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Predictions by the multimedia environmental fate model SimpleBox compared to field data

Intermedia concentration ratios of two phthalate esters

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Abstract

Environmental concentrations of two high production volume phthalate esters, di(2-ethylhexyl) phthalate (DEHP) and di n-butyl phthalate (DBP), are compared to predictions by the multi-media fate model SimpleBox. Concentration *ratios*, with emphasis to those of air/water, were compared because this specific model output is used for harmonizing environmental quality objectives (EQO) for air, water, and soil. In the Netherlands the multi-media model SimpleBox is applied to predict intermedia ratios of steady-state concentrations for comprison with ratios of independently derived EQOs. This comparison, also known as 'testing the coherence of EQOs', provides an indication for the likelihood that a pair of independently derived EQOs is both realistic (or manageable) and protective for an adjacent compartments (to which a chemical may migrate). The SimpleBox procedure for testing the coherence of EQO's has been critically examined by a Committee of the Dutch Health Council in 1995. The Committee recommended testing the validity of this specific application of SimpleBox. Monitoring results of DEHP and DBP in the period 1997 - 2001 were used to validate the SimpleBox model as a whole. The results indicate that predicted concentration ratios do not differ more than a factor of ten from field data. However, further validation research is necessary to gain confidence in applying multimedia environmental fate models for regulatory purposes.

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Contents

Samenvatting

Bij het afleiden van een stelsel van milieu-kwaliteitsdoelstellingen (MKD's) voor lucht, water en bodem wordt door het RIVM het multi-media model SimpleBox toegepast voor het testen van de 'coherentie'. Voor een bepaalde stof wordt met het multi-media model SimpleBox de steady-state concentratieratio (SSCR) berekend en vervolgens vergeleken met de verhouding van onafhankelijk van elkaar afgeleide MKD's. Deze vergelijking is een indicatie van het beschermingsniveau van de set van MKD's (bijvoorbeeld: biedt een MKD ook voldoende bescherming voor het secundaire compartiment, nl. dat compartiment waarin de betreffende stof *niet* geëmitteerd wordt, maar waarnaar het zich wel kan verplaatsen?) en voor de beheersbaarheid (is een bepaalde combinatie van MKD's, gezien de eigenschappen van een gegeven stof, wel realistisch?).

De procedure met SimpleBox waarmee inconsistenties t.a.v. een stelsel van aanbevolen MKD's kunnen worden aangetoond en op grond waarvan een MKD voor een bepaald compartiment kan worden bijgesteld, werd in 1995 door de Gezondheidsraad aan een kritisch onderzoek onderworpen. Allereerst stemde de Gezondheidraad in met het voorstel om bij het afleiden van normen voor water, sediment, bodem en lucht, rekening te houden met de mogelijkheid van transport van stoffen tussen de verschillende milieucompartimenten. SimpleBox werd als een mogelijk nuttig wetenschappelijk instrument beoordeeld ten behoeve van het harmoniseren van MKD's. De Gezondheidsraad adviseerde echter een wetenschappelijke update van het model, inclusief gevoeligheids- en onzekerheidsanalyse, maar vooral validatie van het multi-media model als geheel.

Met betrekking tot dit laatste levert het rapport de eerste resulaten. De onzekerheid van met SimpleBox *voorspelde* SSCR's wordt onderzocht door middel van een vergelijking met concentratieverhoudingen die betrekking hebben op *metingen* van een tweetal ftalaatverbindingen in de verschillende milieucompartimenten van Nederland in de periode 1997-2000.

Di(2-ethylhexyl) ftalaat (DEHP) and di n-butyl ftalaat (DBP) zijn hoog productievolume chemicaliën (HPVC's) waarvan de concentraties in de milieucompartimenten meestal goed meetbaar zijn. Concentratieverhoudingen, met name die voor lucht/water, worden vergeleken omdat juist deze specifieke modeloutput toegepast wordt bij het harmoniseren van MKD's. Voorspelde en gemeten concentratieverhoudingen lucht/water wijken niet meer af dan een factor 10. Hoewel ftalaten niet geheel representatief zijn voor de categorie (semi-) vluchtige stoffen, waarop de coherentietest met behulp van SimpleBox voor het eerst werd uitgevoerd, wordt het gebruik van multi-media modellen voor het harmoniseren van milieunormen ondersteund door de resultaten van onderhavig onderzoek. De conclusie luidt dan ook dat er geen redenen zijn de oorspronkelijk voorgestelde toepassing van SimpleBox te verwerpen, met de aantekening dat een wetenschappelijk alternatief ontbreekt. Voortgezet validatieonderzoek is echter noodzakelijk om met voldoende vertrouwen een dergelijk model als een *scientific tool* te kunnen inzetten in milieuregelgeving.

Summary

In the process of deriving 'coherent' sets of environmental quality objectives (EQOs) for air, water, and soil, the National Institute of Public Health and the Environment applies the multi-media model SimpleBox to predict ratios of intermedia steady-state concentration (SSCRs). These SSCRs are compared with ratios of independently derived EQOs to provide an indication of the likelihood that a pair of independently derived EQOs is both protective (also for an adjacent compartment to which a chemical may migrate) and manageable (in terms of realism). The SimpleBox procedure to identify serious inconsistencies between recommended EQOs, on the basis of which EQOs eventually are adjusted, was critically examined by a Committee of the Dutch Health Council in 1995. The Committee agreed with the proposal of taking the transport of substances between compartments into account when setting EQOs for water, sediment, soil and air. The Committee considered SimpleBox to be a potentially useful model for intercompartmental harmonization of EQOs. However, it recommended validation of the procedure, including sensitivity and uncertainty analysis and, in particular, validation of the model as a whole. The current report presents the first results of this validation. The uncertainty of SSCRs predicted by SimpleBox was investigated by means of a comparison between predicted and measured concentration ratios for two phthalate esters monitored in various compartments in the Netherlands in the period 1997-2001.

The two phthalate esters, di(2-ethylhexyl) phthalate (DEHP) and di n-butyl phthalate (DBP), are high production volume chemicals (HPVC) and measurable concentrations could be found in most environmental compartments. Concentration *ratios*, with emphasis on air/water, were compared to model output (SSCR's) because this specific model output is used for harmonizing environmental quality objectives (EQO). Predicted and measured air/water concentration ratios did not differ more than a factor of 10. Although phthalates are chemicals that are not really representative for the group of (semi-)volatile chemicals to which the SimpleBox coherence test procedure was first applied, the results of this validation study supported the use of multi-media environmental fate models for harmonizing EQOs. In conclusion, there are no reasons for rejecting this specific use of SimpleBox as long as there is no scientific alternative. However, further validation research is necessary to gain confidence in applying multimedia environmental fate models for regulatory purposes.

Abbreviations and definitions

CDF	Cumulative distribution function
CI	Coherence index
CR	Intercompartment ratio of measured concentrations
DBP	Di n-butyl phthalate
DEHP	Di(2-ethylhexyl) phthalate
ECETOC	European Centre for Ecotoxicology and Toxicology of Chemicals
ECPI	European Council for Plasticisers and Intermediates,
EQO	Environmental Quality Objective
Er	Auxiliary parameter that accounts for the uncertainty in relative emission rates of DEHP to air, water and soil
EU RAR	European Union Risk Assessment Report
GM	Geometric mean, exponentiated mean (μ) of log transformed X: $\mu_{\log X} = \log GM$
GSD	Geometric Standard Deviation, exponentiated standard deviation (σ) of log transformed X: $\sigma_{\log X} = \log GSD$. The GSD is a measure of the variation of data
HPVC	High Production Volume Chemical
k	Dispersion factor, or uncertainty factor, related to a variable that is lognormally distributed. k_{95} indicates that 95% of the distribution will be between $1/k_{95}$ times and k_{95} times the median (2.5th and 97.5th percentile, respectively). Dispersion factors are used as a measure for the span of lognormal distributions.
LHS	Latin Hypercube Sampling mode (in bootstrapping techniques)
LOD	Limit of Detection below which data are reported as ‘below LOD’
LOQ	Limit of Quantitation, below which only ‘indicative data’ are reported which do not satisfy certain quality criteria
LOES	National Investigation on Estrogenic Compounds
MPC	Maximum Permissible Concentration
PVC	Polyvinyl chloride, polymer which frequently contains DEHP
RIC	Research Institute for Chromatography (Belgium)
RIKZ	National Institute for Coastal Zone Management
RIZA	Institute for Inland Water Management and Waste Water Treatment
RIVM/ECO	Laboratory for Ecotoxicology of the RIVM
RIVM/LOC	Laboratory for Organic Chemistry of the RIVM
SETAC	Society of Environmental Toxicology and Chemistry
SSC	Steady state concentration as predicted by SimpleBox
SSCR	Steady state concentration ratio as predicted by SimpleBox
STP	Sewage treatment plant

1. Introduction

Multimedia environmental fate models of the category ‘Mackay-type’ (Mackay et al., 1985) have proved useful scientific tools since two decades. Notwithstanding the representation of heterogeneous environmental compartments by homogeneous boxes, these ‘box models’ help to understand the path and fate of a chemical that is emitted into the environment. For example, they may explain differences in the fate or behaviour of various chemicals, or differences in the fate or behaviour of a chemical among environments of a different kind. Chemicals of concern have been evaluated with multimedia fate models in terms of operationally defined ‘properties’ such as ‘persistence in the environment’, ‘potential for long distance transport’ or ‘arctic accumulation potential’ (Klečka et al., 1999). Recently, a multimedia model was used to evaluate the ‘realistic presence’ of 12,000 organic pollutants of the Canadian Domestic Substances List (Mackay et al., 2001) This was done in a screening procedure to select chemicals for persistence, bioaccumulation and toxicity (PBT).

Although the aforementioned applicability has been the main motive to develop multimedia models, exposure concentrations are also assessed in a regulatory context. The Mackay-type model SimpleBox (Van de Meent, 1993; Brandes et al., 1996) has been applied in the Netherlands for both scientific and regulatory purposes. As a tool in regulatory decision making, SimpleBox has been applied to predict

1. concentrations in the regional environment for the purpose of risk assessment of chemicals in technical guidance documents (EC-1996) and
2. steady-state intermedia concentration ratios (SSCR) in a non-equilibrium situation for harmonisation of environmental quality objectives (EQOs).

The present report evaluates the application of SimpleBox with respect to the latter. The SSCR concept was considered necessary to adjust EQOs, which are derived for individual chemicals for different compartments. Originally, each EQO was formulated separately and independently as a result of a sectoral approach, in spite of the awareness that in real-world situation concentrations in air, water and soil are interdependent. The SimpleBox procedure to compute SSCRs as a guiding principle to harmonise EQOs, was proposed by Van de Meent and De Bruijn (1995). Although they mentioned that the procedure was not validated, they advocated its appliance in the absence of alternatives.
A Committee of the Health Council of the Netherlands Health Council of the Netherlands (1995) has critically reviewed this procedure. According to the Committee, the use of SimpleBox in the framework of deriving EQOs would require more stringent demands than when it is applied as a scientific tool to gain insight into environmental fate processes. Model validation, including sensitivity and uncertainty analysis, was considered a prerequisite for application in environmental policy. The Committee advised to validate the model as a whole as well as individual process descriptions (see Insert 1). At the same time, the SETAC Taskforce on Application of Multi-Media Fate Models to Regulatory Decision-Making (Cowan et al., 1995) recommended model validation.

The general validity of the use of multimedia environmental fate models as a screening or scientific tool can not be established. Validation of a particular use of such models may be feasible but depends on the desired level of accuracy. Confidence may be gained by systematically testing model predictions of defined scenarios against specific field data. To this end, two high production volume chemicals (HPVCs) were selected: diethylhexylphthaltate (DEHP) and dibutylphthalate (DBP). For both compounds evaluated data are available which can by used to specify input parameter distributions. This report concentrates on the suitability of SimpleBox to predict SSCRs of phthalate esters in adjacent compartments, in comparison to ratios of measured concentrations collected in the Netherlands in the period 1997-2001.

Insert 1

With respect to the use of SimpleBox, the Committee of the Dutch Health Council recommended:

- to carry out sensitivity and uncertainty analyses;
- validation of specific applications, adapted to the system and the group of chemicals for which the model is used;
- to investigate the differences between model description and reality;
- to take several aspects into account, including: 1) the exchange rate of substances between air, rainwater and aerosol particles, between water and solids, 2) the influence of dissolved organic matter on exchange processes, 3) the influence of terrestrial vegetation on the exchange of gaseous substances between soil and air and on deposition processes;
- to validate the model as a whole on the basis of a concrete situation with a number of ‘model’ substances that are representative for the group of volatile chemicals.

2. SimpleBox and coherence testing of MPCs

Integrated environmental management policy in the Netherlands aims at the development of coherent sets of environmental quality objectives (EQOs). During a technical-scientific course Maximum Permissible Concentrations (MPC) are derived for each compartment. The modeling procedure evaluates the coherence of independently derived MPCs for air, water and soil. The coherence criterion is that MPCs should be both protective and manageable. An MPC for one compartment should also be protective for organisms living in adjacent compartments, since the chemical in question may be transferred across the interface. One may argue that harmonizing MPCs could be achieved sufficiently with partition coefficients, assuming that in the long term thermodynamic equilibrium will be reached between the compartments sediment/water and soil/groundwater. However, air may not be at or even near equilibrium with water and soil. Differences in advective transport processes of the chemical may be considerable because transport in air is more rapid in air than in adjacent compartments. Van de Meent and De Bruijn (1995) calculated steady state concentrations, which are not in equilibrium (so-called Level III computations, Mackay et al., 1985), to investigate the coherence of MPCs of seven model compounds for air, water and soil. Van de Plassche and Bockting (1993) applied the SimpleBox model (see Figure 1) in the evaluation of the coherence of MPCs for 46 volatile substances. A brief explanation of the procedure of coherence testing is given in Insert 2.

Insert 2

A set of MPCs is called incoherent if compliance with an MPC in the primary compartment - the compartment to which the emission takes place - results in MPC violation of an adjacent (secondary) compartment due to transport of the chemical across the interface between both compartments. Here it is convenient to define the environmental fate modeling output parameter, SSC_{pr}, which is the steady state concentration in the compartment to which the emission takes place. SSC_{sec} is the steady state concentration computed by the model for an adjacent compartment. Van de Meent and De Bruijn (1995) introduced a procedure to compare the steady state intermedia concentration *ratio* (SSC_{pr}/SSC_{sec}), computed with SimpleBox, with the quotient of independently derived MPCs (MPC_{pr}/MPC_{sec}).
Ragas (2000) introduced the coherence indicator (*CI*)

$$CI = \frac{MPC_{pr}}{MPC_{\sec}} \times \frac{SSC_{\sec}}{SSC_{pr}}$$

If *CI* is greater than one, the MPCs are not coherent because if emissions cause SSC_{pr} to reach the level of MPC_{pr} the steady state concentration in the secondary compartment will exceed MPC_{sec} (provided that the combined emission and import ratio between the two compartments is not changed).

3. Scope of the validation study

Validating models of such complex processes as 'fate of substances emitted into the environment' is difficult, if not impossible. It may become feasible if a well-defined scenario is concerned in relation to a specific model output and provided that:

- measurable concentrations are encountered in the compartments of a chosen scenario;
- uncertainty of input parameters and environmental processes is limited.

Obviously, high production volume chemicals (HPVCs) are candidates for a validation study since measurable concentrations in environmental compartments and gathered information (e.g. in reports in the frame of Risk Assessment Regulations) are often attributes of such chemicals.

In this report, 'validation of SimpleBox' means a comparison between model predicted steady state concentration ratios (SSCR) and quotients of environmental concentrations of HPVCs obtained from analyzed samples. If uncertainty and variability are to be taken into account, distributions of parameters are used as input instead of fixed values. These distributions propagate through the model, resulting in distributions of the desired output. The aim of this study is to compare a distribution of computed steady-state concentrations with a distribution of a corresponding ratio of measured concentration in the Netherlands.

3.1 History of SimpleBox

SimpleBox version 1.0

SimpleBox is a deterministic model that produces a single value output from single input parameters. Van de Meent and De Bruijn (1995) proposed the coherence test to be carried out with version 1.0 (see Figure 1).

Comments on version 1.0

The first version of SimpleBox has been reviewed by the Committee of the Health Council (Health Council of the Netherlands, 1995). They identified fundamental uncertainty with respect to:

- the assumption that the Netherlands consists of eight boxes (air, three soil boxes, water, and suspended particles in water, biota and sediment). The question was raised if the absence of a separate box for terrestrial vegetation is justified. Ignoring vegetation was suspected to affect estimated steady state air concentrations;
- the assumption of physical and chemical homogeneity in these boxes;
- the equations used in a model.

The Health Council recommended to critically reviewing the model structure and individual process descriptions. This advice was followed with the release of SimpleBox 2.0 (Brandes et al., 1996).

SimpleBox version 2.0

Concerning intercompartment transport of chemicals, this version reflects the present state of the art in multi-media fate modelling. The second version of SimpleBox is a multimedia fate model for evaluating the environmental fate at a regional scale nested in a continental scale. The continental scale consists of a moderate zone, which is linked to the regional scale. The regional scale is nested in a global scale which is connected to both an arctic and a tropic zone (Figure 2).

Other conceptual differences compared to version 1.0 are:

- the option to include a terrestrial vegetation module;
- two separate water compartments, fresh water and (inner)sea water;
- background concentrations at the regional scale resulting from transboundary transport of air and water between continental and regional scale.

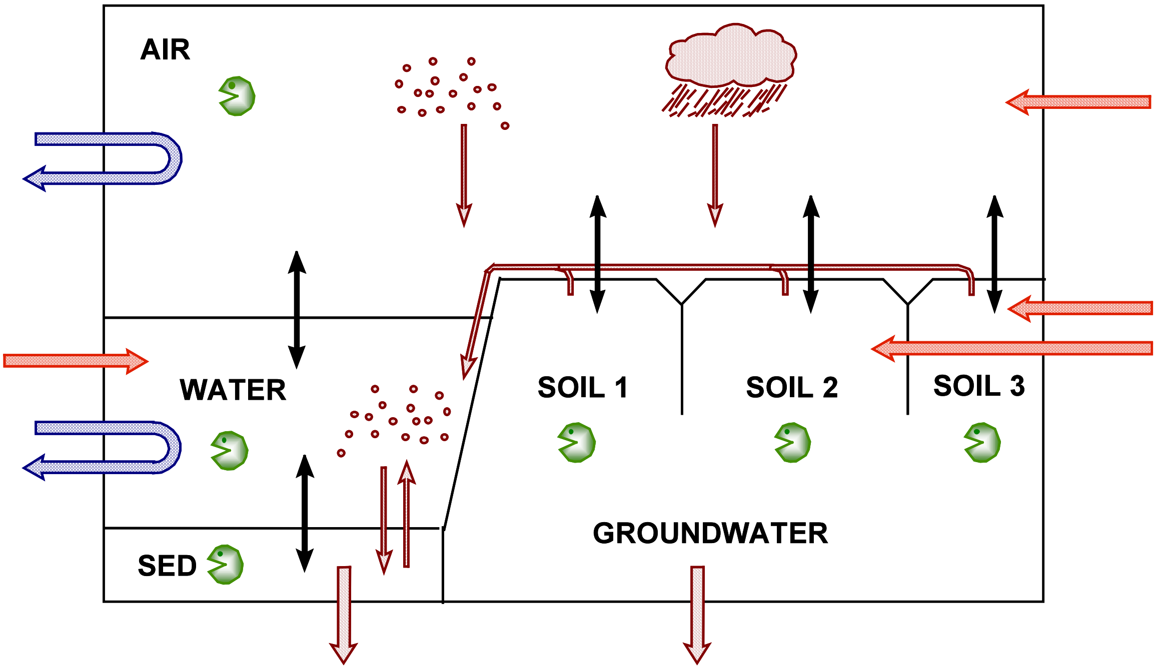

Figure 1. SimpleBox 1.0 (Van de Meent, 1993) has one scale and 8 compartments (air, water, suspended matter in water, aquatic organisms, sediment and three different types of soil: natural, agricultural and urban). Through sediment burial and groundwater the modelled chemical may be removed from the system.

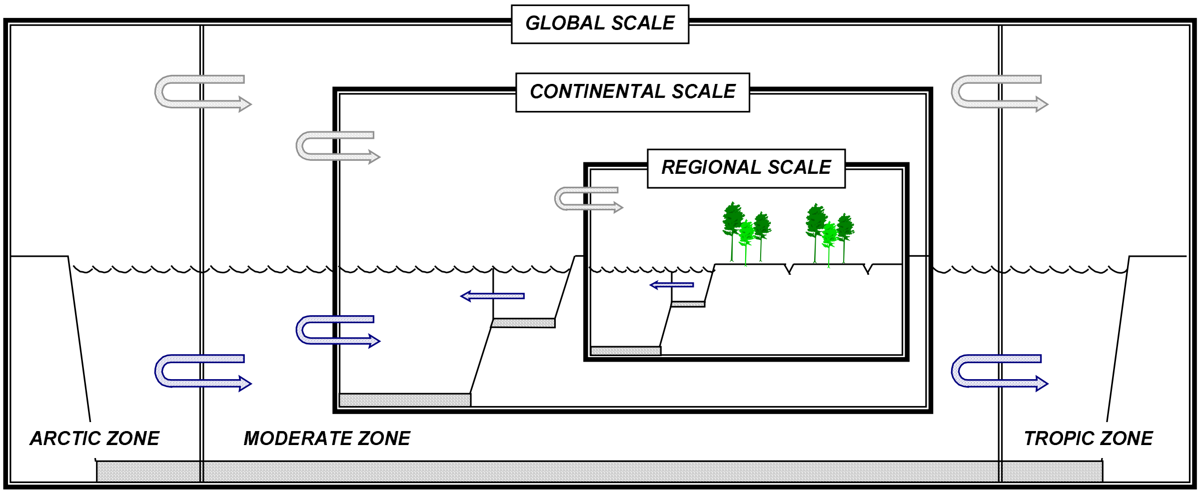

Figure 2. Simplebox 2.0 (Brandes et al., 1996)

3.2 Variability and uncertainty

The release of version 2.0 of SimpleBox reflected the present state of the art in multimedia fate modelling. However, version 2.0 still includes fundamental uncertainty. Since further reduction of fundamental uncertainty is beyond the scope of the validation project, the principal choice is made to conceive assumptions and equations and most of the default settings in SimpleBox 2.0 as scenario choice for this study. Uncertainty was dealt with by quantifying its magnitude and consequences in model estimates.

Sensitivity analysis and operational uncertainty, due to variability of some input parameters or a lack of data with respect to crucial substance-environment interactions, has been done previously by Etienne et al. (1997).

Meteorological data and other parameters that describe the environment (fi. water flows, water depth) are by default represented as yearly average values, typical for the Netherlands. They constitute the scenario in which fate and compartment concentrations of a compound are modeled.

Uncertainty due to spatial and temporal variability is ignored in this study. Ragas (2000) argued that spatial variability should not be included in the operational uncertainty analysis, because it would violate the model structure. Temporal variability due to diurnal and seasonal changes is assumed to even out, which is appropriate in view of the long period of collecting samples that was necessary to obtain sufficient data. The steady state concentration in a compartment is represented by a single value, i.e. the median or mode of a distribution. We assume that the variability is the result of propagation of specified uncertainty in selected input parameters, due to:

- empirical inaccuracy with respect to substance properties;
- lack of knowledge about the interactions between the substance and its environment (partitioning and degradation processes); and
- inaccurate information on emissions.

Only these uncertainties are thought to propagate, causing a certain distribution of the model output. A comparison is made to the distribution of ratios of concentrations, which were measured at locations spread out over the Netherlands over three years.

3.3 Ratios of measured concentrations

Production data and substance properties of two high production volume phthalates, DEHP and DBP, are known. From these figures it was anticipated that concentrations in different compartments in the Netherlands are measurable. Ideally, a large number of adjacent concentration pairs on varying locations are measured. From a logistic point of view, however, this appeared to be not feasible and concessions had to be made. Concentrations of DEHP and DBP in different environmental compartments were sampled at different times over the period 1997 - 2001.

Measured data are presented as:

- a distribution of concentrations per compartment, for comparison with the distribution of SimpleBox predicted steady state concentrations;
- a distribution of fugacity (see Appendix 6) per compartment. Mutual comparison will give insight into relevant issues such as: are the compartments in equilibrium? If not, do different fugacities agree well with the presumed emission patterns (primary compartment) and degradation rates in the different compartments?

- a distribution of a concentration ratio (CR) of adjacent compartments, for comparison with a corresponding SSCR that is predicted by SimpleBox.

3.4 Possible validity criteria

Two chemicals can not be sufficient to provide a solid ground to approve or disprove a particular application of SimpleBox. This study is only a starting point in a longer exercise of validating multi-media environmental fate models. Therefore it is convenient to formulate a priory criteria for testing model predictions against field data. As a guideline we adopt criteria of the SETAC-Workshop[1] (Cowan et al., 1995), during which perceived accuracy factors were tabulated. These factors were discriminated based on chemical types and categories of media. In this table uncertainty factors were given, ranging from 2 to 30, which increase for each inter-media transfer, provided that the emission of the chemical and degradation rates are known exactly. Discharge rates of phthalates, however, are uncertain and this uncertainty may cause even more uncertain results. Nevertheless, we adopt the range of uncertainty discussed by the SETAC-Workshop (Cowan et al., 1995), to formulate criteria for the present study:

- the median predicted steady state concentration ratio (SSCR) does not deviate more than a factor 3 from the median of the ratio of measured concentrations, while more than 60% of the observations fall between the 2.5th and the 97.5th percentiles of predicted SSCR (‘factor 3 criterion’);
- the median SSCR deviates more than a factor 3 from the median of observed concentration ratios but less than a factor of 10 (‘factor 10 criterion’), while more than 40% of the observations fall between the 2.5 and 97.5 percentiles of predicted SSCR. Note that the factor of 10 was already suggested by Van de Plassche and Bockting (1993) to take into account the inaccuracy of model predictions;
- 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’), while more than 30 % fall between the 2.5th and the 97.5th percentiles of predicted SSCR;

The validation study examines the model as a whole. This means that all kinds of uncertainty are included in the question how well SimpleBox predicts the environmental concentration ratios of specific chemicals in the Netherlands.

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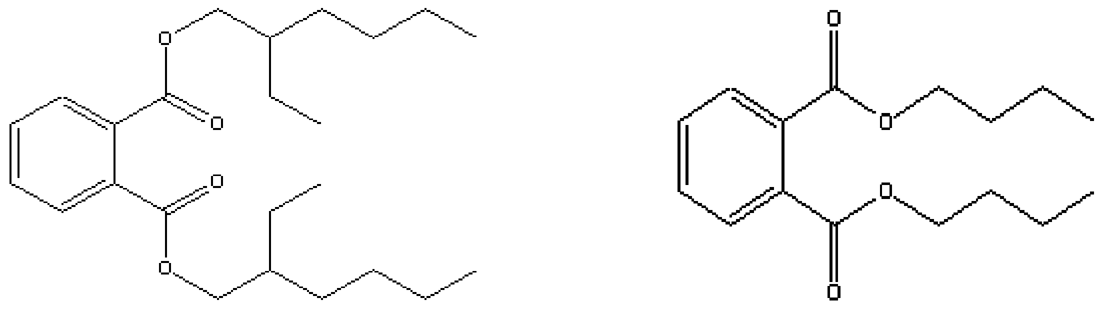
[1] Taskforce on Application of Multi-Media Fate Models to Regulatory Decision-Making

4. Properties of DEHP and DBP

Phthalate esters are industrial chemicals and widely used as plasticizers in PVC resins (ECETOC, 1988). In the EU approximately 1,000,000 tons are produced per year (4,300,000 worldwide) which is at a constant level since 20 years. Because of their properties, high production volumes and widespread use, concentrations in various environmental compartments are measurable and expected to reflect a constant and diffuse release into the environment. DEHP and n-dibutylphthalate (Figure 3) belong to the most common phthalate esters. Of the eighteen commercial phthalate esters, the share of di (2-ethylhexyl)phthaltate (DEHP) is fifty percent. The consumption is expressed on a per capita base, allowing calculation of emission data for a certain region with a known population density.



di(2-ethylhexyl) phthaltate (DEHP)
CAS No. 117-81-7

di n-butyl phthalate (DBP)
CAS No. 84-74-2

Figure 3 Molecular structures of DEHP and DBP

Physico-chemical properties

The chemical structure of a phthalate ester consists mainly of one benzene ring and two alphatic ester groups attached to the benzene ring in an ortho configuration. At ambient temperature, DEHP and DBP are non-volatile liquids with high boiling points. The air-water partition coefficient of both chemicals is well below 0.001 at 20 °C. Data in Table 1 were retrieved from a comprehensive review about physicochemical properties, environmental partitioning, bioaccumulation and (a)biotic transformation processes by Staples et al. (1997). In Table 1, uncertainty due to empirical inaccuracy is expressed in terms of k (dispersion factor or uncertainty factor) assuming that the distribution of a physico-chemical property is lognormal. Dispersion factors are used as a measure for the span of lognormal distributions. The octanol-water partition coefficient (K_{ow}) is related to the water solubility through a regression equation as used in SimpleBox, but slightly adjusted to to link the tabulated values for water solubility and log Kow to each other.

The atmospheric mixture of mainly nitrogen and oxygen, with an average mol weight equal to 28.8 g mol^{-1} has a lower density than atmospheric DEHP and DBP. The molecular weight of DEHP is more than an order of magnitude higher than the air mixture, which implies that the rarefication pattern[2] considerably deviates from that of major components in ambient air

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[2] With partial pressure p_0 (Pa) at sea level, the pressure p at ambient temperature at height h (m) is:

$$\frac{P}{P_0} = \exp(-\frac{Mgh}{RT})$$, with mol weight = M kg mol^{-1}, $g = 9.8$ m s^{-2} , $R = 8.314$ $Jmol^{-1}K^{-1}$, $T = 293$ K.

(Figure 4). In undisturbed atmosphere the concentration of DEHP at 1000 m height is only 23% of the concentration at sea level (DBP: 37%), while the nitrogen-oxygen mixture has still 90% of its sea level pressure. In these calculations the counteracting factor wind has been ignored. During quiet weather considerably higher concentrations can be measured on ground levels, which may increase the variability of measured air concentrations sampled under varying weather conditions.

Table 1. Physico-chemical properties of DEHP and DBP. Medians and k values are derived from Staples et al., 1997.

Property	unit	DEHP		DBP	
		Median	k	Median	k
Mol. Weight	g mol $^{-1}$	390.54	-	278.34	-
Vapour Pressure $_{T=25^{\circ}C}$	Pa	$1.33 \cdot 10^{-5}$	2	$3.6 \cdot 10^{-3}$	2
Solubility $_{T=25^{\circ}C}$	Mg L $^{-1}$	0.003^{*}	2	11.2^{*}	2
K_{ow}	-	$10^{7.5}$	4.5	$10^{4.5}$	3
Melting point	$^{\circ}$C	-47	-	-35	-

*Correlated to uncertainty in K_{ow} (corr. coeff. = -0.96 on log scale).

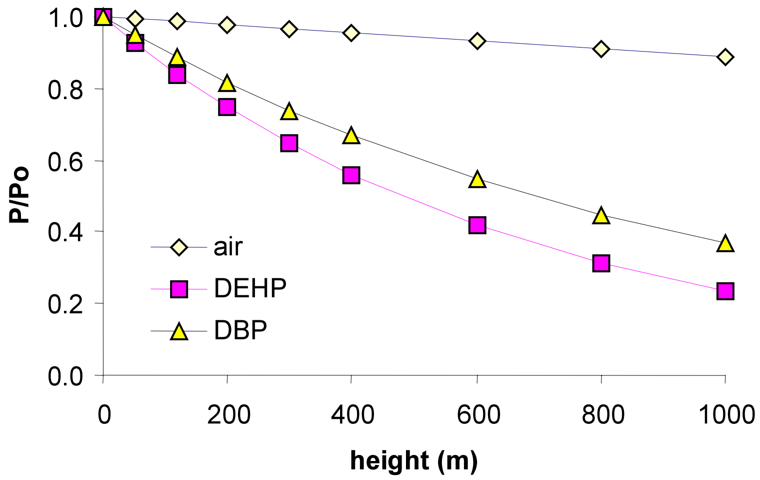

Figure 4. Rarefication of air, DEHP and DBP relative to atmospheric pressure at sea level

Environmental partitioning

The (dimensionless) air-water partition coefficient is derived from the vapour pressure and water solubility (Table 1). As it is assumed that the distribution of these two properties is log normal, with known median and k values, the analytical solution yields the median of Henry's law coefficient as the quotient of median vapour pressure (X_1) and median solubility (X_2). The distribution of this quotient is again log normal with median Y (= X_1/X_2) and a dispersion factor k_Y, which can be specified in terms of the individual uncertainty factors (k_1 and k_2):

$$k_Y = \exp\sqrt{\ln^2 k_1 + \ln^2 k_2}$$

Table 2. Partition coefficients and uncertainty factors of DEHP and DBP

Partition coefficient	Unit	DEHP		DBP	
		median	k	Median	k
Air-water (=H/RT)*	-	$7.4 \cdot 10^{-4}$	2.7	$3.8 \cdot 10^{-5}$	2.7
Suspended particles-water ($K_{p,\ susp.}$)	L kg^{-1}	$2.67 \cdot 10^{4}$	4.5	$1.54 \cdot 10^{3}$	10
Sediment-water ($K_{p,\ sed.}$)	L kg^{-1}	$2.78 \cdot 10^{4}$	7	$4.53 \cdot 10^{2}$	27
Soil-water ($K_{p,\ soil}$)	L kg^{-1}	$2.78 \cdot 10^{4}$	7	$4.53 \cdot 10^{2}$	27

*estimated Henry's law constant (H): quotient of vapour pressure (Pa) and water solubility (mol m^{-3}), R is the universal gas constant (8..314 J mol^{-1} K^{-1}) and T is the absolute temperature (285 K).

K_p values related to solids-water partitioning are assumed to be lognormally distributed. The median as well as uncertainty factor (k) is based on data gathered by Staples et al. (1997). These data relate to the organic carbon normalized partition coefficients, which are here multiplied by the organic carbon content of the solids, f_{oc}, to obtain K_p. Table 2 relates to K_p values with f_{oc} equal to 0.1.

Degradation

Degradation rates in air (Table 3) correspond to atmospheric halflifes of 0.7 and 2.3 d for DEHP and DBP, respectively. The dominant degradation process in water is biodegradation with halflifes of 23 d (DEHP) and 7 d (DBP). Degradation in soil and sediment is roughly one order of magnitude lower than in water. Hydrolysis of DEHP and DBP is slow, with halflifes of 2000 and 22 years (Staples et al. 1997). Estimated aqueous photooxidation halflifes are in the range of months to years. Therefore, abiotic degradation in the water compartment is neglected with respect to biodegradation. Median values and dispersion factors, given in Table 3, are based on a review paper by Staples et al. (1997).

Table 3. First order degradation rate constants and dispersion factors in d^{-1}

First order rate constant	DEHP		DBP	
	Median	k	Median	K
$K_{deg\ (air)}$	1.0	5	0.3	5
$K_{deg\ (water)}$	0.03	5	0.1	5
$K_{deg\ (sediment)}$	0.003	5	0.003	5
$K_{deg\ (soil)}$	0.003	5	0.01	5

Emission

The predicted air/water concentration ratio is very sensitive to the air/water emission ratio. In the case of phthalates the uncertainty with respect to this quotient is considerable, notwithstanding the high production volume of DEHP.

Two literature sources may be applied to estimate emissions of DEHP and DBP to the various environmental compartments. In a global overview on phthalate esters, Parkerton and Konkel (2001) considered lifecycle stages in the evaluation of environmental emission factors. They identified primary sources of production and consumption through literature surveys and unpublished market studies. Production and consumption tonnages of DEHP and DBP in Europe during the late 1990s are given in Table 4.

Table 4. Production (Kton yr^{-1}) of DEHP and DBP in the EU (Parkerton & Konkel, 2001)

Phthalate	Production	Consumption	Export
DEHP	595	476	119
DBP	37	21	16

Industrial processing of phthalates, use and disposal of phthalate containing products cause emission at the European scale. Since the use of phthalates containing products is widespread on this continent, a scaling factor of 16/370 (population ratio of the Netherlands and Europe) is applied to estimate emissions in the Netherlands. Although in the Netherlands phthalate esters are not produced, it is surrounded by equally highly industrialized and high-density population areas like North Rhine-Westphalia and Belgium. Therefore, the scaling factor is also applied to the Netherlands to evaluate emissions due to production, manufacturing and transport.

Besides information on the production, consumption and export of phthalates, SimpleBox also requires information on the distribution of the emissions over the compartments. Parkerton and Konkel (2001) evaluated emission factors (percentages of the annual amount produced or consumed that are emitted to the environment) according to a lifecycle scheme. However, they have applied a simple mass balance computation to estimate the emission to air using *measured* outdoor-air concentrations in the Netherlands (back calculation). Because a mass balance computation is the essence of multi-media environmental fate modeling, these emission factors could not be adopted as the aim of the project was to validate and not to calibrate SimpleBox.

Consequently, emission factors must be obtained from another source. Under the EU Risk Assessment Procedure for existing chemicals (Council Regulation (EEC) 793/93 of 23 March 1993) five phthalates are being evaluated. DEHP and DBP have been assessed (EU Risk Assessment Report, 2001[a,b]) by Sweden and the Netherlands, respectively. Emission data with respect to DEHP and DBP in Europe were retrieved from these sources and differentiated according to the life-cycle scheme of Parkerton and Konkel (2001) (Table 5).

Table 5. Emission factors (% of annual production that is emitted to the various environmental compartments) derived from EU RAR (2001[a,b]).

	DEHP			DBP		
Life Stage	Air	Water	soil	air	Water	Soil
Production	0.0004	0.014	0.0016	0.00	0.04	
Transport & industrial processing	0.0960	0.005	0.0141	0.02	0.05	
Product end use	0.0434	0.203	0.1679	1.67	3.06	
Product disposal	0.0042	0.507	0.5113		0.10	
Total	0.144	0.730	0.695	1.69	3.24	

With respect to Table 5, the following remarks have to be made:

- The great majority of these two phthalate esters either accumulates in the technosphere (without being an emission source) or is incinnerated.
- About half of the releases of DEHP during ‘transport & industrial processing’ is related to the manufacturing of polymers (98% PVC). In EU RAR (2001a) it is assumed that losses from PVC processing operations would be equally distributed between air and wastewater. Parkerton and Konkel (2001) suggested that given the nature of the PVC processing technology, emission would primarily occur to air. Therefore a 9:1 air/water emission distribution is assumed.
- During the life stages production and transport & industrial processing DEHP is emitted to wastewater. It is assumed that only 10% of these emissions will reach surface water as a result of wastewater treatment.
- Interior product end use (inside buildings) of DEHP containing polymers is presumably released to wastewater treatment plants, of which 10% will be emitted to surface water. Exterior (outside buildings) polymer related end use of DEHP is assumed to cause emission to the water compartment directly.

Emissions of both phthalates in the Netherlands are derived (Table 6) from data in Tables 4 and 5, combined with the scaling factor 16/370 (the Netherlands/EU).

Table 6. Emission rates of DEHP and DBP at the regional and the continental scale, derived from Tables 4 and 5

	DEHP (ton yr^{-1})			DBP (ton yr^{-1})		
	E_{air}	E_{water}	E_{soil}	E_{air}	E_{water}	E_{soil}
The Netherlands	35	152	141	13	25	-
EU without the Netherlands	656	3322	3164	291	558	-

Alternative emission factors for DEHP (Table 7) could be evaluated from data by Cadogan et al. (1994). The emission factors given in Table 7 were modified by assuming that in the Netherlands only 10 % of DEHP will reach the surface water (more than 90 % of the wastewater is treated by wastewater treatment plants). The scaling factor 17/370 is combined with Tables 4 and 7, to obtain the emission rates for in the Netherlands as given by Table 8.

Table 7. Alternative emission factors (%) for DEHP based on data by Cadogan et al. (1994), applied to the Netherlands

	DEHP		
Life Stage	Air	Water	soil
Production	0.163	0.003	
Transport & industrial processing		0.013	
Product end use	0.088	0.063	
Product disposal		0.053	
Total	0.252	0.133	

The emission rates on a European scale were based on the assumption that in Europe only 70% of the wastewater is treated by sewage treatment plants in stead of 90% in the Netherlands. This difference causes the discrepancy in emission ratios between the Netherlands and Europe in Table 8.

Table 8. Emission rates of DEHP at the regional and continental scale based on Cadogan et al. (1994)

	DEHP (ton yr^{-1})		
	E_{air}	E_{water}	E_{soil}
The Netherlands	61	28	-
EU without the Netherlands	1331	1535	-

A comparison of both emission scenarios for DEHP may illustrate the uncertainty in emission rates. The air/water emission ratio according to Table 6 equals 0.2, whereas Table 8, based on data of Cadogan et al. (1994), indicates that the ratio is equal to 2.

The above information shows that large variations (approximately a factor of ten) can be observed in the emissions estimates of DEHP. To account for the uncertainty in the emission estimates, the two scenarios are combined by expressing the emissions of DEHP in the Netherlands as follows:

$E_{air} = 35 + Er$
$E_{water} = 152 - 4.77 \cdot Er$
$E_{soil} = 141 - 5.42 \cdot Er$

Parameter Er may have an uniform distribution between 0 and 26. If Er equals zero, the emission scenario is according to EU RAR (2001[a]) as in Table 6. If Er equals 26, the emission scenario given by Table 8 (Cadogan et al., 1994) applies. However, this still may underestimate the uncertainty on the emission rates to each compartment. Therefore, E_{air}, E_{water} and E_{soil} are multiplied by E_a, E_w or E_s, respectively. These factors are lognormally distributed, with median equal to one and uncertainty factor, $k_{a,w,s}$ equal to 10.
For DBP only one emission scenario was found (EU RAR, 2001[b]), yielding emission rates to air and water as given in Table 6. The uncertainty was taken into account by assuming a lognormal distribution of E_{air} and E_{water} in the Netherlands with median values as given in Table 6 and uncertainty factors equal to 15.
Emission data of DEHP and DBP in the EU are the only input data at the continental scale from which SimpleBox 2.0 calculates ‘continental background’ concentrations in air and water.

5. Materials and methods

5.1 Measured concentrations

In 1997, the Laboratory for Ecotoxicology (RIVM/ECO) launched a monitoring campaign in collaboration with the Laboratory for Organic Chemistry (RIVM/LOC), the European Council for Plasticisers and Intermediates (ECPI), AlControl Biochem Laboratory and the Research Institute for Chromatography (RIC). Samples of soil and vegetation were taken in the period 1997-1998. Fish samples were collected in 1998 and sediment samples were taken in 1999. Air sampling took place in 2000-2001.
In the framework of the project LOES (Dutch National Investigation on Estrogenic Compounds, see Vethaak et al., 2002), samples of freshwater were taken during spring, summer and autumn of 1999 for analysis of phthalates. At approximately 50% of the sample locations also suspended particulate material was collected.

Sampling sites and analytical procedures

Sampling locations for air and freshwater are shown in Figure 5; for sediment, fish, soil and vegetation in Figure 6. More detailed information is found in Table 9 (air) and in Appendix 2 (soil, vegetation, sediment and fish). The chemical analysis of phthalates in air, sediment, fish, soil and vegetation is described in Appendix 3. For analysis of DEHP and DBP in samples of water and suspended solids, reference is made to Vethaak et al. (2002).

Air

At four locations duplicate air samples were taken in the period of 2000/2001 (Table 7). The weather conditions of all samples were not typical for the Netherlands. The average wind speed was below 3 m s^{-1}, which is the default value in SimpleBox because it is considered the yearly average in the Netherlands. A penetrating odour was clearly detected at A5 (Table 9) where emissions were observed coming from the petrochemical sites, while there was nearly no wind and smog was present. In the wintertime of 2001, all samples were taken on Sunday. Sampling during the summer of 2001 (A7 and A11) was at high temperature after a long warm and dry period.

Table 9. Air sampling of phthalates in the Netherlands in 2000/2001.

Location (Nr in Figure 5)	Code	Time	Weather
Gilze-Rijen (25), small road	A1	22 Feb 00 (10:00)	5 °C, sunny, mild wind
Between forest and arable land, 2 km	A2	4 Aug 00 (14:30)	20 °C, cloudy, mild wind
From highway; close to airforce base.	A3	14 Jan 01 (Su, 14:30)	1 °C, cloudy, no wind
Pernis (24), industrial	A4	22 Feb 00 (12:00)	9 °C, sunny/cloudy, mild wind
Town in vicinity of Rotterdam,	A5	4 Aug 00 (9:30)	20 °C, sunny/cloudy, no wind
Samples taken in the center of the	A6	14 Jan 01 (Su, 9:30)	2 °C, sunny, mild wind
Town.	A7	2 Aug 01 (10:15)	25 °C, very sunny, mild wind
Speulderveld (27), remote	A8	22 Feb 00 (15:00)	8 °C, sunny, mild wind
Area, nature reserve,	A9	4 Aug 00 (11:30)	24 °C, sunny, mild wind
Sampling at 300 m from motorway.	A10	14 Jan 01(Su, 11:40)	1 °C, cloudy, mild wind
	A11	2 Aug 01 (14:00)	28 °C, hot, sunny, mild wind
Vianen (23), close to	A12	22 Feb 00 (16:00)	9 °C, cloudy, mild wind
Highway crossing 100 m from	A13	4 Aug 00 (13:10)	24 °C, sunny, mild wind
Highway.	A14	14 Jan 01 (Su, 13:20)	2 °C, cloudy, mild wind

The limit of detection is determined by the method blank as described by the method validation (for more about chemical analysis see Appendix 3). The method blank was below 30 pg on the system, corresponding to 2 ng m^{-3} for a single isomer phthalate.

Fresh water

During spring, summer and autumn 1999, 66 freshwater samples were taken from 23 different sites (see Appendix 4) for analysis of the dissolved concentration. From 11 out of 23 locations also samples of suspended material in the water column were taken to yield 32 samples (one was lost) for the determination of the phthalate concentration in suspended particles. Both suspended material and water could be paired, yielding 32 pairs of water and solid concentrations.

The limit of detection (LOD) for dissolved DEHP was between 0.09 and 0.16 μg L^{-1} and for DBP between 0.08 and 0.14 μg L^{-1}. All suspended sediment samples contained DEHP in analyzable amounts. In only a minor fraction of the 32 samples the concentration of DBP in suspended solids could be determined. The methodology of sampling and chemical analysis is given by Vethaak et al. (2002).

Sediment

Early 1999, 30 sediment samples were collected in the Netherlands (Appendix 2, Table A3). The median organic carbon content was 4.6%, ranging from less than 0.5% (clean pond in Oud Beijerland) to 14% in Wormerveer. The amount of particles smaller than 1 μm varies from 1.7% (Noordwijk) to 26 % in Alkmaar and Assendelft, with a median of 9.4%.

The LOD for DEHP and DBP in sediment was 15 and 25 μg/kg dry weight, respectively.

Fish in freshwater

In 1998 local fishermen collected twenty-five samples were at different locations in the Netherlands (see Appendix 2, Table A4) by. The fat content of the fish varied between 0.1 and 5.1% (median: 0.5%; 90th percentile: 2.2%). The limit of detection was 100 ng g^{-1} (fat) for both phthalates.

Soil and vegetation

During the summer and autumn 1997 and spring and summer 1998, 34 soil samples and 47 vegetation samples were taken by RIVM. Tables A1 and A2 (Appendix 2) contain information on the sample sites. The dry weight content of soil ranged from 63 to 96% (median 83%); dry matter of vegetation varied between 11 and 64% (median 18.6%). The LOD for DEHP and DBP in soil was 15 and 25 μg kg^{-1} dry weight, respectively.

For vegetation 50 μg kg^{-1} dry weight was reported as the ‘limit of quantitation’ (LOQ) of both phthalates. ‘Indicative’ levels were reported in the range between 1 and 50 μg kg^{-1} dry weight.

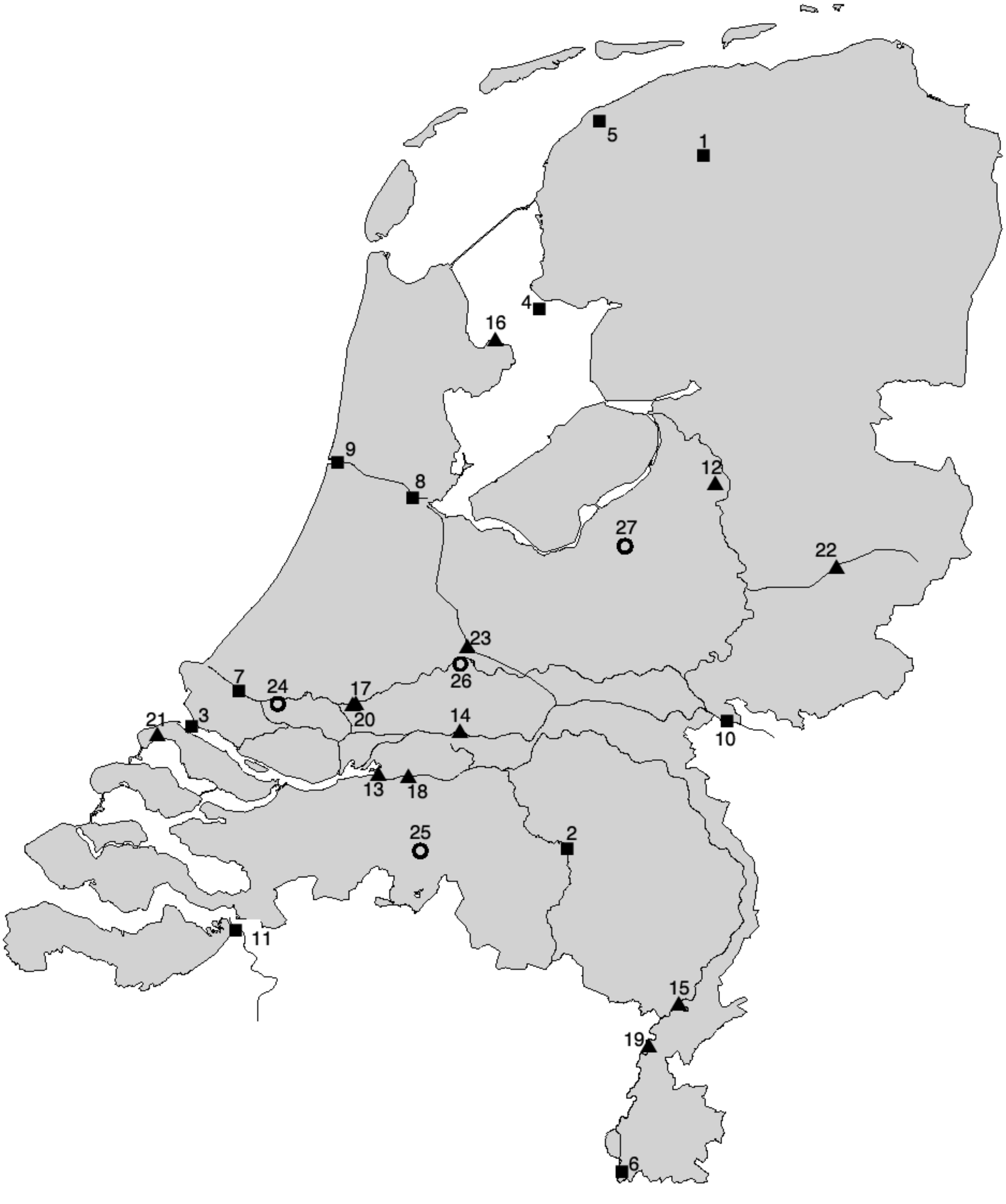

Figure 5. Overview of sampling locations in the Netherlands for air (open circles) and water (black triangles: only water; black squares: both water and suspended matter).

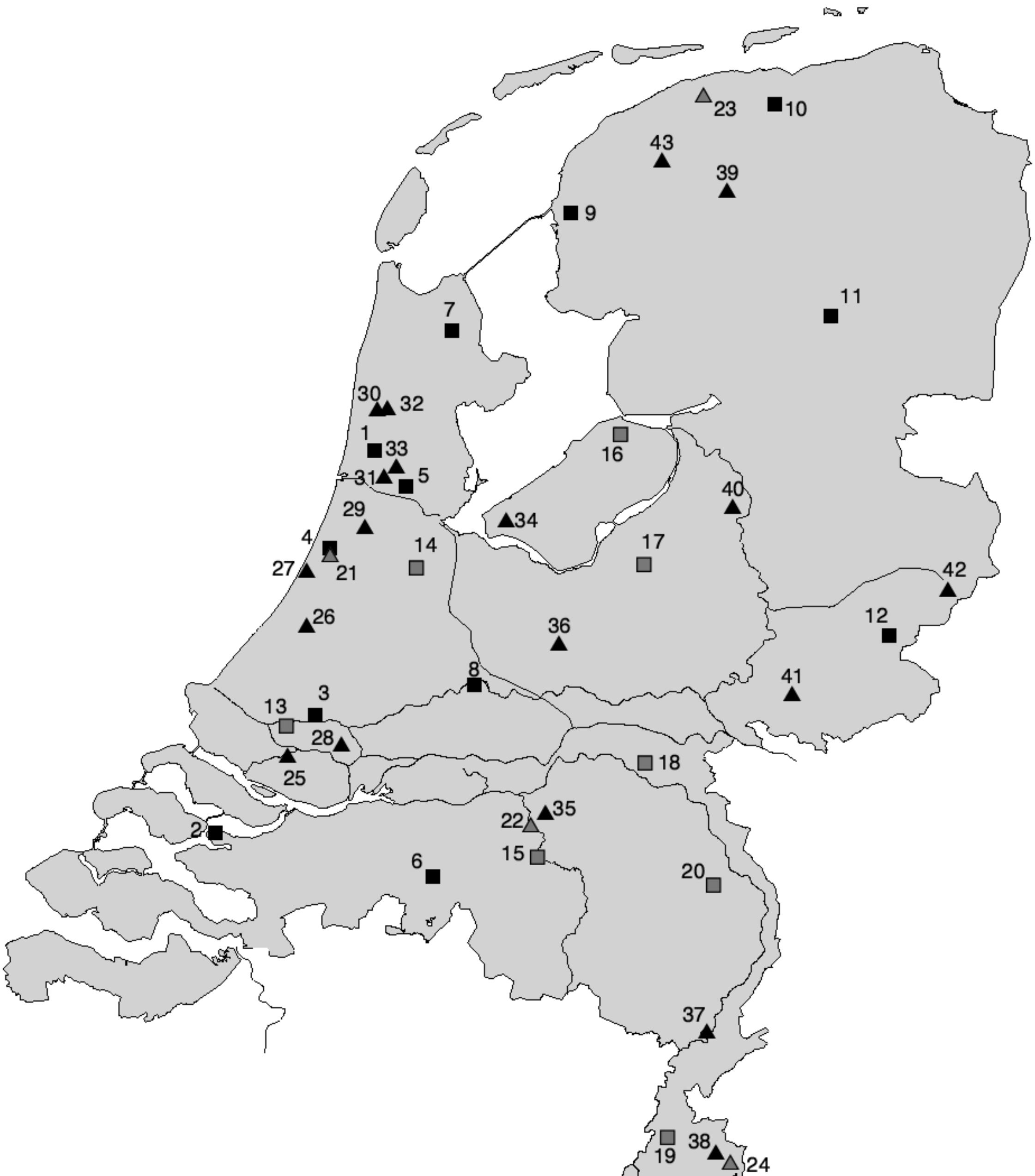

Figure 6. Overview of sampling locations in the Netherlands for sediment (grey triangles), both sediment and fish (black triangles), vegetation (grey squares) and both soil and vegetation (black squares).

Treatment of measured data: premisses and methods

The premise is that the distribution of concentrations in all compartments is lognormal. DEHP levels in 4 out of 14 air samples were below the LOD (2 ng m^{-3}). The DEHP concentrations above LOD were tested in a quantile-quantile plot to verify the log normal distribution. The method to assign a value to samples below LOD is described in Appendix 4.

Cumulative probability plots, the geometric mean (GM) and the geometric standard deviation (GSD) were calculated for the total concentration in air and for the dissolved concentration in water (concentration measured after filtration of the water sample).

Measured concentrations in sediment samples were expressed in units of mg kg^{-1} dry weight. Substitute values for samples with concentrations below the detection limit were calculated (Appendix 4). All concentrations were subsequently multiplied by corresponding dry weight fractions to obtain a set of concentrations in units of µg kg^{-1} wet sediment. The GM and GSD were calculated from this data set.

Concentrations in 25 fish samples were determined in the fat fraction of the fish. The results were converted into units of µg kg^{-1} wet fish, with LOD equal to 1 µg kg^{-1} wet fish. Substitute values were calculated according to Appendix 4. From this data set GM and GSD were calculated.

In more than half of the 34 soil samples DEHP levels (in µg kg^{-1} dry matter) were above the LOD and the median was determined in a straightforward manner. The resulting were multiplied by dry weight fractions to obtain concentrations in units of µg kg^{-1} wet soil. For DBP only 30 % was above the LOD and the median had to be estimated. In Appendix 4 methods are given for the substitution of values below the LOD and the estimation of the median.
The concentration of DBP in units of µg kg^{-1} wet soil was obtained from the product of this estimated median in µg kg^{-1} dry matter and the median value of the dry matter content of all samples (kg dry soil per kg wet soil).

For DEHP only two out of 47 vegetation samples were below the LOQ whereas the vast majority (42) contained less DBP than the LOQ. In the concentration range of 1 to 50 µg kg^{-1}, there are 14 samples to which ‘indicative’ concentrations were assigned. These values were included in the data analysis in order to obtain a better estimate of the 90th percentile for DBP. The median concentration of DBP in vegetation was estimated and all concentrations (including the substituted values) were multiplied by the dry matter fraction to obtain concentrations in µg kg^{-1} wet vegetation. This data set was used to calculate the median concentration and the 90th percentile.

5.2 Modelling steady state concentrations

The spreadsheet programme Microsoft Excel 97 was employed to perform the calculations with the spreadsheet file ‘SimpleBox 2.06.xls’. The uncertainty propagation was conducted with Monte Carlo analysis in the Latin Hypercube sampling mode (LHS) in Crystal Ball^{TM} version 4.0 (Decisioneering, 1996).

Characteristics of the regional environment

All parameters that characterize the regional environment are similar to default settings (Brandes et al., 1996), with the exception of parameters given in Table 10. The default parameters reflect a 40,000 km^2 area (including fresh water), typical for the Netherlands, and an equal area of sea water. The continental scale has dimensions of the European Union, including seawater.

Table 10. Chosen characterization of the regional environment in SimpleBox 2.06

System parameter	Value
Temperature	12 °C
Area sea water	40,000 km^2
Area fresh water	1,200 km^2
Area natural soil	10,800 km^2
Area agricultural soil	24,000 km^2
Area urban/industrial soil	4000 km^2
Wind speed	1.5 m s^{-1}
Mixing height air	300 m

6. Results

6.1 Measured concentrations

Air

In all samples duplicate concentrations of DBP did not deviate more than 30 % from the mean and were above the detection limit of 2 ng m^{-3} (Table 11). From a quantile/quantile plot[3] the conclusion is justified that a lognormal distribution is most likely (Figure 7). The cumulative distribution function (CDF) is given by Figure 8, in which the measured concentrations are represented by Hazen plotting positions (Cunnane, 1978). These are midpoints halfway empirical CDF jumps.

Interpretation of the DEHP dataset appeared less obvious. The samples collected during the third session (winter 2001) were below the system blank. However, there were no reasons to suspect the data of analytical artefacts or to consider them outliers. The concentrations show a wider dispersion compared to DBP, but the duplicates were yet satisfactory in that they differ less than 20% from the mean, with the exception of sample A11 (33%). Concentrations below the sample blank (2 ng m^{-3}) were substituted by 0.73 ng m^{-3} (Appendix 4).

Table 11. Average of duplicate concentrations in air (ng m^{-3})

Location (Nr in Fig 5)	date	Code	DEHP	DBP
1. Gilze-Rijen	22 Feb 00 Wednesday	A1	25	19
(25)	4 Aug 00 Friday	A2	57	25
.	14 Jan 01 Sunday	A3	0.73*	5
2. Pernis	22 Feb 00 Wednesday	A4	31	9
(24)	4 Aug 00 Friday	A5	333	70
	14 Jan 01 Sunday	A6	0.73*	4
	2 Aug 01 Thursday	A7	48	7
3. Speulderveld	22 Feb 00 Wednesday	A8	8	11
(27)	4 Aug 00 Friday	A9	9	31
	14 Jan 01 Sunday	A10	0.73*	7
	2 Aug 01 Thursday	A11	20	2
4. Vianen	22 Feb 00 Wednesday	A12	52	9
(23)	4 Aug 00 Friday	A13	72	17
	14 Jan 01 Sunday	A14	0.73*	5

* substituted for < 2

The geometric mean (11.9 ng m^{-3}) was chosen as the location parameter of the distribution. The width of the distribution, expressed as GSD, is 7.7 which corresponds to the 2.5th and 97.5th percentile equal to 0.2 and 660 ng m^{-3}, respectively (see also Table 14).

The distribution of DBP was relatively narrow with GM and GSD equal to 10.3 ng m^{-3} and 2.5, respectively. The 2.5th and 97.5th percentile values were equal to 1.5 and 55.8 ng m^{-3}, respectively.

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[3] A quantile-quantile (Q-Q) plot is a graphical 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 with an abscissa of zero (y=x). If both distributions have different locations and shape parameters but both are samples from the same distributions, the Q-Q plot is a straight line (y = ax + b).

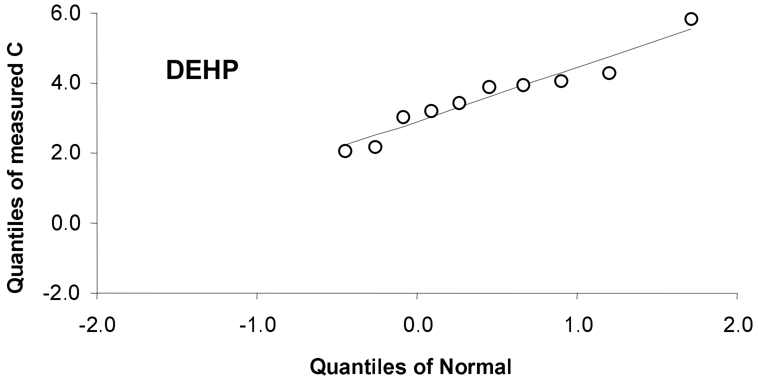

Figure 7. Q-Q plot of log transformed DEHP concentrations in air samples

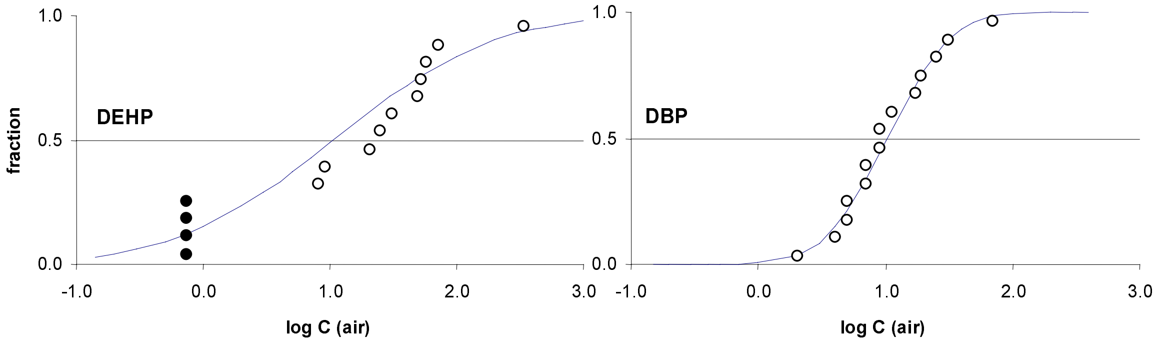

Figure 8. Cumulative probability plots (CDF) and Hazen plotting positions of phthalate concentrations in air. The solid circles in the left plot represent substituted data (0.73 ng m^{-3}) for determinations of DEHP below LOD

Fresh water column

In one freshwater sample the dissolved concentration of DEHP was 1000 times higher than the average and therefore it was removed from the dataset. The limit of detection varied between 0.08 and 0.14 µg L^{-1} per sampling session. Because only a small minority of the measured phthalate concentrations (dissolved) in surface water was below this limit, for pragmatic reasons '<LOD' was replaced with LOD/2.

Concentrations measured as dissolved and sorbed to suspended matter are given in Appendix 5 and represented as empirical CDF plots in Figure 9.

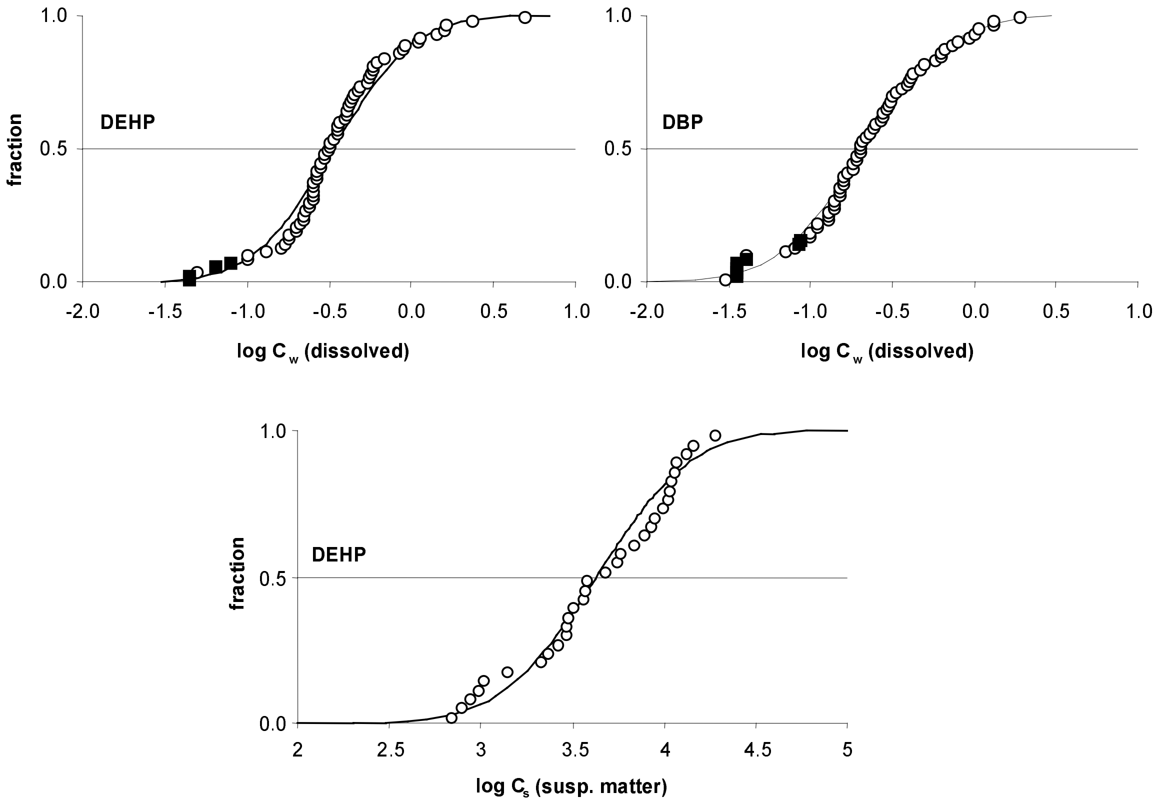

Figure 9. CDF plots and Hazen plotting positions of concentrations dissolved in fresh water (C_w in µg L^{-1}) and in (dry) suspended solids (C_s in µg kg^{-1}). Black squares are substituted values for censored data.

Analyzing DBP in suspended material appeared problematic. In one sample the result of the determination was reported as 'below 4139 mg kg^{-1}', in 9 samples this limit was 2008, in 5 samples 900 and in 5 other 80 mg kg^{-1}. Only in 12 samples determination appeared possible, resulting in a lowest and highest value of 34 and 379 mg kg^{-1}, respectively. The median of the 12 concentrations was 88 mg kg^{-1}. Because of the limited number of data, no CDF plot is given for DBP in suspended solids in Figure 9.

Freshwater sediment

In sediment samples 23% (DEHP) and 20% (DBP) of the samples were below LOD (Figure 10). The data set including substituted values can be reasonably well described by the lognormal CDF curve. The distribution of DEHP concentrations in sediment is wider than for DBP.

Fish

In 10 out of 25 samples the concentration of DEHP was below LOD, whereas in 7 samples DBP levels were below LOD. The probability plots in Figure 11 show a roughly 10 times wider distribution of DEHP concentrations compared to DBP levels. The GM was 1.8 and 1.0 µg kg^{-1}wet fish for DEHP and DBP respectively (see also Table 12).

Soil and vegetation

In 12 out of 34 soil samples the concentration of DEHP was below LOD. Two vegetation samples were not analysed for DEHP and therefore not further considered part of the data set, the remaining 45 samples appeared above LOD (Figure 12). The GM values were 31.8 and

41.8 μg kg^{-1} (wet) for soil and vegetation, respectively. Both distributions display a comparable width (soil: GSD = 2.3; vegetation: GSD = 2.9). Most soil and vegetation samples contained DBP concentrations below the LOD. The median DBP concentration in soil, 6.0 μg kg^{-1} (wet), was estimated through extrapolation according to Appendix 4.

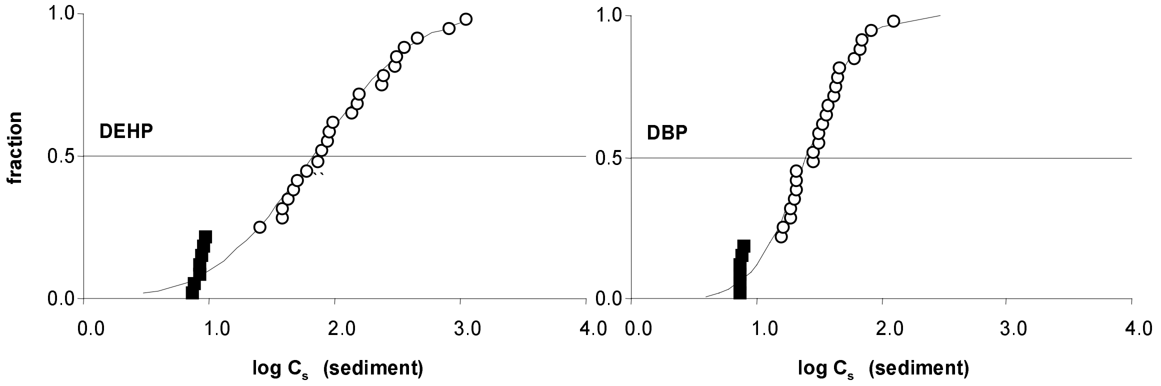

Figure 10. CDF plots and Hazen plotting positions of phthalate concentrations in fresh water sediment (C_s in μg kg^{-1} wet weight). Black squares are substituted values.

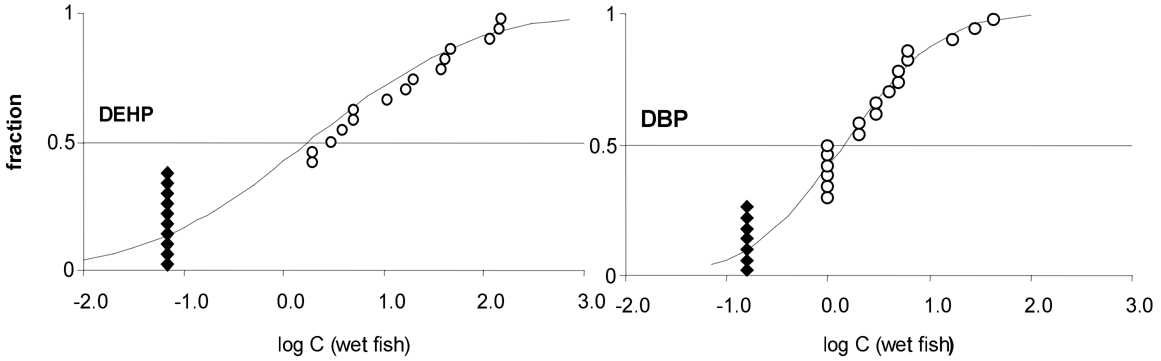

Figure 11. Probability plots (CDF) and Hazen plotting positions of phthalate levels in fish. Black diamonds are substituted values.

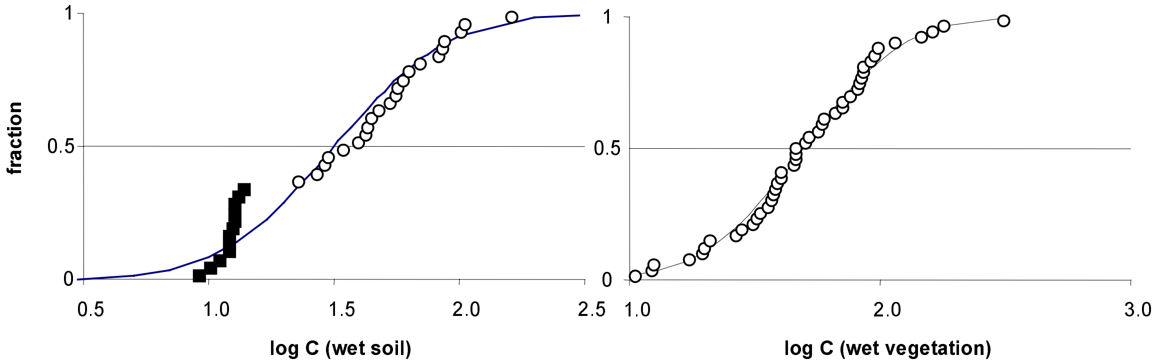

Figure 12. DEHP concentrations in soil and vegetation. Black squares are substituted values.

It appeared relatively close to the geometric mean (6.7) calculated from the whole data set, including substituted values below LOD which range from 3.1 to 4.5 μg kg^{-1} (wet). The 95th percentile (29.1 μg kg^{-1}) relative to the median was used to quantify the width of the distribution.
The median concentration in vegetation (Table 12) was calculated in a similar way. The difference with respect to the geometric mean of all data (included substituted values), 0.54 μg kg^{-1} (wet), was greater than for soil. The accuracy, however, is poor due to the fact that most of the data were indicative values. This may have caused the rather high dispersion: the 95th percentile exceeds the median by a factor of 14.

The significance of the observed concentrations

Table 12 is a summary of all parameters that specify the location and dispersion of the measured data. Note that the concentration of DEHP in vegetation is higher than in soil.

Table 12. Median and 95th percentile values of assumed lognormally distributed environmental concentrations of DEHP and DBP.

		DEHP		DBP	
Compartment	units	median	95th perc.	median	95th perc.
Outdoor air	ng m^{-3}	11.9	163.4	10.3	44.7
Freshwater dissolved	μg L^{-1}	0.33	1.56	0.21	1.06
Freshwater susp. Sediment	μg kg^{-1}(dry)	4311	13800	88^{+}	372^{+}
Sediment	μg kg^{-1}(wet)	67.4	649	25.3	77.5
Fish	μg kg^{-1}(wet)	1.7	141	1	26
Soil	μg kg^{-1}(wet)	31.7	102.6	6.0*	29.1
Vegetation	μg kg^{-1}(wet)	41.8	176.0	0.8**	33.9

$^{+}$ result of 12 determinations out of 32 samples, *estimated with the dg90 method,
** estimated: concentration in dry weight according to the dg90 method was multiplied with the median dry matter fraction of all vegetation samples.

Fugacity

Table 12 does not disclose whether or not there is equilibrium among the compartments. The fugacity is a thermodynamic quantity related to the chemical activity (or concentration) in some compartment or phase (Mackay, 1982) that characterizes the escaping capacity of the chemical from one phase or compartment to another. Diffusive intercompartment exchange of chemicals is driven by differences in fugacity. At equilibrium all fugacities of a compound among the compartments are equal. It should be noted that there are other transport mechanisms (related to deposition processes) that are not driven by differences in fugacity and may occur in the opposite direction.
Distributions of measured concentraties were converted into distributions of fugacities according to Appendix 6 and plotted in Figure 13. Examination of these plots raises several important issues:
DEHP

- The fugacity of DEHP in water is more than two orders of magnitude higher than in air; apparently there is no equilibrium between air and water, neither between sediment and water (difference more than a factor of 30);
- The highest fugacity of DEHP in water may indicate that water is the primary compartment, where degradation is relatively slow (Table 3). This may implicate diffusive transport from water to air and to other compartments;

- Sediment seems to be a sink for DEHP in the aquatic environment. Transport of DEHP from water to sediment is merely due to settling of suspended material carrying the adsorbed chemical with it. The concentration in sediment is governed by the rates of supply of DEHP (through sedimentation) and degradation. These fugacity plots could be an indication that biodegradation in sediment might be faster than according the rate constant given in Table 3;
- Biotransformation of DEHP in fish seems to be relatively fast: the median fugacity is several orders of magnitude lower than in water;

DBP

- Air, water and sediment are close to equilibrium: their fugacities do not span more than a factor of five;
- For DBP the median fugacity in sediment is only a factor of two lower than in water, indicating that equilibrium is approximated.
- According to Table 6, water would be the primary compartment for DBP, although the fugacity plot of DBP suggests that air is the primary compartment. A relatively high emission may be balanced by rapid biodegradation in the water compartment (t½ = 7 d, Table 3)[4].
- The ratio of degradation rate constants for air and water, given by Table 3, is a factor of 10 higher for DEHP than for DBP. This difference is rather supported by Figure 13 than refuted.

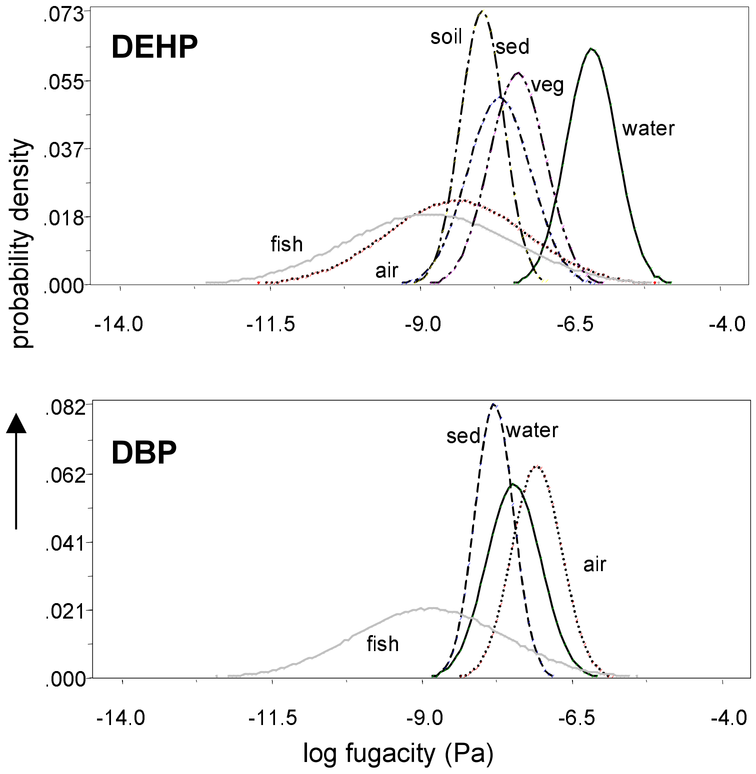

Figure 13. Fugacity distributions calculated from measured concentrations in environmental compartments.

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[4] Although the first order degradation rate constant of DBP in air is a factor of 3 higher than in water, the aquous concentration is several orders of magnitude higher. As the removal rate due to degradation is the *product* of the degradation rate constant and the corresponding concentration, the rate of degradation in water is higher. This is also true for DEHP, even when k_{deg} in air is 30 times higher than in water.

Suspended solids-water partitioning

Frome the 32 pairs of concentrations, given in Table A6 of Appendix 5, a set of 32 $K_{p,\ susp.}$ values was calculated for DEHP (Figure 14). The 5th , 50th and 95th percentiles are 870, 9211 and 41149 mg kg^{-1}, respectively, and the mean and median of log transformed data coincide at 3.95. Table 13 compares $K_{p,\ susp.}$ from field data with data by Staples (see also Table 2). The ratio of the concentration of DBP in suspended solids (C_s) and the corresponding dissolved concentration, yielded 12 values of $K_{p\ susp}$ for DBP, which appear to be log normally distributed (the median and mean of log transformed data converge at 2.8). Table 13 shows that partition coefficients derived from field data are lower than the values derived by Staples et al. (1997). The difference, however, does not exceed a factor of three.

Table 13. Median of suspended-water partition coefficients and uncertainty factors.

Phthalate		*log $K_{p,\ susp.}$*	*k*
DEHP	*Staples et al. (1997)*	*4.42*	*4.5*
	Field data LOES (n = 32)	*3.95*	*8.5*
DBP	*Staples et al. (1997)*	*3.2*	*10*
	Field data LOES (n = 12)	*2.8*	*5.1*

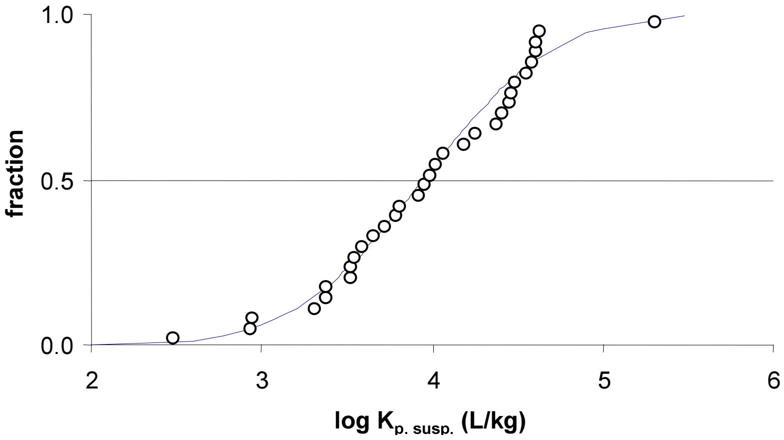

Figure 14. CDF plots and Hazen plotting positions of $K_{p,\ susp}$ for DEHP obtained from 32 pairs of measured concentrations in freshwater samples.

6.2 Model predictions

6.2.1 Environmental partitioning: input parameters

For modeling the concentration (ratios) of phthalates, we have used the physicochemical properties given by Staples et al. (1997). They reported the most likely value of each parameter as well as information from which the empirical uncertainty could be derived. Both characteristics were applied in stochastic modeling. Many relevant interactions between the substance and the environment are derived from these physicochemical properties. In SimpleBox, default environmental property values are estimated using relationships based on a limited number of key characteristics as input. These relationships have been established through recent progress in environmental chemistry. The partition coefficient of a hydrophobic chemical between suspended solids and water is an example. In the default mode, environmental partitioning is calculated as a function of descriptors of both the

environment (organic carbon content of the solids, the temperature, the pH etc.) and the chemical (K_{ow}, acid/base dissociation constant etc.). These relationships are often inaccurate or in some cases far from appropriate and should only be applied if no empirical information on environmental partitioning is available. Therefore, SimpleBox allows the user to overrule the default calculations for environmental partitioning.
In their comprehensive review Staples et al. (1997) provide data on environmental partitioning, which can be used to define a distribution of partition coefficients. If the default parameter estimations of SimpleBox are used, the solids-water partition coefficient of DEHP would be two orders of magnitude higher than derived from the LOES project or reported by Staples et al (1997). The median partition coefficient of DEHP ($K_{p,\,susp}$) as given by Table 13 corresponds to 27,000 L kg^{-1} (dry weight). Note that SimpleBox would calculate a default 1,500,000 L kg^{-1}, based on log K_{ow} (7.5) and the average organic carbon content (0.1) of suspended sediment. The results derived from the LOES project ($K_{p,\,susp} = C_s/C_w$) are in good agreement with data by Staples et al. (1997). Figure 15 demonstrates that real world partition coefficients are of vital importance to describe environmental partitioning of DEHP.

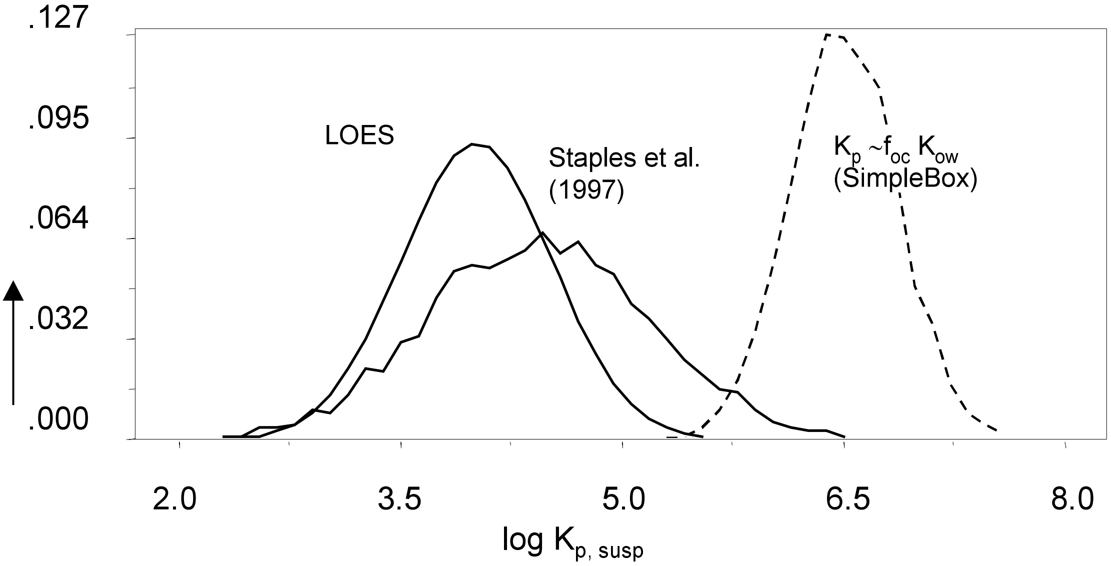

Figure 15. Frequency distributions of the suspended sediment-water partition coefficient $K_{p,\,susp}$ (L kg^{-1} dry weight) of DEHP. $K_{p,\,susp}$ derived from Staples and SimpleBox default are based on lognormally distributed data.

6.2.2 Predicted fugacity, compared to field observations

Fugacity distributions predicted by SimpleBox (see Figure 16) ressemble fugacity plots based upon field data (Figure 13) with respect to the following:

- there is no equilibrium between water and air for DEHP; the differences in median fugacity between air and water are more than three orders of magnitude;
- for DEHP the fugacity pattern of soil is close to that of air;
- both measured and predicted (log) fugacity of DBP is around -7.8 in air, water and sediment. In contrast with Figure 13, predicted fugacity in water is slightly higher than in air.

There are also some differences:

- For DEHP, SimpleBox predicts a scenario close to equilibrium between water and sediment, while measured data indicate a difference of almost two orders of magnitude. Apparently, degradation of DEHP in sediment is largely underestimated by SimpleBox;
- The distribution of fugacity of DEHP in air from field data is much wider than predicted by SimpleBox. The median of the modelled fugacity is lower than the median of the fugacity related to field data.

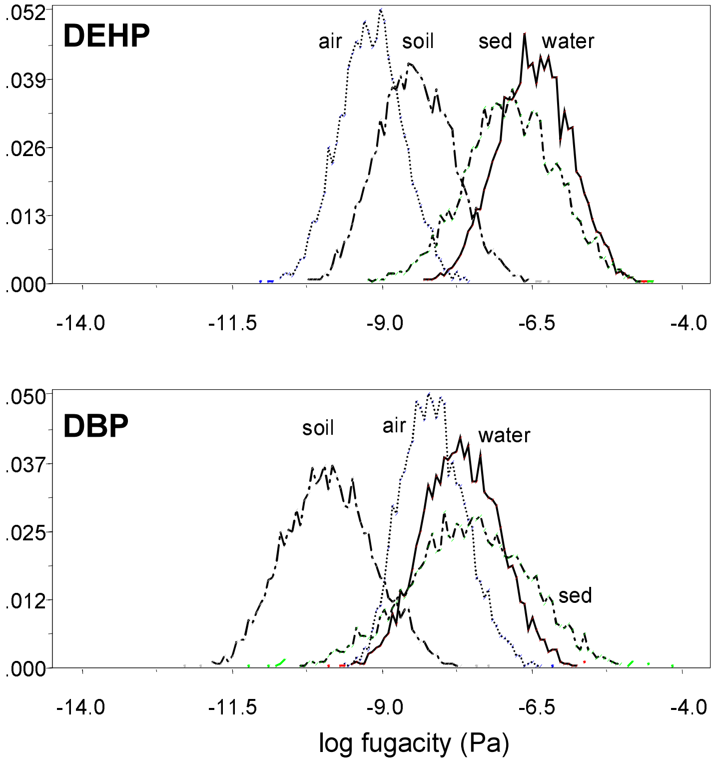

Figure 16. SimpleBox predicted fugacity distributions.

6.2.3 Predicted compared to monitored concentrations

The following remarks can be made if measured and modelled concentrations of DEHP are compared (Table 14, Figure 17 and 18).

Air. The difference between measured and predicted median bulk concentrations is less than one order of magnitude. The distribution of measured concentrations is wider.

Surface water. The measured bulk concentration in freshwater is less than half an order of magnitude lower than predicted. Note that 95% of both predicted and measured distributions fall between 0.01 and 2 $\mu g\ L^{-1}$.

Sediment and fish. Large differences can be observed when comparing measured and predicted concentrations in sediment and fish. This discrepancy is probably due to underestimation of biodegradation and biotransformation rates, respectively. In anoxic sediment, anaerobic degradation of DEHP may proceed more rapidly than according to the rate constant in Table 3. Another explanation is that in the aerobic top layer of the sediment, due to a high density of microorganisms, aerobic degradation is faster than in the water column, whereas lower degradation rates were used in the calculations (Table 3). SimpleBox 2.0 does not account for biotransformation, although it is well known that bioaccumulation of DEHP in fish is limited by biotransformation (Staple et al., 1997). The diversity of fish species as well as the long storage period may explain the extreme high

dispersion factor of the concentration in fish. Thus the actual DEHP level in fish samples shortly after catching of the fish, might have been higher. On the other hand, the computed concentrations are improbably high because only partioning between fish and water is assumed in the model. Note that the 95% confidence intervals of predicted concentrations of DEHP and DBP in water and fish span slightly more than two orders of magnitude.
Soil. The computed soil concentration is the weighted average of three different soil compartments that are distinguished in SimpleBox and is close to field observations.
Vegetation. The fact that the predicted concentration is more than 40 times lower, is partly explained by the underestimation of the air concentration by a factor of 6. Another explanation may be the discrepance in partitioning between aerosol associated and gaseous DEHP. Staples et al. (1997) report that 80% is associated with aerosols, whereas SimpleBox calculates 95%, solely on the basis of physico-chemical properties of DEHP[5] at 12 ºC. Diffusive transport from air to plant tissue is proportional to the gaseous concentration. If the air-arerosol partioning data of Staples et al. (1997) would overrule the default, calculated by SimpleBox, the modelled concentration in the gaseous phase would be three times higher and the modelled DEHP concentration in vegetation would be higher.

Table 14. Measured compared to computed DEHP concentrations.

	measured			SimpleBox		
Compartment	2.5th perc.	median	97.5th perc.	2.5th perc.	Median	97.5th perc.
Outdoor air (ng m^{-3})	0.22	11.9	660.1	0.25	2.0	18.2
Freshwater diss. (µg L^{-1})	0.06	0.33	1.92	0.01	0.16	1.97
Sediment (µg kg^{-1})	3.6	67	1185	42	708	11202
Fish (µg kg^{-1})	0	1.7	614	$1.8 \cdot 10^4$	$2.5 \cdot 10^5$	$3.3 \cdot 10^6$
Soil (µg kg^{-1})	6	32	161	5	36	348
Vegetation (µg kg^{-1})	4.8	41	340	0.05	0.9	13.2

The results obtained for measured DBP (Table 15, Figures 17 and 18) differ from predictions as follows.
Air. The measured median concentration exceeds the predicted by a factor of slightly more than ten; the dispersion coefficients are almost equal.
Surface water. Predicted and measured bulk concentrations of freshwater do not differ that much, both with respect to the median and the dispersion.
Sediment and fish. The same is true for sediment, despite the fact that the input parameter for the biodegradation rate constant in sediment is equivalent to a halflife as high as 230 d. The content in fish is again overpredicted, although less than a factor of 100. The absence of a biotransformation routine in SimpleBox causes a less unrealistic result than for DEHP. This may lead to the unexpected conclusion that, biotransformation of DBP is at least ten times slower compared to DEHP, although we can not ignore the possibility that DEHP accumulates faster than DBP.
Soil and vegetation. Again, the computed concentrations were averaged over the three soil types. Yet the difference with respect to measured concentrations is less than two orders of magnitude. However, the usefulness of the set of measured soil and vegetation data is limited as the majority of the data was below LOD. A fraction of data below LOD were reported as ‘below LOQ’. These data were treated as above LOD.

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[5] In SimpleBox, the fraction of the chemical that is associated with the aerosol phase, $F_{aerosol}$, is estimated on the basis of the chemicals’s vapour pressure (VP in Pa): $F_{aerosol} = 10^{-4}/(VP + 10^{-4})$ according to Junge (1977). For DEHP, SimpleBox calculates $F_{aerosol} = 0.95$ at T = 12 ºC.

Table 15. Measured compared to computed DBP concentrations.

	measured			SimpleBox		
Compartment	2.5th perc.	median	97.5th perc.	2.5th perc.	median	97.5th perc.
Outdoor air (ng m^{-3})	1.8	10.3	59.1	0.1	0.9	12.0
Freshwater dissolv. (μg L^{-1})	0.03	0.21	1.45	0.01	0.13	2.22
Sediment (μg kg^{-1})	6.7	25.3	96	1.1	33.3	950
Fish (μg kg^{-1})	0.1	1.6	42.1	6.4	97.4	1650
Soil (μg kg^{-1})	1*	6*	39*	0.0	0.1	2
Vegetation (μg kg^{-1})	0.01*	0.8*	69*	0.11	1.37	23.8

*unreliable results, see text

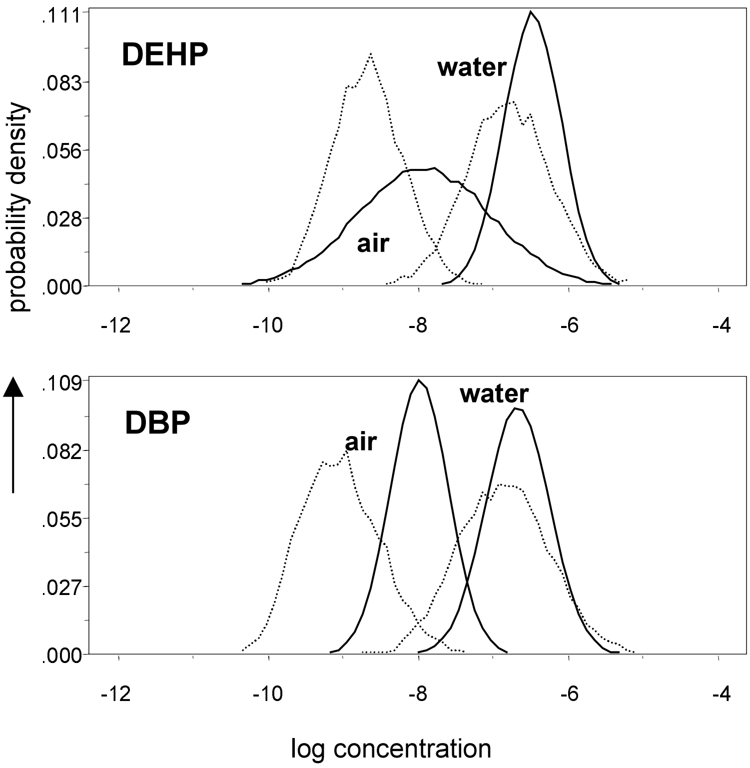

Figure 17. Measured (solid lines) and predicted (dotted lines) concentrations in water (g L^{-1}) and air (g m^{-3}).

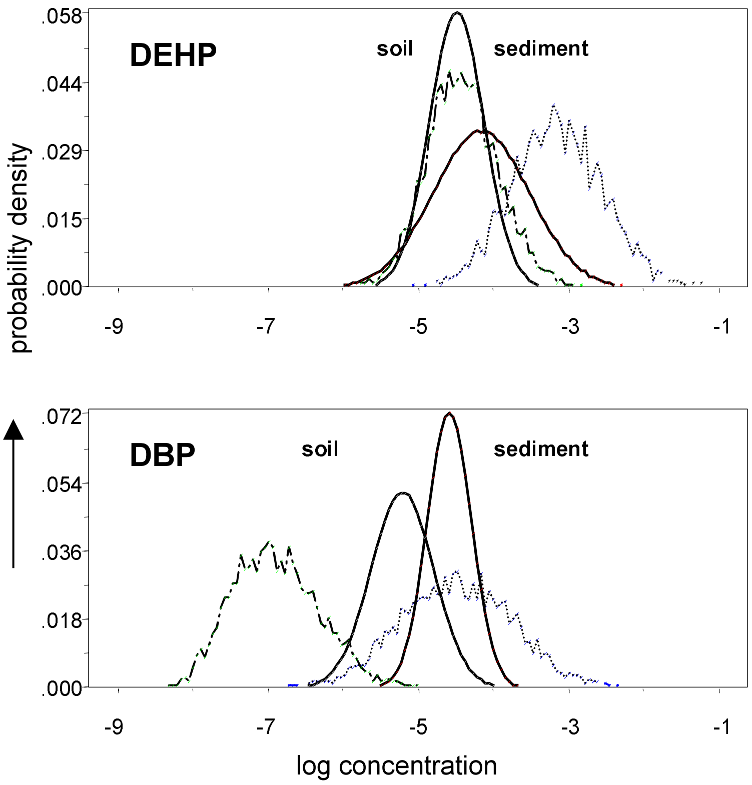

Figure 18. Measured (solid lines) and predicted (dotted lines) concentrations in soil and sediment (g kg $^{-1}$ (wet)).

6.2.4 Predicted compared to observed concentration ratios

Dispersion factors of CR based on measured concentrations of DBP are considerably smaller than for DEHP (Table 16). This may be explained by the fact that the partition coefficients of DBP are lower.

DEHP

Differences between measured and predicted concentration ratios are in the order air/water < air/soil < sediment/water for DEHP (Figure 19, Table 16). The predicted air/water SSCR satisfies the ‘factor 3 criterion’. The predicted SSCR for both air/soil and sediment/water fulfills the ‘factor 10 criterion’. The estimated sediment/water concentration ratio is overrated, probably because the rate of degradation processes is underestimated.

Table 16. Measured compared to computed concentration ratios.

	measured			SimpleBox		
Ratio (units) phthalate	2.5th perc.	median	97.5th perc.	2.5th perc.	Median	97.5th perc.
Air/water (L m^{-3}) DEHP	$4.7\cdot10^{-4}$	$3.5\cdot10^{-2}$	2.6	$8.9\cdot10^{-4}$	$1.2\cdot10^{-2}$	$3.5\cdot10^{-1}$
Air/soil (L kg wet^{-1}) DEHP	$4.8\cdot10^{-6}$	$3.8\cdot10^{-4}$	$3.0\cdot10^{-2}$	$2.4\cdot10^{-6}$	$6.3\cdot10^{-5}$	$5.8\cdot10^{-4}$
Sediment/water (L kg wet^{-1}) DEHP	7.3	$2.1\cdot10^{2}$	$5.8\cdot10^{3}$	$2.5\cdot10^{2}$	$1.5\cdot10^{3}$	$6.0\cdot10^{3}$
Air/water (L m^{-3}) DBP	$3.8\cdot10^{-3}$	$4.8\cdot10^{-2}$	$6.5\cdot10^{-1}$	$2.5\cdot10^{-4}$	$6.2\cdot10^{-3}$	$2.6\cdot10^{-1}$
Air/soil (L kg wet^{-1}) DBP	$1.3\cdot10^{-4}$	$1.7\cdot10^{-3}$	$2.1\cdot10^{-2}$	$1.7\cdot10^{-3}$	$7.3\cdot10^{-3}$	$2.5\cdot10^{-2}$
Sediment/water (L kg wet^{-1}) DBP	12	$1.2\cdot10^{2}$	$1.2\cdot10^{3}$	32	$2.3\cdot10^{2}$	$2.5\cdot10^{3}$

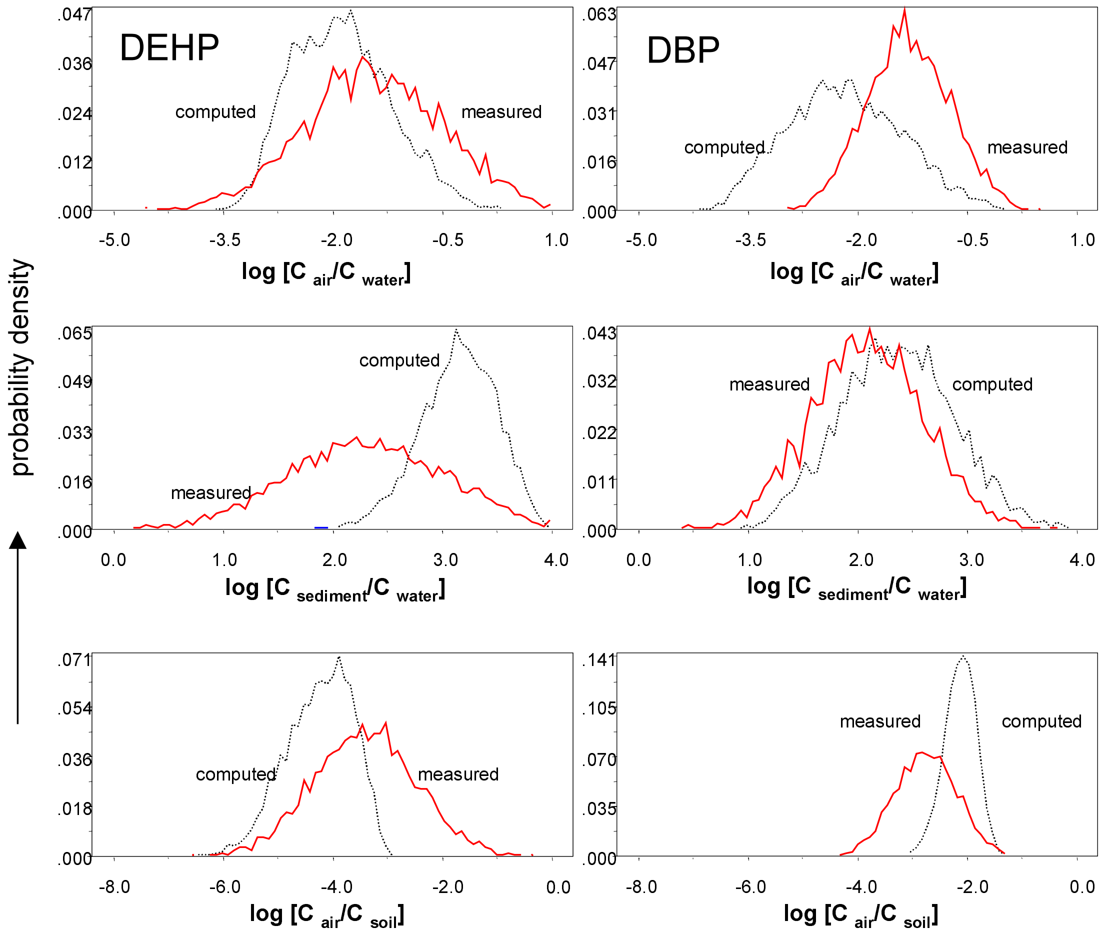

Figure 19. Frequency distributions of concentration ratios air/water, sediment/water and air/soil for DEHP (left) and DBP (right). Units according to Table 16.

<u>DBP</u>

The predicted median of the air/water SSCR (Table 16) deviates less than a factor of 10 from the measured CR (Table 16). For sediment/water the predictions are very satisfactory: the difference is less than a factor of 2. For air/soil the discrepancy between predicted and measured is again within the ‘factor 10 criterion’.

7. Discussion

7.1 Sampling air/water field data in pairs

The focus of this verification study is on the performance of SimpleBox with respect to the air-water concentration ratio. Testing the coherence of EQOs by means of SimpleBox was until now only applied to this the air-water concentration quotient. Measured concentrations indicate that 1) the concentration of both phthalates in water can be described by a log normal distribution; 2) although the data set concerning DBP in air is small, a log normal distribution can be used as will be demonstrated below. The log normal distribution of the DEHP concentration in air is not so clear. This data set is characterized by two clusters: a smaller fraction (28%) which contains censored data (below the limit of detection) for which we replaced '< 2 ng m^{-3}' with 0.73 and a major fraction around a value which is more than one order of magnitude higher than 2 ng m^{-3}. In the upper part of the major fraction one observation (333 ng m^{-3}) might be an outlier, probably due to the combination of extreme weather conditions and the physical properties of DEHP (high fraction associated with aerosols) better than a lognormal distribution. If this value is omitted, a normal distribution seems to fit the data (including the cluster of censored data) seems to be normally distributed. However, this would lead to an unrealistic scenario, because the average and the standard deviation would imply that 40% of the data is negative. This type of distribution was rejected and a log normal distribution was assumed.

It is unclear whether the cluster of low DEHP concentrations in air is the result of strongly reduced emissions on Sunday or due to specific weather conditions. If emissions on Sunday are indeed significantly lower, then 4 out of 14 observations is an overrepresentation by a factor of 2 and a weighing factor of ½ should be applied. It may also be the result of typical weather conditions.

An alternative approach to obtain a distribution of air/water concentration ratios is sampling in pairs. At random one concentration is drawn from the set of 14 air concentrations and one from the set of 66 water data and from each pair a quotient is calculated. In case of DBP the distribution of quotients obtained from sampling in pairs (Figure 20) ressembles the quotient of distributions (upper right plot in Figure 19). This is expected since both the water and air concentrations are log normally distributed. For DEHP, however, 28% of the quotients falls in the low region because the numerator equals 0.73 and 72% of the ratios has a numerator in the range between 8 and 333. The result is a bimodal distribution as given in Figure 20, with the median of the model output in between both modes. Also from this comparison the conclusion is justified that the model predictions for DEHP are in good agreement with realistic air-water concentration ratios in the field. Nevertheless, in the high region computed output is lower than measured, however the difference is less than a factor of 2.

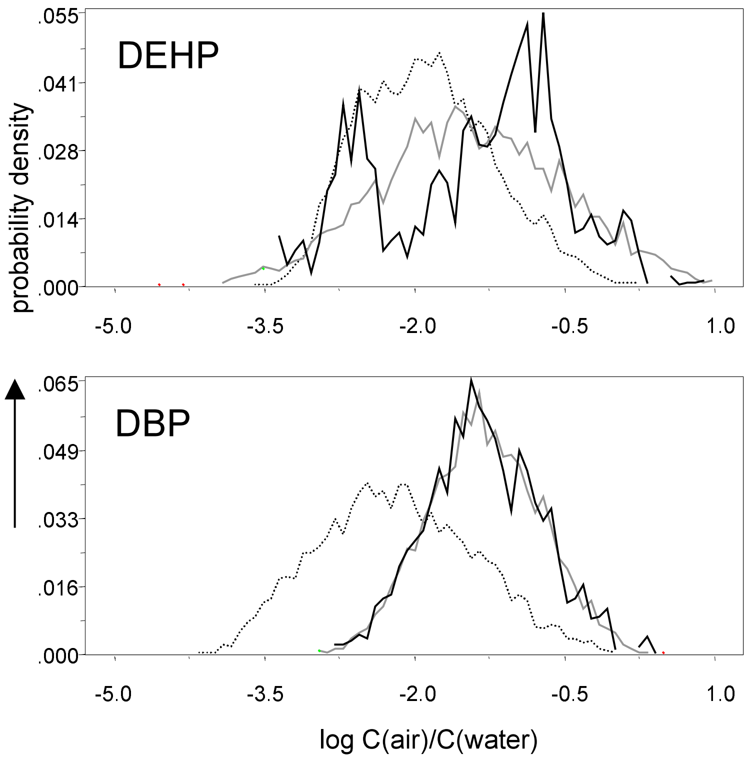

Figure 20. Frequency distributions of air-water concentration ratios: modeled (dotted lines) and measured (solid lines). Grey solid and dotted are similar to upper two plots of Figure 19; the black solid line results from paired sampling in air and water.

7.2 The vegetation module

The distribution of the measured DEHP concentration is wide both in air and vegetation. As a consequence the concentration ratio also varies over four orders of magnitude. The modelled analogue is inside the measured range but has a variability of less than two orders of magnitude (Figure 21). Running the model with terrestrial vegetation module switched off does not alter the results in computed air/water SSCRs. This is in agreement with the SimpleBox output with respect to the distribution of DEHP over the different compartments (Table 17), because terrestrial vegetation is not a reservoir for DEHP. Consequently, vegetation concentrations will not influence in the air compartment. The median air/water SSCR for DBP increases from 5.8 10^{-3} to 6.9 10^{-3} when the terrestrial vegetation is switched off.

Table 17. The distribution of phthalates (%) over the compartments

Compartment	DEHP (%)	DBP (%)
air	0.0	0.7
Freshwater	0.2	18.0
column	25.0	55.0
sediment		
Seawater column	0.2	7.2
sediment	4.8	1.3
soil	69.8	15.8
vegetation	0.0	1.9

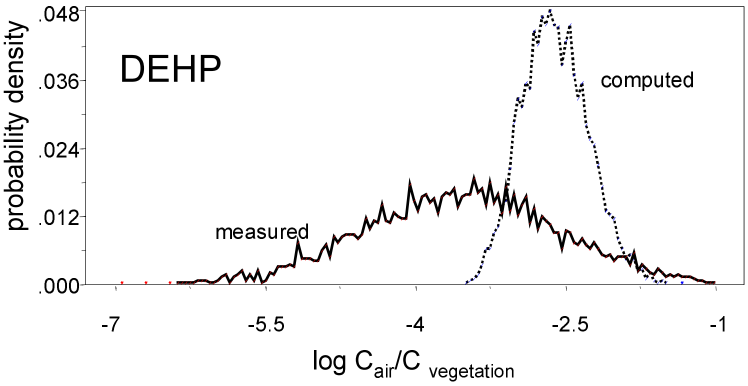

Figure 21. The predicted and measured DEHP concentration ratio for air and vegetation

7.3 How accurate should SSCRs be for coherence testing?

The feasibility of 'validation' may be enhanced if there is good insight into both achievable and required accuracy of model predictions. Narrow margins of model output may not be necessary if the target of application has wide margins of uncertainty, while still the complexity of environmental fate processes makes the use of a model indispensable. In principle an EQO is a deterministic quantity and this is also true for the ratio of EQOs. However, EQOs are scientifically based on MPCs, which are usually derived from a limited toxicity data set. As a consequence, most MPCs are surrounded by uncertainty margins of at least one order of magnitude.

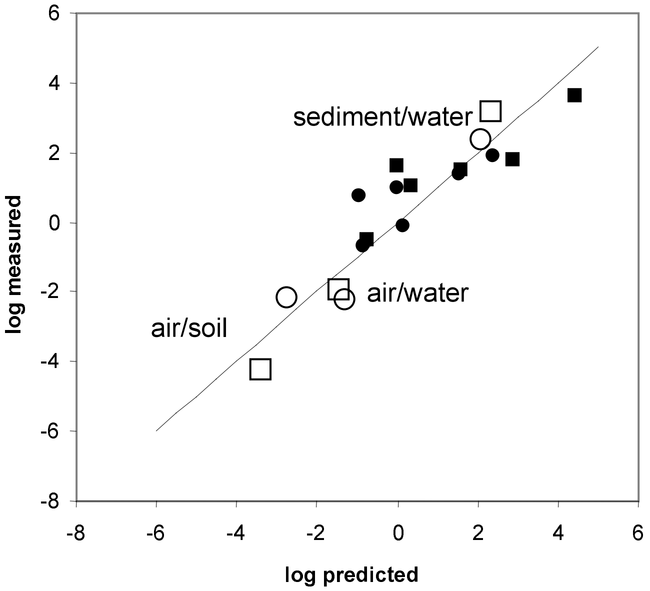

Figure 22. Predicted versus measured concentrations (black) and ratios (open) for DEHP (squares) and DBP (circles); data (median) derived from Tables 14, 15 and 16.

The uncertainty of effect based MPCs generally increases in the following order: refined effect assessment < preliminary effect assessment < equilibrium partitioning method (Posthuma et al., 2002). However, even when derived according to the refined effect assessment, the uncertainty of the MPC estimate can easily be as high as a factor of 10. In Chapter 4, we showed that if two independent MPCs are lognormally distributed, the quotient of MPCs has also a log normal distribution. Furthermore, if we assume that k = 10 for both MPC_a and MPC_b, the uncertainty factor related to the lognormal distribution of MPC_a/ MPC_b approximates 26 (Jager and Slob, 1995).
This has implications for the demands with respect to uncertainty and accuracy we may put on computed concentration ratios. Given the aformentioned uncertainty of the ratio of MPCs, it seems not appropriate to pursue a better accuracy in estimated SSCRs than a factor of three. Furthermore, it seems unrealistic to expect that the uncertainty in SSCRs will be less than a factor of ten. MPCs have been adjusted by Van der Plassche and Bockting (1993) if the discrepancy between SSCR and the ratio of MPCs was greater than a threshold factor of ten. Expected uncertainty of model predictions was the reason to apply this treshold. The current report confirms (see Figure 22) this approach, although verification with more chemicals is necessary.

7.4 The target chemicals

In this first stage of validation, we have not investigated substances which are representatives of the 46 volatile compounds (Van de Plassche and Bockting, 1993) as recommended by the Health Council (1995). There is a trade-off between physico-chemical properties on one hand and the type and rate of the emission on the other. Concentrations in the relevant compartments have to be measurable to be able to make a comparison between measured concentration ratios, which presumably represent a steady state situation given the constant (diffuse) emission rates, and predicted SSCR. We were able to compare observable concentrations ratios of DEHP and DBP in the Netherlands with model predictions. In the near future we will report the results of a comparative study on 5 chemicals of which environmental concentrations have been published in reports of local authorities.

7.5 Import through air and rivers

At the continental scale, SimpleBox calculates steady state concentrations in air and water based on default settings, which reflect the whole of the EU. Since the emission of phthalates is merely due to transport, product end use and disposal, emission to air and water are diffuse. As a consequence the emission rates of phthalates are scaled up according to the population of the EU. However, the population density in the EU is assumed homogeneous (104 persons per squared km) in the calculations at the continental scale. Thus the emission density of phthalates to air and water is almost a factor of 5 lower than in the Netherlands (460 persons per squared km). That the Netherlands is surrounded by a highly industrialized and a equally densely populated area (North Rhine Westphalia and Belgium) is not accounted for in SimpleBox, as SimpleBox is a general model that lacks real-life spatial variability. As a consequence, steady state concentrations of DEHP and DBP in water that flows into the Netherlands is computed by SimpleBox as given in Table 18. Import via river water is underestimated because diffuse emission to water in the continental region adjacent the Netherlands is underestimated by a factor of 5. The LOES project (Vethaak et al., 2002) clearly shows that the concentrations in water in the river Meuse in Belgium and the river Rhine in Germany are virtually equal to Dutch freshwater (Table 18).

Import by advective transport via the air compartment may be overestimated. Transport of the chemical with air (wind) across the boundaries of the Netherlands is calculated from the rate of airflow from the continental scale (EU) multiplied with the corresponding concentration in air. Although the air concentration is relatively underestimated due to a high population density at the east and south borders this is probably more than compensated by transport through wind from the direction of the sea. As wind from sea direction prevails, air with low concentrations of phthalates is imported. Concentrations of xenobiotic compounds in air above the North Sea are considerably lower than in air from a highly industrialized and populated area.

Table 18. Predicted and measured (median) concentrations (µg L^{-1}) in fresh water inside the Netherlands (SimpleBox: regional) and outside (continental)

	DEHP		DBP	
	SimpleBox	LOES*	SimpleBox	LOES*
Germany/Belgium	0.05	0.30	0.04	0.21
The Netherlands	0.19	0.33	0.13	0.21

* Vethaak et al. (2002)

7.6 Sensitivity analysis

Figure 23 shows input parameters for modelling air/water SSCRs of DEHP and DBP which matter most. Obviously, the output is highly dependent on emission rates to air and water. In case of DEHP the predictions are relatively sensitive for the scenario parameter Er (see end of Chapter 4) and the suspended sediment/water partition coefficient. For DBP, the air/water estimate seemed to depend more on the degradation in water.

The SSCR with respect to air/soil is sensitive to most of the emission parameters in case of DEHP. Discharge rates to air and soil, including the auxiliary parameter Er were expected to have a high impact on the $SSCR_{air/soil}$, but surprisingly for DBP (Figure 24) properties of the compound and the environment are more important. Although emission of DBP to soil was set to zero and not considered an input parameter, the emission rate to air seems to have a minor impact. The $SSCR_{air/soil}$ for DBP is merely governed by the water solubility, the vapour pressure (at 25 °C), the biodegradation rate in soil and the temperature.

The $SSCR_{sediment/water}$ of DEHP is sensitive to the partition coefficient with respect to suspended but not with respect to settled solids (Figure 25). Note that there is some positive influence of the water solubility of DEHP, due to the reciprocal relationship to Henry's law coefficient (higher solubility results in more accumulation in the water compartment and subsequent irreversible transport to the sediment due to high value of $K_{p\ susp}$). The sensitivity chart emphasizes the high priority of knowing the degradation rate of DEHP in sediment. This input parameter has less influence on $SSCR_{sediment/water}$ of DBP.

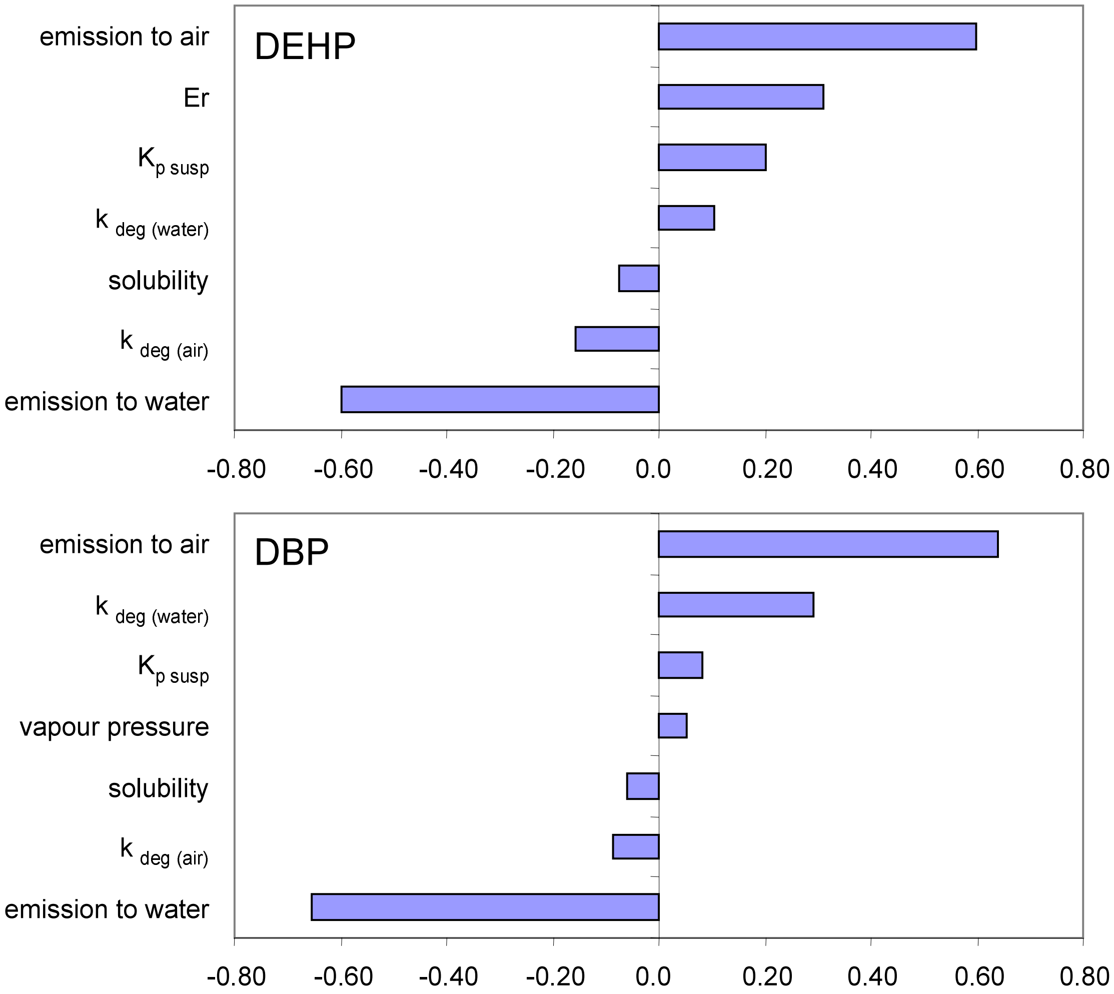

Figure 23. *Sensitivity of the air/water concentration ratio for most important input parameters. Vapour pressure at 25 °C.*

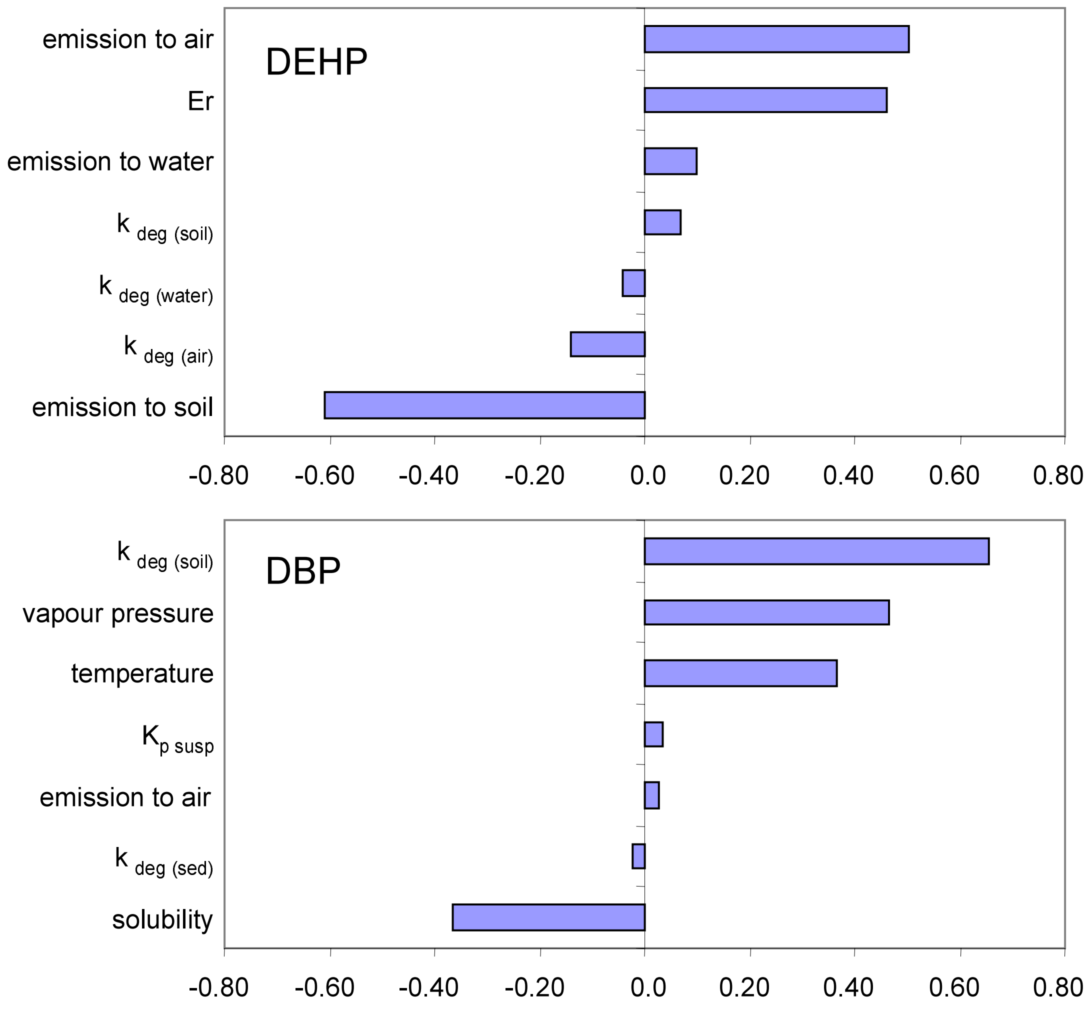

Figure 24. Sensitivity charts of the air/soil concentration ratio. Solubility and vapour pressure at 25 °C.

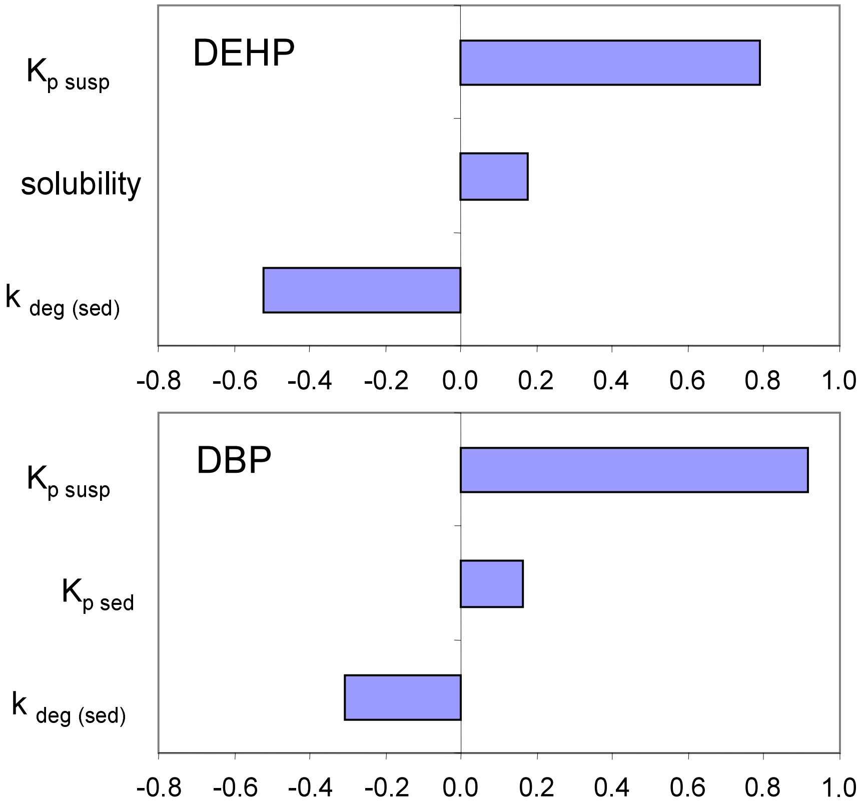

Figure 25. Sensitivity charts of the sediment/water concentration ratio. Solubility at 25 °C.

8. Conclusions

1. All predicted median air-water, air-soil and sediment-water concentration ratios of the two phthalates esters, DEHP and DBP, do not deviate more than a factor of 10 from analogues which are based on measured environmental concentrations in the Netherlands.
2. The median predicted air-water concentration ratio deviates less than a factor of 3 with regard to field observations in case of DEHP and less than a factor of 10 for DBP. The results of the current study do not give cause to increase or decrease the incoherence threshold of 10. This threshold implies that if the ratio of two independently derived Environmental Quality Objectives (EQOs) deviates less than a factor of 10 from steady state concentration ratios predicted by the multimedia fate model SimpleBox, the EQOs should not be adjusted.
3. From measured concentrations in air, water and sediment it can be derived that these compartments are not in equilibrium for DEHP (air and water are even far from equilibrium), but close to equilibrium for DBP. These differences in environmental behaviour are fairly well predicted by SimpleBox.
4. The two model compounds are well-known HPVCs. Important environmental characteristics such as solid-water partitioning appeared to be available from empirical studies. As a consequence, default estimations partition coefficients (based on the octanol-water partition coefficient) could be avoided. For DEHP the difference between measured and estimated partitioning coefficients is several orders of magnitude. If the validation study would be based on less well-known substances, a greater discrepancy between model output and field observations may be expected.
5. The span of modelling results is greatly affected by uncertainty with regard to emission of the phthalates, especially caused by slow release of DEHP to air and water during the product end-use stage.
6. In SimpleBox default values for the windspeed and the mixing height of the air compartment are suggested of 3 m s^{-1} and 1 km, respectively. A mixing which is dependent height on windspeed and/or on the molecular weight of the modelled chemical should be considered.
7. The monitoring data concerning the air compartment are not satisfactory. The data set is small and weather conditions appeared not representative for the Netherlands. This forced us to deviate from default settings with respect to air mixing height and the windspeed.
8. In view of conclusions 5. and 6., we recommend to expand collaboration with the chemical industry to collect more data on emission and occurence of HPVCs in the environment with the aim to verify multi-media fate models.

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Appendix 2 Sampling sites soil, vegetation, sediment and fish

Table A1. Soil sampling dates, location, code, percentage dry matter (% DM)

Location	Code	% DM	Remarks	Date
Uitgeest	B01	88.5	± 5 m from highway	8 Aug 97
	B06	85.2	Duplicate B01	8 Aug 97
	B02	65.7	± 400 m from highway	8 Aug 97
	B03	76.3	± 20 m from highway	8 Aug 97
	B05	73.3	± 100 m from highway	8 Aug 97
	B07	63.4	± 800 m from highway	8 Aug 97
Zaandam	B04	88.1	near waste incinerator	8 Aug 97
Eibergen	B09	84.4	sampled by RIVM/LLO	26 Aug 97
	B32	87.0	sampled by RIVM/LLO	28 Nov 97
Gilze-Rijen	B10	92.1	sampled by RIVM/LLO	5 Sep 97
Kollumerwaard	B11	83.5	sampled by RIVM/LLO	28 Aug 97
De Zilk	B12	91.0	sampled by RIVM/LLO	28 Aug 97
	B33	95.7	sampled by RIVM/LLO	3 Jun 98
Rotterdam	B16	87.5	near waste incinerator (AVR)	20 Okt 97
Anna Jacobapolder	B17	81.9		7 Aug 97
Vianen	B18	66.7	A27 – approx. 400 m from highway	21 Oct 97
	B19	74.6	A27 – approx. 10 m from highway	21 Oct 97
	B23	75.4	duplicate B19	21 Oct 97
	B20	82.5	A27 – approx. 800 m from highway	21 Oct 97
	B21	87.4	A27 – approx. 3 m from highway	21 Oct 97
	B22	78.9	A27 – approx. 100 m from highway	21 Oct 97
Vlijmen	B24	89.9		26 Jul 97
Schraard	B26	69.7		8 Aug 97
	B30	72.6		10 Apr 98
Middenmeer	B27	85.9		8 Aug 97
Lheebroekerzand	B31	64.6		06 Aug 97
	B34	96.5		1 Apr 98

Table A2. Vegetation sampling sites and dates, code, percentage dry matter (% DM)

Location	Code	% DM	Remarks	Date
Zaandam	G02	28.7	(mixed grassy) vegetation	8 Aug 97
	G10	27.8	Duplicate	8 Aug 97
Beek	G13	16.6	mixed grassy vegetation	28 Aug 97
Eibergen	G18	14.3	mixed grassy vegetation	26 Aug 97
	G31	53.7	mixed grassy vegetation	28 Nov 97
	G41	18.5	Grass	7 May 98
Gilze-Rijen	G16	19.7	mixed grassy vegetation	5 Sep 97
Kollumerwaard	G15	49.5	grass	28 Aug 97
De Zilk	G14	57.1	mixed grassy vegetation	28 Aug 97
	G32	54.5	mixed grassy vegetation	28 Nov 97
	G45	46.2	grass (mixed grassy vegetation)	3 Jun 98
Speulderveld	G17	47.4	mixed grassy vegetation	28 Aug 97
	G43	64.5	mixed grassy vegetation	1 Jun 98
Venray	G11	17.6	maize, sugar beat (leaves) & lily (leaves)	27 Jul 97
	G19	17.7	sugar beat (leaves) & lily (leaves)	4 Oct 97
	G44	22.6	grass (mixed grassy vegetation)	2 Jun 98
Pernis	G09	19.7	grass (mixed grassy vegetation)	7 Aug 97
	G20	20.7	grass (mixed grassy vegetation)	20 Oct 97
	G47	24.9	mixed grassy vegetation	22 Jun 98
Rotterdam	G21	19.8	mixed grassy vegetation	20 Oct 97
Anna Jacobapolder	G04	11.5	sugar beat (leaves)	7 Aug 97
	G22	13.9	sugar beat (leaves)	20 Oct 97
	G35	17.5	grass	3 Apr 98
Vianen	G23	11.4	grass (mixed grassy vegetation)	21 Oct 97
Vlijmen	G01	14.4	sugar beat (leaves)	26 Jul 97
	G24	17.1	sugar beat leaves	26 Oct 97
	G33	13.9	leaves of Brussels sprouts	1 Mar 98
	G42	24.2	grass	9 May 98
Nes aan de Amstel	G12	21.4	(mixed grassy) vegetation	8 Aug 97
	G25	17.5	grass, leaves & vegetation (mixed grassy vegetation)	5 Nov 97
	G28	16.7	duplicate	5 Nov 97
	G39	15.2	mixed grassy vegetation	10 Apr 98
Schraard	G03	24.7	grass & maize	8 Aug 97
	G08	23.0	duplicate	8 Aug 97
	G26	23.6	grass (mixed grassy vegetation)	5 Nov 97
	G37	12.5	nettle, dandelion & sorrel (mixed grassy vegetation)	10 Apr 98
Middenmeer	G07	14.2	curly kale	8 Aug 97
	G29	15.0	curly kale	5 Nov 97
	G38	18.6	grass	10 Apr 98
	G46	18.4	grass, cleavers & tree leaves (mixed grassy vegetation)	15 Jun 98
Swifterbant	G05	13.9	sugar beat leaves & grass	8 Aug 97
	G27	15.4	farm crop (sugar beat leaves & grass)	5 Nov 97
	G36	15.0	grass	10 Apr 98
Lheebroekerzand	G06	43.8	(grassy) vegetation	6 Aug 97
	G30	33.7	mixed grassy vegetation	3 Nov 97
	G34	41.6	mixed grassy vegetation	1 Apr 98
Boxtel	G40	15.0	grass	26 Apr 98
Wijchen	G48	23.0	grass	25 Jun 98

Table A3. Sediment sampling sites: percentages dry matter (DM), total organic carbon (TOC) and clay content expressed as % < µm

Location/remarks	code	date	% DM	% TOC	% < µm
Opeinder Kanaal (canal).	S1	18 Jan 99	77.6	1.9	7.5
Hantummervaart (canal).	S2	18 Jan 99	64.6	2.0	19.0
River 'Maas' near Ool. Sandy sediment.	S3	21 Jan 99	56.4	5.1	21.0
River 'Maas' near Ool. Duplicate of S3.	S4	21 Jan 99	58.7	5.4	19.0
Castle 'Strijthagen' in Landgraaf. Contains leaf material.	S5	21 Jan 99	62.6	4.3	12.0
Heerlen/Landgraaf. Sandy sediment. Fishing club 'N.O. Hoek'	S6	21 Jan 99	73.3	2.5	6.5
Assendelft	S7	22 Jan 99	41.7	8.3	26.0
Wormerveer.	S8	22 Jan 99	42.2	14.0	8.8
Alkmaar – Hoornse/Hoevevaart (canal).	S9	22 Jan 99	39.8	6.1	25.0
Alkmaar … Duplicate of S9	S10	22 Jan 99	58.3	5.0	26.0
Alkmaar – Noord-Hollands kanaal (canal)	S11	22 Jan 99	78.5	0.5	2.2
Alkmaar – Noord-Hol. Duplicate of S11	S12	22 Jan 99	79.8	0.5	2.0
Haarlem – Ringvaart Vijfhuizen (canal)	S13	22 Jan 99	73.2	1.9	2.9
Haarlem – Ringv…Duplicate of S13	S14	22 Jan 99	75.4	1.4	3.1
Noordzijderpolder in Noordwijk.	S15	22 Jan 99	74.1	0.8	1.7
Leidse trekvaart (canal).	S16	27 Jan 99	78.4	0.9	2.7
Apeldoorn canal, Hoorn the Heerde district.	S17	28 Jan 99	40.8	7.7	16.0
City lake Enschede (Fishing club 'VIOS')	S18	28 Jan 99	66.2	9.1	7.6
Yacht-basin 'Oude IJssel' te Doetinchem	S19	28 Jan 99	62.3	5.3	10.0
'De Zoomwijckvijver' (a more than 10 year old pond in Oud-Beijerland).	S20	29 Jan 99	75.5	<0.5	3.3
Het Waaltje, Hendrik Ido Ambacht. Fishing club 'ERHV de Waal' in Ridderkerk.	S21	29 Jan 99	73.7	6.9	11.0
River 'Dommel', Vught, near motorway A2.	S22	30 Jan 99	49.2	7.0	12.0
River 'AA', near Rosmalen. Reported: -35	S23	30 Jan 99	73.9	0.8	4.5
River 'AA', near Rosm.. Duplicate of S23.	S24	30 Jan 99	74.9	1.0	3.0
Pond 'Wipperveld' Kennedyln Woudenberg	S25	5 Feb 99	41.0	5.2	16.0
Pond 'Wipperveld'… Duplicate of S25.	S26	5 Feb 99	48.2	5.4	17.0
Canal around Almere, Harl.singl 31, Almere	S27	5 Feb 99	67.5	6.3	17.0
Canal around Almere, Duplicate of S27.	S28	5 Feb 99	51.7	4.6	14.0
Fishing club 'De Vliet', Voorschooten	S29	8 Feb 99	77.9	0.8	3.8
Fishing club 'De Vliet' Duplicate of S29	S30	8 Feb 99	78.3	0.6	3.5

Table A4. Fish sampling

Location	Code	sampling date	species	% fat	Remark
Haarlem	F1	20 Mar 98	bream	0.1	
Noordwijk	F2	31 Mar 98	roach	0.5	
Noordwijk	F3	31 Mar 98	bream	0.2	Samples not found
Rosmalen	F4a	Unknown	bream	1.6	Collected on 4/4/98
Rosmalen	F4b	Unknown	roach	0.8	Collected on 4/4/98
Doetinchem	F5	Unknown	bream	0.1	Collected on 3/4/98
Ridderkerk	F6	Unknown	roach	0.2	Collected on 3/4/98
Zaandijk	F7	Unknown	bream	0.2	Collected on 10/4/98
Voorschoten	F8	Unknown	roach	0.7	Collected on 10/4/98
Woudenberg	F9	Unknown	bream	0.5	Collected on 7/5/98
Alkmaar	F10	Unknown	bream	0.2	Collected on 13/5/98
Alkmaar	F11	Unknown	bream	0.4	Collected on 13/5/98
Assendelft	F12	Unknown	roach	1.0	Collected on 13/5/98
Herten	F13a	Unknown	white bream	0.8	Collected on 15/5/98
Herten	F13b	Unknown	roach	0.6	Collected on 15/5/98
Herten	F14	Unknown	bream	0.4	Collected on 15/5/98
Almere	F15	Unknown	bream	0.5	Collected on 27/5/98
Oud-Beijerland	F16	Unknown	bream	1.4	Collected on 28/5/98
Landgraaf	F17	24 May 98	bream	0.2	
Landgraaf	F18	24 May 98	roach	1.6	
Landgraaf	F19	Unknown	roach	1.7	Collected on 25/6/98
Heerde	F20	Early June 98	roach	0.3	Collected on 29/7/98
Enschede	F21	8 June 98	bream	5.1	Packed in plastic
Opeinde	F22	22 July 98	roach	2.6	Collected on 5/8/98
Leeuwarden	F23	Unknown	roach	2.6	Collected on 5/8/98

Appendix 3 Analytical procedures

Air samples:

Sampling was performed on 5% PDMS (polydimethylsiloxane) sorption tubes, following the validated method. Sampling was done at 500 mL min^{-1} during 15 - 30 min using a calibrated universal constant flow sampling pump (SKC, Dorset, UK). Special precautions are taken to avoid contamination. All sampling tubes are preconditioned and checked for blank levels of phthalates before sampling.

Samples are taken in duplicate. During this first sampling session, also one sample was collected using a glass fiber filter.

The analyses were performed by thermal desorption – GC-MS using the validated method. The thermal desorption tubes are desorbed at 300 °C during 10 min. The desorbed compounds were analysed by GC-MS in scan mode.

The limit of detection is determined by the method blank as described by the method validation (see below). The method blank was below 30 pg on the system, corresponding to 2 ng m^{-3} for the single isomer phthalates.

The validation of the sampling method and analysis is described by Tienpont et al. (2000). The validated method specifies a sampling speed of 500 mL min^{-1} during 30 min. During the third sample session the sampling time was increased to 60 min and the sampled volume was between 25 and 40 L. This is still below the breakthrough volume of DBP and DEHP (100 L). These phthalates are thus retained quantitatively on the sampling tube using the increased sample volumes.

More details are given by David and Sandra (2001).

Soil and sediments samples

Samples were provided by RIVM and analyzed by AlControl Biochem Laboratoria, Hoogvliet, The Netherlands. Methods and results were reported in ‘The Analysis of Phthalate Esters in Soil and Sediments’ (12 p, 15 Tables and 2 Figures).

Vegetation samples

The samples were collected by RIVM in 1997 and 1998. The samples were stored in RIVM at –40 °C. RIC collected the samples on March 24, 2000 for analysis. The samples were homogenized the next day and stored at –18° C until extraction. The origin of each sample is unknown and only the RIVM code was given.

Approximately 5 g sample was extracted with 10 mL cyclohexane during 2 x 30 min. The extracts were analysed by GC-MS using the previously described method.

Method validation
A complete method validation has been done before sample analysis. Extraction recovery and linearity were tested. Method and instrument blanks were performed. A method validation report will be prepared in the next weeks.

During the sample sequence, also instrument and method blanks were included next to spiked samples. The calibration curves for the individual compounds had correlation coefficients better than 0.995 for all single isomer phthalates. The recoveries are between 75% and 120%. The method repeatability is better than 10% for the single isomer phthalates. Blank values were always below LOQs. Lower detection limits are not possible. Extract concentration always resulted in higher blank values.

More details are given by David and Sandra (2001).

Fish samples
In first instance, a fat extraction was performed according to ‘Analytical Methods for Pesticide Residues in Foodstuffs’, published by the Ministry of Public Health, The Netherlands. This includes extraction with cyclohexane/acetone. The organic phase is isolated and concentrated to dryness for fat determination.
The phthalates were isolated from the fat matrix by gel permeation chromatography. The phthalates fraction was collected and concentrated. An additional fractionation was done by solid phase extraction. The analyses were performed by GC-MS using d4-DEHP as internal standard.

The method validation is described in a separate report. RSDs are in the order of 20-30% on a fat basis. The limit of detection is determined by the method blank and is different for the different phthalates. DBP and DEHP were detected in the method blanks, but the levels were constant (around 50 ppb). The LOD (lowest observed detection) for these compounds were set at 2 times the average blank values. Both for DBP and DHEP the LOD appeared to be 100 ng g^{-1} fat.

Remarks :
1. The samples were stored at RIVM from mid 1998 to early 2000 at –40°C. RIC collected the samples on March 24, 2000. At RIC, samples were stored at –18°C.
2. Before sample extraction, the fish head and tail was removed. The remaining part was homogenised using a household blender. From the homogenised sample, a subsample was taken for analysis. After de-freezing, it was not possible to remove bones in an efficient way.
3. Approximately 2 years have passed between sampling and analysis.
4. Although RIVM mentioned in the sampling protocol that all samples should be wrapped in Al-foil, it was observed that some samples were not completely wrapped.

Appendix 4 Applied methods for censored data

DEHP in air

The set of 14 air samples contained 4 samples with concentrations of DEHP below the limit of detection (LOD) of 2 ng m^{-3}. For these samples '< 2 ng m^{-3}' was substituted with 0.73 ng m^{-3}. This value (x_i) is calculated according to Swaving and De Vries (2000):

$$x_i = LOD \cdot \left[\left(\frac{LOD}{x_{0.9}} \right)^{frac} \right]$$

$$frac \leq 0.5$$

in which the fraction of censored data, *frac*, is lower than or equal to ½ and $x_{0.9}$ is the 90th percentile of the dataset.

Sediment and fish

Substitute values for both phthalates concentrations below the limit of detection were calculated with the equation used above because *frac* ≤ ½.

Soil and vegetation

All concentrations of DEHP in vegetation were above the LOD, whereas in soil they were most often above the LOD. Substituted values for censored data were calculated according to the equation above. For DBP both in soil and vegetation, the fraction of censored data was higher than ½, and the substituted values were computed according to Swaving and De Vries (2000):

$$x_i = LOD \cdot \left[\left(\frac{LOD}{x_{0.9}} \right)^{-1.6+4.2 \cdot frac} \right]$$

$$frac \geq 0.5$$

The median was obtained as:

$$median = LOD \cdot \left[\left(\frac{LOD}{x_{0.9}} \right)^{-2.1+4.2 \cdot frac} \right]$$

$$frac \geq 0.5$$

Appendix 5 Measured concentrations of DEHP and DBP in surface water

Table A5 DEHP and DBP concentrations (µg L^{-1}) in dissolved in freshwater

Location	Spring		Summer		Autumn	
	DEHP	DBP	DEHP	DBP	DEHP	DBP
Biesbosch (Gat van de Kerksloot)	0.18	0.16	0.22	0.27	0.28	0.19
Border Meuse (Roosteren)			0.32	0.36	0.16	0.32
Brakel	0.18	0.20	outlier$^{\#}$	1.88	0.84	0.58
Canal Apeldoorn	0.27	0.15				
De Dommel	0.20	0.13				
Ditch agriculture under glass	0.45	0.80			0.05	0.09*
Haringvliet sluices	0.21	0.16	1.13	0.92	0.36	0.33
Keizersveer	0.40	0.11	0.31	0.16	0.10	0.07
Koudevaart (St Annaparochie)	0.27	0.22	1.64	0.18	0.59	0.28
Lake Bergum	0.25	0.19	2.35	0.28	1.10	0.15
Lake IJssel (Andijk)	0.43	0.50	0.44	0.47	0.49	0.10
Lake IJssel (Vrouwenzand)	0.24	1.07	0.69	0.20	1.45	0.63
Lateraal canal Heel			0.34	0.04*	0.20	0.11
Lekkerkerk	0.05*	0.04*	0.42	0.40	0.10	0.13
Meuse (Eijsden)	0.28	0.31	0.62	1.33	0.36	0.10
Nieuw Lekkerland	0.05*	0.14	0.08*	0.14	0.41	0.03
Nieuwe Waterweg (Maassluis)	0.25	0.15	1.60	0.30	0.22	1.32
Nordsea Canal (Amsterdam)	0.37	0.14	0.25	0.39	0.27	0.62
Nordsea Canal (IJmuiden)	0.56	0.08	0.57	0.73	0.48	1.02
Ouddorp			0.32	0.18	0.13	0.04
Rhine (Lobith)	0.58	0.04*	0.92	0.29	0.54	0.20
Scheldt (Schaar van Oudendoel)	0.30	0.04*	0.17	0.42	0.07*	0.25
Surface water (canal)					0.25	0.09*
Surface water De Dommel					4.96	0.67
Twente canal	0.41	0.24	0.36	0.23	0.90	0.41
WRK Nieuwegein	0.24	0.04*	0.27	0.21	0.25	0.15

* ½ detection limit; $^{\#}$ reported value: 200.4 µg L^{-1}

Table A6 DEHP in suspended solids (Cs in μg kg^{-1}) and in water (Cw in μg L^{-1})

Location		Spring	Summer	Autumn
De Dommel	Cs	8481	n.d.	11809
	Cw	0.20	n.d.	4.96
Haringvliet sluices	Cs	3734	10768	2944
	Cw	0.21	1.13	0.36
Koudevaart (St Annaparochie)	Cs	1039	1404	2662
	Cw	0.27	1.64	0.59
Lake Bergum	Cs	876	697	970
	Cw	0.25	2.35	1.1
Lake IJssel (Vrouwenzand)	Cs	792	2300	8900
	Cw	0.24	0.69	1.45
Meuse (Eijsden)	Cs	9858	14598	10849
	Cw	0.28	0.62	0.36
Nieuwe Waterweg (Maassluis)	Cs	2906	3215	5601
	Cw	0.25	1.6	0.22
Nordsea Canal (Amsterdam)	Cs	10483	3821	7854
	Cw	0.37	0.25	0.27
Nordsea Canal (IJmuiden)	Cs	5843	3625	19258
	Cw	0.56	0.57	0.48
Rhine (Lobith)	Cs	2993	2149	4802
	Cw	0.58	0.92	0.54
Scheldt (Schaar van Oudendoel)	Cs	11400	6808	13178
	Cw	0.30	0.17	0.065

Appendix 6 Conversion of concentration into fugacity

The concentration in air (Table 8) are bulk concentrations. In order to calculate the fugacity, the concentrations need to be multiplied by the fraction (Fr) not associated to aerosols to obtain the gaseous concentrations (Table A7).

Table A7 Assumed fractions of air bulk concentrations ***not*** *associated with aerosols*

Phthalate	Fr (gas phase)
DEHP	0.050
DBP	0.930

Fugacity of a chemical in air is a simple function of the gaseous concentration and the temperature (Table A8). In water it is estimated from the dissolved concentration in water and two properties, water solubility and vapour pressure, which are both temperature dependent. In soil and sediment also the partition coefficients and density are needed.

Table A8 Expressions for fugacity, vapour pressure (V_p) in Pa; all concentrations ($C_{g,w,s,sed.}$) and water solubility (S) in mol m^{-3}; K_p in L kg^{-1}; ρ in kg L^{-1}

Fugacity (Pa)	Expression	symbols, units
f air	$C_g{\cdot}R{\cdot}T$	C_g (air conc. not associated); R (8.314 J K^{-1} mol^{-1}); T (temperature, K)
f water	$C_w{\cdot}V_p{\cdot}S^{-1}$	C_w (dissolved conc.); V_p (Pa) S (water solubility)
f soil	$C_s{\cdot}V_p{\cdot}S^{-1}K_{p,soil}{}^{-1}\rho_{soil}{}^{-1}$	C_s (conc. in soil), $K_{p,soil}$ (partition coeff.), ρ_{soil} (density soil)
f sediment	$C_{sed}{\cdot}V_p{\cdot}S^{-1}K_{p,sed}{}^{-1}\rho_{sed}{}^{-1}$	Csed (conc. in sed.), $K_{p,sed}$ (partition coeff.), ρ_{sed} (density sed.)

As an approximation, the water samples during spring, summer and autumn were assumed to be taken at 8, 17 and 12 °C, respectively. The water solubility and the vapour pressure were adjusted accordingly (Table A9).

Table A9 Temperature dependent vapour pressure and water solubility of DEHP and DBP used to convert water concentrations of Table A5 into fugacities

Temperature (° C)	DEHP		DBP	
	V_p (Pa)	S (mol m^{-3})	V_p (Pa)	S (mol m^{-3})
8 (spring)	$3.9\ 10^{-6}$	$6.0\ 10^{-6}$	$1.4\ 10^{-3}$	$3.4\ 10^{-2}$
17 (summer)	$7.6\ 10^{-6}$	$6.9\ 10^{-6}$	$2.1\ 10^{-3}$	$3.6\ 10^{-2}$
12 (autumn)	$5.4\ 10^{-6}$	$6.4\ 10^{-6}$	$1.1\ 10^{-3}$	3.210^{-2}