

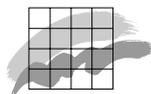


Ministry of Environment and Energy
National Environmental Research Institute

On the fate of Xenobiotics

The Roskilde region as case story

NERI Technical Report No. 366



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Abstract: The report summarizes the main findings of the project "Xenobiotic Compounds". The single chapters correspond to the different subprojects, such as the modelling approach, basic studies on phthalates (PAE's) and nonylphenols (NP's), sources to PAE's and NP's, emissions of Linear Alkylbenzene Sulphonates (LAS's), PAE's and NP's, the wastewater treatment plant (WWTP), the terrestrial environment, the aquatic environment and model validation, respectively.

Keywords: Xenobiotics, nonylphenols (NP), nonylphenol ethoxylates (NPE), phthalates (PAE), Linear Alkylbenzene Sulphonates (LAS), emission, wastewater treatment plant (WWTP), modelling.

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Summary

The project "Xenobiotic Compounds" was initiated in Jan. 1996. The project has been conducted as an integrated part of the research activities in the Department of Environmental Chemistry during the period Jan. 1996 to May 2000.

The present report summarises the main findings of the project. The single chapters correspond to the different subproject: The modelling approach (chap. 2), Basic studies on phthalates (PAE's) and nonylphenols (NP's) (chap. 3), Sources to PAE's and NP's (chap. 4), Emissions of Linear Alkylbenzene Sulphonates (LAS's), PAE's and NP's (chap. 5), The wastewater treatment plant (WWTP) (chap. 6), The terrestrial environment (chap. 7), The aquatic environment (chap. 8) and Model validation (chap. 9). A list of the products originating from the project, i.e. papers, reports and lectures is given in an appendix.

The report is as such without references. However, each chapter gives at the end the reference to the appropriate report or paper resulting from the single subprojects.

The project has been financed based on special funding from the Ministry of Energy and Environment.

Resumé

Projektet "Xenobiotic Compounds" blev startet i januar 1996. Projektet har været gennemført som en integreret del af forskningsaktiviteterne i Afdeling for Miljøkemi i perioden januar 1996 til maj 2000.

Nærværende rapport sammenfatter hovedresultaterne for projektet. De enkelte kapitler svarer til de forskellige delprojekter: Modellerings fremgangsmåde (kap. 2), Grundlæggende undersøgelser af phthalater (PAE'er) og nonylphenoler (NP'er) (kap. 3), Kilder til PAE'er og NP'er (kap. 4), Emissioner af Lineære Alkylbenzen Sulfonater (LAS'er), PAE'er og NP'er (kap. 5), Rensningsanlægget (kap. 6), Det terrestriske miljø (kap. 7), Det akvatiske miljø (kap. 8) og Model validering (kap. 9). En liste over de produkter, der er kommet fra projektet, dvs. artikler, rapporter og foredrag, findes i et appendix sidst i rapporten.

Rapporten er som sådan uden referencer. Der er imidlertid som afslutning på hvert kapitel en henvisning til de(n) rapport(er) eller artikler, der er resultatet af de enkelte delprojekter.

Projektet har været finansieret gennem en speciel bevilling fra Miljø- og Energiministeriet.

1 Introduction

In 1996 the project "Xenobiotic Compounds" was initiated based on funding from the Ministry of Energy and Environment. The project has been conducted as an integrated part of the research activities in the Department of Environmental Chemistry during the period January 1996 to May 2000.

The project has been followed by a group including the NERI scientist engaged in the project and representatives from The Danish Environmental Protection Agency and The Denmark and Greenland Geological Survey.

The present report "On the fate of Xenobiotics. The Roskilde region as case story" summarises the main finding of the project.

1.1 Background

Although a wide range of studies on the distribution and fate of organic chemicals in the environment has appeared over the years, a complete picture of the distribution pathways for the fate of xenobiotic compounds in the environment has not yet developed. In addition only limited information on the environmental impact and thus possible health effects is available. In order to be able better to evaluate the actual environmental, as well as health impact of chemical substances, it is crucial that an enhanced knowledge on the environmental fate of xenobiotics are developed, the eventual objective being the development of predictive tools for this purpose.

Investigations of this type have to be carried out as a combination of experimental and theoretical studies. Experimental results originating from field and laboratory studies formed together with available data from the literature the input to the modelling part of the project.

It was immediate clear that it was possible to cover only a rather limited number of compounds within the frame of the experimental studies. Hence, it was agreed that the main focus should be plasticizers of the phthalate type, and surface active agents such as NP's and NPE's and LAS's (Linear Alkylbenzene Sulphonates). The project has focussed on 3 main environmental compartments:

The terrestrial environment

- *The terrestrial environment*, where a series of soils samples in the Roskilde area was investigated. The single soils were selected based on a series of criteria, which should ensure comparable, representative and relevant results. The soils should be typical for Danish agriculture with respect to soil type, encompass a broad range of dressing/fertilisation and cultivating methods, have a known history including known characteristics of dressing/ fertiliser, be exposed for a time sufficient to allow the dressing/ fertilisation method to have a significant impact on the xenobiotics studied in the soil and have

identical or similar and known soil characteristics. For this purpose 8 sampling sites around Roskilde were selected.

The aquatic environment

- *The aquatic environment*, where the Roskilde Fjord was selected as target area. The fjord is close to agricultural fields and is recipient of water from small rivers. The municipal WWTP in Roskilde discharge its cleaned wastewater into the fjord as is cleaned wastewater from a series of smaller cities.

The wastewater treatment plant

- *The WWTP* in Roskilde, which is the main recipient of industrial as well as municipal wastewater from the Roskilde area.

1.2 Objectives

Compounds studied

The main objective for the project has been to set up and validate one or more models to determine the fate, e.g. PEC (Predicted Environmental Concentrations) values for PAE's and surface active ingredients as NP's, nonylphenol ethoxylates (NPE's) and LAS's. Selected models are used to evaluate the generic compartment model used in the EUSES risk assessment system.

Further an objective for the project has been to establish a general modelling paradigm for the construction of concentration profiles for single compounds or classes of compounds in environmental matrices.

As an important part of the project experimental work has been conducted to establish environmental concentrations of the compounds under investigation. In addition fundamental studies dealing with the solubility and possible micelle formation of PAE's and NP's has been carried out.

2 The Modelling Approach

2.1 Model uncertainty

Predictive models involving theoretical studies combined with empirical knowledge, such as field and laboratory experiments are useful as support for decision in relation to environmentally related problems. These models can help to take action before the actual problems become serious and to evaluate the possible consequences of different future scenarios formed by different actions taken. Therefore, model calculations have a central place in e.g. the risk assessment of chemicals. More and more sophisticated models have been developed over the last 20 years and the boundary for the possible calculations has been extended dramatically during the years. But a wide gap has opened up between "what-is-possible" calculations and "what-is-realistic" calculations the latter yielding some kind of new (not realised) information. The quantification and minimisation of uncertainty have become key issues in the attempt to make useful mathematical models for decision support.

Uncertainty analyses

A multimedia model involves a high level of complexity, which often is associated with a high degree of uncertainty. Thus, the use of the models needs to be supported with a careful uncertainty analysis, which is one of the major challenges in model application. Uncertainty analyses are being increasingly used as an integrated part of risk analysis and denoted probabilistic risk assessment. However, even though the basic principle of probabilistic risk assessment is sound, there exist some pitfalls to be aware of. It is important to realise that also the uncertainty estimate may be uncertain. An incomplete uncertainty estimate can easily underestimate the true uncertainty and thereby end up with conclusions of falls realism.

As an integrated part of the present project a systematic approach is described to guide a systematic uncertainty analysis in relation to risk assessment. The problem can in general be formulated as a duality between models which: "Say-much-about-little" and models which "Say-little-about-much". If the goal is to make a detailed prediction ("to say much") by a model then the model needs to be so complex in order to take many processes into account that only a limited system ("about little") can be described. On the other hand, if less detailed predictions are the topic ("Say little") then the needed model complexity is more limited and it will be possible to say something about a larger system ("about much"). This is the dualism in any prediction and thus also for mathematical models.

Different sources of uncertainty

The present study relates the decision support problem to mathematical modelling on a conceptual basis. The focus is risk assessment of chemicals but the relevance is broader and covers decision support based on mathematical models in general. Two basically different sources of uncertainty are considered:

- Input uncertainty and variability arise from missing information about actual values and natural variability due to a heterogeneous environment.
- Structural (model) uncertainties arise from the fact that every model is a simplification of reality and the mathematical expressions are approximations for real systems due to a limited systemic knowledge.

Input uncertainty

The input uncertainty can in principle be solved in most cases either analytical or more often by using a Monte Carlo type analysis. However, in practice it can be difficult to get the necessary information about the variability of the input parameters and results from Monte Carlo calculations needs to be interpreted with caution due to this problem. The structure uncertainty is more problematic to quantify and a complete determination is in principle impossible because this will demand a complete knowledge about the system to be modelled and thus there will be no need for a model! In this study it is shown, however, how the structural uncertainty improvement can be determined for sub-processes in a model. In this way it is possible to answer the question: Are there any sub-processes (sub-models) in the model which is unnecessary and harmful for the total uncertainty. This may well be the case that a model having many sub-models performs poorer compared to a simpler model even if every sub-model is theoretical relevant and well described. A combined uncertainty analysis using the concept of respectively input and structure uncertainty is useful to investigate these problems. In very simple models the necessary input parameters are often available at low uncertainty level, yielding output values with low uncertainty. On the other hand the very simple models will exhibit high structural uncertainties resulting in low accuracy. With very complex models the reverse trend is seen. High input uncertainties are introduced from a large number of input parameters and furthermore default values cases have to be applied in several cases. The structural uncertainties will on the other hand be lower.

Structure uncertainty

Conventional probabilistic risk assessment will only quantify input uncertainty. Thus, this type of assessment will unequivocally underestimate the uncertainty in cases where the assumptions behind the model are so restrictive that significant structural uncertainties are involved.

Sources of uncertainty

Even though the total uncertainty seems complicated to quantify, there will typically only be a few dominating sources of uncertainty. A model can be said to be discordant (inharmonious) when some parts of the model operates with a relatively low uncertainty while other parts of the model includes a higher level of uncertainty. In a discordant model minor uncertainty sources have been improved at the expense of major uncertainty sources. However, if all information needed for an existing discordant model is available then the model can be used without consideration as a 'best obtainable knowledge approach'. The problems arise if such a model is used to identify data necessary for the decision making, because resources are wasted on collecting superfluous information. Furthermore, a discordant model can easily produce conclusions of false realism where detailed parameter studies of low uncertainty sources are considered when the emphasis should be on other parts of the model.

Integrating uncertainty analyses

It is crucial, although often a forgotten issue, to integrate the uncertainty analysis with the need for decision support. This is a result of the fact that the structure uncertainty will increase and thus more complex structures have to be implied for the desire of more detailed information (higher information level). This is very important to realise for a decision-maker that asks an 'expert' about a prediction to support a certain decision. If the question is formulated by the decision-maker to the expert at a higher information level than strictly necessary for the decision then significant resources may easily be wasted. This problem has been formulated in the statistical learning theory for problem solution using a restricted amount of information as: *When solving a given problem, try to avoid solving a more general problem as an intermediate step.*

Evaluation of model uncertainty

A close evaluation of model uncertainty is in general a rather resource demanding task and in reality the user of a model can easily be brought into a situation where a model have to be used without the possibility for such an evaluation. A tiered approach is therefore suggested in order to investigate model uncertainty in relation to a specific problem. A guideline for such an approach is shown in Figure 2.1 and will be explained in the following.

Step 1. The formulation of the problem to be solved in terms of a question is crucial for the model selection. It is therefore important to make a precise formulation of the question.

Step 2. The model is selected based on expert judgement, which again is based on reported validation results and an evaluation of critical assumptions. The magnitude of the structural uncertainty needs to be quantified so much as possible. The structural uncertainty is difficult to quantify precisely, however, some kind of judgement is necessary and in most cases possible.

Step 3. As a first approach a few model calculations are done using relatively few combination of realistic input parameters. There will often exist a priori knowledge, about which of the input parameters that are the most important for the model and about an interval of variation, which is smaller than the true variability. If the variation of input parameter values in this analysis yields results of unacceptable high uncertainty then is possible to reject the model as a candidate for valid calculations.

Step 4. If the model uncertainty was acceptable in step 3, the next step will be to over estimate the input-uncertainty, where unrealistic variations is applied to the input. More effort is needed in this step compared to step 3 but in many cases it will be a rather easy task to set up an over estimation of the variability intervals. If the input-uncertainty is acceptable then the model prediction will be valid otherwise more detailed and thus also much more resource demanding uncertainty analysis needs to be applied.

Step 5 a. The structural and input uncertainty together yields a picture of the total uncertainty. It is then possible to compare with the demand of information needed and thereby see if the model is acceptable or not when the model is acceptable it can be used to answer the question.

There may exist a more complex model, which can make an answer at a higher information level than the actual question.

Step 5 b. A detailed uncertainty analysis is made for input-uncertainty. The information needed is knowledge about the distribution function for input-parameter variability, which can be used, in a Monte Carlo simulation. In some cases a sensitivity analysis can be used before the Monte Carlo analysis to identify the parameters for which the model is most sensitive. Such a sensitivity analysis can help to focus the Monte Carlo analysis and thus minimise the resources needed.

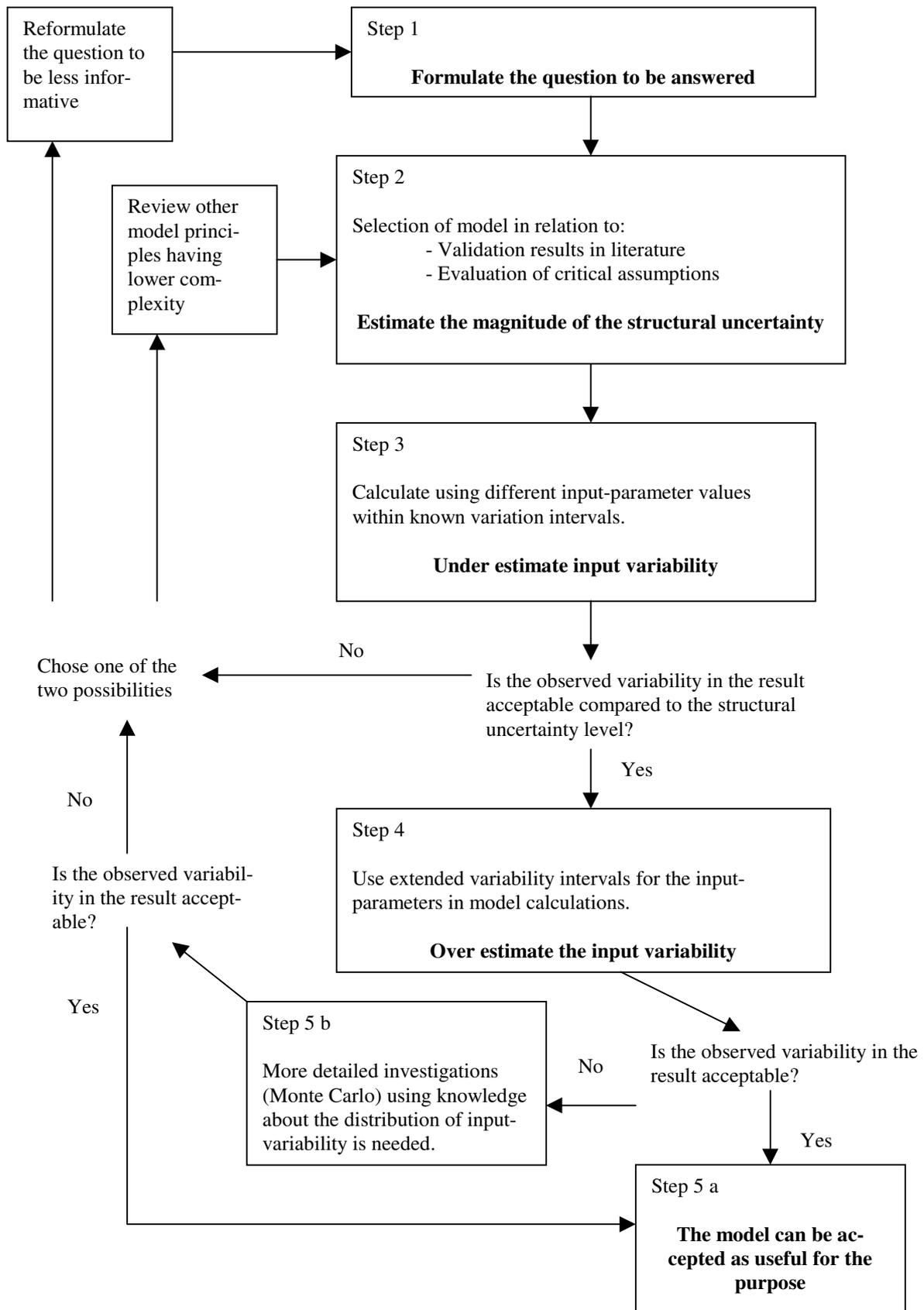


Figure 2.1 The guideline for a tiered approach in the model evaluation.

The study is comprehensively described in:
Paradigm for analyzing complex model uncertainty
 Peter B. Sørensen, Lars Carlsen, Patrik Fauser, Jørgen Vikelsøe, Research Notes from NERI No. 141, 2001.

3 Basic Studies

Obviously correct values for physical-chemical data, such as solubility are crucial in order to describe the fate of chemical substances in the environment. Further correct experimental data are mandatory in order to develop models such as QSAR models for the prediction of characteristics for hitherto uninvestigated species.

Nonyl phenols

In the present project basic studies on NP's were conducted partly to establish the correct value for the solubility of these species and partly verify the possible formation of micelles of these compounds.

Phthalates

In the case of PAE's the main objective of the studies has been to establish the correct values for the solubility and octanol-water partitioning and possibly to retrieve some information on the interaction with dissolved organic matter.

3.1 Nonylphenol (NP)

In recent years NPE's have received considerable attention due to the apparent endocrine disrupting effect of the primary degradation products, i.e., NP's and NPE's with 1 or 2 ethoxy units.

NP's and NPE's with 1 or 2 ethoxy units (NPEO1, NPEO2) are found in relatively high concentrations in the environment.

The environmental fate of NP's is closely linked to the solubility of the compound. Thus, an increased solubility may result in an increased leachability from topsoil layers to the underlying aquifers and hereby being a potential threat to the ground water and catchments. Further NP's may constitute a potential risk due to its possible amphiphilic nature thus possibly being subject to micelle formation whereby the bulk concentration in water can be increased significantly above the unimeric saturation value. A formation of micelles may a priori constitute a vehicle for hydrophobic pollutants, such as PAH's, whereby the mobility of the latter may be significantly enhanced.

3.1.1 Solubility

The dissolution process of NP in water appears to be relatively slow. Thus, it was demonstrated that even following stirring for ca. 160 h we were unable to dissolve more than ca. 5 mg/L of NP, which *a priori* is in contradiction with a formation of micelles. The aqueous solubility of NP was, by means of a gas chromatographic method determined to be to be 4.9 ± 0.4 mg/L, corresponding to $(2.22 \pm 0.18) \times 10^{-5}$ mol/L at 25°C.

It is concluded that the low solubility in combination with an observed rather slow dissolution process will limit the leachability of NP in the terrestrial environment.

3.1.2 Micelle formation

The possible formation of micelles upon dissolution of NP in water was elucidated applying surface tension measurements of NP solutions, the bulk concentrations of which ranged from significant oversaturation to concentrations well below the above estimated water solubility.

Figure 3.1 visualises the surface tension measurements as a function of bulk NP concentration in water. The unimeric solubility of NP is determined as the intercept concentration between the steepest first part of the curve and the flat, last part of the surface tension curve to approx. 5.0 mg/L in accordance with the above given value based on gas chromatographic determination.

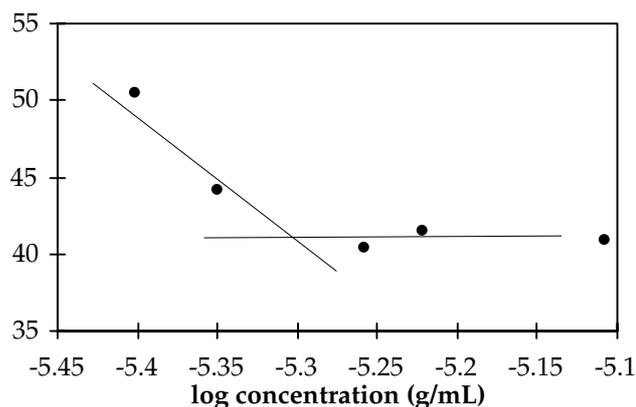


Figure 3.1 Surface tension of aqueous solutions of nonylphenol as function of the bulk aqueous concentration. All concentrations are corrected based on Tyndall measurements to eliminate contributions from micro-droplets.

A priori the shape of the curve is in agreement with a formation of NP-micelles at total concentrations above approx. 5.0 mg/L. However, in the present case it is strongly suggested that the shape of the curve simply reflect that solutions above approx. 5.0 mg/L become oversaturated. Thus, it was, based on indirect evidence, suggested that nonylphenol, in contrast to NPE with, *e.g.*, 12 ethoxylate moieties, is not subject to micelle formation, and as such does not constitute a potential vehicle for the transport of hydrophobic pollutants in the environment. For NPE's with a very high number of ethoxy moieties, *e.g.* 100, the compounds appear virtually water soluble without apparent micelle formation.

NP does not form micelles!

It should be emphasised that the conclusion that NP does not form micelles is based on circumstantial evidence as it is not possibly unequivocally to verify if the inflection in the surface tension curve (Fig. 3.1) is caused by micelle formation or phase separation. Thus, it can be concluded that NP apparently will not be able to promote the transport of hydrophobic xenobiotics in the environment.

The study is comprehensively described in:

Solubility of nonylphenol and nonylphenol ethoxylates. On the possible role of micelles. Rikke Brix, Søren Hvidt, Lars Carlsen. *Chemosphere*, **44** (2001) 759-763.

3.2 Phthalate (PAE)

PAE's (phthalates or phthalic acid esters), have caused increasing concern due to reported weak carcinogenic and estrogenic effects of some of these compounds, thus, possibly affecting the male reproductive health. PAE are continuously used in very high amounts, and are regarded as being omnipresent throughout the environment.

3.2.1 Solubility and Octanol-Water Partitioning

Based on available literature a high variability in solubility measurements was disclosed. Furthermore the experimental derived solubilities showed a not unexpected increase with increasing alkyl chain length up to 6 carbons in each alkyl chain. For longer alkyl chains the apparent solubilities appeared more or less constant. The patterns in the measured solubilities for the PAE's was investigated by use of *structure-activity relationships* (SAR) using empirical descriptors, i.e. molecular connectivity indices and electrotopological atomic state indices as explanatory variables.

Through uni- and bivariate regression analysis simple equations were developed for estimating the solubility of PAE's, however, regression coefficients for these models was unacceptable low. The regression analysis indicated that both solubility and partitioning coefficients was described by a combination of hydrophilic and hydrophobic descriptors. The nearly constant solubilities for the PAE's with more than 6 carbon atoms in the alkyl chain, however, questioned the reliability of the experimental derived data.

UNIFAC

The average experimental solubilities and octanol-water coefficients ($\log K_{ow}$) found in the literature as function of the UNIFAC calculated values are illustrated in Fig. 3.2.

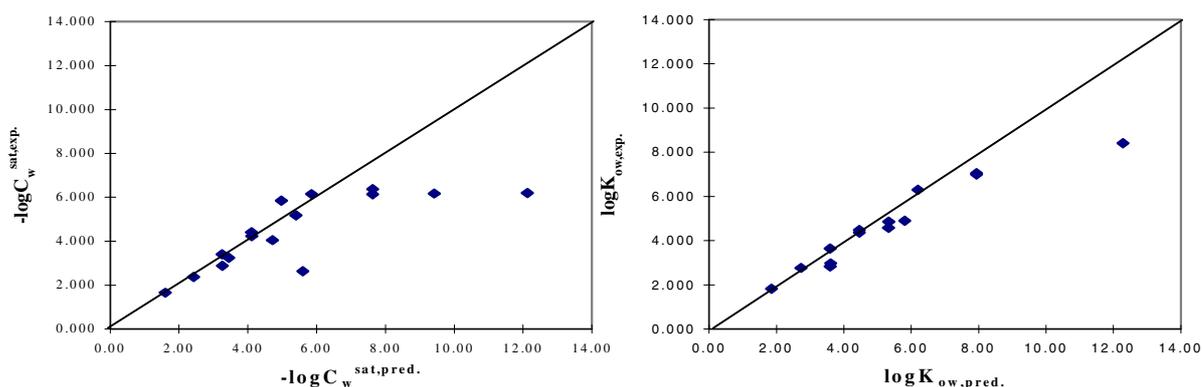


Figure 3.2 Average experimental solubilities and octanol-water partition coefficients vs. the corresponding UNIFAC derived values.

It is demonstrated (cf. Fig. 3.2) that the UNIFAC calculated solubilities are significantly underestimated when compared to experimental solubilities for PAE's with more than 6 C atoms in each alkyl chain. The opposite is observed for the UNIFAC calculated octanol-water coefficients, i.e. for PAE's with more than 6 C atoms in the alkyl chain, the $\log K_{ow}$

values are overestimated relative to the experimental data. The discrepancy between experimental and UNIFAC calculated data are however, most pronounced for the solubility measurements.

Model for phthalate dissolution

Further, experimental investigations of the solubility of DEP, DnBP and DEHP have indicated that discrepancies between estimated solubilities, might be due to the formation of an emulsion of aggregates PAE's within the bulk water phase as illustrated in Figure 3.3.

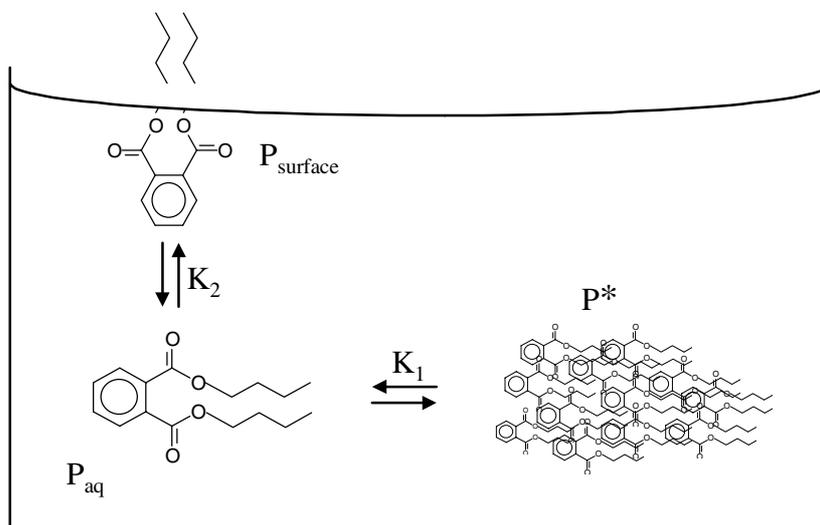


Figure 3.3 The partition of PAE's between a liquid phthalate phase and the bulk water phase system, $P^* \rightleftharpoons P(aq)$, and the partition of PAE's between the bulk water phase and the surface, $P(aq) \rightleftharpoons P_{surface}$.

Due to virtually identical densities of the solute and the solvent, an emulsion is formed when exceeding the unimeric solubility, the aggregates being distributed throughout the bulk water phase. The three-phase system is analogous to micellar systems; however, in contrast to micelles the emulsions are not expected to consist of well defined ordered structures, apparently due to the less pronounced amphiphilic nature of the PAE's.

Surface tension measurements

The true unimeric solubility of PAE's was determined by measuring the surface tension as function of bulk concentration at temperature between 10 and 35°C. The solubility of PAE's depends on temperature as shown for DEP in Figure 3.4. The solubility determined by the concentration break in the curve decreases with increasing temperature as commonly observed for hydrophobic organic compounds at environmentally relevant temperatures.

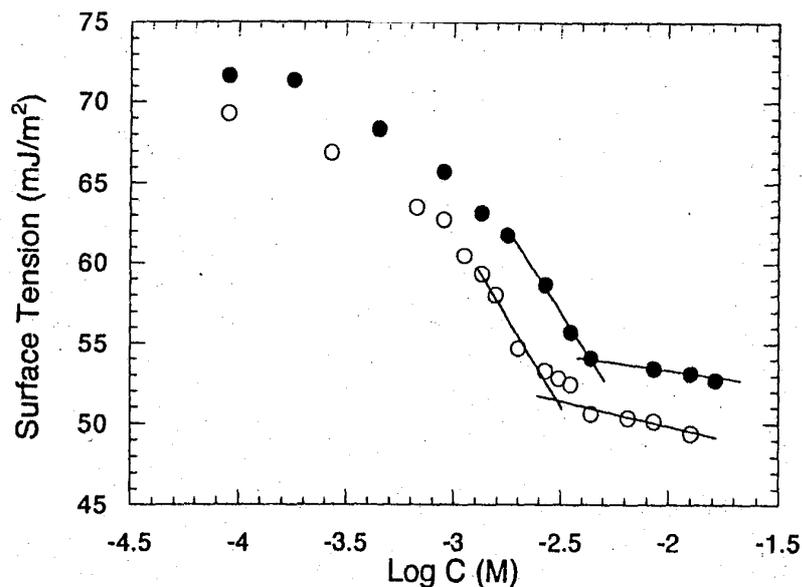


Figure 3.4 The surface tension of diethyl Phthalate as function of concentration in bulk water at 10°C (filled circles and 35°C (open circles)

The true solubility

The measured solubility of DEHP is 0.0019 mg/L, which is approximately one order of magnitude lower than the earlier measured solubility of 0.017 ± 0.003 mg/L in nice agreement with the UNIFAC calculated solubilities at 25°C.

Because of the very similar densities of PAE's and water, transport from natural surface waters is most likely to occur through adsorption to dissolved organic matter followed by sedimentation, or by uptake by microbes feeding on surface waters followed by turn-over sedimentation of non-degraded PAE's. Transport through continental surface waters may be different than expected when assessing the risk of this class of compound based on the "solubilities" given in the literature, since the nature of an emulsion differs significantly from the properties of a true solution. An aqueous emulsion of PAE's can be expected to behave similarly to dispersed organic matter, since both are aqueous dispersions of colloidal size. In the terrestrial environment the presence of PAE's in the form of microemulsions may, in respect to the above comparison, cause an increased potential risk for leaching of these substances to underlying aquifers, since it seems unlikely that microemulsions will be retained in soil to any significant extent when compared to PAE's present in their unimeric form.

These studies are comprehensively described in:

Prediction of aqueous solubilities and octanol - water coefficients of phthalates by the UNIFAC group contribution method. Angélique G. Rasmussen. Research Notes from NERI No. 69, 1998

SAR/QSAR approaches to solubility, partitioning and sorption of phthalates. Marianne Thomsen, Angélique G. Rasmussen, Lars Carlsen. *Chemosphere* **38** (1999) 2613-2624

Solubility of phthalates revisited. Environmental implications. Marianne Thomsen, Søren Hvidt, Lars Carlsen. in: Walker, J.D. ed., *Handbook on*

QSARs for predicting Environmental Fate of Chemicals. Society of Environmental Toxicology and Chemistry, Pensacola, FL, USA, 2001, in press.

Solubilities and surface activities of phthalates investigated by surface tension measurements. Marianne Thomsen, Lars Carlsen, Søren Hvidt. Environ. Toxicol. Chem. 20 (2001) 127-132.

Further the environmental chemistry of PAE's has been compiled in: *Phthalater i Miljøet. Opløselighed, Sorption og Transport.* Marianne Thomsen, Lars Carlsen. Faglig rapport fra DMU, nr. 249, 1998

3.2.2 Interactions with DOM

The environmental mobility of PAE may be significantly influenced by the possible interaction with natural organic material. In reality the presence of dissolved organic matter (DOM) may influence physical/chemical, hydrological as well as ecological processes, e.g., simply by increasing the apparent solubility, which eventually may influence the transport of xenobiotics with respect to increased washout and run-off to the groundwater and surface waters, respectively. In order to illustrate this interaction the sorption mechanisms and complex formation between humic acid (HA) and an successively increasing number of diethyl phthalate (DEP) molecules have been studied theoretically using molecular mechanics, the number of DEP molecules being varied from 1 to 30 according to the equation:



The energy components of the single HA•nDEP complexes have been used as explanatory variables in a principal component analysis for exploring the presence of similarities/dissimilarities in the energetic properties of the individual complexes.

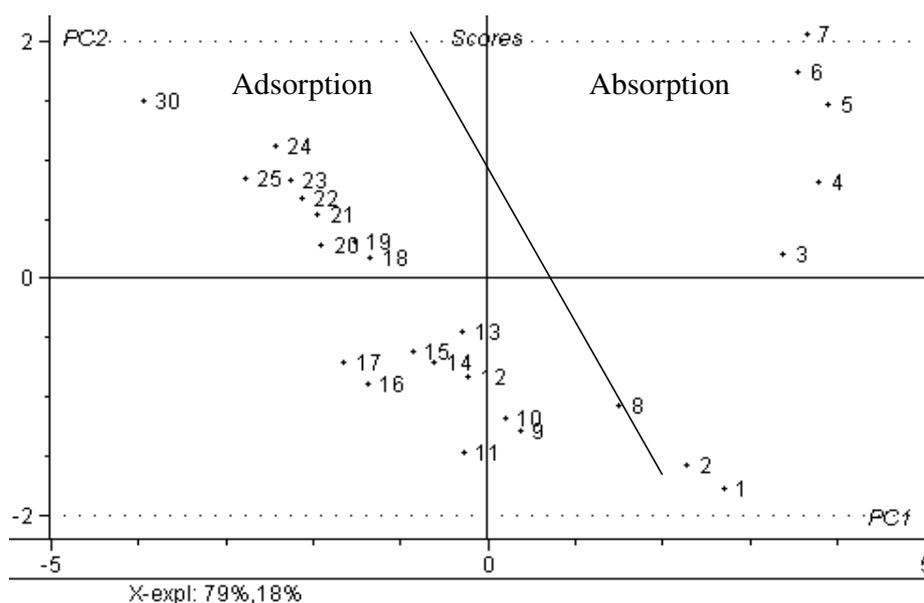


Figure 3.5 Principal component analysis (score plot) based on energy components for the interaction between diethyl phthalate and humic acid for 1 to 30 phthalate molecules (the single complexes are denoted with a number corresponding to the number of phthalate molecules in the complex).

The DEP-HA can be explained in terms of a two-step mechanism. Absorption takes place as long as the host humic acid structure offers a) enough internal docking space and b) favourable interactions (energy release) with the guest molecule. This takes place for up to 7 DEP molecules. Further increase in the number of DEP molecules will, due to the lack of free available internal voids lead to surface controlled adsorption.

Structural features at the atomic level, such as partial atomic charges and high aromaticity of the humic acid, are observed to be dominating the intermolecular interactions in the complexes at the specific sorption sites. Mainly hydrogen bonds (electrostatic energy) and pi-pi intermolecular aromatic interactions (Van der Waals energy) describe the intermolecular forces. The modelled sorption process is not conflicting with experimental derived data on sorption thermodynamics, but need to be further evaluated by experimental data.

The study is comprehensively described in:

Humic complexes of di-ethyl phthalates: molecular modelling of the sorption process. Hans-Rolf Schulten, Marianne Thomsen, Lars Carlsen. *Chemosphere*, **45** (3), 2001, 357-369

4 Sources to PAE and NP

Institutions and industries

The identity and relative importance of the sources to PAE's and NP's is of major interest in the evaluation of the environmental fate of these compounds. Thus, the present study investigated the presence of selected PAE and NP in the wastewater from an array of pre-selected industries and institutions in order to identify and evaluate the absolute and relative importance of single sources including car wash centres, a hospital, a kindergarten, an flue factory and an industrial laundry.

Furthermore, the deposition in the area, as well as the concentration levels in two local rivers was investigated.

Finally, the wastewater inlets to the local WWTP, where the sources converge at a single point, were analysed.

The average concentrations in wastewater from institutions and industry are summarised in Table 4.1, which also show the average WWTP inlet concentrations for November 1996 and January 1997.

Table 4.1 Average concentrations in wastewater from institutions and industry, $\mu\text{g/l}$

	<i>NP</i>	<i>NPDE</i>	<i>DBP</i>	<i>DPP</i>	<i>BBP</i>	<i>DEHP</i>	<i>DnOP</i>	<i>DnNP</i>	<i>DiNP</i>
Car wash	140	0.2	73	0.1	16	112	12	10	269
Hospital	0.4	0.6	36.6	0.3	0.1	15	0.4	0.7	nd
Kindergarten	1637	10832	nd	131	315	nd	311	277	399
Laundry	nd	nd	nd	nd	nd	111	4.7	4.2	nd
Glue factory	1003	31	nd	94	209	nd	277	nd	7515
WWTP	3.1	na	32	0.8	0.9	44	8.8	2.1	na

Deposition

The deposition was sampled in bulk at a station located about 6 km to the north of Roskilde. The most abundant substances found were DEHP and DBP, followed by BBP and DnOP. The concentrations of DEHP ranged from 0.27 to 1.6 $\mu\text{g/l}$, and the deposition rate from 140 to 540 $\mu\text{g/m}^2/\text{y}$. The results indicated a larger and more random variation for the deposition concentrations than for the deposition rate, shown in Fig. 4.1 for the four most abundant PAE's.

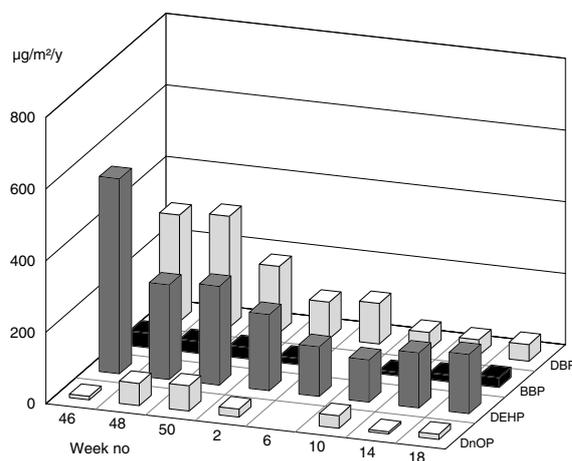


Figure 4.1 Seasonal variation of deposition rates (annual deposition per m²) of the four PAE's occurring in the highest concentrations.

Streams

Two small rivers/streams in the Roskilde Fjord catchment were investigated. The most abundant PAE's found were BBP, DEHP and DnOP. The concentrations were very low compared to wastewater.

In Table 4.2 the averages for deposition and streams are shown. Remarkably, the concentrations in the streams are generally lower than in the deposition.

Table 4.2 Average concentrations in deposition and streams, ng/l

Site	NP	NPDE	DBP	DPP	BBP	DEHP	DnOP	DnNP	DiNP
Deposition	7	nd	268	nd	38	465	43	nd	nd
Hove Stream	nd	nd	nd	1	56	130	51	11	nd
Maglemose Stream	nd	nd	50	7	145	460	18	34	nd

In Table 4.3 the total emissions for the Roskilde area are shown, calculated from the measured concentrations and the water flow. For the deposition a receiving area of 16 km² is assumed.

Table 4.3 Mass flow balance for total project (The glue factory and the rivers are not included in the sum).

Site	NPDE	DBP	DPP	BBP	DEHP	DnOP	DnNP	DiNP
	Total annual mass flow, kg/y							
Carwashing	0,004	1,3	0,003	0,28	2,1	0,19	0,22	5,4
Hospital	0,042	2,7	0,02	0,006	1,1	0,031	0,53	
Kindergartens	197		2,4	5,7		5,7	5,0	7,3
Laundries					7,3	0,31	0,27	
Deposition		1,8		0,31	3,3	0,36		
Sum	197	5,9	2,4	6,3	28	7,2	6,1	13
WWTP	ia	174	4,5	5,0	240	49	12	ia
Streams		0,033	0,009	0,25	0,65	0,15	0,052	
	Percentage of flows relative to the WWTP, %							
Carwashing	-	0.7	0.1	5.6	0.9	0.4	1.9	-
Hospital	-	1.6	0.4	0.1	0.5	0.1	0.5	-
Kindergartens	-	0	53	116	0	12	43	-
Laundries	-	0	0	0	3.0	0.6	2.3	-
Deposition	-	1.1	0	6.2	1.4	0.7	0	-
Sum	-	3.4	54	128	12	15	52	-
WWTP	-	100	100	100	100	100	100	-
Streams	-	0.02	0.2	5.0	0.3	0.3	0.4	-

There are large uncertainties inherent in the calculations. Nevertheless, they do give an indication of the absolute and relative contribution of the sources. A more accurate estimate would require a significant larger number of samples.

The study is comprehensively described in:

Sources of phthalates and nonylphenols in municipal waste water. A study in a local environment. Jørgen Vikelsøe, Marianne Thomsen, Elsebeth Johansen. NERI Technical Report No. 225, 1998

5 Emissions of LAS, PAE and NP

In the previous section the relative contributions to the WWTP from selected sources were reported in an experimental approach to account for measured concentrations in the WWTP inlet. Below estimation of the concentrations in the WWTP inlet based on a theoretical investigation meant for future assessment in the WWTP is described. This approach addresses the uncertainty aspects that are essential for the interpretation of risk assessment models.

When environmental hazards of xenobiotics are investigated it is of fundamental interest to determine the major sources of emission; i.e. to identify the major products, consumption figures and the quantities of the investigated chemicals used in these products. It is essential to understand in which way the products are used and if the chemicals are “lost” to the atmospheric, aquatic or terrestrial compartment. Some chemicals, such as the surfactants, are almost completely disposed in the wastewater, while others, such as the PAE’s, enter the environment in a more complex way, e.g. through waste.

The emission survey summarises this information in emission factors that easily can be used in risk assessment modelling. The substrate emission is often the weak link in the sense that it is very uncertain with respect to emitted mass and transport mechanisms and therefore the overall fate model becomes associated with considerable uncertainties that makes decision making doubtful.

Compounds studied

As a part of a project the emission and fate of LAS’s, six different PAE’s, NP’s and NPE’s in Roskilde municipality comprising a WWTP, Roskilde Fjord and a sludge amended field has been evaluated. The emission survey supplies input values to the sewer and WWTP which in turn defines the xenobiotic concentrations in the effluent water that is discharged to the Fjord and the sludge that is stored on a field adjacent to the Fjord.

The starting point to this overall fate model is thus the emission survey. The reliability, or uncertainty, of the combined model will depend strongly on the uncertainties associated with the survey. However, consumption can not be standardised and will always display local variations. Disclosure of the consumption pattern of the individual consumer or industry is, however, beyond the scope of this project.

Annual mean inlet concentration to WWTP

The result from the emission survey comprises annual mean inlet concentrations to Roskilde WWTP of LAS’s, total PAE’s and NPE’s

$$C_{\text{LAS}} = 20 \pm 20 \frac{\text{mg LAS}}{\text{liter}}$$

$$C_{\text{NPDE}} = 2 \frac{\text{mg NPDE}}{\text{liter}}$$

$$C_{\text{PAE}} = 150 \pm 128 \frac{\text{mg PAE}}{\text{liter}}$$

(no deviation is stated due to insufficient data)

These figures are obtained from import/export data, producers, previous investigations and estimates concerning the fate of the substrates in the different environmental compartments.

The study is described in:

Phthalates, Nonylphenols and LAS in Roskilde Wastewater Treatment Plant - Fate Modelling Based on Measured Concentrations in Wastewater and Sludge. Patrik Fauser, Peter B. Sørensen, Jørgen Vikelsøe, Lars Carlsen. NERI Technical Report No. 354, 2001.

6 The Waste Water Treatment Plant (WWTP)

In the EUSES risk assessment system for chemicals the description of the processes in a WWTP is central. The compartment description paradigm is used to calculate the partitioning between different phases in the wastewater treatment combined with assumed first order degradation. As a part of EUSES the SimpleTreat model assumes continuous flow through the system where different reactors are connected in series.

However, in Denmark it is often the case that the sewage is not treated in a continuous process but rather in a discontinuous operation, where the redox potential changes discontinuously during alternation between aeration and no aeration respectively. Furthermore the outlet is taken from different reactors during time. Thus, it is not necessarily true that the continuous operation approach used in SimpleTreat is sufficient for risk assessment when alternating operation treatment facilities are considered. A central issue in this work is therefore to investigate the importance of the actual mode of operation (continuous/discontinuous) in order to identify the need for adjustments in SimpleTreat if the alternating operation needs to be covered by the conclusions from the model.

Bjergmarken WWTP

As a model plant Bjergmarken WWTP in Roskilde, Denmark, treating the waste water from 80000 PE in an alternately operated BIO-DENIPHO activated sludge operation, is employed. Furthermore, the model set-up for Bjergmarken WWTP is used to calculate a mass balance for selected xenobiotics.

6.1 Continuous vs. discontinuous model set-up

The complex system functionalities associated with the WWTP are incorporated into 2 models of varying complexity according to the general modelling paradigm.

Model 1

Model 1 comprises the alternating operation cycle and includes aerobic and anoxic degradation, respectively, expressed through the corresponding pseudo 1st order degradation rates k_{IN} and k_{ID} respectively. Furthermore adsorption is described through the retention factor, $R = 1 + K_d \cdot X_B$, where K_d is the partition coefficient and X_B is the concentration of particulate matter.

Model 2

In model 2 the biological treatment cycle is aggregated into one reactor with a continuous flow equal to the daily mean flow. Different from SimpleTreat model 1 and 2 do not include volatilisation, stripping, acid/base dissociation, temperature dependencies and diffusion in settled particulate matter thus reducing the uncertainties related to the large number of input variables.

The reactor hydraulics of model 2 thus resembles SimpleTreat and the deviations between the more complex model 1 and the simple model 2

are used to evaluate the uncertainties in employing SimpleTreat in the simulation of an alternately operated WWTP.

Steady-State

The dissolved outlet concentration calculated in model 1 reveals the dynamic alterations in the plant. After a period of constant inlet concentrations and flow steady state occurs and the outlet concentration curve fluctuates around a mean “cycle steady-state” value, cf. Fig. 6.1. The amplitude can be calculated from

$$\text{Amplitude} = 1.6 \cdot 10^4 \cdot \frac{k_{IN}}{R} + 2 \cdot 10^{-2} \quad [\%] \quad (6.1)$$

and reaches approximately 3 % for a hydrophobic and easily degradable substrate such as LAS.

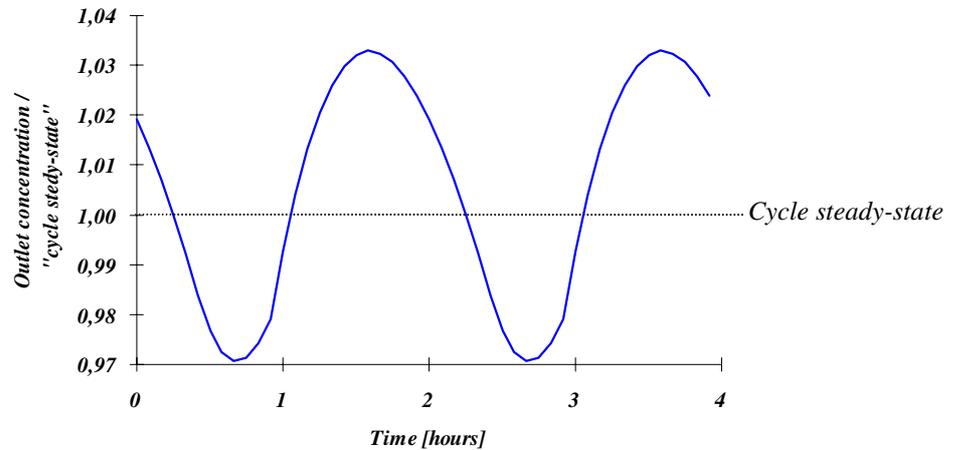


Figure 6.1 Calculated steady-state fluctuations of outlet concentration from Bjergmarken WWTP during one operation cycle (4 hours). Simulated with model 1.

If the same process parameters are used in model 2 the deviation between the steady-state outlet concentration in model 2 and the mean “cycle steady-state” concentration in model 1 lies in the interval from 2 to 35%, with the largest values for easily degradable, hydrophilic substrates.

Modification of the degradation rate a calibrated empirical 1st order degradation rate for model 2, k_1 (model 2) can be calculated from

$$\frac{k_1(\text{model 2})}{R} = \frac{2279 \cdot \left(\frac{k_{IN}}{R}\right)^2 + 0.963 \cdot \left(\frac{k_{IN}}{R}\right)}{\left(0.275 \cdot \left(\frac{k_{ID}}{k_{IN}}\right)^2 - 0.822 \cdot \frac{k_{ID}}{k_{IN}} + 1.55\right)} \quad (6.2)$$

If this value is inserted in model 2 the deviations are no more than 2% between the outlet concentrations in model 1 and 2. However, for substrates with aerobic half-lives longer than approximately 2 hours k_1 (model 2) can be set equal to k_{IN} .

An integrated 1st order sensitivity and uncertainty analysis approach concludes that the uncertainties related to the input parameters in model 2 results in uncertainties in the outlet concentrations that are much larger than the periodic fluctuations in model 1. Thus, the complex operation cycle in model 1 can be reduced to a single biological reactor, analogous to Sim-

pleTreat, with continuous flow when the 1st order degradation rates, k_{1N} and k_{1D} are substituted with the empirical degradation rate in Equation 6.2.

6.2 Using model 2

An experimental series was performed during 8 days in May 1999. Each day one composite inlet sample and one outlet grab sample was collected from Bjergholmen WWTP. Further one grab sample from the primary sludge and one from the secondary sludge was collected.

The experimental concentrations are used to calibrate model 2 with respect to K_d and k_{1N} for the 9 investigated xenobiotics.

Table 6.1 Calibration parameters based on model 2 and experimental data.

	<i>Mean aerobic half life $t_{1/2}$ [hours]</i>	<i>Mean partition coefficient K_d [l · kg⁻¹]</i>
Linear alkylbenzene sulfonate, LAS	1.3	2760
Di-(2ethylhexyl)-phthalate, DEHP	21.6	13060
Dibutylphthalate, DBP	insufficient data	insufficient data
Dipentylphthalate, DPP	19.0	2570
Benzylbutylphthalate, BBP	79.1	3530
Di-(n-octyl)-phthalate, DnOP	29.0	19200
Di-(n-nonyl)-phthalate DnNP	32.8	28600
Nonylphenol, NP	7.2	2080
Nonylphenol-diethoxylate, NPDE	6.3	3640

The calculated aerobic half lives are generally low for the PAE's compared to literature values, typically found for soil experiments, but it is important to note that the experimental conditions are never coherent with the highly favourable conditions in the WWTP where the high concentration of micro-organisms are adapted to the prevailing conditions in terms of temperature, flow, substrate concentrations etc.

The mean values in Table 6.1 and mean experimental inlet concentrations and flows are employed in model 2 to calculate a mass balance for the fate of the investigated xenobiotics, i.e. the fraction of the influent mass that can be found in the outlet, degraded fraction, primary sludge and secondary sludge, respectively. A further differentiation into dissolved and adsorbed fractions is performed

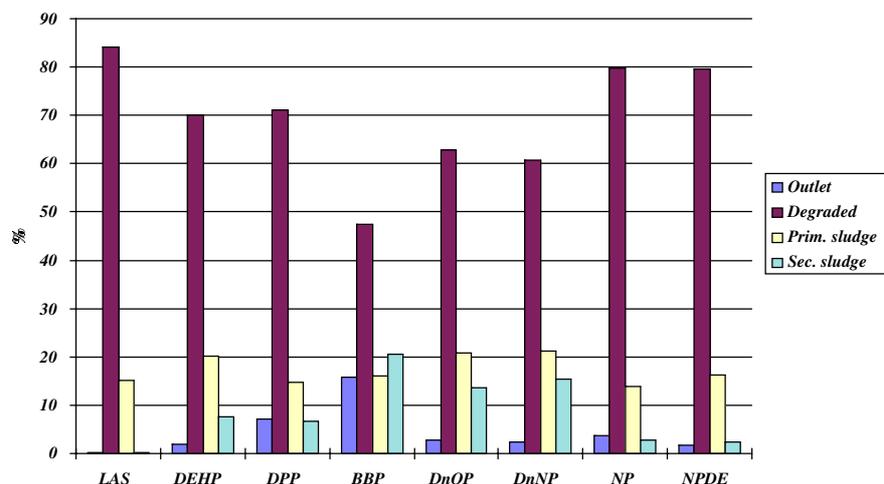


Figure 6.2 Fate of investigated xenobiotics in the alternately operated WWTP. Calculations are performed with model 2.

From the experimental and model results it can be concluded that the alternate plant operation is highly efficient with respect to degradation of hydrophilic as well as hydrophobic substrates.

The study is comprehensively described in:

Phthalates, Nonylphenols and LAS in Roskilde Wastewater Treatment Plant - Fate Modelling Based on Measured Concentrations in Wastewater and Sludge. Patrik Fauser, Peter B. Sørensen, Jørgen Vikelsøe, Lars Carlsen. NERI Technical Report No. 354, 2001.

7 The Terrestrial Environment

The study of the terrestrial compartment compiles results of a field study, investigating the occurring of xenobiotics in a series of soils samples.

Selection criteria

In order to ensure comparable, representative and relevant results, a series of criteria were adopted for the selection of soils. These comprise that the soils should

- be typical for Danish agriculture with respect to soil as well as to methods
- encompass a broad range of dressing/fertilisation and cultivating methods, comprising high and low level sludge, organic manure, artificial fertiliser and an uncultivated area for background reference
- have a known history including known characteristics of dressing/fertiliser
- be exposed for a time sufficient to allow the dressing/fertilisation method to have a significant impact on the xenobiotics studied in the soil. It is in the present study assumed that this applies when the same method has been in operation for at least two years
- have identical or similar and known soil characteristics, i.e. the content of humus, clay, silt and sand, in order not to confuse the picture developed due to different dressing/fertilisation and cultivating methods.

Obviously, it is not possible to fulfil all five criteria completely at every single location selected. Thus, quantitative data of soil characteristics is only known from the Danish Square Grid Database, which may deviate substantially from those in the actual soil samples because of the distance between the database sampling points and the sampling positions on the locations.

It is also emphasised that the actual amount of sludge, manure or artificial fertiliser applied is known only approximately. Further the possible contents of xenobiotics may have changed over the years in an unknown way.

The present study includes soil samples from eight locations selected according to the above criteria

1. Preserved natural area not cultured for 50 -100 years, cattle grazing (Ejby). Sampled Oct. 5, 1996.
2. Ecologically cultured for 40 years (Ledreborg). Sampled Oct. 5, 1996.
3. Manured sustainable in ecologically culture for 5 years, formerly conventionally cultured (Kirke Såby). Sampled Oct. 5, 1996.
4. Conventionally cultured using artificial fertiliser (Ågerup). Sampled Oct. 5, 1996.
5. Sludge amended, medium amounts, cultured (Jyllinge). Sampled Sep. 26, 1996

6. Sludge amended, low amounts, cultured (Sundbylille). Sampled Sep. 26, 1996.
7. Sludge amended with high amounts for 25 years, changed to artificial fertiliser 6 years before first sampling, cattle grazing (Bistrup). Sampled Oct. 25, 1996 and Nov. 4, 1998.
8. Meadow in run-off zone from sludge storage, cattle grazing (Bistrup). Sampled Oct. 25, 1996.

7.1 PAE and NP in Soils

Several Danish investigations of PAE's in waste water and sewage sludge have confirmed the omnipresence of PAE's. These substances tend to be concentrated in the sewage sludge from the wastewater by processes in the WWTP's. The sources, abundance, distribution and fate of PAE and NP in agricultural soils dressed with and without sludge have been studied as a part of the project. The vertical distribution of these substances in soil depth profiles has not previously been studied.

The results shows that DEHP were the most abundant phthalate in most samples, but high concentrations of DiNP occurred occasionally. NP's seemed to occur in high concentrations only in the two soils exposed to high amounts of sludge.

In Table 7.1 the results for DEHP, the most abundant phthalate, are shown.

Table 7.1 Concentration of DEHP in depth profiles, $\mu\text{g}/\text{kg}$ d.m. (7a and 7b refer to sampling Oct. 1996 and Nov. 1998, respectively)

Depth, cm	1. Uncultured	2. Ecol. 40 y	3. Man. 5 y	4. Artif. fertil	5. Med. sludge	6. Low sludge	7a. High sludge	7b. High sludge	8. Runoff zone
0-10	8	16	16	34	18	22	991	1400	674
10-20	41	45	18	12	13	18	1707	1700	76
20-30	27	32	8	9	9	17	1406	1800	9
30-40	4	14	18	15	6	23	881	3400	26
40-50	0	20	1	20	15	21	586	1200	5
50-60								550	

It appears that low concentrations with only minor differences are found at site 1 to 6, whereas site 7 and 8 display much higher levels.

The artificially fertilised soil at location 4 and the low sludge amended soils at the locations 5 and 6 do not differ significantly from the unfertilised soil in the preserved area at location 1 or the two ecologically cultured soils at locations 2 and 3.

In contrast, very high concentrations of NP's and PAE's were found in the high sludge amended soil location 7 throughout the profile, showing a build-up of DEHP. Thus a close relationship was found between the concentration levels in the profiles, and the method of dressing.

Location 7 was revisited after 2 years, without significant difference in concentration level, suggesting a rather low degradation rate.

In Figs 7.1 – 7.4, the average concentrations of all substances as a function of depth are shown for selected soils as bar graphs.

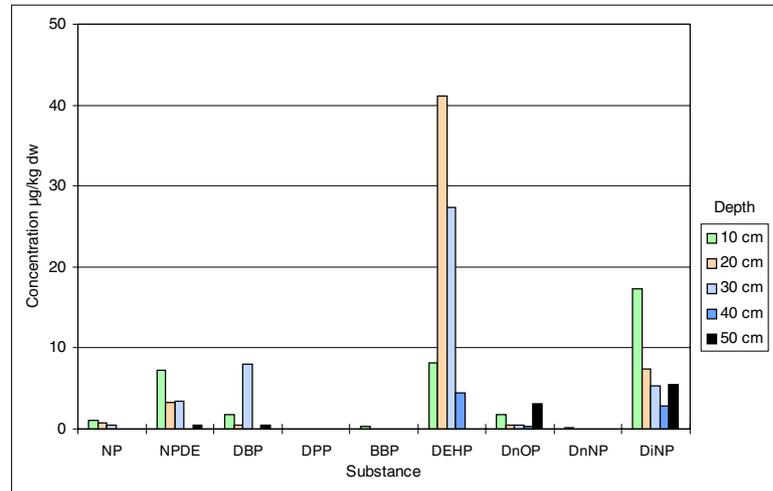


Figure 7.1 Concentration profiles for location 1, preserved area not cultured for more than 50 years.

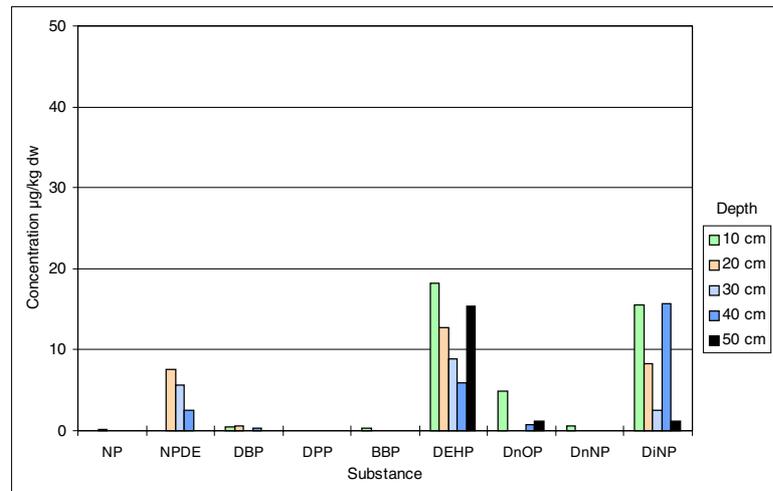


Figure 7.2 Concentration profiles for location 5, amended with medium amounts of sludge.

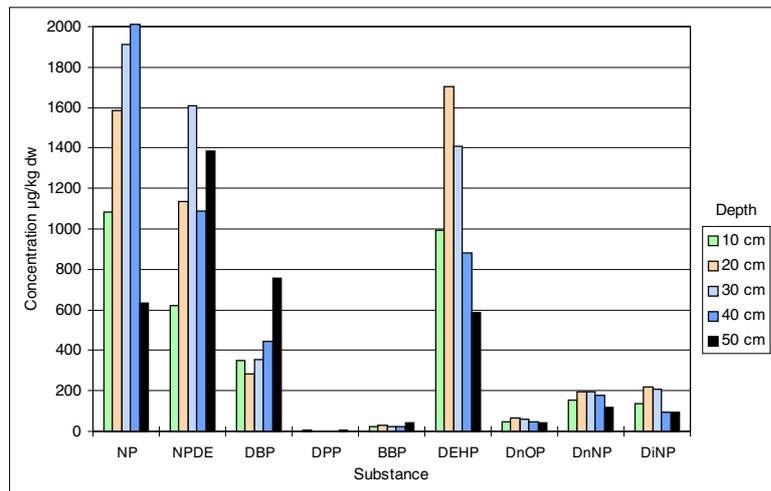


Figure 7.3 Concentration profiles for location 7, heavily sludge amendment (ceased 1991) sampled 1996.

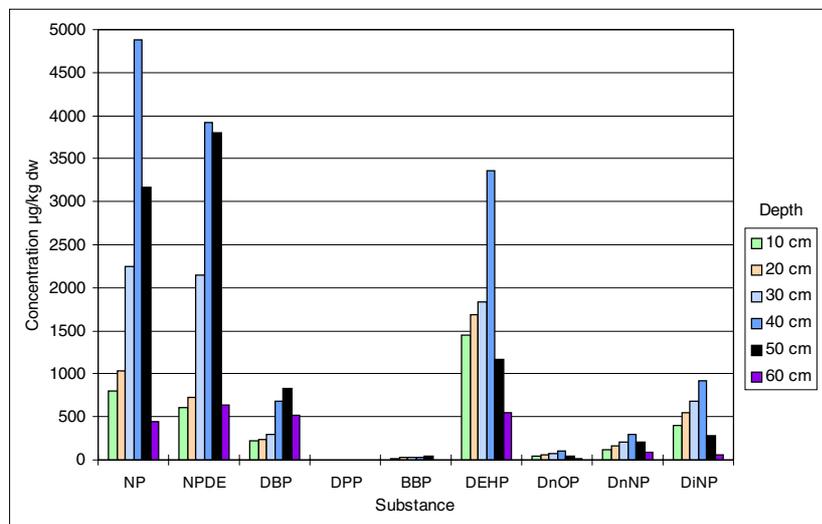


Figure 7.4 Concentration profiles for location 7 sampled 1998 (2 years later).

Modest sludge application

A modest application of sludge for soil amendment apparently does not give rise to elevated concentrations of NP's and PAE's, compared to the manured or artificially fertilised soils. Further, the concentrations are very close to those found in a not cultivated preserved soil.

Preserved areas

PAE's were detected in the preserved soil not cultivated for more than 50 years, thus other sources than dressing must be present. The most likely source in this case is atmospheric deposition.

Heavy sludge - amendment

Very high levels of PAE and NP were found in heavily sludge-amended soils, exceeding the Danish soil quality criteria for some of the compounds. Even 8 years after the sludge amendment had ceased; high concentrations remained in the soil. In these circumstances the substances studied behave as persistent organic pollutants.

The study is comprehensively described in:
Phthalates and nonylphenols in soil. A field study of different soil profiles. Jørgen Vikelsøe, Marianne Thomsen, Elsebeth Johansen, Lars Carlsen. NERI Technical report No. 268, 1999

Phthalates and nonylphenols in differently dressed soils. Jørgen Vikelsøe, Marianne Thomsen, Lars Carlsen. Submitted for publication.

7.2 LAS in soils

In recent years LAS have caused significant concern, the main concern being the lack of degradation of LAS under anaerobic conditions.

Over the last decades the fate and effect of LAS in the aquatic environment have been studied extensively, whereas it is still to be disclosed to what extent LAS's constitute a problem in the terrestrial environment as the fate and effect of LAS in the latter environmental compartment have been studied only scarcely.

LAS may enter the terrestrial environment by several pathways such as irrigation with wastewater or by amendment of the soil by sewage sludge.

In Table 7.2 the LAS concentrations determined in the soil samples originating from the 8 locations are given. The results are corrected for recovery.

Table 7.2 Concentrations of LAS in soil samples from the 8 different locations. If one or more of a priori identical samples did show a concentration below the detection limit the concentration was set equal to 0 in the calculation of the average concentration. These results are given in parentheses. If both samples displayed concentrations below the detection limit no value is given.

Depth (cm)	LAS mg/kg dw	Sdev
Location 1:		
<i>Preserved natural area not cultured for 50 -100 years, cattle grazing</i>		
0-10	(0.45)	0.34
10-20	0.53	0.04
20-30	(0.23)	0.32
30-40	0.71	0.06
40-50	(0.98)	1.09
Location 2:		
<i>Ecologically cultured for 40 years</i>		
0-10	0.83	0.09
40-50	(0.49)	0.33
Location 3:		
<i>Manured sustainable in ecologically culture for 5 years, formerly conventionally cultured</i>		
0-10	(0.40)	0.35
10-20		
20-30	- not included in the analysis program	
30-40	0.71	0.28
40-50	(0.63)	0.63
Location 4:		
<i>Conventionally cultured using artificial fertiliser</i>		
0-10	(1.19)	0.64
40-50	(0.36)	0.37
Location 5:		
<i>Sludge amended, medium amounts, cultured</i>		
0-10	1.12	0.40
10-20	(1.07)	1.24
20-30	0.6	0.31
30-40	(0.36)	0.32
40-50	(0.56)	0.33
Location 7:		
<i>Sludge amended with high amounts for 25 years, changed to artificial fertiliser 6 years before first sampling, cattle grazing</i>		
0-10	11.23	0.21
10-20	9.92	1.96
20-30	9.72	0.78
30-40	9.4	0.007
40-50	7.13	1.64
Location 7:		
<i>Sludge amended with high amounts for 25 years, changed to artificial fertiliser 8 years before first sampling, cattle grazing</i>		
0-10	10.35	4.03
10-20	19.25	1.87
Location 8:		
<i>Meadow in run-off zone from sludge storage, cattle grazing</i>		
0-10	1.86	0.74
10-20	4.01	0.85
20-30	0.78	9.19
30-40	1.65	0.80
40-50	0.92	0.26

It is immediately noted that only very low LAS concentrations could be detected in the different soils included in the present investigation apart from the samples originating from location 7, i.e. sludge amended with high amounts for 25 years. In the latter case concentrations up to approx. 20 mg/kg soil were detected.

For other soils (locations 1, 2, 3, 4 and 5) concentrations of LAS were found to be in the order of < 1 mg/kg dw.

For location 8, i.e. a meadow in run-off zone from sludge storage used for cattle grazing, the concentrations in the top 20-cm were found to be somewhat elevated.

Preliminary soil quality criteria

On the above basis it can be concluded that apart from location 7 and 8 concentrations of LAS in all soil samples were found to be below 1 mg/kg, which is well below the a proposed preliminary soil quality criteria for LAS at 5 mg/kg. Thus, it can be concluded that LAS does not constitute an ecotoxicological hazard in the terrestrial environment as long as the amendment of soils are carried out according to the prevailing regulations.

On the other hand it is apparent that it heavy sludge amendment is carried out as at location 7, the soil quality criteria may well be exceeded.

The study is comprehensively described in:

Linear alkylbenzene sulphonates (LAS) in soils. A field study of different soil profiles. Lars Carlsen, Mai-Britt Volfing, Jeannette Kjelsmark. Research Notes from NERI No. 134, 2000.

7.3 Modelling of sludge amended soils

Sludge amendment of agricultural soil is an obviously way of nutrient recycling and furthermore a cheap way of waste management. However, further aspects need to be considered regarding the contents of xenobiotics in the sludge. A large variety of xenobiotics arrive to the WWTP in the wastewater. Many of these components are hydrophobic and thus will accumulate in the sludge solids and are removed from the plant effluent. This may yield a sufficient cleaning of the effluent and a good water quality, but the resulting accumulation in the sludge many cause problems in the subsequent sludge disposal. The agricultural re-use of the sludge nutrients needs to be associated with a risk assessment concerning the accumulated xenobiotic substances.

Exposure assessment

Exposure assessment for the soil compartment (root zone) is important in relation to terrestrial organisms and human consumption of agricultural products originating from sludge amended soil. The topsoil represents the upper 20-cm layer and is the most biological active zone. The biological activity will typically decrease rapidly with depth under the topsoil layer and the total root zone depth for agricultural crops will typical be about one meter. The focus in this work is the topsoil. The local Predicted Environmental Concentration (PEC) level for the soil compartment as calculated in the European Union System for the Evaluation of Substances (EUSES) is related to the upper 20 cm layer of top soil.

The model

A simple model for the topsoil is used. The substance is assumed homogeneously distributed as suggested in the European Union System for the Evaluation of Substances (EUSES). It is shown how the fraction of substance mass, which may leach, from the top soil is a simple function of the ratio between the degradation half lifetime and the adsorption coefficient. If the degradation is insignificant ($q \ll x_1 \cdot K_d \cdot \rho \cdot k'$) the ratio X_L approach one i.e. all the substance supplied is leached. The equation can be rewritten using the relationship for $T_{1/2}$.

$$\frac{T_{1/2}}{K_d} = \frac{\ln(2) \cdot \rho \cdot x_1}{q_m} \cdot \frac{X_L}{1 - X_L} \quad 7.1$$

Eq. 7.1 predicts a unique combination of K_d and $T_{1/2}$ to be related to specific fractions of leached material. X_L is the ratio between the degraded and the leached mass ($X_L=0$ means no leaching), q is the mean flux of water leaching from the top-soil (cm/d), ρ is the dry bulk density (kg/dm^3), x_1 is the top soil depth (cm), $T_{1/2}$ is the degradation half lifetime for the substance in the top soil (d), and K_d is the adsorption coefficient (L/kg). Using numeric values representative for Danish condition this equation predict the leached mass ratio to be about 0.3 % of the numeric value for the $T_{1/2}/K_d$ ratio.

Input parameters

The simple topsoil model is applied in an analysis of the field scale measurements of DEHP contamination in agricultural soil. In this investigation sludge amended agricultural soil is analysed. The intensity of the actual sludge amendment (load) is calculated based on the input parameters: (1) The number of person equivalent (pe) connected to the WWTP, (2) The sludge production per pe, and (3) The concentration of DEHP in the sludge. This calculation is subject to some uncertainty and the value of this is estimated using considerations about the uncertainty in each input parameter yielding a log-normal distribution for possible sludge load values. The measured concentration values are also associated with some variability and a normal distribution is estimated based on the recorded measurements.

Disappearance coefficient

The topsoil model can relate the sludge load to a resulting soil concentration value which is compared to the measured concentrations, by using a first order disappearance coefficient (K_{dis}). The calculated concentration values can be compared to the measurements and thus it is possible to adjust the K_{dis} value in order to obtain the best agreement between the model calculations and the measurements. The result is a close to normal distribution for the K_{dis} values and the interval for about 95% of the probability is identified to be a half lifetime in the topsoil from 7 to 38 years.

This model can be used in a probabilistic risk assessment of agricultural soil. The results are strongly related to the experimental values which have been used to calibrate the K_{dis} distribution function. Thus, the use of the model is mostly a numerical example of probabilistic risk assessment. Based on the soil quality criterion, the maximum allowable soil concentration level is identified and is a key parameter in the risk assessment.

The recovery time period need for a polluted soil to recover after contamination, in which the soil concentration decreases below the soil quality criterion is identified as a distribution function. It is shown how missing information about the soil concentration level at the beginning of the recovery time period can lead to much longer estimated time periods if the prediction needs to be safe (low probability for under estimation of the recovery time period). The maximum period of sludge amendment is calculated for three different load intensities. The results are compared to the critical load where the soil quality criteria are fulfilled at infinite time (the disappearance sufficient to remove the substance from the topsoil at the same rate as the load). It is shown that this critical load value in this case is much lower than the tolerable load for a long time period (up to 48 years).

The study is comprehensively described in:

Modeling Analysis of Sewage Sludge Amended Soil. Peter B. Sørensen, Lars Carlsen, Jørgen Vikelsøe, Angélique G. Rasmussen. NERI Technical Report No. 361, 2001.

8 The Aquatic Environment

One of the characteristics of the Roskilde region is the fjord, which leads from Roskilde at the bottom of the fjord to the outlet in Kattegat. Thus, the Roskilde fjord system constitute an interesting example of an aquatic environment where xenobiotics are transported to the fjord by several pathways including discharge of waste water from the WWTP, run-off from a sludge storage, discharge from a series of small rivers as well as deposition.

As part of the present study the fate of PAE and NP in the fjord system, including the water as well as the sediment compartment, has been studied experimentally as well as theoretically.

8.1 PAE and NP in the fjord system

Compounds studied

The occurrence sources, transport and fate of NP's and PAE's in the aquatic environment of a fjord were investigated. The substances analysed were NP, NPDE, DBP, DPP, BBP, DEHP, DnOP and DnNP. The analytical methods were specifically developed for the investigation, using high resolution GC/MS. The investigation comprised measurements of water and sediment in the fjord as well as in sources.

Temporal and spatial variation

The level and the temporal and spatial variation of the xenobiotics in the water of the fjord were studied during three seasonal campaigns, involving widespread different locations. Very low concentrations were found. DEHP was the most abundant substance, followed by much lower concentrations of DBP, BBP, DPP and NP. NPDE was not found. The concentrations of the higher PAE's were highly significantly inter-correlated. On a large geographical scale the spatial variation was insignificant, but a significant seasonal variation was present, indicated by a maximum for June and a minimum for December, confirmed by analysis of variance. The largest seasonal variation and a significant short-term variation were present at the narrow middle location, where the current velocity is high. The broad innermost part, near Roskilde, was most constant.

Sediment samples

Sediment was studied in the innermost part of the fjord (Roskilde Vig). Much higher concentrations were found than in the water, DEHP, DBP NP and NPDE being most abundant. A decreasing gradient from the WWTP outlet to a location 6-km away was observed, approaching the concentrations found in the other less polluted fjord, Isefjord. Thus, horizontal transport through the water is limited to some kilometres, and the main transport process seems to be sedimentation, or binding to sediment in the fjord bottom.

Sediment core

The sediment study including a core 22 cm deep (~80 y old) from Roskilde Vig. A decreasing tendency with depth/age was observed for DEHP and BBP, reflection the historical development in consumption of PAE's. For NP and NPDE, a more complicate pattern was found, char-

acterised by low concentrations in the upper/youngest part and two deeper maxima, probably caused by variation in the use of NPE's .

Streams and Lake

The seasonal sampling also comprised three streams and a lake, including sediment. In the water of the streams, the DEHP concentrations ranged up to the triple of the fjord. The spatial and temporal variations were more pronounced and random, certainly because the streams - unlike the fjord - are hydraulic and geographic separate entities having different sources and flows. The lake sediment indicated a significant sedimentation of all substances – in particular NP and NPDE – in the deepest part of the lake.

Numerical models were set up in order to describe the fate of the substances in the water and sediment compartments of the fjord. Only DEHP data was used since DEHP was the most abundant substance and the only one to occur in concentrations that are of environmental significance.

Physico-chemical processes

The physico-chemical processes in the fjord that were considered to influence the fate of DEHP, were: 1st order degradation of dissolved DEHP, adsorption to particulate matter, sedimentation of particulate matter, vertical diffusion in the sediment and dispersive mixing in the water. DEHP sources to the fjord were streams, WWTP discharges and atmospheric deposition. Water exchange with the surrounding sea removes DEHP, since the DEHP concentrations is negligible in the sea.

In order to establish a simple robust model, the seasonal variations were not considered. More data concerning the growth and wilting cycle of the vegetation and the influence of changing emission patterns from consumers and WWTP's were needed and therefore mean annual conditions were simulated based on constant flows and concentrations.

The numerical models were validated with analytical expressions. The experimental sediment core data was used to calibrate the sediment model yielding a sedimentation rate of 2.5-mm pr. year, corresponding well to a rate previously found for the fjord. Furthermore a distribution coefficient equal to 10000 L/kg dm and a 1st order degradation rate of $2 \cdot 10^{-5} \text{ sec}^{-1}$ were found.

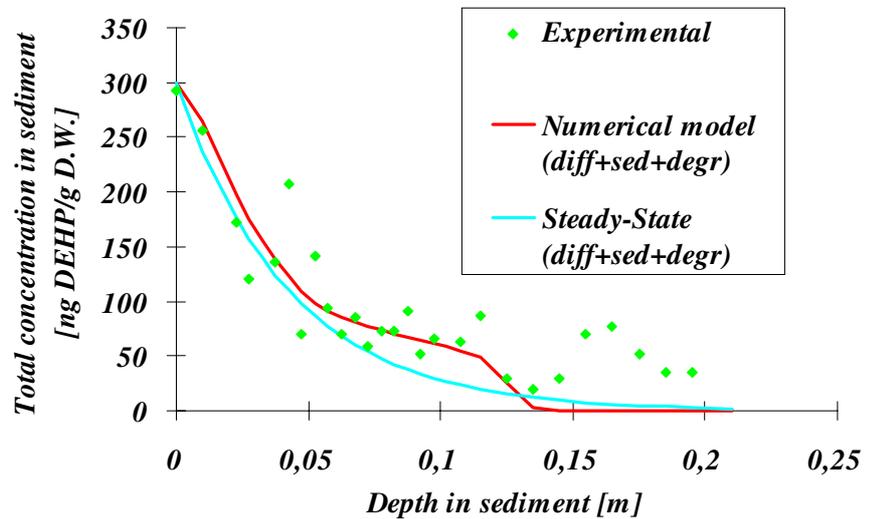


Figure 8.1 Experimental and numerically modelled concentration profile for DEHP in sediment core

The sediment simulations showed that it is the sedimentation process that governs the vertical transport of substance in the sediment. Diffusion is only significant in the theoretical upstart of the system, where the concentration gradient is large at the surface. This fact has further been investigated in relation to evaluating the generic compartment model, SimpleBox, comprised in the European Union System for the Evaluation of Substances, EUSES.

The water model was made by dividing the fjord into two sections of total mixing along the horizontal axis, where the surface areas were large and into a narrow dispersive section where the horizontal flow was high. The shallow water was considered to be totally mixed along the vertical axis in the whole fjord. The experimental water concentrations were approximately constant only displaying minor spatial variations that could not be modelled, probably because of short-term effects such as tidal flow. The mean experimental concentration was a factor of 5 higher than the mean calculated concentration.

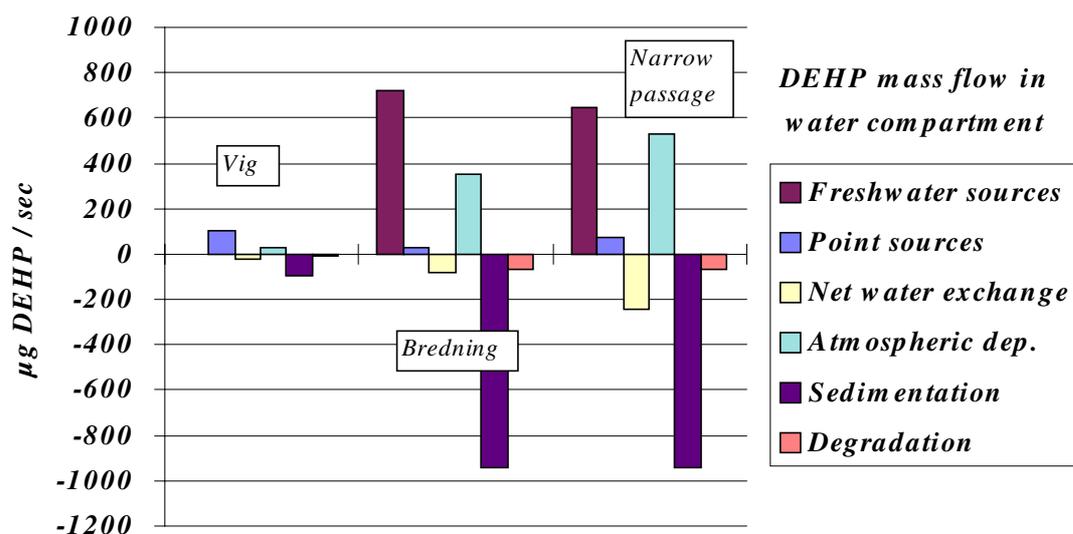


Figure 8.2 DEHP mass flow in the different water compartments included in the analysis

Mass flow

Freshwater from streams were the predominant DEHP source to the fjord, followed by atmospheric deposition and WWTP's. Sedimentation was the predominant removal mechanism followed by water exchange with the sea and degradation.

In spite of the deviation between the experimental and calculated DEHP concentrations in the water, the used modelling approach is considered to simulate the complex interactions that take place in a system such as Roskilde Fjord, satisfactorily. However, in order to employ the model as a risk assessment tool it is necessary to further investigate analytical detection limits, source contributions and temporal variations of the system.

The study is comprehensively described in:
Phthalates and Nonylphenols in Roskilde Fjord - A Field Study and Mathematical Modelling of Transport and Fate in Water and Sediment.
 Jørgen Vikelsøe, Patrik Fauser, Peter B. Sørensen, Lars Carlsen. NERI Technical Report No. 339, 2001.

9 Model evaluation

EUSES

As an integrated part of the project generic compartment models are investigated. Such models are developed and used and forms the basis in the European Uniform System for the Evaluation of Substances (EUSES) for risk assessment. As part of the present project the environmental concentration is considered having focus on the substance exchange between the water column and the sediment.

Uncertainty analysis

The uncertainty analysis is crucial for mathematical models as decision support and a systematic approach in the uncertainty analysis is needed for determination of the total model uncertainty. One approach of a systematic divides the overall uncertainty sources in two types. The first type is input uncertainty attributed to the uncertainty in the input parameters for the model. The second type is the systemic uncertainty as a result of the assumption taken in the model. Only the systemic uncertainty is considered in this investigation as the input uncertainty is investigated elsewhere.

Systemic uncertainty

The systemic uncertainty is difficult to quantify. Nevertheless, one possible way is to investigate different elements (sub-models) in the model separately and formulate a more complete model, which avoids some of the assumptions in the sub-model. The discrepancy between the sub-model under investigation and the more complete model formulation will quantify the importance of the sub-model assumptions avoided in the more complete model. Additional assumptions included in the model under consideration compared to the more complete model will be quantified for each sub model isolated. Many of the simplifications in the generic compartment models are a naturally consequence of the goal to make generic and manageable calculations for decision-makers. However, one has to secure that the uncertainty coming from to the simplifications in the generic sub-models is acceptable (small).

The systemic uncertainty introduced in the simplified mathematical formulation of the diffusive sediment uptake is in the present study addressed at the regional scale. The sediment water system is important when hydrophobic substances are considered. Measurements of a series of hydrophobic substances actually show a high occurrence in the sediment layer (cf. chap. 8). In the generic compartment models a mean diffusive transport length approach is taken for a sediment box of a specific arbitrary thickness.

Transfer mechanisms

Two major transfer mechanisms seem relevant:

- Transfer carried by net deposition of solids from the water column to the sediment surface
- Transfer due to diffusion in the sediment pore structure

In relation to the description of the sediment/water transfer in generic models the following questions appear relevant:

1. When will the transfer due to diffusion dominate the overall substance mass transfer?
2. What is the uncertainty in the generic models introduced when the diffusion transfer is described using a one box approximation for the sediment?

Flux

The flux of substance between the water column and the sediment is driven by diffusion and solids deposition respectively. Initially when a substance appears in the water column (start of emission) the diffusion will dominate the sediment uptake due to large concentration gradients in the sediment surface. However, as time progresses, the diffusion-induced flux will decrease rapidly, as the concentration gradients at the top of the sediment will level out because more substance enters the sediment layer. In contrast, the substance transfer due to solids deposition will not display a high flux initially but rather a value that is proportional to the dissolved water column concentration.

The dissolved water concentration is assumed constant in time and the degradation and the laminar boundary layer at the sediment/water column interface is neglected. In this case the initial diffusive flux is infinitely high and decrease rapidly during time. The Flux due to solids deposition will not display a high initial value but be constant during time and will thus become the dominating transfer mechanism after duration of a specific time period. An equation is derived to calculate the time period of diffusive flux dominance. However, an additional time period needs to progress before the mass of substance in the sediment will become governed by deposition and a maximum value of this time period (t_{cr}) is calculated to be $t_{cr} = D_s/V^2 \cdot R_s$, where D_s is the diffusion coefficient in the sediment, V the thickness of the layer deposited on the sediment surface per time unit and R_s the retention factor in the sediment.

Degradation

Under some circumstances it may be doubtful to neglect the degradation in the sediment. Thus, the degradation is included and simple relationships are obtained by assuming steady state sediment concentration and negligible laminar boundary layer at the sediment/water column interface. This yield an estimate of the final importance for diffusion and deposition, respectively, after steady state is obtained in the sediment.

Diffusive transfer

The description of diffusive transfer seems not well established in the generic compartment model, the latter using a mean transfer length for diffusion, which damages the nature of diffusion. In reality or as a result of the full solution of the governing equation for sediment diffusion the rate of substance transfer can be extremely high, as long the contamination in the sediment is limited. On the other hand, the compartment model tends to have constant rate diffusion in the first time period for simulation. After a specific period the mean length approach in the compartment models, to describe diffusion, becomes more valid. However, this time period may well be in the magnitude of many years! In case of steady state where the emission of substance into the system equals the sediment uptake by diffusion the one box approach will always overestimate the dissolved water concentration in relation to the more complete sediment description. Obviously, the discrepancy in the diffusive transfer

description will vanish as the transfer due to deposition of solids on the sediment surface starts to dominate in the total transfer of substance mass to the sediment. In many cases the transfer by deposition will dominate after a rather short time period and thus the concept in the compartment models will become acceptable simply because the diffusive transfer is negligible. Thus, it is concluded that the one sediment box approach seems insufficient to include a realistic diffusion mechanism. But in many cases the deposition and thus the burial from the sediment box of fixed thickness will become the dominating factor in the sediment/water column exchange of substance and in that case the inadequate description of diffusion will not be important.

The study is comprehensively described in:

Theoretical evaluation of the sediment/water exchange description in generic compartment models (SimpleBox). Peter B. Sørensen, Patrik Fauser, Lars Carlsen & Jørgen Vikelsøe. NERI Technical Report No. 360, 2001.

10 Conclusions and Outlook

The project "Xenobiotic Compounds" has been conducted as an integrated part of the research activities in the Department of Environmental Chemistry during the period January 1996 to May 2000.

The present study has been carried out as a combination of experimental and theoretical studies. Experimental results, originating from field and laboratory studies, formed together with available data from the literature the input to the modelling part of the project.

The studies have been focused on plasticizers of the phthalate type, and surface active agents such as NP and NPE and LAS. Three main environmental compartments have been included in the investigations, i.e., the terrestrial environment, where a series of soils samples in the Roskilde area was investigated, the aquatic environment, where the Roskilde Fjord was selected as target area and the WWTP in Roskilde, which is the main recipient of industrial as well as municipal wastewater from the Roskilde area.

The main objective for the project has been to set up and validate one or more models to determine Predicted Environmental Concentrations (PEC) for the compounds under investigation, i.e., PAE's, NP's, NPE's and LAS's, and to evaluate the generic compartment model used in the EUSES risk assessment system. In addition, an objective for the project has been to establish a general modelling paradigm for the construction of concentration profiles for single compounds or classes of compounds in environmental matrices.

In the following the main findings are summarised.

The Modelling Approach - Model uncertainty

The evaluation of model uncertainty has been approached and a 5-step procedure/guideline has been formulated

Step 1. The formulation of the problem to be solved in terms of a question to answer is crucial for the following choice and evaluation of the model.

Step 2. The model is selected based on expert judgement, which again is based on reported validation results and an evaluation of critical assumptions, the structural uncertainty being quantified to the extent possible. The structural uncertainty level makes the reference for the acceptable input-uncertainty, where the input-uncertainty is acceptable for values below or equals the judgement for the structure-uncertainty.

Step 3. A few model calculations are initially carried out a few different combinations of realistically selected input parameters. If the variation of input parameter values in this analysis yields results in unacceptable high uncertainty the model may be rejected as a candidate for valid calculations.

Step 4. If the model uncertainty was acceptable in *step 3*, the next step will be to over estimate the input-uncertainty, where unrealistic variations is applied to the input. If the input-uncertainty is acceptable then the model prediction will be valid (*step 5a*) otherwise a more comprehensive uncertainty analysis is needed (*step 5b*).

Step 5 a. The model is acceptable and can be used to answer the question. More complex models, which may give answers at higher information levels than the actual question, may exist.

Step 5 b. A detailed uncertainty analysis is made for input-uncertainty based on knowledge about the distribution function for input-parameter variability, possibly applying MonteCarlo simulations.

Basic Studies

A series of basic studies on physico-chemical features, i.e., solubility, partitioning and possible micelle formation of NP and PAE's has been carried out

Nonylphenols

NP is only slightly soluble in water, the solubility being determined as 4.9 ± 0.4 mg/L at 25 °C corresponding to $(2.22 \pm 0.18) \times 10^{-5}$ mol/L. The dissolution of NP in water seems to be a rather slow process (characteristic time scales of several days), which in combination with the low solubility will limit the potential leachability of NP in the terrestrial environment.

Due to an unfavourable ratio of sizes of the hydrophilic and hydrophobic parts of the molecule, NP is not subject to micelle formation. Thus, NP is not expected to be able to mobilise e.g. hydrophobic pollutants like polycyclic aromatic hydrocarbons (PAH's).

Taking the above into account, as well as the apparent slow degradation rate of NP, it strongly suggests that NP brought to topsoils will remain immobile for a significant period of time.

Phthalates

The unimeric solubility of the PAE's DEP, DnBP, DEH(6)P and DEHP has been determined to be 938, 14.6, 0.52 and 0.017 mg/L, measured at 22°C for DEHP and 25°C for the remaining PAE's. The solubility of the PAE's decreases significantly with increasing temperature in the range from 10 to 35°C. The PAE's apparently form micro emulsions within the bulk water phase upon exceeding the unimeric solubility. Compared to linear alkylbenzene sulfonates and NPE's, the surface activities of the PAE's are significantly less pronounced. In spite of this they show high affinity for adsorption at air-water interfaces, the standard free energy for adsorption increasing with increasing with the number of methylene-groups in the alkyl chain.

PAE's with more than six carbon atoms in their ester chains exhibit much lower unimeric solubilities in pure water than previously argued. This may have pronounced effects with respect to the environmental fate of these compounds in natural waters.

Comparing the solubility data with experimental data on bioconcentration of DEHP revealed that the linear relation between aqueous exposure concentration and bioconcentration is inversed from positive to negative upon exceeding the unimeric solubility. This strongly indicates a significant lowering of the bioavailability of the aggregated PAE's within bulk water.

Transport of PAE's may be different than expected when assessing the risk of this class of compound based on the "solubilities" previously stated in the literature, as the nature of emulsions differs significantly from the properties of a true solution. Like dissolved organic matter, an aqueous emulsion of PAE's of colloidal size will not be fixed within the soil matrix. Thus, precautions have to be taken in the case of intensive sludge amendment to soils. In these cases washout processes after heavy rain fall leaves the formation of microemulsions in the topsoil water as a possibility, which may lead to an altered migration potential, i.e. increased mobility.

Sources to PAE and NP

The investigation on possible sources of PAE's and NP's comprises car wash centres, a hospital, a kindergarten and an industrial laundry. Waste water inlet from the local WWTP, where the emissions from the sources converge, were analysed, as well as the deposition and two small rivers in the area.

The car wash results were based on 26 individual car washes. The kindergarten result is uncertain being based on only a single sample.

The order of importance of sources for DEHP, the most abundant phthalate in the waste water, were the laundries, followed by the deposition, the car wash centers and the hospital, accounting for about 12% of the influx of this substance to the WWTP.

For NP and di-iso-nonyl phthalate, the kindergarten and the car wash centres were significant sources.

The PAE concentrations in the deposition were very low compared to the wastewater.

The concentrations in the two small rivers were on the same or lower level as the deposition, indicating insignificant direct pollution.

A reasonable consistent balance for the mass flows of the measured substances shows that other sources the above mentioned must be present.

Emissions of LAS, PAE and NP

The result from a simple emission survey comprises annual mean inlet concentrations to the Roskilde WWTP of LAS's, PAE's and NP's derived from export/import figures, manufacturers, previous investigations and estimates concerning the fate of the substances in the different environmental compartments.

$$C_{\text{LAS}} = 20 \pm 20 \frac{\text{mg LAS}}{\text{liter}}$$

$$C_{\text{PAE}} = 150 \pm 128 \frac{\text{mg PAE}}{\text{liter}}$$

$$C_{\text{NPDE}} = 2 \frac{\text{mg NPDE}}{\text{liter}}$$

In the case of NP's no deviation is given due to insufficient data.

These figures are employed in the WWTP model to estimate the sensitivity of the outlet concentrations towards variations in the inlet and process parameters.

The Waste Water Treatment Plant

The steady-state compartment description of the biological reactors and settlers in WWTP's as employed in SimpleTreat has been evaluated with respect to an alternately operated WWTP situated in Roskilde, Denmark. The effect of substituting a complex discontinuous operation, involving alternating degradation and flow conditions between two reactors, with one single biological reactor with continuous flow (SimpleTreat) has been investigated by setting-up two models representing the respective operation schemes.

Through model simulations an empirical relationship between an aggregate pseudo 1st order degradation rate for the simple model and the aerobic and anoxic 1st order degradation rates, respectively, for the alternate operation has been established. When employing this aggregate degradation rate in the simple model an outlet concentration can be calculated that deviates no more than 2% from the alternate operation model. For substrates with aerobic half-lives longer than approximately 2 hours, the aggregate 1st order degradation rate can be set equal to the aerobic 1st order degradation rate.

To calibrate the simple model an experimental series was performed where inlet, outlet, primary sludge and secondary sludge samples were taken and analysed for PAE's, NP's and LAS's. The aerobic 1st order degradation rate and the partition coefficient between solid phase and water were used as calibration factors for each individual compound. Generally the modelled half-lives for the PAE's were low and the removal efficiencies of the NP's and PAE's were high compared to literature values. LAS half-life and adsorption properties corresponded well with previous investigations. The alternately operated WWTP is thus found to be very efficient with respect to biodegradation and overall removal of the investigated xenobiotics.

The Terrestrial Environment

The studies on the terrestrial environment included soil samples from eight locations:

- Preserved natural area not cultured for 50 -100 years.
- Ecologically cultured for 40 years.
- Manured sustainable in ecologically culture for 5 years, formerly conventionally cultured.
- Conventionally cultured using artificial fertiliser

- Sludge amended, medium amounts, cultured.
- Sludge amended, low amounts, cultured.
- Sludge amended with high amounts for 25 years, changed to artificial fertiliser 6 years before first sampling,
- Meadow in run-off zone from sludge storage

In addition to the soil samples selected samples of the applied sludge and other fertilisers were analysed for their possible contents of PAE, NP and LAS.

PAE and NP in soils

It can be concluded that as long as the different types of dressing are administered rationally the procedure apparently does not constitute as a potentially route of pollution with PAE's and NP.

PAE's and NP can be detected even in soils being uncultivated for at least 75 years, strongly indicating that other sources than dressing must be brought into play in order to explain the results. The most reasonable explanation seems to be contributions due to precipitation.

In the case of intensive sludge amendment applying high level sludge it appears that even 6-8 years after sludge was last administered significant concentrations of PAE's and NP's can be found. It is in this connection worthwhile to note that laboratory experiments have demonstrated that the half-life of e.g. DEHP is around 20 days under aerobic conditions.

Six years after the last amendment with high level sludge the concentration levels of, e.g., DnBP, DEHP and NP have been found to approach or even exceed the Danish soil quality criteria for these compounds (DnBP: 100 µg/kg, DEHP: 1000 µg/kg, NP: 10 µg/kg).

LAS in soils

Apart from locations subjected to intensive sludge amendment concentrations of LAS in all soil samples were found to be below 1 mg/kg, which is below a proposed preliminary soil quality criteria for LAS at 5 mg/kg. Thus, it is concluded that LAS's is unlikely to constitute a major ecotoxicological hazard in the terrestrial environment as long as the amendment of soils are carried out according to the prevailing regulations.

On the other hand it developed that if heavy sludge amendment is carried, the soil quality criteria may well be exceeded.

The presence of LAS even long after introduction to the soil is suggested to originate from presently undisclosed sources to LAS contamination in combination with the presence of minor areas of anaerobic nature.

Modelling of sludge amended soils

A simple model for the topsoil has been applied assuming the substance to be homogeneously distributed (completely mixed) as suggested in the European Union System for the Evaluation of Substances (EUSES). It is shown how the fraction of substance mass, which is leach from the topsoil, is a simple function of the ratio between the degradation half life-time and the adsorption coefficient.

It is concluded that the 'completely-mixed-condition' assumed in the simple soil model is a valid assumption when the retention factor (R) in the topsoil is in the magnitude for 50 or higher, and when the ploughings happens once a year. The 'completely-mixed-condition' in the topsoil is valid for both slightly and highly hydrophobic substances.

The simple topsoil model is applied in an analysis of the field scale measurements of DEHP contamination in agricultural soil. The topsoil model has been used to relate the sludge load to a resulting soil concentration value which is compared to the measured concentrations, by using a first order disappearance coefficient (K_{dis}). It appeared that the result was close to normal distribution for the K_{dis} values and the interval for about 95% of the probability is identified to be a half life of DEHP in the range of 7 to 38 years.

The model was subsequently used to approach a probabilistic risk assessment of the agricultural soil. Based on the soil quality criterion, the maximum acceptable concentration level in the soil was disclosed as a key parameter in the risk assessment. The recovery time period need for a polluted soil to recover after contamination, in which the soil concentration decreases below the soil quality criterion has been identified as a distribution function. It is shown how missing information on the DEHP concentration level at the beginning of the recovery time period can lead to much longer estimated time periods if the prediction needs to be safe. The maximum period of sludge amendment has been calculated for three different load intensities, the results being compared to the critical load where the soil quality criteria is fulfilled at infinite time.

The Aquatic Environment

Roskilde Fjord system, which leads from Roskilde at the bottom of the fjord to the outlet in Kattegat constitute an interesting example of an aquatic environment where xenobiotics are transported to the fjord by several pathways including discharge of waste water from the WWTP, run-off from a sludge storage, discharge from a series of small rivers as well as deposition.

PAE and NP in the fjord system

DEHP was the most abundant substance found in the fjord water, followed by much lower concentration of DBP, and minute amounts of BBP, DPP and NP. NPDE was not detected. The concentrations were very low, i.e., about a third of that in deposition and half of that in the streams, respectively.

No significant spatial variation for the concentration for any of the substance was found in the fjord water on a large geographical scale. A significant seasonal variation was found for DEHP and BBP having maxi-

mum in June and minimum in December. The variation was lesser at the inner part compared to the middle and the outer part of the fjord. At the narrow middle part the seasonal variation was highest, and a significant short-term variation was observed having a time-scale of hours.

For the rivers, the concentrations in the water were about the double of the fjord, the spatial and temporal variations being more pronounced and random.

In the fjord sediment DEHP and DBP were most abundant, occurring in much higher concentrations than in the water. The concentrations decreased by a factor of about 20 depending on the distance from the WWTP outlet. In a 22 cm deep core of fjord sediment, the DEHP concentrations decreased by approx. one order of magnitude from top to bottom, reflecting a significant historical increase of pollution level.

The concentrations found in the fjord water seem too low to adversely affect the environment, whereas the substances found in the sediments may influence the bottom living organism, and through them enter the food chain.

The experimental results are interpreted through model simulations of the water-sediment system. The shallow water compartment is considered to be totally mixed along the vertical axis. The fjord is divided into two sections of total mixing along the horizontal axis where the surface areas are large and into a narrow section where the horizontal flow is governed by dispersion on account of high flow.

A mass balance for the water compartment for the annual mean DEHP concentrations, comprising contributions from WWTP's, atmospheric deposition and freshwater contributions and removal mechanisms comprising microbial degradation and sedimentation, was performed. It revealed that the main removal process in the fjord is sedimentation of particle bound substances, or binding of dissolved substances to sediments, whereas horizontal transport through the water seems to be of lesser significance. The main contributors are freshwater intrusions from streams followed by atmospheric deposition and discharges from WWTP's.

The DEHP concentration profile in the sediment core was modelled by incorporating vertical diffusion, degradation and sedimentation from the water phase. A sedimentation rate of 2.5 mm per year and a degradation rate corresponding to the aerobic degradation rate in Roskilde WWTP were found.

The simple modelling approach, where the water and sediment compartments are treated separately only connected through substance exchange through sedimentation, seems appropriate in describing the fate of DEHP in the complex multi media fjord system.

Model evaluation

The sediment/water exchange was selected as a key-process in generic compartment models as SimpleBox. It appears that the description of diffusive transfer is not well established in the generic compartment model. The full solution of the governing equation for sediment diffusion

indicates an extremely high rate of substance uptake, as long the contamination in the sediment is limited. Contrary, initially the single sediment box approach yields a constant diffusion rate. After a specific period the single box description approaches validity although it was concluded that the time period can easily be in the magnitude of many years. In case of steady state the one box approach will always overestimate the dissolved water concentration in relation to the more complete sediment description. In conclusion it appears that the one sediment box approach is insufficient to include a realistic diffusion mechanism. But in many cases the deposition and thus the burial from the sediment box of fixed thickness will become the dominating factor in the sediment/ water column exchange of substance and in that case the inadequate description of diffusion will not be important.

The generic compartment models needs to be mathematically simple in order to be usable as decision support and a more realistic description of the diffusive transfer into the sediment will introduce a rather high level of mathematical complexity. Thus, it is suggested simply to accept the generic compartment models as valid when the diffusive description is negligible.

Suggestions for future work

The present work suffers from a shortage in data, i.e., the analytical data are vitiated by significant uncertainties. Further the statistical analyses are based on few samples only. This is especially the case in the studies on sources to PAE's and NP's and in the study on selected xenobiotics in the terrestrial environment. Obviously future studies call for larger number of samples in order to improve the statistical treatment of the data and thus the subsequent modelling approach. In these context further studies of critical processes, e.g., in connection with sludge amendment should be conducted

The studies on the fate of PAE's, NP's and LAS's in the terrestrial environment, the investigated location 7 (*vide supra*) constitutes an excellent field site for further studies. Thus, it is suggested that a major field experiment be initiated including a substantial amount of samples, the single samples being taken to a depth of not less than 2 m, which will allow disclosure of concentration profiles as a result of vertical migration. The study should be extended for a longer period of time in order to verify any variation in the concentration profiles due to degradation and/or downward transport.

It seems further appropriate to include a broader range of xenobiotics in the study. Thus, the fate of selected POP's, PAH's and pesticides should be addressed.

In relations to the aquatic environment further studies should address dating sediment cores in the fjord in combination with appropriate analyses for selected xenobiotics. The aim of this study would be to elucidate the actual nature of the pollution history of the fjord taking into account the various sources such as atmospheric deposition and input due to the WWTP. In the latter case further studies on the transformation of a broader range of xenobiotics should be addressed. The investigated WWTP comprise nitrification as well as denitrification which gives an

opportunity to investigate the fate of the xenobiotics as a function of the operating conditions.

Further studies, e.g., using the above mentioned field location, should definitely look in the possible combination with effect studies in order to obtain both effect and fate data, i.e., both PNEC and PEC values to be included in the risk assessment.

The above projects would lead to a highly valuable data material which would enable comprehensive modelling including SAR/QSAR modelling and ranking studies to elucidate the mutual importance of different scenarios for the pollution and subsequent remediation of the various environmental matrices.

The ultimate aim with the further studies on probabilistic risk assessment is to develop appropriate toolboxes for decision-makers to evaluate, e.g., remediation times for contaminated areas. In more general terms the present study calls for further studies to improve the predictive models to be used in study of fate of xenobiotics in various environmental compartments.

Appendix: Products originating from the project

Papers (with peer review):

SAR/QSAR approaches to solubility, partitioning and sorption of phthalates. Marianne Thomsen, Angélique G. Rasmussen, Lars Carlsen. *Chemosphere* **38** (1999) 2613-2624

Solubility of phthalates revisited. Environmental implications. Marianne Thomsen, Søren Hvidt, Lars Carlsen. in: Walker, J.D. ed., *Handbook on QSARs for predicting Environmental Fate of Chemicals.* Society of Environmental Toxicology and Chemistry, Pensacola, FL, USA, 2001, in press

Solubilities and surface activities of phthalates investigated by surface tension measurements. Marianne Thomsen, Lars Carlsen, Søren Hvidt. *Environ.Toxicol.Chem.* **20** (2001) 127-132

Humic complexes of di-ethyl phthalates: molecular modelling of the sorption process. Hans-Rolf Schulten, Marianne Thomsen, Lars Carlsen, *Chemosphere*, **45** (3), 2001, 357-369

Solubility of nonylphenol and nonylphenol ethoxylates. On the possible role of micelles. Rikke Brix, Søren Hvidt, Lars Carlsen. *Chemosphere*, **44** (2001) 759-763.

Phthalates and nonylphenols in differently dressed soils. Jørgen Vikelsøe, Marianne Thomsen, Lars Carlsen. Submitted to *Science of the total Environment*.

Model Description of an Alternately Operated Wastewater Treatment Plant - Evaluation of the Applicability of SimpleTreat. Patrik Fauser, Peter B. Sørensen, Lars Carlsen, Jørgen Vikelsøe. Submitted to *Chemosphere*.

Phthalates, Nonylphenols and LAS in an Alternately Operated Wastewater Treatment Plant – Fate Modelling Based on Measured Concentrations in Wastewater and Sludge. Patrik Fauser, Jørgen Vikelsøe, Peter B. Sørensen, Lars Carlsen. Submitted to *Water Research*.

Papers (other):

Kilder til og forekomst af nonylphenoler og phthalater i spildevand og jord. Jørgen Vikelsøe, Marianne Thomsen, Lars Carlsen. in: 'Diffuse forureninger på landbrugs- og byjord', Akademiet for de Tekniske Videnskaber (ATV), 1998

Reports:

Sources of phthalates and nonylphenols in municipal waste water. A study in a local environment. Jørgen Vikelsøe, Marianne Thomsen & Elsebeth Johansen. NERI Technical Report No. 225, 1998

Prediction of aqueous solubilities and octanol - water coefficients of phthalates by the UNIFAC group contribution method. Angélique G. Rasmussen. Research Notes from NERI No. 69, 1998.

Phthalater i Miljøet. Opløselighed, Sorption og Transport. Marianne Thomsen & Lars Carlsen. Faglig rapport fra DMU, nr. 249, 1998.

Phthalates and nonylphenols in soil. A field study of different soil profiles. Jørgen Vikelsøe, Marianne Thomsen, Elsebeth Johansen & Lars Carlsen. NERI Technical report No. 268, 1999.

Linear alkylbenzene sulphonates (LAS) in soils. A field study of different soil profiles. Lars Carlsen, Mai-Britt Volting & Jeannette Kjelsmark. Research Report from NERI No. 134, 2000.

Theoretical evaluation of the sediment/water exchange description in generic compartment models (SimpleBox). Peter B. Sørensen, Patrik Fauser, Lars Carlsen & Jørgen Vikelsøe. NERI Technical Report No. 360. 2001.

Paradigm for analyzing complex model uncertainty. Peter B. Sørensen, Lars Carlsen, Patrik Fauser, Jørgen Vikelsøe. Research Notes from NERI, No. 141, 2001.

Modeling Analysis of Sewage Sludge Amended Soil. Peter B. Sørensen, Lars Carlsen & Angélique G. Rasmussen. NERI Technical Report No. 361, 2001.

Phthalates and Nonylphenols in Roskilde Fjord - A Field Study and Mathematical Modelling of Transport and Fate in Water and Sediment. Jørgen Vikelsøe, Patrik Fauser, Peter B. Sørensen & Lars Carlsen. NERI Technical Report No. 339, 2001.

Phthalates, Nonylphenols and LAS in Roskilde Wastewater Treatment Plant - Fate Modelling Based on Measured Concentrations in Wastewater and Sludge. Patrik Fauser, Peter B. Sørensen, Jørgen Vikelsøe, Lars Carlsen. NERI Technical Report No. 354, 2001.

Persistent Organic Pollutants in Soil, Sludge and Sediment - A Multi Analytical Field Study of Selected Organic Chlorinated and Brominated Compounds

Jørgen Vikelsøe, Marianne Thomsen, Lars Carlsen, Elsebeth Johansen
Research Report from NERI, Denmark (in prep)

On the fate of Xenobiotics. The Roskilde region as case story. Lars Carlsen, Peter B. Sørensen, Jørgen Vikelsøe, Patrik Fauser, Marianne Thomsen. Research Report from NERI, Denmark (draft version for comments) [FINAL report]

Diverse:

Undersøgelse af Nonylphenoler og Phthalater i Spildevand og Jord. Jørgen Vikelsøe. Det Må Ud, nr. 4, sept. 1998.

Conference contributions and lectures:

QSAR approaches to solubility, partitioning and sorption of phthalates. Marianne Thomsen, Angélique G. Rasmussen & Lars Carlsen. contribution to the 7th Annual Meeting of SETAC-Europe, Amsterdam, Apr. 1997.

SAR/QSAR approaches to solubility, partitioning and sorption of phthalates. Marianne Thomsen, Angélique G. Rasmussen & Lars Carlsen. contribution to Kemisk Forenings Årsmøde, Odense, juni 1997

The fate of xenobiotic compounds in soil. Marianne Thomsen, Jørgen Vikelsøe, Elsebeth Johansen & Lars Carlsen. Contribution to the 8th Annual Meeting of SETAC Europe, Bordeaux, Apr. 1998

Model analysis for the fate of anthropogenic substances in differently dressed soils. Angélique G. Rasmussen, Peter B. Sørensen, Marianne Thomsen, Jørgen Vikelsøe & Lars Carlsen. Contribution to the 8th Annual Meeting of SETAC-Europe, Bordeaux, Apr. 1998

Forekomst af alkylphenoler og phthalater i miljøet. Roskildeområdet som case-story. Lars Carlsen. Lecture at workshop arr. af Center for ØstrogenlignendeStoffer (SMP), Apr. 1998

Solubility of phthalates revisited. Environmental implications. Marianne Thomsen, Søren Hvidt & Lars Carlsen. Contribution to the 8th International Workshop on Quantitative Structure-Activity Relationships (QSARs) in the Environmental Sciences - QSAR 98, Baltimore, May 1998.

Kilder til og forekomst af nonylphenoler og phthalater i spildevand og jord. Jørgen Vikelsøe, Marianne Thomsen & Lars Carlsen. ATV møde: 'Diffuse forureninger på landbrugs- og byjord', May 1998.

Solubility of phthalates revisited. Environmental implications. Marianne Thomsen, Søren Hvidt & Lars Carlsen. Contribution to Kemisk Forenings Årsmøde, Odense, juni 1998

Determination of remediation times for sludgeamended agricultural soils. Peter B. Sørensen, Jørgen Vikelsøe and Lars Carlsen. Contribution to the 9th Annual Meeting of SETAC-Europe, Leipzig, May 1999

Integrated uncertainty analysis of LAS emission/fate models. Patrik Fauser, Peter B. Sørensen and Lars Carlsen. Contribution to the 9th Annual Meeting of SETAC-Europe, Leipzig, May 1999

Solubility of phthalates revisited. Environmental implications. Marianne Thomsen, Søren Hvidt and Lars Carlsen. Contribution to Dansk Miljøforskning 1999, DMU, Copenhagen, Aug. 1999

Determination of remediation times for sludgeamended agricultural soils. Peter B. Sørensen, Jørgen Vikelsøe and Lars Carlsen. Contribution to Dansk Miljøforskning 1999, DMU, Copenhagen, Aug. 1999

The fate of xenobiotic compounds in soil. Marianne Thomsen, Jørgen Vikelsøe, Elsebeth Johansen and Lars Carlsen. Contribution to Dansk Miljøforskning 1999, DMU, Copenhagen, Aug. 1999

Phthalates in Aqueous Solution and at Surfaces (oral). Marianne Thomsen. Seminar, Roskilde University, Nov., 1999.

Emission and Fate of DEHP in Roskilde Municipality with Emphasis on Roskilde Fjord. P. Fauser, P.B. Sørensen, J. Vikelsøe and L. Carlsen. Contribution to SETAC 2000: 3rd SETAC Word Conference and 10th Annual Meeting of SETAC-Europe, Brighton, May 2000.

Evaluation of the one box approach in the generic compartment modelling for the sediment/water transfer. P.B. Sørensen and P. Fauser. Contribution to SETAC 2001: 11th Annual Meeting of SETAC-Europe, Madrid, May 2001

Specialerapporter:

Phthalaters miljøkemi. Marianne Thomsen. Specialeprojekt, DMU-MIKE/Københavns Universitet, 1997.

Opløselighed og sorption af Nonylphenol. Rikke Brix. Specialeprojekt, DMU-MIKE/Københavns Universitet, 1998

LAS i det terrestriske miljø, herunder udvikling af mikrobølgeekstraktions- og isomerspecifik HPLC – metode. Jeannette Kjelsmark. Specialeprojekt, DMU-MIKE/Københavns Universitet, 2000

Projektrapporter:

Phthalaters opløselighed og migration. Helene Hodal, Louise Askjær Pedersen, Ketil Koop-Jakobsen & Ole Sørensen. semester projekt, Roskilde Universitetscenter, NAT-BAS, 1998.

National Environmental Research Institute

The National Environmental Research Institute, NERI, is a research institute of the Ministry of Environment and Energy. In Danish, NERI is called *Danmarks Miljøundersøgelser (DMU)*.

NERI's tasks are primarily to conduct research, collect data, and give advice on problems related to the environment and nature.

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Publications:

NERI publishes professional reports, technical instructions, and the annual report. A R&D projects' catalogue is available in an electronic version on the World Wide Web.

Included in the annual report is a list of the publications from the current year.

Faglige rapporter fra DMU/NERI Technical Reports

2000

- Nr. 327: Konsekvenser af ny beregningsmetode for skorstenshøjder ved lugtemission. Af Løfstrøm, L. (Findes kun i elektronisk udgave)
- Nr. 328: Control of Pesticides 1999. Chemical Substances and Chemical Preparations. By Krongaard, T., Petersen, K.K. & Christoffersen, C. 28 pp., 50,00 DKK.
- Nr. 329: Interkalibrering af metode til undersøgelser af bundvegetation i marine områder. Krause-Jensen, D., Laursen, J.S. & Larsen, S.E. (i trykken)
- Nr. 330: Digitale kort og administrative registre. Integration mellem administrative registre og miljø-/naturdata. Energi- og Miljøministeriets Areal Informations System. Af Hansen, H.S. & Skov-Petersen, H. (i trykken)
- Nr. 331: Tungmetalledfald i Danmark 1999. Af Hovmand, M.F. Kemp, K. (i trykken)
- Nr. 332: Atmosfærisk deposition 1999. NOVA 2003. Af Ellermann, T., Hertel, O. & Skjødt, C.A. (i trykken)
- Nr. 333: Marine områder – Status over miljøtilstanden i 1999. NOVA 2003. Hansen, J.L.S. et al. (i trykken)
- Nr. 334: Landovervågningsoplande 1999. NOVA 2003. Af Grant, R. et al. (i trykken)
- Nr. 335: Søer 1999. NOVA 2003. Af Jensen, J.P. et al. (i trykken)
- Nr. 336: Vandløb og kilder 1999. NOVA 2003. Af Bøgestrand J. (red.) (i trykken)
- Nr. 337: Vandmiljø 2000. Tilstand og udvikling. Faglig sammenfatning. Af Svendsen, L.M. et al. (i trykken)
- Nr. 338: NEXT I 1998-2003 Halogenerede Hydrocarboner. Samlet rapport over 3 præstationsprøvnings-runder . Af Nyeland, B. & Kvamm, B.L.
- Nr. 339: Phthalates and Nonylphenols in Roskilde Fjord. A Field Study and Mathematical Modelling of Transport and Fate in Water and Sediment. The Aquatic Environment. By Vikelsøe, J., Fauser, P., Sørensen, P.B. & Carlsen, L. (in press)
- Nr. 340: Afstrømningsforhold i danske vandløb. Af Ovesen, N.B. et al. 238 s., 225,00 kr.
- Nr. 341: The Background Air Quality in Denmark 1978-1997. By Heidam, N.Z. (in press)
- Nr. 342: Methyl t-Buthylether (MTBE) i spildevand. Metodeafprøvning. Af Nyeland, B. & Kvamm, B.L.
- Nr. 343: Vildtudbyttet i Danmark i jagtsæsonen 1999/2000. Af Asferg, T. (i trykken)

2001

- Nr. 344: En model for godstransportens udvikling. Af Kveiborg, O. (i trykken)
- Nr. 345: Important summer concentrations of seaducks in West Greenland. An input to oil spill sensitivity mapping. By Boertmann, D. & Mosbech, A. (in press)
- Nr. 346: The Greenland Ramsar sites. A status report. By Egevang, C. & Boertmann, D. (in press)
- Nr. 347: Nationale og internationale miljøindikatorssystemer. Metodeovervejelser. Af Christensen, N. & Møller, F. 161 s., 150,00 kr.
- Nr. 348: Adfærdsmodel for persontrafik. Modelkoncept. ALTRANS. Af Rich, J.H. & Christensen, L. (i trykken)
- Nr. 349: Flora and fauna in Roundup tolerant fodder beet fields. By Elmegaard, N. & Bruus Pedersen, M. (in press)
- Nr. 350: Overvågning af fugle, sæler og planter 1999-2000 med resultater fra feltstationerne. Af Larusen, K. (red.) (i trykken)
- Nr. 351: PSSD – Planning System for Sustainable Development. A Methodical Report. By Hansen, H.S. (ed.)
- Nr. 352: Naturkvalitet på stenrev. Hvilke indikatorer kan vi bruge? Af Dahl, K. et al. 128 s., 140,00 kr.
- Nr. 353: Ammoniakemission fra landbruget siden midten af 80'erne. Af Andersen, J.M. et al. 45 s., 50,00 kr.
- Nr. 354: Phthalates, Nonylphenols and LAS in Roskilde Wastewater Treatment Plant. Fate Modelling Based on Measured Concentrations in Wastewater and Sludge. By Fauser, P. et al. 103 pp., 75,00 DKK.
- Nr. 355: Veststadil Fjord før og efter vandstandshævning. Af Søndergaard, M. et al. (elektronisk)
- Nr. 356: Landsdækkende optælling af vandfugle, vinteren 1999/2000. Af Pihl, S., Petersen, I.K., Hounisen, J.P. & Laubek, B. 46 s., 60,00 kr.
- Nr. 357: The Danish Air Quality Monitoring Programme. Annual report for 1999. By Kemp, K. & Palmgren, F. (electronic)
- Nr. 358: Partikelfiltre på tunge køretøjer i Danmark. Luftkvalitets- og sundhedsvurdering. Af Palmgren, F. et al. (Foreløbig elektronisk udgave)
- Nr. 359: Forekomst af "afvigende" isbjørne i Østgrønland. En interviewundersøgelse 1999. Af Dietz, R., Sonne-Hansen, C., Born, E.W., Sandell, H.T. & Sandell, B. (i trykken)
- Nr. 360: Theoretical Evaluation of the Sediment/Water Exchange Description in Generic Compartment Models (Simple Box). By Sørensen, P.B., Fauser, P., Carlsen, L. & Vikelsøe, J. 58 pp., 80,00 DKK.
- Nr. 361: Modelling Analysis of Sewage Sludge Amended Soil. By Sørensen, P., Carlsen, L., Vikelsøe, J. & Rasmussen, A.G. (in press)
- Nr. 362: Aquatic Environment 2000. Status and Trends – Technical Summary. By Svendsen, L.M. et al. (in press)
- Nr. 363: Regulering af jagt på vandfugle i kystzonen. Forsøg med døgnregulering i Østvendssyssel. Af Bregnballe, T. et al. (i trykken)
- Nr. 364: Vingeindsamling fra jagtsæsonen 2000/2001 i Danmark. Wing Survey from the 2000/2001 Hunting Season in Denmark. Af Clausager, I. (i trykken)

The report summarizes the main findings of the project “Xenobiotic Compounds”. The single chapters correspond to the different sub-projects, such as the modelling approach, basic studies on phthalates and nonylphenols, sources to phthalates and nonylphenols, emissions of LAS, phthalates and nonylphenols, the wastewater treatment plant, the terrestrial environment, the aquatic environment and model validation, respectively.

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