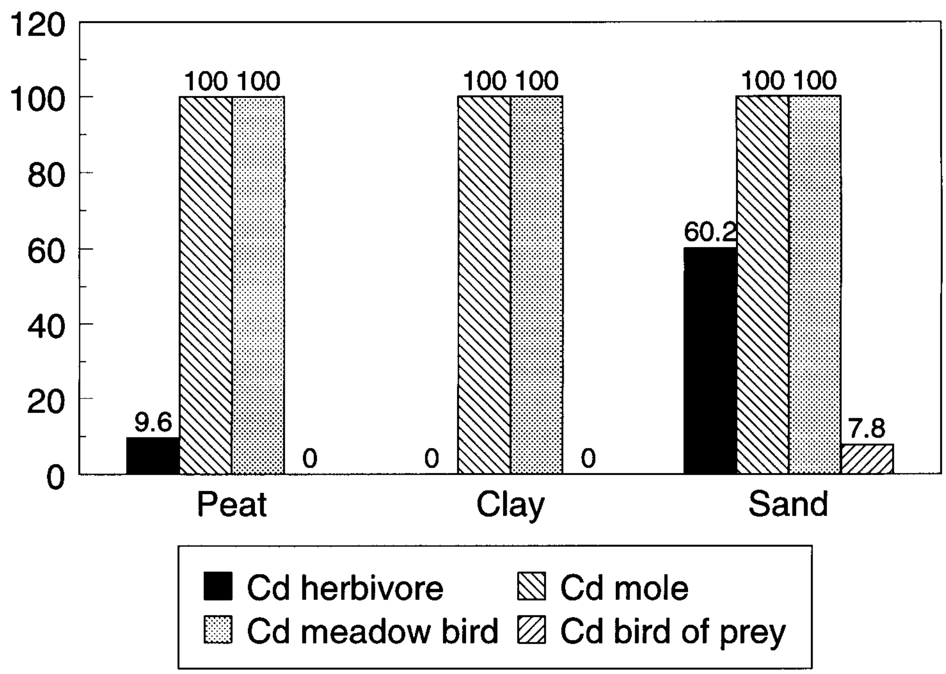

Figure 17: Risk at exceeding critical Cd concentrations in food of different functional groups in 2015.

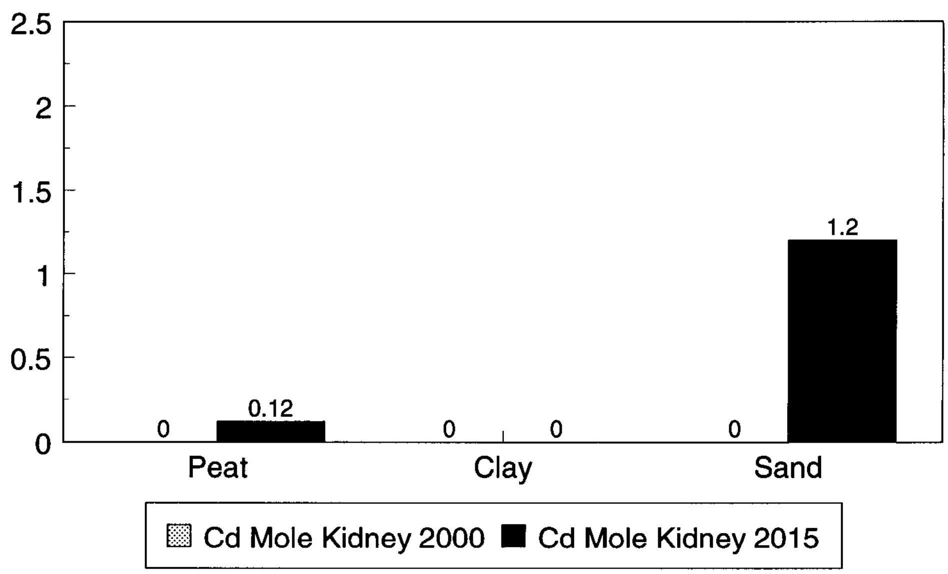

Figure 18: Risk at exceeding critical Cd concentrations in mole kidney.

Bioaccumulation of Cd in the food web of grassland is judged by comparing a MPC for food concentrations (0.35 mg/kg dm, 76) with calculated food concentrations in the year 2015 (Figure 17). Meadow birds and moles, with a high proportion of earthworms in their diet, seem to be at risk, but risks are absent or very low for herbivorous mice and their predators. The potential risks for all groups from Figure 17 are derived from extrapolation of toxicity tests with other animals. When bioaccumulation risk for the mole is assessed with an empirical bioaccumulation factor for kidney damage (Ma 1987), chronic kidney damage seems improbable (Figure 18).

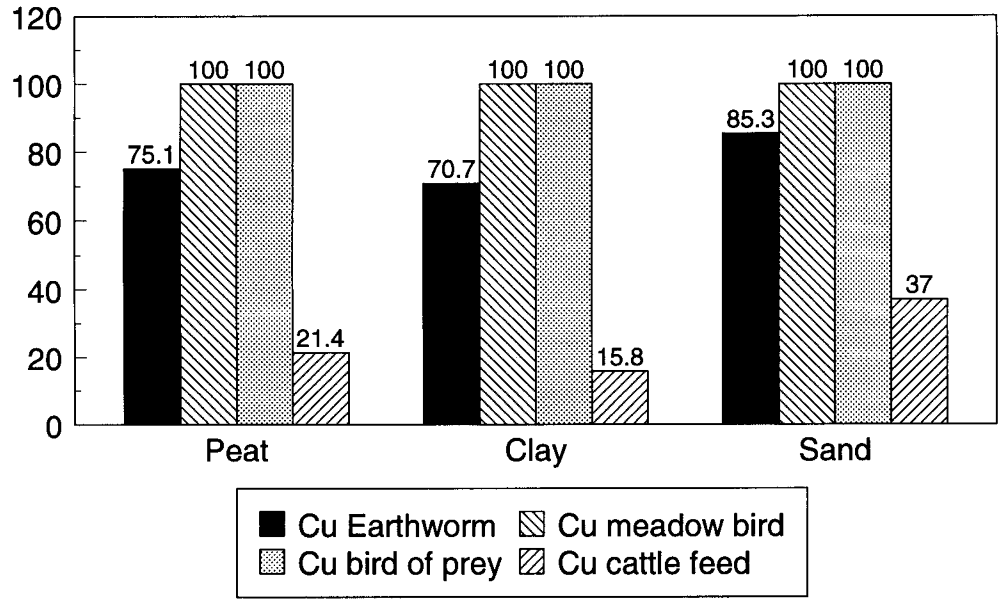

Figure 19: Risk at exceeding critical Cu concentrations in food of different functional groups in 2015.

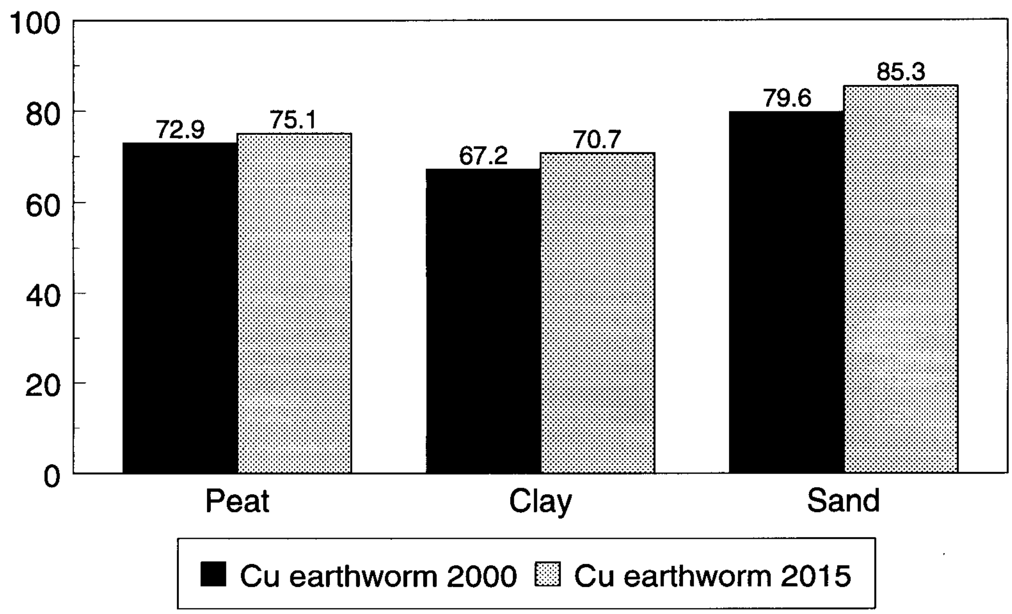

Figure 20: Risk at exceeding critical concentrations of Cu in earthworms.

An MPC for Cu in food was only available for mammals (84), therefore an MPC of 2.4 mg/(kg.d) was used for general assessment of food quality in the year 2015. For birds, Cu toxicity is expected in 2015 since the MPC is exceeded 100% (Figure 19). Due to the high toxicity of Cu to sheep, a substantial risk for cattle of 37% is predicted for Cu on sandy soils and lower but not negligable for the other soil types. Cu accumulation in earthworms (Figure 20) is already a problem in the year 2000 and risks increase only marginally with maximum 5% on sandy soil towards 2015.

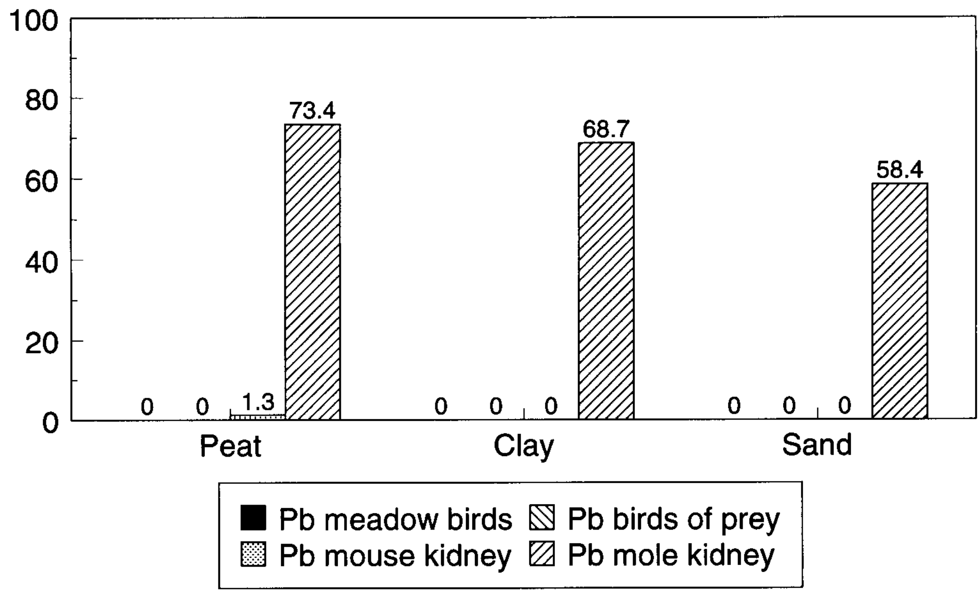

Figure 21: Risk at exceeding critical Pb concentrations in food of different functional groups in 2015.

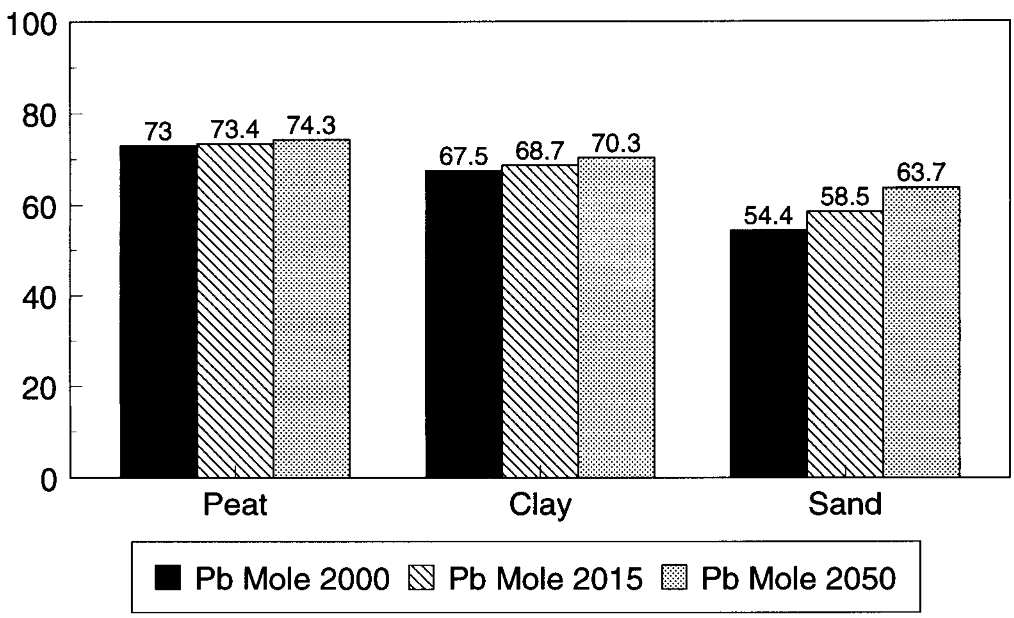

Figure 22: Risk at exceeding critical concentrations of Pb in mole kidney.

Risks for lead intoxication of birds are calculated by comparing an ADI for kidney damage (20 ug/(g.d), 78) with calculated food intake rates. Predicted lead accumulation in soils in 2015 does not lead to chronic Pb intoxication of birds (Figure 21). A very low risk is predicted for mice on peat soils in 2015. For moles, kidney damage is expected for all soil types. Due to the ongoing, but slow Pb accumulation in soils and earthworms, risks for moles are expected to increase slowly but steadily for all soil types (Figure 22).

4.4 Discussion

Initial conditions and load scenario

Bioaccumulation of several heavy metals shows large differences between different metals and different soils. The predicted bioaccumulation strongly depends on the adopted load scenario and initial soil concentrations resulting from heavy metal inputs in the past. The load scenario used here is that of 'business as usual' which may already be too pessimistic if load reductions have been realized. The uncertainty associated with initial concentrations and load was evaluated. In the present analysis, quite wide ranges of initial concentrations and loading had to be used because of the distribution of the chosen soil types over the entire country. A more site-specific analysis, e.g. for mapping of bioaccumulation risks on a grid scale, seems only sensible if uncertainty about initial concentration, load and soil parameters is reduced considerably by combining information with a Geographical Information System (GIS).

Soil sorption

Sorption of heavy metals to soils was described with relatively simple functions. The contribution of the soil parameters soil density, organic matter and clay content to model predictions for total soil concentration and dissolved concentration is therefore dominant. These parameters are known well, and can be extracted from geographical databases. More complex sorption models (e.g. 79,80) can be used to predict soil sorption if such models show a significant improvement in model fit to available soil accumulation time series. More detail such as depth profiles of metal concentrations is not necessarily better for an estimate of exposure concentrations, because most soil fauna is exposed either through the litter layer or the upper 20 cm (for burrowing organisms, grasses and herbs). Metal uptake of shrubs and trees occurs over a deeper soil layer, for which metal profiles are probably necessary.

Bioavailability

Estimation of bioavailability of toxicants is a main issue in risk analysis of toxicants. In CATS models, vegetation is exposed to the available dissolved concentration by root uptake only. Soft-bodied organisms such as earthworms are exposed both through food and pore water, and other organisms only through food uptake. These uptake processes are calibrated on a specific soil, whereafter the uptake mechanisms effectively react to changes in soil equilibria, governed by soil and loading parameters (see above). These mechanisms therefore take over the role of bioconcentration factors. In some cases, regression equations have been derived for the relation between soil properties and bioconcentration such as for heavy metals and earthworms (e.g. 57). The validity of the bioavailability mechanisms used in this CATS model can be assessed by comparison with field data from monitoring programmes (e.g. 67). A more statistical approach to biomonitoring data on different soil types is the most pragmatic way to generate regressions for bioaccumulation on different soil types. A more mechanistic approach is studying bioaccumulation in the laboratory of organisms on different soil types (Notenboom & Posthuma in prep.). It has been suggested that the concentration free ions (ion activity) is the true bioavailable fraction (81, Bril pers. med.) but this may be hard to establish if competition for binding sites occurs (82).

Bioaccumulation in the food web

Bioaccumulation of all metals was studied well for earthworms, mice, moles, vegetation and cattle and could be incorporated in the model by calibrating on accumulation studies (Appendix B). Bioaccumulation of heavy metals by birds is less well-known, and therefore assimilation efficiencies and excretion rates could only be calibrated within wide ranges.
Model simulations indicate that Cd, Cu and Pb concentrations in organisms on sandy soils increase if no load reduction measures are taken. The same 1985 load scenarios lead to a much slower increase for peat and clay soils, especially so for Pb.

Risk analysis

Comparison of accumulation in soil and leachate of different metals is made possible by the consistent quality objectives of the Ministry of Housing, Spatial Planning and Environment. The exceedance of quality objectives for foodweb bioaccumulation is much less comparable since critical concentrations, NOECs etc. are not always available for all metals. For heavy metals, a Maximum Permissible Concentration (MPC) was derived for cadmium and copper in food of birds and mammals, but not lead (76). Cu is an essential metal and critical organ concentrations, such as established for Pb and Cd in kidney, are not an appropriate criterion to judge Cu intoxication. A more unifying concept could be found if, instead of bioaccumulation, population effects could be studied for all metals. This requires a high degree of definition of the ecosystem studied, availability of specific dose-response functions and adequate description of ecosystem effects. Although case studies, such as the CATS-4 model for effects of Chlorpyrifos in microcosms (59) showed good promise, there is still a long way to go for routine application in regional risk assessment.

Mapping of risk predictions

The maximum achievable goal for mapping of bioaccumulation risks seems to be mapping of exceedance of quality objectives, NOECs or critical concentrations. With the present computing power, a dynamic risk prediction for a specific toxicant per geographical unit, using Monte Carlo analysis of CATS models, takes about one hour to complete. By simplifying the model, this time can be brought down to a factor of two to four, depending on the time horizon (e.g. 5, 25 or 50 years) of risk prediction. Calculation of risks, expressed as % runs above a certain quality objective, can be performed automatically with a simple program.
By using a steady state model for bioaccumulation in food chains, without the environmental chemistry, risk calculations using Monte Carlo sampling in spreadsheets can be brought down to 2-5 minutes per geographical unit. Example calculations were performed with the SIGMA spreadsheet model for Cu and Cd (83). Unfortunately, it is only possible to calculate exceedance probabilities manually. This procedure is most time consuming and partly defeats the time gained by implementing the model in a spreadsheet. The most efficient implementation

for routine application seems to be either a reprogramming of SIGMA or similar models or a simplification of CATS.

5. CONCLUSIONS

General conclusions

- Application of CATS models for regional assessment of bioaccumulation risks proved feasible. Case studies on heavy metals in meadow agro-ecosystems and organotin in a freshwater lake showed that initial concentrations, toxicant loading of the system and sorption coefficients strongly influence the prediction of bioaccumulation risks.

- Comparison of accumulation in water, sediment, soil and leachate of different metals is made possible by a consistent set of quality objectives of the Ministry of Housing, Spatial Planning and Environment. The exceedance of quality objectives for foodweb bioaccumulation is much less comparable since critical concentrations, NOECs etc. are not always available for all toxicants.

- Instead of bioaccumulation, population effects could be studied for all toxicants. This requires a high degree of definition of the ecosystem studied, availability of specific dose-response functions and adequate description of population effects. Although attempts have been made by studying and subsequent modelling of laboratory-scale ecosystems, there is still a long way to go for population effect modelling in regional risk assessment.

- Although effect modelling on an ecosystem level might be preferable for ecological risk analysis, exceedance of quality objectives, NOECs or critical concentrations seems to be the most realistic goal for mapping of ecosystem risks of toxicants.

Organotin study

- Dutch quality standards based on ecotoxicity testing, i.e. maximum permissible concentrations (MPC) were compared with concentrations calculated in water and newly formed sediment. MPCs for dissolved TBT were exceeded in the whole lake, indicating the necessity of the ban on TBT.

- After the ban on TBT, the quality standard for dissolved TBT is reached reasonably fast in the lake but not so in the marina. TBT accumulation in new sediment takes much longer to arrive at acceptable levels since risk levels do not fall below 80% for the lake simulation. Sediment quality standards are exceeded for both the lake and the marina and a time span of 50 years could be needed to arrive at levels conforming to quality standards in the Netherlands.

- System loading, sorption and to a lesser extent degradation in water dominated model uncertainty. Uncertainty of ecotoxicological processes tended to be overshadowed by this. Simple monitoring of water, susp. matter and sediment in risk areas could reduce uncertainty about abiotic behaviour and increase the influence of (eco)toxicological parameters on model outcome. True biological variability could then be separated better from uncertainty of essentially abiotic behaviour of TBT.

- TBT Risks in marinas as judged by a lethal body concentration are predicted to be substantial for most fish especially whitefish and predatory fish. When the ban is as effective as we presume in our scenario, risks can be reduced to very low levels on a timescale of approximately 10 years. Risk assessment for fish in the lake did not show any risk during the simulation period.

- The relative importance of exposure pathways for TBT was calculated (FWU ratio). The median FWU ratio for mussels is about 0.7, indicating that water uptake is the major pathway. The median FWU ratio for predatory fish is also below 1, but when loading is reduced, the food uptake starts to dominate bioaccumulation rising to median values of 2 before decreasing again. The median FWU ratio for whitefish and eel is never below 1 indicating that food is the dominant exposure route for TBT in lake Westeinder.

Heavy metals in meadows

- Calculated distributions of total heavy metal content of the three different soil types were used to calculate the risk that quality objectives used in the Netherlands are exceeded in the year 2000 and 2015. Target Values for Cd are not exceeded for any soil type in 2000. In 2015 however, ongoing accumulation leads to a small risk of 0.44% on sandy soil, and 5.4% on peat. The Maximum Tolerable Risk level in soil (MTR), based on extrapolation of laboratory toxicity, is exceeded in 2000 and 2015 for all soil types but least for clay with 57% exceedance in 2000.

- Target Values for Cu are exceeded most for peat and sandy soil, but increase fast between 2000 and 2015 on clay from 8.2 to 43.1%. For Target Values of Pb, the situation is more favourable since only on peat, a slight increase in risk from 12.3 to 22.7% from 2000 to 2015 is expected.

- Bioaccumulation of Cd in the food web of grassland is judged by comparing an MPC for food concentrations with calculated food concentrations in the year 2015. Meadow birds and moles, with a high proportion of earthworms in their diet, seem to be at risk, but risks are absent or very low for herbivorous mice and their predators. However, when bioaccumulation risk for moles is assessed with an empirical bioaccumulation factor for kidney damage, chronic kidney damage seems improbable.

- Predicted copper accumulation in soils seems to lead to risks for birds. Due to the high toxicity of Cu to sheep, a substantial risk of 37% is predicted for Cu on sandy soils and lower but not negligable for the other soil types. Cu accumulation in earthworms is already a problem in the year 2000 and risks increase marginally towards 2015

- Predicted accumulation of Pb in soils in 2015 does not lead to chronic Pb intoxication of birds. A very low risk is predicted for mice on peat soils in 2015. For moles, kidney damage is expected for all soil types. Due to the ongoing, but slow Pb accumulation in soils and earthworms, risks for moles are expected to increase slowly but steadily for all soil types.

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APPENDIX A: CALIBRATION AND REGIONAL RISK CALCULATIONS

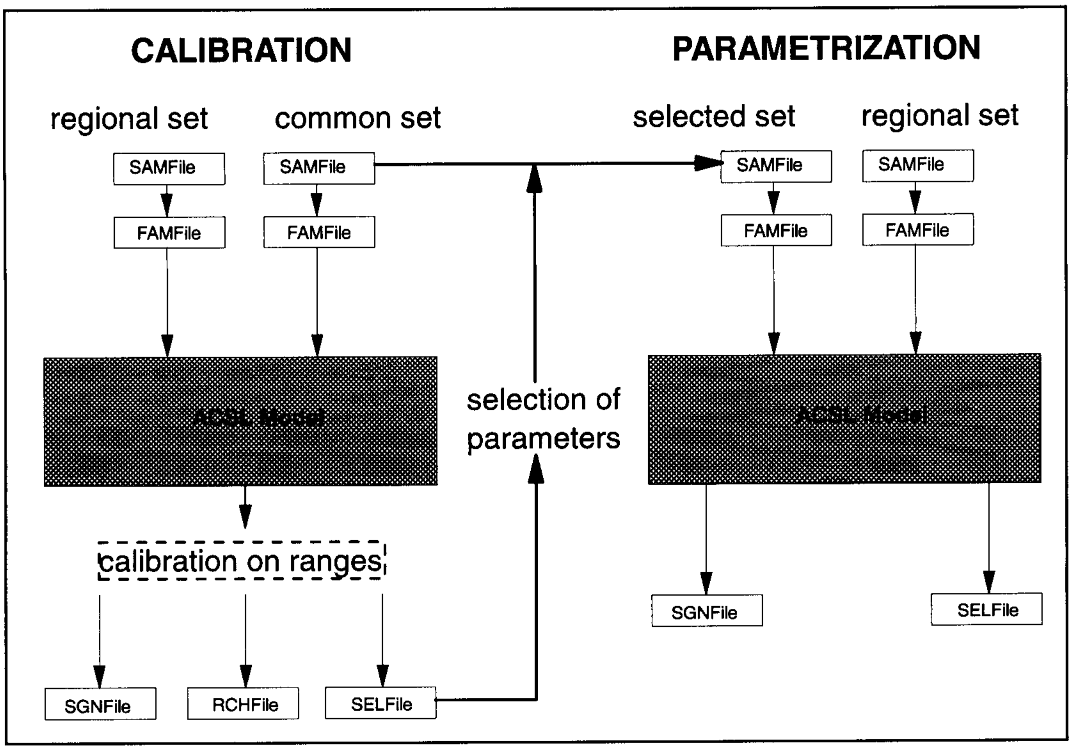

Figure 23: Diagram of calibration procedure

CATS models are calibrated by a comparison of model calculations with field or laboratory ranges. Calculations outside these ranges are rejected (13). Parametervalues, responsible for wrong model results, are discarded. This results in a selection of the parameters that are common for different ecosystems (the *common set* in Figure 23). This selected set is then used to apply the model to different regions or ecosystems. Those parameters that are specific for ecosystems or regions, are fed to the model in the *regional set*. This set of regional parameters must be adapted for each different region, and is responsible for the differences in model behaviour between regions. The additional Fortran code to run an ACSL model in Monte-Carlo mode was adapted from previous versions (63) and is available from the authors.

Table 4: specification of soil paramaters for CATS-1, according to (64). Uni = uniform distribution, his= histogram distribution.

PEAT					
cRhoSIM	uni	0.7	0.8		
cEpsSoil	uni	0.7	0.8		
cThetaSoil	uni	0.45	0.55		
pH	uni	4.9	5.1		
Lutum	his	0.175	0.65	0.175	
		10	18	25	40
OM	uni	15	35		
CEC	uni	23.8	63.8		
CLAY					
cRhoSIM	uni	1.2	1.4		

cEpsSoil	uni	0.4	0.5
cThetaSoil	uni	0.28	0.32
pH	uni	5.4	5.6
Lutum	uni	8	35
OM	uni	3	10
CEC	uni	7.8	30.0
SAND			
cRhoSIM	uni	1.1	1.4
cEpsSoil	uni	0.405	0.455
cThetaSoil	uni	0.22	0.27
pH	uni	5.0	5.6
Lutum	uni	2.0	4.0
OM	uni	5	10
CEC	uni	6.3	14.5

Table 5: specification of load and initial concentrations for CATS-1

CADMIUM	PEAT	CLAY	SAND
Load (g/ha y)	5 - 8	5 - 7	6 - 9
COPPER	PEAT	CLAY	SAND
Load (g/ha y)	200 - 400	200 - 400	400 - 800
LEAD	PEAT	CLAY	SAND
Load (g/ha y)	150 225	175 225	150 250

APPENDIX B: SPECIFICATION OF PARAMETERS

Cu uptake and excretion parameters

parameter	50 perc.	mean	minimum	maximum
Assimilation Efficiencies (-)				
fXAssC	3.33371E-01	3.38015E-01	1.00282E-01	5.99631E-01
fXAssW	1.23798E-01	1.23759E-01	5.00932E-02	1.99934E-01
fXAssT	6.99636E-01	6.99909E-01	6.00742E-01	7.99842E-01
fXAssM	3.25620E-01	3.25567E-01	2.50017E-01	3.99898E-01
fXAssB	3.25902E-01	3.25294E-01	2.50099E-01	3.99903E-01
fXAssMi	4.49155E-01	4.49438E-01	3.00031E-01	5.99747E-01
fXAssR	3.25607E-01	3.25405E-01	2.50071E-01	3.99882E-01
Excretion rates (y-1)				
kXExcrC	8.48568E+00	8.44009E+00	5.10339E-01	1.49877E+01
kXExcrW	2.24518E+01	2.25114E+01	1.50144E+01	2.99911E+01
kXExcrT	3.99607E+00	3.97925E+00	2.00292E+00	5.99883E+00
kXExcrM	1.49389E+01	1.49965E+01	1.00123E+01	1.99942E+01
kXExcrB	1.49496E+01	1.49925E+01	1.00095E+01	1.99935E+01
kXExcrMi	1.51225E+01	1.50664E+01	1.00093E+01	1.99780E+01
kXExcrR	1.51246E+01	1.50689E+01	1.00106E+01	1.99948E+01
Uptake rates (y-1)				
kXUpCr	5.51508E-05	5.51024E-05	3.00095E-05	7.99604E-05
kXUpW	8.84578E-04	8.83319E-04	7.70066E-04	9.99545E-04
Half Sat. constants				
hXUpCr	6.00258E-02	6.00221E-02	5.00151E-02	6.99949E-02
hXUpW	8.72481E-03	8.73995E-03	6.50230E-03	1.09960E-02
cBCFMoKidWorm	1.05063E+00	1.04951E+00	8.00066E-01	1.29992E+00
cBCFMiKidTot	1.49936E+00	1.50168E+00	1.00074E+00	1.99885E+00

Pb Uptake and excretion parameters

parameter	50 perc.	mean	minimum	maximum
Assimilation Efficiencies (-)				
fXAssC	1.23756E-01	1.24118E-01	5.00847E-02	1.99889E-01
fXAssW	7.46978E-02	7.48227E-02	5.00311E-02	9.99781E-02
fXAssT	3.47785E-01	3.50676E-01	1.00319E-01	5.99604E-01
fXAssM	1.23509E-01	1.24240E-01	5.00174E-02	1.99898E-01
fXAssB	1.24633E-01	1.24864E-01	5.00994E-02	1.99903E-01
fXAssMi	1.16764E-01	1.19371E-01	5.00154E-02	1.99874E-01
fXAssR	1.24702E-01	1.25577E-01	5.00711E-02	1.99882E-01
Excretion rates (y-1)				
kXExcrC	4.28169E+00	4.28010E+00	5.14135E-01	7.99378E+00
kXExcrW	1.23475E+01	1.24336E+01	5.01437E+00	1.99911E+01
kXExcrT	4.21275E+00	4.21517E+00	5.05481E-01	7.99781E+00
kXExcrM	4.21230E+00	4.25780E+00	5.00525E-01	7.99562E+00
kXExcrB	4.28576E+00	4.24417E+00	5.07138E-01	7.99513E+00
kXExcrMi	4.70405E+00	4.57341E+00	5.49737E-01	7.99315E+00
kXExcrR	4.24313E+00	4.26359E+00	5.03871E-01	7.99611E+00
Uptake rates (y-1)				
kXUpCr	7.04119E-05	7.02983E-05	4.00114E-05	9.99525E-05
kXUpW	8.81510E-04	8.82912E-04	7.70066E-04	9.99545E-04
Half Sat. constants				
hXUpCr	5.99997E-02	5.99858E-02	5.00151E-02	6.99949E-02
hXUpW	8.76173E-03	8.75807E-03	6.50230E-03	1.09960E-02

Bioconcentration factors kidney [kg/kg]

cBCFMoKidWorm	6.99291E-01	7.00777E-01	4.00079E-01	9.99899E-01
cBCFMiKidTot	6.98805E-01	7.00268E-01	4.00446E-01	9.99474E-01

APPENDIX C: QUALITY OBJECTIVES USED FOR RISK ASSESSMENT

Table 6: calculated target and intervention values for soil (for standard soil taken from (39))

	Peat	Clay	Sand		Lead	Copper	Cadmium		HC5
OM	20	21	3	trg	85	36	0.8	targ	0.26
Lutum	25	6.5	7.5	int.	530	190		int	
	Peat	Clay	Sand						
Lood, trg	95.00	77.50	60.50						
Lood, int.	592.35	483.24	377.24						
Koper, trg	42.00	31.50	21.30						
Koper, int	221.67	166.25	112.42						
Cadm, trg	1.01	0.90	0.53						
Cadm, HC5	0.33	0.29	0.17						

APPENDIX D: ESTIMATION OF TBT LOAD

Total TBT emission to the lake was estimated from the number of ships present in lake Westeinder (Municipality of Aalsmeer, pers. comm.) and the TBT flux per ship as estimated in USES (RIVM 1994). The fraction of ships that are actually treated with TBT-containing anti-fouling paint and the fraction of the year that ships are in the water are considered uncertain parameters. State variables in CATS-2 are expressed as g/m^2, therefore Load is calculated per m^2:

$$Load = (NShip \bullet AShip \bullet fShipW \bullet fShipP \bullet Leach) / Area$$

with *Load* = g Sn/m^2 y
NShip = number of Ships (5700)
AShip = average sub surface area per ship (5 m^2)
fShipW = fraction of the year that ships are in the water (0.5-0.8)
fShipP = fraction of ships treated with anti-fouling paint (0.5-1)
Leach = leaching of TBT (3.74 g Sn/m^2 y)
Area = area of lake Westeinder (8.8375E+06 m^2)

TBT load for an average marina (250 ships) was estimated using the equations from the anti-fouling section from USES (RIVM 1994), with the addition of uncertainty in parameters *fShipW* and *fShipP* (as specified above). TBT load in 1975 was estimated for Westeinder and marinas as described above:

Westeinder: 0.0012 - 0.0055 (g Sn/m^2 y)
marina: 0.094 - 0.524 (g Sn/m^2 y)

A logistic load reduction scenario was calculated with

$$Load(t) = Load(0) \bullet \frac{1}{1 + \exp(\frac{t - a}{b})}$$

with t = time of simulation (50 years, period 1975 - 2025), a = half time of reduction, (17 year; 1992), b = slope parameter (2/year), and *Load (0)* = estimated TBT emission in 1975