

**REVIEW OF EUSES MODELLING
FOR DI-2 ETHYLHEXYL
PHTHALATE (DEHP)**

Final Report Prepared for the European Chemical
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EXECUTIVE SUMMARY

CEFIC contracted with JSC International and the Canadian Environmental Modelling Centre (CEMC) to undertake an analysis of parts of the May 2000 draft European Union risk assessment report for bis (2-ethylhexyl) phthalate (di-2 ethylhexyl phthalate or DEHP) which has been prepared by Sweden. (KemI - Kemikalieinspektionen or The National Chemical Inspectorate). The specific objectives were:

- Examine/comment on the input data, including physical-chemical properties
- Identify key parameters influencing model calibration / results
- Review the consistency between predicted and monitored concentrations
- Ascertain if the EUSES model calculations agree with independent multimedia modelling results.

This task was facilitated by exploiting information from an ongoing project at the CEMC funded by the American Chemistry Council that focuses on the multimedia modelling of phthalate esters.

The KemI report was reviewed in detail and comments conveyed to CEFIC orally and in a progress report. This final report summarizes key findings.

A detailed analysis was conducted on the large quantity of monitoring data for DEHP in air, water, soil and sediment. These data extend over a wide range of concentrations thus selection of appropriate averages is problematic. A technique was devised in which, using histograms, the data were separated into groups indicative of concentrations in local, regional and continental scale environments. These concentrations are discussed and satisfactorily compared with the results of EUSES and Level III fugacity models. The high variability in environmental concentrations is attributed to two factors, ranging proximity of collected field samples to sources and the inherent short residence time or persistence of DEHP, which tends to cause a heterogeneous pattern in observed concentrations.

The physical-chemical EUSES input data are reviewed and found to be in accord with current estimates. The only exception was a low value of the octanol-water partition coefficient, K_{OW} , but the results are relatively insensitive to this quantity.

Degradation rate data in the form of half-lives were compared with current estimates and found to be reasonable, except in the case of bottom sediments. The half-life assumed in the E.U. draft risk assessment for deeper sediments is much longer than the 300 days used for the surface sediments and results in an overall half-life for sediments of 3000 days. The selection of such a long half-life for deeper sediments is questionable given the presence of bioturbation and episodic resuspension. However, selection of this long half-life for deeper sediments has little effect on the magnitude of predicted sediment concentrations. In the CEMC modelling a single well-mixed sediment layer with a half-life of 300 days was used and this resulted in predicted environmental concentrations for sediments that were similar to those predicted in the E.U. risk assessment.

Emission data were examined and while the total emission rate to all media is judged to be correct in magnitude, KemI's assumed emission release scenario used in EUSES calibration is believed to assign too small a fraction to air and too much to surface water and soil. Improved agreement with monitoring data is obtained by adjusting the release scenario with higher emission to air and reduced emissions to soil and water.

When the EUSES and CEMC fugacity models are provided with identical input data, similar results are obtained as expected given similar structure and descriptive equations. The results of the model predictions compare favourably with the monitoring data.

Since DEHP has been in use for many decades, we believe that it must have reached a steady state condition in the environment, thus the use of a steady state model is fairly justified. Fears that conditions may be getting progressively worse as a result of accumulation of DEHP from past discharges are, in our view, unfounded. The fact that

emission rates and observed concentrations were reconciled with a steady state model is further support for DEHP being at a steady state condition.

Any DEHP present above the solubility limit must be in a non-aqueous phase and therefore not available for bioconcentration. The use of such supersaturated concentrations in bioaccumulation models is thus invalid. It would be useful for models such as EUSES to contain such a check and stop or at least flag such situations thus avoiding misinterpretation of results.

We hypothesise that many of the samples showing high levels of DEHP actually contain plastic material (notably PVC) in which the DEHP is present as a plasticiser. DEHP in this state is not readily “available” and does not contribute to the dissolved concentration or the fugacity of the substance. For example, it is not readily bioavailable, nor can it evaporate.

Subject to the issues outlined above, it is concluded overall that both the KemI/EUSES and CEMC/fugacity models give a satisfactory simulation of the environmental fate of DEHP. The models play the role of synthesising disparate data on physical-chemical properties, emission rates and environmental characteristics into a prediction of fate and multimedia concentrations. Since predictions are consistent with monitoring data, it can be asserted that the environmental fate is adequately and quantitatively known. This provides a sound foundation for decisions relating to the management of this substance. It is hoped that this example will be followed for other chemicals of commerce.

Recommendations are made for particular and general studies that will improve future modelling efforts.

1.0 INTRODUCTION

1.1 Background

KemI (Kemikalieinspektionen or The National Chemical Inspectorate), a Swedish-based government organization, has recently carried out a risk assessment on bis (2-ethylhexyl) phthalate (di-2 ethylhexyl phthalate or DEHP) based, in part, on EUSES modelling (NCI, 2000). EUSES (European Union System for the Evaluation of Substances) is the preferred modelling tool for risk assessments as outlined in 1995 by the European Union (EU) Technical Guidance Document for risk assessment of new and existing substances, developed and approved by the EU Member States (ECB, 1997). In order to undertake the required EUSES modelling it was first necessary for KemI to define a number of critical model input parameters that ultimately dictate the predicted fate, exposure and risk of DEHP in the environment. Comparisons of observed and simulated concentrations of DEHP suggest that critical parameters may be defined inaccurately. Following discussion with the European Council for Plasticizers and Intermediates (ECPI) in July 2000, JSC International Ltd. and the Canadian Environmental Modelling Centre (CEMC) at Trent University were contracted to undertake a detailed review of the EUSES modelling of DEHP undertaken by KemI. The aim was to identify any deficiencies in the EUSES model calibration, application or interpretation and make constructive recommendations for possible improvement.

O'Connor Associates Environmental Inc. (OAEI) and CEMC were separately contracted by the American Chemistry Council (ACC) to model the fate of phthalate esters in the environment and to estimate human exposure to phthalate esters.

In the CEMC funded project we draw on the findings of this companion project to assist in the interpretation of the EUSES modelling.

1.2 Specific objectives of the CEFIC funded project

- Scrutinise each model input parameter used by KemI in setting up EUSES

- Identify key parameters defining steady-state exposure
- Propose alternative data choices, where appropriate
- Undertake EUSES modelling using alternative input data
- Compare EUSES predicted environmental concentrations with observed DEHP concentrations in our in-house field monitoring database
- Compare predictions from EUSES with predictions from in-house fugacity models using the same set of model input data
- Draw conclusions and make recommendations based on the project's findings

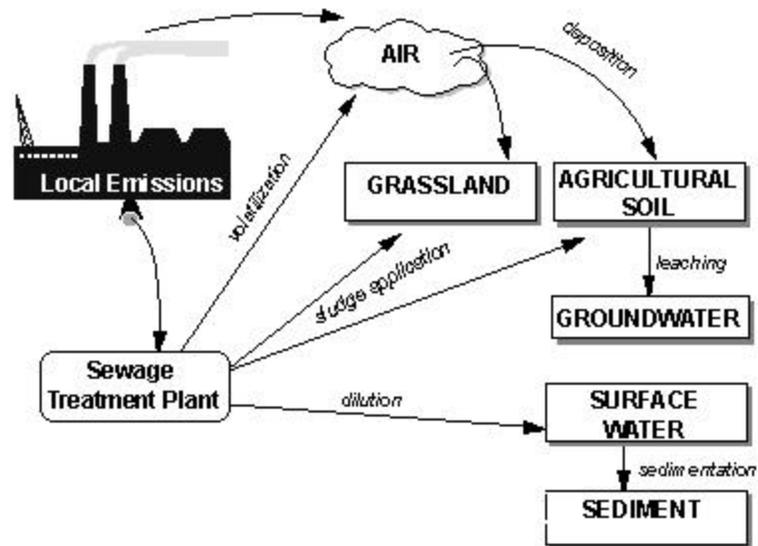
2.0 ANALYSIS OF MONITORING DATA

2.1 Using appropriate monitoring data for model calibration

Multimedia environmental models predict an average concentration for the entire region being modelled. EUSES has three separate modelling scenarios that apply to different spatial scales, namely: “local”, “regional” and “continental” (Figure 1). The “local” scenario represents an exposure scenario for humans or wildlife near to a point source (e.g. in proximity to a manufacturing plant). The “regional” scenario represents an exposure scenario for humans or wildlife living in a densely populated industrial region (e.g. in the Netherlands). The “continental” scenario represents an exposure scenario for human or wildlife living in a region remote from sources (e.g. in a rural area). It is vitally important to compare the PECs from these three modelling scenarios with the appropriate monitoring data when undertaking model calibration i.e. to compare like with like. For example, an EUSES regional modelling scenario predicts average PECs for a densely populated region (20 million people living in an area of 40,000 km² i.e. 500 people per km²). This is roughly equivalent to the population density of the Netherlands (420 people per km²), which is one of the most densely populated countries in Europe. It is not appropriate therefore to compare PECs from a regional EUSES simulation with concentrations from sites remote from sources or from sites in close proximity to sources.

It is essential that environmental concentrations representative of the spatial scale being simulated are required for model calibration. These concentrations could be obtained (1) from a sampling program with the aim of providing concentrations representative of the required spatial scale and/or (2) analysing all available monitoring data and extracting concentrations representative of the required spatial scale. In this study we were able to use both approaches for calibration of the EUSES “regional scale” simulation, and we were able to extract out concentrations representative of remote locations from available monitoring data for calibration of the EUSES “continental scale” simulation.

Local Scale



Continental and Regional Scales

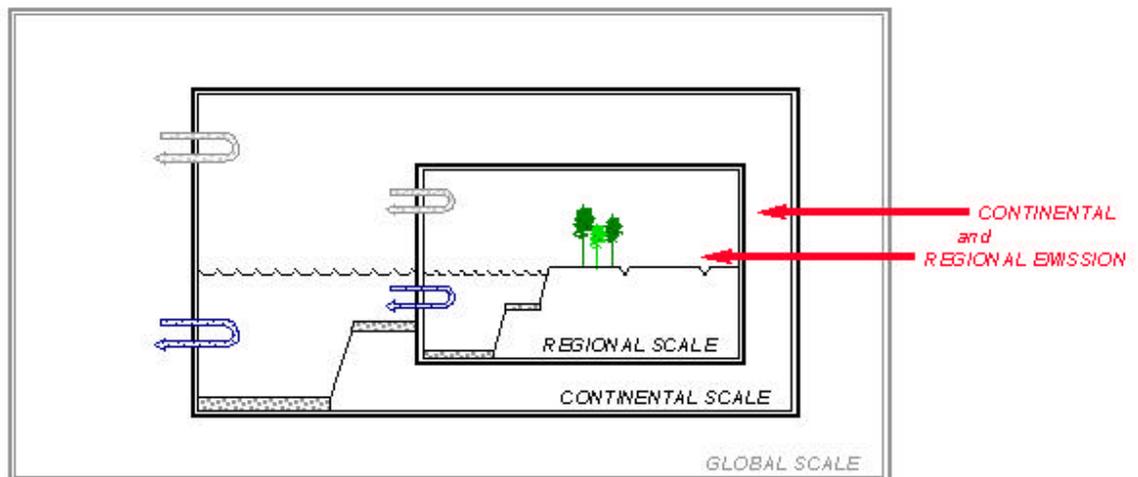


Figure 1. Spatial scales in EUSES

2.2 ECPI/RIVM field monitoring campaign

Over the last few years RIVM (Rijksinstituut voor Volksgezondheid en Milieu or National Institute of Public Health and the Environment) and ECPI have recently collaborated on a multimedia sampling program throughout the Netherlands, which provides an ideal dataset for calibrating the EUSES “regional scale” scenario. It is particularly appropriate because the Netherlands has a similar population density to that assumed in the EUSES regional model, possibly because the EUSES model was developed in the Netherlands. Air, water, soils, sediments, vegetation, fish and cow’s milk have been analysed for DEHP (Alberti et al., 2000; AIControl, 1999; RIC, 2000). These published monitoring data are combined with some additional unpublished RIC data, and are summarised in Table 1.

Table 1. Summary of DEHP monitoring data from the ECPI/RIVM monitoring campaign

Medium	Number of samples	Median	10 th percentile	90 th percentile	Units
Outdoor air	24	17	1.0	85	ng/m ³
Surface water	18	0.46	0.087	1.3	µg/L
Soil	33	1,420	630	3,100	µg/kg OC
Sediment	30	5,000	1,300	15,000	µg/kg OC
Vegetation	48	220	82	480	µg/kg dry
Fish	25	450	50	5,600	µg/kg fat
Cow’s milk	29	670	310	1,300	µg/kg fat
Sewage sludge	70	260	64	1,700	mg/kg OC

2.3 ACC monitoring database

As part of a contract between the American Chemistry Council’s Environmental Research Task Group, CEMC and O’Connor Associates an extensive database of

concentrations of phthalate esters (including DEHP) in the environment has been compiled in an ExcelTM spreadsheet. The data were categorized into regions including Canada, United States, Europe, and Asia. The data were also categorized in terms of data quality. The following ranking scheme was employed:

- 1 Reliable without restrictions
- 2 Reliable with restrictions
- 3 Not reliable
- 4 Unassignable

The monitoring data have been evaluated using several different methods as discussed in further detail in the reports by EMBSI (1999) and Clark et al. (2001). A table summarising DEHP concentrations in the primary environmental media in Europe (taken from the ACC database) is included below (Table 2). On the whole these data compare favourably with the data reported in the recent ECPI/RIVM monitoring campaign (Table 1).

Table 2. A summary of selected DEHP monitoring data from the ACC database

Medium	Number of samples	Median of study averages	10th percentile	90th percentile	Units
Outdoor air	397	18	1.3	130	ng/m ³
Surface water	405	0.21	0.018	1.9	µg/L
Soil	3	50	29	66	µg/kg dry
Sediment	85	0.29	0.019	8.2	mg/kg dry

Since the individual data points were not available for every study in the data base it was decided to calculate the median of the reported study averages and the 10th and 90th percentiles of study averages. Non-detectable data were included in the calculations by assuming a concentration equal to one-half the detection limit. A few potential limitations with the methodology used to collate the monitoring database and to calculate average concentrations are summarized below:

- Temporal trends may introduce a positive bias because regulatory controls in the past few decades may have contributed to lower concentrations.
- Positive bias may also be introduced by the tendency to focus field sampling near to point sources.
- Systematic bias may be introduced by using half the detection limit in the calculation of arithmetic mean.

The above problems all tend to introduce a positive bias and thus introduce a degree of conservatism to the estimates of DEHP environmental concentrations.

2.4 Analysis using histograms

It is difficult to visualize the distribution of the monitoring data by examining the raw data contained in the ExcelTM monitoring database or by examining the summary tables and statistics. Therefore, it was decided to display the monitoring data graphically using both frequency histograms and cumulative distribution plots derived from these histograms. For the purpose of this report these plots are termed “cumulative histograms”.

Environmental concentrations in each medium were divided logarithmically into classes or bins, with a factor of approximately 3 between adjacent bins. For example, for surface water concentrations the following bins were allocated

Bin	Range ($\mu\text{g/L}$)	Midpoint of range ($\mu\text{g/L}$)
1	0.01 - 0.03	0.017
2	0.03 - 0.1	0.055
3	0.1 - 0.3	0.17
4	0.3 - 1.0	0.55
5	1.0 - 3.0	1.7
6	3.0 - 10	5.5
7	10 - 30	17
8	30 - 100	55

The bins allocated can be adjusted to fit the range of environmental concentrations in the database.

The frequency histograms were constructed by the number of study averages in the monitoring database that fell within each bin. A weighted frequency histogram was constructed by adding up the number of samples that contribute to each study average within a particular bin. For example, if there are three study averages within a bin ranging from 0.1 to 0.3 $\mu\text{g/L}$ of 0.12 $\mu\text{g/L}$ ($n=10$), 0.20 $\mu\text{g/L}$ ($n=1$), 0.25 $\mu\text{g/L}$ ($n=5$) then this bin will have a frequency of 3 in the unweighted histogram and a frequency of 16 in the weighted histogram.

The cumulative histograms were constructed by calculating the cumulative percentage contribution of each successive bin to the total number of study averages in the case of an unweighted cumulative histogram, or to the total number of samples in the case of a weighted cumulative histogram.

Four types of histogram have been plotted to show the distributions of concentrations of DEHP in air, surface water, and sediment in Europe i.e. unweighted frequency, weighted frequency, unweighted cumulative and weighted cumulative. Thus, in total, 12 histograms have been plotted for DEHP (see Figures 2-7). The location of a calculated

weighted arithmetic mean concentration is shown on each histogram, which accounts for the fact that different studies analyse variable numbers of samples. The weighted arithmetic mean concentration was calculated by multiplying each individual study average by the number of samples in the study, summing all of these weighted study averages, and dividing the sum by the total number of samples.

Weighted histograms often display a markedly different distribution from the unweighted histograms. Further, the weighted arithmetic mean is greatly influenced by a few high concentrations, which heavily bias the mean to the high-side. This is evidenced by the cumulative histograms, which show that the 50th percentile is usually at a lower concentration than the weighted arithmetic mean concentration. It was concluded that the unweighted histograms provide a better description of the distribution of DEHP concentrations. It is also concluded that because weighted arithmetic means can be strongly biased by a few studies reporting high concentrations, median concentrations are a better indication of average regional environmental concentrations.

The histograms show that DEHP concentrations are characterized by a very wide range, which makes interpretation and averaging difficult. For example, water concentrations vary from 0.003 to 10 µg/L i.e. a factor of 3000. Many of the concentrations at the extreme low end may be below the limit of quantification, although this was not always clearly stated in scientific articles. Concentrations in excess of the solubility limit for DEHP are attributable to partitioning onto non-aqueous phases including dissolved and suspended particulate matter possibly in colloidal form. Such partitioning processes can increase the total concentration of such substances in surface water well above the solubility limit.

We believe that the wide distribution in observed DEHP concentrations is due to variable proximity to sources i.e. the concentrations on the right-hand side of the histograms are probably representative of local contaminated sites and those on the left-hand side are likely to be representative of regional background or continental environmental concentrations. Separation of the monitoring data into groups based on proximity to

sources would require going back to the source references and allocating concentrations to different classifications such as “urban/industrial” or “rural/background”. Even after careful scrutiny of source references separation of the data may not be possible.

We have sought to interpret the monitoring data objectively based on the unweighted cumulative histograms as follows:

1. One third represent “remote from source” samples.
2. One third represent “close to source” samples.
3. One third represent “intermediate” samples.

This classification into three distinct ranges is consistent with the three spatial scales of risk assessment that are undertaken with EUSES. The “remote from source”, “close to source” and “intermediate” samples correlate with the “continental”, “local” and “regional” spatial scales, respectively. The cumulative histograms for DEHP (Figures 3, 5 and 7) were used to assign these three concentration ranges and average values for DEHP in surface waters, sediments and air in Europe as illustrated for DEHP surface water concentrations in Figure 8.

For surface water, 90% of the reported data lie between 0.01 and 10 $\mu\text{g/L}$ with a weighted average of 0.93 $\mu\text{g/L}$. We interpret the distribution to indicate that in water which is remote from sources of DEHP the concentration probably lies in the range 0.01 to 0.1 $\mu\text{g/L}$ i.e. typical values of 0.03 $\mu\text{g/L}$ plus or minus a factor of 3. In waters that are in the vicinity of discharges, concentrations probably lie in the range 1.0 to 10 $\mu\text{g/L}$ with a typical value of 3.0 $\mu\text{g/L}$ plus or minus a factor of 3. The “intermediate” or “regional-scale” concentrations therefore lie in the range 0.1 to 1.0 $\mu\text{g/L}$ i.e. typical values of 0.3 plus or minus a factor of 3.

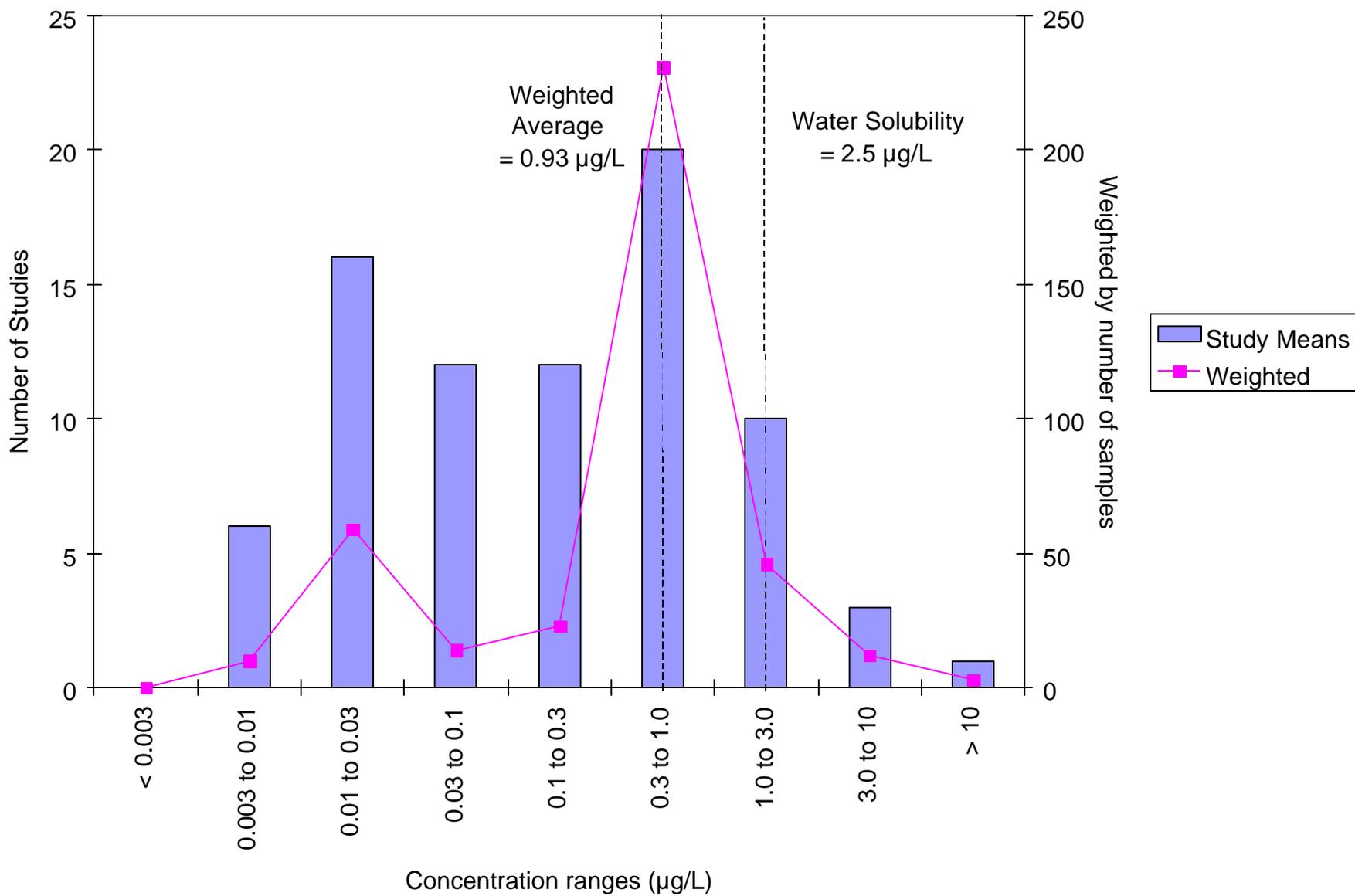


Figure 2. Frequency histogram showing the distribution of DEHP water concentrations in Europe from published studies

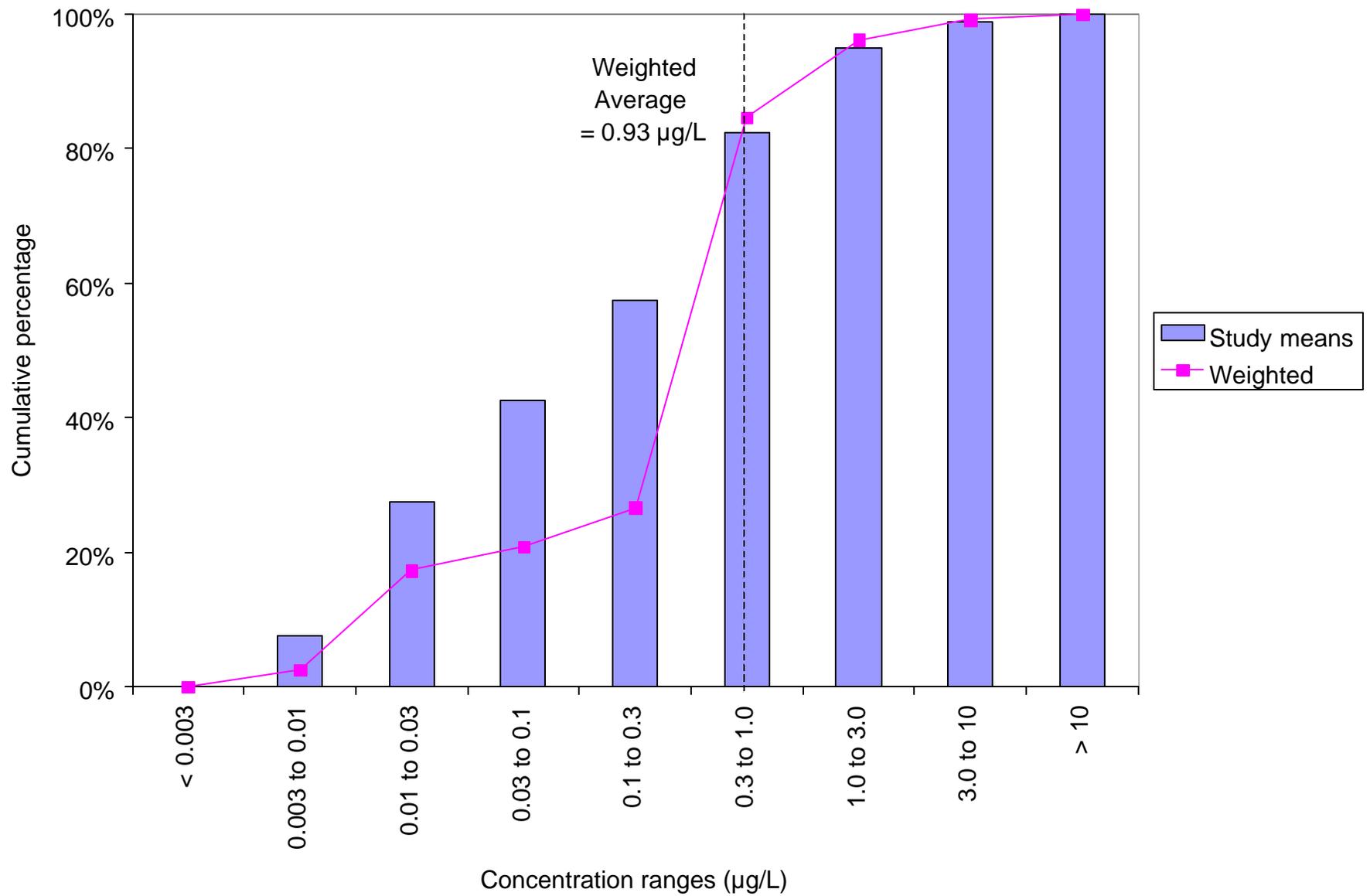


Figure 3. Cumulative histogram showing the distribution of DEHP water concentrations in Europe from published studies

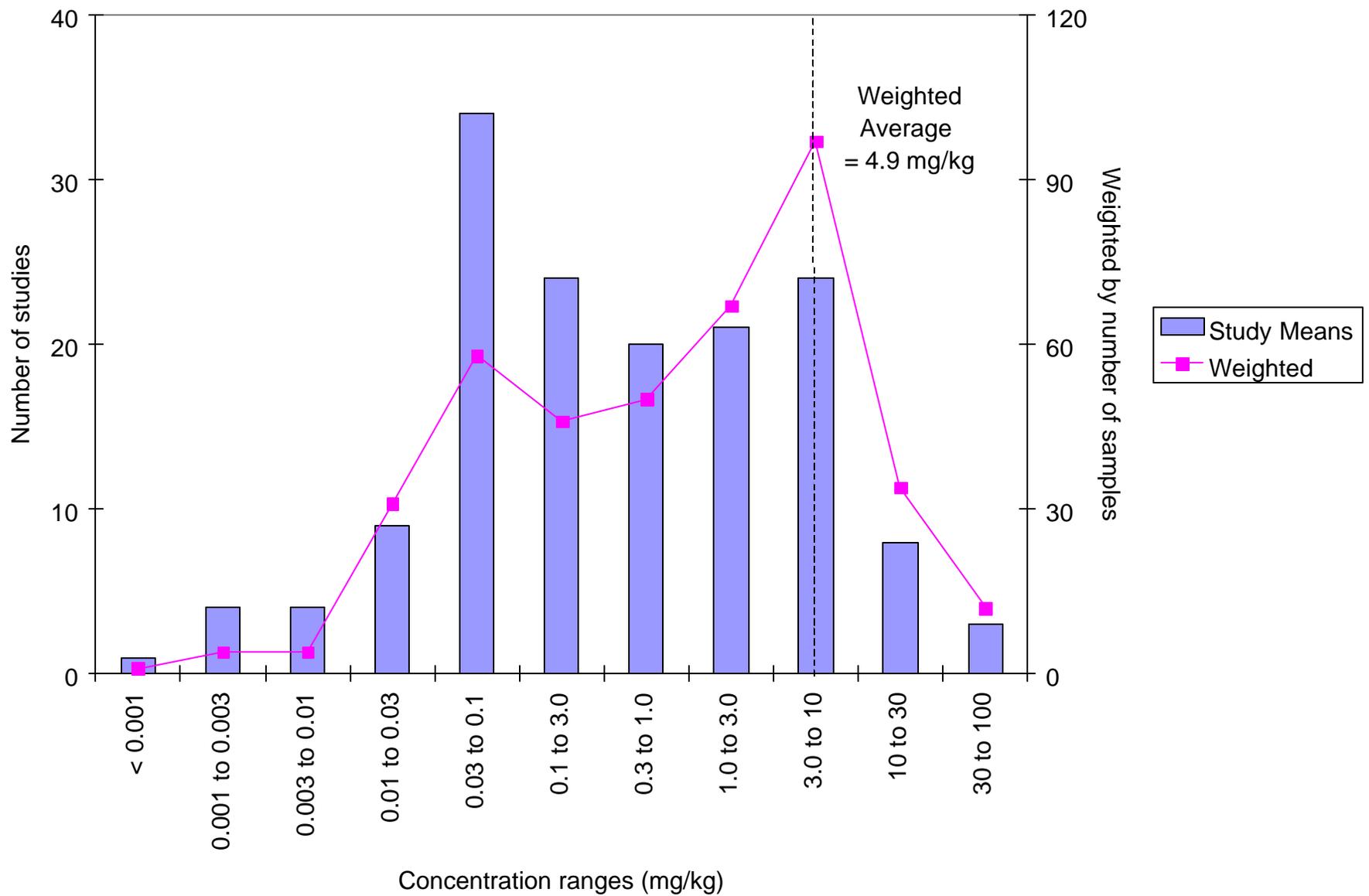


Figure 4. Frequency histogram showing the distribution of DEHP sediment concentrations in Europe from published studies

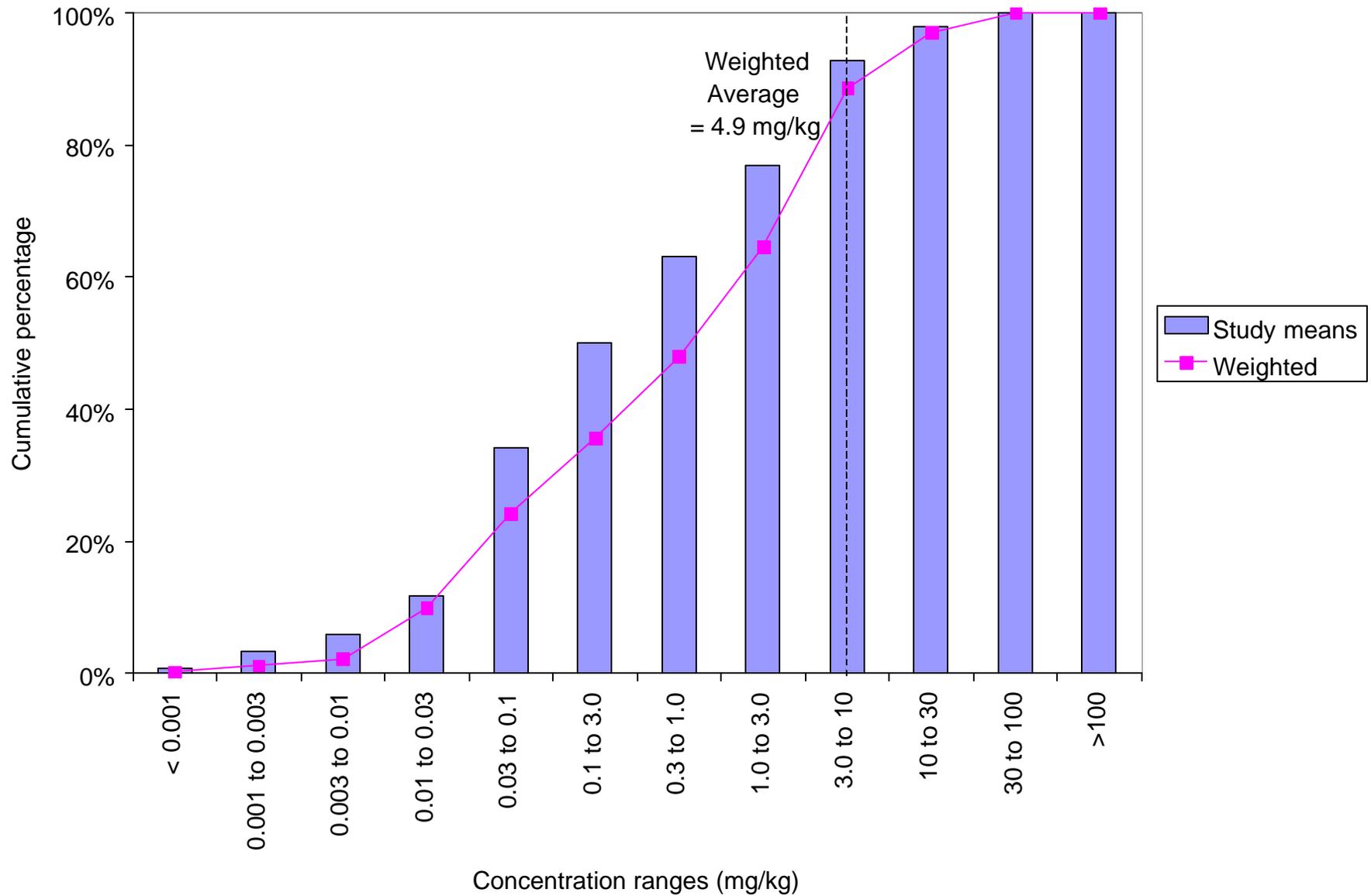


Figure 5. Cumulative histogram showing the distribution of DEHP sediment concentrations in Europe from published studies

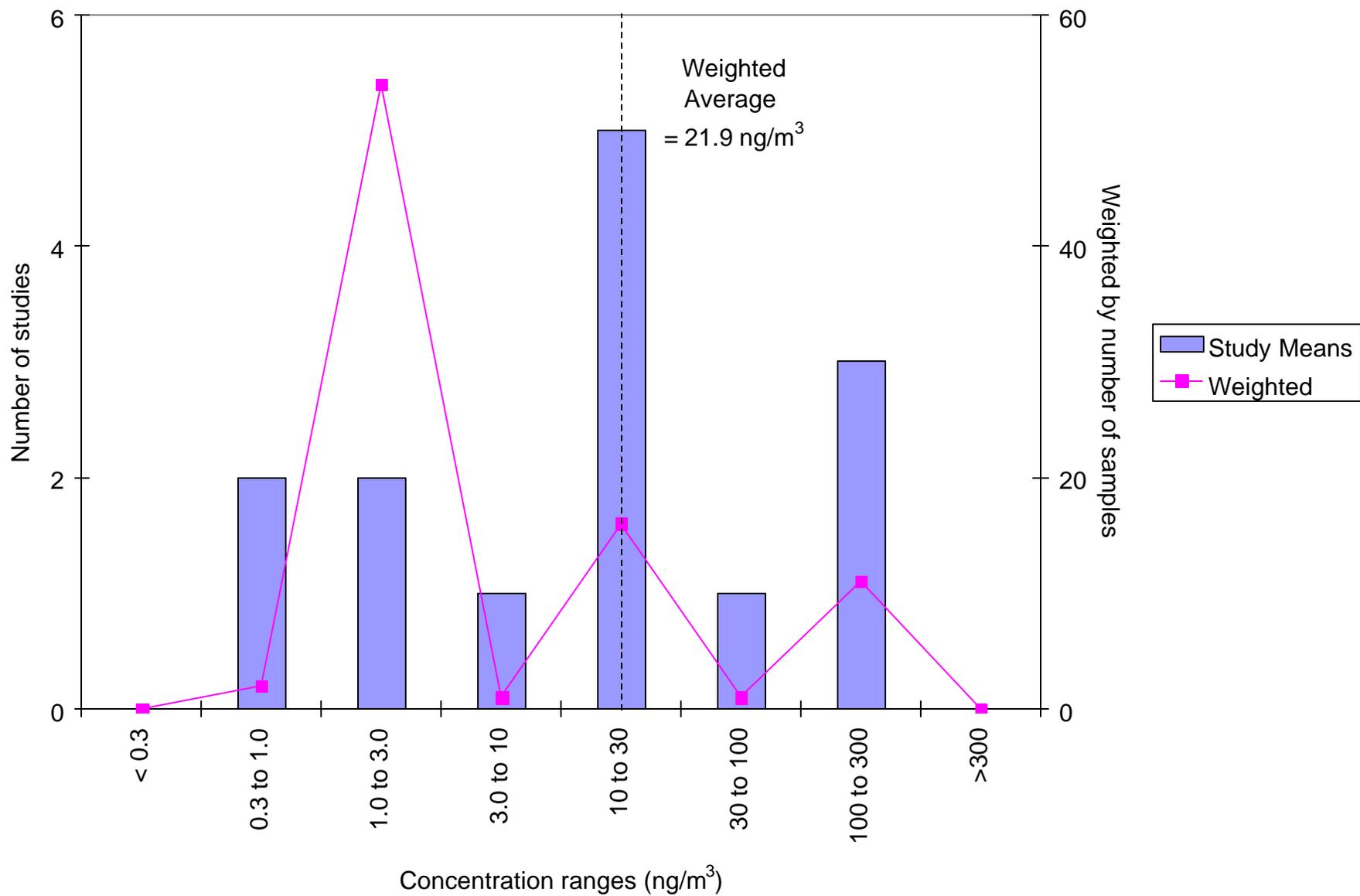


Figure 6. Frequency histogram showing the distribution of DEHP air concentrations in Europe from published studies

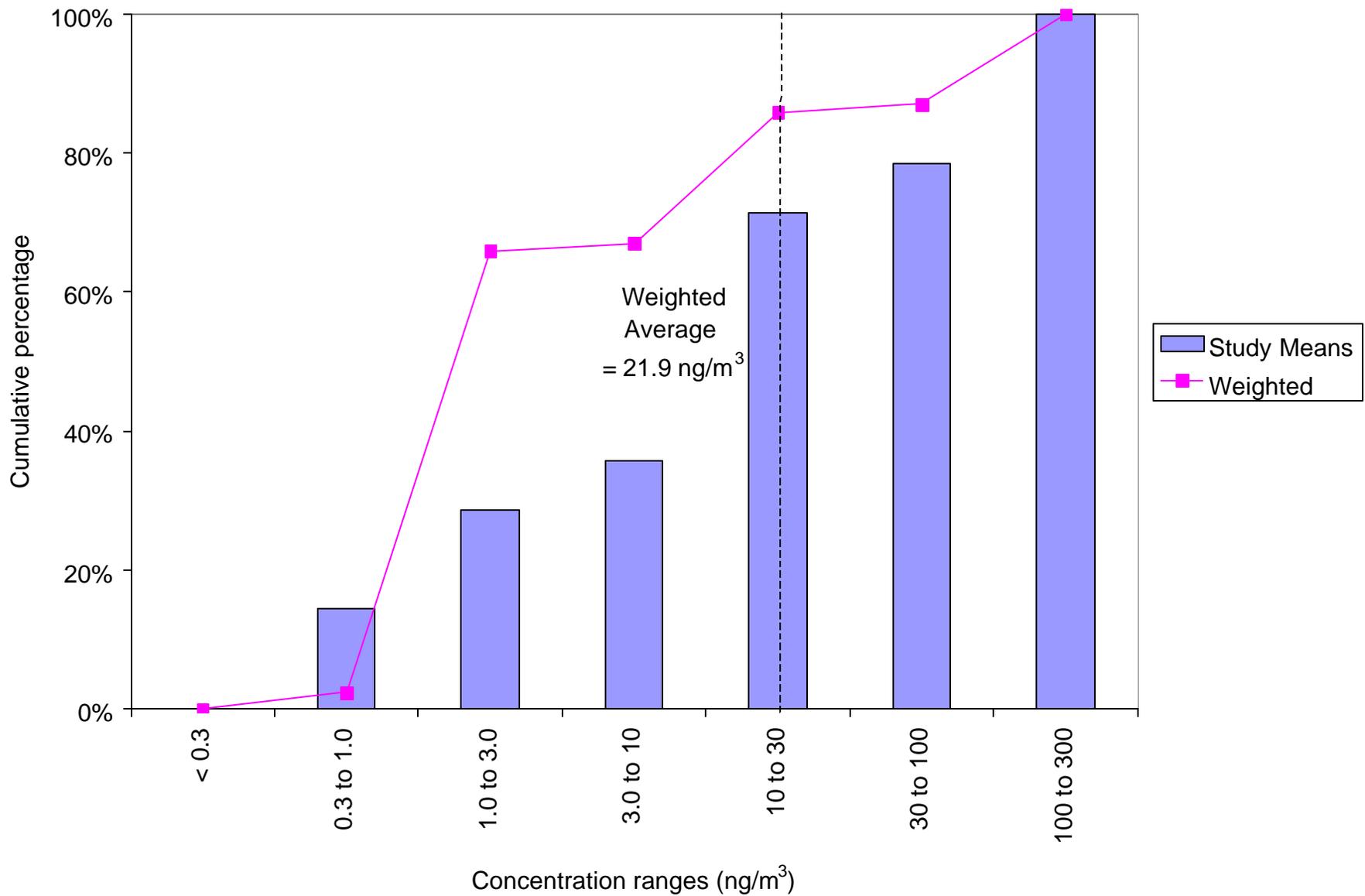


Figure 7. Cumulative histogram showing the distribution of DEHP air concentrations in Europe from published studies

For sediments, 90% of the reported data lie between 0.001 and 10 mg/kg with a weighted average of 4.9 mg/kg (dry). We interpret the distribution to indicate that in sediments associated with water which is not subject to direct discharge of DEHP the concentration probably lies in the range 0.001 to 0.1 mg/kg i.e. typical values of 0.01 mg/kg plus or minus a factor of 10. In sediments that are in the vicinity of discharges, concentrations probably lie in the range 1.0 to 10 mg/kg with a typical value of 3 mg/kg plus or minus a factor of 3. The “intermediate” or “regional-scale” concentrations therefore lie in the range 0.1 to 1.0 mg/kg i.e. typical values of 0.3 mg/kg plus or minus a factor of 3.

For air, 90% of the reported data lie between 0.3 and 100 ng/m³ with a weighted average of 21.9 ng/m³. We interpret the distribution to indicate that in air which is not subject to direct discharge of DEHP the concentration probably lies in the range 0.3 to 3.0 ng/m³ i.e. typical values of 1.0 ng/m³ plus or minus a factor of 3. In air that is in the vicinity of discharges concentrations probably lie in the range 30 to 300 ng/m³ with a typical value of 100 ng/m³ plus or minus a factor of 3. The “intermediate” or “regional-scale” concentrations therefore lie in the range 3.0 to 30 ng/m³ i.e. typical values of 10 plus or minus a factor of 3.

It is not possible to undertake a similar analysis for soil because of the lack of monitoring data available. We estimate that the weighted average soil concentration of 48 µg/kg is representative of an “intermediate” or “regional-scale” concentration.

From an examination of the frequency histograms it is possible to infer what may be a bimodal distribution in the environmental concentrations of DEHP. For example, the histograms in Figures 4 and 6 appear to be two separate distributions superimposed on top of each other. It is, unfortunately, difficult to separate out these two distinct groups of samples from the database because of insufficient information on each individual study. It could be hypothesized that the bimodal distribution represents the “remote from source” samples and the “near to source” samples. An alternative hypothesis is that the right-hand peak in the histograms represents phthalates released from sources associated with PVC particles and thus have not achieved equilibrium partitioning, whereas the left-

hand peak represents phthalates that have reached equilibrium partitioning conditions.
We discuss this in more detail later.

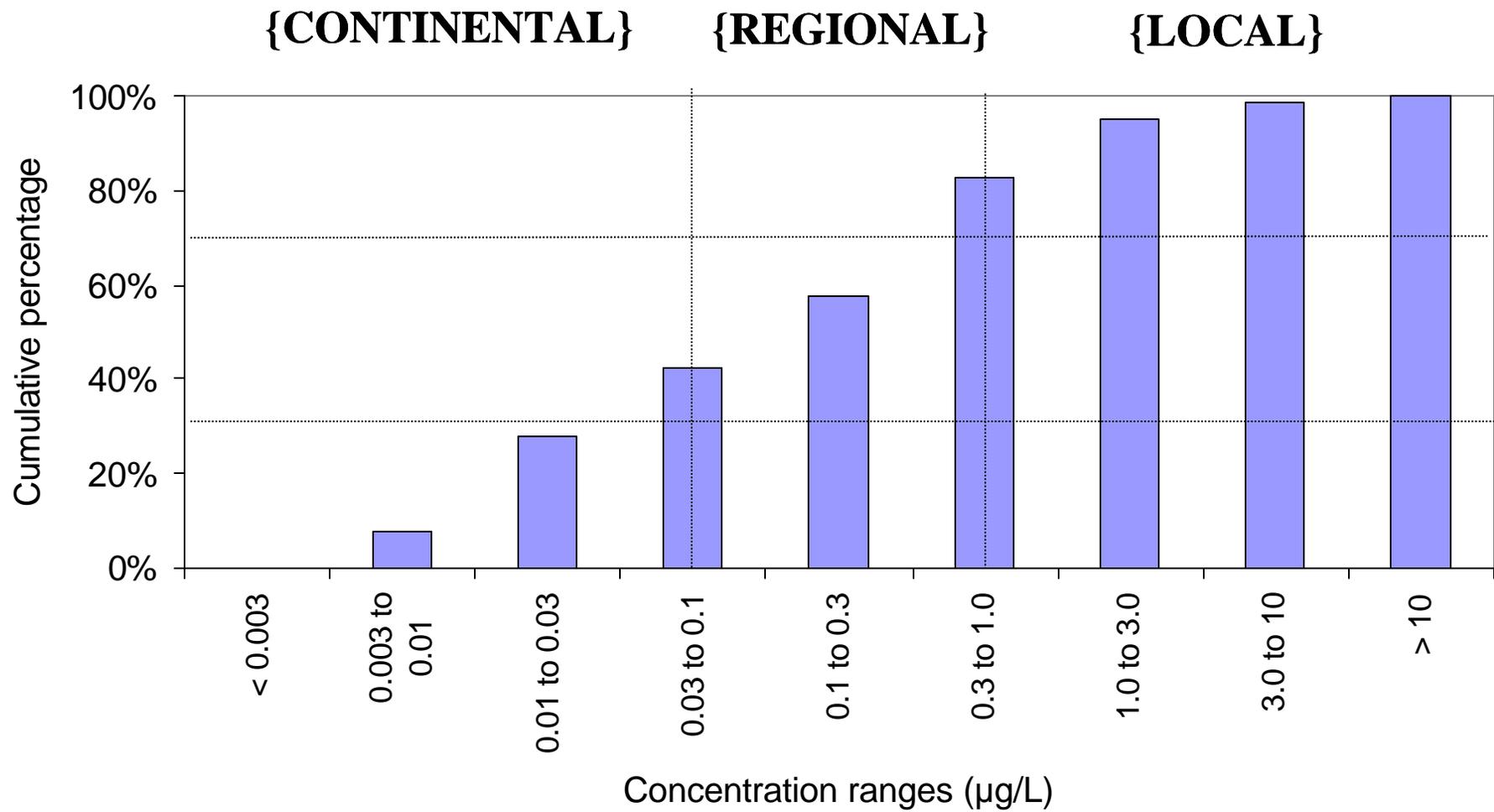


Figure 8. Method of analysing cumulative histograms

3.0 ANALYSIS OF EUSES INPUT DATA

There are three key types of chemical input data that will influence the predicted environmental concentrations in EUSES, namely

- Physical-chemical data (i.e. vapour pressure, water solubility and octanol-water partition coefficient (K_{OW})),
- Environmental degradation rates, and
- Environmental emissions

The same EUSES-environments were used for all simulations, so only the variation in chemical input data will influence the predicted environmental concentrations of KemI and CEMC models. Table 3 summarizes the assumed environmental inputs including compartment dimensions, air and water flow rates.

3.1 Physical-chemical properties

The physical-chemical properties of phthalate esters have been recently reviewed by Cousins and Mackay (2000). The values for water solubility, vapour pressure and K_{OW} , used by KemI are in reasonable agreement with the values suggested in this review. The value of K_{OW} of $10^{7.0}$ is slightly lower than the value suggested by Cousins and Mackay of $10^{7.65}$, but KemI were constrained with the upper bound of $10^{7.0}$ that is acceptable for use in EUSES. A sensitivity test was undertaken to determine the effect of K_{OW} on the predicted environmental concentrations and it was shown that using a value for K_{OW} of either $10^{7.0}$ or $10^{7.65}$ yielded near identical results. This is because compounds with K_{OW} of $10^{7.0}$ and above are sufficiently highly hydrophobic to be mainly associated with organic or lipid phases and a small increase in hydrophobicity does not appreciably increase the already high extent of association.

For consistency we have used the same physical-chemical input data as KemI in our EUSES modelling calculations (Table 4).

Table 3. Dimensions and properties of the EUSES/SimpleBox 1.0 region used for regional risk assessment

Parameter	Value	Unit
Total area of region	4×10^{10}	m ²
Water surface area	1.2×10^9	m ²
Environmental temperature	12	°C
Area fraction of natural soil	0.6	-
Area fraction of arable soil	0.27	-
Area fraction of industrial soil	0.1	-
Water depth	3	m
Air mixing height	1000	m
Industrial/natural soil mixing depth	0.05	m
Arable soil mixing depth	0.2	m
Sediment mixing depth	0.03	m
Volume fraction of particles in air	2×10^{-11}	-
Volume fraction of particles in water	1.5×10^{-5}	-
Volume fraction of air in soil	0.2	-
Volume fraction of water in soil	0.2	-
Volume fraction of soil solids	0.6	-
Volume fraction of sediment pore water	0.8	-
Volume fraction of sediment solids	0.2	-
Organic carbon fraction of particles in water	0.1	-
Organic carbon fraction of soil solids	0.02	-
Organic carbon fraction of sediment solids	0.05	-
Residence time of air	0.684	days
Residence time of water	40.1	days

Table 4. Physical-chemical properties and degradation rates of DEHP used as EUSES inputs by CEMC and KemI

EUSES Substance Property	Values used by CEMC	Values used by KemI
Molar mass (g/mol)	390.57	390.57
Melting Point (°C)	-55	-55
Boiling Point (°C)	230	230
Vapour Pressure (Pa)	3.4×10^{-5}	3.4×10^{-5}
Water solubility (g/m ³)	3×10^{-3}	3×10^{-3}
Log K _{OW} (unitless)	7.0 ¹	7.0 ¹
Overall degradation half-life in air (days)	1.0	1.0
Overall degradation half-life in water (days)	22	50
Overall degradation half-life in soil (days)	250	300
Overall degradation half-life in sediment (days)	365	300 ²

¹ K_{OW} is the octanol-water partition coefficient. The maximum value allowed in EUSES is 10^{7.0}.

² This only applies to the surface sediment (upper 3 cm) in the KemI EUSES simulation. The overall sediment degradation half-life (upper and buried sediment) is 3000 days.

3.2 Degradation rates

It is noteworthy that degradation half-lives of organic compounds cannot be viewed in the same way as radionuclide half-lives, which are a fundamental, reproducible property of the radionuclide. Degradation half-lives are functions of both the chemical and the environment and are by their nature hard to assign as they vary temporally and spatially. Given the difficulties in assigning reliable half-lives we have drawn on several available pieces of evidence available for assessing the degradability of DEHP in the environment.

3.2.1 Literature data

The first obvious place to look for experimental evidence for the degradability of DEHP is in the scientific literature and we were fortunate that Staples et al. (1997) have recently published a review of the environmental fate of a range of phthalate esters including DEHP. Staples et al. (1997) found that biodegradation is the dominant loss process for phthalate esters in all media except the atmosphere where they are likely to be susceptible to rapid photo-oxidation. A photo-oxidation half-life, based on hydroxyl radical attack, for DEHP of 0.2-2 days was predicted by Staples et al using the Atmospheric Oxidation Program (AOP) (Meylan and Howard, 1993). One study is available to compare with this prediction indicating an atmospheric half-life for DEHP of about 1 day. The confirmation of the atmospheric half-life is important because it is a critical parameter as is discussed later. Primary aerobic biodegradation half-lives of phthalate esters in natural waters and soils have been estimated by Staples et al. based on analysis of available measured data. Aerobic biodegradation half lives in natural waters and soils tend to increase with increasing alkyl chain length. DEHP was shown to have aerobic biodegradation half-lives in natural waters of 2 to 22 days and half-lives in soils of 25 to 250 days respectively. Staples et al reported that there are only limited data available on biodegradation of phthalate esters in sediments, but the data suggests that primary biodegradation of phthalate esters in sediments is slower than in soils and of the order of several months (>100 days).

The above analysis of measured biodegradation half-life data from Staples et al. has been used to define approximate half-lives. We have taken a conservative approach and

allocated the upper end of the range suggested by Staples et al. as the half-lives used for input into the multimedia models (Table 3).

3.2.2 Evidence for biodilution in food chains

The study of both aquatic and terrestrial ecosystems has shown that one enlightening way of studying food chain bioaccumulation is through transforming environmental concentrations into fugacities (McLachlan, 1996). Fugacities offer the advantage of using use a single “currency” to compare levels of contamination in different environmental media and organisms. This approach helps determine if a chemical significantly biomagnifies or biodilutes in food chains. Persistent compounds tend to biomagnify whereas compounds that are readily metabolised, however hydrophobic, tend to biodilute in food chains.

The fugacity f (Pa) of a compound in a particular phase can be calculated from the concentration C (mol/m³) using the following equation

$$f = C / Z$$

where Z is the fugacity capacity of the phase for the compound (mol/m³/Pa). Hence if the fugacity capacity of phase can be calculated, then the fugacity can be calculated from measured concentrations. Using this approach, concentrations of phthalates in Europe have been transformed into their corresponding fugacities for air, surface water, vegetation, soil, sediments, fish, cow’s milk and human milk. Only monitoring data from the recent RIVM/ECPI monitoring campaign were used for calculating fugacities (summarized in Table 1), except for human milk concentrations, which were taken from the ACC concentration database. The fugacity capacities or Z values for the phases were estimated using methods outlined in Mackay (1991). Physical-chemical data used in the calculations such as the octanol-water partition coefficient, Henry’s law constant and octanol-air partition coefficient were taken from Cousins and Mackay (2000). These calculations were undertaken in an ExcelTM spreadsheet, which is available from the authors on request if detailed examination of the calculations is desired.

The discussion of the trends of DEHP fugacities in environmental media has been reiterated below based the report of Clark et al. (2001). A plot of DEHP fugacities for a range of environmental media is shown in Figure 9. The error bars represent the 10th and 90th percentiles reported environmental concentrations.

Fugacities of DEHP in different media decrease by 3 log units or a factor of 1,000 from left to right on the plot, from air to fish. The fugacities of DEHP in fish, cow's milk and human breast milk are considerably lower than in most other media. This decrease in fugacity represents a biodilution effect as DEHP is transferred through aquatic and terrestrial food chains. As discussed by McLachlan (1996), three factors combine to cause these biodilution effects:

1. Chemical degradation.
2. Reduced absorption of highly hydrophobic compounds in the digestive tract.
3. Kinetically limited uptake of involatile, hydrophobic compounds by plants.

It is believed that for DEHP all three factors are likely to have contributed to the observed biodilution effects.

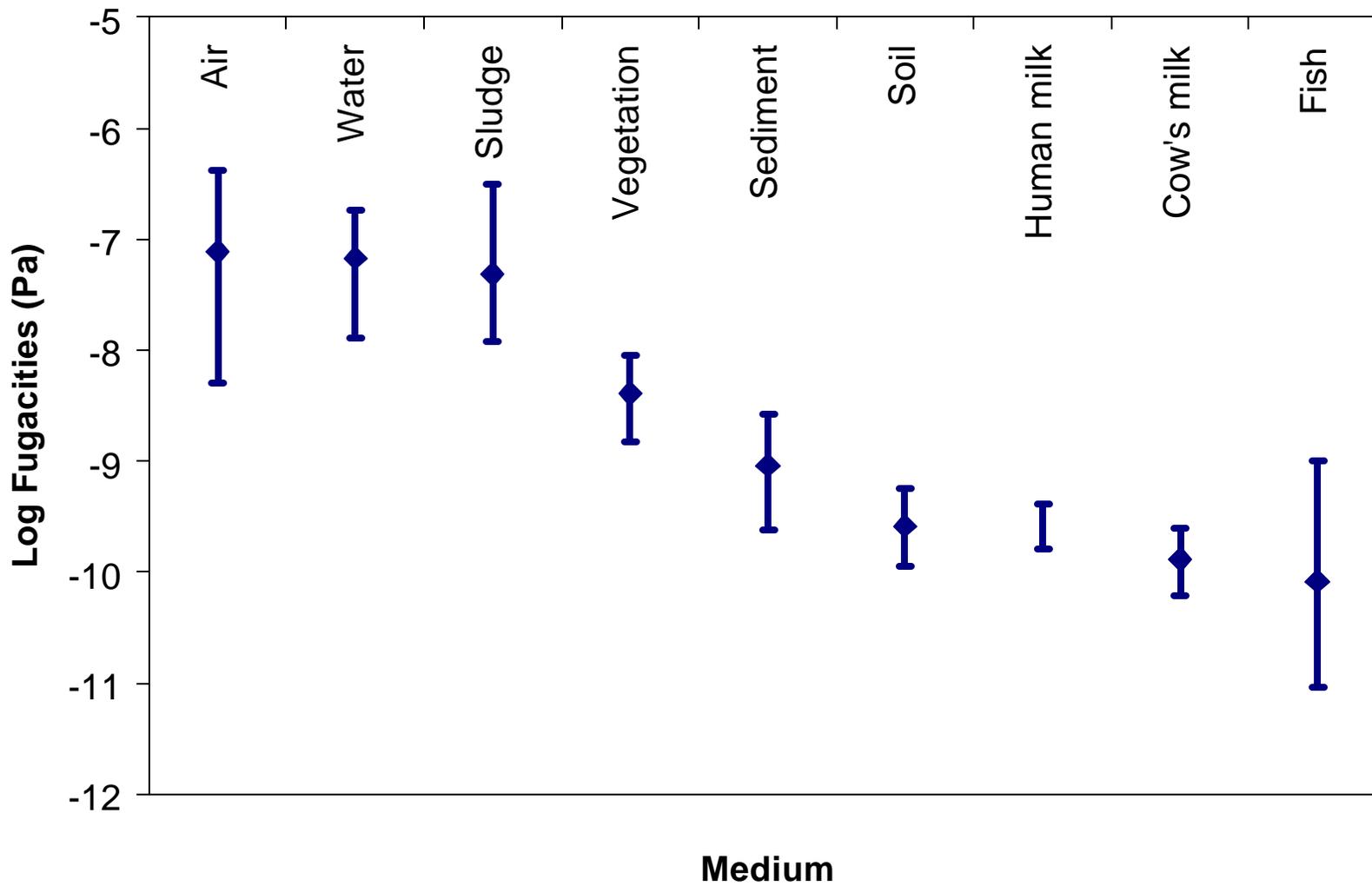


Figure 9. Estimated fugacities of DEHP in environmental media

McLachlan (1996) focussed on the air/soil-plant-cow-milk-human food chain, which is important for the human exposure via the terrestrial food chain. In Figure 10 the fugacities of DEHP in European air, soil, plants, cow's milk and human milk have been compared to fugacities reported by McLachlan for hexachlorobenzene (HCB) in samples collected in Germany. This provides an interesting comparison of two contrasting chemicals in the same food chain. The fugacities of HCB clearly increase by a factor of 300 (or 2.5 log units) between air and human breast milk indicating a pronounced biomagnification effect. In contrast, DEHP biodilutes by a factor of 1,000 (or 3 log units). There is strong biodilution from air to plant (a factor of 13) and from plant to cow (a factor of 32). The drop in fugacity from air to plant is probably the result of the third factor listed above; kinetically limited uptake by plants. The drop in fugacity from plant to cow may be a combination of the first and second factors; degradation and reduced absorption in the digestive tract. McLachlan (1996) found that the 2,3,7-8-substituted polychlorinated dibenzo-p-dioxins and furans, which have similar hydrophobicities (K_{OW} of $10^6 - 10^8$) to DEHP (K_{OW} of $10^{7.65}$), but are highly persistent, may biodilute by a factor of 10 to 100 between air and human breast milk. This is lower than the biodilution effect observed for DEHP of >300 and suggests that for DEHP degradation (i.e. biotransformation) contributes to the biodilution effect (Figure 11).

The observed biodilution of DEHP must be regarded as fortuitous because it reduces human exposure, which would be much greater if the food supply was in equilibrium with the air. Further, the lack of DEHP biomagnification will limit the exposure of upper trophic levels to the more toxic metabolite of DEHP, the monoethylhexyl ester, MEHP, which is formed by enzymatic hydrolysis of DEHP in the intestine and liver of organisms. MEHP is water soluble and will not bioaccumulate or biomagnify in the food chain, but rather will be excreted (or conjugated and excreted) in the urine of the organism in which it is formed.

This approach of plotting fugacity as a function of medium can, we believe, provide interesting insights into chemical fate. We expand on its basis below.

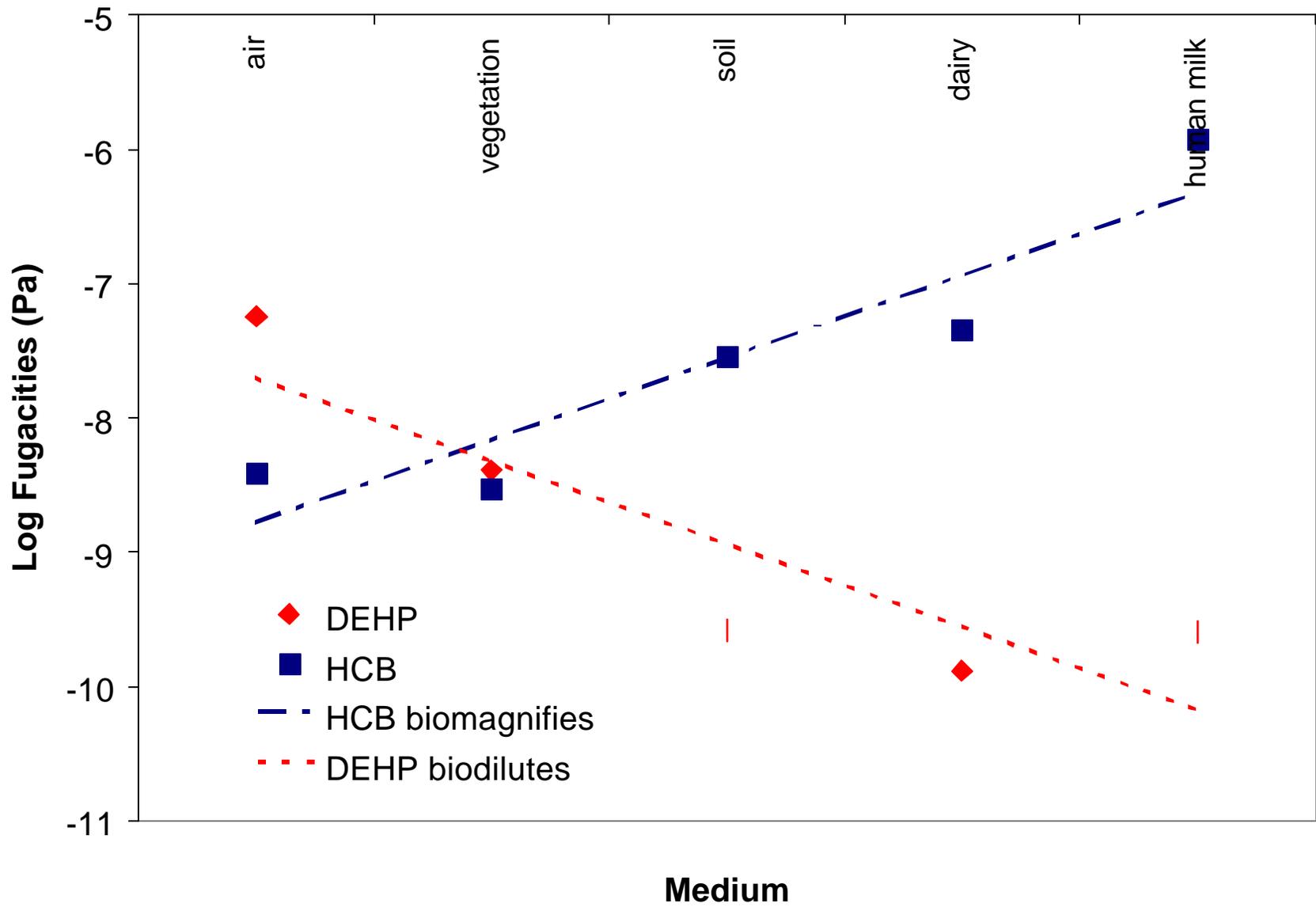


Figure 10. Comparison of food chain bioaccumulation for two contrasting organic compounds

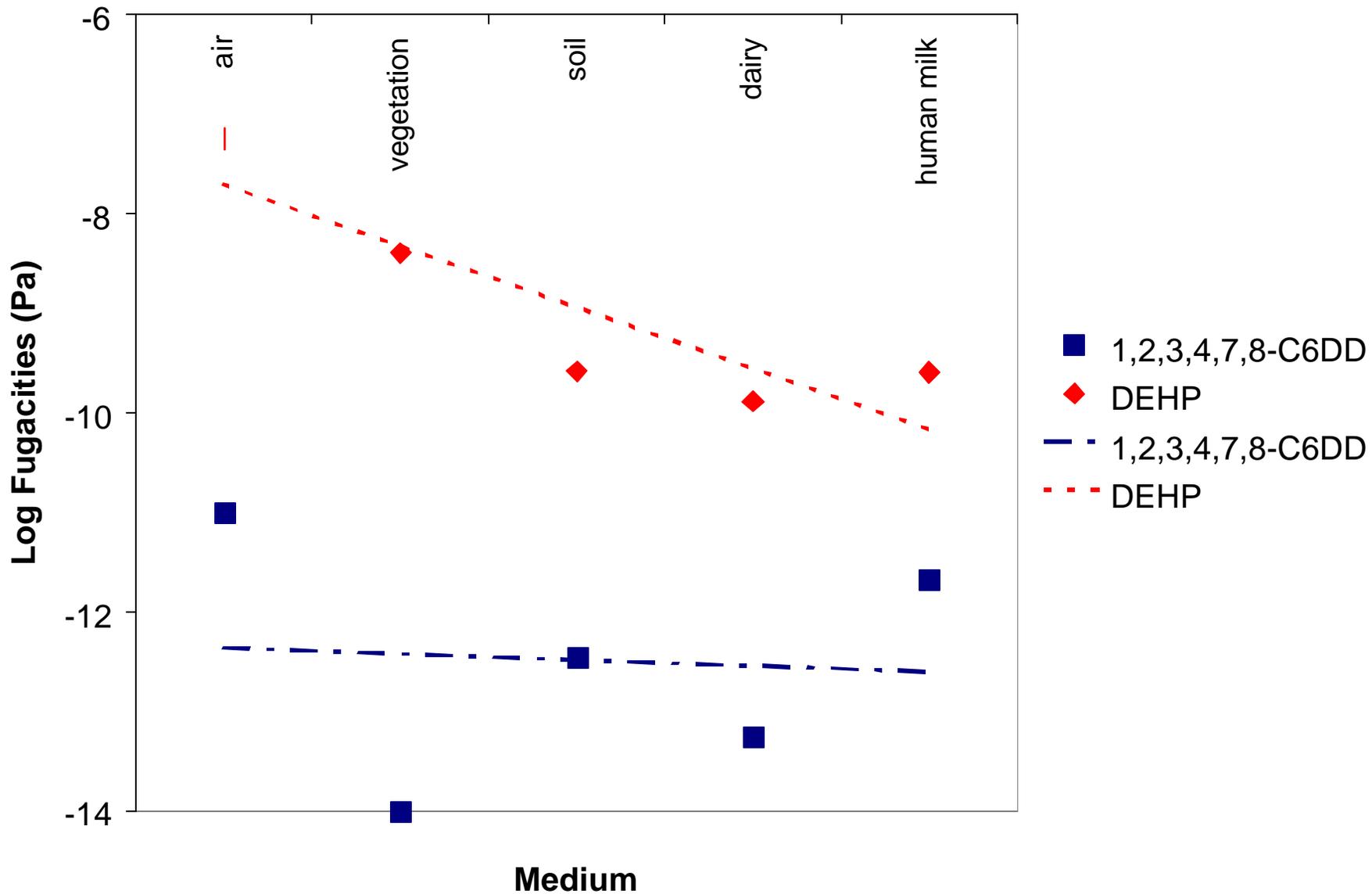


Figure 11. Comparison of the biodegradation of two compounds with similar hydrophobicities but different metabolism rates

To a first approximation a chemical present in the environment is seeking to equalise its fugacity in all media. Some natural processes such as food digestion can cause an increase in fugacity for some substances resulting in an increase in concentration i.e. bioconcentration. As a result, a persistent hydrophobic substance will tend to display a constant fugacity across all media, but higher fugacities in media subsequent to digestion, such as in milk. This is observed for HCB (above) and some PCBs.

A hydrophobic substance that is less persistent (i.e. more reactive) will display a decreasing fugacity from source to sink because the rate of loss in “sink” media is sufficient to reduce fugacities, there being insufficient time for the solute to diffuse in adequate quantities to equalise the fugacity. A fugacity gradient approach of this type thus indicates two features of the chemical’s behaviour:

1. It is likely that the highest fugacity medium is the primary source and the lowest fugacity media tend to be sinks subject to transport from the source.
2. The downward source to sink slope is an indication of reactivity, i.e. high negative slope corresponds to high reactivity and short half-lives or persistence.

3.2.3 Heterogeneity in concentrations as further evidence for DEHP degradability

A characteristic of persistent organic substances is that they tend to have fairly homogeneous concentrations in a specific medium. This is because the quantity in the medium is large relative to the input or output rate of chemical. Note that the ratio of quantity/input rate represents a residence time. The net result is that although there may be local discharges, the substance has time to mix throughout the medium and migrate between media. If the substance degrades more rapidly and is less persistent there is less time to mix, the quantity in medium is less, and greater heterogeneity in concentrations is expected.

3.2.4 Summary of findings on degradability of DEHP in the environment

In the case of phthalate esters the high medium heterogeneity and the “biodilution” discussed above strongly indicate that these substances have relatively short environmental half times. They are not persistent to the same extent as compounds such as HCB, DDT and higher molecular weight PCBs.

The degradation rates selected by CEMC and KemI for their EUSES simulations are summarised in Table 3 and appear to be in reasonable agreement.

3.3 Environmental emissions

As part of the ACC contract, discussed earlier in the Introduction, Exxon-Mobil Biomedical Sciences have estimated the environmental emissions of a range of phthalate esters including DEHP (EMBSI, 2000). The emissions estimates of EMBSI were calculated on a per capita basis, which facilitates the calculation of emissions to different EUSES scenarios based on human population assumptions. The human population of the entire EU, which is the area modelled in the EUSES “continental” scenario, is 370 million and the human population of the EUSES “regional” scenario used by KemI is 20 million.

The estimated emissions to the EUSES region used by CEMC, which are based on the work of EMBSI (2000), are tabulated together with the emission estimates used by KemI in their EUSES based risk assessment of DEHP (Table 5). The total amounts of DEHP emissions estimated by KemI for the EUSES “continental” and “regional” exposure scenarios are a factor of approximately 1.6 and 3 higher, respectively, than the emissions used by CEMC. More importantly, there are large differences in the relative amounts emitted to the different environmental media. EMBSI (2000) estimate a much greater proportion being emitted to air and relatively less being emitted to surface waters and soils. This different emission profile has a large influence on the predicted environmental concentrations in environmental media.

Emissions to wastewater treatment plants have been set to zero for the CEMC EUSES simulations, but this does not mean we have neglected to include releases from wastewater treatment plants in the emission inventory. EMBSI (2000) included wastewater emissions in the “emissions direct to surface water” category. The emissions of DEHP directly to surface waters calculated by KemI are 0.1×3620 (assuming 90% is removed during wastewater treatment) + 7330, which sums to a total of 7692 tonnes/year. This compares to the total of 333 tonnes/year used by CEMC, which includes emissions direct to surface waters and those coming via wastewater treatment works.

There are three types of soil in EUSES, namely “natural”, “agricultural” and “industrial” soil. KemI assume that all emissions to soil are to the “industrial” soil. For consistency, CEMC have made the same assumption.

Table 5. Environmental Emission Rates (tonnes/year) of DEHP used in the EUSES simulations by CEMC and KemI

Continental Emissions	CEMC	KemI
Emission to air	7,438	682
Emission to surface water	333	4,124
Emission to industrial soil	417	8,247
Total	8,187	13,053
Regional emissions	CEMC	KemI
Emission to air	402	76.1
Emission to surface water	18	488
Emission to industrial soil	22.5	931
Total	443	1,495

4.0 DISCUSSION OF EUSES MODELLING RESULTS

4.1 Comparison of EUSES PECs with monitoring data

KemI and CEMC EUSES predicted regional and continental environmental concentrations (PECs) are compared with observed concentrations from the recent ECPI/RIVM monitoring program (Table 6, Figure 12). The two sets of monitoring data represent (1) the median of the concentrations reported in various media by ECPI/RIVM and (2) the estimated ranges for concentrations at different spatial-scales estimated from the cumulative histograms of the ACC data.

The CEMC EUSES regional and continental simulations compare favourably with the monitoring data, whereas the KemI EUSES regional simulations overestimate the water, sediment and soil concentrations and underestimate the air concentrations. As the physical-chemical properties and degradation half-lives that were used as inputs in both simulations are similar, the main cause of the disparity between CEMC's and KemI's PECs is the difference in the emissions release scenario.

A validation issue that arises with these, and indeed with all mass balance models is that there may be some cancellation of errors. For example, a concentration may be correctly predicted by using an over-estimate of emission rate and an over-estimate of reactivity (or correspondingly an under estimate of half-life). The model provides a constraint on the relationship between these variables, for example, in this case the product of emission rate and half-life is known. There are also constraints of "reasonableness" for each variable that tends to narrow the range of possible values. In the present situation the various parameter values selected by the CEMC are judged to be both reasonable and in accord with monitoring data. We do, however, preclude the possibility of some error cancellation.

The discrepancy between the KemI/EUSES concentration in air and the monitoring data suggests that the product of their emission rate and half-life is in error, i.e. it is too low. This could be satisfied by an increase in emission rate by a factor of 5 to 10 or a

corresponding decrease in half-life in air. It seems inconceivable that the half-life in air is much shorter than the assumed 1 day, thus the evidence is compelling that the emission rate must be in error, by being underestimated.

4.2 Comparison of PECs from EUSES and fugacity models

In Figure 13 the PECs from the EUSES regional modelling scenario are compared to PECs from a Level III regional fugacity model calibrated to the EUSES environment. The same chemical inputs have been used for both models. The Level III fugacity model has been calibrated by changing the bulk properties of the environmental compartments and mass-transfer coefficients in the model to those used in the EUSES regional environment. Equations used to describe environmental partitioning, however, have not been altered in the fugacity model. As can be observed (Figure 13) the EUSES and the Level III fugacity model are in good agreement with each other. This is not unusual as the regional model within the EUSES framework, known as SimpleBox (van de Meent, 1996) is essentially a Level III model. Further, SimpleBox and Level III fugacity models have previously been shown to give very similar predictions, using the same chemical input data and a standardised environment (Cowan et al., 1995).

4.3 Persistence

The model predicts that when total emissions to the environment are 440,000 kg/year (about the amount estimated to be emitted to the EUSES-region) the total inventory in the environment is 126,000 kg. As a result the residence time is $126,000/440,000$ or 0.3 years. Mathematically this is a “characteristic time” describing DEHP dynamics in the system. A dynamic model of DEHP under initial conditions of zero concentrations, then sustained constant emissions would display an approach to a steady state that would be essentially complete after three characteristic times or 0.9 years. Similarly, if DEHP emissions were stopped entirely the system would clear of DEHP almost entirely in 0.9 years.

The implication is that, since DEHP has been in use for many decades, it must have reached a steady state condition in the environment, thus the use of a steady state model

is fairly justified. Fears that conditions may be getting progressively worse as a result of accumulation of DEHP from past discharges are unfounded.

4.4 Bioaccumulation

Conventional bioaccumulation models as used in Level III and EUSES are based on equilibrium partitioning of the chemical between its dissolved concentration in water and the organism's tissues (as characterised by K_{OW}), but supplemented by a possible concentration increase resulting from food ingestion and digestion. This calculation contains the implicit assumption that ratios of lipid to water concentrations are potentially of the order of K_{OW} , but modified by possible biomagnification and metabolism which respectively increase and decrease the ratio. To be realistic, the concentration in water must be below the solubility limit. Any DEHP present above the solubility limit must be in a non-aqueous phase and therefore not available for bioconcentration. The use of such supersaturated concentrations in bioaccumulation models is thus invalid. It would be useful for models such as EUSES to contain such a check and stop or at least flag such situations thus avoiding misinterpretation of results.

This issue is of particular importance in the local exposure scenarios where concentrations tend to be highest. The use of solubilities above the water concentration in bioconcentration calculations has occurred in the draft E.U. risk assessment of DEHP (NCI, 2000). For example, in the EUSES predicted local water concentration resulting from production of DEHP (Use Pattern 1 in EUSES terminology) was 0.8 mg/L, which is nearly 270 times higher than the water solubility. The bioconcentration factor for fish used in EUSES simulations is 840, thus if the predicted local concentration is used to calculate a fish concentration a value of 672 mg/kg is obtained, which is at least 270 times too high.

Table 6. Comparison of EUSES PECs with monitoring data

Media	EUSES Spatial Scale	Monitoring data		Model PECs		
		Derived from ACC database	RIVM/ECPI monitoring data	CEMC EUSES PECs	KemI EUSES PECs	CEMC PECs from a Level III fugacity model ¹
Total air (ng/m ³)	Continental	1	-	5.0	0.002	-
	Regional	10	17	14	0.02	11
Total surface water (µg/L)	Continental	0.03	-	0.015	0.36	-
	Regional	0.3	0.46	0.06	3.0	0.05
Soil (µg/kg dry)	Continental	-	-	8.2	38	-
	Regional	48 ²	28 ³	26 ⁴	350 ⁴	41
Sediment (mg/kg dry)	Continental	0.01	-	0.24	4.0	-
	Regional	0.3	0.5 ⁵	1.0	23	0.87

¹ Calibrated to the EUSES regional scenario.

² Weighted-average calculated from three studies reporting soil concentrations.

³ Assuming soil has an organic carbon content of 0.02 w/w.

⁴ Weighted average of three soil types: “natural”, “agricultural” and “industrial” based on fraction of total soil surface area covered by each soil type i.e. average soil concentration = (area fraction industrial soil x concentration industrial soil) + (area fraction natural soil x concentration natural soil) + (area fraction agricultural soil x concentration agricultural soil).

⁵ Assuming sediment has an organic carbon content of 0.1 w/w.

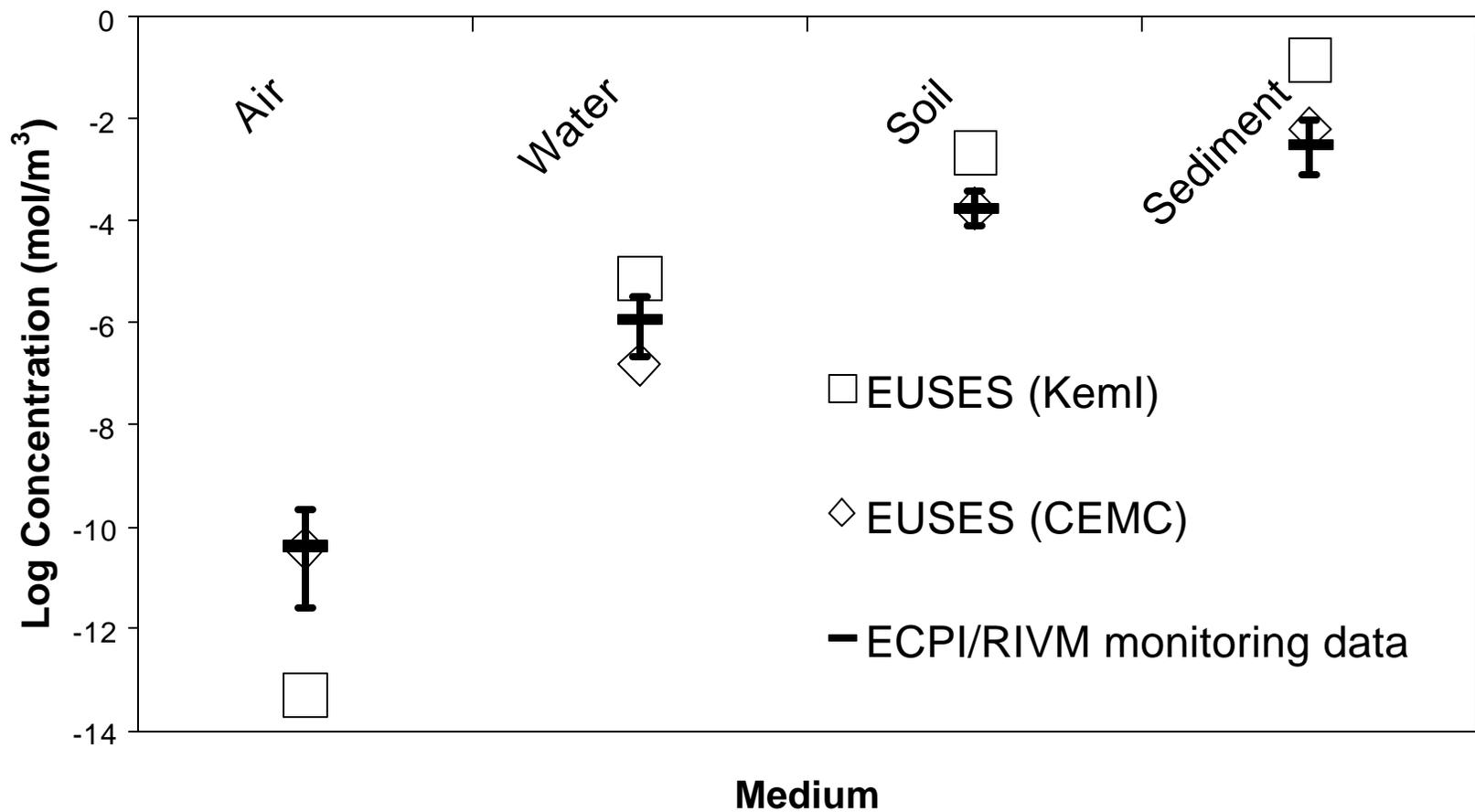


Figure 12. Comparison of regional PECs from EUSES with available monitoring data (error bars represent 10th and 90th percentiles of ECPI/RIVM monitoring data)

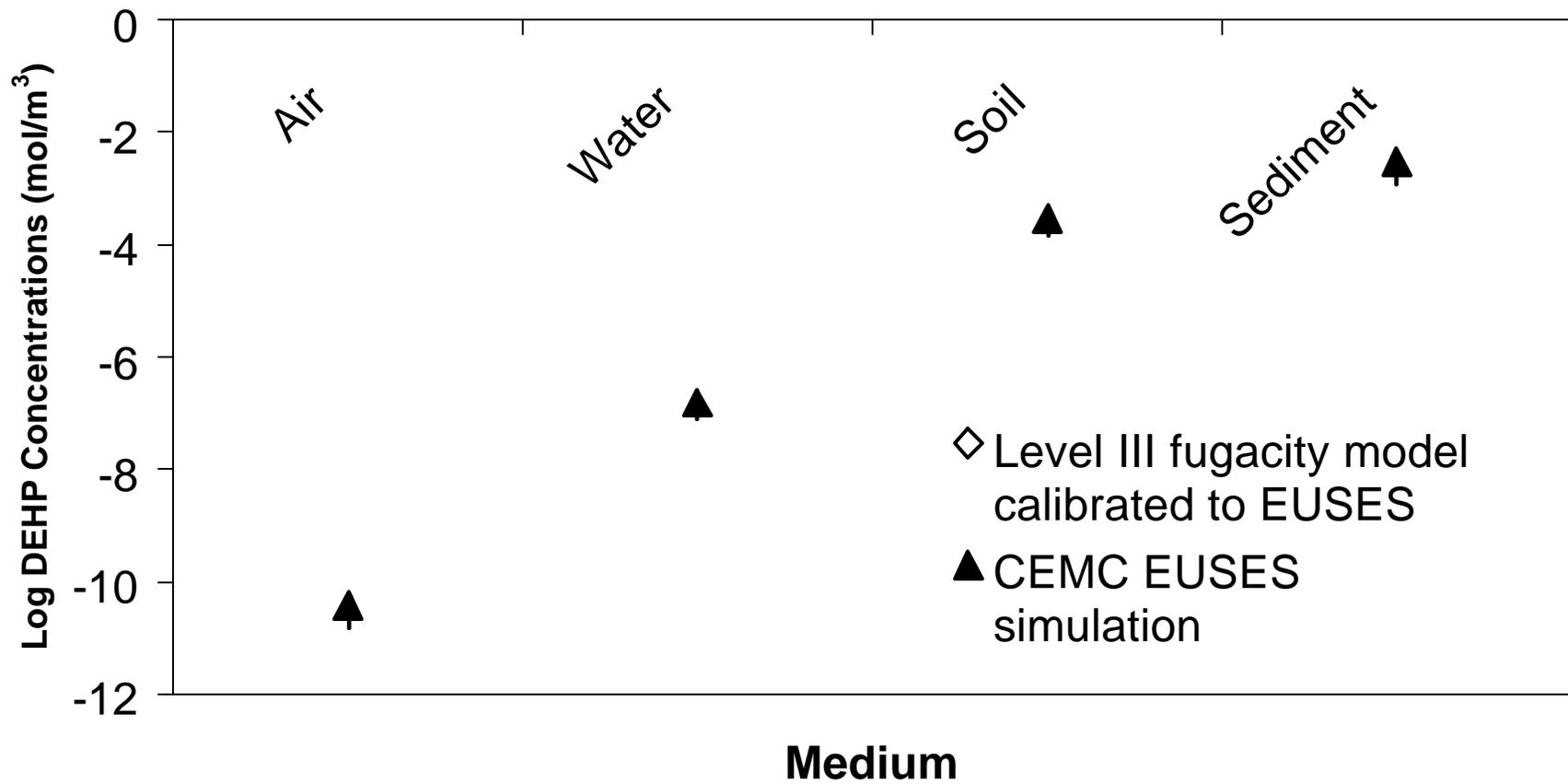


Figure 13. Comparison of EUSES PECs with PECs from a Level III fugacity model

5.0 CONCLUSIONS

It has been shown that a careful analysis of field monitoring data is vital for meaningful calibration of mass balance models. Either a specific monitoring program is needed or a large effort is needed to extract appropriate data from the literature. The high variability in environmental concentrations is attributed to two factors, ranging proximity to sources and the inherent short residence time or persistence of DEHP, which tends to cause heterogeneous concentrations. Plotting monitoring data as histograms provides useful insights into the distribution of the monitoring data and provides a tool for partitioning monitoring data into the three EUSES spatial scales, which are based on proximity to local sources. By transforming environmental concentrations into fugacities it was clearly demonstrated that DEHP biodilutes by several orders of magnitude in aquatic and terrestrial food chains.

The physical-chemical properties and degradation rates used as inputs by KemI to the EUSES model are in good agreement with those recommended with CEMC. The only exception was a low value of the octanol-water partition coefficient, K_{OW} , but the results are relatively insensitive to this quantity. Degradation rate data in the form of half-lives were compared with current estimates and found to be reasonable. The sediment half-lives are problematic in that the estimate of an approximately 300 day half life in surface sediment seems reasonable. The suggestion that in deeper sediments the half-life is orders of magnitude larger is, in our view, questionable given the presence of bioturbation and episodic resuspension. For DEHP to experience such a difference in half-life implies very different conditions that are sustained for a period of ten or more years. A further implication is that any such DEHP is not “available”.

Based on a comparison of model predictions with actual environmental concentrations, DEHP emissions to air appear underestimated, whereas emissions to surface water appear overestimated in the draft EU risk assessment undertaken by KemI.

CEMC, using recent emission estimates obtained by EMBSI (2000), have successfully reconciled measured environmental concentrations with emission estimates for both the continental-scale and regional-scale EUSES simulations. In our opinion this supports the view that these more recent emission estimates are realistic. The model has thus successfully reconciled the known properties of DEHP with the proposed emission rates and the monitoring data. There is the caveat that there has been some cancellation of errors within the model to give a good agreement between PECs and monitoring data, but such errors are believed to be relatively small in magnitude given the constraints between the various parameters.

Since DEHP has been in use for many decades, we believe that it must have reached a steady state condition in the environment, thus the use of a steady state model is fairly justified. Fears that conditions may be getting progressively worse as a result of accumulation of DEHP from past discharges are, in our view, unfounded. The fact that emission rates and observed concentrations were reconciled with a steady state model is further support our supposition.

The EUSES “regional” modelling scenario was shown to give very similar output to Level III (non-equilibrium steady state) fugacity models. This is expected as the EUSES “regional” model is based on SimpleBox, which in turn was based on a Level III fugacity model.

Any DEHP present above the solubility limit must be in a non-aqueous phase and therefore not available for bioconcentration. The use of such supersaturated concentrations in bioaccumulation models is thus invalid. It would be useful for models such as EUSES to contain such a check and stop or at least flag such situations thus avoiding misinterpretation of results.

We hypothesise that many of the samples showing high levels of DEHP actually contain plastic material (notably PVC) in which the DEHP is present as a plasticiser. This has been observed previously for dust and sludge samples (Tienpont et al., 1999). During

sample work-up the DEHP is extracted from the polymer matrix. It is likely that the plastic material consists of small particles that have been abraded from plastic items, or represent the remnants of degrading plastic products. DEHP in this state is not readily “available” and does not contribute to the dissolved concentration or the fugacity of the substance. For example, it is not readily bioavailable, nor can it evaporate.

6.0 RECOMMENDATIONS

We recommend that when undertaking EUSES based risk assessments that the wealth of available monitoring data is fully utilised to better characterize and distinguish continental, regional versus local exposure scenarios. Visualising monitoring data, for example by plotting histograms, is recommended as a useful way to delineate spatial scales. Ideally monitoring programs should be designed specifically to obtain data for the different spatial scales simulated by EUSES. Model calibrations can be meaningless if inappropriate monitoring data are used. Further multimedia modelling programs should be set up in Europe for the calibration of EUSES. Soil data are often neglected, but they are important for DEHP, because soil is the primary medium of accumulation for this hydrophobic compound.

We recommend that the assumptions regarding the emission release scenarios (i.e. fraction released to air versus water) for DEHP be reassessed. There seems to be convincing evidence, based on relative fugacities in media and on modelling results, that air is the primary medium of discharge.

Finally we recommend that environmental degradation half-lives should be reassessed as new data become available. These vital input data are often difficult to obtain because there are no standard methods for measuring overall degradation half-lives in environmental media. Model calibration exercises such as those presented in this report help to build confidence that the assumed environmental degradation half-lives are indeed consistent with field measurements.

We suggest that in future monitoring programs of DEHP and other polymer additives it is desirable to test the hypothesis that samples containing high levels of DEHP contain PVC. This can be done by the following procedures which should be done under sterile conditions:

1. Sequentially extract a sample of sediment with water under equilibrium conditions to determine if the sediment-water partition coefficient remains constant. This will also show if a fraction of the solute is not extractable.
2. Using a field sample of sediment, equilibrate it with water, sample and measure the concentrations and determine the partition coefficient, then add more DEHP and determine the new partition coefficient. This will show if the “old” and “new” solute are subject to the same partitioning phenomena.
3. An examination of biota-sediment accumulation factors (BSAF) may reveal anomalies. If the solute is present in a non-available form the BSAF will be smaller than expected. This may, unfortunately, be complicated by metabolism.
4. Companion analysis for PVC content should be done using pyrolysis-GC-MS (Tienpont et al., 1999) to obtain an indication of the potential for DEHP in PVC to contribute to the sediment concentrations. A statistical analysis of DEHP and PVC contents may reveal a relationship indicative of DEHP being present in a PVC phase.

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