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# Validating SimpleBox-Computed Steady-state Concentration Ratios

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## ABSTRACT

The SimpleBox procedure for testing the coherence of environmental quality objectives was critically examined by a Committee of the Dutch Health Council in 1995. The result was a recommendation by the Committee to test the validity of this specific application of SimpleBox. The multi-media model SimpleBox version 2.0 was chosen as the most suitable model for use in the procedure to test the coherence of independently derived environmental quality objectives. Environmental concentrations of five substances, tetrachloroethylene, lindane, benzo[a]pyrene, fluoranthene and chrysene, were compared to predicted concentration. More specifically, the monitoring data were used to derive concentration ratios for adjacent compartments; these were then compared to modelled steady-state concentration ratios, taking uncertainties in the model input parameters into account. From the results calculated concentration ratios were, in general, found not to deviate much more than a factor of 10 from the "observed" data. The discrepancy between the computed and "observed" ratios of concentrations in the air and soil compartments were much larger, exceeding a factor of 30.

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# SUMMARY

The Dutch Health Council identified model validation as a pre-requisite for applying models for regulatory purposes. Validation of multi-media models for estimating environmental fate was recommended by a SETAC Taskforce on the Application of Multi-Media Fate Models to Regulatory Decision-Making. This report documents the evaluation of the validity of the multi-media fate model, SimpleBox, version 2.0, with respect to its specific use in testing the coherence of independently derived environmental quality objectives. The objective of the evaluation was to test whether the model could predict steady-state intermediate concentration ratios well enough for the purpose of coherence testing. Testing the validity of the underlying mechanistic assumptions in the model was considered to be beyond the scope of this project.

Predicted steady-state concentration ratios (SSCRs) were compared with measured environmental concentration ratios (MECRs). SimpleBox calculations of SSCRs require information on emission ratios, chemical properties and environmental settings. Monte Carlo sampling of input distributions takes the uncertainty of the SSCRs into account. Useful information, both on emission ratios and environmental concentrations, was either scarce or difficult to obtain. Chemicals, measured in air in the Netherlands, were generally not measured or detected in water or soil. Concentration data from outside the Netherlands, e.g. the Great Lakes in Canada, were only available from the literature and resulted in a small set of air and water concentrations measured over a long period of time in different geographic areas. These data were therefore not particularly useful for validation. It also had to be considered that for modelling concentrations outside the Netherlands, a lot of region-specific environmental information would be needed that might be difficult to obtain.

Nevertheless, measured environmental concentrations in The Netherlands of five substances, lindane, tetrachloroethylene, fluoranthene, chrysene and benzo[a]pyrene, were used to calculate air-water concentration ratios, and water sediment, water-suspended-matter and air-soil concentration ratios. These “measured” ratios were compared to the modelled concentration ratios. Concentration ratios for air and water were, generally speaking, not found to deviate by more than a factor of 10. For water-sediment and water-suspended matter concentration ratios, the computed ratio of only benzo[a]pyrene was found to differ by just more than a factor of 3. Only for the air-soil concentration ratios large differences were observed, and then generally more than a factor of 30.

The uncertainties in the “measured” and calculated concentration ratios have about the same magnitude. Uncertainties in Environmental Quality Objectives are also about the same so there is no direct need to reduce uncertainties in predicted concentration ratios. There is also no reason to reject the application of SimpleBox in the procedure of testing the coherence of independently derived environmental quality objectives, at least, as long as there is no scientific alternative.

Comparison of modelled and observed concentration ratios indicates that the degree of certainty with which the predicted ratios fall within a chosen uncertainty interval, obviously tends to be higher using wider intervals. Certainty levels of the related uncertainty factors, i.e. 3, 10, 30 and 100, come to about 20%, 50%, 70% and 80%, respectively.

# SAMENVATTING

In dit rapport komt de validatie van het verspreidingsmodel SimpleBox 2.0 aan de orde. Bij de validatie is er met name gekeken naar een specifieke toepassing van het model, namelijk het toetsen van de ‘coherentie’ van onafhankelijk van elkaar afgeleide milieukwaliteitsdoelstellingen. Het doel van dit rapport is om na te gaan of het model de verhoudingen van steady-state concentraties in aan elkaar grenzende compartimenten voldoende goed voorspelt voor het aantonen van inconsistenties in de onafhankelijk van elkaar afgeleide milieukwaliteitsdoelstellingen.

Dit naar aanleiding van het advies van de Nederlandse Gezondheidsraad waarin zij heeft aangegeven dat validatie een eerste vereiste is voor een model dat wordt toegepast in beleidsontwikkeling. Tevens adviseerde de gezondheidsraad een wetenschappelijke update van het model, inclusief gevoeligheids- en onzekerheidsanalyse. De SETAC taakgroep voor het toepassen van multi-media verspreidingsmodellen bij het ontwikkelen van beleidsvoorschriften gaf eveneens een aanbeveling voor het valideren van verspreidingsmodellen.

De onzekerheid in de door het model voorspelde concentratieverhoudingen wordt onderzocht door het vergelijken van de voorspelde ratios met de verhouding van de in het milieu gemeten concentraties in aan elkaar grenzende compartimenten. Daartoe is informatie benodigd over zowel fysisch-chemische eigenschappen, emissies als omgevingsvariabelen. Met behulp van de Monte Carlo techniek wordt de onzekerheid in de invoer parameters doorberekend naar de modeluitvoer, de steady-state concentratieverhoudingen.

De hoeveelheid bruikbare informatie was vrij beperkt met betrekking tot zowel gemeten concentraties als emissies. Het komt vaak voor dat chemische stoffen die in de lucht worden gemeten niet worden aangetroffen of worden gemeten in het oppervlaktewater of in de bodem. Buitenlandse meetgegevens, zoals aangetroffen in de openbare literatuur kwamen vaak niet overeen in plaats en tijd. Voor regios buiten Nederland geldt tevens dat het verkrijgen van representatieve omgevingsvariabelen lastig kan zijn.

Voor een vijftal stoffen zijn de meetgegevens gebruikt om concentratieratios te berekenen. Het betreft: lindaan, tetrachlooretheen, fluorantheen, chryseen en benzo[a]pyreen. Deze zogenaamde ‘gemeten’ concetratieverhoudingen zijn vergeleken met de door het model SimpleBox berekende concentratieverhoudingen. De concentratieratios voor lucht-water verschillen meestal niet meer dan een faktor tien met de berekende ratios. Voor de concentratieverhoudingen van water-sediment en water-gesuspendeerd materiaal is het verschil voor slechts één stof meer dan een factor drie. Grote verschillen worden waargenomen voor de verhouding tussen de concentraties in lucht (aerosolen/regenwater) en de bodem. Het verschil is meer dan een factor dertig.

De onzekerheid in de ‘gemeten’ en de gemodelleerde ratios is ongeveer even groot, en vergelijkbaar met de onzekerheid in de afgeleide milieukwaliteitsdoelstellingen. Daarom is het niet direct noodzakelijk om de onzekerheden in de modeluitkomsten te reduceren. Er is eveneens geen directe aanleiding om het model SimpleBox af te wijzen met betrekking tot het gebruik bij het afleiden van een coherente set van milieukwaliteitsdoelstellingen, waarbij moet worden opgemerkt dat een goed wetenschappelijk alternatief niet voorhanden is.

Vergelijking van gemodelleerde en ‘gemeten’ ratios geeft aan dat de mate van zekerheid waarmee voorspelde ratios binnen een vooraf vastgestelde onzekerheidsmarge vallen, groter wordt naarmate grotere onzekerheidsmarges worden gebruikt. Deze mate van zekerheid is berekend voor verschillende onzekerheidsmarges en bedraagt voor de onzekerheidsfactoren 3, 10, 30 en 100 respectievelijk 30%, 50%, 70% en 80%.

# 1. PROBLEM DEFINITION

## 1.1 Background

SimpleBox (Van de Meent, 1993 and Brandes et al., 1996) is a multi-media environmental fate model. Models of this so-called Mackay-type are used and have been proposed for use in various regulatory frameworks (Cowan et al., 1995). In The Netherlands, SimpleBox has been used:

1. to predict steady-state intermedia concentration ratios for the purpose of harmonisation of environmental quality objectives (Health Council of The Netherlands, 1995);
2. to predict concentrations in the regional environment for the purpose of evaluation of chemicals (Van der Poel, 1997a).

*Harmonisation of Environmental quality objectives*

Within the research program 'Setting Integrated Environmental Quality Objectives for Water, Soil and Air' (INS-project), The Netherlands Directorate-General of the Environment (DGM) has started to derive harmonised or 'coherent' sets of environmental quality objectives. Maximum permissible concentrations (MPCs) in the environment are derived on the basis of the estimated 5th percentile of the distribution of NOECs. MPC-values are derived independently for air (human toxicity data), water (aquatic ecotoxicity data), sediment (sediment toxicity data), and soil (terrestrial ecotoxicity data). These sets of MPC-values may not be coherent in the sense that maintaining the environmental concentration in a given compartment exceeds the MPC derived for another compartment. Van de Meent and De Bruijn (1995) have proposed to use the steady-state intermedia concentration ratios (SSCR), as computed by SimpleBox, as a test for coherence of independently derived MPC-values. This SSCR procedure has been applied to derive harmonised environmental quality objectives for a number of volatile organic chemicals (Van de Plassche and Bockting, 1993). In the past, the same modelling procedure has been used for computing critical concentrations in air, starting from MPC-values for soil (Van de Meent, 1995). The SSCR-procedure has been critically reviewed by a Committee of the Health Council of The Netherlands (Health Council of The Netherlands, 1995). The Health Council recommended that validation of SimpleBox is urgently needed. The Committee advised amongst others to validate the model as a whole as well as individual process descriptions.

*Substances and Products Evaluation*

The SimpleBox model has found application as a regional distribution model in the Uniform System for Evaluation of Substances (USES) (RIVM, VROM, WVC, 1994; Van der Poel, 1997a; EC, 1996). In this application, Predicted Environmental Concentrations (PEC) in air, water, sediment and soil at a regional spatial scale (The Netherlands) are computed on the basis of (predicted) emission rates. In the computation, the regional concentrations are computed, taking the continental concentrations as a 'background' (Van der Poel, 1997a). This application has drawn attention outside The Netherlands.

In Denmark, research has been carried out to evaluate the possibilities for use of SimpleBox in typical Danish settings, and to adapt the model to these specific needs (Fredenslund et al., 1995; Severinsen et al., 1996). The regional modelling part of USES has been applied to Life Cycle Analysis, for evaluating the impact of toxic substances emitted during the ‘cradle-to-grave sequence’ of products (Guinée et al., 1996). For this purpose, the model was set to European proportions as much as the USES framework allowed. The European Commission finished a European System for the Evaluation of Substances (EUSES) in 1997, taking the Dutch USES model as a starting point (EC, 1996; Jager et al., 1997).

## 1.2 Need for validation of SimpleBox

Until recently, multi-media fate models have primarily been used as research tools, to gain insight into the possible importance of intermedia transfer mechanisms, and to improve understanding of the importance of properties of chemicals in this respect. Hardly any serious attempt has been made so far to test the validity of this type of model as a tool for predicting concentrations or concentration ratios. Van de Meent and De Bruijn (1995) characterised the multi-media modelling concept as ‘non-validated’, and suggested at the same time to apply the concept, in absence of alternatives. While the usefulness of multi-media models in regulatory decision making is clear, the need for validation of this model type is even more evident.

Model validation was recommended by a SETAC Taskforce on Application of Multi-Media Fate Models to Regulatory Decision-Making (Cowan et al., 1995). The Health Council of The Netherlands identified model validation as a prerequisite for application of the model in regulatory practice (Health Council of The Netherlands, 1995).

## 1.3 Goal

The goal of the research described in this report was to evaluate the validity of the multi-media fate model SimpleBox with respect to its specific use in the procedure of testing the coherence of independently derived environmental quality objectives. The subject of this report is to validate the model as a whole: how well does the model describe the environmental concentration ratios of specific chemicals in The Netherlands?

## 1.4 Approach

### *Scope of the validation*

Focusing on the specific use for testing coherence of environmental quality objectives, has a number of implications:

With respect to the model output to be validated, the study is primarily restricted to quotients of pairs of steady-state concentrations at the regional spatial scale: the air-water, air-soil and water-sediment concentration ratios.

In line with this, first priority is given to validating the model as a whole; validation of individual process descriptions has a lower priority.

With respect to the model input, the study is restricted to situations in which the quantitative knowledge of *ratios of emissions* to the different environmental compartments is defined; knowledge of absolute rates of emission is not required because the SimpleBox model is a so-called linear model, the output (concentration ratios) is linearly dependent on the input (emission ratios).

With respect to the chemicals, the study focuses on the chemicals for which integrated environmental quality objectives are being set in the INS-project: the typical micropollutants supposed to have toxic effects on humans and ecosystems. No particular set of chemicals has been identified a priori for this study. The model claims to be applicable to all chemicals, provided that the necessary model input in terms of partition coefficients is available. Therefore, in principle, validity needs to be tested for all chemicals.

With respect to the system, the study focuses on environmental situations that can be interpreted as representative for typical Dutch circumstances.

*Validity*

Criteria for accepting or rejecting the model validity are to be found in the level of certainty that is required for the proposed application of the model result. In this case: the possible decision to adjust an environmental quality objective if it is concluded that the derived Maximum Permissible Concentrations (MPCs) for two compartments are incoherent. In the proposed procedure, MPCs are called incoherent if the computed Steady-State Concentration Ratio exceeds the ratio of the independently derived MPCs by more than a factor of 10. The Health Council has recommended to base this judgement on actual uncertainties, rather than on this implicitly perceived uncertainty factor of 10. In this light, model calculations of SSCRs are considered valid if the uncertainty as it appears from comparison of computed and observed data is small enough to yield practically useful criteria for coherence of MPCs. The validation study is done with the SimpleBox version 2.0.

*Uncertainty in model output*

Taking the recommendations made by the Health Council and others into consideration, the assumptions made in SimpleBox -the possible sources of uncertainty and error- are reviewed, and prior to this study an uncertainty analysis was carried out. The methods and results of this uncertainty analysis are given in Etienne et al. (1997). In this study we have taken the uncertainty in the model output into account by Monte Carlo sampling of input distributions. The result is a distribution of the steady-state air/water- and air/soil etc., concentration ratios.

*Model*

The original version (Figure 1.2) of the multimedia fate model SimpleBox is revised as a starting point for this validation study. A technical description of this version of SimpleBox (Figure 1.1) can be found in Brandes et al. (1996).

In the new version of SimpleBox the environment is modelled as a regional scale nested in continental and global scales. The regional and continental scale represent a densely populated Western European region and the whole of the European Union, respectively.

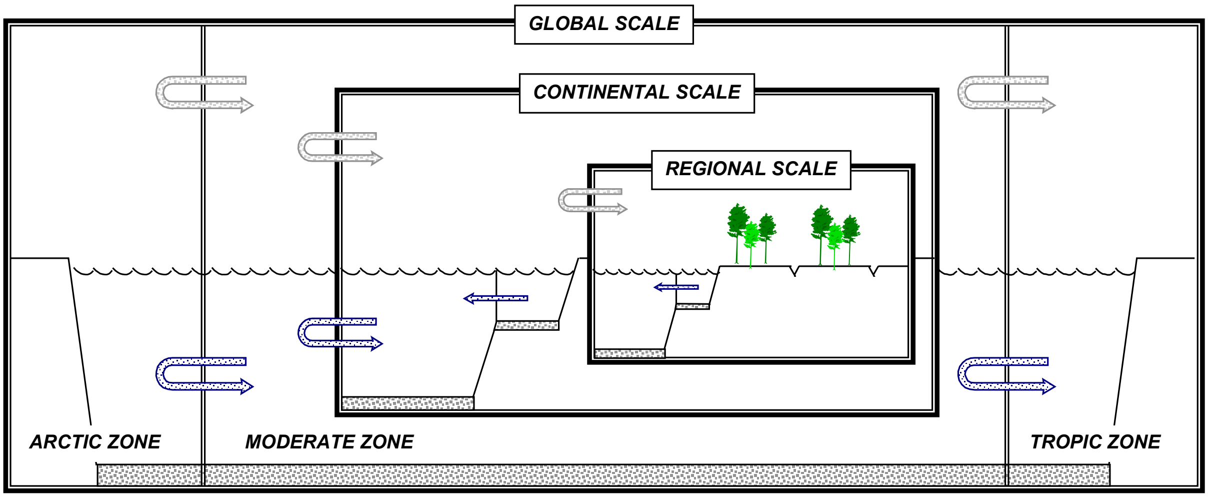

*Figure 1.1: Geographic scales in SimpleBox 2.0 (Brandes et al., 1996)*

The spatial scales include homogeneous environmental compartments: air, freshwater and seawater compartments, sediments, three soil types and vegetation on natural and agriculturally used soil. The global scale is divided in three zones: a moderate, arctic and tropic zone. Each zone consists of an air, seawater, sediment and soil compartment.

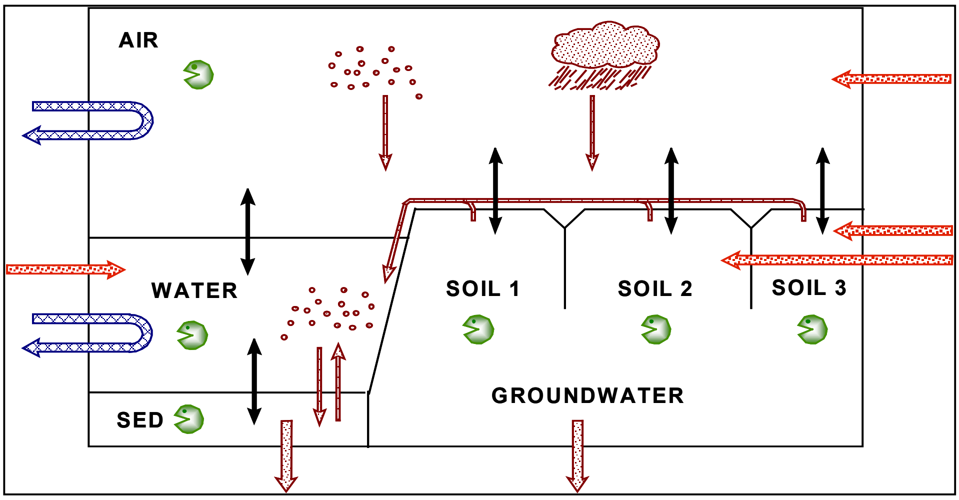

*Figure 1.2: Six compartments (air, water, sediment three different soil types) in SimpleBox 1.0 (Van de Meent, 1993).*

In SimpleBox 2.0, four compartments (marine water and sediment and vegetation on natural and agricultural soil) have been added (Brandes et al., 1996)

The model requires information on chemical properties and emission rates and calculates the distribution of the chemical between the environmental compartments. This study concentrates on the regional scale, the model defaults are modified to represent the typical Dutch settings.

# 2. APPROACH TO MODEL VALIDATION

## 2.1 Introduction

Computed steady-state concentration ratios were compared with observed concentration ratios. Concentration data were obtained from the literature, databases of monitoring networks and by consultation of experts. An additional monitoring program was started for phthalates. However, this monitoring program is not a part of this project and the validation results are separately reported by Struijs (2002). It was anticipated that measured concentrations in The Netherlands would be available for a limited number of well-known chemicals only, and that this selection of chemicals might not be as representative for the chemicals of the INS-list as one would like. Simultaneously measured concentration data for air, water, sediment and soil at the same locations in The Netherlands were expected to be exceptional. Data obtained from measurements outside The Netherlands are considered to be potentially useful in this validation project too (Japan, Denmark, Great Lakes in North America). For these data, the SimpleBox model definitions must be adjusted to represent the environmental situations for which the measurements were obtained.

## 2.2 Data collection

Four sorts of data are needed:

- *loadings*: amounts of a chemical that enter the system to be modelled (‘import’ with air and water, emissions to air, water and soil) and their probability distributions. Only relative amounts (percentage of total loadings) are needed because the model is linear in the emissions and the resulting concentrations and only relative statements on concentrations are to be validated. But loadings are not exactly known and therefore the uncertainty has been accounted for.
- *environmental descriptors*: if the validity test is done for environmental settings other than the model default settings (The Netherlands), the characteristic parameters for that specific environmental situation are needed.
- *concentrations*: preferably concentrations in air, water, sediment and soil, measured at the same location, and at the same time, but concessions may be inevitable in case of lack of data.
- *properties*: physical and chemical properties, to be used as input to the model (partition coefficients, degradation rate constants) and their probability distributions.

Emission and concentration data are the most difficult categories. A selection of representative, ‘INS-like’, chemicals was made on the basis of apparent data availability. Obvious candidates for selection were chemicals that have been addressed in other, similar model studies and for which monitoring data and fate parameters are known to be available.

Van de Meent and De Bruijn (1995) used benzene, 1,4-dichlorobenzene, 1,1,1,-trichloroethane, dichlorophenol, atrazine, benzo[a]pyrene and lead, to illustrate the harmonization procedure. Mackay and others (1985,1992) have published model test results with benzene, chlorobenzene, 1,2,3-trichlorobenzene, hexachlorobenzene, and p-cresol. Devillers et al., and Bintein and Devillers used isobutylene (1995), lindane (1996a) and atrazine (1996b) to test the ChemFrance model. Verbruggen et al. (1997) used DDT, PCBs, DEHP and lead to test their global fate model. We have carried out a literature search for concentration data in air, water, sediment and soil, measured at the same regions and times. Two sorts of difficulties were foreseen: unstructured data plentifulness and data scarcity. To solve these problems, a scoping search was done first for DEHP and PCBs, using easily accessible open literature. Data was collected from the public literature and by actively searching for additional sources of data.

## 2.3 Modelling

For all suitable data sets, the output distributions of the SSCRs were calculated with SimpleBox 2.0 after parameterisation of the model for the type of environment from which the data originate. Considering the uncertainties in model inputs, probability distributions of compound specific and non-compound specific input parameters (environmental parameters) are required for the output distribution of the SSCRs. These resulting uncertainties in the model output refer to the assumption of well-mixed compartments and space- and time-averaged concentrations. The output distributions were obtained from Monte Carlo simulations.

## 2.4 Testing methods for validity

There are several statistical methods, which may be useful for assessing the performance of model output (Boekhold et al., 1993):

1. Graphical methods
2. Factor-of-*f*-approach
3. Comparison of confidence intervals
4. Comparison of mean values
5. Comparison of variances

*Graphical methods*

Graphs can be very useful in showing trends and distributions. Because the validation results must be readily interpretable by users of the system, the choice for a graphical representation seems to be more appropriate, instead of presenting the results of a validation study with statistical methods (Jager, 1995).

Graphical methods may include comparison of observed and predicted values, comparison of ranges of observed and predicted values and comparison of (cumulative) distribution functions of observed and predicted values.

*Factor-of-f-approach*

The Factor-of-*f*-approach is a method for testing whether model predictions fall within a prescribed factor of true values. Parrish and Smith (1990) describe the method of the Factor-of-f-approach.

*Comparison of confidence intervals*

By means of Monte Carlo simulation techniques one can obtain the characteristics of the probability density functions (PDF) of the output, which result from the uncertainties in the input parameters. If the shape and characteristics of the PDF of model output parameters is known, a particular confidence interval can be constructed. This confidence interval is dependent on the desired level of significance $\alpha$. Comparison of the confidence intervals resulting from the model simulations with the confidence intervals of the measurements is described by Parrish and Smith (1990).

*Comparison of mean values*

Statistical tests such as a Student’s t-test can be used to test whether model predictions are the same as true values. But, in practice predicted values will rarely equal the true values, thus the hypothesis will be rejected routinely. For the application of environmental models in management, the hypothesis of equality and this testing approach may be too stringent (Parrish and Smith, 1990).

An approach to design a statistically meaningful test is to test the hypothesis that the difference between predicted and measured mean values does not exceed a predefined value. This value can be chosen such, that a certain amount of imprecision is allowed (Boekhold et al., 1993). Further statistical details can be found in Mood et al. (1974).

*Comparison of variances*

For comparison of variances multiple measurements and multiple model outputs must be known. This can be achieved by using Monte Carlo simulations. The Kolmogorov-Smirnov procedure tests for goodness of fit of model predictions to the distribution of measurements (D’Agostino and Stephens, 1986).

## 2.5 Criteria for validity[1]

Model predictions of SSCRs are valid if the uncertainty, as it appears from comparison of computed and observed data, is small enough to be useful in the practice of coherence testing.

Coherence criteria:

Maximum Permissible Concentrations (MPCs) are called incoherent if the computed steady-state concentration ratio exceeds the ratio of the independently derived maximum permissible concentrations by more then a factor of 10 (Van de Meent and De Bruijn, 1995). Example: if a certain chemical is emitted to air, and MPCs of 1 mg/m$^3$ and 1 µg/l, for air and water, respectively, are derived, and the SimpleBox calculation predicts an air-water steady-state concentration ratio of 90 l/m$^3$, then the ratio of MPCs, Maximum Permissible Concentration Ratio (MPCR), exceeds the ratio of Steady-State Concentrations (SSCs), SSCR, by more than a factor 10:

$$MPCR_{air-water} = \frac{MPC_{air}}{MPC_{water}} = \frac{10^{-3}\,g/m^3}{10^{-6}\,g/l} = 1000\ l/m^3 \geq 10 \cdot SSCR_{air-water}$$

In this example, the model predicts that if the concentration in air would be maintained at the level of MPC$_{air}$, the concentration in water would exceed the MPC$_{water}$ by more than a factor of 10:

$$C_{water} = \frac{MPC_{air}}{SSCR_{air-water}} = \frac{10^{-3}\,g/m^3}{90 l/m^3} = 11.1 \mu g/l > 10 \cdot MPC_{water}$$

As pointed out by the Health Council, there is no scientific rationale for the use of a factor of 10 as a threshold criteria for incoherence, other than perhaps that this is the perceived uncertainty of the predicted SSCR. No formal probabilistic basis has been proposed for coherence criteria. A useful probabilistic criterion for example could be the 90% confidence level of the quotient of MPCR and SSCR. A set of MPCs could be called incoherent, if the quotient MPCR and SSCR differs from the value 1 with more than 90% certainty. If the MPCR/SSCR quotient has a lognormal distribution with an uncertainty factor of ten[2], this probabilistic criterion would match with the factor-of-10 criteria.

$$P\left\{-10 < \frac{MPCR}{SSCR} < 10\right\} > 0.90$$

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[1] In case of validating SimpleBox by means of comparing calculated SSCR with Measured Environmental Concentration Ratios (MECR); MPCR can be replaced by MECR and MPC by the environmental concentration (C) through out this paragraph.

[2] In this case, the 90% confidence interval has a range of : mean/10 - mean·10.

Application of the criteria requires quantitative assessment of the distributions (uncertainties) of both the SSCR and the MPCR. There are three situations possible:

1. The relative uncertainty in MPCR is much greater than the relative uncertainty in SSCR. In this case, the uncertainty in SSCR is negligible, and the practical usefulness of the coherence test is determined by the uncertainty in MPCR only.
2. The relative uncertainty in SSCR is much greater than the relative uncertainty in MPCR. In this case, the practical usefulness of the coherence test is fully determined by the uncertainty in SSCR.
3. The relative uncertainties have similar magnitudes. In this case both uncertainties contribute to the practical usefulness of the coherence criteria.

Clearly, probabilistic criteria for validity of the model calculations of SSCR can only be set if the required level of confidence (acceptable level of certainty) for coherence test is defined, and the uncertainty in MPCR is known.

As a guideline, a priory criteria for testing model predictions against field data of the SETAC-Workshop (Cowan et al., 1995) can be used. The perceived accuracy factors are based on the assumption that the emission rate is known exactly, that the degradation rates are well characterised and that only the uncertainties in chemical properties and chemical transfer between media determine the actual predicted concentrations. The uncertainty in the model results may in fact be much larger due to considerable uncertainty in emissions rates, however the uncertainty ranges as discussed by the SETAC-Workshop (Cowan et al., 1995) were used to formulate criteria for this study:

- the median predicted steady state concentration ratio (SSCR) does not deviate more than a factor of 3 from the median of the ratio of measured concentration ratio (‘factor 3 criterion’).
- the median SSCR deviates more than a factor 3 from the median of the observed concentration ratios but less than a factor of 10 (‘factor 10 criterion’)
- the median SSCR deviates more than a factor of 10 but less than a factor of 30 from the median of observed concentration ratios (‘factor 30 criterion’)

Formal probabilistic coherence criteria can be derived for predefined levels of confidence (acceptable level of certainty) using uncertainty analysis and comparing model results (SSCR) with measured environmental concentrations. This procedure will be further outlined in chapter 5.

As stated earlier, uncertainties in the model output (SSCRs) can be obtained by the uncertainties in model inputs, e.g., by Monte Carlo simulations. As a consequence of the assumptions of well-mixed compartments, and of steady-state, the model output relates to space- and time-averaged concentrations. For a good comparison, space and time-averages of ‘observed’ concentrations should be obtained, attempting to simulate the concentrations that would be obtained by analysing properly prepared blends of samples taken at various locations and times (variability). The distributions of concentrations are used to derive the distribution of concentration ratios of adjacent compartments. The environment should be characterised to define a regional scenario in SimpleBox.

# 3. OBSERVED ENVIRONMENTAL CONCENTRATIONS

## 3.1 Introduction

We have looked for suitable data for the validation of SimpleBox in three different ways:

*1. Open literature search, 2. Japanese data* and *3. Databases* of measured concentrations from other Laboratories at RIVM; Air Research Laboratory (LLO), Laboratory for Waste Materials and Emissions (LAE), Laboratory for Water and Drinking-water Research (LWD) and the Soil and Groundwater Research Laboratory (LBG), other research institutes in The Netherlands; Institute for Inland Water Management and Waste-Water Treatment (RIZA), National Institute for Coastal and Marine Management (RIKZ) and The Netherlands Institute for Sea Research (NIOZ) and provinces, regional polder-boards and drinking water companies; Association of Rhine and Meuse Water Supply Companies (RIWA).

## 3.2 Literature Search

An open literature search is conducted for concentration data of three chemicals. The search procedure was as follows: *1. Selection of chemicals* for which a lot of data are available (PCBs, DDT and DEHP are selected). *2. Formulation of the search routine* in cooperation with the library of the RIVM (Databases: Toxline and Chemical Abstracts). *3. Selection* of possible useful literature by glancing through the abstracts. *4. Request of data* from the authors.

*Results of the literature search*

In order to acquire relevant data for validating the SimpleBox 2.0 model we have looked for measured concentrations of some selected chemicals in the environmental compartments air and water in the public literature.

Our objective was to put together a set of data for some chemicals consisting of concentrations in the environmental compartments air, water and soil measured during a comparable period and in a well definable geographical area.

For three selected chemicals, namely diethylhexylphthalate (DEHP), DDT and PCBs we searched the literature by means of Medline Express, Chemical Abstracts and the Toxline Plus databases. We only have gone through the literature published from 1985 until 1996; the use of older data seemed to be not useful to us because of the increasing accuracy of the analytical procedures, which might influence the concentrations measured. In the case of DEHP our search yielded about eighty hits of which only twenty seemed to be relevant relying on title and abstract. The data obtained originated from different countries and also from different periods so they did not meet our criteria.

For DDT and PCBs we revised our search strategy a bit to keep the number of hits in control. For these chemicals we searched for concentrations in water **and** (air or soil). In spite of this limitation we obtained some hundreds of hits. It was remarkable that about ninety percent of the articles found were dealing with effects of these chemicals on a diversity of organisms. Nevertheless we encountered the same problems as we did with DEHP; the resulting data did not meet to our objective to be a coherent set in time and location.

We conclude that the use of literature data for validating SimpleBox 2.0 was unsuccessful. Some results of the literature search on concentrations of PCBs and DDT are given in Appendix II.

## 3.3 Japanese Data

The Environmental Health and Safety division of the Environment Agency of Japan has been conducting successive investigations of chemicals in the Japanese Environment. The results which were potentially suitable for this study are taken from reports entitled Environmental Survey and Wildlife Monitoring of Chemicals in fiscal year 1992, 1993 and 1994 (Environmental Agency Japan, 1995, 1996).

In these reports measured concentrations of a large group of (persistent) chemicals are given in water, sediment, fish and occasionally in air and rainwater. Concentrations of chemicals in soil are not given in these reports.

We used the following selection procedure: concentrations of chemicals in air at specific locations are compared with measurements of these chemicals in water at the same locations and in the same year. Series of air and water concentrations are reported in Table 3.1. We conclude that the Japanese data do meet the formulated criteria for the literature search but are not useful in validating SimpleBox 2.0 because of either the limited number of measurements above the detection limit or the limited number of geographical sites or both.

*Table 3.1: Japanese Data: measured air and water concentrations.*

| Chemical | Location | year | Air Min. ng.m$^{-3}$ | Air Max. ng.m$^{-3}$ | Air Med. ng.m$^{-3}$ | D | N | Water Min. ng.ml$^{-1}$ | Water Max. ng.ml$^{-1}$ | Water Med. ng.ml$^{-1}$ | D | N |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1,2-Dichloroethane | 31421 | 1988 | 64 | 380 | | 6 | 6 | 0.1 | 0.13 | | 3 | 3 |
| Melamine | 2041 | 1994 | | 3.9 | | 1 | 3 | | 0.37 | | 1 | 3 |
| Melamine | 3121 | 1994 | 2 | 5.8 | 2.2 | 3 | 3 | | 0.4 | | 1 | 3 |
| Melamine | 3141 | 1994 | 2 | | | 1 | 3 | | 0.14 | | 1 | 3 |
| Tributyl phosphate | 3121 | 1993 | | 2.5 | | 1 | 1 | 0.011 | 0.018 | 0.012 | 3 | 3 |

D= above detection limit, N= total number of measurements.

## 3.4 Air and Rainwater Quality Monitoring

Air and rainwater quality data are available from the Dutch National Air Quality Monitoring Network (LML) and the Dutch National Rainwater Quality Monitoring Network (LMRw) are managed by the Laboratory of Air Research of the National Institute of Public Health and the

Environment in The Netherlands. Besides the Monitoring Networks, regional boards (DCMR-Rijnmond) and the provinces of Zeeland and Noord-Holland perform air quality monitoring.

Concentration data which are expected to be useful for validation of SimpleBox include measurements of Volatile Organic Components (VOC) in air, lindane (and other pesticides) and polycyclic aromatic hydrocarbons in rainwater and aerosols. The list of VOCs, which are detected in air, can be found in Table 3.2.

*Table 3.2: Detected chemicals in air in The Netherlands.*

| *Chemical* | *Chemical* |
|---|---|
| 1,1,1-trichloroethane | 1,4-ethylmethylbenzene |
| 1,2,3-trimethylbenzene | 1.4-dimethylbenzene |
| 1,2,4-trimethylbenzene | benzene |
| 1,2-dimethylbenzene | ethylbenzene |
| 1,2-ethylmethylbenzene | tetrachloroethylene |
| 1,3,5-trimethylbenzene | tetrachloromethane |
| 1,3-dimethylbenzene | toluene |
| 1,3-ethylmethylbenzene | |

VOC concentrations in air are measured at ten different sites in The Netherlands. These locations are part of the National Air Quality Monitoring Network. Sampling is done at three site types:

| | |
|---|---|
| regional | these sites are thought to be representative for the area around the site with a radius of 5 to 50 km |
| city | these sampling sites are located in a city with 40 000 or more inhabitants and are not directly influenced by traffic |
| street | these sampling sites are located in an urban environment with a traffic intensity of 1000 vehicles per 24-hour period. |

Five of the ten sites are classified as regional sites, two as city and three as street sampling sites. Sampling is done in a four weekly cycle during which seven 24-hour period samples are taken. A total of 47 VOC components are being analysed.

The results of the measurements for tetrachloroethylene at all sites are used to estimate the average concentration in air. Traffic is not known to contribute to tetrachloroethylene emissions. On the other hand dry-clean facilities are predominately located in urban areas. As the influence of this source on the measured concentrations is not clear we also used the information from the sampling sites located in the large cities to derive typical concentrations, see Table 3.3.

*Table 3.3: Average concentration of tetrachloroethylene in air in The Netherlands in period 1993-1994.*

| Chemical | sampling technique | Average µg.m$^{-3}$ | Stdev ng.m$^{-3}$ | N | Location | Reference |
|---|---|---|---|---|---|---|
| Tetrachloroethylene | carbon sorption | 0.33 | 0.40 | 733 | 10 sites | Vermeulen (1997) |

N is the number of measurements.

Several different authorities in The Netherlands monitor PAH concentrations in air. Measurements by the provincial authority of Noord-Holland were taken near industrial sources and Schiphol airport, as well as at a background station in the middle of the province Noord-Holland (De Rijp). Measurements of the advisory environmental service Rijnmond (DCMR-milieudienst) were taken at urban locations in Rotterdam. The provincial authority of Zeeland measured at a remote site, though influenced by industrial sources (Nieuwdorp). The National Institute of Public Health and the Environment in The Netherlands took air samples mainly at urban sites, which are influenced by traffic. For this study only concentrations measured at De Rijp and Nieuwdorp were used (Table 3.4). The concentrations of the selected PAHs at Nieuwdorp with an industrial burden, is approximately 3 to 5 times higher. Sampling by the province of Noord-Holland was carried out with a high volume sampler (HVS) with a PM10 inlet.

*Table 3.4: Measured concentrations of PAHs in aerosols (Total Suspended particles) in 1991 and 1992 at regional sites in The Netherlands.*

| Chemical | Year/sampling technique | Average ng.m$^{-3}$ | Stdev ng.m$^{-3}$ | N | Location | Reference |
|---|---|---|---|---|---|---|
| Chrysene | 1991 (HVS) | 0.45 | 0.61 | 21 | De Rijp (Noord-Holland) | Van der Meij (1997) |
| Benzo[a]pyrene | 1991 (HVS) | 0.19 | 0.42 | 21 | De Rijp (Noord-Holland) | Van der Meij (1997) |
| Chrysene | 1992 (HVS) | 0.38 | 0.29 | 14 | De Rijp (Noord-Holland) | Van der Meij (1997) |
| Benzo[a]pyrene | 1992 (HVS) | 0.21 | 0.30 | 14 | De Rijp (Noord-Holland) | Van der Meij (1997) |
| Chrysene | 1992 | 1.54 | 1.98 | 50 | Nieuwdorp (Zeeland) | Vermeulen (1997) |
| Benzo[a]pyrene | 1992 | 0.54 | 0.66 | 50 | Nieuwdorp (Zeeland) | Vermeulen (1997) |

HVS stands for the High Volume Sampling technique, which measures Total Suspended Particles (TSP). N is the number of measurements.

The National Precipitation Chemistry Monitoring Network consisted of 14 stations in 1991. At all stations samples were analysed for main components and heavy metals. Additionally, at three stations samples were taken to be analysed for organic microcomponents like alpha-hexachlorocyclohexane, gamma-hexachlorocyclohexane, hexachlorobenzene and thirteen representatives from the group of polycyclic aromatic hydrocarbons.

The results of these three sampling stations are presented in Table 3.5 for the selected chemicals. Sample values below the limit of detection (LOD) were substituted with half the LOD. Rain samples were taken with wet-only collectors during a four-week period and concentrations in the free soluble phase as well as bound to aerosols were determined.

*Table 3.5: Measured concentrations of PAHs in rain in 1991 in The Netherlands.*

| **Chemical** | **Comp.** | **Median** $ng.l^{-1}$ | **Average** $ng.l^{-1}$ | **Stdev** $ng.l^{-1}$ | **Location** | **D** | **N** |
|---|---|---|---|---|---|---|---|
| Fluoranthene | aero | 24 | 28 | 32 | De Bilt (628) | 10 | 13 |
| Fluoranthene | solu | 57 | 103 | 105 | De Bilt (628) | 13 | 13 |
| Fluoranthene | aero | 16 | 27 | 25 | Leiduin (540) | 11 | 13 |
| Fluoranthene | solu | 40 | 76 | 75 | Leiduin (540) | 13 | 13 |
| Fluoranthene | aero | 32 | 70 | 113 | Rotterdam (434) | 11 | 13 |
| Fluoranthene | solu | 83 | 138 | 147 | Rotterdam (434) | 13 | 13 |
| Chrysene | aero | 19 | 22 | 23 | De Bilt (628) | 13 | 13 |
| Chrysene | solu | 14 | 23 | 24 | De Bilt (628) | 12 | 13 |
| Chrysene | aero | 14 | 21 | 20 | Leiduin (540) | 13 | 13 |
| Chrysene | solu | 15 | 22 | 20 | Leiduin (540) | 12 | 13 |
| Chrysene | aero | 24 | 55 | 79 | Rotterdam (434) | 13 | 13 |
| Chrysene | solu | 16 | 30 | 39 | Rotterdam (434) | 13 | 13 |
| Benzo[a]pyrene | aero | 11 | 12 | 8 | De Bilt (628) | 12 | 13 |
| Benzo[a]pyrene | solu | 2 | 2 | 2 | De Bilt (628) | 8 | 13 |
| Benzo[a]pyrene | aero | 10 | 15 | 13 | Leiduin (540) | 12 | 13 |
| Benzo[a]pyrene | solu | 2 | 3 | 2 | Leiduin (540) | 9 | 13 |
| Benzo[a]pyrene | aero | 17 | 30 | 40 | Rotterdam (434) | 12 | 13 |
| Benzo[a]pyrene | solu | 4 | 4 | 4 | Rotterdam (434) | 10 | 13 |

*Aben and Laan (1995).

Detection limits are 1 $ng.l^{-1}$ for B[a]p and 0.3 $ng.l^{-1}$ for chrysene in solution (solu) and for the fraction associated with aerosols (aero): 0.3 $ng.l^{-1}$ for fluoranthene. N is the number of measurements and D is the number of measurements above the detection limit.

For lindane rain samples were taken with open precipitation collectors. This means that both wet and dry deposition was measured. Four-weekly samples were taken. Again for pragmatic reasons values below the LOD were replaced with LOD/2 (Table 3.6).

*Table 3.6: Concentrations of lindane in precipitation in The Netherlands in 1991 and 1992*.*

| **Location, year** | **Comp.** | **D** | **N** | **Median** µg.l$^{-1}$ | **Average** µg.l$^{-1}$ | **Stdev** µg.l$^{-1}$ |
|---|---|---|---|---|---|---|
| De Bilt (628), 1991 | solu | 9 | 13 | 0.02 | 0.03 | 0.03 |
| Leiduin (540), 1991 | solu | 11 | 13 | 0.02 | 0.03 | 0.02 |
| Rotterdam (434), 1991 | solu | 13 | 13 | 0.02 | 0.04 | 0.03 |
| De Bilt (628), 1992 | solu | 13 | 13 | 0.02 | 0.05 | 0.09 |
| Leiduin (540), 1992 | solu | 13 | 13 | 0.02 | 0.06 | 0.09 |

* Buijsman and Stolk (1997A)

N is the number of measurements and D is the number of measurements above the detection limit.

The presence of pesticides in rainwater is studied in several research projects by provincial authorities and polder boards of which some of the results for lindane are presented in Table 3.7. We used the data for 1991 presented in Table 3.6.

*Table 3.7: Measured concentrations of lindane in precipitation in The Netherlands*.*

| **Location, year** | **D** | **N** | **DL** µg.l$^{-1}$ | **Average** µg.l$^{-1}$ | **Max** µg.l$^{-1}$ |
|---|---|---|---|---|---|
| Breda, 1988 | 2 | 3 | 0.001 | 0.0016 | 0.020 |
| Fleverwaard, 1990,1991 | 5 | 80 | 0.01 | 0.018 | 0.030 |
| Rijnland, 1988 | 36 | 36 | 0.01 | 0.14 | 0.68 |
| Westland, 1988, 1989 | 21 | 21 | 0.001 | 0.027 | 0.11 |
| Westland, 1990 | 3 | 3 | - | 0.016 | 0.021 |
| Zuid-Holland, 1991, 1992 | 65 | 65 | 0.001 | 0.041 | 0.24 |

*Teunissen-Ordelman et al. (1996)

DL is the detection limit, N is the number of measurements and D is the number of measurements above the detection limit.

## 3.5 Water data

Concentrations in water and sediment as well as suspended matter are obtained from the Institute for Inland Water Management and Waste-Water Treatment (RIZA) and the National Institute for Coastal and Marine Management (RIKZ) which under the commission of the Department of Public Works executes a monitoring program called Monitoring the Condition of State waters (MWTL).

Monitoring data concerning chemicals in fresh water and seawater (see also Van Meerendonk et al., 1994, Phernambucq et al., 1996) are stored in the DONAR-database. Data were also available from the AQUAview database (Dagelet and Puijenbroek, 1997) which contains water quality data from the RIWA (RIWA, 1994).

The IJsselmeer (Andijk) and Markermeer Haringvliet and other major watersystems like Westerschelde and the rivers Rhine and Meuse are selected as 'representative sites' for the concentration in fresh water in The Netherlands. In the fresh water samples 25% (chrysene) and 52% (lindane and benzo[a]pyrene) of the samples was below the detection limit, see Table 3.8. Several statistical procedures can be used to calculate average concentration and the standard deviation. In these cases Quantile-Quantile plots were used to derive the location parameter and the spread of the distribution (D'Agostino and Stephens, 1986*),* see Appendix IV.

*Table 3.8: Average concentrations of PAHs, lindane and tetrachloroethylene in major surface waters in The Netherlands, 1992*.*

| **Chemical** | **D** | **N** | **DL** $\mu g.l^{-1}$ | **Average** $\mu g.l^{-1}$ | **Stdev** $\mu g.l^{-1}$ |
|---|---|---|---|---|---|
| Fluoranthene | 224 | 271 | 0.006-0.02 | 0.037 | 0.036 |
| Chrysene | 53 | 70 | 0.01 | 0.019 | 0.014 |
| Benzo[a]pyrene | 112 | 213 | 0.004-0.01 | 0.017 | 0.064 |
| Lindane | 91 | 175 | 0.001-0.01 | 0.011 | 0.014 |
| Tetrachloroethylene | - | 135 | 0.01 | 0.273 | 0.117 |

*Dagelet and Puijenbroek (1997); RIWA yearly report (1993 and 1994) and RIZA yearbook (1996).

DL is the detection limit, N is the number of measurements and D is the number of measurements above the detection limit.

*Provinces and regional polder boards*

The coordination commission on the enforcement of the act on contamination of fresh surface waters in The Netherlands (CIW/CUWVO) makes an annual inventory (1992-1993) of the measurements performed by the water quality administrators. The data contain monitoring data of regional surface waters and the adjoining sediments. These data are under control of the RIZA-institute. For lindane a summary of these data is presented in Table 3.9 and 3.10. We used the results of Table 3.8, which are well in line with de data shown in Table 3.9 and 3.10

*Table 3.9: Measured concentrations of lindane in major surface waters in The Netherlands*.*

| **Location, year** | **D** | **N** | **DL** $\mu g.l^{-1}$ | **Average** $\mu g.l^{-1}$ | **Max** $\mu g.l^{-1}$ |
|---|---|---|---|---|---|
| IJsselmeer, 1992 | 2 | 5 | 0.001 | 0.02 | 0.02 |
| Hollands Diep, Haringvliet, 1992 | 16 | 23 | 0.001 | 0.019 | 0.08 |
| Oosterschelde, 1992 | 2 | 2 | 0.001 | 0.0085 | 0.014 |
| Overijsel, 1992 | 3 | 3 | 0.001 | 0.005 | 0.005 |
| meren, 1992 | 2 | 4 | 0.01 | 0.01 | 0.01 |
| rivieren, meren en plassen, 1993 | 37 | 107 | 0.001 | 0.004 | 0.05 |

*Teunissen-Ordelman et al. (1996).

DL is the detection limit, N is the number of measurements and D is the number of measurements above the detection limit.

*Table 3.10: Measured concentrations of lindane in regional surface water in The Netherlands*.*

| **Location, year** | **D** | **N** | **DL** µg.l$^{-1}$ | **Average** µg.l$^{-1}$ | **Max** µg.l$^{-1}$ |
|---|---|---|---|---|---|
| Groningen, 1992 | 88 | 140 | 0.002 | 0.007 | 0.114 |
| Groningen, 1993 | 228 | 296 | 0.002 | 0.0078 | 0.275 |
| Friesland, 1992 | 16 | 22 | 0.001 | 0.0029 | 0.012 |
| Friesland, 1993 | 35 | 36 | 0.0001 | 0.0016 | 0.0039 |
| Drenthe, 1992 | 57 | 60 | 0.001 | 0.007 | 0.035 |
| Drenthe, 1993 | 59 | 64 | 0.001 | 0.0049 | 0.017 |
| West-Overijssel, 1992 | 22 | 171 | 0.01 | 0.026 | 0.08 |
| West-Overijssel, 1993 | 9 | 41 | 0.01 | 0.106 | 0.72 |
| Regge en Dinkel, 1992 | 31 | 33 | 0.01 | 0.01 | 0.04 |
| Regge en Dinkel, 1993 | 33 | 42 | 0.001 | 0.028 | 0.302 |
| Oost-Gelderland, 1992 | 18 | 62 | 0.01 | 0.029 | 0.2 |
| Oost-Gelderland, 1993 | 6 | 51 | 0.01 | 0.062 | 0.20 |
| Amstel en Gooiland, 1992 | 93 | 96 | 0.001 | 0.008 | 0.033 |
| Amstel en Gooiland, 1993 | 76 | 108 | 0.001 | 0.013 | 0.09 |
| Uitwaterende sluizen, 1992 | 3 | 70 | 0.01 | 0.013 | 0.02 |
| Uitwaterende sluizen, 1993 | 5 | 143 | 0.01 | 0.016 | 0.03 |
| Rijnland, 1992 | 54 | 87 | 0.001 | 0.017 | 0.20 |
| Rijnland, 1993 | 185 | 189 | 0.001 | 0.006 | 0.025 |
| Delfland, 1992 | 308 | 312 | 0.001 | 0.025 | 0.47 |
| Delfland, 1993 | 277 | 289 | 0.001 | 0.012 | 0.59 |
| Schieland, 1992 | 53 | 53 | 0.001 | 0.011 | 0.11 |
| Schieland, 1993 | 40 | 40 | 0.001 | 0.0048 | 0.015 |
| Hollandse Eilanden en Waarden, 1992 | 5 | 18 | 0.01 | 0.044 | 0.08 |
| Hollandse Eilanden en Waarden, 1993 | 1 | 18 | 0.01 | 0.12 | 0.12 |
| West-Brabant, 1992 | 73 | 98 | 0.001 | 0.018 | 0.2 |
| West-Brabant, 1993 | 341 | 392 | 0.001 | 0.011 | 0.25 |
| WS de Dommel, 1992 | 1 | 40 | 0.01 | 0.01 | 0.01 |
| Limburg, 1992 | 225 | 299 | 0.005 | 0.028 | 0.43 |
| Limburg, 1993 | 221 | 232 | 0.0005 | 0.018 | 1.2 |
| Rivierenland, 1992 | 5 | 9 | 0.005 | 0.029 | 0.045 |
| Veluwe, 1993 | 7 | 7 | 0.01 | 0.011 | 0.020 |

*Teunissen-Ordelman et al. (1996).

DL is the detection limit, N is the number of measurements and D is the number of measurements above the detection limit.

*Suspended matter and sediment*

Sediment monitoring data are available from five different sites, which are sampled once a year. Sediment concentrations are expressed on a dry weight basis (Table 3.11).

*Table 3.11: Measured concentrations of PAHs in sediments [$\mu$g.kg$^{-1}$(dry)] of major and regional surface waters in The Netherlands*.*

| **Chemical** | **Average** mg.kg$^{-1}$ (dry). | **Stdev** | **N** | **D** |
|---|---|---|---|---|
| Fluoranthene | 1.08 | 1.23 | 6 | 5 |
| Chrysene | 0.49 | 0.52 | 6 | 5 |
| Benzo[a]pyrene | 0.59 | 0.63 | 6 | 5 |
| Lindane | <0.001 | - | 44 | 0 |

*RIZA, Yearbook (1995).

N is the number of measurements and D is the number of measurements above the detection limit.

Concentrations in suspended matter are monitored on a more regular basis through out a year. Average concentrations for the major surface waters in The Netherlands are presented in Table 3.12

*Table 3.12:* M*easured concentrations of PAHs in suspended solids [$\mu$g.kg$^{-1}$(dry)] in major surface waters in The Netherlands in 1992*.*

| **Chemical** | **Average** mg.kg$^{-1}$ (dry) | **Stdev** | **N** | **D** |
|---|---|---|---|---|
| Fluoranthene | 1.33 | 1.33 | 93 | 87 |
| Chrysene | 0.68 | 0.56 | 92 | 91 |
| Benzo[a]pyrene | 0.73 | 0.68 | 93 | 91 |
| Lindane | 0.002 | 0.003 | 97 | 81 |

*RIZA, DONAR-data base.

N is the number of measurements and D is the number of measurements above the detection limit.

## 3.6 Soil quality data

Concentrations in the soil are measured in the Dutch National Soil Quality Monitoring Network (LMB). The network is one of the responsibilities of the Laboratory of Soil and Groundwater Research at the National Institute of Public Health and the Environment. Soil and Groundwater quality assessment in The Netherlands for different combinations of soil use (grassland, arable land, forest soils) and soil types (sand, fluvial and marine clay, peat and loam) is one of their main objectives. Concentration data on PAHs, PCBs (Appendix III), pesticides and heavy metals for agriculturally used soils and natural soils in 1992, 1993 and 1994 are available (Lagas and Groot, 1996; Groot and van Swinderen, 1993 and Groot et al., 1996). Average concentrations and standard deviations of selected chemicals for different agricultural soil uses are summarised in Table 3.13.

*Table 3.13: Measured concentrations of PAHs and lindane [$\mu$g.kg$^{-1}$(dry)] in top level (10 cm) of agricultural soils in The Netherlands in 1992 *.*

| Chemical | Grassland | | Arable land | | Maize culture | | Bulb growing | | Fruit culture | |
|---|---|---|---|---|---|---|---|---|---|---|
| | avg | std | avg | std | avg | std | avg | std | avg | std |
| Lindane | 0.64 | 0.36 | 0.80 | 0.66 | 1.28 | 0.86 | 0.17 | - | 0.30 | - |
| Chrysene | 64 | 71 | 20 | 9 | 25 | 20 | 13 | - | 96 | - |
| Pyrene | 96 | 124 | 29 | 14 | 35 | 30 | 17 | - | 142 | - |
| Benzo[a]pyrene | 56 | 68 | 16 | 8 | 19 | 15 | 8 | - | 60 | - |

*Lagas and Groot (1996).

## 3.7 Summary

The data from the various monitoring networks in The Netherlands provided concentration data for five substances to construct concentration ratios for adjoining compartments which, are assumed to be representative for The Netherlands. Air(aerosol)-water concentration ratios can be deduced from data on benzo[a]pyrene, pyrene and tetrachloroethylene (tetra). Rain-water concentration ratios can be derived from data on benzo[a]pyrene, fluoranthene, pyrene and lindane. Data about lindane and benzo[a]pyrene, fluoranthene and pyrene also could be used to derive water-sediment and water-suspended matter concentration ratios. Air(aerosol)-soil concentration ratios can be estimated for benzo[a]pyrene and pyrene and rain-soil concentration ratios can be derived for benzo[a]pyrene, fluoranthene, pyrene and lindane. The data are summarised in Table 3.14.

*Table 3.14: Measured concentrations of selected compounds used in validation procedure.*

| | | | measured concentrations | | |
|---|---|---|---|---|---|
| **substance** | **compartment** | **units** | **average** | **median** | **stdev** |
| Tetrachloroethylene | water | µg.l$^{-1}$ | 0.273 | 0.185 | 0.413 |
| | air | µg.m$^{-3}$ | 0.331 | 0.220 | 0.399 |
| Lindane | rainwater | µg.l$^{-1}$ | 0.055 | 0.020 | 0.094 |
| | freshwater | µg.l$^{-1}$ | 0.011 | 0.005 | 0.014 |
| | sediment | µg.kg$^{-1}$(dry) | < 1.00 | - | - |
| | suspended matter | µg.kg$^{-1}$(dry) | 2.19 | 1.00 | 2.85 |
| | agricultural soil | µg.kg$^{-1}$(dry) | 0.67 | 0.55 | 0.45 |
| Benzo[a]pyrene | aerosols | ng.m$^{-3}$ | 0.38 | 0.21 | 0.55 |
| | rainwater | ng.l$^{-1}$ | 22.8 | 13.8 | 27.0 |
| | freshwater | µg.l$^{-1}$ | 0.017 | 0.008 | 0.064 |
| | sediment | mg.kg$^{-1}$(dry) | 0.59 | 0.45 | 0.63 |
| | suspended matter | mg.kg$^{-1}$(dry) | 0.73 | 0.60 | 0.68 |
| | agricultural soil | µg.kg$^{-1}$(dry) | 40.8 | 22.0 | 57.1 |
| Chrysene | aerosols | ng.m$^{-3}$ | 0.96 | 0.48 | 1.49 |
| | rainwater | ng.l$^{-1}$ | 58.8 | 31.0 | 70.5 |
| | freshwater | µg.l$^{-1}$ | 0.018 | 0.010 | 0.014 |
| | sediment | mg.kg$^{-1}$(dry) | 0.49 | 0.35 | 0.53 |
| | suspended matter | mg.kg$^{-1}$(dry) | 0.68 | 0.50 | 0.56 |
| | agricultural soil | µg.kg$^{-1}$(dry) | 51.9 | 31.9 | 60.5 |
| Fluoranthene | aerosols | ng.m$^{-3}$ | | | |
| | rainwater | ng.l$^{-1}$ | 147 | 95 | 172 |
| | freshwater | µg.l$^{-1}$ | 0.037 | 0.026 | 0.036 |
| | sediment | mg.kg$^{-1}$(dry) | 1.07 | 0.70 | 1.22 |
| | suspended matter | mg.kg$^{-1}$(dry) | 1.33 | 1.10 | 1.32 |
| | agricultural soil | µg.kg$^{-1}$(dry) | 112 | 60 | 152 |

# 4. MODELLING

## 4.1 Introduction

SimpleBox version 2.0 was used for the calculation of the probability distributions of steady-state concentration ratios. The SimpleBox settings must be adjusted to simulate the environment in which the measurements are carried out. The various sources and types of uncertainty and the specific settings of both SimpleBox and the Monte Carlo simulation - which will be performed to examine the range of the SSCRs- are presented in this chapter.

## 4.2 Monte Carlo Simulations

Monte Carlo simulation is a useful tool to get insight in the uncertainties of the steady state concentration calculations of SimpleBox. The Monte Carlo simulation is performed with Crystal Ball, an add-in for Microsoft Excel (Decisioneering, 1993). This method samples values of the input parameters at random from the probability distribution for each input parameter (sampling method: Latin hypercube).

## 4.3 Variability and uncertainty

In this research we considered both uncertainty due to empirical inaccuracy, lack of data and uncertainty due to temporal variability. Spatial variability cannot be applied simply because spatial variability is not modelled within SimpleBox. The boxes within SimpleBox are considered to be homogeneous, so one value of a parameter is valid for the entire box. Uncertainty due to temporal variability is operational. Since an average over a box may vary in time.

Model domain parameters may vary temporally. For example, mixing height of air and mean water depth are model domain parameters but have no domain scenario uncertainty since they are well defined, but still uncertain due to unavoidable empirical uncertainty and lack of data. Uncertainty due to lack of data may be explained by estimating a value and an uncertainty factor or a range in case there are not enough data.

We assumed that the variability in the model estimates is the result of the uncertainty in selected input parameters, due to:

- empirical inaccuracy with respect to substance properties
- inaccurate information on emissions
- lack of data and temporal variability with respect to model domain parameters as mixing height of air and water depth. Meteorological data and other data that describe the environment (e.g. windspeed and rainfall) are represented as variable parameters.
- lack of knowledge about interactions between the substance and its environment

These uncertainties are thought to propagate, causing uncertainty in the model output.

Information on the distribution types for the different environmental settings etc. is extracted from the sensitivity/uncertainty analysis of SimpleBox by Etienne et al. (1997), see Table 4.2. The distributions are defined by assigning a type of distribution, normal, lognormal triangular etc. and specific distribution parameters. Depending on the importance of its influence on the model output and the availability of data it is required to define the right distribution. The final result is a probability distribution (= output uncertainty) of the SSCR which will be compared with the distribution of concentration ratios, which were derived from measured concentrations at various locations over The Netherlands over one or two years.

## 4.4 Model settings for The Netherlands

The SimpleBox 2.0 defaults of the regional scale simulate a typical Western-European region. The model parameters are adjusted to model The Netherlands. In this case, we have decided that the dimensions of the system (The Netherlands) are not subject to Monte Carlo sampling. Thus, the system area and area fractions are part of the scenario. Table 4.1 gives the scenario assumptions for this validation study. We made three exceptions: mixing height of air, the depth of the fresh surface water compartment and the depth of the soil compartments. The mixing height of air and the depth of the fresh surface water compartment have a large influence on the model output as was shown by Etienne et al. (1997). The mixing height of air and the depth of the water compartment determine the volume of the air and fresh surface water compartment, respectively. The mixing height varies temporally, it shows daily and seasonal variation. For water depth typical representative values were used based on what can be found for real water systems. The depth of the soil compartment is calculated from the chemical specific penetration depth (Brandes et al., 1996; Cowan et al. 1995). The vegetation compartment was turned off during the model calculations.

The time scale for temporally varying parameters as *WINDspeed*, mixing layer height, and *TEMPERATURE* is set to 24 hours-daily average values were taken. For the *RAINRATE* monthly average values typical for The Netherlands were applied. This is believed to be more appropriate concerning the sampling duration. Other distributions are chosen based on expert judgement of the authors.

*Table 4.1: Scenario assumptions.*

| Parameter name | Unit | Regional |
|---|---|---|
| *SYSTEMAREA* | km$^2$ | 84,000* |
| *Area fresh water* | km$^2$ | 4,200 (5%) |
| *Area sea water* | km$^2$ | 42,000 (50%) |
| *Area natural soil* | km$^2$ | 16,800 (20%) |
| *Area agricultural soil* | km$^2$ | 20,200 (24%) |
| *Area urban soil* | km$^2$ | 840 (1%) |
| *Depth sea water* | m | 25 |
| *Average residence time sea water* | d | 76 |

*The area soil + area fresh water in The Netherlands is 50% of the total SYSTEMAREA, the other fraction is sea water.

- *Chemical dependent penetration depth in soils*

Introducing the chemical dependent penetration depth gives a more accurate estimate of the exchange between the soil compartment and the air compartment. Within SimpleBox 2.0 (Brandes et al., 1996) the diffusion coefficients have default values of $11 \cdot 10^{-6}$ and $11 \cdot 10^{-10}$ [m$^2$.s$^{-1}$] for soil air and water, respectively. They are used for the calculating the chemical dependent penetration depth for soils. It is thought to be more accurate to make the diffusion coefficients in air and water substance dependent, although no sensitivity analysis was performed.

- *Tropospheric OH-radical concentration*

For most substances reaction with hydroxyl radicals is the major atmospheric removal pathway although transformation pathways like reaction with ozone and the night-time reaction with nitrate-radicals also contribute. Hydroxyl radical reaction rate constants are used in estimating the atmospheric degradation. These reaction rate constants are calculated by the contribution method by Atkinson (Atkinson, 1988) and were reported by Howard (1991b). The atmospheric degradation based on hydroxyl radical reaction rate is not only dependent on atmospheric hydroxyl radical concentrations, which vary seasonally as will be shown below, but is also temperature dependent. Because of lack of data on the substances we studied, we use as an approximation the rule of thumb known as Van ‘t Hoff’s law.
It states that in general the reaction rate lowers by half, respectively doubles with every 10 degrees of temperature drop or rise. Reaction rates estimated by Atkinson’s method refer to room temperature (25 °C).

Atmospheric hydroxyl radical concentrations change daily and seasonally. Hydroxyl radicals are generated by atmospheric photochemical reactions, hence the daily and seasonal changes result from the intensity of the solar radiation which reaches the earth (troposphere). Consequently atmospheric hydroxyl concentrations drop to zero at night. Hydroxyl radical concentrations differ by latitude, concentrations in the tropic regions are generally higher than atmospheric concentrations at the Northern or Southern part of the hemisphere. Many studies were aimed at measuring tropospheric hydroxyl radical concentrations. An overview is given by Hewitt and Harrison (1985) and GDC (1992). In addition to these measurements several models (Lu and Khalil, 1991; Perner et al., 1987 and Crutzen and Gidel, 1983) have been developed to predict tropospheric hydroxyl radical concentrations. From these measuring results and model predictions, monthly 24-hour average tropospheric hydroxyl radical concentrations at the Northern hemisphere are derived. A custom distribution function with continuous ranges is used to model the monthly variation of the tropospheric hydroxyl radical concentration. Characteristics of the custom distribution of hydroxyl radicals are reported in Appendix V.

- *Correlations*

The parameter *TEMPERATURE* on the regional and continental spatial scale is assumed to correlated with a correlation coefficient of 0.9. Similarly, the degradation half-lives in the compartments of the spatial scales are correlated with a correlation coefficient of 0.9. *WINDspeed* and $HEIGHT_{\mathrm{air}}$ are also correlated with a correlation coefficient of 0.85 (Etienne et al., 1997).

*Table 4.2: Characteristics of the probability distributions of non-compound-specific input parameters.*

| Parameter name | Unit | Distribution | Mean (L)<br>Mode (T)<br>Value (C)<br>Scale (W) | St. Dev. (L)<br>Range min. (T,C)<br>Location (W) | Range max. (T,C)<br>Shape (W) | Source/ Remarks |
|---|---|---|---|---|---|---|
| *CORG*$_{\text{susp i}}$ | %C | L | 10 | 4 | | |
| *SUSP*$_{\text{water 1 [R]}}$ | mg.l$^{-1}$ | L | 24.4 | 23.5 | | |
| *SUSP*$_{\text{water 2 [R]}}$ | mg.l$^{-1}$ | L | 5 | 4 | | |
| *FAT*$_{\text{fish i}}$ | % | L | 5 | 4 | | |
| *BIO*$_{\text{water i}}$ | mg.l$^{-1}$ | T | 1 | 0.1 | 10 | |
| *CORG*$_{\text{sed i}}$ | %C | L | 5 | 4 | | |
| *CORG*$_{\text{soil i}}$ | %C | L | 5 | 4 | | |
| *TEMPERATURE* [R] | $^0$C | C | 10 | -5 | 30 | Corr. 0.9 |
| *TEMPERATURE* [C] | $^0$C | C | 10 | -5 | 30 | Corr. 0.9 |
| *Depth*$_{\text{water 1}}$ | m | W | 3 | 2 | 15 | |
| *Flow*$_{\text{water 1[C]-water 1 [R]}}$ | m$^3$. s$^{-1}$ | L | 2247 | 887 | | DGW (1993) |
| *Flow*$_{\text{water 1[C]-water 2 [R]}}$ | m$^3$. s$^{-1}$ | L | 212 | 86 | | |
| *HEIGHT*$_{\text{air}}$ | m | C | 400 | 77 | 1138 | Corr. 0.85 |
| *OH*$_{\text{air}}$ | molecules.cm$^{-3}$ | C | 1. 10$^6$ | 8.10$^5$ | 1.3.10$^6$ | |
| *Depth*$_{\text{sed i}}$ | cm | T | 3 | 1 | 10 | |
| *FRwater*$_{\text{sed i}}$ | - | T | 0.8 | 0.5 | 0.999 | |
| *Depth*$_{\text{soil i (i=1,2,3)}}$ | cm | 3≤calc.≤100 | | | | |
| *FRwater*$_{\text{soil i}}$ | - | T | 0.20 | 0.003 | 0.67 | |
| *FRsolid*$_{\text{soil i}}$ | - | T | 0.60 | 0.30 | 0.95 | |
| *RHOsolid* i | kg.m$^{-3}$ | T | 2500 | 2000 | 3000 | |
| *WINDspeed* | m.s$^{-1}$ | C | 5 | 1.65 | 13.6 | Corr. 0.85 |
| *AEROSOLdeprate* | cm.s$^{-1}$ | L | 0.1 | 0.1 | | |
| *RAINrate* | mm.d$^{-1}$ | C | 2.03 | 0.02 | 6.59 | |
| *COLLECTeff* | - | T | 20000 | 5000 | 35000 | |
| *kasl(soilair)* | m.s$^{-1}$ | T | 5.56·10$^{-6}$ | /3 | *3 | |
| *kasl(soilwater)* | m.s$^{-1}$ | T | 5.56·10$^{-10}$ | /3 | *3 | |
| *SETTLvelocity* | m$_{\text{water}}$.s$^{-1}$ | T | 2.89·10$^{-6}$ | 3.0·10$^{-6}$ | 3.0·10$^{-5}$ | |
| *SUSPeff*$_{\text{stp}}$ | mg.l$^{-1}$ | T | 30 | 25 | 35 | |
| *PRODsusp 1* | g(d).m$^{-2}$.y$^{-1}$ | T | 10 | 5 | 20 | |
| *PRODsusp 2* | g(d).m$^{-2}$.y$^{-1}$ | T | 1 | 0.5 | 2 | |
| *kws(water)* | m.s$^{-1}$ | T | 2.78·10$^{-6}$ | /3 | *3 | |
| *kws(sed)* | m.s$^{-1}$ | T | 2.78·10$^{-8}$ | /3 | *3 | |
| *EROSION*$_{\text{soil i}}$ | m(soil).s$^{-1}$ | T | 0.03 | 0 | 0.06 | |
| *FRACrun*$_{\text{soil i-water 1}}$ (=y) | - | T | 0.25 | 0 | 0.5 | |
| *FRACinf*$_{\text{soil i}}$ (=1-y) | - | T | 0.25 | 0 | 0.5 | |
| *CONSTTHETA* | Pa | L | ln(1·10$^{-4}$) | ln(10) | | |
| *PROPCONSTKocKow* | - | T | 0.41 | 0.3 | 1 | |

The distributions are indicated as **N**ormal, **L**ognormal, **T**riangular, **W**eibull and **C**ustom. The various distributions are characterised by different parameters: Normal and Lognormal by the mean and a standard deviation, triangular by mode and range etcetera.

## 4.5 Chemical compound properties

Chemical properties of the selected chemicals (physical-chemical properties and degradation rates) are obtained from different literature sources. Most common sources of chemical properties are:

*Table 4.3: Common sources of chemical properties.*

| Handbooks: | Data bases: |
|---|---|
| 1. EurEco (1990) | A. NIST (1997) |
| 2. BUA (1992) | B. ARS (1995) |
| 3. Howard (1989a, 1989b, 1993) | C. CS (1996) |
| 4. Howard et al. (1991a) | D. Enviro-Net (1996) |
| 5. Howard et al. (1991b) | E. ERL (1994) |
| 6. Lide (1996) | F. JRC (1996a, 1996b) |
| 7. Mackay et al. (1992a, 1992b, 1992c, 1995) | G. MedChem (1996) |
| 8. Verschueren (1983) | H. SCR (1993) |
| 9. Tomlin (1994) | I. University of Akron (1996) |
|  | J. US EPA (1996a) |
|  | K. Beilstein (1996) |
|  | L. US EPA (1996b;1996c), US EPA and SRC (1996) |

Four new parameters are added to the model compared to SimpleBox version 2.0; $K_{oc}$, Half-life, *CONSTTHETA* and *PROPCONSTK*$_{oc}$*K*$_{ow}$ as suggested by Etienne et al. (1997). Henry's law constant was calculated from the solubility and vapour pressure because of the lack of data for the substances we studied. Finally log $K_{ow}$ and *SOLUBILITY* are correlated with a correlation coefficient of -0.85.

The distributions for $K_{ow}$, $K_{oc}$, *VAPOR PRESSURE*, *SOLUBILITY* and *MELTINGPOINT* are mostly composed of data in Mackay et al. (1992). Distributions of half-lives are derived from Howard et al. (1991b), which offered low and high estimations, and Mackay et al. (1992). Data on tetrachloroethylene are largely taken from Etienne et al. (1997) and data on lindane are from various sources, see Table 4.4.

*Hydroxyl radical reaction rates*

Hydroxyl radical reaction rates can be calculated using several methods (Rorije et al., 1997). Our data are based on Atkinson's method, which also provides fragment contribution schemes for ozone and nitrate radicals. For the compounds considered in this study, reaction with ozone and nitrate radicals is not of concern. Hydroxyl reaction rate constants were reported by Howard (1991b).

A triangular distribution was used to model the uncertainty in the estimated hydroxyl radical reaction rate. Atkinson (1988) gave an estimate of the uncertainty in calculated reaction rates for alkanes, alkenes etc. aromatic compounds and oxygen-containing compounds. A comparison of the calculated and experimental room temperature rate constants showed that for 18 out of 270 compounds the rate constants disagree by more than a factor 2. So, 94% of the calculated reaction rates are within a factor of two of the experimental rates.

From other studies it was shown that this might be a factor of three for the majority of the compounds (Rorije et al., 1997). Large deviations may occur for several chemical classes:

perhalogenated compounds, phosphates, small heterocyclic rings, nitroalkanes and aromatics which are not benzene derivatives (Rorije, 1997). Because the substances we studied do not belong to these chemical classes we used the uncertainty factor of 2.

- *Diffusion coefficients*

Diffusion coefficients in air and water may be calculated from several empirical or theoretical relationships (Reid et al., 1988). Diffusion coefficients in air are calculated from empirical correlations for binary gas systems at low pressures following the methods known as Wilke-Lee method and the method by Fuller and co-workers. Binary liquid diffusion coefficients at infinite dilution are calculated by the Wilke-Chang estimation method and Hayduk-Minhas correlations (Reid et al., 1988).

The uncertainty in these methods can be estimated by comparing calculated values with measurements. Doing this for air and water systems results in uncertainties of a few percent, usually 3 to 10 percent error. Differences between methods are of the same magnitude (10-15%). The uncertainty in diffusion coefficients is described by a triangular distribution using the results of the estimation methods as minimum and maximum values.

- *Enthalpy of solution and vaporisation*

Enthalpies of solution are generally calculated from experimentally measured solubilities at various temperatures. The enthalpy of solution can then be estimated from so called Van 't Hoff's plots using linear regression. Enthalpies of solution of polycyclic aromatic hydrocarbons in aqueous solutions were estimated by May and Wasik (1978), Schwarz (1977) and Wauchope and Getzen (1972). We used the most recent solubility data in the temperature range of 5-30 °C from May and Wasik (1978) because we believe the most recent data are the most accurate. The uncertainty in the estimated values can be obtained from regression statistics and we assumed a normal distribution.

The heat of solution of lindane is calculated from solubility data at various temperatures provided by Dannenfelser and Yalkowsky (1991) in the temperature range of 15 to 45 °C, using the same method as described above.

The heat of vaporisation can be estimated according to the same method, using measured vapour pressures at various temperatures instead. We used the most recent data on the heat of sublimation, which were provided by Sonnefeld et al. (1983) and NIST (1997). The uncertainty in the heat of sublimation is described by a normal distribution.

The heat of volatilisation is calculated from the heat of solution and the heat of sublimation providing the heat of solution and the heat of sublimation refer to the same physical state, e.g., solid or liquid. Consequently the uncertainty in the heat of volatilisation is normally distributed. The data on the heat of volatilisation obtained in this way correspond with the measured values (Ten Hulscher et al., 1992).

*Table 4.4: Characteristics of compound-specific parameters.*

| Parameter name | Unit | Distri-bution | Compound γ-HCH | Fluoranthene | Chrysene | Benzo[a]pyrene | Tetrachloroethylene | Source/ Remarks |
|---|---|---|---|---|---|---|---|---|
| CAS Registry Number | | | 58-89-9 | 206-44-0 | 218-01-9 | 50-32-8 | 127-18-4 | |
| *MOLWEIGHT* | $g.mol^{-1}$ | - | 290.85 | 202.26 | 228.29 | 252.32 | 165.82 | 6,7,9 |
| log *Kow* | $\log(m_{wat}^3.m_{oct}^{-3})$ | T | 3.72 [3.2;3.85] | 5.16 [4.7;6.5] | 5.73 [5.01;7.10] | 5.97 [4.05;8.5] | 3.4 [2.39;3.78] | 3,7,abcdnG Corr.-0.85 |
| log *Koc* | $\log(l_{water}.kg_{carbon}^{-1})$ | T/N | 3.1 [2.8;4.1] | 5.36 [4.00;6.38] | 5.72 [4.0;6.9] | 6.3 [4;8.3] | 2.38 [1.81;4.03] | 3,7acdnB |
| *VAPOR PRESSURE* | Pa | T | 3.63E-3 [1.20E-3;5.60E-3] | 1.24E-3 [1.65E-4;9.92E-1] | 1.50E-6 [5.70E-7;4.00E-6] | 5.71E-7 [8.53E-10;1.22E-5] | 2500 [2100;2666] | 7,9acdnB |
| $\Delta H_{vaporisation}$ | $kJ.mol^{-1}$ | N | 106.6; 0.9 | 84.6; 0.9 | 118; 1 | 118.3; 2.2 | 34.7; 0.8 | eA |
| *SOLUBILITY* | $mg.l^{-1}$ | T | 7.3 [6.6;17] | 0.255 [0.119;1.430] | 2.4E-3 [1.0E-3;6.9E-3] | 2.73E-3 [1.74E-4;1.09E-2] | 150 [117;489] | 7,8,9abcdln B |
| $\Delta H_{solution}$ | $kJ.mol^{-1}$ | N | 49.1; 9.6 | 39.83; 1.59 | 41.25; 1.00 | 79.3; 7.2 | 34.17 | gh |
| *H* | $Pa.m^3.mol^{-1}$ | calc. (T) | | | | | | |
| $\Delta H_{volatalisation}$ | $kJ.mol^{-1}$ | calc. (N) | | | | 39;7 | 0.53; 0.03 | fo |
| *MELTINGPOINT* | °C | T | 112.5 [112;113] | 109 [107;111] | 254[252;256] | 176.5 [175;179] | -22 [-22.7;-19] | 6,7,8,9bB |
| $D_{air}$ | $m^2.s^{-1}$ | T | 6.0E-6 [5.38E-6;6.6E-6] | 6.01E-6 [5.06E-6;6.97E-6] | 5.51E-6 [4.72E-6;6.31E-6] | 5.27E-6 [4.47E-6;6.06E-6] | 1.07E-5 [1.01E-5;1.13E-5] | j (calc.) |
| $D_{water}$ | $m^2.s^{-1}$ | T | 5.48e-10 [4.8E-10;6.15E-10] | 5.99E-10 [5.40E-10;6.57E-10] | 5.32E-10 [4.62E-10;6.02E-10] | 5.12E-10 [4.38E-10;5.85E-10] | 8.7E-10 [8.4E-10;9.01E-10] | j (calc.) |
| $K_{OH}$ | $cm^3.molecules^{-1}.s^{-1}$ | T | 6.95E-12 [3.47E-12;1.39E-11] | 3.18E-11 [1.59E-11;6.37E-11] | 8.00E-11 [4.00E-11;1.60E-10] | 1.5E-10 [7.5E-11;3E-10] | 1.67E-13 [8.36E-14;3.34E-13] | 5,7m |
| *Half-life* $_{water}$ | days | T | 54 [12;240] | 150 [140;160] | 70 [13;372] | 14 [3;57] | 270 [180;360] | 5,7abcdk |
| *Half-life* $_{sediment}$ | days | T | 49 [6;413] | 580 [280;880] | 1218 [742;2000] | 491 [114;2118] | 402 [98;1653] | 5,7abcd |
| *Half-life* $_{soil}$ | days | T | 130 [12;1406] | 290 [140;440] | 609 [224;993] | 174 [57;529] | 270 [180;360] | 5,7abcd |

For triangular distributions (T) the location parameter is given together with the mininum and maximum value, which is given between brackets. The Normal distribution (N) is characterised by the location parameter (median, average) and the standard deviation.

a. Linders (1994)
b. Slooff (1988)
c. Theunissen-Ordelman (1995)
d. Theunissen-Ordelman (1996)
e. Sonnefeld et al. (1983)
f. Ten Hulscher et al. (1992)
g. May and Wasik (1972)
h. Dannenfelser and Yalkowsky (1991)
i. Russom et al. (1991)
j. Reid (1988)
k. Zepp and Schlotzhauer (1979)
l. Jacobs (1996)
m. Atkinson (1988)
n. Etienne et al. (1997)
o. Ashworth (1988)

## 4.6 Emissions

Emission ratios between water, soil and air are based on expert judgement of the Laboratory for Waste Materials and Emissions of the RIVM (Wesselink and Van der Poel, 1997), emission estimates from Integrated Criteria documents (Slooff and Matthijsen, 1988 and Slooff et al., 1989) and Registration (Berdowski et al., 1994 and Draaijers et al., 1997), see Table 4.5.

*Table 4.5: emissions estimates for The Netherlands per compartment.*

| Chemical | Main Application/ Sources | Emission to compartment | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Air | | | Water | | | Soil$^{2}$ | | |
| | | *a* | *b* | *c* | *a* | *b* | *c* | *a* | *b* | *c* |
| γ-HCH | insecticide | | 10% | | | | | 100%$^{3}$ | 90%$^{3}$ | |
| Fluoranthene | creosoting/burning | 75% | 85% | 87% | 10%$^{1}$ | 5% | 6% | 15% | 10% | 7% |
| Chrysene | creosoting/burning | 81% | 60% | | 7% | 15% | | 12% | 25% | |
| Benzo[a]pyrene | creosoting/burning | 60% | 65% | 68% | 30%$^{1}$ | 10% | 32% | 10% | 25% | |
| Tetrachloroethylene | solvent | 100% | 99.7% | | | 0.3% | | | | |

[1] emission to surface water (direct sources) and emissions resulting from effluents of sewage water treatment plants

[2] emission to natural, agricultural and urban or industrially used soil

[3] emission to agricultural used soil

Estimates are based on registration (a); integrated criteria documents (b) and (c) RIVM (1996).

### *Transboundary emissions*

Transport across the boundaries of The Netherlands may to a large extend contribute to the emissions in The Netherlands. Two studies (Thijssen, 1985 and Slooff et al., 1989) indicate that atmospheric import of PAHs may contribute up to 30-80% to the total atmospheric emissions in The Netherlands for lower and higher PAHs respectively, see also Table 4.7. The transboundary contributions for lindane and tetrachloroethylene are calculated by SimpleBox by taking the European region (EU-15) as continental scale and using consumption estimates of lindane for the European Community, because there are no other data to quantify import by advective transport via the air compartment for these substances. Transport of the chemical with air and water across the boundaries of the regional scale (The Netherlands) in SimpleBox is calculated from the rate of air and water flow from the continental scale multiplied with the corresponding concentration. The consumption of lindane in the European union was estimated to be 1044 tonnes.year$^{-1}$ (excl. The Netherlands) (Bakker, 1997; Klepper, 1997). EU-15 emission estimates for tetrachloroethylene are taken from EU RAR (2001). Tetrachloroethylene emissions to air and water for The Netherlands in 1993 are 2380 and 15.1 tonnes, respectively as reported by Berdowski et al. (1995).

The amount of PAHs that is imported by the rivers Rhine and Meuse, into The Netherlands and their contribution to the total water emissions was estimated from concentration profiles and water flows in the Rhine and Meuse in 1993. Monthly average concentrations are calculated using concentration data from the water works (RIWA, 1994; Dagelet and Puijenbroek, 1997). River flows are based on average 24 hour values which were used to calculate monthly average river flows (RIKZ, 1994). Combining the monthly average concentrations with the monthly average flows provides monthly averaged loads, which were added for benzo[a]pyrene, fluoranthene and chrysene. The 1993 figures are used to calculate the contribution of rivers to the emissions to fresh surface waters in 1994 (Draaijers, 1997) because few concentration data for 1994 were available. The bias caused by comparing 1993 river loads with 1994 emissions is expected to be small because yearly average concentrations are rather constant in the period of 1992-1995 (RIZA, 1996). From these calculations appears that the rivers Rhine and Meuse contribute approximately 25-45% to the total emission of fluoranthene and benzo[a]pyrene to the Dutch fresh surface waters, respectively (Table 4.6). Calculations by Berdowski et al. (1994) for the sum of the six PAHs of Borneff (25%) support these estimates. Comparing the calculated river loads with the 1993 emission estimates by RIVM (1996) results in contributions of 30-35% to the total emissions to fresh surface waters in The Netherlands for fluoranthene and benzo[a]pyrene, respectively. For chrysene the contribution was estimated to be higher, 65%.

*Table 4.6: The contribution to total emissions to fresh surface water in The Netherlands through border crossing river inputs (ton/year).*

| Load | Benzo[a]pyrene | Fluoranthene | Chrysene |
|---|---|---|---|
| Rhine | 1.4 | 3.2 | 1.3 |
| Meuse | 0.2 | 0.6 | 0.5 |
| Total rivers | 1.6 | 4.8 | 2.4 |
| Emission to water | 2.09 | 13.9 | 1.3 |
| Contribution rivers | 43% | 26% | 65% |

*Table 4.7: Import by rivers and atmospheric transport.*

| Chemical | Rivers | | Air | |
|---|---|---|---|---|
| | *a* | *b* | *b* | *c* |
| Fluoranthene | 25% | 80% | 50% | 30% |
| Chrysene | 65% | 80% | 75% | 85% |
| Benzo[a]pyrene | 40% | 88% | 75% | 85% |

The percentages indicate the contribution of foreign sources to the emissions in The Netherlands as a percentage of the total emission to the specified compartment. Rivers indicate the input by the Rhine and the Meuse to the fresh surface waters in The Netherlands. The input of the Scheldt and the Ems to the estuaria (West-Scheldt and Ems-Dollard) is not included. Estimated loads are from (a) this study; (b) Slooff and Matthijsen (1989) and (c) Thijssen and Huygen (1985).

### *Emission scenarios*

Emission estimates of benzo[a]pyrene, fluoranthene and chrysene for The Netherlands by Draaijers et al. (1997) and the estimates of contributions from abroad, via air and water, are used to assess the relative emissions to the compartments in The Netherlands, Table 4.8. For lindane the 1991 sales volume of 21 tonnes is used (Theunissen-Ordelman and Schrap, 1996).

*Table 4.8: Emission scenarios. Relative emission estimates to compartments.*

| Compartment | Chemical | | | | |
|---|---|---|---|---|---|
| | Lindane | Fluoranthene | Chrysene | Benzo[a]pyrene | Tetrachloroethylene |
| $EMIS_{\mathrm{air}}$[R] | 10% | 49% | 16% | 17% | 83% |
| $IMPORT_{\mathrm{air}}$ [R] | clac.[a] | 33% | 78% | 67% | calc.[a] |
| $EMIS_{\mathrm{water1}}$[R] | 0% | 6% | 1% | 8% | 0.4% |
| $IMPORT_{\mathrm{water1}}$[R] | calc.[a] | 2% | 3% | 5% | calc.[a] |
| $EMIS_{\mathrm{natural\ soil}}$[R] | 0% | 0% | 0% | 0% | 0% |
| $EMIS_{\mathrm{urban\ soil}}$[R] | 0% | 3% | 1% | 1% | 0% |
| $EMIS_{\mathrm{agr.\ soil}}$[R] | 90% | 7% | 1% | 2% | 0% |

[a] no data available on transboundary emissions, in stead the contributions from the continental scale, as an integral part of SimpleBox vs 2.0 are used.

### *Emissions and uncertainties*

The uncertainties in the emission rates for PAHs to each compartment was taken into account by assuming a relative error. This relative error is based on the emission quality rating system used by the EPA (1995) and Harmelen et al. (1999). Each emission factor has been given a quality rating: A, B, C, D, and E, with the latter representing the highest uncertainty. This classification has more or less subjectively been translated into a quantitative relative error by Berdowski et al. (1997). The relative error reflects the emission factor range as a 95%-

confidence interval with an estimated mean value. Uncertainty in PAH emissions increase for each compartment from air<water<soil and were mainly designated with an E-rating (Harmelen et al., 1999). The relative error for an E-rating was assumed to be 3 as was done by Berdowski et al. (1997) for particulate matter. This can by adopted for PAH because PAH and particulate matter are closely related with respect to sources and the fact that especially the higher PAHs are present in the atmosphere as particulate matter.

The uncertainty in the PAH emissions to each compartment was expressed by applying a relative error of 3. Assuming that the emissions have a log-normal distribution, this means that the emissions to air (Eair), water (Ewater) and soil (Esoil) have a minimum of Ecomp./3 and a maximum of Ecomp.*3

In The Netherlands lindane is mainly used in agriculture in non-aerial applications like seed and soil treatment. In 1991, 21 tonnes of lindane were used. Direct emissions to surface water were assumed not to be relevant. The emission factor to air was assumed to be 10% of the consumption rate at the maximum and 1% at the minimum with a uniform distribution. The remainder of the consumed amount is emitted to soil: Esoil = Consumption – Eair. The European emission scenario for lindane was thought to be the same as for The Netherlands.

Major uses of tetrachloroethylene are as a chemical intermediate and dry-cleaning solvent. Other smaller uses are metal cleaning and extraction processes. Some minor uses include stain remover, paint remover and application as fumigant. Emissions to air and water are calculated from consumption figures (EU RAR, 2001). Final emission rates may not completely correspond with the emission reported rates because different average emission factors have been applied. Uncertainties in emission rates were based on reasonable applicable ranges from emission estimates and more or less subjective expert judgements, see table 4.9.

*Table 4.9: European consumption (ktonne.year$^{-1}$) and emission rates (tonne.year$^{-1}$) of tetrachloroethylene including uncertainty estimates.*

| Source | Volume [ktonne.year$^{-1}$] | Compartment | Emission factor [-] | Emission [tonne.year$^{-1}$] | Uncertainty |
|---|---|---|---|---|---|
| Production | 164 | Air | 1.00E-03 | 164 | r.e. 5 |
| | | Water | 3.00E-06 | 0.5 | r.e. 5 |
| Intermediate | 66 | Air | 1.00E-03 | 66.0 | r.e. 5 |
| | | Water | 3.00E-06 | 0.2 | r.e. 5 |
| Dry Cleaning | 62.4 | Air | 8.00E-01 | 49 920 | +/-20% |
| | | Water | 3.00E-04 | 18.7 | r.e. 5 |
| Metal Cleaning | 14 | Air | 9.00E-01 | 12 600 | +/-10% |
| | | Water | 1.00E-02 | 140 | +/-50% |
| Other | 1.6 | Air | 9.00E-01 | 1 440 | +/-10% |
| | | Water | 4.00E-02 | 64.0 | r.e. 5 |
| Waste | | Air | | 3 000 | +/-50% |
| Total | | Air | | 64 200 | +/-15% |
| | | Water | | 223.4 | +/- 60% |

# 5. COMPARISON OF COMPUTED AND OBSERVED DATA

## 5.1 Introduction

This chapter gives a description of the calculated environmental concentration ratios. Simultaneous measured concentrations in two or more (adjacent) compartments are not available and therefore measured environmental concentration ratios (MECRs) have to be calculated using data from different locations all over The Netherlands. It is assumed that the average concentrations are representative for the average situation in The Netherlands during the considered period of time. Computed steady-state concentration ratios (SSCRs) are also presented in this chapter. At the end of this chapter a comparison is made between the MECRs and the SSCRs in order to test the validity of the model.

## 5.2 Computed steady-state concentrations and concentration ratios

In this paragraph the results of the Monte Carlo simulations with SimpleBox are presented. The distribution of the model output is characterised by the median estimate and the corresponding 95%-confidence interval. We assumed lognormal distributions of the calculated concentrations. Consequently the computed concentration ratios are also lognormally distributed, formula 5.1. According to the shape of the output distributions the $\log_{10}$ values fit the normal distribution generally reasonable well (e.g. figure 5.1 and Appendix VI and VIII).

$$\log\left(SSCR_{air-water}\right) = \log\left(\frac{Css_{air}}{Css_{watrer}}\right) = \log\left(Css_{air}\right) - \log\left(Css_{water}\right) \qquad \mathbf{5.1}$$

in which:

$SSCR_{air\text{-}water}$ : SimpleBox Steady-State concentration ratio for air and water

$Css_{air}$ : steady state concentration in air

$Css_{water}$ : steady state concentration in water

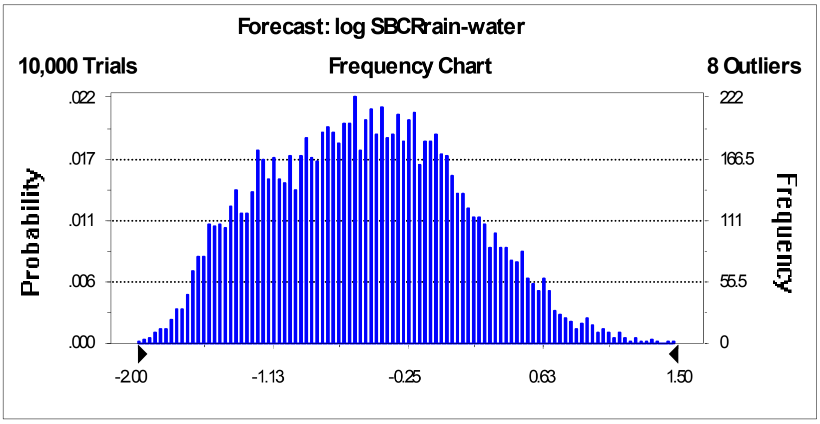

*Figure 5.1: Output frequency distribution of* $SSCR_{rain\text{-}water}$ *for lindane.*

The concentration in rainwater is not an output parameter of SimpleBox but it can be calculated from parameters used in SimpleBox to describe intermedia partitioning. Rainwater samples were collected with both wet-only samplers (PAHs) and bulk samplers (lindane). The calculation of the rainwater concentrations from both wet-only and bulk sampler is described below.

*Concentration in precipitation, wet only samplers:*

Gaseous and particle-bound chemicals are removed from the atmosphere through rain scavenging. Two processes can be distinguished. Equilibrium partitioning of the chemical compound present in the gaseous phase with the raindrops and scavenging of aerosol particles by rain droplets. The concentration of the chemical compound in rain results from both processes:

$$Css_{rain} = SCAVratio \cdot Css_{air} \qquad \mathbf{5.2}$$

$$SCAVratio = \frac{1 - FRass_{aerosol}}{K_{air-water}} + FRass_{aerosol} \cdot COLLECeff \qquad \mathbf{5.3}$$

$Css_{rain}$ : steady-state concentration in rain [$kg \cdot m_{rain}^{-3}$]

$Css_{air}$ : steady-state concentration in air (total) [$kg \cdot m_{rain}^{-3}$]

SCAVratio : scavenging ratio (quotient of the total concentration in rainwater and the total concentration in air [-]

$FRass_{aerosol}$ : fraction of the chemical compound in air that is associated with aerosol particles [-]

$K_{air-water}$ : air-water equilibrium distribution constant [$kg \cdot m_{air}^{-3}/kg \cdot m_{water}^{-3}$]

COLLECTeff : aerosol collection efficiency at [-]

The first term represents an estimate of the equilibrium distribution between rainwater and the gas phase of air. The second term represents the scavenging of aerosol particles by rain droplets.

*Concentration in precipitation, total (wet and dry) deposition from bulk samplers:*

The concentration in rain water collected from bulk samplers results from the input of both wet and dry deposition and is derived as follows:

Wet deposition, washout of material by rain:

$$DEPwet = SCAVratio \cdot Css_{air} \cdot RAINRATE \qquad \mathbf{5.4}$$

DEPwet : wet deposition flux [$kg \cdot m^{-2} \cdot s^{-1}$]

SCAVratio : scavenging ratio (quotient of the total concentration in rainwater and the total concentration in air [-]

$Css_{air}$ : total concentration in air [kg·m$^{-3}$]

RAINRATE : wet precipitation rate [$m_{rain}$·s$^{-1}$]

Dry deposition, gravitational settling of particles (aerosols):

$$DEPdry = AEROSOLDEPRATE \cdot FRass_{aerosol} \cdot Css_{air} \qquad \textbf{5.5}$$

DEPdry : dry deposition flux [kg·m$^{-2}$·s$^{-1}$]

AEROSOLDEPRATE : deposition velocity of the aerosol particles with which the chemical compound is associated [m·s$^{-1}$]

$FRass_{aerosol}$ : fraction of the chemical compound in air that is associated with aerosol particles [-]

$Css_{air}$ : computed total concentration in air [kg·m$^{-3}$]

Concentration of chemical compound in rain from bulk samplers:

$$DEPtotal = DEPwet + DEPdry$$

DEPtotal : total deposition flux [kg·m$^{-2}$·s$^{-1}$]

$$Css - open_{rain} = \frac{DEPtotal}{RAINRATE} = SCAVratio \cdot Css_{air} + \frac{DRYDEP_{aerosol}}{RAINRATE} \cdot Css_{air} \qquad \textbf{5.6}$$

$Css\text{-}open_{rain}$ : SimpleBox computed steady-state concentration in rain from bulk samplers [kg·m$^{-3}$]

## 5.3 Monitored compared to computed concentrations

Measured and computed concentrations are compared in this section (Table 5.1). The median was chosen as the location parameter of the distributions to be compared. The 2.5th and the 97.5th percentiles give some information about the form of the distributions. As stated before the measured concentrations were assumed to be log-normally distributed. Consequently the log values of the measured concentrations are symmetrically distributed around the mean (median). The distribution or dispersion can therefore be expressed with a factor, k. The factor k covers the range between the location parameter and the lower and the upper confidence limits, here the 2.5th and the 97.5th percentiles.

The shape of non-symmetrical distributions cannot be expressed with a factor, k. In some cases though calculated distributions will be more or less tailed to either of the sides of the distribution curve.

The distributions of the measured and computed concentrations are graphically displayed in Appendix VI. An overview of the scores on the criteria posed in section 2.5 is given in Appendix VII.

*Tetrachloroethylene*

*Air:* The measured concentration in air is overestimated by a factor of 5. The width of the distribution curve of field observations is somewhat larger than the distribution of the calculated concentrations, 6 against 4.

*Water:* The computed median value of the freshwater concentration is almost a factor of 4 lower than observed water concentrations. It is important to note that the observed concentrations do not contain any values of the largest fresh surface water body in The Netherlands, IJsselmeer, for the considered period. In previous years it was shown that concentrations in IJsselmeer are about a factor of 10 lower. The dispersion factor of the measured concentrations is 4 times larger compared to the dispersion factor of the calculated concentrations.

*Table 5.1: Measured versus computed concentrations, tetrachloroethylene.*

| | | **measured** | | | **simplebox** | | |
|---|---|---|---|---|---|---|---|
| **substance/ compartment** | **unit** | **2.5 th perc.** | **median** | **97.5 th perc.** | **2.5 th perc.** | **median** | **97.5 th perc.** |
| **perchloroethylene** | | | | | | | |
| air | g.m$^{-3}$ | 3.29E-08 | 2.11E-07 | 1.35E-06 | 2.55E-07 | 5.56E-07 | 1.79E-06 |
| freshwater | g.l$^{-1}$ | 1.77E-08 | 1.51E-07 | 1.28E-06 | 2.29E-08 | 3.93E-08 | 6.18E-08 |

*Lindane*

*Air:* The predicted mean of the rainwater concentration is about 5 times smaller than the observed concentrations. The distribution of measured concentrations is wider.

*Water:* The measured dissolved concentration in fresh surface water is a factor of 3 lower than predicted. The distribution of the modelled concentrations is much wider. The modelled distribution is somewhat tailed to the right.

*Suspended matter:* The computed median concentration of lindane in suspended matter is about two times higher. The distribution of the calculated concentrations is much wider, having a dispersion factor of about 15. The dispersion factor of measured concentrations is about 7. The computed distribution of the concentration in suspended matter is somewhat tailed to the right.

*Soil:* Comparing measured and modelled concentrations in agricultural soil shows that modelled concentrations are about 11 times higher. The computed concentration of the weighted average of the three soil types distinguished in SimpleBox is about 3 times higher. The width of the calculated distribution for agricultural soil is about the same, the width of the distribution of the average soil is also about the same. The distributions of the estimated concentrations in agricultural soil and the average soil are slightly tailed to the left. It seems possible that soil samples were taken from low contaminated parcels with input mainly resulting from atmospheric deposition and that concentrations are not directly related to the application of lindane to agricultural soils, but it seems also likely that soils samples from contaminated sites were included as modelled concentrations solely resulting from atmospheric deposition (natural soil) are lower.

*Table 5.2: Measured versus computed concentrations, lindane.*

| | | **measured** | | | **simplebox** | | |
|---|---|---|---|---|---|---|---|
| **substance/ compartment** | **unit** | **2.5 th perc.** | **median** | **97.5 th perc.** | **2.5 th perc.** | **median** | **97.5 th perc.** |
| **lindane** | | | | | | | |
| rain | g.l$^{-1}$ | 2.85E-09 | 2.81E-08 | 2.75E-07 | 1.28E-09 | 5.89E-09 | 2.46E-08 |
| freshwater | g.l$^{-1}$ | 9.60E-10 | 6.65E-09 | 4.58E-08 | 1.40E-09 | 1.76E-08 | 3.11E-07 |
| sediment | g.kg$^{-1}$(dry) | | | | | | |
| susp. matter | g.kg$^{-1}$(dry) | 1.89E-07 | 1.33E-06 | 9.37E-06 | 2.26E-07 | 3.06E-06 | 5.20E-05 |
| agricultural soil | g.kg$^{-1}$(dry) | 1.67E-07 | 5.56E-07 | 1.84E-06 | 1.05E-06 | 6.15E-06 | 1.66E-05 |
| average soil | g.kg$^{-1}$(dry) | 1.67E-07 | 5.56E-07 | 1.84E-06 | 2.78E-07 | 1.51E-06 | 4.01E-06 |

### *Benzo[a]pyrene*

*Air:* The measured and computed concentration in rainwater differ less than a factor of 2. The computed concentration in air of benzo[a]pyrene which is bound to aerosols is slightly less than a factor 3 higher than the measured concentration. The distribution of the measured concentrations is about the same as the distribution of the calculated concentrations. Note that for aerosols the calculated distribution is tailed to the left. The estimated distribution of rainwater concentrations resembles the observed concentrations even better.

*Fresh surface water:* Difference between the predicted and observed concentration in freshwater is less than a factor of 3. The distribution of measured concentrations is much larger than the distribution of estimated concentrations.

*Suspended matter and sediment:* Comparing the measured concentration in suspended matter and sediment shows that the difference is less than a factor of 4 for sediment and about a factor of 2 for suspended matter. For both compartments the measured concentration is higher. The distribution of calculated sediment concentrations is somewhat tailed to the left, but of the same order of magnitude as the measured concentrations, this is also true for the measured concentrations in suspended matter.

*Soil:* Large differences can be observed between calculated concentrations in agricultural soil (low emissions) and the measured concentrations in agricultural soils, factor 160 lower. The calculated concentrations in the average soil match the measured concentrations better, but is still more than a factor 60 smaller than measured concentrations. The width of the distribution of the calculated concentrations is about the same for agricultural soil and smaller for the weighted average concentration in soil.

*Table 5.3: Measured versus computed concentrations, benzo[a]pyrene.*

| | | **measured** | | | **simplebox** | | |
|---|---|---|---|---|---|---|---|
| **substance/ compartment** | **unit** | **2.5 th perc.** | **median** | **97.5 th perc.** | **2.5 th perc.** | **median** | **97.5 th perc.** |
| **b[a]pyrene** | | | | | | | |
| aerosols | g.m$^{-3}$ | 2.66E-11 | 2.15E-10 | 1.73E-09 | 1.18E-11 | 6.33E-10 | 5.38E-09 |
| rain | g.l$^{-1}$ | 2.36E-09 | 1.47E-08 | 9.21E-08 | 1.66E-09 | 1.74E-08 | 1.30E-07 |
| freshwater | g.l$^{-1}$ | 1.76E-10 | 4.37E-09 | 1.10E-07 | 1.68E-09 | 8.09E-09 | 3.99E-08 |
| sediment | g.kg$^{-1}$(dry) | 7.37E-05 | 4.06E-04 | 2.23E-03 | 8.99E-06 | 1.14E-04 | 5.79E-04 |
| susp. matter | g.kg$^{-1}$(dry) | 1.13E-04 | 5.35E-04 | 2.52E-03 | 5.20E-05 | 2.74E-04 | 2.27E-03 |
| agricultural soil | g.kg$^{-1}$(dry) | 3.80E-06 | 2.71E-05 | 1.93E-04 | 3.22E-08 | 1.69E-07 | 1.01E-06 |
| average soil | g.kg$^{-1}$(dry) | 3.80E-06 | 2.71E-05 | 1.93E-04 | 1.15E-07 | 4.25E-07 | 1.86E-06 |

*Chrysene*

*Air:* The predicted concentration in air for chrysene bound to aerosol and chrysene in rainwater are about a factor 2 larger than the measured concentration. The distribution of the calculated concentrations in aerosols is not symmetrical around the median, but to some extend tailed to the left. Apart from this, the curves are comparably wide. The distribution of the calculated rainwater concentrations is relatively wide compared to the measured distribution with distribution coefficients of 8 and 6, respectively.

*Water:* The calculated concentration in freshwater is close to field observations also with respect to the dispersion.

*Suspended matter and sediment:* For both suspended matter and sediment, the predicted median of the concentrations is about a factor 2 lower than for the measured concentrations. The width of the distributions does not differ that much with dispersion coefficients of about 5.

*Soil:* The predicted concentration in agricultural soil is a factor of 26 lower than the observed concentration in agricultural soil. The predicted concentration in the weighted average soil is about a factor 15 lower than the observed concentrations. The predicted concentration in agricultural soil (emission) is even lower than the concentration in natural soil (no emission). This is largely due to the larger mixing depth of 20 cm vs. 3 cm for natural and urban soil. The distribution curve of the predicted concentration in agricultural soil is rather symmetric around the median. The dispersion factors for the estimated concentrations are somewhat smaller compared to observed concentrations in agricultural soils.

*Table 5.4: Measured versus computed concentrations, chrysene.*

| | | **measured** | | | **simplebox** | | |
|---|---|---|---|---|---|---|---|
| **substance/ compartment** | **unit** | **2.5 th perc.** | **median** | **97.5 th perc.** | **2.5 th perc.** | **median** | **97.5 th perc.** |
| **chrysene** | | | | | | | |
| aerosols | $g.m^{-3}$ | 5.89E-11 | 5.20E-10 | 4.55E-09 | 1.45E-11 | 1.12E-09 | 1.19E-08 |
| rain | $g.l^{-1}$ | 5.95E-09 | 3.77E-08 | 2.39E-07 | 1.02E-08 | 8.54E-08 | 6.81E-07 |
| freshwater | $g.l^{-1}$ | 4.01E-09 | 1.48E-08 | 5.48E-08 | 3.57E-09 | 1.63E-08 | 7.02E-08 |
| sediment | $g.kg^{-1}$(dry) | 5.98E-05 | 3.34E-04 | 1.86E-03 | 2.72E-05 | 1.69E-04 | 6.69E-04 |
| susp. matter | $g.kg^{-1}$(dry) | 1.28E-04 | 5.27E-04 | 2.16E-03 | 8.77E-05 | 3.46E-04 | 2.22E-03 |
| agricultural soil | $g.kg^{-1}$(dry) | 5.48E-06 | 3.38E-05 | 2.08E-04 | 2.84E-07 | 1.29E-06 | 7.12E-06 |
| average soil | $g.kg^{-1}$(dry) | 5.48E-06 | 3.38E-05 | 2.08E-04 | 5.88E-07 | 2.20E-06 | 1.19E-05 |

### *Fluoranthene*

*Air:* Rainwater concentrations are underestimated by slightly less than a factor 3. The dispersion is notable larger for the computed concentrations.

*Water:* Computed freshwater concentrations are almost a factor 2 larger than observed concentrations. The width of the distributions are approximately the same.

*Suspended matter and sediment:* Concentrations in suspended matter and sediment are underestimated by a factor of somewhat more than 1 and about a factor of 3, respectively. The distribution of the modelled sediment concentrations is tailed to the left. Apart from this the width of computed and measured distributions are about the same for both sediment and suspended matter.

*Soil:* Larger differences can be observed between computed concentrations and the measured concentration in agricultural soil, about a factor of 48. Urban soil concentrations are overestimated by a factor of almost 7, on the other hand. The concentration in agricultural soils is even lower than the predicted concentration in natural soil, although emissions to agricultural soils are taken into account. As discussed with benzo[a]pyrene, this can largely be explained by the larger mixings depth of agricultural soils. As a consequence the weighted average concentration is a factor of 13 lower than the observed concentration. The width of the distributions of the calculated concentrations is much smaller (k = 2) compared to the distribution of the measured concentration in agricultural soils, k = 7.

*Table 5.5: Measured versus computed concentrations, fluoranthene.*

| **substance/ compartment** | **unit** | **measured** | | | **simplebox** | | |
|---|---|---|---|---|---|---|---|
| | | **2.5 th perc.** | **median** | **97.5 th perc.** | **2.5 th perc.** | **median** | **97.5 th perc.** |
| **fluoranthene** | | | | | | | |
| aerosols | $g.m^{-3}$ | | | | | | |
| rain | $g.l^{-1}$ | 1.54E-08 | 9.53E-08 | 5.91E-07 | 2.68E-09 | 3.26E-08 | 3.78E-07 |
| freshwater | $g.l^{-1}$ | 5.14E-09 | 2.61E-08 | 1.31E-07 | 8.44E-09 | 4.93E-08 | 2.44E-07 |
| sediment | $g.kg^{-1}$(dry) | 1.20E-04 | 7.12E-04 | 4.26E-03 | 4.42E-06 | 2.86E-04 | 1.63E-03 |
| susp. matter | $g.kg^{-1}$(dry) | 1.87E-04 | 9.50E-04 | 4.78E-03 | 7.50E-05 | 7.15E-04 | 3.90E-03 |
| agricultural soil | $g.kg^{-1}$(dry) | 9.22E-06 | 6.74E-05 | 4.91E-04 | 4.40E-07 | 1.44E-06 | 4.93E-06 |
| average soil | $g.kg^{-1}$(dry) | 9.22E-06 | 6.74E-05 | 4.91E-04 | 1.69E-06 | 5.17E-06 | 1.58E-05 |

To get more insight into the quality of the SimpleBox output, it was determined whether the modelled concentrations meet the criteria mentioned in paragraph 2.5. The results are presented in Appendix VII. Here we give an overview of the findings.

*Air:* the predicted concentrations of the three PAHs in rain or aerosols meet the ‘factor 3 criterion’. For lindane and tetrachloroethylene the ‘factor 10 criterion’ is met.

*Water:* For all substances the ‘factor 3’ criterion is fulfilled.

*Suspended matter and sediment:* For sediment concentrations, the model predictions for fluoranthene and chrysene satisfy the ‘factor 3 criterion’. The results for benzo[a]pyrene do not meet this criterion, but fulfil the ‘factor 10 criterion’. For all substances the computed concentration in suspended matter meet the ‘factor 3 criterion’. For tetrachloroethylene there were no data available

*Soil:* When comparing the measured concentrations in agricultural soil with computed concentrations in agricultural soil for lindane the ‘factor 30 criterion, is met. When comparing the measured concentration in agricultural soils with the weighted average concentration in soil, the ‘factor 3 criterion’ is fulfilled. For the three PAHs measured concentrations are also compared to predicted concentrations in agricultural soil and average soil. For agricultural soil the ‘factor 30 criterion’ is not satisfied for benzo[a]pyrene and fluoranthene. Chrysene meets the ‘factor 30 criterion’. For the average soil the ‘factor 30 criterion’ is fulfilled for both fluoranthene and chrysene. For benzo[a]pyrene even the ‘factor 30 criterion’ is not met.

The best scores of the model predictions are in the order of water/suspended matter>sediment>air>soil.

The results of the comparison have been displayed in Figure 5.2 for all substances. The solid line represents a perfect match between the predictions and observations. The dashed lines give the upper and lower limits corresponding with an uncertainty factor of 10.

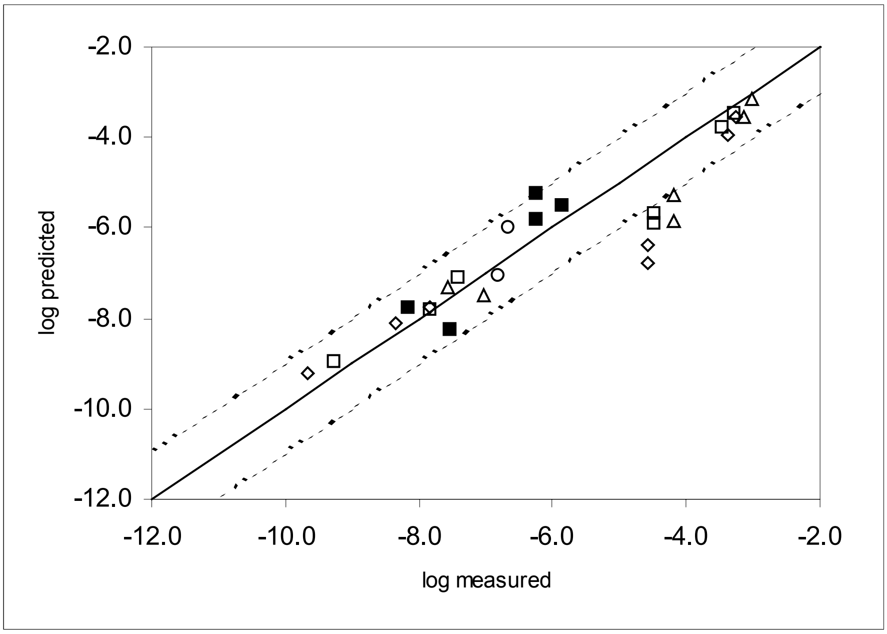

*Figure 5.2: measured versus predicted concentrations. Open diamond: benzo[a]pyrene; open square: chrysene; open triangle: fluoranthene; open circle: tetrachloroethylene; closed square: lindane. Data derived from Tables 5.1 to 5.5.*

## 5.4 Observed compared to computed concentration ratios

For each substance statistical parameters of the computed concentration-ratios an the concentration ratios resulting from the observed field concentrations are given in Tables 5.6 through Table 5.10.The distributions of the measured and computed concentration ratios are graphically displayed in Appendix VIII. An overview of the scores on the criteria posed in section 2.5 is given in Appendix IX.

### *Benzo[a]pyrene*

Predicted rain-water steady state concentration ratios are a little underestimated but satisfy the ‘factor 3 criterion’. The computed aerosol-water SSCRs on the other hand are overestimated, again the ‘factor 3 criterion’ is fulfilled. Modelled water-sediment concentration ratios deviate about a factor of 6 from the measured concentration ratios. Measured water-suspended matter concentration ratios are about a factor of 3 smaller than the predicted concentration ratio. The computed rain-soil concentration ratio for agricultural soils is overestimated compared to the observed field concentration ratio, the discrepancy is about a factor of 187. This is also true for the computed aerosol-soil concentration ratio, the concentration ratio is overrated by a factor of more than 400. Large differences can also be observed when computed rain/aerosol-soil concentration ratios for the average soil were compared to observed concentration ratios. Computed concentration ratios are 78 times and more than 180 times higher for rain-soil and aerosol-soil CRs, respectively. This is mainly caused by the underestimation of the soil concentration.

*Table 5.6: Measured versus prediction concentration ratios for benzo[a]pyrene.*

| | | **measured** | | | **simplebox** | | |
|---|---|---|---|---|---|---|---|
| **substance/ compartment** | **unit** | **2.5 th perc.** | **median** | **97.5 th perc.** | **2.5 th perc.** | **median** | **97.5 th perc.** |
| **b[a]pyrene** | | | | | | | |
| rain-water | - | 8.60E-02 | 3.34E+00 | 1.33E+02 | 1.30E-01 | 2.17E+00 | 2.47E+01 |
| aero-water | $l.m^{-3}$ | 1.10E-03 | 4.84E-02 | 2.34E+00 | 1.09E-03 | 7.46E-02 | 1.05E+00 |
| water-sediment | $kg(dry).l^{-1}$ | 2.75E-07 | 1.09E-05 | 4.01E-04 | 1.48E-05 | 6.04E-05 | 1.64E-03 |
| water-susp | $kg(dry).l^{-1}$ | 2.25E-07 | 8.16E-06 | 3.10E-04 | 5.52E-06 | 2.72E-05 | 1.83E-04 |
| rain-agri. soil | $kg(dry).l^{-1}$ | 3.92E-05 | 5.38E-04 | 8.05E-03 | 1.58E-02 | 1.00E-01 | 4.65E-01 |
| rain-avg. soil | $kg(dry).l^{-1}$ | 3.92E-05 | 5.38E-04 | 8.05E-03 | 5.42E-03 | 4.22E-02 | 1.71E-01 |
| aero-agri. soil | $kg(dry).m^{-3}$ | 4.48E-07 | 7.90E-06 | 1.37E-04 | 1.27E-04 | 3.45E-03 | 1.78E-02 |
| aero-avg. soil | $kg(dry).m^{-3}$ | 4.48E-07 | 7.90E-06 | 1.37E-04 | 3.87E-05 | 1.47E-03 | 6.66E-03 |

### *Chrysene*

The predictions of the rain-water, aerosol-water, water-suspended matter and water-sediment concentration ratios are very satisfactory, the difference is about a factor of 2. For the ‘air’-soil concentrations ratios the same accounts as for benzo[a]pyrene. The median of the modelled concentration ratio for agricultural soil is almost 60 times higher. The median of the weighted average soil concentration ratio is more than a factor 30 overestimated.

*Table 5.7: Measured concentration ratios compared to computed concentration ratios, chrysene.*

| substance/ compartment | unit | measured | | | simplebox | | |
|---|---|---|---|---|---|---|---|
| | | **2.5 th perc.** | **median** | **97.5 th perc.** | **2.5 th perc.** | **median** | **97.5 th perc.** |
| **chrysene** | | | | | | | |
| rain-water | - | 2.68E-01 | 2.54E+00 | 2.40E+01 | 4.60E-01 | 5.40E+00 | 4.88E+01 |
| aero-water | $l.m^{-3}$ | 2.94E-03 | 3.52E-02 | 4.65E-01 | 7.60E-04 | 6.62E-02 | 9.38E-01 |
| water-sediment | $kg(dry).l^{-1}$ | 4.93E-06 | 4.40E-05 | 3.73E-04 | 2.13E-05 | 8.55E-05 | 1.08E-03 |
| water-susp | $kg(dry).l^{-1}$ | 4.08E-06 | 2.81E-05 | 1.99E-04 | 9.84E-06 | 4.25E-05 | 2.50E-04 |
| rain-agri. soil | $kg(dry).l^{-1}$ | 8.87E-05 | 1.11E-03 | 1.51E-02 | 1.36E-02 | 6.49E-02 | 2.76E-01 |
| rain-avg. soil | $kg(dry).l^{-1}$ | 8.87E-05 | 1.11E-03 | 1.51E-02 | 8.26E-03 | 3.74E-02 | 1.56E-01 |
| aero-agri. soil | $kg(dry).m^{-3}$ | 8.91E-07 | 1.53E-05 | 2.61E-04 | 1.56E-05 | 8.71E-04 | 4.93E-03 |
| aero-avg. soil | $kg(dry).m^{-3}$ | 8.91E-07 | 1.53E-05 | 2.61E-04 | 9.38E-06 | 5.12E-04 | 2.59E-03 |

### *Fluoranthene*

For the rain-water concentration ratio the 'factor 10 criterion' is fulfilled, the difference is roughly a factor of 5. Water-sediment and water-suspended matter concentration ratios are overestimated with a factor of nearly 4 and 2, respectively. Comparing computed rain-agricultural soil concentration ratios with measured concentration ratios shows a larger discrepancy, the 'factor 30 criterion' is just fulfilled. The rain-average soil concentration ratio is overestimated with about a factor of 5.

*Table 5.8: Measured concentration ratios compared to computed concentration ratios, fluoranthene.*

| | | measured | | | simplebox | | |
|---|---|---|---|---|---|---|---|
| **substance/ compartment** | **unit** | **2.5 th perc.** | **median** | **97.5 th perc.** | **2.5 th perc.** | **median** | **97.5 th perc.** |
| **fluoranthene** | | | | | | | |
| rain-water | - | 3.22E-01 | 3.64E+00 | 4.21E+01 | 5.22E-02 | 6.70E-01 | 1.05E+01 |
| aero-water | $l.m^{-3}$ | | | | | | |
| water-sediment | $kg(dry).l^{-1}$ | 3.22E-06 | 3.65E-05 | 4.24E-04 | 2.06E-05 | 1.37E-04 | 2.52E-02 |
| water-susp | $kg(dry).l^{-1}$ | 2.74E-06 | 2.73E-05 | 2.67E-04 | 8.15E-06 | 6.03E-05 | 1.19E-03 |
| rain-agri. soil | $kg(dry).l^{-1}$ | 1.01E-04 | 1.43E-03 | 2.02E-02 | 1.76E-03 | 2.48E-02 | 1.79E-01 |
| rain-avg. soil | $kg(dry).l^{-1}$ | 1.01E-04 | 1.43E-03 | 2.02E-02 | 4.82E-04 | 6.68E-03 | 6.43E-02 |
| aero-agri. soil | $kg(dry).m^{-3}$ | | | | | | |
| aero-avg. soil | $kg(dry).m^{-3}$ | | | | | | |

*Perchloroethylene*

The air-water concentration ratio for perchloroethylene is overestimated with just more than a factor of 10. The air concentration is overestimated and water concentrations underestimated giving a larger deviation for the concentration ratio.

*Table 5.9: Measured versus predicted concentration ratios, tetrachloroethylene.*

| | | measured | | | simplebox | | |
|---|---|---|---|---|---|---|---|
| **substance/ compartment** | **unit** | **2.5 th perc.** | **median** | **97.5 th perc.** | **2.5 th perc.** | **median** | **97.5 th perc.** |
| **perchloroethene** | | | | | | | |
| air-water | $l.m^{-3}$ | 8.34E-02 | 1.40E+00 | 2.30E+01 | 6.51E+00 | 1.45E+01 | 4.35E+01 |

*Lindane*

The rain-water concentration ratio is underestimated, the ‘factor 30 criterion’ is satisfied. The computed water-sediment concentration ratio is less than a factor 3 smaller than measured. The predicted water-suspended matter concentration ratio is almost equal to the measured ratio, the predicted ratio is just a little more than a factor one larger. The same is true for the rain-natural soil concentration ratio. The ‘factor 30 criterion’ is not met for the rain-agricultural soil concentration ratio. The CR is underestimated with about a factor 50. Giving an indication of relatively uncontaminated agricultural soil from which samples were taken.

*Table 5.10: Measured versus predicted concentration ratios, lindane.*

| substance/<br>compartment | unit | measured |  |  | simplebox |  |  |
|---|---|---|---|---|---|---|---|
|  |  | **2.5 th perc.** | **median** | **97.5 th perc.** | **2.5 th perc.** | **median** | **97.5 th perc.** |
| **lindane** |  |  |  |  |  |  |  |
| rain-water | - | 2.12E-01 | 4.17E+00 | 8.13E+01 | 2.37E-02 | 3.05E-01 | 5.57E+00 |
| water-sediment | kg(dry).l$^{-1}$ |  |  |  |  |  |  |
| water-susp | kg(dry).l$^{-1}$ | 3.17E-04 | 4.99E-03 | 7.79E-02 | 1.34E-03 | 5.94E-03 | 2.59E-02 |
| rain-agri. soil | kg(dry).l$^{-1}$ | 3.90E-03 | 5.12E-02 | 6.33E-01 | 1.60E-04 | 1.02E-03 | 8.41E-03 |
| rain-avg. soil | kg(dry).l$^{-1}$ | 3.90E-03 | 5.12E-02 | 6.33E-01 | 6.64E-04 | 4.18E-03 | 3.12E-02 |

The results of the comparison have been displayed in Figure 5.3 for all substances and compartments. The solid line represents a perfect match between the predictions and observations. The dashed lines give the upper and lower limits corresponding with an uncertainty factor of 10.

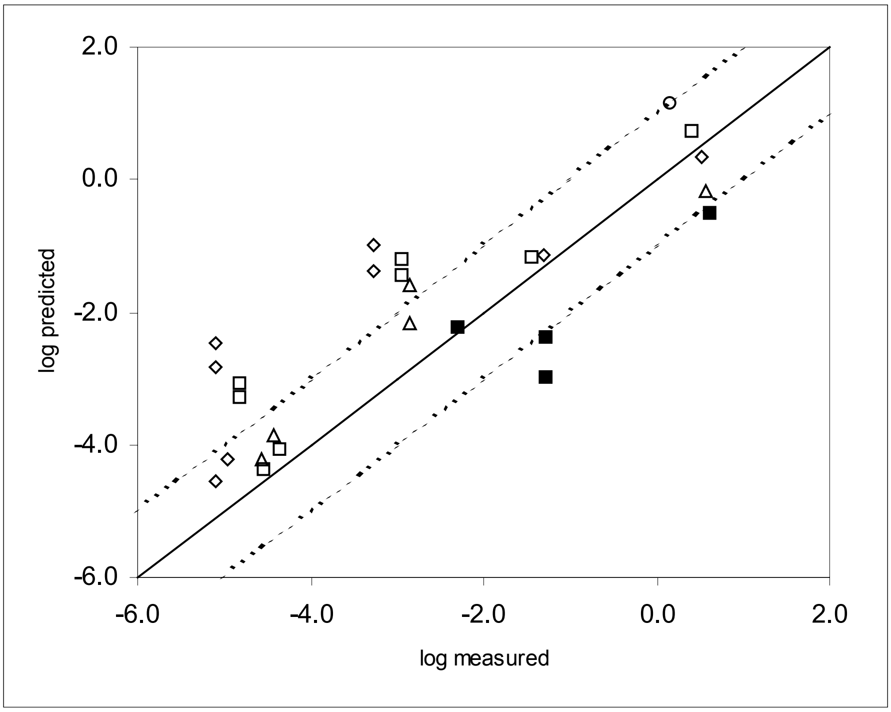

*Figure 5.3: Measured versus predicted concentration ratios. Open diamond: benzo[a]pyrene; open square: chrysene; open triangle: fluoranthene; open circle: tetrachloroethylene; closed square: lindane. Data derived from Table 5.6 to 5.10.*

## 5.5 Deriving coherence criteria

Possible coherence criteria as posed in section 2.5 should be derived from actual validation studies, giving a scientific rationale for the use of threshold criteria for coherence testing and quantification of this threshold.

The results of the present uncertainty analysis can be used to derive probabilistic criteria. Confidence levels can be derived from the distributions of the quotient of SSCR and MECR applying predefined uncertainty factors. For instance one can determine the probability of the quotient of SSCR and MECR exceeding a predefined factor *k* of say 10 or 3 from unity, see Formula 5.7.

$$P\left\{-\log k > \log\left(\frac{SBCR_{comp1-comp2}}{MECR_{comp1-comp2}}\right) > \log k\right\} = x \qquad \mathbf{5.7}$$

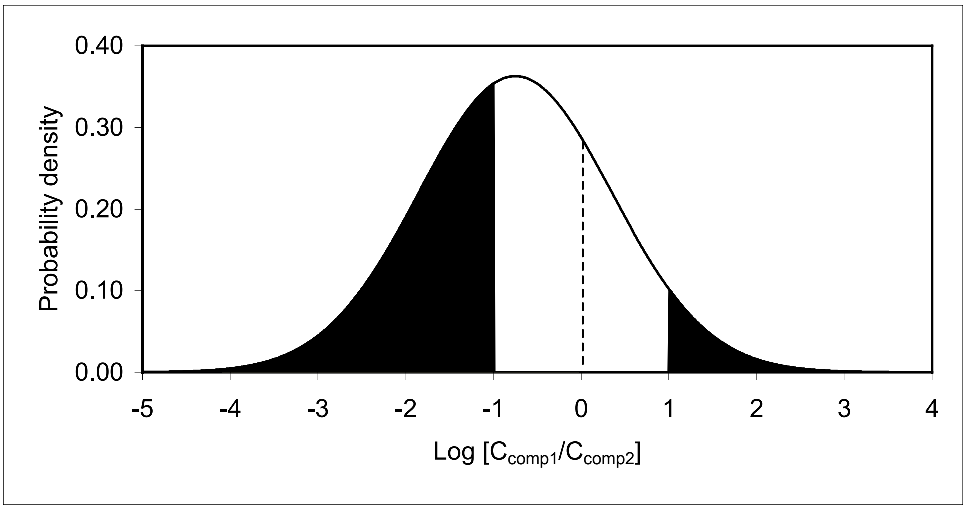

*Figure 5.4: Example of a lognormal distribution of concentrations ratios. Concentrations ratios can be read instead of concentrations ($C_{comp1}$ and $C_{comp2}$).*

Assuming the SSCR/MECR quotient has a lognormal distribution and the uncertainty factor of 10 is applied, the white area in Figure 5.4 is the probability of the SSCR/MECR quotient deviating less than a factor of 10 from unity, log (1) = 0. A probability of say 50% means that 50% of the $SBCR_{air-water}$ lie within a range of ± 10 of the $MECR_{air-water}$, or there is 50% chance that the $SBCR_{air-water}$ deviates less than a factor of 10 from the $MECR_{air-water}$, see Formula 5.8

$$P\left\{-1 < \log\left(\frac{SBCR_{air-water}}{MECR_{air-water}}\right) < 1\right\} = 0.5 \qquad \mathbf{5.8}$$

$$\log \frac{SBCR_{air-water}}{MECR_{air-water}} = \log \frac{Css_{air} / Css_{water}}{C_{air} / C_{water}} \qquad \textbf{5.9}$$

in which:

$SBCR_{air\text{-}water}$ : computed steady-state concentration ratio for air and water [-]

$MECR_{air\text{-}water}$ : measured environmental concentration ratio for air and water [-]

$Css_{air}$ : simplebox computed steady-state concentration in air [$g \cdot m^{-3}$]

$Css_{water}$ : simplebox computed steady-state concentraton in water [$g \cdot l^{-1}$]

$C_{air}$ : measured concentration in air [$g \cdot m^{-3}$]

$C_{water}$ : measured concentration in water [$g \cdot l^{-1}$]

The results of this analysis are presented in Appendix X. A better match of computed concentration ratios with measured concentration ratios gives a higher probability of the computed concentration ratio deviating less than the assigned uncertainty factor of concern. In a glance it was roughly estimated from Appendix X that going from uncertainty factors 100-30-10-3 the probability of the computed concentration ratio deviating less than this factor from the perceived concentration ratio are about 80-70-50-30%.

# 6. DISCUSSION

## 6.1 Data

*Data survey*

Data, which can be used to derive measured concentration ratios for the validation of SimpleBox, are limited. The data should provide coherent sets of environmental concentrations for various combinations of compartments but were of limited use, at least for the data sources we referred to. Chemicals, which are measured in air in The Netherlands are generally not detected or measured in water or in soil. Concentrations of substances measured outside The Netherlands e.g. Canada, Great Lakes, were accessible from open literature. This resulted in a small set of air and water concentrations measured over a large period of time, hence not feasible for the validation. Also, it must be considered that in case of concentrations measured outside The Netherlands a lot of environmental information is needed for that specific region, which may not be easy to retrieve

## 6.2 Required accuracy of SSCRs for coherence testing

As discussed by Struijs and Peijnenburg (2002) the feasibility of validation may be enhanced if there is good insight into both achievable and required accuracy of model predictions. Margins of the model output have therefore to be compared to the margins of the application target. Environmental Quality Objectives (EQOs) are based on Maximum Permissible Concentrations (MPCs), which are usually derived from a limited toxicity data set. The uncertainty of the MPC estimate can easily be as high as a factor of 10. The uncertainty factor of the quotient of two MPCs, assuming a log normal distribution, approximates 26. Taking this into account, it seems unrealistic to expect that the uncertainty in the SSCRs will be less than a factor of 10. The uncertainty in predicted concentration ratios is generally of the same order of magnitude except for some tailed distributions giving much wider distributions.

## 6.3 Studied chemicals

In a validation exercise it is desirable to consider chemicals of different classes. Cowan et al. (1995) recommended that a validation study should include at least one chemical from each of the following five classes:

- volatile or partially volatile organic chemicals (e.g., chlorobenzenes, PCBs, PAHs)
- involatile chemicals (e.g., metals, surfactants)
- insoluble chemicals (e.g., chloroparafins, silicones, waxes)
- dyes and polymers (e.g., involatile and insoluble)
- fast-reacting chemicals (e.g., mercury, phenols, hydroquinone)

The five substance regarded in this study can be classified as volatile or partially volatile organic chemicals. PAHs are a group of chemicals consisting of two or more condensed aromatic rings with a wide range of properties ranging from moderate to low soluble and volatile (semi-volatile) to virtually insoluble and involatile. Chrysene and benzo[a]pyrene have much similarity with chemicals from class ‘dyes and polymers’ they are both insoluble and involatile. Fluoranthene and lindane are typical representatives of semi-volatile chemicals with low solubility. Tetrachloroethylene has rather different properties than those characterising PAHs, e.g., volatile and moderately soluble. Thus these five substance covering at least two of the recommended five classes, but the classes involatile and insoluble chemicals are also covered.

With respect to environmental releases it is also good to realise that the substances have rather different release patterns. PAHs have significant releases to air, water and soil resulting from their use (wood preservatives) and unintended release from combustion. Lindane is used as a pesticide and mainly released to soil. Tetrachloroethylene is largely released to air and to some extend to water. The main source being it’s use as dry-cleaning solvent.

## 6.4 Soil compartments

Comparison of statistical properties (confidence intervals, medians and uncertainties) of the distribution functions of the MECRs with those of the SimpleBox computed steady-state concentration ratios, (SB)SSCRs, may lead to the conclusion that for the five substances considered in this study, SimpleBox predicts their concentration ratios reasonable well. There are some differences though between sets of concentration ratios. Especially air-water and water-sediment and water-suspended matter concentration ratios are well predicted. Computed air-soil concentration ratios do not resemble, large differences between the estimated and measured median of the concentration ratios are observed. A part can be explained by the fact that the soil compartment is a very heterogeneous compartment both in the sense of soil properties and in used. SimpleBox assumes the soil compartment to be homogeneous, although three different soil types are distinguished within SimpleBox vs. 2.0 the overcome part of these differences. Another reason for the difference between the predicted and measured concentrations may be the specific use of certain substances, f.i. lindane is not expected to be applied to grassland and only specific parcels will be treated. From the comparison of the measured and predicted soil concentration it may be concluded that soil samples were apparently taken from parcels with low contamination of lindane primarily resulting from atmospheric deposition and not directly related to the application of lindane to agricultural soils although the latter may not be excluded because estimated background concentration in natural soil are lower than measured concentrations. In case of PAHs natural background concentrations or natural sources may explain part of the observed discrepancy for PAHs. Edwards (1983) suggested that typical levels of endogenous PAHs in soil are in the range of 1-10 $\mu g.kg^{-1}$, resulting from microbial and plant synthesis, plant fossilisation and natural fires. In addition emissions to soil are rather uncertain as they can be very site specific.

Elevated concentrations may also result from certain activities in the past. For peat-pasture areas located in the West of The Netherlands it is known that higher soil concentrations result from the use of city compost containing coal residues and ashes, for so called ‘toemaakdekken’ in the past. The flooding of river foreland with fresh surface water is also known to be a source of PAHs in particular for river clay soil.

Also emissions to soil may be underestimated especially for benzo[a]pyrene and chrysene. The emission to agricultural soil due to the application of compost for land enrichment may be a considerable and underestimated source of PAHs as for compost only quality standards for heavy metals are implemented in regulation.

# 7. CONCLUSIONS

1. The calculated median of the water-sediment and water-suspended matter concentration ratios do not deviate more than a factor of 10 from the measured environmental concentration ratios in The Netherlands. Actually only for benzo[a]pyrene the ‘factor 3 criterion’ is not met.
2. For lindane and tetrachloroethylene the prediction air-water concentration ratios differ just more than a factor of 10, 13.7 and 10.1, respectively from the observed concentration ratios. For the three PAHs the differences are less than a factor of 3
3. For nearly all substances air(rain/aerosol)-soil concentration ratios, deviations are more than a factor of 30.
4. The results of the current study do not give cause to increase or decrease the incoherence threshold of 10 possibly with the exception of air-soil concentration ratios, but uncertainties with respect to the heterogeneity in composition and use of this compartment are too large to draw hard conclusions.
5. The threshold of 10 implies that if the ratio of two independently derived Environmental Quality Objectives (EQOs) deviates less than a factor of 10 from modelled steady state concentration ratios, the EQOs should not be adjusted Accepting this threshold of 10 results in chance of roughly 50 percent or less that the EQOs have not been adjusted even though they should. For a threshold of 3 this risk is about 70% or less and for a threshold of 30 the risk is about 30 percent or less.
6. The uncertainty in model predictions is of the same order of magnitude as the uncertainties in observations and the uncertainties in EQOs and it seems therefore unrealistic to reduce uncertainties in SSCRs

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# APPENDIX II: RESULTS OF THE LITERATURE SEARCH, CONCENTRATIONS OUTSIDE THE NETHERLANDS

*Table II.1: Measured concentrations of chlorobenzenes, PCBs and pesticides in water in the Great Lakes ecosystem*.*

| **Chemical** | **Comp.** | **Range** ng.l$^{-1}$ | **Region** | **Average** ng.l$^{-1}$ | **Region** | **Remark** | **year** |
|---|---|---|---|---|---|---|---|
| 1,3-dichlorobenzene | water | 0.3-1 | offshore | 0.25-1.2 | Toronto Waterfront | av.October-May,June | 1987 |
| 1,4dichlorobenzene | water | 2-3 | offshore | 0-9.4 | Toronto Waterfront | av.October-May,June | 1987 |
| hexachlorobenzene | water | | | 0.05-0.074 | Toronto Waterfront | av.October-May,June | 1987 |
| alfa-BHC | water | 3-5 | Waterfr. | 2.5-4.7 | Toronto Waterfront | av.October-May,June | 1987 |
| gamma-BHC (lindane) | water | 0.5-1 | Waterfr. | 0.58-1.1 | Toronto Waterfront | av.October-May,June | 1987 |
| pp'-DDE | water | | | 0.021-0.035 | Toronto Waterfront | av.October-May,June | 1987 |
| pp'-DDD | water | | | 0.012-0.028 | Toronto Waterfront | av.October-May,June | 1987 |
| pp'DDT | water | | | 0-0.004 | Toronto Waterfront | av.October-May,June | 1987 |
| Total PCBs | water | | | 0.58-2.5 | Toronto Waterfront | av.October-May,June | 1987 |

*Halfon and Poulton (1992).

*Table II.2: Measured concentrations of chlorobenzenes, PCBs and pesticides in air in the Great Lakes ecosystem*.*

| **Chemical** | **Comp.** | **Range** ng.m$^{-3}$ | **Average** ng.m$^{-3}$ | **Region** | **Remark** | **year** |
|---|---|---|---|---|---|---|
| Hexachlorobenzene | air | 0.1-0.3 | 0.2 | Great Lakes | | 1980 |
| Total DDT | air | 0.01-0.05 | 0.03 | Great Lakes | | 1980 |
| alfa-BHC | air | 0.25-0.4 | 0.3 | Great Lakes | | 1980 |
| gamma-BHC (lindane) | air | 1-4 | 2 | Great Lakes | | 1980 |
| Total PCBs | air | 0.4-3 | 1.0 | Great Lakes | | 1980 |

*Eisenreich et al. (1981).

# APPENDIX III: OBSERVED CONCENTRATIONS OF PESTICIDES AND PCBs

*Table III.1: Measured concentrations of agricultural pesticides in air (rain) and water in The Netherlands*[*]*.*

| Chemical | Region | Comp. | Range µg.l$^{-1}$ | Average µg.l$^{-1}$ | Median µg.l$^{-1}$ | Remark | D | N |
|---|---|---|---|---|---|---|---|---|
| Atrazine | 2 | air | <0.1-0.9 | 0.3 ± 0.2 | | rain | 25 | 95 |
| Atrazine | 2 | water | <0.1-1.8 | 0.5 ± 0.4 | 0.4 | | 26 | 95 |
| Azinphos-methyl | 2 | air | <0.1-0.3 | 0.2 ± 0.03 | | rain | 21 | 95 |
| Azinphos-methyl | 2 | water | <0.1-0.2 | 0.2 ± 0.05 | 0.2 | | 4 | 95 |
| Bentazone | 2 | air | <0.1-0.2 | 0.2 ± 0.04 | | rain | 8 | 95 |
| Bentazone | 2 | water | <0.1-2.7 | 0.5 ± 0.6 | 0.2 | | 41 | 95 |
| Chlorpropham | 2 | air | <0.1-5.3 | 1.5 ± 1.3 | | rain | 11 | 95 |
| Chlorpropham | 2 | water | <0.1-0.8 | 0.5 ± 0.2 | 0.5 | | 6 | 95 |
| 2,4-D | 2 | air | <0.1-0.3 | 0.3 | | rain | 2 | 95 |
| 2,4-D | 2 | water | <0.1-1 | 0.5 ± 0.4 | 0.4 | | 8 | 95 |
| 1,2-dichloropropane | 2 | air | <0.05-0.3 | 0.3 ± 0.1 | | rain | 11 | 95 |
| 1,2-dichloropropane | 2 | water | <0.05-0.08 | 0.07 ± 0.01 | 0.08 | | 3 | 95 |
| Dimethoate | 2 | air | <0.1-1.6 | 0.9 ± 0.6 | | rain | 4 | 95 |
| Dimethoate | 2 | water | <0.1-5 | 0.7 ± 1.1 | 0.2 | | 20 | 95 |
| Diuron | 2 | air | <0.1-0.4 | 0.2 ± 0.1 | | rain | 8 | 95 |
| Diuron | 2 | water | <0.1-3.2 | 0.7 ± 0.9 | 0.4 | | 24 | 95 |
| MCPA | 2 | air | <0.1-0.2 | 0.2 ± 0.05 | | rain | 14 | 95 |
| MCPA | 2 | water | <0.1-1.5 | 0.3 ± 0.3 | 0.2 | | 21 | 95 |
| MCPP (mecoprop) | 2 | air | <0.1-0.4 | 0.2 ± 0.1 | | rain | 13 | 95 |
| MCPP (mecoprop) | 2 | water | <0.1-2.1 | 0.3 ± 0.5 | 0.2 | | 15 | 95 |
| Metoxuron | 2 | air | <0.1-40 | 2.2 ± 8.5 | | rain | 22 | 95 |
| Metoxuron | 2 | water | <0.1-1.9 | 0.5 ± 0.5 | 0.3 | | 11 | 95 |
| Organotin | 2 | air | <0.002-0.4 | 0.03 ± 0.07 | | rain | 64 | 95 |
| Organotin | 2 | water | <0.002-0.4 | 0.02 ± 0.05 | 0.005 | | 62 | 95 |
| Propachlor | 2 | air | <0.1-4 | 0.7 ± 0.9 | | rain | 18 | 63 |
| Propachlor | 2 | water | <0.1-0.7 | | 0.2 | | 3 | 63 |

[*]Tas et al. (1996); Van Boom (1993).

N is the number of measurements and D is the number of measurements above the detection limit.

*Table III.2: Measured concentrations of lindane in suspended solids in The Netherlands, 1992*.*

| **Location, year** | **D** | **N** | **DL** µg.kg-1 | **Average** µg.kg-1 | **Max** µg.kg-1 |
|---|---|---|---|---|---|
| Noordelijk Deltagebied | 28 | 31 | 1 | 2.74 | 6.5 |
| Hollands Diep, Haringvliet | 15 | 16 | 1 | 2.77 | 4.6 |
| IJsselmeer | 4 | 5 | 1 | 1.17 | 2.0 |
| Markermeer | 2 | 3 | 1 | 1.26 | 1.3 |
| Westerschelde | 9 | 12 | 1 | 4.85 | 8.6 |

*TeunissenOrdelman et al. (1996).

DL is the detection limit, N is the number of measurements and D is the number of measurements above the detection limit.

*Table III.3: Measured concentrations of lindane in sea water in The Netherlands, 1992*.*

| **Location, year** | **D** | **N** | **DL** $\mu g.l^{-1}$ | **Average** $\mu g.l^{-1}$ | **Max** $\mu g.l^{-1}$ |
|---|---|---|---|---|---|
| Monding Westerschelde | 6 | 6 | 0.001 | 0.0093 | 0.017 |
| Noordzee, 1992 | 22 | 22 | 0.001 | 0.0036 | 0.008 |
| Waddenzee, 1992 | 8 | 8 | 0.001 | 0.0046 | 0.008 |
| Eems-Dollard, 1992 | 12 | 12 | 0.001 | 0.0053 | 0.01 |

*Teunissen-Ordelman (1996).

DL is the detection limit, N is the number of measurements and D is the number of measurements above the detection limit.

*Table III.4: Measured concentrations of PCBs in top level soil in The Netherlands*.*

| **Chemical** | **Range** $\mu g.kg^{-1}$ | **Average** $\mu g.kg^{-1}$ |
|---|---|---|
| PCB 28 | | 1.0 |
| PCB 52 | 0.58 - 2.48 | 1.34 |
| PCB 101 | 0.53 - 1.43 | 0.89 |
| PCB 118 | 0.51 - 0.58 | 0.55 |
| PCB 138 | 0.54 - 4.49 | 1.84 |
| PCB 153 | 0.6 - 1.6 | 0.97 |
| PCB 180 | 0.7 - 2.6 | 1.20 |

*Van Duijvenbooden et al. (1992).

*Table III.5: Measured concentrations of PCBs in top level soil in The Netherlands [*].*

| Chemical | Range µg.kg$^{-1}$ | Average µg.kg$^{-1}$ |
|---|---|---|
| PCB 28 | 0 - 0.8 | 0.25 |
| PCB 52 | 0 - 1.7 | 0.2 |
| PCB 101 | 0 - 2.5 | 0.45 |
| PCB 118 | 0 - 2.0 | 0.26 |
| PCB 138 | 0 - 2.7 | 0.6 |
| PCB 153 | 0 - 2.5 | 0.6 |
| PCB 180 | 0 - 1.2 | 0.35 |
| Σ6 PCBs | | 2.45 |
| Total PCBs | | 12.25 |

*Lagas et al. (1994).

*Table III.6: Measured concentrations of PCBs in suspended solids in IJsselmeer IJ23 *.*

| Chemical | Average µg.kg$^{-1}$ d.w. O.M. 20% | N |
|---|---|---|
| PCB 28 | 2 | 6 |
| PCB 52 | 1 | 6 |
| PCB 101 | 3 | 6 |
| PCB 118 | 3 | 6 |
| PCB 138 | 4 | 6 |
| PCB 153 | 4 | 6 |
| PCB 180 | 2 | 6 |
| Σ6 PCB (excl. 118) | 16 | |
| total PCB (= 5*Σ6 PCB) | 80 | |

*Venema (1991).

N is the number of measurements.

*Table III.7: Measured concentrations of PCBs in surface sediments in IJsselmeer *.*

| **Chemical** | **Average** µg.kg$^{-1}$ d.w. | **N** |
|---|---|---|
| PCB 28 | 6 | |
| PCB 52 | 6 | |
| PCB 101 | 4 | |
| PCB 138 | 7 | |
| PCB 153 | 6 | |
| PCB 180 | 4 | |
| Σ PCB (excl. 118) | 33 | 28 |
| total PCB (= 5*Σ PCB) | 165 | |

*Winkels (1993).

N is the number of measurements.

*Table III.8: Measured concentrations of PCBs in air*.*

| **Chemical** | **Range** ng.m$^{-3}$ | **Average** ng.m$^{-3}$ | **Location** | **References** |
|---|---|---|---|---|
| total PCB | 0.1 - 0.5 | | | Atlas et al., 1986, |
| total PCB | | 0.9 | Delft, The Netherlands | Annema, 1995 |
| total PCB | - 2.7 | 0.9 | Vlaardingen, de Bilt, Witteveen | Annema, 1995 |

*Annema (1995).

# APPENDIX IV: ESTIMATING STATISTICAL PARAMETERS FROM LIMITED DATA SETS

The average value and the standard deviation of data set with many concentations below the detection limit can be estimated with quantile-quantile plots. A quatile-quantile (Q-Q) plot is a grapical display to compare a data set (empirical) to a theoretical probability distribution (assumption). If both distributions are the same, the Q-Q plot is a straight line. If both distributions have different locations and shape parameters but both are samples from the same type of distribution, the Q-Q plot is a straight line (y = ax + b) in which b is the median of the empirical distribution and a is the standard deviation.

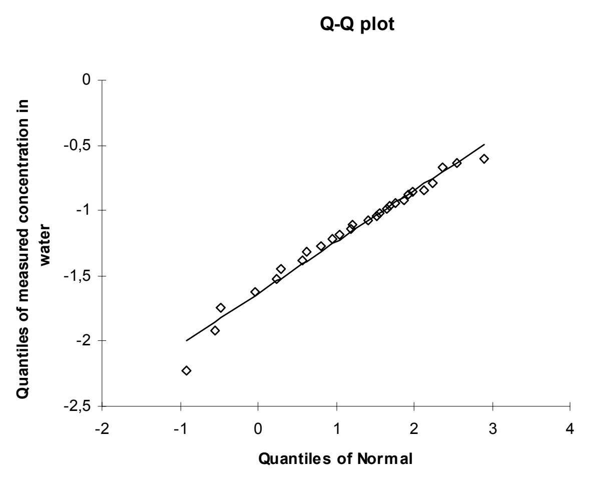


*Figure IV.1: Q-Q plot of log tranformed concentrations in water. Straight line: y = 0.39x – 1.63.*

The Q-Q plot is solely based on all concentrations above the detection limit. The figure below shows no data in the lower tail of the cumulative distribution function of the log transformed concentrations in water (below detection limit).

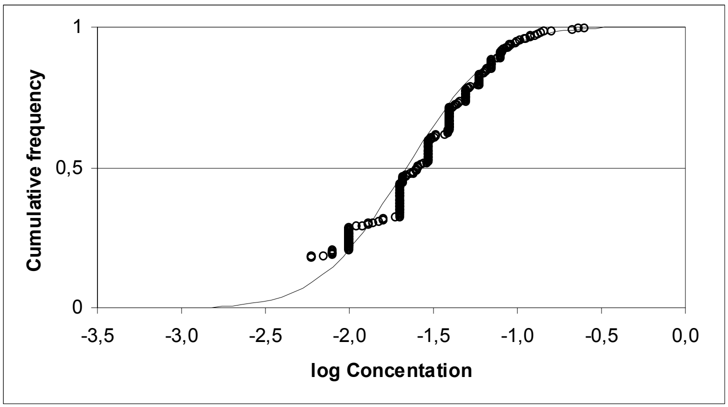


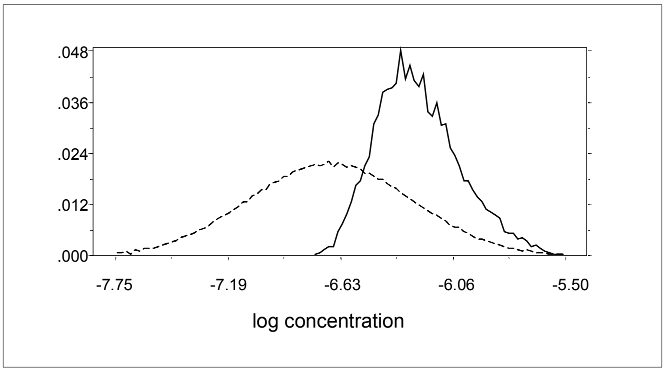
*Figure IV.2: Cumulative distibution function of the log transformed concentrations in water (open circles) and the estimated cumulative distribution function (solid line).*

# APPENDIX V: CHARACTERISTICS OF THE DISTRIBUTION OF OH-RADICAL CONCENTRATIONS ($10^6$ MOLECULES.CM$^{-3}$)

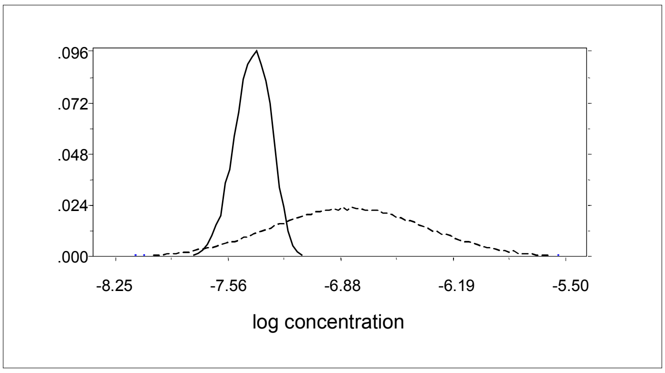
| Range OH concentartions | | relative frequency | frequency |
|---|---|---|---|
| 0.8 | 0.9 | 0.33 | 4 |
| 0.9 | 1 | 0.08 | 1 |
| 1 | 1.1 | 0.17 | 2 |
| 1.1 | 1.2 | 0.25 | 3 |
| 1.2 | 1.3 | 0.17 | 2 |

# APPENDIX VI: FREQUENCY DISTRIBUTIONS OF OBSERVED AND COMPUTED CONCENTRATIONS

## Tetrachloroethylene

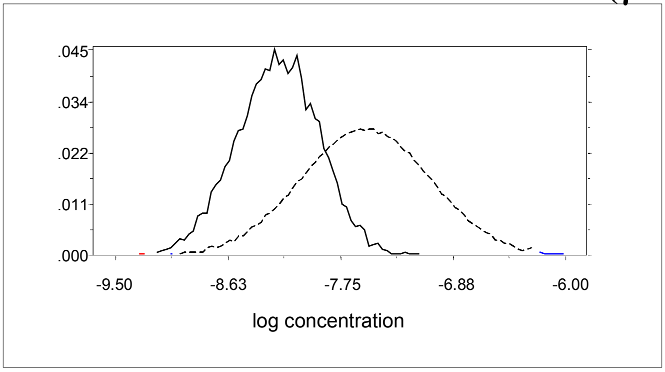


Measured (dotted lines) and predicted (solid lines) distributions of concentrations in air [g.m$^{-3}$].



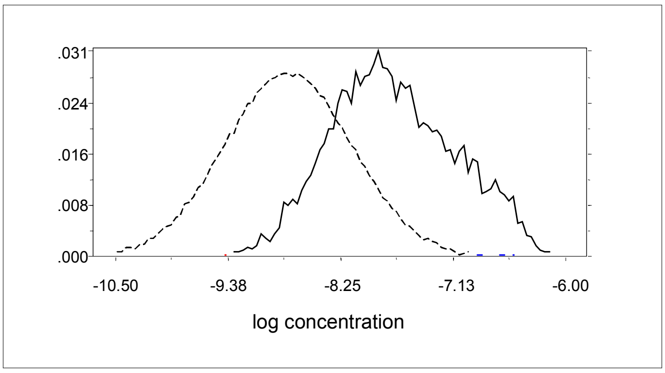
Measured (dotted lines) and predicted (solid lines) distributions of concentrations in water [g.l$^{-1}$].

# Lindane ($\gamma$-HCH)

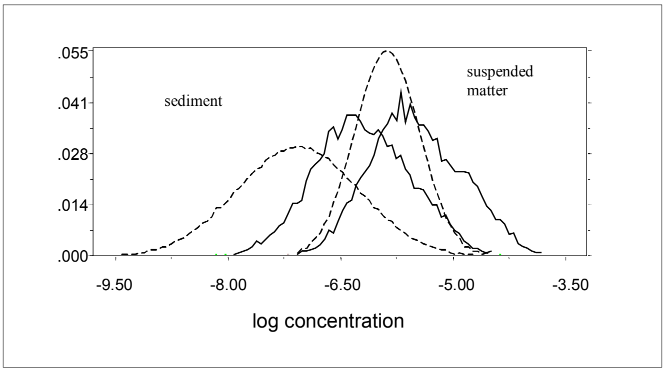


aerosol

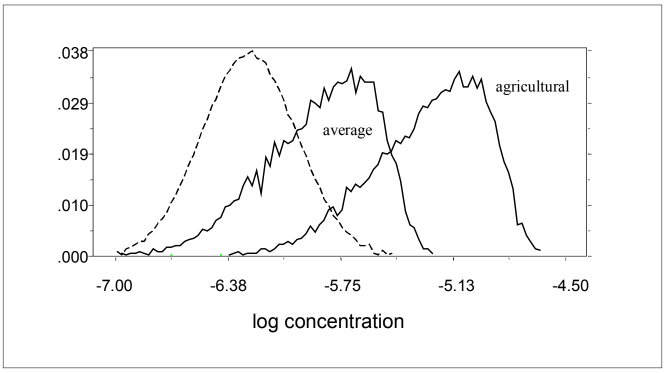
Measured (dotted lines) and predicted (solid lines) concentrations in rain [g.l$^{-1}$].



Measured (dotted lines) and predicted (solid lines) concentrations in water [g.l$^{-1}$].

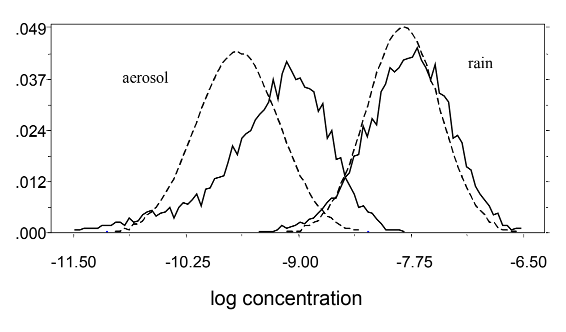


Measured (dotted lines) and predicted (solid lines) concentrations in sediment and suspended matter [g.kg$_{dwt}^{-1}$].

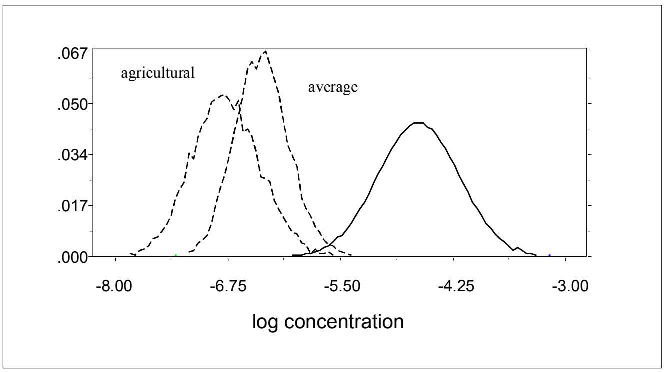


Measured (dotted lines) and predicted (solid lines) concentrations in agricultural soil and average soil [g.kg$_{dwt}^{-1}$].

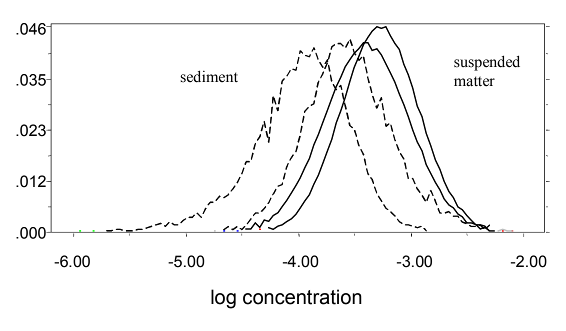
# Benzo[a]pyrene



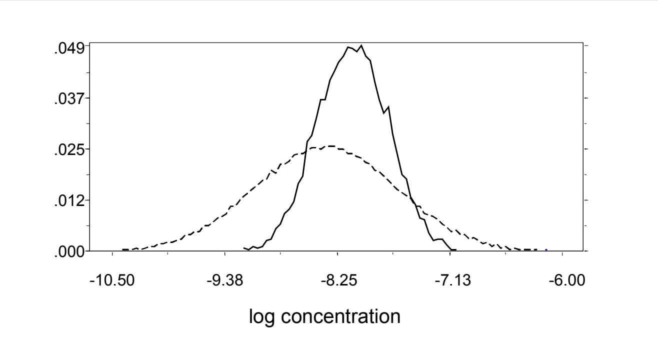
Measured (dotted lines) and predicted (solid lines) concentrations in aerosol [g.m$^{-3}$] and rain [g.l$^{-1}$].



Measured (dotted lines) and predicted (solid lines) concentrations in agricultural soil and average soil [g.kg$_{dwt}^{-1}$].

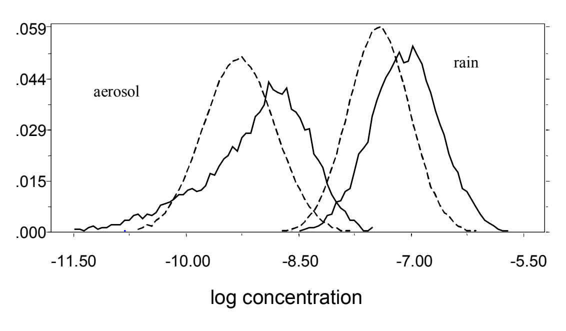


Measured (dotted lines) and predicted (solid lines) concentrations in sediment and suspended matter [g.kg$_{dwt}^{-1}$] of fresh surface water [g.kg$_{dwt}^{-1}$].

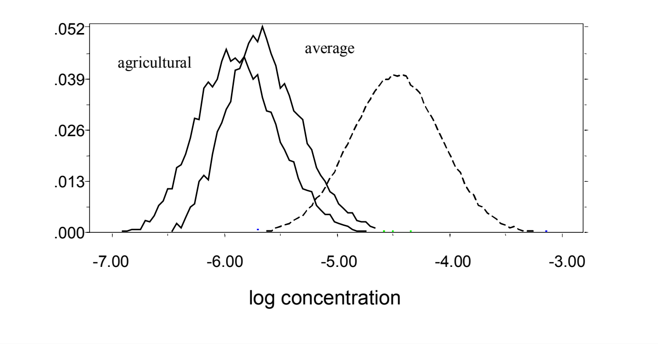


Measured (dotted lines) and predicted (solid lines) concentrations in fresh surface water [g.l$^{-1}$].

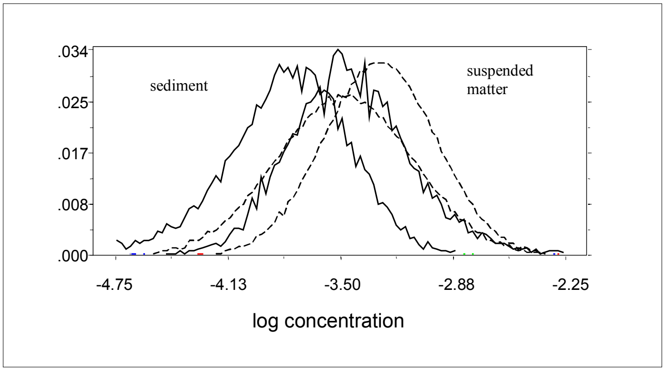
## Chrysene



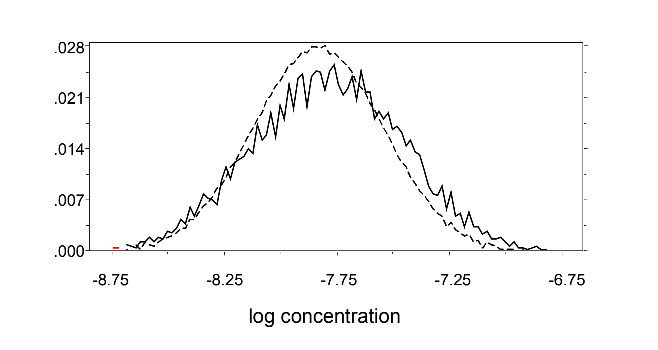
Measured (dotted lines) and predicted (solid lines) concentrations in aerosols [g.m$^{-3}$] and rain [g.l$^{-1}$].



Measured (dotted line) and predicted (solid lines) concentrations in agricultural soil and average soil [g.kg$_{dwt}^{-1}$].

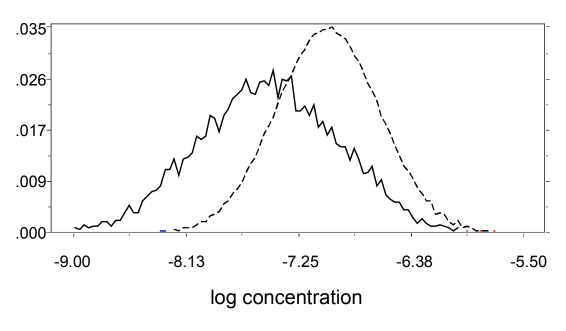


Measured (dotted lines) and predicted (solid lines) concentrations in suspended matter and sediment [g.kg$_{dwt}^{-1}$] of fresh surface water.

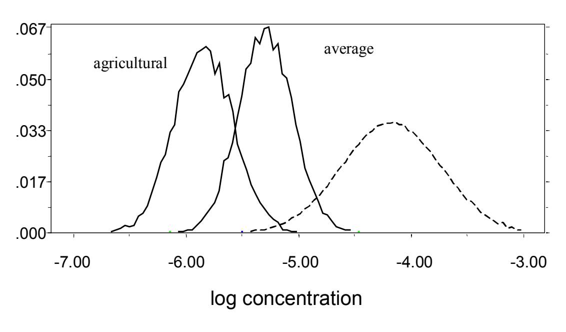


Measured (dotted lines) and predicted (solid lines) concentrations in fresh surfacewater [g.l$^{-1}$].

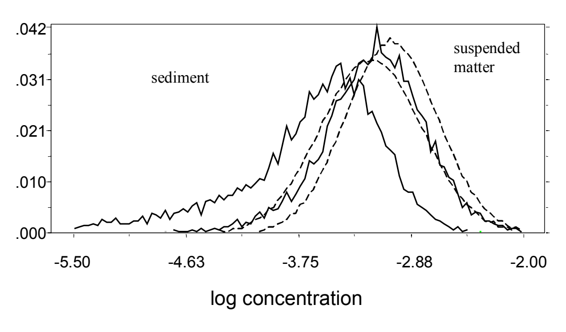
# Fluoranthene



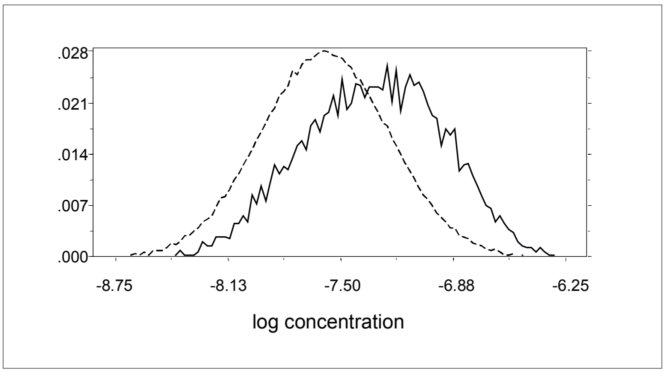
Measured (dotted lines) and predicted (solid lines) concentrations in rain [$g.l^{-1}$].



Measured (dotted lines) and predicted (solid lines) concentrations in agricultural soil and average soil [$g.kg_{dwt}^{-1}$].



Measured (dotted lines) and predicted (solid lines) concentrations in sediment and suspended matter [$g.kg_{dwt}^{-1}$]of fresh surface water.



Measured (dotted lines) and predicted (solid lines) concentrations in fresh surface water [$g.l^{-1}$].

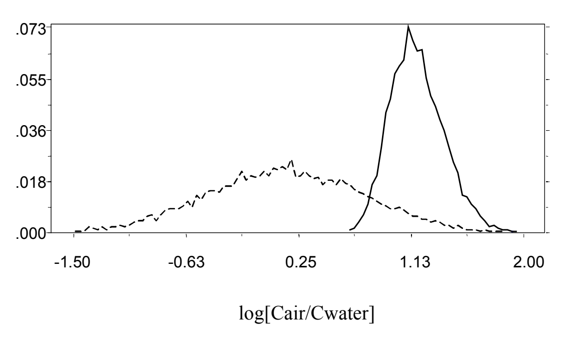
# APPENDIX VII: SCORES OF COMPUTED CONCENTRATIONS ON THE FACTOR 3, 10 AND 30 CRITERIA, ARE THE CRITERIA FULFILLED?

| | | **Criteria factor k for** | | |
|---|---|---|---|---|
| **substance** | **compartment** | **3** | **10** | **30** |
| | | | | |
| tetrachloroethylene | air | no | yes | yes |
| | fresh water | yes | yes | yes |
| | | | | |
| lindane | rain | no | yes | yes |
| | freshwater | yes | yes | yes |
| | sediment | | | |
| | suspended matter | yes | yes | yes |
| | agricultural soil | no | no | yes |
| | average soil | yes | yes | yes |
| | | | | |
| benzo[a]pyrene | aerosols | yes | yes | yes |
| | rain | yes | yes | yes |
| | freshwater | yes | yes | yes |
| | sediment | no | yes | yes |
| | suspended matter | yes | yes | yes |
| | agricultural soil | no | no | no |
| | average soil | no | no | no |
| | | | | |
| chrysene | aerosols | yes | yes | yes |
| | rain | yes | yes | yes |
| | freshwater | yes | yes | yes |
| | sediment | yes | yes | yes |
| | suspended matter | yes | yes | yes |
| | agricultural soil | no | no | yes |
| | average soil | no | no | yes |
| | | | | |
| fluoranthene | aerosols | | | |
| | rain | yes | yes | yes |
| | freshwater | yes | yes | yes |
| | sediment | yes | yes | yes |
| | suspended matter | yes | yes | yes |
| | agricultural soil | no | no | no |
| | average soil | no | no | yes |
| | | | | |

# APPENDIX VIII: FREQUENCY DISTRIBUTIONS OF OBSERVED AND COMPUTED CONCENTRATION RATIOS

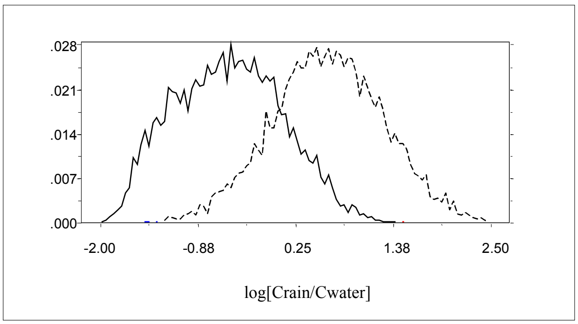
soil(2) = agricultural soil
soil(4) = average soil

## Tetrachloroethylene

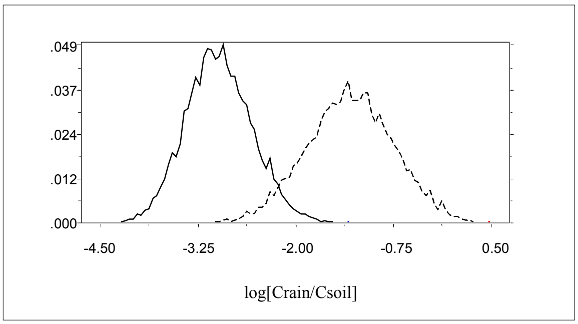


Measured (dotted) and computed (solid) air-water concentration ratios.

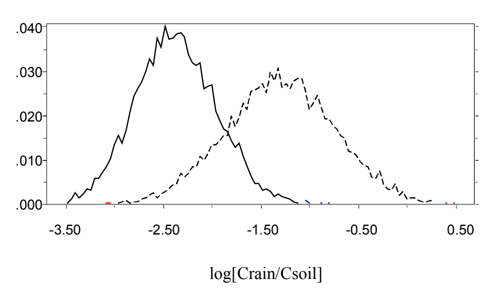
## Lindane



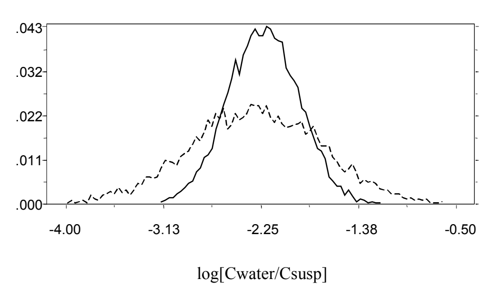
Measured (dotted) and computed (solid) frequency distributions of rain-water concentration ratios.



Measured (dotted) and computed (solid) frequency distributions of rain-soil(2) ratios.

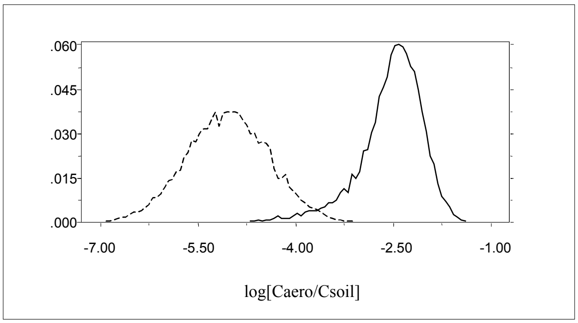


Measured (dotted) and computed (solid) frequency distributions of rain-soil(4) ratios.

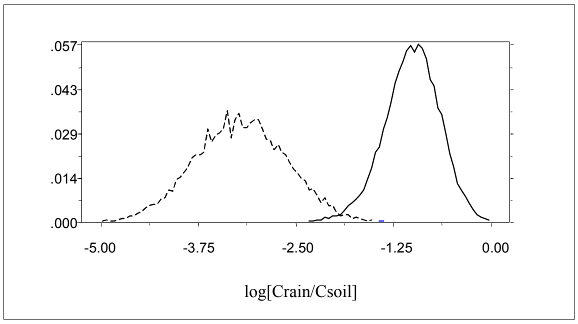


Measured (dotted) and computed (solid) frequency distributions of water-sediment ratios.

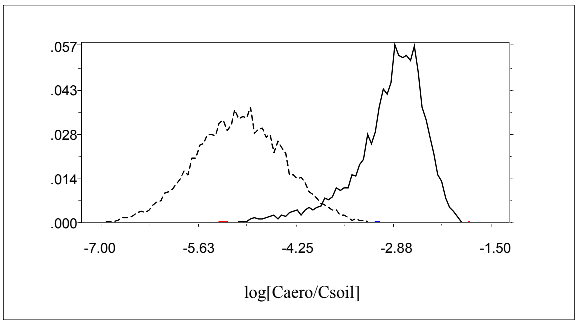
## Benzo[a]pyrene



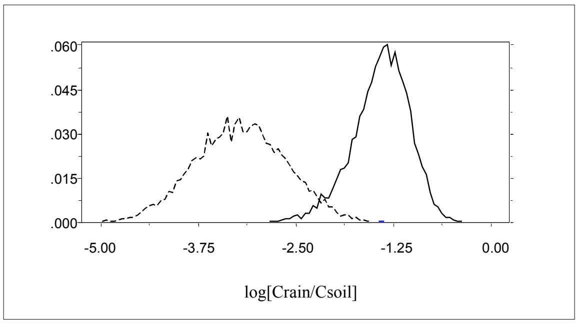
Measured (dotted) and computed (solid) frequency distributions of aerosol-soil(2) concentration ratios.



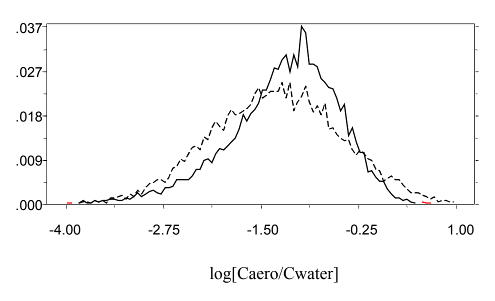
Measured (dotted) and computed (solid) frequency distributions of rain-soil(2) concentration ratios.



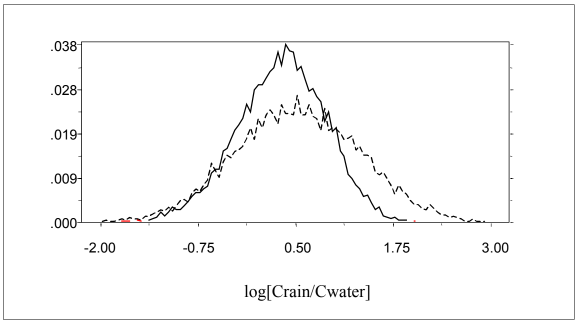
Measured (dotted) and computed (solid) frequency distributions of aerosol-soil(4) concentration ratios.



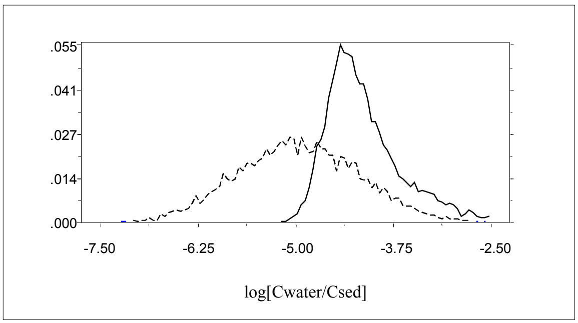
Measured (dotted) and computed (solid) frequency distributions of rain-soil(4) concentration ratios.



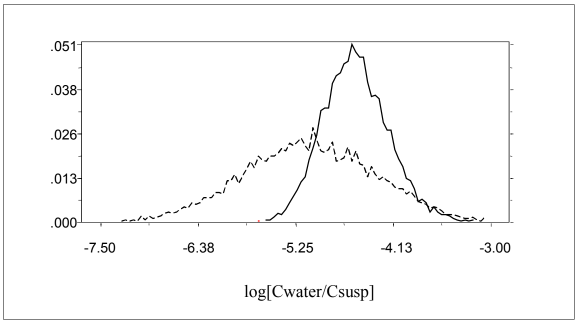
Measured (dotted) and computed (solid) frequency distributions of aerosol-water concentration ratios.



Measured (dotted) and computed (solid) frequency distributions of rain-water concentration ratios.

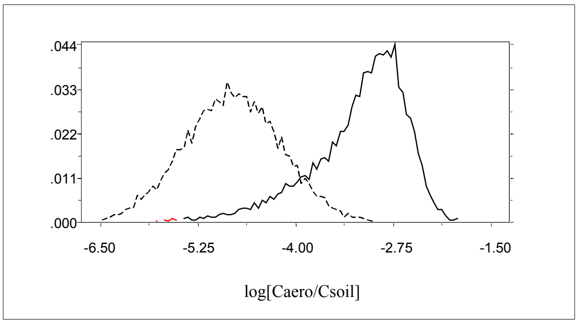


Measured (dotted) and computed (solid) frequency distributions of water-sediment concentration ratios.

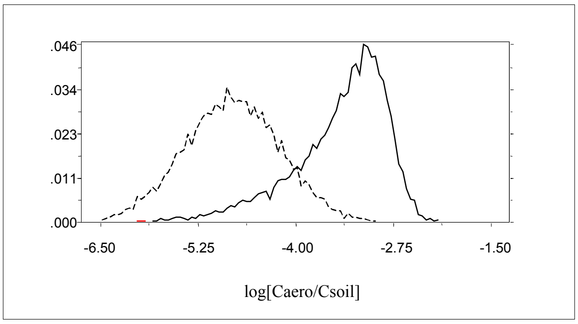


Measured (dotted) and computed (solid) frequency distributions of water-suspended matter concentration ratios.

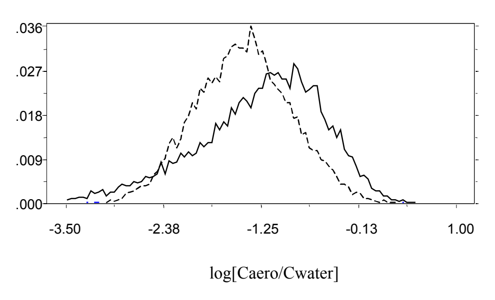
## Chrysene



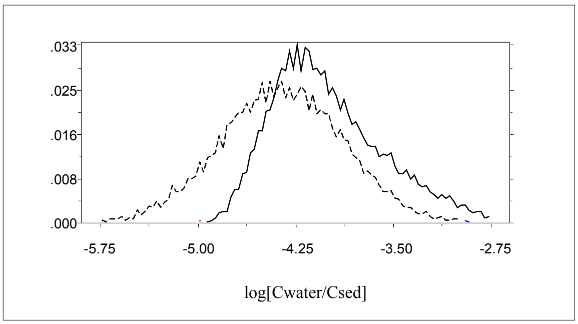
Measured (dotted) and computed (solid) frequency distributions of aerosol-soil(2) concentration ratios.



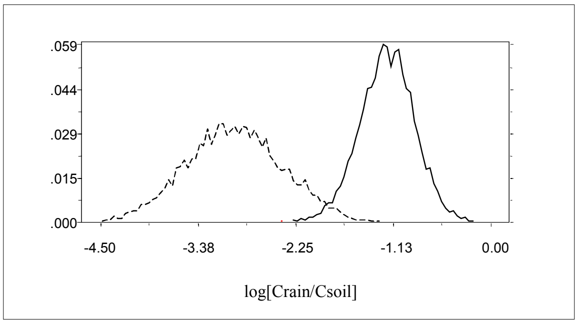
Measured (dotted) and computed (solid) frequency distributions of aerosol-soil(4) concentration ratios.



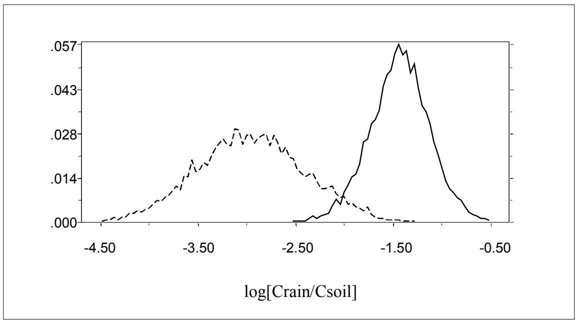
Measured (dotted) and computed (solid) frequency distributions of aerosol-water concentration ratios.



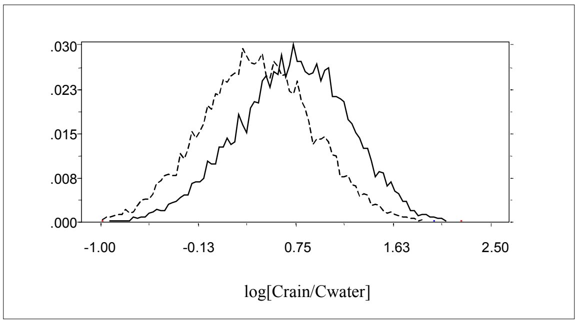
Measured (dotted) and computed (solid) frequency distributions of water-sediment concentration ratios.



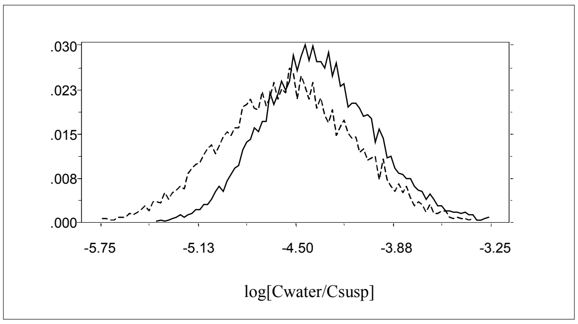
Measured (dotted) and computed (solid) frequency distributions of rain-soil(2) concentration ratios.



Measured (dotted) and computed (solid) frequency distributions of rain-soil(4) concentration ratios.

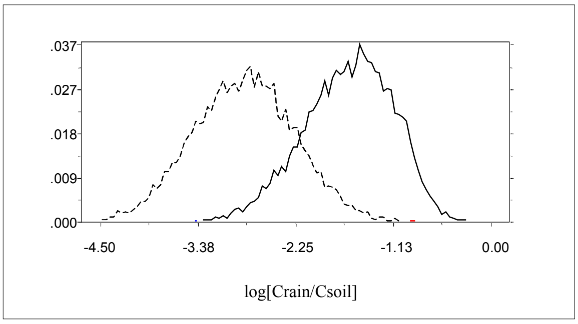


Measured (dotted) and computed (solid) frequency distributions of rain-water concentration ratios.

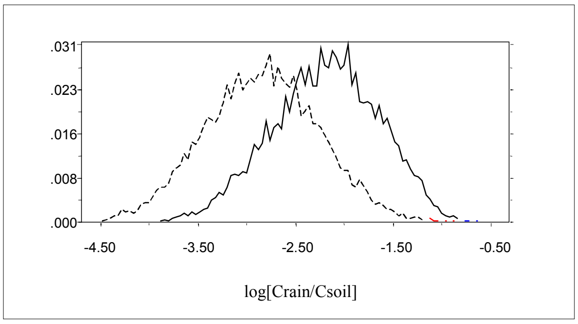


Measured (dotted) and computed (solid) frequency distributions of water-suspended matter concentration ratios.

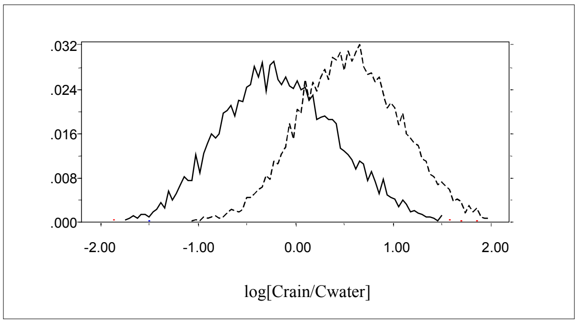
## Fluoranthene



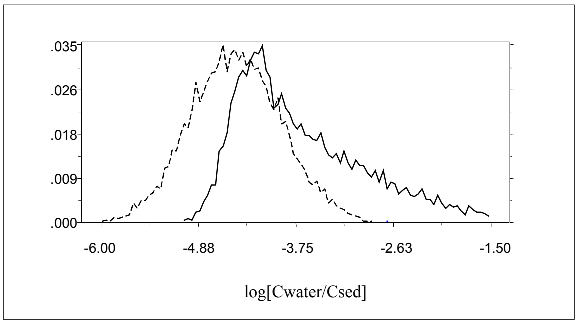
Measured (dotted) and computed (solid) frequency distributions of rain-soil(2) concentration ratios.



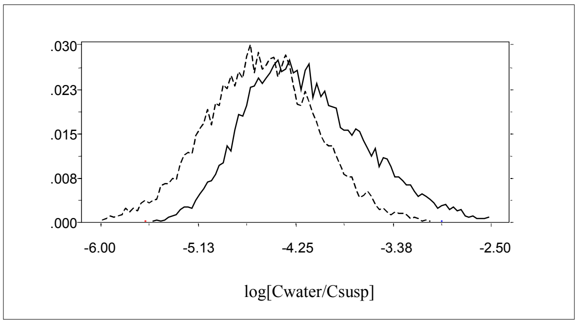
Measured (dotted) and computed (solid) frequency distributions of rain-soil(4) concentration ratios.



Measured (dotted) and computed (solid) frequency distributions of rain-water concentration ratios.



Measured (dotted) and computed (solid) frequency distributions of water-sediment concentration ratios.



Measured (dotted) and computed (solid) frequency distributions of water-suspended matter concentration ratios.

# APPENDIX IX: SCORES OF COMPUTED CONCENTRATION RATIOS (CRS) ON THE FACTOR 3, 10 AND 30 CRITERIA, ARE THE CRITERIA MET?

| | | **Criteria factor k for** | | |
|---|---|---|---|---|
| **substance** | **ratio** | **3** | **10** | **30** |
| tetrachloroethylene | air-water | no | no | yes |
| | | | | |
| lindane | rain-water | no | no | yes |
| | water-sed | 🟩 | 🟩 | 🟩 |
| | water-susp | yes | yes | yes |
| | rain-agricultural soil | no | no | no |
| | rain-average soil | no | no | yes |
| | | | | |
| benzo[a]pyrene | rain-water | yes | yes | yes |
| | aero-water | yes | yes | yes |
| | water-sed | no | yes | yes |
| | water-susp | no | yes | yes |
| | rain-agricultural soil | no | no | no |
| | rain-average soil | no | no | no |
| | aero-agricultural soil | no | no | no |
| | aero-average soil | no | no | no |
| | | | | |
| chrysene | rain-water | yes | yes | yes |
| | aero-water | yes | yes | yes |
| | water-sed | yes | yes | yes |
| | water-susp | yes | yes | yes |
| | rain-agricultural soil | no | no | no |
| | rain-average soil | no | no | no |
| | aero-agricultural soil | no | no | no |
| | aero-average soil | no | no | no |
| | | | | |
| fluoranthene | rain-water | no | yes | yes |
| | aero-water | | | |
| | water-sed | no | yes | yes |
| | water-susp | yes | yes | yes |
| | rain-agricultural soil | no | no | yes |
| | rain-average soil | no | yes | yes |
| | aero-agricultural soil | | | |
| | aero-average soil | | | |
| | | | | |

# APPENDIX X: PROBABILITY OF COMPUTED CRS FALLING WITHIN PREDEFINED UNCERTAINTY RANGES

Comparison of logarithmic value of measured en computed concentration ratios. Degree of similarity expressed as the percentage of outcomes witin a given range of unity. The range is given by a factor k, a factor k=100 giving a lower limit of 1/100 and a upper limit of 1*100

| | | **Factor k for relative range (1/k,1*k)** | | | |
|---|---|---|---|---|---|
| **substance** | **ratio** | **100** | **30** | **10** | **3** |
| tetrachloroethylene | air-water | 92 | 74 | 48 | 20 |
| | | | | | |
| lindane | rain-water | 82 | 64 | 46 | 19 |
| | water-sediment | 94 | 83 | 64 | 34 |
| | water-suspended matter | 100 | 97 | 85 | 51 |
| | rain-agricultural soil | 67 | 38 | 17 | 5 |
| | rain-average soil | 91 | 72 | 45 | 18 |
| | | | | | |
| benzo[a]pyrene | rain-water | 95 | 85 | 67 | 36 |
| | aerosols-water | 92 | 81 | 63 | 33 |
| | water-sediment | 88 | 75 | 55 | 28 |
| | water-suspended matter | 95 | 85 | 66 | 36 |
| | rain-agricultural soil | 38 | 15 | 5 | 1 |
| | rain-average soil | 61 | 32 | 13 | 4 |
| | aerosol-agricultural soil | 25 | 10 | 4 | 1 |
| | aerosol-average soil | 42 | 21 | 9 | 3 |
| | | | | | |
| chrysene | rain-water | 99 | 95 | 80 | 45 |
| | aerosols-water | 96 | 87 | 69 | 38 |
| | water-sediment | 99 | 95 | 83 | 50 |
| | water-suspended matter | 100 | 99 | 91 | 59 |
| | rain-agricultural soil | 64 | 33 | 12 | 2 |
| | rain-average soil | 77 | 47 | 21 | 6 |
| | aerosol-agricultural soil | 65 | 41 | 22 | 9 |
| | aerosol-average soil | 74 | 52 | 31 | 12 |
| | | | | | |
| fluoranthene | rain-water | 94 | 82 | 61 | 31 |
| | aerosols-water | | | | |
| | water-sediment | 88 | 77 | 62 | 34 |
| | water-suspended matter | 98 | 91 | 77 | 44 |
| | rain-agricultural soil | 85 | 63 | 38 | 16 |
| | rain-average soil | 95 | 85 | 64 | 33 |
| | aerosol-agricultural soil | | | | |
| | aerosol-average soil | | | | |
| Criteria limits | | 80 | 70 | 50 | 20 |