THE DEVELOPMENT AND HARMONISATION OF RISK ASSESSMENT PROCEDURES TO EVALUATE THE ENVIRONMENTAL IMPACT OF TOXIC SUBSTANCES

A thesis submitted to Brunel University for the degree of Engineering Doctorate

by

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Environment Agency.

VOLUME 1

SEPTEMBER 2001

ABSTRACT

The environmental risk assessment of substances is introduced and the various controls used to protect the environment are outlined. The European notification system and the risk assessments required as part of the system are detailed. Through an examination of the existing European Union System for the Evaluation of Substances tool and sensitivity analyses based on variability in the measurement of physico-chemical properties for a substance, a spreadsheet model was developed to allow multiple risk assessments for the same substance to be calculated simultaneously. The development and testing of the NECXES spreadsheet tool are documented in detail.

Data for the capacity and dilution factor at Sewage Treatment Plants (STPs) in England and Wales were collated and statistically analysed and compared to European default values used for generic risk assessments. The default capacity value for STPs (10,000 population equivalents) was protective of 70% of the STPs sampled. The remaining 30% however, a small number of large works, contributed 94% of the total effluent discharged from STPs in England and Wales.

The STP data were used with the NEXCES tool to perform and compare probabilistic risk assessments to those calculated using deterministic methods for a number of test substances. The probabilistic calculations produced a lower median exposure concentration for water than the generic assessment for all of the test substances. Regression analysis allowed the probability of adverse effects to be quantified for the various deterministic risk values. The NEXCES tool was also used to develop a rapid assessment tool for new substances, in the form of contour plots, which can be used to assess the risk of substances using minimal data.

The main conclusions and contributions to the academic and industrial fields, as well as the field of environmental technology are presented. Areas where there are opportunities for further research are also outlined.

ACKNOWLEDGEMENTS

I would like to acknowledge the efficient and effective supervision and support given by my academic and industrial supervisors, Dr. Sue Grimes of the Centre for Environmental Research, Brunel University and Dr. Jim Wharfe of the National Centre for Ecotoxicology and Hazardous Substances, Environment Agency. I also extend my gratitude to the two sponsors of this Engineering Doctorate, the Engineering and Physical Science Research Council and the National Centre for Ecotoxicology and Hazardous Substances. Particular thanks go to the managers and members of the teams in which I completed my research: Dr. Steve Robertson, for his vision and drive; Dr. Geoff Brighty, for the opportunity to work on a real pollution incident; and Dr. Derek Tinsley, for his enthusiasm and the chance to get first-hands experience at the laboratory.

I would also like to thank Oliver Warwick for his encouragement and critical appraisal, and Jan Krokowski, Anthony Williamson and Rachael Dils to mention but a few colleagues who have made the four years fly by. I would like to acknowledge Dr. Jack de Bruijn, RIVM for making the SimpleTreat model available to me, and Dr. Tjalling Jager for his interest and ideas.

I would like to thank my fellow Research Engineers on the Engineering Doctorate programme who in our meetings at modules and other social occasions have made the light at the end of the tunnel seem closer. To my friends and family who have been unwavering in their support of me and particularly those who have commented on the many drafts of this thesis, you know how much your efforts have meant to me and your help has been instrumental in the completion of my doctorate.

Finally thanks go to the Brunel Engineering Doctorate team and particularly Carole Carr, the lynch-pin of the Engineering Doctorate programme at Brunel university, for her help, support and the many coffees and biscuits through the years.

It has been said (Sutter II, 1993) that Prometheus was the patron deity of risk assessors:

> *Prometheus (Greek: forethought) collected all the hazards in the World and placed them in a box. He warned his brother Epimetheus (Greek: afterthought) to keep the hazards contained. Epimetheus however, allowed Pandora (Greek: all-giving) access to the box, which without proper instruction she opened, releasing all the hazards within. Prometheus was the only one to be punished by Zeus.*

May we be more promethean in our assessment of risks, and ensure all hazards are accompanied with clear and understandable instructions and warnings. To do this our risk assessments need to be rapid and transparent and the resulting controls effective.

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EXECUTIVE SUMMARY

Introduction to the Engineering Doctorate Programme

The Engineering Doctorate is a four-year research degree, based in industry and supported by a programme of professional development courses. The Engineering and Physical Science Research Council (EPSRC) sponsored EngD programmes were set up in response to industry needs for more industrially orientated research students.

Of an original five centres set up to run EngD programmes the Brunel/Surrey centre was unique in that all of its projects followed a distinct theme, that of 'Environmental Technology', all new and existing centres are now required to follow a theme. The Brunel/Surrey EngD aims to provide graduates with the necessary skills to balance environmental risk along with all of the traditional variables of cost, quality, productivity, shareholder value, legislative compliance etc.

The Brunel/Surrey EngD programme involves a balance of pulls (Figure 1), the Research Engineer must balance the academic and industrial requirements of the research while considering the environmental issues inherent in the project or projects undertaken.

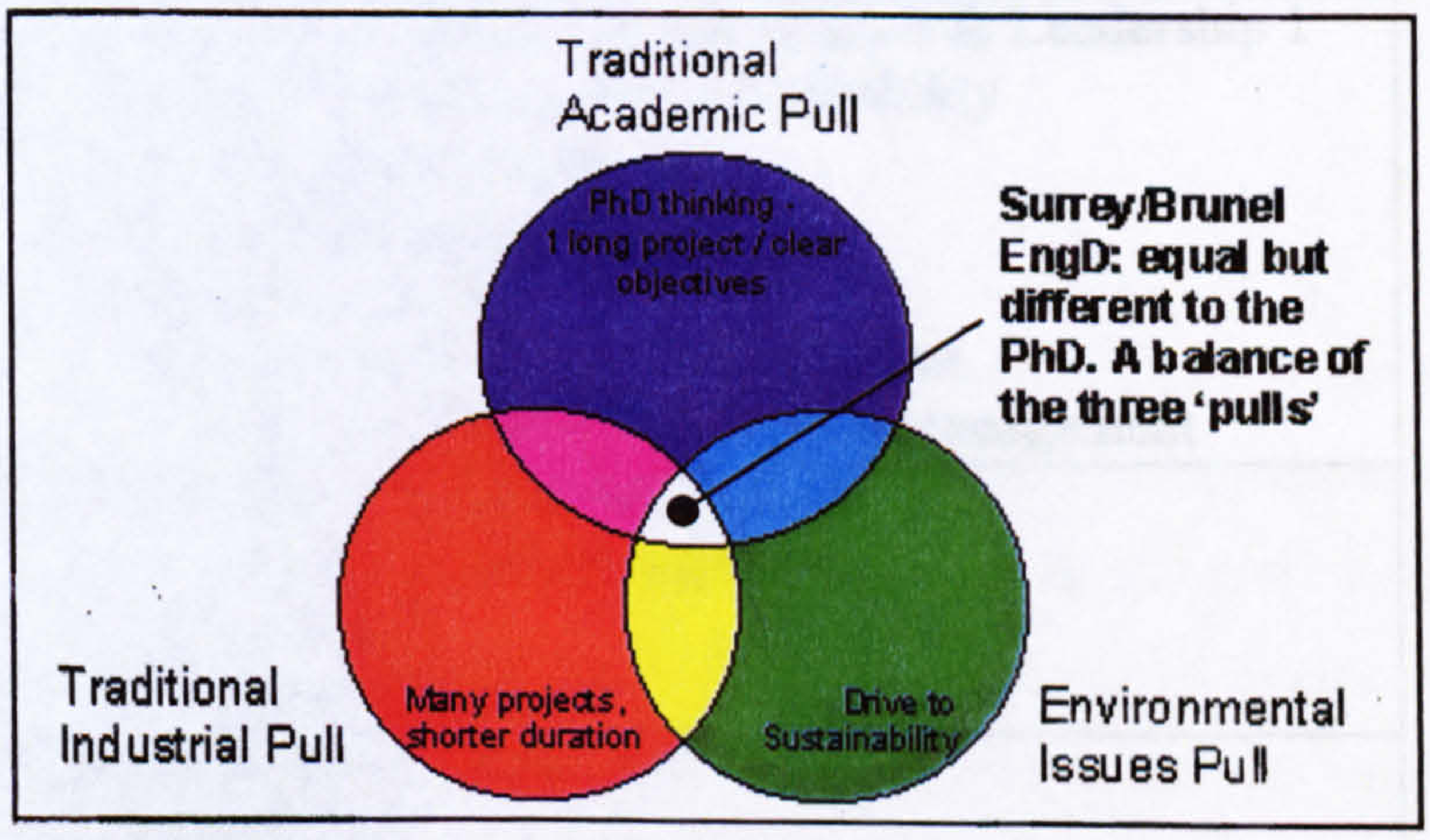

Figure 1 – The three elements of an EngD research project

The overall objective of the Brunel/Surrey EngD programme is:

> "...to create graduate Research Engineers with the necessary background knowledge, skills and expertise to understand the relationship between the environment, technology and business and to apply this understanding to the development, promotion and execution of corporate strategy."
>
> Brunel & Surrey EngD Course Handbook 2000-2001

The EngD is distinguished by its programme of complementary courses that must be completed by the Research Engineers (REs). These courses have the following aims:

- To present a view of the relationship between engineering and the environment including sociological aspects
- To provide professional development in key business skills and competencies
- To close any gaps in the knowledge required to undertake the research project

The programme of courses is comprised of compulsory and elective modules, and the completion of a relevant assignment is usually requires after the course. The modules taken and completed during this research are outlined in the following table:

Year 1	Induction course: Communication & Leadership 1 Clean Technology and Sustainability Project Management Life Cycle Approaches Hands on Audit Risk Perception & Communication + elective – Conference Project Management
Year 2	Sociology 1 Research Methods Sociology 2 Environmentalism Leadership 2 Environmental Law
Year 3	Financial Management Marketing Risk Management
Year 4	Talking to the Media Materials in the Environment Environmental Economics and Sustainability + elective – EPSRC Graduate School

During the four-year research programme the REs are required to submit progress reports on a six-monthly basis. The six-monthly reports are a record of progress toward the ongoing research objectives. These reports do not necessarily describe work at a conclusive stage, simply the progress made towards the set deliverables in previous reports.

The Structure of this Portfolio

This portfolio comprises two volumes, the first of which contains the main thesis from this research, including this executive summary, a more detailed introduction into the area of research, the development of the research and the main findings, conclusions and contributions to the field of environmental technology as well as the academic and industrial fields. A list of publications has been included in this first volume along with supporting information and documentation in the form of appendices.

The second volume contains a set of bound six-monthly reports charting the progress of this research along with the progress towards the agreed objectives from the previous period and set objectives for the following six-months. At each six-month interval the aims and objectives of the EngD programme and progress towards these were also considered. The main research has been presented in the first volume of this portfolio and the second volume and the six-monthly reports contained should be should be considered as progress summary notes for each six-month period.

Outline of the Research

The importance of chemicals in our society, their potential to cause harm and their risk assessment are introduced in *Chapter 1*. The development of environmental legislation to control hazardous substances is briefly outlined. The role and responsibilities of the Environment Agency, the primary regulatory body in England and Wales, and one of its main national centres, the National Centre for Ecotoxicology and Hazardous Substances, is described.

In *Chapter 2* the risk assessment procedure required under the European Notification System for new and existing substances is outlined. Both the EU Technical Guidance Document and the European Union System for the Evaluation of Substances (EUSES) for performing risk assessments are introduced. The quantitative structural activity relationships (QSAR) that are used to predict partition coefficients are detailed along with the "base set" physico-chemical data used to calculate the risk assessments.

Initial sensitivity analysis investigations to determine the effect of the variability in the measurement of physico-chemical properties on the exposure assessment are reported. The boiling point and melting point values had no effect, while variations in the vapour pressure and solubility in water values were found to have a small effect (±3%) on the assessment. Variations in the *Kow* value had a much larger effect (±13%) for most of the substances tested.

The choice of QSAR used to estimate *Koc* from *Kow* was also found to have a large effect (±30%) on the resulting assessment. The EU default QSAR was found to produce a value below the average of the range, which cannot be considered to be a worst case for the aquatic compartment.

The development of a spreadsheet-based model (NEXCES) for performing risk assessments for the aquatic compartment on the local scale is reported in *Chapter 3*. There is a need for such a model due to the inability of EUSES to perform multiple treatments of the same assessment.

Construction of the spreadsheet is documented and addresses how some of the problems, as detailed in the EUSES Blacklist, were overcome. This included the latest SimpleTreat model and the ability to select the QSAR for predicting the partition coefficient *Koc* from *Kow*.

Validation of the spreadsheet is outlined. Investigations into the effect of variance in the measurement of the vapour pressure and *Kow* values are used to demonstrate the power of the NEXCES tool. Five thousand calculations were run for variations in each physico-chemical property producing distributions and ranges for the risk characterisation ratios.

In *Chapter 4*, two parameters, dilution and capacity, used in the modelling of sewage treatment plants (STP) in the risk assessment system are examined. The value for the dilution factor available at the point of discharge from a STP can be a critical value in the risk assessment. Data were collated from the 8 administrative regions in England and Wales. These were statistically analysed to determine how the data for England and

Wales compared with the generic default values used in the European risk assessment system.

By capacity, 30% of STPs were larger than the EU default value of 10,000 population equivalents and contribute to more than 90% of the total effluent discharged by STPs in England and Wales. The dilution data produced a median value of 5.2, which is less than the EU default value of 10, which means generic risk assessments may under-predict risk. Geographical information system techniques were used to produce geographical plots to highlight areas of particular concern.

The data collated in *Chapter 4* were then re-sampled and used to perform probabilistic assessments for test substances in *Chapter 5*, using the spreadsheet model developed in *Chapter 3*. The developed NEXCES tool was used to perform probabilistic risk assessments using STP capacity and dilution factor data. The data collated were re-sampled to produce 5000 pairs of values to run a similar number of risk assessments.

Probabilistic and deterministic risk assessments for a number of test substances were performed and compared. Regression analysis of the results from these was used to determine the probability values for the deterministic RCR thresholds (>1, >10, etc.).

The development of a rapid risk assessment tool for new substances is described in Chapter 6. The tool was developed in response to a real need by the UK competent authority for the European notification system. Preliminary contour plots of risk depending on a substance's *Koc* value and the soluble fraction discharged from the STP are examined.

The procedure was refined to include consideration of the SimpleTreat model, measuring local exposure in water rather than risk. These analyses illustrate that local exposure is independent of the Henry's law constant (*HENRY*) at low values of *HENRY*. These findings have led to the final development of the rapid assessment tool for new cosmetic substances, where *HENRY* value is less than 0.1. The contour plots allow risk assessments for substances to be rapidly performed based on the *Kow*, and toxicity alone.

The research presented in this thesis is briefly reviewed in *Chapter 7*. The main findings from the research are presented, with a consideration of how the work fits into the wider context of the control and risk assessment of substances in the environment.

The contributions to the academic and industrial fields are outlined along with the contributions to the field of environmental technology. Some of the areas where there are opportunities for further work are also outlined.

Main Conclusions

The initial aim of this research was to examine the different ways in which hazardous substances are controlled and this was done through working with a number of the key groups in the National Centre for Ecotoxicology and Hazardous Substances. The various risk and hazard assessment systems used by the CAU, ETS and DTA were reviewed.

From the review process two main areas of interest were proposed for further investigation, using an Environment Agency format, and the two project proposals were presented as part of the 24-month dissertation:

1. Sensitivity analysis of values in the environmental exposure section of the European Notification risk assessment system as performed in the EUSES system.
2. Comparative study of single substance and whole sample toxicity risk assessments on selected discharges

The first of these project proposals became the focus of the remainder of this research. The spreadsheet tool was developed to initially facilitate the sensitivity analyses but then allowed the project proposal to be expanded to include probabilistic risk assessments and the development of the rapid assessment contour plots.

The main contributions arising from this research have led, for the first time to:

- Quantification of some of the sensitivities in the exposure assessment of the EU generic risk assessment system
    - Confirmation that measurement errors for *Kow* have the greatest effect on the resulting risk assessment of all physico-chemical properties examined
    - Demonstration that the European default QSAR for predicting *Koc* from *Kow* does not produce a worst-case assessment for the aquatic compartment

- Development, documentation and testing of a spreadsheet tool implementing the latest model for sewage treatment works and capable of rapidly performing multiple treatments of the same assessment making probabilistic risk assessments feasible

- Demonstration of the critical nature of the dilution factor in the risk assessment process through the collated and analysis of paired data for dilution and capacity of STPs in England and Wales

- Demonstration that the EU generic risk assessment overstates the capacity of STPs in 70% of cases and as a result the default value of <10,000 PE is protective of this works

- Quantification of the risk associated with deterministic values through comparative probabilistic risk assessments for a number of test substances, thus providing a better indication of the need for additional testing

- Development of a rapid risk assessment tool for new substances, to produce a visual "litmus test" which allows preliminary assessments to be made using minimal data for a substance

CHAPTER 1

INTRODUCTION

SUMMARY

The importance of chemicals in our society, their potential to cause harm and their risk assessment are introduced. The development of environmental legislation to control hazardous substances is briefly outlined. The role and responsibilities of the Environment Agency, the primary regulatory body in England and Wales, and one of its main national centres, the National Centre for Ecotoxicology and Hazardous Substances, is described.

The European Notification System and the risk assessment of new and existing substances is reviewed. Principles of ecotoxicology and the tests performed to produce toxicity data for risk assessments are explained along with the interpretation of these data.

The scope of this thesis is set out and the research undertaken introduced.

1 INTRODUCTION

The UK chemical industry is one of the largest in the world. Chemicals are ubiquitous and are used extensively in our society in almost every activity:

- Agriculture
- Industry
- Medicines
- Petrochemicals

The various chemical substances are used in our society in differing volumes and under different conditions. All chemical substances represent a risk at some level, whether it is practically negligible or an extremely high risk. Paracelsus (1493-1541) made the observation that (Moriarty, 1993):

> "All things are poisons, for there is nothing without poisonous qualities. It is only the dose which makes a thing a poison."

Similarly all things and activities can pose a hazard. It is the probability of occurrence combined with the severity of the hazard that represents the risk. The risk is defined as the intrinsic ability to cause harm (hazard) and the probability of this happening.

In all stages of the life cycle of a chemical substance there is therefore a need to identify hazards, quantify risks, and where necessary reduce the risks. This four-year Engineering Doctorate has focused on the development of new and existing risk assessment procedures as used and practised within the Environment Agency for England and Wales.

Current systems for the assessment of substances were reviewed and compared. An understanding of the underlying sciences was obtained through investigating the field of ecotoxicology and engaging in the practical tasks of performing ecotoxicology tests.

In the sections that follow the size of the potential problem is outlined by reviewing the magnitude of the chemical industry, and the role of the Environment Agency as the relevant regulatory body. In particular, the role of the National Centre for Ecotoxicology and Hazardous Substances is described, along with the groups within which risk assessment procedures were studied. A brief examination of the history and development of the relevant environmental legislation is presented.

1.1 THE CHEMICAL INDUSTRY

There are more than 100,000 chemicals on the European Inventory of Existing Chemical Substances, (EINECS) that are marketed within Europe. Several hundred chemicals are added to this figure annually. The Organisation for Economic Co-operation and Development (OECD) classes more than 4000 substances as *high production volume chemical* (HPVC), those manufactured in quantities greater than 1000 tonnes/year.

The chemical industry is the 4th largest manufacturing industry in the UK with 10.8% of manufacturing output and 2-3% of UK GDP[1]. The industry can also claim in the region of £36 billion in sales annually. Figure 1.1 details the division by value (GDP), of chemicals for different uses in the chemical industry.

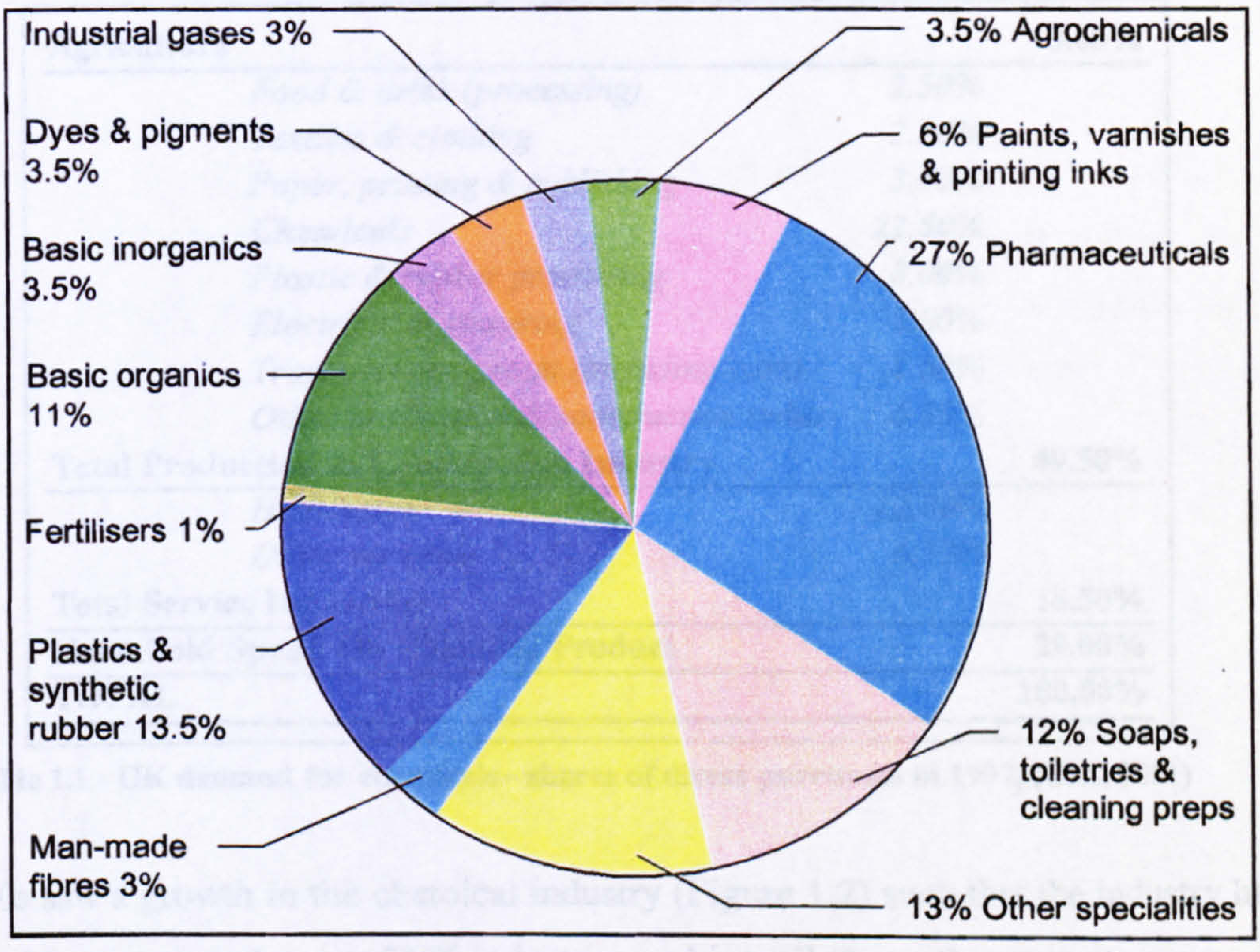

Figure 1.1 - UK chemical industry sector contributions to gross value added[2], 1996 (adapted from CIA, 2001)

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[1] GDP, Gross Domestic Product – an economic term used as a measure of the value of output produced within the domestic boundaries of the UK. The value now includes the output of foreign owned firms that are located in the UK following high levels of foreign direct investment in the UK economy in the 1980s and 1990s. The value of GDP can be calculated in three ways (from output, income or expenditure) all of which should be equal (Riley, 1999).

[2] Gross Valued Added, under new definitions introduced in 1998, GDP is now known as Gross Valued Added (Riley, 1999)

Pharmaceuticals represent the largest sector of the chemical industry, closely followed by plastics and then soaps and cleaning products.

There is a large demand for chemicals in the UK both by consumers and industry. Table 1.1 shows this demand for chemicals by various industry groups and consumers as measured by direct sales.

The production and construction industry accounts for nearly half of all direct sales of chemicals, and consumer (household) spend represents a further 30%, a significant proportion. Within the production and construction sector the chemical industry itself accounts for almost 23% of demand. This suggests that many of the chemicals produced remain in the chemical industry possibly as intermediates or feedstock for other production or formulation processes.

Agriculture			**3.00%**
	Food & drink (processing)	*2.50%*	
	Textiles & clothing	*2.50%*	
	Paper, printing & publishing	*3.00%*	
	Chemicals	***22.50%***	
	Plastic & rubber processing	*8.00%*	
	Electrical engineering	*3.00%*	
	Transport equipment (including cars)	*1.50%*	
	Other production & construction indus	*6.50%*	
Total Production & Construction Industry			**49.50%**
	Healthcare	*12.00%*	
	Other services	*6.50%*	
Total Service Industries			**18.50%**
Household Spend On Chemical Product			**29.00%**
TOTAL			100.00%

Table 1.1 - UK demand for chemicals - shares of direct purchases in 1997, (CIA, 2001)

The 1990s saw a growth in the chemical industry (Figure 1.2) such that the industry had the second largest growth rate of UK industries and is well above the average.

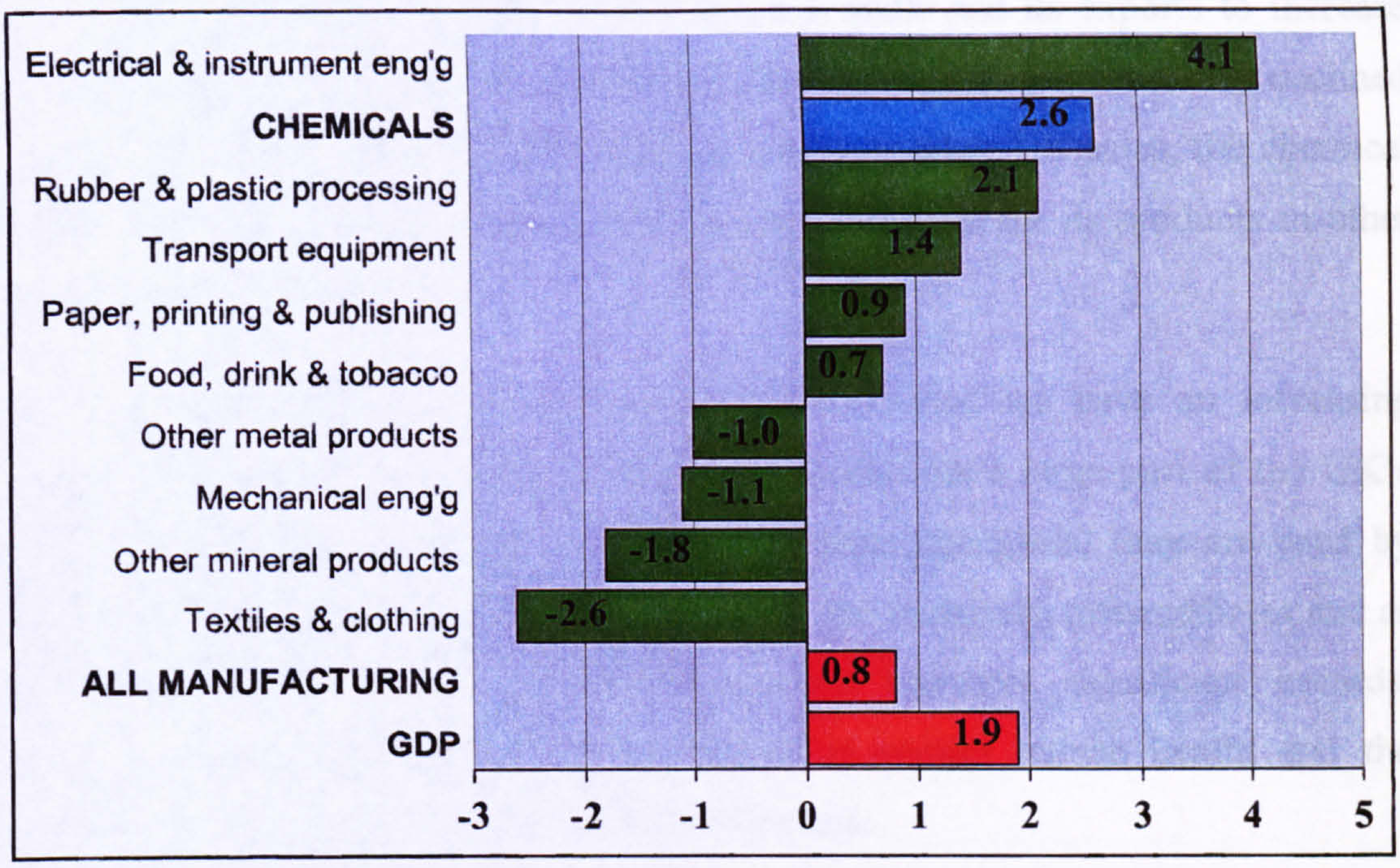

Figure 1.2 -UK industrial growth rate comparisons 1988-98, (CIA, 2001)

This growth is reflected in the fact that the chemical industry is the UK's largest export industry with a trade surplus of approximately £4.4 billion. Furthermore, the UK chemical industry is ranked 5th largest in the World[3]. Figures 1.3 (a, b) demonstrate the continuing growth within the industry.

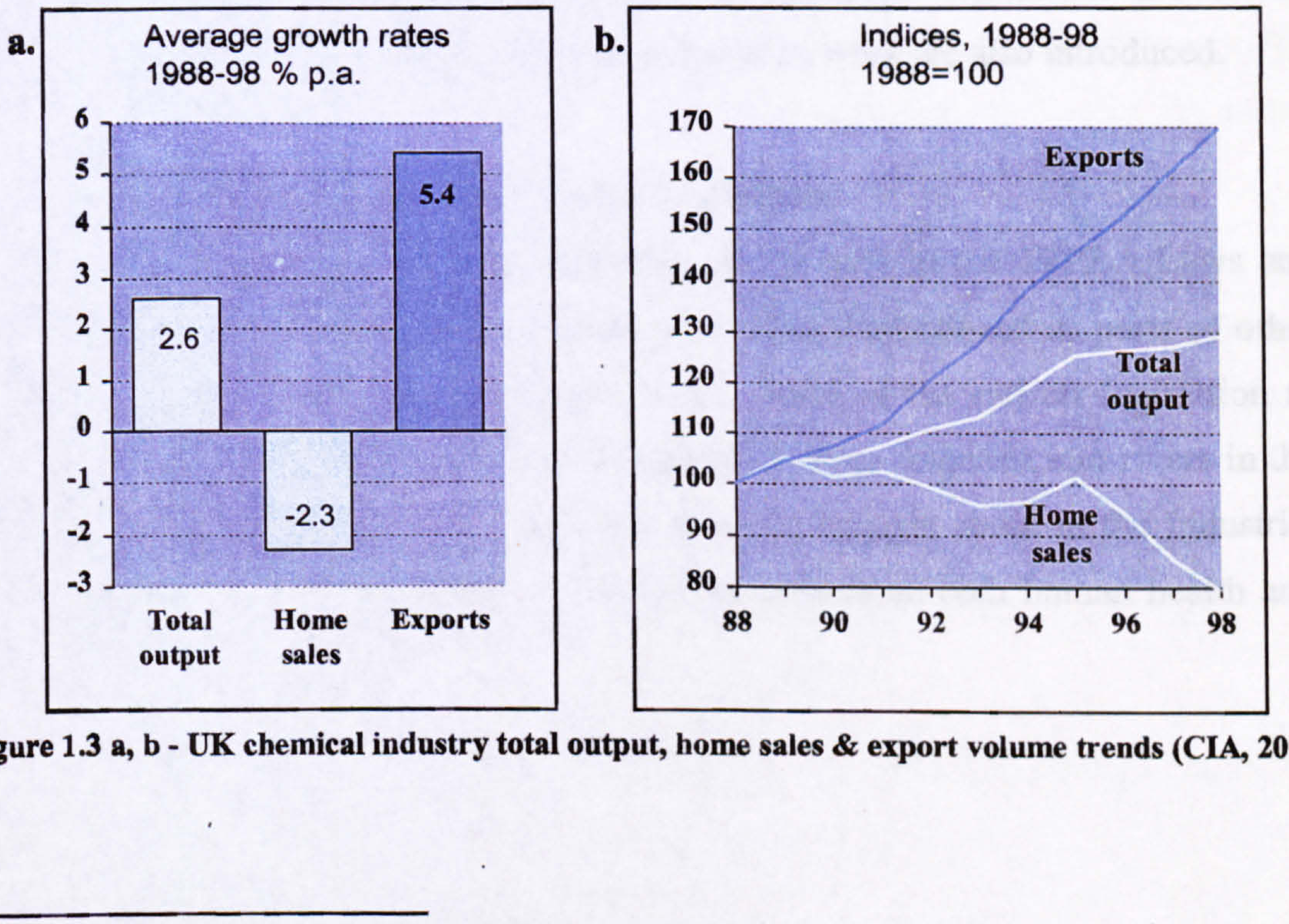

Figure 1.3 a, b - UK chemical industry total output, home sales & export volume trends (CIA, 2001)

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[3] Facts and figures from the Chemical Industries Association, the UK chemical industry's leading trade and employer organisation, Kings Buildings, Smith Square, London, SW1P 3JJ

There is a trend for both the chemical industry as a whole and its exports to increase over the coming years, whilst UK sales in the industry seem to have steadily declined throughout the 1990s. Whether or not there is a turnaround in UK sales, the chemical industry in the UK is getting larger. There is a high demand for its products in other industries and by consumers.

There is a large quantity of chemicals in our society and we have an increasing dependency upon them. The chemical industry accounts for a large part of the UK's manufacturing economy. Society clearly benefits from chemicals, they are used by consumers at home, and in other industry sectors as raw materials, intermediates and as final products. Some of these chemicals however represent significant hazards. Adequate controls and guidelines need to be set to protect human health and the environment from the adverse effects of these chemicals.

1.2 ENVIRONMENTAL LAW AND CHEMICAL MANAGEMENT

The extent and influence of the chemical industry has been outlined in brief. In this section the control and regulation of chemicals in the form of environmental legislation will be examined. These controls have developed over many decades; the impetus for and influences upon these developments in environmental legislation are briefly reviewed. The Environment Agency and the scope of its work are also introduced.

1.2.1 The Development of Environmental Legislation

Environmental law is a relatively new concept, dating back to the 1970s. Laws and other controls were in place prior to this but were usually introduced as parts of other issues rather than environmental protection itself. Some of the earliest legislation to affect the environment was the regulation of emissions from tanneries into rivers in the medieval period. Much later the growth and advances brought about in the Industrial Revolution (circa 1750-1900) however, resulted in impacts on both human health and the environment.

As a result of this the 1800s saw three key pieces of legislation introduced in an attempt to control the escalating problems (Lindner, 2001):

- The Alkali Act, 1863 – created the Alkali Inspectorate, principally to control atmospheric emissions from the chlor-alkali industry
- The Public Health Act, 1875 – provided changes in housing, town and country planning, as well as public health issues
- The Rivers Pollution Prevention Act, 1876 – introduced a framework for water pollution controls, although there were problems with enforcement

A large part of environmental law has its roots in planning legislation. Back in the 19th Century public health and housing legislation controlled planning, this was later followed in the early 20th century by a system of town planning. In 1947 the Town and Country Planning Act (TCPA 1947) was passed, under which some controls were set out for hazardous processes and hazardous substances. Although not specifically environmental law it provided a framework for the implementation of later environmental legislation.

A resurgence in environmental issues occurred in 1962 when Rachel Carson's book 'Silent Spring' was published. The book warns of the dangers in the indiscriminate use of pesticides, using as an example the insecticide DDT (dichloro-diphenyl-trichloroethane). Her call for action led to the eventual US ban of the substance (Park, 2001). Her book was also instrumental in the establishment of two of the main environmental pressure groups, namely *Friends of the Earth* and *Greenpeace.*

The first United Nations Conference on the environment was held in 1972 in Stockholm, Sweden. It was at the Conference on the Human Environment where the concept of *sustainable development* was introduced. The Declaration of Principles suggested that (IEMA, 2000):

> "… we have a right now to a life of dignity and equality in an environment of quality but that we also have a solemn responsibility to protect and improve the environment for present and future generations."

Conference on the Human Environment: Draft Declaration, 1972

Although the Stockholm conference did not suggest how the aims in the declaration might be achieved, it led to the establishment of Ministries of the Environment all over the World and the United Nations Environment Programme (UNEP).

The report, 'Our Common Future' written by the former Norwegian Prime Minister Gro Harland Brundtland and published in 1987 by the UN Commission on Environment and Development (UNCED) linked economic and environmental issues in a way that the Stockholm declaration failed to do. The report which has become known as the "Brundtland Report" sets out the now familiar definition of sustainable development as (Brundtland, 1987):

> "Development that meets the needs of the present without compromising the ability of future generations to meet their own needs"

Implicit in the term sustainable development is the recognition that there will continue to be 'development' while minimising impacts on the environment from further resource depletion, emissions and waste generation. The Brundtland Report laid the foundation for the Earth Summit held in Rio de Janeiro in 1992.

The Rio Earth Summit at the United Nations Conference on Environment and Development agreed four main principles for moving towards a sustainable future:

- Humans are at the centre of concerns for sustainable development
- The right to develop must be exercised in such a way that the development and environmental needs of both present and future generations are met
- Environmental protection must be considered as an integral part of the development process
- There is a need to reduce and eliminate unsustainable patterns of production and consumption

These four principles all emphasise man's dependence on the environment. Traditionally nature has been seen as a resource for human use; the UK Biodiversity Action Plan (1993) was the first formal recognition that nature itself could have inherent importance. The increasing adoption of a precautionary approach towards development demonstrates this change in perception of nature's inherent value.

Within sustainable development the Precautionary Principle is an emerging and important concept. The effects of this philosophy were outlined at the Rio Declaration on Environment and Development (DETR, 1998):

> "In order to protect the environment, the precautionary approach shall be widely applied by States according to their capabilities. Where there are threats of serious or irreversible damage, lack of full scientific certainty shall not be used as a reason for postponing cost-effective measures to prevent environmental degradation."
>
> Rio Declaration on Environment and Development, 1992

There are problems however with the Precautionary Principle. In the 1960s the United States Food and Drug Administration (US FDA) set a precautionary limit for the human carcinogen (*aflatoxin*) found in peanuts at the analytical limit of detection, then 20 ppb (parts per billion). A decade later however analytical science had advanced and the toxin could then be measured at 5 ppb and even 1 ppb, the problem faced by the FDA was whether it was scientifically defensible to lower the standard to the new analytical limit of detection (Rodricks, 1992). They did not, due to the economic costs that industry would face in trying to achieve such a standard. The problem with precautionary action is the constant need for re-evaluation due to new scientific evidence.

Environmental legislation in the UK has become increasingly influenced by the European Union (EU) and international agreements. The role of the EU (formerly the European Community, EC) was originally to achieve co-ordination of the economic policies of the EC through a single European Market; this role was later extended to policies within social, environmental and other fields (Malcolm, 1994). EU Regulations are directly applicable to all Member States and are binding in their entirety (e.g. Exiting Substances Regulations, ESRs[4]). EU Directives however, are only binding to those Member States that it addresses (Humphreys, 1996) and each Member State uses their own legal mechanisms to implement the measures detailed in the Directive (e.g. Dangerous Substances Directive[5]).

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[4] Commission Regulation 793/93/EEC on the evaluation and control of the risks of exiting substances

[5] Commission Directive 67/548/EEC on the approximation of the laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances.

A trend appearing in EU law is the use of directives that set out a framework or structure of controls, which are then applied to specific situations through further 'daughter Directives' (Ball & Bell, 1994). An example of such a Framework Directive is the *Water Framework Directive* through which it is hoped an integrated and co-ordinated approach to water management can be introduced (Foster *et al.*, 2001).

Environmental legislation and the regulation of potential impacts to the environment have built up in a rather haphazard fashion. Many of the Acts and revisions of legislation were made on a reactive basis. Park (2001) outlines the development of what he terms as environmentalism (the social and societal pressures leading to these environmental regulatory changes) as three waves of environmentalism:

- First Wave – The conservation era launched by Roosevelt and Pinchot in the US (c1915-1960s)
- Second Wave – The explosion of pollution control laws and regulations, during the 1960s and 1970s
- Third Wave – The current solution-orientated environmental climate

Malcolm, (1997) suggests that environmental regulation has grown in direct proportion to environmental awareness. In the last decade alone there has been an explosion of international treaties and protocols, European laws and domestic legislation concerned with the environment.

For further details on the history and development of environmental law readers are directed to 'Environmental Law' (Ball & McGillivray, 2000). This book is now in its 5th edition, previously Ball and Bell (2nd edition, 1994), which testifies to the speed at which environmental legislation is developing. For issues relating to the planning and process control side of environmental legislation, which is beyond the scope of this introduction another valuable resource is 'A Guide to Environmental Law' (Malcom, 1994).

1.2.2 Environmental Legislation – The Current Situation

Having presented a brief history of the development of environmentalism and environmental legislation, some of the main pieces of legislation shall now be considered in further detail. The regulatory controls for water, air, integrated pollution control, and the establishment of the environment regulatory bodies shall be considered. The list below is not an exhaustive list, but includes some of the major legislative instruments particularly those with relevance to the control of hazardous substances in the environment.

- Regulation of water
  - Water Resources Act 1991
  - Ground Water Regulations 1998
- Regulation of atmospheric pollution
  - Clean Air Act 1993
  - Air Quality Regulations 1997
- Integrated pollution control regulations
  - Environmental Protection Act 1990
  - Pollution Prevention and Control Act 1999
- Establishment of environmental regulators
  - Environment Act 1995

Regulation of Water

The regulation of water is divided in to two distinct areas:

- Water used for specific uses
  - Drinking water
  - Bathing water
  - Water for fish and shellfish habitats
- Dangerous substances in water

Up to the 1940s water supply and sewage disposal were mainly controlled through municipal authorities (Garbutt, 2000). It was the River Boards Act 1948, and subsequently the Water Resources Act 1963 (WRA 1963) that established a regional structure of authorities based upon river basins.

A further major restructuring of the industry was brought about by the Water Act 1989 (WA 1989), Water Resources Act 1991 (WRA 1991) and the Water Industry Act 1991 (WIA 1991). This included the privatisation by the Government of the operational side of the water industry (water supply, sewage services and some recreational services). The Office of Water Services (OFWAT) was formed, regulating water supply and sewage provisions, while the National Rivers Authority (NRA) was created (WA 1989) with powers including the regulation of pollution and water abstraction in watercourses.

While these developments split the regulation of water into that of provision and protection, another major step was taken with the Rivers (Prevention of Pollution) Act 1951. This legislation required consents for sewage and industrial discharges to inland waters. The WRA 1963 extended this consenting to certain underground waters. The geographical coverage of discharge consenting was further increased by the Control of Pollution Act 1974 (COPA 1974) which covered inland waters, underground waters, tidal and coastal waters (up to 3 miles). COPA 1974 also introduced a public register of information and allowed the possibility of private prosecutions.

The Dangerous Substances Directive 76/464 [6] relates to dangerous substances discharge to water, (not to be confused with the Dangerous Substances Directive concerning packaging and labelling). This directive is a "framework directive" setting out a programme of action to be followed by later "daughter" directives which in this case deal with individual chemicals.

The Directive outlined two lists of chemicals, the first of substances the pollution from which should be eliminated and the second of substances where pollution is to be reduced (See Appendix 1):

List I - Black List

Particularly toxic, persistent or bioaccumulating substances.

List II - Grey List

Groups and families of substances which affect the smell and taste of water, also substances affecting the balance of oxygen in the water.

The daughter directives detail limits for these chemicals, threshold volumes which discharges should not exceed. The Groundwater Regulations 1998[7], ensure the UK is compliant with the EC 1980 directive on Groundwater[8]. The regulations concern the protection of groundwaters from List I and List II substances as outlined in the (discharge to water) Dangerous Substances Directive. Further details about the UK's

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[6] Council Directive 76/464 on pollution caused by dangerous substances discharged into the aquatic environment

[7] Groundwater Regulations, Statutory Instrument 1998 No. 2746

[8] Council Directive 80/68/EEC on the protection of ground water against pollution caused by certain dangerous substances

Environmental Quality Standards (EQS) system are outlined in the section on the Environmental Toxicology Section (Section 1.4.2).

Regulation of Atmospheric Pollution

Regulations controlling atmospheric pollution developed from the legislation against smoke and smog nuisances. The Clean Air Act 1956, which was supplemented by the Clean Air Act 1968, imposed controls on atmospheric pollution. This included controls for all commercial activities not previously covered by regulations and for the first time also referred to domestic fires.

During the 1970s a gradual improvement in air quality took place (Ball & McGillivray, 2000). However at a similar time there was a growing awareness of the problems related to sulphurous emissions from vehicles and chimneys. The resulting NO_x and SO_x particles that are formed in the atmosphere were linked with acid rain and acid deposition particularly in Scandinavian regions.

Other growing issues such as ozone depletion and the threat of global warming led to various emission standards being set. There were also prohibitions on some substances, e.g. chlorofluorocarbons (CFCs). The Air Quality Standards Regulations 1989[9] set quality standards for the atmosphere; these standards detail limit levels for sulphur dioxide, nitrogen dioxide, lead and smoke as measured by a system of sampling stations around the UK.

Historically local authorities have been responsible for enforcing atmospheric pollution limits and nuisance controls. Under emerging, integrated approaches to pollution control the newly formed environmental regulators are now responsible for the most polluting industries.

Integrated Pollution Control Regulations

The compartmentalised approach to pollution control in the UK has been criticised for its failure to view the environment as a whole (Ball & McGillivray, 2000). Instead individual environmental compartments (air, land and water) are considered and regulated separately. There was previously no consideration of the possible consequences of imposing a control on one environmental compartment or media and the effects it would have on the others. Under such a situation by changing an industrial

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[9] Air Quality Standards Regulations, Statutory Instrument 1989 No. 317

process the controls for water may be met while transferring the environmental burden to the land or air compartments.

The Environmental Protection Act 1990 (EPA 1990) introduced a system of integrated pollution control for industrial processes. The legislation is a process-orientated control system and has two main parts. The first part, Integrated Pollution Control (IPC) relates to more polluting processes (Figure 1.4) and addresses the minimisation of pollution to all environmental media. The second part, Air Pollution Control (APC) is aimed at the less polluting industries and only controls atmospheric emissions.

Prescribed Processes:

Fuel and power industry
Gasification, carbonisation, combustion and petroleum processes.

Chemical industry
Petrochemical, organic, chemical pesticide, pharmaceutical, acid manufacturing, halogen, chemical fertiliser, bulk chemical storage, and inorganic chemical processes.

Minerals industry
Cement, asbestos, fibre and ceramic processes.

Metal industry
Iron and steel, smelting and non-ferrous processes.

Waste disposal industry
Incineration, chemical recovery, and waste derived fuel processes.

Miscellaneous industry
Paper manufacturing, di-isocyanate, tar and bitumen, uranium, coating, coating manufacturing, timber and animal and plant treatment processes.

Figure 1.4 – Prescribed processes as outlined in schedule to the environmental protection regulations under EPA 1990, (Ball & McGillivray, 2000)

The EPA 1990 refers to IPC being administered by an 'enforcing authority'. The authority in England and Wales is the Environment Agency as formed by the Environment Act 1995. The Scottish Environmental Protection Agency (SEPA) is similarly responsible for IPC in Scotland. Meanwhile local authorities carry out the duties under APC for the less polluting industries.

A number of regulations were passed under the framework of EPA 1990 outlining the 'prescribed' processes incorporated and detailing the system of authorisations for these processes:

- Environmental Protection (Prescribed Processes and Substances) Regulations 1991[10]
- Environmental Protection (Applications, Appeals and Registers) Regulations 1991[11]
- Environmental Protection (Authorisation of Processes) (Determination Periods) Order 1991[12]

The UK Pollution Prevention and Control Act 1999, implemented the requirements of the European Integrated Pollution Prevention and Control Directive 1996 (IPPC)[13]. This legislation broadens the scope of IPC and includes specific requirements for the use of a Best Available Technology (BAT) approach to pollution prevention. There is a 7-year rolling programme for applying the IPPC regulations to those processes and installations detailed in the legislation. This was due to start in 1997, but actually commenced in 2000.

IPPC continues the trend of integrating environmental legislation and considering a more holistic approach that considers the interactions and consequences of controls on processes and chemicals. IPPC also aims to promote sustainability by requiring BAT to meet the process controls.

1.2.3 Establishment of Environmental Regulators

Along with the integration of regulatory approaches such as the EPA 1990 an integration of the regulatory bodies for the environment was made with the Environment Act 1995 (EA 1995). The Act introduced key changes in the organisation and enforcement of environmental legislation in the UK.

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[10] Environmental Protection (Prescribed Processes and Substances) Regulations, Statutory Instrument 1991, No. 472 as amended

[11] Environmental Protection (Applications, Appeals and Registers) Regulations, Statutory Instrument 1991, No. 507

[12] Environmental Protection (Authorisation of Processes) (Determination Periods) Order, Statutory Instrument 1991, No. 513

[13] Council Directive 96/61/EEC on integrated pollution prevention and control

The Environment Agency, for England and Wales, and SEPA for Scotland were formed by the EA 1995. In England and Wales, the EA 1995 brought together and merged a number of bodies:

- *The NRA* - National Rivers Authority
- *HMIP* - Her Majesty's Inspectorate of Pollution
- *The Waste Authorities* - local waste regulatory authorities

From the 1st April 1996 onwards the duties of the former NRA, HMIP and waste regulatory authorities were passed onto the newly formed Environment Agency and Scottish Environmental Protection Agency.

One of the main aims of the Environment Agency is to contribute towards sustainable development, and part of this includes the use of the precautionary principle. Section 39 of the EA 1995 is one of the most controversial provisions of the Act, it states that the Agency, in considering whether or not to exercise any power or in deciding the manner in which to exercise such power, shall unless unreasonable to do so:

> "...take account the likely costs and benefits of the exercise or non-exercise of the power or its exercise in the manner in question."
>
> Section 39, Environment Act 1995

Also in Section 4 the Act briefly mentions that the Agency is required to "take into account any likely costs". Cost and benefit analyses are nothing new as far as the disciplines of planning, management and business are concerned, however these instances referring to the use of cost-benefit analysis are the first time such cost considerations have ever appeared formally in UK legislation affecting the environment (Malcolm, 1996).

Not all environmental regulation however rests with the Environment Agency, the EPA 1990 places the administration of IPC with the Environment Agency, while local authorities are responsible for APC. Furthermore, there is no legal framework for liaison and consultation between the two parties with respect to their environmental protection roles.

1.2.4 Control of Hazardous Substances Entering the Environment

Controls exist for industrial processes to limit pollution, various controls are also in place for environmental compartments, placing limits on emissions to water, air, etc. A further approach to protecting the environment is the regulation of hazardous substances themselves.

A large part of legislation has developed around the classification and labelling of hazardous substances. The Dangerous Substances Directive[14] (packaging and labelling) 1967 was implemented in the UK by the Chemical Hazard Information and Packaging Regulations 1993[15] (CHIP 1993). The directive initially focussed on the harmonisation and avoidance of barriers to trade between Member States. Subsequent legislation has been concerned however, with the assessment and better understanding of potential risks to man and the environment.

The 6th amendment[16] to the Dangerous Substances Directive introduced the requirement and procedures for the notification of new substances prior to marketing. For the purpose of notification, all chemicals are classed as either *Existing Substances* or *New Substances.* Existing chemicals are listed on the European Inventory of Existing Commercial Substances (EINECS), which includes all substances deemed to be on the Community market on 18 September 1981. There are approximately 110,000 chemicals listed on EINECS.

The Dangerous Substances Directive was amended a seventh time[17] in which the requirement of risk assessments for man and the environment were detailed. The Notification of New Substances Regulations 1993[18] (NONS 1993) implements the 7th amendment of the Dangerous Substances Directive in the UK. All notified new chemicals are placed on the European List of Notified Chemical Substances (ELINCS), which currently lists approximately 2000 substances, with about 300 being added annually. The UK completes One third of these assessments for the whole of Europe.

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[14] Council Directive 67/548/EEC on the approximation of laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances

[15] Chemical Hazard Information and Packaging Regulations, Statutory Instrument 1993, No. 1746

[16] Council Directive 79/831/EEC amending for the sixth time Directive 67/548/EEC on the approximation of laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances

[17] Council Directive 92/32/EEC amending for the seventh time Directive 67/548/EEC on the approximation of laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances

[18] Notification of New Substances Regulations, Statutory Instrument, 1993, No. 3050

Directive 93/67/EEC[19] and Regulation 1488/94/EEC[20] detail a system for the risk assessment of new and existing substances respectively. This risk assessment system comprises four stages of assessment, namely hazard identification, dose-response assessment, exposure assessment and risk characterisation. Further details on the European notification system and the implementation of the system within the UK can be found in the section on the Chemical Assessment Unit (Section 1.4.1).

1.2.5 Future Environmental Legislation

The development of environmental legislation has become less reactive and there is a continued move towards general policies and an integration of approaches. Framework directives are being used increasingly to rationalise and consolidate existing environmental media specific controls. Examples include the Water Framework Directive[21] and the Air Framework Directive[22]. The intention of the Water Framework Directive is to address and resolve the fragmented approach to the legislation on water in Europe. The key objectives of the Directive are outlined in Article 1 as (Foster *et al*, 2001):

- Prevent further deterioration and protect and enhance the status of aquatic ecosystems and associated wetlands
- Promote sustainable water consumption
- Contribute to mitigating the effects of floods and droughts

Another trend with framework directives is the passing of a directive outlining a system of controls and then future daughter Directives detail process or chemical specific controls, as required. Examples of such controls being the Dangerous Substances Directive (on discharges to water) and the IPC Directive.

Specific to England and Wales, the Environment Agency is preparing a 'Chemical Strategy'. The intention is to form an overarching strategy enabling the Agency to effectively regulate and manage chemicals in the environment, and help to promote their sustainable production, use and disposal. This is an example of another holistic

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[19] Commission Directive 93/67/EEC laying down the principles for the assessment of risks to man and the environment, notified in accordance with Council Directive 67/548/EEC

[20] Commission Regulation 1488/94/EEC laying down the principles for the assessment of risks to man and the environment of existing substances in accordance with Council Regulation 793/93/EC

[21] Council Directive 2000/60/EC establishing a framework for community action in the field of water policy

[22] Commission Directive 84/360/EEC on the combating of air pollution from industrial plants

view of potential impacts to the environment (and human health). By taking such a view, the consequences of any individual control can hopefully be anticipated.

Finally the idea of cost, and particularly costs and benefits have entered environmental legislation. This, in itself can be problematic, in particular in assigning values to the environment. The introduction of cost-benefit considerations however may force the development of environmental economics and result in the use of such procedures becoming more common in planning and the regulation of processes and chemicals.

1.3 THE ENVIRONMENT AGENCY

The primary department for the environment within Central Government was the Department of Environment, Transport and the Regions (DETR). The DETR was formed through the amalgamation of the Department of the Environment and the Department of Transport and Industry in 1997. In June 2001 however the Department of Environment, Food and Rural Affairs (DEFRA) was created. This new department brought together parts of DETR, the entire Ministry of Agriculture, Fisheries and Food (MAFF), the Home Office's responsibilities for animal welfare and foxhunting.

As mentioned, the Environment Act 1995 (EA 1995) established the Environment Agency to cover England and Wales, SEPA for Scotland. The Act made provisions for, amongst other things:

> "...the control of pollution, the conservation of natural resources and the conservation or enhancement of the environment..."
>
> (The Environment Act, 1995)

The EA 1995 brought together the separate bodies that were previously, disparately controlling environmental protection, namely:

The NRA - National Rivers Authority, set up in September 1989 as a result of the privatisation of the water authorities, with duties in respect to the control and protection of watercourses, including:

- Water resources management, Water Resources Act 1991 (WRA 1991), Part II
- Control of pollution of water resources, WRA 1991, Part III
- Flood defence, WRA 1991, Part IV, and Land Drainage Act 1991.

HMIP - Her Majesty's Inspectorate of Pollution, developed from the Alkali Inspectorates of the 19th century, controlling industrial pollution, particularly to air, including:

- Integrated Pollution and Control (IPC) regulations, Environmental Protection Act 1990 (EPA 1990)
- Industrial air pollution, Alkali, &c, Works Regulation Act 1906

The Waste Authorities - local authorities had powers over smaller scale processes and industries, powers including:

- Integrated Pollution and Control (IPC) regulations, EPA 1990
- Local Authority Air Pollution Control (LAAPC)

From the 1st April 1996 onwards the duties of the former NRA, HMIP and waste regulatory authorities were passed onto the newly formed Environment Agency and Scottish Environmental Protection Agency. Also transferred to the two Agencies were functions of the Secretary of State (via the then Department of Environment, DoE) such as the control of disposal of radioactive waste under the Radioactive Substances Act 1993, and powers under the Water Industry Act 1991 in relation to special category effluent.

Malcolm (1996) describes the Agency's principle aims (from Section 4 of EA 95) to be the, "discharge of its functions so as to protect or enhance the environment so as to make a contribution towards achieving Sustainable Development".

The Agency is officially a 'non-departmental public body' which means they work for the public with specific duties and powers. The Agency has a Board of up to 15 members including the Agency's Chairperson and Chief Executive. Prior to the formation of DEFRA the Board members were appointed by DETR, MAFF and the Welsh Office.

The total annual budget for the Agency is in the region of £585 million, 75% of which is produced through charges and licensing, the rest being funded by the Government. The Agency's remit covers the whole of England and Wales, which includes about 15 million hectares of land, 36,000 km of river, 5,000 km of coastline including over 2 million hectares of coastal waters (EA, 1997a).

The Agency divides its work areas into Directorates, for example Water Management and Environmental Protection, then within each of these directorates there are a number of functions. In 1997 the Agency produced a strategy outlining the new approach the organisation intended to take towards regulating the environment, 'An Environmental Strategy for the Millennium and Beyond'. As part of this the Agency outlined nine key themes within which the majority of their work fell (EA, 1997b):

- Addressing CLIMATE CHANGE
- Improving AIR QUALITY
- Managing our WATER RESOURCES
- Enhancing BIODIVERSITY
- Managing our FRESHWATER FISHERIES
- Delivering INTERGRATED RIVER-BASIN MANAGEMENT
- Conserving THE LAND
- Managing WASTE
- Regulating MAJOR INDUSTRIES

In 2000 the Agency updated their strategy and published the following vision (EA, 2000):

> "Our vision for the environment and a sustainable future is: a healthier, rich and diverse environment in England and Wales, for present and future generations."

To achieve this vision a new set of nine themes were developed (EA, 2000):

Fundamental goals:
  - a better quality of life
  - an enhanced environment for wildlife

Environmental outcomes:
  - cleaner air for everyone
  - improved and protected inland and coastal waters
  - restored, protected land with healthier soils

Changes:
  - a 'greener' business World
  - wiser, sustainable use of natural resources

Risks and problems:
  - limiting and adapting to climate change
  - reducing flood risk

For each of the environmental themes in the Agency's vision a "Framework for Change" has been written. These documents set out medium-term plans and proposals to ensure progress towards the long-term objectives. The frameworks outline the objectives under each themes and specific goals for the Agency to achieve as well as the actions necessary to achieve these goals. Furthermore tests for progress are also detailed so that measures of success can be made.

Geographically the structure of the Agency is divided into 8 Regions including Welsh Region or what is also known as Environment Agency Wales (Figure 1.5). Each Region is also split, into a number of Areas, there being a total of 26 Area offices.

Figure 1.5 – Map of England and Wales indicating the 8 Regions and the 26 Areas within the Environment Agency (adapted from EA, 1997a)

Approximately 9500 staff work for the Environment Agency in England and Wales. Each Region has three statutory Regional Committees covering environmental protection, flood defence and fisheries and includes local authority and business representatives. The Regional and Area structures are aimed at ensuring local issues and requirements are considered and addressed in the work of the Agency.

The boundaries of the Regions were inherited from the water authorities, which were in turn based on main river catchments; Midlands Region demonstrates this most starkly with its Areas being named after the upper and lower sections of the Rivers Trent and Severn. The municipal boundaries that the former waste regulatory authorities worked within differ slightly to these boundaries, most notable between Welsh and Midlands Region, however the catchment based Regions were adopted.

The Agency has a wide range of duties and powers relating to environmental management and the improvement in the quality of air, land and water. Throughout the exercising of the Agency's strategy there is an attempt to 'think globally while acting locally' and this is reflected in documents called LEAPs (Local Environment Agency Plans). In these reports, actions and efforts for individual river catchment areas are outlined, focusing on local targets and actions while attempting to fulfil the wider Agency strategy. The fact that these reports are based on river catchments however, echoes the fact that although the Agency is meant to be addressing multi-media concerns, i.e. land, air and water; many initiatives are still focused on the aquatic compartment (the water environment).

The Agency recognises that to deliver its Vision an investment in relevant science, engineering and technology is required (EA, 1997b), however it admits that a large proportion of its research and development programme will be, and is, carried out externally. The annual research and development (R&D) budget for the Agency is in the region of £11 million.

One of the problems the Agency found with the dispersed Regions and Areas structure, was that much of the expertise and knowledge in various areas was also dispersed within the Regions and Areas. 8 National Centres were set up as centres of expertise to provide strategic direction and a focus of national expertise.

The 8 National Centres by work area are:

Environmental Strategy

- National Centre for Environmental Data and Surveillance
- National Centre for Risk Analysis and Options Appraisal

Environmental Protection

- National Centre for Ecotoxicology and Hazardous Substances
- National Groundwater & Contaminated Land Centre

Water Management

- National Coarse Fisheries Centre
- National Salmon and Trout Fisheries Centre
- National Water Demand Management Centre
- National Flood Warning Centre

The National Centre for Ecotoxicology and Hazardous Substances (NCEHS) receives a large proportion of the £8.6 million total operating budget for National Centres compared to the other centres (Figure 1.6). The NCEHS is also one of the larger centres as measured by staff, full-time equivalents (FTEs), (Figure 1.7).

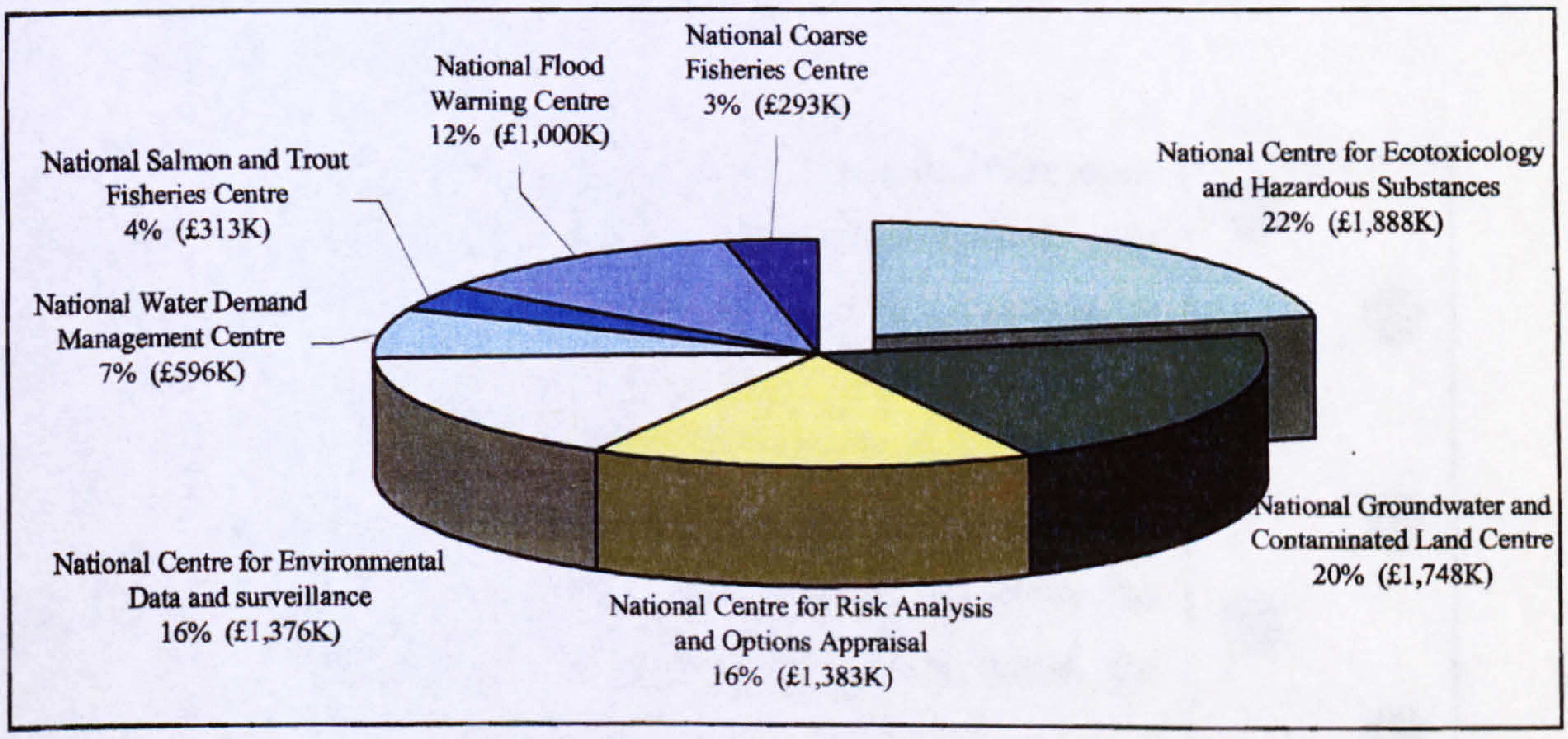

Figure 1.6 - Operating budgets for national centres (adapted from Wharfe, J. unpublished work)

Environmental Protection centres – shaded green;

Environmental Strategy centres – shaded yellow;

Water Management centres – shaded blue;

Total operating budget for national centres = £8,597,000

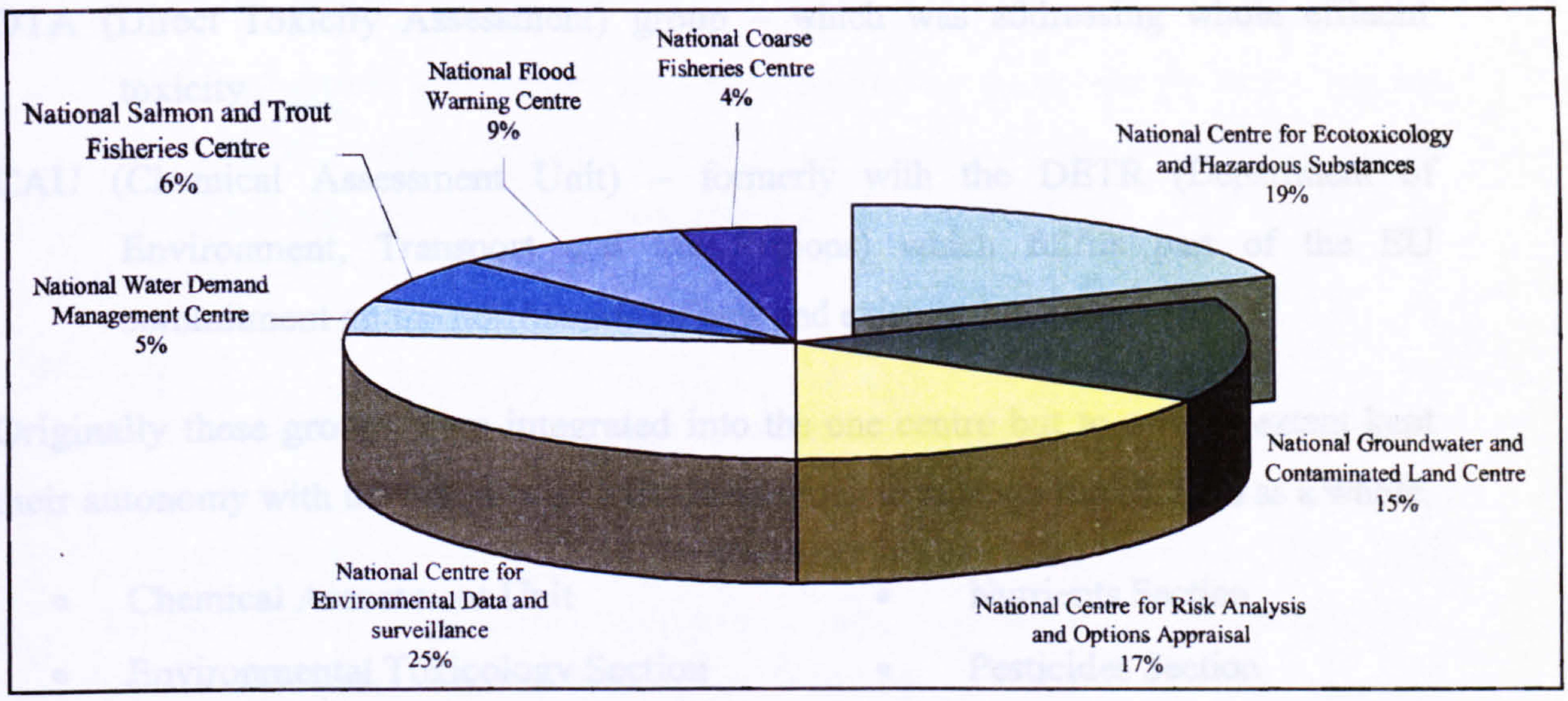

Figure 1.7 – Size of national centres by FTE (adapted from Wharfe, J. unpublished work)
Environmental Protection centres – shaded green;
Environmental Strategy centres – shaded yellow;
Water Management centres – shaded blue;
Total number of FTEs = 172

This Engineering Doctorate, and the research presented was jointly sponsored by and undertaken within the National Centre for Ecotoxicology and Hazardous Substances.

1.4 THE NATIONAL CENTRE

The National Centre for Ecotoxicology and Hazardous Substances (NCEHS) was established to provide scientific expertise and strategic direction in respect to chemicals in the environment for the Agency. The main centre is based in Wallingford in Oxfordshire with an accredited ecotoxicology laboratory in Waterlooville near Portsmouth, UKAS No. 1878 (UK Accreditation Service). The Centre's logo (Figure 1.8) attempts to capture the wide remit of chemicals in the environment within which the NCEHS works.

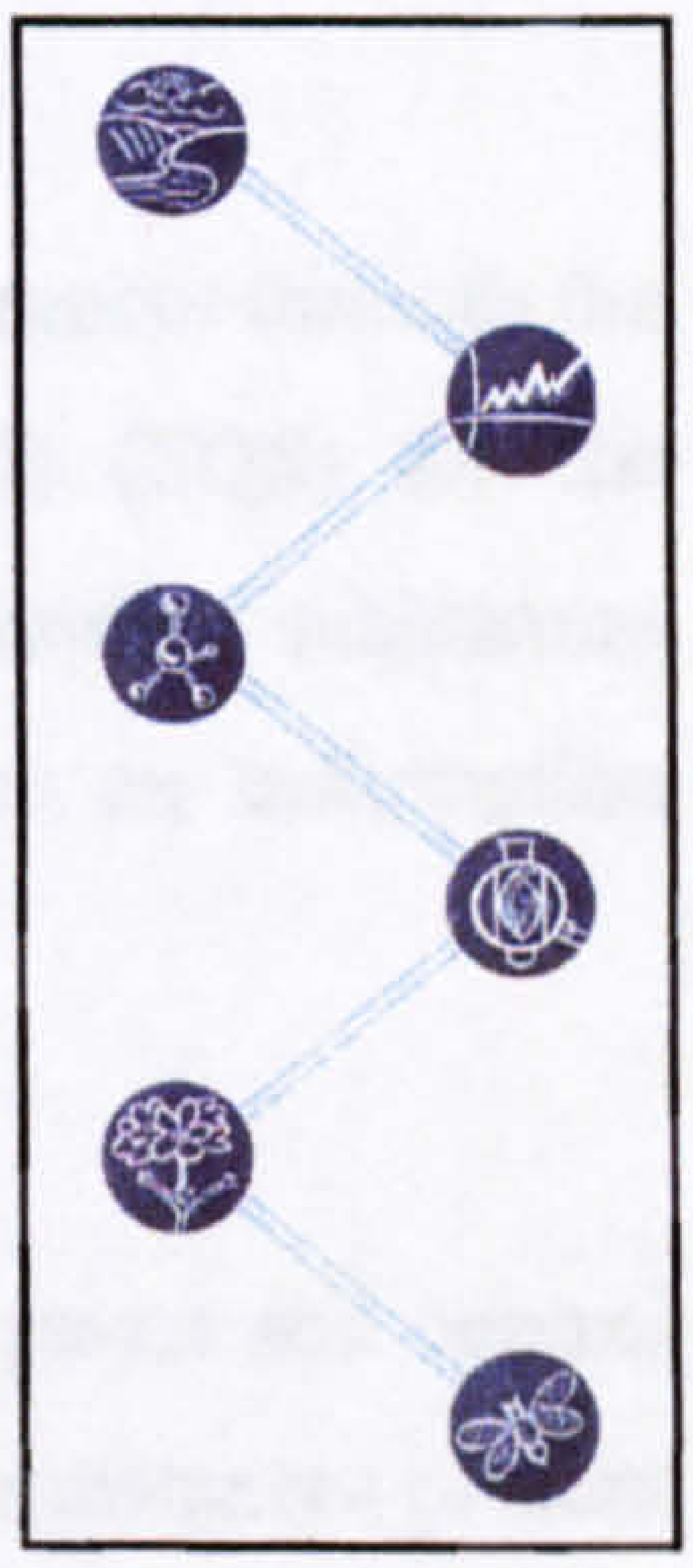

Figure 1.8 - NCEHS logo

The Centre was formed from various previously existing groups as outlined below:

TAPS (Toxic and Persistent Substances) group – which encompassed Nutrients, Pesticides and Environmental Toxicology sections

DTA (Direct Toxicity Assessment) group – which was addressing whole effluent toxicity

CAU (Chemical Assessment Unit) – formerly with the DETR (Department of Environment, Transport and the Regions) which fulfils part of the EU commitment on the notification of new and existing substances.

Originally these groups were integrated into the one centre but to a large extent kept their autonomy with the addition of a Business group to manage the NCEHS as a whole.

- Chemical Assessment Unit
- Environmental Toxicology Section
- Direct Toxicity Assessment
- Nutrients Section
- Pesticides Section
- Business Development

An organisational chart for the NCEHS can be found in Appendix 2, and a brief description of each of the groups follows.

Chemical Assessment Unit (CAU)

On behalf of DEFRA, and previously the DETR, the CAU acts as part of the joint UK competent authority under the Notification of New Substances Regulation (NONS) and the Existing Substances Regulation (ESR). The UK competent authority comprises of the CAU and the Health and Safety Executive (HSE). The CAU is responsible for reviewing the environmental data and risk assessment of all new chemicals notified in the UK.

Environmental Toxicology Section (ETS)

This group addresses the control of toxic substances entering the environment through the development and implementation of environmental quality standards (EQS) for the protection of aquatic life. Other areas of work include endocrine disrupting substances and the Dangerous Substances Directive. The group also provides an information service, the Environmental Toxicology Advisory Service (ETAS).

Direct Toxicity Assessment (DTA)

DTA involves the use of whole-effluent biological effect measures to assess and control complex effluents. Through examining the combined effects of all the substances present in an effluent it provides a more holistic measure of harm than substance specific measures and allows synergistic and antagonistic interactions of substances in mixtures to be taken into account. Their work includes a Demonstration Programme of the use and implementation of the DTA methodology.

Nutrients

This group provides the Agency's focus for nutrients and eutrophication issues. Aquatic eutrophication is where waters are enriched by nutrients giving rise to ecological and use related problems, the process is accelerated by human activities. The work of the Nutrients section also includes a Blue-Green algal advisory service.

Pesticides

The Pesticide Section provides expert and authoritative advice to government committees and to Area and Regional Agency staff on the use and effects of pesticides. By their nature such substances are lethal to organisms and require special attention. The section also provides extensive advice to Government on the development of pesticides policy, other areas of work include, pesticide approvals and risk indicators.

Business Development

The Business Development team is responsible for all financial and business planning for the Centre. Their work includes consultation with the Centres' customers and stakeholders both inside and out of the Agency and with Head Office.

At the start of the new financial year in 2001 the Environmental Toxicology Section and Direct Toxicity Assessment group combined to form a single Environmental Toxicology Section. The reasoning behind this was to develop new ideas through the integration of two closely related science groups. The work remits of the two groups were complementary in many areas and through the merger it is intended that more flexible use can be made of the available resources. The merger is timely due to the completion of the DTA demonstration Programme. DTA work is continuing however it is focusing on policy decision lines. It is hoped that the experiences from each group will help address various cross-cutting issues.

The organisational chart for the Centre reflecting the changes in structure plus the addition of some temporary groups (1-year positions funded by Head Office) can be found in Appendix 3. These new temporary positions are set to address the Water Framework Directive and human health issues. These positions introduce new areas of work and expertise, from which further interaction the groups may benefit. There is a general trend towards more interaction and cross-group initiatives on projects that seem to be advantageous for all involved, however knowledge management and data storage and retrieval does seem to be a problem. These issues may be addressed in the

Agency's proposed Knowledge Management (proposal X1A(01)04) and Science Plan (proposal X1A(01)02) projects.

The NCEHS's annual budget is approximately £2 million, and of the Agency's annual R&D budget of £11 million, £¾ million is accounted for by the NCEHS through National R&D programmes. More than 500 projects are currently running as part of the Agency's R&D portfolio 10% of which are managed by the NCEHS.

The Centre is currently funded for its work on a function basis, the split by Agency function is shown in Figure 1.9. The resource deployment by the Centre (predicted for 2000-2001) is shown in Figure 1.10 in response to business needs.

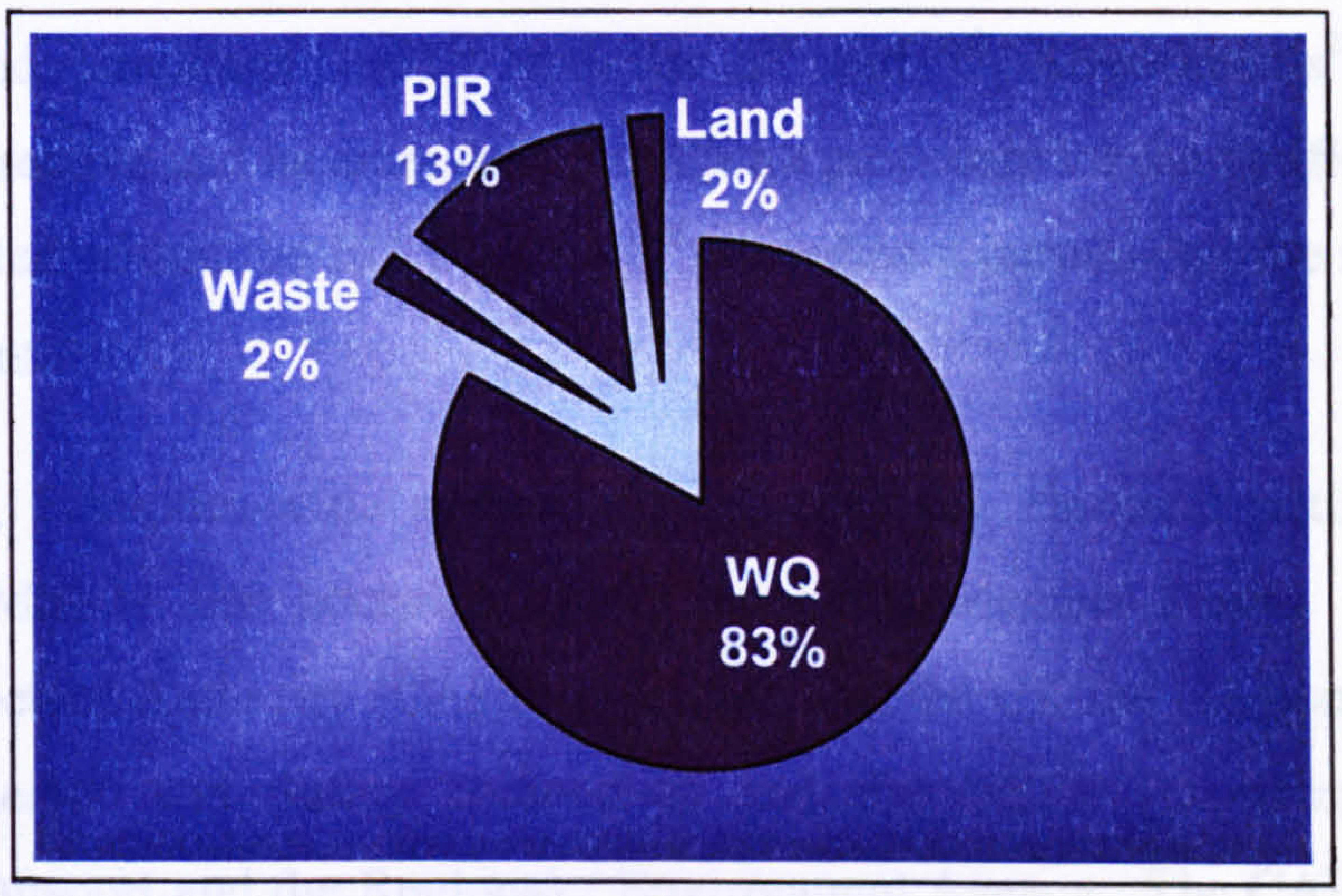

Figure 1.9 –Pie Chart demonstrating split in NCEHS funding (NCEHS, 1999)
Where, PIR - Process Industry Regulation; WQ - Water Quality

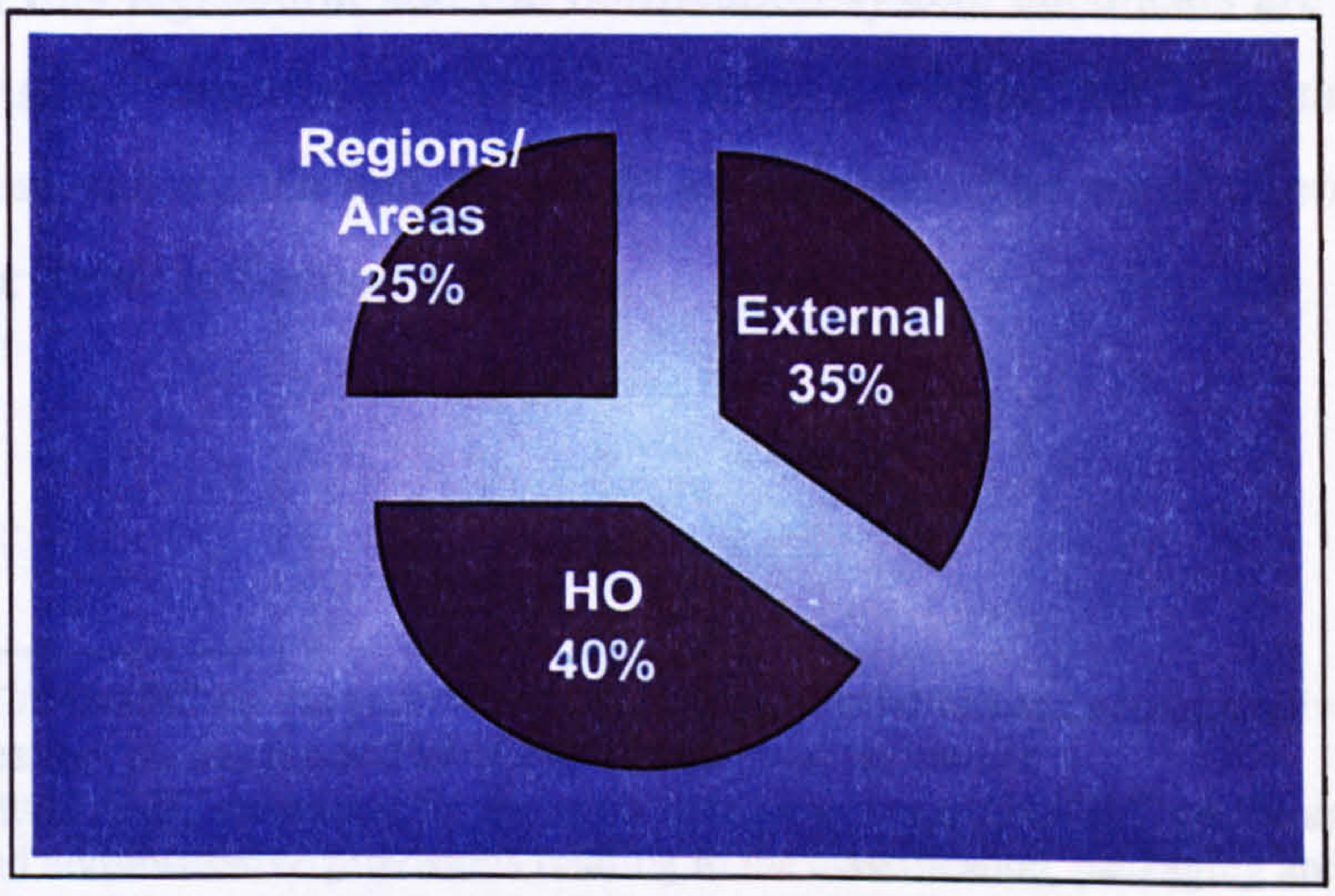

Figure 1.10 –Pie Chart demonstrating deployment of NCEHS resources (NCEHS, 1999)
Where, HO – Head Office

The majority of the Centre's funding comes from the Water Quality side of its work, however although this trend is continuing the Centre does hope to redress the balance in the future. Groups such as the human health section are broadening the Scope of work in the NCEHS, and there are definitely more multi-media considerations being made in the combined Environmental Toxicology section.

More detail on the activities of the three sections (CAU, ETS and DTA) within which this research was conducted is now given.

1.4.1 The Chemical Assessment Unit

The main part of the CAU's work comes under the EU Dangerous Substances Directive (classification and labelling) 1967[23] and the 6th and 7th Amendments[24&25] to the directive. The directive and its amendment outline a procedure for the notification of all chemicals marketed within the EU with the 7th amendment introducing the requirement for risk assessment.

The harmonised, European-wide system ensures that any chemical notified in one Member State (MS) is also accepted in the remaining Member States. There is a nominated Competent Authority (CA) in every MS. In the UK the CA consists jointly of the HSE (Health and Safety Executive) and the DETR (Department of the Environment, Transport and the Regions) / Environment Agency. The CAU within the NCEHS fulfils the Agency's commitment.

For the purpose of this legislation and the notification system chemicals are defined as either new or existing chemicals. There is then a process for the gathering of information on these substances and their risk assessment. The notification system is described in further detail in Section 1.5.

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[23] Council Directive 67/548/EEC on the approximation of laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances

[24] Council Directive 79/831/EEC amending for the sixth time Directive 67/548/EEC on the approximation of laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances

[25] Council Directive 92/32/EEC amending for the seventh time Directive 67/548/EEC on the approximation of laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances

1.4.2 The Environmental Toxicology Section

The Environmental Toxicology Section (ETS) provides information and expertise on the control of substances that enter the environment. Their work includes the development and implementation of Environmental Quality Standards (EQSs) and the Section runs an Environmental Toxicology Advice Service (ETAS).

The Environmental Toxicology Advice Service

The ETAS supplies information and advice on the impact of chemicals on the environment, including physical and chemical properties, any relevant EQS, World Health Organisation (WHO) or other limit values. The service works on a tiered structure of contacts that respond to queries from Area and Regional staff. The ETS organise the training and supporting of the Regional Contacts (RCs) who form the first tier of response. If the RCs and the NCEHS cannot provide the information required there is a technical service contract with WRc (a research contractor) for further information and assistance. The tiered response system is detailed in Figure 1.11.

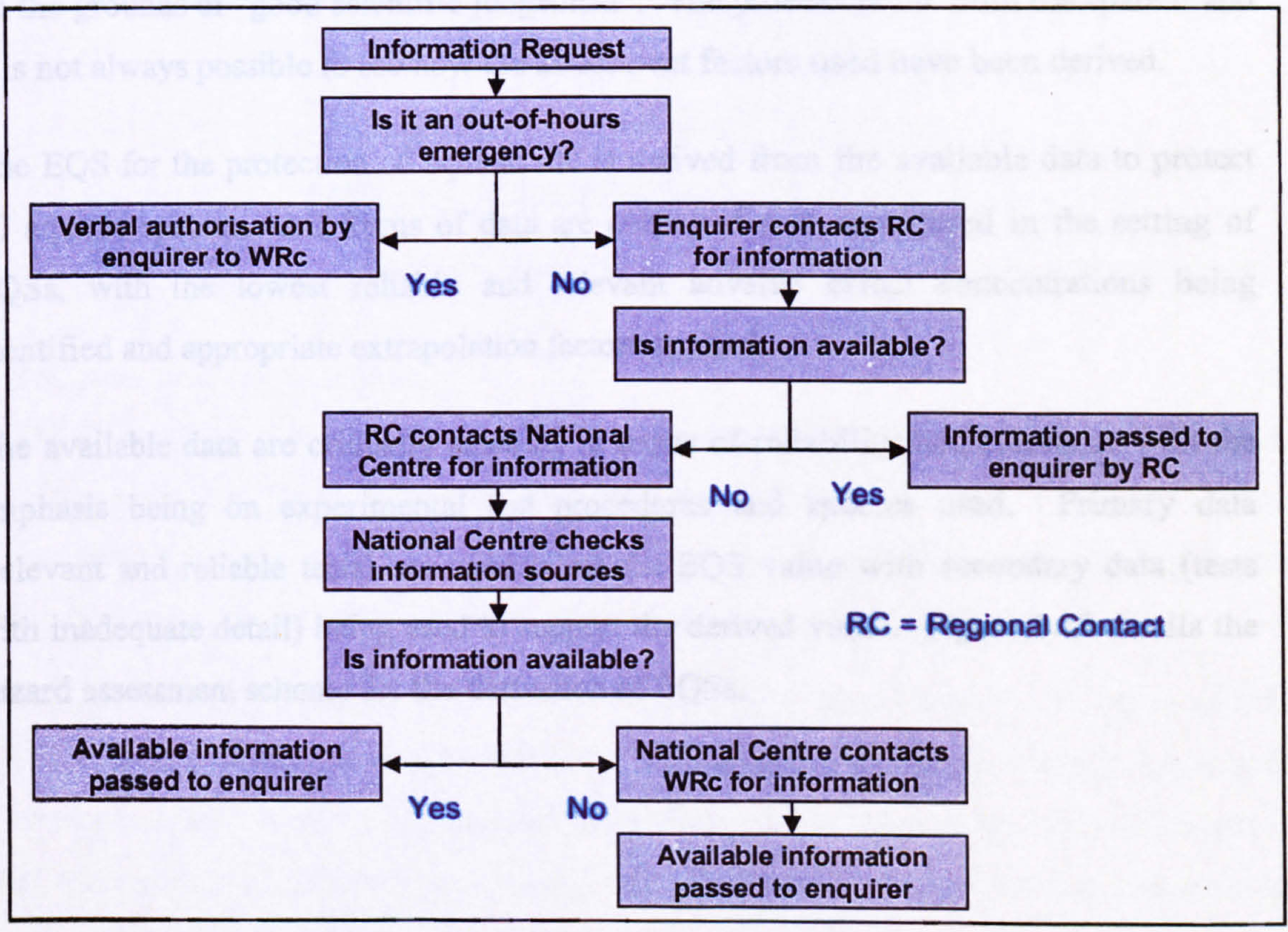

Figure 1.11 – Flow chart of the Environmental Toxicity Advisory Service

Environmental Quality Standards

In the Dangerous Substances Directive[26] (discharges to water), two methods of control are outlined for List I (black list) and List II (grey list) substances (Appendix 1). The first method, Limit Values (LV) are uniform, fixed emission limits that must be complied with irrespective of the size or number of plants, and the nature of the receiving water (ENDS, 1992). Most MS in Europe have adopted this method of implementation. The second method, as adopted by the UK, is that of Environmental Quality Standards (EQSs), which are concentration limits not to be exceeded at particular locations in the receiving water (ENDS, 1992). EQSs have been defined as, (Whitehouse & Fawell, 1997):

> "the concentration of a substance which should not be exceeded in the receiving water in order to protect the use of the water"

The system used to evaluate and set EQSs is less prescribed than the European notification system. Many of the decisions and the interpretations on data are justified on the grounds of "good scientific judgement". The process is far from transparent and it is not always possible to see how the assessment factors used have been derived.

The EQS for the protection of aquatic life is derived from the available data to protect all aquatic species. All forms of data are consulted and considered in the setting of EQSs, with the lowest reliable and relevant adverse effect concentrations being identified and appropriate extrapolation factors applied.

The available data are critically assessed in terms of reliability and relevance with the emphasis being on experimental test procedures and species used. Primary data (relevant and reliable tests) are used to set the EQS value with secondary data (tests with inadequate detail) being used to support the derived value. Figure 1.12 details the hazard assessment scheme for the derivation of EQSs.

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[26] Council Directive 76/464 on pollution caused by dangerous substances discharged into the aquatic environment

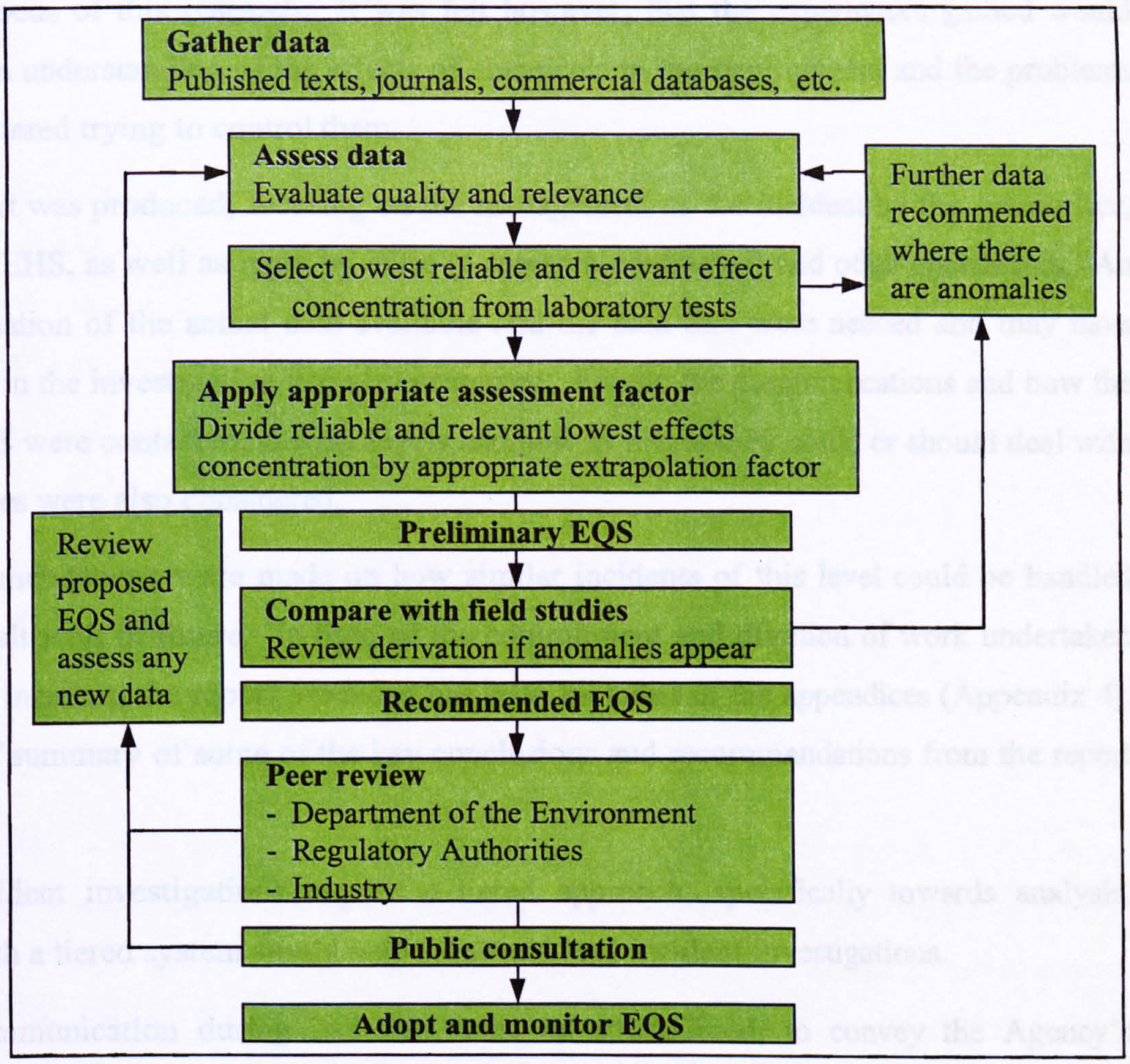

Figure 1.12 - Hazard assessment scheme for the derivation of EQSs (Whitehouse & Fawell, 1997)

The Kennet & Avon Incident

The ETS provided technical support and information throughout the handling of a large "Category 1" pollution incident during the period of this research. An objective was set, aside from the core of this research, to assess the NCEHS's contribution to the incident management and to look at how and what could be done in future.

The Kennet and Avon incident involved a fish kill of approximately 150 tonnes of fish at a fish farm in Hungerford, Berkshire. The incident was unusual in many ways, both because of the complicated hydraulics of the river system where it occurred and because of the number of different groups and organisations involved. The decision making process, "what was done and why", was considered along with the structure of the incident management approach and how this changed during the investigation.

Analysis of the management and communication in this incident was not core to the main focus of this research. It was felt however, that the experiences gained would offer an understanding of the effects of chemicals in the environment and the problems encountered trying to control them.

A report was produced, focusing on the management of the incident by the Area office, the NCEHS, as well as input by WRc (a research contractor) and other contractors. An examination of the actual data available and the data that were needed and may have helped in the investigation was also presented. Finally the communications and how the NCEHS were contacted, at what levels and how in future they could or should deal with enquiries were also considered.

Recommendations were made on how similar incidents of this level could be handled and dealt with in future. In light of the commitment and duration of work undertaken on this incident, the report produced has been included in the appendices (Appendix 4). A brief summary of some of the key conclusions and recommendations from the report follow:

- Incident investigations require a tiered approach, specifically towards analysis. Such a tiered system would help focus and lead incident investigations.
- Communication during incidents must be streamlined, to convey the Agency's control of the incident to the public, media and stakeholders. Incident rooms must have scientific staff available to understand and convey technical information.
- Increased awareness of the NCEHS's ETAS information service is needed. Adherence to the hierarchical, tiered structure of contacts must be maintained.
- Clarification on the remit of ETAS is required and must be communicated to its customers. High levels of support, for incidents further afield would have ramifications on other NCEHS work and obligations.
- Computer processing of routine monitoring data would highlight potential pollution problem areas. Combining several existing databases of chemicals and their physical, chemical and ecotoxicological properties, would generate a larger knowledge base to help direct and lead analyses and investigations.

1.4.3 The Direct Toxicity Assessment Section

The Direct Toxicity Assessment (DTA) Section within the NCEHS primarily develops applications, methods and risk assessment approaches for effluent control, receiving water assessment and contaminated land. Direct toxicity assessment (DTA) as an approach uses biological effect measures to control mixed effluent discharges. The benefit of a DTA approach is that the whole toxicity of a mixture is measured, therefore considering and measuring any additive or synergistic effects in the mixture. Johnson *et al.* (1999) have suggested the application of DTA where there are:

- Existing discharges causing damage
- New discharges or process changes are made
- Problems with biological surveys
- Potential risk to vulnerable sites
- Changes in policy
- Sites where BAT is being implemented

Apart from a few toxicity-based discharge consents (under the WRA 1991) most existing chemical control systems in England and Wales are based on single substance controls. It is however unusual for chemicals to be discharged singularly and in a pure form. It is also rare for the complete composition of these sometimes complex, mixed discharges to be known or characterised. A discharge may contain unknown contaminants, but also additive and even synergistic toxic effects may arise through interaction between chemicals in the effluent.

The DTA approach is a more holistic way of assessing the toxicity of substances compared to substance specific measures. The approach implicitly considers the additive, antagonistic and synergistic effects of chemicals in the mixture being tested, without the need for complete characterisation of the effluent. Although DTA has not been used in a regulatory capacity to any great extent in the UK to date, there has been extensive use of similar principles such as 'Whole Effluent Toxicity' (WET) in the US by the US EPA.

The Development of DTA

In the initial stages, the DTA method has been used to target river catchments, those showing greatest effects from pollution or those showing effects that cannot be explained through chemical analysis alone. The assessment includes the following stages:

- Review of existing catchment data
- Screening of discharges (hazard data)
- Risk assessment, using dilution and dispersion data
- Confirmation of toxicity through use of bioassays

The discharges entering the target catchment are firstly screened to identify those of concern and suspected of contributing to the in-stream effects. Risk assessments are then performed using toxicity and dilution data as well as other information about the receiving water to confirm earlier predictions. Where necessary, a Toxicity Reduction Evaluation (TRE) stage is then conducted to reduce the likely in-stream toxic effects of problem discharges. The TRE stage basically involves examining the problem and assessing solutions to mitigate the effects.

One advantage of the DTA approach is that an effluent does not need to be fully chemically characterised (each chemical in the effluent does not have to be individually identified) in order for the effluent to be assessed and controlled. Some effluents can contain many hundreds of different components and it is very unusual for complete characterisation data to be available for most discharges. Furthermore in effluents where synergistic effects occur between chemicals (e.g. a number of chemicals react to cause greater than additive toxicity), the DTA approach ensures the most efficient and effective control.

The DTA Demonstration Programme

The DTA Demonstration Programme (EA National R&D Project P2-094) was a collaborative project between industry, water companies and environmental regulators. In 1996 a group formed from the Environment Agency, SEPA and the Department of Environment Northern Ireland (DENI), produced a consultation document and set up the demonstration programme to demonstrate the use of DTA as a ecotoxicological tool for assessing polluting effluents.

The programme aimed to test the proposed protocol for the use of the DTA approach. The original protocol outlined the following four steps (Forrow *et al.*, 1998):

1. Discharge prioritisation
2. Discharge characterisation
3. Toxicity reduction and licensing
4. Compliance monitoring

This was later revised and became a seven-stage protocol (Figure 1.13). An initial location prioritisation stage was introduced prior to selection and prioritisation of discharges. Separate steps to cover the characterisation of the toxicity, and fate and dispersion in the receiving waters were also incorporated. Finally, a stage for the assessment of the need to reduce the discharge was added into the protocol, before moving on to the toxicity reduction evaluation and implementation stages.

Through applying DTA it was found that more emphasis was needed on the assessment of the need to reduce toxic discharges and the planning of a TRE approach to achieve this. Focus was also given to monitoring and appraising the improvement plans once in operation, reflecting the importance of these stages within the method.

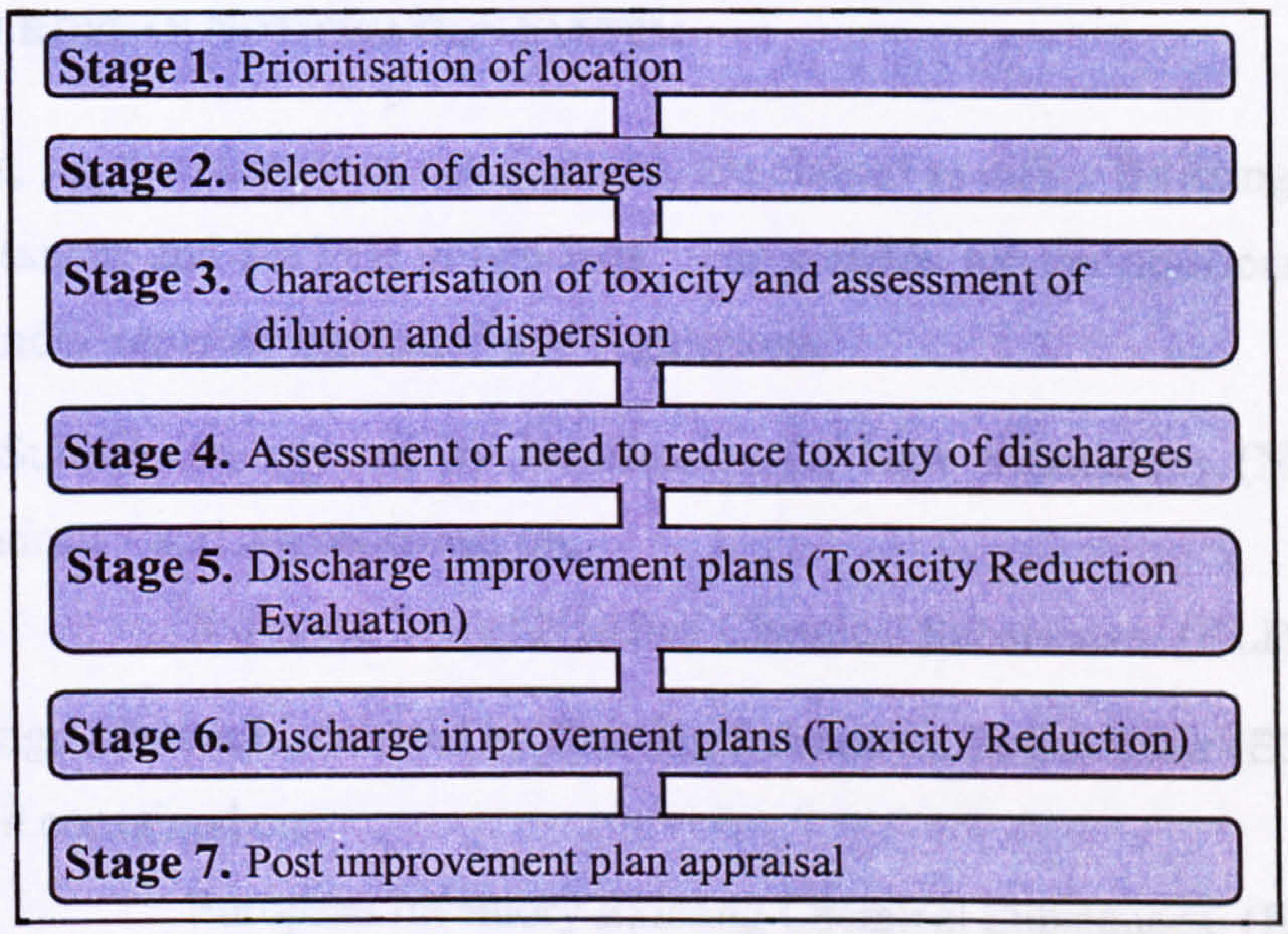

Figure 1.13 - Seven-stage protocol for DTA (Tinsley, 1998)

The collaborating groups completed the DTA demonstration programme in September 2000, some of the learning points highlighted by the group were:

- Early screening of discharges is vital to ensure efficient use of resources
- Need to synchronised testing of chemistry, biology and fisheries to ensure the data is current
- Some levels of water hardness cause culturing
- Correlation between *Daphnia* test results and chemical and biological luminescence test results is poor, possibly requiring a larger test battery
- Inter laboratory variation was low, with good accuracy using the rapid *daphnia* tests
- Courier services are variable and affect the transportation of samples

These along with other points may lead to changes in the DTA protocol (Figure 1.13), and the proposed risk assessment framework. In moving towards implementation of DTA as a tool for the control of pollution in the environment, the next step will involve demonstrating how the method of assessment can be integrated into existing control systems and educating industry and regulators in its use and value.

1.5 THE EUROPEAN NOTIFICATION SYSTEM

All chemicals, for the purpose of notifications, are classed as either Existing Substances or New Substances and are held in two lists. The systems for the notification of each are covered under separate legislation and regulations:

New Substances, covered by Notification Of New Substances (NONS) regulations - and are contained on,

European List of Notified Chemical Substances, (ELINCS)

Existing Substances, covered by Existing Substances Regulations (ESRs) - and are contained on,

European Inventory Existing Chemical Substances, (EINECS)

The term "new substance" refers to any chemical marketed in the EC since 18th September 1971, (EC, 1996a).

1.5.1 Existing Substances Regulations

For existing substances the initial information required for the notification is requested from any company who produced or imported into the EC more than 10 tonnes in any one year between 23rd March 1990 and 22nd March 1994. These data are used to assess the hazardous nature of the substances and aids the compiling of priority lists.

Of approximately 110,000 substances that are named on EINECS, CAs in European Member States are currently assessing 110 of them. There are currently three priority lists and a fourth is being drawn up (Appendix 5).

There are three main stages to the Existing Substances Regulations, each of which is outlined below.

1. Data collection stage, companies who import or produce substances covered by the ESRs are required to send summaries of relevant readily available data to the European Chemicals Bureau (ECB).
2. Selection of priority substances, the EC is responsible together with the CAs for producing priority lists of the substances for assessment according to the preliminary data.
3. The evaluation and risk assessment of the selected priority substances is usually the longest stage. A suggested risk assessment process is outlined in guidance accompanying the regulations. These risk assessments can be very complicated for substances with extensive use patterns.

The first priority list produced was basically formed listing substances that Member States wished to see on it, whilst at the same time the Informal Priority Setting method (IPS) was being devised by the work group of the same name. The IPS ranking method was never really used to any great extent however. A second priority list was formed, which used data in the International Uniform Chemical Information Database, (IUCLIDS) to automatically rank substances. The chemicals that did not make the second list along with others proposed by MS were used to produce a third priority lists. A forth priority list is being constructed using the European Ranking Method (EURAM) which is similar to the original IPS method (Hansen *et al.*, 1999).

Member States then bid for substances on the various priority lists, with a number of reasons influencing their choice and quantity of substances; industrial pressures, research interests, data availability, etc. (Brooke, 1997, *pers. com.*). Member States having opted to carry out assessments on various chemicals, then collate available data and interpret the various tests and results. Not all tests and data will be to the required Organisation for Economic Co-operation and Development (OECD) Test Guidelines or to Good Laboratory Practice (GLP). A comprehensive risk assessment is then completed leading to one of three conclusions (EC, 1996a):

1. There is no need, at this stage, for further information or for controls beyond those already being applied.
2. Risks are not well enough understood and further information, which may include further testing, is required.
3. The case for further controls, beyond those already in operation, should be considered.

The CA presents the conclusion to the EC, who present the risk evaluations to a committee of Member States. The risk assessment is discussed and agreed on by technical experts and then the committee returns a verdict by majority vote on the proposed conclusion. If the assessment is accepted the EC will publish the evaluation and proposals.

Of the 110 priority chemicals the first draft risk assessment reports are available for 81 of the substances. Of these the conclusions have been agreed for 45 substances, however final risk assessment reports have only been published for 3 substances to date.

- 2-(2-methoxyethoxy)ethanol
- 2-(2-butoxyethoxy)ethanol
- Benzene, C_{10-13} alkyl derivatives

1.5.2 Notification of New Substances

The regulations require that those placing a new substance on the market to:

(i) Notify to a CA their intention to place a new substance on the market.

(ii) Provide the CA with certain information on the substance.

Completion of these two tasks comprises a notification. As part of the second stage, the notifier is required to produce and supply the CA with a technical dossier providing the following details concerning the substance:

- Data on its chemical identity
- Estimate on the quantity to be placed on the EC market
- Details of the substance's functions and uses
- Data on its Physiochemical, toxicological and ecotoxicological properties
- Recommended precautionary, disposal and emergency measures
- Proposals for classification and labelling, and if dangerous, a safety data sheet

This data is supplied in a standard format called *the Structured Notification Interchange Format* (SNIF), the structure of which is outlined in Table 1.2.

Base Set Information		
0	Manufacturer and notifier identity and location of production site	
1	Identity of the substance	
	1.1 Name	1.3 Composition of substance
	1.2 Molecular, structural formula	1.4 Methods of detection & determination
2	Information on the substance	
	2.0 Production	2.4 Emergency action in case of spillage
	2.1 Purpose of use	2.5 Emergency action in case of injury
	2.2 Estimated production/imports	2.6 Packaging
	2.3 Recommended precautions	
3	Physiochemical properties	
	3.0 Standard state	3.8 Partition Coefficient o/w
	3.1 Melting point	3.9 Flash point
	3.2 Boiling point	3.10 Flammability
	3.3 Relative density	3.11 Explosive properties
	3.4 Vapour pressure	3.12 Self-ignition temperature
	3.5 Surface Tension	3.13 Oxidising properties
	3.6 Water solubility	3.15 Granulometry
4	Toxicological studies	
	4.1 Acute toxicity	4.3 Other effects
	4.2 Repeated dose	
5	Ecotoxicological studies	
	5.1 Effects on organisms	5.3 Sorption tests
	5.2 Degradation	
6	Possibility of rendering substance harmless	
	6.1 For industry/skilled trades	6.2 For the public at large
7	Risk Assessment	
9.1	Declaration of unfavourable effects on man and environment	
9.2.1	Proposed classification and labelling	
9.2.3	Proposed safety data sheet	

Table 1.2 – SNIF structure of *base set* information

Not all sections of the SNIF are completed for all substances. There are a number of levels of notification, dependent on the weight (tonnage) to be placed on the EC market (Table 1.3). The higher the level of notification the more data that will be required.

Level 2	>1000 tonnes/annum or >5000 tonnes in total	*Base set*, plus additional toxicity, including birds, and long term soil and water data, and further degradation tests.
Level 1 (upper)	>100 tonnes/annum or >500 tonnes in total	*Base set*, plus chronic, long term and biotoxicity data and sorption characteristics.
Level 1 (lower)	>10 tonnes/annum or >50 tonnes in total	*Base set*, plus some relevant data from Level 1 (upper) tests.
VII A	>1 tonnes/annum or >5 tonnes in total	*Base set* data
VII B	>100 kg/annum or >500 kg in total	Reduced *base set*, physical and chemical data, biodegradation and acute toxicity.
VII C	>10 kg/annum or >50 kg in total	Reduced *base set*, chemical identity, indication of use and acute toxicity.

Table 1.3 - Level of notification and the relevant data requirements (EC, 1996a)

The *base set* is the usual level of data required for substances marketed between 1 and 10 tonnes/annum. At lower tonnage levels, a reduced *base set* of data may be submitted, and at higher tonnage levels further testing will be requested. The reduced *base set* is mainly data on the physiochemical properties of the substance. Detailed ecotoxicological and environmental fate and behaviour data are not required at lower notification levels.

A Technical Guidance Document (TGD) was produced (EC, 1996a) that describes a suggested risk assessment process for the notification regulations. This TGD details a risk assessment system for both new and existing substances. In principle the risk assessments produced should be valid for all Member States, therefore generic, European-wide exposure scenarios are used.

The assessment calculations are conducted for what is defined in the TGD as a (EC, 1996a):

> "non-existing model environment with predefined, agreed environmental characteristics. These environmental characteristics can be average values or reasonable worst-case values depending on the parameter in question,"

If a new company applies to notify a substance that has already been previously notified the company must still submit a *repeat notification*. This contains the same information as a full notification, however the two or more companies involved are encouraged to share data. The contact details of the previous notifier are made available to the new notifier and the sharing of test data is encouraged. This data sharing procedure aims to minimise the amount of animal testing that is required in the notification process. From experience, the UK CA has noted that most companies when faced with a repeat notification, decide either not to produce/import the substance (due to industrial competition etc.) or do enter into data sharing agreements.

If a company has notified at an initial tonnage level but later exceeds this level a notification upgrade is required. When a company is upgrading to a new level (except for Levels 1 & 2), they are required to send in a new notification with the extra data required as outlined in Table 2. For upgrades to Level 1 or 2 the CA will advise on what specific tests are deemed necessary, tailoring each test programme to the uncertainties and data requirements for that substance.

From the data that is collated for the notification a risk assessment must then be prepared. This is an "assessment of the actual and potential risks created by each notified new substance to people and the environment" (EC, 1996a). The risk assessment forms part of the NONS process, and is intended to be "an holistic approach, which covers the lifecycle of a substance, and considers the effects on all environmental compartments and on people as workers or consumers" (EC, 1996a). This risk assessment process is considered in greater detail in the following section.

1.6 ENVIRONMENTAL RISK ASSESSMENT

In this section risk assessment in general and more specifically environmental risk assessment is considered. The same underlying aim and approach applies to all risk assessment systems. However the methodologies may differ. The processes used by the ETS for setting EQSs, the proposed DTA risk assessment framework and risk assessments as part of the European notification system are all examined.

For a risk to exist three things are needed, an intrinsic **hazard** (e.g. lead, which can harm both man and the environment), there also needs to be a **receptor** (man, fish, etc.) and most importantly a **pathway** (e.g. digestion, deposition) between the two.

Hazard → Pathway → Receptor

Without these three components there is no, or very limited risk. The process of risk assessment is a multistage process in which the probability that specified harmful effects might occur is calculated (Figure 1.14).

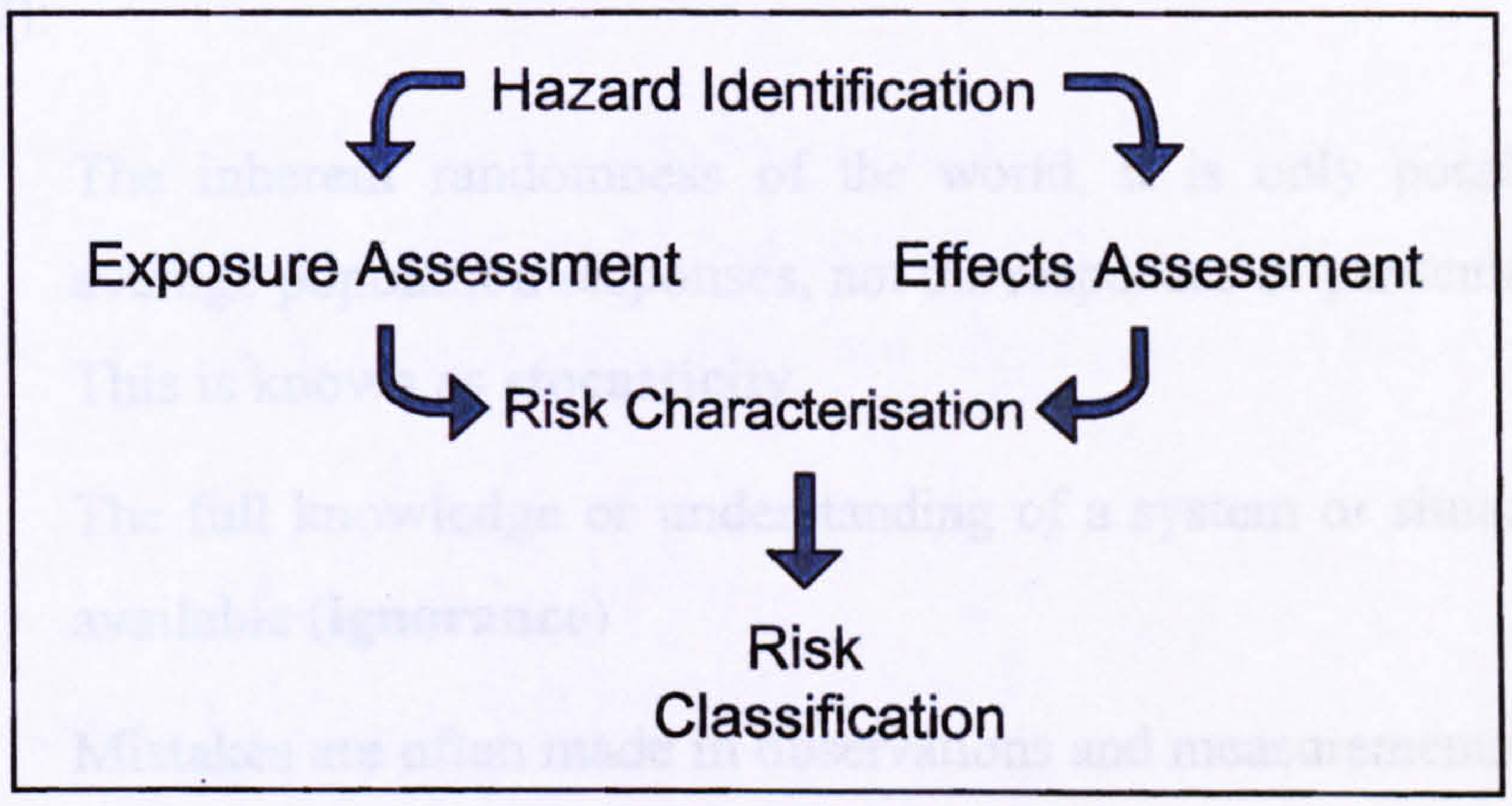

Figure 1.14 - The risk assessment process, (Robinson *et al.*, 2001)

The first step in this process is that of hazard identification, where the possibility of there being a cause for concern is determined. For new substances in the European notification system the hazard identification stage is intrinsic, risk assessments being performed for all substances. In other systems, for example DTA and ESRs hazard identification is carried out using initial data supplied. In the case of DTA this data is used to select and prioritise discharges for further assessment.

The next two stages involve the assessment of the exposure to, and effects of the substance. The exposure assessment attempts to approximate the concentration of the substance that may be found in the environment, often termed as the Predicted Environmental Concentration (PEC). In calculating this value the volume of the substance produced and imported may be considered as well as the fate and behaviour of the substance in the environment. To assess the potential adverse effects of a substance, usually the effects on a small number of organisms are measured and these results extrapolated to protect all species. This value is often termed as a Predicted No-Effect Concentration (PNEC).

At the risk characterisation stage of the assessment the likely exposure level (PEC) and the likely effect level (PNEC) are compared and a ratio or summary value calculated. It is from the magnitude of this value that further risk management options such as risk reduction or risk elimination may be taken.

In the calculation of risk there are many uncertainties. There may be limited knowledge of the processes in production, formulation or use of the substance. Uncertainty also arises when extrapolating the results of a few effect test to protect all species. The sources of these uncertainties can be summarised as (Suter II & Barnthouse, 1993; Calow, 1997):

(i) The inherent randomness of the world, it is only possible to define average population responses, not the responses of particular individuals. This is known as **stocasticity**

(ii) The full knowledge or understanding of a system or situation are rarely available **(ignorance)**

(iii) Mistakes are often made in observations and measurements **(fallibility)**

Some of the assessment systems for substances in the environment that are used within the NCEHS are considered below.

1.6.1 The Environmental Quality Standard system

The EQS assessment system was examined. The assessment scheme as detailed (Figure 1.12) involves the collation of ecotoxicological data, the assessment of this data for suitability and then the application of an assessment or uncertainty factor (AF) to derive a EQS value.

Some consideration of the fate and behaviour of a substance in water is made, however the likelihood of exposure is not considered. The procedure cannot be considered as a risk assessment because only the effects of the substance have been considered.

1.6.2 NONS risk assessments

The 7th amendment to the Dangerous Substances Directive[27] (packaging and labelling) encourages notifying companies to produce their own risk assessments (RA). The notification fee of approximately £6000 is partially refunded if the CA accepts the notifier's RA. It is however, ultimately the CA's duty to produce the RA and pass it on to the EC. The proposed environmental risk assessment procedure for new substances is outlined in detail in the EC TGD (EC, 1996a). The exposure and effect assessment stages shall be considered in turn.

Exposure Assessment

As part of the exposure assessment, the releases of a substance are considered, along with the fate and behaviour of the substance in the environment.

The environment is potentially at risk to exposure of chemical substances at all stages of the substance's lifecycle. The lifecycle of a substance and the various stages in it are shown in Figure 1.15. The lifecycle stages that are principally considered in this RA system are:

- Production
- Processing
- Transport and storage
- Formulation
- Use - Professional large scale use (industry)
    - Professional small scale use (trade)
    - Private or consumer use
- Disposal, including waste treatment

The emission patterns from each life stage vary widely from one or more well-defined point sources to diffuse releases from many small point sources (e.g. households) or line sources (e.g. a road or motorway). Emissions can also be either continuous or intermittent releases.

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[27] Council Directive 92/32/EEC amending for the seventh time Directive 67/548/EEC on the approximation of laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances

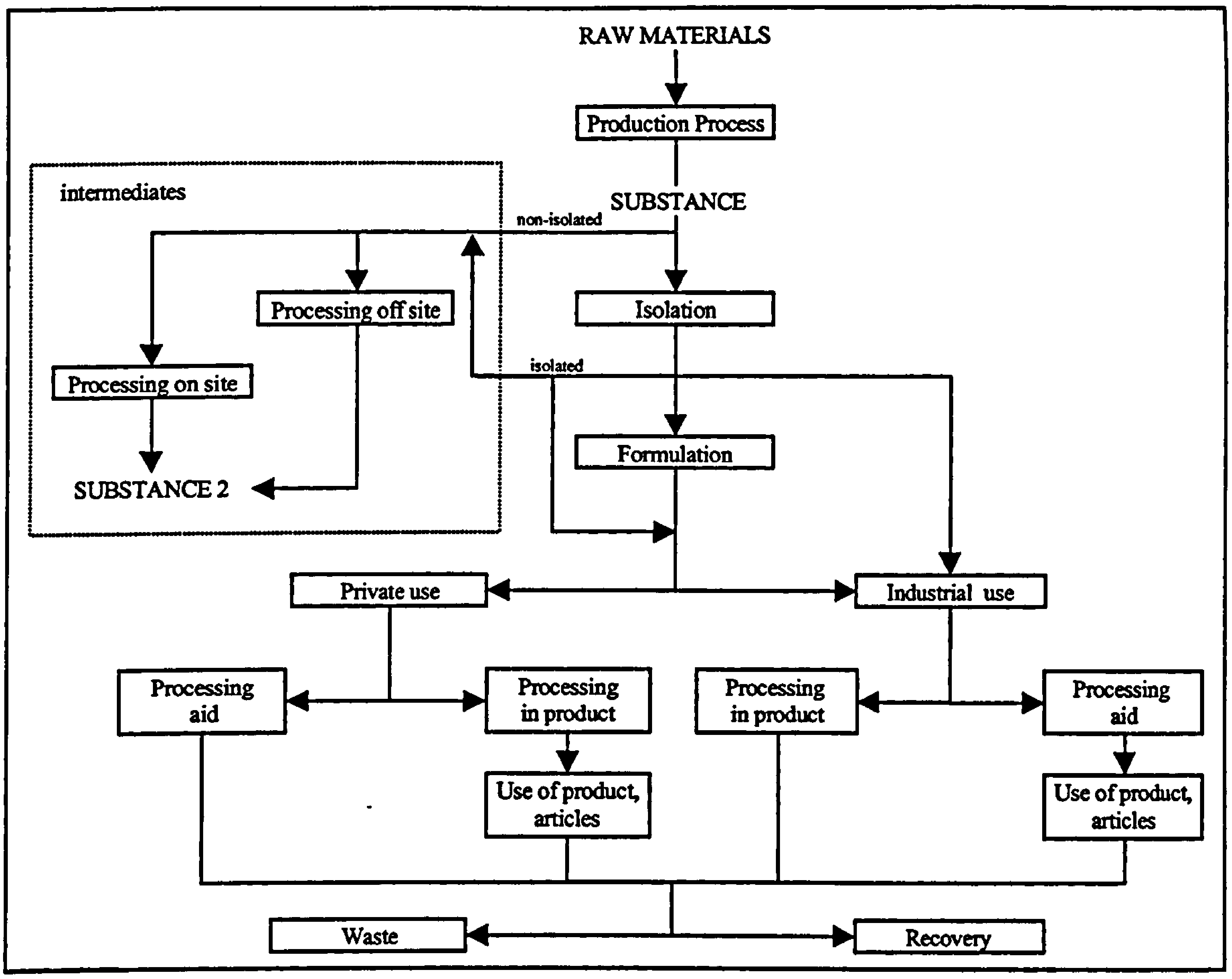

Figure 1.15 - Schematic representation of the lifecycle of a substance, (EC, 1996a; Poel, 1997)

For new substances there will be no measured levels of the chemical in the environment, therefore the concentration of a substance that will be emitted to the environment must be estimated. A PEC is calculated, primarily using data supplied by the producers and importers of a substance, but also data from emission scenario documents (data on generic emission properties by industry type). These standard emission scenarios are detailed in the A and B Tables of the TGD (EC, 1996a).

There is much discussion on the accuracy of the values in these tables on the Internet (http://ecb.ei.jrc.it/Euses/blacklst.htm, EUSES Blacklist; ECB, January 2001), however they serve as a reasonable worst-case estimate for the intended generic assessments.

Emissions of the substance will occur throughout the lifecycle of the chemical. These emissions may be directed to different parts of the environment. Furthermore, once emitted the substance may transfer from the air to water, or from soil to water. Figure 1.16 shows some of the emission and distribution routes a substance may follow.

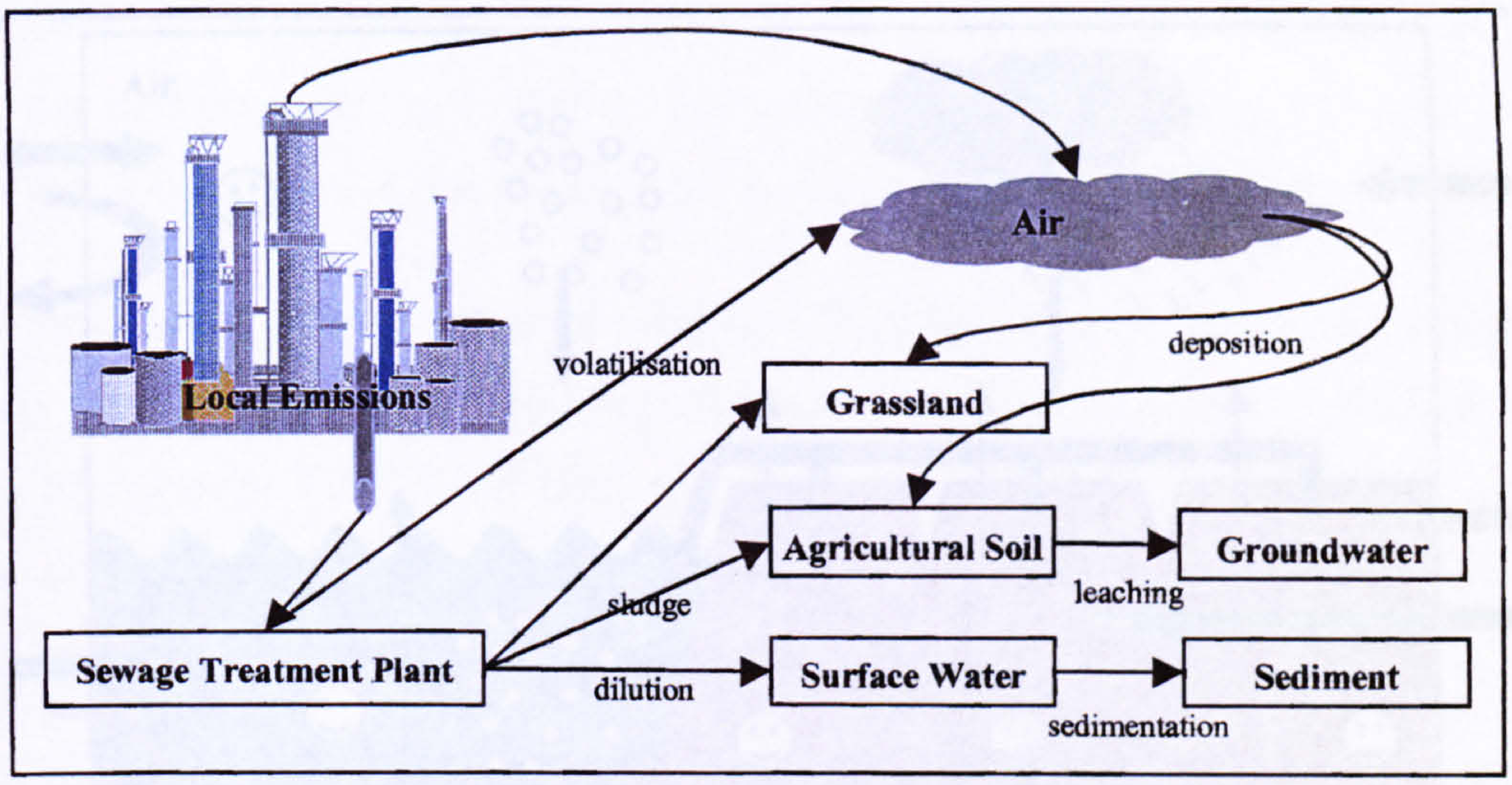

Figure 1.16 - Possible emissions and distribution routes, (redrawn from EC, 1996a)

For the purpose of the assessment a standardised generic environment is defined to allow European wide risk assessments to be calculated. Environment default values are set for properties such as the density of soil and air; temperature (12°C); and various other characteristics. The model used to describe the environment is called a multimedia compartment model (Figure 1.17). These models represent the environment as a set of spatially homogenous (zero dimensional) boxes, one box for each compartment. Most of the models use six compartments to describe the environment. The environmental compartments used in the exposure assessment are:

Air - this is a bulk compartment, consisting of a gas phase, an aerosol and a rainwater phase. Airflow (wind), evaporation (from soil and water) wet and dry deposition, and degradation all influence the concentration of a substance in air.

Aquatic - this compartment (also termed 'water compartment') refers to the truly dissolved state of a substance. Colloidal or macromolecular materials are considered to be part of the compartment's suspended matter and biota. These phases influence the fate of chemicals by binding the substance and preventing mass transfer and degradation processes in the aquatic phase. Suspended matter acts as a physical carrier across the sediment-water interface.

Suspended matter - refers to all abiotic colloidal or macromolecular materials in the aquatic compartment that are not truly dissolved. There is a continual flux across the sediment-water interface through sedimentation and re-suspension, sewage treatment plants, and aquatic organisms are other sources of suspended matter.

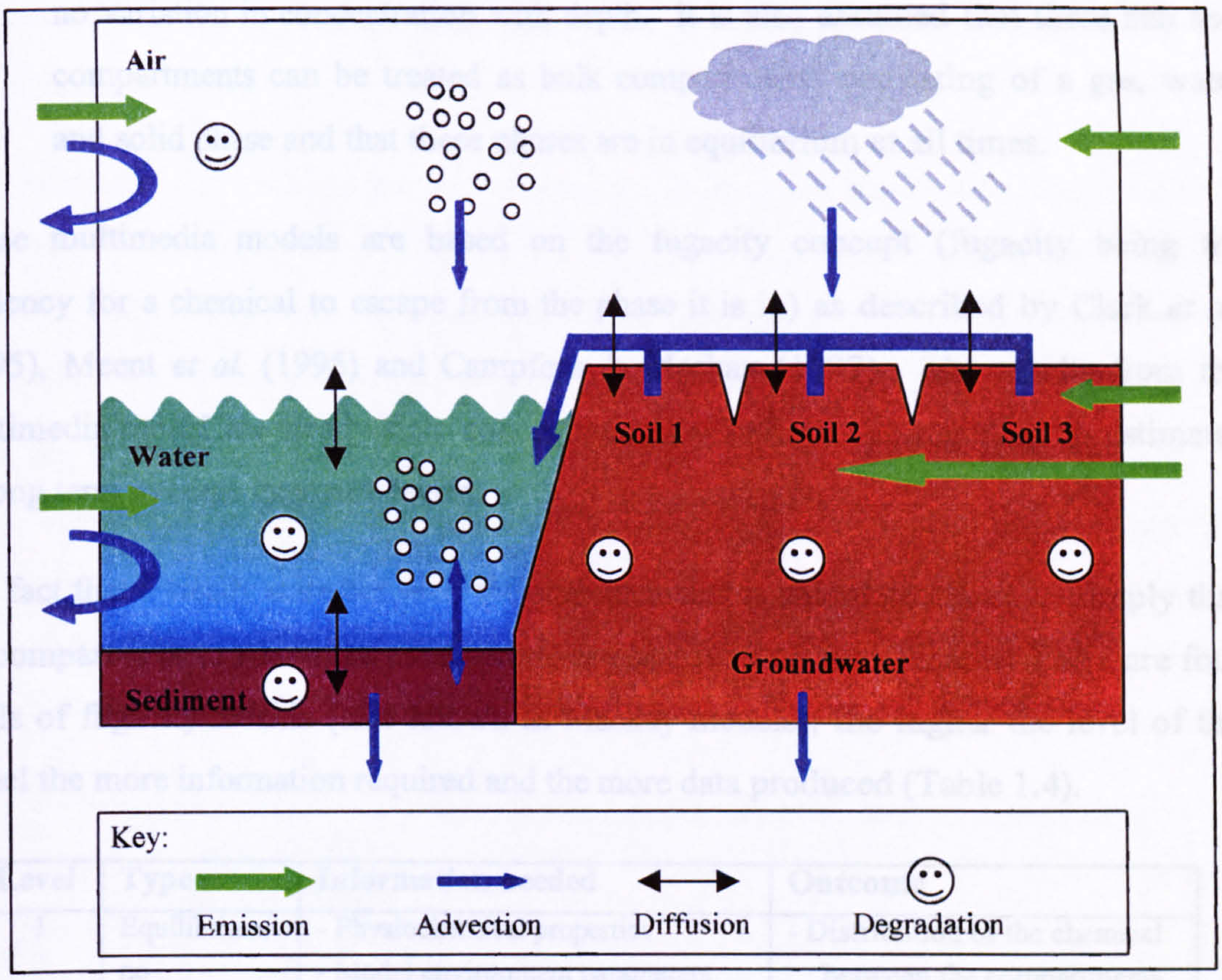

Figure 1.17 - Multimedia compartment model, (redrawn from Meent *et al.*, 1995)

Aquatic Biota - this compartment refers to all living organisms in the aquatic compartment, from bacteria to mammals. The compartment is small and usually plays an insignificant role with regard to the overall fate of a substance.

Sediment - this compartment can be treated as a bulk compartment, consisting of a water phase and a solid phase. Equilibrium is assumed between these two phases, however, if the sedimentation of particles is greater than the re-suspension this top layer will be continually refreshed.

Soil - this is the most stationary, and therefore most spatially inhomogeneous of all the environmental compartments. Unfortunately, the fate of chemicals is largely dependent on the characteristics that vary widely between soil types. Also the soil's use is a factor determining the means by which chemical loading occurs. A single soil compartment is not sufficient to reflect the role of soil in multimedia chemical fate models, therefore soil is subdivided into natural soil (Soil 1), agricultural soil (Soil 2) and industrial soil (Soil 3). Usually only the topsoil layer is considered, and assumed to be homogeneous in as far as there is no variation in concentration with depth. It is also assumed that these sub soil no variation in concentration with depth. It is also assumed that these sub soil compartments can be treated as bulk compartments consisting of a gas, water and solid phase and that these phases are in equilibrium at all times.

These multimedia models are based on the fugacity concept (fugacity being the tendency for a chemical to escape from the phase it is in) as described by Clark *et al.* (1995), Meent *et al.* (1995) and Campfens & Mackay (1997). The results from the multimedia model are steady-state concentrations, which can be regarded as estimates of long term average exposure levels.

The fact that a steady state between the compartments is calculated does not imply that the compartment to which the emission takes place is of no importance. There are four levels of fugacity-models (also known as Mackay-models); the higher the level of the model the more information required and the more data produced (Table 1.4).

Level	Type	Information needed	Outcome
I	Equilibrium, no degradation	- Physiochemical properties - Model environment parameters - Amount of chemical in the system	- Distribution of the chemical between the compartments
II	Equilibrium, degradation	- Level I plus, - Overall discharge rate - Transformation and advection rates in different compartments	- Distribution between compartments - Environmental life time
III	Steady state, degradation	- Level II plus, - Compartment specific discharge rates - Inter-media transfer rates	Greater accuracy in - Life time - Chemical quantities and conc. in different compartments
IV	Non-steady state, degradation	- Similar to Level III	- Time before steady state achieved - Time needed to disappear after final discharge

Table 1.4- Hierarchy of multimedia fugacity models, from Meent *et al.* (1995)

The major simplification that compartmentalisation represents in the box model is both a strength and a weakness. Removing spatial considerations and interactions allows a focus on the inter-media distribution of a substance and its fate within these media. With the assumption of homogeneity however, comes the risk that small scale and localised risks may be overlooked. When these models are used to predict exposure concentrations for large areas, the homogeneity of the compartments becomes a far less realistic assumption.

To overcome this problem the use of a nested multimedia model was suggested at the Society of Environmental Toxicology and Chemistry (SETAC) conference 1993 (Meent, 1993). In a nested model, interactions between a number of spatial scales (e.g. regional, continental, global etc.) are considered as shown in Figure 1.18.

For the risk assessment of new notified substances the model environment is divided into three spatial scales, these being continental, regional and local. The concentrations of a chemical substance in the continental scale are used for background and inflow concentrations for the regional scale, which in turn provides background and inflow concentrations for the local scale estimates.

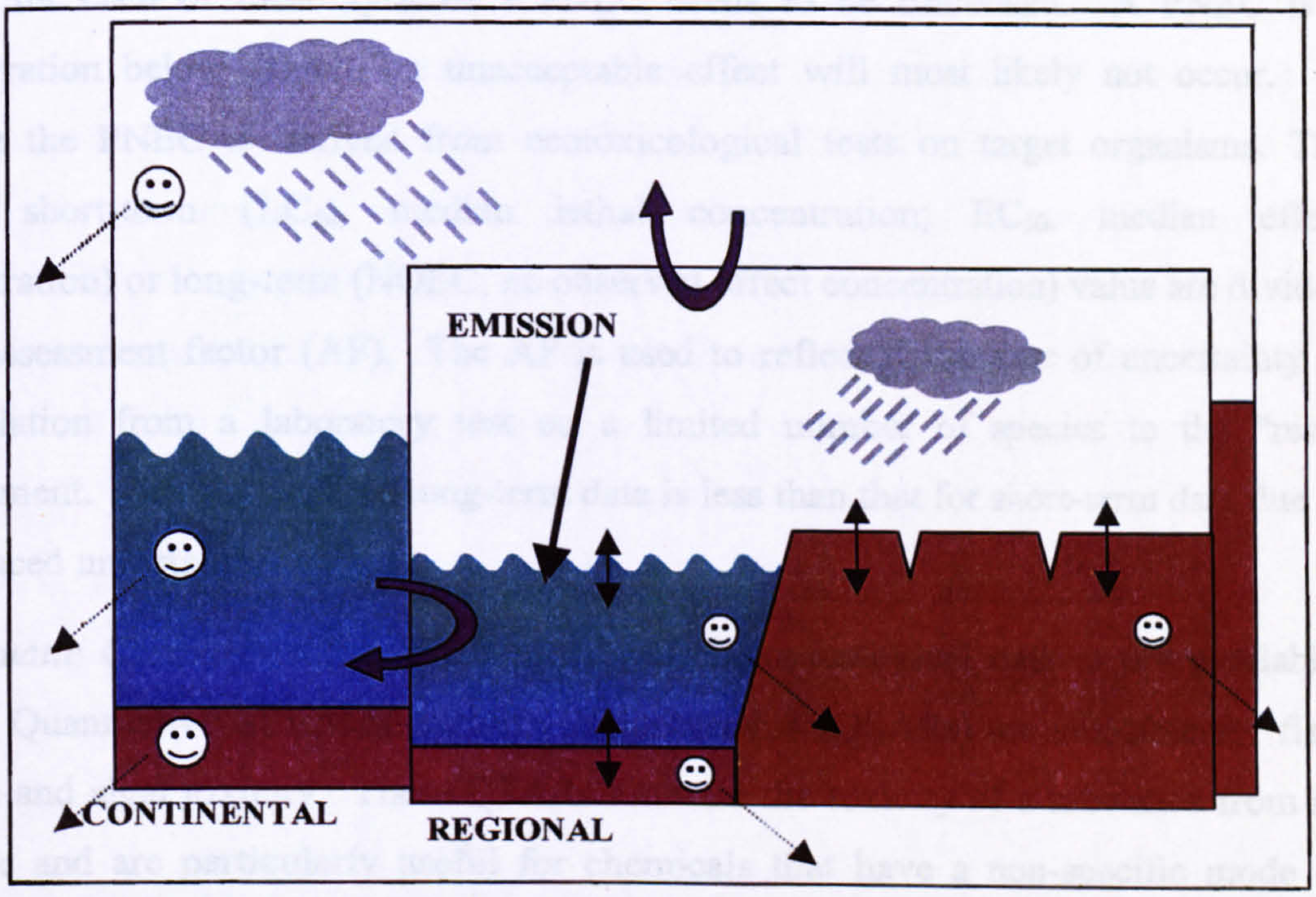

Figure 1.18 - A nested multimedia compartment model, (redrawn from Meent *et al.*, 1995)

For new substances at low tonnage volumes the assessments tend towards site specific assessments of point source emissions and the local environmental concentration has the major impact (PEC_{local}). However, at the higher tonnage levels and in cases of high toxicity and/or persistency, the larger regional environmental concentrations are also of interest ($PEC_{regional}$). PEC values for each spatial scale and each environmental compartment are calculated.

Effect Assessment

The protection goals for the environment are:

- Aquatic ecosystems
- Terrestrial ecosystems
- Atmosphere
- Top predators
- Microbial activity in a sewage treatment plants

The three compartments are specifically considered, as well as fish eating and worm eating "top predators". The micro-organisms in sewage treatment plants (STPs) are considered due to their importance in controlling the exposure to the aquatic compartment.

Ideally for each of these systems a PNEC needs to be calculated. A PNEC is a concentration below which, an unacceptable effect will most likely not occur. In practice the PNEC is derived from ecotoxicological tests on target organisms. The lowest short-term (LC_{50}, median lethal concentration; EC_{50}, median effect concentration) or long-term (NOEC, no observed effect concentration) value are divided by an assessment factor (AF). The AF is used to reflect the degree of uncertainty in extrapolation from a laboratory test on a limited number of species to the "real" environment. The AF used for long-term data is less than that for short-term data due to the reduced uncertainty.

The Aquatic Compartment – When measured ecotoxicological data is not available, reliable Quantitative Structural Activity Relationships (QSARs) are available for fish, daphnia and algal toxicity. These QSARs estimate the toxicity of a substance from its structure and are particularly useful for chemicals that have a non-specific mode of action.

Once the lowest, $L(E)C_{50}$ has been determined an assessment factor based on the quantity of data that was available for the extrapolation is used to give a $PNEC_{aquatic}$ value, (Equation 1.1 and Table 1.5).

$$PNEC_{aquatic} = L(E)C_{50_{\min}} \div AF$$ **Equation 1.1**

Data Available	Assessment Factor
At least one short-term $L(E)C_{50}$ from each of three trophic levels of the base-set (fish, *daphnia* and algae)	1000
One long-term NOEC (either fish or *daphnia*)	100
Two long-term NOECs from species representing two trophic levels (fish and/or *daphnia* and/or algae)	50
Long-term NOECs from at least three species (normally fish, *daphnia* and algae)	10
Field data or model ecosystems	Reviewed on a case-by-case basis

Table 1.5– Assessment factors for PNEC derivation (EC, 1996a)

Risk Characterisation Ratio

Having calculated PEC and PNEC values as part of the exposure assessment and the dose-response assessment, risk characterisation is then conducted. This process involves the calculating of PEC/PNEC ratios, also termed as risk characterisation ratios (RCRs). For substances notified under NONS there are four possible conclusions from the risk assessment and risk characterisation process as detailed in Article 3.4 of Directive 93/67/EEC[28]:

PEC/PNEC ≤ 1

(i) The substance is of no immediate concern and need not be considered again until further information is made available in accordance with Articles 7(2), 8(3), 8(4) or 14(1) of Directive 67/548/EEC.

PEC/PNEC > 1

(ii) The substance is of concern and the competent authorities shall decide what further information is required for revision of the assessment, but shall defer a request for that information until the quantity placed on the market reaches the next tonnage threshold.

(iii) The substance is of concern and further information shall be requested immediately.

(iv) The substance is of concern and the competent authority shall immediately make recommendations for risk reduction.

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[28] Commission Directive 93/67/EEC laying down the principles for the assessment of risks to man and the environment, notified in accordance with Council Directive 67/548/EEC

The evaluation procedures linked with the testing for the aquatic environment have resulted in a highly structured decision scheme for the aquatic compartment, (Figure 1.19). If there is cause for concern further information will be required either when the volume of the substance reaches the next tonnage level, or immediately depending on the extent of this concern.

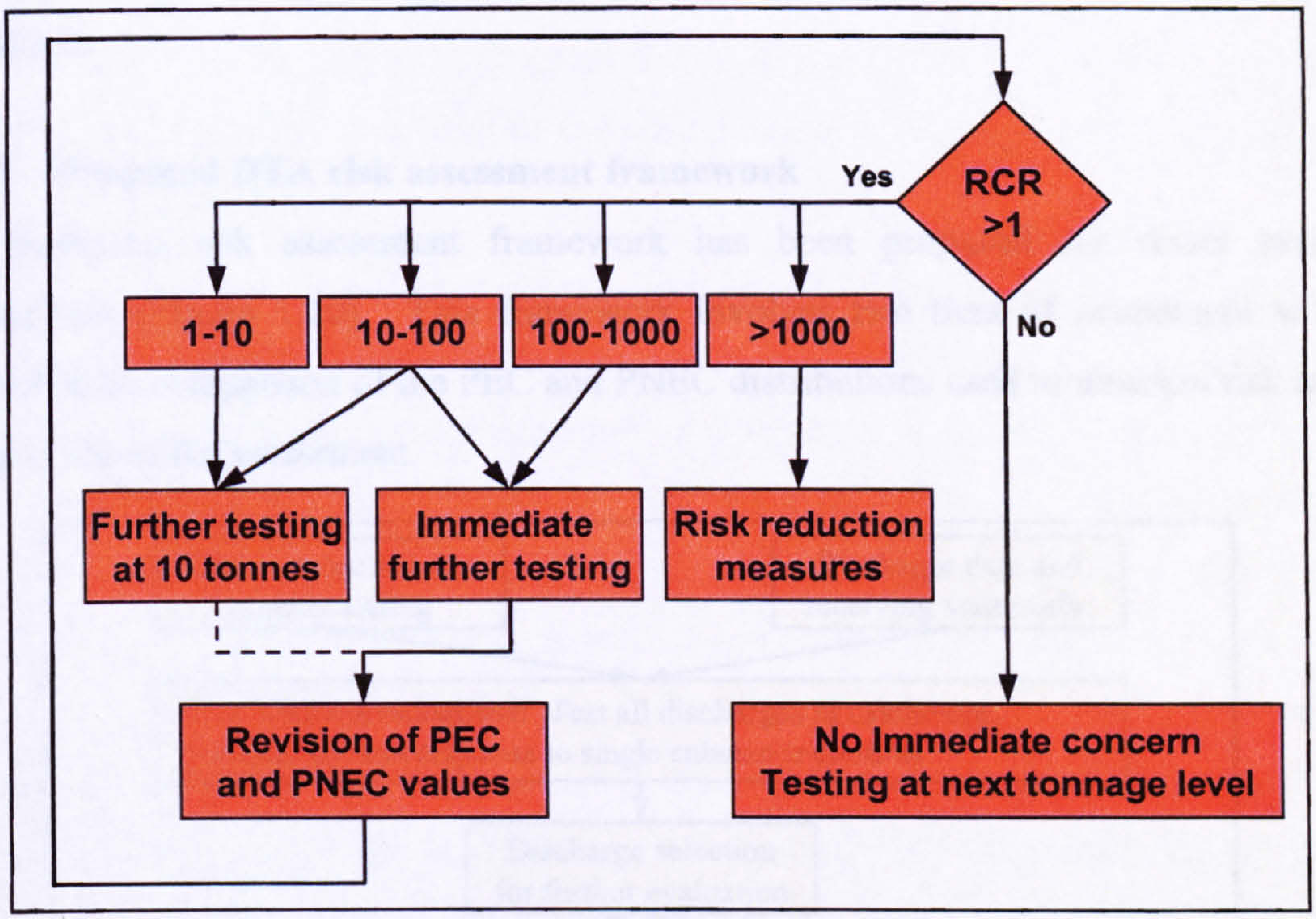

Figure 1.19 – Risk characterisation decision diagram for the aquatic compartment (adapted from Vermeire & Zandt, 1995; EC, 1996a)

This system of risk characterisation uses a deterministic value, the risk quotient (PEC/PNEC), to characterise and summarise the risk assessment. Such an approach bases the final outcome on single values for parameters that are reasonable or worst-case approximations of the values. The drawbacks of such an approach are (Suter II & Barnthouse, 1993):

- Worst cases may not be multiplicative or additive
- Worst case scenarios are inconsistent, e.g. the possibility of still worse cases
- Worse cases do not consider the probability of a particular event
- Conservative assumptions presume limited or no cost resulting from the regulation of false positives.

Probabilistic risk assessments, where distributions are considered rather than single values, are becoming more wide spread, particularly in the field of pesticide assessment (Solomon, 1996; Maund *et al.*, 1998). Through the use of a probabilistic risk assessment procedure the level of uncertainty acceptable in the risk assessment becomes a matter of policy rather than being implicitly considered within the assessment (Jager *et al.*, 1997). The proposed risk assessment framework for DTA includes a probabilistic approach.

1.6.3 Proposed DTA risk assessment framework

A theoretical risk assessment framework has been proposed for direct toxicity assessment (Figure 1.20). This framework involves two tiers of assessment with a probabilistic comparison of the PEC and PNEC distributions used to measure risk at the second tier of the assessment.

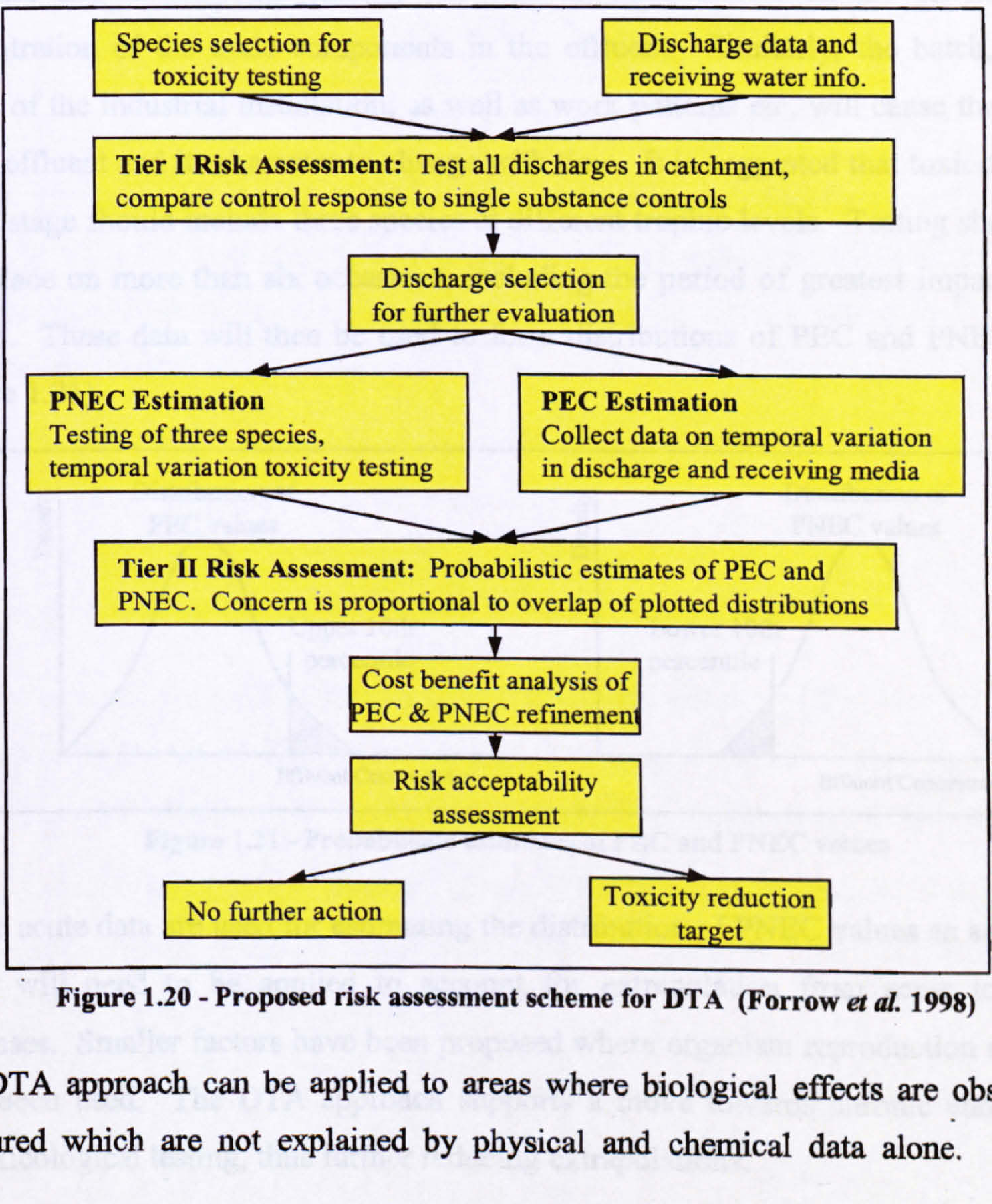

Figure 1.20 - Proposed risk assessment scheme for DTA (Forrow *et al.* 1998)

The DTA approach can be applied to areas where biological effects are observed or measured which are not explained by physical and chemical data alone. The risk assessment would be carried out based on whole effluent toxicity using representative organism, ecotoxicology tests and environmental and receiving water data

Tier I, Preliminary Risk Assessment – Under the proposed framework all discharges in a impacted catchment will be subject to a preliminary risk assessment stage. The hope here is that through the use of acute lethal testing of an invertebrate (and possibly another catchment specific sensitive organism) those discharges contributing to the observed toxic effect can be highlighted for further assessment. For this stage to be effective and worthwhile, the cost of the testing needs to be minimised, while ensuring environmental protection.

Tier II, Refined Risk Assessment – Those discharges showing acute lethal toxicity in the preliminary assessment stage will then go on to be considered in greater detail. The second stage will be probabilistic in nature. Variations in flow rate, seasonal variations, upstream and downstream effects, etc. will all have effects on the environmental concentration of the toxic components in the effluent. Similarly, the batch, or shift nature of the industrial installation, as well as work patterns etc. will cause the amount of the effluent and its character to change with time. It is suggested that toxicity testing at this stage should include three species at different trophic levels. Testing should also take place on more than six occasions, including the period of greatest impact, where known. These data will then be used to form distributions of PEC and PNEC results (Figure 1.21).

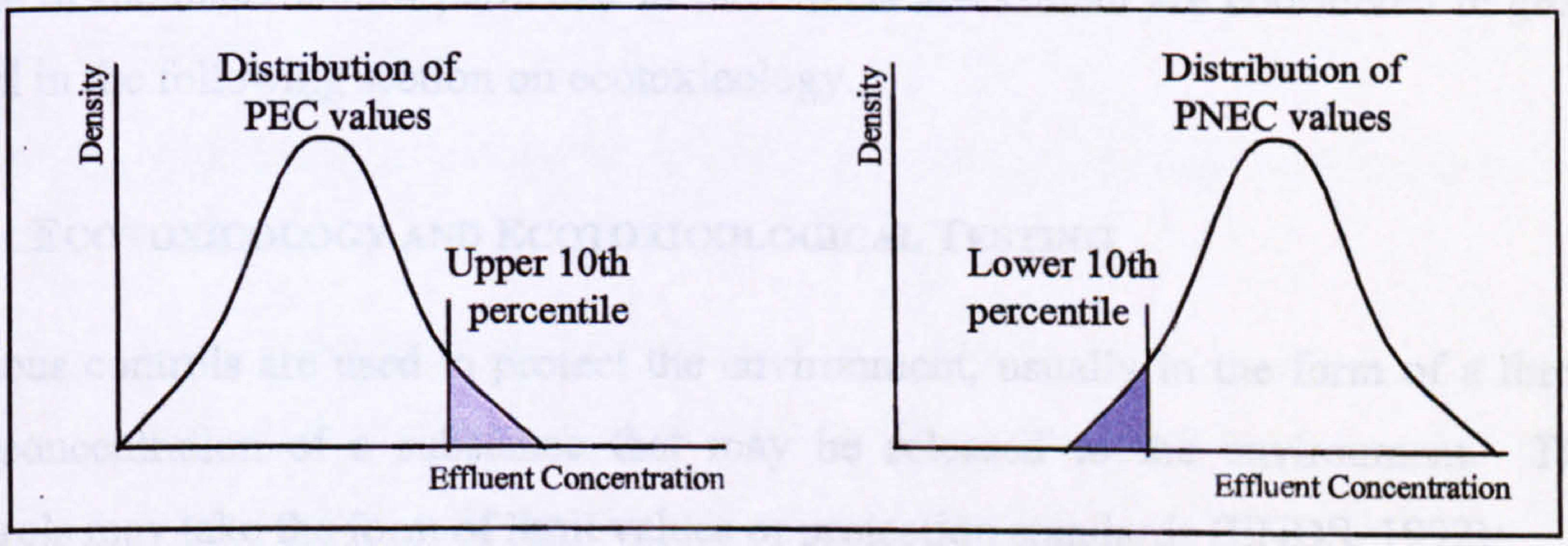

Figure 1.21 - Probabilistic estimates of PEC and PNEC values

Where acute data are used for estimating the distribution of PNEC values an assessment factor will need to be applied to account for extrapolation from acute to chronic responses. Smaller factors have been proposed where organism reproduction endpoints have been used. The DTA approach supports a move towards chronic endpoints in ecotoxicological testing, thus further reducing extrapolations.

A comparison of the probabilistic PEC and PNEC distributions (Figure 1.22) gives a measure of the concern, the greater the overlap of the PEC and PNEC the greater the probability that the concentration of the effluent in the environment will cause effects to organisms. The setting of a limit level for this concern is a matter of policy, however an unacceptable risk has been proposed as being where the upper 10th percentile of the PEC distribution is greater than the lower 10th percentile of the PNEC. That is to say where the higher probable environmental concentrations are greater than the lower probable no-effect concentrations, there is cause for concern.

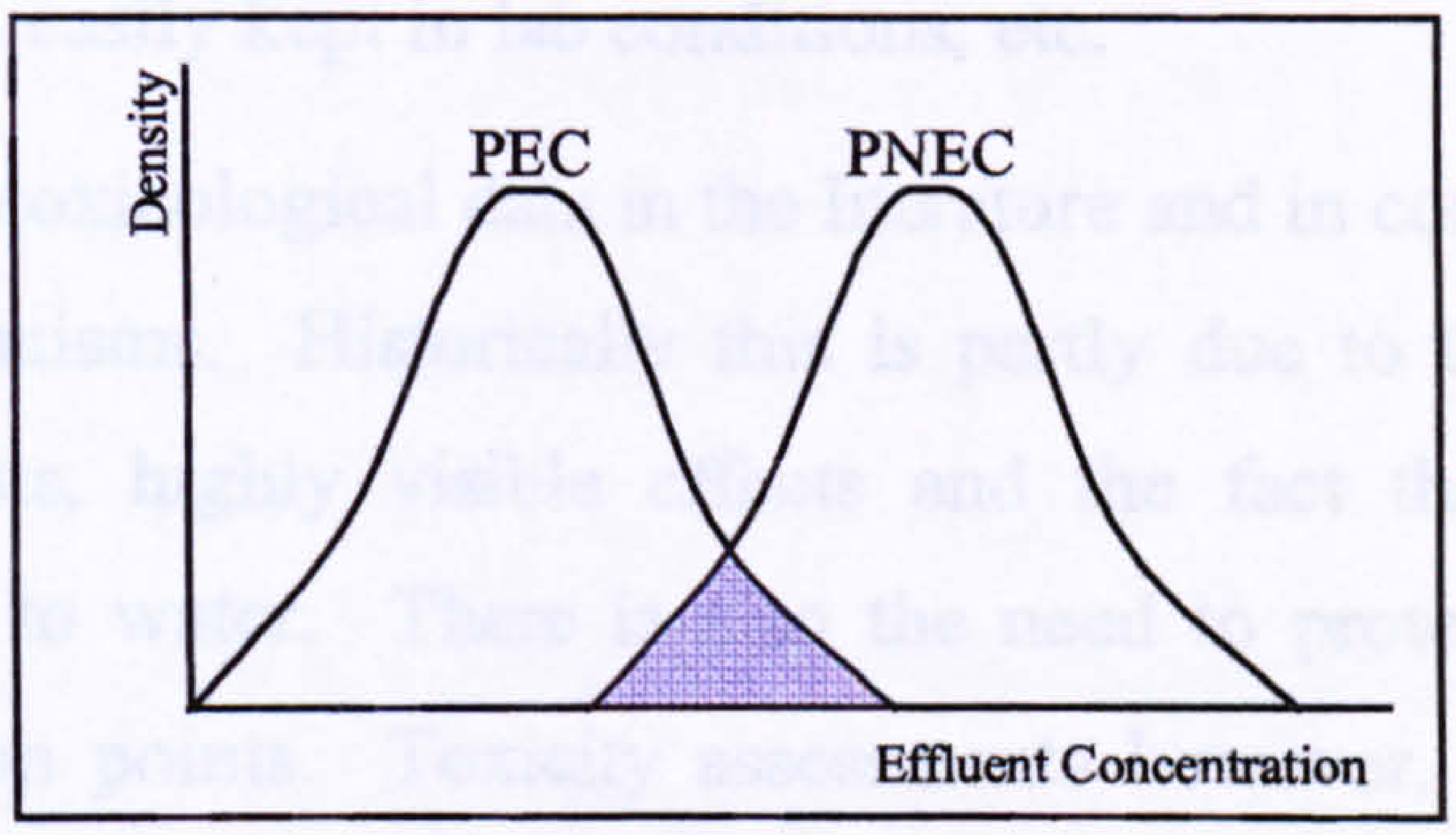

Figure 1.22 - Comparison of PEC and PNEC distributions

Where an unacceptable risk is identified a programme of toxicity reduction will be agreed between the discharger and the regulator. This programme will contain long and short-term goals, including the identification of the toxicant of concern, and the source of the toxicant in the industrial process.

Some of the uncertainties particular to the effects assessment are considered in greater detail in the following section on ecotoxicology.

1.7 ECOTOXICOLOGY AND ECOTOXICOLOGICAL TESTING

Various controls are used to protect the environment, usually in the form of a limit to the concentration of a substance that may be released to the environment. These controls may take the form of limit values or protection standards (ENDS, 1992):

- Limit Values (LVs) – these are fixed values for particular industrial sectors with no account taken of the local situation, based on what is achievable using best available technology (BAT)

- Environmental Quality Standards (EQS) – more flexible controls allowing consideration of the total input of chemicals from both diffuse and point sources into a particular watercourse

These protection standards and limit values are usually based on ecotoxicological tests conducted on target species. Also in the effect assessment stage of risk assessment, PNEC values can be derived from the results of ecotoxicological test results. Ideally the species tested are those likely to be affected by the contamination, or those that the controls aim to protect. Practical considerations must also be addressed, such as species that are readily available, easily kept in lab conditions, etc.

The major part of the ecotoxicological data in the literature and in commercial databases is based on aquatic organisms. Historically this is partly due to the relative ease of carrying out aquatic tests, highly visible effects and the fact that many industrial effluents are discharged to water. There is also the need to protect water quality at drinking water abstraction points. Toxicity assessments however, do not have to be limited to the aquatic compartment and an increasing amount of work is being carried out upon other environmental compartments e.g. sediment and soil.

Most toxicity tests are performed using single life stages (e.g. juvenile or adult), of single species, affected by a single substance. Although a few different species tests may be performed using the same chemical, to represent different functional groups or trophic levels in an ecosystem, the limit value used for protection is usually based on the most sensitive tested species.

An assessment, uncertainty or safety factor (AF) is normally then applied to account for the various uncertainties:

- Intra- and inter-laboratory variation of toxicity data.
- Intra- and inter-species variations (biological variance).
- Short-term to long-term toxicity extrapolation.
- Laboratory data to field impact extrapolation.

1.7.1 What is ecology?

Ecology is the study of the interactions that determine the distribution and abundance of organisms. To help us understand the complexity of ecosystems, various sub-systems have been defined. One of the earliest divisions came from Limnaeus, 1707-1778

(Moriarty, 1993), who laid out the foundations for the current classification system by defining each distinct type of organism as an individual 'species', drawing an analogy with crystals. The definition has since been refined by, Mayr, 1963 (in Moriarty, 1993) as:

> *Species are groups of interbreeding populations that are reproductively isolated from other such groups.*

Some of the other levels of organisation that are considered are:

Populations – These are individuals of one species that occur in a defined area, usually populations do not exists alone they form communities

Community – Defined as populations of different species that exist in the same area

Below the level of species, it is possible to study biological-chemical e.g. reaction of pollutants with enzymes, proteins etc. However at these levels of study the relevance of results to whole species, populations and ecosystems decreases. Figure 1.23 shows how the level of ecological organisation effects the uncertainty, relevance and errors in the tests performed and the resulting data.

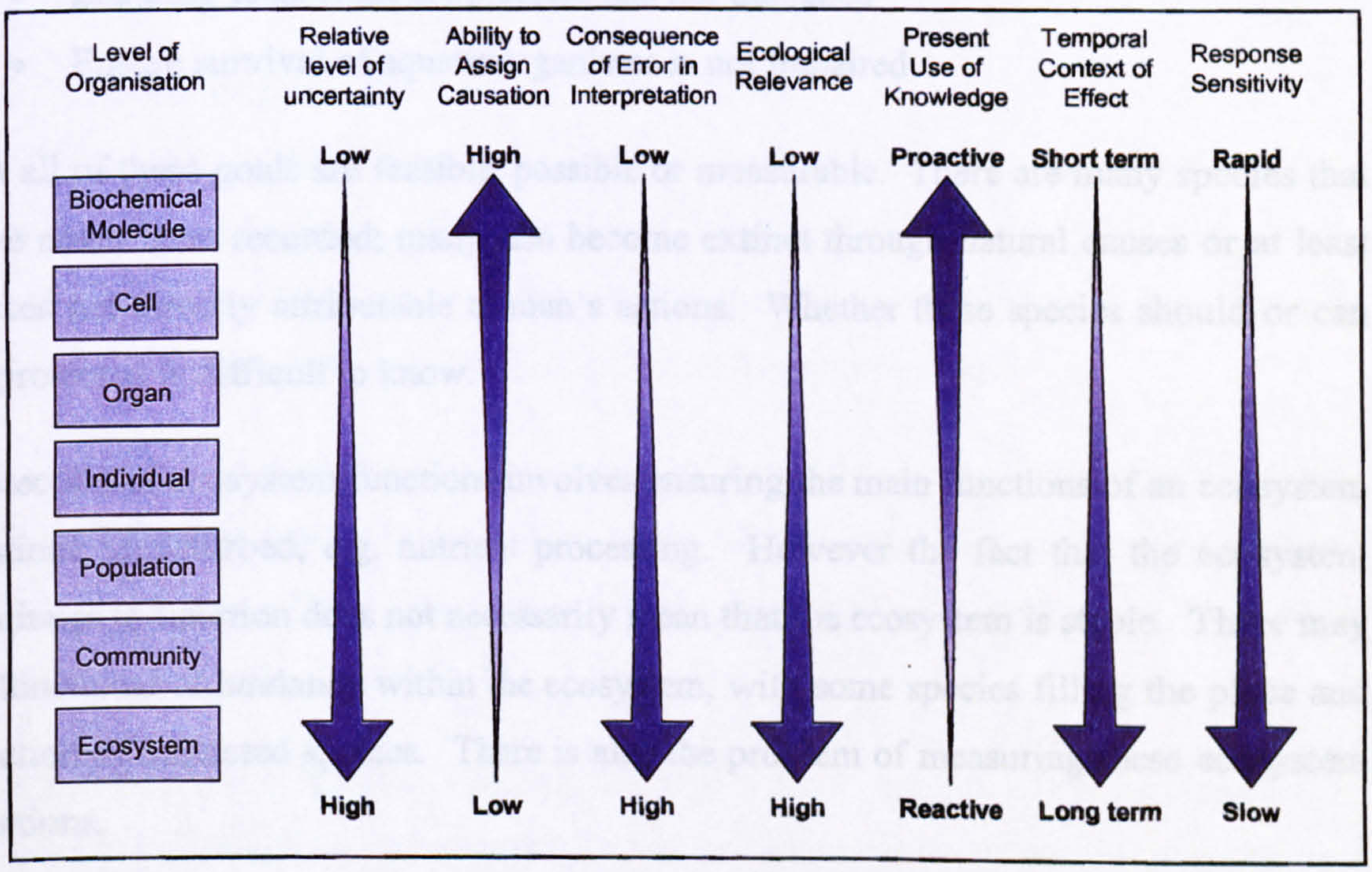

Figure 1.23 - Level of ecological organisation and relevance and uncertainty (Newman, 1995)

1.7.2 What is ecotoxicology?

Ecotoxicology was a term coined by Truhaut in 1969 (Moriarty, 1993), it was seen as a natural extension of toxicology in the environment; this being the study of effects of poisons on individual organisms (toxicology) while considering the ecological effect of these pollutants (the environment). Calow (1993) states that ecotoxicology is concerned with protecting ecological systems from adverse effects that might arise synthetic chemicals. The first definition referred to "poisons" and their effects on "individual" organisms, this being partly due to ecotoxicology's historic roots in the field of toxicology, whereas Calow's definition encompasses a wider scope, protecting "ecosystems" from "synthetic chemicals".

1.7.3 What are we trying to protect?

When attempting to protect the environment from chemical pollution many different objectives can be set as protection goals, these include:

- Protection of ecosystem functions
- Protection of biodiversity
- Ensuring no further species become extinct
- Ensuring the environment provides necessary raw materials and resources
- Ensuring local areas are pleasant and not degraded
- Ensure survival of aquatic organisms is not impaired

Not all of these goals are feasible, possible or measurable. There are many species that have never been recorded; many also become extinct through natural causes or at least causes not directly attributable to man's actions. Whether these species should or can be protected is difficult to know.

Protection of ecosystem functions involves ensuring the main functions of an ecosystem continue undisturbed, e.g. nutrient processing. However the fact that the ecosystem continues to function does not necessarily mean that the ecosystem is stable. There may be functional redundancy within the ecosystem, with some species filling the place and function of impacted species. There is also the problem of measuring these ecosystem functions.

Protecting biodiversity alone may not achieve the desired goals. Although it is possible to gain an indication of the biodiversity in a system, this does not necessarily indicate a stable system. There are however arguments to say that a more diverse community is more stable to pollutant effects in the long term than less diverse communities (Calow, 1997).

Pollution in the environment tends to reduce species diversity (Forbes & Forbes, 1994) and shortens food-chain length. Calow (1997) makes the point that whether this is actually detrimental to the ecosystem or not is a matter for debate, however it represents a change from the ecosystems original state and as such should be avoided. The relationship between biodiversity and ecosystem stability is by no means a clear one and arguments both for and against can be found in the literature (Forbes & Forbes, 1994).

Most aims in ecotoxicology are currently directed towards maintaining biodiversity through the protection of ecosystems. This links into the Government's commitment to maintaining biodiversity through the Government's Biodiversity Action Plan (1994) as a result of the Rio Convention on Biodiversity (1992).

What is needed is a protection goal explicitly incorporating both of the above criteria (biodiversity and ecosystem function), which through their protection should ensure many other goals are met such as the prevention of loss of species, etc.

1.7.4 What do we measure?

One of the reasons ecotoxicology is studied is to try and predict the adverse effects that may occur if a synthetic chemical is released into the environment. This then allows safety measures and controls to be enforced to protect against a dangerous concentration level of the substance entering or accumulating in the environment.

Ecotoxicologists measure the effects that a pollutant has on the environment through testing sample organisms with controlled doses of toxicants. The concentration values tested and resulting effects are then used in an attempt to predict the No Effect Concentration, (NEC)

The NEC is the actual No Effect Concentration, the "real" toxicity of the substance, and the predicted no effect concentration (PNEC) is the ecotoxicologist's and risk assessor's attempt at estimating this value. We cannot know whether or not we have measured the true NEC in our tests we can only hope to perfect the accuracy of our measurements.

Effects on ecosystems are usually measured using single species tests, on representative organisms. The effects are measured on individual and an attempt is made to gauge the ecological significance of these effects. This requires measured effect data from singularly tested species to be applied and used in the assessment of structural and functional attributes of communities and ecosystems in the field (Versteeg *et al.*, 1999). In performing this extrapolation from single species in the laboratory to ecosystems in the field the following assumptions are made, (Versteeg *et al.*, 1999):

- Laboratory data can be used to effectively protect populations of organisms in the field
- Appropriate protection levels based on single species tests will offer protection to whole communities and ecosystem even though all species have not been directly tested.

To do this requires a level of extrapolation, which is usually performed by the use of assessment factors or species sensitivity distribution, whilst considering the ecological significance of the test or endpoint that has been used. The concept of "ecological significance" is an important one (Moriarty, 1993), and this should be considered when designing a test system or examining results:

> *"The fact that a pollutant kills, say, half of the individuals in a species population may be of little or no ecological significance, whereas a pollutant that kills no organisms, but retards development may have a considerable ecological impact."*

For this reason it is vital that the following are all chosen carefully when performing ecotoxicological tests:

- Test species
- End-point (lethal/effect)
- Timescale (acute/chronic)
- Assessment factor

Harrass (1996) states,

> *"quality is critical, test species must be relevant and reliable, [because] extrapolations will dominate decisions"*

Various standard test guidelines and protocols are used in the performing of these tests as set by many organisations including:

- European Community - EC
- United States Environmental Protection Agency - US EPA
- International Standards Organisation - ISO
- Organisation for Economic Co-operation and Development - OECD
- American Society for Testing and Materials - ASTM

The test system is the macro-environment in which the ecotoxicological tests are carried out. For aquatic toxicity tests this can be one of three types of system as detailed here:

Static - Test vessel is stocked with media at initial test concentration and the test run

Semi-static - Test vessel is stocked with media at initial test concentration, media being replaced at set intervals throughout test

Flow through - Test vessel has input and out-put valves with a continual flow-through of test media into and out-of the vessel, ensuring test concentration is maintained

A flow-through test is a closer representation of the natural system but the test is more labour intensive and costly and requires greater test solution, time and resources than the simpler test systems. There are also problems with various types of toxicants in such systems; e.g. maintaining concentration levels of volatile substances in this case closed systems may be used, where the test vessel is sealed to limit loss of volatile substances.

1.7.5 Ecotoxicological Testing

The National Centre has an ecotoxicology laboratory at Waterlooville. The Laboratory has UKAS accreditation (No. 1878) to perform the following tests:

- Microtox acute toxicity (5-30 min bacteria test)
- *Daphnia magna* acute juvenile immobilisation (48h crustacean test)
- Oyster embryo acute larval development (48h mollusc test)

Work is also carried out on the development of other test methods including the following, some of which are particularly pertinent to DTA toxicity testing:

- *Lemna minor* growth inhibition (72h aquatic plant test)
- *Gammarus pulex* juvenile lethality (96h freshwater invertebrate test)
- *Chironomous riparius* mortality (10 day freshwater invertebrate test)
- *Daphnia magna* reproduction (10 or 21 day freshwater invertebrate test)
- *Tisbe battagliai* reproduction (10 day marine/estuarine invertebrate test)

The method development work includes the evaluation and development of tests to measure sub-lethal endpoints, chronic effects and rapid tests (see Figure 1.24). The laboratory takes part in ring tests for some of the newly developed methods, where five or more laboratories carry out tests to standard methods with reference toxicants to assess the accuracy and precision of the developed test methods.

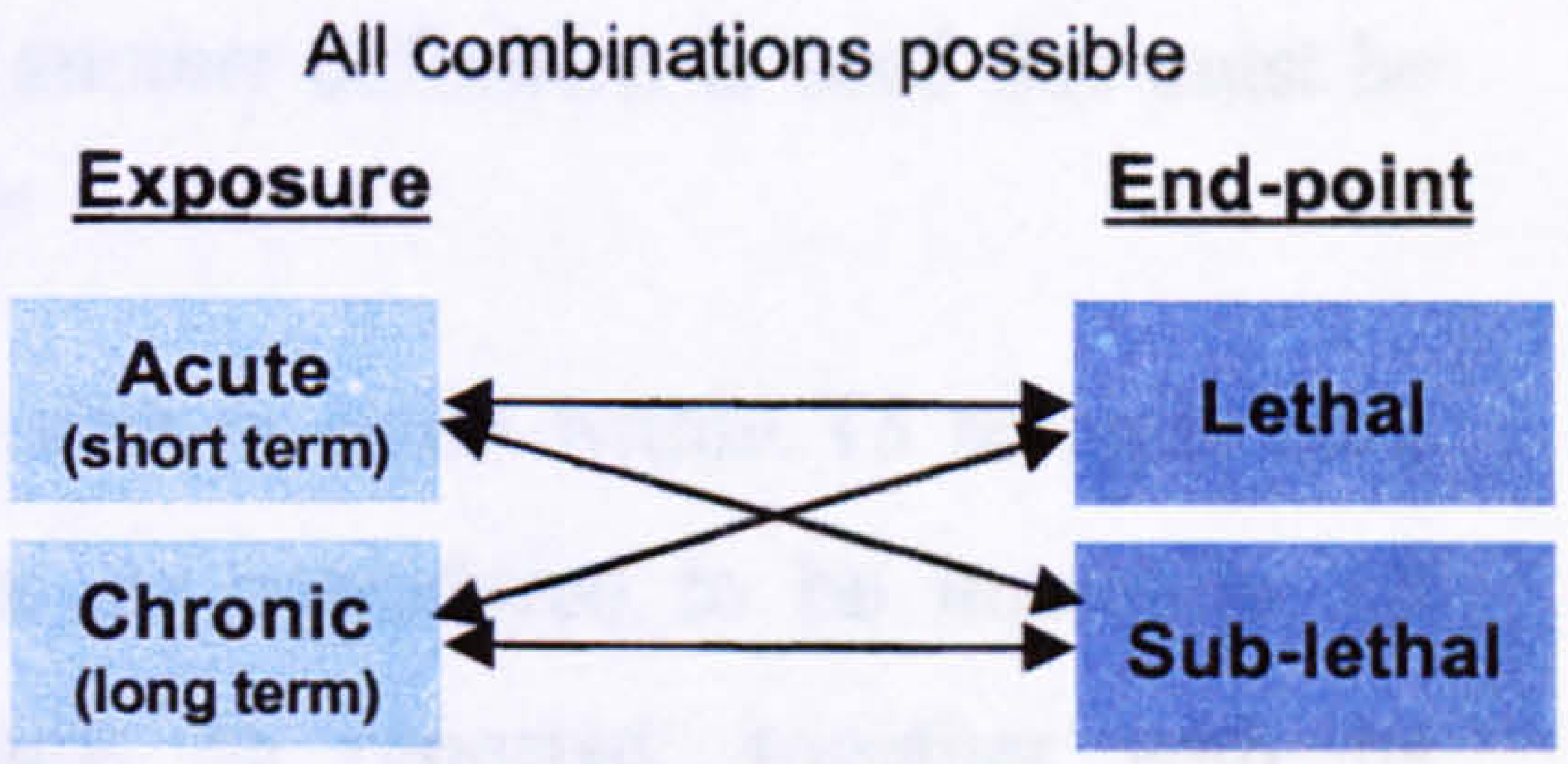

Figure 1.24 – Toxicity test parameters

Some time was spent at the Waterlooville laboratory to gain an understanding of some of the ecotoxiciological tests, the data from which are used in risk assessment. It is important to have an appreciation of the problems, and uncertainty inherent in the tests that produce the data that are used in risk assessment. Two particular tests were examined in detail.

Test Descriptions

Daphnia magna – This is a freshwater invertebrate commonly known as a water flea (see Figure 1.25) that is used widely in ecotoxicity tests. The organisms are cultured to provide a stock of the required test organisms, each culture is developed from ten gravid females (females with eggs) which are placed in new media. The media is either a standard water solution or one where the physical and chemical attributes reflect the receiving water, e.g. for the River Esk samples from the

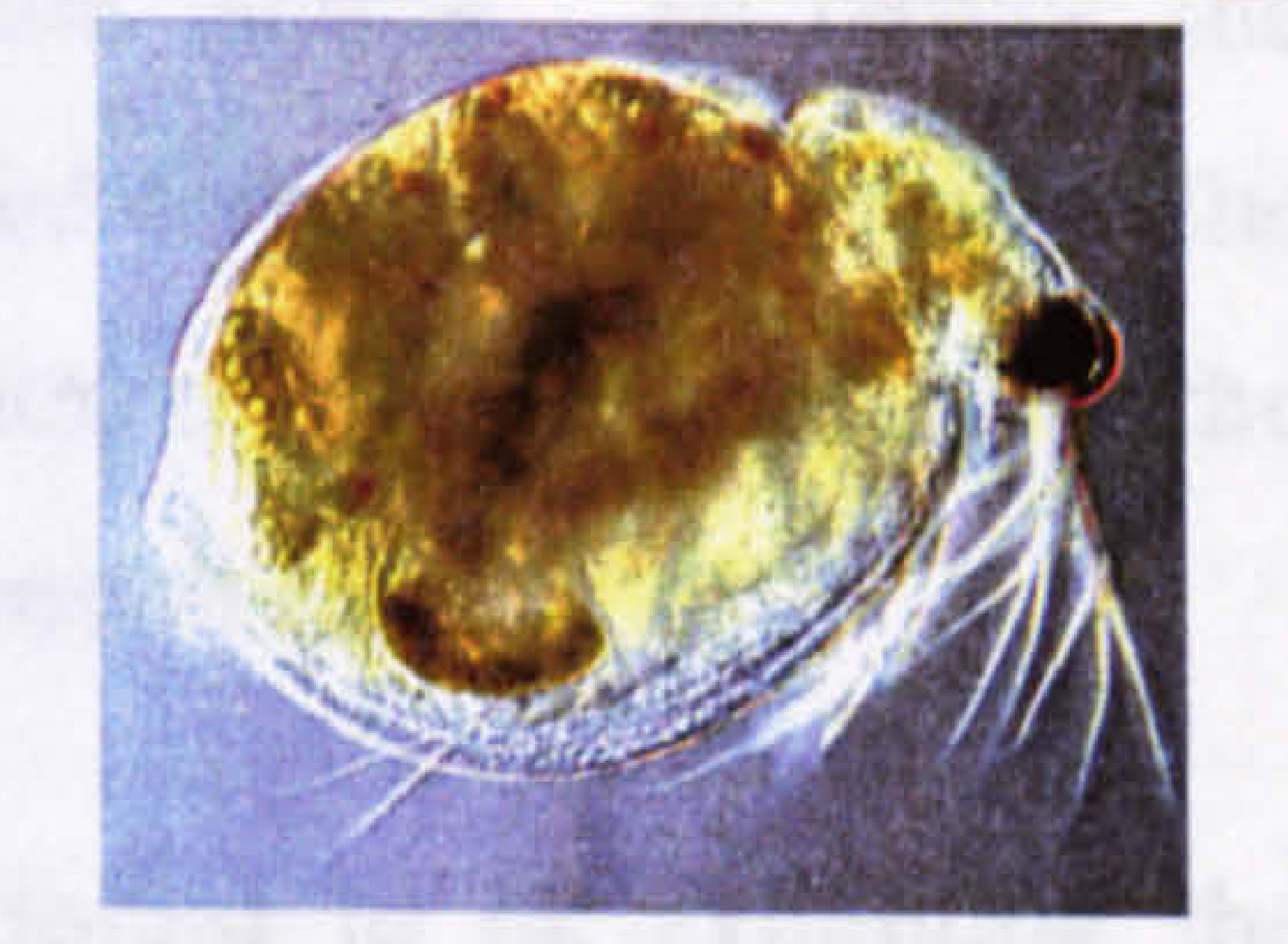

Figure 1.25- ***Daphnia magna***

DTA demonstration programme water samples were adjusted so that the water hardness was lower than standard, (100mg/L $CaCO_3$).

Stressed and poor culturing conditions can lead to *Daphnia* with ephippia (resting eggs), which give the egg sack a black appearance), in such cases the whole culture is discarded.

Two of the tests performed for this species are the 24 or 48 hour EC_{50} and the 14-day reproduction test. For the 48 hour test standard agreed OECD test guidelines are available where all terms and methods are clearly defined:

> "48h EC_{50} – is the concentration estimated to immobilise 50 per cent of the Daphnia after 48 hours exposure. (If another definition is used this must be reported, together with its reference.)"
>
> "Immobilisation – those animals not able to swim within 15 seconds after gentle agitation of the test container are considered to be immobile. (If another definition is used this must be reported, together with its reference.)"

For the test, the organisms to be used must not be more than 24 hours old at the commencement of the test. To ensure this, a number of gravid females are removed from the cultures and placed in separate media 24 hours prior to the test. Any juveniles removed from this new culture can be used for the test and will clearly be less than 24 hours old.

The test also requires that at least 20 animals be tested at each test concentration. These organisms are usually split into four groups of five for the testing. To reduce the variance and uncertainty in the test, the organisms are not fed over the test period. The addition of food could possibly lead to absorption or reaction of the pollutant with the organic matter, and other uncertainties due to feeding and growth rates.

The data produced represent the proportion of animals found to be exhibiting the required effect (immobilisation) after 48 hours at each concentration tested. From these data dose/response analyses can be made.

Gammarus pulex – This is a fresh water invertebrate commonly known as a freshwater shrimp (see Figure 1.26). The test method outlined below is one that is currently in the method development stages to provide a short term, acute toxicity test for use in direct toxicity assessment.

Figure 1.26- *Gammarus pulex*

96 hour acute toxicity method for *Gammarus pulex*

- A stock of the organisms is gathered via "kick sampling" from suitable locations, details of the location and chemical analysis of the water being recorded as part of the test data.
- Collected animals are transferred to Artificial Pond Water (APW) with aeration and an excess of feed material (conditioned alder leaves). Animals are then left to acclimatise for a week. Feed material being removed a day prior to test.
- 20 cages (plastic tubing with net over bottom end) are placed in each test tray containing a test solution. A single juvenile and a leaf disc (feed material) are placed in each cage.
- The test is observed and recorded at 24, 48, 72, and 96 hours, death being defined as no movement of pleopods over 5 seconds, dead organisms being removed from test tray, and the test solution being changed at each reading.

The data produced from this test represents the number of animals found dead at each concentration at each observation time, allowing both time/response and dose/response analyses to be conducted.

Uncertainty

Where cloned or stock animals are used (as in the case of *Dahnia magna*) then there is a large degree of control over the test, and precision can be increased. However where sampled animals (from natural habitat) and organisms of later life stages are used, there is a higher degree of variability within the test design. Although the use of cloned organisms (e.g. *Daphnia magna*), in the tests reduces inhernet variability, the data obtained is less environmentally relevant the tests being even further from the real-world situation. There is a conflict between the requirements for repeatability and reproduceability and ecological relevance since natural ecosystems are variable and complex (Forbes & Forbes, 1994 cited in Calow, 1996).

Instead of single-species test, ecotoxicological tests can be performed on communities, and on multispecies systems. The belief is that these multispecies tests are more relevant to real ecosystems than single-species tests (Calow, 1996). These systems however are not easily controlled, either in composition or system dynamics. Such tests also tend to produce a large amount of data, which must be interpreted in a correct and valid way. Calow (1996) argues that there is no reason that the results obtained from one multispecies test are any more generalisable than the results from different single-species tests.

1.8 ECOTOXICOLOGICAL DATA AND ITS INTERPRETATION

1.8.1 Toxicity Test Standards

In this section the way ecotoxicology test data are used and interpreted is considered. It should be remembered that the aim of the toxicity testing is to obtain meaningful and accurate estimates of the effects of chemicals on organisms in the environment. From concentration/effect (dose/response) data, time-to-event, and other such data, limits are likely to be set to ensure that levels of concentration that may result in harm to the environment are not reached.

1.8.2 Toxicity Test Data

When performing an ecotoxicological test an initially range-finding test is performed to find the concentration range where toxic effects occur. Approximately 5 test concentrations and one control will be selected in the area of interest, and each concentration replicated (approx. 5 times).

Table 1.6 shows an example of ecotoxicity test data. There are 4 test concentrations and a control and 4 replicates at each concentration. 5 test organisms were used in each replicate, therefore each organism represents a proportion of 0.20 of the sample. Data like this, where an effect is either present or it is not, is termed quantal data.

	1	2	3	4	Ave.
Control	0.00	0.00	0.00	0.00	0.00
0.75 mg/l	0.40	0.40	0.40	0.40	0.40
1.00 mg/l	0.40	0.80	0.60	0.40	0.55
1.25 mg/l	0.60	1.00	1.00	0.60	0.80
1.50 mg/l	1.00	0.80	1.00	1.00	0.95

Table 1.6 - Table of ecotoxicity test data

Plotting the average response at each concentration gives a sigmoid or S-shaped curve of dose versus response (Figure 1.27). The data are usually plotted on a logarithmic concentration scale, or the concentration data transposed by the log function. This means that the (zero value) control concentration cannot be plotted on the graph, hence only four data points.

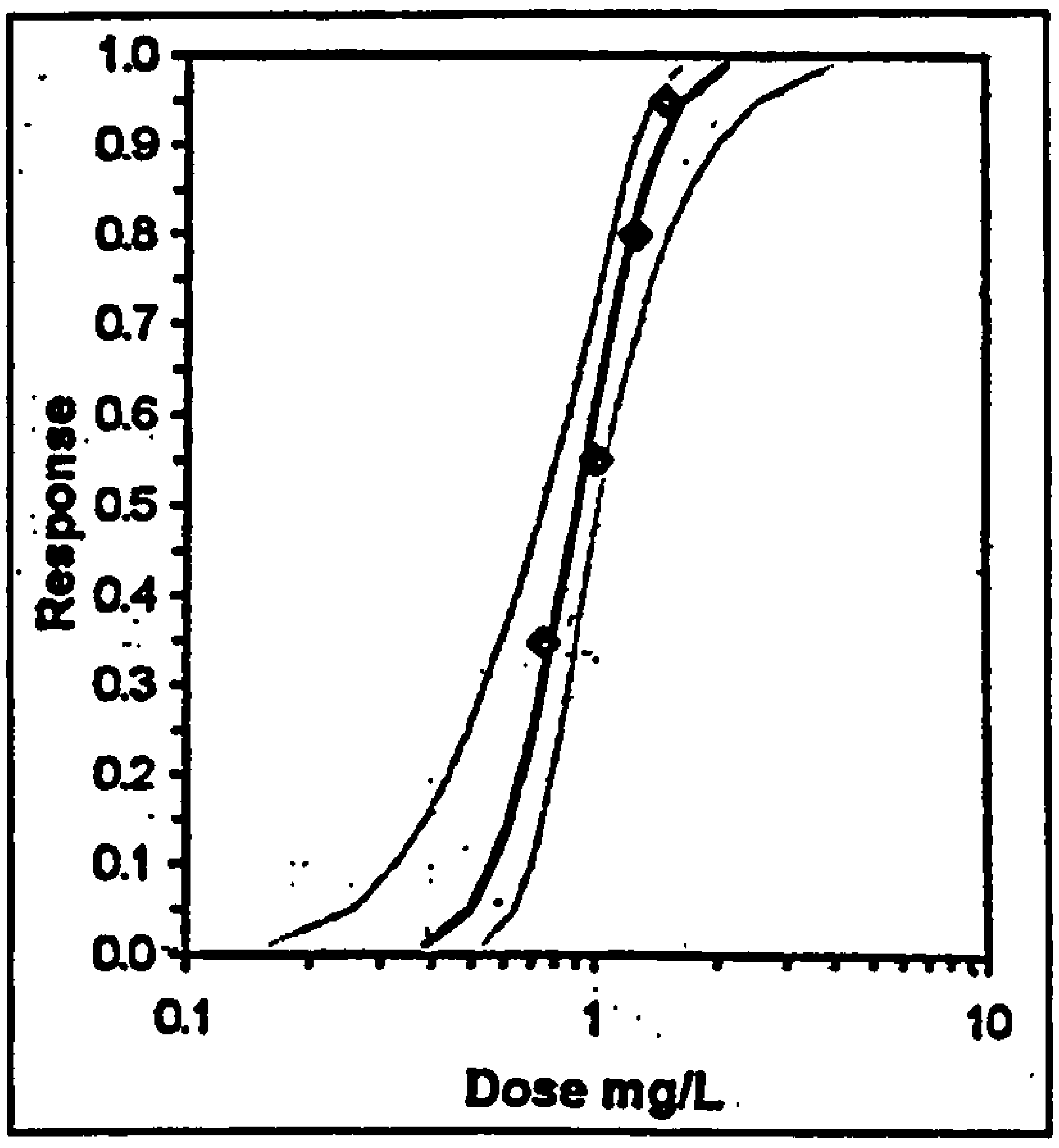

Figure 1.27 - Dose response curve for reference toxicant (Waterlooville Laboratory)
Heavy line indicates dose-response curve, light lines indicate error limits

The data shown (Table 1.6) and plotted (Figure 1.27) are for a reference toxicant and test, indicating the four data points, the dose-response curve and limits of allowable variation.

The ecotoxicological test data are then usually converted into usable indicators, or summaries of the data. Protection limits will be based on these summary values. It should be noted however that it is argued (Chapman *et al.*, 1996), that the guidelines and procedure for selecting summary statistics that adequately describe results from toxicity tests are currently thought to be sub-optimal. The first summary statistics that will be considered are the LOEC (Lowest Observable Effect Concentration) and the NOEC (No Observable Effect Concentration) values.

1.8.3 The NOEC and LOEC Summary Statistics

The values obtained from the toxicity tests are transformed using a mathematical metameter and analysed to see if there is a significant diffence between the mean control value and each mean concentration value. This is usually carried out by using an analysis of variance (ANOVA) method. The first concentration showing a significant difference in means is labelled the LOEC (Figure 1.28). This is the lowest concentration that shows an effect statistically significantly different from the control value. The next test concentration below this is then labelled the NOEC, the first test concentration to show no statistically significant difference from the control data.

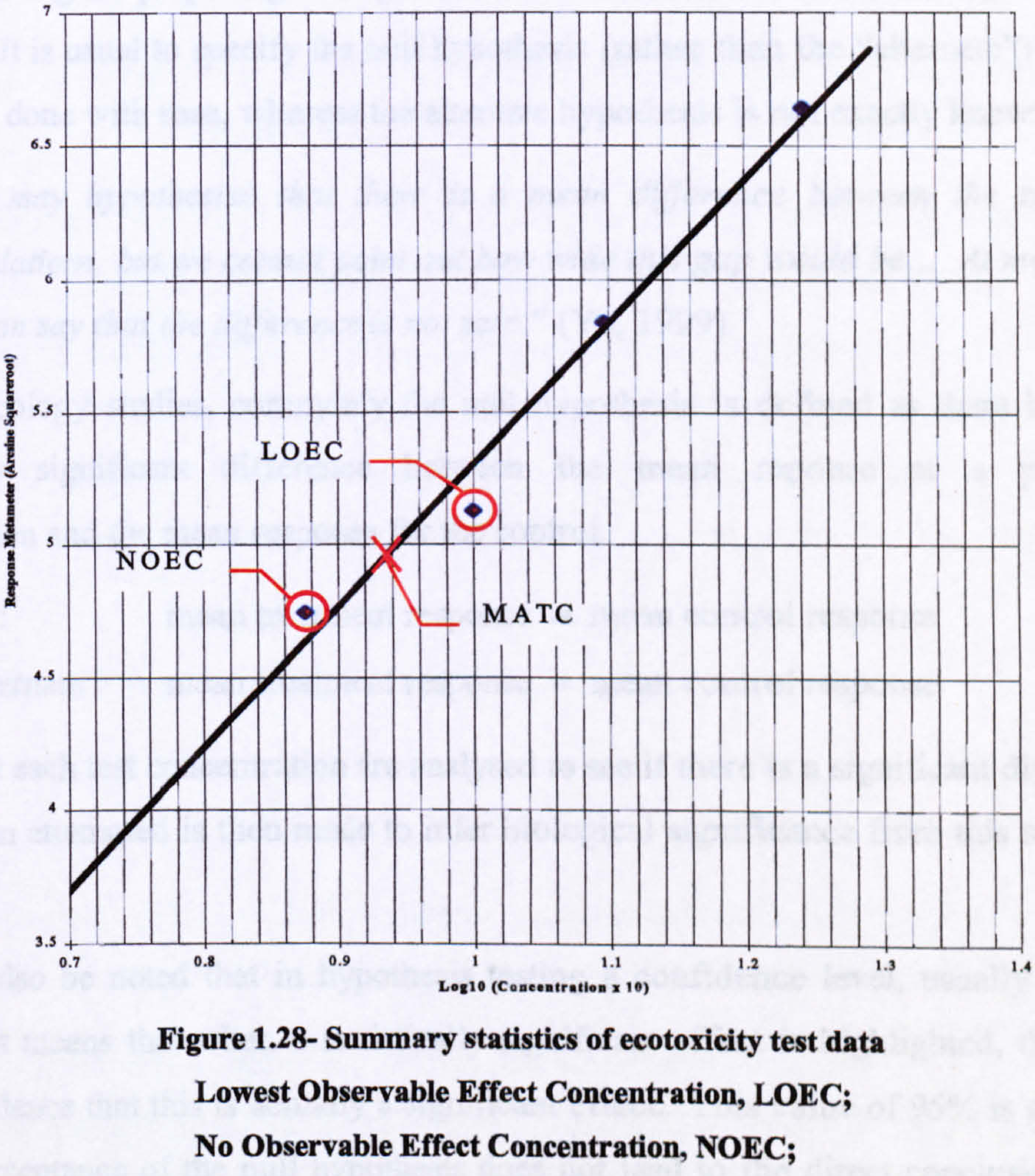

Figure 1.28- Summary statistics of ecotoxicity test data

Lowest Observable Effect Concentration, LOEC;
No Observable Effect Concentration, NOEC;
Maximum Acceptable Toxicant Concentration, MATC

A further value, the MATC (Maximum Acceptable Toxicant Concentration) is taken to be the geometric mean between the NOEC and the LOEC and has been described as, (Rand & Petrocelli, 1985 cited in Newman, 1995):

> *"An undetermined concentration within the interval bounded by the NOEC and LOEC that is presumed safe by virtue of the fact that no statistically significant adverse effect was observed"*

Newman (1995) also makes the point that although there maybe a statistically significant effect this does not mean this effect is adverse. To determine whether an effect is adverse or benign is a difficult process.

The method of data analysis as outlined above is termed as hypothesis testing, where a hypothesis is proposed and then an attempt is made to disprove this hypothesis. The testing of the "null hypothesis" was introduced by Fisher (1949, cited in Newman, 1995) involving the proposing of a specific and bold statement and then subjecting it to criticism. It is usual to specify the null hypothesis (rather than the "alternate") because this can be done with ease, whereas the alternate hypothesis is not exactly known.

> *"We may hypothesise that there is a mean difference between the two populations, but we cannot point out how wide this gap would be... At most we can say that the difference is not zero."* (Yu, 1999)

In ecotoxicology studies, commonly the null hypothesis is defined as there being no statistically significant difference between the mean reponse at a particular concentration and the mean response for the control.

H_0 : mean treatment response $\equiv$ mean control response
Alternate : mean treatment response $\neq$ mean control response

The data at each test concentration are analysed to see if there is a significant difference, and if so an attempted is then made to infer biological significance from this statistical difference.

It should also be noted that in hypothesis testing a confidence level, usually 95%, is used. This means that when a statistically significant effect is highlighted, there is a 95% confidence that this is actually a significant effect. This value of 95% is arbitrary, so strict acceptance of the null hypothesis does not lead to the direct conclusion of no effect. It simply indicates that there is no significant difference between the test response and control response at the 95% confidence level.

Newman (1995) goes on to state:

> *"Even assuming an adverse effect, sound decisions regarding the consequences of toxicant release to an aquatic system require more than these statistical methodologies. A profound lack of any ecological or temporal context for these rudimentary effects detected during structured and temporally deficient experiments often precludes sound decision making."*

Further, there are two possible types of statistical error that can arise in hypothesis testing:

Type I error – the rejection of a null hypothesis which is in fact true
(false negative)

Type II error – no rejection of null hypothesis which is in fact false
(false positive)

Lane (1999) takes the view that a Type II error is only an error in the sense that an opportunity to reject the null hypothesis correctly was lost. It is not an error in the sense that an incorrect conclusion is drawn, since no conclusion is drawn when rejecting the null hypothesis. However it should also be understood that accepting the null hypothesis only means that there is not sufficient data to convincingly show that the difference between two means is not zero, but this does not however prove that the difference is zero.

In environmental terms:

- Type I errors - unsafe substance considered safe
  (could result in environmental harm)
- Type II errors - safe chemical considered as being of concern
  (could result in over protection and cost to industry)

Yu (1999), argues that a careful researcher should balance the Type I and Type II errors. Whereas Neyman and Pearson (1933) who introduced the concept of Type I and Type II errors, recommend that controlling Type II errors should be favoured in scientific research. Ludbrook and Dudley (1998) however, argue that in biomedical research it is the controlling of Type I errors that should be favoured.

It is obviously in the regulators interest to limit the possibility of both types of error, however the favouring of control of Type I errors (Ludbrook & Dudley, 1998), as mentioned above is in line with the precautionary principle. The more stringent limiting of Type I errors would mean that some chemical that should be considered as safe would be considered as being of concern. However when concern is highlighted for a chemical, this generally leads to further testing which would hopefully clarify and correct the earlier conclusion. If however a substance of concern was concluded as being safe, such a chemical may not to be revisited in terms of ecotoxicological testing until perhaps biological effects are noted or further data comes to light.

Lipsey (1990) states in reference to basic research that it is desirable to keep the probability of Type I errors low, because the researcher should be very conservative about adopting new facts or changing facts of existing knowledge. The ability, through hypothesis testing, to detect a difference when there is one depends to a greater extent on experimental design rather than on the magnitude of the effects. High variability and poor experimental design favours Type II errors, causing higher LOEC and NOEC values – poor experimental practices are rewarded. This could result in ecotoxicology laboratories known for poor experimental practices being favoured by industry.

Many other problems have been highlighted in the use of this statistical summary:

- The precision of the derived values goes down as the number of concentration replicates and animals per concentration goes down.
- A NOEC value cannot always be derived, if no data points show no statistically significant difference in mean to the control.
- Only actual test concentrations can be taken as values for the LOEC and NOEC which puts bias on the choice of test concentrations (linearly scaled or not etc.)

And the use of the summary statistics has been criticised on both theoretical and practical grounds in many other publications as cited by Chapman *et al.*, (1996).

Furthermore, the statistical analysis of the data is carried out by analysis of variance (ANOVA). To perform the ANOVA a transformation of the quantal (e.g. dead/alive) data is required and for this commonly the arcsine squareroot function is used.

However the ANOVA method assumes that:

- observations are independent
- data is normally distributed
- there is common and homogeneous variance

The data should therefore be considered to ensure that the best transformation and analyses are used on a case by case basis, resulting in a sound scientific and statistical background to the summary statistics produced.

1.8.4 The EC_x and LC_x Summary Statistics

The LC_x and EC_x are summary statistics that represent the concentrations of a substance producing x percent lethality or effect (respectively) in the test population.

With data obtained from toxicity tests the frequency distribution of individual organism responses in a population is often skewed, therefore some form of mathematical transformation is often used to normalise the distribution (Newman, 1995). Through the use of a mathematical metameter such as probit, logit etc. the data is transformed and the plot made linear. Hence most dose/response curves are plotted as a Response Metameter (probit, logit etc) against Log Concentration, (Figures 1.29 and 1.30).

From the linear graph an EC_x value can then be quoted for any given response value, linear regression allowing extrapolation of values between measured points on the graph (Figure 1.30). It is obvious from the sigmoid plot of the data (Figure 1.29) that there is more precision around the $L(E)C_{50}$ value. This value is more statistically reliable due to the high slope of the graph at this point, than at the tail ends of the graph. Whereas values taken at either end, $L(E)C_{10}$ or $L(E)C_{90}$ values, are likely to be subject to greater uncertainty.

As is shown on the graph a ±5% change in response has a much larger effect on the dose at the EC_{10} level than at the EC_{50} level. In opposition to this though it has also been demonstrated (Whitehouse *et al.*, 1996) that variability in measured response at intermediate response levels is generally much greater than at the extremes. That is to say there is less variation within the test about the 0% and 100% response levels.

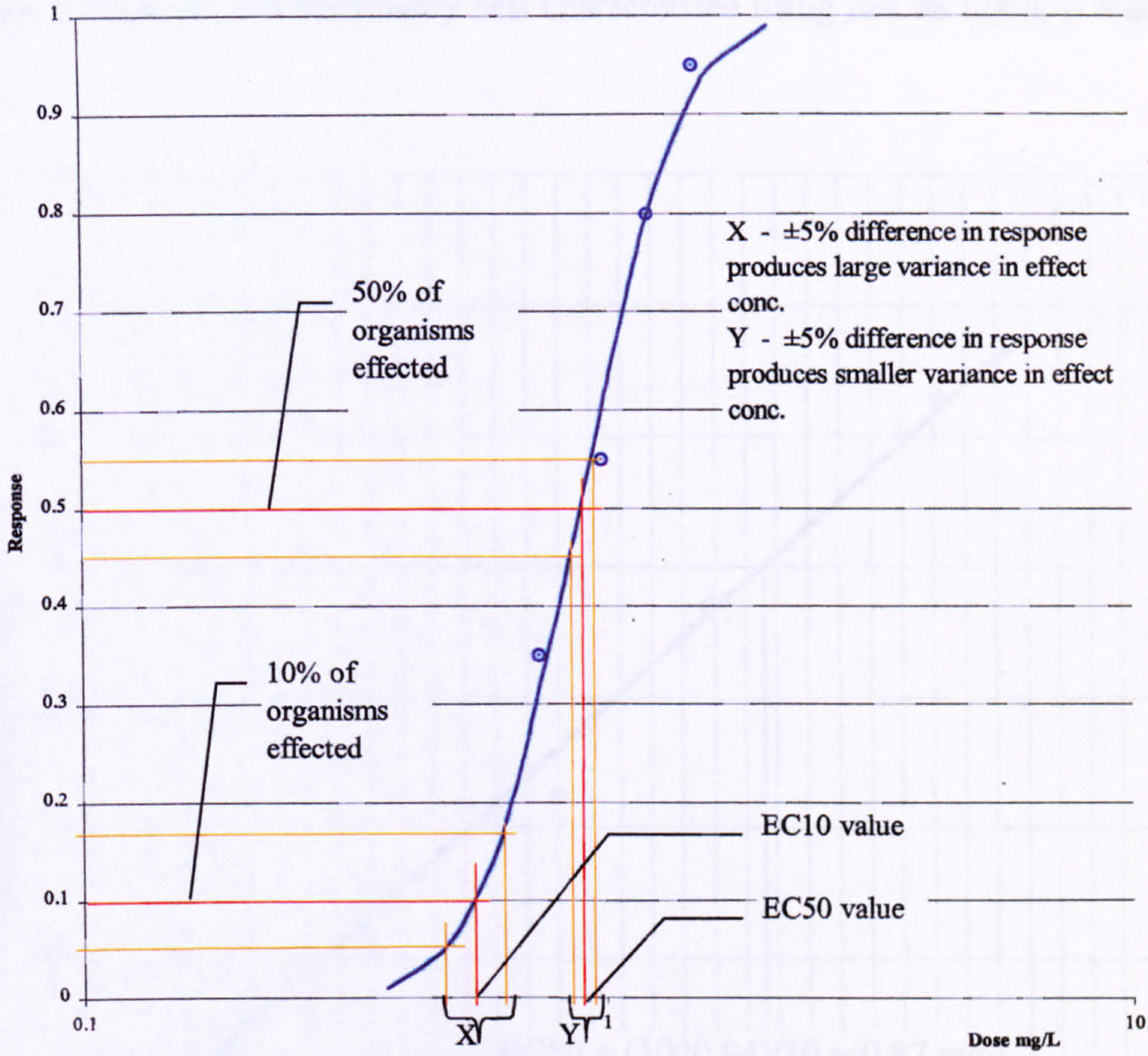

Figure 1.29- Concentration response curve plotted from ecotoxicological data

Newman (1995) notes however that the LC_{50} does not indicate the environmental safety of a substance, rather it is a measure of toxicity that is best employed in a relative context. However Harrass (1996) points out that a review of whole effluent toxicity data in the US suggested that the use of an EC_{25} values was equivalent in level to a NOEC value. An EC_{25} values would be preferable to a NOEC due to the ability to quote confidence limits (as shown later) and because it is statistically valid to interpolate values between data points.

Another suggestion in the literature is instead of quoting just an $L(E)C_{50}$ value, by quoting a slope, S value as well, the graph can be completely characterised allowing any $L(E)C_x$ value to be estimated, (Chapman *et al.*, 1996). However in opposition to this it has been shown that where a $L(E)C_{50}$ value is required test concentrations are best equally spaced along a log scale between 25% and 75% response. Whereas for $L(E)C_{10}$ estimates, one or two data points above 90% response and the majority between 5% and 25% response has been shown to work best. This would suggest that different experimental designs are required depending on the $L(E)C_x$ value of interest, and therefore the data are not necessarily best characterised using just an L(E)C_{50} and slope value.

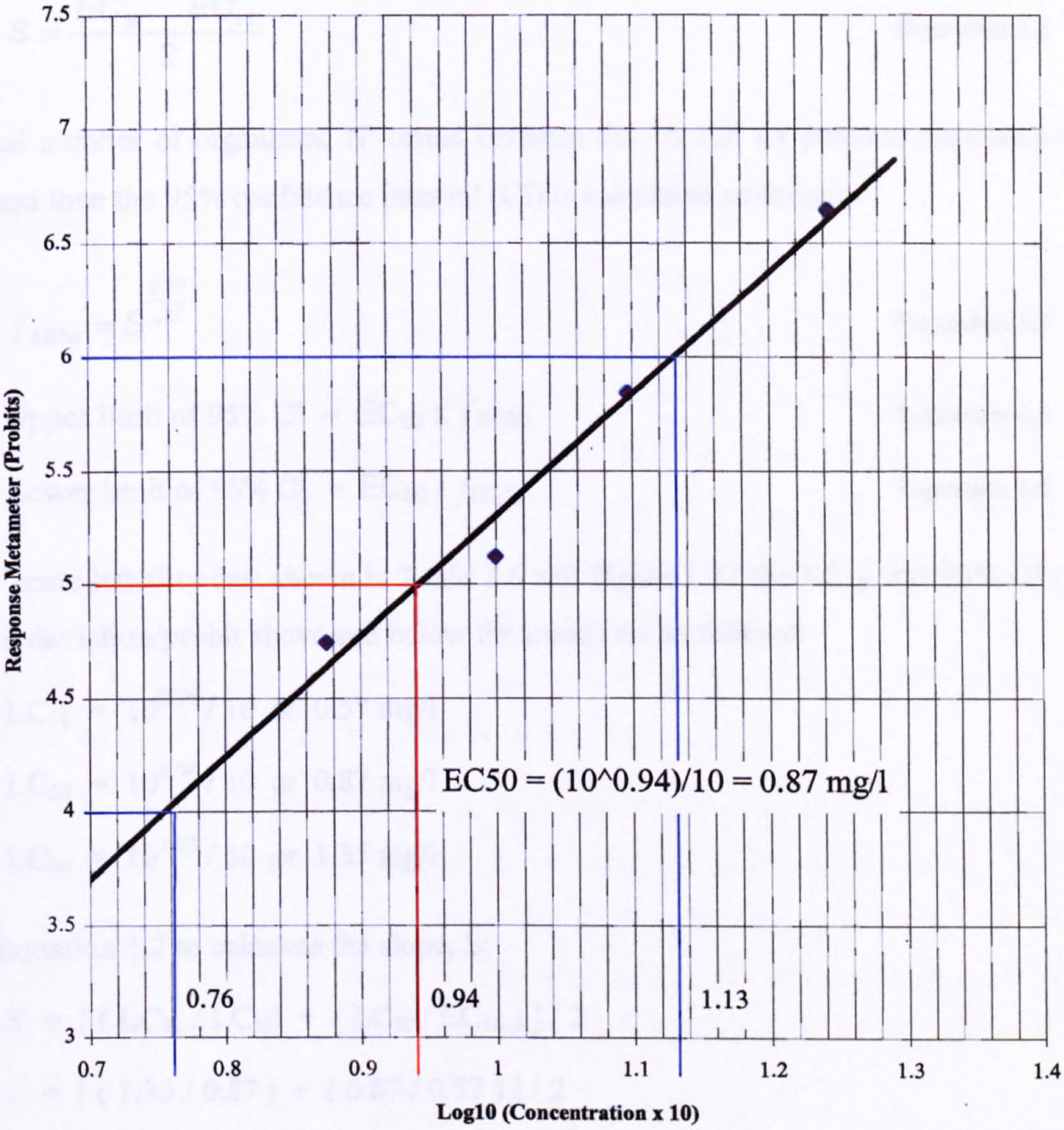

Figure 1.30- Probit-Log concentration graph of dose-response data

The ability to calculate confidence limits supports the use of the EC_x summary. There follows a description of the process involved in calculating the confidence limits for an EC_{50} value.

The confidence limits are calculated using the concentration values for EC_{16} and EC_{84}, the nearest whole percentage values that represent ±1 standard deviations about the mean.

The slope of the graph is calculated as follows:

$$S = \frac{\frac{EC_{84}}{EC_{50}} + \frac{EC_{50}}{EC_{16}}}{2} \qquad \textbf{Equation 1.2}$$

The total number of organisms, N′ tested between the 16 and 84 percent responses is found and then the 95% confidence interval (CI) is calculated as follows:

$$f_{EC50} = S^{\frac{2.77}{\sqrt{N'}}} \qquad \textbf{Equation 1.3}$$

$$\text{Upper limit of 95\% CI} = EC_{50} \times f_{EC50} \qquad \textbf{Equation 1.4}$$

$$\text{Lower limit of 95\% CI} = EC_{50} / f_{EC50} \qquad \textbf{Equation 1.5}$$

For the acute lethality data shown in Table 1.6 and Figure 1.27 the LC_{50} and 95% CI (1 standard deviation/probit above and below the mean) are as follows:

$LC_{16} = 10^{0.76} / 10$ or 0.57 mg/l

$LC_{50} = 10^{0.94} / 10$ or 0.87 mg/l

$LC_{84} = 10^{1.13} / 10$ or 1.35 mg/l

Using Equation 1.2 to calculate the slope, S:

$$\begin{aligned} S &= [(LC_{84} / LC_{50}) + (LC_{50} / LC_{16})] / 2 \\ &= [(1.35 / 0.87) + (0.87 / 0.57)] / 2 \\ &= 1.54 \end{aligned}$$

And then finding the total number of test organisms this represents, N′:

$$N' = 8 + 11 + 16 = 35$$

These values are then entered into Equation 1.3:

$$\begin{aligned} f_{LC50} &= S^{(2.77/\sqrt{N'})} \\ &= 1.54^{(2.77/\sqrt{35})} \\ &= 1.54^{0.47} \\ &= 1.22 \end{aligned}$$

And in turn Equations 1.4 and 1.5 are used to calculate the 95% CIs:

$LC_{50} \times f_{LC50} = 0.87 \times 1.22$ $\quad$ $LC_{50} / f_{LC50} = 0.87 / 1.22$

$= 1.06$ $\quad$ $= 0.71$

$LC_{50} = 0.87$ mg/l (95% CI = 1.06 & 0.71)

1.8.5 Further Interpretation

To further refine the current practice in calculating summary statistics, it has been argued that a small sample of animals is unlikely to contain the most sensitive or resistant animal of the population or even species. Therefore it is likely that in any single sample the L(E)C50 is likely to be biased due to small sample size. It is suggested (Abel & Axiak, 1991) that this bias can be accounted for by reducing the observed percentage effect/mortality by half the percentage value of one animal in the sample. *Example:* For a sample size of 10 animals where 1 animal is dead you do not plot 10% but 5%, this does at least allow the plotting of a corrected 100% mortality result, which on a probability scale would be at infinity.

Whichever tests are used, and whichever methods are used to derive the summary statistics, the values obtained are then used to set standards and emission limits. To do this the summary statistics for one or more species need to be calculated and extrapolated in order to protect whole communities, and the whole ecosystem. The extrapolation used from laboratory generated data, to the protection of the real environment needs to be considered carefully.

1.9 SCOPE OF THESIS

Through reviewing the hazard and risk assessment systems as used within the NCEHS an understanding of the importance of the control of chemicals in the environment was gained. Controls that address both point-source (e.g. emissions from industrial buildings) and diffuse emissions (e.g. emissions from consumer use) are necessary.

The EQS and DTA systems of control aim to target chemicals that are currently in use and may be causing adverse effects in the environment. The system for the risk assessment of new chemicals however, aims to highlight substances that may be of concern before environmental effects arise.

1.9.1 Risk Assessment of New Substances

The new chemicals risk assessment system as outlined in the 7th amendment to the Dangerous Substances Directive[29] requires an initial basic assessment based on limited data. If the conclusion that there is cause for concern is reached, or if the substance is marketed at a greater volume, more data will be required to refine the risk assessment.

The risk characterisation ratios that are calculated as part of this system constitute deterministic risk assessments; it is based on a single PEC value divided by a single PNEC value. Such calculations do not directly consider the quantity of data supplied, however there are provisions in the TGD for lower AF to be used where chronic, long-term toxicity data is available for one or more species. Likewise in the exposure assessment, in order to maintain a generic system, parameters representing reasonable worse case and European-wide average values are used.

Both sensitivity and uncertainty analyses have been applied to the 'Uniform System for the Evaluation of Substances' (USES) and the update to this program 'European Union System for the Evaluation of Substances' (EUSES) (Jager & Slob, 1995; Jager *et al.*, 1997).

These tools although complementary are distinctly different in what they examine, (Ricotti & Zio, 1999):

> Sensitivity analysis – used to study the behaviour of systems or models and how the outputs or results are dependent upon selected input parameters
>
> Uncertainty analysis – used to determine the uncertainty in model predictions resulting from the variation or uncertainty in input variables or parameters

Often sensitivity analyses are performed to identify the values that have the greatest effect on the results of a model; uncertainty analyses, which can often become costly, can then be focused on the values of greatest interest.

A study into the feelings towards uncertainty analysis by representatives of European Member States and Industry showed a general resistance to uncertainty analyses and probabilistic assessments (Jager, 1998). It was felt that uncertainty analyses may generate a significant increase in workload and time required producing assessments. It was also thought that the extra information created might suggest a greater level of accuracy than is actually present. It was accepted however, that uncertainty analyses could be used to demonstrate the level of confidence in a particular assessment. The report suggested that the best way to develop the use of uncertainty analysis would be to demonstrate the benefit to risk management and the decision making process.

1.9.2 Probabilistic Approaches

The use of a probabilistic approach to risk assessments, similar to that proposed in the DTA risk assessment framework was considered. The introduction of probabilistic considerations to risk assessment is not a new concept, and has been used in the field of engineering for some time (Vanotterloo, 1995). The probabilistic approach has also been used increasingly in the field of pesticide assessments (Solomon *et al.*, 1996; Maund *et al.*, 1998; Hall *et al.*, 2000), and guidance for its use has been issued by the US EPA (1997).

Probabilistic considerations can be introduced into both the exposure and effect assessment procedures. Instead of a single value being taken for each environmental parameter a distribution is described and used to reflect the range of values that a parameter might take. In this way distributions of values that can be found in natural systems are incorporated into the assessment.

Probabilistic Effect Assessments

In the effect assessment stage of risk assessment one of two methods are generally used to relate observations on standardised laboratory tests and systems to natural ecosystems (Calow, 1996):

1. Assessment Factor (AF) used to extrapolate test data, the AF implicitly covers both variability and uncertainty although the basis for a particular value is often not clearly defined
2. Natural variability is defined using limited test observations to produce likely sensitivity distributions

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[29] Council Directive 92/32/EEC amending for the seventh time Directive 67/548/EEC on the approximation of laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances

The assessment factor approach which include the use of acute-to-chronic ratios (ACRs) has been accused of a lack in scientific basis (Isnard, 1998). ACRs are a variation in the AF approach and tend to be more specific i.e. for particular substances or organisms (Chapman *et al.*, 1998). The ACR value is a measure of the ratio when scaling from acute (short-term) to chronic (long-term) effects.

The probabilistic method for interpreting effect data has been demonstrated in the assessment of pesticides (Maund *et al.*, 1998). Versteeg *et al.* (1999) compared the results of single-species toxicity test to microcosm, model ecosystem and field data to assess how representative the single-species test results were. To do this cumulative probability plots were constructed using single-species test data. It was concluded that chronic test data for more than 5 test species could be used to set concentration limits protective of model and possibly real ecosystems (Versteeg *et al.*, 1999).

In the notification system for new substances at the *base set* level acute toxicity data is only required for three aquatic species (fish, *Daphnia* and algae). In a study into which of the test species was most sensitive the algal (growth inhibition) test was found to result in strictest classification in 43.5% of cases (Weyers *et al.*, 2000). There is a trend to infer more from less data, it is unlikely that sufficient data will be available to produce cumulative probability plots for new substances.

Probabilistic Exposure Assessments

The exposure assessment stage of risk assessment is complex and less understood compared to the effect assessment stage (BEC, 1999). Due to the limited data available for new substances and uncertainties in the models a reasonable worse-case approach is taken to avoid Type I errors (under estimation of potential risks). Slob & Nijs (1989) describe a probabilistic approach to assessing new chemicals by assigning lognormal distributions to 6 parameters in the exposure assessment. The result is a probability distribution for the PEC value. A similar uncertainty analysis on new substances using the EUSES program was performed by Jager *et al.* (1997) using three different types of distribution (lognormal, uniform and triangular) for more than 30 parameters.

The US EPA use 'Probabilistic Dilution Model 4' (PDM4) to estimate the dilution of substances released directly from wastewater treatment plants, while Environment Canada use data for a suite of Canadian rivers and are developing a tool similar to PDM4 (BEC, 1999).

Monte Carlo Analysis

Monte Carlo analysis is an approach to performing an uncertainty analysis; it has become increasingly popular for quantifying uncertainty in ecological risk assessment (Slob, 1994; Moore, 1996). In a Monte Carlo simulation point estimate values in a model or equation are replaced with probability distributions. Random samples are taken from these distributions and the model or calculation is run many times and the results tallied to produce a probability distribution function or cumulative density function (Jager *et al.*, 1997; Liu *et al.*, 1999). The resulting distribution describes both the range of values and the likelihood that the result might take those values.

Various computer software packages are available for running Monte Carlo simulations including Crystal Ball™ [30] and @Risk™ [31]. The time taken to run a Monte Carlo simulation is highly dependant on the number of iterations being performed and the memory (RAM) and other hardware specifications of the computer running the model.

A further drawback of the Monte Carlo method is the need for precise characterisation of parameter distributions, even when the underlying empirical information is actually insufficient. Moore (1996) suggests that parameter characterisation usually entails a combination of professional judgement, limited empirical information, and blind faith. An alternative to defining distributions is the re-sampling or bootstrap method. Large datasets are required to perform reliable simulations by this method.

1.9.3 Research Undertaken

The TGD and the EUSES program describe a detailed system for the assessment of substances. Such a prescribed system lends itself to uncertainty analysis and probabilistic assessments. EUSES however, does not provide the facility to enter distributions instead of discreet values, or the possibility to carry-out or run multiple assessments at the same time. Initially small investigations were performed by repetitive runs of EUSES with changes in parameters in each run.

To perform useful probabilistic assessments a spreadsheet model was required. Other authors (Jager *et al.*, 1997; Berding, 2000 and Schwartz, 2000) have used spreadsheet

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[30] Crystal Ball™, Decisioneering UK, 58-60 Kensington Church Street, London.

[31] @Risk™, Palisade Corporation, Newfield, New York.

models of the risk assessment system, however such a system had not been described in the literature.

From a preliminary sensitivity analysis of various parameters, and following a review of the literature (Jager *et al.* 1997; BEC, 1999) it was decided to investigate the dilution factor in the exposure assessment in greater detail. Data were collated for the dilution factor and the capacity of sewage treatment plants in England and Wales. These data were analysed and probabilistic assessments performed using a re-sampling method.

This introductory chapter has considered the role of chemicals in society, their potential to cause harm, their risk assessment and the regulatory controls in place to control their use. This is followed in Chapter 2 with a review of the risk assessment procedures required under the European notification system for new and existing substances, and an introduction to the parameters used in the calculation is given. An initial examination of variability in physico-chemical parameters and the effect of this variability on the resulting PEC and RCR are considered.

The construction of a spreadsheet model developed in this work, for performing risk assessments of the aquatic compartment on the local scale is described in Chapter 3. Validation of the model is tested and probabilistic risk assessments are performed.

In Chapter 4, the two environmental parameters, dilution and capacity, used in the modelling of sewage treatment plants in risk assessment systems, are examined statistically, and the data are compared with the generic default values used in the European risk assessment system.

Using the NEXCES tool developed, and described in Chapter 3, probabilistic and deterministic risk assessments of a number of test substances are reported in Chapter 5.

This work is extended in Chapter 6 where the development of a rapid assessment tool for new substances using contour plots is demonstrated. The conclusions from these findings are summarised and the contribution of this work to the field of environmental technology are given in Chapter 7.

CHAPTER 2

EUROPEAN RISK ASSESSMENT SYSTEM

SUMMARY

The risk assessment procedure required under the European Notification System for new and existing substances is outlined. Both the EU Technical Guidance Document and the European Union System for the Evaluation of Substances for performing risk assessments are introduced. The quantitative structural activity relationships (QSAR) that are used to predict partition coefficients are detailed along with the "base set" physico-chemical data used to calculate the risk assessments.

Initial sensitivity analysis investigations to determine the effect of the variability in the measurement of physico-chemical properties on the exposure assessment are reported. The boiling point and melting point values had no effect, while variations in the vapour pressure and solubility in water values were found to have a small effect (±3%) on the assessment. Variations in the Kow value had a much larger effect (±13%) for most of the substances tested.

The choice of QSAR used to estimate Koc from Kow was also found to have a large effect (±30%) on the resulting assessment. The EU default QSAR was found to produce a value below the average of the range, which cannot be considered to be a worst case for the aquatic compartment.

2 EUROPEAN RISK ASSESSMENT SYSTEM

The detailed risk assessment system set out for notified new and existing substances in the European Union lends itself to close analysis. Comprehensive guidance is given in the supporting Technical Guidance Document (TGD). In this chapter the risk assessment process and its automation in the European Union System for the Evaluation of Substance (EUSES) program are considered. Some of the problems with EUSES are identified and initial investigations into uncertainty analyses of the exposure assessment completed using the program are described.

2.1 THE RISK ASSESSMENT SYSTEM

The stages within the risk assessment process shown schematically in Chapter 1, Figure 1.14 include hazard identification, exposure and effect assessment and risk characterisation and classification. These various steps are presented in more detail for the European risk assessment system in Figure 2.1.

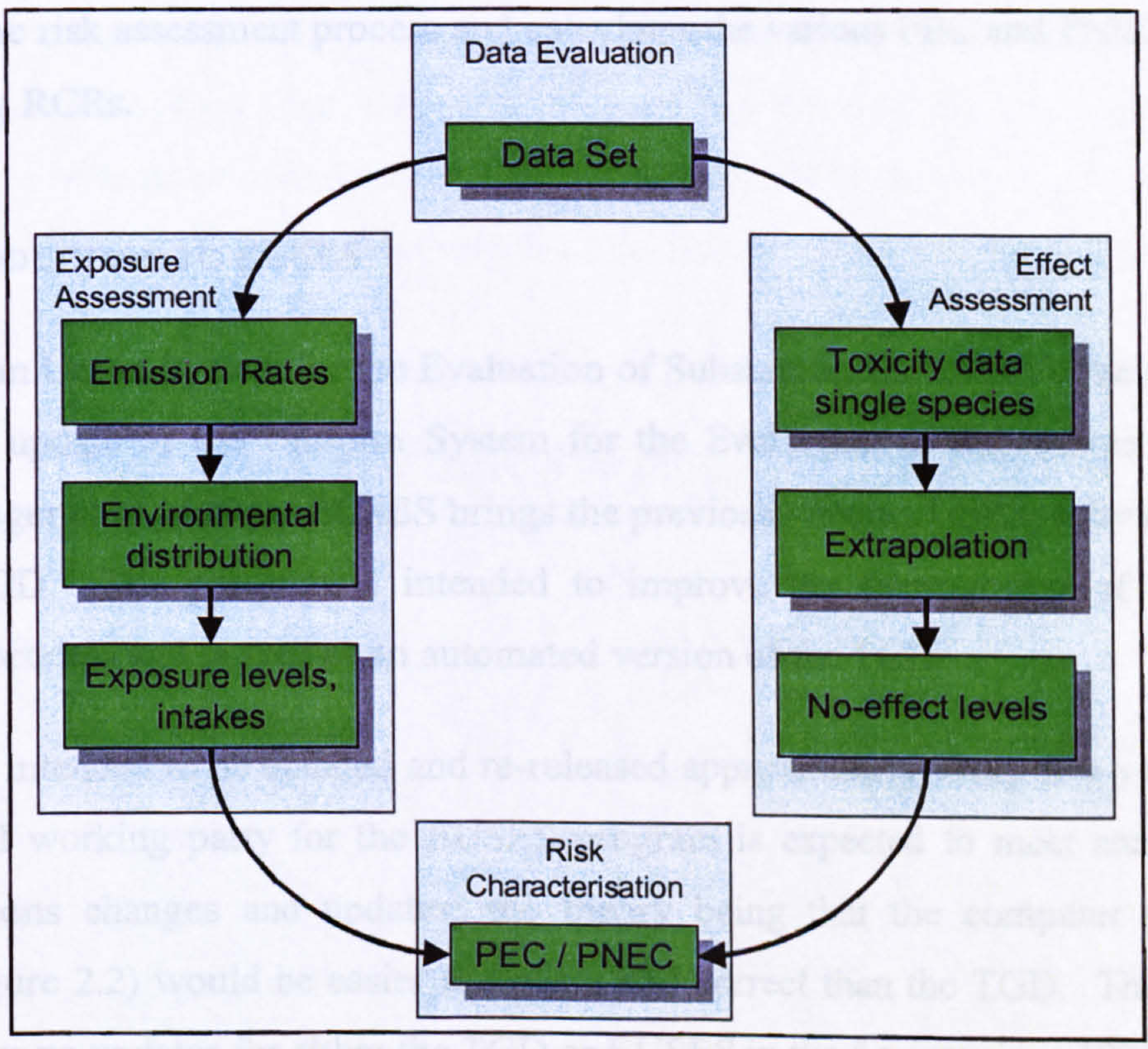


Figure 2.1– The European Union environmental risk assessment process (adapted from EC, 1996b)

The data supplied by notifiers are checked in the data evaluation stage to ensure correct test methods and good laboratory practice have been applied. For substances notified in the UK, the environmental exposure and effect assessments are then carried out by the CAU, while human health effects are considered by HSE.

In the effect assessment, single-species test data are extrapolated to generate a predicted no-effect concentration (PNEC). Emission rates and scenarios are used to predict the concentration of the chemical entering the various environmental compartments (air, land, water, etc.) for the exposure assessment. Distribution parameters are used to calculate how the chemical degrades and is transported within and between the environmental media, and finally predicted environmental concentrations (PECs) are calculated for each environmental compartment.

In the risk characterisation stage the ratio of the PEC/ PNEC is calculated to produce a risk characterisation ratio (RCR). The magnitude of this value is used to a substance's risk classification and to determine whether or not further data or testing are required immediately or at a higher specified tonnage level. The computer program EUSES automates the risk assessment process and calculates the various PEC and PNEC values and resulting RCRs.

2.2 INTRODUCTION TO EUSES

The European Union System for the Evaluation of Substances, EUSES (Vermeire *et al.*, 1997) is an update of the Uniform System for the Evaluation of Substances (USES) program, (Jager *et al.*, 1994). EUSES brings the previous version, USES, fully into-line with the TGD. The program is intended to improve the transparency of the risk assessment process and is seen as an automated version of the TGD.

The TGD is intended to be updated and re-released approximately every five years, and the technical working party for the EUSES program is expected to meet annually to make decisions changes and updates; the theory being that the computer program EUSES (Figure 2.2) would be easier to update and correct than the TGD. There have however been no updates for either the TGD or EUSES in the 5 years since 1996.

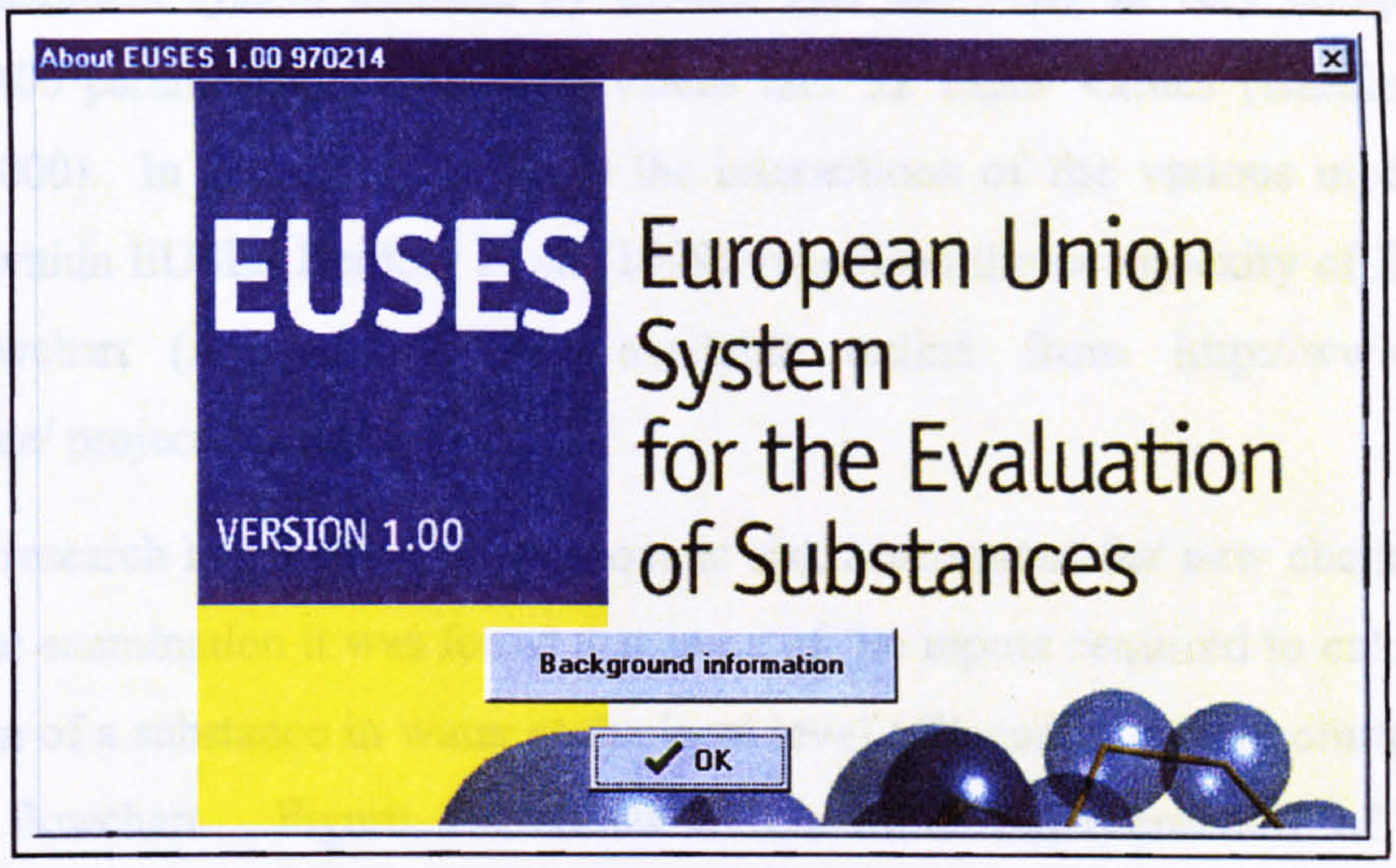
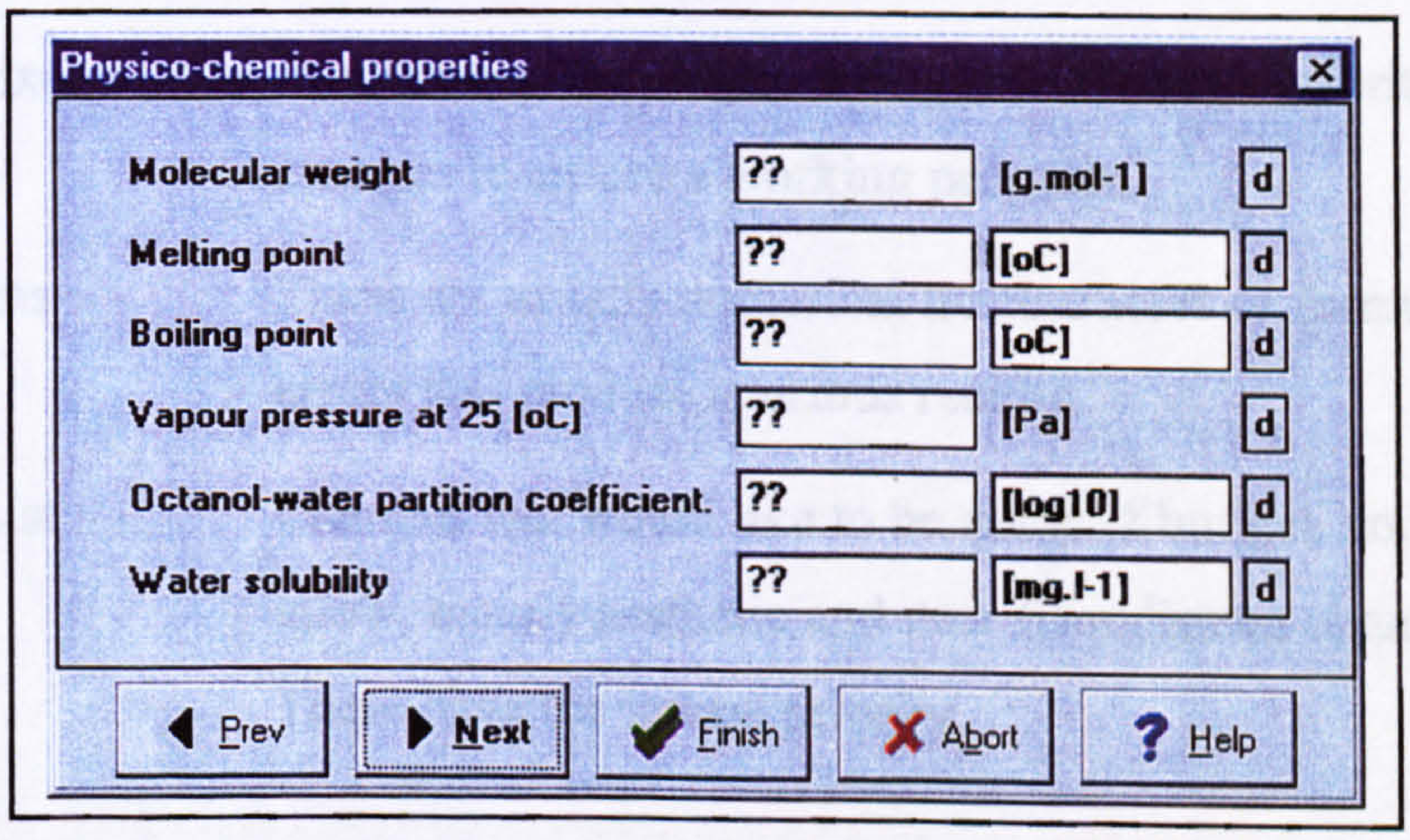


Figure 2.2 - EUSES opening screen (screen shot from the computer program EUSES[1])

2.2.1 Modular Assessments

The EUSES program has a modular system, which for environmental risk assessments follows the schematic as detailed in Figure 2.1. A series of input windows lead the risk assessor through the assessment process requesting data as required (Figure 2.3). Values can be entered in any accepted units and the program will perform the necessary conversions. Calculated (denoted by 'o') and default (denoted by 'd') values can be over-written with user-entered values (denoted by 's'). It is mentioned in the EUSES manual but is worth reiterating that calculated or default values that are changed by the user are not back-calculated.



Physico-chemical properties

Molecular weight ?? [g.mol-1] d
Melting point ?? [oC] d
Boiling point ?? [oC] d
Vapour pressure at 25 [oC] ?? [Pa] d
Octanol-water partition coefficient. ?? [log10] d
Water solubility ?? [mg.l-1] d

Figure 2.3 – Physico-chemical data entry window (screen shot from EUSES program)

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[1] EUSES, European Union System for the Evaluation of Substances, available from the European Chemicals Bureau, Ispra, Italy

The risk assessment system outlined by EUSES and the TGD is very complex with more than 400 parameters, 132 default values and 32 input values (Berding, 2000; Schwartz, 2000). In an attempt to study the interactions of the various modules and parameters within EUSES Berding *et al.* (1999) visualised the complexity of EUSES in a data flowchart (Appendix 6 also available online from http://www.usf.uni-osnabrueck.de/ projects/david/).

The current research has focused on the aquatic risk assessment for new chemicals and through close examination it was found that some of the inputs required to calculate the concentration of a substance in water at the local level ($Clocal_{water}$) were omitted in the complexity flowchart. Figure 2.4 shows a schematic representation of the risk assessment process focusing on the aquatic environment at the local scale as applied in this work, and amended and modified from the work of Berding *et al.* (1999).

2.2.2 The EUSES Blacklist

The European Chemical Bureau (ECB) hosts a supporting web-site on the Internet for EUSES (http://ecb.ei.jrc.it/Euses/) with basic information on the use of the program, its development and how to order copies. There is also an online list of problems and bugs documented for the EUSES program called "The EUSES Blacklist" (Appendix 7; ECB, 1998).

At technical meetings of the EUSES working group problems and improvements are discussed and placed on the list in order of priority:

1. Bug[2] Fixes -	Problems in the programming that are high priority changes to ensure a working program.
2. Problems -	These are usually numerical inaccuracies or formula errors that produce spurious results.
3. Wish List -	Changes that would like to be made if budget, and time allow, mainly aesthetic and user friendliness changes. These have the lowest priority.

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[2] Bugs – errors in a computer program that disrupt normal operation and cause inaccuracies in results.

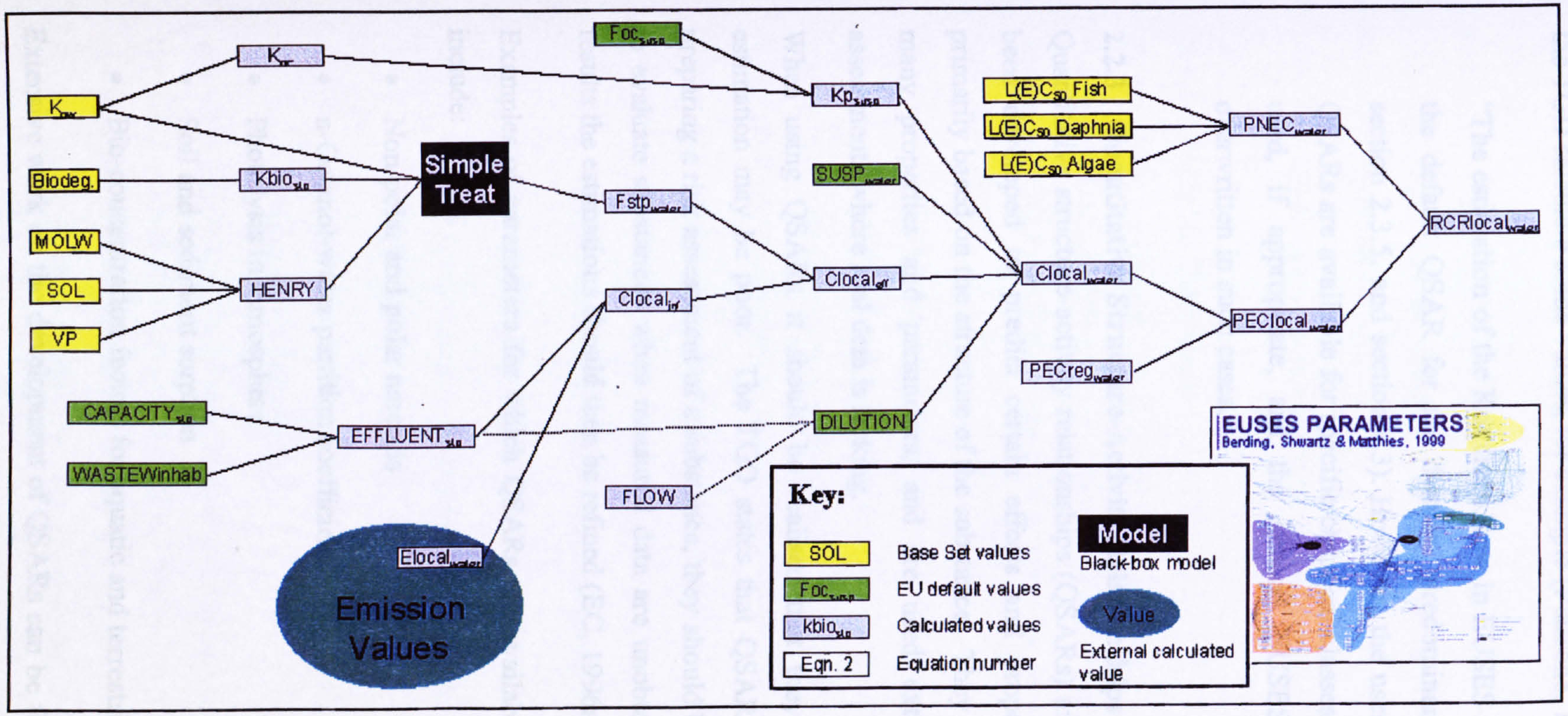


Figure 2.4 – Parameters involved in calculating the local PEC value for water (amended and adapted from Berding *et al.* (1999)

Where

Biodeg. - Descriptive value for the biodegradation rate
$CAPACITY_{stp}$ - Capacity of the STP
$Clocal_{eff}$ - Concentration of chemical in STP effluent
$Clocal_{inf}$ - Concentration in untreated wastewater
$Clocal_{water}$ - Local concentration in surface water
DILUTION - Dilution factor (from river flow)
$EFFLUENT_{stp}$ - Effluent discharge rate of STP
$Elocal_{water}$ - Local emission rate to water during an episode
Foc_{susp} - Fraction of organic carbon in suspended matter
FLOW - Flow rate of river
$Fstp_{water}$ - Fraction of emission directed to water by STP
HENRY - Henry's Law constant
$Kbio_{stp}$ - Rate constant for biodegradation
Koc - Carbon normalised partition coefficient
Kow - Partition coefficient for octanol and water
Kp_{susp} - Solid-water partition coefficient of suspended matter
$L(E)C_{50}$ (species) - Lethal or effect concentration to 50% of population
MOLW - Molecular weight
$PEClocal_{water}$ - Predicted environmental concentration
$PECregional_{water}$ - Regional concentration in surface water
$PNEC_{water}$ - Predicted No-Effect Concentration in water
$RCRlocal_{water}$ - Risk Characterisation Ratio for local water
SOL - Solubility in water
$SUSP_{water}$ - Concentration of suspended matter in river
VP - Vapour pressure
WASTEWinhab - Sewage flow per inhabitant

Many of the items on the Blacklist arise because of discrepancies in how EUSES and the TGD calculate some values, for example (Plassche, 1997):

> "The estimation of the Koc from Kow in EUSES is performed according to the default QSAR for the domain 'predominantly hydrophobics' (TGD section 2.3.5. and section 4.3). However, the user is not warned that other QSARs are available for specific chemical classes. These QSARs should be used, if appropriate, and the general EUSES estimate needs to be overwritten in such cases."

2.2.3 Quantitative Structure-Activity Relationships

Quantitative structure-activity relationships (QSARs) are estimation methods that have been developed to predict certain effects and properties of chemical substances, primarily based on the structure of the substance. They are available for approximating many properties and parameters, and are used extensively in the field of risk assessments where real data is lacking.

When using QSARs it should be realised that they are estimations and that the estimation may be poor. The TGD states that QSARs cannot be the only basis for preparing a risk assessment of a substance, they should be used, as a contemporary tool to evaluate substances when measured data are unobtainable, and in the light of the results the estimations should then be refined (EC, 1996a).

Examples of parameters for which QSARs are available and used in risk assessment include:

- Non-polar and polar narcosis
- n-Octanol-water partition coefficient
- Photolysis in atmosphere
- Soil and sediment sorption
- Biodegradation
- Hydrolysis
- Henry's Law constant
- Photolysis in water
- Bio-concentration factors for aquatic and terrestrial organisms

Extensive work on the development of QSARs can be found in the literature and, there is also much discussion on their use, (Russom *et al.*, 1991; OECD, 1992 & 1993a). Some computer automated QSARs have been developed for parameters (Howard &

Meylan, 1992; Syracuse, 1992). The research into QSARS for exposure parameters is focused in particular on the following values:

- Partition coefficients (Bockting *et al.*, 1993; Bintein & Devillers, 1994)
- Henry's Law Constant (Nirmalakhandan & Speece, 1988; Meylan & Howard 1991)
- Biodegradation rates (Muller & Klein, 1991; OECD, 1993b)

2.2.4 Partition Coefficients

A partition coefficient is a ratio of the equilibrium concentrations of a substance, usually between two immiscible solvents. They are important factors in the exposure assessment for modelling transport of a substance between the various environmental compartments.

Adsorption of the substance to solid surfaces can be a significant removal process in the environment, and reduces the concentration in aqueous solution. The adsorption coefficient normalised to the organic content of soil (*Koc*) is used to calculate the solid-water partition coefficients for each compartment (soil, sediment, suspended matter).

These values and/or the *Koc* value can be derived in a number of ways (in order of decreasing accuracy):

- Direct measurement of individual partition coefficients
- *Koc* measured by adsorption studies (OECD test guideline 106)
- *Koc* approximation, measured by High Performance Liquid Chromatography (HPLC) method
- *Koc* may be estimated from the n-octanol/water partition coefficient, *Kow* (for non-ionic substances)

For some substances however, measurement of *Koc* can be difficult experimentally. In the UK, a measured *Koc* by the HPLC-method is usually required as part of the notification for substances for which the QSAR calculations are not appropriate. Further data may be requested subject to the results of the risk assessment.

The TGD outlines QSARs for estimating *Koc* (Table 2.1) based on linear regression analysis, with *Kow* as the descriptor variable. The TGD states that the QSAR for the chemical class "predominantly hydrophobics" should be used as a default, however values are given for other classes as well. The *Koc* value is derived as detailed in Equation 2.1:

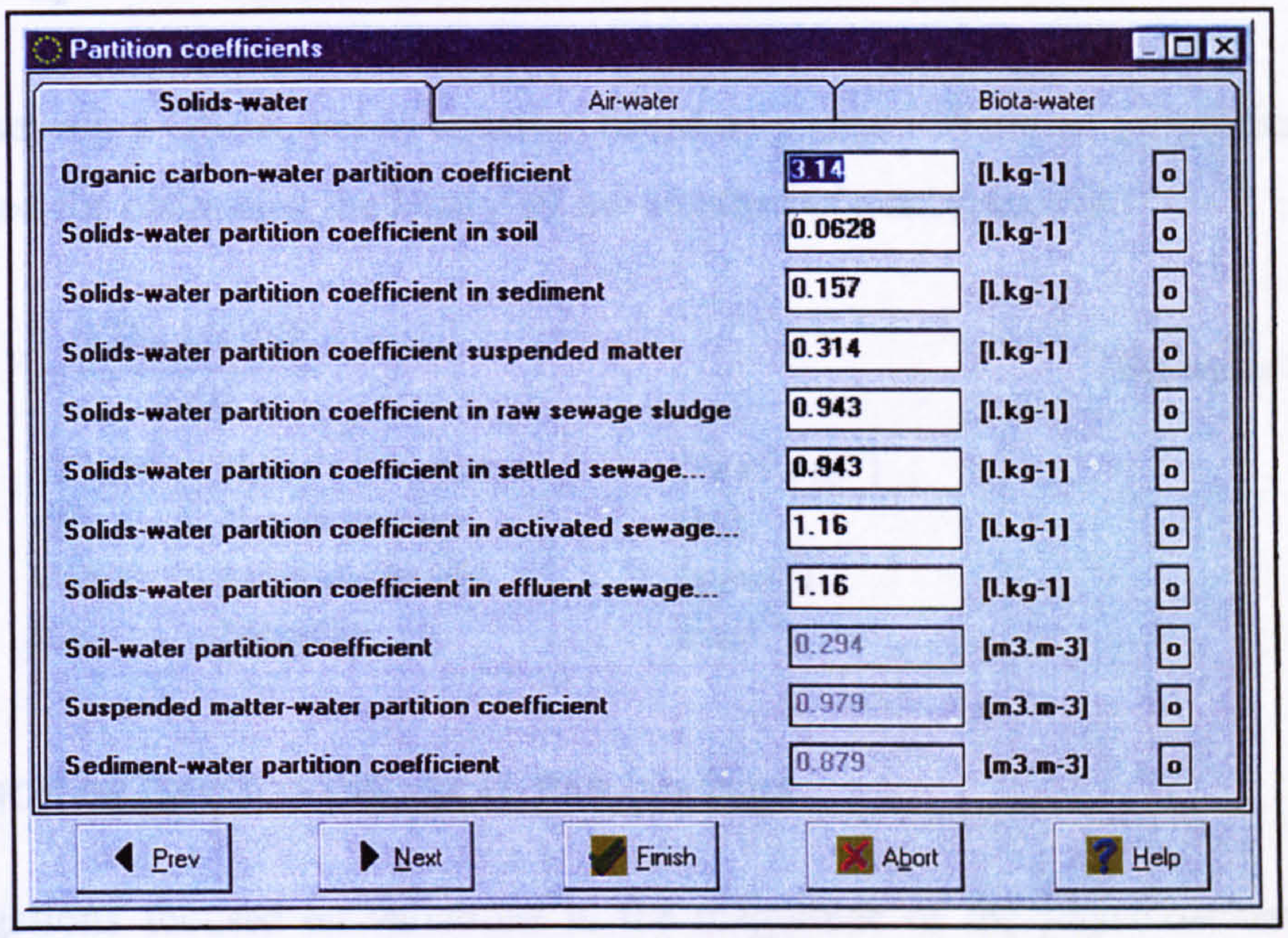
$$LogKoc = x \cdot LogKow + y$$ **Equation 2.1**

LogKoc the carbon normalised partition coefficient in log units
LogKow the n-octanol/water partition coefficient in log units
x & y are variables as detailed in Table 2.1

Chemical Class	**x**	**y**
Acetanilides	0.4	1.12
Acetanilides, carbamates, esters, phenylureas, phosphates, triazines, triazoles, uracils	0.47	1.09
Alcohols	0.39	0.5
Alcohols, organic acids	0.47	0.5
Amides	0.33	1.25
Anilines	0.62	0.85
Carbamates	0.37	1.14
Dinitroanilines	0.38	1.92
Esters	0.49	1.05
Nitrobenzenes	0.77	0.55
Non-hydrophobics	0.52	1.02
Organic acids	0.6	0.32
Phenols, anilines, benzonitriles, nitrobenzenes	0.63	0.9
Phenols, benzonitriles	0.57	1.08
Phenylureas	0.49	1.05
Phosphates	0.49	1.17
Predominantly hydrophobics	0.81	0.1
Triazines	0.3	1.5
Triazoles	0.47	1.41

Table 2.1 - QSARs for the partition coefficient of organic carbon-water (EC, 1996a)

Within the EUSES program, unless the *Koc* value is overwritten with a measured value, *Koc* is calculated from the *Kow* value using the default equation. If a measured or calculated value is available this should be entered at the Partition Coefficients screen (Figure 2.5); other solid/water partition coefficients are then calculated from this value. A wish-list item on the EUSES Blacklist is for the possibility to choose which adsorption QSAR is used.



Organic carbon-water partition coefficient	3.14	[l.kg-1]
Solids-water partition coefficient in soil	0.0628	[l.kg-1]
Solids-water partition coefficient in sediment	0.157	[l.kg-1]
Solids-water partition coefficient suspended matter	0.314	[l.kg-1]
Solids-water partition coefficient in raw sewage sludge	0.943	[l.kg-1]
Solids-water partition coefficient in settled sewage...	0.943	[l.kg-1]
Solids-water partition coefficient in activated sewage...	1.16	[l.kg-1]
Solids-water partition coefficient in effluent sewage...	1.16	[l.kg-1]
Soil-water partition coefficient	0.294	[m3.m-3]
Suspended matter-water partition coefficient	0.979	[m3.m-3]
Sediment-water partition coefficient	0.879	[m3.m-3]

Figure 2.5 - Partition coefficients window (screen shot from EUSES computer program) Organic carbon-water partition coefficient (*Koc*) is used to calculate a number of other solid-water partition coefficients

2.2.5 Henry's Law Constant

The partitioning of a substance between the water and air phases is a physical property described by the Henry's Law constant, (*HENRY*). The magnitude of this constant gives an indication as to which of the two phases a substance is likely to partition into at equilibrium. Substances with low values of *HENRY* will tend to partition into the aqueous phase.

The Henry's Law constant may be expressed in either of the following ways:

$$HENRY = {}^{P}\!/_{C_w} \qquad HENRY' = {}^{C_a}\!/_{C_w}$$ **Equation 2.2 a/b**

HENRY	Henry's Law constant	$(Pa.m^3.mol^{-1})$
HENRY'	Dimensionless Henry's Law constant	(-)
P	Partial pressure	(Pa)
C_w	Concentration in water	$(mol.m^{-3})$
C_a	Concentration in air	$(mol.m^{-3})$

Although not strictly a QSAR, but an equation based on physico-chemical properties, the formula used for estimating the Henry's Law constant of a substance is:

$$HENRY = \frac{VP \times MOLW}{SOL}$$ **Equation 2.3**

HENRY	Henry's law constant	$(Pa.m^3.mol^{-1})$
VP	Vapour pressure	(Pa)
MOLW	Molecular weight	$(g.mol^{-1})$
SOL	Solubility	$(mg.l^{-1})$

2.3 VARIATION OF PHYSICO-CHEMICAL PARAMETERS

Initial investigations focused on variations in the magnitude of the physico-chemical input parameters in the EUSES model. OECD agreed guidelines are available for the measurement of many physical and chemical properties; within each guideline an acceptable error is usually quoted that repeat measurements should satisfy.

It was assumed that the tests producing the physico-chemical data supplied as part of a notification are performed to GLP and to a similar test standard as that of the OECD. Submitted data are checked by HSE prior to assessments being carried out at which point non-standard tests or poor laboratory practice should have been highlighted.

These analyses were restricted to new substances, where the full *base set* of data were available. The assessments were restricted to the calculation of the local PEC value for the aquatic compartment ($PEClocal_{water}$) in order to both simplify and focus the resulting data.

The value quoted in the notification for a particular property was taken to be the mean value. By varying the mean value of a property by the OECD quoted acceptable error maximum and minimum values were found, providing a range for $PEClocal_{water}$ due to experimental variability. A number of substances were analysed in this way with only one parameter being varied at a time in each assessment.

2.3.1 *Base Set* Physico-Chemical Properties

The effect of variability in measurement was investigated for the following properties:

- Melting point (*MP*)
- Boiling point (*BP*)
- Vapour pressure (*VP*)
- Solubility in Water (*SOL*)
- n-octanol-water partition coefficient (*Kow*)

Melting Point

This property is a measure of the temperature (or range) at which a substance changes its physical state from solid to liquid. The measurements are normally carried out at standard atmospheric temperature (101.325 kPa). The accuracy for measuring the melting point of a substance is quoted as ±1.0 K based on the least accurate test method (Kofler hot bar) in OECD Guideline 102[3].

Boiling Point

Similar to the melting point the boiling point of a substance indicates the temperature (or range) at which a substance physically changes state from a liquid to a gas. The approximate accuracy for the measurement of this property is quoted as ±1.4 K (for values <374 K) and ±2.5K (for values ≥ 374 K) by Ebulliometer method in OECD Guideline 103[4].

Vapour Pressure

This value indicates the extent to which a substance will volatilise and become gaseous. More correctly known as the saturated vapour pressure, it is the saturation pressure above a solid or liquid substance. At thermodynamic equilibrium, the value is only a function of temperature. The vapour pressure value is significant environmentally in

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[3] OECD Guideline 102 for testing of chemicals, adopted 12 May 1981; Melting Point/Melting Range (-Capillary Method, using liquid bath, metal block, photocell detection – Hot Stage Method, using Kofler hot bar, melt microscope, meniscus method – Freezing Point Method); OECD, Paris, France

[4] OECD Guideline 103 for testing of chemicals, adopted 12 May 1981; Boiling Point/Boiling Range (Ebulliometer Method – Dynamic Method – Distillation Method – Sicooloboff Method – Photo Detection Method); OECD, Paris, France

estimating atmospheric concentrations. The average accuracy in measuring the values is given as ±25% in OECD Guideline 104[5].

Solubility in Water

This value is a measure of how soluble a substance is in water, and is a measure of the saturation mass concentration of a substance in water. This value is a function of temperature. The value is of environmental importance because the transport of the substance in the environment is significantly affected by the solubility of the substance in water. Water soluble substances are also readily biologically available to humans and other organisms. The accuracy for the test is quoted as ±30% based on least accurate test method (column elution) in OECD Guideline 105[6].

n-Octanol/Water Partition Coefficient

This value is important environmentally because it gives a measure of how the substance will partition between aqueous and organic phases. A significant relationship has also been shown between the n-octanol/water partition coefficient for a substance and the potential for bioaccumulation in fish. The accuracy quoted for the measurement of this value is quoted as ±0.3 log units for the flask shaking method in OECD Guideline 107[7]. This method can be analytically difficult particularly for substances which are poorly soluble in one or other of the test solvents, in such cases a newly agreed estimation method using HPLC can be used (OECD Guideline 117).

Molecular Weight

More correctly termed as the relative molecular mass, this is the gram weight of one mole of a substance referred to ^{12}C (12.000 g/mol). This value is directly calculated from the chemical structure/formula of the substance.

2.3.2 Substances Investigated

For these investigations sets of real *base set* values for a number of new substances were used (Table 2.2). These substances are classified as "Commercially Confidential" as described in the NONS 1993 Regulations, for this reason the identity of the

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[5] OECD Guideline 104 for testing of chemicals, adopted 12 May 1981; Vapour Pressure Curve (Dynamic Method – Static Method – Isoteniscope – Vapour Pressure Balance – Gas Saturation Method); OECD, Paris, France

[6] OECD Guideline 105 for testing of chemicals, adopted 12 May 1981; Water Solubility (Column Elution Method – Flask Method); OECD, Paris, France

[7] OECD Guideline 107 for testing of chemicals, adopted 12 May 1981; Partition Coefficient (n-octanol/water) (Flask Shaking Method); OECD, Paris, France

substances is not given, instead associated codes are used. Full details on the values amended with negative and positive variation, and the resulting $PEClocal_{water}$ values can be found in Appendix 8.

	MOLW	*MP*	*BP*	*VP*	Log *Kow*	*SOL*
Units	*g/mol*	*K*	*K*	*Pa*	-	*mg/l*
Accuracy	~	*±1.0*	*±1.4 (<373K)* *±2.5 (≥373K)*	*Ave.* *±25%*	*±0.3* *log units*	*±30%*
101P	197	223	578	0	4	7.5
652F	284	<24	133-303	23.3	4.68	2.95
909F	187	-	-	0.75	3.34	109
1062F	158	-	-	130	3.07	2710
1084F	234	-	-	0.7	5.3	19
672D	434	-	-	0	5.5	0.2
724D	404	-	-	11	4.3	0.2
745D	445	-	-	0	3.9	1.2
969D	485	-	-	0.1	3.8	1

Table 2.2 – *Base set* data for substances used in initial investigations

2.3.3 Effect of Variability in Measurement on $PEClocal_{water}$

Graphs were produced indicating the range of $PEClocal_{water}$ values produced with reference to that of the PEC calculated using the *base set* data. In the first two analyses it was found that variations in melting point and boiling point did not significantly affect $PEClocal_{water}$. Through closer examination of the data flowchart (Berding *et al.*, 1999) and Figure 2.4 it was found that the two temperature values did not directly affect the calculation of the $PEClocal_{water}$, therefore these properties were not considered in the remaining analyses in this section. Figures 2.6 – 2.14 show the ranges for $PEClocal_{water}$ produced by variability in the *base set* properties.

Although a few substances showed large effects caused by variation in *VP* or *SOL*, all the substances examined showed large variations in $PEClocal_{water}$ with variation in *Kow*. The range of PEC values produced for each substance were compared (Figure 2.15), and a tendency towards grouping of the PEC values of some substances is observed, however there is no clear relationship between any single physico-chemical parameter and the spread and/or grouping of the ranges on this chart.

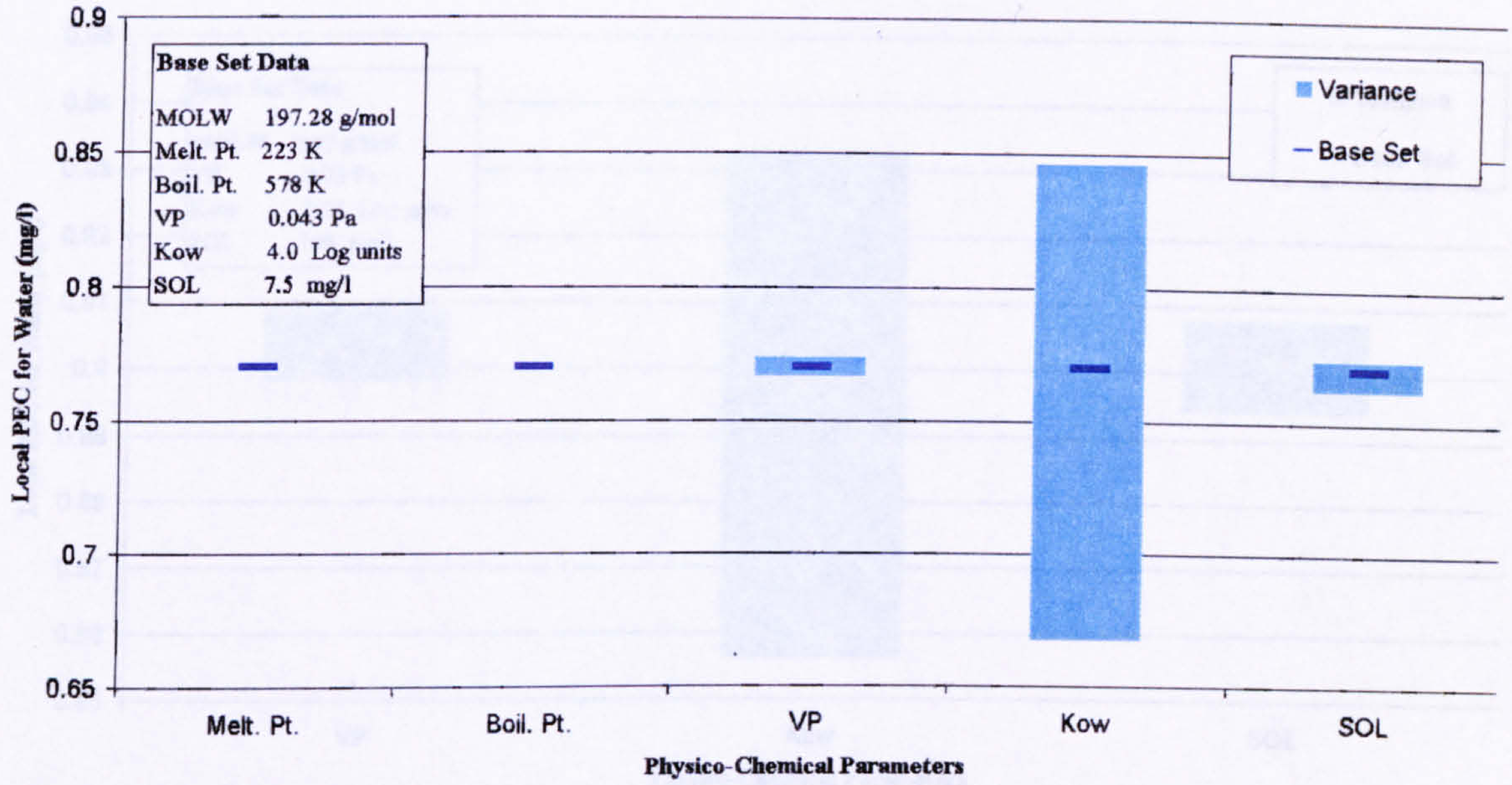

Figure 2.6 - Effect of variability in measurement of physico-chemical values on local PEC value for water - substance 101P

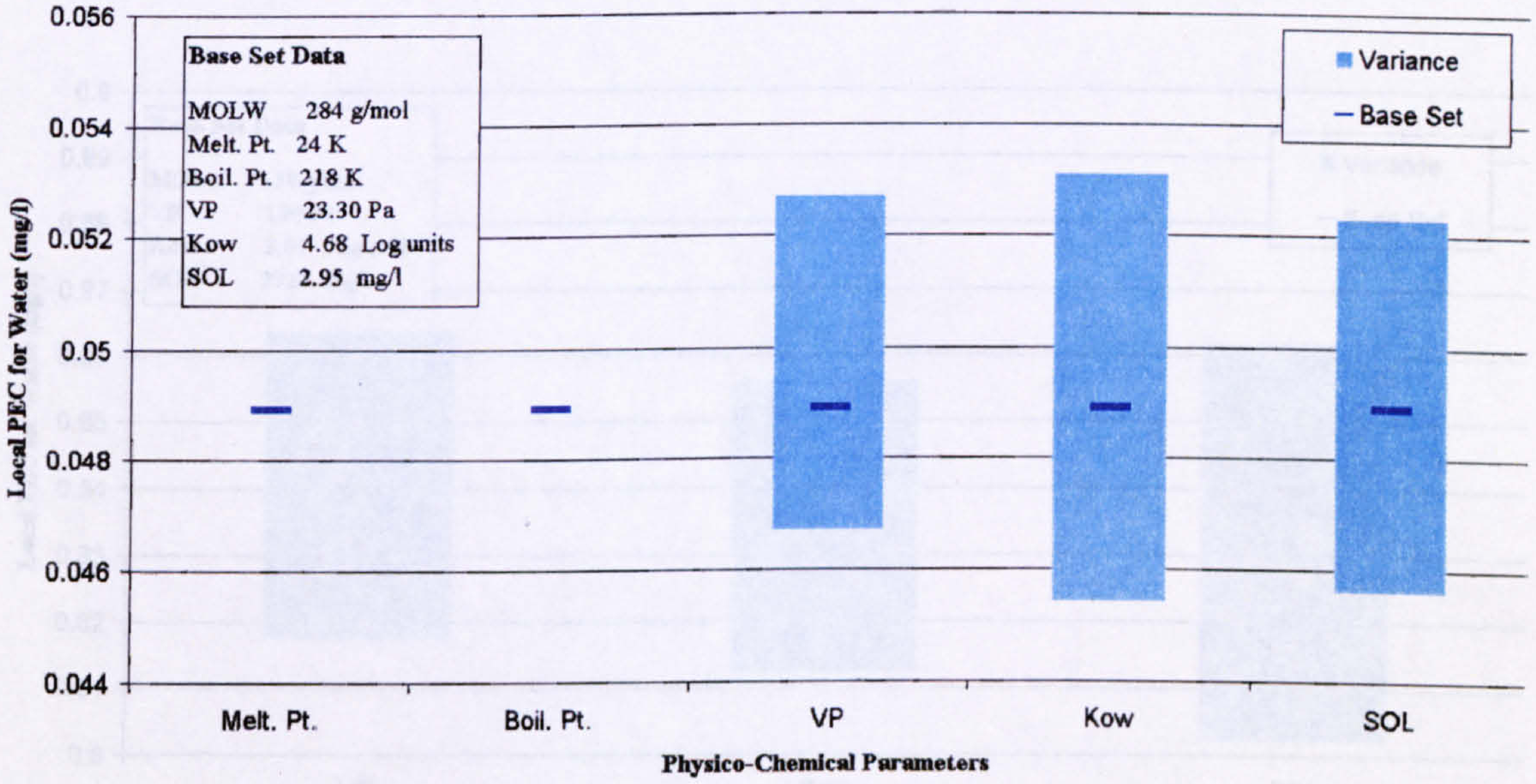

Figure 2.7 - Effect of variability in measurement of physico-chemical values on local PEC value for water - substance 652F

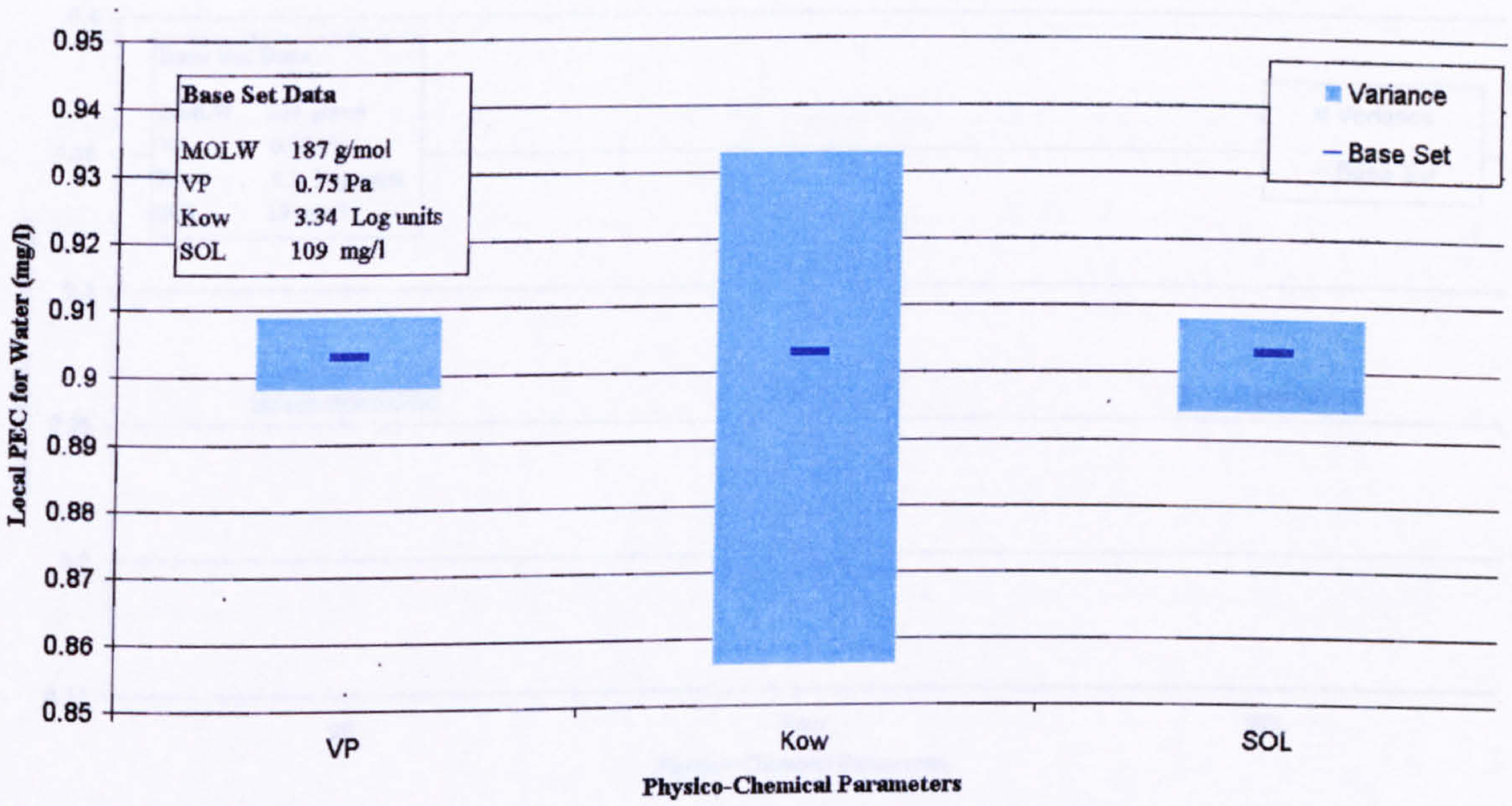

Figure 2.8 - Effect of variability in measurement of physico-chemical values on local PEC value for water - substance 909F

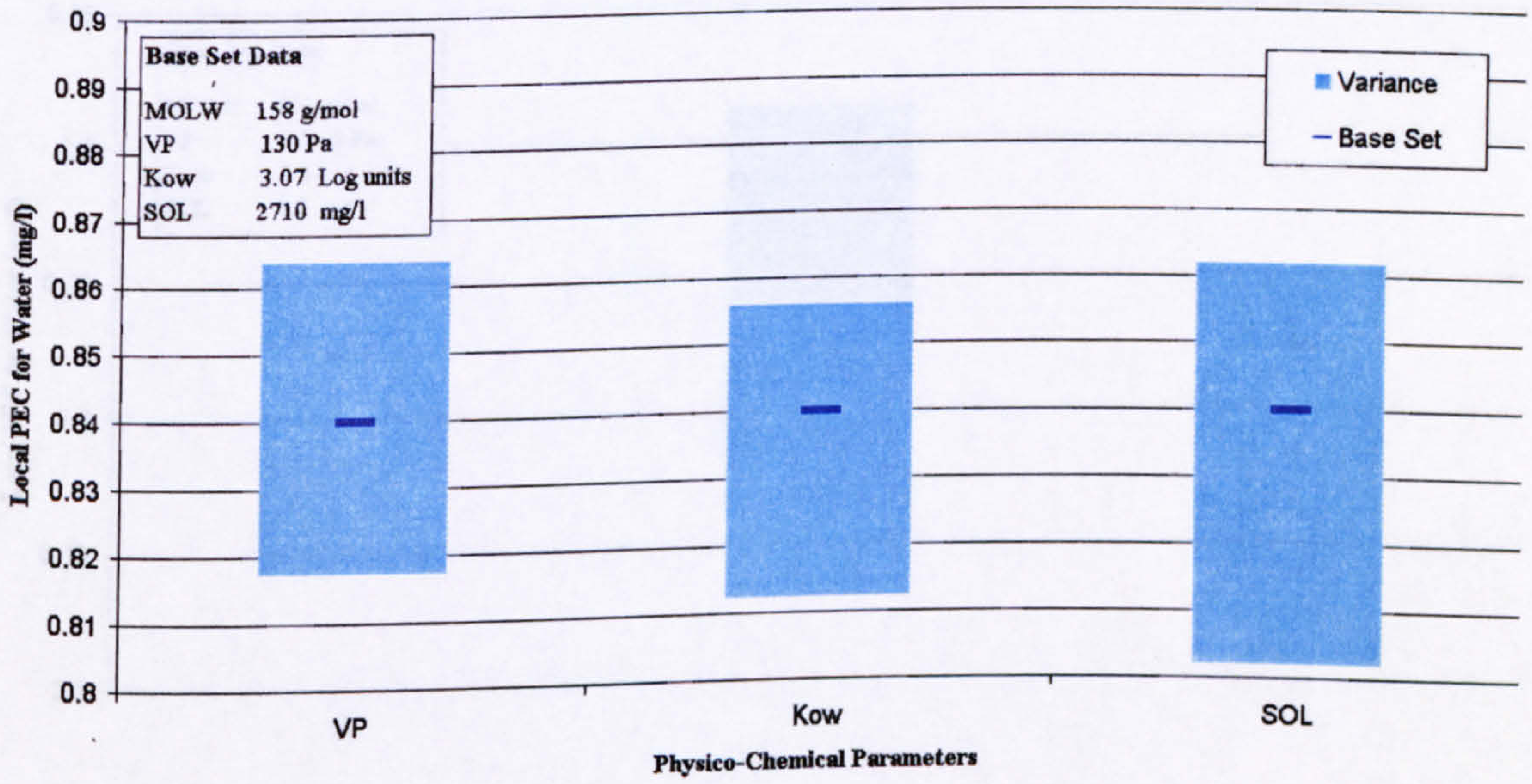

Figure 2.9 - Effect of variability in measurement of physico-chemical values on local PEC value for water - substance 1062F

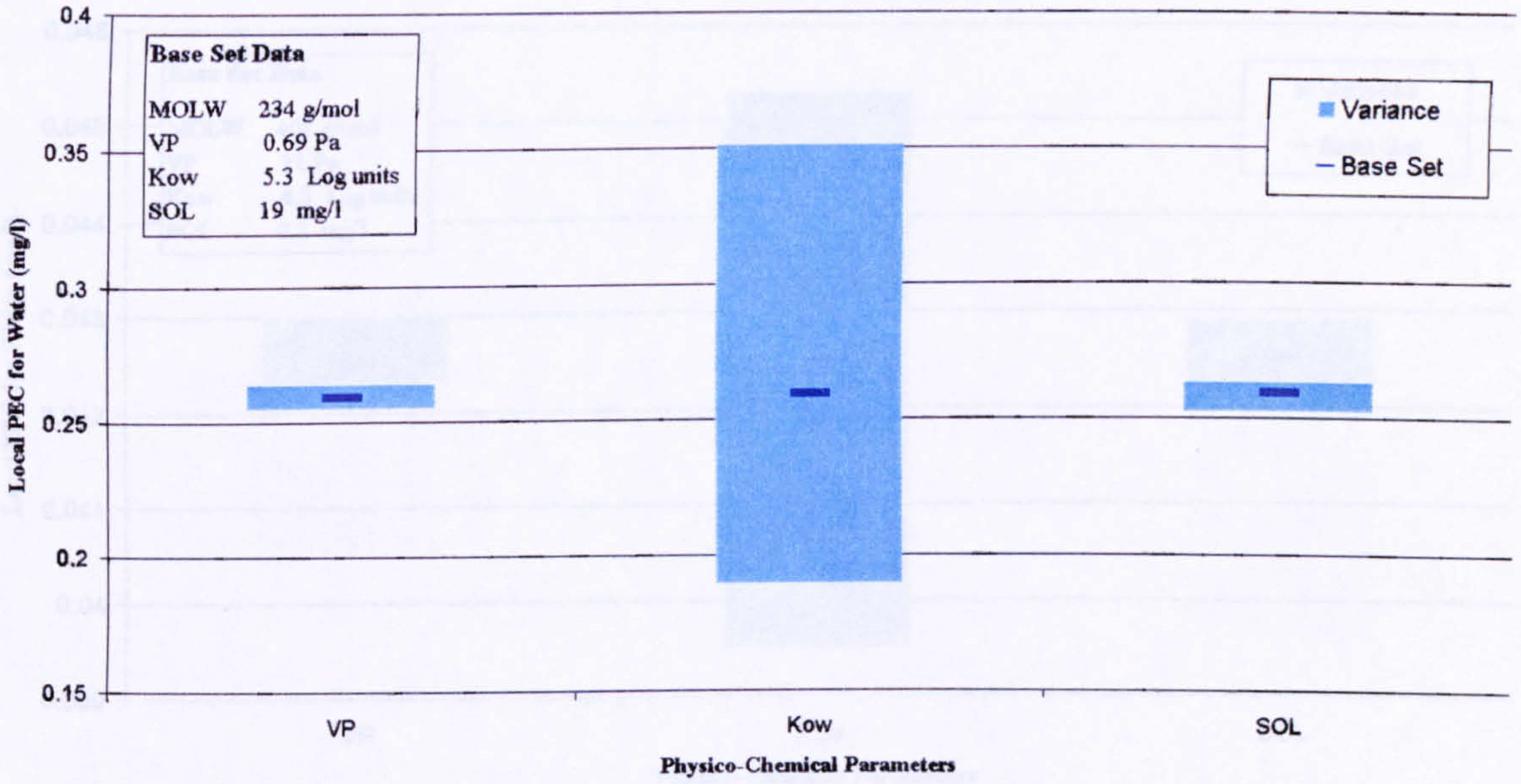

Figure 2.10 - Effect of variability in measurement of physico-chemical values on local PEC value for water - substance 1084F

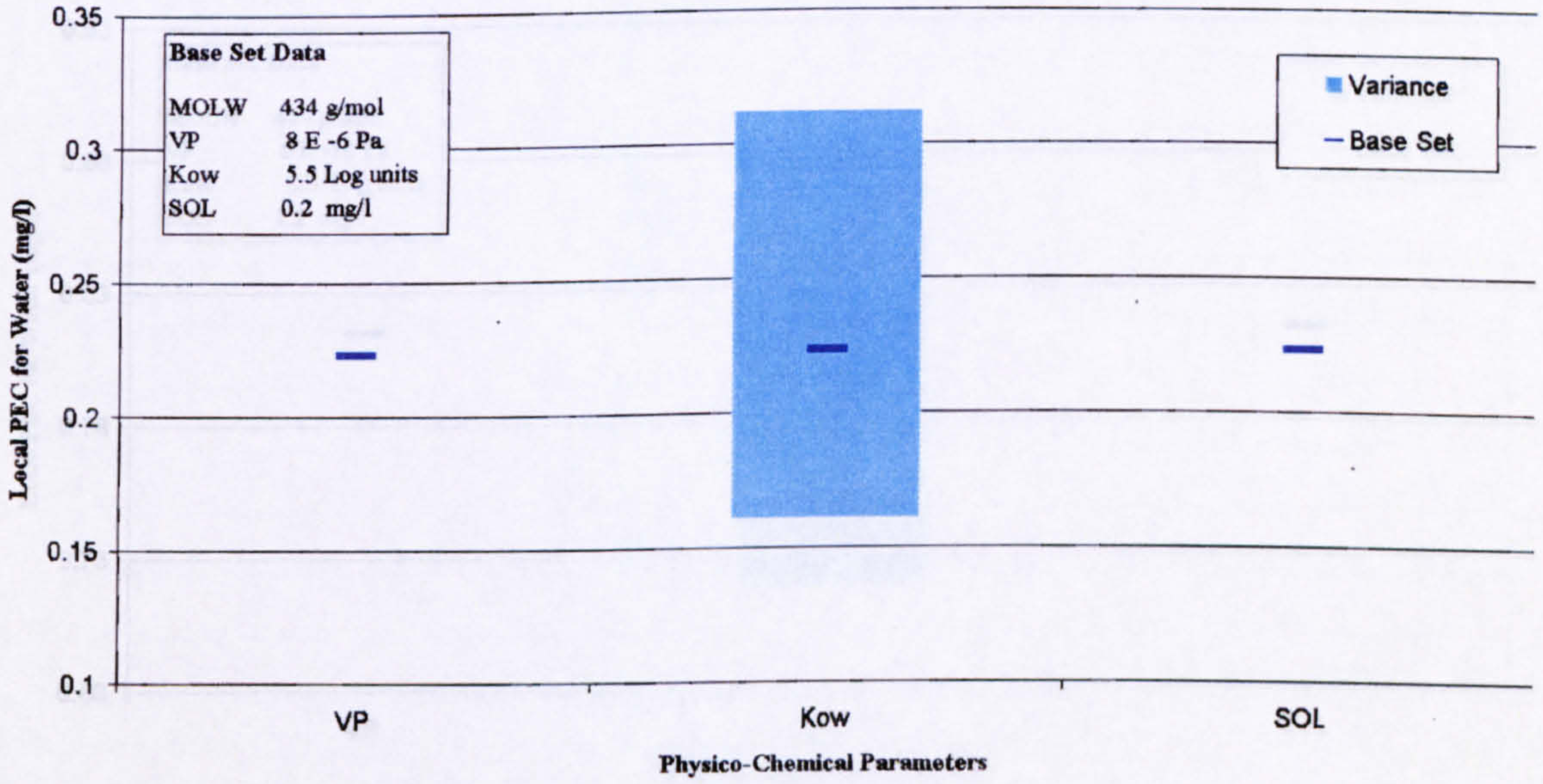

Figure 2.11 - Effect of variability in measurement of physico-chemical values on local PEC value for water - substance 672D

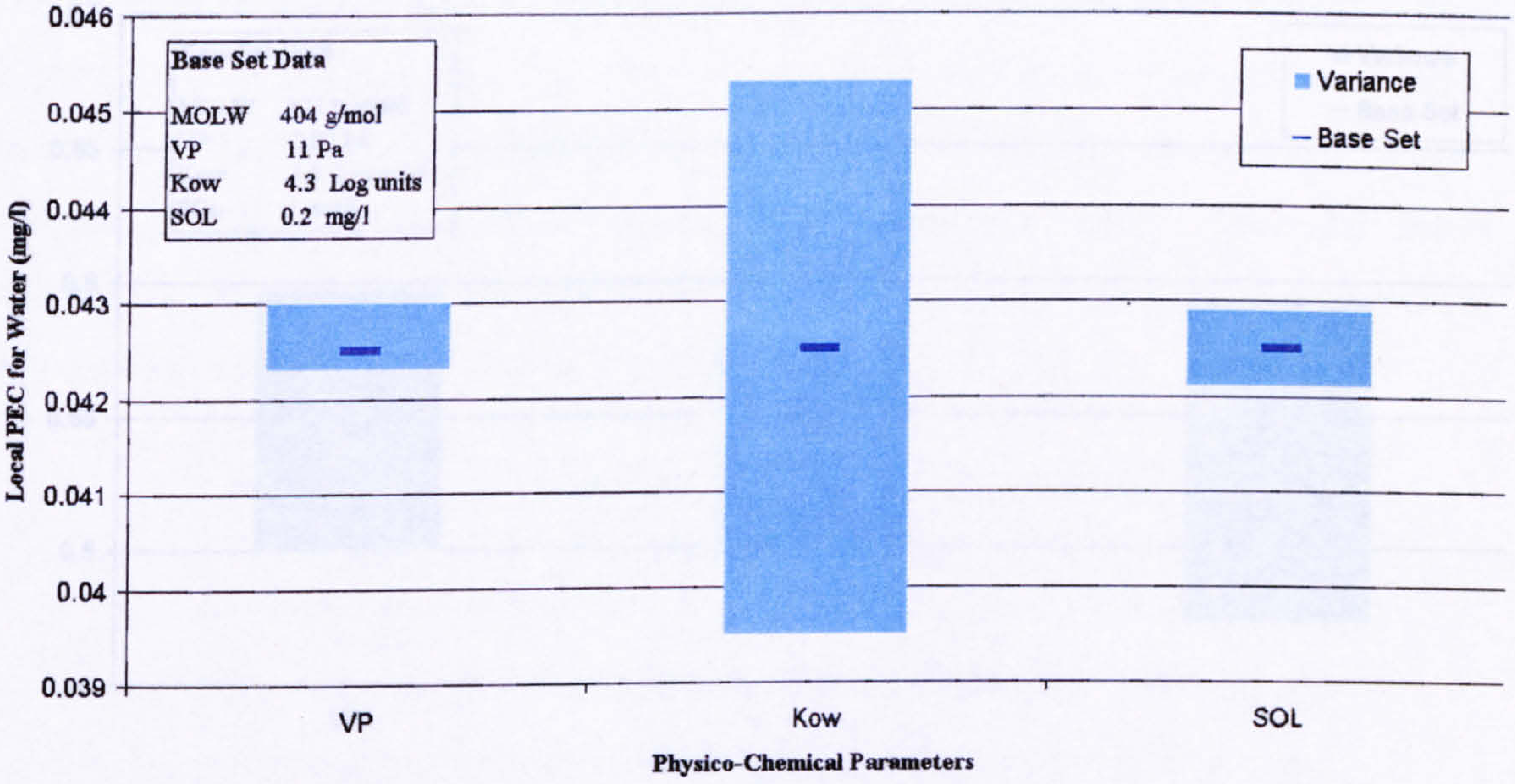

Figure 2.12 - Effect of variability in measurement of physico-chemical values on local PEC value for water - substance 724D

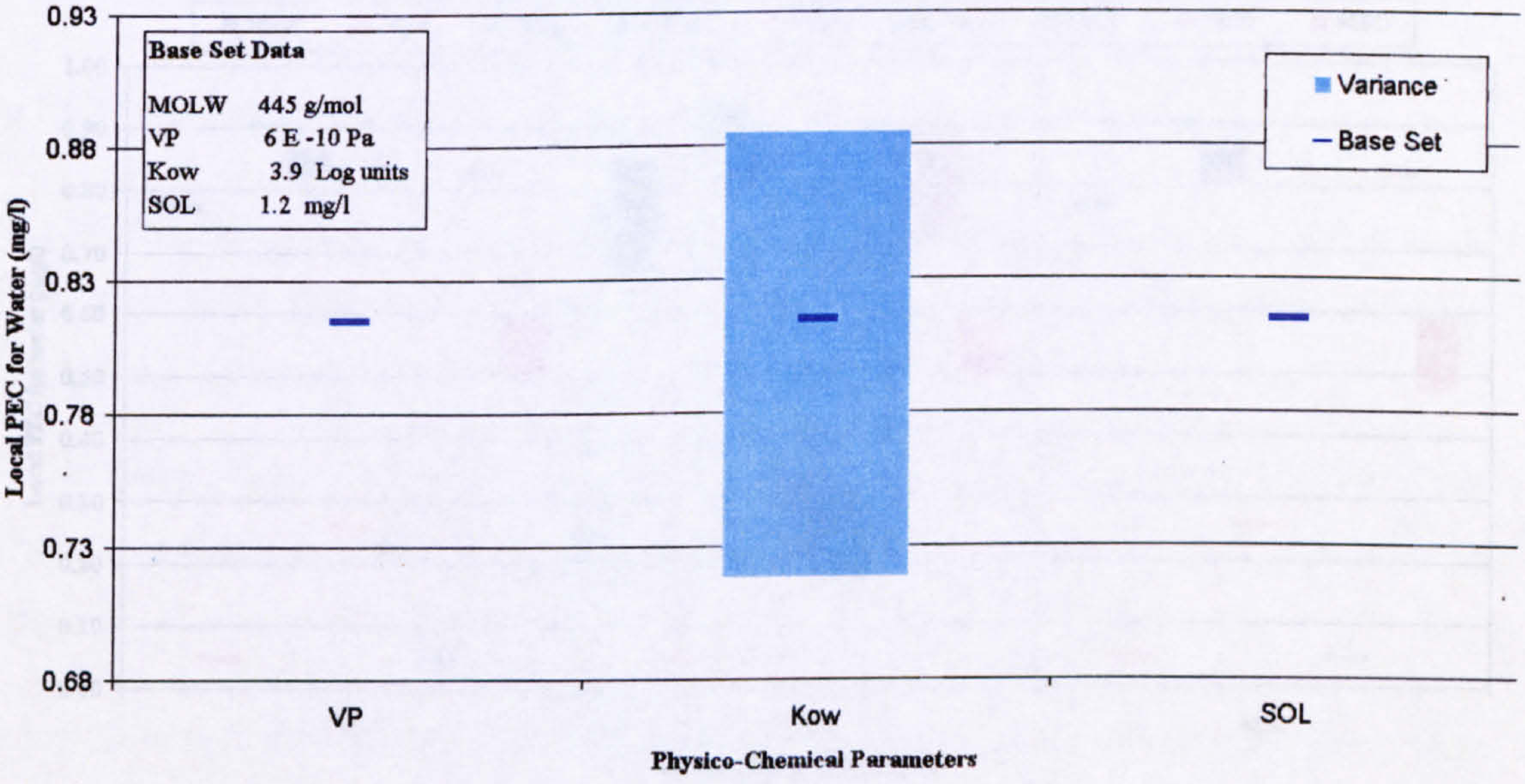

Figure 2.13 - Effect of variability in measurement of physico-chemical values on local PEC value for water - substance 745D

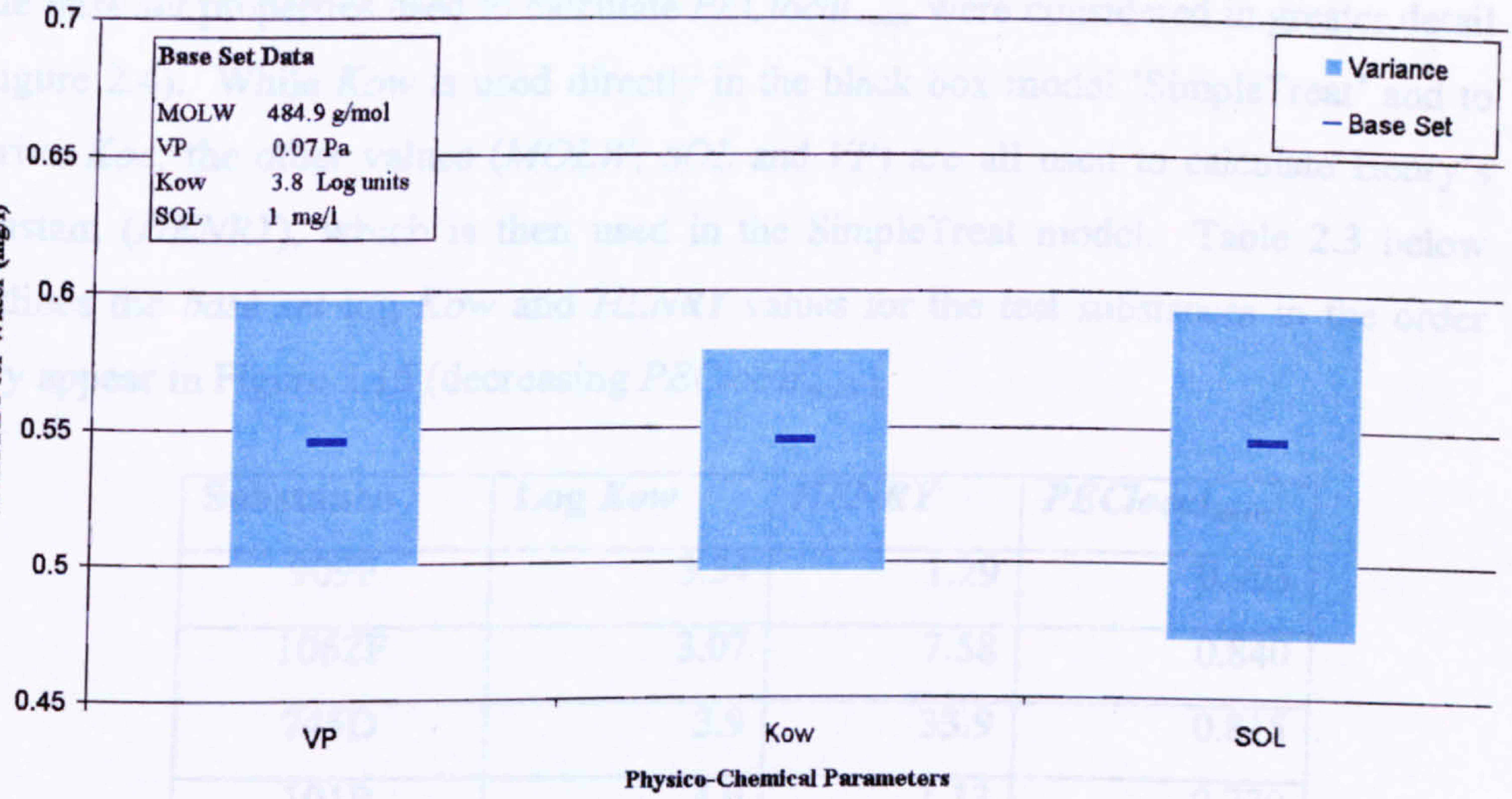

Figure 2.14 - Effect of variability in measurement of physico-chemical values on local PEC value for water - substance 969D

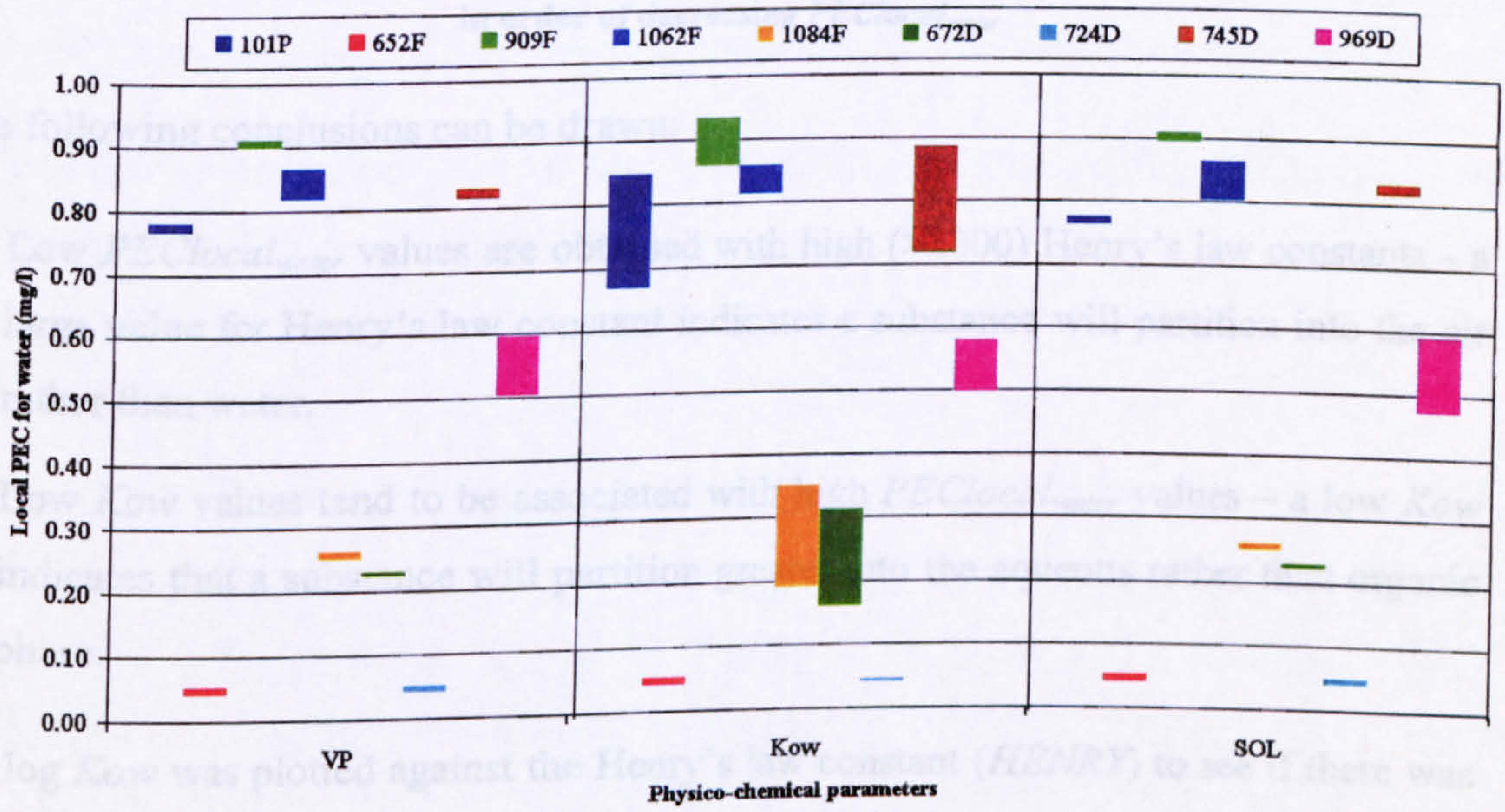

Figure 2.15 - Comparative examination of the effect of variability in measurement of physico-chemical properties on local PEC value for water

The *base set* properties used to calculate $PEClocal_{water}$ were considered in greater detail (Figure 2.4). While *Kow* is used directly in the black box model 'SimpleTreat' and to derive *Koc*, the other values (*MOLW*, *SOL* and *VP*) are all used to calculate Henry's constant (*HENRY*), which is then used in the SimpleTreat model. Table 2.3 below outlines the *base set* log *Kow* and *HENRY* values for the test substances in the order they appear in Figure 2.15 (decreasing $PEClocal_{water}$).

Substance	**Log *Kow***	***HENRY***	$PEClocal_{water}$
909F	3.34	1.29	0.903
1062F	3.07	7.58	0.840
745D	3.9	33.9	0.815
101P	4.0	1.13	0.770
969D	3.8	2.22 E^{-7}	0.545
1084F	5.3	8.5	0.259
672D	5.5	0.02	0.223
652F	4.68	2243	0.0489
724D	4.3	22220	0.0425

Table 2.3 - Log *Kow* and *HENRY* values for test substances in order of decreasing $PEClocal_{water}$

The following conclusions can be drawn:

- Low $PEClocal_{water}$ values are obtained with high (>2000) Henry's law constants - a large value for Henry's law constant indicates a substance will partition into the air rather than water.
- Low *Kow* values tend to be associated with high $PEClocal_{water}$ values – a low *Kow* indicates that a substance will partition greater into the aqueous rather than organic phase.

The log *Kow* was plotted against the Henry's law constant (*HENRY*) to see if there was a correlation between the two values (Figure 2.16). No correlation was found with the data from the test substances used.

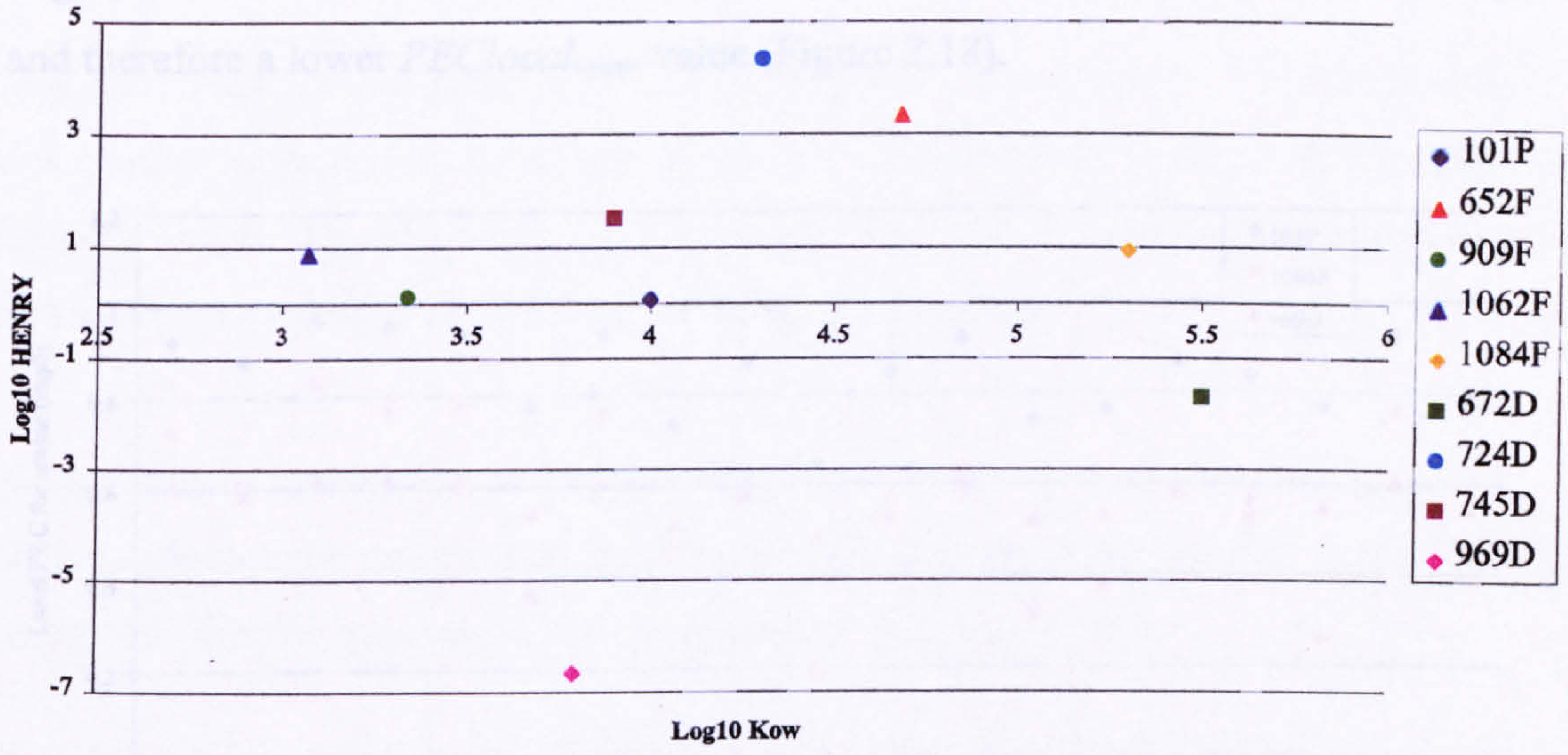

Figure 2.16 - Comparison of log *Kow* and log *HENRY* for various test substances

2.3.4 Effect of Estimation Method of *Koc* on *PEClocal*$_{water}$

QSARs can be used to approximate the carbon normalised adsorption coefficient (*Koc*), from the n-octanol/water partition coefficient (*Kow*) using Equation 2.1 and the values in Table 2.1. The *Koc* value is then subsequently used to calculate the solid-water partition coefficients for each compartment (soil, sediment, and suspended matter). EUSES uses the default QSAR for 'predominantly hydorphobic' substances in all cases.

The effect of the choice of QSAR for predicting *Koc* on the resulting *PEClocal*$_{water}$ was investigated for a sample of the test substances detailed (Figure 2.17). The resulting *PEClocal*$_{water}$ using maximum, minimum, mean and default predicted *Koc* values are given in Table 2.4.

	Default	Mean	Max.	Min.
101P	0.770	0.844	0.964	0.645
1084F	0.259	0.549	0.830	0.190
969D	0.545	0.570	0.625	0.483

Table 2.4 – Resulting *PEClocal*$_{water}$ from various QSAR estimated *Koc* values

The resulting *PEClocal*$_{water}$ using the default QSAR appears to be close to a minimum value. This means that the default QSAR predicts a higher than average *Koc* value.

High *Koc* values are associated with greater partitioning to the solid than water phase and therefore a lower $PEClocal_{water}$ value (Figure 2.18).

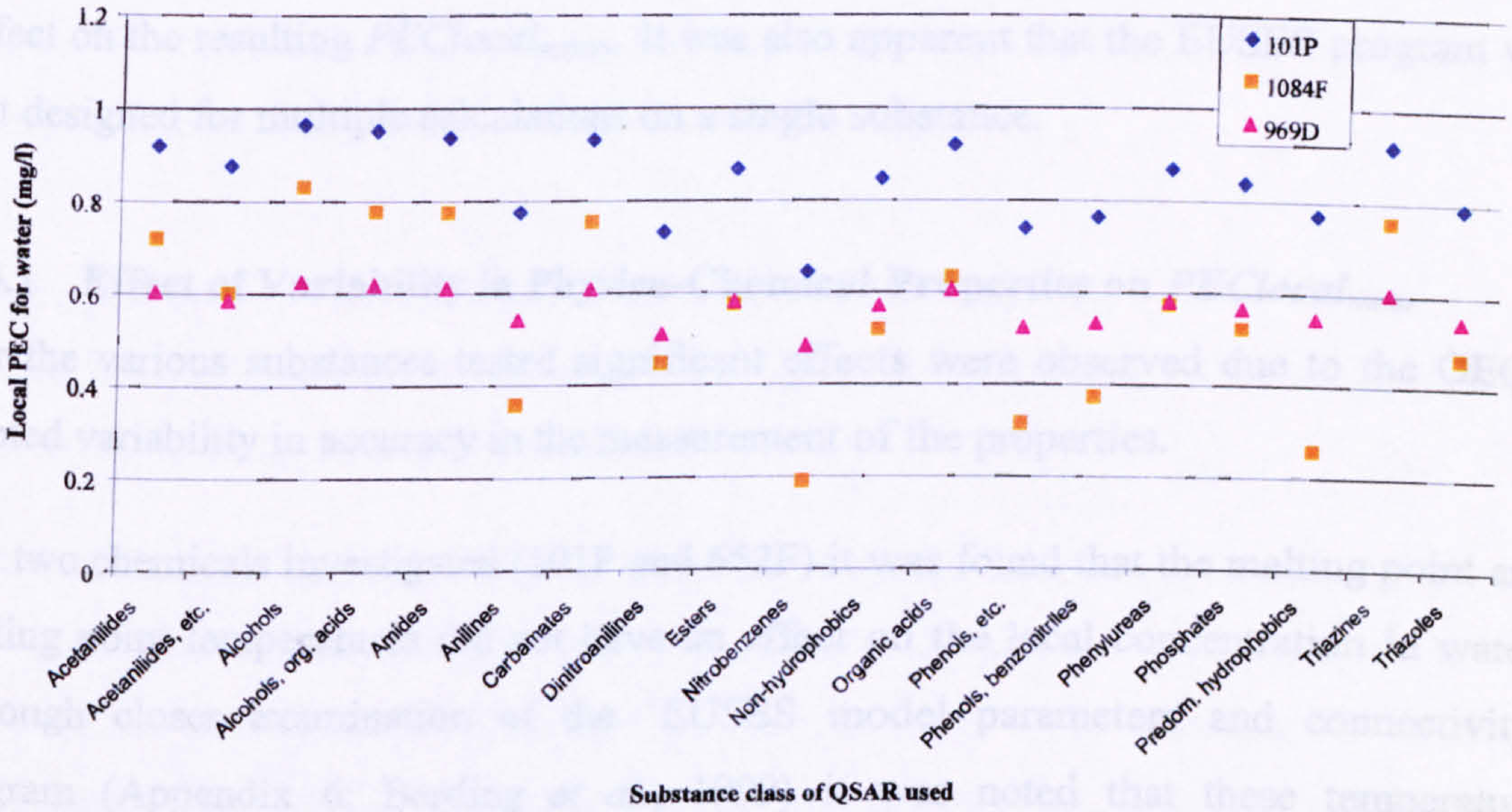

Figure 2.17 - The effect of choice of QSAR in predicting *Koc* from *Kow* for test substances

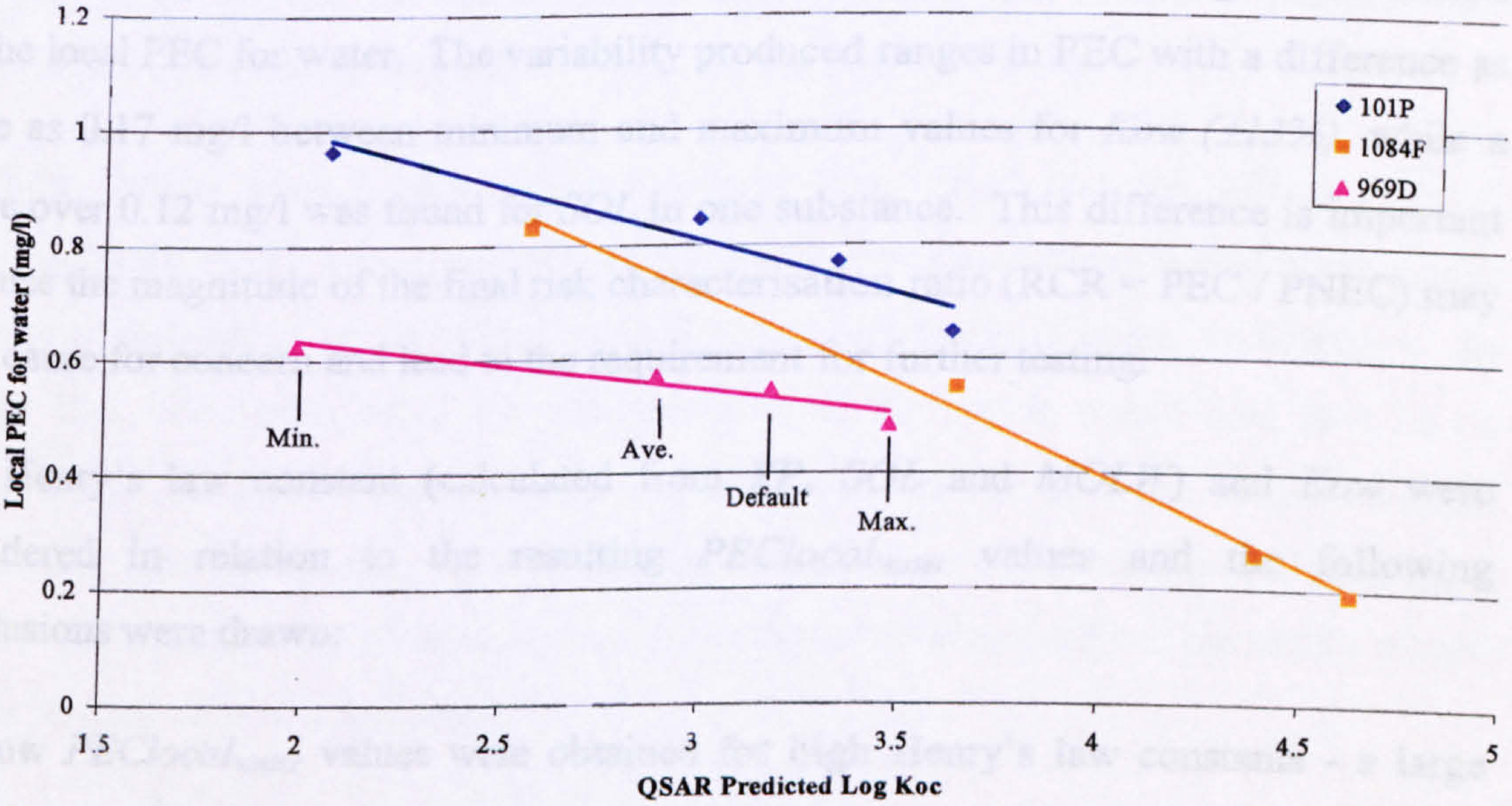

Figure 2.18 - Correlation between estimated log *Koc* value and resulting $PEClocal_{water}$

2.4 SUMMARY AND DISCUSSION

From the initial investigations it was clear that experimental variability due to measurement accuracy, or the choice of QSAR when estimating *Koc* had a significant effect on the resulting $PEClocal_{water}$. It was also apparent that the EUSES program was not designed for multiple calculations on a single substance.

2.4.1 Effect of Variability in Physico-Chemical Properties on $PEClocal_{water}$

For the various substances tested significant effects were observed due to the OECD quoted variability in accuracy in the measurement of the properties.

For two chemicals investigated (101P and 652F) it was found that the melting point and boiling point temperatures did not have an effect on the local concentration in water. Through closer examination of the 'EUSES model parameters and connectivity' diagram (Appendix 6; Berding *et al.*, 1999) it was noted that these temperature measurements were used in a different part of the model (for human health and food chain calculations).

The magnitudes of the vapour pressure (*VP*), solubility in water (*SOL*) and n-octanol/water partition coefficient for a substance, did however have significant effects on the local PEC for water. The variability produced ranges in PEC with a difference as large as 0.17 mg/l between minimum and maximum values for *Kow (±13%)*, while a range over 0.12 mg/l was found for *SOL* in one substance. This difference is important because the magnitude of the final risk characterisation ratio (RCR = PEC / PNEC) may give cause for concern and lead to the requirement for further testing.

The Henry's law constant (calculated from *VP*, *SOL* and *MOLW*) and *Kow* were considered in relation to the resulting $PEClocal_{water}$ values and the following conclusions were drawn:

- Low $PEClocal_{water}$ values were obtained for high Henry's law constants - a large value for *HENRY* indicates a substance will partition into the air therefore reducing the concentration in water.

- Low *Kow* values were associated with high $PEClocal_{water}$ values – a low *Kow* indicates a substance will partition greater into the aqueous rather than organic phase, therefore increasing the concentration in water.

No correlation however was found between *HENRY* and *Kow* based on the limited data from the substances examined.

2.4.2 Effect of Estimation Method of *Koc* on $PEClocal_{water}$

The EUSES program only uses the default QSAR for calculating *Koc* from *Kow* when a measured value for *Koc* is not available.

It was found that the default QSAR produces a greater than average value for *Koc*. A high *Koc* values indicates greater partitioning of a substance into the solid rather than water phase and therefore a lower $PEClocal_{water}$ value. The resulting $PEClocal_{water}$ using the default QSAR is therefore a below average value and cannot be considered as a worst case value for the aquatic compartment.

The values produced by the different QSARs, produced a range of PEC values of 0.6 mg/l for one substance (±30%). It would seem that if QSAR estimate values are to be used the most suitable QSAR should be selected, however it should be noted that the default QSAR is not the worse case value for the aquatic system.

In these initial investigations each property was varied and the effects assessed independently of the other properties. Although in this case the effect of experimental accuracy was being considered for each value separately, if larger variations in the values had been considered the interrelations of the values would also have to be considered. Mackay & Shiu (1981) presented a correlation between the solubility in water and vapour pressure of over 100 organic compounds by chemical class (Figure 2.19). This shows that in considering the variation in a property or parameter related values should also be considered.

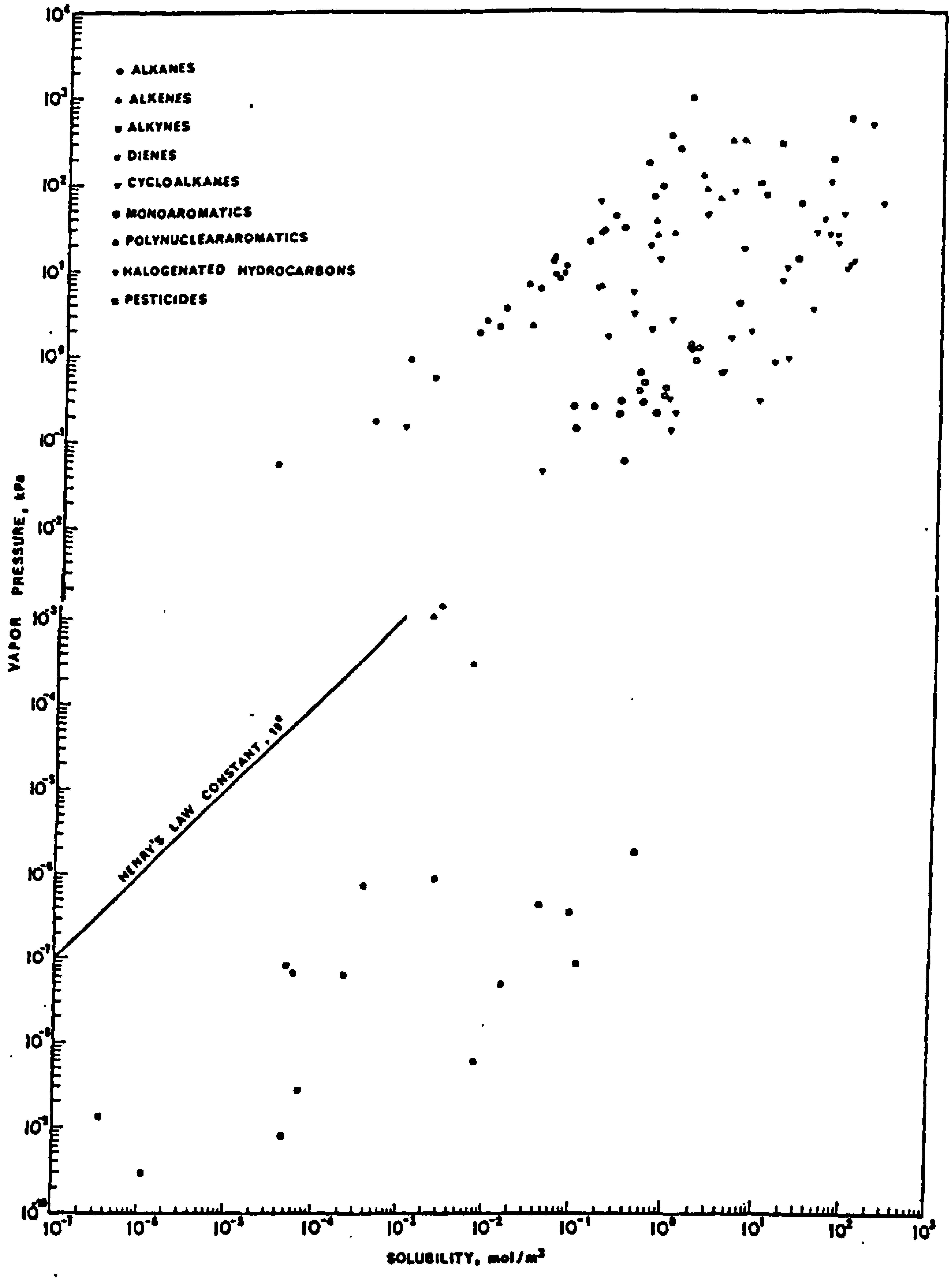

Figure 2.19 - Henry's law constants for organic compounds (Mackay & Shiu, 1981)

2.4.3 EUSES Program

The EUSES program has been shown to be far more complicated than the transparent model that was intended by the EU. It has also not been updated as often as was proposed, and the numerous entries on the EUSES Blacklist (http://ecb.ei.jrc.it/Euses/) indicate the need for a revision of the program.

The program has a strict linear structure for the entering of data in a series of 'data entry' windows. It is not a simple operation to run many calculations on the same substance with slight variations in parameters and properties to assess the effect of such variations. In this way the EUSES program does not lend itself to sensitivity or uncertainty analyses.

Spreadsheet models based on the calculations in EUSES and the TGD have however been used before to carry out such sensitivity and uncertainty analyses (Jager *et al.*, 1997; Berding, 2000 and Shwartz, 2000), although details on their calculations and assumptions have not been documented. The EUSES Blacklist draws attention to many discrepancies in the use of parameters and calculations applied in the EUSES/TGD models. Any spreadsheet model developed must therefore document the parameters and calculations used, the assumptions made and any limitations in the application of such a model, to allow scrutiny and the development of existing and further modules and models.

In Chapter 3 the development and production of such a spreadsheet model limited to local aquatic assessments for new substances is presented. This model was developed so that the effects in variations of parameters and properties in the model could be assessed with greater ease.

CHAPTER 3

NEXCES SPREADSHEET MODEL

SUMMARY

The development of a spreadsheet-based model (NEXCES) for performing risk assessments for the aquatic compartment on the local scale is reported. There is a need for such a model due to the inability of the European Union System for the Evaluation of Substances (EUSES) to perform multiple treatments of the same assessment.

Construction of the spreadsheet is documented and addresses how some of the problems, as detailed in the EUSES Blacklist, were overcome. This included the latest SimpleTreat model and the ability to select the QSAR for predicting the partition coefficient Koc from Kow.

Validation of the spreadsheet is outlined. Investigations into the effect of variance in the measurement of the vapour pressure and Kow values are used to demonstrate the power of the NEXCES tool. Five thousand calculations were run for variations in each physico-chemical property producing distributions and ranges for the risk characterisation ratios.

3 NEXCES SPREADSHEET MODEL

3.1 A SPREADSHEET FOR PERFORMING RISK ASSESSMENTS

The EUSES program does not facilitate numerous assessments of the same substance with small variations in properties and parameters. The program is therefore unsuitable for sensitivity and uncertainty analyses.

Recently, the use of spreadsheet models of the TGD and EUSES risk assessment system has been cited, (Berding, 2000; Jager *et al.*, 2000; Schwartz *et al.*, 2000). The advantage of a spreadsheet model is the ability to run multiple treatments of the same assessment allowing sensitivity and uncertainty analyses to be performed. Such a spreadsheet for the risk assessment of new substances has never been completely documented.

In this chapter the construction of such a spreadsheet model, NEXCES (New EXcel Calculation for the Evaluation of Substances) is outlined. The scope of the risk assessment in the spreadsheet was limited to focus efforts and to ensure that this first module worked and was effective. Further modules could be added in the future if required. The assessment was limited to the calculation of the risk characterisation ratio (RCR) for water on the local scale. The model was also limited to new chemicals of low tonnage for which regional environmental concentrations would be negligible.

Figure 3.1 shows the schematic representation of the risk assessment process amended and modified from the work of Berding *et al.* (1999) and previously illustrated as Figure 2.4. It is used as the template for the model described in this chapter.

Through documenting the spreadsheet the intention was to provide the basis for a transparent and practical risk assessment tool. As the model is extended and new modules are added to the assessment, the tool can be developed in an "open source"[1] manner so that users understand the underlying calculations and interactions. This should ensure that the resulting tool meets the needs of those who actively use it.

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[1] Open source - A program for which the programming code and calculations are freely distributed.

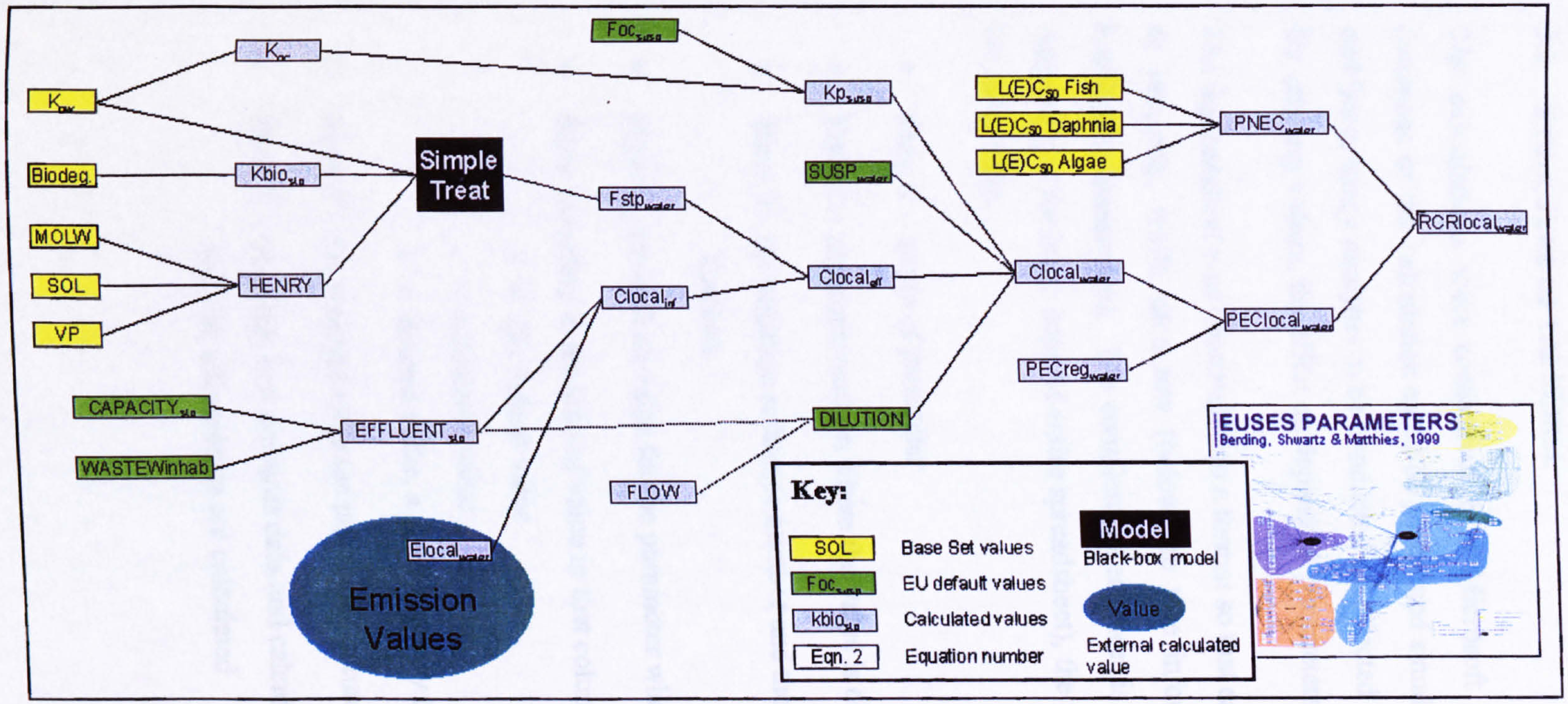

Figure 3.1 - Parameters involved in calculating the local PEC value for water (amended and adapted from Berding *et al.* (1999)

Where

Biodeg. **- Descriptive value for the biodegradation rate**
$CAPACITY_{stp}$ - Capacity of the STP
$Clocal_{eff}$ - Concentration of chemical in STP effluent
$Clocal_{inf}$ - Concentration in untreated wastewater
$Clocal_{water}$ - Local concentration in surface water
DILUTION **- Dilution factor (from river flow)**
$EFFLUENT_{stp}$ - Effluent discharge rate of STP
$Elocal_{water}$ - Local emission rate to water during an episode
Foc_{susp} - Fraction of organic carbon in suspended matter
FLOW **- Flow rate of river**
$Fstp_{water}$ - Fraction of emission directed to water by STP
HENRY **- Henry's Law constant**
$Kbio_{stp}$ - Rate constant for biodegradation

Koc **- Carbon normalised partition coefficient**
Kow **- Partition coefficient for octanol and water**
Kp_{susp} - Solid-water partition coefficient of suspended matter
$L(E)C_{50}$ *(species)* - Lethal or effect concentration to 50% of population
MOLW **- Molecular weight**
$PEClocal_{water}$ - Predicted environmental concentration
$PECregional_{water}$ - Regional concentration in surface water
$PNEC_{water}$ - Predicted No-Effect Concentration in water
$RCRlocal_{water}$ - Risk Characterisation Ratio for local water
SOL **- Solubility in water**
$SUSP_{water}$ - Concentration of suspended matter in river
VP **- Vapour pressure**
WASTEWinhab **- Sewage flow per inhabitant**

3.2 STRUCTURE OF THE MODEL

The calculations were constructed in a Microsoft Excel spreadsheet, so that many instances of the calculation could be performed simultaneously. This allows sensitivity and uncertainty analyses to be conducted on selected variables and default values used. By altering values, the effect on dependent parameters can be assessed.

The Spreadsheet was constructed in a format so that each column represents a parameter or property, while each row (below the title information rows 1-6) represents an individual assessment. The complete spreadsheet is detailed in Table 3.1a, b, c (See Appendix 9 for large copy of entire spreadsheet), the title and information rows contain the following:

- Row 1 – name of parameter
- Row 2 - any comments on where the value is obtained
- Row 3 - the equation reference number and the TGD equation number in brackets
- Row 4 - the default value for the parameter where applicable
- Row 5 - refers to the kind of value in that column:
  d = EU default value
  c = calculated value
  e = entered value, a value input by the user
- Row 6 – the standard units the parameter is entered in
- Row 7 – from this row onwards data and calculations are input and varied and the risk assessments are calculated

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	P	Q
1	**Name**	*MOLW*	*Kow*	*VP*	*SOL*		*Chemical Class*	*Biodeg*	*Prod Vol*	*Import*	*Export*	*L(E)C50 Fish*	*L(E)C50 Daphnia*	*L(E)C50 Algae*	*$PECregional_{water}$*	
2	**Comment**	*Base set*	*Base set*	*Base set*	*Base set*		From pick list AX4:AX22	From pick list BB4:BB8	*Base set*	*Base set*	*Base set*	*Base set*	*Base set*	*Base set*	Assumed to be negligible	
3	**Eqn. No.**	~	~	~	~		~	~	~	~	~	~	~	~	~	
4	**Value**															
5	**d/c/e**	e	e	e	e		e	e	e	e	e	e	e	e	e (c)	
6	**Units**	g/mol	~	Pa	mg/l		~	~	Tonnes/Yr	Tonnes/Yr	Tonnes/Yr	mg/l	mg/l	mg/l	mg/l	
7	**Calc.**	197.3	10000	0.043	7.5		Predom. Hydro.	No Biodeg.	10	0	0	0.6	2.3	0.86	0	

Table 3.1 (a) - Complete spreadsheet for risk assessment of water compartment at local scale

	A	R	S	T	U	V	W	X	Y	Z	AA	AB	AC
1	**Name**	$Capacity_{stp}$	$Waste_{inhab}$	$Effluent_{stp}$		$Elocal_{water}$	$Kbio_{stp}$	*Log Koc*	*Koc*	*HENRY*	$Fstp_{water}$	$Clocal_{inf}$	
2	**Comment**	Default	Default	= $Capacity_{stp}$ * $WASTE_{inhab}$		= Manually entered	Rate from descriptive value	Log *Koc* = x log *Kow* + y (from QSAR and chemical class)		= *MW* * *VP* / *SOL*	= Value from ST3 model	= $Elocal_{water}$ * 10000000 / $Effluent_{stp}$	
3	**Eqn. No.**	~	~	1 (19)		(2)	2, DEG1	4, QSAR1	5	6 (7)	ST3	7 (17)	
4	**Value**	10000	200			0.05							
5	**d/c/e**	d	d	c		e (c)	c	c	c	c	c	c	
6	**Units**	eq	l/d/eq	l/d		kg/d	h^{-1}	~	l/kg	$Pa.m^3/mol$	~	mg/l	
7	**Calc.**	10000	200	=R7*S7		0.05	=VLOOKUP (H7, $BB$4:$BC $8, 2)	=(VLOOKUP (G7, $AX$4:$AZ$22 ,2) * LOG10 (C7)) + VLOOKUP (G7, $AX$4:$AZ$22 ,3)	= 10^(X7)	= D7 * B7 / E7	From ST3 debugged using macro	=V7 * (10 ^ 6) / T7	

Table 3.1 (b) - Complete spreadsheet for risk assessment of water compartment at local scale (continued)

	A	AD	AE	AF	AG	AH	AI	AJ	AK	AL	AM	AN	AO	AP
1	**Name**	$SUSP_{water}$	*DILUTION*	Foc_{susp}		Kp_{susp}	$Clocal_{eff}$	$Clocal_{water}$ *(prov)*	$Clocal_{water}$	$PEClocal_{water}$	Min *L(E)C50*	*AF*	$PNEC_{water}$	RCR_{water}
2	**Comment**	Default	Default	Default		= Foc_{susp} * *Koc*	=$Clocal_{inf}$ * $Fstp_{water}$	= $Clocal_{eff}$ / ((1 + (Kp_{susp} * $SUSP_{water}$ * 10E-6))* *DILUTION*)	Check if value > water solubility	=$Clocal_{water}$ + $PECregional_{water}$	= min[*L(E)C50* (fish, *daphnia*, algae)]	= 1000 (at *base set*)	= min. *L(E)C50* / *AF*	= $PEClocal_{water}$ / $PNEC_{water}$
3	**Eqn. No.**	~	~	~		9 (9)	10 (18)	11 (30)	12	13 (33)	14	~	15	16
4	**Value**	15	10	0.1								1000		
5	**d/c/e**	d	d	d		c	c	c	c	c	c	c	c	c
6	**Units**	mg/l	~	kg/kg		l/kg	mg/l	mg/l	mg/l	mg/l	mg/l	~	mg/l	~
7	**Calc.**	15	10	0.1		=AF7 * Y7	=AB7 * (AA7 / 100)	= AI7/((1+(AH7 * AD7 * (10 ^ -6))) * AE7)	= IF (AJ7>E7, E7, AJ7)	= AK7 + P7	= MIN(L7:N7)	1000	= AM7 / AN7	= AL7 / AO7

Table 3.1 (c) - Complete spreadsheet for risk assessment of water compartment at local scale (continued)

For ease of explanation and for validation purposes a set of real *base set* values was used in Row 7, these values are given in Table 3.2. The example substance used is classified as "Commercially Confidential" as described in the NONS 1993 Regulations, for this reason the identity of the substance has not been given, but this does not affect the calculations in any way. Where applicable the calculations used in the spreadsheet are also detailed in Row 7. The formulae given are those found in Microsoft Excel 97, although similar functions are available in other versions and software packages.

Parameter	**Units**	**Value**
MOLW	g/mol	197.3
Kow	~	10000
VP	Pa	0.043
SOL	mg/l	7.5
Chemical Class	~	Predom. Hydro.
Biodeg	~	No Biodeg.
Prod Vol	Tonnes/Yr	10
Import	Tonnes/Yr	0
Export	Tonnes/Yr	0
$L(E)C_{50}$ Fish	mg/l	0.6
$L(E)C_{50}$ Daphnia	mg/l	2.3
$L(E)C_{50}$ Algae	mg/l	0.86
$PECregional_{water}$	mg/l	0
$Elocal_{water}$	kg/d	0.05

Table 3.2– *Base set* data for example substance

3.3 CALCULATION OF PEC

3.3.1 *Base Set* Data

The following physical and chemical data are supplied as part of the *base set* of data required in a notification and are used in performing risk assessments:

MOLW	Molecular weight (Column B), this is the gram weight of one mole of the substance
Kow	Partition coefficient for octanol and water (Column C), this gives a measure of how the substance will partition between aqueous and organic phases
VP	Vapour pressure (Column D), this value indicates to what extent the chemical will volatilise and become gaseous
SOL	Solubility in water (Column E), this value is a measure of how soluble the substance is in water

Columns G-N (Table 3.1a) detail the remaining *base set* data entered into the spreadsheet.

The Chemical Class (Column G) was used to indicate which QSAR the model should use to estimate the *Koc* value from *Kow*. The first column of Table 3.3 (cells AX4:AX22) was set as a "look-up"[2] table for the chemical class.

The biodegradeability value (*Biodeg.*, Column H) was used to derive a degradation rate constant ($Kbio_{stp}$). The first column of Table 3.4 (cells BB4:BB8) was set as a look-up table for the classifications that test results could meet.

The production, import and export volumes of the substance (Columns I, J, K) were not actually used in the calculations in this spreadsheet but appear in the model in case future modules such as exposure scenarios are added to the model.

Ecotoxicological data for the three acute aquatic tests, fish, *Daphnia* and algae (Columns L, M, N) were used in the effect assessment in the calculations.

---

[2] Look-up table – a device used in computing to constrain the possible values for a parameter, a table of acceptable values is declared and entry values are selected from this table to reduce the risk of syntax and input errors

	AX	AY	AZ
3	**Chemical Class**	x	y
4	Acetanilides	0.4	1.12
5	Acetanilides, carbamates, esters, phenylureas, phosphates, triazines, triazoles, uracils	0.47	1.09
6	Alcohols	0.39	0.5
7	Alcohols, organic acids	0.47	0.5
8	Amides	0.33	1.25
9	Anilines	0.62	0.85
10	Carbamates	0.37	1.14
11	Dinitroanilines	0.38	1.92
12	Esters	0.49	1.05
13	Nitrobenzenes	0.77	0.55
14	Non-hydrophobics	0.52	1.02
15	Organic acids	0.6	0.32
16	Phenols, anilines, benzonitriles, nitrobenzenes	0.63	0.9
17	Phenols, benzonitriles	0.57	1.08
18	Phenylureas	0.49	1.05
19	Phosphates	0.49	1.17
20	Predominantly hydrophobics	0.81	0.1
21	Triazines	0.3	1.5
22	Triazoles	0.47	1.41

Table 3.3 - QSAR1 for predicting *LogKoc* from *LogKow* look-up table (AX4:AZ22)

	BB	BC
3	**Degradation Description**	**$Kbio_{stp}$ (h^{-1})**
4	Ready biodegradable (within 10 day window)	1.0
5	Ready biodegradable (failing 10 day window, but within 28 days)	0.3
6	Inherent biodegradable (fulfilling specified criteria)	0.1
7	Inherent biodegradable (failing specified criteria)	0.0
8	Not biodegradable	0.0

Table 3.4 - DEG1, descriptive biodegradation rates look-up table (BB4:BC8)

3.3.2 Derivation of Intermediate Values

A number of values need to be calculated for use later in the assessment, these are explained below

Regional PEC for Water

For new substances, marketed in low volumes, it is fair to assume that the regional concentration in water will be negligible. This is because there is unlikely to be an existing background concentration in the environment, and while marketed at low volume, this background or regional concentration is unlikely to accumulate in the short term.

By limiting the scope of the model to new, low volume substances the value for the regional environmental concentration in water ($PECregional_{water}$) was set at 0. If actual or calculated values were available they could be entered directly into the model here.

Effluent Discharge Rate of STP

The capacity of the sewage treatment plant (STP) was given the EU default value of 10,000 population equivalents (Column R) and the volume of waste per inhabitant was given the EU default value of 200 l/d/eq (Column S). From these two parameters the value of the effluent discharge rate ($EFFLUENT_{stp}$) was calculated (Column T) as shown in Equation 3.1.

$$EFFLUENT_{stp} = CAPACITY_{stp} \cdot WASTEWinhab$$

Spreadsheet formula = R7 * S7 **Equation 3.1**

$EFFLUENT_{stp}$	Effluent discharge rate of STP	(l/d)	
$CAPACITY_{stp}$	Capacity of the STP in population equivalents	(eq)	default = 10000
$WASTEWinhab$	Sewage flow per inhabitant	(l/d/eq)	default = 200

Emissions to Local Water

The concentration of the substance emitted to water in the local scale of the model, $Elocal_{water}$ (Column V) is usually calculated using the production and import/export volumes (given in Columns I, J, K). These values are used with the "A and B tables" in the TGD or, where available, actual or estimated emission values. The accuracy of this information, however is questioned in the EUSES Blacklist (Appendix 7; ECB, 1998).

Measured or estimated data are often used, leading assessments to become more site-specific rather than giving generic result. For this reason, and to simplify and retain flexibility in the model, this value (*$Elocal_{water}$*) was entered directly. The input value was set at 0.5 kg/d to represent 10 Tonnes of a substance on the EU market as detailed in the calculations below, but could be calculated using the TGD method, or measured or modelled values could be entered directly.

$$Elocal_{water} = Fmainsource \frac{1000}{Temission} \cdot RELEASE$$

Equation 3.2

$Elocal_{water}$	Local emission rate to water during an episode	(kg/d)
Fmainsource	Fraction of release at local main source	
Temission	Number of emission days per year	(d/yr)
RELEASE	Volume released	(kg/yr)

For domestic substances the release volume can be assumed to be the whole tonnage because the entire volume of the substance will be washed down a drain or sink etc. at some point during the use phase. The number of emission days (*Temission*) will be 365, and the fraction to be counted as the main local source (*Fmainsource*) is given as 0.002 by the TGD (EC, 1996a).

$$\Rightarrow \quad Elocal_{water} = 0.002 \cdot \frac{1000}{365} \cdot 10$$

Equation 3.3

$$\Rightarrow \quad Elocal_{water} = 0.548$$

Equation 3.4

Rate of Biodegradation

To derive the biodegradation rate (Column W) for use in the fate and behavioural calculations the descriptive value (Column H) was used to look-up the corresponding rate constant (*$Kbio_{stp}$*) from Table 3.4. Values were originally proposed by Struijs and Berg (1992), the values in the table are those as agreed and published in the TGD.

The calculation in the spreadsheet was entered as follows:

= VLOOKUP (H7, $BB$4:$BC$8, 2) **Equation 3.5**

This function looks-up *Biodeg.* (Column H) in the DEG1 table (BB4:BC8) and retrieves the value from the second column along, which is the $Kbio_{stp}$ value. The dollar signs "$" in the cell references ensured the same table was used in each row (individual assessment), all other cell references in the formulae remained relative (i.e. in the next row down the value was H8 not H7).

Carbon Normalised Partition Coefficient

Adsorption of the substance to solid surfaces can be a significant removal process, and reduce the concentration in solution. The carbon normalised partition coefficient (*Koc*) is used to calculate the solid-water partition coefficients for each compartment (soil, sediment, suspended matter). These values and/or the *Koc* value can be derived in a number of ways (most accurate to least accurate):

- Direct measurement of individual partition coefficients
- *Koc* measured by adsorption studies (OECD test guideline 106)
- *Koc* approximation, measured by HPLC-method
- *Koc* may be estimated from *Kow* (for non-ionic substances)

For some substances the measurement of *Koc* can be difficult experimentally. In the UK, a measured *Koc* by the HPLC-method is usually required as part of the notification for substances for which the QSAR calculations are not appropriate. Further data may then be requested subject to the results of the initial risk assessment.

The TGD outlines various QSARs by chemical class for estimating *LogKoc* (Column X) based on linear regression analysis with *LogKow* as the descriptor variable. The default QSAR used in EUSES and the TGD is for "predominantly hydrophobics", however as the initial investigations proved, the choice of QSAR can significantly affect the resulting $PEClocal_{water}$. It is preferable to select the most appropriate QSAR for each chemical because the default QSAR does not give a worse case scenario for the aquatic environment.

The available QSARs are outlined in Table 3.3 for the various chemical classes (Column G). The 'x' and 'y' values in Table 3.3 were used in Equation 3.6 to derive the *LogKoc* value.

$$LogKoc = x \cdot LogKow + y$$ **Equation 3.6**

LogKoc Carbon normalised partition coefficient in log units
LogKow n-octanol-water partition coefficient in log units

The calculation in the spreadsheet is as follows:

=(VLOOKUP (G7, $AX$4:$AZ$22, 2) (i)
* LOG10(C7)) (ii)
+VLOOKUP (G7, $AX$4:$AZ$22, 3) (iii) **Equation 3.7**

i. Finding 'x' – the Chemical Class (G7) is looked up in the QSAR table (AX4:AZ22) and the value from the second column along retrieved
ii. Multiply by *LogKow* – is calculated the Log of the *Kow* value (C7)
iii. Addition of 'y' - the Chemical Class is looked-up in the QSAR table and the value from the third column along retrieved

The *Koc* value (Column Y) is then calculated from the *LogKoc* value (Equation 3.8)

$$Koc = 10^{LogKoc}$$

Spreadsheet formula = 10 ^ (X7) **Equation 3.8**

Koc Carbon normalised partition coefficient *(l/kg)*
LogKoc Carbon normalised partition coefficient in log units

Henry's Law Constant

Volatilisation and the partitioning of a substance between the water and air phases can occur direct from surface water and in the aeration tank in the STP. The magnitude of the Henry's law constant (Column Z) gives an indication of which of the two phases a substance is likely to partition into at equilibrium. Substances with low values will tend to partition into the aqueous phase.

Where a measured value for Henry's law constant is not available it is estimated using Equation 3.9.

$$HENRY = \frac{VP \cdot MOLW}{SOL}$$

Spreadsheet formula = D7 * B7 / E7 **Equation 3.9**

HENRY	Henry's Law constant for the substance	(Pa m^3/mol)
VP	Vapour pressure of the substance	(Pa)
MOLW	Molecular weight of the substance	(g/mol)
SOL	Solubility of the substance in water	(mg/l)

3.3.3 Fate of Substance in STP

Fraction Emitted form STP

On the local scale the TGD makes the assumption that all wastewater will pass through a STP before being discharged to the environment. A 9-compartment box-model is outlined in the TGD (Struijs *et al.*, 1991) and implemented through the use of the SimpleTreat 3.0 model in EUSES. A set of look-up tables substitute for the full SimpleTreat model in the TGD, these tables being based on an older version of the model and provide approximate values (Appendix 10).

SimpleTreat 3.0 (Struijs, 1996) the debugged version is the latest version of the model and is different to the one used in EUSES. It was this latest and debugged version that was used in the spreadsheet model.

The values to calculate Henry's constant (*HENRY*), *Kow* and $Kbio_{stp}$ were entered into the SimpleTreat model (ST3) and the fractions of emissions directed to the three environmental compartments (air, water, sludge) were obtained as outputs. The ST3 model was implemented as a black-box model added to the spreadsheet model. The required inputs were entered and the value for the fractions of emissions to water ($Fstp_{water}$) was taken from ST3 and entered into the spreadsheet (Column AA). A macro was written to automate the process of using the ST3 model, this macro and the use of the SimpleTreat model is explained further in Section 3.5.

Concentration of Substance Entering STP

To find the concentration of the substance entering the STP (Column AB) Equation 3.10 was used.

$$Clocal_{inf} = \frac{Elocal_{water} \cdot 10^6}{EFFLUENT_{stp}}$$

Spreadsheet formula = V7 * (10 ^ 6) / T7 **Equation 3.10**

$Clocal_{inf}$	Concentration of substance in untreated wastewater	(mg/l)
$Elocal_{water}$	Local emission rate to water during an episode	(kg/d)
$EFFLUENT_{stp}$	Effluent discharge rate of the STP	(l/d)

Default Values in Model

The following parameters are all default values defined in the TGD:

- Concentration of suspended matter in river - $SUSP_{water}$ (Column AD)
  default = 15 mg/l
- Dilution factor, from river flow - *DILUTION* (Column AE)
  default = 10
- Solid-water partition coefficient of suspended matter - Foc_{susp} (Column AF)
  default = 0.1 kg/kg

The value for the dilution factor from mixing in the receiving water at point of discharge (*DILUTION*) can be calculated if data are available using Equation 3.11, otherwise the default value of 10 is used.

$$DILUTION = \frac{EFFLUENT_{stp} + FLOW}{EFFLUENT_{stp}}$$ **Equation 3.11**

DILUTION	Dilution factor calculated from river flow	-
$EFFLUENT_{stp}$	Effluent discharge rate of the STP	(l/d)
FLOW	Flow rate of river	(l/d)

Partition Coefficients

The solid-water partitioning coefficients are used to calculate the extent to which the substance is absorbed into other compartments (soil, sediment and suspended matter). The value for suspended matter (Column AH) was calculated using Equation 3.12.

$$Kp_{susp} = Foc_{susp} \cdot Koc$$

Spreadsheet formula = AF7 * Y7 **Equation 3.12**

Kp_{susp}	Solid-water partition coefficient for suspended matter	(l/kg)	
Foc_{susp}	Weight fraction of organic carbon in suspended matter	(kg/kg)	default = 0.1
Koc	Carbon normalised partition coefficient	(l/kg)	

Concentration of Substance Emitted from STP

The SimpleTreat model was used to assess the fate and behaviour of substances within the STP in the assessments. The concentration emitted to water from the STP (*Column AI*) was calculated using the fraction emitted to water ($Fstp_{water}$) obtained from the ST3 model using Equation 3.13.

$$Clocal_{eff} = Clocal_{\inf} \cdot Fstp_{water}$$

Spreadsheet formula = AB7 * (AA7 / 100) **Equation 3.13**

$Clocal_{eff}$	Concentration of chemical in STP effluent	(mg/l)
$Clocal_{inf}$	Concentration in untreated wastewater	(mg/l)
$Fstp_{water}$	Fraction of emission directed to water by STP	-

The value for the fraction emitted is divided by a factor of 100 in the spreadsheet formula due to the ST3 model returning the value as a percentage, thus the output value from ST3 is converted to a decimal value.

3.3.4 Concentration of Substance in the Environment

Concentration of Substance in Local Water

In the assessment scenario, the effluent from the STP is discharged direct to surface waters, two assumptions are then made:

- Complete instantaneous mixing occurs at the point of discharge
- Immediate exposure takes place (volatilisation, degradation and sedimentation are ignored)

The first assumption simplifies the assessment, although instantaneous mixing is unlikely the conservative dilution factor of 10 is said to account for some of the uncertainty due to this assumption. The second assumption is a worst case scenario and although degradation and other transformation and transport processes are likely to take place calculations are made on the basis of the whole concentration remaining in the water.

The concentration of the substance in local water (Column AJ) was calculated using Equation 3.14.

$$Clocal_{water} = \frac{Clocal_{eff}}{\left[1 + \left(Kp_{susp} \times SUSP_{water} \times 10^{-6}\right)\right] DILUTION}$$

Spreadsheet formula = AI7 / ((1 + (AH7 * AD7 * (10 ^ - 6))) * AE7)

Equation 3.14

$Clocal_{water}$	Local concentration in surface water during an emission episode	(mg/l)	
$Clocal_{eff}$	Concentration of chemical in the STP effluent	(mg/l)	
Kp_{susp}	Solid-water partition coefficient for suspended matter	(l/kg)	
$SUSP_{water}$	Concentration of suspended matter in river	(mg/l)	default = 15
$DILUTION$	Dilution factor at point of discharge	-	default = 10

It is noted in the TGD and EUSES Blacklist (Appendix 7) that values for the concentration of the substance in water in excess of water solubility (*SOL*) can arise. Such results should be interpreted on a case-by-case basis, however in this model, if the concentration in local water exceeded water solubility, the concentration was set to the solubility in water as suggested in the EUSES Blacklist. A provisional value for

$Clocal_{water}$ was calculated (Column AJ) as detailed in Equation 3.14, then this figure was checked against the value for solubility in water (E7). In the spreadsheet an "IF" statement was used to check and produce the final value for $Clocal_{water}$ (Column AK):

=IF (AJ7 > E7,	(i)	
E7,	(ii)	
AJ7)	(iii)	**Equation 3.15**

i. "IF" argument – the concentration in STP effluent (AJ7) is checked to see if it is greater than the solubility in water (E7)

ii. Answer – if argument is true ($Clocal_{eff}$ is greater than *SOL*) then the answer is set to the solubility in water (E7)

iii. Alternative answer – if argument is false (i.e. the concentration in water is less than water solubility) the concentration in water is as calculated (AJ7)

Local PEC for Water

The PEC value for local water (Column AL) was derived from the sum of the concentration in local water ($Clocal_{water}$) and PEC for regional water ($PECregional_{water}$), which was assumed to be 0 for new chemicals at low volumes (Equation 3.16).

$$PEClocal_{water} = Clocal_{water} + PECregional_{water}$$

Spreadsheet formula = AK7 + P7 **Equation 3.16**

$PEClocal_{water}$	Predicted environmental concentration during an episode	(mg/l)
$Clocal_{water}$	Local concentration in surface water during an emission episode	(mg/l)
$PECregional_{water}$	Regional or background concentration in surface water	(mg/l)

3.4 CALCULATION OF PNEC AND RCR

3.4.1 Calculation of PNEC Value

The lowest $L(E)C_{50}$ value (Column AM) was calculated from the three acute toxicity values supplied (fish, *Daphnia* and algae), this was calculated as detailed in Equation 3.17.

$$Min\ L(E)C_{50} = \left\{ \begin{array}{c} L(E)C_{50}\ (fish) \\ L(E)C_{50}\ (daphnia) \\ L(E)C_{50}\ (algae) \end{array} \right\}_{MIN}$$

Spreadsheet formula = MIN (L7:N7) **Equation 3.17**

$Min\ L(E)C_{50}$	Lowest lethal or effect concentration for 50% of the population	(mg/l)
$L(E)C_{50}\ (fish)$	Lethal or effect concentration for 50% of the population for fish	(mg/l)
$L(E)C_{50}\ (daphnia)$	Lethal or effect concentration for 50% of the population for *daphnia*	(mg/l)
$L(E)C_{50}\ (algae)$	Lethal or effect concentration for 50% of the population for algae	(mg/l)

The EU default assessment factor (AF) for substances with acute toxicity data for three trophic levels is 1000 (Column AN). The PNEC for water (Column AO) was calculated by applying the default *AF* to the lowest ecotoxicological test value, (Equation 3.18).

$$PNEC_{water} = Min\ L(E)C_{50} \div AF$$

Spreadsheet formula = AM7 / AN7 **Equation 3.18**

$PNEC_{water}$	Predicted No-Effect Concentration of the substance in water	(mg/l)	
$Min\ L(E)C_{50}$	Lowest lethal or effect concentration for 50% of the population	(mg/l)	
AF	Assessment Factor or uncertainty factor	-	default = 1000

3.4.2 Calculation of RCR Value

Finally in the risk characterisation stage the RCR was calculated for local water (Column AP) by dividing the $PEClocal_{water}$ by the $PNEC_{water}$ (Equation 3.19).

$$RCRlocal_{water} = \frac{PEClocal_{water}}{PNEC_{water}}$$

Spreadsheet formula = AL7 / AO7 **Equation 3.19**

$RCRlocal_{water}$	Risk Characterisation Ratio for local water	-
$PEClocal_{water}$	Predicted Concentration of the substance in local water	(mg/l)
$PNEC_{water}$	Predicted No-Effect Concentration of the substance in water	(mg/l)

Different conclusions are drawn regarding the RCR value as set down in the Directive on Risk Assessment for New Notified Substances (93/67/EEC). When RCR ≤ 1, the following conclusion is drawn in accordance with Article 3.4(i) of the Directive:

- The substance is of no immediate concern and need not be considered again until further information is made available when the volume on the market reaches the next tonnage threshold

When RCR > 1, then further information is usually required to refine the risk assessment and one of the following conclusions as set out in Article 3. 4(ii), 3.4(iii) or 3.4(iv) will be reached, depending on the magnitude of the RCR and the extent to which the exposure assessment has been refined already:

- The substance is of concern and the competent authorities shall decide what further information is required for revision of the assessment when the volume on the market reaches the next tonnage threshold

- The substance is of concern and further information shall be requested immediately

- The substance is of concern and the competent authority shall immediately make recommendations for risk reduction

Figure 3.2 shows the schematic representation of the risk assessment process, indicating the equations used to calculate the various values as detailed in this chapter.

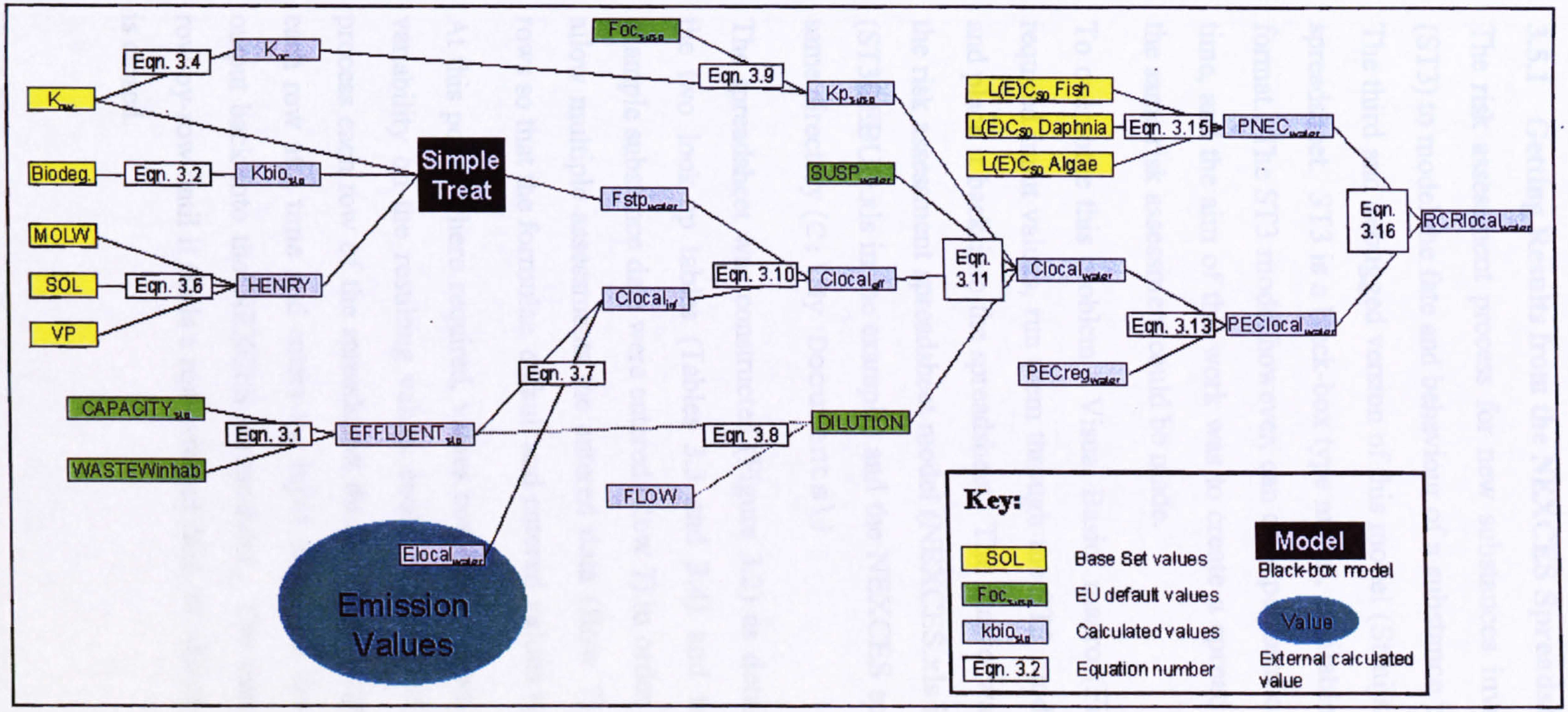

Figure 3.2 - Parameters involved in calculating the local PEC value for water indicating the equations used to obtain values

Where

Biodeg. - Descriptive value for the biodegradation rate
$CAPACITY_{stp}$ - Capacity of the STP
$Clocal_{eff}$ - Concentration of chemical in STP effluent
$Clocal_{inf}$ - Concentration in untreated wastewater
$Clocal_{water}$ - Local concentration in surface water
DILUTION - Dilution factor (from river flow)
$EFFLUENT_{stp}$ - Effluent discharge rate of STP
$Elocal_{water}$ - Local emission rate to water during an episode
Foc_{susp} - Fraction of organic carbon in suspended matter
FLOW - Flow rate of river
$Fstp_{water}$ - Fraction of emission directed to water by STP
HENRY - Henry's Law constant
$Kbio_{stp}$ - Rate constant for biodegradation

Koc - Carbon normalised partition coefficient
Kow - Partition coefficient for octanol and water
Kp_{susp} - Solid-water partition coefficient of suspended matter
$L(E)C_{50}$ *(species)* - Lethal or effect concentration to 50% of population
MOLW - Molecular weight
$PEClocal_{water}$ - Predicted environmental concentration
$PECregional_{water}$ - Regional concentration in surface water
$PNEC_{water}$ - Predicted No-Effect Concentration in water
$RCRlocal_{water}$ - Risk Characterisation Ratio for local water
SOL - Solubility in water
$SUSP_{water}$ - Concentration of suspended matter in river
VP - Vapour pressure
WASTEWinhab - Sewage flow per inhabitant

3.5 PRODUCING RESULTS AND VALIDATION

3.5.1 Getting Results from the NEXCES Spreadsheet

The risk assessment process for new substances involves the use of SimpleTreat 3.0 (ST3) to model the fate and behaviour of a substance in a sewage treatment plant (STP). The third and debugged version of this model (Struijs, 1996) was used in the NEXCES spreadsheet. ST3 is a black-box type model, available in a Microsoft Excel spreadsheet format. The ST3 model however, can only perform calculations on one set of data at a time, and the aim of this work was to create a spreadsheet where multiple instances of the same risk assessment could be made.

To overcome this problem a Visual Basic[3] macro (Figure 3.3) was written to take the required input values, run them through the ST3 model and then take the output value and place it back into the spreadsheet. The macro was written as a module attached to the risk assessment spreadsheet model (NEXCES.xls in this example). The ST3 model (ST3DEBUG.xls in the example) and the NEXCES spreadsheet were both saved in the same directory (`C:\My Documents\`)

The spreadsheet was constructed (Figure 3.2) as detailed (Table 3.1 a, b, c) including the two look-up tables (Tables 3.3 and 3.4) and the macro (Figure 3.3), then the example substance data were entered (Row 7) in order to perform a risk assessment. To allow multiple assessments the entered data (Row 7) were copied down a number of rows so that the formulae, default and entered values were all reproduced in each row.

At this point, where required, values could have been varied so that the effect of such variability on the resulting values could be assessed. Finally the macro was run to process each row of the spreadsheet through the SimpleTreat model. The macro takes each row at a time and enters the input data into the ST3 model and then copies the output back into the NEXCES spreadsheet. The macro continues to process the data row-by-row until it finds a row without data, at which point it stops and the ST3 model is closed.

---

[3] Visual Basic macro – a macro is a series of commands and instructions written in the Visual Basic programming language that are grouped together as a single command to accomplish the task automatically, instead of manually performing a series of time-consuming, repetitive actions within a computer software package

```
Sub SimpleTreat()
 ' SimpleTreat Macro  -  Macro recorded 09/08/00 by Research Engineer
 'Declare offset variable “var2” and set it equal to 0
      Dim var2 As Integer
      var2 = 0
 'Open SimpleTreat3 model workbook
      ChDir "C:\My Documents\"
      Workbooks.Open FileName:="C:\My Documents\ST3DEBUG.xls"
 'Start a Do routine
           Do
 'Select all phys chem properties (MOLW, Kow, VP, SOL) from NEXCES
 spreadsheet
                Windows("NEXCES.xls").Activate
                Range("B7:E7").Select
 'Offset (rows, cols) by “var2” (will be zero to start) then copy
                ActiveCell.Offset(var2, 0).Select
                Selection.Copy
 'Change to ST3 spreadsheet and paste values in transposing row to column
                Windows("ST3DEBUG.xls").Activate
                Sheets("input").Select
                Range("B6").Select
                Selection.PasteSpecial Paste:=xlValues, Operation:= _
                xlNone, SkipBlanks:=False, Transpose:=True
 'Select biodegradation rate (Kbio.stp) from NEXCES spreadsheet
                Windows("NEXCES.xls").Activate
                Range("W7").Select
 'Offset (rows, cols) by “var2” (will be zero to start) then copy
                ActiveCell.Offset(var2, 0).Select
                Selection.Copy
 'Change to ST3 spreadsheet and paste values in
                Windows("ST3DEBUG.xls").Activate
                Sheets("input").Select
                Range("B48").Select
                Selection.PasteSpecial Paste:=xlValues, Operation:= _
                xlNone, SkipBlanks:=False, Transpose:=False
 'Get output value from ST3
                Sheets("output").Select
                Range("C27").Select
                Application.CutCopyMode = False
                Selection.Copy
 'Change to NEXCES spreadsheet
                Windows("NEXCES.xls").Activate
                Range("AA7").Select
 'Offset by “var2” (will be zero to start) then paste
                ActiveCell.Offset(var2, 0).Select
                Selection.PasteSpecial Paste:=xlValues, Operation:= _
                xlNone, SkipBlanks:=False, Transpose:=False
 'Add 1 to offset variable “var2” so next row is used in all operations
                var2 = var2 + 1
 'Check for data in next row
                Range("B7").Select
                ActiveCell.Offset(var2, 0).Select
 'If empty close ST3 and end
                     If ActiveCell.Value = "" Then winClose
 'If values present start Do routine again
          Loop
End Sub

'Routine to close ST3 window
Sub winClose()
    Windows("ST3DEBUG.xls").Close (0)
    If ActiveCell.Value = "" Then End
End Sub
```

Figure 3.3 - Module 1, macro to run the SimpleTreat 3.0 model from NEXCES spreadsheet

3.5.2 Validation of the NEXCES Spreadsheet

For validation purposes the actual data for a test substance were used (Table 3.2) and the resulting RCR value was found to be 1.915615. Assessments performed using EUSES and the TGD process using the same data gave slightly different values (Table 3.5). On close inspection it was found that these discrepancies were due to the different versions of the SimpleTreat model used by EUSES and the TGD. The following investigations were carried out to demonstrate how the model worked and an example of the power of this spreadsheet model.

Model	SimpleTreat Version	$Fstp_{water}$	$PEClocal_{water}$	$RCRlocal_{water}$
TGD	1	56	0.0014	2.79
TGD (revised*)	3	77	0.0019	3.84
EUSES	3	77.3	0.00193	3.85
NEXCES	3 debugged	46.13	0.001149	1.92

Table 3.5 - Comparison of the values calculated using different versions of risk assessment models

*** A set of revised tables for the SimpleTreat model are available for the TGD**

In the example the inherent variability in measuring the n-octanol/water partition coefficient (*Kow*) and the vapour pressure (*VP*) of the test substance were investigated. Similar to the initial investigations using EUSES, the test guidelines as produced by the OECD (1993b) for the two methods were used as detailed in Table 3.6. It was assumed that variability would be normally distributed around the mean (*base set*) value and the error given in the test guidelines would be equal to 3 standard deviations (SD) about this mean. Mathematically, three standard deviations encompass 99.7% of normally distributed data (Figure 3.4).

Property	Test Guideline	Error	Mean	SD
Vapour Pressure	104	Average ± 25%	0.043 Pa	$25\% \div 3 \times 0.043$ $= 0.00358$ Pa
Partition Coefficient (*Kow*)	107	± 0.3 log units	4 log units	$0.3 \div 3$ $= 0.1$ log unit

Table 3.6 - Physical properties and respective error, mean and standard deviations (SD)

The problems with the accuracy of statistical procedures within the Microsoft Excel 97 software are well documented (McCullough & Wilson, 1999). Of particular concern was the Random Number Generator (RNG) algorithm, which performed badly in the test run by McCullough & Wilson (1999). Unfortunately superior software packages for performing such operations were not available. Therefore, to find the optimal number of runs for the investigations an analysis of the normality of distributions of numbers generated by Microsoft Excel 97 was made, (see Appendix 11 for full details).

It was found that 5000 data points from separate runs of the calculation were an optimal sample size based on a good approximation to a normal distribution and the time taken to process a sample of this size. Using the RNG in Microsoft Excel 5000 values were produced normally distributed for each value with the relevant mean and SD.

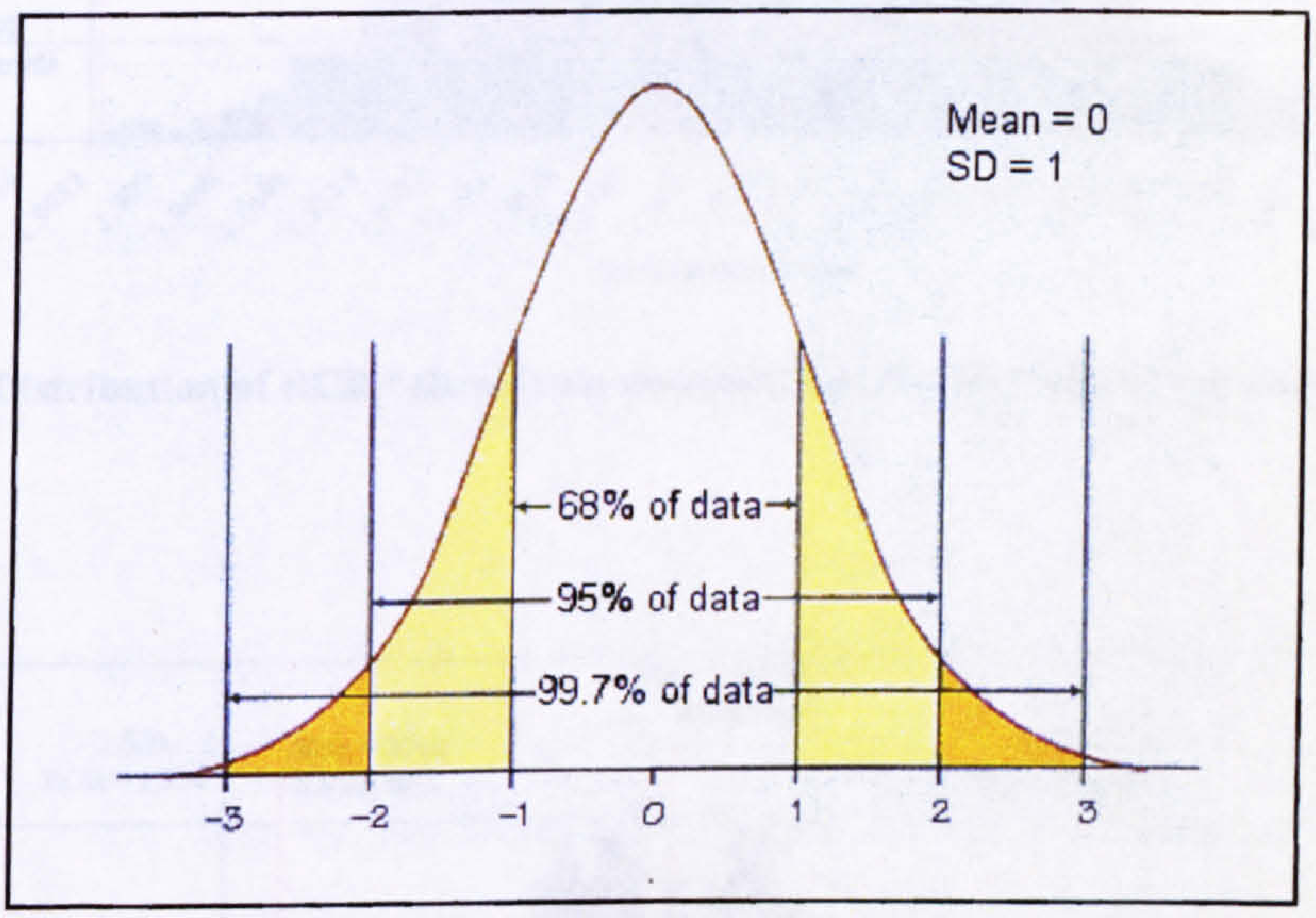

Figure 3.4 – Normal distribution indicating the percentage of sample falling within 1, 2 & 3 standard deviations of the mean, (Moore & McCabe, 1999)

The investigation was run twice, once for *Kow* and once for *VP*. 5000 rows were created in the NEXCES spreadsheet and then the randomly generated property values were placed in the relevant column (the *Kow* values were converted to decimal values from log units).

Once complete the RCR values (Column AP) were examined. Two graphs were produced of the resulting RCR values from normally distributed *VP* values and from normally distributed log *Kow* values (Figures 3.4 & 3.5 respectively).

The accuracy in measurement for the *Kow* value can cause a far greater effect on the resulting RCR than vapour pressure. The resulting range for the RCR within ±2 SD (this encompasses 95% of the data) of the mean, is 1.5 - 2.3 for variation in *Kow* and only 1.91 – 1.92 for variation in *VP*.

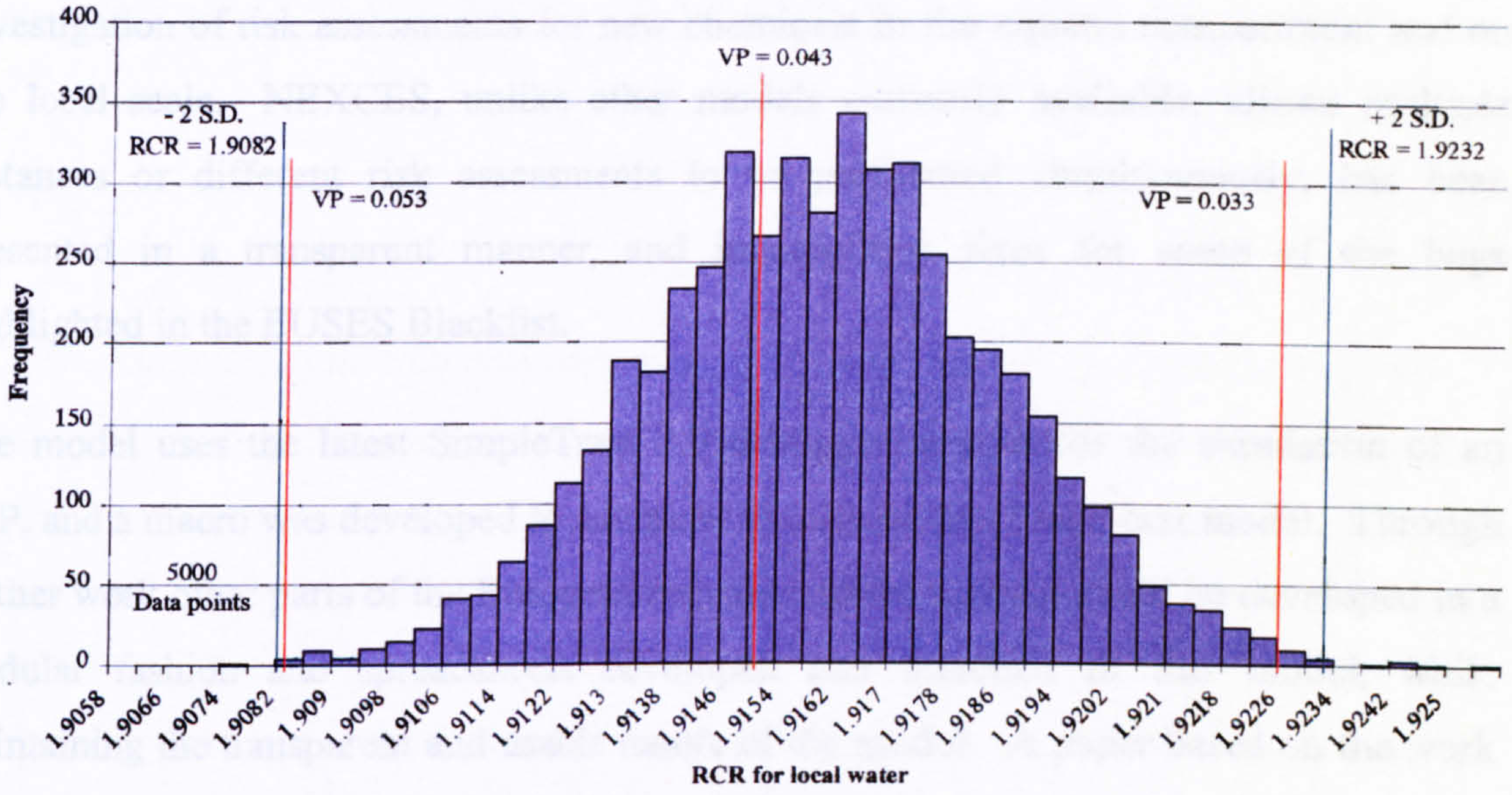

Figure 3.5 - Distribution of RCR values from normally distributed vapour pressure (*VP*) values

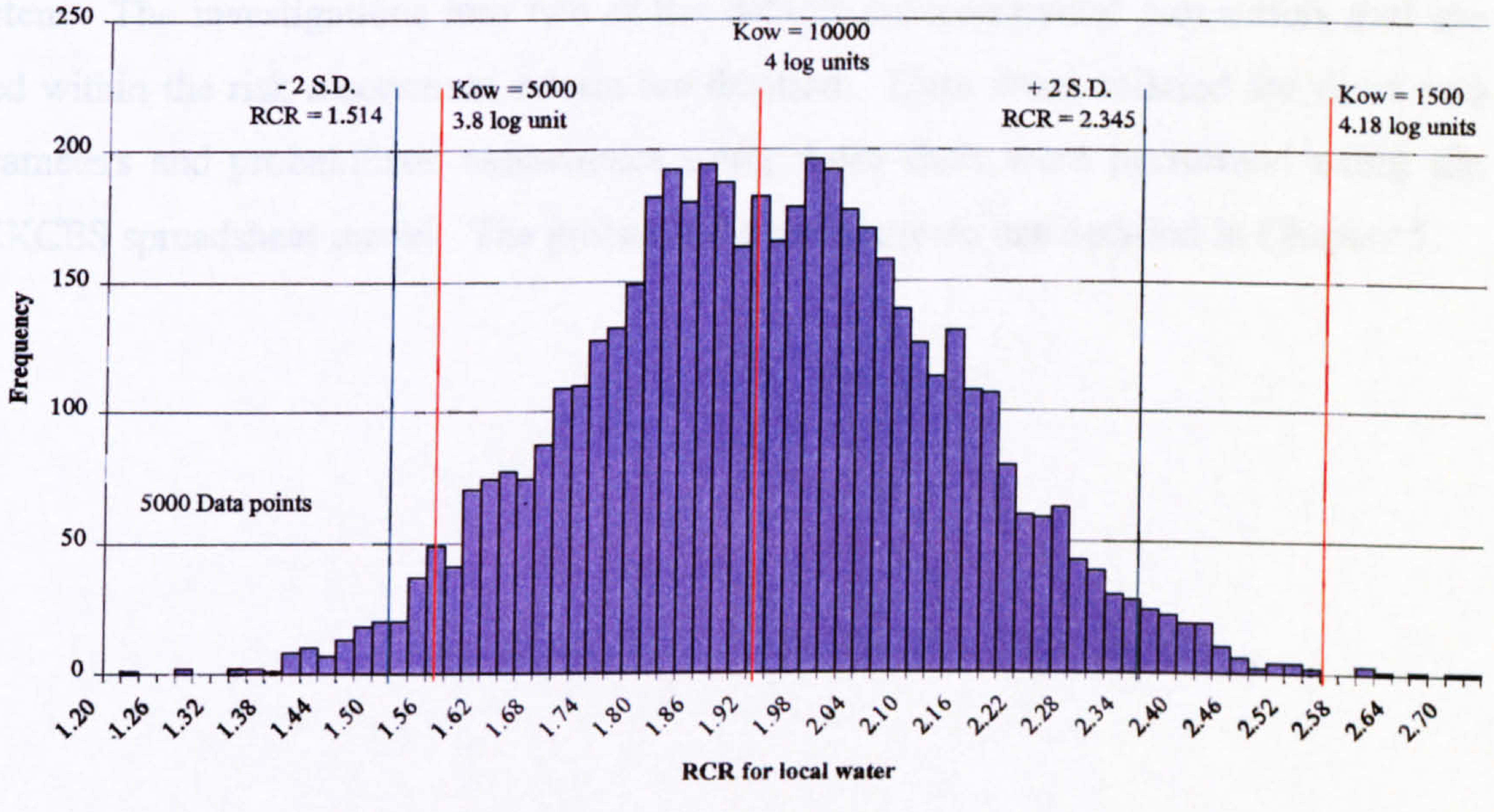

Figure 3.6 - Distribution of RCR values from normally distributed log *Kow* values

3.6 SUMMARY

The NEXCES spreadsheet model provides a usable and powerful tool for the investigation of risk assessments for new chemicals in the aquatic compartment and on the local scale. NEXCES, unlike other models currently available, allows multiple instances or different risk assessments to be performed simultaneously, has been presented in a transparent manner, and incorporates fixes for some of the bugs highlighted in the EUSES Blacklist.

The model uses the latest SimpleTreat 3.0 debugged model for the simulation of an STP, and a macro was developed to automate the use of this black-box model. Through further work other parts of the European risk assessment system could be developed in a modular fashion and spreadsheets developed and attached to this model, while maintaining the transparent and usable nature of the model. A paper based on the work in this chapter has been accepted for publication by the journal 'Environmental Toxicology and Chemistry' and is likely to be published early 2002 (Appendix 12).

The following chapter outlines initial sensitivity analyses on the EU risk assessment system. The investigations into two of the default environmental parameters that are used within the risk assessment system are detailed. Data were collated for these two parameters and probabilistic assessments using these data were performed using the NEXCES spreadsheet model. The probabilistic assessments are detailed in Chapter 5.

CHAPTER 4

STATISTICAL ANALYSIS OF ENVIRONMENTAL PARAMETERS

SUMMARY

Two parameters, dilution and capacity, used in the modelling of sewage treatment plants (STP) in the risk assessment system are examined. The value for the dilution factor available at the point of discharge from a STP can be a critical value in the risk assessment. Data were collated from the 8 administrative regions in England and Wales. These were statistically analysed to determine how the data for England and Wales compared with the generic default values used in the European risk assessment system.

By capacity, 30% of STPs were larger than the EU default value of 10,000 population equivalents and contribute to more than 90% of the total effluent discharged by STPs in England and Wales. The dilution data produced a median value of 5.2, which is less than the EU default value of 10, which means generic risk assessments may under predict risk. Geographical information system techniques were used to produce geographical plots to highlight areas of particular concern.

4 STATISTICAL ANALYSES OF ENVIRONMENTAL PARAMETERS

4.1 INTRODUCTION

The risk assessments performed for new substances are based upon physical, chemical, ecotoxicological and fate and behaviour data supplied for each notified substance. The risk assessments are then performed using EUSES or the system detailed in the TGD. Early sensitivity analyses on the PEC calculation within the risk assessment system were carried out by Slob & Nijs, (1989).

It has been noted that data relating to non-negative physical entities (e.g. size measurements, chemical measurements etc.) usually exhibit good fit with lognormal distributions (Slob, 1994). A measure for the uncertainty of a value with a lognormal distribution was described as,

> "K is the factor for which the probability that the value of a true parameter differs more than a factor of K from the nominal value is smaller than α"
>
> (Slob & Nijs 1989 cited in Greef & Nijs, 1990)

This means for a 95% CI ($\alpha = 0.05$), 95% of the data will fall within a factor K of the median value. Using this measure, some of the values used to calculate the PEC in the risk assessment system were presented (Table 4.1) however it was not clearly demonstrated how these figures were derived. Slob & Nijs (1989) quoted the total uncertainty factor (K) for the PEC calculation as 139. It is clear however, that with these figures the greatest contribution to this uncertainty is from the value for the effluent discharge and stream flow.

Parameter	Uncertainty Factor, K
No. of emission points	1.5
No. of emission days	1.5
Percentage loss to waste water	2
Retention factor	2
effluent discharge + stream flow	122

Table 4.1 - Uncertainty factors for values used to calculate PEC (Slob & Nijs, 1989)

When the equation for calculating the concentration of a substance in local water is examined it can be seen that the dilution factor is one of the main determining values.

$$Clocal_{water} = \frac{Clocal_{eff}}{\left[1+\left(Kp_{susp} \times SUSP_{water} \times 10^{-6}\right)\right]DILUTION} \qquad \textbf{Equation 4.1}$$

$Clocal_{water}$	Local concentration in surface water during an emission episode	(mg/l)	
$Clocal_{eff}$	Concentration of chemical in the STP effluent	(mg/l)	
Kp_{susp}	Solid-water partition coefficient for suspended matter	(l/kg)	
$SUSP_{water}$	Concentration of suspended matter in river	(mg/l)	default = 15
$DILUTION$	Dilution factor at point of discharge	-	default = 10

Substituting the default values and Equation 3.9 for Kp_{susp}:

$$Clocal_{water} = \frac{Clocal_{eff}}{\left[1+\left(0.1 \times Koc \times 15 \times 10^{-6}\right)\right]DILUTION} \qquad \textbf{Equation 4.2}$$

$$\Rightarrow \quad Clocal_{water} = \frac{Clocal_{eff}}{\left[1+\left(Koc \times 1.5 \times 10^{-6}\right)\right]DILUTION} \qquad \textbf{Equation 4.3}$$

$$\Rightarrow \quad Clocal_{water} \approx \frac{Clocal_{eff}}{x \cdot DILUTION} \qquad \textbf{Equation 4.4}$$

Where *Koc* <700,000 the factor x will be approximately 1, whereas where *Koc* ≥700,000 the factor x will be greater than 1. Thus it can be seen that the PEC for local water which is dependent upon the concentration in local water ($Clocal_{water}$) is particularly sensitive to the value of the dilution factor. An analysis of the real distribution of values for the dilution factor was therefore felt to be of great importance in order to understand the uncertainties inherent in the generic risk assessment of new substances.

During the data collation activities, it became apparent that information concerning the capacity of STPs was also readily available. For this reason the capacity of STPs was also investigated.

Data were collated on the two chosen environmental parameters and each parameter statistically investigated separately.

4.2 THE DATA

Data were collated from each of the Environment Agency's eight administrative regions and the number of records available are detailed in Table 4.2. Not all of the required data was available for all works in all Regions. Of the 3588 municipal STPs in England and Wales, usable data were collated for about 25% (880 STPs). Three regions did not supply suitable data within the timeframe to be included in these investigations.

Region	No. of STPs	Fraction of total	Usable data records	Fraction of Regional total
Anglian	690	23 %	310	45 %
Midlands	395	11 %	107	27 %
North East	447	10 %	0	0 %
North West	354	12 %	196	55 %
Southern	281	6 %	0	0 %
South West	408	9 %	0	0 %
Thames	374	12 %	174	47 %
Wales	639	17 %	93	15 %
Totals:	*3588*		*880*	

Table 4.2 - Numbers of data records available by region for England and Wales

The range of values exhibited by the two parameters is quite large (Figure 4.1) with each ranging over about 5 orders of magnitude. There is also no distinct trend displayed by the data shown, with larger STPs not always being associated with larger dilution factors.

The $\log_{10}$ of each value was given because of the large range in values for each parameter. Distributions are usually characterised by a population mean (μ) and a standard deviation (σ) or population variance (σ^2) value. Slob (1994) however, for lognormal distributions, suggests the use of the population median (M) and the population coefficient of variation (CV).

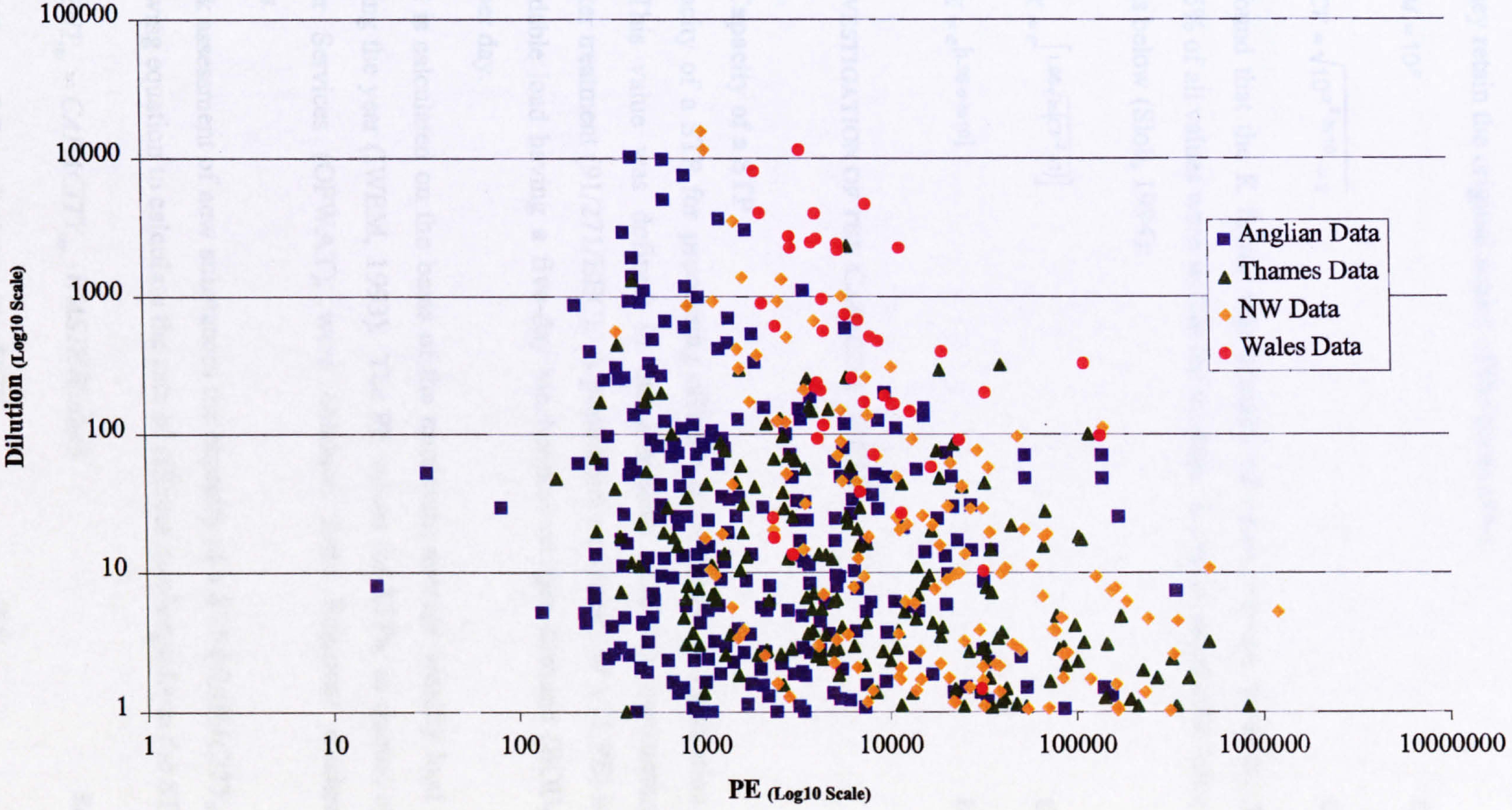

Figure 4.1 - Distribution of capacity in population equivalents and dilution factor at point of discharge for STPs in England and Wales

Equations 4.5 & 4.6 detail the calculation of the population median (M) and the population coefficient of variation (CV) respectively. The advantage of these measures is that they retain the original scales of the parameters.

$$M = 10^{\mu} \qquad \text{Equation 4.5}$$

$$CV = \sqrt{10^{\sigma^2 \ln 10} - 1} \qquad \text{Equation 4.6}$$

It was found that the K factor was actually of more interest, detailing the factor by which 95% of all values were within the median. K can be calculated using either of the equations below (Slob, 1994):

$$K = e^{\left[1.96\sqrt{\ln\left(CV^2+1\right)}\right]} \qquad \text{Equation 4.7}$$

$$K = e^{[1.96 \cdot \sigma \cdot \ln 10]} \qquad \text{Equation 4.8}$$

4.3 INVESTIGATION OF THE CAPACITY OF STPS

4.3.1 Capacity of a STP

The capacity of a STP for processing effluent is measured in Population Equivalents (PE). This value was defined in the European Directive concerning municipal wastewater treatment (91/271/EEC). A population equivalent of 1 (1 PE) is the organic biodegradable load having a five-day biochemical oxygen demand (BOD_5) of 60g of oxygen per day.

The load is calculated on the basis of the maximum average weekly load entering the STP during the year (IWEM, 1993). The PE values for STPs, as quoted by the Office of Water Services (OFWAT), were obtained from Regional discharge consent databases.

In the risk assessment of new substances the capacity of a STP ($CAPACITY_{stp}$) is used in the following equation to calculate the rate of effluent discharge from the STP.

$$EFFLUENT_{stp} = CAPACITY_{stp} \cdot WASTEWinhab \qquad \text{Equation 4.9}$$

$EFFLUENT_{stp}$	Effluent discharge rate of STP	(l/d)	
$CAPACITY_{stp}$	Capacity of the STP in population equivalents	(eq)	default = 10000
$WASTEWinhab$	Sewage flow per inhabitant	(l/d/eq)	default = 200

The value $EFFLUENT_{stp}$ is subsequently used to calculate the concentration of the substance entering the STP, and hence leaving the STP, which in turn is used in the calculation of the Predicted Environmental Concentration (PEC) for local water. The effluent discharge rate can also be used to calculate a dilution factor value (Figure 4.2).

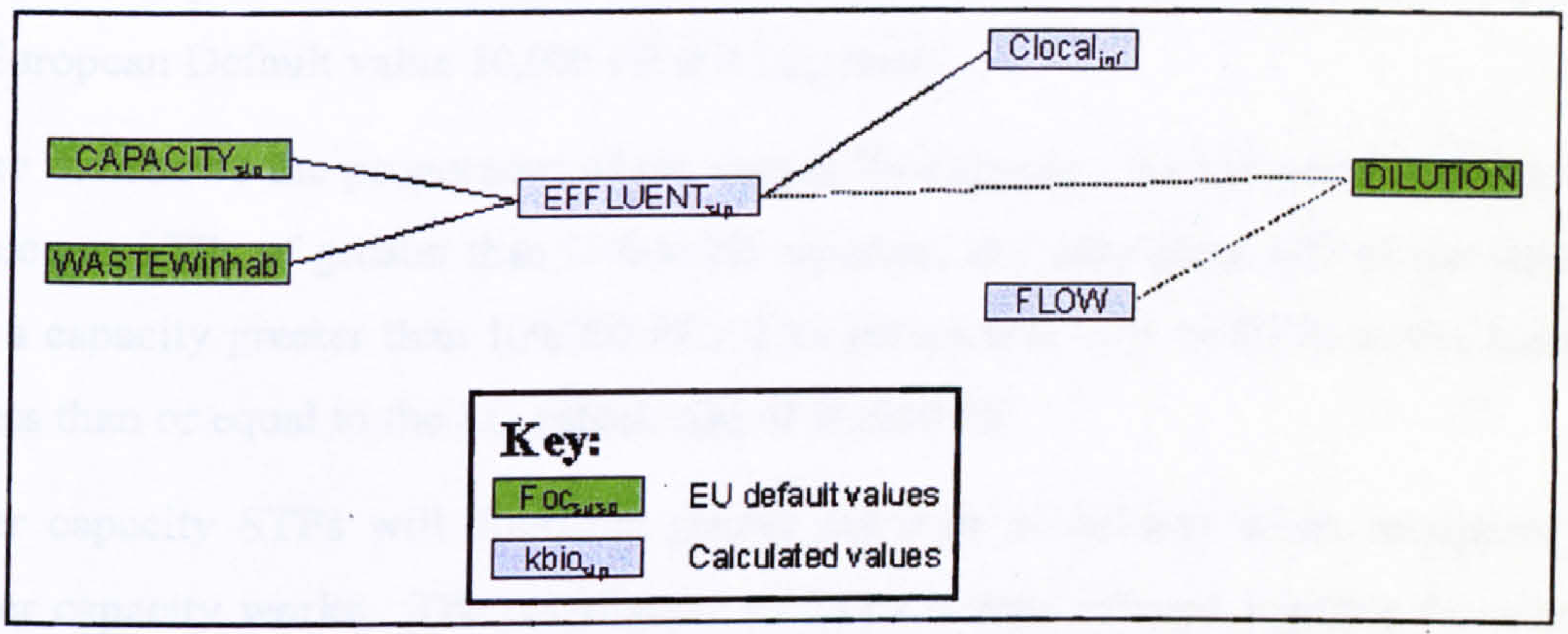

Figure 4.2 – Parameters in risk assessment system dependent upon the capacity of a STP value

Due to the large range in PE values (Figure 4.1) $\log_{10}$(PE) was used in these analyses. Figure 4.3 shows the histogram of data for $\log_{10}$(PE), the European default value of 10,000 PE (at 4 log units) is also marked.

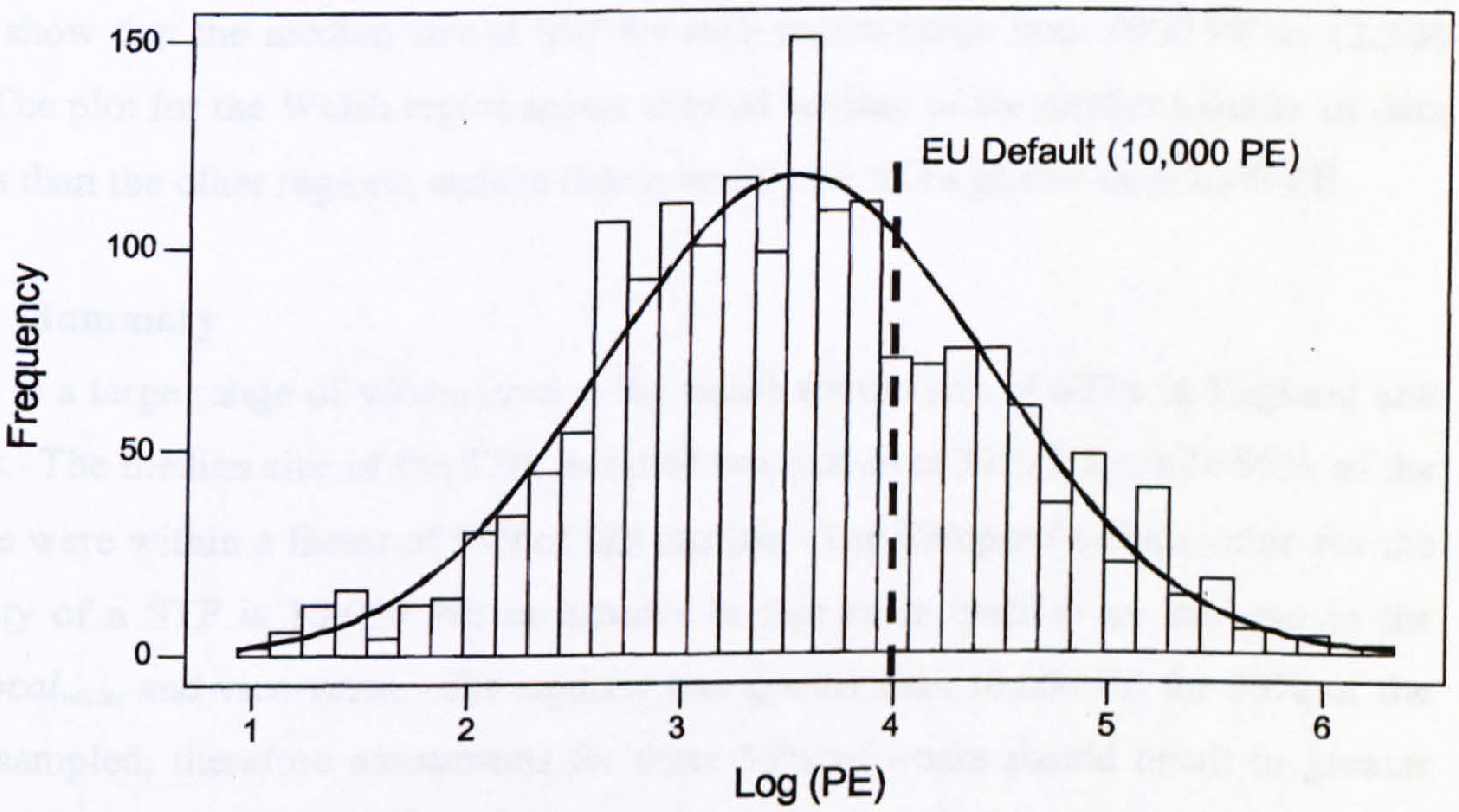

Figure 4.3 - Histogram of Log_{10}(PE) with normal curve and EU default value indicated; N = 880, M = 3300 PE, K = 58.9

4.3.2 Results

The mean value for the data was 3.52 log units giving a sample median, M ≈ 3300 PE. The uncertainty factor K was 58.9 (range for capacity of STP, 95% CI: 56 → 194000). The Anderson-Darling normality test returned a value of 0.025, demonstrating only a small tendency towards normality. It can be seen that the median value was less than the European Default value 10,000 PE at 4 Log units.

Figure 4.4 shows the proportions of the sample by capacity. As indicated, 30% of the sample are STPs of greater than 10,000 PE capacity, and only about 6% of the sample have a capacity greater than 100,000 PE. This means that 70% of STPs in the sample are less than or equal to the EU default size of 10,000 PE.

Larger capacity STPs will discharge greater volumes of effluent when compared to smaller capacity works. The contribution of STPs to total effluent loading, by size is shown in Figure 4.5. STPs with a capacity less than 10,000 PE contribute 8% of the total effluent load. STPs with a capacity of 100,000 PE and less, account for 35% of the sample, with 65% of the total effluent being contributed by STPs with a capacity greater than 100,000 PE.

The data were analysed separately by region (Figure 4.6). The cumulative frequency plots show that the median size of STP for each region range from 1000 PE to 12,500 PE. The plot for the Welsh region appear skewed because of the smaller number of data points than the other regions, and the data is mainly for STPs greater than 2000 PE.

4.3.3 Summary

There is a large range of values (over 6 log units) for the size of STPs in England and Wales. The median size of the STPs sampled was just over 3000 PE, while 95% of the sample were within a factor of 58.9 of this median. The European default value for the capacity of a STP is 10,000 PE; an increase in this value leads to an increase in the $PEClocal_{water}$ and vice-versa. The capacity was greater than 10,000 PE for 30% of the STPs sampled, therefore assessments for these 30% of works should result in greater $PEClocal_{water}$ values than calculated using EU default parameters. For the remaining 70% of STPs sampled the generic European assessment will calculate a higher level of concentration in water than is likely to occur and is therefore protective.

STPs with a higher capacity will proportionally discharge a greater amount of effluent than smaller sites. The data showed that STPs with a capacity of >10,000 PE contributed 94% of the total effluent load. The European default value of 10,000 PE, is precautionary for STPs of lower capacity and therefore encompasses 70% of the STPs sampled, which however only contribute 6% of the total effluent load.

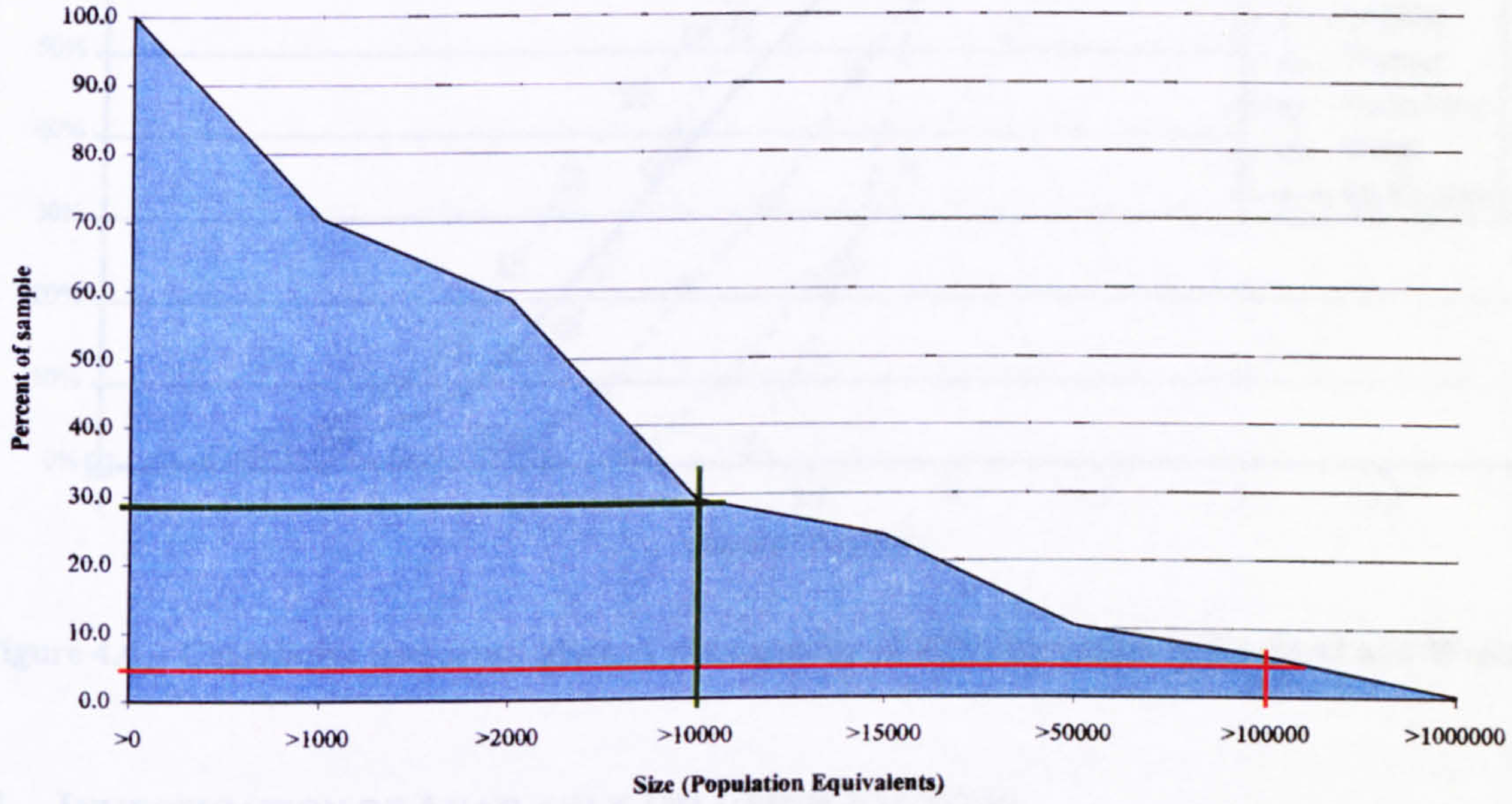

Figure 4.4 - Proportion of STPs by capacity in England and Wales

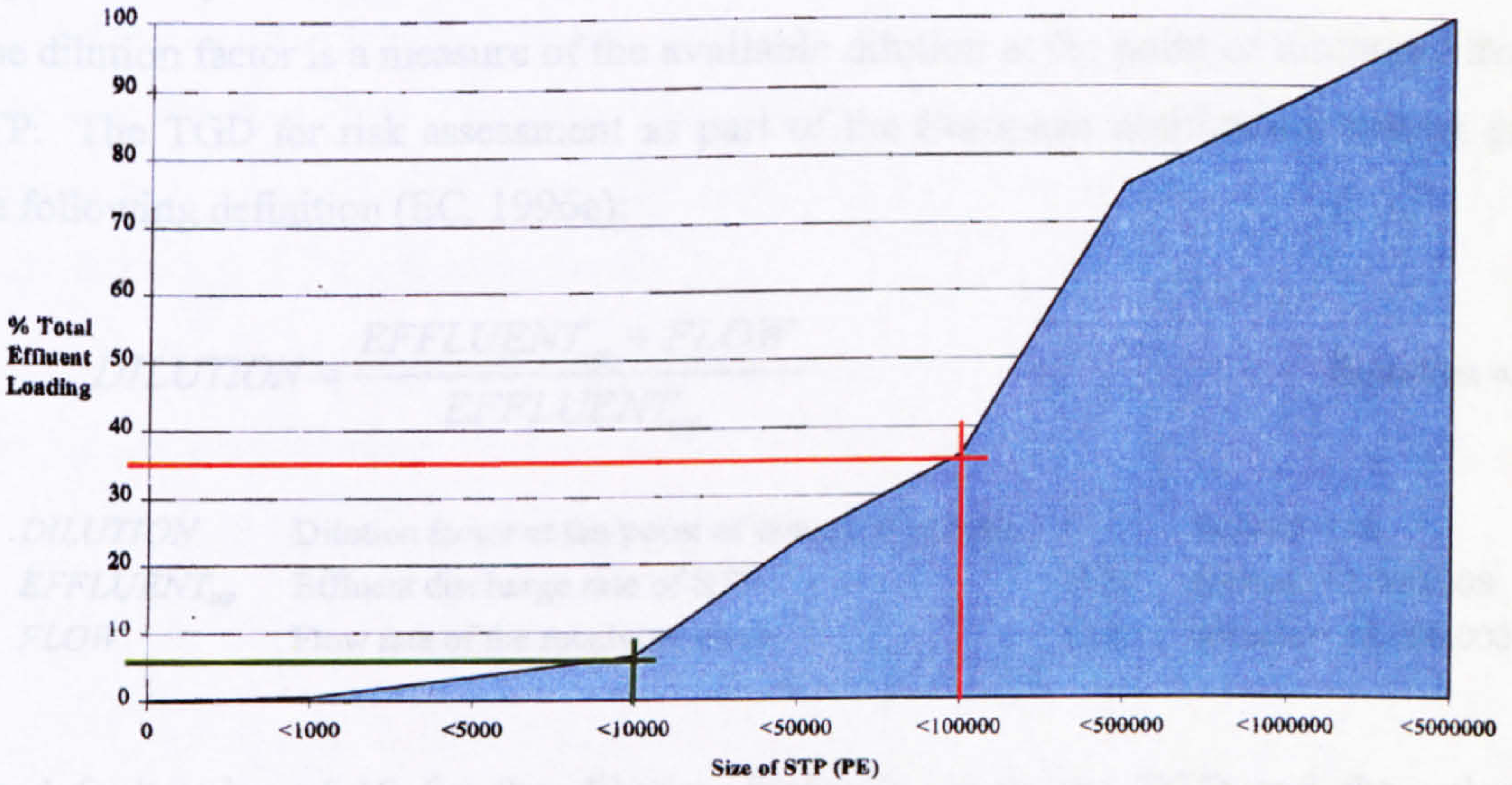

Figure 4.5 - Proportion of STPs by capacity contributing to total effluent load

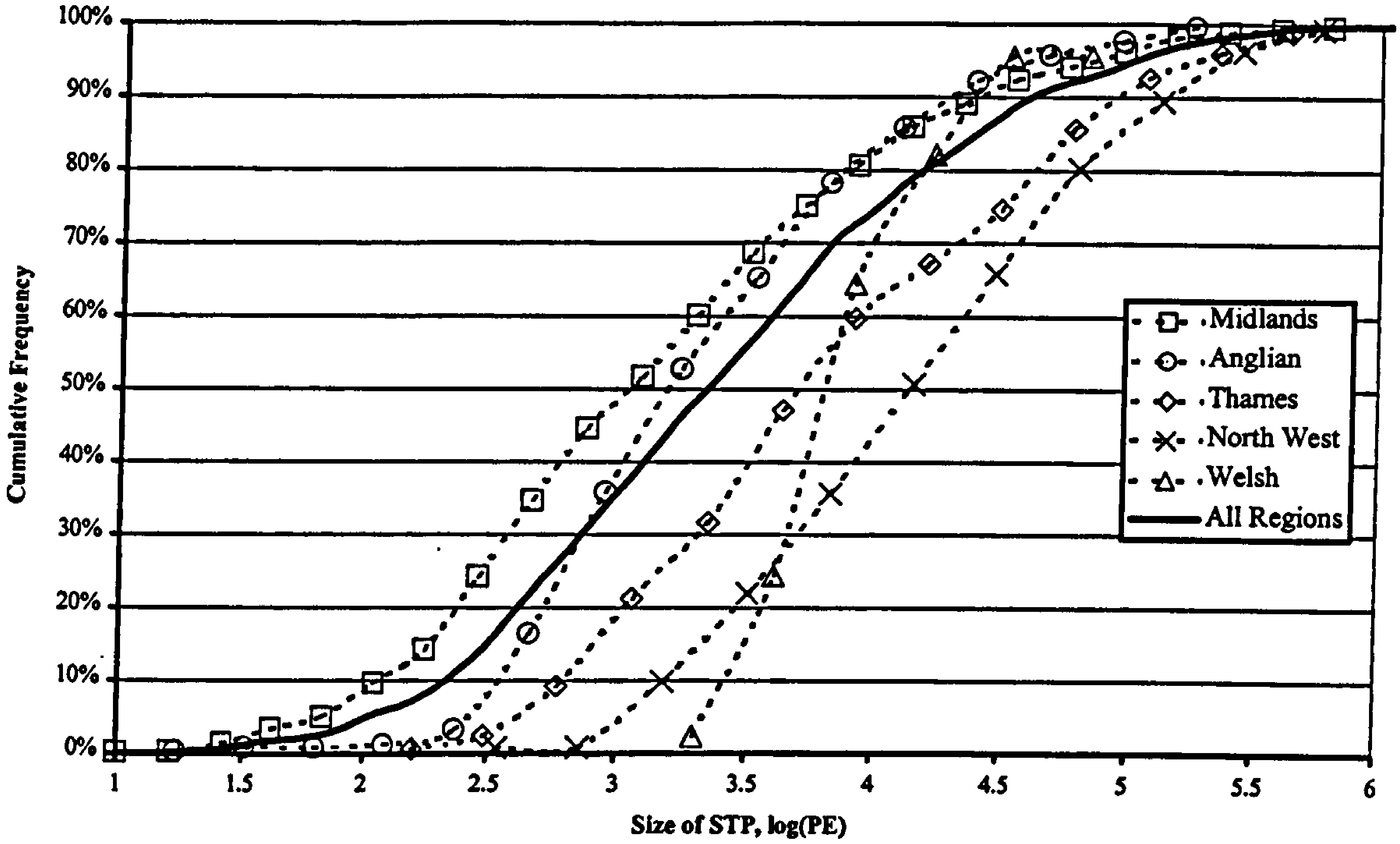

Figure 4.6 – Cumulative frequency plots of the capacity of STPs by region in England and Wales

4.4 INVESTIGATION OF AVAILABLE DILUTION FACTORS

4.4.1 Available Dilution

Importance of the Dilution Factor

The dilution factor is a measure of the available dilution at the point of discharge from a STP. The TGD for risk assessment as part of the European notification system gives the following definition (EC, 1996a):

$$DILUTION = \frac{EFFLUENT_{stp} + FLOW}{EFFLUENT_{stp}}$$

Equation 4.10

DILUTION	Dilution factor at the point of complete mixing	-	default = 10
EFFLUENT$_{stp}$	Effluent discharge rate of STP	(l/d)	default = 2,000,000
FLOW	Flow rate of the receiving river	(l/d)	default = 18,000,000

The default value of 10 for the dilution factor is set in the TGD and the value is attributed to the studies by Greef & Nijs (1990). This work reviewed approximately 500 Waste Water Treatment Plants (WWTP) in The Netherlands and concluded that, "a common dilution factor is an inadequate measure for exposure to new chemicals". The authors particularly noted that dilution factors do not take into account transverse concentration distributions, which can result in actual areas of concentration being higher than predicted. The default value for generic risk assessments in the EU is however a factor of 10, which is intended to represent the dilution factor at the point of complete mixing some distance downstream from the point of discharge.

Other investigations of the dilution factor have been made; a study in Germany of 112 industrial WWTP found that the 10th low percentile mean river flow was 60 m^3/s compared to the EU default river flow of 18,000,000 l/d $\approx$ 0.21 m^3/s (Magaud & Diderich, 2000). 643 industrial WWTP were investigated in France and the 10th low percentile mean river flow was approximately 1 m^3/s and led to the proposal of the median value (due to the shape of the distribution) of 3.25 m^3/s (Magaud & Diderich, 2000). This would result in a dilution factor of 141.

In the US the 'Probabilistic Dilution Model 4' (PDM4) is used to estimate the dilution available at the point of discharge from WWTPs, while in Canada, data from a suite of Canadian rivers are currently used. The Canadian EPA are however, developing a tool similar to the US EPA's PDM4 (BEC, 1999). Further research on dilution factors for MS in the EU is currently being undertaken, (Jager, 2001, *pers. com.*). There have however, been no detailed studies into the available dilution at point of discharge from STPs in the UK.

Calculation of the Dilution Factor

The Dry Weather Flow (DWF) permitted discharge value for each STP was taken as an approximation of the $EFFLUENT_{stp}$ value; the DWF being the average daily flow calculated during 7 days without rain.

The TGD suggests that the 10th low percentile mean river flow or the 1/3 mean value can be used to calculate river flow (EC, 1996a). In this work the nearest upstream measured mean river flow value was used to approximate *FLOW*.

None of the data submitted by Midlands region were usable for calculating dilution factors. Without these data and some unsuitable records from other regions the sample size was decreased to 608 records. The dilution factor was calculated for each STP (Equation 4.10) using the surrogate values as described. Due to the large range in values for *DILUTION* (Figure 4.1) the Log_{10}(*DILUTION*) values were used in analyses. Figure 4.7 shows the histogram of the data with the European default value of 10 (at 1 log unit) indicated.

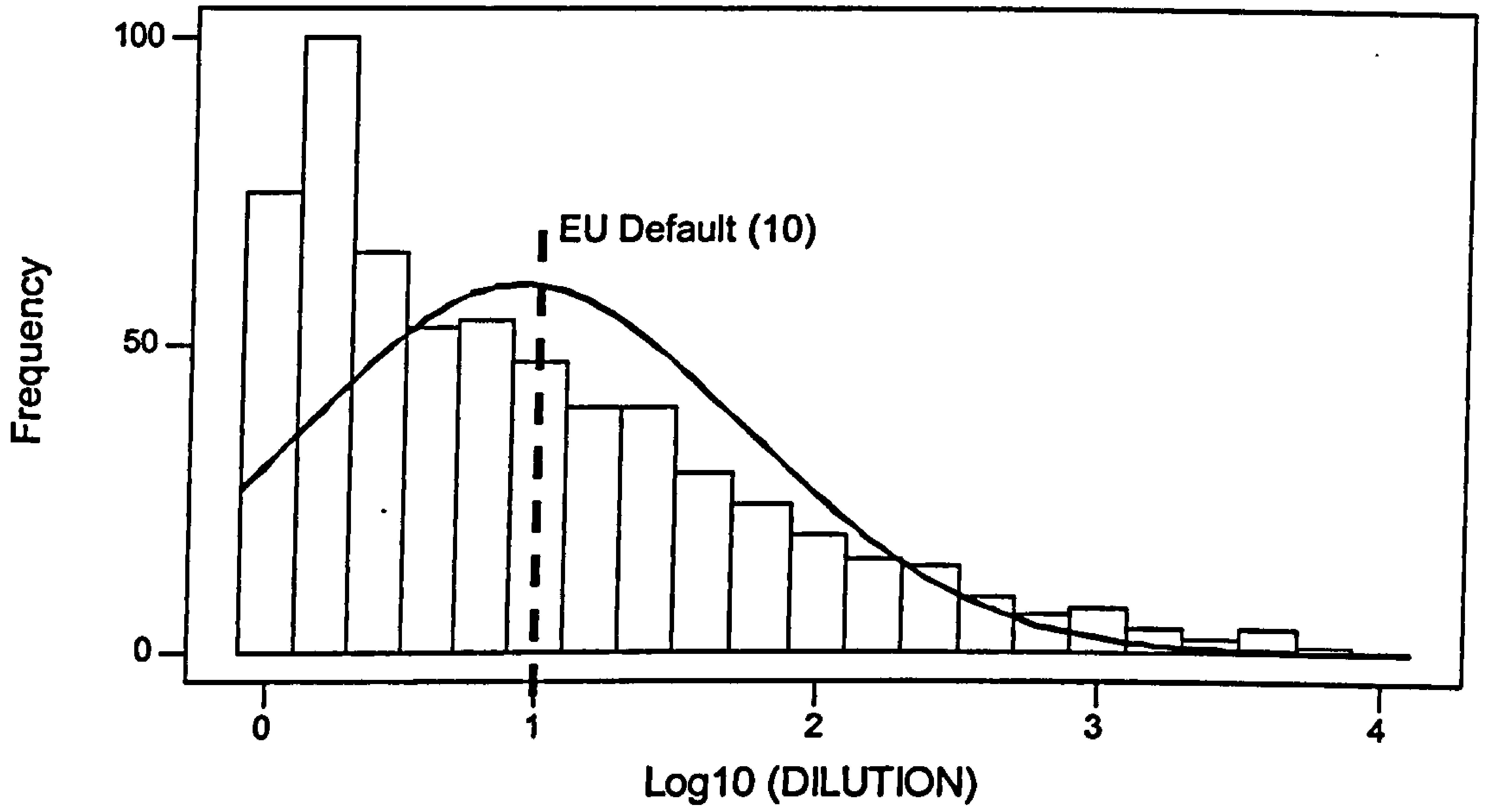

Figure 4.7 - Histogram of Log_{10}(*DILUTION*) with normal curve and EU default value indicated. The sample size is 608

4.4.2 Results

The mean value for the data was 0.93 log units giving a sample median, M ≈ 5.2. The uncertainty factor K was 38.7 (range of dilution factor, 95% CI: 0.14 → 203). The Anderson-Darling normality test returned a p-value of 0.000, confirming the observation of a non-normal distribution with a heavy positive skew. The median value was less than the European Default value of 10.

The data were analysed by region (Figure 4.8) and it can be seen that the Welsh data do not follow the same trend as the other regions. Wales is a hilly region that has frequent high rainfall, and the region has fewer but larger STPs which discharge into rivers with comparatively higher dilution factors. The other regions all follow a similar trend with the mean value for *DILUTION* ranging from 0.9 log units (dilution factor ≈ 8) to 1.2 log units (dilution factor ≈ 16).

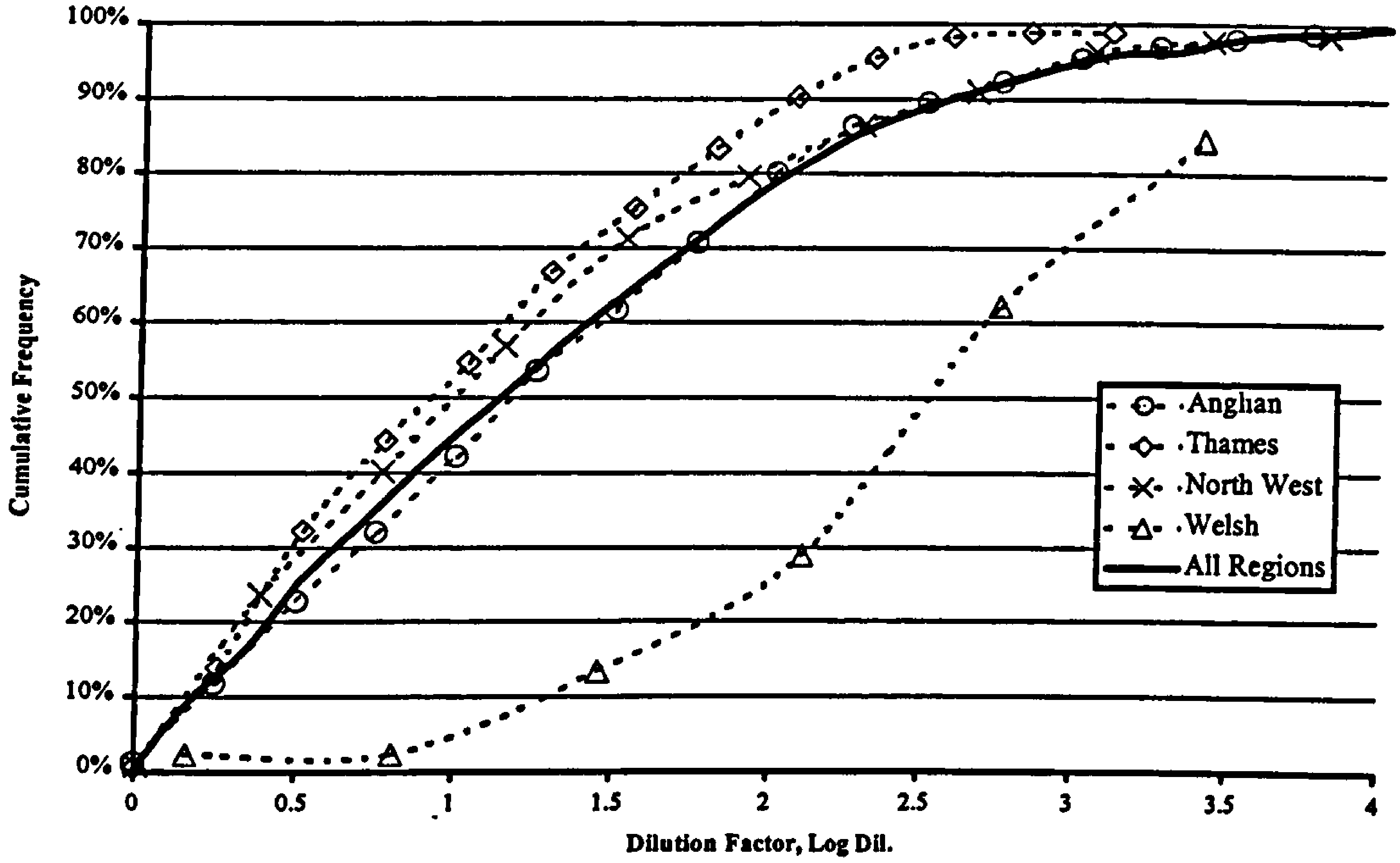

Figure 4.8 – Cumulative frequency plot of dilution factor at STPs by Region

Considering the data for all regions (Figure 4.8), 45% of the sample receive lower dilution factors than 10 (1 log unit) while 55% of the STPs obtain a dilution factor >10, whereas, only 25% receive lower dilution factors than 3 (≈ 0.5 log units), with 75% of STPs obtaining a higher factor of dilution than 3. It should be realised however, that these dilution factors do not consider a zone of mixing as in the European risk assessment system. A mixing zone is an area where secondary mixing processes are permitted, ensuring that no environmental degradation occurs beyond the mixing zone boundaries. As calculated, instantaneous and complete mixing of the two flows is assumed at the point of discharge.

4.4.3 Summary

There is a large range in values for the dilution factor at point of discharge from STPs in England and Wales, the values range over 5 log units. The median dilution factor was found to be approximately 5. The default value of 10 used in the European risk assessment system would be precautionary for 55% of the STPs sampled.

Analysis of individual data points, indicated that larger STPs did not always receive larger dilution factors. Examining individual data points in Figure 4.1 it was noted that a number of very large STPs (100,000 – 1,000,000 PE) were associated with very low dilution factors (<10). Some of these points were examined in detail and it became apparent that in some situations STP discharges were to small drains, ditches and streams.

These ditches and drains act as tributaries to larger streams and rivers, where eventually much greater dilution will be gained. This is a limitation of the data, and a problem with the method of measurement and sampling taken in England and Wales. Some dilution factors as calculated for STPs will be very low due to the low flow in these tributary ditches and drains. In some cases the flow in these drains may be the effluent itself (dilution factor of 1). The effect of this is that low dilution factor values can appear, particularly for larger STPs.

4.5 GEOGRAPHICAL ANALYSIS OF DATA

As part of the data collated for these analyses grid references were associated with each set of values for a STP. A Geographical Information Systems (GIS) tool was used to plot the data for the dilution available at STPs in England and Wales spatially with respect to the Environment Agency's administrative regions and the river infrastructure (Figure 4.9). It can clearly be seen where the available dilution is less than the European default value of 10.

The data relating to the capacity of the STPs were then added to the GIS plot (Figure 4.10). By using a coloured scale for both the available dilution and the capacity of the STPs, individual points where the capacity is very large whilst the dilution factor is low can be identified. From these GIS analyses it was found that Thames and North West regions both contain a significant number of STPs where the dilution factor is less than 10 for STPs with capacities of greater than 100,000 population equivalents. These sites would serve as ideal locations to undertake further investigations.

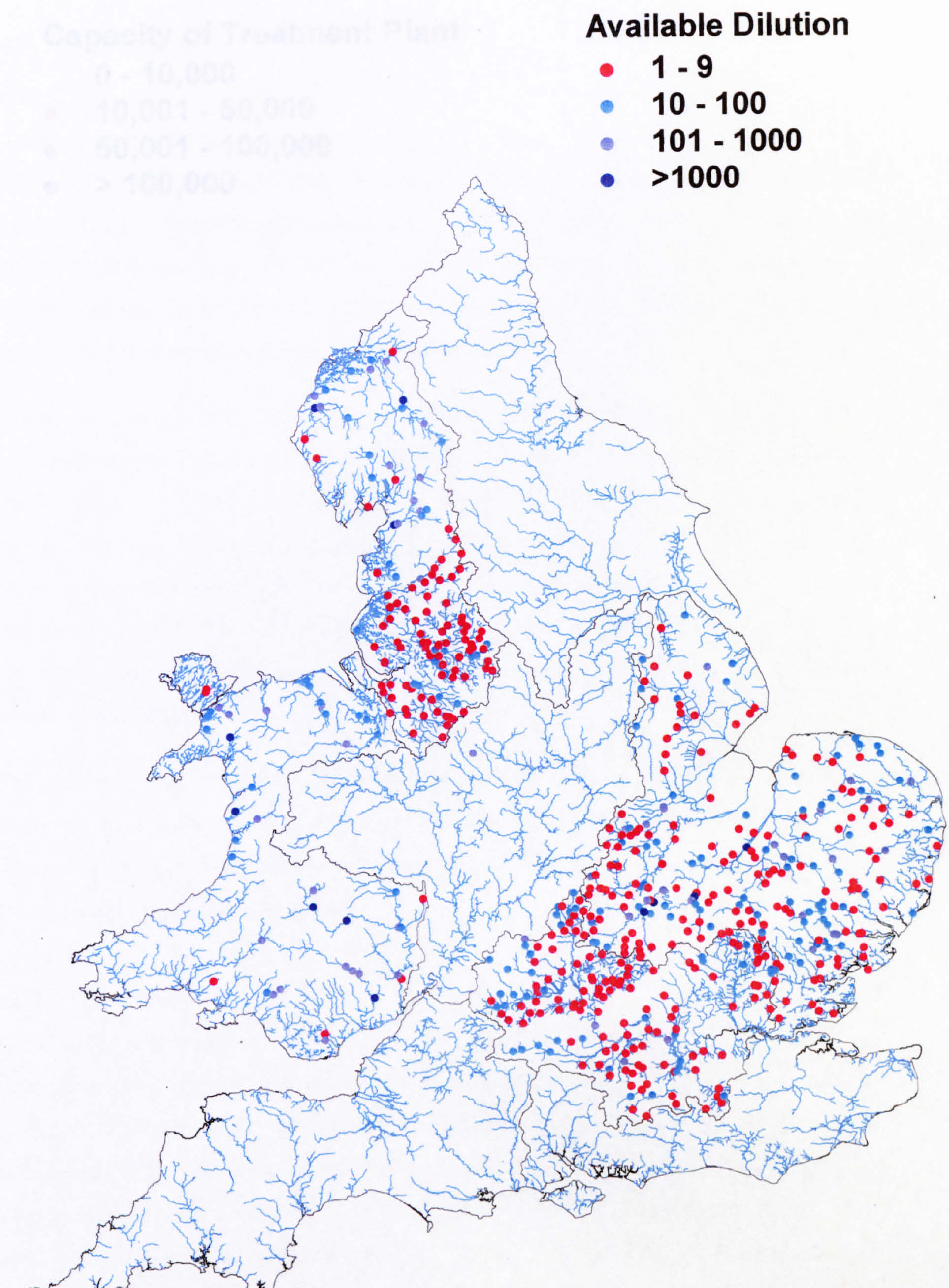

Figure 4.9 - GIS plot of the dilution available at STPs across England and Wales

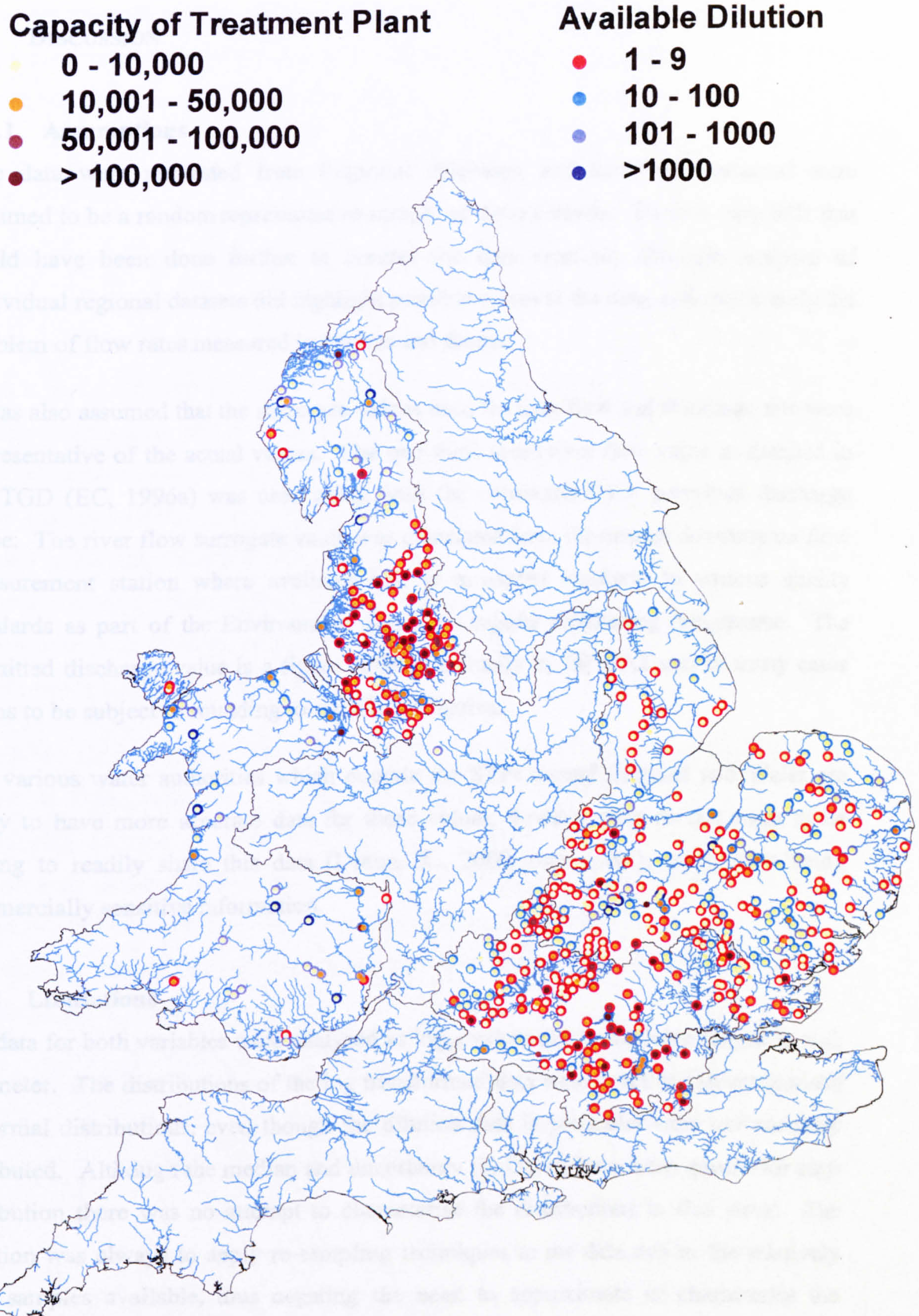

Figure 4.10 - GIS plot of the capacity of and dilution available at STPs across England and Wales

4.6 DISCUSSION

4.6.1 Assumptions

The data were requested from Regional databases, and those data returned were assumed to be a random representative sample of those datasets. There is very little that could have been done further to control the data received, although analyses of individual regional datasets did highlight possible biases in the data, and importantly the problem of flow rates measured in ditches and drains.

It was also assumed that the surrogate values used for river flow and discharge rate were representative of the actual values. The one-third mean river flow value as detailed in the TGD (EC, 1996a) was used along with the consented DWF permitted discharge value. The river flow surrogate value was calculated from the nearest downstream flow measurement station where available and is measured regularly to various quality standards as part of the Environment Agency's regular monitoring programme. The permitted discharge value is a figure collated annually by OFWAT and in many cases seems to be subject to rounding to significant figures.

The various water authorities which operate the STPs around England and Wales are likely to have more accurate data for these values, however they do not seem to be willing to readily share this data (Dixon, K., 2000, *pers. com.*), much of it being commercially sensitive information.

4.6.2 Limitations

The data for both variables were analysed as $\log_{10}$ values due to the large ranges in each parameter. The distributions of the log transformed data were described in comparison to normal distributions, even though the dilution data in particular were nor normally distributed. Although the median and uncertainty (K-factor) have been quoted for each distribution there was no attempt to characterise the distributions in this work. The intention was always to apply re-sampling techniques to the data due to the relatively large samples available, thus negating the need to approximate or characterise the distributions. This work is presented in Chapter 5.

Data for a limited number of Regions were available for these analyses even though all 8 Regions were requested for the data. With data for all 8 Regions, regional differences could have been examined in greater detail.

4.7 SUMMARY

These analyses have highlighted areas for further investigation, and problems in the collation of adequate data. The measuring of flow rates in ditches and drains that lead to larger rivers where greater dilution will occur can lead to very low dilution values. This is particularly apparent for the larger STPs. For situations like this a measurement of flow in the drain and in the eventual receiving water would be of greater interest. The GIS analyses can be used to highlight sites where there are low dilution factors for large capacity STPs, some of which may be caused by flow rates being measured in ditches and drains. Further examination of these sites would help to initially investigate the scope of the problem regarding the measurement of flow rates in ditches and drains. When appraising the data an indication of the type of watercourse that the discharge enters would also be of great value.

The wide ranges for both parameters demonstrates the difficulty in generalising for either of these parameters. Current research in the EU seems to be focused on calculating a single dilution factor that can be used as a generic value in risk assessments (Magaud & Diderich, 2000). It would however, seem more appropriate to develop a large dataset that can be used in probabilistic assessments, so that the type of rivers, or the magnitude of the range in dilution factors can be selected and probabilistic assessments made from this.

The following chapter details probabilistic risk assessments for new substances that were performed using the distributions obtained in this work for the capacity of STPs and the dilution available at point of discharge.

CHAPTER 5

PROBABILISTIC RISK ASSESSMENTS

SUMMARY

The developed NEXCES tool was used to perform probabilistic risk assessments using STP capacity and dilution factor data. The data collated were re-sampled to produce 5000 pairs of values to run a similar number of risk assessments.

Probabilistic and deterministic risk assessments for a number of test substances were performed and compared. Regression analysis of the results from these was used to determine the probability values for the deterministic RCR thresholds (>1, >10, >100, etc.).

5 PROBABILISTIC RISK ASSESSMENTS

5.1 INTRODUCTION

The data collated for the two parameters (capacity and dilution) at STPs in England and Wales were used in the NEXCES model to perform probabilistic assessments for a number of new substances.

The existing TGD and EUSES system generate a deterministic assessment based on point estimate values (RCR = PEC / PNEC). Further information may be requested or controls placed on a substance depending on the magnitude of the resulting RCR value. The disadvantages of such point estimate values in risk assessments have been cited to include (Jager *et al.*, 1997):

- It is not normally possible to determine where a point estimate lies in the distribution of possibilities
- Point estimate values may mislead risk managers by producing precise but false estimates
- Point estimates can eliminate the incentives for producing further information to refine assessments

The point estimates for values can be replaced by distributions that describe the various parameters; such an approach is termed a probabilistic assessment. Probabilistic methods can be used in risk assessments in three ways, illustrated in Figure 5.1 along with the standard deterministic assessment, which are currently performed for new substances:

- Probabilistic exposure assessment with a point estimate for effect assessment (Figure 5.1b)
- Probabilistic effect assessment with a point estimate for exposure assessment (Figure 5.1c)
- Probabilistic exposure and effect assessments (Figure 5.1d)

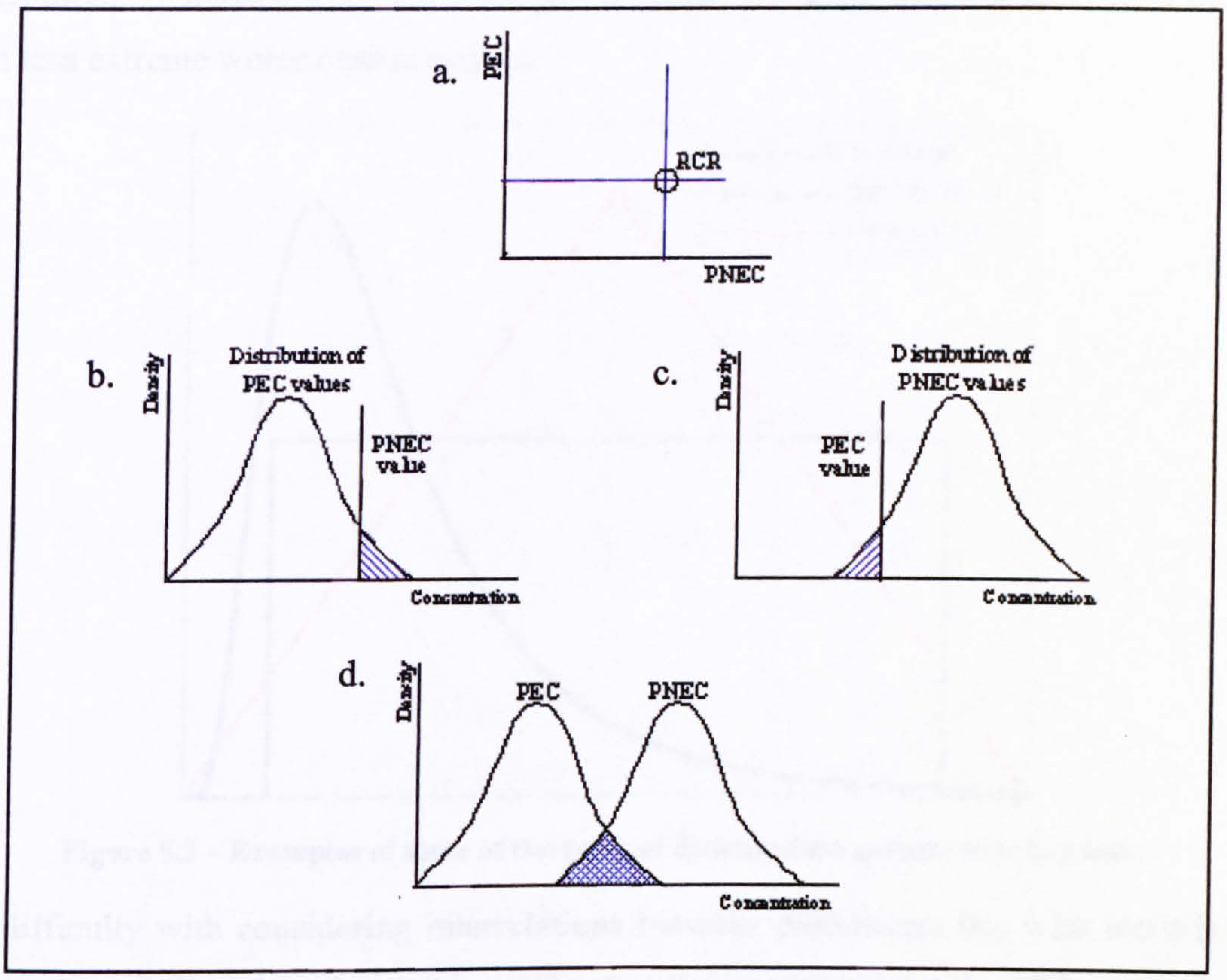

Figure 5.1 - Integration of probabilistic approaches into the risk assessment of chemical substances

a. Deterministic approach, RCR = PEC / PNEC

b. Uncertain PEC, with point estimate of PNEC

c. Uncertain PNEC with point estimate for PEC

d. Uncertain PEC and PNEC

Jager *et al.* (1997, 2000) carried out probabilistic assessments for two substances using distributions for more than 30 of the parameters used in the EUSES risk assessment system. The uncertainty in each parameter was characterised by either a uniform, triangular or lognormal distribution (Figure 5.2). The authors noted that the characterisation of parameters by the chosen distributions was by no way complete and that the distributions used were only a 'starting point'.

In the work of Jager *et al.* (1997, 2000) however, the interrelation of values was not explicitly considered. Many physical, chemical and environmental parameters are interrelated, not always directly and sometimes in complex manners. Mackay & Shiu (1981) reported for example, the correlation between the vapour pressure and solubility in water of a substance. When interrelations between parameters are ignored in a probabilistic assessment extreme worst-case values can arise, albeit with low probability. This has the effect of "stretching-out" the tails of the resulting assessment distribution. Whereas, when interrelations are considered the distribution will be tighter with less extreme worse case scenarios.

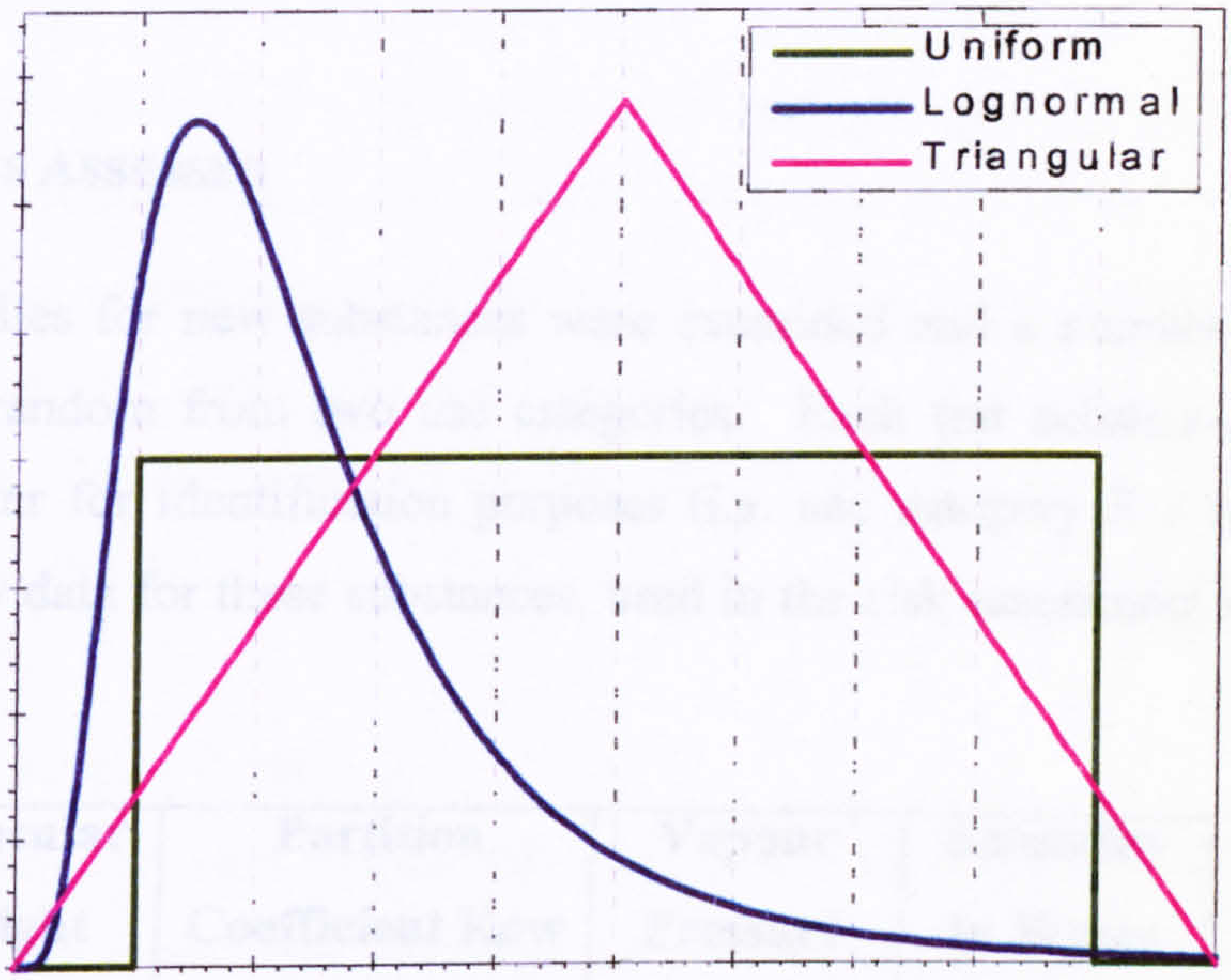

Figure 5.2 – Examples of some of the types of distributions parameters may take

The difficulty with considering interrelations between parameters lies with identifying them and modelling the relationships. The data that were collated for STPs in England and Wales were however already paired, each value for the capacity of an STP was associated with a dilution factor for the same site. The data and distributions for the two parameters could have been used separately for each parameter, however this would have included the consideration of unseen combinations of values from Figure 5.3 (e.g. low capacity, <100; with high dilution factor, >100).

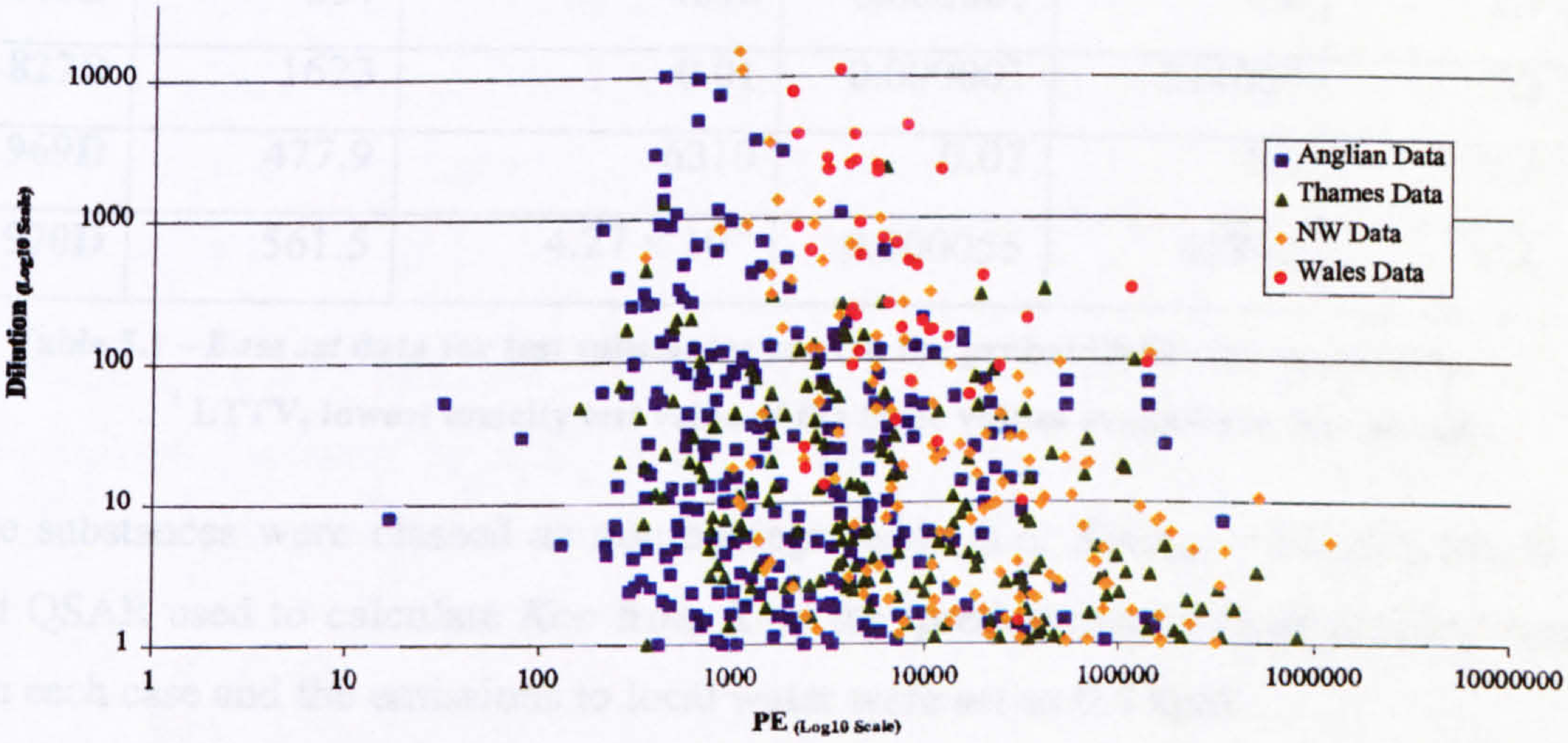

Figure 5.3 – Paired data for capacity of STPs and dilution factor available in England and Wales

By considering the data for the parameters in pairs the resulting probabilistic exposure assessments more closely model the situation for England and Wales, as characterised by the data.

5.2 SUBSTANCES ASSESSED

The notification files for new substances were examined and a number of substances were selected at random from two use categories. Each test substance was given a number and a letter for identification purposes (i.e. use category F – fragrance, D – dye). The *base set* data for these substances, used in the risk assessment are detailed in Table 5.1.

ID No.	**Molecular Weight** *(g/mol)*	**Partition Coefficient Kow** *(-)*	**Vapour Pressure** *(Pa)*	**Solubility in Water** *(mg/l)*	**LTTV**[†] *(mg/l)*
652F	284	47863	23.3	2.95	1.1
909F	187	2188	0.75	109	4.6
1062F	158	1175	130	2710	16.3
1084F	234	199526	0.69	19	0.5
672D	434	316228	0.000008	0.2	0.2
724D	404	19953	10	0.2	0.2
745D	445	7943	6.0×10^{10}	1.2	48.1
803D	357	4898	0.000001	0.4	2.7
827D	1623	0.01	0.000001	214000	7.3
969D	477.9	6310	0.07	1.0	1.0
970D	561.5	4.27×10^{-5}	0.000055	42800	8.4

Table 5.1 – *Base set* data for test substances used in the probabilistic risk assessments

[†] LTTV, lowest toxicity test value of the three values available in *base set* data

All the substances were classed as non-biodegradable (i.e. $Kbio_{stp}$ = 0.0 h^{-1}), the EU default QSAR used to calculate *Koc* from *Kow* for 'predominantly hydrophobics' was used in each case and the emissions to local water were set as 0.5 kg/d.

5.3 METHOD

5.3.1 Preparation of NEXCES Spreadsheet

The NEXCES spreadsheet was opened and the calculations as detailed in Chapter 3 were copied down the spreadsheet to create 5000 calculation rows. Five-thousand iterations for the assessment were chosen to produce results from good normal distributions (Chapter 3, Section 3.5.2 and Appendix 11). The spreadsheet was checked to ensure that all calculations and values had been reproduced correctly throughout the 5000 rows of calculations.

5.3.2 Entering *base set* Data

For each substance in turn the *base set* data were copied into the first row of calculation cells in the NEXCES spreadsheet and these values were copied down the spreadsheet to fill all 5000 rows.

5.3.3 Re-sampling of STP Data

Conventional statistical approaches rely on the central limit theorem to allow characterisation of a sample distribution. With the increase in affordable computer processing power, more sophisticated computer-intensive statistical methods involving re-sampling of data are being used more frequently. By reshuffling, re-sampling a data set thousands of times to empirically define a sample distribution, the only assumption necessary is that the original data are randomly sampled and that the chance of re-sampling a value is random (Pitt & Kreutzweiser, 1998). Such re-sampling techniques do not require the distribution assumptions inherent in the conventional statistical characterisation processes.

To re-sample the STP data, sets of paired data cells (STP capacity and dilution factor) were randomly selected from the available data, in this way real combinations of dilutions and capacity values were reproduced. The process used to do this is detailed in Table 5.2.

A	B	C	D	E
STP Capacity (PE)	Dilution Factor	=CONCATENATE(RANDBETWEEN(3,607)) *	=INDIRECT(CONCATENATE("A",C4)) †	=INDIRECT(CONCATENATE("B",C4)) ‡

Table 5.2 – Excel™ formulae used to re-sample STP data in sets of paired values

*** Generates a uniformly distributed random number between 3 and 607 the range of rows that contained STP data**

† Finds the STP capacity value (column A) in random row (column C)

‡ Finds the dilution factor value (column B) in same random row (column C)

5.4 RESULTS

In turn the *base set* data for each test substance were entered into the NEXCES spreadsheet and then a set of 5000 paired and randomly sampled values from the collated STP data were generated and entered into the spreadsheet in the respective columns for dilution factor and capacity of STP. The spreadsheet macro was then run to process each row of the spreadsheet through the SimpleTreat 3.0 model.

The resulting PEC values were then analysed and compared to PEC, and RCR values generated using default values and the deterministic risk assessment method. Figures 5.4 - 5.14 detail the histograms for each substance showing the probabilistic distribution of PEC values and the deterministic PNEC value. The larger the portion of the distribution to the right of the PNEC line the greater the probability that the PEC will exceed the PNEC (i.e. an adverse effect may occur).

Table 5.3 provides a comparison of the results of both deterministic and probabilistic risk assessments for the test substances. This comparison is represented graphically in Figure 5.15. Using both assessment processes, a low risk is observed for substance 745D, and the substance of most concern is 672D. The advantage of the probabilistic assessments however are that the level of risk as well as the probability of adverse effects occurring are quantified.

ID No.	Deterministic RCR value	Probability PEC exceeds PNEC (%)
652F	0.10	30.4
909F	0.42	52.3
1062F	0.12	32.0
1084F	0.53	56.3
672D	1.2	67.4
724D	0.45	53.2
745D	0.027	11.8
803D	0.58	57.3
827D	0.34	47.9
969D	0.99	64.6
970D	0.30	45.3

Table 5.3- Comparison of the resulting risk from deterministic and probabilistic risk assessments

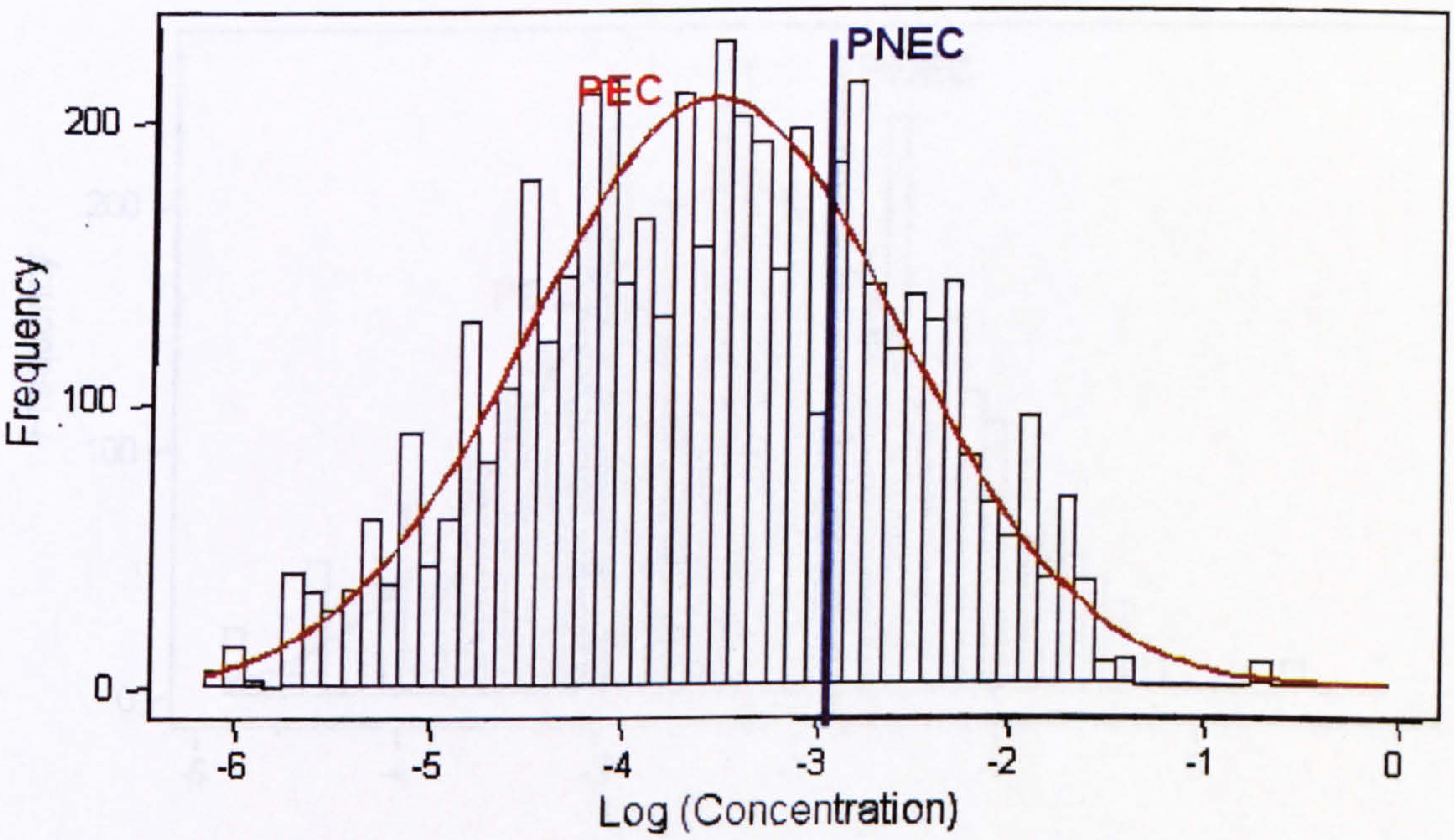

Figure 5.4 - Histogram of probabilistic exposure concentrations (in Log units) for substance 652F, with deterministic PNEC indicated

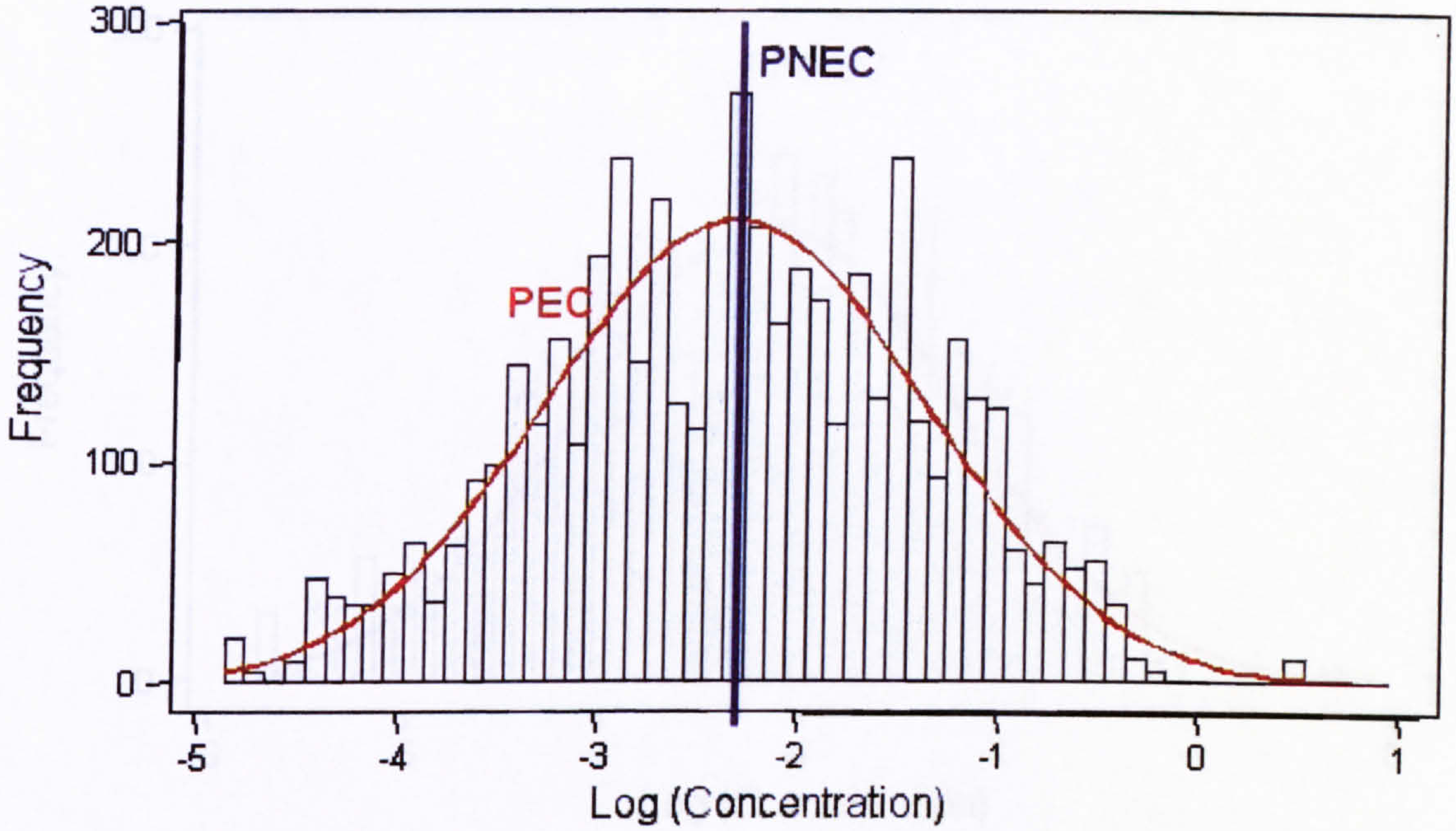

Figure 5.5 - Histogram of probabilistic exposure concentrations (in Log units) for substance 909F, with deterministic PNEC indicated

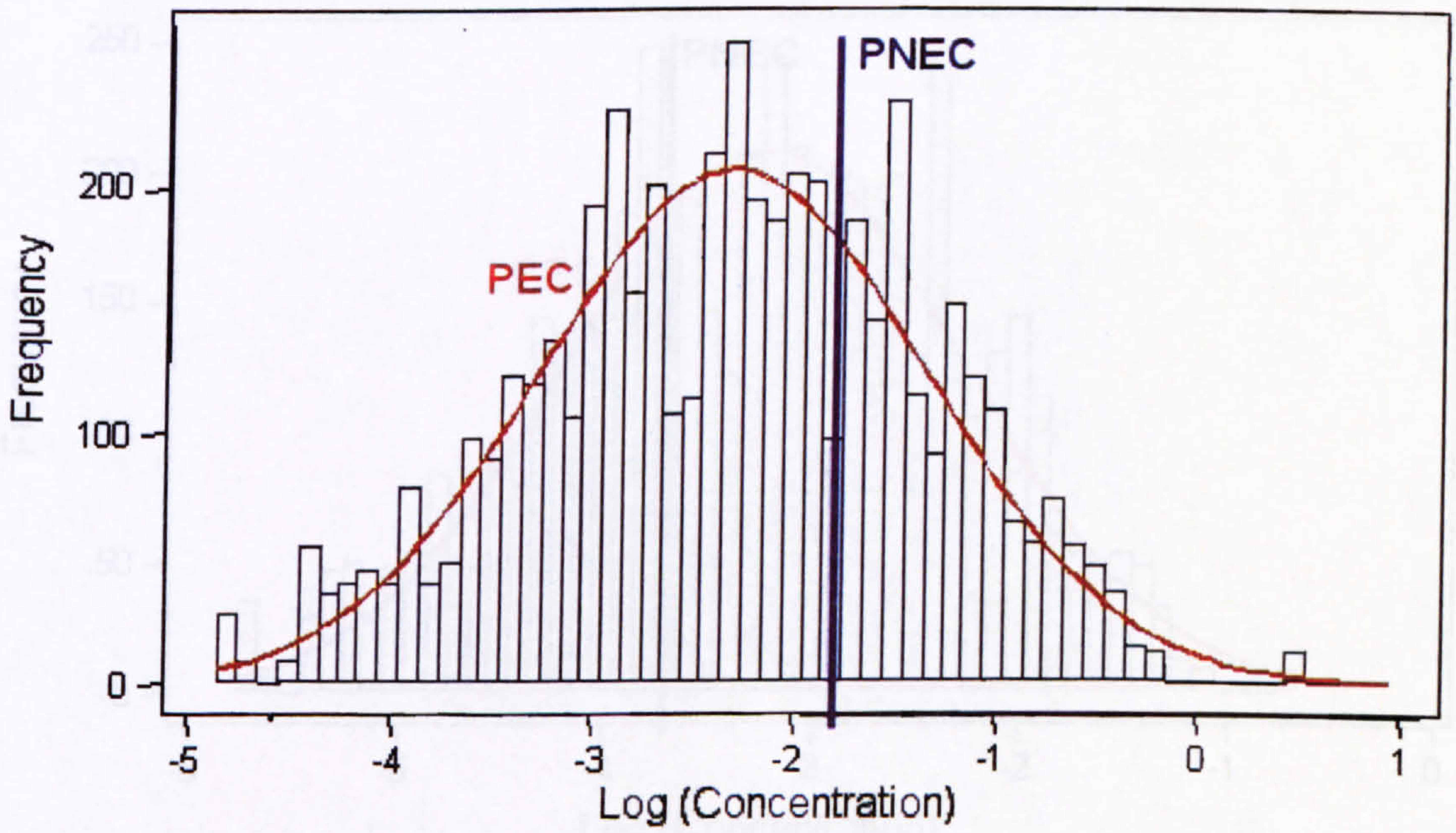

Figure 5.6 - Histogram of probabilistic exposure concentrations (in Log units) for substance 1062F, with deterministic PNEC indicated

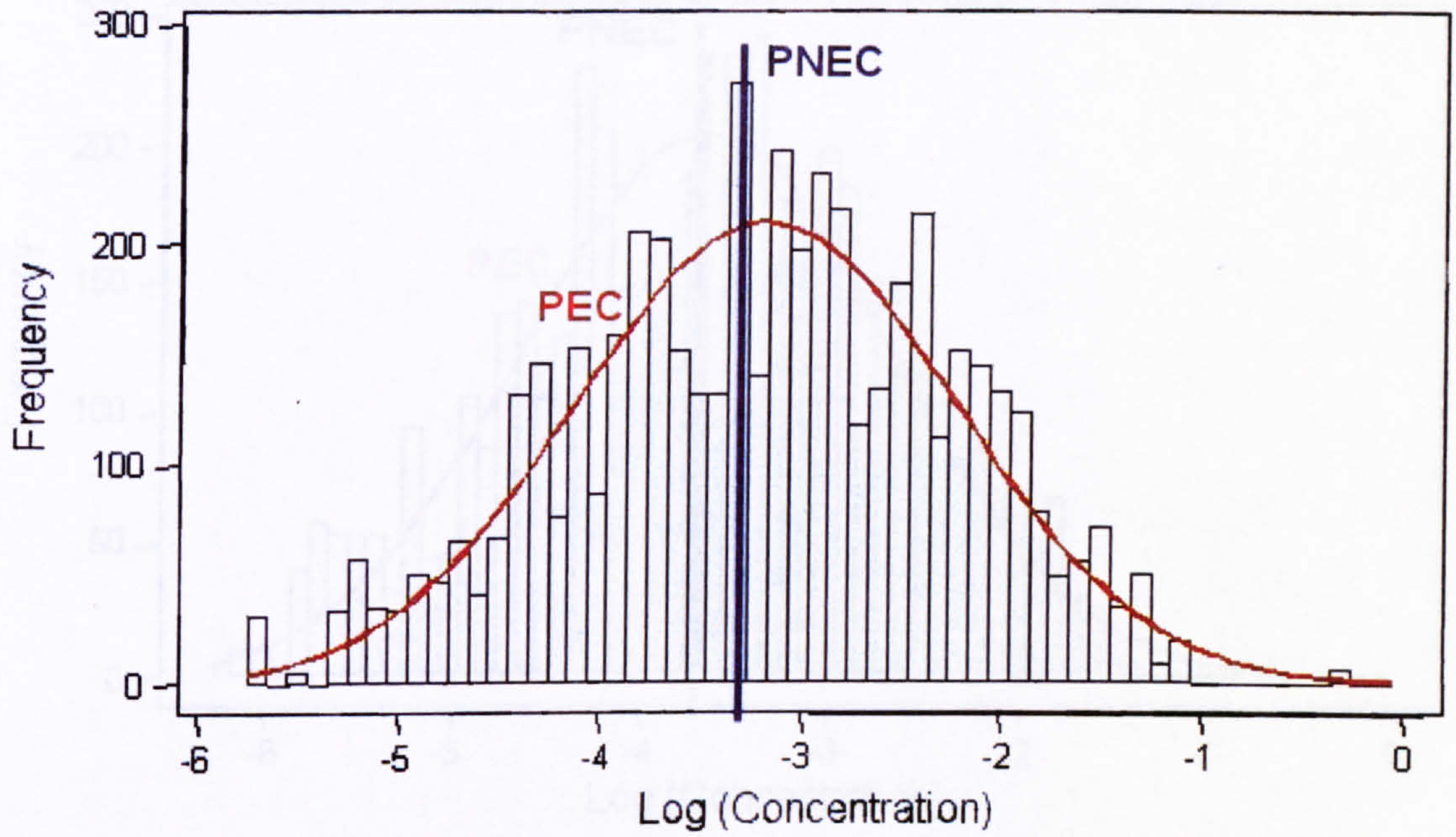

Figure 5.7 - Histogram of probabilistic exposure concentrations (in Log units) for substance 1084F, with deterministic PNEC indicated

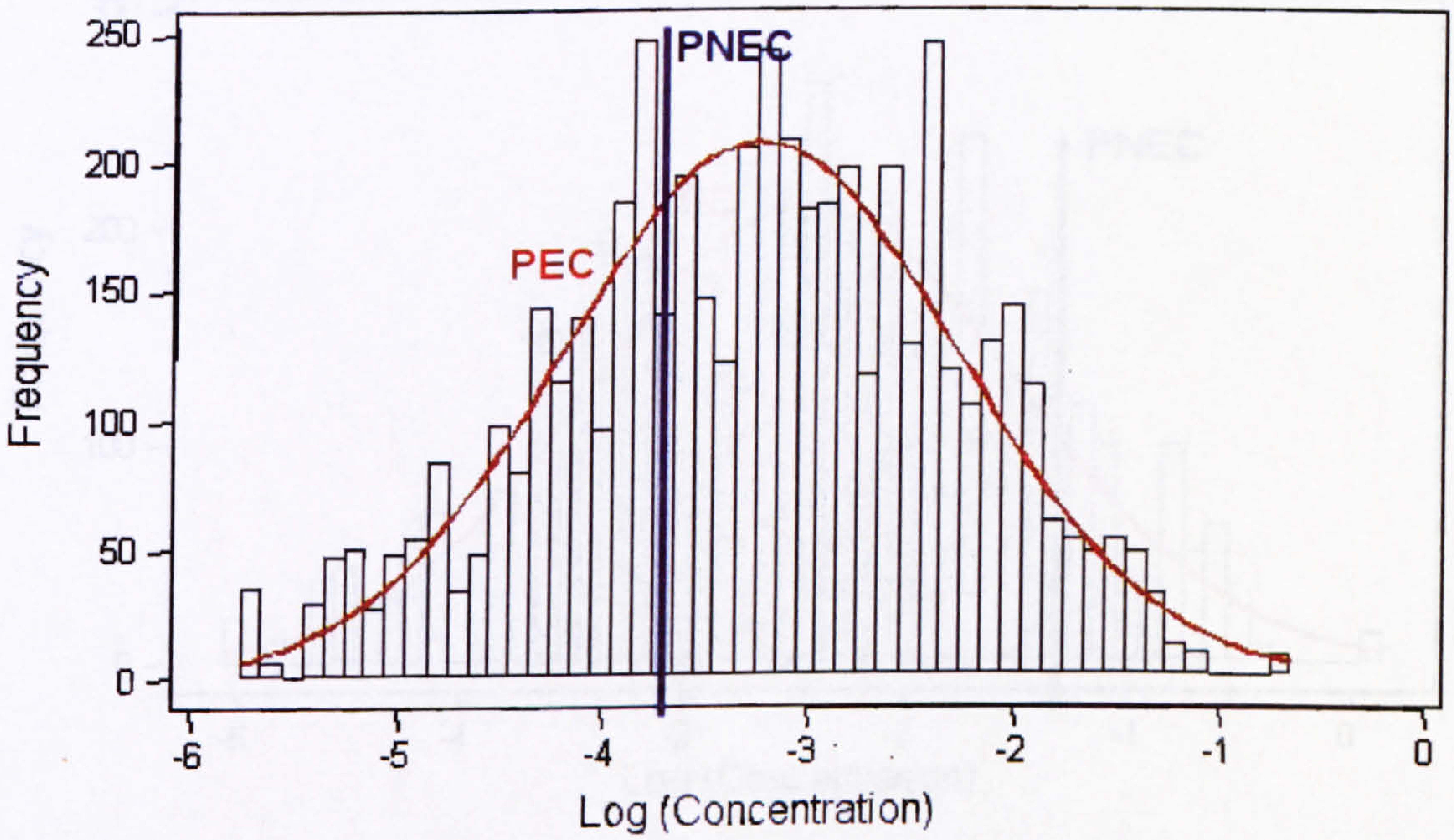

Figure 5.8 - Histogram of probabilistic exposure concentrations (in Log units) for substance 672D, with deterministic PNEC indicated

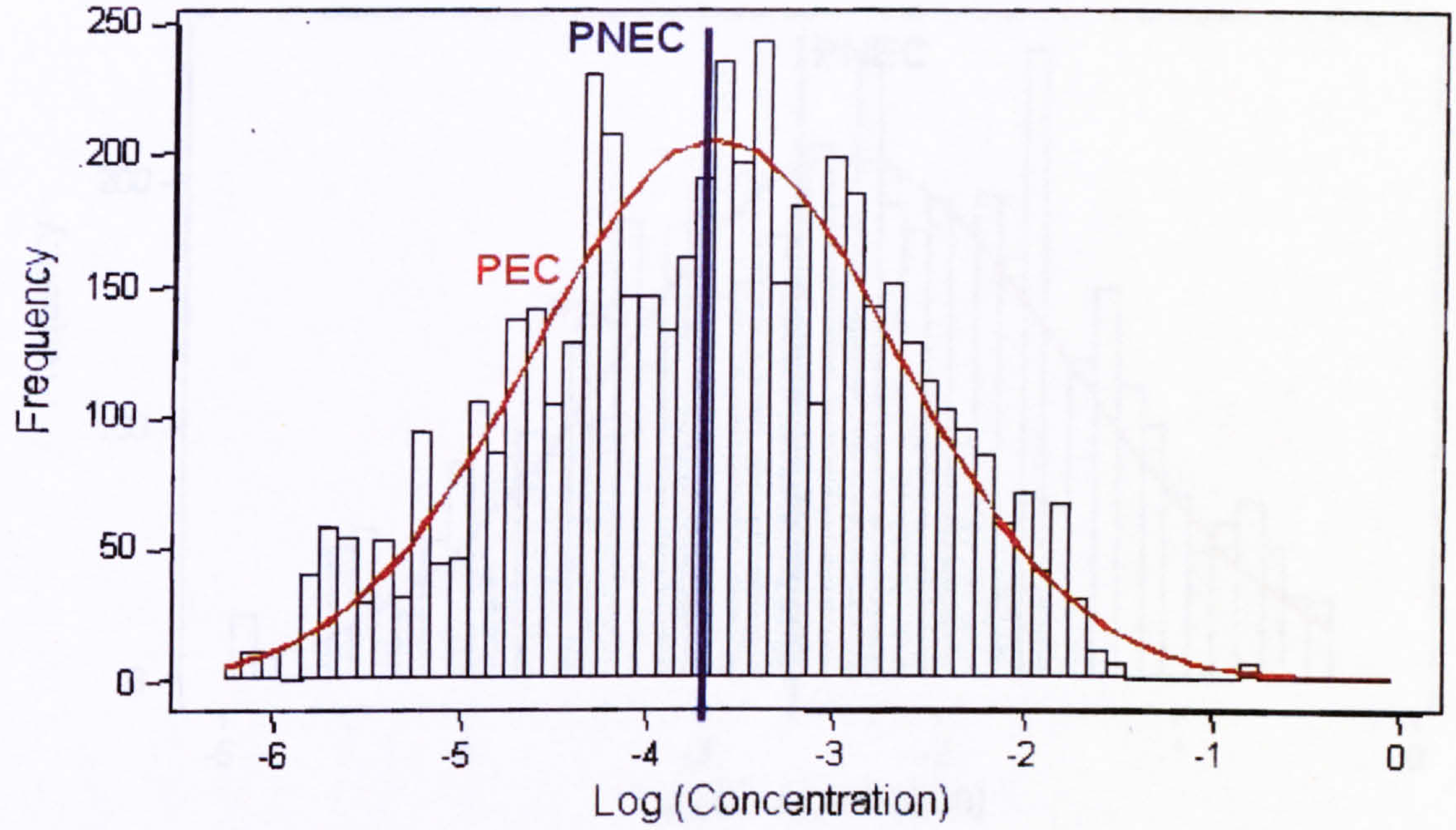

Figure 5.9 - Histogram of probabilistic exposure concentrations (in Log units) for substance 724D, with deterministic PNEC indicated

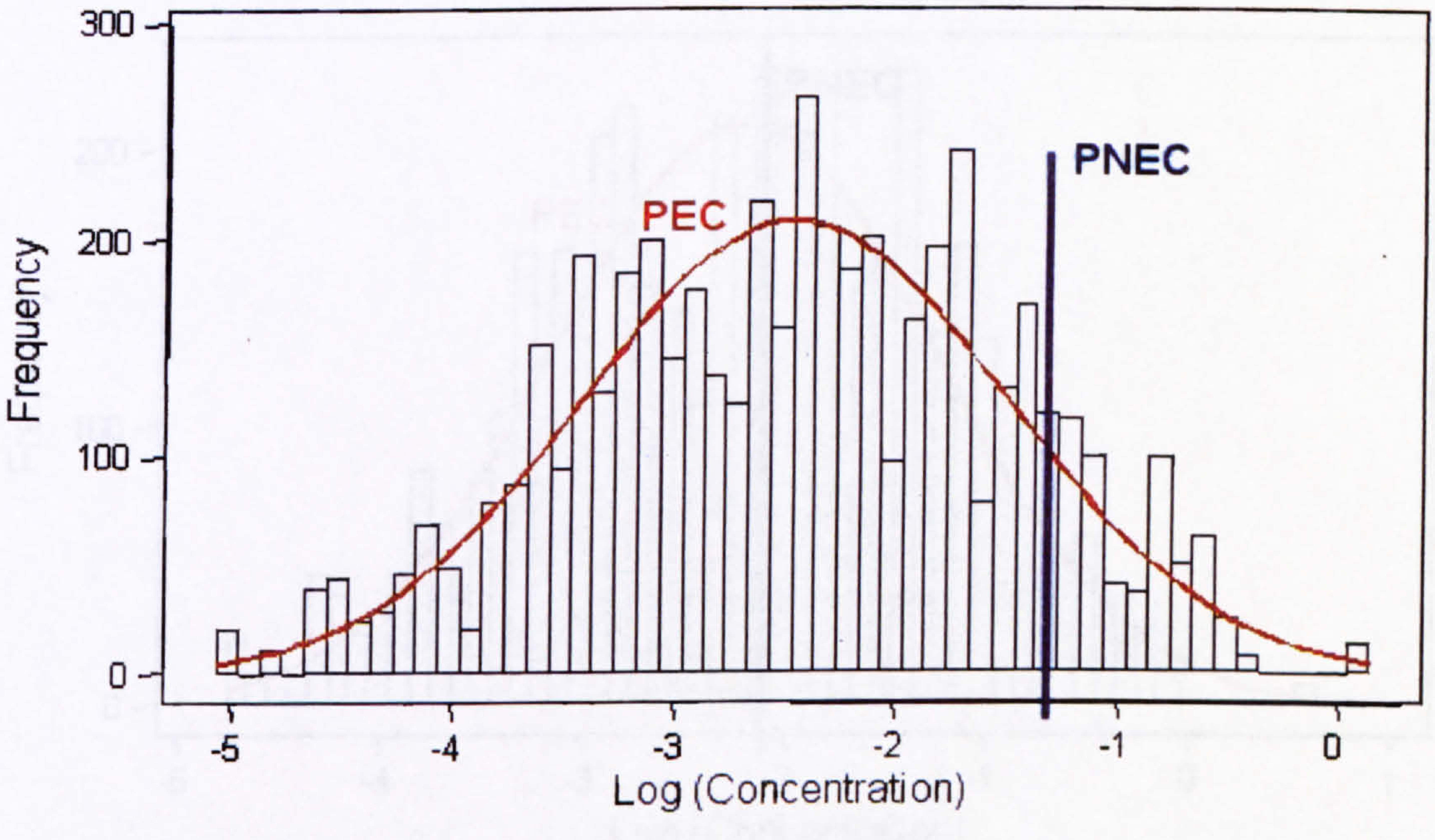

Figure 5.10 - Histogram of probabilistic exposure concentrations (in Log units) for substance 745D, with deterministic PNEC indicated

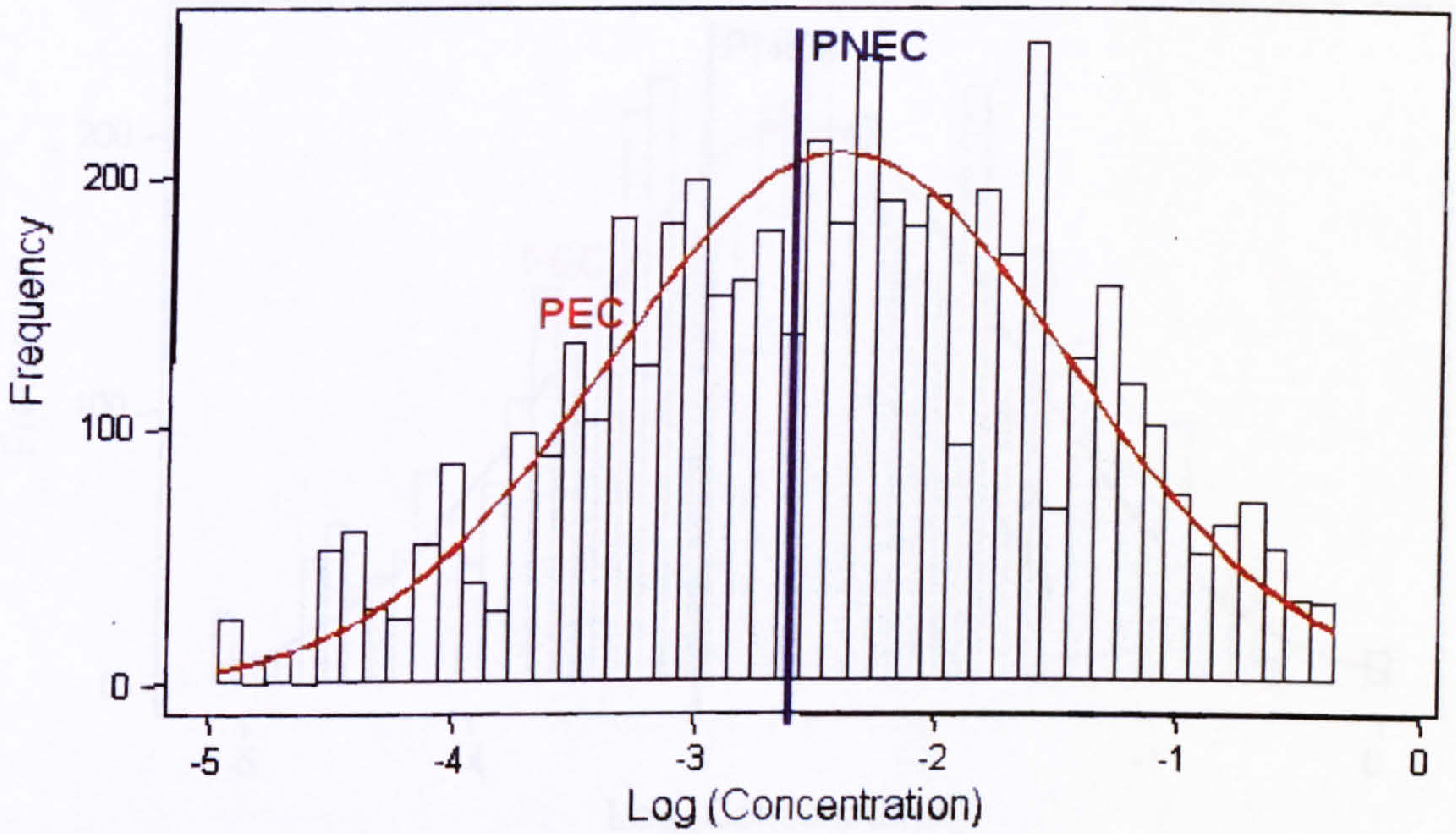

Figure 5.11 - Histogram of probabilistic exposure concentrations (in Log units) for substance 803D, with deterministic PNEC indicated

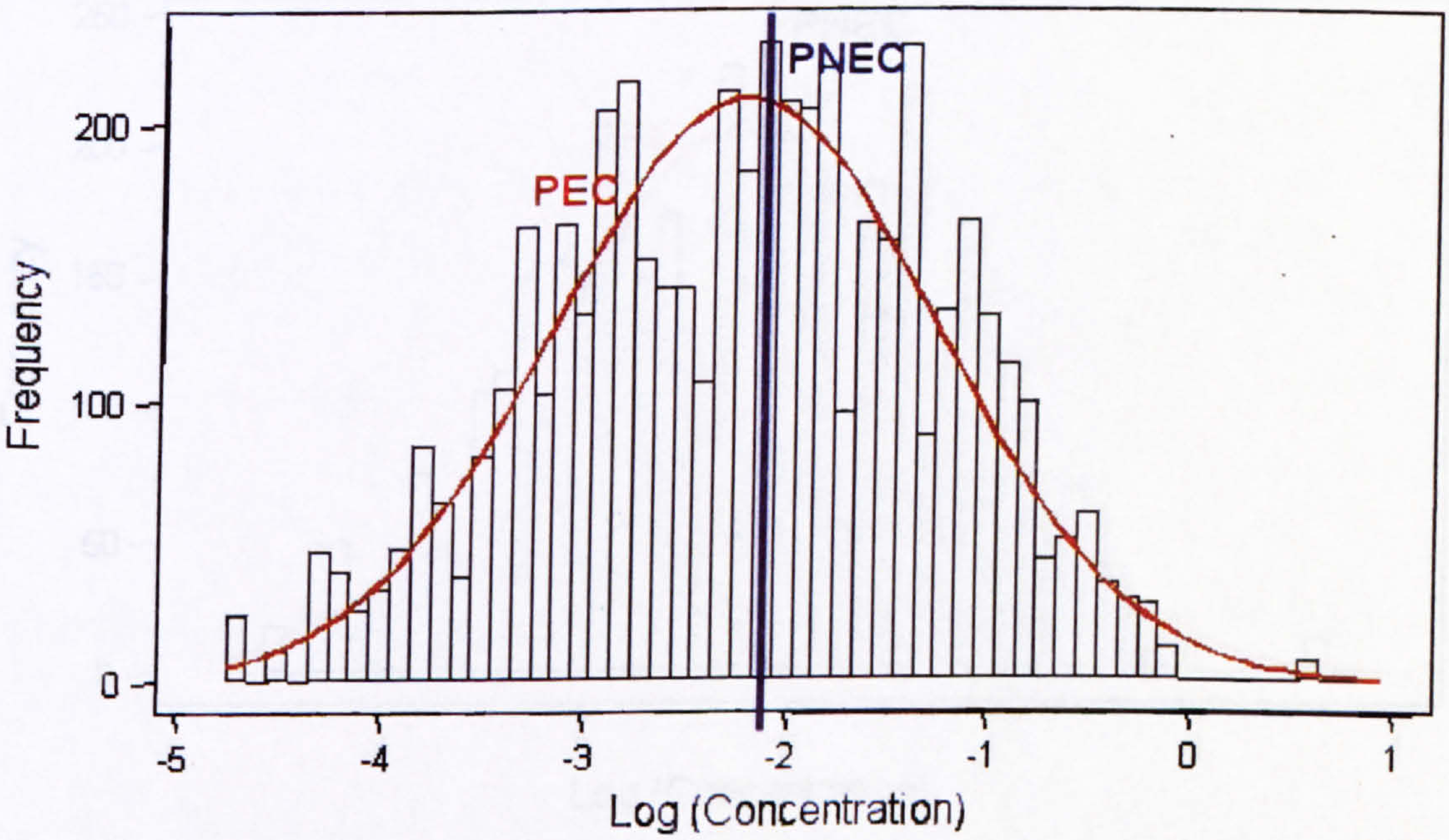

Figure 5.12 - Histogram of probabilistic exposure concentrations (in Log units) for substance 827D, with deterministic PNEC indicated

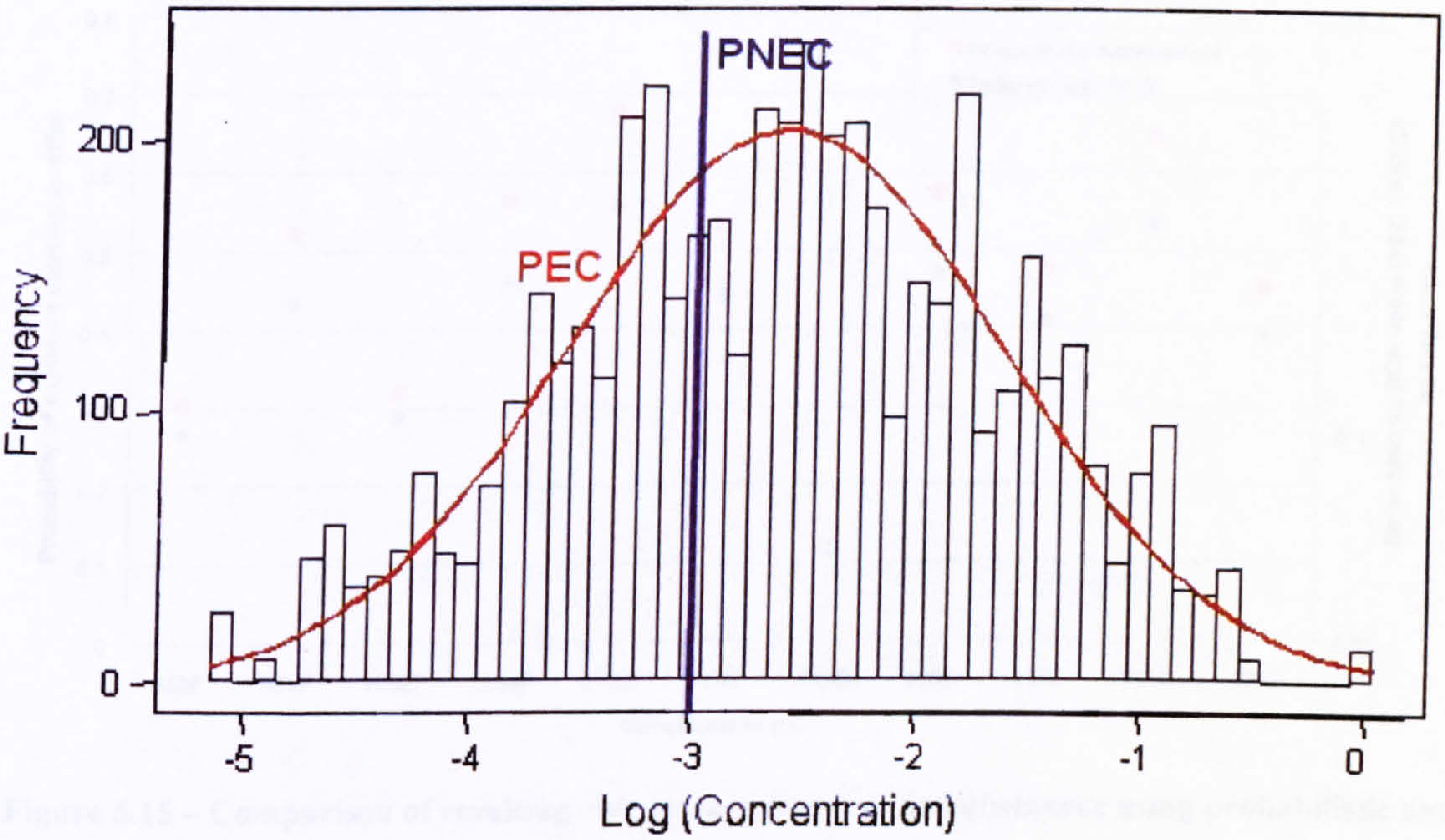

Figure 5.13 - Histogram of probabilistic exposure concentrations (in Log units) for substance 969D, with deterministic PNEC indicated

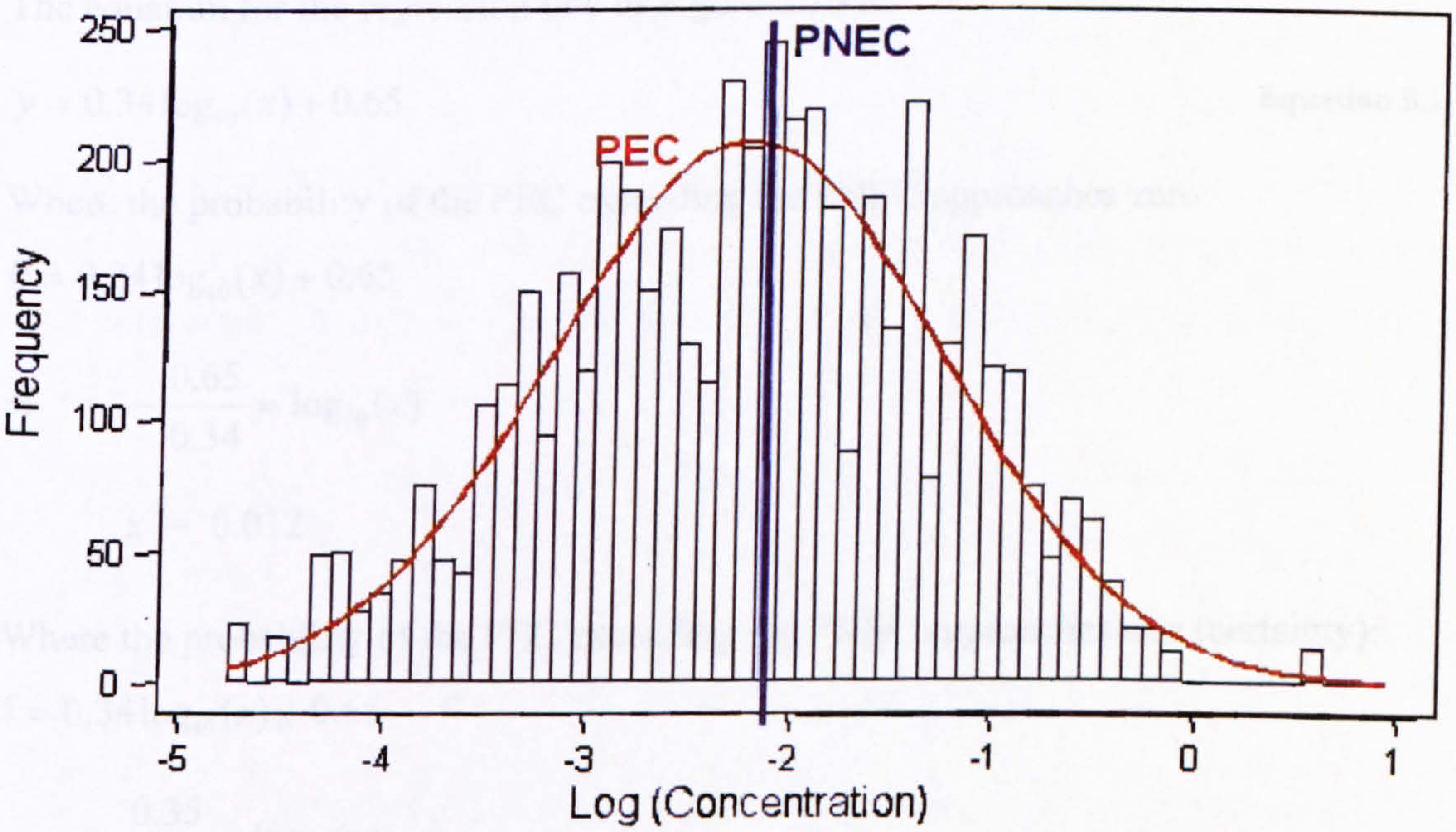

Figure 5.14 - Histogram of probabilistic exposure concentrations (in Log units) for substance 970D, with deterministic PNEC indicated

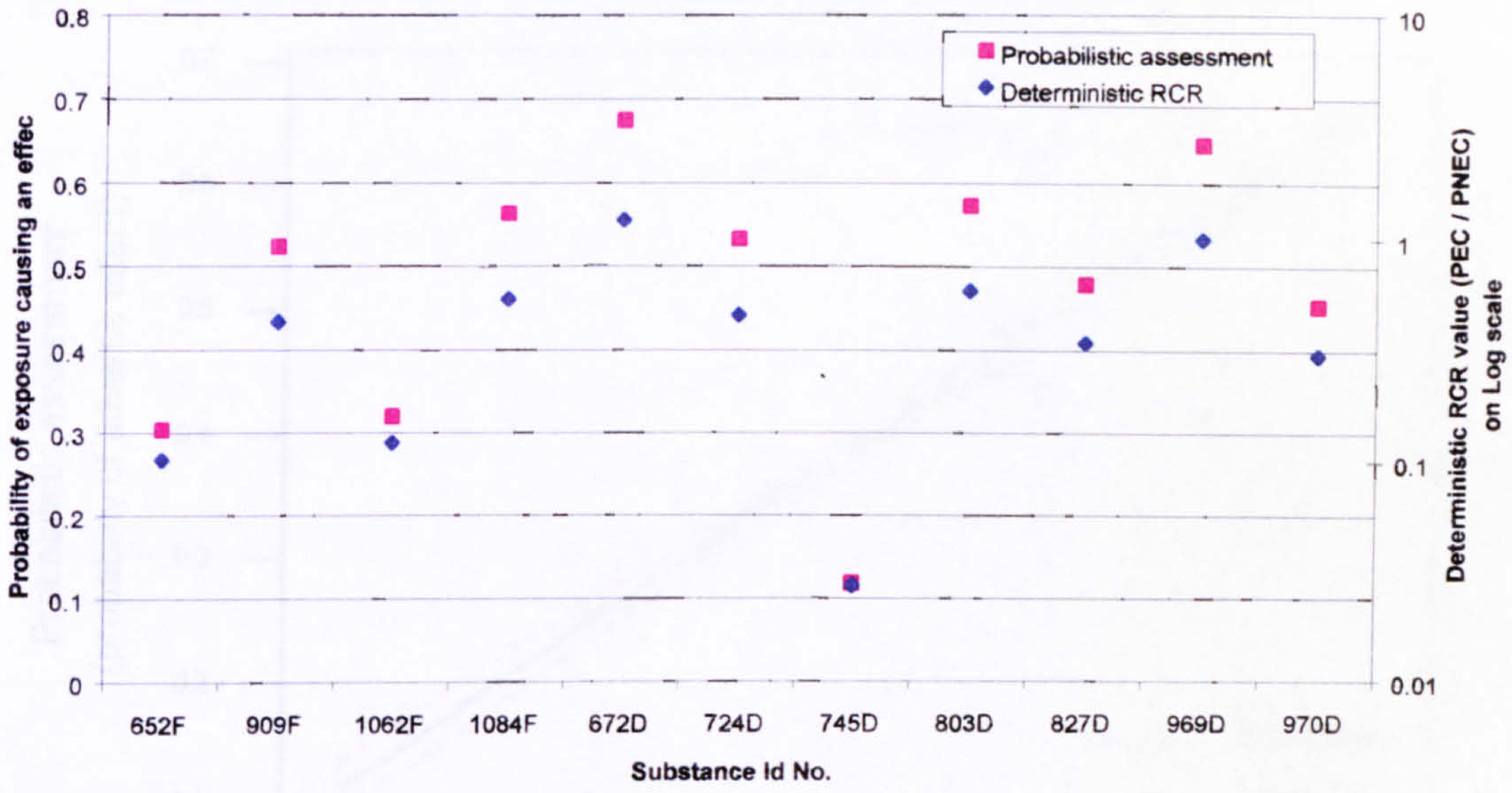

Figure 5.15 – Comparison of resulting risk assessments for test substances using probabilistic and deterministic methods, deterministic RCR on log scale

The differing results using the two risk assessment methods were examined to assess any correlation (Figure 5.16). A correlation was found exhibiting reasonable fit and by analysing the trend the limits were derived. Deterministic RCR values and the corresponding probability of the PEC exceeding the PNEC were calculated.

The equation for the regression line in Figure 5.16 is:

$$y = 0.34\log_{10}(x) + 0.65$$ **Equation 5.1**

Where the probability of the PEC exceeding the PNEC approaches zero:

$$0 = 0.34\log_{10}(x) + 0.65$$

$$\Rightarrow \quad -\frac{0.65}{0.34} = \log_{10}(x)$$

$$x = 0.012$$

Where the probability of the PEC exceeding the PNEC approaches one (certainty):

$$1 = 0.34\log_{10}(x) + 0.65$$

$$\Rightarrow \quad \frac{0.35}{0.34} = \log_{10}(x)$$

$$x = 10.70$$

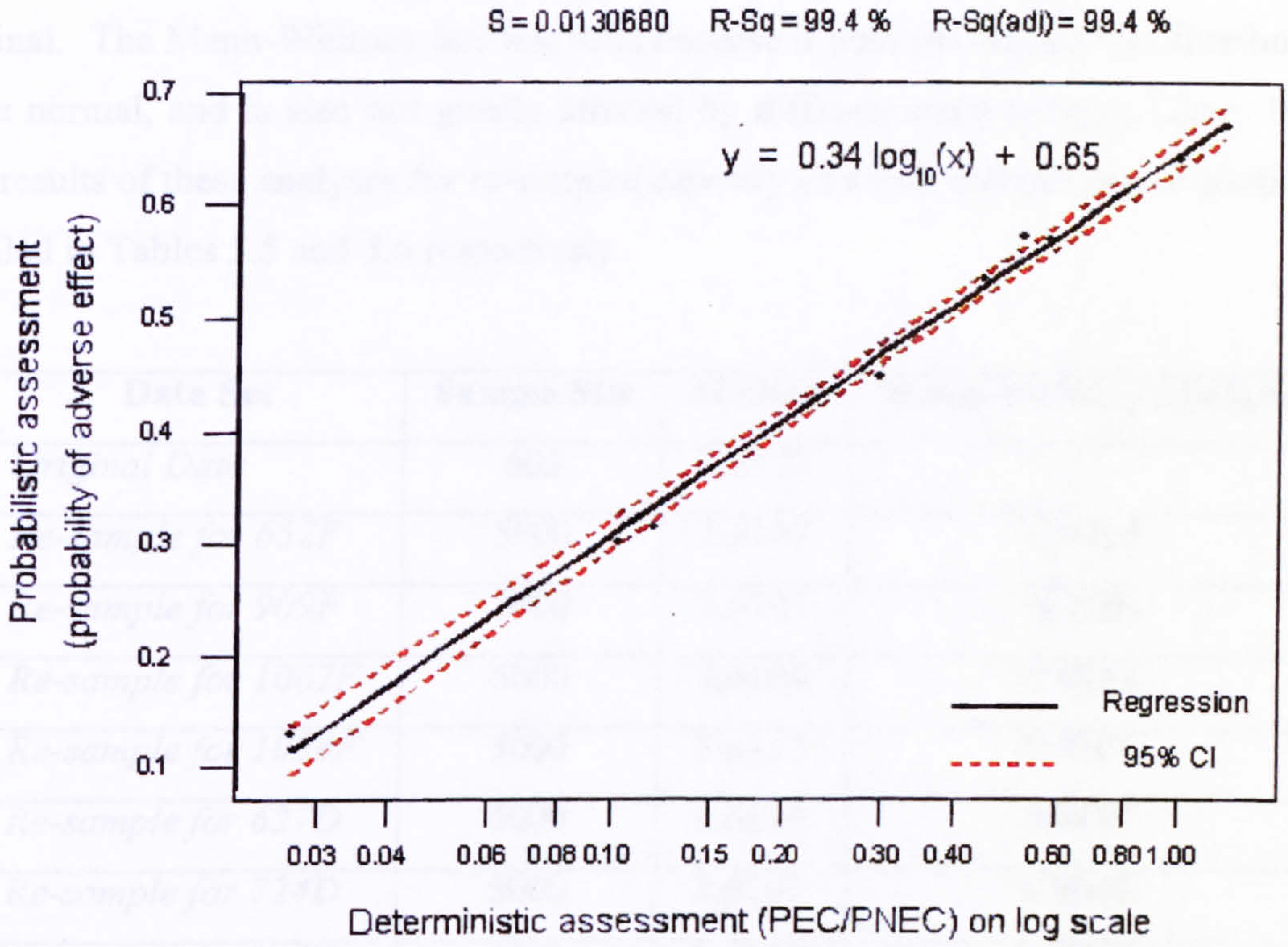

Figure 5.16 – Regression line for risk assessments using deterministic and probabilistic methods
S - related to S^2 which is an estimate of the variance in the data considering any relationship
R-Sq, R-Sq(adj) –the proportion of variation in the response data explained by predictors

Therefore when the RCR > 10.0 there is a very high probability that effects may occur and when the RCR < 0.01 there is a very low probability of adverse effects occurring. It should be remembered however, that an assessment factor of 1000 has been used to account for uncertainty in the effect assessment based on organism tests on three trophic levels. It can also be calculated that for a deterministic RCR value of 1, the probability of adverse effects is 0.65, and for an RCR of 0.1, the probability would be 0.31 (Table 5.4).

Deterministic RCR value	0.02	0.05	0.1	0.5	1	5	10
Probabilistic of adverse effects	0.07	0.21	0.31	0.55	0.65	0.89	0.99

Table 5.4 – Probability of adverse effects associated with deterministic RCR values

Retrospectively the re-sampled data for the two STP parameters were each compared to the original distributions to confirm that the re-sampling method was reproducing the distributions accurately. The Mann-Whitney test, a two-sample rank test of the equality of two population medians, was used to compare each re-sampled data set to the original. The Mann-Whitney test was used because it does not require the distributions to be normal, and is also not greatly affected by different sized samples (Zarr, 1996). The results of these analyses for re-sampled capacity of a STP and dilution available are detailed in Tables 5.5 and 5.6 respectively.

Data Set	Sample Size	Median	Mann-Whitney Statistic
Original Data	605	3.6117	-
Re-sample for 652F	5000	3.6167	0.9924
Re-sample for 909F	5000	3.6107	0.7596
Re-sample for 1062F	5000	3.6180	0.9927
Re-sample for 1084F	5000	3.6117	0.9867
Re-sample for 627D	5000	3.6114	0.9597
Re-sample for 724D	5000	3.6107	0.9048
Re-sample for 745D	5000	3.5877	0.7727
Re-sample for 803D	5000	3.6153	0.9210
Re-sample for 827D	5000	3.6091	0.7607
Re-sample for 969D	5000	3.6117	0.9082
Re-sample for 970D	5000	3.6114	0.9648

Table 5.5 – Mann-Whitney test results for re-sampled capacity of STP data
Mann-Whitney test statistic is the resulting significance level of the test

The majority of the re-sampled data sets for STP capacity produce a Mann-Whitney statistic > 0.90 (909F, 745D, 827D perform badly in the test) suggesting, at a 10% CI, that the samples are not significantly, statistically different. For the re-sampled dilution data only two samples produce a Mann-Whitney statistic > 0.90 (724D, 803D perform well in the test), with some values only achieving a Mann-Whitney statistic of about 0.50.

Data Set	Sample Size	Median	Mann-Whitney Statistic
Original Data	605	0.7132	-
Re-sample for 652F	5000	0.7073	0.7576
Re-sample for 909F	5000	0.7424	0.5371
Re-sample for 1062F	5000	0.7116	0.8683
Re-sample for 1084F	5000	0.7042	0.8102
Re-sample for 627D	5000	0.7272	0.6488
Re-sample for 724D	5000	0.7088	0.9240
Re-sample for 745D	5000	0.6986	0.4850
Re-sample for 803D	5000	0.7129	0.9397
Re-sample for 827D	5000	0.7116	0.7066
Re-sample for 969D	5000	0.7042	0.6236
Re-sample for 970D	5000	0.7160	0.7332

Table 5.6 - Mann-Whitney test results for re-sampled dilution available at discharge from STP data Mann-Whitney test statistic is the resulting significance level of the test

Re-sampling the data does not require characterisation of a distribution, however it may result in some features in a distribution becoming accentuated. Peaks and troughs differing from the overall trend of the distribution may be emphasised in the re-sampling process, increasing the importance of these features in analyses. Although the Mann-Whitney test statistic is said to be independent of the normality of a distribution, making it suitable for comparisons such as this, it should be noted that the dilution data were clearly non-normal, while the capacity data did exhibit a bell-shaped distribution.

To check the significance of the different re-sampled distributions and their effect on the overall results, probabilistic assessments were run on all the test substances using the same re-sampled data sets for the STP capacity and dilution in each case. The re-sampled parameter data sets for substance 803D were selected because both parameter distributions scored over 0.90 in the Mann-Whitney tests. Table 5.7 details the results of the probabilistic assessments using individually re-sampled parameter distributions, and the single distributions used for substance 803D.

The results from both sets of assessments are very similar, the difference between the resulting risk assessments being, at the most 1.4%. Although the Mann-Whitney test statistics were unable to support the re-sampled data sets as being statistically similar, it has been shown that the two re-sampled data sets showing greatest similarity (those for substance 803D) when used for each assessment produced similar results to those where the data were re-sampled for each test substance.

ID No.	Probability that PEC exceeds PNEC (%) †Individual re-samples	 ‡Single re-sample	Difference
652F	30.4	30.2	0.2
909F	52.3	52.0	0.3
1062F	32.0	31.6	0.4
1084F	56.3	57.7	1.4
672D	67.4	67.3	0.1
724D	53.2	53.8	0.6
745D	11.8	13.2	1.4
803D	57.3	*57.3*	-
827D	47.9	48.6	0.7
969D	64.6	64.3	0.3
970D	45.3	45.3	0.0

Table 5.7- Comparison of probabilistic risk assessment results

† Individually re-sampled data sets for each assessment

‡ Re-sampled data sets for 803D used for each individual assessment

5.5 SUMMARY AND DISCUSSION

Probabilistic risk assessment methods allow distributions for parameters to be used in the calculations rather than estimate point values which may be average, worse case, etc. Such probabilistic assessments for a number of test substances have been demonstrated. The assessments were performed for new substances, focusing on the local scale. The values for the parameters for the capacity of a STP and the dilution factor available at point of discharge were re-sampled from the data that were collated for England and Wales (Chapter 4).

In all cases $PEClocal_{water}$ values generated using the generic EU default parameters resulted in lower values than the median value generated using probabilistic methods.

The deterministic value was generally a factor of 3 less than the probabilistic PEC value. This means that for England and Wales using the distributions obtained the risk assessment system under-predicts the concentration in the environment.

The results of probabilistic risk assessments are easily visualised and more readily compared than the results of deterministic assessments. Since a probability or percentage value can be quoted as part of the risk assessment the results are more transparent than deterministic risk assessment methods. Whilst the limit levels (>1, >10, >100 etc.) of the deterministic system seem arbitrary in nature, probabilistic assessments can be used to ensure a chosen level of protection (i.e.95%) with declared confidence limits.

Examination of the relation between the results of the two types of risk assessment shows a linear relationship exists. With the distributions and assumptions used in these assessments it was found that where the deterministic RCR value was greater than 10.0 there would be a high probability of adverse environmental effects, while for assessments with an RCR less than 0.01 there is a very low probability of harm.

For the European notification system the generic risk assessments outlined in the TGD must be performed, however probabilistic investigations such as those presented here help to show the level of protection offered by the deterministic risk assessments for specific situations. Probabilistic assessments based on distributions for two parameters in England and Wales have been presented demonstrating that on average a high level of concentration in the environment can be expected for all the substances examined.

CHAPTER 6

NEW SUBSTANCES RAPID ASSESSMENT TOOL

SUMMARY

The development of a rapid risk assessment tool for new substances in response to a real need by the UK competent authority for the European notification system is described. Preliminary contour plots of risk depending on a substance's Koc value and the soluble fraction discharged from the STP are examined.

The procedure was refined to include consideration of the SimpleTreat model, measuring local exposure in water rather than risk. These analyses illustrate that local exposure is independent of the Henry's law constant (HENRY) at low values of HENRY. These findings have led to the final development of the rapid assessment tool for new cosmetic substances, where HENRY value is less than 0.1. The contour plots allow risk assessments for substances to be rapidly performed based on the Kow, and toxicity alone.

6 NEW SUBSTANCES RAPID ASSESSMENT TOOL

6.1 INTRODUCTION

In the work discussed in this thesis a model was developed to perform multiple assessments simultaneously, which made it possible to perform probabilistic risk assessments. Real data were collated for two parameters in the model and the distributions from these data sets used to calculate probabilistic assessments for a number of substances. The results from generic assessments were then reviewed in the light of the probabilistic results obtained.

Such probabilistic assessments use a great deal of data and require distributions to be assigned for various parameters, the more data available the closer the assigned distributions will model real scenarios. There is however a trend to infer more, from less data, particularly at the preliminary risk assessment stages in the control of substances.

Contour plots were developed to demonstrate the effects of parameter on the resulting PEC and RCR values. The application of the NEXCES spreadsheet tool has made it feasible, for the first time, to calculating the many hundreds of points required to construct these contour plots in an efficient manner.

In response to a real need by the UK Competent Authority for the European Notification System, contour plots were developed demonstrating the effects of the n-octanol/water partition coefficient (*Kow*) and the toxicity of a substance on the resulting toxicity, as measured by the generic risk assessment process.

6.2 PRELIMINARY INVESTIGATIONS

The ability of the NEXCES spreadsheet to generate many assessments based on small changes to the input data has already been demonstrated earlier in this work. The ease with which many assessments can be calculated allowed the effect on the risk assessments of incremental variations in the physico-chemical properties to be examined.

6.2.1 Method

To generate a contour plot, a matrix of values needs to be constructed. The column headings represent one of the parameters being investigated while the rows represent the other. The values within the matrix are the resulting risk values calculated using the NEXCES spreadsheet to perform assessment using the parameter values detailed by the relevant row and column (Table 6.1).

RCR		Soluble fraction discharged					
		0.75	**0.80**	**0.85**	**0.90**	**0.95**	**1.00**
log Koc	**4.75**	28.82	30.74	32.66	34.58	36.50	38.43
	5.00	27.17	28.99	30.80	32.61	34.42	36.23
	5.25	24.67	26.31	27.96	29.60	31.25	32.89
	5.50	21.20	22.61	24.02	25.44	26.85	28.26
	5.75	16.95	18.08	19.21	20.34	21.47	22.60
	6.00	12.50	13.33	14.17	15.00	15.83	16.67

Table 6.1 - Part of a matrix used in the construction of a contour plot showing the effect of log *Koc* and from STP on the RCR value, e.g. the matrix value of 24.02 (highlighted) represents the RCR value calculated for a log *Koc* value of 5.50 and where the soluble fraction discharged was 0.85

6.2.2 Results

Initially contour plots were generated to demonstrate the effects of the physico-chemical properties of a substance on the RCR (Figure 6.1), that result from various combinations of log *Koc* and the soluble fraction discharged from the STP.

The values for the local aquatic compartment were calculated for a non-biodegradable test substance. A fixed emission volume was used and it was assumed that all of the local concentration ($Elocal_{water}$) went through a STP. In this initial stage the validity of these assumptions was not closely scrutinised. The contour plot clearly shows a steep increase in risk as log *Koc* decreases from 5.5 to about 4, and the higher the fraction of emissions directed to the STP effluent, the greater the risk. There is also a distinct plateau in the RCR value at any given emission fraction for log *Koc* values less than 3; a low *Koc* value indicates that a substance will partition into the aqueous phase more than the organic phase.

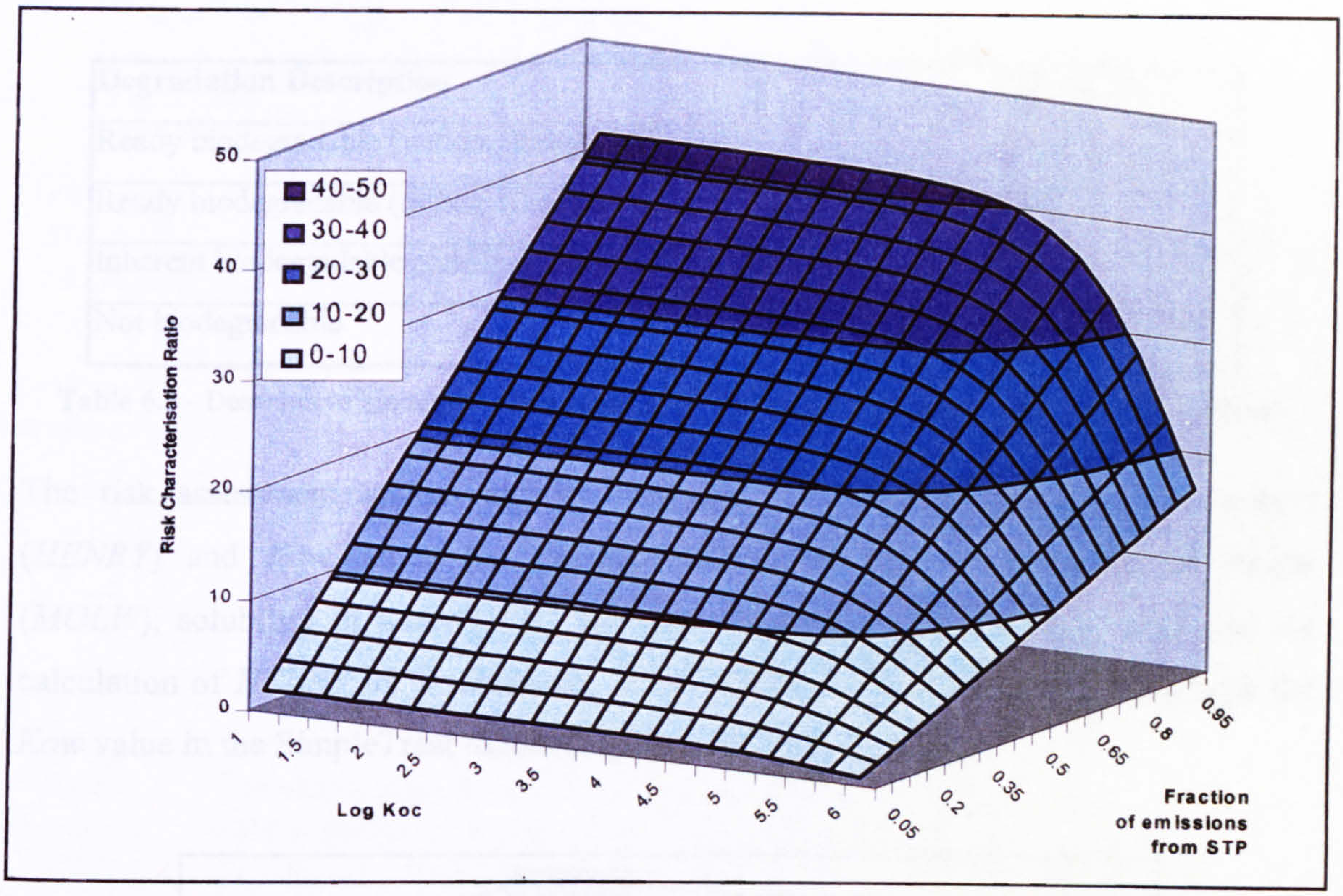

Figure 6.1 - Contour plot of the resulting risk for a test substance dependent upon the fraction emitted from the STP and the log *Koc*

The interrelation of the *Koc* value and the soluble fraction discharged from the STP was omitted from these early analyses, the *Koc* value is however used to calculate other partition constants in the STP model. At the time of these early investigations the details of the SimpleTreat model had not been obtained. It should also be noted that an assumption was made on the level of toxicity so that the RCR values could be calculated.

6.3 DETAILED INVESTIGATIONS

The fate and behaviour of a substance in a STP is modelled by the SimpleTreat spreadsheet (Struijs *et al.*, 1991). The TGD outlines a number of summary tables derived from the SimpleTreat model to allow risk assessors to look up the Henry's constant and n-octanol/water (*Kow*) partition coefficient for a substance and find the fraction of the influent that will be directed to air, water, or sludge (Appendix 10). The tables also detail the fraction of the substance that will be degraded and how much will be removed. Sets of summary tables are available for each level of biodegradability (Table 6.2).

Degradation Description	$Kbio_{stp}$ (h^{-1})
Ready biodegradable (within 10 day window)	1.0
Ready biodegradable (failing 10 day window, but within 28 days)	0.3
Inherent biodegradable (fulfilling specified criteria)	0.1
Not biodegradable	0.0

Table 6.2 - Descriptive biodegradation rates and the corresponding degradation rate constants

The risk assessment system can be expressed in terms of Henry's law constant (*HENRY*) and *Kow*, since the physico-chemical properties of molecular weight (*MOLW*), solubility in water (*SOL*) and vapour pressure (*VP*) are only used for the calculation of *HENRY* for a substance. The *HENRY* value is then used along with the *Kow* value in the SimpleTreat model (Figure 6.2).

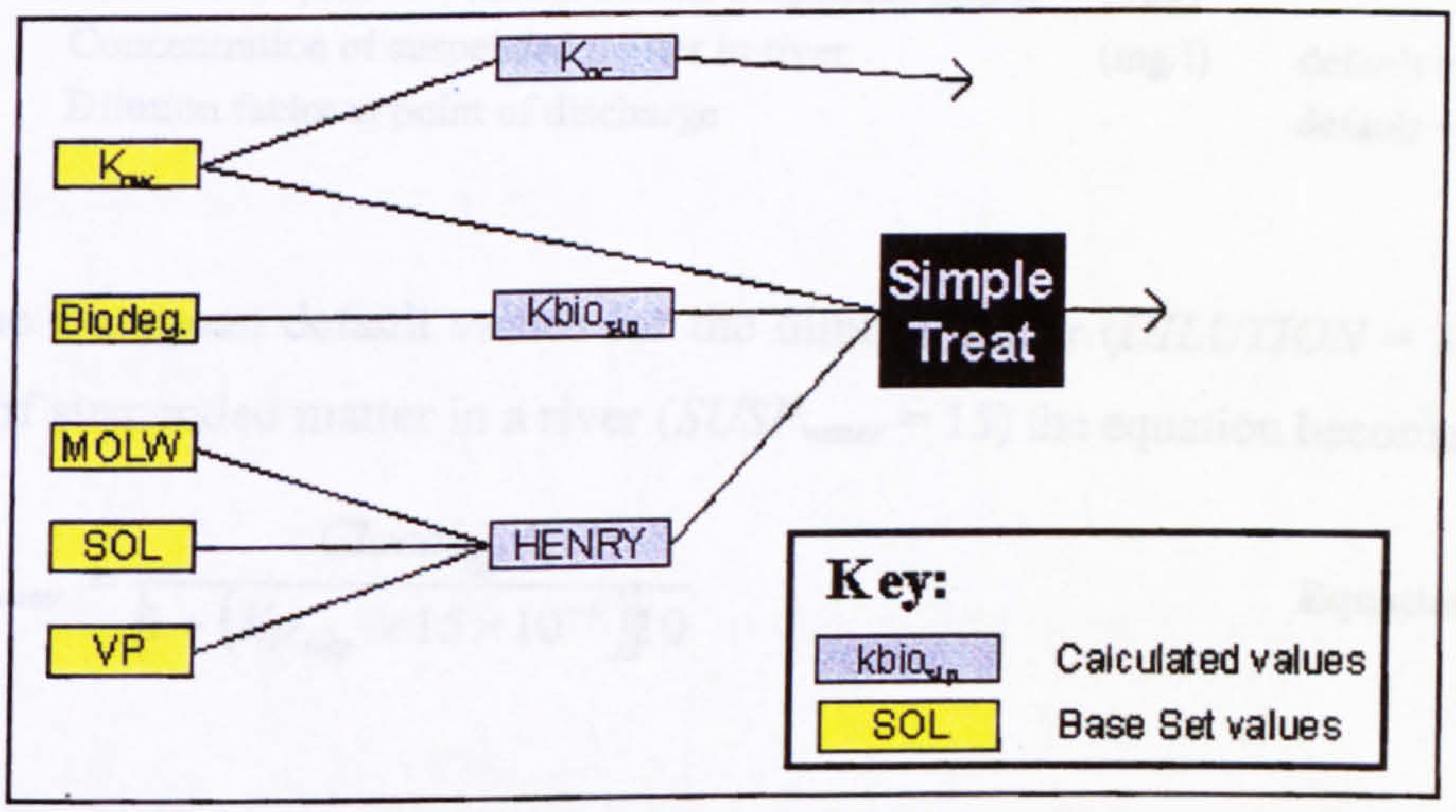

Figure 6.2 - Physico-chemical properties used in the risk assessment system

From the interrelation of the parameters it can be seen that for each level of biodegradation it should be possible to arrange the risk assessment in terms of the Henry's law constant, *HENRY* and *Kow*.

6.3.1 Deriving the local PEC for water

The risk assessment calculations were examined and the local PEC value for water was derived in terms of the physico-chemical properties, Henry's law constant and *Kow*. The PEC value for local water is defined as the sum of the concentration in local water ($Clocal_{water}$) and PEC for regional water ($PECregional_{water}$), which can be assumed to be negligible for new chemicals marketed at low volumes (Equation 6.1).

$$PEClocal_{water} = Clocal_{water} + PECregional_{water}$$ **Equation 6.1**

$$\Rightarrow \quad \boxed{PEClocal_{water} = Clocal_{water}}$$ **Equation 6.2**

$PEClocal_{water}$	Predicted environmental concentration during an episode	(mg/l)
$Clocal_{water}$	Local concentration in surface water during an emission episode	(mg/l)
$PECregional_{water}$	Regional or background concentration in surface water	(mg/l)

Therefore the PEC for local water is equivalent to the concentration in local water, which is calculated as detailed in Equation 6.3.

$$Clocal_{water} = \frac{Clocal_{eff}}{\left[1 + \left(Kp_{susp} \times SUSP_{water} \times 10^{-6}\right)\right] DILUTION}$$ **Equation 6.3**

$Clocal_{water}$	Local concentration in surface water	(mg/l)	
$Clocal_{eff}$	Concentration of substance in the STP effluent	(mg/l)	
Kp_{susp}	Solid-water partition coefficient for suspended matter	(l/kg)	
$SUSP_{water}$	Concentration of suspended matter in river	(mg/l)	default = 15
$DILUTION$	Dilution factor at point of discharge	-	default = 10

Substituting the European default values for the dilution factor ($DILUTION = 10$) and concentration of suspended matter in a river ($SUSP_{water} = 15$) the equation becomes:

$$\Rightarrow \quad Clocal_{water} = \frac{Clocal_{eff}}{\left[1 + \left(Kp_{susp} \times 15 \times 10^{-6}\right)\right] 10}$$ **Equation 6.4**

The solid-water partition coefficient for suspended matter (Kp_{susp}) is defined as follows:

$$Kp_{susp} = Foc_{susp} \cdot Koc$$ **Equation 6.5**

Kp_{susp}	Solid-water partition coefficient for suspended matter	(l/kg)	
Foc_{susp}	Weight fraction of organic carbon in suspended matter	(kg/kg)	default = 0.1
Koc	Carbon normalised partition coefficient	(l/kg)	

Substituting Equation 6.5 into Equation 6.4:

$$\Rightarrow \qquad Clocal_{water} = \frac{Clocal_{eff}}{\left[1+\left(0.1\times Koc\times 15\times 10^{-6}\right)\right]10} \qquad \textbf{Equation 6.6}$$

The *Koc* value can be approximated from the *Kow* value using QSARs, the European default QSAR for 'predominantly hydrophobic' substances is detailed in Equation 6.8:

$$LogKoc = 0.81\cdot LogKow + 0.1 \qquad \textbf{Equation 6.7}$$

Where,

$$Koc = 10^{LogKoc} \qquad \textbf{Equation 6.8}$$

Koc	Carbon normalised partition coefficient	*(l/kg)*
LogKoc	Carbon normalised partition coefficient in log units	
LogKow	n-octanol-water partition coefficient in log units	

Substituting Equation 6.8 into Equation 6.7:

$$Koc = 10^{(0.81\times LogKow+0.1)} \qquad \textbf{Equation 6.9}$$

Substituting Equation 6.9 into Equation 6.6 the concentration in local becomes:

$$Clocal_{water} = \frac{Clocal_{eff}}{\left[1+\left(10^{(0.81\times LogKow-0.1)}\times 1.5\times 10^{-6}\right)\right]10} \qquad \textbf{Equation 6.10}$$

Equation 6.11 is used to calculate the concentration of the substance in the STP effluent ($Clocal_{eff}$):

$$Clocal_{eff} = Clocal_{\inf}\cdot Fstp_{water} \qquad \textbf{Equation 6.11}$$

$Clocal_{eff}$	Concentration of substance in STP effluent	(mg/l)
$Clocal_{inf}$	Concentration in untreated wastewater	(mg/l)
$Fstp_{water}$	Fraction of emission directed to water by STP, from SimpleTreat model	

The concentration of the substance in the STP influent ($Clocal_{inf}$) in Equation 6.11 is calculated using the following equation:

$$Clocal_{\inf} = \frac{Elocal_{water} \cdot 10^6}{EFFLUENT_{stp}}$$ **Equation 6.12**

$Clocal_{inf}$	Concentration of substance in untreated wastewater	(mg/l)	
$Elocal_{water}$	Local emission rate to water during an episode	(kg/d)	
$EFFLUENT_{stp}$	Effluent discharge rate of the STP	(l/d)	default = 2,000,000

Substituting Equation 6.11 and 6.12 into Equation 6.10, and after entering the European default value for the effluent discharge rate of the STP ($EFFLUENT_{stp}$ = 2,000,000), the concentration in local water is given by the equation below:

$$Clocal_{water} = \frac{\left(\frac{Elocal_{water} \times 10^6}{2 \times 10^6}\right) \times Fstp_{water}}{\left[1 + \left(10^{(0.81 \times LogKow - 0.1)} \times 1.5 \times 10^{-6}\right)\right]10}$$ **Equation 6.13**

The fraction of emissions from the STP directed to water ($Fstp_{water}$) is calculated by the SimpleTreat model and is a function of Henry's law constant and *Kow*.

$$\Rightarrow \quad Clocal_{water} = \frac{Elocal_{water} \times 0.5 \times f(HENRY, Kow)}{\left[1 + \left(10^{(0.81 \times LogKow - 0.1)} \times 1.5 \times 10^{-6}\right)\right]10}$$ **Equation 6.14**

For new substances at low tonnages on the local scale the $PEClocal_{water}$ is equivalent to the concentration in local water ($Clocal_{water}$). The value for the local emissions of the substance ($Elocal_{water}$) in Equation 6.14 was set to unity, removing the value from the calculation. An $Elocal_{water}$ value of 1 represents approximately 200 tonnes of a domestic substance (Equation 6.15 and 6.16).

$$Elocal_{water} = Fmainsource \frac{1000}{Temission} \cdot RELEASE$$ **Equation 6.15**

$Elocal_{water}$	Local emission rate to water during an episode	(kg/d)
Fmainsource	Fraction of release at local main source	
Temission	Number of emission days per year	(d/yr)
RELEASE	Volume released	(kg/yr)

For a domestic substance, for instance, a cosmetic or a surfactant, the release volume can be assumed to be the whole tonnage because the entire volume of the substance will be washed down a drain or sink etc. at some point during the use phase. The number of emission days will be 365, and the fraction to be counted as the main local source is given as 0.002 by the TGD (EC, 1996a).

$$\Rightarrow \quad Elocal_{water} = 0.002 \cdot \frac{1000}{365} \cdot 200 \qquad \textbf{Equation 6.16}$$

$$\Rightarrow \quad Elocal_{water} = 1.096 \qquad \textbf{Equation 6.17}$$

Thus for other emission concentrations the resulting $Clocal_{water}$ and hence $PEClocal_{water}$ values can be calculated from a factor representing the real $Elocal_{water}$ value to obtain the actual value for the $PEClocal_{water}$.

It has been demonstrated how the $Clocal_{water}$, and hence $PEClocal_{water}$ under the assumptions made, can be expressed as a function of the values *HENRY* and *Kow*:

$$\boxed{PEClocal_{water} \equiv Clocal_{water} = \frac{0.5 \times f(HENRY, Kow)}{\left[1 + \left(10^{(0.81 \times LogKow - 0.1)} \times 1.5 \times 10^{-6}\right)\right]10}} \qquad \textbf{Equation 6.18}$$

6.3.2 Results

Graphs were constructed (Figures 6.3-6.6), one for each category of biodegradability, showing the effects of Henry's law constant and *Kow* on the resulting $PEClocal_{water}$ value. By presenting the predicted concentration in local water an assumption on the magnitude of toxicity was not required.

A feature of all the graphs is a plateau in the $PEClocal_{water}$ at low values for Henry's law constant (-1 to -4 log units). The Henry's law constant gives an indication into which of the two phases, air and water, a substance is likely to partition. Substances with low values for Henry's law constant will tend to partition into the aqueous phase, and as the graphs demonstrate for any given *Kow* value there is little change in the $PEClocal_{water}$ for Henry's law constants between -1 and -4 log units.

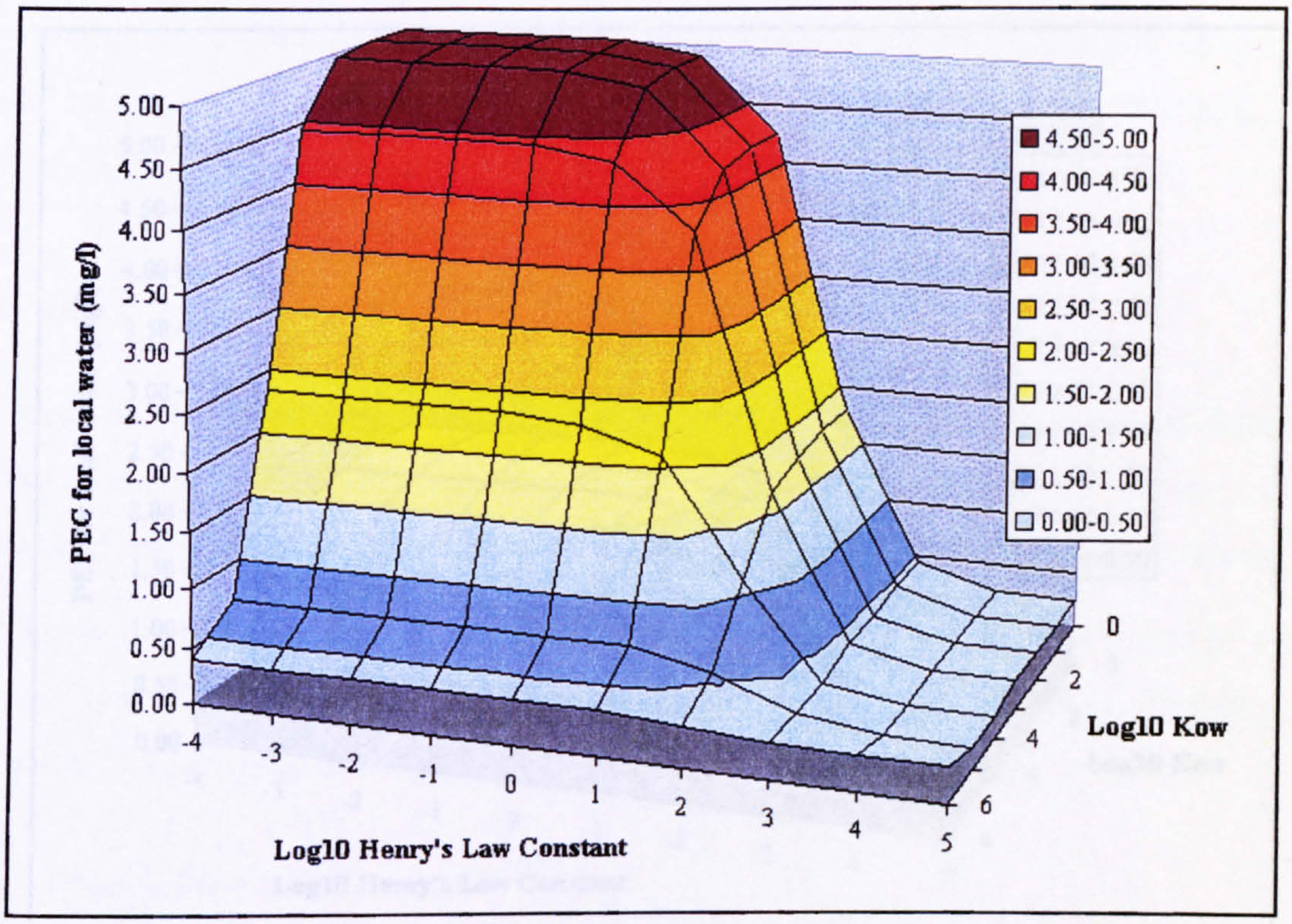

Figure 6.3 - Contour plot of the local aquatic PEC for non-biodegradable, substances dependent upon Henry's law constant and log *Kow*

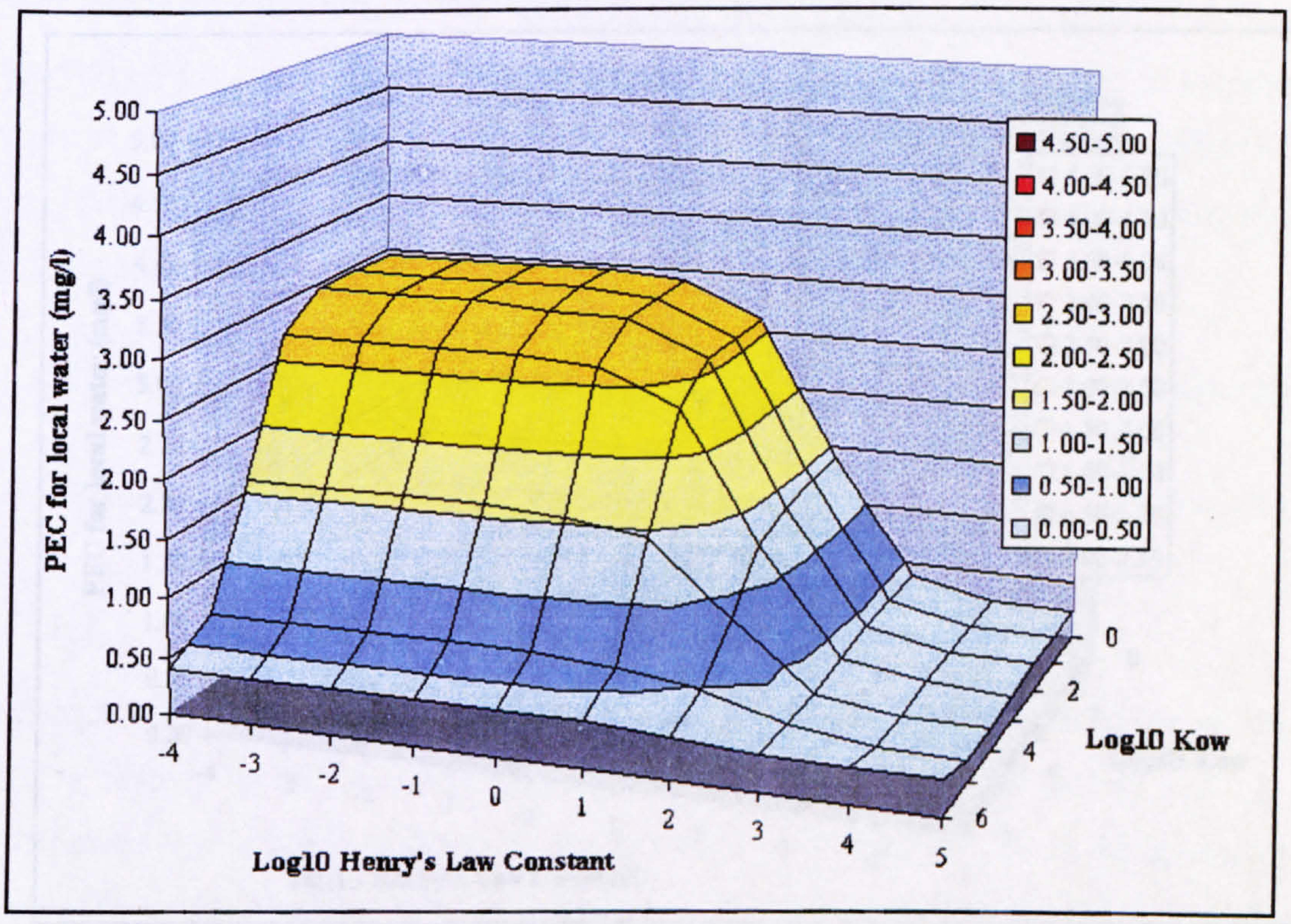

Figure 6.4 - Contour plot of the local aquatic PEC for inherently biodegradable, substances dependent upon Henry's law constant and log *Kow*

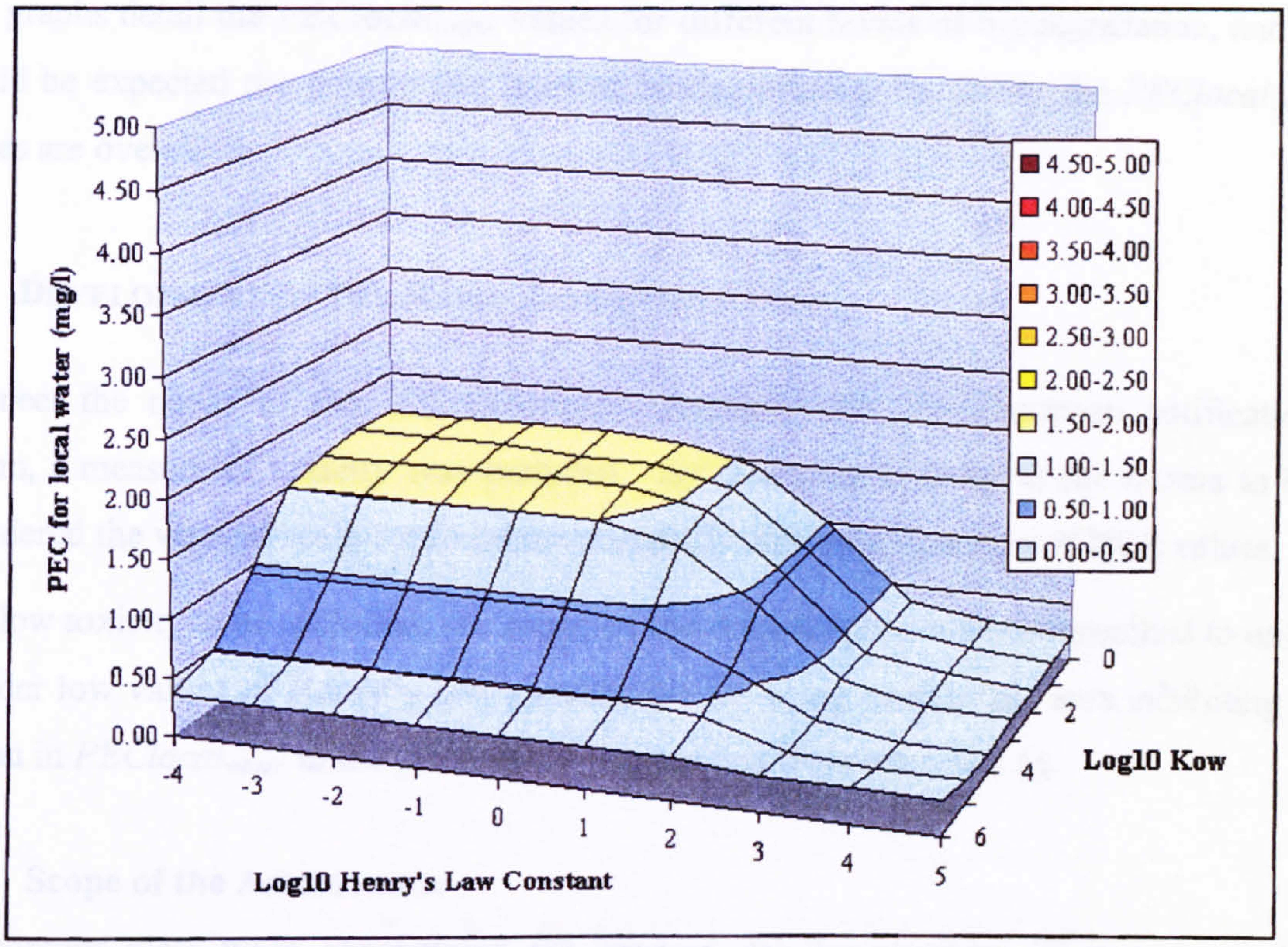

Figure 6.5 - Contour plot of the local aquatic PEC for readily biodegradable (outside 10-day window), substances dependent upon Henry's law constant and log *Kow*

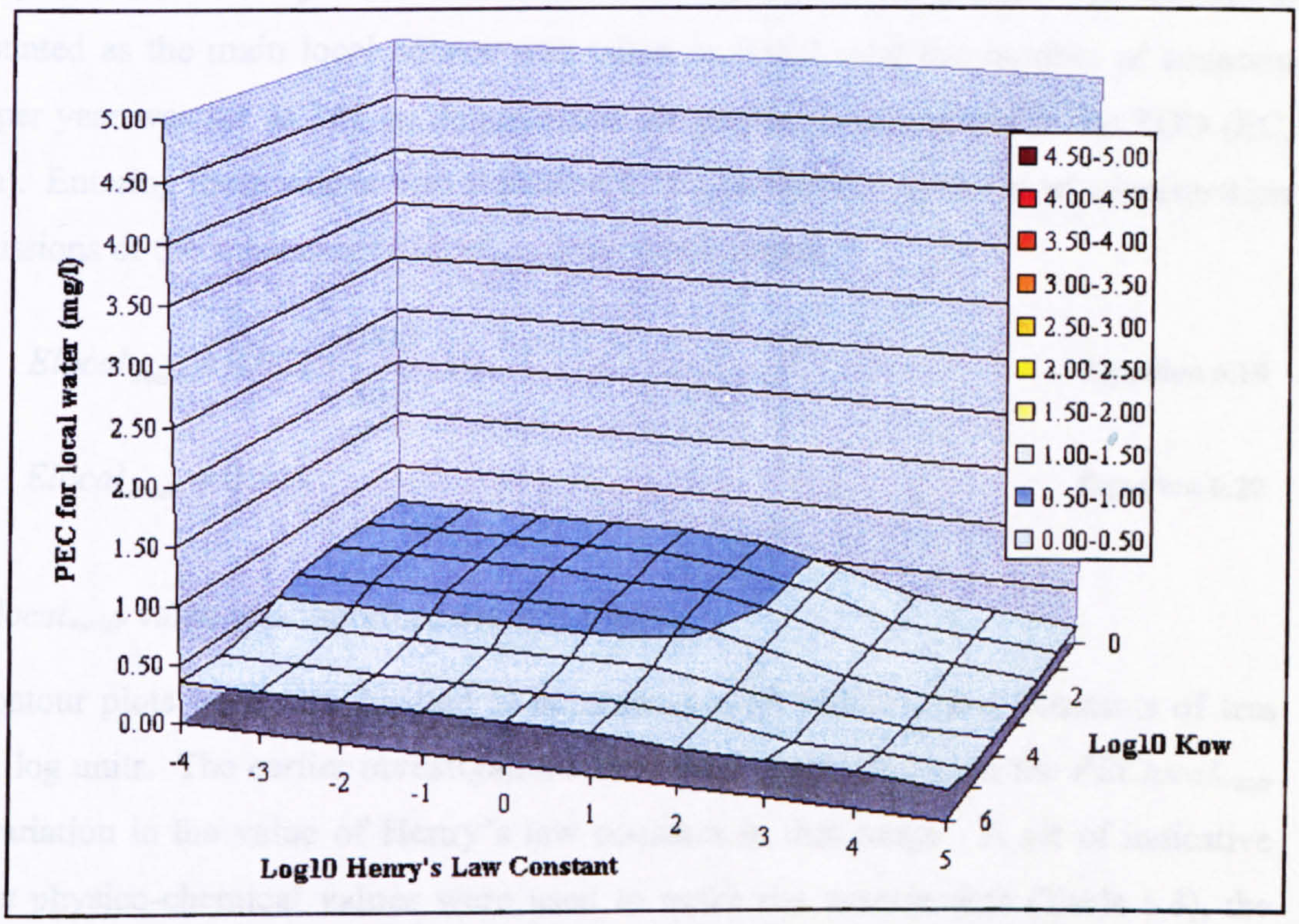

Figure 6.6 - Contour plot of the local aquatic PEC for readily biodegradable (inside 10-day window), substances dependent upon Henry's law constant and log *Kow*

The graphs detail the $PEClocal_{water}$ values for different levels of biodegradation, and as would be expected the greater the level of biodegradation the lower the $PEClocal_{water}$ values are overall.

6.4 DEVELOPMENT OF THE RAPID ASSESSMENT TOOL

To meet the needs of the UK Competent Authority for the European notification system, a measure of toxicity was included. By including toxicity in the factors to be considered the vertical scale could be meaningfully displayed in terms of RCR values.

To allow toxicity to be included, the scope of the contour plots were constrained to only consider low values of Henry's law constant (-1 to -4 log units), that area exhibiting a plateau in $PEClocal_{water}$ in the previous investigations (Figures 6.3-6.6).

6.4.1 Scope of the Assessments

The contour plots were constructed for generic risk assessments of new domestic substances, with no regional concentration. It was assumed that the volume on the market would be 10 tonnes (the *base set* threshold volume) and that the volume in its entirety would eventually enter the environment during the use phase. The fraction to be counted as the main local source was taken as 0.002, and the number of emission days per year was set as 365 as documented for domestic substances in the TGD (EC, 1996a). Entering these values into Equation 6.15 (Section 6.3.1) the local concentration of emissions of the substance ($Elocal_{water}$) were calculated.

$$\Rightarrow \quad Elocal_{water} = 0.002 \cdot \frac{1000}{365} \cdot 10 \qquad \textbf{Equation 6.19}$$

$$\Rightarrow \quad Elocal_{water} = 0.548 \qquad \textbf{Equation 6.20}$$

The $Elocal_{water}$ value was therefore set at 0.5 kg/d.

The contour plots were also limited to substances with Henry's law constants of less than -1 log units. The earlier investigations showed limited effects on the $PEClocal_{water}$ from variation in the value of Henry's law constant in this range. A set of indicative *base set* physico-chemical values were used to make the assessments (Table 6.3), the physico-chemical values were selected to ensure the resulting Henry's law constant was less than -1 log unit. The level of toxicity of the substance, as measured by the value for the lowest toxicity test value was varied along with the *Koc* value to produce contour plots for each level of biodegradability.

Parameter	Units	Value
MOLW	g/mol	600
VP	Pa	0.0005
SOL	mg/l	164
HENRY	Pa m^3/mol	0.0018
Kow	~	*Note 1*
Biodeg	~	*Note 2*
Min. LC_{50}	mg/l	*Note 3*
Volume in EU	Tonnes/Yr	10
Chemical Class	~	Predom. Hydro.
PECregional$_{water}$	mg/l	0.0
Elocal$_{water}$	kg/d	0.05

Table 6.3– Base Set data for the test substance

1. ***Kow* varied from 0.0 – 5.0 log units**
2. **A contour plot was produced for each level of biodegradability**
3. **The toxicity (minimum LC_{50} value) was varied on a log scale from 0.01 - 40**

6.4.2 Method

To generate the contour plots, a matrix of values was constructed for each level of biodegradability. The values within the matrix are the resulting risk values calculated using the NEXCES spreadsheet (Table 6.1).

RCR		Toxicity (mg/l) on a log scale					
		0.7	0.8	0.9	1	2	3
log *Koc*	1.0	3.57	3.12	2.77	2.51	1.25	0.83
	1.2	3.56	3.12	2.77	2.51	1.25	0.83
	1.4	3.56	3.12	2.77	2.51	1.25	0.83
	1.6	3.55	3.11	2.76	2.51	1.24	0.83
	1.8	3.54	3.10	2.76	2.50	1.24	0.83
	2.0	3.53	3.09	2.74	2.49	1.23	0.82

Table 6.4 - Example of part of a matrix for the construction of a contour plot showing the effect of log *Koc* and toxicity on the RCR value

6.4.3 Results

Four contour plots were produced, one for each level of biodegradability (Figures 6.7 - 6.10). The graphs show that as the level of biodegradability increases the respective RCR value is reduced. Higher levels of biodegradability will result in more of the substance being removed from the environment.

The graph for non-biodegradable substances (Figure 6.7), acts as a worse case scenario, and from this, it can be seen that if the substance is less toxic (i.e. the magnitude of the toxicity value is greater) the risk decreases (the RCR value is plotted on a log scale). The steps that are apparent in the contour plot are just a feature of the log scale for toxicity that was used to gain a visualisation of a greater range of toxicity values.

It is noted that as the *Kow* value increases above 3.5 the toxicity of the substance in water decreases rapidly. This occurs because substances with high *Kow* values will partition into the organic phase more than the aqueous phase, thus reducing the concentration and hence toxicity in the aqueous phase.

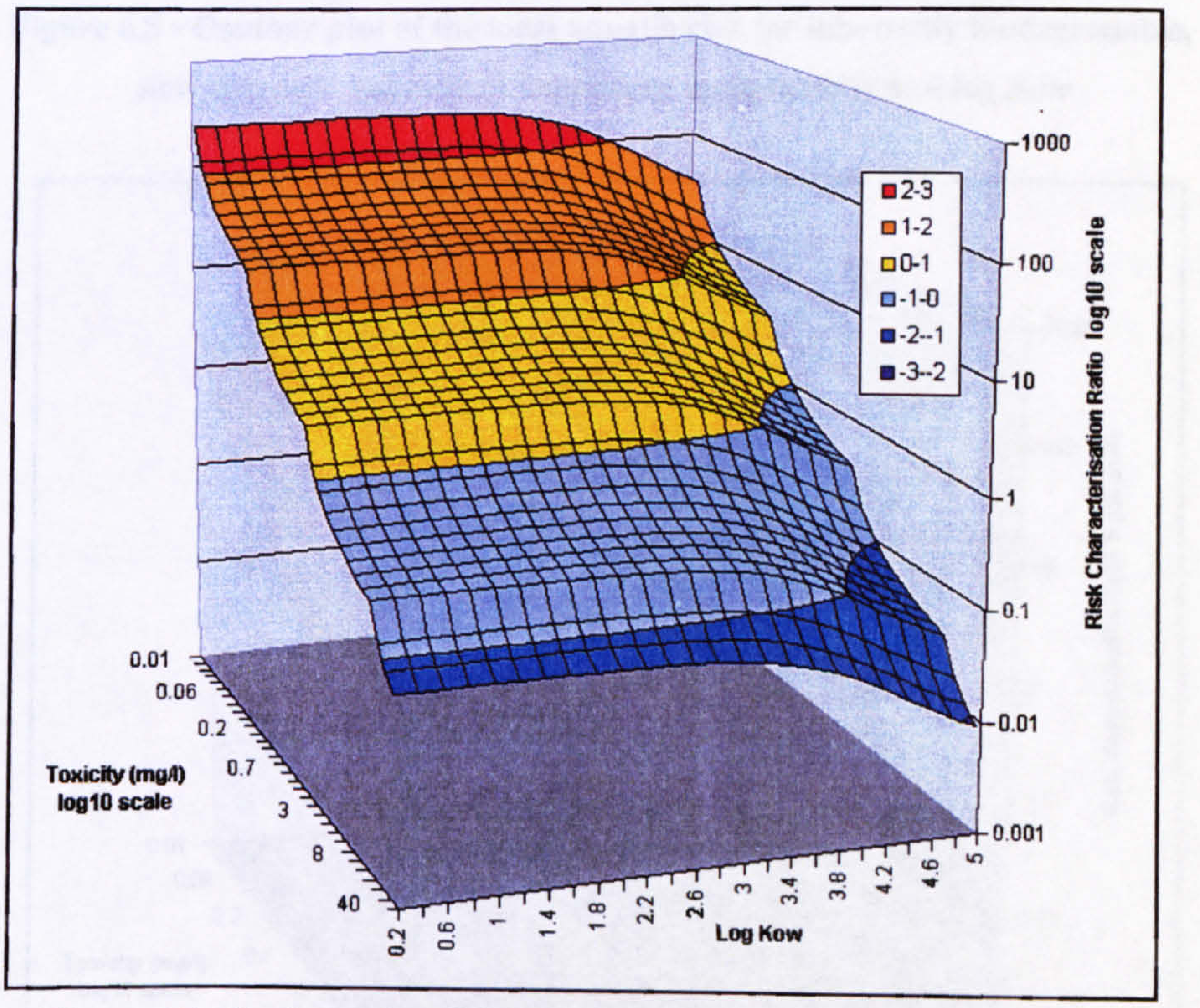

Figure 6.7 - Contour plot of the local aquatic risk for non-biodegradable, new domestic substances dependent upon toxicity and log *Kow*

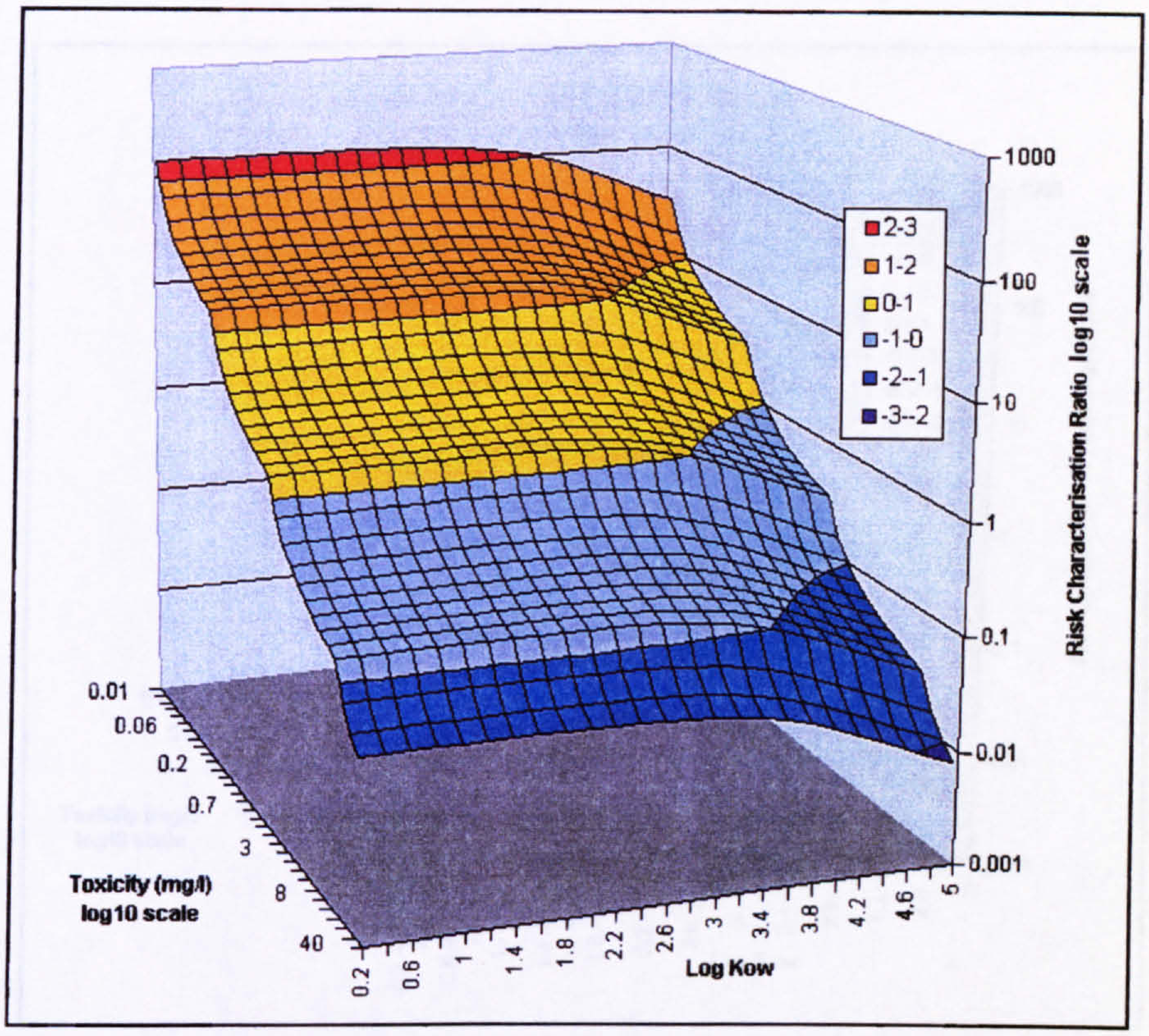

Figure 6.8 - Contour plot of the local aquatic risk for inherently biodegradable, new domestic substances dependent upon toxicity and log *Kow*

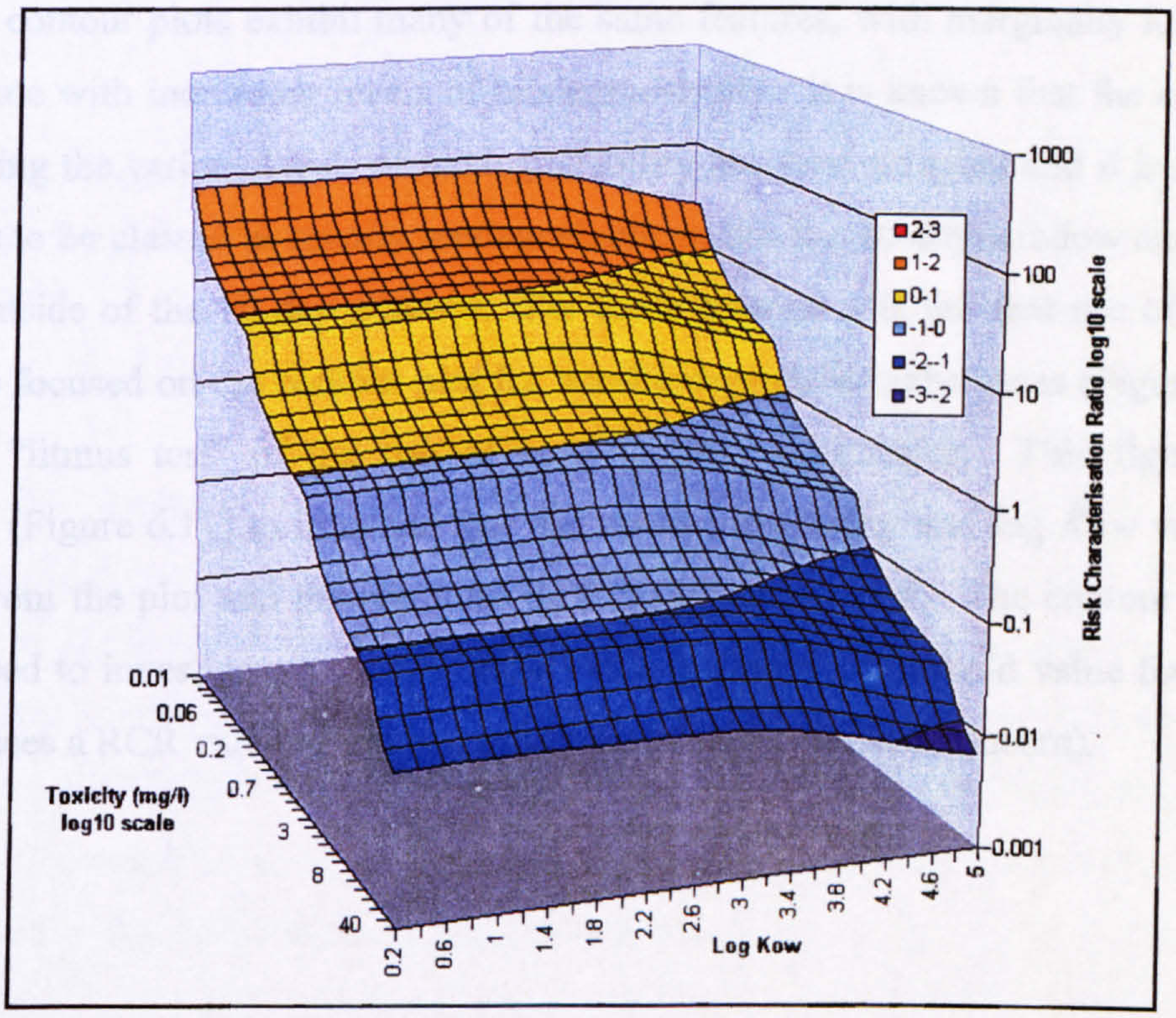

Figure 6.9 - Contour plot of the local aquatic risk for readily biodegradable (outside 10-day window), new domestic substances dependent upon toxicity and log *Kow*

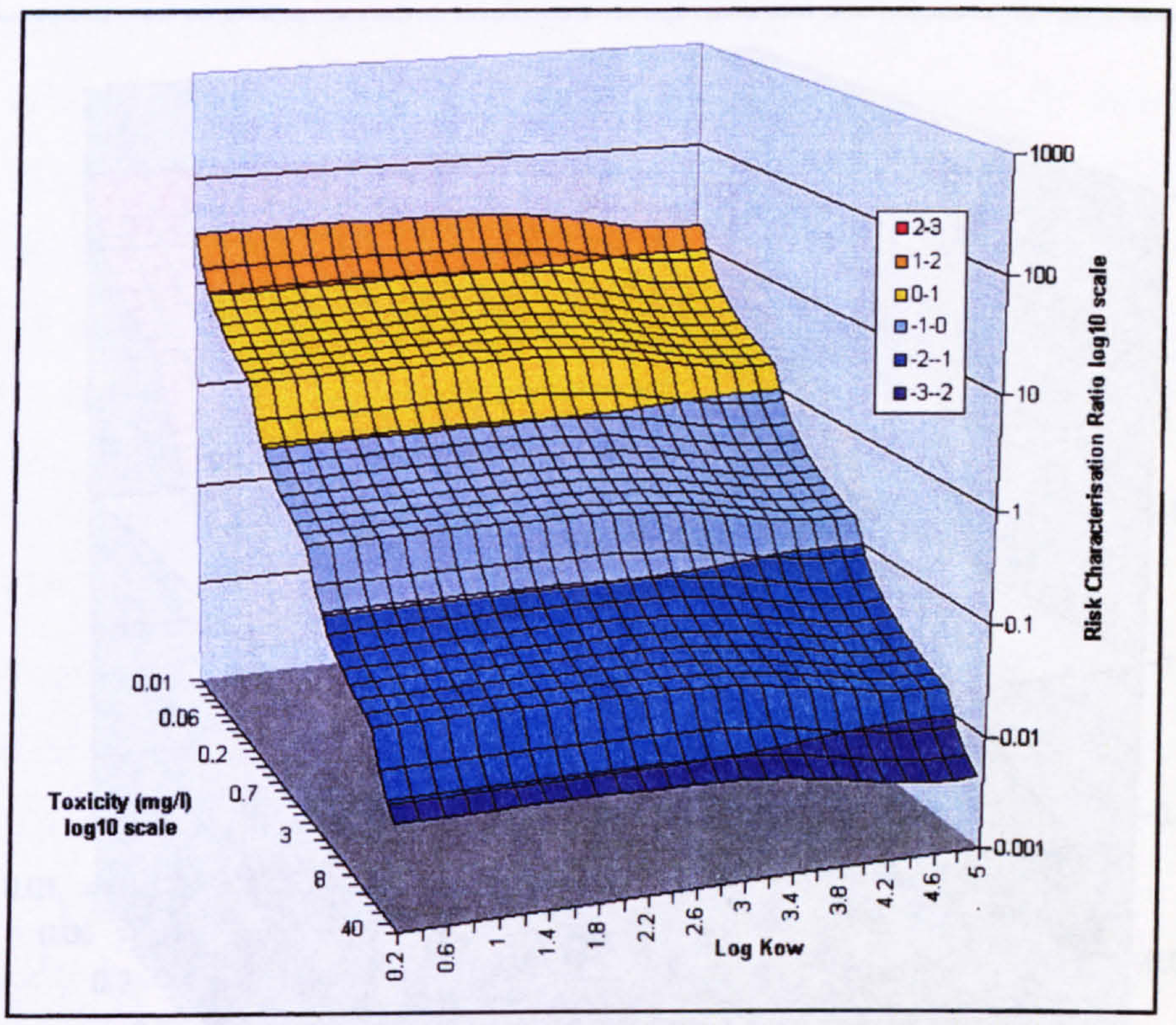

Figure 6.10 - Contour plot of the local aquatic risk for readily biodegradable (inside 10-day window), new domestic substances dependent upon toxicity and log *Kow*

The four contour plots exhibit many of the same features, with marginally lower RCR values scale with increasing levels of biodegradability. It is known that the criteria set for attaining the various levels of biodegradability are very stringent and it is rare for a substance to be classed as readily biodegradable within the 10-day window and slightly less so outside of the 10-day window. For these reasons it is felt that use of this tool should be focused on the contour plot for non-biodegradable substances (Figure 6.7) as a simple "litmus test" of the risk of new domestic substances. This figure is re-presented (Figure 6.11) to illustrate that the measured toxicity and log *Kow* values can be read from the plot and the resulting RCR value determined. The contour plot can also be used to investigate a specific *Kow* value to find the threshold value for toxicity that produces a RCR value of 1 (i.e. a substance of no immediate concern).

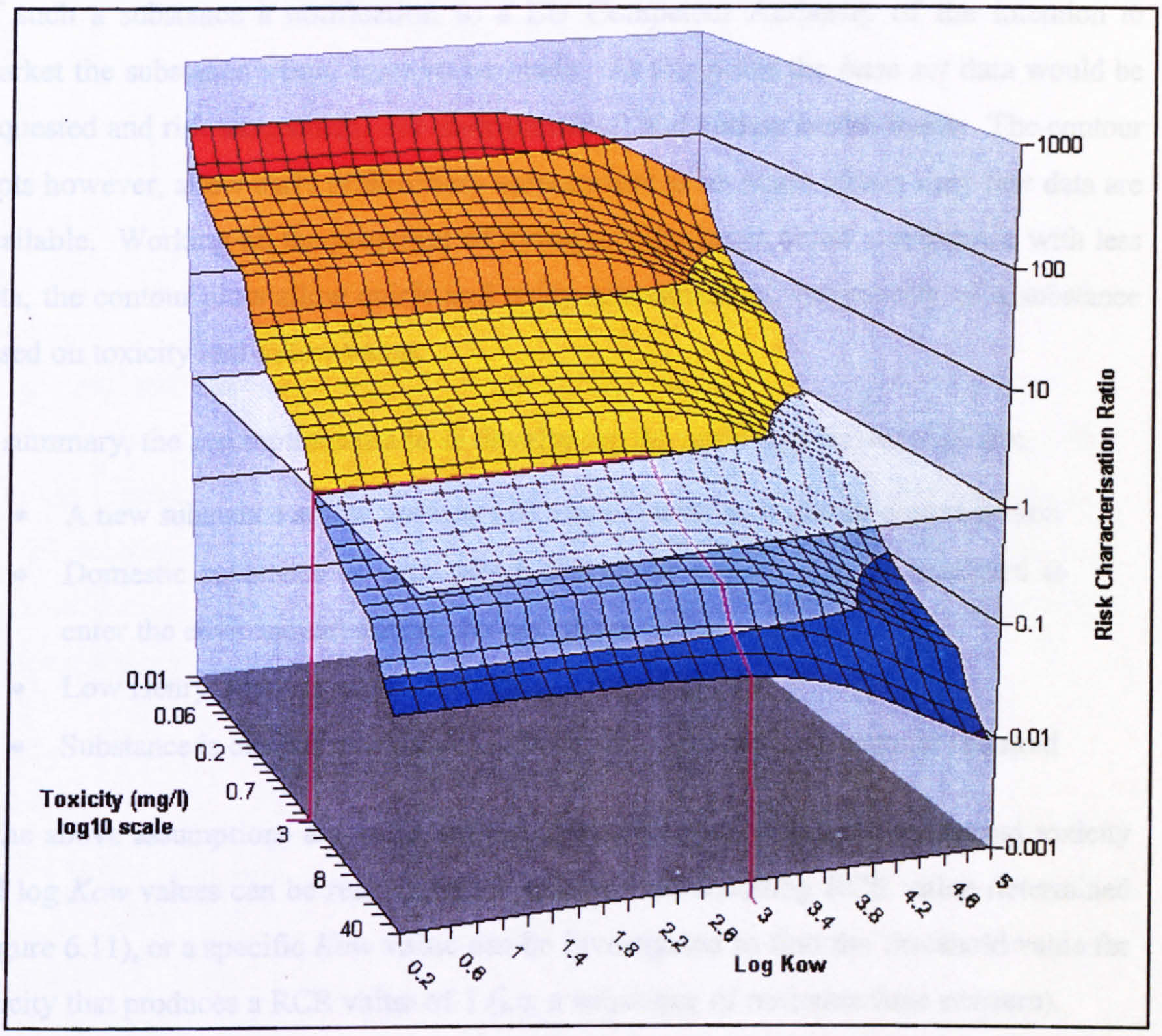

Figure 6.11 – Example of determining critical values from the non-biodegradable contour plot
For a substance with log *Kow* 3.0 the toxicity of the substance must be less than 2 mg/l

6.5 SUMMARY

The research presented documents the development of a graphical tool for rapid assessment of domestic new substances based on a few *base set* data values. The construction of the tool was in response to the needs of the CAU within the NCEHS, and the many hundreds of calculations needed to produce the contour plots were made feasible by the NEXCES spreadsheet that had been developed in an early stage of this research. The result is a visual "litmus test" for substances based on very few data, giving an indication of the toxicity of the substances.

Most new substances are initially marketed in low volumes, and at worse can be assumed to enter the environment in their entirety and as a precaution may be classed, in the first instance as non-biodegradable. During the development and prior to marketing of such a substance a notification to a EU Competent Authority of the intention to market the substance would have to be made. At this point the *base set* data would be requested and risk assessments for environmental and human health made. The contour plots however, allow early preliminary assessments to be made where very few data are available. Working on the principal of trying to infer more about a substance with less data, the contour plots allow quick and ready assessment of the toxicity of a substance based on toxicity and a *Kow* value.

In summary, the assumptions made in developing the rapid assessment tool are:

- A new substance at low volume (10 tonnes) with no regional concentration
- Domestic substance or one where the entire volume can be assumed to enter the environment during the use phase
- Low Henry's law constant (less than -1 log unit)
- Substance is classed non-biodegradable, or worse case assessment required

If the above assumptions are valid and/or acceptable then either the measured toxicity and log *Kow* values can be read from the plot and the resulting RCR value determined (Figure 6.11), or a specific *Kow* value can be investigated to find the threshold value for toxicity that produces a RCR value of 1 (i.e. a substance of no immediate concern).

The information from the contour plot can both give an immediate indication of the risk of a substance based on a small number of assumptions and pieces of measured data, as well as indicating where further testing is required to refine the assessment. Depending upon where on the surface the measured values place a substance it may be more economical to perform a further toxicity test to refine the toxicity value, or further testing may be focused on the physico-chemical values to either refine the Henry's law constant or *Kow* value.

CHAPTER 7

CONCLUSIONS AND FURTHER WORK

SUMMARY

The research presented in this thesis is briefly reviewed. The main findings from the research are presented, with a consideration of how the work fits into the wider context of the control and risk assessment of substances in the environment. The contributions to the academic and industrial fields are outlined along with the contributions to the field of environmental technology. Some of the areas where there are opportunities for further work are also outlined.

7 CONCLUSIONS AND FURTHER WORK

7.1 SUMMARY OF THE RESEARCH

Through an initial examination of the different methods by which hazardous substances can be controlled in the environment it was found that the European notification system could be developed through the application of probabilistic risk assessment methods as used in pesticide assessments and in the DTA risk assessment framework.

The generic European risk assessment system is a highly prescribed process used to assess new and existing substances marketed within Europe. Initial sensitivity analysis investigations detailed in *Chapter 2* demonstrated that variations in some physico-chemical properties could cause marked effects in the resulting risk assessment (±13%), while the choice of QSAR used to predict *Koc* from *Kow* can result in even larger variation (±30%).

Chapter 3 documented the development and testing of the NEXCES spreadsheet model that allows multiple assessments to be performed simultaneously while incorporating solutions for some of the problems and computer bugs documented for the EUSES program.

The collation and statistical analysis of the dilution and capacity parameters for STPs were reported in *Chapter 4.* The collated data for England and Wales were also compared to the European default parameter values used to perform generic risk assessments. These data were then re-sampled and used to perform probabilistic assessments for test substances in *Chapter 5*, using the spreadsheet model developed in *Chapter 3.* The results from deterministic and probabilistic risk assessments were compared and through regression analysis the probability of adverse effects occurring was quantified for various deterministic RCR thresholds.

In *Chapter 6*, the NEXCES spreadsheet model from *Chapter 3* was used to process data so that a rapid risk assessment tool for new substances, based on contour plots, could be developed. The contour plots produced act as a "limus-test" for new domestic substances, indicating the likely risk based on a limited number of properties of the substance.

7.2 MAIN CONCLUSIONS

The initial aim of this research was to examine the different ways in which hazardous substances are controlled and this was done through working with a number of the key groups in the National Centre for Ecotoxicology and Hazardous Substances. The various risk and hazard assessment systems used by the CAU, ETS and DTA were reviewed.

From the review process two main areas of interest were proposed for further investigation, using an Environment Agency format, and the two project proposals were presented as part of the 24-month dissertation:

1. Sensitivity analysis of values in the environmental exposure section of the European Notification risk assessment system as performed in the EUSES system.
2. Comparative study of single substance and whole sample toxicity risk assessments on selected discharges

The first of these project proposals became the focus of the remainder of this research. The spreadsheet tool was developed to initially facilitate the sensitivity analyses but then allowed the project proposal to be expanded to include probabilistic risk assessments and the development of the rapid assessment contour plots.

The main contributions arising from this research have led, for the first time to:

- Confirmation that variations in the measurement of *Kow* had the greatest effect (±13%) of all physico-chemical properties examined on the resulting risk assessment.

  This confirms that accuracy in the measurement of the Kow value is important and if a risk assessment is to be refined the refining of this value should appear early in any consideration.

- Demonstration that the default QSAR for predicting *Koc* as used in EUSES does not produce a worst-case assessment for the aquatic compartment.

  This is a serious flaw in the EUSES model (which automatically selects the default QSAR, the value from which needs to be manually over-written).. If a worst case *assessment is to be made then depending upon which environmental compartment is being considered different QSARs may be used to produce real worst case values.*

- Development, documentation and testing of a spreadsheet tool capable of performing multiple treatments of the same assessment.

  A spreadsheet model of the TGD/EUSES had never been completely documented and where authors had referred to the use of such a model it was impossible to find what assumptions had been made, which version of SimpleTreat had been used etc. The NEXCES spreadsheets makes the calculation of the many thousands of risk assessments required to produce probabilistic risk assessments feasible.

- Demonstration that the dilution is a critical factor in the risk assessment process through the collated and analysis of paired data on the dilution and capacity of STPs in England and Wales.

  The data collated represents a large sample of the population and includes geographical information for GIS analyses. It was only through thorough analysis of this data that the issues regarding how discharge flow is measured in the UK was discovered.

- Demonstration that the generic risk assessment overstates the capacity of STPs in 70% of cases and as a result the default value is protective.

  Although the European default value for STP capacity is protective of the 70% of STPs which are <10,000 PE, the remainder are large works and actually contribute the bulk of the effluent load.

- Quantification of the risk associated with deterministic values by employing a probabilistic risk assessment, thus providing a better indication of the need for additional testing.

  By quantifying the probability of adverse effects for England and Wales, associated with values of deterministic risk assessments the levels at which further testing or other controls are needed can be seen more transparently.

- Development of a rapid risk assessment tool for new substances, to allow preliminary assessments to be made using minimal data for a substance.

  Responding to a real need, this visual "litmus test" for the risk that new domestic substances pose to the local aquatic compartment addresses the need for rapid preliminary assessments based on limited data for a substance.

These contributions span both the academic and industrial fields, while all contributing to the field of environmental technology.

Through collating environmental data such as the STP data, the environment and the fate of hazardous substances within it, can be modelled more closely in the future. Jager (pers. com. 2001) has been collating similar data for rivers and STPs in Germany and The Netherlands, and along with the UK data collated in this work these data can be used to develop the generic risk assessment system.

The probabilistic risk assessments performed for test substances used the large amount of data obtained for STPs in England and Wales. These assessments could be considered more site-specific than the generic European risk assessments based on national data. Although such assessments do not meet the generic requirements of the notification system, they help to demonstrate how protective the generic risk assessments are of England and Wales. Also in this work, probabilities for England and Wales were associated with the deterministic values obtained in risk assessments to better guide the requirement for further data or more controls on substances.

Risk assessments need to be balanced, type I errors must be avoided, so worst-case assumptions are used in order to ensure substances that may cause harm are not considered safe. If the risk assessment system is too precautionary however, the type II errors that result (safe substances being considered as a concern) will increase the costs to industry. Tools such as the rapid assessment tool for new substances can be used as part of a tiered system to review substances so that costs are limited.

7.3 FURTHER RESEARCH

Areas that have been highlighted where further research could be developed include the other project proposed in the 24-month dissertation:

> Comparative study of single substance and whole sample toxicity risk assessments on selected discharges

During the course of the research areas where further research could be undertaken were highlighted:

- Investigation and site visits to the individual STPs highlighted as being of concern by the GIS plots of the STP data

  Investigation of the individual site where high capacities are linked to low dilution factors will indicate the scope of the problem involved in flow measurement. Combined with an investigation into ways in which better flow measurements could be taken, this work would help to direct the measurement and use of STP discharge flow data in the future.

- Addition of other modules to the NEXCES spreadsheet model

  Other modules could be developed and added to the NEXCES tool, including an emission calculation module, regional-scale calculations and the inclusion of other environmental compartments.

- Further probabilistic risk assessments performed in comparison to deterministic risk assessments for new substances.

  By performing further investigations and comparisons of probabilistic assessments and deterministic assessments acceptance for the method can be gained and its use may be integrated into the European notification system. This would require either the agreement on standard distribution shapes for various parameter values, or more preferably the collation of more real environmental data.

GLOSSARY

ACR	Acute-to-Chronic Ratio
AF	Assessment Factor
ANOVA	Analysis of Variance
APC	Air Pollution Control
APW	Artificial Pond Water
ASTM	American Society for Testing and Materials
BAT	Best Available Technology
BEC	Bonnell Environmental Consulting
BOD_5	5-day biochemical oxygen demand
Bugs	Errors in a computer program or system that disrupt operation
CA	Competent Authority
$CaCO_3$	Calcium Carbonate
CAU	Chemical Assessment Unit
CFCs	Chlorofluorocarbons
CI	Confidence Interval
CIA	Chemical Industries Association
CV	Coefficient of Variance
DDT	Dichloro-Diphenyl-Trichloroethane
DEFRA	Department for Environment, Food and Rural Affairs
DENI	Department of Environment Northern Ireland
DETR	Department of the Environment, Transport and the Regions
DoE	Department of the Environment
DTA	Direct Toxicity Assessment
DWF	Dry Weather Flow
EA	Environment Agency
EC	European Community
EC_x	Effect Concentration for x percent of population
EC_{50}	Effect Concentration for 50 percent of population
ECB	European Chemical Bureau
EEC	European Economic Community
EINECS	European Inventory of Existing Commercial Substances

ELINCS	European List of Notified Chemical Substances
ENDS	Environmental Data Services
EPA	Environmental Protection Agency
EQS	Environmental Quality Standard
ESR	Existing Substances Regulations
ETAS	Environmental Toxicology Advisory Service
ETS	Environmental Toxicology Section
EU	European Union
EURAM	European Ranking Method
EUSES	European Union System for the Evaluation of Substances
FDA	Food and Drug Administration
FTE	Full Time Equivalent
GDP	Gross Domestic Product
GIS	Geographical Information System
GLP	Good Laboratory Practice
GVA	Gross Value Added
HMIP	Her Majesty's Inspectorate of Pollution
HO	Head Office
HPLC	High Performance Liquid Chromatography
HPVC	High Production Volume Chemicals
HSE	Health and Safety Executive
IEMA	Institute of Environmental Management and Assessment
INERIS	Institut National de l'Environnement Industriel et des Risques
ISO	International Standards Organisation
IPC	Integrated Pollution Control
IPPC	Integrated Pollution Prevention and Control
IPS	Informal Priority Setting
IUCLIDS	International Uniform Chemical Information Database
IWEM	Institution of Water and Environmental Management
K	Uncertainty factor
LAAPC	Local Authority Air Pollution Control
LC_x	Lethal Concentration for x percent of population
LC_{50}	Lethal Concentration for 50 percent of population

LEAPs	Local Environment Agency Plans
L(E)C_x	Lethal (or Effect) Concentration for x percent of population
LOEC	Lowest Observed Effect Concentration
Look-up table	Used in spreadsheets to constrain possible values for a parameter
LTTV	Lowest Toxicity Test Value
LV	Limit Value
M	Median
Macro	A small group of commands used within a computer program
MAFF	Ministry of Agriculture, Fisheries and Food
MATC	Maximum Acceptable Toxicant Concentration
MS	Member State
N	Population
NCEHS	National Centre for Ecotoxicology and Hazardous Substances
NEC	No Effect Concentration
NEXCES	New EXcel Calculation for the Evaluation of Substances
NOEC	No Observed Effect Concentration
NONS	Notification of New Substances
NO_x	Nitrous Oxides
NRA	National Rivers Authority
OECD	Organisation for Economic Co-operation and Development
OFWAT	Office of Water Sources
Open source	A program for which the code is freely distributed
p.a.	Per annum
PDM4	Probabilistic Dilution Model 4
PE	Population Equivalent
PEC	Predicted Environmental Concentration
PIR	Process Industry Regulation
PNEC	Predicted No Effect Concentration
ppb	Parts per billion
QSAR	Quantitative Structural Activity Relationship
R&D	Research and Development
RA	Risk Assessment
RAM	Random Access Memory

RC	Regional Contact
RCR	Risk Characterisation Ratio
RIVM	National Institute of Public Health and the Environment
RNG	Random Number Generator
S	Slope
SD	Standard Deviation
SEPA	Scottish Environmental Protection Agency
SETAC	Society for Environmental Toxicology and Chemistry
SNIF	Structured Notification Interchange Format
SO_x	Sulphurous Oxides
ST3	SimpleTreat 3.0 model
STP	Sewage Treatment Plant
TAPS	Toxic and Persistent Substances group
TGD	Technical Guidance Document
TRE	Toxicity Reduction Evaluation
UN	United Nations
UNCED	United Nations Commission on Environment and Development
UNEP	United Nations Environment Programme
UK	United Kingdom
UKAS	United Kingdom Accreditation Service
US	United States
US EPA	United States Environmental Protection Agency
USES	Uniform System for the Evaluation of Substances
US FDA	United States Food and Drug Administration
Visual Basic	A computer programming language
WET	Whole Effluent Toxicity
WHO	World Health Organisation
WQ	Water Quality
WWTP	Waste Water Treatment Plant
μ	Population mean
σ	Standard deviation
σ^2	Population variance

LEGISLATION

CHIP 1993	Chemical Hazard Information and Packaging Regulations 1993
COPA 1974	Control of Pollution Act 1974
EA 1995	Environment Act 1995
EPA 1990	Environmental Protection Act 1990
NONS 1993	Notification of New Substances Regulations 1993
TCPA 1947	Town and Country Planning Act 1947
WA 1989	Water Act 1989
WIA 1991	Water Industry Act 1991
WRA 1963	Water Resources Act 1963
WRA 1991	Water Resources Act 1991

MODEL PARAMETERS

Biodeg.	Descriptive value for the biodegradation rate
BP	Boiling Point
$CAPACITY_{stp}$	Capacity of the STP (in population equivalents)
$Clocal_{eff}$	Concentration of chemical in STP effluent
$Clocal_{inf}$	Concentration in untreated wastewater
$Clocal_{water}$	Local concentration in surface water during emission episode
$DILUTION$	Dilution factor (from river flow)
$EFFLUENT_{stp}$	Effluent discharge rate of STP
$Elocal_{water}$	Local emission rate to water during an episode
$FLOW$	Flow rate of river
$Fmainsource$	Fraction of release at local main source
Foc_{susp}	Weight fraction of organic carbon in suspended matter
$Fstp_{water}$	Fraction of emission directed to water by STP
$HENRY$	Henry's Law constant
$Kbio_{stp}$	Rate constant for biodegradation
Koc	Carbon normalised partition coefficient
Kow	Partition coefficient for octanol and water

Kp_{susp}	Solid-water partition coefficient of suspended matter
$L(E)C_{50}$ *(algae)*	Lethal or effect concentration to 50% of population for algae
$L(E)C_{50}$ *(daphnia)*	Lethal or effect concentration to 50% of population for daphnia
$L(E)C_{50}$ *(fish)*	Lethal or effect concentration to 50% of population for fish
MOLW	Molecular weight
MP	Melting Point
$PEClocal_{water}$	Predicted environmental concentration during episode
$PECregional_{water}$	Regional concentration in surface water
$PNEC_{water}$	Predicted No-Effect Concentration of the substance in water
$RCRlocal_{water}$	Risk Characterisation Ratio for local water
RELEASE	Volume released
SOL	Solubility in water
$SUSP_{water}$	Concentration of suspended matter in river
Temission	Number of emission days per year
VP	Vapour pressure
WASTEWinhab	Sewage flow per inhabitant

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APPENDICES

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APPENDIX 1 – DANGEROUS SUBSTANCES DIRECTIVE, LIST I AND LIST II SUBSTANCES

THE DANGEROUS SUBSTANCES DIRECTIVE

OFFICIAL TITLE: Council Directive 76/464/EEC on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community (Official Journal L 129, 18/5/76)

Directive 76/464/EEC outlined two lists of chemicals, the first of substances from which pollution should be eliminated and the second of substances where pollution is to be reduced:

List I - Black List

Particularly toxic, persistent or bioaccumulating substances.

List II - Grey List

Groups and families of substances which affect the smell and taste of water, also substances affecting the balance of oxygen in the water.

The directive applies to inland surface water, territorial waters, and internal coastal waters but not groundwater. Daughter directives detail limits for these chemicals, threshold volumes that discharges should not exceed. The Water Framework Directive, which is currently being implemented in the UK, will repeal directive 76/464/EEC and its daughter directives.

DIRECTIVE 76/464/EEC - LIST I

List I contains certain individual substances which belong to the following families and groups of substances, selected mainly on the basis of their toxicity, persistence and bioaccumulation with the exception of those which are biologically harmless or which are rapidly converted into substances which are biologically harmless.

1. Organohalogen compounds and substances which may form such compounds in the aquatic environment
2. Organophosphorus compounds
3. Organotin compounds

4. Substances in respect of which it has been proved that they possess carcinogenic properties in or via the aquatic environment. (Where certain substances in List II are carcinogenic they are included in this category)

5. Mercury and its compounds

6. Cadmium and its compounds

7. Persistent mineral oils and hydrocarbons of petroleum origin

And for the purposes of implementing Articles 2, 8, 9 and 14 of this Directive:

8. Persistent synthetic substances which may float, remain in suspension or sink and which may interfere with any use of the waters

DIRECTIVE 76/464/EEC -LIST II

List II contains:

- Substances belonging to the families and groups of substances in List I for which the limit values referred to in Article 6 of the Directive have not been determined
- Certain individual substances and categories of substances belonging to the families and groups of substances listed below.

The list also contains substances which have a deleterious effect on the aquatic environment, which can, however, be confined to a given area and which depend on the characteristics and location of the water into which they are discharged.

1. The following metalloids and metals and their compounds:

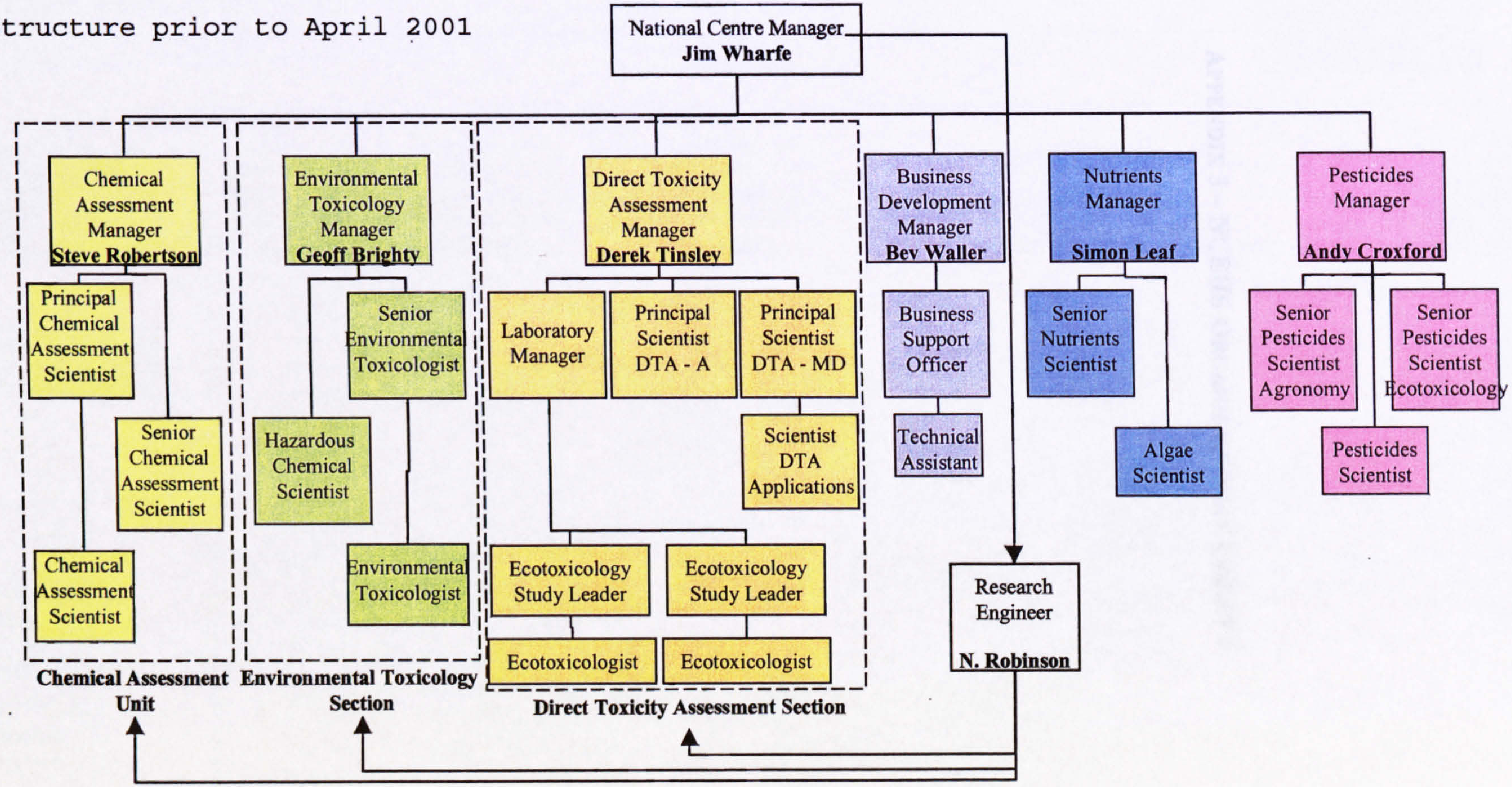
(1) Zinc
(2) Copper
(3) Nickel
(4) Chromium
(5) Lead
(6) Selenium
(7) Arsenic
(8) Antimony
(9) Molybdenum
(10) Titanium
(11) Tin
(12) Barium
(13) Beryllium
(14) Boron
(15) Uranium
(16) Vanadium
(17) Cobalt
(18) Thallium
(19) Tellurium
(20) Silver

2. Biocides and their derivatives not appearing in List I.
3. Substances which have a deleterious effect on the taste and/or smell of the products for human consumption derived from the aquatic environment, and compounds liable to give rise to such substances in water.
4. Toxic or persistent organic compounds of silicon and substances which may give rise to such compounds in water, excluding those which are biologically harmless or are rapidly converted in water into harmless substances.
5. Inorganic compounds of phosphorus and elemental phosphorus.
6. Non persistent mineral oils and hydrocarbons of petroleum origin.
7. Cyanides, fluorides.
8. Substances which have an adverse effect on the oxygen balance, particularly: ammonia, nitrites.

APPENDIX 2 – NCEHS ORGANISATIONAL CHART 1

Organisational Chart National Centre for Ecotoxicology and Hazardous Substances

Structure prior to April 2001



APPENDIX 3 – NCEHS ORGANISATIONAL CHART 2

Organisational Chart National Centre for Ecotoxicology and Hazardous Substances

Structure from April 2001

APPENDIX 4 – THE KENNET & AVON INCIDENT – NCEHS INVOLVEMENT REPORT

ENVIRONMENT
AGENCY

BRUNEL
UNIVERSITY

Engineering Doctorate in Environmental Technology

The Kennet and Avon Incident

National Centre EHS Involvement Report

By
Nik Robinson

> with legal regulatory requirements, using enforcement powers including prosecution, is an important part of achieving this aim."

This means that the Agency must prevent damage to the environment, try to find those who do cause environmental damage, accumulate evidence and where possible prosecute them. To do this there needs to be the provision for twenty-four hour availability for response, both from operational and pollution inspection staff as well as the laboratory and analysis functions that are needed to support any incident investigation. For large businesses the Agency usually just has to ensure that protection/remediation processes are being carried out, through monitoring and assessment, however with smaller companies the need to ensure protection sometimes requires the Agency to act, due to a party not being able to handle the situation themselves. This was the case with the moribund fish in the tanks at the Hungerford Fish Farm, the weight of the dead and dying fish were straining the tank walls posing a possible pollution risk. These fish were removed and the area cleared by Area staff to prevent the pollution of downstream waters.

The initial response to any incident requires sampling and observations to investigate and identify the pollutant. In the K&A canal incident, the problem of negative results arose and by the second and third week of the investigations, even after the resurgence in toxicity, the toxicant had still not been identified, although much was known of its properties by this stage.

The Agency defines an incident as anything that fulfils the following criteria:

- A specific event
- Brought to the Agency's attention
- Within the Agency's area of responsibility
- Has an environmental and/or operational impact

The Hungerford Fish Farm incident certainly meets these criteria and an Emergency Response was initiated. However as the focus of the incident moved from the fish farm to the K&A canal and as the duration of the investigation moved from days to weeks, the incident response could and maybe should have moved towards an Operational Investigation. However the K&A canal incident was classed as an Emergency Response for the duration of the incident. Under the Agencies new CIC (Common Incident Classification) system this incident would have been classed as high impact due to the media attention as well as the high value of the watercourse and the sensitivity of the area. It seems though that the point at which an incident's investigation becomes an operational investigation either needs to be clarified or more rigorously adhered to.

There are competing interests in the above two types of incident management, an investigation (whether operational or not) tries to identify the pollutant, whilst an Emergency Response aims to control the pollution, of which remediation is one option. When, as in this incident, control options are discovered before the pollutant's identity is known, a question arises, should the control option be carried out (remediation in this case) destroying any of the pollutant remaining, or should the pollutant be investigated until identified? Identification would mean that the pollutant could be detected and treated more quickly from a more informed viewpoint in the current and future situations, however when considering the Agency's aims, where possible control options should be put in place. Allowing a pollutant to remain in a watercourse for an unknown length of time, even if this is to study the pollutant for future reference would prove hard to defend against the Agency's current aims. Whether or not remediation was the right control option to choose, and what other control options would have been successful and would have met the Agency's aims is hard to argue in retrospect, very few samples being available after the incident for further investigation.

6.4 Control Options –

During the incident investigations some of the process steps alone used in analyses seemed to render toxic samples no longer toxic, indicating that the pollutant was very unstable to temperature, pH and other physical and chemical changes. The use of these process steps that could have lead to the breaking down of the pollutant would have affected the investigations. This shows the importance of the information produced by the TIE, and these findings need to be communicated to those performing the analysis as soon as possible to ensure their analyses process methods

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2 Executive Summary

This report briefly outlines the main stages in the invetigation of the Kennet and Avon canal pollution incident that started on March 4th 1998, at the Berkshire Trout Farm in Hungerford. The procedures adopted and applied in the technical investigation and the incident management are considered. Areas where lessons can be learnt are also highlighted and outlined.

This particular incident was unusual because of a number of factors:

i. Where it occurred
ii. What it affected
iii. The numbers of interested parties involved in the investigation.

The decision making process, 'what was done and why', is considered along with the management structure and how this changed as the investigation progressed.

Finally the involvement of the NCEHS is considered, how and why they became involved in the investigations, and to what extent the Centre should get involved in similar future incidents.

3 Aims And Objectives

The National Centre for Ecotoxicology and Hazardous Substances (NCEHS) is a relatively new centre within the Environment Agency. This report looks at how the Environmental Toxicology Section within the NCEHS and the technical service they offer, Environmental Toxicology Advisory Service (ETAS) supported the incident investigation.

This report aims to highlight areas where lessons can be learnt to ensure the National Centre's involvement in similar incidents in the future is at its most effective. The technical investigations that took place and the incident management that supported them have been considered along with an analysis of the decisions that were taken and why, and a review of the management structure and how it developed through the course of the investigation.

4 Introduction

During the early morning March 4th 1998, the owner of the Berkshire Trout Farm in Hungerford reported a large fish kill to the Environment Agency. By mid-morning the large scale of the incident was becoming apparent, the farm abstracting its water from the River Dun upstream of its confluence with the River Kennet. The primary cause of fish death appeared to be asphyxiation, but dissolved oxygen (DO) levels were high enough to rule out lack of oxygen in the water as a cause.

Visual inspections were made along the watercourses above and below the farm and dead fish were found in the Kennet and Avon (K&A) canal and the River Dun but not in the River Kennet. Later, electric fishing surveys, involving qualitative, semi- and fully- quantitative methods were used. At the fish farm there were no deaths in fry (young fish) supplied by water that was not abstracted from the River Dun, although there were some survivors in the affected tanks as well.

The Agency set up an incident room at Wallingford and a range of water, sediment and fish samples were collected for chemical analysis by the Agency's National Laboratory Service (NLS). The National Centre for Ecotoxicology and Hazardous Substances (NCEHS) were asked to help direct the analysis through their Environmental Toxicology Advisory Service (ETAS), by providing target lists of possible toxicants that could cause the observed effects.

Agency staff removed an estimated 150 tonnes of dead fish from the fish farm to prevent pollution downstream. Initial chemical investigations did not identify the causative agent but did eliminate some potential toxicants including cyanide, heavy metals and organotins, as well as physico-chemical parameters such as pH, dissolved oxygen, ammonia and nitrate levels. Further investigations at premises within the locality and discussions with British Waterways (BW) shed no new light on the potential sources of the causal agent. Chemicals found at these premises were listed and water samples analysed for these toxins, but none were present at high enough concentrations to be toxic. No pollutants were identified at significantly higher concentrations than in control samples throughout investigations by the NLS.

On day three of the incident the K&A canal was closed to boat traffic and lock gates remained closed along affected reaches to protect downstream sites, including another large fish farm. Deployments of mixed coarse fish were made at four sites along the K&A canal by the Agency. Within 48 hours many deployed fish died at sites where dead fish had been found previously, but there were no mortalities at an upstream, unimpacted site.

Macroinvertebrate surveys and analyses revealed a limited number of mortalities at some of the sample sites, however these may not have been directly related to the pollution event. Algal analyses found the main species present to be centric diatoms, however the diatom populations were healthy with few bacteria present; the pollution event did not seem to be due to any known toxic algae including blue-green strains. There were no positive results obtained from the `in vitro` Enhanced Chemi-Luminescence (ECL) tests or the `in vivo` Microtox bacterial bioluminescence test. Analysis of moribund fish showed histopathological changes in the gills of most of the fish sampled, it was observed that death appeared to be rapid, and the cause of death seemed to be asphyxia through gill damage.

With no clear leads, a week into the investigation the Environmental Protection (EP), Water Management (WM) and Operations (Ops.) groups at the Agency's Head Office requested Geoff Brighty's Environmental Toxicology Section (ETS) within the NCEHS to take over the scientific investigation and to manage this aspect of the incident. WRc who were initially contacted under their technical service contract which supports the ETS's ETAS, later became formally involved and over the following four weeks the identity, source and potential treatment options of the causative agent were investigated. They were contracted to:

- Identify the causal substance
    - Review chemical determinations
    - Analyse historical water samples
- Evaluate toxicity
    - Assessment of historical toxicity
    - Assessment of current toxicity
    - Sediment toxicity

- Toxic Identification and Evaluation (TIE)
- Modes of toxic action

WRc approached the work in a discrete number of areas:

1. Field monitoring – sentinel fish deployments to gauge toxicity in the field
2. Laboratory monitoring – field observations confirmed for sampled water
3. Toxicant investigation – samples found to be toxic used to identify the pollutant
4. Other analytical work – analyses used to support results from above work

Field deployments were used to monitor the extent of toxicity in the Rivers Dun and Kennet and the K&A Canal and to identify toxic canal pounds (stretches between lock gates). Laboratory tests on sediment and water samples from these toxic pounds were then performed, first to verify toxicity levels observed in the field and, where toxicity was confirmed, samples were further investigated in an attempt to identify the causal substance, and to recommend remediation options.

WRc initially made a review of work carried out by the NLS and performed their own analyses on historical samples. Particular attention was given to substances that cause acute fish toxicity but have no effect on invertebrates, that are toxic at low concentrations and those that may have been present below the previous limits of detection. Limits of detection were later lowered through use of larger samples. This work discounted many possible causes as outlined below:

- Reduced DO (Dissolved Oxygen) or large changes in pH.
- High concentrations of ammonia, nitrite, cyanide, or heavy metals.
- Organotin compounds, phenols, petroleum products, detergents and narcotics with a boiling point below 500°C.
- Known agrochemicals highly toxic to fish.

In addition to the field deployments, laboratory toxicity testing, chemical analysis and algology carried out by the Agency and WRc, additional analyses were carried out by other specialist organisations, these included:

- Fish histopathology by the Agency National Fisheries Laboratory (NFL) and DB Aquatic Pathology Services.

(List Continued Overleaf)

- SEM (Scanning Electron Microscopy) of fish tissues by Royal Holloway College, University of London.
- TIE by CEFAS, (Centre for Environmental, Fisheries and Aquaculture Science).
- Fish blood analysis by the University of Plymouth.
- Analysis for blue-green algal toxins at the University of Dundee.
- Algal identification and ecological indexing by Freshwater Biological Assoc.
- Zooplankton studies by the Institute of Freshwater Ecology.
- SEMs of `Stephanodiscus hantzschii` (planktonic diatom) by University of Bristol.
- Polysaccharide cleavage analysis undertaken by M-Scan Ltd.
- Electrospray Mass Spectroscopy (MS) analysis of water samples carried out by Micromass Ltd.
- Review of microbiological information by the University of Lancaster.

Sediment toxicity tests were carried out, but showed no conclusive evidence of sediment toxicity. Tests were also performed on material that had been dredged from the canal and left on the banks. Water and moribund fish tissue samples were sent for mouse bioassays, these tests confirmed that neither toxic water nor moribund or affected fish were likely to cause secondary toxicity to mammalian organisms.

During the field deployments toxicity levels increased along one stretch of the canal from the levels measured in the first deployment (week 2) to those measured at the beginning of the second deployment (week 3), at which point fish were dying within 24 hours. At the same time algal blooms were sighted along some reaches of the canal, although this would not have been unusual it was noted. As a result of the increase or resurgence in toxicity, and the shortening in time of the fish mortality endpoint (now less than 17 hours in standard samples), a TIE investigation was requested by the NCEHS and undertaken by CEFAS. Samples of water with increased toxicity were sent for further mammalian toxicity testing and chemical analysis as in the initial stages of the investigation. Algal samples were also taken for analysis and identification.

The toxicity within the pounds was also varying spatially. The resurgence and the spatial variations in toxicity were unlikely to be caused by a single point source, the lock gates now being closed. It appeared that either substances were being released from the sediment or a biological source in the water was responsible. Sediment toxicity tests gave negative results, therefore the possibility of a biological source was investigated further. The toxicity was associated with pounds that appeared clear, while those showing algal blooms were deemed either low in toxicity or non-toxic. Algal surveys performed on samples from three reaches of the canal showed dense blooms of centric diatoms and high densities of motile and non-motile bacteria.

During the TIE investigation, a third set of field deployments were performed indicating toxicity remained at some sites and was slowly moving downstream, therefore treatment options were investigated in the laboratory. Hydrogen peroxide (H_2O_2) was found to be successful at rendering toxic samples non-toxic, many other remediation methods tested also reduced the toxicity of samples to no-effect after 96 hours. However, filtration alone (used as a preparation step in many of the procedures) was also found to temporarily remove the toxicity in some cases. The filtration removed the majority of the toxicity but some went through and after a time the toxicity was back to its original level again. Because of continuing toxic effects and the Agency's experience in using hydrogen peroxide, this treatment option was implemented from the upstream control site, to Hungerford Bridge. However some downstream sites on the K&A canal, which had been toxic at times during the incident, were not treated and the River Dun was not remediated. Emphasis had been put on the fact that treatment of an unknown toxicant was not ideal and that there was a requirement for adequate mixing of the hydrogen peroxide (H_2O_2) in the water column, which was ensured by dosing from a motorboat into the vessel's wake. The H_2O_2 solution was also dyed to act as a visual indication to the extent of mixing. A final fish deployment at each of the sites used in the deployments was made with negative results at all sites which had been affected during the incident. The canal was therefore reopened to boat traffic (a month after the incident began) and the management of the incident closed shortly after.

The causative agent is thought to have been a biological toxin, and to have been bacterial in nature. The production of this toxin appears connected to the crashing of the algal blooms in the canal and may be linked to the dredging of the canal in the previous months, and the unusual weather conditions prior to the event. Warm and dry conditions would have meant that microbial communities in the dredgings would have changed dramatically to that which was present in the canal sediment. Bacterial spores that were dormant in the submerged sediment would have germinated in the relatively oxygen-rich environment at the surface of the dredged material, with a general shift from an anaerobic to an aerobic microbial community.

Heavy rain might then have washed some of the dredgings, associated microbes and nutrients into the canal, leading to two potential explanations:

- That the material washed back into the canal contained a large enough 'pulse' of the toxin to cause rapid fish mortality.
- That the microbial community in the dredgings formed an inoculum for continued growth in the canal, leading to the production of greater amounts of the toxin in the canal days or weeks later.

The limited boat traffic on the canal meant that the micro-nutrients and microbes washed into the canal remained there rather than being washed downstream into the River Kennet. The presence of polysaccharides in the water from the algal blooms, micro-nutrients from the dredgings and the relatively warm temperatures and low flows would have provided ideal conditions for the establishment of a thriving microbial community in the canal.

5 The Technical Investigation

5.1 Unusual nature of incident

The pollution incident was unusual due to:

- Lack of leads on potential source
- Highly valued and complex watercourse
- What the pollution affected

`Lack of leads on potential source` - It is very unusual for inspectors dealing with an incident not to find any clues as to a source in a pollution event. Normally the toxic agent is either easily identified as one of the main toxicants known to affect the aquatic environment, or a barrel, container or other source is easily identified, this information then allows the analysis processes to be directed towards the target chemical.

The incident management started as it would in any other instance, sampling and analysis starting in the early hours of the morning and continuing throughout the day. However by late afternoon no major breakthrough had been made, the first analyses showed nothing. For this reason analyses were repeated and detection limits lowered where possible. The repetition of the initial analyses was interpreted by the media to signify a lack of confidence in the initial testing, and the media questioned why more rigorous testing had not been employed in the first instance. It was, however the lack of clues "on the ground" and significant peaks in the initial scans that led to the re-testing. Normally repeat analyses would be carried out, where significant peaks in the initial scans were matched to those of known chemicals. This was not possible in this incident because by day two, even the chemical group/family of the pollutant was still known. Due to the lack of these results the possibility of the pollution being due to something other than a chemical was considered. There was a belief though that whatever the toxin was it would have to be large in quantity or high in concentration to account for the observed effects.

`Highly valued and complex watercourse` - The location of the incident was also unusual. The interrelation of the K&A canal and the Rivers Kennet and

Dun produces a very complex water system, (see Map of the Kennet and Avon Canal and the Rivers Dun and Kennet, Appendix - Section 10.1). The system has a high value due to abstraction for potable supply downstream, various fish farms along its length and a high leisure and amenity value. These factors make the location particularly special and the incident very high in public profile.

`What the pollution affected` - Finally the `modus operandum`, of the pollution was very unusual as well. Only fish seemed to be affected by the toxin with invertebrates, birds and mammals being unaffected, and no significant effects on bacteria were observed.

5.2 Monitoring, sampling & analysis

This section considers the:

- Routine and investigative monitoring
- Availability of adequate sample volumes
- Whether routine monitoring and analysis could have predicted the incident

`Routine and investigative monitoring` - The watercourse is routinely monitored with sampling and analysis being carried out by the Agency. The Scientific Investigation Group who perform this standard procedural monitoring stepped-up these monitoring efforts and added to them for the incident. Monitoring continued throughout the incident and continued after the incident management was closed, to continue to track the pollution and confirm that the remediation efforts were successful. Operational staff and contractors also carried out investigative sampling and monitoring with sampling sites being kept uniform where possible.

Although bacterial sampling and testing were carried out right from the beginning of the incident there is no routine bacterial sampling, the initial samples only being taken because the equipment was to hand. There is also a question concerning whether less routine monitoring should be carried out, if so this would mean the historical data that were available leading up to the event would not have been available.

`Availability of adequate sample volumes` – A problem that soon became apparent during the incident was that the required volumes of samples for the analyses being performed were not always available, especially during the initial stages of the investigation. The samples that were initially received from the field were of no fixed volume, although 1 litre volume was typical and normally sufficient. This suggests that communication links between the operational/sampling staff and those performing the analyses at the laboratories were not working efficiently enough. Although adequate sample volume was not the reason that the pollutant was not identified in initial analyses, it may have been one of the reasons supporting the repeating of tests. Greater volumes of samples would have allowed lower detection limits in the analyses. The highlighting of this communication problem allows the situation to be targeted for improvement in any future pollution incidents.

`Whether routine monitoring and analysis could have predicted the incident` – It should be considered whether the event should or could have been predicted from the existing routine monitoring that is carried out. Could the data that are produced from this routine monitoring have predicted the event or highlighted the area as being at risk? It is unlikely that such judgements prior to the event could have been made, however now the conditions for such an event are, at least partially, known it might be possible that future events could be predicted. However the likelihood of a similar event occurring is slim and probably not worth the time and resources necessary for such analysis, despite the high consequences. Although initially predictive monitoring and analysis may seem to be resource-intensive, it would be possible to analyse the routine data in an automated process, which checked various parameters and highlighted "hot spots" or areas of concern.

Examples of indicators of areas of concern include a drop in DO, which is usually linked with an increase in BOD (biological oxygen demand). Also algal concentration, water hardness, metal ion concentration and pH level are of particular concern and can indicate increasing toxicity and/or problem areas in some cases. The routine monitoring is not however at headwaters, monitoring points usually being at the downstream end of pounds/reaches, and although some routine analysis is carried out the results are not checked to the extent as outlined above.

If routine monitoring data were used in a predictive manner, it would represent a significant move towards a preventative rather than reactionary approach to pollution at least in some areas. The Agency in its 'Enforcement and Prosecution Policy' document state that,

> "The Agency regards prevention as better than cure. It offers information and advice to those it regulates and seeks to secure co-operation avoiding bureaucracy or excessive cost. It encourages individuals and businesses to put the environment first and to integrate good environmental practices into normal working methods."

However this tendency towards prevention, is hard to implement in the control of pollution events, with much of the work necessarily being reactive. The decline in pollution incidents per annum, a move from many minor incidents to a few major incidents and a move from more man-made to more natural incidents would all suggest that pollution prevention efforts were having a positive effect on pollution incidents.

It is unlikely that the K&A canal pollution incident could have been predicted using existing routine monitoring data. The use of fish monitors, usually based on ventilatory and movement responses, may have given an indication of the toxicity, however these are resource intensive and tend to be used more in protecting portable water abstraction points [van der Schalie et al 1988]. The incident seems to have been due to a series of complex interactions, the high levels of bacteria, the local weather pattern and the availability of organic matter (the polysaccharides from the collapsing algal blooms) and nutrients to sustain or even promote the bacterial community once in the watercourse. However some form of modelling system using routine monitoring data may help to predict future pollution events of this and other natures.

unaffected, showing effect levels similar to other affected pounds on the canal at least once during the investigation. When deciding on sites to be used as control sample sites care needs to be taken that these are far enough removed from the affected area so as not to provide a false background level. A comparison between a local unaffected watercourse and the Site 3 sample may have highlighted the problem of background toxicity, care would have to be taken in the comparisons ensuring suitable and unaffected sources from both the canal and the rivers were used for sampling.

`Adequate historical data for controls/comparisons` – There needs to be adequate historical data available for comparisons to be made with monitored data. At some point in the investigation dead invertebrates and dead fish were found yet the mortalities seemed unlinked to the pollution event. Good historical data on abundance of species and other details would allow more informed decisions to be made when deciding whether to count or discount mortalities that may not be linked to the pollution. A reduction in routine monitoring as mentioned earlier would mean such conclusions would become harder or even impossible to draw. There is a real need for historical data to be available for use in similar investigations, and a reduction in the routine monitoring would compromise the strength of this historical data.

5.4 Investigations

This section considers the field and laboratory investigations undertaken during the incident as shown in the decision-tree diagram:

- Field deployments
- Laboratory analyses

`Field deployments` – The "decision-tree diagram" (see Appendix, Section 10.3) of the actions and investigations and their related decisions helps to show how the various monitoring, sampling and analysis phases were inter-linked. It also attempts to demonstrate why some actions arose due to the result of previous tests and monitoring data. After the initial investigations in the incident, the WRc set up a number of field deployments at different sites, the four sets of deployments made serve as a timescale for the remainder of the incident.

The field monitoring showed that toxicity was migrating slowly downstream in the first deployment, and so field deployments were continued, along with the parallel laboratory fish testing. The second deployment saw the resurgence in toxicity and sightings of algal blooms with various links being drawn between the two. It was because of the resurgence and the migrating toxicity that Site 2 was split, to further refine the toxicity data and to investigate the algal bloom link.

The third deployment saw further sub-dividing of sites and continued field monitoring to track the toxicity while remediation options were considered in the laboratories. Finally, after the remediation at the end of the third deployment a fourth and final deployment was instigated to monitor the effectiveness of the treatment, with the canal being re-opened at the end of this final deployment, when the toxicity was confirmed as cleared.

These deployments, as indicated, placed a timescale on the incident allowing the laboratory analyses to fit in with the field monitoring, each set of laboratory analyses tying in with a deployment. They also allowed the migration of the pollution to be tracked effectively. Once these deployments had been set-up the investigation seemed to take on a more structured approach. Although such a monitoring program is a major undertaking and is not always necessary in a pollution incident, in incidents of a similar scale such a program helps the tracking of the pollution, establishes immediate exposure routes and adds structure to the investigations.

`Laboratory analyses` – Along with the first `in-situ` fish deployment various laboratory analyses and tests were also carried out. As a result of the data from the daphnia, mouse, ECL and Microtox studies, these lines of investigation were discontinued. While the fish test showed positive toxicity and for this reason these laboratory analyses were continued along with the field deployments. During the second deployment fish samples from the first deployment were sent for analyses.

The resurgence in toxicity during the second deployment led to the splitting of some pounds and re-deployment of test fish. The resurgence was treated as a separate event, which is why the Daphnia, ECL, Microtox, tests were repeated along with the continuing fish test, with fish samples being again sent for SEM and blood analysis. However, similar results to the first set supported the increased toxicity as being a resurgence of the earlier event. At this point because there was now a more acute end point CEFAS were contacted regarding a TIE investigation, which continued through the third deployment. Because toxicity was now high again, WRc were asked to consider and test remediation options, CEFAS's TIE helping to identify the unstable nature of the pollutant.

After the canal had been treated with hydrogen peroxide a fourth and final deployment was setup to monitor the success of the treatment efforts. Again fish samples were taken to confirm there were no longer any observable acute effects.

The strategy to run field deployments and laboratory tests simultaneously resulted in effects, noted in the field, being replicated soon after in the laboratories, allowing the investigative analysis to target the most toxic samples. The re-running of all analyses on new samples after the resurgence, worked well also, clearly supporting the main hypothesis that the second wave of toxicity was indeed a resurgence of the original. Finally, the four major fish deployments allowed the whole pollution incident to be monitored over time making it possible to plot a profile of the toxicity throughout the incident, and to clearly see the migration of the toxicity supporting the visual observations of algae and crashing blooms.

5.5 Toxicity Identification Evaluation

This section considers the TIE investigation undertaken by CEFAS:

- Before the resurgence in toxicity
- After the resurgence in toxicity

`Before the resurgence in toxicity` – A TIE could not be performed during the early stages of the investigation due to the fish test endpoint being greater than 48 hours. Such investigations rely on acute toxicity tests that can be performed after each step in the process and no reliable short (acute) endpoint was available at this point in the investigation.

`After the resurgence in toxicity` – After the resurgence, the time to mortality was reduced significantly enough for the TIE method to be employed. Due to the particular nature of the pollutant and the late point at which these investigations commenced the toxicant was not fully identified, yet much data and many physical and chemical properties of the pollutant were investigated. This information lent further support to the remedation options being researched and helped to characterise the pollutant more than had been possible before.

For most common pollutants, limit values or EQSs are defined, and would be used to gauge whether or not a pollutant is likely to cause ecological damage. However this requires that the pollutant is known, can be analysed for, identified, and the concentrations in the watercourse can be calculated. For this reason a full identification would have meant future incidents involving the same pollutant, would not necessarily require the same extensive fish deployments. TIE as a method is an effective and structured approach to gaining data on and eventually identifying a polluting substance. However to be effective, an acute toxic endpoint is necessary, with a sufficiently short time-to-effect (or time-to-death) that the test can be performed after each step of the TIE investigation.

If a TIE investigation had been started during the earlier stages of the investigation, despite an endpoint of days rather than hours, the pollutant would have been more fully identified or maybe treated earlier than in this incident. However this has to be weighed against the cost of the TIE investigation, and the fact that it appeared that the toxicity was receding during the opening stages of the incident.

5.6 Biological Source Investigation

The two factors and the possible link between these, which triggered the biological side of the investigation, will be considered:

- Algal blooms
- Resurgence in toxicity

• Link between algal blooms and toxicity

`Algal blooms` – When tested the main algal species present were centric diatoms, also high counts of bacterioplankton were found on the 9th March. However it seems that the high bacteria levels and fish mortalities were not linked, or considered together at that stage in the investigation. In one case the laboratory testing of a sample from Site 3 resulted in total mortality after 72 hours. This result was surprising considering no mortality had been noted in the field, also Site 3 was being used as a control site. It was noted however, that between taking the sample and performing the tests, algae present in the sample had settled out of suspension, possibly linking the toxicity to the breakdown of the algae in the sample.

`Resurgence in toxicity` – The main factor supporting pollution of a biological nature was the resurgence in toxicity. Particularly the fact that toxicity was seen to increase in more than one separated pound, which would be very unlikely if the source had been chemical in nature.

`Link between algal blooms and toxicity` – At about the same time as the resurgence in toxicity, algal blooms were sighted along the canal. Approximately half of the Site 2 pound appeared to contain an algal bloom which led to the splitting of the site to investigate the blooms and increased toxicity. After 24 hours total mortality was observed at Site 2a (downstream, clear water) but no mortalities were seen at Site 2b (upstream, algal bloom). These results helped confirm earlier beliefs that algal blooms characterised non-toxic pounds while clear water was characteristic of toxic pounds. However there appears to be some confusion in WRc's report which states that,

> "The crash of the diatom bloom appears to be linked to toxicity in the canal water, but it is not clear how. Field observations suggest that at non-toxic sites where the diatom bloom crashed, a lag period of 2-3 days occurred before fish toxicity was recorded."

However the algal bloom was moving slowly downstream. The bloom entered the upstream part of Site 2 on the 20th March while the downstream half, which the bloom had not yet infiltrated, was clear and toxic. This does not agree with the suggestion of the crashing bloom resulting in an increase in toxicity; a bloom having not been noted in the downstream end of the reach before it became toxic again. The exact link between the two events is not known, there were no reports of crashing blooms before the original event, however at this time nobody was specifically looking for such signs either.

5.7 Incident response

This section considers the level of emergency and incident response provided:

- Emergency response by the National Fisheries Laboratory
- Emergency response by the National Laboratory Service
- Provision of emergency response

`Emergency response by the National Fisheries Laboratory` – During the investigations the level of response offered by the NFL became an issue. The question was of their capabilities and availability for emergency incident response. The NFL were no longer equipped for emergency response, for this reason John Sutton contacted David Bucke of DB Aquatic Pathology Services, for histopathology work on the moribund fish.

`Emergency response by the National Laboratory Service` – The chemical analysis required for the investigation meant that the NLS worked around-the-clock when necessary and in some cases were unable to continue routine programme work for Anglian and Thames Regions. This resulted in a slip in their legal obligations as part of that programme, however the NLS's remit does require response to emergencies to be the main priority in such situations.

`Provision of emergency response` – The level of response the national services offer and what is within their remits for similar incidences would seem in need of clarification, and this should be compared to what responses are required by operations in such situations. In this incident many outside contractors with particular areas of expertise were brought into the investigation. The organising and inter-communication between all these groups is a potential problem, and one that is considered in a later section. The alternative would be to promote and keep this expertise "in-house", which may cause some slip in normal operational work, which would have to be overcome and managed accordingly. However it seems better to keep the knowledge base and experience within the Agency so that the recurrence of similar incidents can be handled in the light of experience and previous knowledge, rather than contracting out for these skills. The Agency's National Centres of expertise and National Laboratories are an ideal place for this experience to be centred and held, so that any Area or Region can draw upon the expertise and national patterns or other trends or effects can be highlighted. One of the other points highlighted by the need for many experts in different fields was the need for a list of key contacts. Contacts for contracting out laboratory analyses, SEM work, pathology work, and even the supply of test species need to be readily available, perhaps on National or Regional lists. As is evident when the later deployments are reviewed, the availability of test organisms was becoming limited due to the need to work with the same batch, resulting in fewer fish being deployed at each site, causing the usual problems (including statistical relevance) associated with low test populations.

5.8 Initial Conclusions

Conclusions based on the initial monitoring, sampling and analysis:

- Pollutant could be very soluble in water and not be amenable to extraction methods used
- Pollutant could have high molecular weight and not be amenable to analysis methods used
- Pollutant only affected fish and no other species to any great extent
- Pollutant could be extremely toxic to fish in concentrations below level of detection

Pollutant could be very soluble in water and not be amenable to extraction methods used - The GC-MS (Gas Chromatograph-Mass Spectrometry) analysis employed requires that the substance can be extracted, and concentrated in a solvent and that the substance can be analysed in a volatile phase. It is obviously easier to choose a suitable solvent when the target substance is known. Other types of analysis may well have been better suited to detecting the polysaccharides but detection of an unknown substance by these methods present the same sorts of problems. So it would have been possible to detect if not identify the polysaccharide, however this would have required the use of other analysis techniques and significantly added time to the analyses processes. Another problem with the analysis used in detecting a substance like a polysaccharide is that the MS detector, as part of the analysis, fragments the molecule into smaller components, which are analysed. As a result of this fragmentation it may be very difficult to identify the parent molecule from the identities of the constituent parts.

It is unlikely if the polysaccharide had been detected, even if not fully identified, that it would have aided the incident management during the initial investigations. Depending on the concentration of the polysaccharide, although the peak may have been unusual in the watercourse, it would not have represented a major toxic concern, just a high level of organic material in the sample. If this fact along with the idea of a biological, even bacterial toxin, had been considered at this point, then the investigation may have been significantly directed by these findings. It should be remembered though that at this point the pollution was still being considered as a point source chemical dosing-type incident.

Another point concerning the analyses is whether chemicals that are not amenable to the extraction processes would be significantly toxic? A list of chemical groups/families that are unlikely to be detected by each standard analysis method, available to incident controllers would help direct sampling and requests for analysis, the incident managers being able to see what chemical families might not be detected by standard methods.

`Pollutant could have high molecular weight and not be amenable to analysis methods used` – Substances with particularly high molecular weights have a longer "residence time" in the GC column, the higher the molecular weight the longer the analysis time. When analysing for unknowns if the substance is believed to be of high molecular weight then a suitable solvent can be used and the column run, however the analysis will take longer. Different columns can be used to tailor the analysis to the substance but this obviously requires the knowledge of at least the chemical family of the unknown substance.

`Pollutant only affected fish and no other species to any great extent` - The `modus operandum` of the pollutant was highly specific, only significantly affecting fish with very acute effects apparent, whereas invertebrates and other taxa seemed unaffected. There does not seem to be any readily available database for searching for likely pollutants by these kinds of parameters. A database that you could search for possible pollutants, using known data to refine the list would help direct the analysis, if not identify the pollutant. In this case the highly acute toxicity to fish but low toxicity to invertebrates were very characteristic, and may have helped to focus the analysis efforts. Such a database would require the combining or "data-mining" of several large but existing databases. Data from the setting of Environmental Quality Standards (EQSs), from the Notification of new and existing substances and other ecotoxicological databases could be merged to form a large dataset that could be searched using the known parameters from a pollution investigation. The creating of such a database tool would be quite resource intensive initially, but would then only need updating for new chemicals, and most of the data would already have been checked to European Union (EU) or other standards.

`Pollutants could be extremely toxic to fish in concentrations below level of detection`

Also the pollutant could have been extremely toxic to fish in low concentrations, below those detection limits and/or an 'unknown' not held in the spectra libraries. However most of the unknowns that were found would have had to be extremely toxic because none were present above 100ng^{-1}

`Toxicity and Concentration` - Finally, if the substance had been any of the unknown chemicals that were not in the GC-MS's spectral database then they would have had to be highly toxic but at low concentration. These properties are not very common, with very few chemicals of this nature known. Again a database that allowed you to search for chemicals that are highly toxic but at concentrations less than 100ng^{-1} may help focus, if not identify, the toxin.

On the basis of these initial findings monitoring and analyses were continued however there was still no clearer direction than before but much data to support the elimination of a number of pollutants from further consideration. The information that finally helped to move the investigation along was the fact that the pollution was biological in nature, and this was supported by the resurgence, particularly because there was increased toxicity in a number of separated pounds, highly unusual for an anthropogenic source. There were some thoughts along the lines of biological toxins at this stage, particularly concerning toxic algae, however it was not until the resurgence after the lock gates had been closed that these ideas were confirmed.

5.9 Information Handling and Requirements

This section considers the handling and requirements for information during the investigation:

- Negative results
- Area/Regional specific information
- External expertise

`Negative results` – A major problem during the investigation was that much of the analysis data conveyed negative results. Although a full TIE was not suitable during the early stages of the investigation, a similar tiered approach would have helped in managing the negative results and further structured the continued analyses. Initially perhaps, chemical pollutants would be investigated (being the most common cause of pollution events), then after the initial chemical investigation, if no leads are generated the second tier of investigation could begin. This next stage would involve more refined chemical analysis, targeting more unusual pollutants, as well as some basic biological analysis and tests. The tiered investigation model would help to focus and lead the investigation and this structured model would need to be developed using data from many previous incidences and the analyses most useful in their investigation.

`Area/Regional specific information` – A considerable level of area-specific information aids the management process in incidents like this. Not only at the level of monitoring sites (Pollution Prevention databases provided valuable information on sites in the area) and possible polluters along the watercourse, but also the knowledge of any historical events that may be linked, studies, reports or other factors that may help in the investigation. In this incident many of the operational staff had many years of experience of the particular watercourses, however this can neither be relied upon nor hoped for in all cases. For this reason records of all incidents, related data (for instance any modelling that has been performed on the watercourse) and other useful information need to be recorded and held in archives, and more importantly effectively catalogued so the information is easily retrieved. A great deal of archived information about watercourses and catchments is held at Regional and Area offices, however this is of little use if no-one is aware of or uses the information or makes use of it.

During the investigation for the causative substance, all chemicals contained in the Agrochemicals Handbook and the Pesticide Manual were considered, as well as those not approved for UK use. However, no similar list seemed to be consulted for veterinary actives, yet a cursory review found that "Vade Mecums" were available for bovine and equine drugs, with volumes for other species probably being available. Lists of this nature would be useful for future investigations, as were the agrochemicals and pesticides lists. Even a chemical-by-industry database similar to those discussed previously, with searchable fields, would help to direct and inform investigations.

External expertise – As mentioned previously, particular expertise was brought in as and when it was required and a list of these kinds of contacts for scientific expertise would be a considerable advantage if available to incident management teams in future events. The use of so many different groups working on their own specific angle of the incident did however mean that at stages, more than ten groups were working on different directions in the investigation simultaneously. The reconciling of all the information produced from each of these avenues of investigation, and the job of over-viewing the investigation and information produced by it, was at times problematical. This was one of the reasons the management structure for the incident changed during the course of the incident, (see Section 6.1 for further details).

5.10 NCEHS

The NCEHS's involvement was twofold:

- Initial ETAS response
- ETSs led technical investigation

`Initial ETAS response` – The NCEHS were initially contacted via the Thames Regional Contact (RC) under the ETAS service run by the ETS. The ETAS system has three tiers for responding to information requirements on toxic substances.

1. Regional Contacts
2. Environmental Toxicology Section of NCEHS
3. WRc

Initially the RCs who all have EQS and other basic information for substances should be contacted. If they are then unable to answer the query it is passed on to the ETS, who hold more extensive datasets and databases. If the query still can not be resolved it is passed to WRc who also operate the out-of-hours support for ETAS. Field operatives in their day-to-day work most commonly use ETAS, when minor incidents occur and remediation or environmental protection is required.

However, the existing hierarchical system does not always seem to be adhered to, with queries short-cutting the RC and being made directly to the NCEHS. If the strength and use of the RCs is to be reinforced then queries and even the replies (when ETS or WRc are consulted) must be direct through them. In this investigation this system was bypassed, because of the proximity of the Area Office to the NCEHS (both on the same site), and poor connections and communications between the Area Office and the RC. The types of information provided and extent of the ETAS service should be reviewed, also Area, Regional and other possible customers' awareness of the service, its availability and how queries should be made and to whom should be strengthened.

`ETSs led technical investigation` – Due to the close proximity of the West Area and NCEHS sites Geoff Brighty (head of ETS) was contacted informally by the Area Office, and was present at a meeting held within a few days of the incident. Initially the requirement of the NCEHS had been to highlight possible target toxicants that might aid and help to direct the chemical analysis and identification of the pollutant. Geoff Brighty at this point discussed and agreed the approaches to the on-going monitoring strategy, however, requests from Head Office required greater involvement by the ETS and resulted in Geoff Brighty moving into a more co-ordinating and managing role in the investigation than is normally undertaken. One particular area of input was that of outside expertise, not only that of WRc's investigation, which came about through the ETS's contacts within WRc. Geoff Brighty also commissioned the mammalian toxicity testing at Dundee University and the TIE conducted by CEFAS.

It became apparent during the investigation that the incident was of greater magnitude than first anticipated, this being highlighted by situations such as the unavailability of sufficient sample quantities and the shortage of fish for deployments. It was for this reason that the management of the incident required inputs from so many parties. The number of groups involved and the fact that the scale of the event had not been foreseen may have resulted in the sometimes confused handling and management of these parties and the flow of data between them. Whether ETAS should take such a senior or management role in future incidents needs to be considered. Like the NLS, other work is compromised by the level of attention required by the incident and may, as was the case for the NLS, involve the slip of other obligations, however as previously mentioned, the NLS's remit does give priority to emergency responses.

6 The Incident Management

6.1 Communications and Incident Management

There were many groups requiring up-to-date communication during this incident, and it is the efficient controlling of these lines of communication that can help to streamline the investigation and convey the Agency's control over the situation to the public, media and other stakeholders.

Results from analysis work were reported to the incident room as and when they were available as well as a hard copy daily update report being sent. However, response communications from the incident room tended to be scarce which did not help to direct the investigations. Also often only non-scientific staff were available as contacts at the incident room causing problems in the relaying of messages, sometimes even incorrectly. Technical staff need to be available, or even handling communications in the incident room, otherwise the significance of some data or results may be overlooked when verbal communications are passed on.

The incident management structure changed quite significantly during the course of the investigation, and this resulted in a more complex communication chain in the later part of the investigations. Two organisational charts can be found in the Appendix (Section 10.4), the first outlines the initial incident management structure, and the second outlines the structure after the NCEHS and WRc became involved.

It can be seen that in the initial management structure the West Area office called in the services of the NLS, NFL and NCEHS. The NLS provided laboratory analysis work and the NFL was initially contacted for fish histopathology work, but this was passed on to DB Aqautic Pathology Services because the NFL no longer had emergency response capabilities. Finally the NCEHS was contacted through the ETAS service they provide, initially via the Thames Region RC, with the required information being returned directly to the Area office. Later, pressures from the DETR (Department of the Environment, Transport and the Regions) and the EP, WM and Ops. functions of the Agency's Head Office resulted in this management structure changing significantly. The NCEHS took a co-ordinating role over the technical investigation and the many outside groups who later joined the investigation. A strong two-way link between John Sutton, Fisheries and Ecology Manager in the West Area Office and Geoff Brighty of the NCEHS helped agree and manage the monitoring and analysis strategy. The Area Environmental Protection office dealt with the operational side of the incident as well as public relations (communications with BW and local Councils etc.) and the media.

The initial contact with NCEHS arose partly due to the proximity of the incident room and the NCEHS, both being located on the same site. This was in addition to the ETS receiving a request from West Area through the Thames Region ETAS RC regarding lists of possible toxins that could be causing the pollution. However, the proximity of the two groups was not necessary, the NCEHS being able to offer the same support to a similar incident even if it was further afield. The delegation of some parts of the incident's management to Geoff Brighty was seen as essential. In this particular incident however, this could have been more a matter of manpower, although his presence in the management team did mean his expertise was more easily available to direct and agree monitoring, sampling and other strategies. Such an integral role in the management would not always be possible though, especially if the incident had been further afield.

When we look at the communication system during the incident the number of interested parties created a very complicated network of communication, (see Appendix, Section 10.5, K&A Canal Incident Communication System). We can see how initially the West Area Office was in contact with many different groups, foremost their operational staff some of whom were the first at the incident. Initially the media contacting these Agency staff members in the field and then later media enquiries were directed through the Regional Media Team. As has been mentioned the Thames RC was contacted under the ETAS service and the query was passed on to the NCEHS.

After taking the lead in the technical investigation, the NCEHS contracted WRC along with other outside groups to perform the investigations, however the communication links between these contractors and the incident room became very complex. Most of the contractors reported back to WRc or the NCEHS, depending on who had brought them into the investigations, however Royal Holloway College reported their results back to WRc and not the NCEHS. David Bucke passed his results back to the West Area office as well as to Geoff Brighty via the NFL.

The pressures that came from Head Office both to the West Area Office and the NCEHS can also be seen, with A. Robertson (Ops), contacting the West Area office, while the NCEHS were requested by M. Griffiths (EP) and T. Owen (WM) to lead the technical investigation. These routes of communication were at times varied and confusing, with there seldom being a central point of contact for information. The second communication system diagram (see Appendix, Section 10.5, Possible Incident Communication System) shows a simpler communication system with the Area Office and the Incident Room being the two main hubs for information.

Similar to the earlier communication system, the initial response would be from the Area Office with operational staff visiting the site, sampling monitoring etc. The Area Office and Incident Room would be the main lines of contact with the Regional Media Team, with all responses to the media and other stakeholders coming from this team.

If technical information was needed under the ETAS service, the Area Office would contact the RC in the first instance. If the data were immediately available it would be returned directly to the Area Office, however if the RC was unable to answer the query it would be passed on to the NCEHS in the usual way in the tiered ETAS system. All responses would go back through the RC to the Area strengthening the communications between Area and RC and to avoid higher levels of the service being pulled wholly into one investigation or incident.

If the scale of the incident increased, or if the amount of information required warranted it the RC could work from the Incident Room, this becoming the primary route for communications. This would provide a technical knowledge base on hand and bring the ETAS service more closely in contact with the incident. At each level of the ETAS service, contractors could be brought in as necessary to handle technical areas of the investigations. The RC and NCEHS could also advise what expertise was available, who and where, from a contacts/contractors list if this was held at the National Centre.

One further point that arises from the NCEHS's involvement in this incident is that of its profile. The initial contact was more due to location than through the Area's awareness of the NCEHS and it's activities. Indeed the Area office did not feel that there was particularly much support from the Regional office. If the incident had been in a different location, then the RC may have been involved more in the process. Area offices need to know the procedures of the RC/NCEHS possibly by way of a procedural guideline document. This could outline the boundaries of involvement and what the NCEHS can and cannot provide. These issues need to be addressed, if the centre is to offer similar support in other such incidents, firstly the existence of the NCEHS needs to be known at Area level, and by the people who are most likely to need to call on their support. These Areas then need to know how the tiered ETAS system works and finally what information is available through the system. If however the RCs are overlooked or excluded from the process, the Area Offices will get use to dealing directly with the NCEHS rather than following the ETAS enquiry structured system.

If the NCEHS is to continue providing this kind and level of support, they really need to have details of the incident much earlier in the management process. The existing ETAS tiered structure could be used, information on all incidents being internally e-mailed to the relevant RC during the initial stages of an incident, (see Appendix, Section 10.6 for Flow Diagram). In most cases this may be as far as the ETAS's involvement goes, however if information is required the RC then has some background to the incident. If the RC provides information, the initial e-mailed information on the incident can be forwarded to the National Centre. This would then mean that a database of incidents would develop along with the information provided through the ETAS service. The strength in this way of operating being that information is available on an incident ready for when an ETAS query is made. This information then travels up the tiers of the service one step ahead of the enquiry, allowing events to be monitored and those requiring response targeted. The initial information that would be e-mailed to the RC is probably already being made available to a different audience; it just requires the local RC to be included in the list of those who should be informed with initial details in the case of a pollution event. This system would mean greater data handling by the RC and the NCEHS, but as long as the tiered system is adhered to this extra data should not cause excessive problems, only serving to improve the profile and responses of the centre to its customers. It would also mean a large dataset on pollution incidents in England and Wales would be being collated as part of an existing process, this dataset then being available for analysis to look for trends in and to target pollution incidents.

The existing ETAS system and any expansion to it or other system that may be implemented requires considerable training both of NCEHS staff and the RCs. The RCs' training needs are the most notable because of the number of RCs there are, their diverse locations across the country and because of the turnover that is seen among those holding the post. For these reasons the training of RCs needs to be on a continual basis accounting for those who take-over the positions of others.

6.2 Containment vs. Dilution

The lock gates along the affected reaches of the K&A canal were closed on the 7th March 1998 and were not opened again until 3rd April, after the last deployment which was to confirm the remediation had been affective. Arguments have been put forward both for and against closing the lock gates to contain the pollution. Containment could have concentrated the pollution, while leaving the gates open may have resulted in diluting the toxicity.

However

- Which is the most preferable action containment or dilution, and what factors affect this decision?
- Should the decision to contain be made earlier or later in the incident, what about future incidents?

The containment option was chosen because downstream of the affected canal pounds, were high quality fisheries and points of potable water abstraction and the pollutant hadn't been identified. Live fish had been found downstream at the confluence of Shalbourne Brook with the canal, suggesting local effects in a contained toxic stretch of the watercourse. However more importantly, opening lock gates would have meant knowingly permitting pollution, an action that by the Agency's own working laws they could have been prosecuted by, Water Resources Act 1991, Chapter II – Pollution Offences:

> "A person contravenes this section if he knowingly permits any poisonous, noxious or polluting matter or any solid waste matter to enter any controlled waters."

Section 85.-(1), Water Resources Act 1991, Chapter II - Pollution Offences

So for these reason the decision was made to close the affected pounds; i.e. the lock gates were no longer operated/opened, effectively containing the pollution as far as possible.

The option of containment is usually a matter of logistics; it is not normally possible to contain rivers where the management of pollution incidents tends more towards a monitoring/tracking response. Examples are a stream in Thames Region that was polluted with pesticides, which was dammed, it being practical to do so, whereas previously when there was a DDT (Dichloro Diphenyl Trichloroethane) pollution incident on the River Dun, the pollution was watched and monitored, there being no practical option for containment. In this incident the Agency was faced with two to three polluted pounds on the K&A canal, containing an unknown toxicant. If they had allowed the canal to remain open, or the lock gates to continue to operate, they would have been 'knowingly permitting pollution', an action for which they could have been held responsible.

6.3 Incident Management and the Agency's Aims and Objectives

The Agency's duty is to protect/enhance the environment, in its 'Enforcement and Prosecution Policy' document the Agency says the following (emphasis added),

> "The Environment Agency's aim is to `provide a better environment` for England and Wales both for the present and for the future. It will achieve much of this through education, by providing advice and by regulating the activities of others. Securing compliance

with legal regulatory requirements, using enforcement powers including prosecution, is an important part of achieving this aim."

This means that the Agency must prevent damage to the environment, try to find those who do cause environmental damage, accumulate evidence and where possible prosecute them. To do this there needs to be the provision for twenty-four hour availability for response, both from operational and pollution inspection staff as well as the laboratory and analysis functions that are needed to support any incident investigation. For large businesses the Agency usually just has to ensure that protection/remediation processes are being carried out, through monitoring and assessment, however with smaller companies the need to ensure protection sometimes requires the Agency to act, due to a party not being able to handle the situation themselves. This was the case with the moribund fish in the tanks at the Hungerford Fish Farm, the weight of the dead and dying fish were straining the tank walls posing a possible pollution risk. These fish were removed and the area cleared by Area staff to prevent the pollution of downstream waters.

The initial response to any incident requires sampling and observations to investigate and identify the pollutant. In the K&A canal incident, the problem of negative results arose and by the second and third week of the investigations, even after the resurgence in toxicity, the toxicant had still not been identified, although much was known of its properties by this stage.

The Agency defines an incident as anything that fulfils the following criteria:

- A specific event
- Brought to the Agency's attention
- Within the Agency's area of responsibility
- Has an environmental and/or operational impact

The Hungerford Fish Farm incident certainly meets these criteria and an Emergency Response was initiated. However as the focus of the incident moved from the fish farm to the K&A canal and as the duration of the investigation moved from days to weeks, the incident response could and maybe should have moved towards an Operational Investigation. However the K&A canal incident was classed as an Emergency Response for the duration of the incident. Under the Agencies new CIC (Common Incident Classification) system this incident would have been classed as high impact due to the media attention as well as the high value of the watercourse and the sensitivity of the area. It seems though that the point at which an incident's investigation becomes an operational investigation either needs to be clarified or more rigorously adhered to.

There are competing interests in the above two types of incident management, an investigation (whether operational or not) tries to identify the pollutant, whilst an Emergency Response aims to control the pollution, of which remediation is one option. When, as in this incident, control options are discovered before the pollutant's identity is known, a question arises, should the control option be carried out (remediation in this case) destroying any of the pollutant remaining, or should the pollutant be investigated until identified? Identification would mean that the pollutant could be detected and treated more quickly from a more informed viewpoint in the current and future situations, however when considering the Agency's aims, where possible control options should be put in place. Allowing a pollutant to remain in a watercourse for an unknown length of time, even if this is to study the pollutant for future reference would prove hard to defend against the Agency's current aims. Whether or not remediation was the right control option to choose, and what other control options would have been successful and would have met the Agency's aims is hard to argue in retrospect, very few samples being available after the incident for further investigation.

6.4 Control Options –

During the incident investigations some of the process steps alone used in analyses seemed to render toxic samples no longer toxic, indicating that the pollutant was very unstable to temperature, pH and other physical and chemical changes. The use of these process steps that could have lead to the breaking down of the pollutant would have affected the investigations. This shows the importance of the information produced by the TIE, and these findings need to be communicated to those performing the analysis as soon as possible to ensure their analyses process methods are not destroying the pollutant. In this incident it was decided to remediate the affected reaches of the canal, remediation being chosen due to the high value of the watercourse and surrounding area and because of the favourable logistics. Hydrogen peroxide solution (H_2O_2) was used for the remediation, because Agency staff had experience in its use and due to the low probability of adverse effects to the environment. Some biologists expressed concerns over the use of hydrogen peroxide, and its effects on macroinvertebrates, flora and fauna. However the arguments supporting the action seemed to outweigh those against in this situation. It is worth noting that when taking a decision upon remediation options the methods and effects of that option to the environment are considered by the Agency.

All the pounds between Lock 74 and Lock 68 were treated with hydrogen peroxide, but no treatment was carried out on the River Dun or the River Kennet. To monitor the effectiveness of the dosing a final deployment was made at all treated sites and the control site. Although the WRc report states that no mortalities occurred in these deployments, the raw data as available in the annex to the report indicates two fatalities were recorded to small chub at Site 6 after 96 hours. This reach on the River Kennet, down stream of its confluence with the river Dun had not been treated even though in the previous deployments (Deployment 3) there had been mortalities at this site. These mortalities, in both cases, may have been due to stress or other unrelated affects but because of the small number of fish deployed and the lack of further details about these two fatalities no further conclusions can be made.

As quoted earlier, the Agency aims to “provide a better environment”. The word ‘better’ can be taken to mean returned to full health, however it is usually associated with the suggestion of improvement. Whether or not nature can be improved upon is a philosophical debate and depends on which viewpoint the improvement is being considered from. However if we consider the Agency’s aim is to return the environment to full health, does remediation as a control method fulfil this goal? If you are adding something extra to the environment, whether it is another chemical, to combine with or breakdown a pollutant or water to aid the dilution process you are taking the system further from its original or natural state. The ideal goal would be for no chemicals or substances from anthropogenic sources to enter the environment, however this is not attainable, even limiting emissions takes great changes in our social arrangements and domestic and business paradigms. This brings social and also economic factors into consideration. If we cannot avoid some emissions into the environment, then the next best option after limiting these would be to allow, where possible the environment to deal with these pollution incidents in a natural way. Allowing chemicals to breakdown under natural actions, but again this is not always possible, particularly when considering social and economic factors. If a polluted area has a high amenity value then the pressure to "clean-up" the pollution will be high, as will areas of high economic value, e.g. fisheries.

Pollution incidents need to be considered and assessed on a case by case basis, and to make the decision processes transparent, actual values need to be put on the environment and social value of areas. Although this is not ideal, these values will be considered, in the management of an incident and so the thought process behind the setting of these values needs to be defendable. Such a system for putting a value on an area would then aid the decision process in such situations as whether to remediate or just to sample and monitor. However such a system if used, needs to be widely accepted, involving the education of stakeholders as to why values have been set and the reasons for their magnitudes. These figures also need to be supported and agreed by the Government to avoid cases like the Thames Water, Axford abstraction licence decision, where the value of "non-use" related benefits of a watercourse as calculated by the Agency were amended from £13.2 million down to £0.3 million by the Government Inspector. Cases like this undermine the Agency's position and promote mistrust in the values they give to the environment.

7 The Media

7.1 National Press

Throughout the K&A canal incident media attention was high both at local and national level. The BBC news page on the Internet ran an article on the incident (published 19:38 5th March 1998), outlining how a "mystery pollutant" had killed "more than 3 million fish". They stated that it was thought that the contaminant had "entered" the river and spread down stream. The report stated that "the Environment Agency says it may have traced the source of pollution" and went on to outline some of the investigations being undertaken. On the same day The Times ran an article entitled, "Trout farm loses entire stock to pollution spill". This article stated that the Agency's belief was that the pollutant was a pesticide. An Agency spokesperson was also quoted as having said about the pollutant "We can't remove it. We have to wait for nature to take its course."

The Guardian on the .14th of March, after WRc's investigation had commenced, wrote of the Agency's costly investigation and the continued allusiveness of the pollutant's identity and origin. It was also quoted that the Agency had investigated possible toxicants "from A to Z" and having found nothing had started again. Also highlighted in this report was Mr. Stevenson's allegations of a previous incident that was reported to have occurred in 1994, however it actually occurred in 1995. This report mentioned the Agency's defence to these allegation and described their investigation as "directionless", but also stating that the Agency's investigation was concentrating in the single direction of identifying the pollutant.

On the 27th March the ENDS (ENvironmental Data Services) Report ran an article where the incident was put down to "a combination of rare, natural phenomena". This article stated that the pollution was caused in part by algal growth. It also mentioned that the Agency was only aware of one other similar incident (New Zealand 1994). The lack of effects on invertebrates was also mentioned ruling out insecticides or pesticides. The Agency's remediation plans were also outlined. This report outlined the Agency's "several lines of investigation". The Independent's report on 28th March mirrors that of the ENDS Report in its more factual and clear statement of the problem, believed causes and proposed remediation efforts.

It is unfortunate that a national paper only reported the incident and its associated efforts in a clear and factual manner this late in the response. The reason for this may have been due to the large number of people involved in the incident, and the confusion that may have resulted in the communication between all the interested parties. The message the initial reports conveyed to the Public, one of the Agency's main customers, was one of confusion and a "directionless" approach to the incident. It is not always possible or necessary to identify pollutants, but it would seem that the pollutant's identity is thought important (or at least perceived to be) by the Agency's stakeholders.

The only message which seems to be consistent throughout the different reports, is that of Mr. Stevenson's feelings about the incident and his loss of his entire stock of 150 tonnes of fish, except that The Times quoted the loss of fish to be 300 tonnes. Although more difficult, the Agency needs to convey its messages and report its findings throughout an incident with a similar clarity and focus to the other interested parties. This can be achieved if a single spokesperson represents the Agency's stance on the investigation (or any other issue). However this is not always possible with field staff being put on the spot for answers, so for this reason those likely to be approached for comments need to be up to date on the issues and results of the investigation, in an attempt to show are more united front.

7.2 Internal Press

In the March issue of the Thames Regional internal newsletter the incident was outlined as one of the region's worst. The April issue went into further details of the clean-up operation, the NLS and WRc investigations and the remediation of the site. Finally, in the May issue a column on lessons learnt was run. This article outlined the need for one senior member of staff in overall control and with the authority to make important decisions. Efficient communication, in particular on the incident and Customer Services telephone lines were also highlighted. There was also a need for a technical person to be available at all times in the incident room to keep up with new results and, as has been mentioned, to be able to understand scientific messages that need to be passed on. It was also noted that some of the area management team had been drawn into the hands-on work due to the high work load, when they should have been taking a "helicopter" viewpoint so as to oversee and direct the investigations. However it is worth noting that both the national and regional internal newsletters misrepresented information in their reports. This shows the failings in the communication chain, if even an internal resource can't publish the correct facts.

8 Conclusions

8.1 Management & Communications

The following areas of the incident's management and communications are considered:

- Structured analysis approach
- Data storage
- Clear lines of communication
- Incident room communications
- Development of incident

Structured analysis approach – A tiered approach to incident investigations is required, most specifically in the analysis used in these investigations. This tiered system would then help to focus and lead the incident investigations. Such an approach needs to be developed by reviewing many pollution incidents and the analyses used in their investigations and the analytical tools that were of most use. A tiered structure of analysis steps in future pollution incidents could then be proposed.

Data storage – Incident related and local or watercourse specific data both at Area and Regional level needs to be stored and effectively catalogued for future retrieval.

Clear lines of communication – Communication between parties involved in an incident investigation need to be streamlined. This would then help to convey the Agency's control over an incident to the public, the media and other stakeholders. Effective lines of communication between field operators and incident managers needs to ensured, with all communications going through one central hub, rather than some reports returning to the Area Office and others to the incident room.

Incident room communications – Scientific staff need to be available in the incident room as contacts for dealing with, understanding and conveying detailed technical information. There also needs to be effective return communications from the incident room to the analytical laboratories and other parties in the investigation to help lead their work.

`Development of incident` – As the scope and spatial effect of an incident increases, and as its duration increases there should be a point at which an emergency response becomes an operational investigation; these two approaches having different and competing interests (control versus investigation/identification). The point at which the status of an incident changes from an emergency response to an operational investigation needs to be clarified, and adhered to.

8.2 Emergency Response

The following areas of emergency response to incidents are considered:

- Availability of emergency response
- Contractors contact list

`Availability of emergency response` – Not all Agency functions will be able to provide an emergency response to incidents (as was the NFL's situation) or their response may result in a slip in their other work and obligations (as in the case of the NLS). There needs to be the provision for 24hr response from operational and management teams, laboratory and other analysis services, and ETAS, to support emergency incident investigations. These areas do not all need to necessarily be covered in-house, some services maybe having alternative support 'out of office hours', however the availability of these services needs to be widely known and clarified along with what is (and is not) within their remits and abilities.

`Contractors contact list` – The services available within the Agency in emergency situations need to be compared to what services are required for the investigations and if the support is not available in-house, external sources need to be investigated. Although it would be better where possible to keep the expertise in-house so that future incidents could be dealt with in light of previous experiences, this is not always possible, and a contact list for external experts needs to be compiled. This contact list also needs to contain details of commonly needed resources (e.g. test organisms) and test and analysis institutes as well as external experts. The list needs to be maintained and kept up to date and be readily available to incident managers, this could be done through the NCEHS, possibly forming part of the ETAS service.

8.3 The NCEHS

The following areas of the NCEHS and it's response to incidents are considered:

- Profile and contact
- Kennet & Avon Incident Response
- Incident information

`Profile and contact` – Awareness of the information service, its availability, and how and to whom queries should be made needs to be increased. Also the hierarchical, tiered contact structure of ETAS is not always adhered to, with queries often bypassing the RC and being directed directly to the NCEHS. To reinforce and increase their positions all queries and replies (even if passed up to the NCEHS) must be directed through the RC's.

`Kennet & Avon Incident Response` – Although initially contacted under ETAS for possible target toxicants, Geoff Brighty was also asked to discuss and agree the monitoring strategy. Then when the Agency's Head Office required greater involvement, Geoff Brighty moved into a more co-ordinating/management role of outside expertise. Like the NLS such a level of involvement has ramifications on other work within the ETS and can (and did) result in slip of other obligations. For this reason the remit of ETAS and its level of support need to be clarified and communicated to its customers.

The same level of information support as provided in this incident would have been possible further afield and did not require the close proximity of the NCEHS and West Area Office. The delegation of some sides of the investigation to Geoff Brighty were seen as essential by the Area Office, although this may have been partly due to the shortage of manpower. However Geoff Brighty's close involvement did provide valuable technical support and ensured the expertise to discuss and direct monitoring and analyses were easily available. Such an integral role would not be possible if the incident had been further afield, for this reason the RC could provide this close contact, even by working from the incident room to provide on-hand technical knowledge and support should the level of the incident require it. This would also bring the ETAS service closer to the incident.

Incident information – The NCEHS needs to receive pollution incident details earlier in the management of an incident than currently occurs. This would allow the ETS to have the required information on an incident to-hand in case of an enquiry under ETAS. The existing tiered structure of ETAS could be employed with incident information travelling up the tiered system one step in advance of a query. This would require incident managers to send pollution incident details to RC's, so the information was available to them if a query came through. This system although requiring greater data handling than at present, would mean that a national database of incidents was compiled as part of an existing system, and would improve the profile and responses of the ETS and the NCEHS.

8.4 Incident Investigation -

The following areas of the NCEHS and it's response to incidents are considered:

- Routine monitoring
- Sampling
- Algal blooms
- TIE
- Monitoring program
- Analysis
- Treatment

Routine monitoring – Routine monitoring needs to continue at the current or higher level, otherwise only limited or out-dated historical/background data will be available for reference in future pollution incidents. Although there is no routine bacterial monitoring or sampling, and it is not always required, the testing facilities should be available if not to-hand for operational staff in the field.

Monitoring program – The four main deployments along with the parallel laboratory analyses worked very well, the field deployments setting a timescale for the investigations and allowing the pollutant to be tracked. This approach also helped to structure the investigations. When necessary the monitoring sites were added to or split to refine investigations, however such a large-scale field-monitoring program is resource intensive and not always necessary depending on the scale of the incident.

`Sampling` – The required volumes of samples necessary for effective analyses were not always available, effective lines of communication between the laboratory and the field need to be ensured to so sampling can be at least partially directed by those analysing the samples. Adequate comparisons and sample controls also need to be ensured, there being no direct comparisons made of the toxicity found at the fish farm and River Dun with toxicity in the K&A canal. Also, the designated control site was found to be toxic at least once during the investigation (although this was at a late stage in the investigations), a comparison of the intended control site with a different local but unaffected watercourse might add support to the validity of chosen control sites.

`Analysis` – Results from the TIE investigation suggested that some process steps in the sample preparation stages of analyses may have rendered the samples non-toxic. This is an area where greater understanding of the analysis process and work-up stages could help inform the investigation managers. Incident managers need to be aware of the limitation of each analysis method so that the results obtained are viewed in context. Only after continued negative results from chemical analyses were other (biological, natural) pollution sources considered, a structured analysis program should be developed (as outlined above) to direct the analyses. The re-running of analyses after the increase in toxicity and the treatment of the increase as a separate incident allowed the hypothesis of a resurgence to be clearly tested.

`Algal blooms` – There is confusion in the WRc report, which states that non-toxic pounds, characterised by algal blooms, became toxic 2-3 days after the algal blooms crashed. Observations and monitoring data show that after the splitting of the site the upstream section was found to be non-toxic while the downstream section was toxic. The bloom crashed the day after the site was split yet the upsteam section remained non-toxic for the remainder of the investigation. Observations need to be clearly recorded in incidents of this nature, and in similar situations, regular visual surveys may help to support results observed in the field and laboratory analyses.

`Treatment` – The Agency successfully carried out the chosen treatment option, in which its staff had experience. There was no treatment of the River Dun and although the WRc reported that no mortalities were observed in the final deployment, the raw data indicates mortalities did occur at a site on the River Dun. The Rivers Dun and Kennet were not treated because they were flowing and only seem to be toxic when canal water over-spilled into them. However, dilution in the canal had been discounted, partly due to the feasibility of H_2O_2 treatment and these considerations should have been discussed in greater depth in the Technical Report on the incident. Also the incident highlighted the need for adequate test organism populations for deployments so that unrelated mortalities can be discounted.

`TIE` – The TIE investigation proved to be an effective, structured tool in the gathering of physical and chemical data leading towards identifying a pollutant. The results from the investigation helped to characterise the pollutant and support treatment options. TIE does however require an acute endpoint to provide results promptly; an analysis of the cost versus the benefit (information provided) and on what timescale depending on the length of the endpoint would help to support future use of this tool.

8.5 Databases

The following areas were databases could be developed to aid in future incident investigations are considered:

- Predictive monitoring and analysis
- Pollutant targeting
- Chemicals by industry and use

`Predictive monitoring and analysis` – Data obtained from the current (and if possible increased) routine monitoring and analysis could be analysed in an automated computer process. This system would search for groups of parameters that are indicative of potential pollution problems and areas of concern. The highlighted "hot spot" indicated as of concern could then be targeted by the relevant Areas.

Pollutant targeting – By combining several existing databases of chemicals and their physical, chemical and ecotoxicological properties, a large database could be created which could be queried using known properties in a pollution incident, (e.g. chemicals causing piscine toxicity <3.6 $mg.l^{-1}$). The target list would then be further refined as other properties of the toxin were found. In this way a target chemical list would be generated which would help to direct and lead analyses and investigations.

Chemicals by industry and use – There was a need for information on chemicals by their use during the investigations, the argochemicals and pesticides handbooks being consulted. A searchable database should be compiled containing this data, much of which will already be available in other data sources (e.g. ECB's new substances database). This information could be included as extra fields in the database above, and would again help managers to direct investigations by including or discounting chemicals from their possible target list, by their industry and use.

9 Glossary and References

9.1 Glossary

Term	**Definition**
ADZ	Aggregated Dead-Zone (model)
BOD	Biological Oxygen Demand
BW	British Waterways
CEFAS	Centre for Environmental, Fisheries and Aquaculture Science
DDT	Dichloro diphenyl trichloroethane
DETR	Department for the Environment, Transport and the Regions
DO	Dissolved Oxygen
ECL	Enhanced Chemi-Luminescence
ENDS	Environmental Data Services
EP	Environmental Protection
EQS	Environmental Quality Standards
ETAS	Environmental Toxicology Advisory Service
ETS	Environmental Toxicology Section
EU	European Union
Fry	Young or juveniles of a species
GC	Gas Chromatograph
H_2O_2	Hydrogen peroxide
K&A	Kennet and Avon (canal)
Motile	Capable of moving spontaneously
MS	Mass Spectrometry
NCEHS	National Centre for Ecotoxicology and Hazardous Substances
NFL	National Fisheries Laboratory
NLS	National Laboratory Service
Ops.	Operations
Pound	The reach/stretch of water between two lock gates on a canal
RC	Regional Contact
SEM	Scanning Electron Microscopy
TIE	Toxic Identification and Evaluation
WM	Water Management

9.2 References

M. J. Grimwood; (1997); Fate and Toxicity of Hydrogen Peroxide in Aquatic Environments and Sewage Effluents; Technical Report No. G11, WRc Report No. EA4348, WRc plc., for the Environment Agency.

W. H. van der Schalie, T. R. Shedd and M. G. Zeeman; (1988); Ventilatory and Movement Responses of Rainbow Trout Exposed to 1,3,5-trinitrobenzene in an Automated Biomonitoring System; in Automated Biomonitoring Ed. D. Gruber and J. Diamond; Chichester: John Wiley & Sons

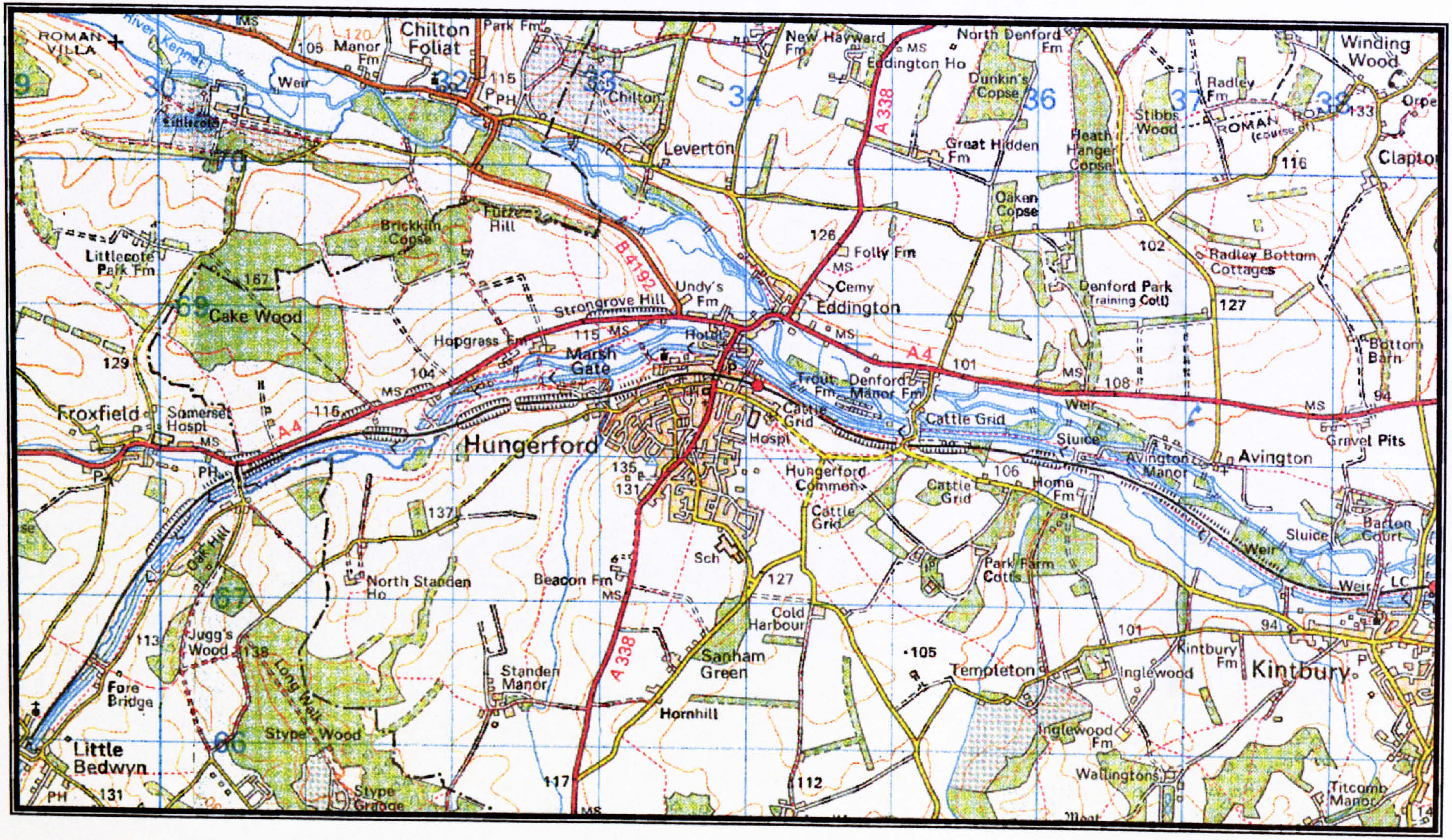
T. Wilkes; (1997); Pollution Incident Prediction Using the Aggregated Dead Zone Model, Lancaster University

10 Appendix

Section	Title
10.1	Map of the Kennet and Avon Canal and the Rivers Dun and Kennet
10.2	Toxicity Profile of the Kennet and Avon Canal
10.3	Decision-Tree Diagram of the Investigations for the Kennet and Avon Canal Incident
10.4	Kennet and Avon Canal Incident Investigation Organisational Charts
10.5	Kennet and Avon Canal Incident Investigation Communication System Charts
10.6	ETAS Incident Flow Diagram

10.1 Map of the Kennet and Avon Canal and the Rivers Dun and Kennet

Map of the Kennet and Avon Canal and the Rivers Dun and Kennet



10.2 Toxicity Profile of the Kennet and Avon Canal

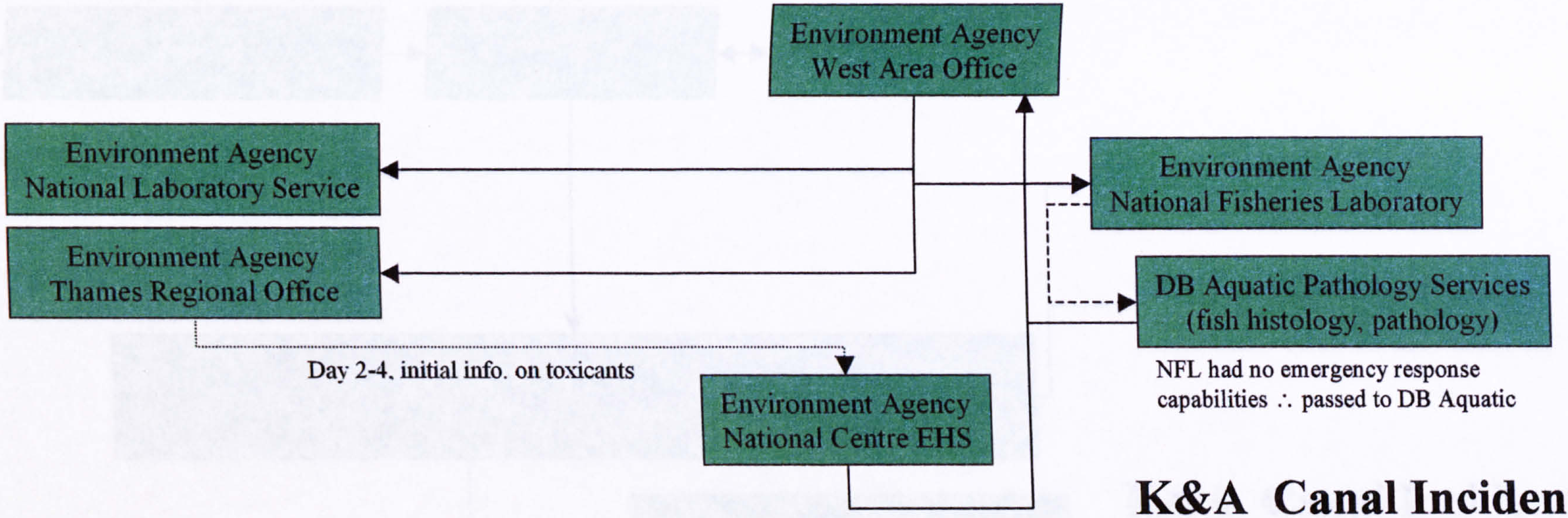
Profile of Toxicity of Pollution Throughout the Course of the Incident

10.3 Decision-Tree Diagram of the Investigations for the Kennet and Avon Canal Incident

River Dun Pollution Incident - Technical Investigation

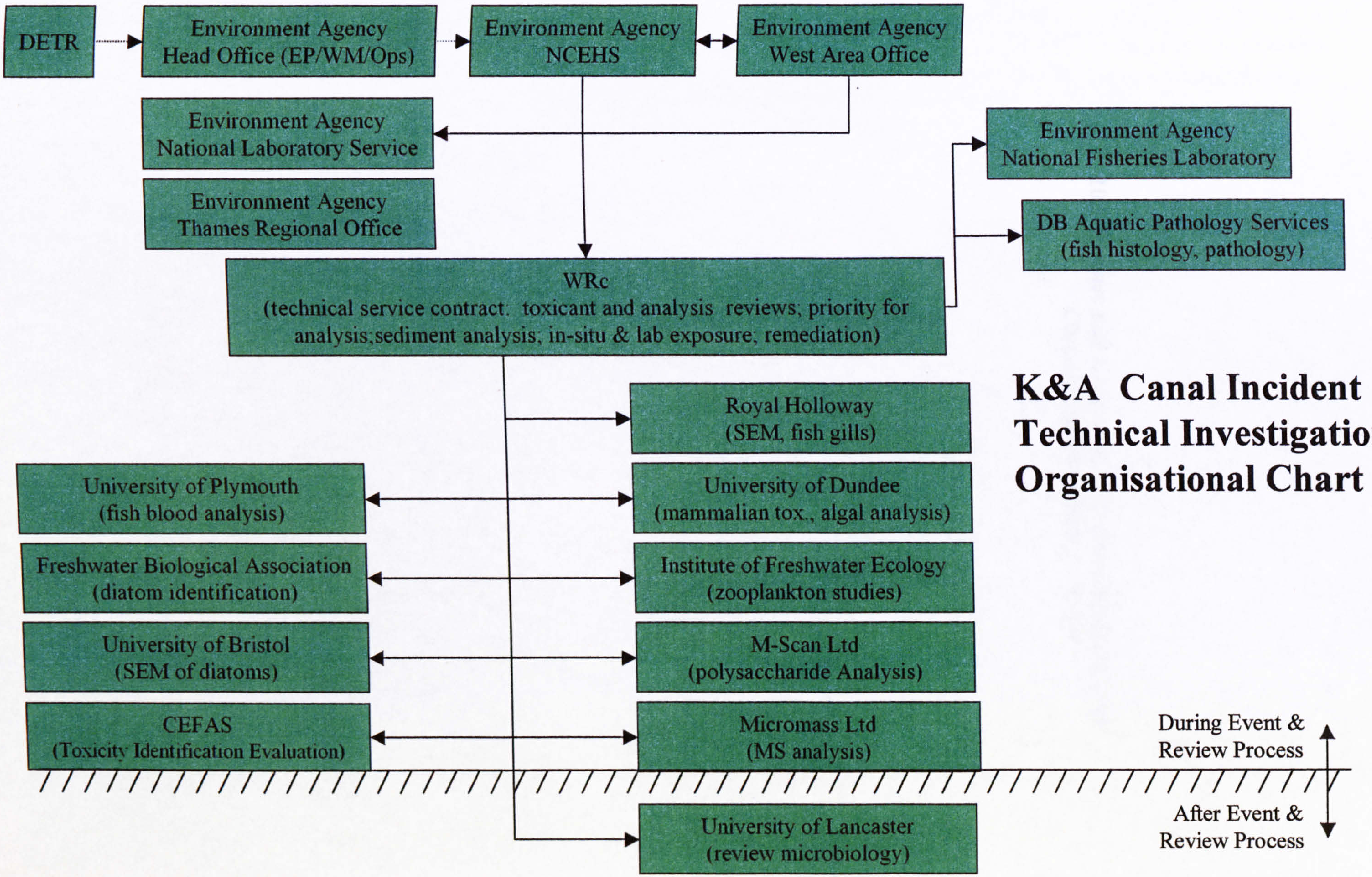
10.4 Kennet and Avon Canal Incident Investigation Organisational Charts

K&A Canal Incident
Initial Investigation
Organisational Chart



NFL had no emergency response capabilities ∴ passed to DB Aquatic

K&A Canal Incident Technical Investigation Organisational Chart



10.5 Kennet and Avon Canal Incident Investigation Communication System Charts

K&A Canal Incident Communications System

K&A Canal Incident Communications System

Notes from communication system diagram:

Order of communications:

① - Initially the response was from the West Area Office, with operational staff being some of the first at the incident

② - The Thames Region RC was contacted under the ETAS service for information on possible pollutants

③ - This query was then passed from the RC to the NCEHS to deal with

④ - Responses from the NCEHS went back, at first via the RC

⑤ - Responses from the NCEHS also went back directly to the West Area office. This last line of communication became the main line between the Area office (John Sutton) and the NCEHS for the remainder of the incident, after the pressures from Head Office (see ❻)

General notes:

→ -Represents temporary lines of communication

❶ - Initially the media were contacting EA operational staff in the field, this meant that these initial statements to the media had not gone through the Regional Media Team

❷ - After the initial incident most media enquiries were directed through the Regional Media Team, however some staff were still being contacted directly in the field

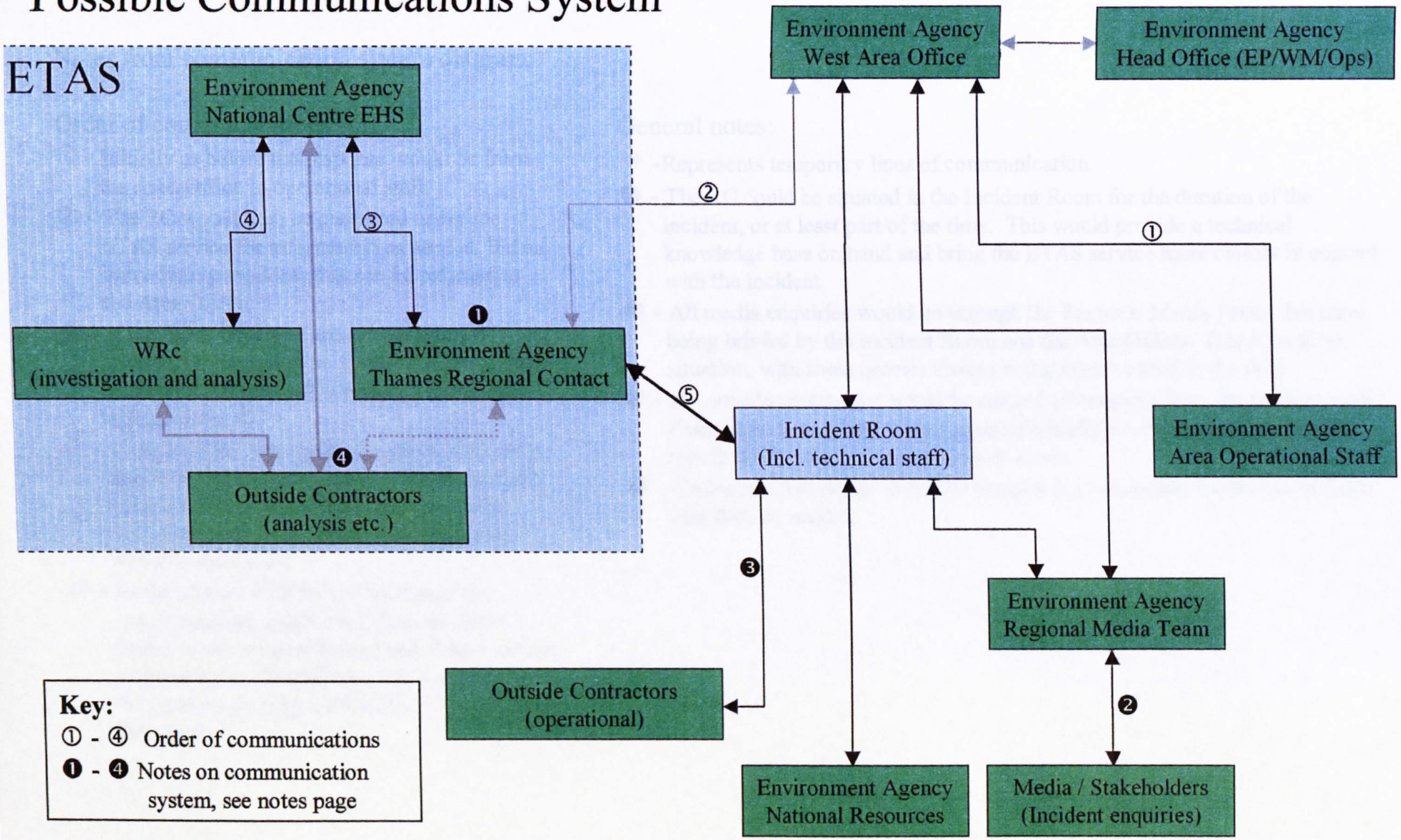
❸ - Royal Holloway College reported the results of their work back to WRc and John Sutton not the NCEHS

❹ - David Bucke passed his results back to John Sutton and the West Area office as well as through the NFL to Geoff Brighty at the NCEHS

❺ - The dotted line between the NLS and WRc represents the initial communications, when WRc first started their investigations during which time they reviewed the earlier work by the NLS.

❻ - Pressures from Head Office came from three functions, with A. Robertson (Ops), communicating with the West Area office, while M. Griffiths (EP) and T. Owen (WM) requested the NCEHS to lead the technical investigation

Possible Communications System



Possible Communications System

Notes from communication system diagram:

Order of communications:

① - Initially as before the response would be from the Area Office to operational staff

② - The RC would then be contacted under the ETAS service for information as needed, if data immediately available this can be returned to the Area Office

③ - If the RC is unable to answer the query it would then be passed on to the NCEHS to deal with, with answers being returned to the Area office via the RC

④ - If the NCEHS was unable to answer the query then it would be passed on to WRc under their contract to the ETS. Responses from WRc would be returned to the Area office via the NCEHS and the RC

⑤ - As the contact with the RC increased the communication would shift from the Area Office to the Incident Room, and if the incident required it the RC could actually be based in the Incident Room providing the ETAS support from their

General notes:

→ -Represents temporary lines of communication

❶ - The RC could be situated in the Incident Room for the duration of the incident, or at least part of the time. This would provide a technical knowledge base on hand and bring the ETAS service more closely in contact with the incident

❷ - All media enquiries would go through the Regional Media Team, this team being briefed by the Incident Room and the Area Office. This is an ideal situation, with some queries always being made to staff in the field

❸ - All outside contractors would be controlled centrally from the incident room. Even if the contractors were contacted initially by a third party the control would still be centred in the Incident Room

❹ - Technical Contractors would be brought in as necessary by the RC NCEHS and WRc as needed.

10.6 ETAS Incident Flow Diagram

ETAS Flow Diagram

As the incident progresses the connection with the RC may become greater and the RC may even work from the Incident Room, being available for information requests and to receive incoming technical data.

APPENDIX 5 – EXISTING SUBSTANCES PRIORITY LISTS

EXISTING SUBSTANCES PRIORITY LISTS

Article 8 of the Regulation states that the Commission, in consultation with the Member States, will regularly draw up lists of priority substances which require immediate attention because of their potential effects to human health and the environment. Basic data collected during the initial stages are used as the basis for selecting priority substances. Four such priority lists have been published to date.

National priority lists are incorporated into the working lists that are formed from various ranking methods.

Key to Member States:

A	Austria	B	Belgium
D	Germany	DK	Denmark
E	Spain	EL	Greece
F	France	FIN	Finland
I	Italy	IRL	Ireland
N	Norway	NL	The Netherlands
P	Portugal	S	Sweden
UK	United Kingdom		

FIRST PRIORITY LIST

Commission Regulation (EC) No 1179/94 concerning the first list of priority substances as foreseen under Council Regulation (EEC) No 793/93

Official journal of the European Communities, No L 131, 26/05/1994, P 0003 - 0004

CAS No.	EINECS No.	Chemical Name	Member State
60-00-4	200-449-4	edetic acid	D
62-53-3	200-539-3	aniline	D
64-02-8	200-573-9	tetrasodium ethylenediaminetetraacetate	D
71-43-2	200-753-7	benzene	D
75-05-8	200-835-2	acetonitrile	E

CAS No.	EINECS No.	Chemical Name	Member State
79-01-6	201-167-4	trichloroethylene	UK
79-06-1	201-173-7	acrylamide	UK
79-10-7	201-177-9	acrylic acid	D
79-20-9	201-185-2	methyl acetate	D
79-41-4	201-204-4	methacrylic acid	D
80-62-6	201-297-1	methyl methacrylate	D
84-74-2	201-557-4	dibutyl phtalate	NL
91-20-3	202-049-5	naphthalene	UK
95-76-1	202-448-4	3,4-dichloroaniline	D
95-80-7	202-453-1	4-methyl-m-phenylenediamine	D
98-82-8	202-704-5	cumene	E
100-41-4	202-849-4	ethylbenzene	D
100-42-5	202-851-5	styrene	UK
101-77-9	202-974-4	4,4& prime;-methylenedianiline	D
103-11-7	203-080-7	2-ethylhexyl acrylate	D
106-46-7	203-400-5	1,4-dichlorobenzene	F
106-99-0	203-450-8	buta-1,3-diene	UK
107-02-8	203-453-4	acrylaldehyde	NL
107-13-1	203-466-5	acrylonitrile	IRL
107-64-2	203-508-2	dimethyldioctadecylammonium chloride	D
108-05-4	203-545-4	vinyl acetate	D
108-95-2	203-632-7	phenol	D
110-49-6	203-772-9	2-methoxyehtyl acetate	NL
110-65-6	203-788-6	but-2-yne-1,4-diol	D
110-82-7	203-806-2	cyclohexane	F
111-77-3	203-906-6	2-(2-methoxyethoxy)ethanol	NL
112-34-5	203-961-6	2-(2-butoxyethoxy)ethanol	NL
117-84-0	204-214-7	dioctyl phthalate	NL
127-18-4	204-825-9	tetrachloroethylene	UK
141-97-9	205-516-1	ethyl acetoacetate	D

CAS No.	EINECS No.	Chemical Name	Member State
1163-19-5	214-604-9	bis(pentabromophenyl)ether	F/UK
1570-64-5	216-381-3	4-chloro-o-cresol	DK
7664-39-3	231-634-8	hydrogen fluoride	NL
32536-52-0	251-087-9	diphenyl ether, octabromo derivative	F/UK
65996-92-1	266-027-7	Distillates (coal tar)	NL
67774-74-7	267-051-0	Benzene, C10-13 -alkyl derivs.	I
85535-84-8	287-476-5	Alkanes, C10-13, chloro	UK

SECOND PRIORITY LIST

Commission Regulation (EC) No 2268/95 concerning the second list of priority substances as foreseen under Council Regulation (EEC) No 793/93

Official journal of the European Communities, No. L 231, 28/09/1995, P. 0018 - 0019

CAS No.	EINECS No.	Chemical Name	Member State
67-66-3	200-663-8	chloroform	F
71-23-8	200-746-9	propan-1-ol	D
75-45-6	200-871-9	chlorodifluoromethane	I
75-56-9	200-879-2	methyloxirane	UK
77-78-1	201-058-1	dimethyl sulphate	NL
88-12-0	201-800-4	1-vinyl-2-pyrrolidone	UK
90-04-0	201-963-1	o-anisidine	A
95-33-0	202-411-2	N-cyclohexylbenzothiazole-2-sulphenamide	D
98-01-1	202-627-7	2-furaldehyde	NL
100-97-0	202-905-8	methenamine	D
108-88-3	203-625-9	toluene	DK
109-66-0	203-692-4	pentane	N
110-80-5	203-804-1	2-ethoxyethanol	D

CAS No.	EINECS No.	Chemical Name	Member State
111-15-9	203-839-2	2-ethoxyethyl acetate	D
115-96-8	204-118-5	tris(2-chloroethyl) phosphate	D
117-81-7	204-211-0	bis(2-ethylhexyl) phthalate	S
120-82-1	204-428-0	1,2,4-trichlorobenzene	DK
123-91-1	204-661-8	1,4-dioxane	NL
557-05-1	209-151-9	zinc distearate	NL
1314-13-2	215-222-5	zinc oxide	NL
7440-66-6	231-175-3	zinc	NL
7646-85-7	231-592-0	zinc chloride	NL
7681-52-9	231-668-3	sodium hypochlorite	I
7722-84-1	231-765-0	hydrogen peroxide	FIN
7733-02-0	231-793-3	zinc sulphate	NL
7779-90-0	231-944-3	trizinc bis(orthophosphate)	NL
25154-52-3	246-672-0	nonylphenol	UK
25167-70-8	246-690-9	2,4,4-trimethylpentene	D
25637-99-4	247-148-4	hexabromocyclododecane	S
26761-40-0	247-977-1	di-"isodecyl" phthalate	F
28553-12-0	249-079-5	di-"isononyl" phthalate	F
32534-81-9	251-084-2	diphenyl ether, pentabromo derivative	UK
61790-33-8	263-125-1	Amines, tallow alkyl	D
68515-48-0	271-090-9	1,2-Benzenedicarboxylic acid, di-C8-10-branched alkyl esters, C9-rich	F
68515-49-1	271-091-4	1,2-Benzenedicarboxylic acid, di-C9-11-branched alkyl esters, C10-rich	F
84852-15-3	284-325-5	Phenol, 4-nonyl-, branched	UK

THIRD PRIORITY LIST

Commission Regulation (EC) No 143/97 concerning the third list of priority substances as foreseen under Council Regulation (EEC) No 793/93

Official journal of the European Communities, No. L 025 , 28/01/1997 P. 0013 - 0014

CAS No.	EINECS No.	Chemical Name	Member State
75-91-2	200-915-7	tert-butyl hydroperoxide	NL
79-11-8	201-178-4	chloroacetic acid	NL
80-05-7	201-245-8	4,4'-isopropylidenediphenol	UK
81-14-1	201-328-9	4'-tert-butyl-2',6'-dimethyl-3',5'-dinitroacetophenone	NL
81-15-2	201-329-4	5-tert-butyl-2,4,6-trinitro-m-xylene	NL
85-68-7	201-622-7	benzyl butyl phthalate	N
98-95-3	202-716-0	nitrobenzene	D
110-85-0	203-808-3	piperazine	S
120-12-7	204-371-1	anthracene	EL
122-39-4	204-539-4	diphenylamine	D
1306-19-0	215-146-2	cadmium oxide	B
1333-82-0	215-607-8	chromium trioxide	UK
1634-04-4	216-653-1	tert-butyl methyl ether	FIN
3033-77-0	221-221-0	2,3-epoxypropyltrimethylammonium chloride	FIN
3327-22-8	222-048-3	(3-chloro-2-hydroxypropyl) trimethylammonium chloride	FIN
5064-31-3	225-768-6	trisodium nitrilotriacetate	D
7440-02-0	231-111-4	nickel	DK
7440-43-9	231-152-8	cadmium	B
7775-11-3	231-889-5	sodium chromate	UK
7778-50-9	231-906-6	potassium dichromate	UK
7782-50-5	231-959-5	chlorine	I

CAS No.	EINECS No.	Chemical Name	Member State
7786-81-4	232-104-9	nickel sulphate	DK
7789-09-5	232-143-1	ammonium dichromate	UK
10039-54-0	233-118-8	bis(hydroxylammonium) sulphate	D
10588-01-9	234-190-3	sodium dichromate	UK
11138-47-9	234-390-0	Perboric acid, sodium salt	A
13775-53-6	237-410-6	trisodium hexafluoroaluminate	D
15096-52-3	239-148-8	trisodium hexafluoroaluminate	D
26447-40-5	247-714-0	methylenediphenyl diisocyanate	B
30899-19-5	250-378-8	pentanol	D
65996-93-2	266-028-2	Pitch, coal tar, high-temp.	NL
85535-85-9	287-477-0	Alkanes, C14-17, chloro	UK

FOURTH PRIORITY LIST

Commission Regulation (EC) No 2364/2000 concerning the fourth list of priority substances as foreseen under Council Regulation (EEC) No 793/93

Official journal of the European Communities, No. L 273 , 26/10/2000 P. 0005 - 0007

CAS No.	EINECS No.	Chemical Name	Member State
77-47-4	201-029-3	Hexachlorocyclopentadiene	NL
79-94-7	201-236-9	2,2',6,6'-tetrabromo-4,4'-isopropylidenediphenol	UK
88-72-2	201-853-3	2-nitrotoluene	E
98-54-4	202-679-0	4-tert-butylphenol	N
98-73-7	202-696-3	4-tert-butylbenzoic acid	D
107-98-2	203-539-1	1-methoxypropan-2-o1	F
108-65-6	203-603-9	2-methoxy-1-methylethyl acetate	F
111-76-2	203-905-0	2-butoxyethanol	F
112-07-2	203-933-3	2-butoxyethyl acetate	F
112-90-3	204-015-5	(Z)-octadec-9-enylamine	D

CAS No.	EINECS No.	Chemical Name	Member State
121-14-2	204-450-0	2.4-dinitrotoluene	E
124-30-1	204-695-3	Octadecylamine	D
994-05-8	213-611-4	2-methoxy-2-methylbutane	FIN
1222-05-5	214-946-9	1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylin-deno[5,6-c]pyran	NL
1309-64-4	215-175-0	Diantimony trioxide	S
1310-73-2	215-185-5	Sodium hydroxide	p
1 330-4 3-4	215-540-4	Disodium tetraborate, anhydrous	A
1506-02-1	216-133-4	1-(5,6,7,8-tetrahydro-3,5,5,6,8,8-hexamethyl-2-naphthyl)ethan-1-one	NL
3333-67-3	222-068-2	Nickel carbonate	DK
7718-54-9	231-743-0	Nickel dichloride	DK
7784-18-1	232-051-1	Aluminium fluoride	NL
7789-75-5	232-188-7	Calcium fluoride	NL
10043-35-3	233-139-2	*Boric acid, crude natural	A
11113-50-1	234-343-4	Boric acid	A
13138-45-9	236-068-5	Nickel dinitrate	DK
13674-84-5	237-158-7	Tris(2-chloro-1-methylethyl) phosphate	IRL/UK
13674-87-8	237-159-2	Tris[2-chloro-1-(chloromethyl)ethyl] phosphate	IRL/UK
26523-78-4	247-759-6	Tris(nonylphenyl) phosphite	F
38051-10-4	253-760-2	2,2-bis(chloromethyl)trimethylene bis(bis(2-chloroethyl)phosphate)	IRL/UK
61788-45-2	262-976-6	Amines, hydrogenated tallow alkyl	D
61788-46-3	262-977-1	Amines, coco alkyl	D

(*) Containing not more than 85% of H_3BO_3 calculated on the dry weight.

APPENDIX 6 – EUSES MODEL PARAMETERS AND CONNECTIVITY

EUSES MODELS
PARAMETERS AND CONNECTIVITY

"This assessment is transparent and easy to perform." (EUSES documentation, page v)

05 May 1999

Volker Berding, Stefan Schwartz
Institute of Environmental Systems Research
University of Osnabrück

http://www.usf.uni-osnabrueck.de/projects/david/

Statistics:

- ○ 466 parameters
- ○ 26 PECs and 41 other concentrations
- ● 6 physico-chemical properties
- ● 37 inputs
- ● 132 defaults
- ● 967 connections

Legend:

▭	Substance-dependent parameters
🟨	Physico-chemical parameters
▱	Concentrations
▭	Scenario parameters
A — B	B depends on A
A B	Closed parameters
A*	Different values on continental and regional scale
⬬	Black box

APPENDIX 7 – THE EUSES BLACKLIST

BLACKLIST EUSES 1.00

The EUSES Blacklist is a list of problems, inconsistencies and computer bugs users and developers have encountered with the EUSES program. A selection of wishes and desires for improvements or increased functionality are also included.

RIVM/CSR - ECB
2 September 1998

Contents

I. Bugs

- Ia. Bugs which can be circumvented
- Ib. Bugs which cannot be circumvented

II. Suggestions for improvement and omissions

III. Inconsistencies

I. Bugs

Ia. Bugs which can be circumvented

1.
Source: K. den Haan, ECETOC/Shell
Date: 27 March 1997
After clicking the "finish" button the program does not always present the risk characterisation table, but falls back to the outline. Usually a second trial is successful.

2.
Source: T. Vermeire, RIVM
Date: 23 April, 1997
The screen "Risk characterisation [..]" only appears in the outline mode, but not in the interactive assessment. Normally this is no problem, since the interactive mode does show the summary risk characterisation table. However, the parameters "Intermittent release" and "Extra factor applied to PEC" (applied for PEC soil/sediment in case logKow 5) only appear in the detailed screen and not in the summary table. In this way the user is not made aware in the interactive mode that the emission pattern is "intermittent" and that the PEC is increased with a factor of 10.

3.
Source: M. Rikken, RIVM
Date: 23 April, 1997
Printing a full report following a preview is not possible. The "Print" button on the preview screen shows the "Customise Print" screen. However, no output is obtained from the printer following the choice "Full document". A full document can be obtained, however, by choosing "Select pages to print" and entering the full page range of the document. The "Current page" command also works without problems.

4.
Source: M. Mons, RIVM
Date: 10 July, 1997
Error: The summary report does not contain the risk characterisation results for consumers. These results can only be found in the full report and in the compact report.

5.
Source: B. Scharenberg, UBA
Date: 22 October 1997
In case of IC/UC 3/33 and "Substance not processed elsewhere" the "Fraction of the main source" for production and processing are now different, whereas they should be the same. At present, the user has to overwrite the estimated values.

6.
Source: B. Scharenberg, UBA
Date: 22 October 1997
The compact report does not contain any PECs. The full and summary report do contain PECs.

7.
Source: S. Bintein, Ministère de l'environnement
Date: 22 October 1997
Emission factor in TGD and EUSES manual for IC 4, processing, soil, MC 3 is 0.01. EUSES gives 0.001. This has to be corrected manually.
For HPVC, IC = 16, no emission fractions are given by EUSES for formulation, whereas Table B2.3 should have been implemented. These fractions now have to be put in manually.

8.
Source: S. Bintein, Ministère de l'environnement
Date: 22 October 1997
Emissions for type of dyes used for continuous dying are implemented in EUSES during private use, but in the TGD emissions during private use must be considered only for type of dyes used for batch dying.

9.
Source: Theo Vermeire, RIVM
Date: 1 November 1997
Emission edit screen: if "production" is switched off the corresponding MC-box does not become grey. Switching production on again results in the MC box becoming grey. However, after going to the next screen and subsequently returning to the edit emission screen it turns out that the MC-box has the right colour.
For IC/UC 3/33 the MC shows a default Ic, which should be III.

10.
Source: Tjalling Jager, RIVM
Date: 10 November 1997.
Changing the dilution factor in the defaults section does not influence the assessment. The dilution factor has to be changed for each life cycle stage in the screen "Local STP input and configuration".

11.
Source: Margreet Mons, RIVM
Date: 20 November 1997
The summary report does not include the inhalatory NOAEL, whereas it does include the oral NOAEL.

12.
Source: EUSES Short Course, Helsinki
Date: 14 November 1997
Consumer inhalatory exposure: if the Cair is set, the intake is not recalculated and has to be adapted manually.

13.
Source: Paul van der Poel, RIVM
Date: 6 April 1998
If a substance has more than one use pattern, the estimated emission rate for production may depend on the IC to which this stage has been assigned in EUSES (Screen "use patterns"). This is due to the fact that the B-tables have been designed considering that "typical" chemicals can be used for certain ICs with a specific production regime. However, for substances such as pigments it does not matter whether they are used in printing inks, plastics or paints: the production takes place in chemical industry specialised in pigment production and not in chemical industry specialised in chemicals for a specific branch. In this example the production would give rise to the application of the following tables of EUSES depending on the IC to which the production stage is assigned to:

IC	Table NSEC	Table HPVC	default tonnage (_)
11	B1.9	B1.4	3000
12	B1.8	B1.4	2500
14	B1.2	B1.6	7000

This can lead at lower tonnages to considerable differences in the "fraction of the main sources" (fms) and "number of processing days" (nd). To avoid this two strategies may be followed
This problem could be solved by:
1. inserting an extra use pattern IC2 (chemical industry: basic chemicals) and UC 0/55 with the fraction of application set at 1 (this should be the last use pattern inserted since EUSES always automatically calculated the default value for the remaining use patterns by subtracting the sum of the use patterns input from 1; the total fraction in the end will be 2).
2. assigning the stage of production to the main use pattern. This should for instance be chosen in the case of dyes for leather, paper and/or textile industry because a specific A-table exists for dyes.

14.
Source: Charles Bodar, RIVM
Date: 18 June 1998
The STP can be switched off. However, in that case EUSES still calculates a PEC/PNEC for STP micro-organisms. This should be ignored.

15.
Source: Peter van Iersel, RIVM
Date: 1 October 1998
A substance with category 11/43 should get the emission factor of category VB according to A-table 3.11. However, EUSES assigns the value for category IV. The wrong factor should be overwritten.

16.
Source: Louwrens Verdam, RIVM
Date: 28 October 1998
In case a regional emission rate is overwritten, EUSES erroneously also changes the local emission rate by the same factor. The user should put in the original local value.
Remark: Not a bug, the EUSES calculations are correct (see equation 7, page III-13, EUSES manual)

17.
Source: Pauline Gingnagel, RIVM
Date: 10 November 1998
In one particular case with 9 IC/UC categories, regional PECs were shown as 0 (s), whereas no PECs had been entered and non-zero values had been expected. The non-zero values (o) appeared after deleting the zero-values.

Ib. Bugs which cannot be circumvented

1.
Source: P. Gingnagel, RIVM
Date: 13 March 1997
Mammalian effects input: once input is given, e.g. a NOAEL, this value can be replaced by another value as expected, but it cannot be erased (e.g. by replacing it with '??'). EUSES always "remembers" the input. This error is probably related to the gap filling behaviour in this screen and therefore this error also occurs in the screen "Human effects input"..

2.
Source: L. Verdam, RIVM
Date: 7 April 1997
New substance, very low vapour pressure, category 4/55, tonnage EU and regional 0.35 tonnes.year-1 , resulted in emission to waste water for production of 7 kg.d-1 production for 1 day. File subsequently saved as export file. After importing this file the emission rate remained unchanged (i.e. at 7 kg.d-1) after increasing the production volume to 999 tonnes/year and keeping the number of emission days at 1. The emission fractions are OK. For other life cycle stages there was no problem.
After starting the assessment from scratch no more problems were encountered. The emission rate increased, as expected, linearly with the production volume.

3.
Source: C. Heidorn, ECB
Date 4 June, 1997
In the default screen "Regional and continental distribution defaults" the continental area is given as 3.52E+8 km2, whereas it should be 3.52E+6 km2 (i.e. EU area - Regional area = 3.56E+6 km2 - 4E+4 km2. In the export file the value is correct and the calculations performed also use the right value. Probably the wrong value on the screen is caused by a faulty unit conversion.

4.
Source: C. Heidorn, ECB
Date 4 June, 1997
In the Help-screen "Regional and continental system definition" the number of EU-inhabitants incorrectly given as 3.8E+6 instead of 3.7E+8. This does not influence any calculation.

5.
Source: E. van der Plassche, RIVM
Date: 15 August, 1997
On screen, in the program reports and in the background report the concentration in earthworms for secondary poisoning is indicated as "Local concentration in earthworms from agricultural soil". This should be "Concentration in earthworms from agricultural soil", which is the average of the local and the regional concentration in agricultural soil. The calculation is correct.

6.
Source: S. Bintein, Ministère de l'environnement
Date: 22 October 1997
EASE in EUSES does not produce correct results for an aerosol. Whatever the class of volatility is, the ability to become airborne is chosen as high, whereas other options (moderate) should be available (TGD, page 171; EUSES-report, appendix V, page 3; it is also noted that page 3 in the EUSES-report is different from page 171 in the TGD in that an additional class "volatility very low" is shown for which, in case of an aerosol, TBA appears to be high?).

7.
Source: S. Bintein
Date: 22 October 1997
Import of data into EUSES directly from SNIF or HEDSET is not possible.

8.
Source: J. de Bruijn, RIVM
Date: 1 November 1997
The parameter "Equilibrium Partitioning used for PNEC in soil" always has the value "yes". It should change to "no" in case more than 1 toxicity value for terrestrial organisms is entered.

9.
Source: EUSES Short Course, RIVM
Date: 6 November 1997
In case of IC/UC 3/33, substance not processed elsewhere and production only, the results are reported under processing.

10.
Source: EUSES Short Course, RIVM
Date: 6 November, 1997
Consumer exposure, dermal scenarios: the parameter "duration of contact" is presented as a parameter for both scenarios A and B. However, it only applies to scenario B and should therefore move to the specific entry screen.

11.
Source: EUSES Short Course, RIVM
Date: 6 November, 1997
If only consumer and worker exposure assessment are selected the "human" defaults cannot be approached.

12.
Source: EUSES Short Course, Helsinki
Date: 14 November ,1997
In case a dermal or inhalatory LOAEL or a dietary LOEC for mammals or man is set, any value of the NOAEL or NOEC which has been calculated from the oral NOAEL via route to route extrapolation should not be used in the risk characterisation: a measured LOAEL or LOEC is preferred above a calculated NOAEL or NOEC.

13.
Source: Theo Vermeire, RIVM
Date: 22 December 1997
The ratios between brackets in the screens "Risk characterisation for consumers" for oral and dermal exposure should be reversed, e.g. N(L)OAEL/uptake instead of uptake/N(L)OAEL .

14.
Source: Theo Vermeire, RIVM
Date: 22 December 1997
In the case of assessment types III, IV or V, EUSES still presents the input screens for the environmental effects assessment. This is not necessary except for the mammalian toxicity data input screen.

15.
Source: Theo Vermeire, RIVM
Date: 18 March 1998
It was reported that the yes/no switch for "Exceeds solubility limit" did not work. An export file was sent to me in which this was indeed the case. Is this problem related to no. 8?

16.
Source: Paul van der Poel, RIVM
Date: 6 April 1998
As soon as IC8 is chosen in the "emission input data" window the first grey field for "extra data on use category" turns white and shows as default "Pure oils" with the alternatives "Water based" and "Unknown". This box should be grey, however, for IC8; it is only relevant for UCs 29 and 35. Though it will not affect the outcome of the emission estimation, it is confusing especially when you have to consider usage as a solvent (e.g. for a vapour degreasing installation).

17.
Source: Theo Vermeire, RIVM
Date: 1 June 1998
Saving a non-standard default set leads to another default filename in the statusbar as expected. However, a reset does not lead to a reset of this filename. This name only changes back after choosing default - edit - ok.

18.
Source: Stefan Schwartz, Universität Osnabrück
Date: 16 June 1998
Entering extreme values may give problems: e.g. entering logKow < -308 gives ,1.234; entering Kow 308 gives ??

19.
Source: Stefan Schwartz, Universität Osnabrück
Date: 16 June 1998
The program stops at "Degradation and transformation input" after entering 0 in the field "Fraction connected to sewer systems" in the dialog "Defaults/Release estimation".

20.
Source: S. Bintein, Ministère de l'environnement
Date: 12 January 1999
Table B2.6 is not implemented for IC = 7 / UC = 9, 10 or 31 for HPVC.
This could be confirmed by using, for example, a regional tonnage of substance = 2 E+05. For UC = 6 a f main source of 0.7 is obtained as indicated in Table B2.6. But for UC = 9, 10 or 31 a f main source of 0.4 is obtained as indicated in Table B2.3.

21.
Source: S. Bintein, Ministère de l'environnement
Date: 12 January 1999
Use of Table B2.3 and B2.9 (formulation) for polymer industry (IC = 11), HPVC, for UC = 43. It is not correct that EUSES now always uses Table B 2.9, whatever the extra details on the use category (monomers, catalysts, other process regulators). For UC = 43 (not initiators, retarders & inhibitors) Table B 2.3 must be used and not Table B2.9. This error is restricted to the formulation step, because for the production step Table B1.4 is correctly implemented in EUSES as indicated in the TGD.

22.
Source: Geert Janssen / Theo Vermeire, RIVM
Date: 30 August 1999
Miscalculation of PNEC $_{\text{micro organisms}}$ (page III-95 EUSES documentation).
In the effects assessment for micro organisms it can happen that 2 PNECs are available: one on the basis of an EC50 and one on the basis of a NOEC or EC10. EUSES should choose the lowest PNEC. However, EUSES now chooses the PNEC based on the EC50 when (NOEC or EC10)/AF < EC50/AF and chooses the PNEC based on NOEC or EC10 when (NOEC or EC10)/AF EC50/AF.

23.
Source: Geert Janssen, RIVM
Date: 1 September 1999
Miscalculation of the local PEC agricultural soil.
The local PEC agricultural soil is miscalculated, when using an user defined fraction of emission to sludge ($Fstp_{sludge}$). The local PEC agricultural soil seems to be correctly calculated when the default $Fstp_{sludge}$ is overwritten and the user is not directly starting the assessment, but only uses the next buttons. When the assessment is started (and finished) the old local PEC agricultural soil is used or calculated, despite the fact that the original $Fstp_{sludge}$ is overwritten.

II. Suggestions for improvement and omissions

1.
Source: M. Rikken, CSR, RIVM
Date: 18 February 1997
Separate reporting of $PEC_{air,point\ source}$ and $PEC_{air,STP}$. EUSES now just shows the highest of the two which is used for the risk characterisation.

2.
Source: T. Vermeire, RIVM
Date: 7 April, 1997
Contrary to the Specifications for EUSES (January 1996), the program does not offer a qualitative risk assessment according to the TGD (chapter 3, section 4.5) in case no $PNEC_{water}$ can be calculated (no-effects in short term tests). The program is able to recognise values for toxicity in the environmental effects assessment input fields. However, in case of no values for aquatic toxicity of limit values such as 100 mg.l-1, the program should ask whether a qualitative assessment should be performed and, if the answer is "yes", should calculate a substitute PNEC by dividing the aqueous solubility by 100 and flag this one (only in case log Kow 3 or BCF_{fish}. 100).

3.
Source: T. Vermeire, RIVM
Date: 21 April, 1997
The full report of EUSES does not report regional and continental emission rates for agricultural soil for the individual life cycle steps. However, it does report the total emission rate for agricultural soil.

4.
Source: L. Wijkhuizen-Maslankiewicz, RIVM
Date: 15 May, 1997
In case the molecular weight of a substance is 700 the BCF_{fish} is not calculated because the QSAR is not valid any more. The user, however, does not get a warning and is left in doubt about the cause of the problem that no $PEC_{oral,fish}$ and C_{fish} are calculated and consequently not intakes for predators and humans.
Solution: In case the user would like to have a maximum estimate he has to lower the molecular weight to 700.

5.
Source: E. van de Plassche, RIVM
Date: 11 June, 1997
According to the TGD ecotoxicological data for soil organisms should be normalised for the standard soil containing 2% organic carbon. These ecotoxicological tests can be performed with a variety of soils. This normalisation is not performed by EUSES and should be done by the user before input. The normalisation can only be applied in case of organic substances, assuming these mainly adsorb to organic matter. It is further noted that this normalisation will lead to errors in case of very low (< 2%) or very high (30%) content of organic matter.

6.
Source: E. van de Plassche, RIVM
Date: 11 June, 1997
In de output screen "Local concentrations and depositions" the user is not informed that the concentrations in surface water are dissolved concentrations as is shown in the background report page III-51 and in the output files.

7.
Source: E. van de Plassche, RIVM
Date: 11 June, 1997
The PEClocal concentrations are only shown for the dissolved fraction. Since the total concentrations are not shown the amount adsorbed to suspended matter cannot be derived directly. The amount adsorbed can be calculated using formulae 58 (regional) and 64 (local).

8.
Source: E. van de Plassche, RIVM
Date: 27 June 1997
In some cases the levels of the substance in sewage sludge applied to agricultural soil are known. EUSES allows to overwrite the estimated levels in sludge by these measured ones at the local scale. However, this is not possible at the regional and continental scales. This problem can be solved in EUSES by overwriting the regional and continental emission rate to agricultural soil by this rate multiplied with the ratio between C_{sludge} estimated and C_{sludge} measured.

9.
Source: E. van de Plassche, RIVM
Date: 27 June, 1997
The estimation of the Koc from Kow in EUSES is performed according to the default QSAR for the domain "predominantly hydrophobics" (TGD section 2.3.5. and section 4.3). However, the user is not warned that other QSARs are available for specific chemical classes. These QSARs should be used, if appropriate, and the general EUSES estimate needs to be overwritten in such cases.

10.
Source: C. Bodar/M. Rikken/T. Vermeire, CSR, RIVM and B. Scharenberg, UBA
Date: 15 August, 1997 and 22 October 1997
In case emission rates from part or all sources of a substance are known and used to overwrite the generic estimates for the local average emission rates during emission episodes, both the TGD and EUSES still calculate a generic total regional annual average emission rate. However, the sum of all site-specific and generic local releases, back-calculated to annual averages, should be a better estimate of the total continental annual average emission rate and should also be the basis for the calculation of the total regional emission rates. At present this can only be done manually and the result can be used to overwrite the generic estimates. Note that in the case of the calculation of regional emission rates from 'real' continental emission rates one cannot use the default assumption that the regional emission rate is 10% of the continental emission rate. If the geographic location of all sources is known, one should take account of this somehow.

11.
Source: G. Janssen, RIVM
Date: 14 October 1997
Consumer exposure assessment: EUSES does not automatically check whether the estimated daily uptake exceeds the theoretical maximum as can be derived from the amount of product used, the concentration of the substance in the product and the use frequency. Example: facial cream, 800 mg with 1% substance, 1 time per day. Maximum uptake is 8 mg/70 kg per day or 0.1143 mg.kgbw-1.d-1. EUSES calculates a potential uptake of 1.69 mg.kgbw-1.d-1.

12.
Source: Theo Vermeire, RIVM
Date: 14 October 1997
The risk characterisation for man is performed for each population potentially exposed and for each relevant route of exposure, but not separately for each effect as is indicated in TGD.

13.
Source: Dr. G. Heinemeyer, BgVV
Date: 22 October 1997
Consumer exposure assessment: EUSES only allows consideration of one exposure scenario per exposure route in one run. In case more scenarios per route have to be considered, this calculation needs another EUSES-file. This should be possible in one run with no limit in the number of scenarios. It would be very useful then to have an extra field for a description of each use scenario.

14.
Source: Dr. G. Heinemeyer, BgVV
Date: 22 October 1997
Consumer exposure assessment: a discussion is needed on the inclusion of models for higher tier consumer exposure assessments in EUSES

15.
Source: B. Scharenberg, UBA
Date: 22 October 1997
In case of wrong input of a number as 0,2 or 1,6 etc., EUSES should warn the user, that this is illegal. Presently EUSES accepts such values (as 0 and 1, respectively).

16.
Source: M. Palmquist, KEMI
Date: 22 October 1997
The output could be improved by replacing the number of the use pattern in the headings by text, specifying the use pattern.

17.
Source: EUSES WG, Ispra
Date: 22 October 1997
Updates of EUSES should include a help screen with information on the changes made.

18.
Source: EUSES WG, Ispra
Date: 22 October 1997
The output for the regional model could be improved by presenting the % distribution.

19.
Source: EUSES WG, Ispra
Date: 22 October 1997
The options to select the output to the printer (now possible in different ways via the Assess-Select screen, the RCR-table [not explained in manual] and the File/Print Setup) could be improved.

20.
Source: T. Vermeire, RIVM
Date: 20 November 1997
Terrestrial effects assessment: In case only one test is available EUSES calculates a PNEC both from this value after application of an assessment factor and via the equilibrium partitioning method. Subsequently the lowest of the two is reported and used in the risk characterisation. This is as expected. However, EUSES should report as intermediate result both PNECs.

21.
Source: M. Palmquist, KEMI
Date: 28-10-97
Edit emission screen: No main categories should be shown in case the corresponding life cycle stage is not checked. In case information on all or specific main categories is not needed according to the A-Tables, no value should be given either. The default main category should be shown.

22.
Source: EUSES Short Course, RIVM
Date: 6 November 1997
Text improvements:
- Consumer exposure input - inhalation: “Amount of product released” = “Amount of product used”
- Worker exposure input -dermal: “Amount of dermal contact” = “Frequency of dermal contact”.

23.
Source: Tjalling Jager, RIVM
Date: 11 November 1997
The Previous Button in the Interactive and Direct Modes also cancels de input just made. The input is only confirmed after going to the next screen with the Next Button. It may be considered to change this behaviour: once an input is set (s) by the user it should be considered as confirmed.

24.
Source: Tjalling Jager, RIVM
Date: 11 November 1997
The guidance concerning the Tonnage used to access the A and B Table can be improved.

25.
Source: Charles Bodar, RIVM
Date: 20 November 1997
It would be helpful if a free text field is added under Study in which detailed information on the use pattern can be stored for the first page of the report.

26.
Source: EUSES Short Course, Helsinki
Date: 13 November, 1997
Working in the outline it would be helpful to indicate in the status bar where you are.

27.
Source: P. Gingnagel, RIVM
Date: 21 January 1998
For the physical-chemical property of vapour pressure only one unit (Pascal at 25°C) is available. The data set of existing chemicals can also include data of vapour pressure with different units e.g. atmosphere. More units should be allowed for the input of vapour pressure.

28.
Source: P. Gingnagel, RIVM
Date: 21 January 1998
There is no warning when an user select an invalid industry and use category combination. The appendix VI. "Valid IC/UC combinations" of the EUSES-report should be incorporated in EUSES.

29.
Source: P. Gingnagel, RIVM
Date: 21 January 1998
The TGD indicates that a low-flow rate of a river (or 10-percentile) should be used for calculating the actual dilution factor at the point of complete mixing. However when an average flow is given one third of this average should be taken for calculating the dilution factor (TGD page 303). No information on this calculation is available in the EUSES help function. This calculation should be (1/3 of average flow rate) incorporated in EUSES.

30.
Source: P. Gingnagel, RIVM
Date: 21 January 1998
For the "Flow rate of the river" and "Effluent discharge of this STP" only one unit is allowed in EUSES. More units should be made available.

31.
Source: P. Gingnagel, RIVM
Date: 21 January 1998
In the screen of "Local STP input and configuration" the default of "number of inhabitants feeding this STP" is often changed to generate a site specific "Effluent discharge of this STP". The site specific data of STP are often submitted as effluent discharge rate of a STP. No data on number of inhabitants are given because the site specific STP mainly concerns the industry. At the moment the input for "number of inhabitants feeding this STP" must be changed to get a site specific effluent discharge of a STP. The input of the number of inhabitants or equivalent must be derived from the default parameter of EUSES (200 l/d per equivalent or inhabitant) and the submitted flow rate of a site specific STP. The input of a site specific effluent discharge rate should be allowed directly in the field "Effluent discharge of this STP".

32.
Source: P. Gingnagel, RIVM
Date: 21 January 1998
The print outputs of EUSES are difficult to read especially when many use patterns and life cycle steps are selected. In EUSES a screen on "use pattern" and "Risk characterisation result table for the environment" are presented. These screens should also be presented in the print output because all selected industry and use categories with the relevant life cycle steps and the risk characterisation results are viewed. These tables could be separately incorporated in the print output of EUSES.

33.
Source: P. Gingnagel, RIVM
Date: 21 January 1998
The maximum number of use patterns in EUSES that can be selected is ten (screen "use patterns"). After inserting a 11th use pattern the message "Add usage failed" will follow. The information that only ten use patterns are allowed is not available in the help function. No restrictions should be made on the number of use patterns or more use patterns should be allowed.

34.
Source: T. Vermeire, RIVM
Date: 18 March, 1998
In the case that only 2 LC50-values are available and 2 NOECs for aquatic organisms, the assessment factor chosen by EUSES is 100. It is assumed that in this case it is unknown whether the lowest NOEC is also for the same taxonomic group with the lowest LC50. The documentation and the help should, however, make this more explicit.

35.
Source: Els Smit, RIVM
Date: 23 March
After choosing "new study" in the main menu the programme should ask immediately to enter "name" and "description" to avoid an error message at saving.

36.
Source: Stefan Schwartz, Universität Osnabrück
Date: 16 June 1998
EUSES should also allow to use separate models: it should be possible to enter only the data needed for a specific model.

37.
Source: Stefan Schwartz, Universität Osnabrück
Date: 16 June 1998
The error messages could be improved with regard to the "solutions" provided. In many case one is referred to the manual and no further advice is given.

38.
Source: Stefan Schwartz, Universität Osnabrück
Date: 16 June 1998
It should be able to adjust the width of the columns in the "Use patterns" table to improve readability and to allow printing.

39.
Source: Stefan Schwartz, Universität Osnabrück
Date: 16 June 1998
In the screen "Emission input data" the phrase "main category" should be added on the relevant position.

40
Source: Stefan Schwartz, Universität Osnabrück
Date: 16 June 1998
Remove the "Load defaults" button on the screen "Defaults". It does not belong there and the function can already be approached via the main menu.

41.
Source: Paul van der Poel, RIVM
Date: 23 August 1998
In some cases it should be possible to specify the regional tonnage of a substance per life cycle step (e.g. Screen "Intermediate results tonnages" per life cycle step for each IC/UC combination). This applies, for instance, to a substance imported to 1 formulating source in a region (100 % of EU-tonnage) with subsequent diffuse industrial or private use (10% rule applies: 10 % of the EU-tonnage in a region). This can now be done by entering two identical IC/UC combinations in the "Use patterns" screen, one for each life cycle step. "Intermediate results tonnages" screens will appear for each IC/UC/life cycle step entry.

42.
Source: M. Palmquist, KEMI
Date: 10 November 1998
An EUSES report outprint containing the two columns Value and Reference could only be obtained when printing out in the Outline mode. This should be informed about in the Help screen or changed in the program.

43.
Source: M. Palmquist, KEMI
Date: 10 November 1998
Screen "Release estimation/Intermediate results". In the interactive mode the screen card corresponding to the life cycle step applicable (filled in) to this use pattern (e.g. screen card for processing) should open automatically.

44.
Source: M. Palmquist, KEMI
Date: 10 November 1998
Would it be possible to open several (at least two) studies at the same time to be able to work in parallel with the studies?

45.
Source: M. Palmquist, KEMI
Date: 10 November 1998
Screen "Emission input data". If for certain industrial categories an emission scenario document is available (marked as "yes"), the user should be informed that the document is not implemented in EUSES.

46.
Source: Dennis Kalf, RIVM
Date: 6 April 1999
In the first column of the table on page III-93 (EUSES manual), at 2 NOEC and 3 NOEC there is not mentioned that they must be from different taxonomic groups.

47.
Source: Geert Janssen, RIVM
Date: 23 August 1999
It is recommended that the program additionally could produce a flexible summary report, so that the user can define what results he wants to present. 100% flexible is the most recommendable choice, but the program can be improved considerably by giving some choices for a summary report. The RIVM/CSR can provide suggestions and choices for a flexible report.

III. Inconsistencies

1.
Source: J. de Bruijn, RIVM
Date: 26 March 1997
The officially accepted erratum of Appendix II of chapter 3 does not produce the same results as SimpleTreat in EUSES. The current version of SimpleTreat 3.0 debugged included a different estimation routine for Koc than the TGD and EUSES.

2.
Source: E. van de Plassche, RIVM
Date: 14 October, 1997
In the assessment of secondary poisoning the PEC (concentration in fish or worm) is in mg.kg-1wwt whereas the PNEC is in mg.kg-1dw. The PNEC usually is derived from the NOAEL or NOEC of tests with experimental animals, fed dry laboratory chow. Theoretically a correction is necessary for the conversion from dry weight to fresh weight. In view of the difference in diet (laboratory chow versus worms or fish) such a correction seems difficult to perform.

3.
Source: S. Bintein, Ministère de l'environnement
Date: 22 October 1997
The parameter Surplus Sludge is a fixed value in the TGD (0.011) and a variable in SimpleTreat 3.0 in EUSES.

4.
Source: B. Scharenberg, UBS
Date: 22 October 1997
The concentration of suspended matter in the continental system (25 mg.l-1) is different from the regional value (15 mg.l-1). This makes the region an area with net sedimentation. The TGD only reports the regional value.

5.
Source: Tjalling Jager, RIVM
Date: 10 November 1997
EUSES does not consider direct emission of fertilisers and pesticides to agricultural soil (processing, Table A3.1). The TGD-Erratum of 19 February 1997 (Doc. ECB TGD/01/97) specifies to direct these emissions to agricultural soil on the regional and continental scale.

6.
Source: Tjalling Jager, RIVM
Date: 10 November 1997
Page III-39, Table III-12 mentions concentration of biota in water ($BIOTA_{water}$) of 0.1 kgwwt.m-3. The value in EUSES is 1 mg.l-1, the SimpleBox documentation mentions 1 mgdwt.l-1 (this is not correct as it is multiplied with a BCF on wwt basis!).

7.
Source: Theo Vermeire, RIVM
Date: 18 March 1998
According to the TGD the dry weight solids produced per person per day (SOLIDS) is 0.011 kg.eq-1.d-1; in EUSES the value is 0.09 kg.eq-1.d-1.

APPENDIX 8 – PHYSICO-CHEMICAL DATA FOR TEST SUBSTANCES

INITIAL INVESTIGATION TEST DATA

The data used in the initial investigations are detailed in the tables that follow. The accuracy for measuring the physico-chemical properties as quoted by the OECD for standard test methods are detailed. The *base set* value for each parameter was varied positively and negatively by the quoted accuracy, the resulting values for the parameters are also detailed in the tables along with the $PEClocal_{water}$ value calculated.

Substance Id. 101P

Description of variance	***MOLW***	***MP***	***BP***	***VP***	**log *Kow***	***SOL***	***$PEClocal_{water}$***
Units	*g/mol*	*K*	*K*	*Pa*	-	*mg/l*	*mg/l*
Accuracy	~	*± 1.0 K*	*± 1.4 K*[1] *± 2.5 K*[2]	*ave. =* *±25%*	*±0.3 log units*	*±30%*	~
Base set	197.28	223	578 *	0.043	4.0	7.5	0.770
MP –	197.28	222	500 *	0.043	4.0	7.5	0.770
MP +	197.28	224	500 *	0.043	4.0	7.5	0.770
BP –	197.28	223	500 *	0.043	4.0	7.5	0.770
BP +	197.28	223	500 *	0.043	4.0	7.5	0.770
VP –	197.28	223	500 *	0.03225	4.0	7.5	0.774
VP +	197.28	223	500 *	0.05375	4.0	7.5	0.766
Kow –	197.28	223	500 *	0.043	3.7	7.5	0.846
Kow +	197.28	223	500 *	0.043	4.3	7.5	0.667
SOL –	197.28	223	500 *	0.043	4.0	4.875	0.762
SOL +	197.28	223	500 *	0.043	4.0	10.125	0.774

[1] *(<373K)*

[2] *(≥373K)*

* Maximum allowable value in EUSES 500 K, therefore values entered as 500 K

Substance Id. 652F

Description of variance	***MOLW***	***MP***	***BP***	***VP***	**log *Kow***	***SOL***	***PEClocal***$_{water}$
Units	*g/mol*	*K*	*K*	*Pa*	-	*mg/l*	*mg/l*
Accuracy	~	*± 1.0 K*	*± 1.4 K*[1] *± 2.5 K*[2]	*ave. =* *±25%*	*±0.3 log units*	*±30%*	~
Base set	284	<24*	133-303	23.30	4.68	2.95	0.0489
MP –	284	23	218	23.30	4.68	2.95	0.0489
MP +	284	25	218	23.30	4.68	2.95	0.0489
BP –	284	24	216.6	23.30	4.68	2.95	0.0489
BP +	284	24	219.4	23.30	4.68	2.95	0.0489
VP –	284	24	218	17.475	4.68	2.95	0.0527
VP +	284	24	218	29.125	4.68	2.95	0.0467
Kow –	284	24	218	23.30	4.38	2.95	0.0531
Kow +	284	24	218	23.30	4.98	2.95	0.0454
SOL –	284	24	218	23.30	4.68	2.065	0.0456
SOL +	284	24	218	23.30	4.68	3.835	0.0523

[1] *(<373K)*

[2] *(≥373K)*

* Descriptive values (i.e. <3, >6) are accepted in EUSES however discrete decimal values were used in all cases

The melting point and boiling point values were found to not be of significant interest for the initial investigations (See Section 2.3.3) and were not investigated for the remainder of the substances.

Substance Id. 909F

Description of variance	***MOLW***	***VP***	**log *Kow***	***SOL***	***PEClocal*** $_{water}$
Units	*g/mol*	*Pa*	-	*mg/l*	*mg/l*
Accuracy	~	*ave. = ±25%*	*±0.3 log units*	*±30%*	~
Base set	187	0.75	3.34	109	0.903
VP –	187	0.5625	3.34	109	0.909
VP +	187	0.9375	3.34	109	0.898
Kow –	187	0.75	3.04	109	0.933
Kow +	187	0.75	3.64	109	0.856
SOL –	187	0.75	3.34	76.3	0.894
SOL +	187	0.75	3.34	141.7	0.908

Substance Id. 1062F

Description of variance	***MOLW***	***VP***	**log *Kow***	***SOL***	***PEClocal*** $_{water}$
Units	*g/mol*	*Pa*	-	*mg/l*	*mg/l*
Accuracy	~	*ave. = ±25%*	*±0.3 log units*	*±30%*	~
Base set	158	130	3.07	2710	0.840
VP –	158	97.5	3.07	2710	0.864
VP +	158	162.5	3.07	2710	0.817
Kow –	158	130	2.77	2710	0.856
Kow +	158	130	3.37	2710	0.812
SOL –	158	130	3.07	1897	0.802
SOL +	158	130	3.07	3523	0.862

Substance Id. 1084F

Description of variance	***MOLW***	***VP***	**log *Kow***	***SOL***	***$PEClocal_{water}$***
Units	*g/mol*	*Pa*	-	*mg/l*	*mg/l*
Accuracy	~	*ave. = ±25%*	*±0.3 log units*	*±30%*	~
Base set	234	0.69	5.3	19	0.259
VP –	234	0.5175	5.3	19	0.264
VP +	234	0.8625	5.3	19	0.255
Kow –	234	0.69	5.0	19	0.351
Kow +	234	0.69	5.6	19	0.189
SOL –	234	0.69	5.3	13.3	0.252
SOL +	234	0.69	5.3	24.7	0.263

Substance Id. 672D

Description of variance	***MOLW***	***VP***	**log *Kow***	***SOL***	***$PEClocal_{water}$***
Units	*g/mol*	*Pa*	-	*mg/l*	*mg/l*
Accuracy	~	*ave. = ±25%*	*±0.3 log units*	*±30%*	~
Base set	434	<0.000008 *	5.5	<0.2	0.223
VP –	434	1 E-6 *	5.5	0.2	0.223
VP +	434	1 E-6 *	5.5	0.2	0.223
Kow –	434	1 E-6 *	5.2	0.2	0.312
Kow +	434	1 E-6 *	5.8	0.2	0.160
SOL –	434	1 E-6 *	5.5	0.14	0.223
SOL +	434	1 E-6 *	5.5	0.26	0.223

*** Minimum allowable value in EUSES 1×10^{-6} Pa, therefore values entered as 1×10^{-6} Pa.**

Substance Id. 724D

Description of variance	***MOLW***	***VP***	**log *Kow***	***SOL***	$PEClocal_{water}$
Units	*g/mol*	*Pa*	-	*mg/l*	*mg/l*
Accuracy	~	*ave. = ±25%*	*±0.3 log units*	*±30%*	~
Base set	404	(10-12) 11 *	4.3	<0.2†	0.0425
VP –	404	8.25	4.3	0.2	0.0430
VP +	404	13.75	4.3	0.2	0.0423
Kow –	404	11	4.0	0.2	0.0453
Kow +	404	11	4.6	0.2	0.0395
SOL –	404	11	4.3	0.14	0.0421
SOL +	404	11	4.3	0.26	0.0429

* Geometric mean value from the range was used as base set value

† Descriptive values (i.e. <3, >6) are accepted in EUSES however discrete decimal values were used in all cases

Substance Id. 745D

Description of variance	***MOLW***	***VP***	**log *Kow***	***SOL***	$PEClocal_{water}$
Units	*g/mol*	*Pa*	-	*mg/l*	*mg/l*
Accuracy	~	*ave. = ±25%*	*±0.3 log units*	*±30%*	~
Base set	445	6 E-10	3.9	1.2	0.815
VP –	445	1 E-6 *	3.9	1.2	0.815
VP +	445	1 E-6 *	3.9	1.2	0.815
Kow –	445	1 E-6 *	3.6	1.2	0.885
Kow +	445	1 E-6 *	4.2	1.2	0.718
SOL –	445	1 E-6 *	3.9	0.84	0.815
SOL +	445	1 E-6 *	3.9	1.56	0.815

* Minimum allowable value in EUSES 1×10^{-6} Pa, therefore values entered as 1×10^{-6} Pa.

Substance Id. 969D

Description of variance	***MOLW***	***VP***	**log *Kow***	***SOL***	$\mathit{PEClocal}_{water}$
Units	*g/mol*	*Pa*	-	*mg/l*	*mg/l*
Accuracy	~	*ave. = ±25%*	*±0.3 log units*	*±30%*	~
Base set	(477.9 - 491.9) 484.9 *	0.07	3.8	<1	(0.547 - 0.542) 0.545
VP –	484.9	0.0525	3.8	1	0.597
VP +	484.9	0.0875	3.8	1	0.499
Kow –	484.9	0.07	3.5	1	0.578
Kow +	484.9	0.07	4.1	1	0.496
SOL –	484.9	0.07	3.8	0.7	0.471
SOL +	484.9	0.07	3.8	1.3	0.593

* Geometric mean value from the range was used as base set value, (PEC values calculated using range boundaries quoted in brackets)

APPENDIX 9 – LARGE COPY OF COMPLETE NEXCES SPREADSHEET

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y	Z	AA	AB	AC	AD	AE	AF	AG	AH	AI	AJ	AK	AL	AM	AN	AO	AP
1	Name	MW	Kow	VP	SOL		Chemical Class	Biodeg	Prod Vol	Import	Export	LC50 Fish	LC50 Daphnia	LC50 Algae		PECregional.wat		Capacity.stp	Waste.inhab	Effluent.stp		E.local.water	K.bio.stp	log.Koc	Koc	HENRY	Fstp.water	C.local.inf		SUSP.water	DILUTION	Foc.susp		Kp.susp	C.local.eff	C.local.water(pro	C.local.water	PEC.local.water	min LC50	AF	PNEC.water	RCR.water
2	Comment	Base S	Base S	Base S	Base Set		From pick	From pick	Base S	Base S	Base S	Base S	Base S	Base Set		= Assume		Default	Default	= Capacity s		= Manu	Rate fr	log.Koc	= x log.	= MW	= Value	= E.local.		Default	Default	Default		= Foc.sus	=Clocal.in	= C.local.	Check if v	=C.local.w	= min[L	= 1000	= min. L	= PEC.local.water /PNEC.water
3	Eqn. No.	~	~	~	~		~	~	~	~	~	~	~	~		~		~	~	1 (19)		(2)	DEG1	QSAR1		3 (7)	ST3	4 (17)		~	~	~		5 (9)	6 (18)	8 (30)		9 (33)	~	~	~	~
4	Value															0		10000	200			0.5								15	10	0.1								1000		
5	d/c/e	e	e	e	e		e	e	e	e	e	e	e	e		e (c)		d	d	c		e (c)	c	c	c	c	c	c		d	d	d		c	c	c	c	c	c	c	c	c
6	Units	g/mol	~	Pa	mg/l		~	Tonnes/Yr	onnes/Y	onnes/Y	mg/l	mg/l	mg/l	mg/l		mg/l		eq	l/d/eq	l/d		kg/d	h-1	~	l/kg	a.m3/m	~	mg/l		mg/l	~	kg/kg		l/kg	mg/l	mg/l	mg/l	mg/l	mg/l	~	mg/l	~
7	Calc. 1	561.5	4E-05	6E-05	42798		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
8	Calc. 2	561.5	4E-05	6E-05	42799		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
9	Calc. 3	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
10	Calc. 4	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
11	Calc. 5	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
12	Calc. 6	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
13	Calc. 7	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
14	Calc. 8	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
15	Calc. 9	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
16	Calc. 10	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
17	Calc. 11	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
18	Calc. 12	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
19	Calc. 13	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
20	Calc. 14	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
21	Calc. 15	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
22	Calc. 16	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
23	Calc. 17	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
24	Calc. 18	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
25	Calc. 19	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
26	Calc. 20	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
27	Calc. 21	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
28	Calc. 22	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
29	Calc. 23	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
30	Calc. 24	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
31	Calc. 25	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
32	Calc. 26	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
33	Calc. 27	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
34	Calc. 28	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
35	Calc. 29	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
36	Calc. 30	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
37	Calc. 31	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
38	Calc. 32	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
39	Calc. 33	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
40	Calc. 34	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
41	Calc. 35	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
42	Calc. 36	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
43	Calc. 37	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
44	Calc. 38	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
45	Calc. 39	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
46	Calc. 40	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
47	Calc. 41	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
48	Calc. 42	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
49	Calc. 43	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
50	Calc. 44	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
51	Calc. 45	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
52	Calc. 46	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
53	Calc. 47	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
54	Calc. 48	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
55	Calc. 49	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
56	Calc. 50	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
57	Calc. 51	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
58	Calc. 52	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
59	Calc. 53	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619
60	Calc. 54	561.5	4E-05	6E-05	42800		Predomina	No Biodeg	10	0	0	100	8.4	16		0		10000	200	2000000		0.05	0	-3.44	0.0004	7E-07	100	0.025		15	10	0.1		3.63E-05	0.025	0.0025	0.0025	0.0025	8.4	1000	0.0084	0.297619

Below this line are the two data tables QSAR1 and DEG1

QSAR1

	X	Y
Acetanilides	0.4	1.12
Acetanilides, carbamates, esters, phenylureas, pho	0.47	1.09
Alcohols	0.39	0.5
Alcohols, organic acids	0.47	0.5
Amides	0.33	1.26
Anilines	0.62	0.85
Carbamates	0.37	1.14
Dinitroanilines	0.38	1.92
Esters	0.49	1.05
Nitrobenzenes	0.77	0.55
Non-hydrophobics	0.52	1.02
Organic acids	0.6	0.32
Phenols, anilines, benzonitriles, nitrobenzenes	0.63	0.9
Phenols, benzonitriles	0.57	1.08
Phenylureas	0.49	1.05
Phosphates	0.49	1.17
Predominantly hydrophobics	0.81	0.1
Triazines	0.3	1.5
Triazoles	0.47	1.41

DEG1

kbio.stp	Rate constant (h-1)
Inherent deg.	0.1
No Biodeg.	0.0
Ready deg. inside window	1.0
Ready deg. outside window	0.3

APPENDIX 10 – LOOK-UP TABLES FOR SIMPLETREAT 3.0 AS AMENDED TO TGD

AMENDED SIMPLETREAT 3.0 LOOK-UP TABLES

The look-up tables for the SimpleTreat model as published in the TGD were based on Version one of the model. The values as used in the EUSES programme are from SimpleTreat 3.0. An amendment was circulated to accompany the TGD outlining the new tables based on the new version of the model, it is these tables which are presented here. Four sets of tables are presented, one for each of the levels of biodegradability:

- No biodegradability
- Inherent biodegradability
- Readily biodegradability, 10-day window not fulfilled
- Ready biodegradability, 10-day window fulfilled

For each level of degradation the % of the total concentration of the substance in the influent that is directed to air, water and sludge are detailed. The amount of the substance removed and degraded are also presented.

It should be noted that the SimpleTreat model has been updated once more and it is this SimpleTreat 3.0 debugged that has been used in the NEXCES spreadsheet. Furthermore use of the tables only allows discharge fractions from the STP to be found for whole values of log *HENRY* and log *Kow*. It is suggested that where possible the actual model is used so that exact values can be calculated.

No biodegradability ($kbio_{stp} = 0\ h^{-1}$)

% to air

	Log H									
Log Kow	-4	-3	-2	-1	0	1	2	3	4	5
0	0	0	0	0	0	15	64	91	95	95
1	0	0	0	0	0	15	64	91	95	95
2	0	0	0	0	0	15	64	91	94	94
3	0	0	0	0	0	13	58	84	87	87
4	0	0	0	0	0	7	33	54	57	57
5	0	0	0	0	0	1	8	22	26	26
6	0	0	0	0	0	0	1	5	6	7

% to water

	Log H									
Log Kow	-4	-3	-2	-1	0	1	2	3	4	5
0	100	100	100	100	98	85	36	9	5	5
1	100	100	100	100	98	85	36	9	5	5
2	99	99	99	99	97	84	35	8	5	5
3	89	89	89	89	87	76	33	8	5	5
4	47	47	47	47	46	42	22	6	4	4
5	14	14	14	14	14	14	11	6	4	4
6	9	9	9	9	9	9	8	7	7	7

% to sludge

	Log H									
Log Kow	-4	-3	-2	-1	0	1	2	3	4	5
0	0	0	0	0	0	0	0	0	0	0
1	0	0	0	0	0	0	0	0	0	0
2	1	1	1	1	1	1	1	1	1	1
3	11	11	11	11	11	11	9	8	8	8
4	53	53	53	53	53	52	46	40	39	39
5	86	86	86	86	86	86	81	72	70	69
6	91	91	91	91	91	91	91	88	87	86

% degraded

	Log H									
Log Kow	-4	-3	-2	-1	0	1	2	3	4	5
0	0	0	0	0	0	0	0	0	0	0
1	0	0	0	0	0	0	0	0	0	0
2	0	0	0	0	0	0	0	0	0	0
3	0	0	0	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0	0	0	0
5	0	0	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0	0	0

% removal

	Log H									
Log Kow	-4	-3	-2	-1	0	1	2	3	4	5
0	0	0	0	0	2	15	64	91	95	95
1	0	0	0	0	2	15	64	91	95	95
2	1	1	1	1	3	16	65	92	95	95
3	11	11	11	11	13	24	67	92	95	95
4	53	53	53	53	54	58	78	94	96	96
5	86	86	86	86	86	86	89	94	96	96
6	91	91	91	91	91	91	92	93	93	93

Inherent biodegradability ($kbio_{stp} = 0.1\ h^{-1}$)

% to air

	Log H									
Log Kow	-4	-3	-2	-1	0	1	2	3	4	5
0	0	0	0	0	1	10	50	85	91	91
1	0	0	0	0	1	10	50	85	91	91
2	0	0	0	0	1	10	50	85	90	90
3	0	0	0	0	1	9	46	78	83	84
4	0	0	0	0	1	5	27	50	54	55
5	0	0	0	0	0	1	7	21	25	25
6	0	0	0	0	0	0	1	4	6	7

% to water

	Log H									
Log Kow	-4	-3	-2	-1	0	1	2	3	4	5
0	59	59	59	59	58	52	28	8	5	5
1	59	59	59	59	58	52	28	8	5	5
2	59	59	59	58	58	52	27	8	5	5
3	54	54	54	54	53	47	25	7	5	4
4	32	32	32	32	31	29	17	6	4	4
5	13	13	13	13	13	12	10	6	4	4
6	9	9	9	9	9	9	8	7	7	7

% to sludge

	Log H									
Log Kow	-4	-3	-2	-1	0	1	2	3	4	5
0	0	0	0	0	0	0	0	0	0	0
1	0	0	0	0	0	0	0	0	0	0
2	1	1	1	1	1	1	1	1	1	1
3	10	10	10	10	10	10	9	8	8	8
4	48	48	48	48	48	48	44	40	39	39
5	83	83	83	83	83	83	79	72	70	69
6	91	91	91	91	91	91	90	88	86	86

% degraded

	Log H									
Log Kow	-4	-3	-2	-1	0	1	2	3	4	5
0	41	41	41	41	41	38	22	7	4	4
1	41	41	41	41	40	38	22	7	4	4
2	40	40	40	40	40	38	22	7	4	4
3	37	37	37	37	36	34	20	6	4	4
4	20	20	20	20	20	19	12	4	3	2
5	4	4	4	4	4	4	3	2	1	1
6	0	0	0	0	0	0	0	0	0	0

% removal

	Log H									
Log Kow	-4	-3	-2	-1	0	1	2	3	4	5
0	41	41	41	41	42	48	72	92	95	95
1	41	41	41	41	42	48	72	92	95	95
2	41	41	41	42	42	48	73	92	95	95
3	46	46	46	46	47	53	75	93	95	96
4	68	68	68	68	69	71	83	94	96	96
5	87	87	87	87	87	88	90	94	96	96
6	91	91	91	91	91	91	92	93	93	93

Readily biodegradability, 10-day window not fulfilled ($kbio_{stp} = 0.3\ h^{-1}$)

% to air

	Log H									
Log Kow	-4	-3	-2	-1	0	1	2	3	4	5
0	0	0	0	0	1	6	36	76	84	85
1	0	0	0	0	1	6	36	76	84	85
2	0	0	0	0	1	6	35	75	83	84
3	0	0	0	0	1	6	32	69	77	78
4	0	0	0	0	0	3	20	45	50	51
5	0	0	0	0	0	1	6	19	23	24
6	0	0	0	0	0	0	1	4	6	6

% to water

	Log H									
Log Kow	-4	-3	-2	-1	0	1	2	3	4	5
0	33	33	33	33	32	29	19	7	5	4
1	33	33	33	32	32	29	19	7	5	4
2	32	32	32	32	32	29	19	7	5	4
3	30	30	30	30	30	27	18	7	4	4
4	19	19	19	19	19	18	12	5	3	3
5	10	10	10	10	10	10	9	5	4	4
6	8	8	8	8	8	8	8	7	7	7

% to sludge

	Log H									
Log Kow	-4	-3	-2	-1	0	1	2	3	4	5
0	0	0	0	0	0	0	0	0	0	0
1	0	0	0	0	0	0	0	0	0	0
2	1	1	1	1	1	1	1	1	1	1
3	9	9	9	9	9	9	9	8	8	8
4	45	45	45	44	44	44	42	40	39	39
5	80	80	80	80	80	79	77	71	69	69
6	90	90	90	90	90	90	90	87	86	86

% degraded

	Log H									
Log Kow	-4	-3	-2	-1	0	1	2	3	4	5
0	67	67	67	67	67	64	45	17	12	11
1	67	67	67	67	67	64	45	17	12	11
2	67	67	67	67	66	64	45	17	11	11
3	61	61	61	61	61	58	41	16	11	10
4	36	36	36	36	36	35	25	10	7	7
5	10	10	10	10	10	10	8	5	3	3
6	1	1	1	1	1	1	1	1	1	1

% removal

	Log H									
Log Kow	-4	-3	-2	-1	0	1	2	3	4	5
0	67	67	67	67	68	71	81	93	95	96
1	67	67	67	68	68	71	81	93	95	96
2	68	68	68	68	68	71	81	93	95	96
3	70	70	70	70	70	73	82	93	96	96
4	81	81	81	81	81	82	88	95	97	97
5	90	90	90	90	90	90	91	95	96	96
6	92	92	92	92	92	92	92	93	93	93

Ready biodegradability, 10-day window fulfilled ($kbio_{stp} = 1\ h^{-1}$)

% to air

	Log H									
Log Kow	-4	-3	-2	-1	0	1	2	3	4	5
0	0	0	0	0	0	3	19	55	66	68
1	0	0	0	0	0	3	19	55	66	68
2	0	0	0	0	0	3	19	54	66	67
3	0	0	0	0	0	3	17	50	61	62
4	0	0	0	0	0	2	11	32	40	41
5	0	0	0	0	0	1	4	15	19	20
6	0	0	0	0	0	0	1	2	5	6

% to water

	Log H									
Log Kow	-4	-3	-2	-1	0	1	2	3	4	5
0	13	13	13	13	13	12	9	5	4	3
1	13	13	13	13	13	12	9	5	4	3
2	13	13	13	13	12	12	9	5	4	3
3	12	12	12	12	12	11	8	5	3	3
4	8	8	8	8	8	8	6	4	3	3
5	7	7	7	7	7	7	6	4	4	3
6	8	8	8	8	8	8	7	7	7	6

% to sludge

	Log H									
Log Kow	-4	-3	-2	-1	0	1	2	3	4	5
0	0	0	0	0	0	0	0	0	0	0
1	0	0	0	0	0	0	0	0	0	0
2	1	1	1	1	1	1	1	1	1	1
3	8	8	8	8	8	8	8	8	8	8
4	41	41	41	41	41	41	40	39	39	39
5	73	73	73	73	73	73	72	69	68	68
6	88	88	88	88	88	88	88	86	85	85

% degraded

	Log H									
Log Kow	-4	-3	-2	-1	0	1	2	3	4	5
0	87	87	87	87	87	85	72	41	30	29
1	87	87	87	87	87	85	72	40	30	29
2	87	87	87	86	86	84	71	40	30	29
3	80	80	80	80	80	78	66	37	28	27
4	51	51	51	51	51	50	43	25	18	18
5	20	20	20	20	20	20	18	12	9	9
6	4	4	4	4	4	4	4	3	3	3

% removal

	Log H									
Log Kow	-4	-3	-2	-1	0	1	2	3	4	5
0	87	87	87	87	87	88	91	95	96	97
1	87	87	87	87	87	88	91	95	96	97
2	87	87	87	87	88	88	91	95	96	97
3	88	88	88	88	88	89	92	95	97	97
4	92	92	92	92	92	92	94	96	97	97
5	93	93	93	93	93	93	94	96	96	97
6	92	92	92	92	92	92	93	93	63	94

APPENDIX 11 – THE ACCURACY OF STATISTICAL PROCEDURES WITHIN MICROSOFT EXCEL

NORMAL DISTRIBUTIONS GENERATED BY MICROSOFT EXCEL

The problems with the accuracy of statistical procedures within the Microsoft Excel 97 software have been investigated and reported by McCullough & Wilson (1999). One of the areas where Excel fails particularly is in its generation of random numbers. The random number generator was used to produce normally distributed values for physico-chemical parameters in the early investigations using the NEXCES spreadsheet. For this reason some time was taken to investigate the optimum number of random numbers to generate.

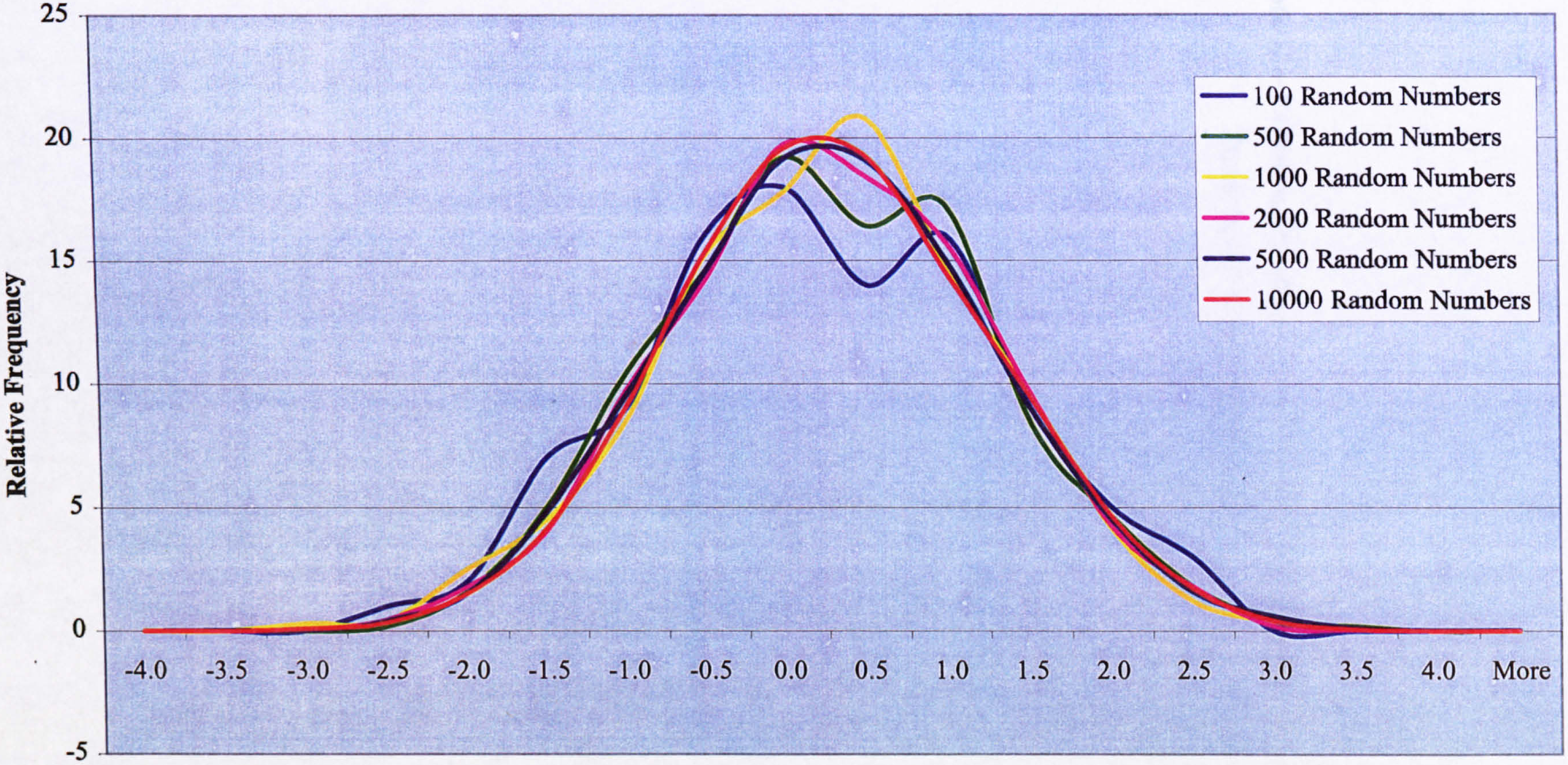
Normally distributed numbers with mean 0.0 and standard deviation 1.0 were generated at sample sizes of 100, 500, 1000, 2000, 5000 and 10000 (Figure A12.1). From the plot of these distributions it was found that visually the plots approached a normal distribution at 5000 samples and above. For this reason 5000 samples were run for each of the investigations, and this number was also used when re-sampling the data for the probabilistic risk assessments.

An attempt was been made to determine through which algorithm the random numbers are generated in Excel, however to date the only information that has been found is for the formula command RAND():

> The first random number:
> random_number=fractional part of (9821 * r + 0.211327),
> `where r = .5`
>
> Successive random numbers:
> random_number=fractional part of (9821 * r + 0.211327),
> `where r = the previous random number`
>
> This formula will provide up to 1 million different numbers.

(http://www.microsoft.com/support/, March 2001)

Distributions from Various Sized Samples of Randomly Generated Normally Distributed Numbers



APPENDIX 12 – PAPER ACCEPTED BY JOURNAL OF ENVIRONMENTAL TOXICOLOGY AND CHEMISTRY

A SPREADSHEET MODEL FOR PERFORMING RISK ASSESSMENTS AS DETAILED IN THE EUROPEAN NOTIFICATION SYSTEM FOR NEW SUBSTANCES

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Abstract-The European Dangerous Substances Directive (67/548/EEC) and its amendments require that environmental risk assessments be performed on all newly notified substances. A technical guidance document (TGD) outlines the procedure for this assessment. This procedure is also automated in the computer program EUSES (European Union System for the Evaluation of Substances). The TGD and EUSES outline a generic system for the assessment of chemicals, using average and reasonable worst case values as default values in the calculations.

Certain problems concerning EUSES have been highlighted, including the lack of transparency, poor user interface and the inability to run multiple assessments side by side for comparison.

The use of a spreadsheet model to perform the risk assessment has been used in some research areas but never completely documented. This paper outlines the construction of a spreadsheet to perform risk assessments for the local aquatic compartment and low tonnage substances in a transparent way, with the opportunity to have multiple runs of the same assessment to compare and highlight sensitive values.

Keywords-EUSES Risk assessment Spreadsheet model

Introduction

The 1967 Dangerous Substances Directive (67/548/EEC) deals with the classification, packaging and labelling of dangerous substances. The 6th amendment to this directive (79/831/EEC) outlined a procedure for the "notification" of all chemicals marketed within the European Union (EU). The 7th Amendment to this directive (92/32/EEC) introduced the requirement for an environmental risk assessment (ERA) to be performed. The role of the EU (formerly the EC) was originally to achieve co-ordination of the economic policies of the EC through a single European Market; this role was later extended to policies within social, environmental and other fields [1]. The principal aim of the legislation is to provide an adequate level of protection for man and the environment, the generic European-wide risk assessments performed also prevent barriers to trade within the EU.

For the purpose of notification, all chemicals are classed as either Existing Substances or New Substances. Existing chemicals are listed on the European Inventory of Existing Commercial Substances "EINECS", which includes all substances deemed to be on the Community market on 18 September 1981. The Notification of New Substances Regulations (NONS 93) implements the 7th Amendment of the Dangerous Substances Directive in the UK, which requires the following prior to placing a new substance (any substance not on the EINECS list) on the market:

- Notification of the intention to place a new substance on the market.
- Provision of certain information on the substance to be made.

The information to be provided includes production, import and export volumes, and physical, chemical, toxicological, ecotoxicological and degradation and behavioural data. From this information risk assessments are then made.

A Technical Guidance Document (TGD) [2] was produced to accompany the regulations, which outlined a suggested risk assessment process. This process is automated in the computer program EUSES (European Union System for the Evaluation of Substances) [3]. Together EUSES and the TGD outline a generic system for the assessment of chemicals. The assessment calculations are conducted for a "non-existing model environment with predefined, agreed environmental characteristics. These environmental characteristics can be average values or reasonable worst-case values depending on the parameter in question," [2].

The strength of such a generic assessment approach, is that it can be applied generally across all European Member States (MS) and the various parameter values have been chosen to ensure protective measures across the whole of Europe.

There are essentially three phases to the notification risk assessment procedure (Figure 1): exposure assessment, effects assessment and then risk characterisation. The potential for a hazard is implicitly assumed by the regulations, requiring a risk assessment on all new chemicals. The exposure is calculated by way of a Predicted Environmental Concentration (PEC) value, and the effect assessment made by calculating a Predicted No-Effect Concentration (PNEC). A Risk characterisation ratio (RCR) is then calculated from these two values for the various environmental compartments: water, air, land, sediment, waste-water treatment plant and biota. Subject to the result of the assessment further data, risk reduction or other risk management options may be required in the risk characterisation and classification stages.

The European system also details three spatial scales in the assessment: local, regional and continental. For this work, the risk assessment of the water compartment is considered for new substances particularly at the local scale.

The European Chemical Bureau (ECB) holds an online list of problems and bugs documented for the EUSES program called "The EUSES Blacklist" (http://ecb.ei.jrc.it/Euses/blacklst.htm, EUSES Blacklist; ECB, 31 January 2001). Many of the items arise because of discrepancies in how EUSES and the TGD calculate some values, for example:

> "The estimation of the Koc from Kow in EUSES is performed according to the default QSAR for the domain 'predominantly hydrophobics' (TGD section 2.3.5. and section 4.3). However, the user is not warned that other QSARs are available for specific chemical classes. These QSARs should be used, if appropriate, and the general EUSES estimate needs to be overwritten in such cases."
>
> E. van de Plassche, RIVM

Berding *et al.* [4] detailed the parameters and interconnectivity of EUSES, in an attempt to visualise its complexity, although in doing so some of the inputs required to calculate the concentration of a substance in water at the local level ($Clocal_{water}$) were missed.

Figure 2 shows a schematic representation of the risk assessment process focusing on the aquatic environment at the local scale amended and modified from the work of Berding *et al.* [4], and equations cited correspond to the equations detailed in this paper.

In other work on ERA, spreadsheet models of the process detailed by the TGD and EUSES have been constructed to allow such investigations as sensitivity analysis and probabilistic assessment [5,6,7]. The construction of such a spreadsheet version of the notification risk assessment system has never been fully documented.

The construction of a spreadsheet to perform risk assessments for the aquatic compartment is outlined ensuring transparency. It provides the opportunity to run multiple instances of the same assessment allowing comparison and sensitive values to be highlighted.

It is hoped that by documenting the spreadsheet in this way will provide the basis for a transparent and practical risk assessment tool. As the model is extended and new modules to the assessment are added the tool can be developed in an "open source" manner so that users understand the underlying calculations and interactions, to ensure that the resulting tool meets the needs of those who actively use it.

Model and method

There follows an outline of the data used and calculations involved in the ERA for the local water compartment, including the calculation of the PEC, PNEC and RCR values. The calculations were constructed in a Microsoft Excel spreadsheet, so that many instances of the calculation could be performed simultaneously. Furthermore it enables a sensitivity analysis to be conducted on selected variables and default values used. By altering these variables, the effect on dependent values can be assessed.

Table 1(a, b, c) detail the completed spreadsheet, each Column in the spreadsheet represents a parameter (as detailed in Figure 2), the rows contain the following:

- Row 1 – name of parameter
- Row 2 - any comments on where the value is obtained
- Row 3 - the equation reference number in this paper and the TGD equation number [2] in brackets
- Row 4 - the default value for the parameter where applicable
- Row 5 - refers to the kind of value in that column:
    - d = EU default value
    - c = calculated value
    - e = entered value, a value input by the user
- Row 6 – the standard units the parameter is entered in
- Row 7 – from this row onwards data and calculations are input and varied from which the risk assessments are calculated

For this worked model and for validating the spreadsheet a set of real Base Set values have been entered in Row 7, these values are shown in Table 2. The example substance is classified as "Commercially Confidential" as described in the NONS 93 Regulations, for this reason the identity of the substance has not been given, however this does not affect the calculations in any way. The calculations used in the spreadsheet (where applicable), are also detailed in Row 7. The formulae given are those found in Microsoft Excel 97, although similar functions should be available in other versions and software packages.

The following physical and chemical data are supplied as part of the "Base Set" of data required for notification and are used in performing the risk assessment:

MOLW	Molecular weight (Column B), this is the gram weight of one mole of the substance.
Kow	Partition coefficient for octanol and water (Column C), this gives a measure of how the substance will partition between aqueous and organic phases.
VP	Vapour pressure (Column D), this value indicates to what extent the chemical will volatilise and become gaseous.
SOL	Solubility in water (Column E), this value is a measure of how soluble the substance is in water.

Columns G-N in Table 1(a) detail the remaining Base Set data entered into the spreadsheet. The first column of Table 3 (AX4:AX22) is set as a look-up table for the value Chemical Class (Column G), this value then indicates which QSAR (Quantitative Structural Activity Relationship) will be used to estimate the *Koc* value.

The first column of Table 4 (BB4:BB8) is set as a look-up table for the biodegradeability value (*Biodeg.*, Column H). A different rate constant ($Kbio_{stp}$) is then used for the biodegradation process (used in the SimpleTreat model) depending on which of these classifications the test results meet.

Data are also provided on production, import and export volumes of the substance (Columns I, J, K). Base Set ecotoxicological data are supplied for the three acute aquatic tests (Columns L, M, N).

For new substances, marketed in low volumes, it is fair to assume that the regional concentration in water will be negligible. This is because there is unlikely to be a background concentration already in the environment, and while marketed at low volume, this background or regional concentration is unlikely to accumulate in the short term. For this reason the value is set at 0 (See Table 1(a), Column P), however if actual or calculated values are available they can be entered directly into the model at this point. That completes the Base Set entries in Table 1(a).

The capacity of a sewage treatment plant (STP) was given the default value of 10,000 population equivalents (Column R, Table 1 (b)) and the volume of waste per inhabitant was given the default value of 200 $l.d^{-1}.eq^{-1}$ (Column S). From these two parameters the value of the effluent discharge rate ($EFFLUENT_{stp}$) was calculated (Column T) as shown in Equation 1.

$$EFFLUENT_{stp} = CAPACITY_{stp} \cdot WASTEWinhab$$

Spreadsheet formula = R7 * S7 (1)

Where,

$EFFLUENT_{stp}$ – is the effluent discharge rate of STP ($l.d^{-1}$)
$CAPACITY_{stp}$ – is the capacity of the STP (in population equivalents, eq) default = 10000
$WASTEWinhab$ – is the sewage flow per inhabitant ($l.d^{-1}.eq^{-1}$) default = 200

The value $Elocal_{water}$ (Column V) is the concentration of the substance emitted to water in the local scale of the model. This value is calculated using the production and import/export values (given in Columns I, J, K) and the "A and B tables" in the TGD or, where available, actual or estimated emission values. There is much discussion in the literature and many points outlined on the EUSES Blacklist about errors and inaccuracies in these tables, however, measured or estimated data are often used, leading assessments to a more site-specific rather than generic result. For this reason, and to simplify and retain flexibility in the model, these values can be calculated using the TGD method, or measured or modelled values may be used and then entered directly into the spreadsheet.

To derive the biodegradation rate for use in the fate and behavioural calculations the descriptive value (in Column H) is used to look up the corresponding rate constant from Table 4. Values were originally proposed by Struijs and Van den Berg [8], the values in the table are those as agreed and published in the TGD.

The calculation in the spreadsheet is as follows

= VLOOKUP (H7, $BB$4:$BC$8, 2) (2)

This function looks up *Biodeg.* (Column H) in the DEG1 table (BB4:BC8) and retrieves the value from the second column along, which is the $Kbio_{stp}$ value. The dollar signs "$" in the cell references ensure the same table is used in each row of the calculation, all other cell references will remain relative.

Adsorption of the substance to solid surfaces can be a significant removal process, and reduce the concentration in solution. The carbon normalised partition coefficient (*Koc*) is used to calculate the solid-water partition coefficients for each compartment (soil, sediment, suspended matter). These values and/or the *Koc* value can be derived in a number of ways (most accurate to least accurate):

- Direct measurement of individual partition coefficients
- *Koc* measured by adsorption studies (OECD test guideline 106)
- *Koc* approximation, measured by HPLC-method
- *Koc* may be estimated from *Kow* (for non-ionic substances)

However, for some substances, measurement of *Koc* can be difficult experimentally. In the UK, a measured *Koc* by the HPLC-method is usually required as part of the notification for substances for which the QSAR calculations are not appropriate. Further data may be requested subject to the results of the risk assessment.

The TGD outlines QSARs (Quantitative Structural Activity Relationships) for estimating *LogKoc* (Table 1(b), Column X) based on linear regression analysis with *LogKow* as the descriptor variable. The TGD states that the QSAR for the chemical class "predominantly hydrophobics" should be used as default, however values are given for other classes as well; the EUSES program automatically selects and uses the default QSAR in all cases. Table 3 outlines the QSARs available and the various chemical classes (the first column of AX4:AZ22, should be used for the values in the look-up table for specifying Chemical Class, Column G). The '*x*' and '*y*' values in Table 3 come from various QSARs and are used in Equation 3 to derive the *LogKoc* value.

$$LogKoc = x \cdot LogKow + y \qquad (3)$$

Where,
LogKoc is the carbon normalised partition coefficient in log units
LogKow is the octanol-water partition coefficient in log units

The calculation in the spreadsheet is as follows:

```
=( VLOOKUP (G7, $AX$4:$AZ$22, 2)     (i)
* LOG10(C7) )                        (ii)
+VLOOKUP (G7, $AX$4:$AZ$22, 3)       (iii)        (4)
```

i. Finds '*x*' - Looks up Chemical Class (G7) in the QSAR table (AX4:AZ22) and retrieves the value from the second column along
ii. Multiplies by *LogKow* – The *Kow* value in C7 in log units
iii. Add '*y*' - looks up Chemical Class in the QSAR table and retrieves the value from the third column along

Column Y calculates the *Koc* value from the *LogKoc* value (Equation 5)

$$Koc = 10^{LogKoc}$$

Spreadsheet formula = 10 ^ (X7) (5)

Where,
Koc is the carbon normalised partition coefficient
LogKoc is the carbon normalised partition coefficient in log units

Volatilisation and the partitioning of a substance between the water and air phases can occur direct from surface water and in the aeration tank in the STP. It is a physical property described by the Henry's Law constant (Table 1(b), Column Z). The magnitude of this constant gives an indication of which of the two phases a substance is likely to partition into at equilibrium. Substances with low values will tend to partition into the aqueous phase.

Where a measured value for Henry's Law constant is not available it is estimated using Equation 6. If no reliable data are available for vapour pressure or solubility both the TGD and OECD guidelines point to the use of Quantitative Structure Activity Relationships (QSARs) to obtain the figure.

$$HENRY = \frac{VP \cdot MOLW}{SOL}$$

Spreadsheet formula = D7 * B7 / E7 (6)

Where,
HENRY is Henry's Law constant for the substance ($Pa.m^3.mol^{-1}$)
VP is the vapour pressure of the substance (Pa)
MOLW is the molecular weight of the substance ($g.mol^{-1}$)
SOL is the solubility of the substance in water ($mg.l^{-1}$)

On the local scale the TGD makes the assumption that all waste water will pass through a STP before being discharged to the environment. A 9-compartment box-model is outlined in the TGD [9] and implemented through the use of the SimpleTreat 3.0 model in EUSES [3]. A set of look-up tables substitute for the full SimpleTreat model in the TGD, these tables being based on an older version of the model, providing approximate values. The latest version available of this program is the SimpleTreat 3.0 version [10], the debugged version of this model is different to the one used in EUSES.

The values for Henry's Constant (*HENRY*), *Kow* and $Kbio_{stp}$ are entered into the SimpleTreat model (ST3) and fractions of emissions to the three compartments (air, water, sludge) are the outputs. The value for the fractions of emissions to water ($Fstp_{water}$) is entered in to the model in Column AA (Table 1(b)). The use of the SimpleTreat model is explained further in the "Getting Results" section.

To find the concentration of the substance entering the STP ($Clocal_{inf}$, Column AB) Equation 7 is used.

$$Clocal_{\mathrm{inf}} = \frac{Elocal_{water} \cdot 10^6}{EFFLUENT_{stp}}$$

Spreadsheet formula = V7 * (10 ^ 6) / T7 (7)

Where,

$Clocal_{inf}$ is the concentration in untreated wastewater ($mg.l^{-1}$)
$Elocal_{water}$ is the local emission rate to water during an episode ($kg.d^{-1}$)
$EFFLUENT_{stp}$ is the effluent discharge rate of the STP ($l.d^{-1}$)

The following parameters are all default values defined in the TGD:

- Concentration of suspended matter in the river - $SUSP_{water}$ (Column AD)
- Dilution factor, from river flow - *DILUTION* (Column AE)
- Solid-water partition coefficient of suspended matter - Foc_{susp} (Column AF)

The value for the dilution factor from mixing in the receiving water at point of discharge (*DILUTION*) can be calculated where data are available, particularly for site-specific assessments in which case Equation 8 is used, otherwise the default value of 10 is used.

$$DILUTION = \frac{EFFLUENT_{stp} + FLOW}{EFFLUENT_{stp}} \qquad (8)$$

Where,

DILUTION is the dilution factor calculated from river flow

$EFFLUENT_{stp}$ is the effluent discharge rate from the STP ($l.d^{-1}$)
$FLOW$ is the flow rate of river ($l.d^{-1}$)

The solid-water partitioning coefficients are used to calculate the extent to which the substance is absorbed into other compartments (soil, sediment and suspended matter). The value for suspended matter (Kp_{susp}, Column AH) is calculated using Equation 9.

$$Kp_{susp} = Foc_{susp} \cdot Koc$$

Spreadsheet formula = AF7 * Y7 (9)

Where,
Kp_{susp} is the solid-water partition coefficient of suspended matter ($l.kg^{-1}$)
Foc_{susp} is the weight fraction of organic carbon in suspended matter ($kg.kg^{-1}$) default = 0.1
Koc is the carbon normalised partition coefficient ($l.kg^{-1}$)

The SimpleTreat model is used to assess the fate and behaviour of substances within the STP in the assessment. Using the fraction emitted to water ($Fstp_{water}$) obtained from SimpleTreat 3.0, the concentration emitted to water from the STP ($Clocal_{eff}$) is given by Equation 10.

$$Clocal_{eff} = Clocal_{\inf} \cdot Fstp_{water}$$

Spreadsheet formula = AB7 * (AA7 / 100) (10)

Where,

$Clocal_{eff}$	Concentration of chemical in STP effluent	($mg.l^{-1}$)
$Clocal_{inf}$	Concentration in untreated wastewater	($mg.l^{-1}$)
$Fstp_{water}$	Fraction of emission directed to water by STP	

The division by a factor of 100 in the spreadsheet formula above is due to the SimpleTreat model returning the 'fraction' emitted as a percentage, this converts the output to a decimal value.

In the assessment scenario the effluent from the STP is discharged into surface water, two assumptions are then made:

- Complete instantaneous mixing is assumed at the point of discharge
- For initial local assessments immediate exposure is assumed (volatilisation, degradation and sedimentation are ignored)

The default dilution factor of 10 is said to account for some variability in these parameters, and these assumptions make for a worst case assessment that can be refined with real measured values where available on a site-specific basis.

The concentration of the substance in local water ($Clocal_{water}$, Column AJ) is calculated using Equation 11.

$$Clocal_{water} = \frac{Clocal_{eff}}{\left[1+\left(Kp_{susp} \times SUSP_{water} \times 10^{-6}\right)\right] DILUTION}$$

Spreadsheet formula = AI7 / ((1 + (AH7 * AD7 * (10 ^ - 6))) * AE7) (11)

Where,

$Clocal_{water}$ is the local concentration in surface water during an emission episode ($mg.l^{-1}$)
$Clocal_{eff}$ is the concentration of chemical in the STP effluent ($mg.l^{-1}$)
Kp_{susp} is the Solid-water partition coefficient of suspended matter ($l.kg^{-1}$)
$SUSP_{water}$ is the concentration of suspended matter in river ($mg.l^{-1}$) default = 15
DILUTION is the dilution factor, default = 10

It is noted in the TGD and EUSES Blacklist (http://ecb.ei.jrc.it/Euses/blacklst.htm, EUSES Blacklist; ECB, 31 January 2001) that values in excess of water solubility (*SOL*) can arise for the concentration of the substance in water. It is suggested that such results be interpreted on a case-by-case basis, however in this model, if the concentration in local water exceeds water solubility, the concentration is set to the solubility in water (Column AK) as suggested in the EUSES Blacklist. In Column AJ a provisional value for $Clocal_{water}$ is calculated as defined in Equation 11, then in Column AK this figure is checked against the value for solubility in water (E7). In the spreadsheet an "IF" statement is used to handle this situation as follows:

```
=IF ( AJ7 > E7,          (i)
E7,                      (ii)
AJ7 )                    (iii)        (12)
```

i. "IF" argument – checks to see if the concentration in STP effluent ($Clocal_{eff}$, AJ7) is greater than the solubility in water (*SOL*, E7)
ii. Answer – if argument is true ($Clocal_{eff}$ is greater than *SOL*) then the answer is set to the solubility in water (*SOL*, E7)
iii. Alternative answer – if argument is false (i.e. the concentration in water is less than water solubility) the concentration in water is as calculated (AJ7)

The PEC value for local water (Column AL) is derived from the sum of the concentration in local water (*$Clocal_{water}$*) and PEC for regional water (*$PECregional_{water}$*), which has been assumed to be 0 for new chemicals at low volumes (Equation 13).

$$PEClocal_{water} = Clocal_{water} + PECregional_{water}$$

Spreadsheet formula = AK7 + P7 (13)

Where,

$PEClocal_{water}$ is the predicted environmental concentration during an episode ($mg.l^{-1}$)

$Clocal_{water}$ is the local concentration in surface water during an emission episode ($mg.l^{-1}$)

$PECregional_{water}$ is the regional or background concentration in surface water ($mg.l^{-1}$)

In Column AM the lowest $L(E)C_{50}$ value is calculated from the three values supplied (algae, fish and *Daphnia*) in the spreadsheet this is calculated as detailed in Equation 14.

$$Min\ L(E)C_{50} = \begin{Bmatrix} L(E)C_{50}\ (fish) \\ L(E)C_{50}\ (daphnia) \\ L(E)C_{50}\ (algae) \end{Bmatrix}_{MIN}$$

Spreadsheet formula = MIN (L7:N7) (14)

Where,

$L(E)C_{50}$ (fish) is the lethal or effect concentration for 50% of the population for fish ($mg.l^{-1}$)

$L(E)C_{50}$ (daphnia) is the 50% lethal/effect concentration for daphnia ($mg.l^{-1}$)

$L(E)C_{50}$ (algae) is the lethal/effect concentration for 50% of the population for algae ($mg.l^{-1}$)

Min $L(E)C_{50}$ is the lowest lethal or effect concentration for 50% of the population ($mg.l^{-1}$)

The PNEC for water (Column AO) is calculated by applying the standard assessment factor (*AF*) of 1000 (Column AN) to the lowest value of the three acute ecotoxicological tests carried out for base set (Column AM) as detailed in Equation 15.

$$PNEC_{water} = Min\ L(E)C_{50} \times AF$$

Spreadsheet formula = AM7 / AN7 (15)

Where,

$PNEC_{water}$ is the Predicted No-Effect Concentration of the substance in water ($mg.l^{-1}$)

Min $L(E)C_{50}$ is the lowest lethal or effect concentration for 50% of the population ($mg.l^{-1}$)

AF is the Assessment Factor or uncertainty factor, default = 1000

Finally in the risk characterisation stage the RCR is calculated for local water (Column AP) by dividing the PEC by the PNEC (Equation 16).

$$RCRlocal_{water} = \frac{PEClocal_{water}}{PNEC_{water}}$$

Spreadsheet formula = AL7 / AO7 (16)

Where,

$RCRlocal_{water}$ is the Risk Characterisation Ratio for local water

$PEClocal_{water}$ is the predicted concentration of the substance in local water ($mg.l^{-1}$)

$PNEC_{water}$ is the Predicted No-Effect Concentration of the substance in water ($mg.l^{-1}$)

Different conclusions are drawn regarding the RCR value as set down in the Directive on Risk Assessment for New Notified Substances (93/67/EEC). When RCR ≤ 1, the following conclusion is set down in Article 3.4(i) of the Directive:

- The substance is of no immediate concern and need not be considered again until further information is made available in accordance with Articles 7(2), 8(3), 8(4) or 14(1) of Directive 67/548/EEC.

When RCR > 1, then further information is usually required to refine the risk assessment, one of the following conclusions as set out in Article 3. 4(ii), 3.4(iii) or 3.4(iv) will be given, depending on the magnitude of the RCR and the extent to which the exposure assessment has been refined already:

- The substance is of concern and the competent authorities shall decide what further information is required for revision of the assessment, but shall defer a request for that information until the quantity placed on the market reaches the next tonnage threshold as indicated in Article 7(2), 8(3) or 8(4) of Directive 67/548/EEC.
- The substance is of concern and further information shall be requested immediately.
- The substance is of concern and the competent authority shall immediately make recommendations for risk reduction.

Getting results

The risk assessment process involves the use of the SimpleTreat (ST3) model. All the data are input to allow proper exposure and effect assessments to be made; the calculation of the fraction of the substance emitted to water from the STP ($Fstp_{water}$) is however an output value from the SimpleTreat model. The third and debugged version of this spreadsheet is available [10]; it is a black-box type model, available in a Microsoft Excel spreadsheet format. The model can only perform calculations on one data set at a time, and the aim of this work was to create a spreadsheet where multiple instances of the same risk assessment could be made, to analyse sensitivity, for example.

To overcome this problem a Visual Basic macro (Box 1) was written to take the required input values, run them through the ST3 model and then take the output value and place it back into the spreadsheet. This macro should be written as a module attached to the risk assessment spreadsheet model (called NEXCES in this example). Also in this example the ST3 model file was called ST3DEBUG and both files were in the following directory:

```
        C:\My Documents\
```

If the spreadsheet is constructed as detailed (Table 1(a, b, c)) including the two look-up tables (Tables 3 and 4) and the macro (Box 1), then starting with Row 7 various input values for risk assessments can be entered. The risk assessment calculations should be copied from Row 7 down, for however many rows are required. Values that are being examined and changed can then be entered. Finally the macro must be run to process each row of the spreadsheet through the SimpleTreat model. The resulting RCR values can be examined and conclusions drawn. For validation purposes the values used were for an actual chemical and if the model is working correctly the resulting RCR value should be 1.915615, EUSES and the TGD will give slightly different values due to the discrepancies in the versions of the SimpleTreat model used. There follows a short example of the power of this spreadsheet model.

Example

In this example the inherent variability in measuring the octanol-water partition coefficient (*Kow*) and the vapour pressure (*VP*) of the test substance were investigated. The test guidelines as produced by the Organisation for Economic Co-operation and Develoment (OECD) [11] for the two methods were used as detailed in Table 5.

For this example it was assumed that variability would be normally distributed around the mean (Base Set) value and the error given in the test guidelines would be equal to 3 standard deviations (99.7 %) about this mean.

A sample size of 5000 data points from separate runs of the calculation was used, based on the good approximation to a normal distribution afforded by such a sample [12]. Then using the random number generator in Microsoft Excel 5000 values were produced normally distributed for each value with the relevant mean and SD.

The investigation was run twice, once for *Kow* and once for *VP*. The whole of Row 7 was copied down for 5000 rows, then the randomly generated values were placed in the relevant column (after being converted from log units to decimal in the case of the *Kow* values). Finally the macro was run, (to find the fraction emitted from the STP using the SimpleTreat model) taking more than an hour depending on the processor speed and RAM availability. When the macro had completed running through the data, the values in the RCR column (Column AP) were examined. Two graphs were produced of the resulting RCR values from normally distributed *VP* values and from normally distributed log *Kow* values (Figures 3 & 4 respectively).

The error from measurement can cause a far greater effect for the *Kow* value than for vapour pressure. The resulting range for the RCR within ±2 SD (this encompasses 95% of the data) of the mean, is 1.5 - 2.3 for variation in *Kow* and only 1.908 – 1.923 for variation in *VP*.

Many other points could be investigated and examined from these data, or through other calculations using this spreadsheet model to run thousands of iterations of the assessment simultaneously.

Conclusions

The model, as presented (referred to as NEXCES, New Excel Calculation for the Evaluation of Substances), provides a usable and powerful tool for the investigation of risk assessments. The spreadsheet model, unlike other models currently available, allows multiple instances or different risk assessments to be performed simultaneously. This spreadsheet model has been presented in a transparent manner, and incorporates many fixes for bugs highlighted in the EUSES Blacklist. It is hoped that by providing the system in an "open source" fashion, the model can be developed and improved, providing a better tool for use by both industry and regulators.

The model uses the latest SimpleTreat 3.0 model for the simulation of an STP, and the macro as detailed, automatically enters the required input values and copies the produced output value back into the NEXCES spreadsheet.

Through further work other parts of the European risk assessment system can be developed in a modular fashion and spreadsheets developed and attached to this model, while maintaining the transparent and usable nature of the model.

Glossary of terms

AF	Assessment Factor

Biodeg.	Descriptive value for the biodegradation rate
Bugs	Errors in a computer program or system
$CAPACITY_{stp}$	Capacity of the STP (in population equivalents)
$Clocal_{eff}$	Concentration of chemical in STP effluent
$Clocal_{inf}$	Concentration in untreated wastewater
$Clocal_{water}$	Local concentration in surface water during emission episode
DILUTION	Dilution factor (from river flow)
EC	European Commission
ECB	European Chemical Bureau
EEC	European Economic Community
EINECS	European Inventory of Existing Commercial Substances
$EFFLUENT_{stp}$	Effluent discharge rate of STP
$Elocal_{water}$	Local emission rate to water during an episode
ERA	Environmental Risk Assessment
EU	European Union
EPSRC	Engineering and Physical Science Research Council
EUSES	European Union System for the Evaluation of Substances
Foc_{susp}	Weight fraction of organic carbon in suspended matter
FLOW	Flow rate of river
$Fstp_{water}$	Fraction of emission directed to water by STP
HENRY	Henry's Law constant
HPLC	High Performance Liquid Chromatography
$Kbio_{stp}$	Rate constant for biodegradation
Koc	Carbon normalised partition coefficient
Kow	Partition coefficient for octanol and water
Kp_{susp}	Solid-water partition coefficient of suspended matter
$L(E)C_{50}$ *(algae)*	Lethal or effect concentration to 50% of population for algae
$L(E)C_{50}$ *(daphnia)*	Lethal or effect concentration to 50% of population for daphnia
$L(E)C_{50}$ *(fish)*	Lethal or effect concentration to 50% of population for fish
MOLW	Molecular weight
MS	Member State
NEXCES	New EXcel Calculation for the Evaluation of Substances
NONS	Notification of New Substances
OECD	Organisation for Economic Co-operation and Development
PEC	Predicted Environmental Concentration

$PEClocal_{water}$	Predicted environmental concentration during episode
$PECregional_{water}$	Regional concentration in surface water
PNEC	Predicted No-Effect Concentration
$PNEC_{water}$	Predicted No-Effect Concentration of the substance in water
QSAR	Quantitative Structural Activity Relationship
RCR	Risk Characterisation Ratio
$RCRlocal_{water}$	Risk Characterisation Ratio for local water
RIVM	National Institute of Public Health and the Environment
SOL	Solubility in water
STP	Sewage Treat Plant
$SUSP_{water}$	Concentration of suspended matter in river
TGD	Technical Guidance Document
VP	Vapour pressure
WASTEWinhab	Sewage flow per inhabitant

Terms in italics represent expressions in equations

Acknowledgements

The authors would like to thank the EPSRC (Engineering and Physical Science Research Council) and the Environment Agency for their financial support of this Engineering Doctorate project. Gratitude is also extended to the members of the National Centre for Ecotoxicology and Hazardous Substances within the Environment Agency the help from whom has been invaluable.

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	A	B	C	D	E	F	G	H	I	J	K	L	M	N	P	Q
1	Name	MOLW	Kow	VP	SOL		Chemical Class	Biodeg	Prod Vol	Import	Export	L(E)C50 Fish	L(E)C50 Daphnia	L(E)C50 Algae	PECregional$_{water}$	
2	Comment	Base Set	Base Set	Base Set	Base Set		From pick list AX4:AX22	From pick list BB4:BB8	Base Set	Base Set	Base Set	Base Set	Base Set	Base Set	Assumed to be negligible	
3	Eqn. No.	~	~	~	~		~	~	~	~	~	~	~	~	~	
4	Value															
5	d/c/e	e	e	e	e		e	e	e	e	e	e	e	e	e (c)	
6	Units	g/mol	~	Pa	mg/l		~	~	Tonnes/Yr	Tonnes/Yr	Tonnes/Yr	mg/l	mg/l	mg/l	mg/l	
7	Calculation	197.3	10000	0.043	7.5		Predom. Hydro.	No Biodeg.	10	0	0	0.6	2.3	0.86	0	

Table 1 (a) - Complete spreadsheet for risk assesment of water compartment at local scale

	A	R	S	T	U	V	W	X	Y	Z	AA	AB	AC
1	Name	Capacity$_{stp}$	Waste$_{inhab}$	Effluent$_{stp}$		Elocal$_{water}$	Kbio$_{stp}$	Log Koc	Koc	HENRY	Fstp$_{water}$	Clocal$_{inf}$	
2	Comment	Default	Default	= Capacity$_{stp}$ * WASTE$_{inhab}$		= Manually entered	Rate from descriptive value	Log Koc = x log Kow + y (from QSAR and chemical class)		= MW * VP / SOL	= Value from ST3 model	= Elocal$_{water}$ * 10000000 / Effluent$_{stp}$	
3	Eqn. No.	~	~	1 (19)		(2)	2, DEG1	4, QSAR1	5	6 (7)	ST3	7 (17)	
4	Value	10000	200			0.05							
5	d/c/e	d	d	c		e (c)	c	c	c	c	c	c	
6	Units	eq	l/d/eq	l/d		kg/d	h^{-1}	~	l/kg	Pa.m^3/mol	~	mg/l	
7	Calculation	10000	200	=R7*S7		0.05	=VLOOKUP(H7, $BB$4:$BC$8 , 2)	=(VLOOKUP (G7, $AX$4:$AZ$22 ,2) * LOG10 (C7)) + VLOOKUP (G7, $AX$4:$AZ$22 ,3)	= 10^(X7)	= D7 * B7 / E7	From ST3 debugged using macro	=V7 * (10 ^ 6) / T7	

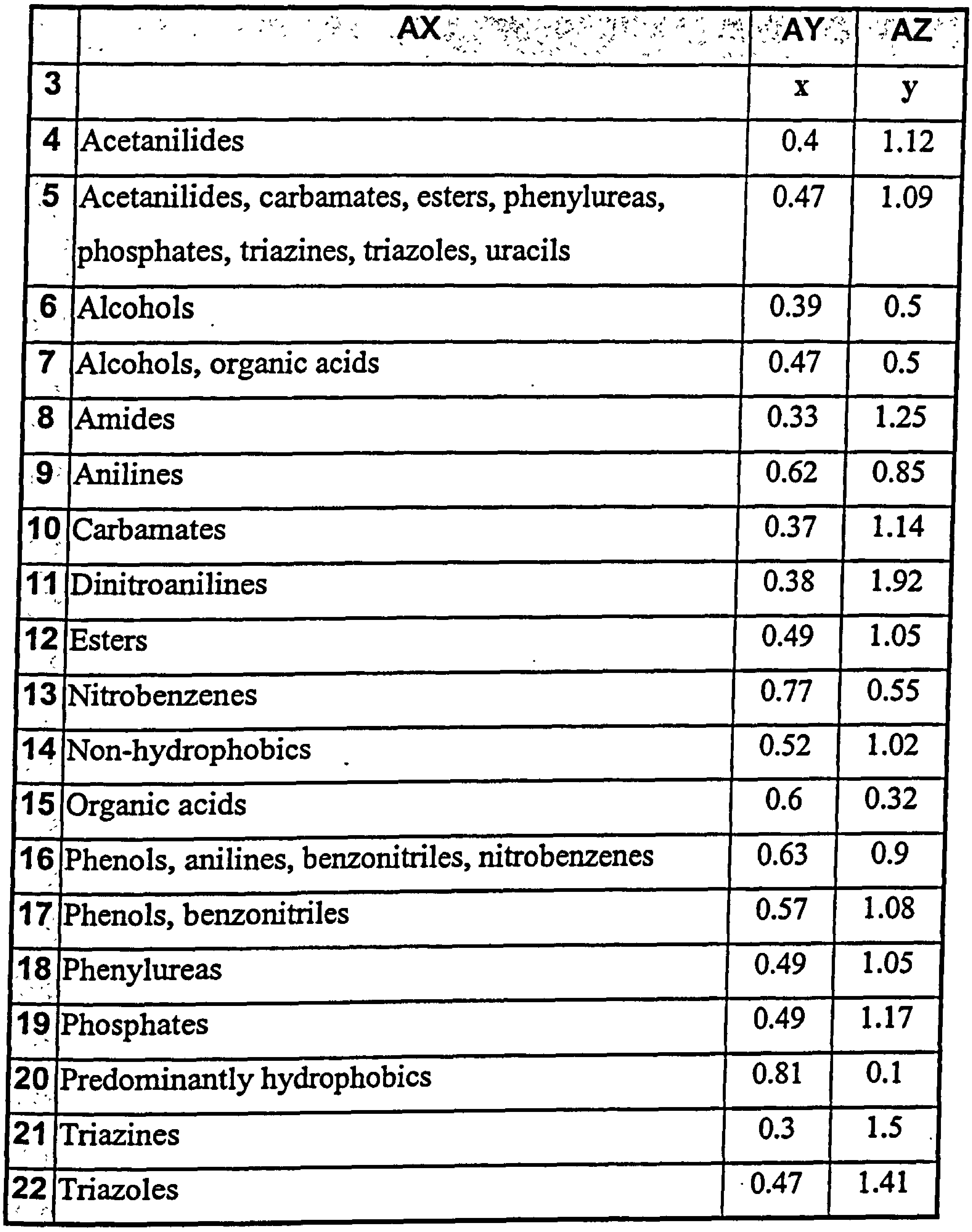
Table 1 (b) - Complete spreadsheet for risk assessment of water compartment at local scale (continued)

	A	AD	AE	AF	AG	AH	AI	AJ	AK	AL	AM	AN	AO	AP
1	Name	SUSP_{water}	DILUTION	Foc_{susp}		Kp_{susp}	Clocal_{eff}	Clocal_{water} (prov)	Clocal_{water}	PEClocal_{water}	Min L(E)C50	AF	PNEC_{water}	RCR_{water}
2	Comment	Default	Default	Default		= Foc_{susp} * Koc	=Clocal_{inf} * Fstp_{water}	= Clocal_{eff} / ((1 + (Kp_{susp} * SUSP_{water} * 10E-6))* DILUTION)	Check if value > water solubility	=Clocal_{water} + $\text{PECregional}_{water}$	= min[L(E)C50 (fish, *daphnia*, algae)]	= 1000 (at Base Set)	= min. L(E)C50 / AF	= PEClocal_{water} / PNEC_{water}
3	Eqn. No.	~	~	~		9 (9)	10 (18)	11 (30)	12	13 (33)	14	~	15	16
4	Value	15	10	0.1								1000		
5	d/c/e	d	d	d		c	c	c	c	c	c	c	c	c
6	Units	mg/l	~	kg/kg		l/kg	mg/l	mg/l	mg/l	mg/l	mg/l	~	mg/l	~
7	Calculation	15	10	0.1		=AF7 * Y7	=AB7 * (AA7 / 100)	= AI7/((1+(AH7 * AD7 * (10 ^ -6))) * AE7)	= IF (AJ7>E7, E7, AJ7)	= AK7 + P7	= MIN(L7:N7)	1000	= AM7 / AN7	= AL7 / AO7

Table 1 (c) - Complete spreadsheet for risk assessment of water compartment at local scale (continued)

Parameter	Units	Value
MOLW	g/mol	197.3
Kow	~	10000
VP	Pa	0.043
SOL	mg/l	7.5
Chemical Class	~	Predom. Hydro.
Biodeg	~	No Biodeg.
Prod Vol	Tonnes/Yr	10
Import	Tonnes/Yr	0
Export	Tonnes/Yr	0
L(E)C_{50} Fish	mg/l	0.6
L(E)C_{50} Daphnia	mg/l	2.3
L(E)C_{50} Algae	mg/l	0.86
$PECregional_{water}$	mg/l	0
$Elocal_{water}$	kg/d	0.05

Table 2 – Base Set data for example substance



	AX	AY	AZ
3		x	y
4	Acetanilides	0.4	1.12
5	Acetanilides, carbamates, esters, phenylureas, phosphates, triazines, triazoles, uracils	0.47	1.09
6	Alcohols	0.39	0.5
7	Alcohols, organic acids	0.47	0.5
8	Amides	0.33	1.25
9	Anilines	0.62	0.85
10	Carbamates	0.37	1.14
11	Dinitroanilines	0.38	1.92
12	Esters	0.49	1.05
13	Nitrobenzenes	0.77	0.55
14	Non-hydrophobics	0.52	1.02
15	Organic acids	0.6	0.32
16	Phenols, anilines, benzonitriles, nitrobenzenes	0.63	0.9
17	Phenols, benzonitriles	0.57	1.08
18	Phenylureas	0.49	1.05
19	Phosphates	0.49	1.17
20	Predominantly hydrophobics	0.81	0.1
21	Triazines	0.3	1.5
22	Triazoles	0.47	1.41

Table 3 - QSAR1 for predicting *LogKoc* from *LogKow* look-up table (AX4:AZ22)

	BB	BC
3	**Degradation description**	**K.bio.stp (h-1)**
4	Ready biodegradable (within 10 day window)	1.0
5	Ready biodegradable (failing 10 day window, but within 28 days)	0.3
6	Inherent biodegradable (fulfilling specified criteria)	0.1
7	Inherent biodegradable (failing specified criteria)	0.0
8	Not biodegradable	0.0

Table 4 - DEG1, discriptive biodegradation rates look-up table (BB4:BC8)

Property	Test Guideline	Error	Mean	Standard Deviation
Vapour Pressure Curve	104	Can be up to 30%	0.043	25% ÷ 3 × 0.043 = 0.0035833
Partition Coefficient (*Kow*)	107	±0.3 log units	4 log units	0.3 ÷ 3 = 0.1 log unit

Table 5 - Physical properties and respective error, mean and standard deviations

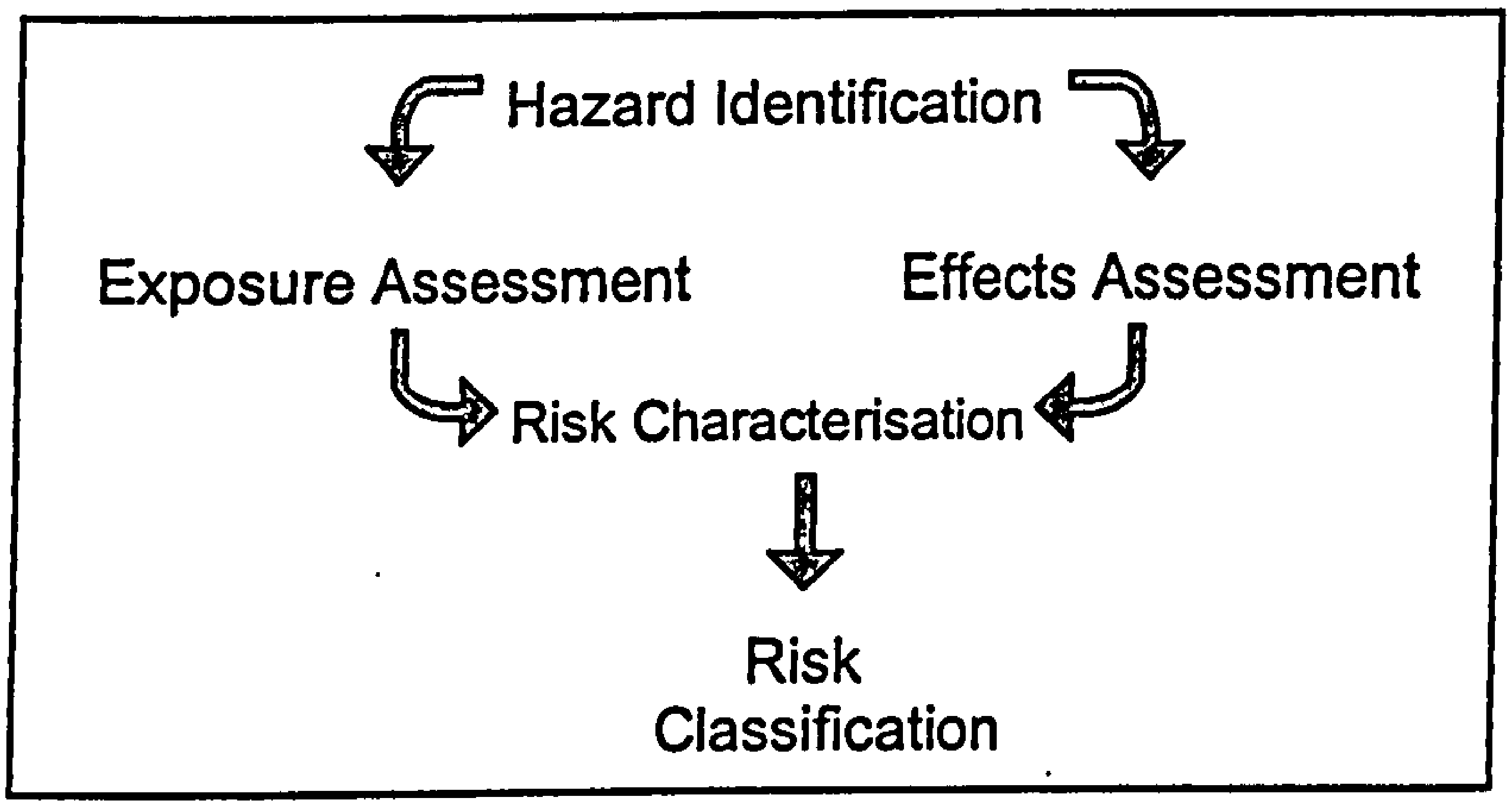


Figure 1 - Risk assessment and risk management process

Figure 2 - Schematic diagram of the parameters involved in calculating the local PEC for water, amended and modified [4]

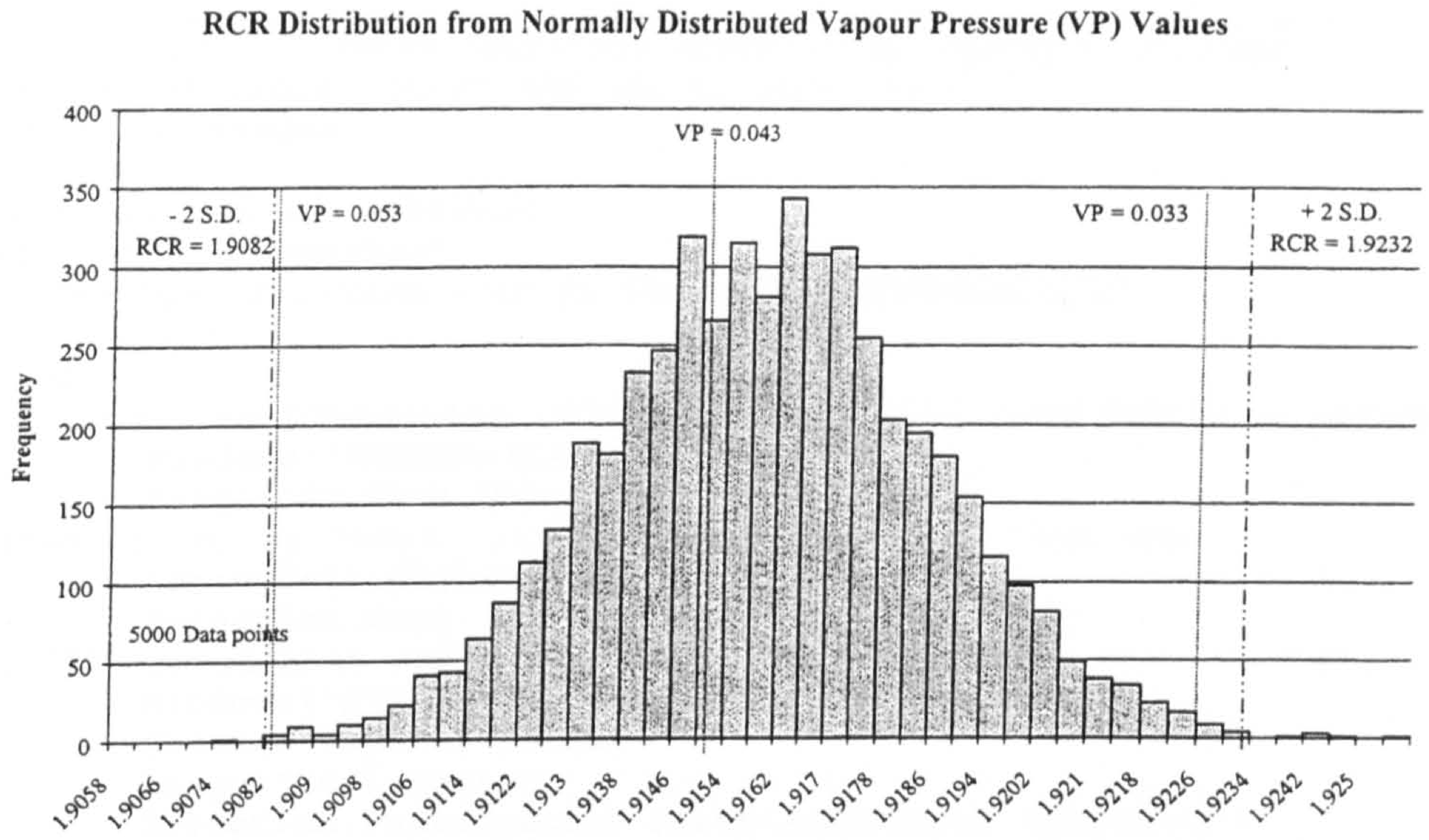


Figure 3 - RCR distribution from normally distributed vapour pressure (VP) values

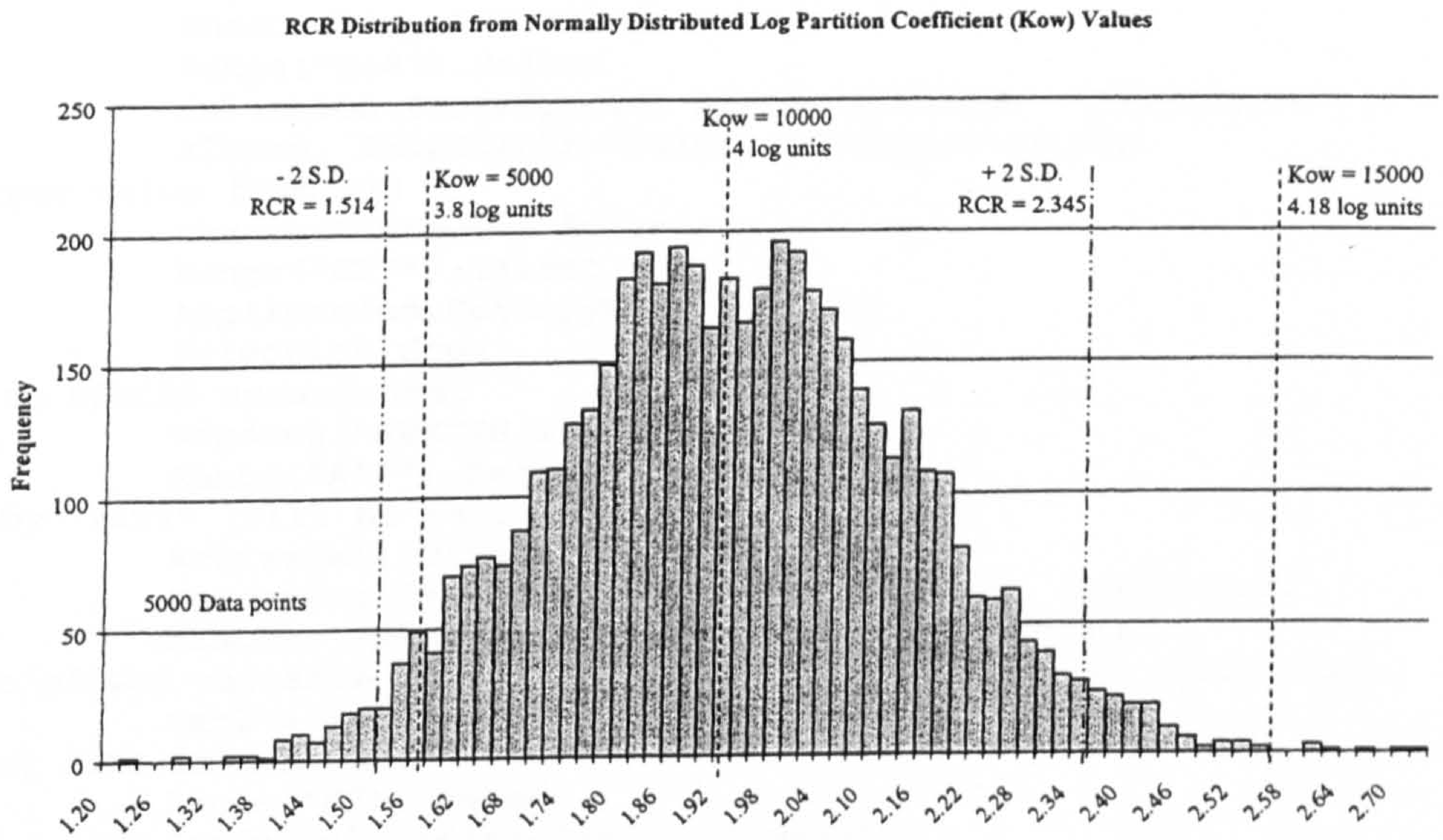


Figure 4 - RCR distribution from normally distributed Log partition coefficient (Kow) values

```
Sub SimpleTreat()
```

```
' SimpleTreat Macro  -  Macro recorded 09/08/00 by Research Engineer
'Declare offset variable “var2” and set it equal to 0
     Dim var2 As Integer
     var2 = 0
'Open SimpleTreat3 model workbook
     ChDir "C:\My Documents\"
     Workbooks.Open FileName:="C:\My Documents\ST3DEBUG.xls"
'Start a Do routine
          Do
'Select all phys chem properties (MOLW, Kow, VP, SOL) from NEXCES spreadsheet
               Windows("NEXCES.xls").Activate
               Range("B7:E7").Select
'Offset (rows, cols) by “var2” (will be zero to start) then copy
               ActiveCell.Offset(var2, 0).Select
               Selection.Copy
'Change to ST3 spreadsheet and paste values in transposing row to column
               Windows("ST3DEBUG.xls").Activate
               Sheets("input").Select
               Range("B6").Select
               Selection.PasteSpecial Paste:=xlValues, Operation:= _
               xlNone, SkipBlanks:=False, Transpose:=True
'Select biodegradation rate (Kbio.stp) from NEXCES spreadsheet
               Windows("NEXCES.xls").Activate
               Range("W7").Select
'Offset (rows, cols) by “var2” (will be zero to start) then copy
               ActiveCell.Offset(var2, 0).Select
               Selection.Copy
'Change to ST3 spreadsheet and paste values in
               Windows("ST3DEBUG.xls").Activate
               Sheets("input").Select
               Range("B48").Select
               Selection.PasteSpecial Paste:=xlValues, Operation:= _
               xlNone, SkipBlanks:=False, Transpose:=False
'Get output value from ST3
               Sheets("output").Select
               Range("C27").Select
               Application.CutCopyMode = False
               Selection.Copy
'Change to NEXCES spreadsheet
               Windows("NEXCES.xls").Activate
               Range("AA7").Select
'Offset by “var2” (will be zero to start) then paste
               ActiveCell.Offset(var2, 0).Select
               Selection.PasteSpecial Paste:=xlValues, Operation:= _
               xlNone, SkipBlanks:=False, Transpose:=False
'Add 1 to offset variable “var2” so next row is used in all operations
               var2 = var2 + 1
'Check for data in next row
               Range("B7").Select
               ActiveCell.Offset(var2, 0).Select
'If empty close ST3 and end
                    If ActiveCell.Value = "" Then winClose
'If values present start Do routine again
          Loop
End Sub

'Routine to close ST3 window
Sub winClose()
     Windows("ST3DEBUG.xls").Close (0)
     If ActiveCell.Value = "" Then End
End Sub
```

Box 1 - Microsoft Excel macro for running SimpleTreat model on multiple risk assessments