SPSD II

DEVELOPMENT OF AN INTEGRATED DATABASE FOR THE MANAGEMENT OF ACCIDENTAL SPILLS (DIMAS)

M. VANGHELUWE, J. MEES, C. JANSSEN

PART 2

GLOBAL CHANGE, ECOSYSTEMS AND BIODIVERSITY

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- MARINE ECOSYSTEMS AND BIODIVERSITY
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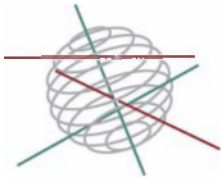

Part 2:

Global change, Ecosystems and Biodiversity

FINAL REPORT

DIMAS

Development of an Integrated Database for the Management of Accidental Spills

EV/41

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LIST OF ABBREVIATIONS

AWZ	Flemish Administration for Waterways and Sea Affairs
BAWG	Bonn Agreement Working Group
BCF	Bioconcentration Factor
BELSPO	Belgian Science Policy
COMMPS	Combined Monitoring-based and Modelling-based Priority Setting
DIMAS	Development of an Integrated Database for the Management of Accidental Spills
ECETOC	European Centre for Ecotoxicology and Toxicology of Chemicals
EDNorth	Endocrine Disruptors in the North Sea
ELSA	Emergency Level Scale Assessment
EC_{50}	Effect Concentration in which 50% of the species are affected
ECB-ESIS	European Chemicals Bureau - official European chemical Substances Information System
ECD	Exposure Concentration Distribution
GESAMP	Group of Experts on the Scientific Aspects of Marine Environmental Protection
GLP	Good Laboratory Practice
GUI	Graphical User Interface
HELCOM	Helsinki Commission
IMDG	International Maritime Dangerous Goods
IMIS	Integrated Marine Information System
IMO	International Maritime Organisation
IUCLID	International Uniform Chemical Information Database
LC_{50}	Lethal Concentration for 50% of the species
$L(E)C_x$	concentration that causes x % change in response (e.g. mortality, immobility)
LOEC	Lowest Observed Effect Concentration
MIMAC	Marine Incidents Management Cluster
MSSQL	Microsoft Structured Query Language
NOEC	No Observed Effect Concentration = test concentration below the lowest concentration that did result in a significant effect in the specific experiment
NSDB	Nordic Substance Database
OSPAR	Oslo and Paris Conventions on the pollution of the North Sea
OTSOPA	Operational, Technical and Scientific Questions concerning Counter Pollution Activities
PAF	Potentially Affected Fraction

PEC	Predicted Environmental Concentration
PNEC	Predicted No Effect Concentration
POP	Persistant Organic Pollutants
RAMA	Risk Analysis of Marine Activities in the Belgian part of the North Sea
REMPEC	Regional Marine Pollution Emergency Response Centre for the Mediterranean Sea
RIVM	Rijksinstituut voor Volksgezondheid en Milieu (Nederland)
SPARC	SPARC Performs Automated Reasoning in Chemistry
SQL	Structured Query Language
SSD	Species Sensitivity Distribution
TSS	Traffic Separation Scheme
UNECE	United Nations Economic Commission for Europe
US-EPA	United States - Environmental Protection Agency
VLIZ	Vlaams Instituut voor de Zee (Flanders Marine Institute)

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ABSTRACT

DIMAS is a 2-year project executed by three Belgian partners (EURAS, VLIZ and Ghent University) and funded by the SPSD II research program of the Belgian Science Policy (BELSPO).

Several shipping accidents in Belgian territorial waters, made the various government agencies involved aware of the need to develop tools to assess the risks and impact on marine resources in the case of an accidental release of hazardous substances. DIMAS aims at the protection of the North Sea and Western Scheldt in case of accidental spills from ships.

In the present project, a relational database is developed, providing reliable, easy to interpret and up-to-date information on marine specific issues. The database contains the latest information on effects (acute and chronic), absorption, distribution, bioaccumulation/biomagnification, GESAMP hazard profiles and physico-chemical properties for a selection of priority substances and is publicly available (http://www.vliz.be/projects/dimas). The selection of the substances is based on criteria such as occurrence on priority lists, volumes transported over sea, frequency of involvement in accidental spills and frequency of transports over sea.

The first beneficiaries of this database are the people directly involved in the first phase of a containment plan for an accidental spill. The final indirect beneficiaries are the general public (scientists, journalists, general public, etc.) who will be better informed about the potential impact to man and the environment.

Keywords: relational database, shipping accidents, accidental spills, hazardous substances, effect modelling, exposure modelling, marine, risk assessment.

INTRODUCTION

The North Sea is one of the most productive ecosystems in the marine environment. There is a general awareness of the need to safeguard this marine ecosystem and to achieve sustainability with respect to human use (OSPAR 2002). However, the North Sea also contains one of the most intensive shipping routes in the world and is being exposed to a significant input of toxicants from very diverse sources, which may harm this ecosystem.

Traditionally, the impact of inputs of contaminants from land including all pathways (e.g. riverine, direct, atmospheric, sewage and sludge formerly deposited, and the dumping of dredged material) has been subject of research since these sources result on an annual basis in large total amounts entering the marine environment. Less attention has been paid to sea-based sources such as pollution caused by accidental spills or leakage from platforms. Although they generally have a smaller contribution to the overall pollution of the North Sea, their impact on a local scale should not be neglected.

Despite present legal, organisational and technical measures currently in place to avoid them, accidental releases of oil and chemicals still happen (Koops 1992, Bonn Agreement 1999). Due to the diversification of transport of crude oil and chemicals in particular and the increasing traffic intensity, there is an increased risk of serious shipping accidents. This applies in particular to the Belgian situation since the Belgian coast is adjacent to the Strait of Dover, which is one of the busiest shipping routes in the world. Two major shipping lanes cross the shallow Belgian maritime area (Noordhinder TSS and Westhinder TSS). Moreover, there is a considerable traffic in the Belgian territorial sea to and from the ports of Antwerp, Zeebrugge, Ghent and Ostend via the Scheldt river. This intense traffic in the narrow shipping lanes creates a substantial risk for pollution mainly resulting from possible collisions. Furthermore, accidents with the shipped products may also occur once they are leaving the harbour and are transported over land.

Although most of the public interest has gone to oil spills and the quantity of chemicals transported over sea is substantially less than oil, the potential harm for the marine environment from a given amount of chemicals spilled can be several orders of magnitude greater. Many of the chemicals transported by sea are highly toxic and/or persistent, can bioaccumulate or cause long-term effects. Recognising that pollution of the sea by oil and other harmful substances in the North Sea area may threaten the marine environment and harm the interests of coastal states, the Bonn agreement was set up (1983). This Agreement for cooperation in dealing with

pollution of the North Sea by oil and other harmful substances was signed by the governments of Belgium, Denmark, France, Germany, the Netherlands, Norway, Sweden, the United Kingdom, Northern Ireland and the European Economic Community.

In the event of an accident at sea, pollutants may contaminate the air, the water surface, the water column and/or the sea floor and indirectly all the organisms in these compartments as well as other users of these compartments. The severity of the impact depends amongst others on the properties of the substance released and the fate and transport of the substance in the marine environment. Therefore, product knowledge and accurate information on environmental partitioning, physical and chemical properties and hazards to the environment are essential to be able to make a good assessment of the potential risks. Sometimes this information is difficult to obtain within the short time frame needed to respond promptly to minimise potential risks of a spill.

With regard to the chemical risk involved in transport by sea, many operational guides have been published by various international and national authorities. Examples are the IMO manuals (IMO 1987, 1992 and 1999), the REMPEC manuals on the Mediterranean Sea (REMPEC 1996 and 1998), the Helsinki Baltic Sea convention (HELCOM 1991), the North Sea Bonn Agreement manual (Bonn Agreement 1985) and other national documents such as the Dutch developed ELSA software (Emergency Level Scale Procedure) (OTSOPA 1990).

At present, federal agencies responsible for evaluating the nature and extent of environmental damage are typically relying on classification systems such as GESAMP hazard profiles, IMDG codes and databases accessible through internet. In most of the cases these sources of information just provide a general overview of the physical hazards represented by the chemicals or their physical and chemical properties in the environment. They often do not take into account the quantity spilled and behaviour of the pollutant or the place where the spill happens and are seldom focused on specific issues such as the impact on marine life, long-term effects, environmental fate and bioaccumulation in marine food chains. Most often the interpretation is left to the user of the database who is confronted with a broad range of reported endpoints and a wide distribution in sensitivities from which it is difficult to select the data needed for the purpose of impact modelling. The absence of easily interpretable databases on marine effects often presents difficulties for the assessment of the impact of accidental spills of oil and chemicals and as such do not provide an easy and understandable basis to inform the officials and others on the seriousness of an accidental spill and the need to initiate risk reduction measures.

Should an accident occur in which substances are discharged into the sea, threatening to be washed up on the beach or even spilled by transportation over land, a prompt reaction to the calamity is essential in order to minimize the potential damage. The choice of effective measures to abate the pollution will depend to a large extent on the direct availability of reliable and up-to-date information on the fate, hazards and risk management procedures to be taken for the spilled product. In this regard it is imperative that all relevant information is made available in a proper format that is easily accessible and interpretable for all stakeholders concerned including the non-expert.

In the DIMAS project, a tool in which environmental data of specific marine pollutants is made available to a broad range of possible end users has been developed. This database provides reliable and up-to date information on marine specific issues, not extensively covered in the above mentioned methodologies while bringing together the information already available in other existing databases (GESAMP 2002, NSDB 2002 etc.). Quite often information on the ecotoxicological effects on marine biota in these databases is limited and if present has most often not been subjected to a thorough data quality assessment. Any assessment of the potential impact of substances entering estuarine and marine waters should ideally be based upon data generated using a range of ecologically relevant saltwater species. However, it is recognized that quite often this information is lacking and the use of freshwater data in lieu of saltwater data can be considered on a case by case evaluation. In this project the ecotoxicological effects were carefully evaluated. It can be expected that due to the nature of an accidental spill, which mostly involves high exposure concentrations for a short period of time, acute effect data are of utmost importance in this regard. However, these spills do also contribute to long-term effects. Subsequently, the database also take these aspects into account.

Since the tool should facilitate and support the decision making in case of an accidental spill, involvement of different stakeholders belonging to different organizational levels was a prerequisite so that specific concerns over the complete chain of command could be taken into account. This was reflected in the composition of the users committee that consisted of representatives of federal and municipal administrations, scientists, port authorities, clean-up and care professionals etc. The users committee was extended with additional experts in the course of the project. As such it could be ensured that the developed database is tailored to the needs of the different end-users.

The project itself consisted of 4 consecutive phases:

(1) Identification and selection of the most important contaminants at the Belgian coast, the Belgian Continental Shelf and the Scheldt estuary.

(2) Collection of physico-chemical and ecotoxicological information regarding the selected contaminants.

(3) Evaluation and interpretation of the gathered data.

(4) Development of an integrated database with a graphical user interface and modelling of the ecotoxicological data.

1 PHASE 1: IDENTIFICATION AND SELECTION OF CONTAMINANTS OF CONCERN

The value of an environmental risk assessment depends to a large extent on the availability of reliable and up-to-date information. Since it would be an enormous task to collect data for all hazardous substances that could be of possible concern to the marine environment, it was deemed necessary to restrict the current project to those substances relevant for the Belgian coast, Belgian Continental Shelf and the Scheldt estuary that would be of highest concern for immediate action.

Thus, in the first phase, the priority contaminants were listed to be included in the database. Selection was performed based on different criteria such as bioaccumulation potential, toxicity, persistence, frequency of involvement in accidental spills, frequency of transport over sea and volumes transported. Furthermore, the intrinsic presence of contaminants in ships and the occurrence of contaminants in dumpsites were taken into account. In this regard the inventory made on the chemical municipal dumpsite 'Paardenmarkt' (Zeebrugge) was of importance (Missiaen & Henriet 2002). Contaminants of concern at this site are arsenic, explosives, chloro-picrine, mustard gas, phosgene and metals present in conventional ammunition.

The prepared list was compared with other existing priority lists (OSPAR priority lists, UNECE POP list, EU Water Framework directive, lists with priority dangerous substances etc.) and validated against transport data from Belgian harbours.

1.1 INITIAL LIST

For the selection of contaminants of concern, a tiered approach was followed. Starting from the NSDB database (Nordic Substance DataBase) with more than 17,500 entries, a selection of products occurring on different lists was made. Therefore, a number of existing lists/databases with substances of concern was retrieved and searched. An overview of the most important lists used in the project, is given in Figure 1.1.

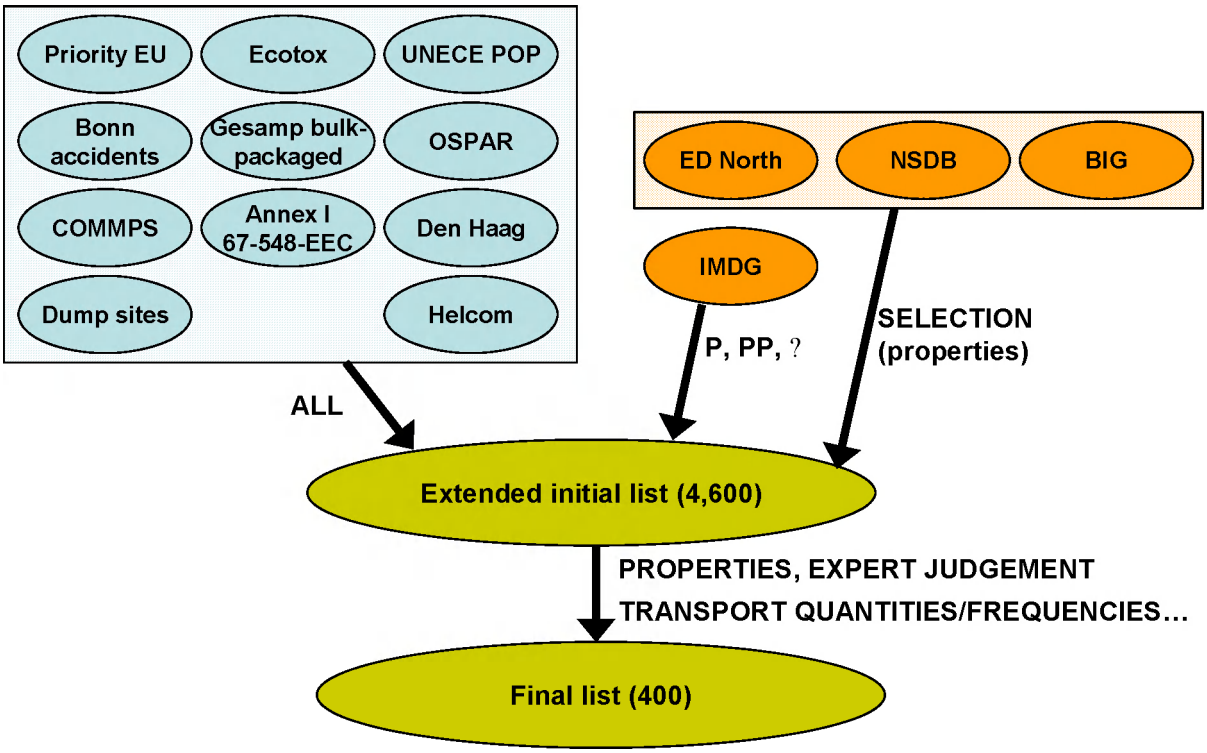


Figure 1.1: Overview of the most important lists/databases used in the selection of substances for DIMAS

The lists mentioned in Figure 1.1 are the following:

- Priority EU: A list of 141 priority substances used by the European Union in the framework of Council Regulation EEC/793/93 on the evaluation and control of the risks of existing substances (http://ecb.jrc.it/esis).
- Bonn accidents: The Bonn Agreement is an international agreement by the North Sea coastal states, together with the EC to offer mutual assistance and co-operation in combating pollution and to execute surveillance as an aid to detecting and combating pollution and to prevent violations of anti-pollution regulations (http://www.bonnagreement.org/). The website contains a list of substances frequently involved in accidental spills at sea.
- COMMPS: In order to establish a list of priority substances in accordance with the provisions of the Water Framework Directive (2000/60/EC) within the European Union, a Combined Monitoring-based and Modelling-based Priority Setting scheme (COMMPS) has been elaborated and a list of priority substances has been derived. This list was used.
- Dump sites: The inventory made on the chemical municipal dumpsite 'Paardenmarkt' (Zeebrugge) was used (Missiaen & Henriet 2002). Contaminants of concern at this site are arsenic, explosives, chloro-picrine,

mustard gas, phosgene and metals present in conventional ammunition. Furthermore, this list of pollutants was extended with compounds found at other dump sites in the North Sea and Baltic Sea derived from literature data.

- Ecotox: The UGent ECOTOX database contains properties and risk and safety phrases of chemicals transported over the North Sea and ecotoxicological profiles on these chemicals (http://www.vliz.be/vmdcdata/ecotox/). This database was constructed in the framework of the project 'Definition and application of ecological criteria and economic indicators for the impact study and cost determination of various types of pollution in the North Sea'.
- GESAMP bulk-packaged: The GESAMP/EHS composite list of hazard profiles of products, transported in bulk and in packaged form, in the framework of the 'Hazard evaluation of substances transported by ships' was used (IMO 2003).
- Annex I 67-548-EEC: Council Directive 67/548/EEC is the EU directive on the approximation of laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances. Annex I to this Directive gives the list of dangerous substances classified according to the greatest degree of hazard.
- UNECE POP: The United Nations Economic Commission for Europe (UNECE) POP protocol covers a list of 16 persistent organic pollutants (POPs).
- OSPAR: The 1992 OSPAR Convention is the current instrument guiding international cooperation on the protection of the marine environment of the North-East Atlantic (http://www.ospar.org/). It combined and updated the 1972 Oslo Convention on dumping waste at sea and the 1974 Paris Convention on land-based sources of marine pollution. The OSPAR Hazardous Substances Strategy sets the objective of preventing pollution of the maritime area by continuously reducing discharges, emissions and losses of hazardous substances, with the ultimate aim of achieving concentrations in the marine environment near background values for naturally occurring substances and close to zero for man-made synthetic substances. To implement this Strategy, the OSPAR Commission has adopted the OSPAR List of Substances of Possible Concern.
- Den Haag: The reference list of dangerous substances annexed to the 'Ministerial declaration of the third international conference on the protection of the North Sea, The Hague, 8 March 1990' was used as an input for the extended list of substances for DIMAS. The following countries were involved:

Belgium, Denmark, Germany, France, the Netherlands, Norway, Sweden, Swiss, the United Kingdom.

- HELCOM: The Helsinki Commission (HELCOM) works to protect the marine environment of the Baltic Sea from all sources of pollution through intergovernmental co-operation between Denmark, Estonia, the European Community, Finland, Germany, Latvia, Lithuania, Poland, Russia and Sweden (http://www.helcom.fi/). HELCOM is the governing body of the 'Convention on the Protection of the Marine Environment of the Baltic Sea Area' - more usually known as the Helsinki Convention. This convention contains a priority list of hazardous substances in the Baltic marine environment.

All these lists/databases were in various formats like PDF documents, Excel sheets, Word documents or they were just available online. The bulk of this data had to be converted to one single format and all substances that appeared twice or more (same name/CAS number/UN number) in the list had to be filtered out. This resulted in an extended initial list of more than 4,600 substances.

The extended list was then converted from an Excel sheet to one hierarchical Microsoft SQL (Structured Query Language) database (MSSQL). This resulted in an easy to manage database of substances, which allowed possible later use/adaptations or extensions. The list was placed on the DIMAS website (restricted area) for online input by the users committee. There was/is the possibility to vote for the compounds to include/exclude them in/from the final list. A comment field could/can be filled in freely to explain the reason for in- or ex-clusion. It was/is also possible to add compounds that were not yet included in the list.

1.2 FINAL LIST

The selection of substances for the final list was partly done by their occurrence on existing lists, expert judgement (properties) and was finalized by comparing to transported quantities and frequencies. The transport quantities were obtained from the RAMA (Risk Analysis of Marine Activities in the Belgian part of the North Sea) project (Le Roy et al. 2006) through MIMAC (Marine Incidents Management Cluster), the cluster that was formed between the complementary projects DIMAS and RAMA.

Within the RAMA project, a list of compound quantities transported and frequency of transport was obtained from the Flemish Administration for Waterways and Sea Affairs (AWZ). UN number, name, IMO and RAMA codes were given, together with information on transported quantities (total quantity, average quantity, number of voyages with a known quantity, total number of voyages). Although some of the data

were incomplete, this list was of utmost importance to the DIMAS project. Transport quantities and frequencies were added to the 'long list' with 4,600 substances in order to be able to adequately select relevant substances for the short list. The substances that were already included into the short list were also validated against the transported quantities/frequencies. An example of how the data are stored in the database is given in Table 1.1 for methane.

Table 1.1: Example of data storage in the 'quantity-frequency' database

UN	name	IMO code	RAMA class	total (tonnes)	voyages with reported quantity	total voyages	average quantity
1972	methane, refrigerated...	2.1	7	5,451,324	59	59	92,395.32

The RAMA class refers to a class defined in the RAMA project (e.g. crude oils, bunkers, marine pollutants…) and was of lesser importance to the DIMAS project. In most cases the number of voyages with reported quantity did not match the total number of voyages with the product. Therefore, an average quantity, based on extrapolation of the available data was made. The products were ranked and products with a high quantity/frequency of transport were included in the DIMAS short list. The selection was further fine tuned with expert judgement and input of the users of the project. This resulted in a short list of 400 compounds. Within the timeframe of the current project, 250 compounds were added to the DIMAS database. The remaining substances could be part of further follow up work.

2 PHASE 2: DATA COLLECTION

In the second phase an extensive literature search was performed using available peer-reviewed literature and already existing databases to gather all information necessary for the database. For each of the compounds, data were collected on physico-chemical properties, ecotoxicology, human effects and GESAMP hazard profiles. Most data on acute, subacute and chronic effects at different trophic levels (fish, algae, plants, invertebrates, micro-organisms) were gathered from international scientific literature. Next to peer reviewed literature, existing databases, national and international reports, research programs etc. were searched.

2.1 PHYSICO-CHEMICAL PROPERTIES

A tiered approach was used to gather physico-chemical properties of the compounds, consulting the following sources:

- ECB-ESIS, the official European chemical Substances Information System from the European Chemicals Bureau, an online available IT system (http://ecb.jrc.it/esis/) containing Risk Assessment Reports and IUCLID (International Uniform Chemical Information Database) Chemical Data Sheets for the physico-chemical properties;
- SPARC online calculator, an online available IT system (http://ibmlc2.chem.uga.edu/sparc/), containing a database with physico-chemical properties of compounds and a module allowing estimations of several physico-chemical properties (vapour pressure, boiling point, solubility, density, log Kow, …);
- the Nordic Substance Database (NSDB), including data on about 18,000 substances or groups of substances from a wide range of data sources, incorporating information from more than 30 important data sources. Experimental data on one or more parameters are included for more than 11,000 of those substances. The basis for the data is laboratory tests;
- peer reviewed literature.

2.2 ECOTOXICOLOGICAL DATA

The main challenge in this project was building the ecotoxicological effect module of the database. For ecotoxicological data, the following sources of data were consulted:

- ECB-ESIS, the official European chemical Substances Information System from the European Chemicals Bureau, an online available IT system (http://ecb.jrc.it/esis/) containing Risk Assessment Reports with high quality ecotoxicological data;
- the US-EPA ECOTOX database, an extensive database for locating single chemical toxicity data for aquatic life, terrestrial plants and wildlife. ECOTOX integrates three previously independent databases (AQUIRE, PHYTOTOX, and TERRETOX) and was created and is maintained by the US-EPA, Office of Research and Development (ORD), and the National Health and Environmental Effects Research Laboratory's (NHEERL's) Mid-Continent Ecology Division (MED). ECOTOX contains toxicity test results and related test information for freshwater and marine organisms, terrestrial plants and terrestrial wildlife extracted predominantly from peer-reviewed literature and is available online (http://cfpub.epa.gov/ecotox/);
- the ED-North database (database on anthropogenic endocrine disruptors in the North Sea), containing the data that where gathered during the SPSD-I research project 'Evaluation of possible impact of endocrine disruptors on the North Sea ecosystem'. The database contains 423 references, 765 chemicals and 2,355 test cases;
- the UGent ECOTOX database, with properties and risk and safety phrases of chemicals transported over the North Sea and ecotoxicological profiles on these chemicals. This database was constructed in the framework of the project 'Definition and application of ecological criteria and economic indicators for the impact study and cost determination of various types of pollution in the North Sea'.
- peer reviewed literature.

The focus of the data collection was on the aquatic and sediment compartment.

While it has been recognised for many years that there is a wider diversity of taxonomic groups (particularly invertebrates) in saltwater environments compared to freshwaters (Russell & Yonge 1928, Moss 1988, Tait 1978), there were relatively few data on the effects of chemical substances on estuarine and marine organisms.

Indeed historically, the patterns of chemical production and use resulting from urban and industrial development have led to the freshwater environment being considered to be the hydrosphere most at risk from these substances. Consequently, most regulatory schemes for evaluating the hazards and risks posed by chemicals have focussed primarily on the protection of freshwater communities. As a result there was a considerable body of data on the ecotoxicity of chemical substances to freshwater organisms (ECETOC 1993), but information for the marine environment was scarce for most compounds. For many marine pollutants, saltwater toxicity data were not even available. In these situations, freshwater data in lieu of data for estuarine/marine species were used to allow read across. Care was taken to avoid pooling freshwater taxa that do not occur in marine ecosystems or are unlikely to occur in strict marine ecosystems (e.g. insects).

The data collection stage yielded a broad range of reported endpoints (mortality, growth, reproduction, …) on different trophic levels (fish, plants, algae, invertebrates, microorganisms, …) and a wide distribution in sensitivities.

2.3 HUMAN TOXICOLOGICAL DATA

Human toxicological data (risk and safety phrases) were mainly gathered from the UGent ECOTOX database and ECB-ESIS.

2.4 GESAMP HAZARD PROFILES

The Revised GESAMP (Group of Experts on the Scientific Aspects of Marine Environmental Protection) Hazard Profiles provide an updated set of criteria for evaluating the hazards of chemical substances to both humans and the marine environment. Over 2,200 substances have been evaluated over the last 30 years.

The GESAMP Hazard Profiles were obtained from the International Maritime Organisation (IMO, kindly provided as the most recent pdf-version by Dr. Jennifer J. Francis). The Revised GESAMP hazard evaluation procedure is shown in Table 2.1.

Table 2.1: The Revised GESAMP hazard evaluation procedure

Columns A & B Aquatic environment

Numerical Rating	A Bioaccumulation and Biodegradation			B Aquatic Toxicity	
	A 1 Bioaccumulation		A 2 Biodegradation	B 1 Acute Toxicity	B 2 Chronic Toxicity
	log Pow	BCF		LC/EC/IC50 (mg/l)	NOEC (mg/l)
0	<1 or > ca. 7	not measurable	**R**: readily biodegradable **NR**: not readily biodegradable	>1,000	>1
1	≥1 - <2	≥1 - <10		>100 - ≤1,000	>0.1 - ≤1
2	≥2 - <3	≥10 - <100		>10 - ≤100	>0.01 - ≤0.1
3	≥3 - <4	≥100 - <500		>1 - ≤10	>0.001 - ≤0.01
4	≥4 -<5	≥500 - <4,000		>0.1 - ≤1	<0.001
5	≥5	≥4,000		>0.01 - ≤0.1	
6				<0.01	

Columns C & D Human Health (Toxic Effects to Mammals)

Numerical Rating	C Acute Mammalian Toxicity			D Irritation, Corrosion & Long term health effects		
	C 1 Oral Toxicity LD50 (mg/kg)	C 2 Dermal Toxicity LD50 (mg/kg)	C 3 Inhalation Toxicity LC50 (mg/l)	D 1 Skin irritation & corrosion	D 2 Eye irritation & corrosion	D3 Long-term health effects
0	>2,000	>2,000	>20	not irritating	not irritating	**C** – Carcinogen
1	>300 - ≤2,000	>1,000 - ≤2,000	>10- ≤20	mildly irritating	mildly irritating	**M** – Mutagenic **R** – Reprotoxic
2	>50 - ≤300	>200 - ≤1,000	>2 - ≤10	irritating	irritating	**S** - Sensitising **A** - Aspiration haz.
3	>5 - ≤50	>50 - ≤200	>0.5 - ≤2	severely irritating or corrosive **3A** Corr. (≤4hr) **3B** Corr. (≤1hr) **3C** Corr. (≤3m)	severely irritating	**T** - Target organ systemic toxicity **L** - Lung injury **N** – Neurotoxic **I** – Immunotoxic
4	≤5	≤50	≤0.5			

Column E Interference with other uses of the sea

E 1	E 2		E 3
Tainting	Physical effects on Wildlife & benthic habitats	**Numerical rating**	Interference with Coastal Amenities
NT: not tainting (tested) **T**: tainting test positive	**Fp**: Persistent Floater **F**: Floater **S**: Sinking Substances	**0**	no interference ***no warning***
		1	slightly objectionable ***warning, no closure of amenity***
		2	moderately objectionable ***possible closure of amenity***
		3	highly objectionable ***closure of amenity***

3 PHASE 3: EVALUATION AND INTERPRETATION OF THE GATHERED DATA

Quite often the information from the above mentioned sources has only been subjected to a preliminary data quality scrutiny. This implies that the initial collection step had to be followed by an expert judgement to evaluate the quality, relevance and representativeness of the underlying data. Therefore a thorough check on data quality was performed before including these data in our database.

This was of utmost importance for the data compiled on the effects on marine biota. Therefore, a detailed quality screening of marine data and a rough quality screening of the (less relevant) freshwater data were carried out.

3.1 MARINE DATA

The data quality and relevance ranking of the marine data points was based on the experience gained in the data evaluation in the EU risk assessment for existing substances (cf. Commission Regulation N° 1488/94 on risk assessment of existing substances) (European Commission 2003).

A checklist for evaluating the data quality of the marine data points is provided in Table 3.1. These criteria are mostly not marine-specific: they simply adhere to the principles of good study conduct.

Table 3.1: Checklist of criteria for the evaluation of the reliability of marine ecotoxicity studies

Type of test – standard test or non-standard test – endpoint used reported – test duration reported – static or flow through
Description of test material and methods – test set-up, measuring chamber/device – test material (including purity), solutions, dilution water if applicable – test organism, including size (age), origin, number of organisms per replicate – test design (# replicates should be used) – type of food given (chronic tests)
Description of physico-chemical test conditions – proper description and control of physico-chemical conditions (e.g. pH, salinity) that may influence the outcome of a test (validity criteria should be met at the end of the test)

Chemical analysis – test concentrations during the test are measured – test concentrations are not measured, but indication is given that the nominal concentrations are close to actual concentrations – evidence is given that concentrations were maintained during the test (< 30% variation)
Concentration-effect relationship – acceptable control mortality, reproduction, growth. – sound statistics used, 95 % confidence limits reported or data on the relationship given amenable to further analysis to derive a suitable $L(E)C_x$ value – concentration range is given – at least 2 different concentrations must have been tested besides the control – a concentration related response should be clear (a progressive effect should be observed as a function of the dose)

The criteria mentioned above should be met, for a study's results to be considered reliable. An experiment can be classified as reliable if it has been carried out according to all criteria, or is missing one or two less important criteria. If one important criterion, or several less important criteria are missing the experiment should be classified as reliable with restrictions, while an experiment should be classified as unreliable if several important criteria are missing. They are outlined in more detail further.

3.1.1 Type of test

Both standard test organisms and non-standard species can be used in the framework of a risk assessment. In general, toxicity data generated from standardized tests, as prescribed by organizations such as OECD and USEPA will need less scrutiny than non-standardized test data, which will require a more thorough check on their compliance with reliability criteria before being used. GLP (Good Laboratory Practice) and non-GLP tests can be used provided that the latter fulfil the stipulated requirements.

In the aquatic environment both static and semi-static tests and flow through tests can be used. In general, flow through tests guarantee a more constant toxicant concentration and water quality.

3.1.2 Description of test material and methods

A detailed description of methods employed in the study should be provided. This description should include at least description of the test medium, time of spiking and recorded observations. Furthermore the organisms used should be uniform in age and represent a sensitive life stage. The test results should allow a proper statistical analysis and the experimental design should provide sufficient replicates per test concentration to derive a high quality L(E)C_x/NOEC value.

3.1.3 Description of physico-chemical test conditions

In Table 3.2 an overview is given of physico-chemical characteristics for each compartment that should preferably be reported and fall within the tolerance limits of the test organisms. If these limits are exceeded the test has to be considered not reliable.

Table 3.2: Physico-chemical parameters that should preferably be reported

Water	Sediment
– temperature – oxygen – hardness – salinity – pH	– temperature – particle size – ammonia/ammonium – organic carbon – oxygen – salinity – pH

3.1.4 Chemical analysis

There is a strong preference for using measured data. Analytical measurements of the toxicant concentrations in the test solution allow to (1) exclude human error related to the preparation/addition of test substance solutions; (2) know the total toxicant concentrations organisms are exposed to, taking into account biodegradation of the compound.

If it is not mentioned whether the reported toxicity values are based on measured or nominal concentrations, they should be considered as nominal concentrations. In cases where no measured data are available the use of nominal concentrations could be considered, based on expert judgement. If the solubility is exceeded the test has to be considered as unreliable. Results from tests where a visual precipitation is observed should be discarded. The absence of a visual precipitation does not

exclude that sometimes colloids may still be present that could still affect the test results.

3.1.5 Concentration-effect relationships

With regard to the acceptability of the test results the following recommendations can be formulated:

- Minimal requirements for endpoints such as mortality, growth, reproduction (e.g. control mortality < 10%) are often given in standard procedures. When these requirements are not met studies should be considered as not reliable.
- When adverse effects are observed in the different treatment groups a clear and consistent (increasing effect with increasing dose) concentration-effect relationship should be present. If no concentration-effect relationship can be established the test should be considered not reliable.
- Because effect concentrations are statistically derived values, information concerning the statistics should also be used as a criterion for data selection. If no methodology is reported and no raw data are reported or if values are 'visually' derived, the data have to be considered unreliable. In absence of sound statistics or no $L(E)C_x$ or NOEC has been calculated or reported in the study itself, the study could still be used if data are available amenable to further analysis that allow to derive a suitable $L(E)C_x$ or NOEC/LOEC value.
- Test concentration intervals should bracket the NOEC with concentrations that are as closely spaced as practical. Increasing the size of the test concentration intervals leads to reduced statistical power for the test. Following new OECD guidelines (e.g. OECD 2001) test concentrations should preferably differ by no more than a factor of 2.

With regard to the proper use of NOEC/LOEC values and $L(E)C_x$ values the following recommendations can be made:

- For acute studies $L(E)C_x$ values should be estimated using appropriate statistical analysis (e.g. probit analysis or linear regression).
- For chronic studies concentration-response modeling such as regression models to calculate $L(E)C_x$ are generally preferred over the classical hypothesis testing ($p< 0.05$) used to derive NOEC values. The latter method has indeed a number of limitations (Moore and Caux 1997). Since the NOEC is by definition an applied dose, its value is to some degree dependent upon the choice of the experimenter. Secondly the NOEC depends upon the variability of the organism to a single dose. Organisms which are particularly

sensitive to small variations in their environment, and hence display a greater variability of response to a given dose, are likely to have higher NOECs than if they were less sensitive, independent of their sensitivity to the toxicant. The use of a regression based approach offers the advantage that all of the information in the concentration-response curve is used and furthermore precludes the use of poor quality information because in those cases an inadequate model fit will be obtained.

- In case a benchmark dose ($L(E)C_x$ is calculated using a regression based approach and this value is to be used as an equivalent for a NOEC value, then typically a cut-off level should be identified representing a low effect percentile. This cut off value to be used should be derived based on the plausibility to detect a statistical significant difference and is depending on the inherent variability observed in the control test. The choice of the appropriate effect level is still an area under discussion and more research is needed (ISO 2004, Environment Canada 2005). A concentration that causes a low level of reduction, such as an EC_5 or EC_{10}, is rarely statistically significantly different from the control treatment. Therefore in some guidance documents the EC_{20} is sometimes proposed as a compromise representing a low level of effect that is generally significantly different from the control treatment (US-EPA 1999). Whatever effect level is chosen, it is recommended that the $L(E)C_x$ value should not be extrapolated below the lowest applied (non-zero) concentration. According to Reiley et al. (2003) and the draft ISO document (ISO 2004) estimation of $L(E)C_x$ values outside the concentration range tested introduces a great deal of uncertainty. If the resulting $L(E)C_x$ value should be below the lowest applied control level (background level) or essentiality level, its reliability/relevance has to be questioned (another confounding factor in this respect is the hormesis phenomenon which for essential metals can be very important). Before estimating the $L(E)C_x$ value it should also be checked, case-by-case if the experimental design is appropriate to be used for regression methods. The statistical design needed for a proper $L(E)C_x$ derivation are more doses with fewer replicates at each dose. For estimating an $L(E)C_x$ value three concentration groups, as well as the control group, is an absolute (theoretical) minimum. However, if there are only three treatment groups and one fails to show any (partial) effect the test would be considered inadequate. Therefore more concentration groups are recommended in practice (ISO 2004). Many of the older toxicity data do not fulfil the statistical requirements in order to derive an $L(E)C_x$ value. In those cases the conventional NOEC and LOEC values should be used. NOEC values could be in the natural range but LOEC values should not.

- If only a LOEC ≥ 20% effect is reported (i.e. no NOEC could be derived as the lowest test group produced a response significantly different from the control group) and a distinct concentration/effect relationship is apparent, the $L(E)C_x$ is calculated and should be evaluated if it can be regarded as the NOEC. If the effect percentage of the LOEC is unknown, no NOEC can be derived. Such an approach is only recommended if insufficient bounded NOECs are available.
- In general, the use of unbounded NOEC values is not recommended. Unbounded NOEC values should only be considered in specific cases. For example, if other toxicity values are not available for a particular species. In that case an unbounded NOEC could be used as a conservative estimate for the 'real' NOEC.

Only reliable marine datapoints were entered in the DIMAS database. A broad range of organisms and endpoints were assessed.

3.2 FRESHWATER DATA

If insufficient data for the marine environment were available, results from freshwater studies were used. Quality screening for freshwater studies was more limited than for the saltwater studies because the high number of freshwater data did not allow such a high detail level within the framework of the current project. Thus, freshwater data were given a quality score ('reliable', 'reliable with restrictions' or 'not fully verifiable') depending on the data source (e.g. data from EU risk assessment reports are classified as reliable whereas data from the US-EPA ECOTOX database are considered not fully verifiable) in combination with expert judgement (e.g. articles from Web of Science were evaluated on a case by case basis).

In order to facilitate the interpretation of the wide range of effect data (cf. 2.2), an effect modelling step was carried out in the last phase of the DIMAS project.

4 PHASE 4: DATABASE DEVELOPMENT AND DATA MODELLING

4.1 DATABASE DEVELOPMENT

Based on the data and insights gained in phase 2 and 3 a relational database with a graphical user interface (GUI) was established. Due to the complexity and the amount of data that had to be entered in the DIMAS database, the best solution appeared to be a relational MS Access database. The advantages of using a relational database over typical archive techniques are the powerful querying capabilities, ease for importing and exporting data in a variety of formats, and faster access to data.

The primary objective of phase 4 was to automate the process of displaying and disseminating the collected data. The database is accessible to all end users (experts and non-experts) as a fully web-enabled search engine using a simple GUI and is retrievable via the project website (http://www.vliz.be/projects/dimas). In case of accidental spills, all end-users, public services, media and the general public will be able to easily gather objective, quality-assured information.

Information that had to be entered in the database included physico-chemical characteristics of the compounds (physical state, melting point, boiling point, density, solubility, vapour pressure, log K_{ow}, …), acute and chronic ecotoxicological data on different marine and freshwater species, risk and safety phrases and GESAMP hazard profiles.

A relational model was built in Access to represent all the substances of the final DIMAS list. The relations in the DIMAS database are represented in Figure 4.1.

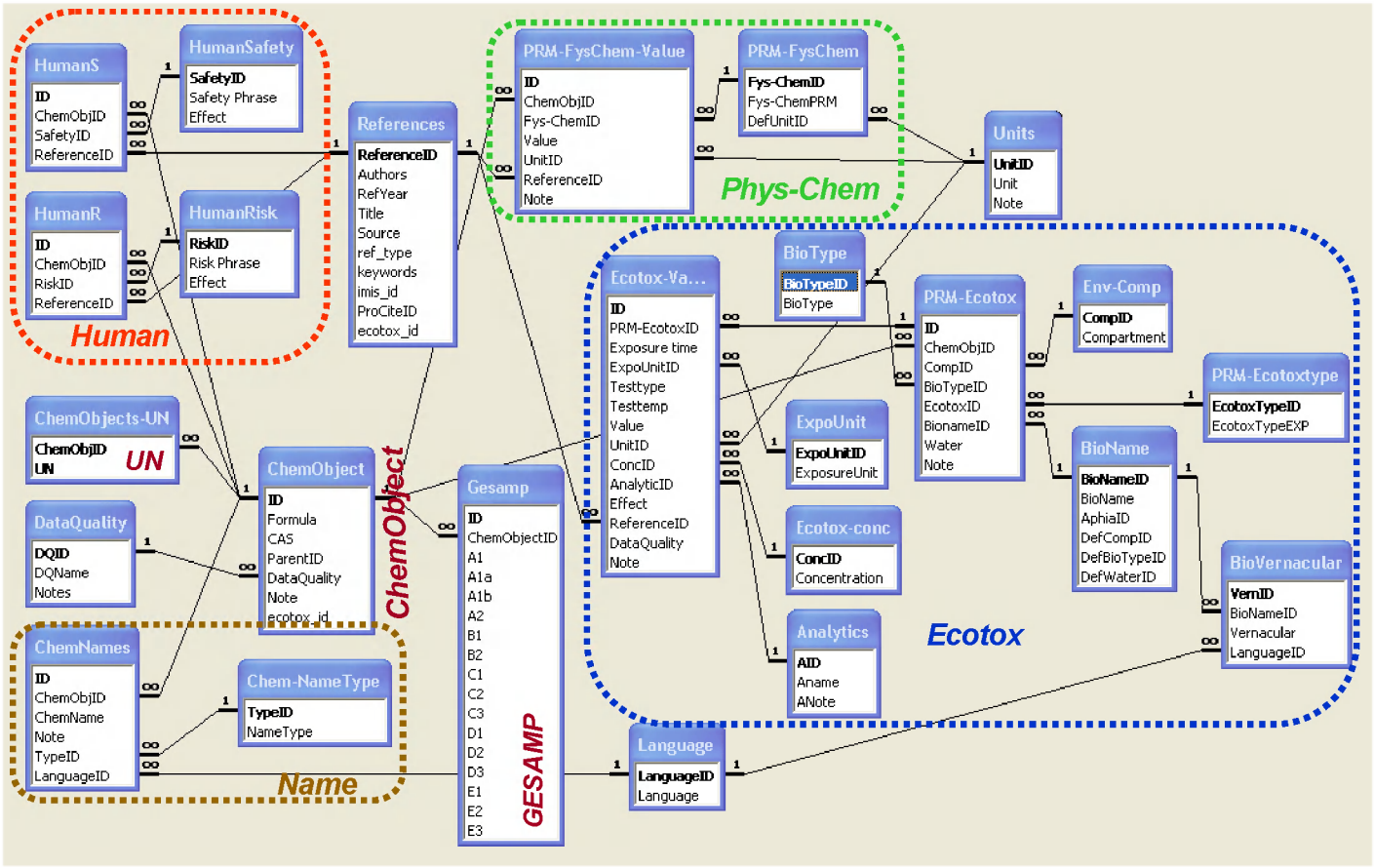


Figure 4.1: Structure of the DIMAS database in Access

The model was composed of four major parts:

- ChemObject: a 'virtual' object to represent any substance or compound. This gave us the possibility lo link one substance to a 'parent' substance, it also allowed us to create groups of substances. Also, this structure allowed us to link more than one name to a substance (a common name, that could be any language, or a IUPAC name). One could attribute more than one UN or CAS number to one ChemObject.
- Physical and chemical parameters: a ChemObject is linked to several physical and chemical parameters. These parameters can even appear twice (i.e. from different references or data sources).
- Ecotox: this is the core of the database where all data is stored for later analysis. All data in this part is fully normalised to avoid typing errors. The structure is a three-tiered system: one ChemObject (1st tier) is linked to several species that can be tested in different circumstances (acute/chronic) (2nd tier).

One circumstance can have several 'Values' (3rd tier), these are the real outcomes of all the tests performed.

- Risk & safety phrases and Gesamp Hazard Profiles: this is data that is freely available for almost all known substances.

There are also a number of predefined lists in the database:

- The reference-list contains all references used for gathering the data. All data records have a reference record linked to it. Where possible, a link has been made to the IMIS database (Integrated Marine Information System - http://www.vliz.be/vmdcdata/IMIS2), which holds data about publications, persons, institutes and datasets;
- The species-list contains species needed in the Ecotox module. Again, where possible, a link has been made with APHIA (the marine species register hosted at VLIZ – http://www.vliz.be/vmdcdata/aphia);
- Some other lists are managed in the DIMAS database for normalisation purposes: units, concentration, data-quality, type of species…

The structure of the database was set up in such a way that in a later stage, new substances can easily be added without the need to modify the structure or damaging existing data. This allows the dataset to be used in any complementary or subsequent project.

After the model was set up, a Graphical User Interface (GUI) was built, so one could easily enter data in the database. After several GUI enhancements and additions, the final version was ready for the production environment, and the database was getting populated.

In total the GUI was composed of seven parts:

- 'ChemObject'
- 'Name'
- 'UN'
- 'Phys-Chem'
- 'Ecotox'
- 'Human'
- 'GESAMP Hazard profile'

4.1.1 ChemObject

This part of the database contains the following fields:

- ChemObjID. This is a unique number for every compound in the database and this field is automatically filled out.
- Formula. In this field, the chemical formula of the compound is entered. Different chemical compounds can have the same formula (isomers) meaning one formula can appear multiple times in the database.
- CAS. The CAS number is a unique numeric identifier for a chemical compound. Each CAS number can only represent one chemical compound. If the same CAS number is entered twice in the database, an error message will appear.
- Parent object. If the compound is part of a group of compounds, the name of the group can be entered in this field.
- Note/reason for inclusion. In this field, the reason for inclusion of the chemical compound in the DIMAS database can be entered. Also, other useful information on the compound that can not be entered elsewhere can be noted in this field.
- DataQuality. This field contains a drop-down menu with the items 'Low', 'Medium' and 'High'.

The completed 'ChemObject' part of the GUI for the compound dibutyl phthalate is shown in Figure 4.2.

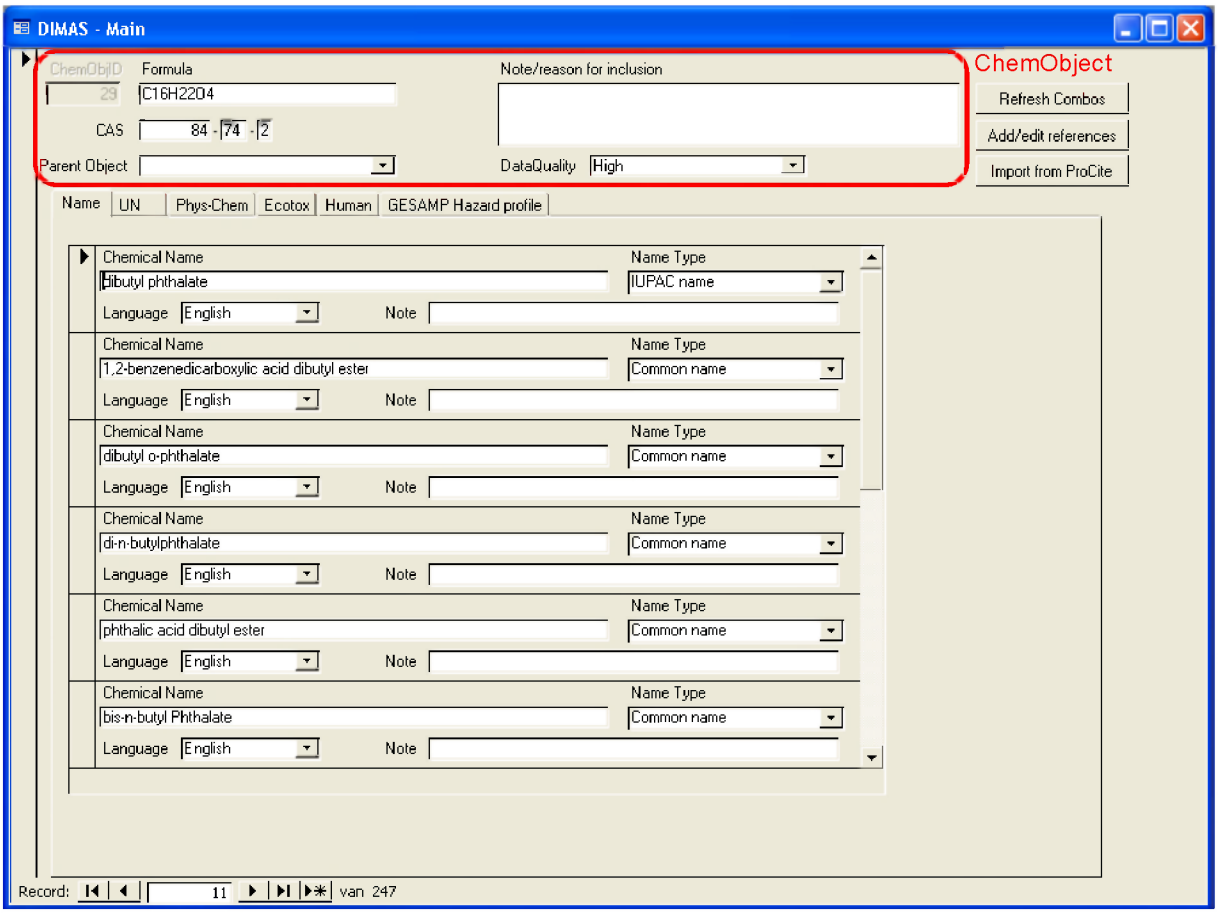


Figure 4.2: 'ChemObject' part of the GUI of the DIMAS database

4.1.2 Name

Several names can be linked to one chemical compound. For every name, the following fields can be entered:

- Chemical Name. In this field, the IUPAC name or a common name of the compound can be entered in English, Dutch or French.
- Name Type. This field contains a drop-down menu with the items 'IUPAC name' and 'Common name'.
- Language. This field contains a drop-down menu with the items 'English', 'French' and 'Dutch'.
- Note. Other useful information on the name of the compound can be entered in this field.

The number of names that can be entered for one compound is unlimited. The completed 'Name' part of the GUI for the compound dibutyl phthalate is shown in Figure 4.3.

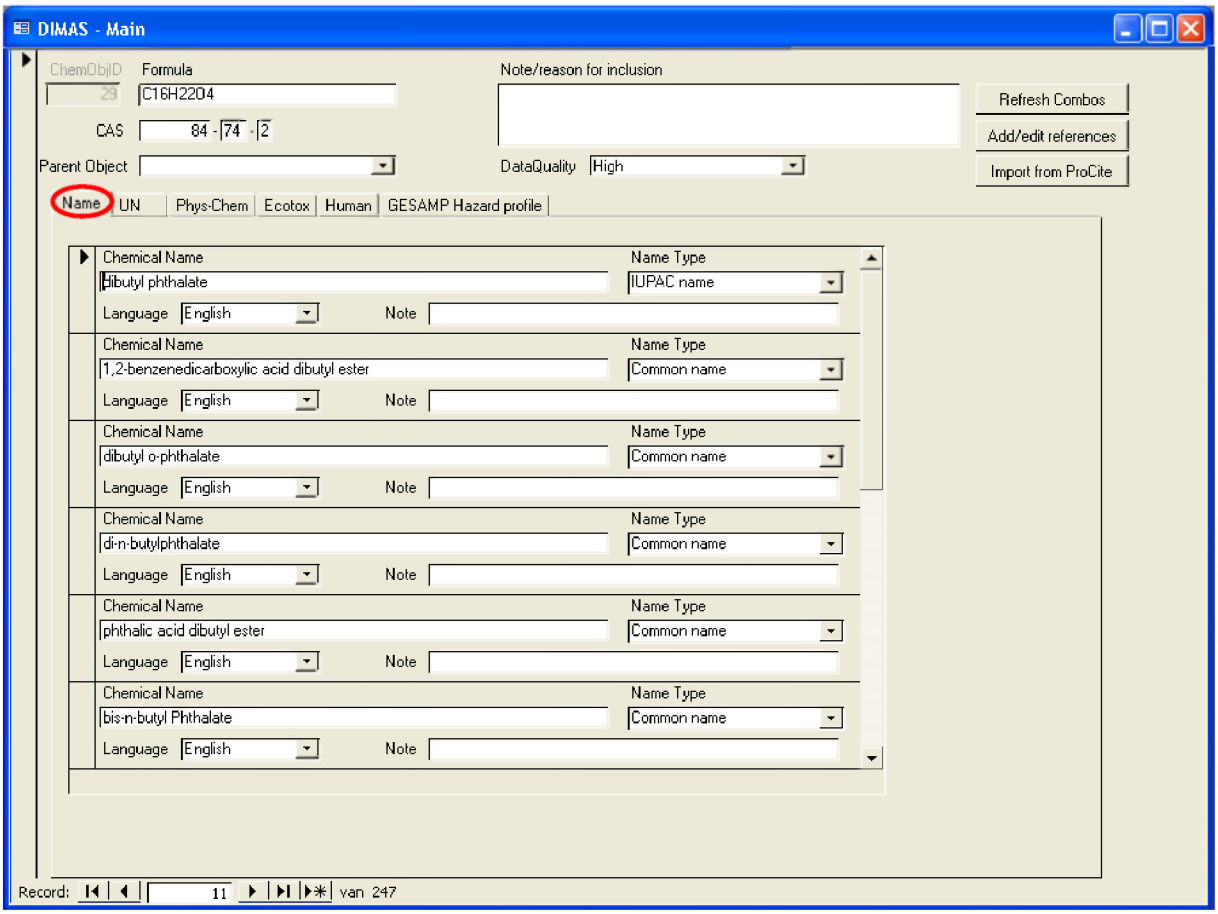


Figure 4.3: 'Name' part of the GUI of the DIMAS database

4.1.3 UN

UN numbers or UN IDs are four-digit numbers that identify hazardous substances and products (such as explosives and poisonous materials) in the framework of international transport. This numbering scheme is widely used in international commerce, for instance to label the contents of shipping containers. Some hazardous substances have their own UN numbers (e.g. acrylamide has UN2074), while sometimes groups of chemicals or products with similar properties receive a common UN number (e.g. flammable liquid, not otherwise specified, have UN1993). A chemical in its solid state may receive a different UN number than the liquid phase if their hazardous properties differ significantly; substances with different levels of purity may also receive different UN numbers. Therefore, different UN numbers can be linked to one compound.

The completed 'UN' part of the GUI for the compound dibutyl phthalate is shown in Figure 4.4.

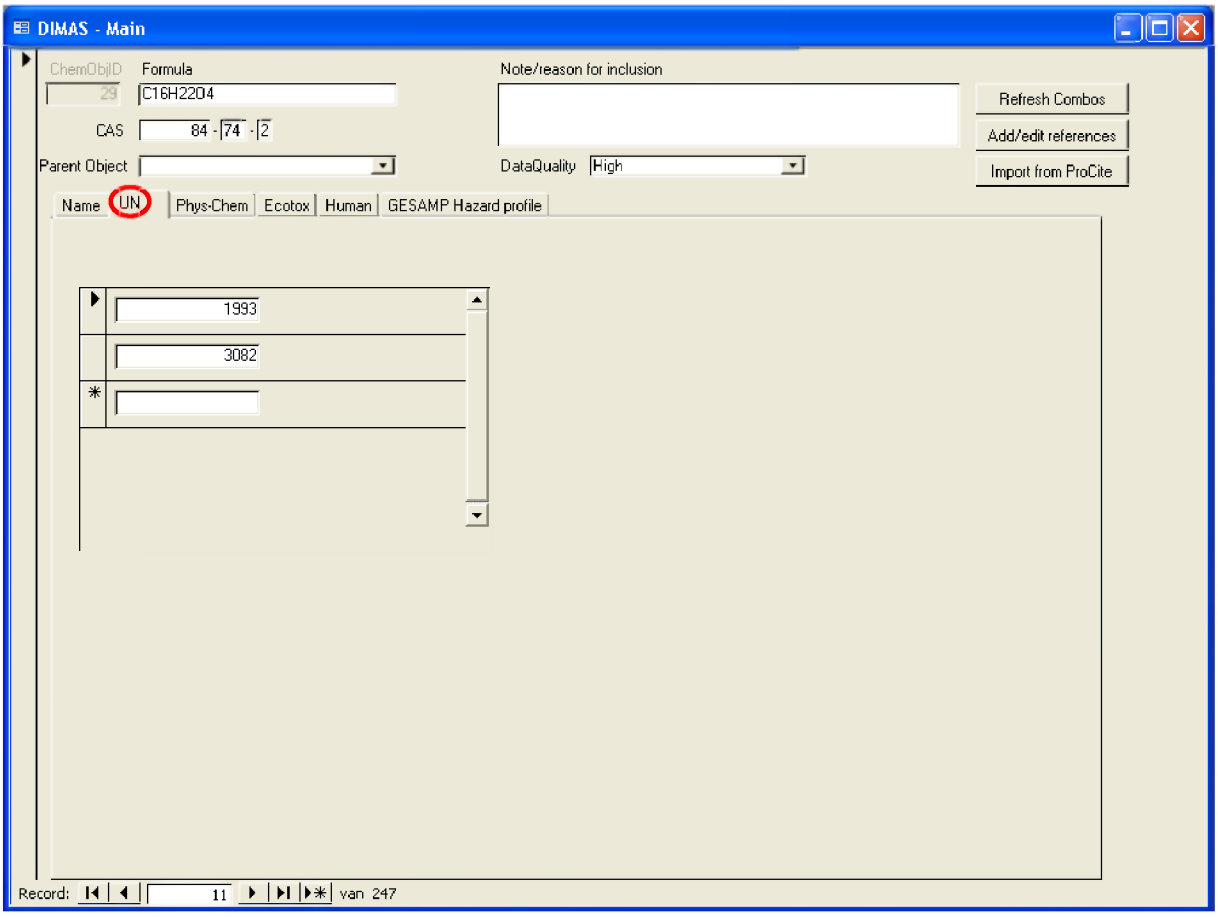


Figure 4.4: 'UN' part of the GUI of the DIMAS database

4.1.4 Phys-Chem

Several physico-chemical parameters can be linked to one chemical compound. For every parameter, the following fields can be entered:

- Physico-Chemical Parameter. This field contains a drop-down menu with the following items:
  - Physical state
  - Melting point
  - Boiling point
  - Relative density
  - Vapor pressure
  - log K_{ow}

- Flash Point
- Autoflammability
- Explosive limits
- Biodegradation
- Water solubility
- Molecular weight

– Value. In this field, the value of the parameter selected in the previous field should be entered. Note that a dot should be used as decimal separator.

– Unit. In this field, the unit of the value entered in the previous field should be selected. This field contains a drop-down menu with 16 different units (dimensionless, °C, g/cm³ at 20°C, hPa at 20°C, vol/vol, g/L, g/mol, Pa, bar, atm, torr, mm Hg, psi, kg/cm², mg/L and µg/L). Each parameter has a default unit assigned to it, which appears in the 'Unit' field when the parameter is selected. This unit can however be adjusted manually to another one in the predefined list.

– Reference. This field contains a drop-down menu with a predefined list of all the references used for the database. If a new reference should be added to this list, this can be done by clicking the 'Add/edit references' button in the main module of the DIMAS GUI. The 'Reference' window will then appear (see Figure 4.5), where new references can be added.

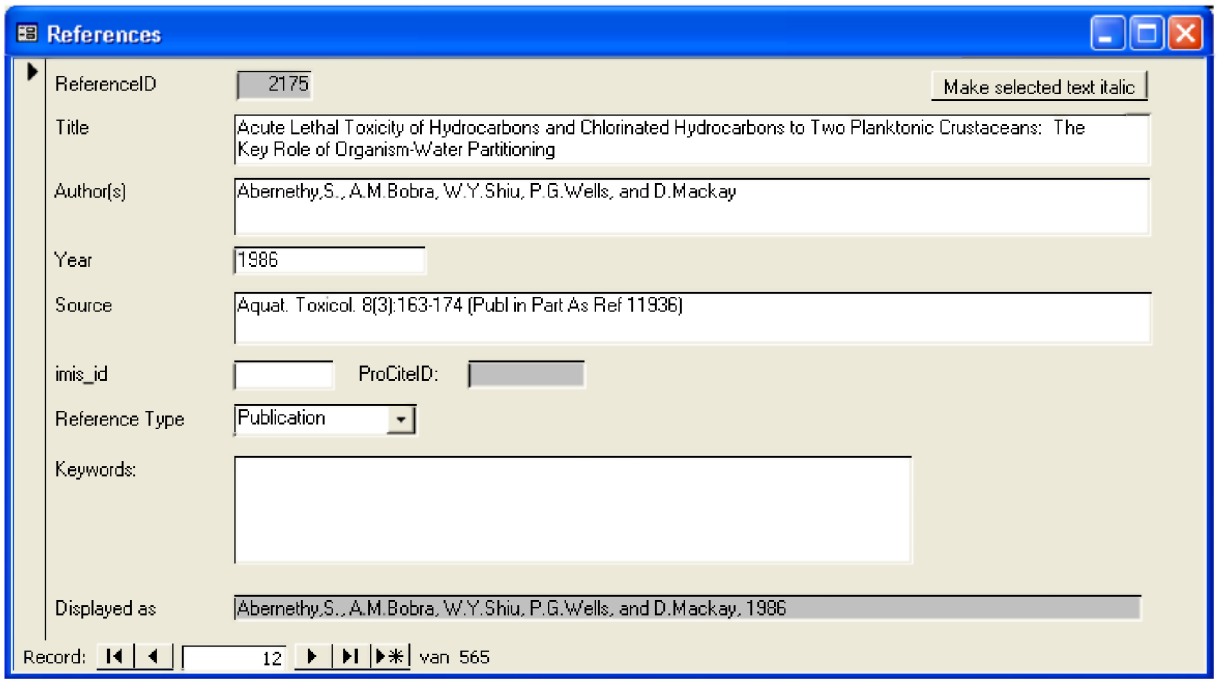


Figure 4.5: 'Reference' window of the GUI of the DIMAS database

– Note. Other useful information on the physico-chemical parameters of the compound can be entered in this field.

The number of physico-chemical parameters that can be entered for one compound is unlimited. The completed 'Phys-Chem' part of the GUI for one of the physicochemical parameters for the compound dibutyl phthalate is shown in Figure 4.6.

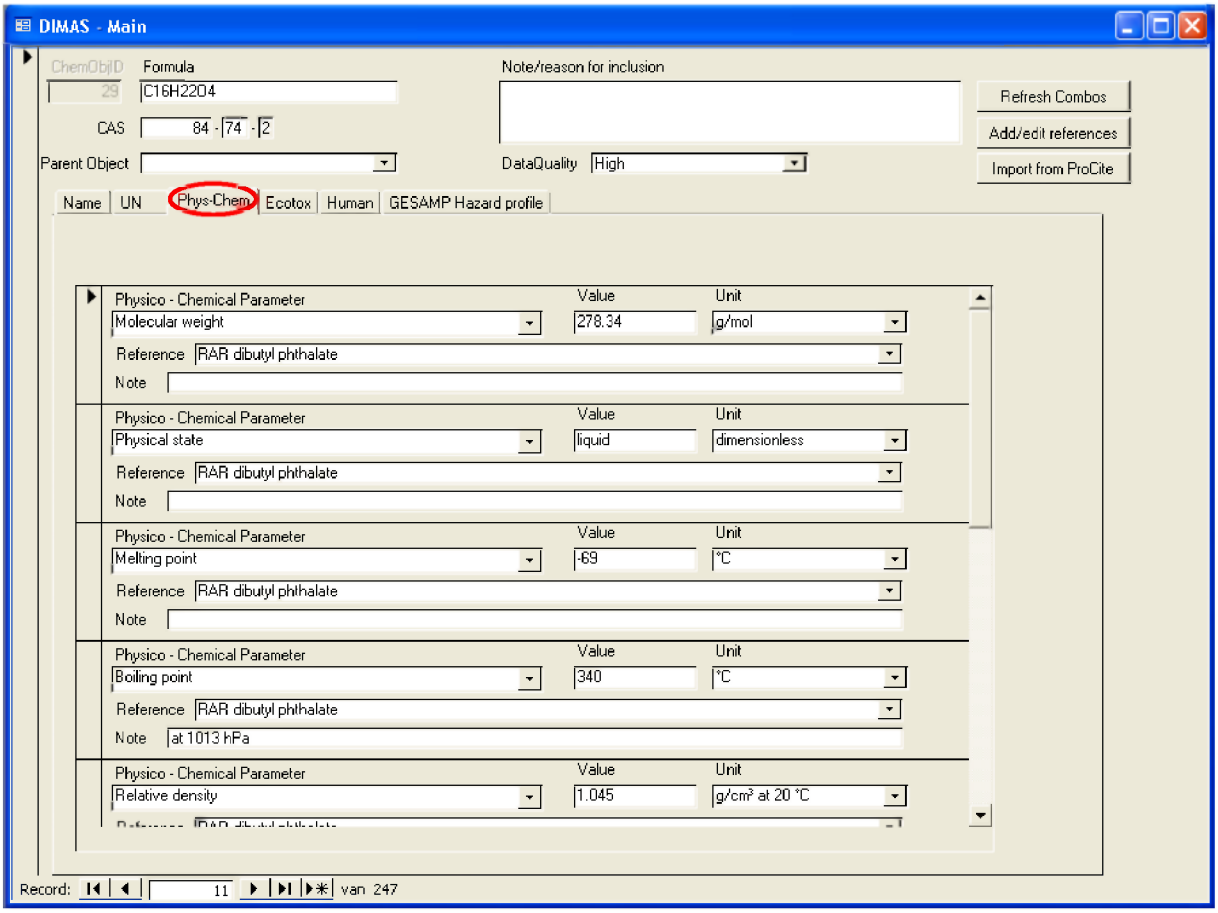


Figure 4.6: 'Phys-Chem' part of the GUI of the DIMAS database

4.1.5 Ecotox

This is the main part of the database, where the effect data are stored. An unlimited number of acute and chronic ecotoxicological effect data for different throphic levels, environments and compartments can be linked to one chemical compound. For every effect datapoint, the following fields should be entered:

– Species/other. This field contains a drop-down menu with a predefined list of all the species used for the database. If a new species should be added to this list, this can be done by clicking the 'Add or edit species and/or vernaculars'

button in the Ecotox module of the DIMAS GUI. The 'BioNames and Vernaculars' window will then appear (see Figure 4.7), where new species can be added. For each species, a default compartment (air, sediment, soil, water), biotype (plant, alga, invertebrate, fish, microorganism, amphibian, insect, other) and water type (salt, fresh) should be entered. Furthermore, an unlimited list of vernaculars can be entered for each species (in Dutch, English or French).

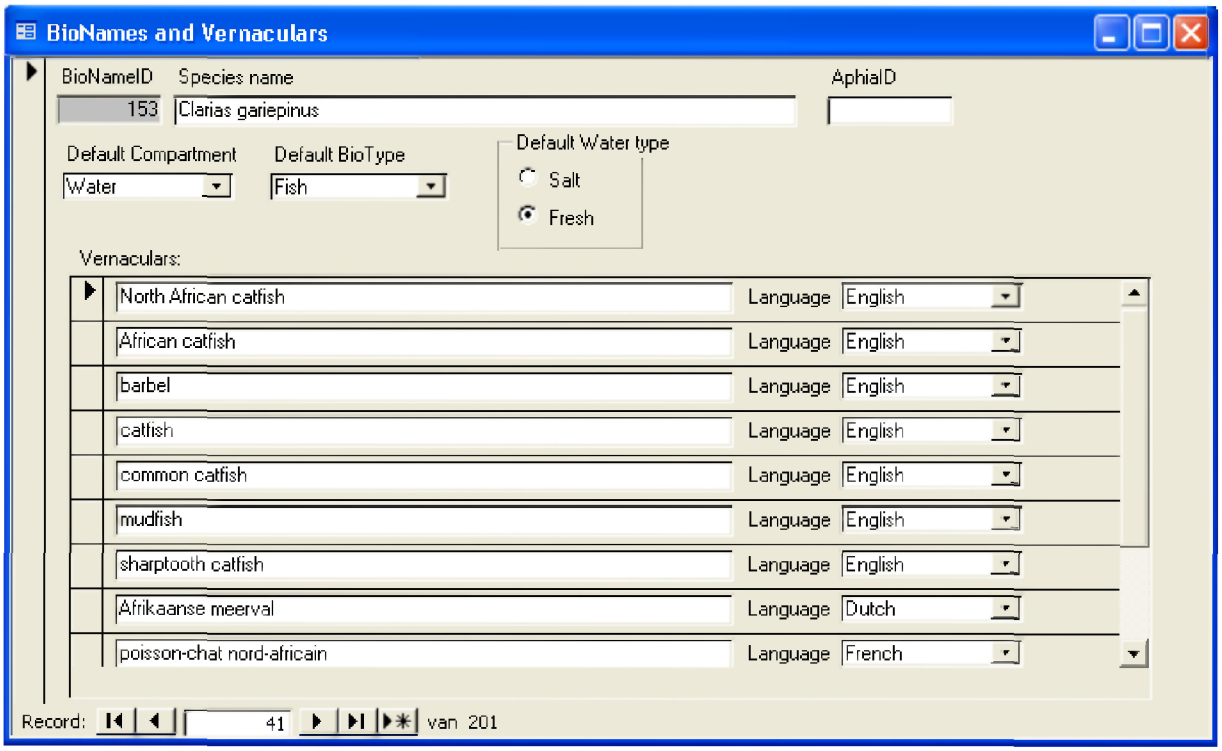


Figure 4.7: 'BioNames and Vernaculars' window of the GUI of the DIMAS database

- Ecotox Exposure Type. This field contains a drop-down menu with the items 'Acute toxicity' and 'Chronic toxicity'. Note that alga toxicity data are always considered chronic.
- Compartment. This field contains a drop-down menu with the items 'Air', 'Sediment', 'Soil' and 'Water'. The default value linked to the species will automatically appear in this field when the species is selected in the 'Species/other' field but can be adjusted manually.
- BioType. This field contains a drop-down menu with the items 'Plant', 'Alga', 'Invertebrate', 'Fish', 'Microorganism', 'Amphibian', 'Insect' and 'Other'. The default value linked to the species will automatically appear in this field when

the species is selected in the 'Species/other' field but can be adjusted manually.

- Water type. This field contains a radiobutton with the items 'Salt' and 'Fresh'. The water type the test was performed in should be selected here. The default value linked to the species will automatically appear when the species is selected in the 'Species/other' field but can be adjusted manually.
- Values. For every species linked to an exposure type, compartment, biotype and water type, several ecotox values can be entered in the database. Per value, the following fields should be completed:
  - Exposure time + unit. The time of exposure of the species to the test compound should be entered here. The unit field contains a drop-down menu with the items 'second(s)', 'minute(s)', 'hour(s)', 'day(s)', 'week(s)' and 'month(s)'.
  - DataQuality. As mentioned in Phase 3: Evaluation and interpretation of the gathered data, quality screening for freshwater studies was more limited than for the saltwater studies because the high number of freshwater data did not allow such a high detail level within the framework of the current project. Thus, freshwater data were given a quality score from the drop-down menu in this field ('reliable', 'reliable with restrictions' or 'not fully verifiable') depending on the data source (e.g. data from EU risk assessment reports are classified as reliable whereas data from the US-EPA ECOTOX database are considered not fully verifiable). Only high quality marine data are entered in the database so these data are all labelled 'reliable'.
  - Value + unit. In this field, the value of the effect concentration should be entered. Note that a dot should be used as decimal separator. In the unit field, the unit of the value entered should be selected. This field contains the same drop-down menu as the unit field in the 'Phys-Chem' part of the GUI with 16 different units (dimensionless, °C, g/cm³ at 20°C, hPa at 20°C, vol/vol, g/L, g/mol, Pa, bar, atm, torr, mm Hg, psi, kg/cm², mg/L and µg/L).
  - Effect concentration. In this field, the effect concentration that was determined in the test should be selected from a drop-down menu (e.g. EC_{50}, LC_{50}, NOEC, LOEC).
  - Analytics. Indicate here if the entered ecotoxicological concentration is a nominal or a measured value. If this information is not available in the reference, this is left empty.

- Endpoint. The endpoint that was determined in the test should be entered here (e.g. mortality, reproduction). If the effect concentration is a lethal concentration (LC), this field will be automatically completed with the endpoint 'mortality'.
- Temperature. If the test temperature of the study is available, this can be entered here.
- Test Type. This field contains a drop-down menu with the items 'static', 'flow through' and 'renewal'.
- Reference. This field contains a drop-down menu with a predefined list of all the references used for the database. If a new reference should be added to this list, this can be done by clicking the 'Add/edit references' button in the main module of the DIMAS GUI. The 'Reference' window will then appear (see Figure 4.5), where new references can be added.
- Note. Other useful information on the ecotox datapoint that can not be entered elsewhere can be noted in this field.

The number of ecotoxicological effect data that can be entered for one compound is unlimited. The completed 'Ecotox' part of the GUI for one of the ecotox datapoints for the compound dibutyl phthalate is shown in Figure 4.8.

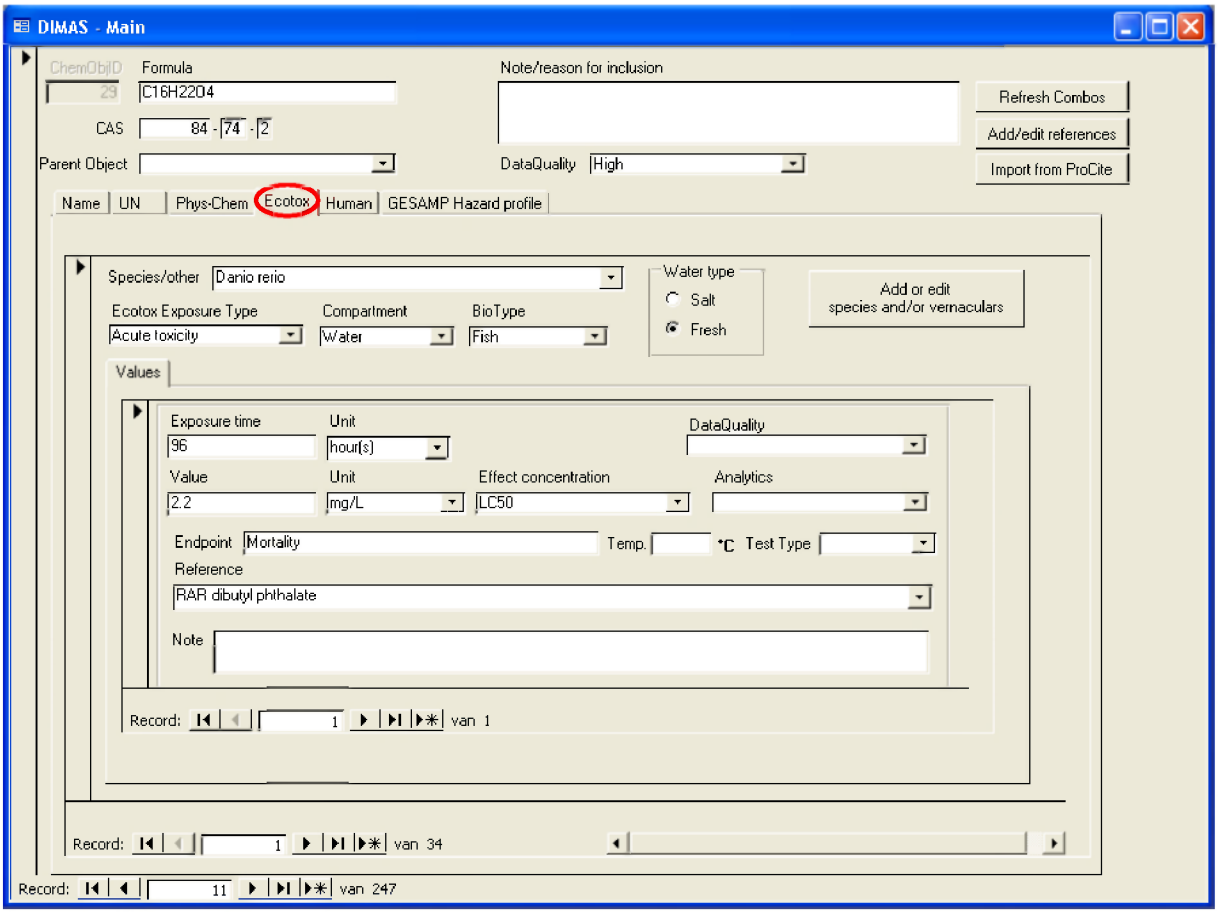


Figure 4.8: 'Ecotox' part of the GUI of the DIMAS database

4.1.6 Human

Human effects are entered in the database as risk and safety phrases. Several risk and safety phrases can be linked to one chemical compound. For every phrase, the following fields can be completed:

- Risk/Safety Phrase. In this field, the code for the risk/safety phrase should be selected from a drop-down menu with all risk/safety phrases.
- Effect. The effect linked to the risk/safety phrase selected in the previous field will automatically appear in this field.
- Reference. This field contains a drop-down menu with a predefined list of all the references used for the database. If a new reference should be added to this list, this can be done by clicking the 'Add/edit references' button in the main module of the DIMAS GUI. The 'Reference' window will then appear (see Figure 4.5), where new references can be added.

The completed 'Human' part of the GUI for the compound dibutyl phthalate is shown in Figure 4.9.

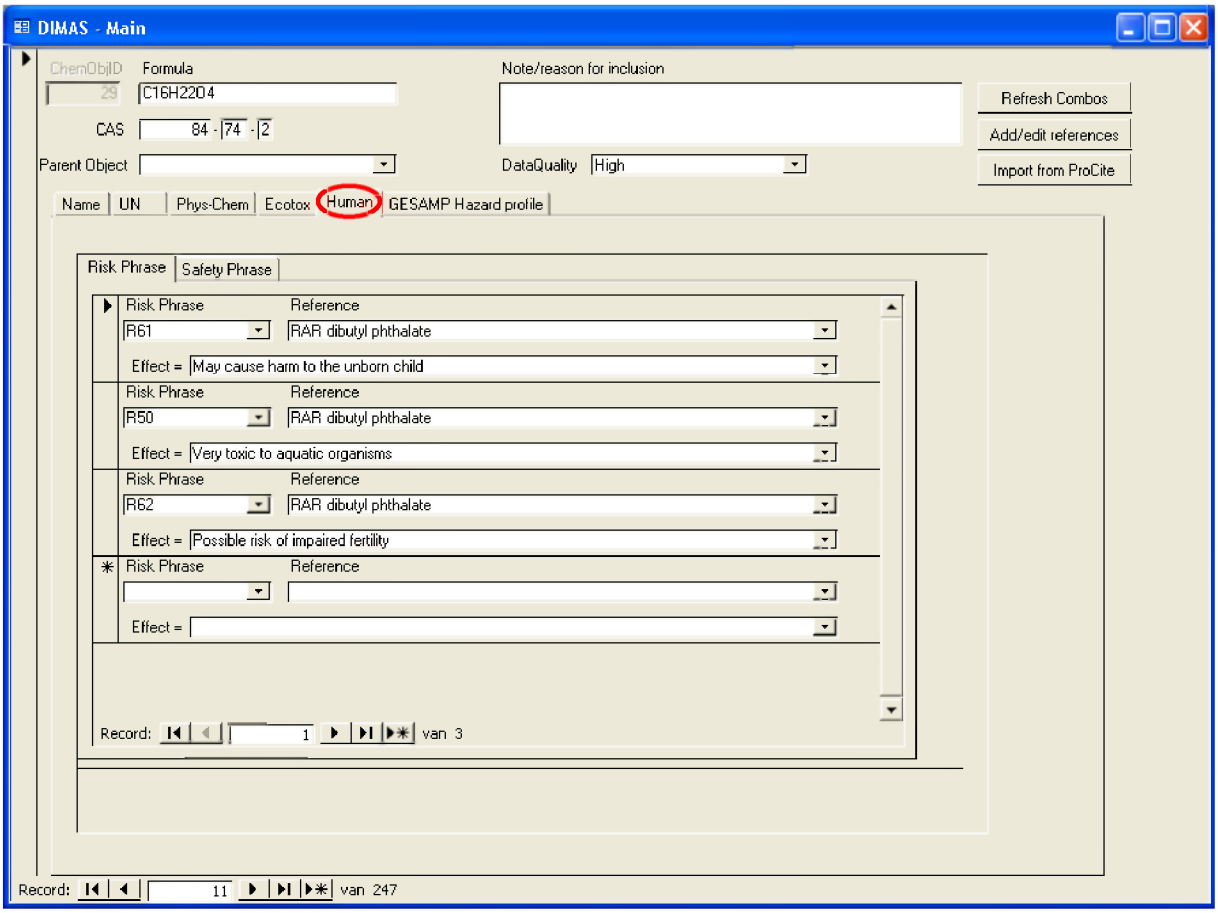


Figure 4.9: 'Human' part of the GUI of the DIMAS database

4.1.7 GESAMP Hazard profile

The GESAMP Hazard Profiles were imported in the database as obtained from the International Maritime Organisation (IMO). The completed 'GESAMP Hazard profile' part of the GUI for the compound dibutyl phthalate is shown in Figure 4.10. The legend for the GESAMP codes is shown in Table 2.1 on p.26.

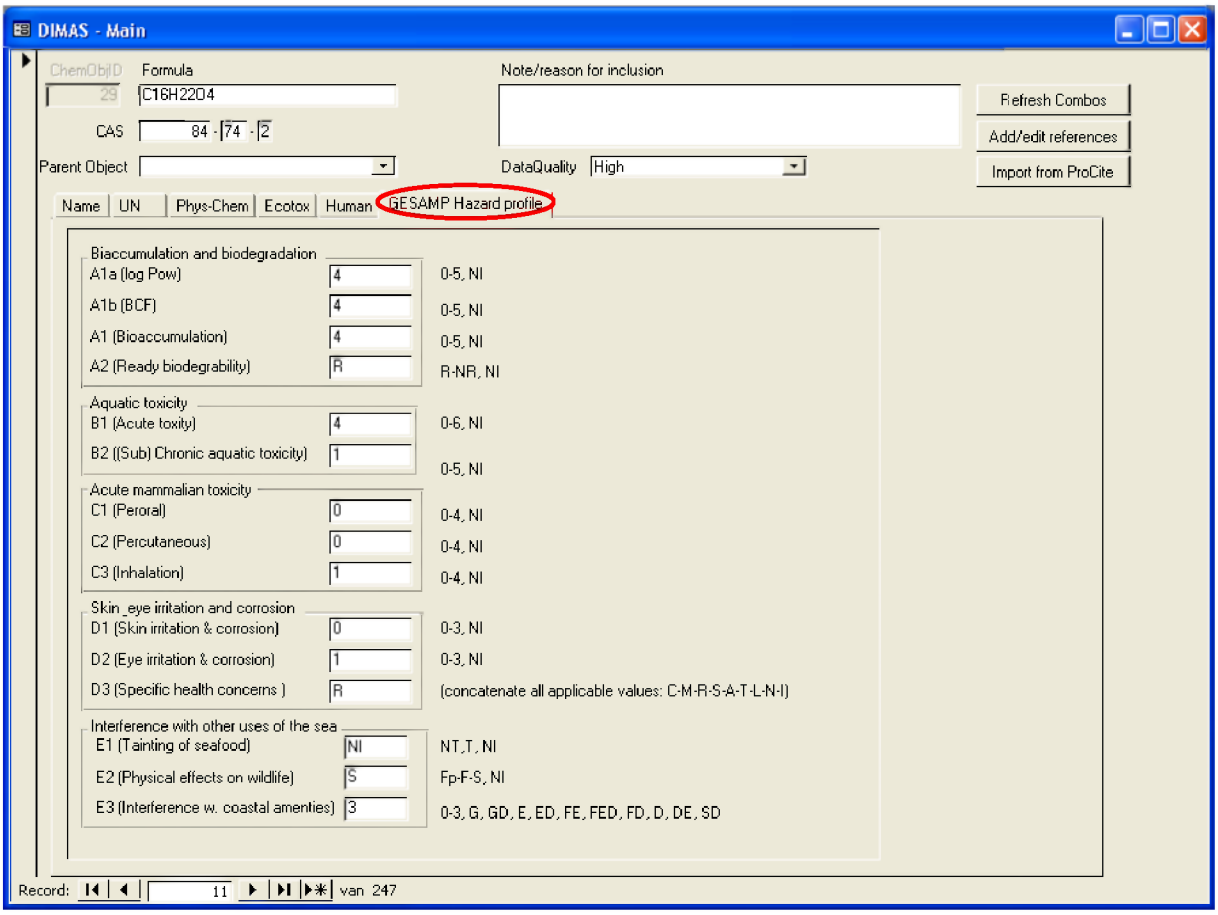


Figure 4.10: 'GESAMP Hazard profile' part of the GUI of the DIMAS database

4.2 DATA MODELLING

When all substances were entered, the DIMAS database was converted back from a local MS Access version to a multi-user MSSQL version, so the database could be consulted online. The necessary PHP and SQL scripts were written to perform the modelling tasks described in 4.2.2 and 4.2.1. These scripts were set up in such a way that the user could select a parameter and then on the fly generate the outcome of the model. This outcome can be text-based or graphic-based.

4.2.1 Exposure modelling

Based on the amount of the compound spilled and the physico-chemical properties of the compound, the compound concentration in different compartments after an accidental spill can be estimated (exposure modelling).

Exposure was estimated by environmental partitioning modelling. It is very important to estimate which of the compartments (water, sediment, air, biota or soil) is most affected by a chemical spill. This can be done by modelling the behaviour of the compound in the environment. For this purpose, the approach developed by Mackay et al. (1996a, 1996b, 1996c) was integrated in the DIMAS database.

Mackay et al. (1996a, 1996b, 1996c) describe a multimedia equilibrium criterion model (fugacity model), which can be used to evaluate the environmental fate of a variety of chemicals. The model treats chemicals that fall into three categories. In the first the chemicals may partition into all environmental media, in the second they are involatile, and in the third they are insoluble in water.

The model consists of level I, II, and III calculations. By sequentially doing level I, II and III calculations, increasing information is obtained about the chemical's partitioning, its susceptibility to transformation and transport, and the environmental process and the chemical characteristics that most influence chemical fate. Level I estimates the equilibrium partitioning of a quantity of organic chemical between the homogeneous environmental media with defined volumes, densities, organic carbon contents, and lipid fraction. There are no in- or out-flows of chemical, and no degrading reactions occur. Level II is similar to the Level I described above, but is a steady state model with a constant input rate, rather than single dose of chemical. There is both advective in- and out-flow of chemical from the unit world. Chemical losses can also occur through degrading reactions. Level III does not assume an equilibrium state, but only steady state. The program uses conventional expressions and typical parameters for intermedia transfer by processes such as wet deposition from the air, sediment deposition in the water, and soil runoff. However, for the DIMAS database, only level I calculations are performed as these require the least input information. Output data give a picture of the chemical's fate in an evaluative or generic environment. For DIMAS, the standard environment was adapted to a marine-specific environment, by virtually eliminating the soil compartment. The volumetric environmental compartment parameters of the Mackay model were adjusted as described below:

- Air: 10×10^{11}
- Aerosol: 2
- Water: 2×10^{8}
- Suspended particles: 1,000
- Fish: 200
- Soil: 9×10^{-9}
- Sediment: 1×10^{5}

For the other environmental properties (densities, fish lipid fractions, organic carbon contents) default values were used.

For each of the compounds in the database, environmental partitioning can be modelled if enough physico-chemical parameters are available (molecular weight, water solubility, vapour pressure, melting point, log K_{ow}). On the DIMAS website, the environmental partitioning can be modelled for all the compounds in the drop-down list by entering the amount of chemical spilled (see Figure 4.11).

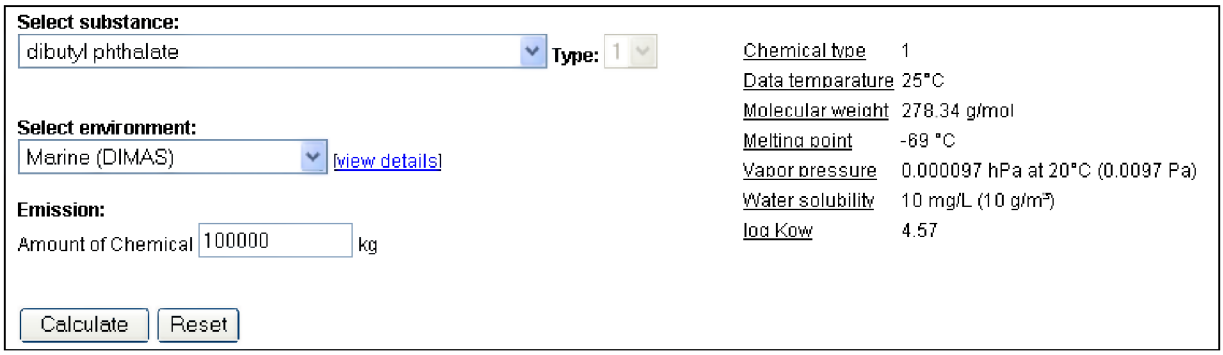
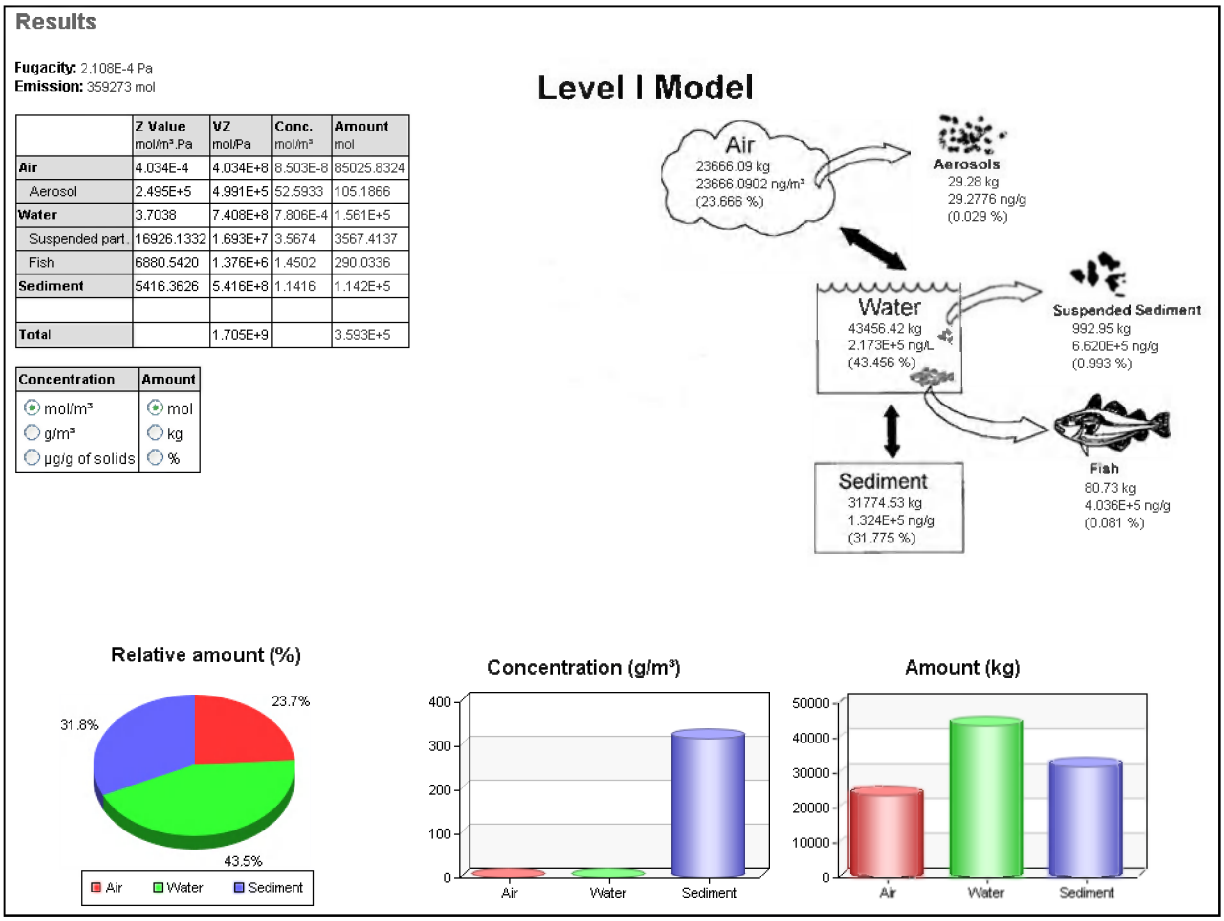


Figure 4.11: Input for environmental fate modelling on the DIMAS website

The output of the environmental fate modelling is a partitioning of the compound between air, aerosols, water, sediment, suspended sediments, and biota (fish). The exposure modelling as calculated on the DIMAS website for 100,000 kg of the compound dibutyl phthalate is shown in Figure 4.12.



	Z Value mol/m³.Pa	VZ mol/Pa	Conc. mol/m³	Amount mol
Air	4.034E-4	4.034E+8	8.503E-8	85025.8324
Aerosol	2.495E+5	4.991E+5	52.5933	105.1866
Water	3.7038	7.408E+8	7.806E-4	1.561E+5
Suspended part	16926.1332	1.693E+7	3.5674	3567.4137
Fish	6880.5420	1.376E+6	1.4502	290.0336
Sediment	5416.3626	5.416E+8	1.1416	1.142E+5
Total		1.705E+9		3.593E+5

Concentration	Amount
mol/m³	mol
g/m³	kg
µg/g of solids	%

Figure 4.12: Output for environmental fate modelling on the DIMAS website

4.2.2 Effect modelling and risk characterization

To facilitate interpretation of the toxicity data, all relevant effect data for a given compound are modelled and visualized in PAF curves (Potentially Affected Fraction) or compiled in a Predicted No Effect Concentration (PNEC).

The PAF concept is based on the combination of species sensitivity distributions (SSD) with site specific exposure concentrations to quantify the potentially affected fraction (PAF) of the species in the environmental compartment of concern. In an SSD, de LC_{50}/EC_{50} values (for acute data) or the NOECs/LOECs (for chronic data) for different species are plotted in a probabilistic way.

The concept was originally developed by the RIVM and the main advantage is that the ecological risk at all levels of contamination can be expressed on the same scale (i.e. from 0% to 100%). Other benefits are that this approach can be automated (which is an advantage if the database is updated), that it can be used for acute as well as for chronic data and that it is easy to interpret.

An example of the application of the PAF concept for risk characterization is given in Figure 4.13. The different PECs (predicted environmental concentrations) are represented in an exposure concentration distribution (ECD), the effects on different species in the SSD. Both curves are compared and the PAF is derived. E.g. for location A, a toxicant concentration that affects 70% of the species is found.

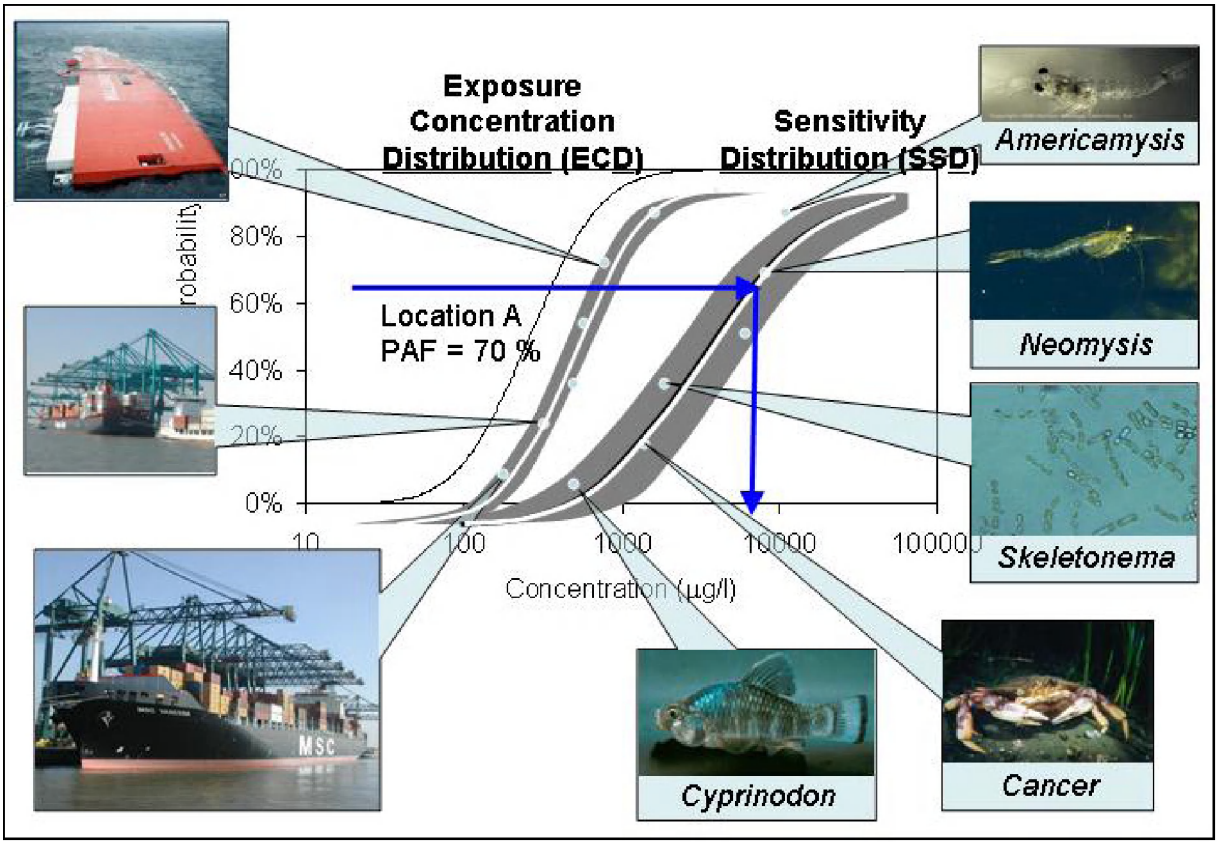


Figure 4.13: Example of the application of the PAF concept for risk characterization

An example of a PAF curve as generated on the DIMAS website is given in Figure 4.14. The cumulative number of species (%) is plotted against the endpoint (LC_{50}, NOEC) and a curve is fitted to the datapoints. This curve allows an estimate of the % species that would be affected at a certain (estimated) environmental concentration and can be calculated for acute and chronic data.

For the PAF curve fitting, a log-normal distribution was chosen. Numerous methods have been proposed for developing species sensitivity distributions (SSDs) and there is no consensus on the most appropriate method. One of the key aspects is the selection of an appropriate distribution model. Many users of SSDs simply employ a standard distribution such as the log-logistic and the log-normal distribution because these have been historically used. In selecting these functions statistical arguments

have been used more frequently than ecological arguments and log-normal distribution fitting is a well-balanced choice when numerous datasets (in casu the datasets of the DIMAS database) without a priori knowledge on the distribution have to be estimated.

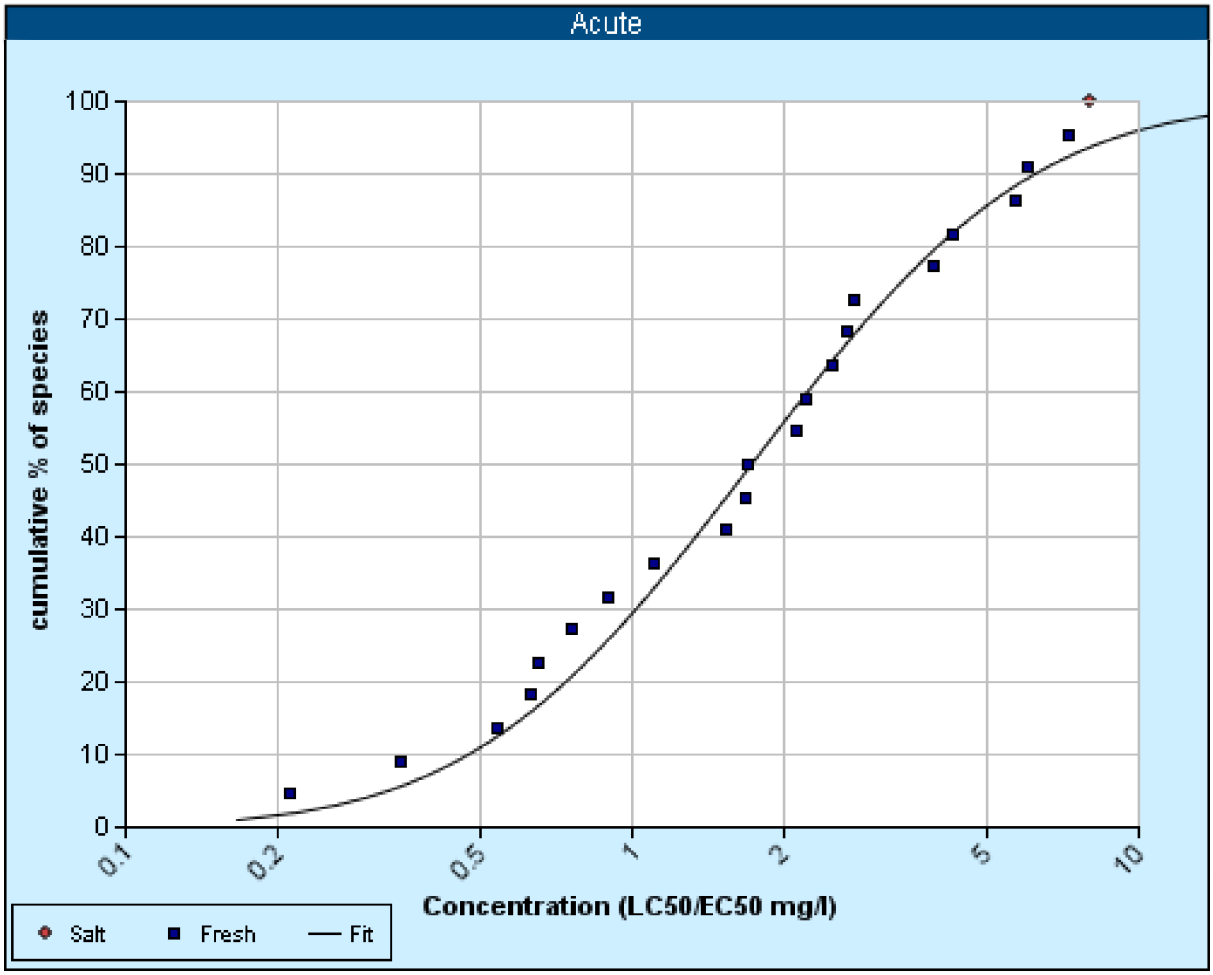


Figure 4.14: PAF curve for acute effects dibutyl phthalate (acute LC_{50} or EC_{50} plotted against the cumulative % of species)

PAF-curves allow characterizing the risk of an accidental spill when combined with the outcome of the exposure modelling. The impact is considered negligible when less than 5% of the species is affected (low risk). Attention has to be paid when 5-25% of the species are affected and there is a major risk when more than 25% of the species are affected. On the DIMAS website, the risk of a spill is represented with pictograms as showed in Figure 4.15.

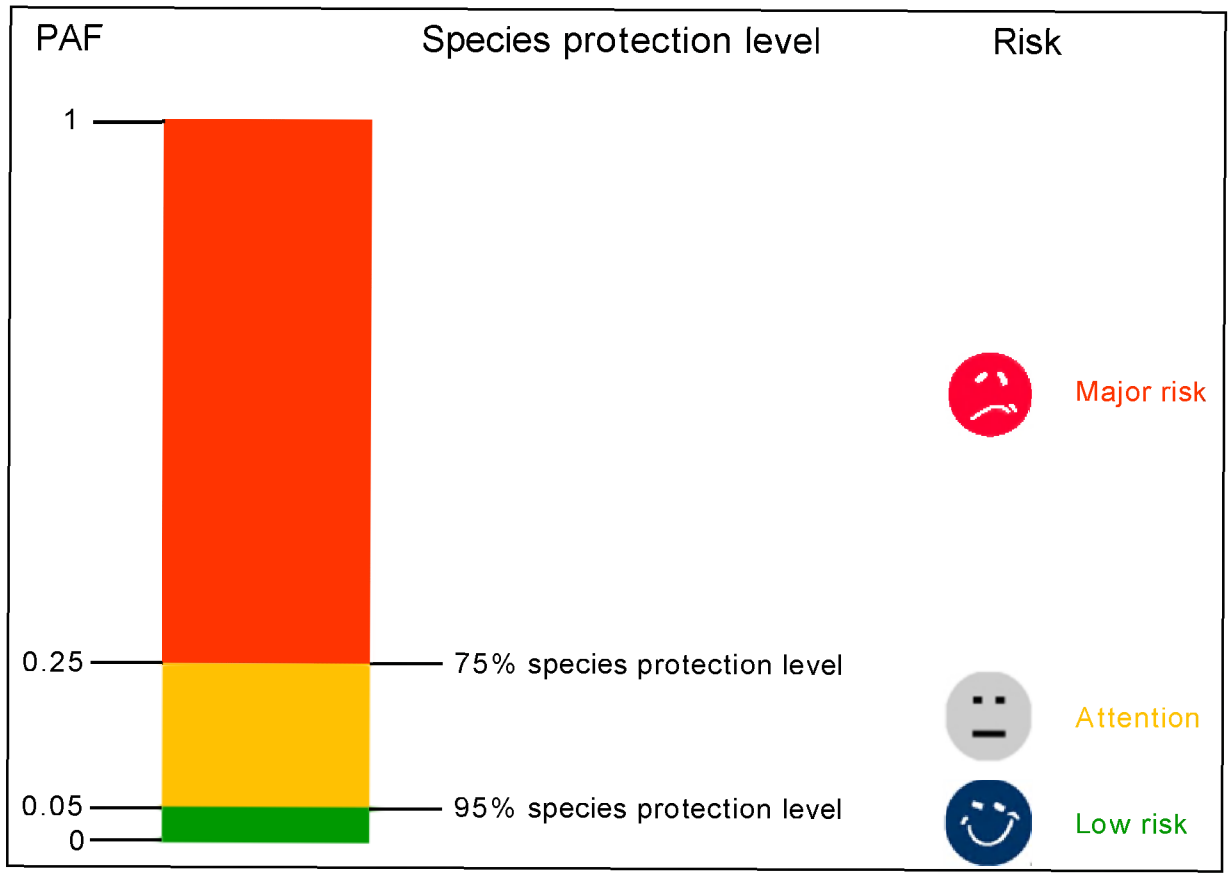


Figure 4.15: Risk characterization of an accidental spill based on the PAF-concept

5 DISSEMINATION

Active dissemination of the compiled information is of key importance for increasing public awareness and understanding by all stakeholders. This is done through a variety of means, e.g. by publication of reports and through the website and by presentation of the activities at scientific congresses and symposia, so as to permit interaction with other scientists active in the field (SETAC Europe 16th Annual Meeting 2006, International conference Marine Incidents Managements Cluster (MIMAC) 2006).

However, the true valorisation of the results consists in the use of the integrated and multi-disciplinary database embedded in a fully web-enabled searching graphical user interface (http://www.vliz.be/projects/dimas). Data accessibility has been improved by using standard formats simplifying data retrieval and use. As such the tool increases transparency and allows for rapid communication. Furthermore, the output compatibility with already existing impact models was taken into consideration.

The database is archived and maintained at VLIZ. Also, a datasheet for each substance is generated from the database, so end users could easily print one or more substance sheets. Furthermore, a CD-ROM version of the DIMAS database was made.

The hosting, maintenance and development of the database and the web application has been done at VLIZ. As VLIZ acts as a data centre for the DIMAS project, the following actions will be performed to preserve all data generated by the project:

- maintenance of the database and the web application;
- backup of the database, the website and the web application;
- archiving of the database, the Access interface and the CD-ROM.

In order to fulfil all these needs, a number of different servers are used by VLIZ. The master copy of the database is stored on a fileserver. This is in fact the newest Access interface with the newest data stored into it. When deploying the web application, a copy of these data is transferred to an SQL server. For a web application with multiple users, an SQL server is commonly used. Furthermore, a web server is used to host the web application and the website itself. The web application is completely written in PHP and has incorporated the models as described in the Data Modelling paragraph (cf. 4.2). Finally, another fileserver with much higher disk capacity then the first fileserver is used to archive the data, the Access interface and the CD-ROM. All these servers are backed up daily on a

backup server. This construction is setup in such a way that data-loss is almost impossible.

The CD-ROM of the DIMAS database is in fact an exact copy of the web application that is running on the VLIZ servers. Some interactive features have been removed, because these are not possible or too complex without a relational database.

The CD-ROM was created by generating all data from the database into static HTML or PDF pages, while the web application was built on dynamic PHP pages. On the CD-ROM the Access interface is also available for any expert to verify the data input, Note that data addition on this interface is not possible, since a CD-ROM is a read-only medium.

The advantage of this system is that all data can easily be printed or exported to PDF. An end-user could even take the CD-ROM with him/her and consult it when needed. The disadvantage of the CD-ROM is that all data is 'fixed', so before printing or consulting any data from the CD-ROM, one should always check the web application if possible and verify if the data are still up to date.

The first beneficiaries of the DIMAS database are the people directly involved in the first phase of a contingency plan for an accidental spill. As such, initial decision making will be facilitated, for example when concerning the level to which the organization should be alerted or mobilized, whether action is required etc. The final indirect beneficiaries are the general public (scientists, journalists, general public, etc.) who will be better informed about the potential impact to man and the environment and ultimately better protected.

6 MIMAC: INTEGRATION RAMA & DIMAS

6.1 INTRODUCTION

To keep the risk of unwanted incidents at sea as low as reasonably feasible and/or acceptable, appropriate measures, both technical and organizational, need to be defined and taken. However, such preventive and mitigating measures can only be taken on the basis of a sound analysis of the risks involved.

The MIMAC cluster aimed to integrate the results of two projects describing technical and organizational measures related to marine incident management, i.e. EV/36: Risk analysis of marine activities in the Belgian part of the North Sea (RAMA) and EV/41: Development of an integrated database for the management of accidental spills (DIMAS).

RAMA dealt with the analysis of the risks and hazards related to shipping, the potential impact of spills and the development of recommendations for improvement of existing contingency plans. DIMAS aimed at developing a database of priority contaminants relevant in case of marine accidents and spills, amendable for interpretation, providing reliable, easy to interpret and up-to-date information on marine specific issues. The most important parts of this database are the quality-assured direct and indirect effects on marine biota.

6.2 OBJECTIVES

The objectives of the cluster were:

1. to create a structure which will increase and optimize the already existing communication and interaction between the different partners in both projects;
2. to avoid duplication and overlap of efforts and data generation and integrate the results and data of both projects;
3. to increase the visibility, dissemination and exploitation of the results by international networking, improving participation of potential end users and integrating recommendations to policy makers;
4. to create added value both for the researchers as well as for the end users of both projects;
5. to minimize gaps in the knowledge by mutual exchange of specific information and data relevant for each others project;

6. to explore opportunities to combine the expertise of both project teams in further research projects.

6.3 RESULTS

6.3.1 More structured co-operation (objective 1, 3, 4)

A structured co-operation was attained through the organization of official and informal partner meetings. In these meetings focus lied on harmonization of data, methods and results as well as on the joint identification of knowledge gaps. This in its turn has lead to more efficient data gathering and increase in the width and relevance of both projects.

Overall, the official as well as the informal meetings were considered very useful by the different partners within the cluster:

- Both projects were clearly optimized in terms of avoiding overlap (e.g. sending out questions to the port authorities, environmental fate and distribution modelling, gathering effects data…).
- The interaction lead to a number of multi-disciplinary new concepts for knowledge gaps in the DIMAS and RAMA projects as well as for future project proposals (mainly in terms of database structure, fate and distribution modelling; see also part 3.3.4 Further research).
- An active exchange of data between Ecolas and EURAS has taken place. As indicated in Figure 6.1, data on transported cargo and the resulting list of relevant dangerous goods were needed by both projects.
    - Based on the shipping and cargo data gathered in the RAMA project, EURAS was able to make up a dangerous goods cargo list of relevant products transported in the Belgian Part of the North Sea. In the DIMAS project, an extended list of compounds was drawn based on physico-chemical properties, intrinsic (eco)toxicity, occurrence on priority lists. From this extended list, the final list with compounds to be fully evaluated in the DIMAS project was made, based on for instance intrinsic properties and – more importantly – on transported quantities. The frequency and quantity of transportation over the North Sea was obtained from the RAMA project and checked with data from the harbour of Ghent.
    - Ecolas in its turn used the ecotoxicological knowledge of EURAS for its effect analysis. Three incident scenarios were selected for the effect

analysis and the ecotoxicological data of the dangerous cargo used in these scenarios were delivered by EURAS. In this way, the quality assurance of the ecotoxicological data will be integrated in the impact analysis of potential spills. Further, the scenario development and choice of marine distribution model parameters in the RAMA project was performed after an informal meeting of EURAS, Ecolas and BMM where possible options and realistic scenarios were thoroughly discussed.

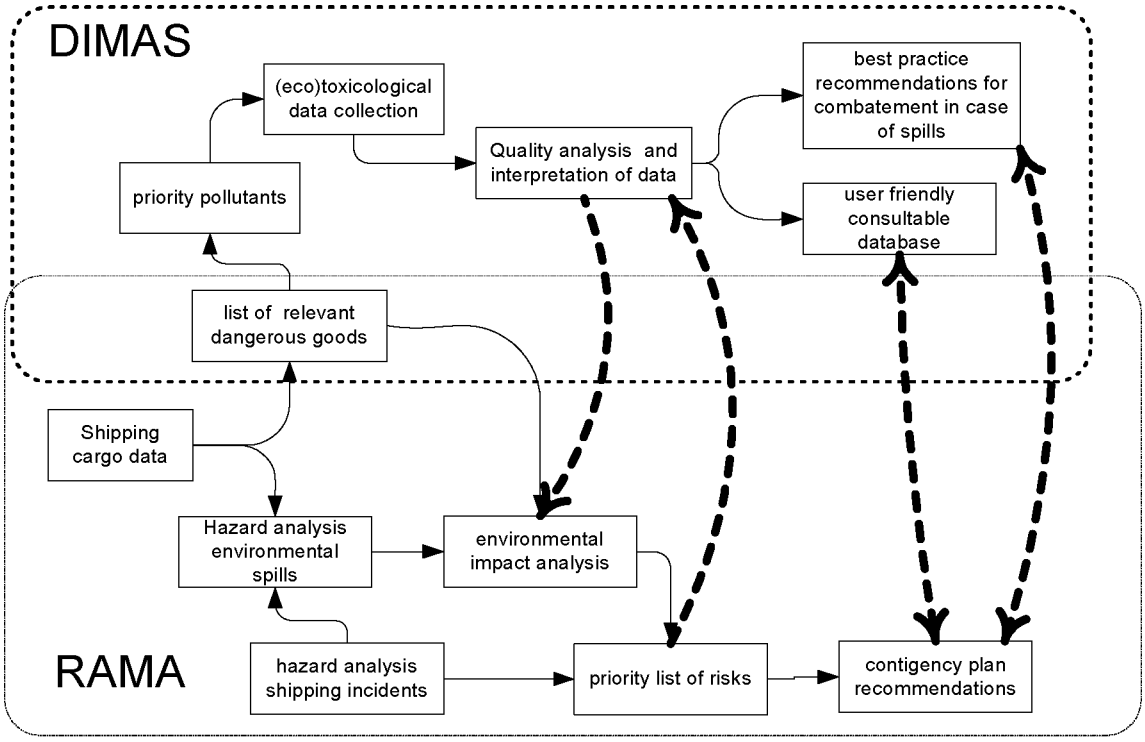


Figure 6.1: Overview of the clustered project (MIMAC) with mutual relationships

6.3.2 Integration of results (objective 2)

The integration of results of both projects resulted in a policy oriented integrated report (Volckaert et al. 2006). This report aims at policy end users, combines the relevant results and reports in an understandable language. The cluster also aimed at improving the visibility, dissemination and exploitation of the results of both projects by organizing a joint end-user meeting, the creation of a cluster website and the organization of an international symposium. During the partner meetings, it became clear that also a clear communication on terminology between RAMA and DIMAS was necessary to optimize the integration of the two projects. Therefore, the terminology was made uniform and easy to interpret (e.g. on the website).

Important with respect to policy, is that both the results of RAMA and DIMAS as well as the outcome of the MIMAC symposium are ready to be used in contingency planning. Currently there are some new developments regarding preparedness and response planning related to spills at sea (organisational, operational, administrative). This provides an excellent opportunity to pick up and integrate some of the results and recommendations put forth by both RAMA and DIMAS. The risk analysis of RAMA forms a basis for the evaluation of the degree of preparedness (products, equipment, response) while the database developed within the DIMAS project forms an operational tool that can be used during pollution combating operations at sea.

6.3.3 Knowledge gaps (objective 5)

A number of knowledge gaps were identified and filled in both projects:

- RAMA:
  - data on ecotoxicity for the selected substances in RAMA were not readily available;
  - data on fate of chemicals were not available.
- DIMAS:
  - data on transport were very limited;
  - data on distribution of chemicals were not available.
- MIMAC: even after clustering the DIMAS and RAMA projects, some data gaps remained:
  - more information (modelling) is needed concerning fate and distribution of chemical spills on the North Sea; current modelling efforts are solely focussed on oil spills (see also 6.3.4);
  - for a number of substances, marine-specific ecotoxicity data are lacking so that extrapolations from freshwater data were needed.

Data gaps for the RAMA and DIMAS projects were filled as much as possible. Through the clustering this could be done without duplication of efforts. Data gaps that are still present are further discussed in 6.3.4.

6.3.4 Further research (objective 6)

A number of research options are suggested below.

- Ecotoxicological research to obtain ecotoxicity data based on marine species for the transported chemical compounds at the North Sea.
- Development of a new approach to assess environmental impact caused by oil and chemical spills. The methodologies for assessing environmental fate and distribution within DIMAS and RAMA are conservative and can supplement each other. A first attempt within RAMA (using the sediment transportation model) for estimating the spatial distribution of a hazardous and noxious substance (HNS) in water over time is novel, but somewhat limited as it assumes no breakdown of the chemical compound in the environment and does not take environmental distribution in the different compartments (air, water, soil, etc.) into account. The approach followed within DIMAS is also limited as only environmental distribution in a steady state environment, without breakdown, is taken into account. Therefore following suggestions can be made:
  - Development of adequate models for calculating the fate and distribution of chemical spills in the marine environment (ideally also taking into account biotic and abiotic breakdown of the product). Currently such models are not available or routinely used in Belgium (and neighbouring countries). This is in contrast to oil spills, where good models are used to evaluate marine pollution.
  - The integration of the approaches of both the RAMA and DIMAS project can form the basis of this new model (Figure 6.2):
    - a Mackay-like distribution of the compound in the environment (DIMAS) followed by
    - a spatial distribution in time (RAMA approach).
  - Refinement of both of these approaches is however necessary to come to an operational and policy relevant tool.

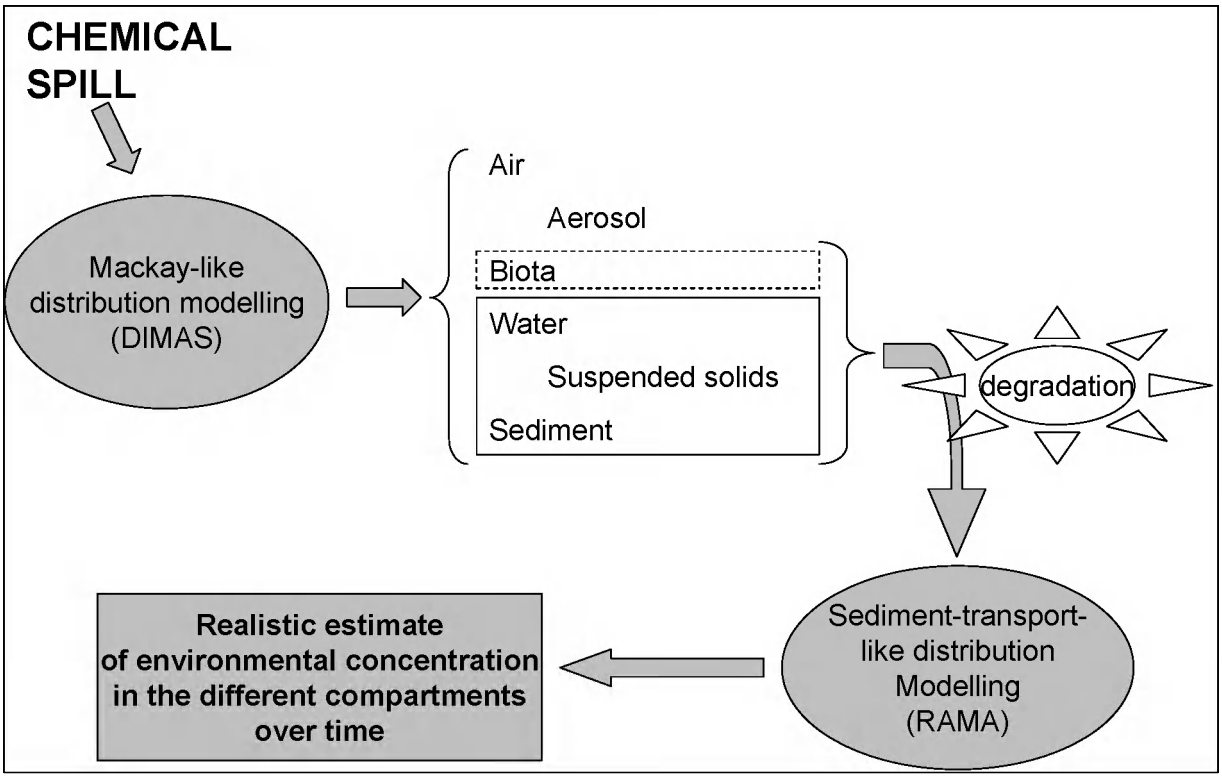


Figure 6.2: Schematized approach for a realistic environmental fate and distribution modeling in the case of an accidental spill

6.4 CONCLUSION

Clustering RAMA and DIMAS was considered to be very successful:

- The integration and bilateral adjustment of methods and data led to more efficient data gathering and increased the width and relevance of both projects by integrating each others experience.
- End users of one project got acquainted with the results of the other project. They also gave valuable advice for the exploitation of the results by other potential end-users (e.g. data from Ghent harbour that was obtained in the DIMAS project was cross-checked with transport data from the RAMA project; distribution modelling from the RAMA project was used as a starting point for developing an environmental fate and distribution model in DIMAS).
- Expertise in both projects was complimentary and this cluster brought together experts in environmental law (RAMA), environmental policy (RAMA), impact assessment (RAMA / DIMAS), risk analysis (RAMA & DIMAS), ecotoxicology and toxicology (DIMAS & RAMA), contingency planning (RAMA), database management (DIMAS). This has lead amongst other to a number of future research options that are considered crucial in spill management/contingency planning, as discussed for instance in 6.3.4.

7 BOTTLENECKS AND FUTURE RESEARCH

A number of bottlenecks/shortcomings were identified within this project.

- Marine ecotoxicological data turned out to be scarce for most substances in the database. Therefore, it was decided to use freshwater data for read-across where appropriate.
- The high number of freshwater data did not allow a detailed quality screening within the framework of the current project. Therefore, quality screening for freshwater studies was more limited than for the saltwater studies.
- For a number of compounds, no ecotoxicological data were found while for other compounds a very high number of datapoints was found (e.g. dibutylphthalate:> 70 high quality datapoints).
- Due to the high number of data for some compounds and the required time to qualify and input data, it was impossible within the framework of this project to enter all substances from the final list into the DIMAS database. However, 250 reviewed compounds are already in the database and the design of the database and the graphical user interface makes it easily possible to update the database with other substances and new datapoints in the future.

A number of future research options are suggested below.

- Ecotoxicological research to obtain ecotoxicity data based on marine species for the transported chemical compounds at the North Sea. With REACH coming into force from July 2007 our knowledge on substances produced in volumes > 1 tonnes will also increase and will be useful in this regard.
- Development of a new approach to assess environmental impact caused by oil and chemical spills (cf. 6.3.4).

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