MonitoringBase Surfactants

Overview and Users' manual

Version 1.0

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Report number

February 11, 2008

This report was commissioned by:

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1. Introduction

Over the last 20 – 30 years, a considerable amount of resources have been spent by the detergent industries (AISE/CESIO), as well as governments and other parties, on the monitoring of surfactant concentrations in various environmental matrices. Recently, the development by CEFIC-LRI of a user-friendly database ((Leslie et al., 2004; MonitoringBase, 2004).) to store metadata and actual measurements of chemicals in the environment has provided a cost-effective opportunity for ERASM to inventorise and centralise field measurements of surfactants. This will now enable ERASM to create a legacy of its work for future product defence as well as demonstrating leadership of the detergent industry in providing information to external stakeholders. A system is required for appraising the quality of data arising from surfactant monitoring studies for inputting into this database.

MonitoringBase, however, contained only a limited number of data on a selected set of surfactants. The objective of the current study was therefore:

1. To develop a database (MonitoringBase Surfactants) to store measured environmental concentration data of surfactants.
2. To retrieve environmental data of anionic, non-ionic, cationic and amphoteric surfactants in the European environment (water, sediment, agricultural soil, biota, waste water and sludge) for the period 1970 to 2005, and to evaluate, score and load the data in MonitoringBase Surfactants.

In the next chapters an overview of the database is given including a manual how to us the database.

2. Technical aspects of MonitoringBase Surfactants

The database was created in Microsoft ®Access 2000 which enables all information to be managed from a single database file. The various types of monitoring programme and measured concentration data were entered into separate tables for each specific data type and stored. Relationships between the tables were defined so that the data could be retrieved and viewed in different ways by users with different queries (selected parameters). Reports of retrieved data were designed for export to Word documents, Excel worksheets or for printing directly.

A list of target substances was prepared in cooperation with ERASM to perform the search of information on measured concentration of surfactants in the environment. The list included four surfactant groups: anionics, non-ionics, cationics and amphoterics. The literature search was performed using the Web of Science and CAB databases, which contain references from peer-reviewed scientific journals dating back to 1945 and 1972, respectively. Several synonyms of the chemicals names combined with matrix names were used. In addition, much data was received from industry or ERASM. An overview of the studies in included in the database are listed in Annex I.

MonitoringBase Surfactants contains measured concentration data from planned, ongoing and completed monitoring, survey and laboratory studies for surfactants in the European environment. The database contains information from 36 studies, and over 2000 measured concentration data for 8 surfactant groups. No information was retrieved for betaines, amine oxides, and SPC. These surfactants are, therefore not included in the database.

3. Using the database

3.1 Installation

To install the database, insert the CD-ROM and copy the file [*MonitoringBase Surfactants*] and [*Users manual*] to your hard disk. The database has been created in Access 2000.

3.2 Operation

When the database has been loaded a title page with start menu (Figure 1) appears, which offers three options:

- *Measured concentrations*: Search for data on measured concentrations that are stored in MonitoringBase Surfactants.
- *Monitoring programmes*: Search for information on European monitoring programmes.
- *Other*: Users' manual

You can choice an option by clicking on the appropriate button. If you want to exit the database choose [*Exit database*].

Briefly, by clicking on one of the buttons of the menu a search screen appears. All search screens have the same lay-out (Figure 2), and contain three major boxes:

· Search: selection of search criteria

· Overview results: search results

· Output: retrieved data export

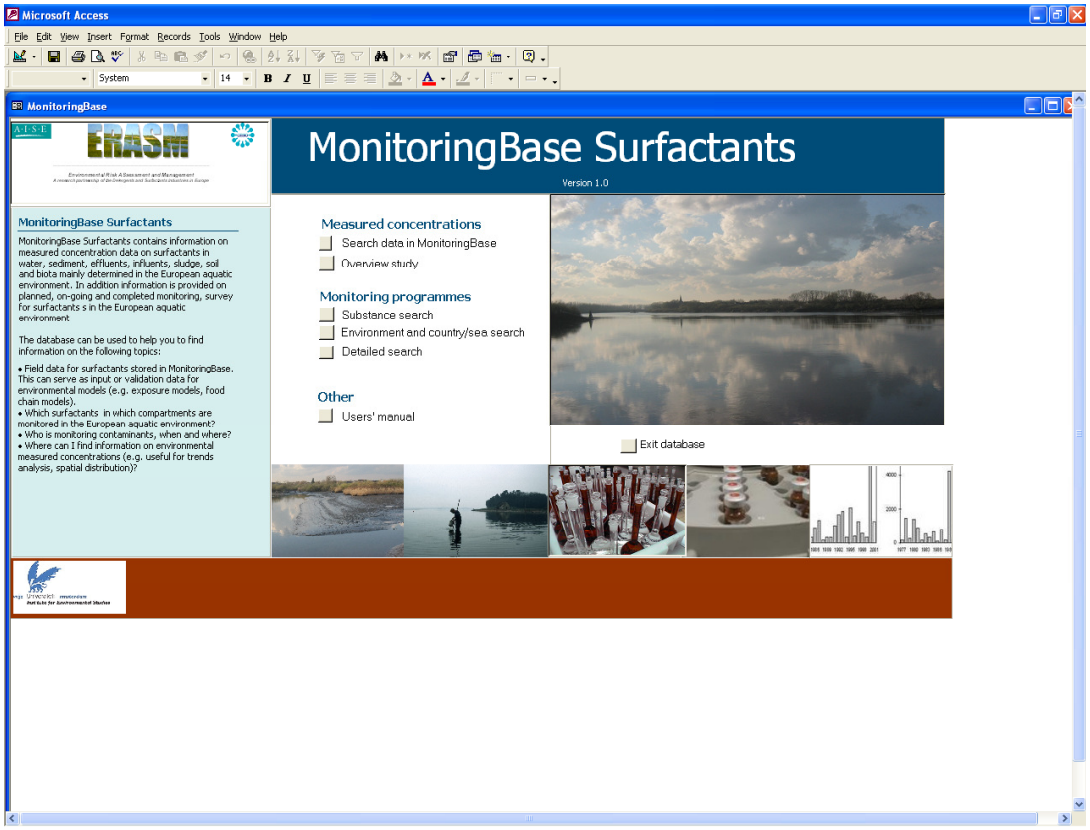

Figure 1: Title page and menu of MonitoringBase Surfactants.

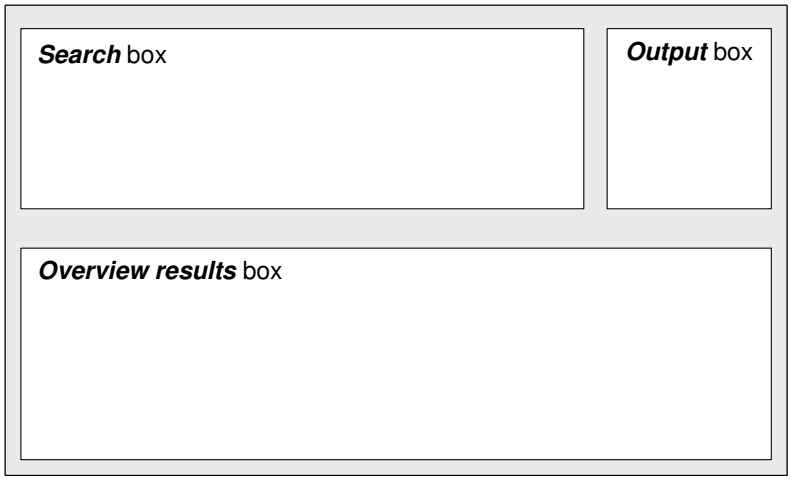

Figure 2: General lay-out of search screens.

The logical sequence for a search is as follows:

- Start with the selection of criteria for your search in the *Search* box (see paragraphs below for selection of search criteria).

- After selection of the criteria, run the search by clicking on the [*Search*] button.
- An overview of the main results is shown in the O*verview Results* box. This box is automatically updated after a search. Not all data available in the database is shown in the results box. To provide an overview of all data available for a specific study double-click on the specific cell of the ID or title column, or us the *Output* box.
- The *Output* box has an option to preview the results on screen, which can be printed, or the option to export and save the results as WORD or EXCEL.

3.2.1 Search Box

For some search criteria a multiple selection can be made. To perform a multiple selection, click on the drop-down menu of a search criteria and select an appropriate item, followed by the *Add* button. The selected item will appear on the list. If you want to add another item to the list, select the item from the drop-down menu and click the *Add* button. If you want to remove one item from the list, select the item on the list and click on the *Delete* button. If you want to remove all items from the list use the *Clear* button.

The results of a search on from a list of items will be an overview of all records in the database that contains one or more items from the list.

EXAMPLE:

Select [*Substance search*] after clicking on the “search data in MonitoringBase” button. Make a multiple selection for the compounds “alcohol ethoxylates (AE)”and ”alcohol ethoxysulfate (AES)” in the *Substance* multiple selection box. After running the search, thirteen programmes appear:

- Analysis of effluent samples for AE as part of ERASM monitoring study (phase I)
- Environmental monitoring for linear alkylbenzene sulfonate, alcohol ethoxylate, alcohol ethoxy sulfate, alcohol sulfate, and soap
- UK Monitoring study on the removal of LAS in trickling filter type STPs. GREAT-ER project #2
- etc.

3.2.2 Overview results box

Double-clicking on a specific cell of the *ID* or *Title* column will show all data of that specific study that is stored in the database (example of project *ID 198* in Figure 3), including general information on the study.

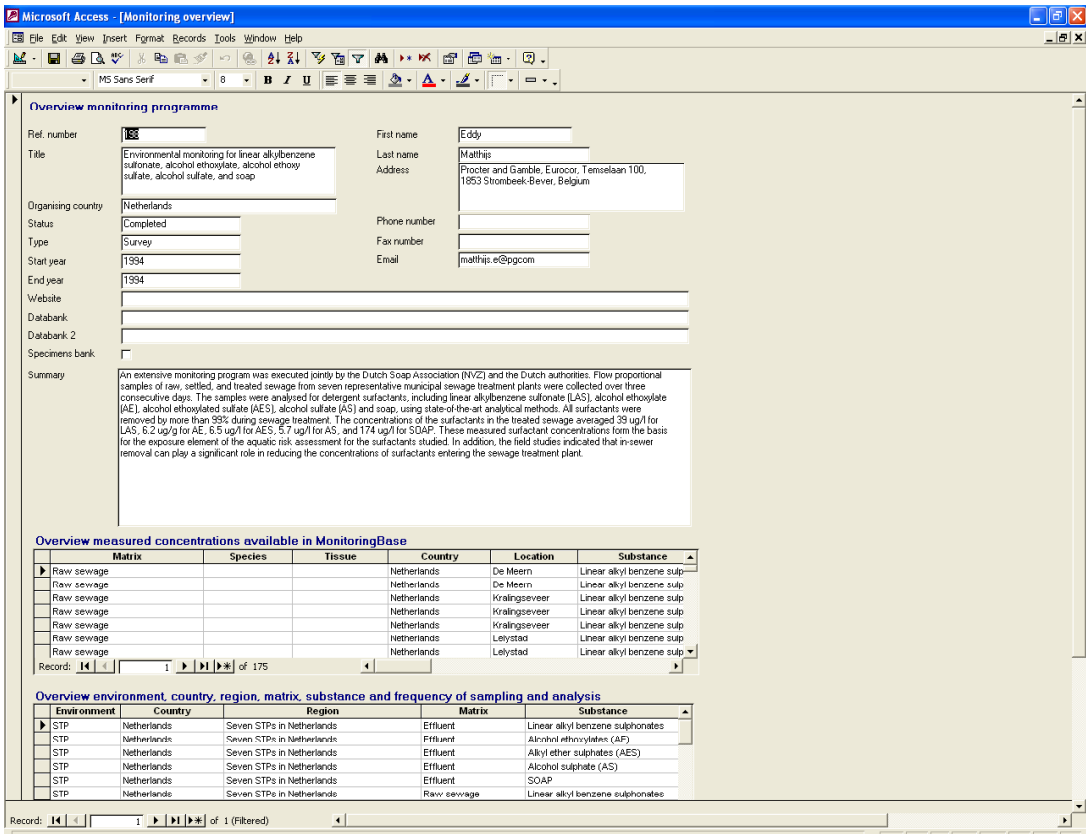

Figure 3: Overview of a study, after double-clicking on the ID or Title cell for a specific programme in the *Overview results* box.

The order of columns in the *Overview results* table can be adapted according to your own wishes. Click on top of the column and hold down your left mouse button. Drag the column to the position you want to move the column. The lay-out is automatically saved.

Sorting and filtering data in results box

If you want to sort data according to a specific parameter (column), click on top of the column, followed by a click on your right mouse button. A drop-down menu appears. Select *Sort Ascending* or *Sort Descending* to order the data, see Figure 4.

If you want to filter data from a specific column, click on a cell in the specific column (parameter), followed by a click on your right mouse button. Filter options will be available (e.g. filter by selection, filter for). If you want to filter for a specific word or data, put the word or data between * *. For example, if you want to filter for “Steenwijk” as STP in the Location column, put *steenwijk* in [*filter for:*].

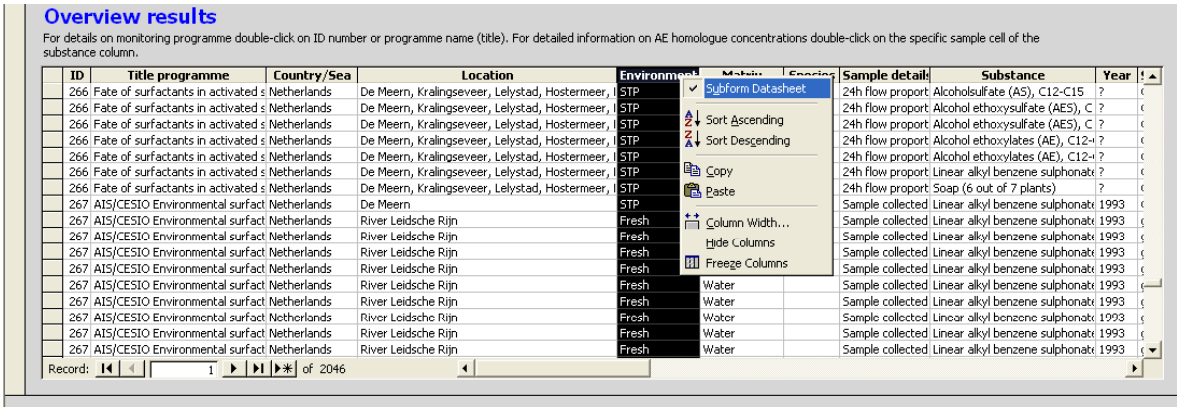

Figure 4: Sorting of data for a specific column in the overview results box.

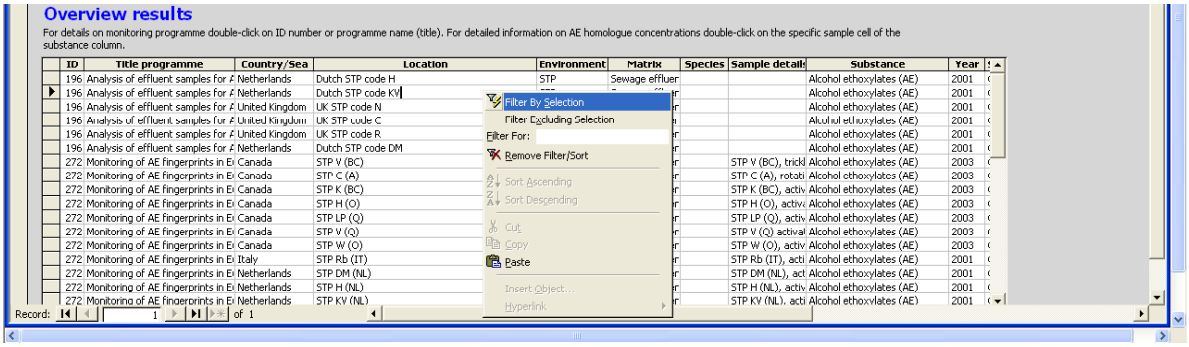

Figure 5: Filtering of data in a specific column in the overview results box.

Copying data

If you want to copy data to another Windows programme, mark the lines you want to copy by clicking on top of the rows or the columns followed by the general Microsoft Windows comments for copying.

3.2.3 Output box

After a search you can export data to various formats.

For a preview on screen select the button  from the *Output* box.

A hard copy will appear on the screen, which can be printed.

If you want to store your search results as a WORD or EXCEL file format select the WORD  button or the EXCEL  button.

To save data as Word file, select the Word file button, and select as output format "Rich text format', followed with OK. Provide a file name and save the report.

To save data as Excel file, select the Excel file button, and select as output format "Microsoft Excel', followed with OK. Provide a file name and save the report.

All reports will contain besides the information on e.g. project title, environment, and substance, also information on the contact person, address, phone/fax number and email address. This information is not shown in the *Overview Results* box.

3.3 Search for data in MonitoringBase Surfactants

1.4.1 "Search data in MonitoringBase"

To look for measured concentrations that is stored in MonitoringBase Surfactants click on [*MonitoringBase Surfactants*]. The following screen appears (Figure 6).

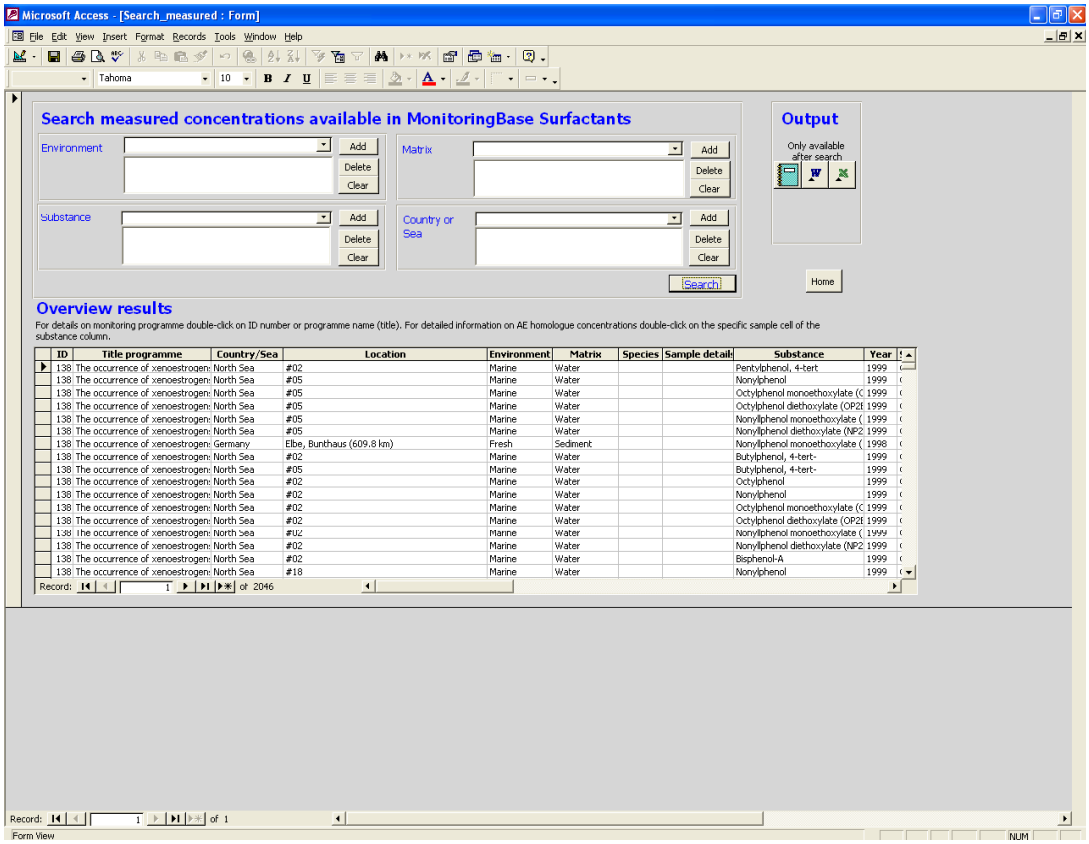

Figure 6: Search form measured concentrations stored in MonitoringBase Surfactants.

Selection of search criteria

The following criteria can be selected for this search:

- Environment
  - Fresh
  - Marine
  - Estuarine
  - Terrestrial
  - STP
- Substance (name of substance)
  - Alcohol ethoxylates (AE)
  - Alcohol sulphate (AS)
  - Alkyl ether sulphates (AES)
  - Alkylated phenols
  - DTDMAC
  - Linear alkyl benzene sulphonates (LAS)
  - Nonylphenols
  - Octylphenols
  - SOAP
- Country/Sea (country or sea where samples are taken)
- Matrix
  - Water

- Sediment
- Sewage influent
- Sewage effluent
- Raw sewage
- Settled sewage
- Aerobic sludge
- Anaerobic sludge
- Soil
- Biota
- Pore water
- Sludge

Overview results box

The *overview results* box for the measured concentrations stored in MonitoringBase Surfactants contains the following information:

- Title programme
- Environment
- Country/Sea
- Region
- Matrix
- Species
- Tissue
- Year
- Substance
- Measured concentration
- Unit
- Quality Scoring (see below or annex 1 for more details)
- Remarks (remarks on the quality of scoring and on the study)
- Sample type (single, composite, pooled)
- Data type (raw, mean, median, range)
- N (number of analysed samples)
- Lipid weight (%)
- Dry weight (%)
- Reference (source of data)
- Author
- Title
- Journal

For scoring of the quality of the study the Klimisch et al. (1997) approach has been used. This approach is widely used by industry and regulators as the basis for assessing the quality of toxicological and ecotoxicological data on products. The approach has been adapted for the assessment of surfactant data (see Annex II). Four categories were derived: 1: Reliable without restriction; 2: Reliable with restriction, 3: Not reliable, 4: Not assignable.

Table 1. Assignment of monitoring studies to the standard Klimisch categories (1-4). More information can be found in Annex II.

Klimisch criteria	Score against the 6 key features of a satisfactory monitoring study	Examples of such studies
1 - reliable without restriction	5 - 6	LAS, AE and AS/AES monitoring studies carried out by ERASM and SDA as part of risk assessment exercises. Other monitoring studies carried out by national authorities (e.g. UK DoE or water authorities). Such studies include most, if not all, of the key aspects of a monitoring study (see Table 1). **Such studies address, as a minimum, the 3 essential key features of a monitoring study (see Table 1)**
2 - reliable with restriction	3 - 4	Includes studies or data from the literature or reports in which certain features of the study have been overlooked or not completely covered (e.g. lack of detailed protocol, recovery studies carried out at only one concentration). However, despite this, the study has sufficient features covered well for an assessor to consider the data to be scientifically acceptable. **Such studies address, as a minimum, the 3 essential key features of a monitoring study (see Table 1)**
3 - not reliable	0 - 2	Obvious and unacceptable problems associated with the study. **For example, one or more of the 3 essential aspects of a monitoring study have not been sufficiently covered such that there are serious doubts about the accuracy of the actual results.**
4 - not assignable	Insufficient details provided to rate the quality of the study.	This includes studies or data from the literature, which do not give sufficient experimental details and which are only listed in short abstracts or secondary literature (books, reviews).

3.4 Search for information on monitoring programmes

Another option of the database is to search for monitoring programmes.

Search criteria

To search for monitoring programmes three options are available. A search based on:

- Substance name [*Substance search*]
- Environment and/or country/sea [*Environment and country/sea search*]
- Project title, type, status, environment, substance, country/sea, matrix, and/or frequency [*Detailed search*]

Click on one of the buttons and a search form appears. An example for the detailed search screen is shown in Figure 6.

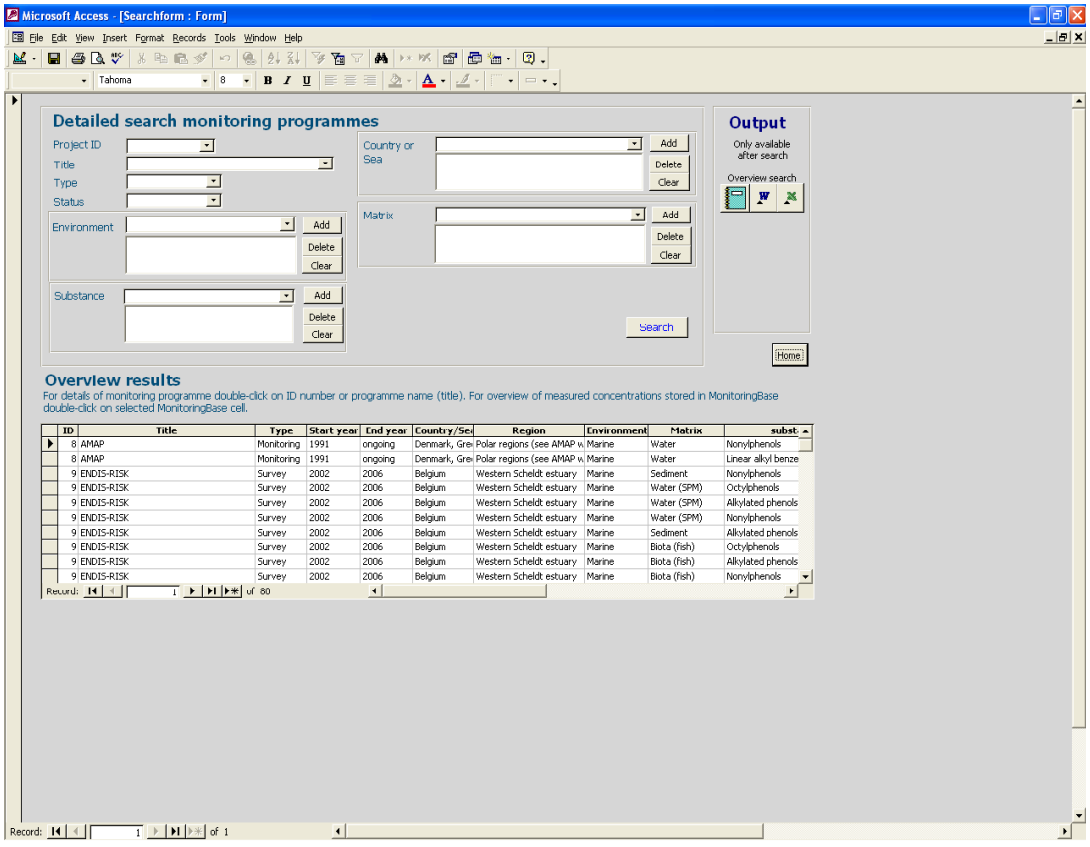

Figure 6: Detailed search screen for monitoring programmes.

The following criteria can be selected for a search:

- Project ID number (unique number of a project in MonitoringBase Surfactants)
- Project title
- Type
    - monitoring
    - survey
    - laboratory
- Status
    - planned
    - ongoing
    - completed
- Environment
    - Fresh
    - Marine
    - Estuarine
    - Terrestrial
    - STP
- Substance (name of substance)
- Country/Sea (country or sea where samples are taken)
- Matrix (ordered from general to more detailed information)
    - Water
    - Sediment
    - Sewage influent
    - Sewage effluent
    - Raw sewage
    - Settled sewage
    - Aerobic sludge
    - Anaerobic sludge
    - Soil
    - Biota
    - Pore water
    - Sludge
- Frequency (frequency of sampling)

Overview results box

The *overview results* box contains the following information:

- ID (unique number of a project in MonitoringBase Surfactants)
- Title
- Type
- Start year (start year of monitoring programme)
- End year (end year of monitoring programme)
- Environment
- Country/Sea (country or sea where samples are taken)
- Location (more detailed description of location/region where samples have been taken)
- Matrix (matrices which are monitoring)
- Substance (substance measured in monitoring programme)
- Website (Website link of homepage of monitoring programme)

- Data available in MonitoringBase Surfactants (if data of monitoring programme is stored in the *Measured Concentration* section of MonitoringBase Surfactants).
- Frequency (frequency of sampling)

4. References

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ANNEX I: Measured concentration data studies stored in MonitoringBase Surfactants.

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ANNEX II: "Application of 'Klimisch' criteria to evaluate the quality of data used in surfactant monitoring studies"

prepared by the ERASM 'MonitoringBase – Surfactants' Task Force
(Diederik Schowanek (P&G) – Project Leader, Andre Rottiers (P&G), Eddy Matthijs (P&G), Thorsten Wind (Henkel), Pim Leonards (VU, Amsterdam), Helmut Klotz (Clariant) and Charles Eadsforth (Shell)

1. Klimisch' methodology

The paper by Klimisch H.J., Andreae M. and Tillmann U., "A systematic approach for evaluating the quality of experimental toxicological and ecotoxicological data", Regulatory Toxicology and Pharmacology, 25, 1-5, 1997 is widely used by industry and regulators as the basis for assessing the quality of toxicological and ecotoxicological data on products.

4 categories/codes of reliability are used

Code	Category
1	Reliable without restriction
2	Reliable with restriction
3	Not reliable
4	Not assignable

In appraising toxicological and ecotoxicological studies, any tests conducted and reported according to internationally accepted test guidelines (e.g. EU, EPA, FDA, OECD) and in compliance with the principle of Good Laboratory Practice (GLP) is normally given the highest grade of reliability (Klimisch - code 1). Studies in which the test parameters documented do not totally comply with the specific testing guidelines but are sufficient to accept the data or in which investigations are described which cannot be subsumed under a testing guideline, but are nevertheless well documented and scientifically acceptable are graded of lower reliability (Klimisch - code 2). Data from these two categories, which are submitted on behalf of industry (e.g. individual companies or consortia) are routinely accepted by regulators.

Klimisch - code 3 - applies to studies, which for a number of reasons (e.g. unacceptable protocol, inappropriate test dosing, poor documentation, etc) are not sufficiently reliable enough to be accepted. The final code - 4 - is applied to studies or data from the literature, which do not give sufficient detail and cannot therefore be assigned to any of the previous categories.

2. Application of 'Klimisch' methodology to surfactant monitoring studies

It is proposed that a similar system be used for appraising the quality of data arising from surfactant monitoring studies that would be inputted into the MonitoringBase database. However, monitoring studies do not have any accepted test guidelines, nor are generated to GLP standards, so it is necessary to develop different selection criteria to monitoring studies that will still allow them to be rated as Klimisch codes 1-4.

In order to assign a monitoring study to one of the Klimisch codes, the main features of a successful monitoring study have been identified in Table 1. Six key features of a monitoring study have been identified which cover:-

(1) design and overall quality of the study

(2) sample collection

(3) sample storage, transportation and receipt

(4) sample preparation

(5) analytical detection

(6) performance of the method.

There are, however, three essential features in any monitoring study that need to have been confirmed before any study can be considered to be 'reliable', i.e. Klimisch criteria 1 and 2. Those are

- That it can be proved that the test substance has not degraded during the period between sampling and the start of sample preparation in the laboratory (e.g. by analysis of spiked field samples, by incorporation of suitable stabilising agent, previous test data that confirms the stability of the material over a period of time, or minimal time between sampling and analysis) - key feature 3

- That the analytical method is sufficiently sensitive and specific enough to measure the test substance of interest to the required limit of determination required for the monitoring study objectives and that there is minimal interference from other constituents in the sample – key feature 5.

- That the recovery of the test substance through the analytical method is sufficiently high (>70%) and repeatable to give confidence that the monitoring data are valid (e.g. by analysis of spiked samples through the analytical method ('recovery' samples)) – key feature 6.

A number of detailed criteria for evaluating each key feature are also included in Table 1 to assist in the evaluation of the quality of the monitoring study. These criteria may not necessarily apply in every case to the particular study under evaluation. For example, under 'Sample storage, transportation and receipt', the use of an appropriate stabilizing agent may not be required for an analyte that is stable under the actual field conditions or where there is analysis of samples directly in or close to the field operation. The evaluator must study the information and make a qualified judgment as to whether each key feature has been satisfactorily addressed in the monitoring study. Obviously, the more details that are documented in the monitoring study report, the easier it will be to evaluate whether the key features have been covered and thereby decide on the quality of the monitoring study.

Table 1. Six key features of a satisfactory monitoring study

No	Feature	Further criteria for evaluating whether a key feature has been properly covered in the monitoring study
1.	Design and overall quality of study	**Desirable to show that sufficient forethought has gone into the design of the monitoring study as well as data collection and retention. Includes:-** • Protocol with clearly defined objectives of the study, accurate locations for sampling (e.g. GIS coordinates), sampling/storage details and a validated analytical methodology to be applied to samples. • Raw data are archived and could be accessed by authorized person to check on the accuracy of data and calculations, if required. • Study has been carried out by an experienced group of workers with monitoring expertise. • Study has been audited internally (within company or group) and/or externally (Journal review).
2.	Sample collection	**Desirable to collect samples of suitable volume and to minimise the possibility of contamination. Additional samples (blank/spiked) will enable further checks to be made in the laboratory, if needed. Includes:-** • Use of appropriate containers for the study/analyte of interest. • Method of sampling and type of sample to be taken (composite or grab sample) is detailed. • Inclusion of 'blank' and 'spiked field' samples. • Care is taken to minimise the possibility of contamination. during sampling (e.g. prewashing of sample containers) • Sufficient sample is taken for analysis requirements

		and to avoid any sub-sampling.
3.	Sample storage, transportation and receipt	**Essential to prove that the test substance has not degraded during the period between sampling and the start of sample preparation in the laboratory. Includes:-** • Previous information on the stability of the analyte(s) of interest. • Use of appropriate stabilising agent to minimise sample deterioration. • Storage conditions in field/lab at suitable temperature to minimise sample deterioration. • Check on efficiency of preservation made (e.g. by analysis of 'spiked field' samples at laboratory). • Details of shipment and receipt ('chain of custody') are provided where appropriate.
4.	Sample preparation	**Desirable to minimise interference from other compounds in the analysis and thereby achieve a sufficiently low limit of determination for the analyte of interest. Includes:-** • Validated method for isolation of analyte of interest. • Isolation removes compounds likely to interfer in method. • Isolation achieves low limit of determination required.
5.	Analytical detection	**Essential that the analytical method is sufficiently sensitive and specific enough to measure the test substance of interest, without interference and to the required limit of determination. Includes:-** • Published/industry accepted and validated analytical method has been employed. • Preferably specific method (e.g. GC/MS, LC/MS). Non-specific methods can give rise to an overestimation of the level of the surfactant of interest due to the presence of structurally similar substances. • Allows quantification of all analytes of interest. • Little or no interference observed in the region of interest, confirmed by analysis of reagent blanks and field blanks. • Sufficiently low limit of determination with details of such parameters (e.g. LoD, LoQ, MDL).
6.	Performance of the method	**Essential that there is satisfactory recovery of the test substance to give confidence that the monitoring data are valid. Includes:-** • A set of recoveries for the analytes of interest have

		been carried out at different spiking levels to cover the likely monitoring concentrations. • Recovery data are >70% and with acceptable standard deviation. • Appropriate external standard has been used for recovery. • Internal standard, if appropriate, has been used in method.

Once the evaluator has made a qualified judgment as to which key features have been satisfactorily addressed in the monitoring study, it is then possible to assign the quality of the monitoring study and its data to the standard Klimisch codes (1-4) using the scoring system shown in Table 2. The details of the scoring and subsequent assignment of a monitoring study are summarized:-

- Any study must have the three essential key features (i.e. 3, 5 and 6) confirmed before it can be considered to be 'reliable', i.e. Klimisch codes 1 and 2. If any of these key features is not sufficiently addressed then the study is assigned Klimisch code 3 (not reliable).

- A monitoring study that has covered at least five and preferably six of these key features would be assigned to Klimisch code 1 – reliable without restriction. The essential features (key features 3,5 and 6) would all be covered as well as 2 or 3 of the desirable features (1,2 and 4).

- A monitoring study that has only covered three or four of these key features would be assigned to Klimisch code 2 – reliable with restriction. The essential features (key features 3,5 and 6) would all be covered as well as possibly one of the desirable features (1,2 and 4).

Table 2. Assignment of monitoring studies to the standard Klimisch categories (1-4)

Klimisch criteria	Score against the 6 key features of a satisfactory monitoring study	Examples of such studies

1 - reliable without restriction	5 - 6	LAS, AE and AS/AES monitoring studies carried out by ERASM and SDA as part of risk assessment exercises. Other monitoring studies carried out by national authorities (e.g. UK DoE or water authorities). Such studies include most, if not all, of the key aspects of a monitoring study (see Table 1). **Such studies address, as a minimum, the 3 essential key features of a monitoring study (see Table 1)**
2 - reliable with restriction	3 - 4	Includes studies or data from the literature or reports in which certain features of the study have been overlooked or not completely covered (e.g. lack of detailed protocol, recovery studies carried out at only one concentration). However, despite this, the study has sufficient features covered well for an assessor to consider the data to be scientifically acceptable. **Such studies address, as a minimum, the 3 essential key features of a monitoring study (see Table 1)**
3 - not reliable	0 - 2	Obvious and unacceptable problems associated with the study. **For example, one or more of the 3 essential aspects of a monitoring study have not been sufficiently covered such that there are serious doubts about the accuracy of the actual results.**
4 - not assignable	Insufficient details provided to rate the quality of the study.	This includes studies or data from the literature, which do not give sufficient experimental details and which are only listed in short abstracts or secondary literature (books, reviews).