

ROYAL BELGIAN INSTITUTE OF NATURAL SCIENCES

MANAGEMENT UNIT OF THE NORTH SEA

MATHEMATICAL MODELS (MUMM)

SECTION 15 –

MARINE ECOSYSTEM MANAGEMENT

SINTEF MATERIALS AND CHEMISTRY





### NEBAJEX Pilot Project – Final Report

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Prepared for EC Grant Agreement Ref. SUB/01/326832 ("NEBAJEX")

March 2004

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### 1. Introduction – NEBA and the NEBAJEX project

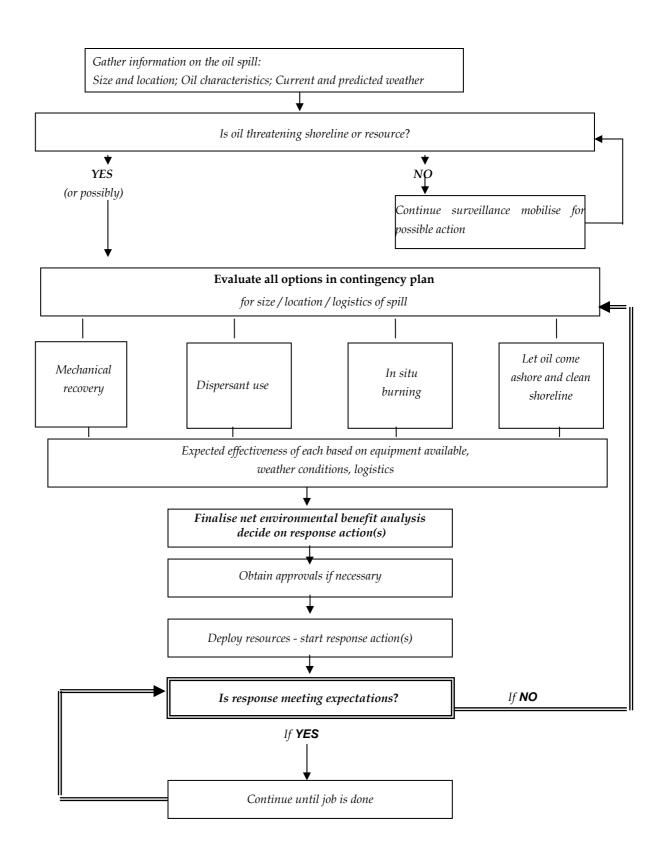
### 1.1. The concept of Net Environmental Benefit Analysis

Three European marine research institutes, MUMM, CEDRE and SINTEF, started in 2001 with a European pilot project called "Net Environmental Benefit Analysis Joint Exercise - NEBAJEX". The main goal of this two-year pilot project was to organize an oil pollution exercise at sea in order to carry out an effective monitoring in real time, and to develop a common monitoring approach, in support of a Net Environmental Benefit Analysis (NEBA) for oil pollution response at sea.

NEBA is an evaluation and decision-making concept for response to major oil spills that is accepted by governmental (e.g. IMO, 1995; Bonn Agreement, 1998) and non-governmental organizations (e.g. IPIECA, 2000; Purnell, 2002). Figure 1 schematically summarizes a NEBA evaluation and decision-making process as described in the Bonn Agreement Counter Pollution Manual (Bonn Agreement, 1998). NEBA can be defined as a means or method to determine the most appropriate response option(s) in order to minimize the overall environmental impact of an oil spill. It can also be described as a method of selecting the best oil spill response alternative through weighting of the advantages and disadvantages of the different response alternatives and of their expected net benefit towards, or net reduction of the overall environmental impact. The NEBAJEX project only deals with the application of NEBA for oil spill response at sea in the light of a (major) oil pollution incident.

Performing a rapid evaluation of the possible impact of an oil spill and taking a well-considered decision of the most appropriate response option according to NEBA is a complex task, especially in case of a major oil spill which is directly threatening sensitive resources. A high number of interacting factors can determine the global environmental impact of an oil pollution (based on O'Sullivan & Jacques, 1998):

- Factors describing the circumstances of the spill: quantity and type of oil spilled, location of the spill, type of spill event (catastrophic sudden release or slow
- **Serepage**) *influencing the spill behaviour*: environmental conditions (weather conditions during the incident, tides and currents, oceanographic factors), and pollution response measures.
- Factors determining the impact of the oil on marine organisms: presence of sensitive environmental resources in impacted/influenced area, seasonal factors (e.g. seasonal sensitivity of marine and coastal environment), duration of exposure, physico-chemical characteristics of the oil, hydrocarbon concentrations in water and sediment, degree of contamination of organisms and substrate, presence of other pollutants, prior exposure to oil, post spill environmental stresses.



<u>Figure 1</u>: Common NEBA evaluation and decision-making scheme (Bonn Agreement, 1998).

<u>Table 1</u>: Important oil pollution aspects to be taken into consideration in a NEBA decision-making process.

## A large variety of oil types transported over sea

- A wide variety of crude oils, transported as cargo on board oil
- Refixeral products, used as fuel or lubricating oil, transported on board all ships, ranging from very light, nonpersistent oils, to very persistent extra heavy fuel oils.
- The behaviour, impact and fate of oil spilt at sea will vary greatly, depending on the type of oil that is being spilt, the location of the spillage, and the environmental conditions.

## Ecological sensitivity of marine and coastal environment

- Sensitivity of marine and coastal natural resources and habitats to oil pollution.
- Depends on oil properties (toxic components, physical impact/clogging).
- Depends on abiotic factors: water depth, sediment/suspended particulate matter (SPM), hydrodynamic regime, different habi-
- Detaymets on ecological factors: specific sensitivity of marine organisms (seabird species, marine mammals, juvenile fish, marine bottom fauna or benthos, such as crustaceans and bivalves.
- Depends on seasonal factors: seasonal variation in sensitivity of an

#### Physico-chemical parameters of oil

- Chemical composition: mineral oil consists of a complex mixture of different hydrocarbon groups (saturates, aromatics, asphaltenes) and other components.
- Important physical properties are: viscosity, density, pour point, flash
- Directiveness of spilt oil will greatly influence the weathering processes, the overall environmental impact and the effectiveness of oil pollution combating techniques.
- Oil properties databases exist, e.g. at SINTEF, Environment Canada, or CEDRE, and are very useful for incident evaluations.

## Vulnerability of human activities, and of coastal communities

- Several human activities at sea or along the coast can be severely impacted by oil spills, such as fisheries or aquaculture.
- A major oil spill can directly lead to a significant impact on coastal communities, if they are depending on sensitive natural resources or the quality of the marine or coastal environment.

#### Weathering of oil

- Process of spreading, evaporation, dispersion, emulsification (forming of water-in-oil (w/o) emulsions), dissolution, photo-oxidation, biodegradation, sedimentation.
- The weathering of oil depends to a

## Pollution response – combating techniques

- Response at sea and along the coast
- Response at sea: availability, effectiveness and limitations of mechanical recovery, dispersants, and in situ burning.

large extent on its properties. A good knowledge of the oil properties leads to a better understanding and evaluation of the weathering of the oil.

- Mobilisation time of response equipment
- The chosen response option(s) should reduce the overall environmental impact of a spill, and not make it

worse.

From the above it is evident that counter pollution officers responsible for the evaluation a major marine oil pollution incident and/or have to take a NEBA decision on the appropriate response action, should have a good understanding of several important and interrelated aspects of marine oil pollution, or should have the possibility to call upon national professionals with the necessary expertise. Table 1 gives an overview of the oil pollution aspects. A lot of information on these aspects can be summarised and incorporated in contingency plans, such as lists and technical fiches of the available oil pollution combating equipment and ecological sensitivity maps, or vulnerable human uses. The overview in table 1 reflects the complexity of major marine oil spills, as well as the complexity of NEBA evaluation and decision-making, when trying to respond in the most appropriate way.

It is important to note that NEBA was first described as a method used for oil spill response planning (pre-spill analysis of different incident scenarios), thus as part of the overall contingency planning process. A good understanding, before a spill takes place, of overall environmental impact of major oil spills and the response possibilities to different oil types, will undoubtedly lead to a better and more complete NEBA evaluation in the light of a real oil pollution incident.

# 1.2. Towards a common NEBA evaluation and decision-making approach

### 1.2.1. Performing an initial, rapid NEBA evaluation

As soon as possible after notification of a pollution incident at sea, a first NEBA is to be performed, and a quick decision is taken on the most appropriate response option(s). This decision is based on:

- information gathered on the size and location of the oil spill, on the type of oil, and on the weather conditions;
- a first threat and overall environmental impact evaluation (see 1.2.2.);
- the weighting of the response options available in the contingency plan, on the basis of the expected effectiveness and the expected overall environmental impact reduction (see 1.2.3.).

### 1.2.2. Initial evaluation of the threat or impact of a marine oil spill

As soon as a coastal state is notified of an oil pollution incident, the competent authorities will immediately try to gather information on the oil spill and the environmental conditions (wind and sea state, current situation + predictions). Based on this information an initial NEBA is performed. A first step is to evaluate

the threat or probable overall environmental impact of the spill. The following questions need urgent answers:

- What are the expected drift, behaviour and fate of the spilled oil?
- *Is the oil threatening a sensitive resource?*
- How toxic is the oil?
- Can the oil spill be combated at sea?

An evaluation of the following **impact factors** should give an answer to these questions:

- oil quantity, type, composition and physico-chemical characteristics,
- oil behaviour: way of oil release/discharge and weathering processes,
- oil spill trajectory/drift,
- oil toxicity,
- ecological sensitivity of marine/coastal environment under threat,
- vulnerable human uses in the impact area,
- expected effectiveness of different pollution response option(s) in contingency plan, as well as expected impact reduction.

### This evaluation can be based upon:

- ecological sensitivity, that can usefully be summarized in ecological sensitivity maps of marine and coastal areas,
- oil characteristics and oil behaviour: some countries dispose of oil properties databases, with characterisation data on different oils (mostly crudes, but also refined products). Such databases are available for instance at SINTEF (Norway), Environment Canada (Canada), CEDRE (France). These oil properties databases enable a better evaluation of a spill, because several important parameters, such as viscosity, pour point, density, etc. or weathering processes (meso-scale flume tests of oils at CEDRE and SINTEF) can be used for modelling purposes and NEBA evaluations,
- information reported from a first aerial surveillance flight over the impacted area,
- assessment tools, such as oil spill trajectory models (MUMM + Météo France), or NEBA models such as 'OSCAR' (SINTEF).

# 1.2.3. Selecting the most appropriate response option(s) for marine pollution combating

In a contingency plan, the different options of pollution combating at sea can be mechanical recovery, dispersants, in situ burning or natural weathering. The advantages and disadvantages of each option have to be evaluated and weighted when performing a NEBA analysis. In case of a major oil spill at sea, past experience shows that the most important response option(s) are mechanical recovery and the use of dispersants.

**Mechanical recovery** is the best NEBA response alternative in theory, because the oil is taken away from the environment. However, mechanical recovery operations at sea can have serious limitations (cf. bad weather conditions, long ETA's, limited storage capacity).

The **use of dispersants** can be a valuable NEBA alternative that can lead to a reduction in the overall environmental impact. Nowadays, it is common practice to use modern dispersants in deeper, offshore waters. In coastal and shallow waters the products could also be used, but the impact is not well understood yet, so the potential risks and effects of dispersant should be carefully evaluated. Dispersants break up the oil slicks and enhance natural dispersion. By applying dispersants, the oil is shifted from the sea surface to the water column. This changes the fate and impact of the oil. The use of dispersants always leads to a *trade-off* between areas, e.g. choosing between an impacted water column offshore or an impact in shallow coastal waters and coastline. The most important questions for weighting the mechanical recovery options against the dispersant option are summarized in <u>Table 2</u>. Generally speaking, dispersants can reduce the overall environmental impact of an oil spill if they are applied in deeper waters (where sufficient dilution can take place) at a reasonable distance from sensitive coastal areas.

<u>Table 2</u>: Questions to be answered in NEBA when weighting the 'mechanical recovery' versus 'dispersant' options.

Examples of questions related to mechanical recovery	Examples of questions related to the use of dispersants
<ul> <li>How effective is mechanical recovery likely to be, from a technical/operational point of view?</li> <li>Will the equipment arrive on time (ETA)?</li> <li>Will the recovery means be sufficient to reduce the expected overall environmental impact?</li> </ul>	<ul> <li>Can chemical dispersion reduce the overall environmental impact?</li> <li>How effective is the dispersant application likely to be?</li> <li>Will the dispersed oil be diluted to low impact levels?</li> <li>What is the fate of the dispersed oil?</li> <li>Will sensitive habitats be impacted, and if yes, what is their estimated time scale for recovery?</li> <li>Will the response time of dispersants be shorter than the time window for their effective use?</li> </ul>

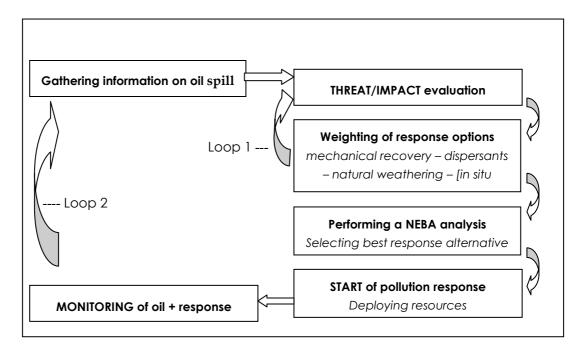
The option of **natural weathering** is only considered reasonable for major spills in case the oil can not be effectively dealt with, e.g. in rough weather conditions, or in the case of non-persistent oils (kerosene, gasoline, diesel) or very viscous oils (residual fuels, tar balls).

**In situ burning** is not further considered in this project. This is mainly because most European countries do not consider the technique of in situ burning as a response option in their contingency plan - except when the oil is already burning because of the accident itself. Several arguments can be mentioned:

- safety concerns in relation to in situ burning,
- the limiting factor of oil thickness (minimum thickness of 3 mm) which is needed for effective burning,
- the limiting factors wave height, wind force and currents (calm conditions are needed),
- the operational challenge of booming the oil in order to perform in situ burning under controlled conditions (if booming succeeds, the oil can also be recovered mechanically),
- the narrow window of opportunity (before lighter components can evaporate).

# 1.2.4. Characterisation, real-time monitoring and modelling of spilt oil in support of a repeated NEBA process

<u>Figure 2</u> is a simplified, schematic overview of NEBA made by MUMM. It is meant to visualize the most important steps in a NEBA process. Also the monitoring aspects are included. Experience from past incidents has shown however that when a coastal state is confronted with a major oil spill, the spill has to be dealt with as soon as possible to prevent further leakage, spreading and weathering of the oil. It is therefore important to note that oil pollution response has to be activated as soon as possible once a (rapid) initial NEBA-decision has been taken. It is obvious that response actions cannot wait for monitoring means to be deployed, especially when the latter have a longer mobilisation time. If real-time monitoring operations are envisaged in a contingency plan, there is an obvious need for a short mobilisation time of monitoring teams.



<u>Figure 2</u>: NEBA evaluation and decision-making scheme, with accent on overall environmental impact evaluation and on monitoring aspects (MUMM).

NEBA however is a continuous evaluation process that is to be repeated during an incident in the light of new information concerning the behaviour of spilt oil, the overall environmental impact, and/or the effectiveness of the activated response technique (see two loops in Fig. 2). During an incident, such valuable new information can be obtained:

- through an early characterisation and real-time monitoring of the spilt oil except if the spilt oil has been characterised in detail before the spill (cf. oil properties databases);
- (2) through real-time aerial (with remote sensing aircraft) and ground-truth monitoring (with ground-truth monitoring teams and platforms) of the oil and of the pollution response;

(3) via mathematical modelling of drift, spreading and behaviour of the spilt oil, using information obtained from the characterisation and real-time monitoring of the spilt oil, sea current data and weather forecasts.

The NEBAJEX pilot project was especially meant to demonstrate in an exercise how useful information obtained in real- or near-time from the monitoring and modelling of oil pollution at sea can feed the continuous NEBA process during a major oil pollution incident.

The NEBAJEX pilot project is <u>not</u> intended to perform a literature review on the environmental impact of a spill in detail. This has been performed a previous European study, resulting in an impact reference system (IRS) (O'Sullivan and Jacques, 1998), which can be found in the European Community Information System or CIS. NEBAJEX is also not intended to describe the advantages and disadvantages of each response technique in full detail, or to study the weighting of the most appropriate response options for various spill scenarios. This part of the NEBA process is extensively dealt with in the Net Environmental-Economic Benefit Analysis (NEEBA) project (Koops *et al.*, 2003). The purpose of this Dutch NEEBA project was to draft operational response guidelines (ORG) intended to aid decision-making in the event of a marine oil spill and to enable coastal states to develop the most appropriate response strategy to a range of different oil spill scenarios, as part of the contingency planning process. Not only the environmental benefits of response actions, but also their efficiency and costs were taken into account when drafting the ORG document.

### 1.3. Overview of NEBAJEX tasks

In Europe, some countries (e.g. Belgium, France, Norway, United Kingdom) have gained valuable experience in *in-situ* and real-time monitoring of oil spilt at sea and of the effectiveness of the response, in the determination of concentrations of monoand poly-aromatic hydrocarbons (BTEX and PAHs), in the large-scale monitoring of an oil spill at sea, and/or the wide application of software tools. All of these monitoring, analysis and modelling aspects are considered useful in support of an ongoing NEBA process.

In view of a catastrophic oil release at sea and future international co-operation between coastal states, it is of prime importance that a common monitoring approach is developed in support of NEBA, and that common monitoring procedures are tested on the occasion of full size exercises involving several monitoring teams. The three European marine research institutes that were involved in NEBAJEX (MUMM, CEDRE and SINTEF) tried to combine their efforts and experience with the aim of developing such a common monitoring approach. An exhaustive list of the monitoring tasks mentioned in the NEBAJEX project proposal is given in <u>Table 3</u>. A real-time monitoring exercise was considered to be of great benefit to the development of a common monitoring approach.

<u>Table 3</u>: Overview of monitoring procedures and strategies to be developed and tested.

 Development of an oil sampling and monitoring strategy of different compartments (focus on surface slick and oil in water column) and of real- or near-time analysis procedures.

<u>Developing + testing a monitoring strategy for the surface slick:</u>

- sampling strategy for surface oil: sampling frequencies (time after release), sampling transects and positions within the slick (time-position recordings with GPS);
- sample handling (how to take the sample, handle and store before analysis);
- analyzing important parameters of the oil or w/o emulsion in real-time in the field (density, viscosity, water content, oil film thickness, emulsion stability and breaking, dispersibility);
- analyzing the chemical composition of the surface oil in a specialized lab: BTEX (mono-cyclic aromatic hydrocarbons), PAHs (poly-aromatic hydrocarbons) and their alkylated C1-C4 homologues.

### <u>Developing + testing a monitoring strategy for the water column:</u>

- developing and testing a monitoring strategy for the dispersed oil (UVF and water sampling): monitoring frequencies and transects, monitoring depth, validation sampling for analysis in a specialised lab;
- determining total hydrocarbon concentration and further analysis (see below).
- (2) Development of procedures for measurement of oil concentrations under an oil slick in the water column, to evaluate the effectiveness of chemical dispersion:
  - Total hydrocarbon concentration (both dispersed and dissolved oil components),
  - BTEX, PAHs, their alkylated C1-C4 homologues, and polar organics.

### (3) Application of software tools (mathematical models):

- For oil spill trajectory, weathering and impact simulations
- For guiding the monitoring efforts (especially the underwater monitoring, since surface and subsurface drift are not at the same speed or direction in general), and for integrating the spatially and temporally patchy data that will be realistically available from even the best monitoring effort, to produce a holistic 3D time series of an event.
- (4) Inter-comparison of the monitoring results obtained by the different monitoring teams.
- (5) Consideration of whether the fate and a mass balance of the spilt oil can be derived from the at-sea monitoring results in combination with simulations from mathematical models.

### 2. Towards a common monitoring approach

### 2.1. Categorisation of oil types

One of the first steps in a Net Environmental Benefit Analysis or NEBA, is an evaluation of the possible threat or impact of an oil spill. Important factors that will largely influence the overall environmental impact are the type of oil, its composition and properties, and its behaviour and drift (see also 2.2.). A categorisation of the major oil types and a description of their weathering processes and ecological impact on coastal and marine ecosystems, resources and fauna can be found in the European IRS (O'Sullivan & Jacques, 1998). Because of its high relevance for NEBA, and because the importance of an oil parameter that is to be monitored in the field varies according to the type of oil being spilt, the general background information of the IRS is partly summarized below. Crude oil and refined petroleum products are in fact mixtures of petroleum hydrocarbons (PHC) and other compounds with widely differing physical and chemical properties that determine their behaviour and fate when spilled as well as their impact on marine life and biological resources. According to each oil type being a mixture of PHC (each hydrocarbon having a specific low, moderate or high molecular weight), four major categories or types of oil can be defined:

- I. **LIGHT VOLATILE OILS:** mostly light, non-persistent products such as petroleum spirit, gasoline, kerosene or paraffin, light automotive diesels.
- II. **MODERATE HEAVY OILS:** most crude oils, and refined products such as marine diesel, gas oil, light fuel oils, light lubricating oils, condensates.
- III. **HEAVY OILS:** very waxy crude oils, asphaltenic crudes, w/o emulsions, heavy lubricating oils.
- IV. **RESIDUAL OILS:** bunker and heavy fuel oils, weathered crude (tarry lumps), asphalt.

Oil entering the marine environment will not generally remain in the same category throughout the duration of an incident. For example, in changing its state, going to different weathering processes, a light crude (type II) will lose its most volatile components and may also form a w/o emulsion ("chocolate mousse"); either of these changes will bring it into types III or IV.

<u>Table 4</u>: classification of oils based on general properties that influence their ecological impact (based on O'Sullivan & Jacques (1998) and recent SINTEF findings).

Oil type	Volatility	Solubility	Natural dispersion	Chemical dispersion	Biological harmfulness
I. light volatile	High	High	Easy	useless <sup>1</sup>	Highly toxic
II. moderate – heavy	Up to 50%	Moderate	Moderate	Effective in a narrow window of opportunity	Variable toxicity, slightly to moderately sticky
III. heavy	Low, < 20%	Low	Low	Low	Smothering, strongly
IV. residual	Non- volatile	Very low	No dispersion	Non-effective	variable acute toxicity

ITOPF uses a similar classification of a list of crude oils and refined products (ITOPF, 1987), dividing the oils in four major types or groups of different density classes. Information on the characteristics of these four oil groups used by ITOPF can be summarised as follows:

**GROUP 1:** Low density $^2 < 0.8$ ,

Low viscosity (at 15°C) of 0.5-2.0 cSt

Low pour point Highly volatile

Light oils, e.g. gasoline, naptha or kerosene;

**GROUP 2:** Medium density 0.8-0.85

Varying viscosity (at 15°C): 4 cSt - solid

Varying pour points<sup>3</sup> Varying evaporation rates

Light to moderate crudes and refined products (gas oil);

**GROUP 3:** Medium to high density 0.85 – 0.95

Varying viscosity (at 15°C): 8 cSt - solid

Varying pour points<sup>8</sup> Low evaporation rates

Moderate to heavy crudes and refined products (medium fuel oil);

**GROUP 4:** High density > 0.95

<u>Or</u> oils with high pour point (> 30°C) High viscosity (at 15°C): 1500 cSt – solid

Very low evaporation rates

Heavy crudes and residual oils (heavy fuel oil/Bunker C).

In ITOPF (1987) it is again described how much the weathering and behaviour of the oil can vary according to the type of oil. The big variety in composition and properties of oils transported at sea largely influences its behaviour, the overall environmental impact and the effectiveness of the different combating options in

<sup>&</sup>lt;sup>1</sup> The chemical dispersion of light volatile oils is useless because of the rapid weathering processes (non-persistent oils characterised by rapid spreading, high evaporation and dissolution rates).

<sup>&</sup>lt;sup>2</sup> Density is described in specific gravity (= density of oil in relation to pure water).

<sup>&</sup>lt;sup>3</sup> Oils with high pour points (> 5°C) behave like group 4 oils if ambient temperature is under their pour point.

case of a major oil spill. A thorough understanding and documentation of these impact factors, where possible supported by quantitative data, is needed to enable a good NEBA of a spill.

Furthermore, as soon as possible after the start of a major oil spill incident, information has to be gathered about the location of the spill, about the environmental conditions at the spill site (wind/currents/sea state) and forecasts, and, via aerial surveillance and oil spill trajectory models, about the dimensions and drift of the oil slick (see 2.2.). A good evaluation of the behaviour and drift of the oil is crucial for the purpose of NEBA, to evaluate the threat of an oil spill to a coastal area or sensitive resource.

Before starting an oil pollution monitoring exercise, a good understanding was needed of the different large categories of oil types, their general composition and properties, and their general behaviour. The characterization and real-time monitoring of spilt oil (objectives of exercise) delivers extra qualitative and quantitative data that can be used to in repeated NEBA evaluations.

## 2.2. Overview of important oil properties for the purpose of NEBA

The impact of a spill, and the way it is most effectively combated, can vary a lot, depending on the type of oil that is spilt, and its properties. An initial characterisation of the original oil, or of oil that is sampled at the sea surface shortly after spillage, offers valuable extra information for a NEBA evaluation of an incident. In order to characterize the type of oil, various physico-chemical properties of the oil can usefully be analyzed in a specialized chemical lab in the initial phase of an incident (see 2.4.).

Via monitoring of a marine oil spill at sea (see 2.5. and 2.6.; aerial and ground-truth monitoring), valuable extra information and data can be obtained in real time on the oil behaviour and weathering, on changes in important physical properties, and on the combatability of the spill.

<u>Table 5</u> summarizes the oil parameters to be chemically analysed in an initial characterisation of the oil and/or in real-time monitoring of the oil at sea. It was proposed during the workshop to make a distinction between the different oil types when listing the parameters that have to be characterised or monitored for the purpose of NEBA. The reason for this is that for each oil type, a different 'importance' can be attached to each parameter. For example:

- in case a major spillage occurs of light volatile oil, it is very important to know the flash point of the oil, for security reasons during an intervention. Due to the high percentage of volatile and toxic compounds, the weight percentages (wt%) are also very important.
- for moderate-heavy oils and heavy-residual oils, it is much more important to know the physical and weathering parameters of the oil (viscosity, density, pour point, emulsification), for combating purposes and for a better understanding of the behaviour and thus probable overall environmental impact of the oil.

In Table 5, the different oil types are grouped in three major oil categories: light volatile oils, moderate to heavy oils and heavy to residual oils. The 'importance' of a given characterisation parameter to be determined for a NEBA evaluation is indicated with '+'. When no '+' is added, this means that the parameter is considered less important for this type of oil. When '+' is mentioned, this means that the parameter is considered relatively important, for a better understanding of the behaviour, impact or combatability of the oil. When '+++' are mentioned, the parameter is considered **very important or crucial** in order to follow the evolution of oil behaviour and weathering, to better evaluate the toxicity and the overall environmental impact of the spilt oil, or for the evaluation of the effectiveness of a response technique. Detailed explanation on each of these parameters is given in 2.2.1, and 2.2.2.

<u>Table 5</u>: Parameters to be chemically analysed during an initial characterisation of original or 'fresh' oil in a specialized lab on land, and/or during real-time monitoring of weathering oil in the field.

Oil parameter	Parameters	Light volatile oils	Moderate- heavy oils	Heavy- residual oils
Physical	- Flashpoint	+++	+++	+
parameters	- Viscosity		+++	+++
(analysis on land	- Density		+	+++
+ at sea)	- Water		+	+++
	content/uptake		+++	+++
	- Emulsion stability		+++	+++
	- Pour point (not at			
	sea)			
Chemical	- Wt% Saturated HC		+	+
parameters	- Wt% Aromatic HC	+++	+++	+++
(analysis only on	- Wt% Waxes		+	+
land)	- Wt% Polar organics	+	+	+
Toxicity	- Wt% of BTEX	+		
(analysis only on	- Wt% of PAHs	+++	+++	+++
land)				
Response	- Dispersibility of oil		+++	+++
effectiveness	- Emulsion breaker		+	+
parameter				
(analysis on land				
+ at sea)				

With table 5 in mind, it was decided at the workshop that in the planned controlled exercise at sea, a moderately heavy oil should be used, that is dispersible and that can form w/o emulsions, in order to test all the procedures and strategies envisaged in NEBAJEX.

2.2.1. Important physical, weathering and combatability parameters

An overview is given of the important physical parameters of oil that can usefully be determined in an initial characterisation of the original oil in lab, and the physical and weathering parameters that can usefully be monitored at sea in real time. The methods or instruments used are also briefly discussed. Important aspects of the oil spill that are monitored via aerial surveillance are also briefly discussed.

Most of the information below is derived from Jokuty *et al.* (2000), Melbye (2003), Resby and Leirvik (2004), and Koops *et al.* (2003).

## (1) Flash point $\rightarrow$ Characterisation of original oil in lab $\rightarrow$ Real-time monitoring at sea

The flashpoint of a fuel is the temperature to which the fuel must be heated to producer a vapour/air mixture above the liquid fuel that is ignitable when exposed to an open flame under specified test conditions. Although not directly important for NEBA evaluations, the flash point is an extremely important factor in relation to the safety of spill cleanup/response operations. Especially light and volatile oils have a low flashpoint. Many freshly spilt crude oils also have low flash points until the lighter components have evaporated or dispersed. Oils with a flashpoint < 61°C can only be safely combated with recovery vessels with special safety regulations. The flashpoint should always be measured, in lab or at sea, especially with light volatile, or other freshly spilt oils. The flashpoint is measured with a flashpoint meter.

(2) Viscosity → Characterisation of original oil in lab → Real-time monitoring at sea

This is probably the most important physical parameter. Many weathering processes, as well as the effectiveness of the response, are heavily influenced by the viscosity of the oil. Viscosity is a measure of a fluid's resistance to flow. The lower the viscosity of a fluid, the more easily it flows. Like density, viscosity is affected by temperature: as temperature decreases, viscosity increases. The unit of *dynamic viscosity* is the millipascal-second (mPa-s), which is equivalent to the unit centipoises (cP). The *kinematic viscosity* (in units of centistokes (cSt)) is also used for the characterisation of an oil, or for mathematical modelling calculations, and can be calculated from dynamic viscosity and density data determined at the same temperature (kinematic viscosity = dynamic viscosity / density).

When spilt oil is weathering at sea after release, the viscosity often increases drastically, mainly due to the process of evaporation and emulsification. Oils with a kinematic viscosity of more than 2.000-5.000 cSt may be difficult to disperse. When the oil reaches a viscosity above 10.000 cSt, chemical dispersion is improbable (IPIECA, 2001), but the latter depends on the oil composition and on the type of dispersant used (some dispersants are known for their chemical dispersion capacity for heavy oils (Daling, 1998)). The viscosity of the original oil at a given temperature is a typical characteristic for each oil category. Heavy or residual oils, or oils with a high pour point, are typically viscous oils.

The dynamic viscosity can be measured using different types of viscosity or rheology meters, such as Haake Rotovisco RV 20, Haake Rotovisco VT 550, Bohlin Visco 88, or Paar Physica Rheometer. The viscosity/rheology characterisation

includes viscosity measurements at different shear rates (between 1 s<sup>-1</sup> and 200 s<sup>-1</sup>). The procedure is instrument specific. For non-newtonian oils, the viscosity values are generally reported as the dynamic viscosity at a shear rate of 10 s<sup>-1</sup>, which can be considered as the reference shear rate for oil and w/o emulsions. During accidents, it may be the only viscosity value reported. For water-free oils, the shear rate of 100 s<sup>-1</sup> is also used, and for highly viscous samples the viscosity at a lower shear rate, (e.g. shear rate of 1 s<sup>-1</sup> for viscosities greater than 32.000 cP) is reported.

For the initial characterisation of the oil, a Haake Rotovisco VT 550 was used by CEDRE, whereas SINTEF used a Paar Physica Rheometer (that is capable of measure higher viscosities).

(3) Density → Characterisation of original oil in lab → Real-time oil monitoring at sea

Density is defined as the mass per unit volume of a substance, and is most often reported for oils in units of g/ml. It is temperature-dependent. Oil will float on sea surface if the density of the oil is less than that of the water. This will be true for all fresh crude oils and most fuel oils. Residual fuel oils may have densities greater than  $1.0 \, g/ml$  and their buoyancy behaviour will vary depending on the salinity and temperature of the water. The density of spilled oil also increases with time, because of evaporation of the lighter volatile components of the oil. After considerable evaporation, the density may increase enough for the oils to submerge below the water surface. For the initial characterisation, the density is an important parameter for moderate to heavy oils, and very important for heavy crudes and fuel oils due to the generally high initial density values.

Monitoring the changes in density of spilt oil at sea is useful in case the density of the (weathered or initial) oil is close to that of seawater (ca. 1.025 g/ml). In such cases, it can be expected that the oil will submerge. Drastic changes in oil density after spillage are logically also an indication of a high evaporative loss of light volatile components of spilt oil.

For the initial characterisation of the oil, CEDRE and SINTEF used an Anton Paar DMA 4500 density meter. For the density measurements at sea during the exercise, MUMM used an Anton Paar SVM 3000 Stabinger viscosity-density meter. The procedure is instrument specific.

#### (4) Pour Point $\rightarrow$ Characterisation of original oil in lab

The temperature when an oil ceases to flow when cooled without disturbance under standardised conditions in the laboratory (ASTM-D97) is defined as the oils pour point. In oil spill clean up situations the pour point provides important information when determining the efficiency of various skimmers, pumping rates and the use of dispersion agents.

The pour point is related to the chemical composition of the parent crude oil, particularly to its wax content. When oil is cooled slowly under static conditions (as used in the laboratory method) small wax crystals can precipitate forming an

interlocking lattice. However, if the oil is cooled rapidly (e. g. in an oil spill) the growth of the wax crystals is disrupted disturbing the formation of the lattice giving lower pour point values. Therefore an oil can for instance flow at temperatures 10 to 15°C lower than determined in the laboratory.

The pour point of an oil with a high wax content will increase dramatically with weathering as the lower weight molecules that contribute in keeping the wax in solution are lost. The pour point of oils with high wax contents can reach 30°C, while low viscous naphthenic oils can have pour points as low as -40°C.

(5) Water content + water uptake → Characterisation of original oil in lab → Real-time oil monitoring at sea

Although it is more important to follow the weathering process of water uptake by the spilt oil to form w/o emulsions, it has been reported that even original oils contain low quantities of water (Jokuty et al., 2000). However, some oils can have a significant water content (>5%). It is therefore useful in an initial characterisation to check the background value of water content of the oil, which can then be compared with the water uptake or emulsification process of weathering oil at the sea surface. Water-in-oil (w/o) emulsification is the most important weathering process that makes oils persistent on the water surface. The formation of w/o emulsions may delay the evaporation and the natural dispersion processes by significantly increasing the viscosity. Almost all petroleum oils contain surface-active compounds which cause them to form w/o emulsions if the energy at the sea surface is sufficient. The presence of breaking waves (wind speed > 5 m/s) has been set as the lowest energy limit for w/o emulsification, but a slower rate of water uptake can also happen in calmer conditions. As a result of the water uptake of oil drifting at the sea surface, the total oil pollution volume can significantly increase. For example, a water uptake of 50% doubles the total volume; a w/o emulsion of 80% volume percentage of water will have a volume of five times that of the originally spilt oil volume.

In lab, the water content, as well as the water uptake, is measured using the Karl Fischer Titration method (standard test method ASTM D 4377-88 (IP 356/87)). At sea on board the research vessel during NEBAJEX, the Alcopol O 60% method was used. With the Alcopol O 60% method, the emulsion water content is measured, based on two parallels, by:

- Adding approximately 5000-10000 ppm of emulsion breaker Alcopol O 60% to the w/o emulsion into a 40 ml sample jar with screw cap or crimp cap; then the sample jar is sealed.
- Mixing the emulsion breaker into the w/emulsion by gently shaking (30 times over 30 seconds) the sealed sample jar.
- Heating the emulsion to 50°C on a hot plate for at least two hours.

The amount of water separated out from the w/o emulsion after 1 hour settling time at 50°C is defined as the water content. Back at the land-based laboratory the water content can be verified by Dean Stark distillation (IP 74/82) and/or Karl Fischer titration.

#### (6) Stability of w/o emulsions $\rightarrow$ Real-time oil monitoring at sea

Asphaltenes, resins and waxes are very important components which influence the stability of w/o emulsions, because they form an interfacial film between the oil and the water droplets. This interfacial film is a physical barrier which prevents coalescence to larger and more unstable water droplets in the oil.

The stability of the w/o emulsions is assessed, based on two parallels, by measuring the value of free water separated out from the w/o emulsion after 1, 3 and 24 hours settling time in a thermostated cooling chamber at sea temperature. This is done following a similar procedure than the Alcopol O 60% test, but without adding of the emulsion breaker.

The properties of a w/o emulsion (water content, viscosity and stability) are also of great importance to the effectiveness of chemical and of mechanical countermeasures. During the Sea Empress incident (UK) for example, it has been shown that unstable emulsions can still be broken by emulsion breakers or dispersants; a second application of dispersants can then be effective on the water-free and less viscous oil slick at the surface. Stable w/o emulsions with a high viscosity can no longer be effectively combated with these chemical products. If mechanical recovery methods are used, the volume increase due to water content will be important (cf. question of sufficient availability of adequate mechanical recovery means). Also the viscosity of the emulsion is important for mechanical recovery. For instance, if the viscosity of w/o emulsions is higher than 10.000 cP, some types of skimmers (e.g. disc and mop skimmers) have a reduced recovery efficiency (ITOPF, 1986).

### (7) Spreading and fragmentation of slicks $\rightarrow$ Real-time oil monitoring at sea

The spreading and fragmentation of an oil spill is rapidly observed on board a remote sensing aircraft. Several features that describe this spreading and fragmentation are important: the dimensions of the spill and changes thereof in time, the film thickness of the surface oil (see below), the presence and dimensions of thicker combatable parts within the slick(s), and the physical shape or form of a spill. The way the spill is spreading and the presence and magnitude of the thicker parts are very important parameters in order to evaluate the probable impact and combatability of a spill. The physical forms can vary. Several forms can be identified:

- Sheen slicks
- Fragmented, semi solid oil (e.g. tar balls), with a very low coverage (< 1%)
- Patches of true oil colour and/or w/o emulsions: rather circular, distinct shapes of thicker oil.
- Trials and ribbons with true oil colour: thicker oil parts, where length >>> width.
- Large homogenous slicks of true oil colour and/or w/o emulsions.

#### (8) Estimated oil volumes + oil film thickness $\rightarrow$ Real-time oil monitoring at sea

Making an estimation of the oil volumes spilt during an incident and observed at the

sea surface is an important parameter in the evaluation of the threat or probable impact of a spill, and of the level of response. The general method used for volume estimations via aerial surveillance, is the colour code method. The new Bonn Agreement Oil Appearance Code (Bonn Agreement, 2003b; see <u>Table 6</u>) was used for oil volume estimations during NEBAJEX.

<u>Table 6</u>: Bonn Agreement Oil Appearance Code, as accepted in BONN Contracting Parties meeting of 2003 (Bonn Agreement, 2003b).

Code	Description	Layer thickness interval (µm)	Volume per km² (in litres or m³)
1	Sheen (silvery-grey)	0.04 – 0.30	40-300 litres
2	Rainbow	0.30 – 5.0	0.3 - 5 m³
3	Metallic	5.0 – 50	5 - 50 m³
4	Discontinuous true oil colour	50 – 200	50 – 200 m³
5	Continuous true oil colour	200 – more than 200	200 m³ – more than 200 m³

A typical guide is that about 90% of oil will be as "thick" patches (e.g. 1-2 mm thick), covering approximately 10 % of the spill area. However, only the thicker parts of a slick (with films that have an appearance of code 4 and 5), are combated at sea. It is therefore important that aerial observers can locate these thicker parts, and correctly evaluate their shape and dimensions. The thickness of continuous true oil colour, and especially of w/o emulsions, can not reliably be estimated from the air.

To measure the thicknesses of oil films of above several mm in real time in the field, SINTEF developed an oil film thickness cylinder. This special constructed sampler consists of a 1 m long Plexiglas cylinder (inner diameter 200 mm) with an open/close-mechanism at the end. The cylinder should be placed through the oil/water interface in open and vertical position, thereafter closed and elevated. In this way, the oil/emulsion surface or film is sampled. The film thickness is read on the spot (e.g. on board a dinghy) from the thickness marks on the cylinder and noted in the log journal. This parameter is very important for a better evaluation of the total volume and combatability of the thicker w/o emulsions.

#### (9) Natural/chemical dispersion + dissolution → Real-time oil monitoring at sea

If sufficient energy is available on the sea surface, waves will start breaking up the oil into droplets with sizes ranging from 1-1000  $\mu$ m in diameter. These will be mixed into the water column. Although mineral oil has a low solubility in water, a minor fraction (mainly low molecular weight hydrocarbons) will also dissolve. This weathering process is called natural dispersion and dissolution. Natural dispersion happens mainly when breaking waves are present (typically at wind speeds higher than 5 m/s). The largest droplets will resurface and, either join the initial slick, or form a sheen oil film behind the spill. Natural dispersion is one of the most important processes that determine the lifetime of the oil at the sea surface. Gradually, the natural dispersion rate will decrease as evaporation and water-in-oil emulsification increase the viscosity of the oil or w/o emulsion.

Chemical dispersants enhance the oil-in-water dispersion rate by reducing the interfacial tension between the oil and water, and by forming smaller oil droplets. Field trials have shown that effective chemical dispersion of surface oil results in an increased oil concentration in the underlying water column down to approximately 10 meters shortly after dispersant application. This concentration can rapidly drop in open marine areas (e.g. deep, offshore areas) where sufficient dilution takes place by vertical and horizontal mixing. In such cases, the remaining oil concentrations in the water column can rapidly drop below the acute toxicity level for most marine organisms.

The monitoring of naturally dispersed/dissolved oil, and especially the monitoring of chemically dispersed oil in the water column can be performed from the air, through the qualitative observation of a sub-surface oil plume (see 2.5.2. and 2.6.). It can also be monitored from the sea surface, by deploying Ultra Violet fluorescence (UVF) instruments on board ground-truth monitoring platforms. In NEBAJEX, two types of UVF fluorometers were used (see 2.5.4. and 2.6.):

- Turner UVF fluorometers: a continuous flow-through Turner model 10 AU 005, used by CEDRE and SINTEF;
- An Aquatracka-MiniBAT integrated system: an Aquatracka UVF fluorometer attached to a miniaturized towed undulating platform, called MiniBAT. This UVF system had recently been purchased by MUMM and was to be tested during the exercise.

(10) Chemical dispersibility  $\rightarrow$  Characterisation of original oil in lab  $\rightarrow$  Real-time oil monitoring at sea

Specialized labs (such as CEDRE and SINTEF) perform dispersibility testing. Two standard dispersibility tests, the WSL (Warren Spring Laboratory) method and the IFP (Institut Français du Petrole) dilution method (NFT 90345), can be used to assess the effectiveness of dispersants for initial characterisation of spilt oil. Both tests are described and compared in e.g. Guyomarch *et al.* (2002). SINTEF also uses the MNS dispersibility test in lab (Mackay test).

At sea, a simple test can be used to give a rapid qualitative check of the chemical dispersibility of weathered oil. The procedure is described by CONCAWE (1988), and consists of a visual observation of dispersant emulsions on seawater in 100 ml measuring cylinders, after 1 minute of gentle hand-tilting of the cylinder. The dispersant dosage is treated Dispersant Emulsion Ratio (DER) = 1:25 for crude oil emulsions, and DER = 1:10 for heavy fuel oil (HFO) emulsions. The procedure can be summarized as follows:

- A 100 ml graded cylinder with stopper is filled with approx. 80 ml seawater;
- 1,5 ml oil or emulsion is added;
- 6 droplets of dispersants are added = approx. 60 μl (for DER 1:25), or 15 droplets of dispersants, for DER 1:10;
- the solution is left for 1 min., then the graded cylinder is gently turned upside down 30 times over 60 sec.

The following three criteria are used for evaluation of the dispersibility:

1. GOOD dispersibility: brown dispersion formed (small oil droplets);

2. REDUCED dispersibility: dark-brown to black dispersion formed (larger oil

droplets);

3. BAD dispersibility: black, very unstable dispersion formed (large oil

droplets, similar to non-treated oil).

### (11) Effectiveness of emulsion breaker $\rightarrow$ Real-time oil monitoring at sea

In some pollution response cases, emulsion breakers can be used to break unstable emulsion, before dispersants are applied. The effectiveness of an emulsion breaker is assessed, based on two parallels, by adding approximately 500 ppm of the emulsion breaker Alcopol O 60% to the w/o emulsion. The amount of water separated out from the w/o emulsion after a 2 min., 1 hour and 24 hour settling period is quantified (Melbye, 2003).

### 2.2.2. Important chemical and toxicological parameters

Crude oil and refined petroleum products are in fact mixtures of petroleum hydrocarbons and other compounds with widely differing physical and chemical properties that determine their behaviour and fate when spilled as well as their impact on marine life and biological resources (see above). Refined petroleum products (incl. gasoline, kerosene, jet fuels, fuel oils (No.2, No.4, No.5, No.6) or bunker fuel oils, and lubricating oils) are obtained from crude oil distillation, cracking, polymerization and reforming. They are blended together to achieve desired chemical properties. They contain all hydrocarbon (HC) classes, but with narrower boiling ranges than corresponding crude oils.

Via analysis of the chemical composition of oil spilt at sea, valuable additional information can obtained for the evaluation of the oil weathering/behaviour/impact, and its probable toxicity. A chemical analysis of a 'fresh' oil sample can consist of two parts:

- (1) the weight percentages of the major hydrocarbon component groups.
- (2) to evaluate the toxicity of the oil, a detailed analysis is useful of the toxic hydrocarbon compounds (BTEX, low molecular weight or LMW PAHs and high molecular weight or HMW PAHs), and of some NSO compounds.

It is important to note that the determination of the weight percentage of the major HC components, and of the toxic compounds, **cannot be obtained in real-time in the field**, but in the order of hours, to one or two days later than the sampling as such. This is because the oil samples are to be analysed in a specialized laboratory, where the requested data can only be obtained via a time-consuming GC-MS analysis, and processing of the results thereof. The chemical composition of the oil is typically performed during the initial characterisation of the original oil or a 'fresh' oil sample (see 2.4.).

#### (1) Weight percentages of major HC groups

A weight percentage (Wt%) of the following major oil components should be

obtained for the purpose of NEBA:

**Saturated HC:** 

Saturated HC consist of alkanes (also called paraffines or aliphatic HC) and cycloalkanes (also called naphthenes, cycloparaffines or alicyclic HC), and olefines (also called alkenes or cycloalkenes; olefines are HC obtained via cracking operations and are only found in refined oil products).

**Aromatic HC:** 

Aromatic HC consist of at least one benzene ring. They comprise:

(1) the highly volatile, soluble and acutely toxic mono-aromatic hydrocarbons (BTEX) and

(2) poly-aromatic hydrocarbons (PAHs); acutely toxic LMW PAHs and less acutely toxic, but carcinogenic/mutagenic HMW PAHs (see also below).

Waxes:

Waxes are HMW paraffines. They can significantly influence weathering processes: a high percentage of waxes leads to high viscosity and low spreading rates, and can positively influence w/o emulsion stability.

Polar organic compounds: (incl. resins & asphaltenes) Polar organic compounds are a group of compounds consisting of resins, porphyrines, metalloporphyrines (Ni/Va/Fe) and asphaltenes. *Resins* comprise the polar and often heterocyclic NSO compounds (sulfur compounds, incl. sulfur aromatics, nitrogen compounds and oxygen compounds). *Asphaltenes* are the fraction of both HMW hydrocarbons HMW NSO compounds effect: the polar and asphaltene components enhance the formation of w/o emulsions.

Toxicity effect: certain resins (e.g. sulfur aromatics) are toxic; oils with a high percentage of sulfur compounds can represent a health and safety hazard for response teams, especially when the oil is burning.

### (2) Toxicity

Figures of weight percentages of the various toxic compounds enable a better evaluation of the possible toxic effects of the oil on the marine environment and its sensitive natural resources (threat/impact evaluation).

BTEX:

BTEX are VOCs (volatile organic hydrocarbon compounds) with one benzene ring or monocyclic aromatic hydrocarbons. BTEX consist of benzene and its alkylated homologues, toluene, ethylbenzene and m-, o- and p-xylene. They have a very high evaporation rate and are highly soluble compared to PAHs. Because of their high solubility they are acutely toxic to marine organisms (membrane dissolving neurotoxins). However, because of their high volatility and high biodegradability, the residence time of BTEX, or VOCs in general, in the marine environment is much shorter compared to PAHs. In case of an oil spill, BTEX have normally disappeared from the marine environment within the first hours after spillage. In case of a spillage of persistent oil in the marine environment, the determination of PAH (see below) is by far more important for evaluation of the probable environmental impact of a spill.

PAH:

PAHs are hydrocarbon compounds with molecules consisting of more than one benzene ring4. Several PAHs are highly toxic and have the tendency to adsorb to sediments and the potential to bioaccumulate. They accumulate in marine invertebrate organisms such as crustaceans and bivalve molluscs which lack efficient mixed-function oxidase (MFO) detoxification mechanisms. In marine vertebrates (e.g. fish) and some polychaetes, that have an efficient MFO detoxification mechanism, PAHs can form carcinogenically active metabolites during the transformation process of the PAH molecule. LMW PAHs are acutely toxic (e.g. naphtalene, fluorene, phenanthrene and anthracene), whereas some of the **HMW PAHs** (e.g. benz[a]anthracene, dibenz[a,h]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene and benzo[a]pyrene) are known to be carcinogenic in mammals and probably also in other vertebrates Auchiandfishtive list of target parent and alkylated (C<sub>1</sub> - C<sub>4</sub> homologues) PAHs that could be considered for environmental monitoring is given in Table 7. Also included in the list are the toxic, aromatic NSO compounds (see below). At present, no internationally agreed list exists with PAHs to be determined for environmental monitoring.

<sup>&</sup>lt;sup>4</sup> In the 'strict' definition, PAH contain at least 3 fused benzene rings, but in practice related 2-ring compounds like naphtalene are often also determined thus enclosed in the PAH-list for environmental monitoring purposes. Aromatics such as Naphthalenes, Phenanthrenes and Dibenzothiophenes, which are not PAHs according to the strict definition, are often also defined as another aromatics group, NPDs.

**Toxic NSO** Also some aromatic NSO compounds are known for their toxic **compounds:** effects, such as dibenzofurane (oxygen compound) and dibenzothiophene (sulphur compound). These compounds are added to the list of Table 7.

The different institutes have different methods for determining the chemical composition of the oil. For this project, the method of CEDRE has been used.

### (3) CEDRE methodology for determining the major HC groups

To determine the hydrocarbons groups (saturates, aromatics, resins and asphaltenes), the method used at CEDRE is as follows:

- 50 ml of n-pentane is added to ca. 100 mg of oil; this is stirred and allowed to stand at room temperature for 2 hours. The asphaltenes, which have precipitated in these conditions, are then removed by vacuum filtration through a GF/F filter and weighed until all the remaining solvent has evaporated.
- The pentane is recovered by rotary evaporation, leaving the maltenes (saturates + aromatics).
- the maltenes are then placed on an open glass column (10 mm I.D.) packed with 6 g silica, topped with 1 cm anhydrous sodium sulfate and saturated with n-pentane.
- the saturates are eluted by 50 ml n-pentane,
- the aromatics are eluted by 70 ml pentane/dichloromethane (80/20) and 20 ml pentane/dichloromethane (70/30),
- the resins are eluted by 25 ml dichloromethane, 30 ml Acetone/MeOH (50/50) and 20 ml MeOH.

The solvents are then evaporated and the different fractions weighed. The calculation of the corresponding relative abundances (%) is done assuming that the volatiles fractions are equally distributed between saturates and aromatics whereas resins and asphaltenes do not evaporate.

## (4) CEDRE methodology for determining weight percentages and quantification of HC saturates & PAHs

The methodology followed and instruments used at CEDRE to determine the weight percentages of major HC groups and PAHs can be summarized as such:

- 10 mg of oil sample were spiked with internal standards (Naphtalene d<sub>8</sub>, Biphenyl d<sub>10</sub>, Phenanthrene d<sub>10</sub>, Chrysene d<sub>12</sub> and Benzo[a]pyrene d<sub>2</sub> for PAHs and Eicosene for n-alkanes).
- Aromatic and saturated fractions were analyzed by Gas Chromatography coupled to Mass Spectrometry (GC-MS). The GC used at CEDRE is an HP 6890 series II (Hewlett-Packard, Palo Alto, CA, USA) equipped with a split/splitless injector (Splitless time: 1 min, flow 50 ml/min). The injector temperature was maintained at 270 °C. The interface temperature was 300°C. The GC temperature gradient was: from 50°C (1 min) to 300°C (20 min) at 5°C/min. The carrier gas was Helium at a constant flow of 1 ml/min. The capillary column used was a VF-5ms (Varian, Middelburg, The Netherlands): 60 m x 0,25 mm ID x 0,25 μm film thickness. The GC was coupled to an HP 5973 Mass Selective Detector (MSD) (Electronic Impact: 70 eV, voltage: 2000V).

- Quantification was done by using Single Ion Monitoring mode with the molecular ion of each PAH and the 57 m/z fragment for n-alkanes at a minimum of 1.4 cycles/s. PAHs and n-alkanes were quantified relatively to the deuterated PAHs introduced at the beginning of the sample preparation procedure (similar with eicosene for n-alkanes). The calibration was performed by analyzing a solution of priority pollutant polycyclic aromatic hydrocarbons (SRM 1647d) purchased from Chiron (Trondheim, Norway).

### (5) MUMM attempts to develop a methodology for selected PAH quantification

MUMM has currently two methods in operation for the analysis of hydrocarbons, being a qualitative method for HC fingerprinting of oil samples and a quantitative method for the determination of selected PAHs in environmental samples. An attempt was made to transpose the quantitative method for the PAHs in environmental samples to the analysis of PAHs in oil samples. Although the method is very selective for the determination of PAHs in the former, it proved to be less selective for the analysis of oil samples as the latter yields more complex patterns. In the oil sample, the selected ions, used for the quantification, alone did not allow for a sufficiently selective identification of the individual PAHs. Many other compounds in the oil have similar masses and identification on the retention time becomes necessary. Unfortunately, the resolution power of the analytical column proved to be insufficient for this task. New, narrow bore (0.18 mm) and longer (40m) columns were tested with this in mind, giving very promising results. For future work, this appears to be the way forward. The narrow bore gives the additional advantage over regular diameters (0,25 mm) that analysis times are reduced without loss on resolution, quite on the contrary even, as they give sharper better defined However, these new methods need to be validated and this proved impossible given the timeframe of the project. Therefore the CEDRE methodology was further used within NEBAJEX.

<u>Table 7</u>: List of target parent and alkylated PAHs, and toxic NSO compounds, for environmental monitoring (OSPAR, 2001; Klungsoyr and Law, 1998; Law *et al.*, 1997)

Compound	MCWG	US EPA priority pollutants	Carcinogeni city
Naphthalene	Х	Х	
C1-naphthalenes	Х		
C2-naphthalenes	Х		
C3-naphthalenes	Х		
C4-naphthalenes	Х		
Acenaphthylene	Х		
Acenaphtene	Х	Х	
Dibenzofurane (O compound)		Х	
Biphenyl	Х		
Fluorene	Х	Х	
C1-Fluorenes	Х		
C2-Fluorenes	Х		
C3-Fluorenes	Х		
Dibenzothiophene (S compound)	Х		
C1-dibenzothiophenes	Х		
C2-dibenzothiophenes	Х		
C3-dibenzothiophenes	Х		
Phenanthrene	Х	Х	
Anthracene	Х	Х	
C1-phenanthrenes/anthracenes	Х		
C2-phenanthrenes/anthracenes	Х		
C3-phenanthrenes/anthracenes	Х		
Fluoranthene	Х	Х	
Pyrene	Х	Х	
C1-fluoranthenes/pyrenes	Х		
C2-fluoranthenes/pyrenes	Х		
Benz[a]anthracene	Х	Х	Х
Chrysene	Х	Х	Х
2,3 benzanthracene	Χ		
Benzo[a]fluoranthene	Χ		
Benzo[b]fluoranthene	Χ	X	X
Benzo[j]fluoranthene	Х		X
Benzo[k]fluoranthene	X	X	X
Benzo[e]pyrene	X		
Benzo[a]pyrene	X	X	X
Perylene	X		
Indeno[1,2,3-cd]pyrene	X	Х	X
Benzo[g,h,i]perylene	X	X	
Dibenz[a,h]anthracene	X	X	X
Dibenzo[a,e]pyrene			X
Dibenzo[a,h]pyrene			X
Dibenzo[a,i]pyrene			X

### 2.3. NEBAJEX objectives

Five primary objectives were defined during the NEBAJEX workshop:

- (1) **the initial characterisation of the spilt oil**, prior to an exercise; and, during the exercise:
- (2) **to validate procedures and strategies** for surface and subsurface oil pollution monitoring, by testing both aerial and ground-truth monitoring procedures;
- (3) to test procedures to evaluate the response effectiveness, with focus on dispersants (aerial and ground-truth monitoring);
- (4) to apply dedicated mathematical models for near-future simulations;
- (5) to use the monitoring and modelling results as input in a NEBA evaluation process.

Several scientific teams participated in the exercise:

- The different monitoring teams at sea had to test procedures and strategies for monitoring of surface oil (via surface oil sampling and analysis) and sub-surface oil (via UV-F measurements and oil-in-water sampling).
- The aerial surveillance teams had to monitor the oil pollution from the air: the surface oil was to be located, its dimensions described and its combatability evaluated; oil-plumes of dispersed sub-surface oil also had to be traced. Procedures for communication and co-ordination were tested between the 'aerial' teams and 'sea-based' teams.
- Mathematical modellers participated to simulate the behaviour of the oil (MUMM, CEDRE, SINTEF). SINTEF modellers planned to make simulations of oil in the water column to guide and support the monitoring efforts. SINTEF modellers also planned calculate the mass balance of the oil.
- Marine chemists would analyse oil samples in the field, on board the Belgian research vessel 'Belgica', in order to obtain new, valuable information in realtime on various important oil properties.

### 2.4. Objective 1: Initial characterisation of spilt oil

Institutes like SINTEF that dispose of an oil properties database have experienced that this is very useful for mathematical modelling and NEBA in case the spilt oil is 'known' because its properties were characterised before the spill and stored in a database. Useful information on the composition and properties of the oil is directly available in such case. As a result of this, a more detailed first evaluation can be performed of the probable oil behaviour, its overall environmental impact, and the combatability of the spill. SINTEF also uses the data in the oil properties database as input for their oil spill models (see 2.7.).

However, when they are confronted with a major oil spill, most coastal states do not have an oil properties database readily available, and the knowledge on the properties of the oil spilt remains general. Even if a database is available, it can happen that the oil is 'unknown'. In these situations, the question arises how the oil

can be characterised in lab in the best and most rapid way for the purpose of NEBA. Experience of past, major oil pollution incidents (e.g. 'Erika' incident) has shown that it is very important to get a 'fresh' oil sample as soon as possible. The sample is then brought to a specialised laboratory on land, where the oil is immediately analysed to obtain quantitative information on the physico-chemical properties of the oil and on its toxicity. The 'fresh' oil sample can be (1) an oil sample (non-weathered) taken on board of the ship in distress, or, if this is not possible, (2) a sample from freshly spilt oil drifting at the sea surface, or (3) an oil sample from the refinery/place where it was produced or shipped.

If sufficient quantities can be collected of freshly spilt oil and/or of the original (not weathered) oil, the weathering processes of the oil can also be simulated: the oil can then be tested in a meso-scale flume basin. Both CEDRE and SINTEF dispose of such a meso-scale flume basin (CEDRE's basin is called Polludrome).

<u>Table 8</u>: Overview of oil properties measured in lab, the method or instrument used, the reference oil analysed, and the institute that performed the analysis for NEBAJEX.

Parameter	Instrument/method	Oil type	Lab performing analysis
Viscosity	Haake Rotovisco VT 550 Paar Physica Rheometer	TRICOLOR reference HFO	CEDRE, SINTEF
Density	Anton Paar density meter	TRICOLOR reference HFO	SINTEF, CEDRE
Pour point	ASTM method D97-65	TRICOLOR reference HFO	SINTEF
Water content	Karl Fischer Titration	TRICOLOR reference HFO	SINTEF
Dispersibility	IFP Test	TRICOLOR reference HFO	SINTEF
Chemical comp. (wt% HC groups)	CEDRE protocol	DEPOL 03 reference oil	CEDRE
PAHs (wt%)	CEDRE protocol, (+ GC-MS)	DEPOL 03 reference oil TRICOLOR reference HFO	CEDRE, MUMM

Table 8 summarizes the parameters that have been analyzed in the specialized labs of CEDRE, SINTEF, and/or MUMM, the type of oil that was characterised, as well as the instrument/method that was used. Before the NEBAJEX exercise, CEDRE had chemically analysed the weight percentages of the different HC groups, and of the PAHs, of the DEPOL 03 oil (oil that would have been spilled in the originally planned NEBAJEX-DEPOL 03 exercise). When the planned NEBAJEX-DEPOL 03 exercise was cancelled just before the exercise week (see 3.1.), and it was decided to organise a NEBAJEX monitoring exercise around the 'Tricolor' wreck, only one reference oil sample of one of the HFOs from the Tricolor (sample from the fuel tanks taken in the beginning of the incident) with a limited volume, could be obtained via CEDRE for use in the NEBAJEX project. Moreover, only the viscosity

and density of the one reference HFO oil had been measured before the exercise. After the exercise, the remaining volume of the one HFO reference sample was used by SINTEF to perform the most important initial characterisation analyses.

### 2.5. Objective 2: real-time in situ monitoring of oil spilled at sea

Monitoring spilt oil in real-time at sea consists of two major, compatible aspects: aerial monitoring and ground-truth monitoring.

# 2.5.1. The research vessel 'Belgica' as central monitoring platform

During the NEBAJEX exercise, the Belgian federal marine oceanographic research vessel 'Belgica' had to take on the role of central monitoring platform, and coordinated the aerial and ground-truth monitoring. Various communication facilities are present on board to fulfil the role of central coordination platform: SATCOM telephone and fax connections, email, marine VHF, and a mobile telephone for coastal areas.

The analyses in real time of the different oil properties listed in 2.5.2. (Table 9) were performed in the laboratory space which is sufficiently present on board of the vessel. The Belgica further disposes of sufficient storage capacity, general lab equipment (fridge/freezers, milliQ water and seawater, two incubators). The Belgica further disposes of a large working deck and powerful hydraulic crane; the two RIBs serving as small monitoring platforms during the exercise were transported to the TRICOLOR site on board the Belgica.

The Belgica has an Oceanographic Data Acquisition System (ODAS) on board, which automatically performs continuous measurements of the position of the vessel, time in UTC, depth, wind speed and direction, sea and air temperature (wet and dry), swell, salinity, and humidity. Sea currents are measured with a hull-mounted Acoustic Doppler Current Profiler or ADCP, for modelling purposes.

### 2.5.2. Aerial monitoring

It is common knowledge that aerial surveillance is crucial for a good and rapid evaluation of a major oil spill, for the purpose of NEBA, and for assisting response operations. In a relatively short period of time, an aircraft can fly over large sea areas. The magnitude, shape and combatability of spotted oil slicks can be rapidly evaluated by trained aerial observers. Dedicated remote sensing aircraft can track oil slicks day and night. Aircraft also play a very important role in guidance of combating units at sea, either recovery vessels or dispersant spraying vessels and aircraft. The NEBAJEX exercise has demonstrated that an aircraft can also usefully guide monitoring units towards or within a slick.

The Belgian remote sensing aircraft participated in the NEBAJEX exercise at the Tricolor site. This aircraft has several sensors on board, such as Side Looking Airborne Radar or SLAR, an Infrared (IR) sensor and a Ultraviolet (UV) sensor. In major oil spills, thicker slick parts and especially w/o emulsions can easily be detected with the IR sensor because these thicker parts are heated up by the sun and

have a higher temperature, whereas thin, sheen-like slick parts have a lower temperature. With an IR sensor in the 'white hot' mode, w/o emulsions become visible as white spots on the IR screen. Other instruments on board of the aircraft are a digital and analogue camera, a video-camera, a GPS, marine VHF, and a portable computer. The aircraft had to combine several monitoring and guidance tasks:

- (1) Observation and documentation of the oil surface slick: location and dimensions of oil spill, oil appearances, coverage and form of slick(s), location and description of thicker parts within the slick(s).
- (2) Observation and documentation of subsurface oil plume (of dispersed oil): location, form, appearance and dimensions (if visible).
- (3) Where needed, guidance of small workboats performing bulk sampling within and/or UVF measurements under the oil slick(s), or in oil plume of chemically dispersed oil.
- (4) Guidance of dispersant spraying and/or mechanical recovery units (if response option initiated).

The most important information on the oil spill that was to be collected by the aircraft is summarized in <u>Table 9</u>. The new Bonn Agreement Oil Appearance Code (see table 6 in 2.2.1.) was used for oil volume estimations.

<u>Table 9</u>: Overview of oil spill parameters obtained in real-time with the Belgian remote sensing aircraft during the NEBAJEX exercise.

Parameter	Instrument/method
Location	GPS
Dimensions of polluted	Visual evaluation, SLAR and UV sensor
area	
(length – width)	
Coverage percentage of	Visual evaluation
oil in polluted area	
Estimated oil volume	Bonn Agreement Oil Appearance Code (BAOAC)
(order of magnitude)	
Thicker parts of slick	Visual evaluation, IR sensor
Presence of w/o	Visual evaluation, IR sensor
emulsions	
Form (shape) of slick	Visual evaluation
Combatability	Evaluation of thicker parts of slick + weather conditions.
Oil plume	Visual evaluation (if observed)
Weather conditions	Visual evaluation (Bft)

A standard reporting format was developed for aerial monitoring (see <u>Figure 3.</u>). This "Reporting format on aerial monitoring of combatable spills" was to be tested during the exercise: the aerial observers should report their oil slick observations to the overall monitoring co-ordinator at sea using the codes and points in this format. Although this aerial monitoring report was largely based on the 'Bonn Agreement Pollution Observation Report on Polluters and Combatable Spills' (Bonn Agreement, 2003a), some elements had been changed, mainly in the parts 'location' and 'description' of the pollution:

- Codes have been proposed for the begin and end of a slick ('S' + 'E'), and for the thicker parts within the slick (' $T_x'$ ); these codes facilitate reporting at sea (just Sierra, Echo and Tango(+nr.) need to be mentioned).
- Special attention is given to the thicker slick parts ('T'). These parts represent the combatable parts, and can consist of discontinuous and continuous true oil colour, and/or w/o emulsions. Also the physical shape or form of these thicker parts can be reported, as well as their dimensions: for thicker patches and homogenous slicks the diameter is reported, and for trails and ribbon-like forms the length and width.
- For dispersed oil, the oil plume location, dimensions, shape and colour or appearance can be reported.
- Point 5. 'Methods of investigation' and point 6. 'weather and sea conditions' are less important in direct communications at sea in the oil spill area, between aerial observers and ground-truth monitoring and combating units. These points however were kept in the reporting format, for reporting to land-based authorities (post-flight reporting), or for in-flight reporting to monitoring and combating units that are not yet in the immediate vicinity of the spill area.

The aerial observation tasks (1) and (2) (see above), are fully covered when the aerial team has correctly filled in this aerial monitoring reporting format. It also allows the observers to report detailed information in a structured and concise way via marine VHF to the overall monitoring coordinator at sea, the On Scene Commander coordinating the response operations, or land-based authorities.

#### Reporting format on aerial monitoring of combatable oil spills 1. REPORTING AIRCRAFT (+ Organisation) 2. DATE & TIME Date (yymmdd) + Time observation (A-B-Z) ..... (.....) 3. LOCATION OF POLLUTION ... ° ...... ' N ... ° ....... ' W/E ... ° ...... ' N ... ° ....... ' W/E Oil slick: Position (lat/long) Pos. slick E: S (Start or begin); $\mathbf{E}$ (End); Thicker parts (only if combatable): $T_n$ (one/more centre(s) of Thicker, $T_1$ : ... ° ..... 'N $T_2$ : ... ° ..... 'N ... ° ..... ' W/E ... ° ..... ' W/E combatable parts of oil slick (incl. emulsions)): T<sub>1</sub>, T<sub>2</sub>, & T<sub>3</sub> $T_3$ : .... ° ...... ' N ... ° ..... 'W/E ... ° ..... ' N ... ° ..... ' N Pos. plume ... ° ...... ' W/E Oil plume: location S (Start); ... ° ...... ' W/E E (End). 4. DESCRIPTION OF POLLUTION a. Oil slick Length - Width (m or km) Slick Length ..... ; Width ..... b. Total coverage (%) Total coverage: ..... % c. Percentage of covered area coloured: (1) % sheen (i.e. silvery, grey, rain-(1) Sheen: bow and metallic); (2) discontinuous true oil colour: (2) % discontinuous true oil colour; (3) continuous true oil colour: (3) % continuous true oil colour; (4) emulsions ..... % (4) % emulsions. Est. Vol. = d. Estimated volume ..... m³ e. physical form/shape of slick O patches O ribbons/trails O homogenous slick O very fragmented/tar balls O other: ..... YES/NO f. Combating possible? f. Dimensions of thicker parts around $T_x$ : (Diameter or length/width, dependent on $T_2$ : Length ....; Width ..... $T_3$ : Length ....; Width ..... shape) (m or km) Plume Length .....; Width ..... g. Oil plume dimensions + shape/colour/appearance 5. METHOD OF INVESTIGATION a. Investigation method(s) a. O visual O SLAR O IR O UV O MWRM O LFS O video camera O identification camera O other: b. Photographs taken b. Photo's: YES / NO 6. WEATHER & SEA CONDITIONS a. Wind dir. .... degr. b. Wind force ..... Bft. a. wind direction; b. wind force; c. Visibility ..... km ..... Octa d. Cloud cov. c. visibility; d. cloud coverage; f. Current dir. .... degr. e. W.height ..... m e. wave height; f. current direction. 7. REMARKS and ADDITIONAL INFORMATION

## 2.5.3. Ground-truth monitoring of surface oil

## 2.5.3. Ground-truth monitoring of surface oil

### (1) Obtaining real-time results in the field of important oil properties

<u>Table 10</u>: Overview of physical, weathering and response effectiveness properties of the oil or w/o emulsion measured in real-time at sea during the exercise, the method or instrument used and the analysis time.

Parameter	Instrument or method	Normal analysis time
Viscosity	Haake Rotovisco VT 550	15 min.
Density	- Anton Paar density meter - Anton Paar SVM 3000 Stabinger viscosimeter	< 15 min.
Water content	Alcopol O 60% + heating	2 hours
w/o emulsion stability	Measuring free water separated from emulsion after period of time	First results: 30' Final results: 24 h A rapid indication on the stability can already be obtained in 2 min. via the emulsion breaker effectiveness
Film thickness (>3mm) of oil or w/o emulsion	Oil film thickness cylinder SINTEF	fesstathtaneous reading from a dinghy
Chemical dispersibility	Small field test (Concawe, 1988)	5 min.
Effectiveness of emulsion breaker	Alcopol O 60%	First results: 2' * Final results: 24 h

From the moment that oil is released from a ship into the marine environment, its behaviour and properties evolve due to various weathering processes. The oil will form a slick at the surface, will start spreading, drifting and fragmenting under influence of winds and currents; light volatile HC compounds will rapidly evaporate or will dissolve; wave energy can induce natural dispersion of the oil, and can trigger the formation of w/o emulsions at the sea surface (see 2.2.).

Via ground-truth monitoring at sea of the oil spill, real-time qualitative and quantitative data can be obtained which describe the weathering process of the oil and enable a better understanding of the fate of the oil spill. Ground-truth monitoring can also lead to a better evaluation of the effectiveness of certain response techniques, like chemical dispersants and type of skimmers to use. The parameters that can rapidly be measured at sea on the basis of oil sampled at the surface, the instrument and method used, and the normal analysis time, are summarized in Table 10.

In 2.2.1., more information is given on the parameters, on the instruments and on the

methods used.

### (2) Sampling strategy

<u>Table 11</u>: Criteria for good data sets from field monitoring (based on experimental field trials).

Environmental data	Good documentation of environmental data is needed: temperatures, wind, waves, currents, etc.	
Sampling frequencies	Typical sampling frequencies are, in time after releases in experimental field trials: 15 min., 30 min., 1 h, 2 h, 4 h, 8 h, 12 h, 24 h (the weathering processes are most drastic in the first hours after spillage)	
Sampling replicates	A high number of sampling replicates is better, because the oil properties can vary considerably within a slick. The number of samples will be limited however shortly after spillage, because of the need for a high sampling frequency.	
Surface w/o emulsions	A correct handing of surface emulsion is very important to obtain reliable samples for analytical characterisation of oil properties.	
Communication with aircraft	Need for good communication procedure between sampling boats and remote sensing aircraft, for guidance, and to enable a combination of both monitoring results.	

Based on the lessons learnt from experimental field trials, a series of criteria are listed (see <u>Table 11</u>) that are necessary in order to obtain good data sets for field monitoring. If a monitoring campaign is set up in the light of a marine pollution incident, these criteria should be carefully considered. However, a major difference between an experimental field trial and an incident is the time of arrival on scene, and the magnitude of an event. In an experimental field trail, monitoring teams are on the spot at the start of a controlled spillage, and sampling frequencies are therefore very high in the beginning.

In an incident with a sudden, accidental oil release however, the oil is being spilt several hours before a ground-truth monitoring team will arrive on site, even with the best effort and level of preparedness. The released oil will already have weathered to a certain extent (depending on the oil type and environmental conditions), and the properties changes will be less drastic at the moment that the monitoring teams arrive on scene and start sampling. Most probably, the oil will also already have spread over a large marine area. In other words: in accidental oil spills, the sampling frequencies can be lower at the start of sampling (depending on the time after spillage), and the sampling effort can be shifted towards the collection of more replicates in a wider area.

The sampling location within a slick must be based on visual inspection of the slick. The major part of the surface samples for analysis on board a research vessel should be taken in the thickest parts of the slick(s). Assistance from remote sensing aircraft

can be very valuable, in indicating and guiding ground-truth monitoring units to the thicker parts, especially the w/o emulsions (e.g. detected as IR white-hot). A sampling strategy for thick oil films and w/o emulsions and film thickness measurements involves a predefined pattern for sampling, with several stations, and several replicate samples per stations (if feasible). For instance, the sampling best starts cruising upwind in the thicker parts in the head of a slick, and going upwind, taking several bulk samples in true oil colour areas and w/o emulsions. Depending on the means available, the size of the monitoring boat(s), and the monitoring tasks, the workboat for surface sampling can be the same workboat as used for monitoring of hydrocarbon concentrations below a slick. The best solution however is to use a dedicated workboat for sub-surface oil monitoring, due to the different strategy for ground-truth monitoring of an oil plume (see 2.5.4. and 2.6.; see also Figure 5).

The prioritisation for analysis of samples in the field must be based on the capacity of the field laboratory. The final sampling plan must be decided in the field, based on the visual observation of the slick(s) (with information on the location, size and shape of the thicker oil/emulsion area(s), the fragmentation of the w/o emulsions), the weather conditions and the overall work load of the field personnel (e.g. will the monitoring of surface oil be in combination with the monitoring of dispersed oil in the water column, or not).

### (3) Bulk sampling and sample handling

At each station the samples of the surface oil/emulsion should be taken in the thicker parts (mainly in the front) of the slicks from a small sampling boat. A specially designed plastic net, or a bucket, is used to collect the oil from the surface. The sampling procedure is illustrated in <u>Figure 4</u>.

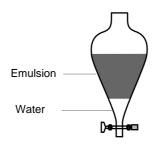
Step 1 of the collection procedure results in collection of considerable amounts of surplus water, which must be drained through a hole in the net. Additional surplus water must be drained off using a 3-L separation funnel. The sampling with the plastic net must be repeated until totally 2.5 - 3 L of water-in-oil emulsion is collected in the separation funnel. In order to obtain a representative w/o emulsion, surplus water must be allowed to settle in the separating funnel for about 10-15 minutes (depending on the oil type) before drained off together with approximately 0.5 L of the oil/emulsion. The funnel with the remaining 2 L of emulsion must gently be tilted 180° 10 times before distributing the oil/emulsion into different bottles and immediately transported to the laboratory at the research vessel for the different analyses. If the work boat for bulk sampling is too small (e.g. zodiac or RIB, i.e. Rigid Inflatable Boat) this sub-sampling can also be performed in the field laboratory on board the research vessel.

All bottles must be carefully labelled with sample ID, local time and weathering time. Additionally, sample ID, local time, weathering time, location in the slick and other relevant comments must be noted in the log journal of the sampling team.

Emulsion — Water —

Collection of surface oil/emulsion with a net (bucket) separating off free water from bottom.

2.



Transfer to a 3 L separation funnel, approximately 15 min. settling for draining of surplus (non-emulsified) water and  $\approx 0.5$  L of bottom emulsion.

- **3.** Gentle homogenisation (10 times 180° tilting) of the remaining bulk sample ( $\approx$ 2 L).
- **4.** Sub-sampling of bulk sample (1 bulk sample divided into different sub-samples for further analysis):
  - 2 x 250 ml bottles (one for field measurements (viscosity, dispersibility, density), the other for additional onshore laboratory measurements); the 250 ml field measurement bottle is subdivided in:
  - 2 x 20 ml bottle (emulsion stability)
  - 2 x 20 ml bottles (water content)
  - 2 x 20 ml bottles (effectiveness of emulsion breaker)
  - 2 x 20 ml bottles (chemical dispersibility)
  - 1 x 70 ml bottle (viscosity)
  - 1 x 20 ml bottle (density)
- **5.** Labelling of sub-samples:

Sample ID, local time and weathering time. Sample ID is for example D1 – A – 12, consisting of codes for the dinghy, the slick (if more than one), and the sample number respectively.

**6.** Logging in journal book:

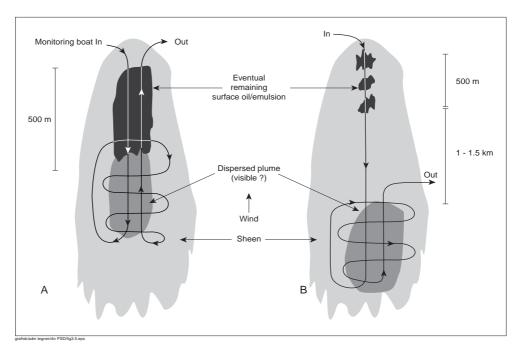
Sample ID, local time, weathering time, location in the slick and other relevant comments.

<u>Figure 4</u>: Procedure for surface oil and w/o emulsion sampling. If not possible to perform all steps in the dinghy, a minimum of step 1, 2 and 5 must be performed in the dinghy prior to delivery of the samples to the field-laboratory (central monitoring platform / research vessel).

### 2.5.4. Ground-truth monitoring of sub-surface oil

### (1) Sub-surface oil monitoring strategy

As already briefly mentioned in 2.2.1., the monitoring of dispersed and dissolved oil in the water column was performed during the NEBAJEX exercise with two types of UVF instruments, a Turner fluorometer (model 10 AU 005, used by CEDRE and SINTEF), and an Aquatracka fluorometer (Aquatracka-MiniBAT integrated system, used by MUMM).



<u>Figure 5</u>: Different strategies for monitoring of a dispersed oil plume in the upper layer of the water column. A: combined surface sampling and monitoring of oil plume from a dinghy; B: dedicated dinghy for monitoring of oil plume (Melbye, 2003).

Different strategies for monitoring of dispersed/dissolved oil (naturally or chemically dispersed) are shown in <u>Figure 5</u>. For the NEBAJEX exercise, a second RIB was dedicated to the task of UVF monitoring of naturally dispersed and dissolved oil and for monitoring of a chemically dispersed oil plume – in case the decision was made to chemically disperse oil from the Tricolor. During the exercise at the Tricolor site, UVF tracking was done with aerial guidance. The subsurface oil monitoring strategy shown in Fig. 5.b. was therefore simplified whereby only one track would be made through an oil slick, following the long axis of the slick downwards, while zigzagging around the axis (the latter only in case of larger slicks). In this way, any subsurface oil would be monitored in one single track from the beginning to the end of the slick.

### (2) Sub-surface oil monitoring with Turner 10 AU fluorometer

The Turner 10 AU 005 field fluorometer can be set up for continuous-flow monitoring of dispersed and dissolved oil in the water column. It can also be set up

to perform discrete sample analyses in a lab. This fluorometer is well-known for monitoring of subsurface oil, and has been used successfully in several experimental sea trials (e.g. Brandvik *et al.*, 1995; Lunel *et al.*, 1995; Hillman *et al.*, 1997). The effectiveness of dispersants, and dispersed oil in general, has also been successfully monitored with Turner fluorometers in a large-scale incident such as the Sea Empress in 1996 (Lunel *et al.*, 1996).

With a Turner fluorometer, concentrations of dispersed and dissolved oil can be measured in the water column, derived from the fluorescent properties of the aromatic components of mineral oil. Oil is pumped from a certain depth through a tube to the Turner UVF instrument e.g. mounted on board a dinghy, where the UVF measurement takes place.

The fluorometer beams a specific wavelength of light to excite fluorescent aromatic compounds, which in turn emit light at a different wavelength. The intensity of the emitted light is proportional to the concentration of the fluorescent compounds. The lower detection range of the Turner fluorometer is 10 parts per billion (ppb) for mineral oil. The fluorometer is calibrated in continuous flow mode before and after each survey. Performing preliminary bench calibration with several types of oil, and with the oil spilt in an accident, enhances the interpretation possibilities of the produced data. Without pre-sampling bench calibration, the fluorometer's signals can be related to oil concentrations only by collecting several water samples from the fluorometer for later laboratory analysis of oil concentration; the UVF signals obtained at sea only provide a qualitative index of differences in oil concentrations between the polluted and non-polluted water column, and between the polluted area with chemically dispersed oil *versus* the area polluted only with naturally dispersed oil.

Many factors in seawater (e.g. turbidity) affect UVF signals, causing background values. For this reason, a UVF sub-surface oil monitoring survey best starts upwind and upstream of a slick, so that the background values of the unpolluted surrounding water can be identified. When moving towards the slick, and pumping polluted seawater from below or behind of the slick, relative increases of fluorescence will be an indication of the presence of dispersed and/or dissolved oil in the water column; if a bench calibration has been performed in lab before the *in situ* monitoring, oil concentrations can be roughly estimated on the basis of the UVF signals in real time. However, absolute oil concentrations can only be obtained after GC-MS analysis in lab of validation samples (samples taken from the Turner UVF to validate the oil concentration results obtained in the field). The validation samples are taken via the Turner UVF pumping system on board of the dinghy, when a peak UVF signal is registered during a survey.

It has been demonstrated that subsurface oil concentrations calculated from UVF signals often underestimate the concentrations in the corresponding water samples, and the discrepancies are larger for samples taken shortly after the start of a discharge. This time variation indicates that the responses from the UVF instruments could be dependent on the size distribution of the oil droplets in the rising oil plume. The surfacing oil droplets will be large shortly after the start of the discharge and will decrease in size with time. It is logical that the UVF response to a certain concentration could be smaller for these large droplets than for the fine droplets

formed in laboratory calibration samples, probably due to the smaller surface to volume ratio and the fact that the fluorescence to a large extent is a 'surface' phenomenon.

### (3) Sub-surface monitoring with the Aquatracka-MiniBAT

In 2002 MUMM purchased a submersible Aquatracka UV fluorometer for the detection of aromatic hydrocarbons in a water body, together with a MiniBAT undulator. The MiniBAT undulator (Guildline 8820 MiniBAT) is a small (75 cm long), remotely controlled towed instrumentation platform with an automatic bottom following and avoidance. The integrated MiniBAT-Aquatracka system (MiniBAT integrated with a SeaBird SBE19 and the Aquatracka fluorometer), can detect relative hydrocarbon concentrations and has an operating depth of 60 m.

The basic UVF measurement principles are not different from the explanation for the Turner UVF (see above). After several test tracks in the Belgian coastal waters, it was concluded that with the Aquatracka-MiniBAT system, significant background fluorescence is measured at varying depths. MUMM performed preliminary bench calibrations for different types of oil before the exercise. A bench calibration with the TRICOLOR oil was performed in lab after the NEBAJEX exercise, to enable a better estimation of oil concentrations found under the oil slicks. However, even with such bench calibrations, an underestimation of oil concentrations of dispersed oil can also take place with this Aquatracka due to the presence of large oil droplets (problem of surface to volume ratio; see above). As for the Turner, the Aquatracka is able to detect the presence of dissolved and naturally or chemically dispersed oil in the water column, through differences in fluorescence values when going through the water column. The lower detection range of the Aquatracka is 1 ppb, the upper detection range depends on the type of oil monitored, varying from 100 ppb for marine diesel (rich of PAHs) to e.g. 1,2 ppm for bunker oil (Di Marcantonio, in prep.). A disadvantage of the Aquatracka-MiniBAT system is that measuring absolute concentrations in the water column is not possible, because water is not pumped on board the RIB, but flows through the submerged fluorometer at a certain depth. Because of this, no validation samples can be taken at the exact moment when a peak UV value is indicated. Water samples had to be taken by means of a Winchester bottle. A Winchester bottle is a shallow water sampler used for hydrocarbon monitoring by CEFAS; it has been in routine use at CEFAS for more than 15 years, and has proved to be both robust and reliable (Kelly et al., 2000). Water samples taken during the exercise with the Winchester bottle were to be brought to a specialised lab for oil concentration measurements with GC-MS, and by doing so served as 'rough' validations of oil concentrations measured in the field.

## 2.6. Objective 3: real-time in situ monitoring of effectiveness of dispersants

Given the considerable limitations of mechanical recovery means (in case of unfavourable environmental conditions, long mobilisation times and/or ETA's, ...) dispersants can be a justifiable response alternative in respect of NEBA. Dispersants can result in a reduction of the overall environmental impact, especially when they

are applied in deeper offshore waters. When applying dispersants, the oil is shifted from the sea surface to the water column. This shift drastically changes the fate and impact of the oil. The use of dispersants therefore always leads to a trade off between impacted areas, e.g. between the less oil sensitive open sea areas and the highly sensitive shallow coastal waters. Two major questions arise when dispersants are used on an oil slick:

- How effective is dispersant application likely to be?
- Is the oil dispersion resulting in a reduced impact to the environment?

In order to evaluate the effectiveness of dispersant application by ground-truth monitoring teams in the field, a two-step approach was to be tested during the NEBAJEX exercise:

- (1) Oil dispersibility testing before application: see dispersibility test of surface oil sample as discussed in 2.5.;
- (2) Effectiveness of chemical dispersion: in case the oil is dispersible, dispersants were to be applied on the slick, and their effectiveness to be monitored:
  - a. via aerial surveillance (observation of oil plume); in this way a rapid qualitative evaluation can be made of the dispersant effectiveness;
  - b. in a semi-quantitative way, through ground-truth subsurface oil monitoring with the UV fluorometers (Turner and/or Aquatracka-MiniBAT; for methodology see 2.5.4.). Validation samples had to be taken to determine the absolute oil concentrations in the oil plume in a specialized lab after the exercise.

As for surface monitoring, a monitoring frequency of a dispersed oil plume is considered beneficial. A typical oil plume monitoring frequency is e.g. performing a UVF track through the water column 1 h, 2 h, 3 h and 4 h after dispersant application.

# 2.7. Objective 4: Application of mathematical models in support of NEBA

Oil spill models are very powerful assessment tools that are commonly used during oil pollution incidents at sea. Most operational models can simulate the trajectory of the spilt oil over a period of a couple of days. CEDRE calls upon Météo France for oil spill trajectory simulations with the Mothy model. MUMM uses its own oil spill behaviour models (Mu-Slick and Mu-Slicklets) to simulate the trajectory, the spreading and the weathering of the spilt oil. SINTEF performs oil spill trajectory simulations and also simulates the weathering process of the oil, via the oil weathering model (OWM). Its OSCAR model can simulate the environmental impact of a spill in three dimensions, and for different response strategies.

The system of models developed at MUMM for modelling oil spills (Scory, 1991; Scory, 2003<sup>5</sup>) is of direct interest for the purpose of NEBAJEX. It is made of (1) an oil spill behaviour model "MU-slicklets" and (2) a set of models and information processing tools, exploiting the results of the surface model in order to assess the consequences of the pollution at the environmental and socio–economical levels.

The environmental conditions which are relevant for the oil spill models are, routinely, provided by the operational forecasting system of MUMM:

- the meteorological conditions (wind intensity and direction) are forecasts issued by the UK Meteorological Office;
- the currents are provided either by MUMM's 2D storm-surge model or by the 2D mode of the operational 3D storm-surge model (based on "COHERENS" community model, see <a href="http://www.ac.be/coherens/">http://www.ac.be/coherens/</a>)6;
- and, finally, significant wave heights, used as a measure of the surface turbulence intensity, are provided by a 2<sup>nd</sup> generation wave model.

The oil spill behaviour model "MU-slicklets" is hybrid (deterministic/probabilistic) model designed to forecast the fate of an oil spill at sea. "MU-slicklets" was developed as an extension of the simpler model "MU-slick". The original "MU-slick" model is based on the concept of a circular slick, (1) spreading under the influence of the endogenous forces (gravity, viscosity, inertia and net surface tension at its edge), and (2) drifting as a whole under the combined influence of wind and currents. The model includes functions to describe the major natural weathering processes that affect the repartition of oil in the marine environment: evaporation, vertical dispersion, emulsification and dissolution.

In the new oil spill behaviour model "MU-slicklets" the oil slick is modelled as an ensemble of particles having their own characteristics and behaviour. Most of the processes described in MU-slick are now modelled as advective processes that affect each of the particles individually. First order estimates of the oil concentrations in the water column and of oil that sediments are derived accordingly. Several parameters that drive these processes still need further tuning. The NEBAJEX exercise offered an extra opportunity to do so.

Finally, a set of models and information processing tools use the results of the oil spill in order to assess the consequences of the pollution at the environmental and socio-economical levels. This post-processing system and the user interface are currently undergoing a major refit.

#### (2) SINTEF Oil Weathering Model (OWM) and OSCAR 2000 model

<sup>&</sup>lt;sup>5</sup> These models are to be considered as research models, undergoing continuous development. Some of their characteristics and the parameterisation used may have been updated since these reports were issued.

<sup>&</sup>lt;sup>6</sup> Work is in progress to take full advantage of the description of the vertical structure of the current given by the 3D hydrodynamic model in the oil behaviour model.

The SINTEF OWM calculates the changes in oil properties due to weathering under user-specified environmental conditions (oil film thickness, sea state and temperatures) and based on data from the standardized laboratory weathering methodology previously described (see Figure 3). The current version of SINTEF-OWM runs under Microsoft Windows on a personal computer. The predictions are compared to measured viscosity values with the same crude weathered in the meso-scale flume basin (simulating wind conditions corresponding to 5-10 m/s wind) and in the field (when the wind speed varied between 5 and 8 m/s during the experiment; NOFO 1995 trial). By combining the predictions of the increase in emulsion viscosity from the weathering modelling with the results of the chemical dispersibility study, the viscosity prediction chart can, for each specific oil, be divided into various "dispersibility areas". This makes it possible to give an estimate of the "time-window" for effective use of dispersant under the chosen sea conditions.

The SINTEF OWM is a powerful tool for evaluation of different oil spill response methods, like for determining the time window for effective use of dispersants for different sea states. The model can show its excellence in cases where the weathering properties have been tested on beforehand in laboratory, which is the case for every Norwegian oil produced. The difference between SINTEF OWM and other models that simulate oil weathering is that it performs a curve fitting of laboratory data on viscosity of emulsions. Other models only use the Mackay curve. In spill situations the SINTEF OWM is used in combination with the OSCAR 2000 model.

SINTEF's OSCAR model system has been developed to supply a tool for objective analysis of alternative spill response strategies. Key components of the system are:

- a data-based oil weathering model,
- a three-dimensional oil trajectory and chemical fates model,
- an oil spill combat model,
- exposure models for fish and ichthyoplankton, birds, and marine mammals and
- tools for exposure assessment within GIS polygons (delineating, for example, sensitive environmental resource areas).

OSCAR has been applied to the analysis of oil spill response strategies for both offshore platforms and coastal terminals. OSCAR provides, for alternative spill response strategies, a basis for comprehensive, quantitative environmental impact assessments in the marine environment. The model calculates and records the distribution in three physical dimensions plus time of a contaminant on the water surface, along shorelines, in the water column, and in the sediments. The model is embedded within a graphical user interface in Microsoft Windows, which facilitates linkages to a variety of standard and customized databases and tools. These latter allow the user to create or import wind time series, current fields, and grids of arbitrary spatial resolution, and to map and graph model outputs. Oil and chemical databases supply physical-chemical and toxicological parameters required by the model. Results of model simulations are stored at discrete time-steps in computer files, which are then available as input to one or more biological exposure models.

OSCAR employs surface spreading, advection, entrainment, emulsification, and volatilization algorithms to determine transport and fate at the surface. In the water column, horizontal and vertical advection and dispersion of entrained and dissolved

hydrocarbons are simulated by random walk procedures. Partitioning between particulate-adsorbed and dissolved states is calculated based on linear equilibrium theory. The contaminant fraction that is adsorbed to suspended particulate matter settles with the particles. Contaminants at the bottom are mixed into the underlying sediments, and may dissolve back into the water. Degradation in water and sediments is represented as a first order decay process. Algorithms used to simulate the various processes controlling physical fates of substances are described in Aamo *et al.* (1993) and Reed *et al.* (1995 and 2004). It should be noted, however, that the model is undergoing continuous development, and that some of the algorithms may have been updated since these papers were published.

Parameters defining the response capabilities for mechanical recovery and dispersant application systems can be supplied by the user or taken from a database. Mechanical recovery systems include specific units such as booms, skimmers and towboats (response vessels), as well as loading barges for storage of recovered oil. Each unit is characterised by parameters such as boom swath, tow velocity, skimmer rate, transfer velocity, loading capacity and loading time. Recovery efficiency is assumed to depend on sea state (significant wave height, which in OSCAR is computed as a function of wind speed, fetch, and water depth). Under ideal conditions, a maximum percentage of the oil entering the boom can be recovered, with the remaining leaking under the boom. Effectiveness is reduced as wave height increases, and goes to zero at a user-supplied threshold wave height. The user can also specify whether operations continue at night (for example if infrared monitoring equipment is available). OSCAR computes sunrise and sunset from latitude and longitude and calendar day.

Chemical dispersant system may be either helicopters or fixed wing aircraft or spray boats, each characterized by parameters such as transfer and operational velocities, endurance (maximum duration of each trip), onboard storage volume of dispersants, spray swath and spray rate. The surface oil mass that can be treated per unit time depends on the spray rate and the dispersant-to-oil ratio, while the dispersing rate (amounts of oil mixed into the water column per unit time as a result of treatment) is supposed to improve with increasing wind. However, dispersant operations are supposed to be limited by a system dependent threshold wind speed.

Each oil spill combat system is located at a certain base station and is given a certain mobilization time. The arrival time of the system at the spill site is thus a sum of the mobilization time and the transfer time – the latter given by the transfer speed and the distance from the base to the spill site.

OSCAR allows the assignment of specific operational strategies to each boom-skimmer or dispersant application system being simulated. A standard strategy for blowout situations is to position mechanical recovery equipment as near the source as possible to increase the potential encounter rate between booms and oil. If all units follow this strategy, then oil that escapes this initial response action will continue to drift unhindered. Unless dispersed naturally or by a directed dispersant action, this oil can later threaten natural resource areas 'down-stream' of the source. The oil response scenarios sometimes therefore employ a mixed strategy, wherein some skimmers work near the source, and others collect oil threatening identified

natural resource areas. Dispersant application units can be deployed in similar ways.

An illustration of the model capabilities is shown in Figure 6.

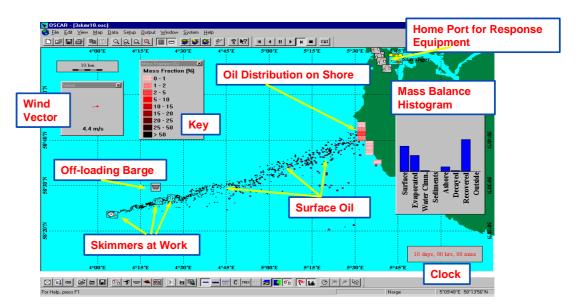


Figure 6: Screen snapshot of OSCAR simulation.

# 2.8. Additional objective: validation of the Bonn Agreement Oil Appearance Code (BAOAC)

During the last meeting of the Bonn Agreement Contracting Parties (Bonn Agreement 2003b), with representatives of Belgium, France, Norway and the European Commission, a new Bonn Agreement Oil Appearance Code or BAOAC was accepted for volume estimations of oil spills at sea (see table 6). At BONN 2003 it was agreed that a further validation of this BAOAC was considered highly useful, and that CP's should try to validate the BAOAC further at the occasion of future field trials.

In the NEBAJEX exercise, an attempt was therefore made to further validate the BAOAC. For this purpose, several pad samples have been taken during the exercise by the RIB dedicated for bulk sampling. Teflon sheets were used to collect sheen oil films, whereas polypropylene pads were used for measurements in patches of discontinuous and continuous true oil colours (Melbye, 2003).

## 3. Preparatory work and preparatory field trials

## 3.1. POLEX 2002, 03 Sept. '02

A first NEBA sea trial was carried out on the occasion of a national pollution response exercise organized by MUMM in Belgian waters in 2002 (POLEX 2002). MUMM deployed an aerial and a ground-truth monitoring team, to test certain monitoring procedures and strategies, instruments and communication procedures to be used in the NEBAJEX project (detail on procedures and strategies, instruments, methods was given in Chapter 2.). In POLEX, a slick would be created at the sea surface with a non-toxic vegetable oil FINAGREEN, that has shown in previous national pollution combating exercise to be a good simulator of oil at the sea surface. MUMM 's means deployed in this exercise were the research vessel 'Belgica' (acting as central monitoring platform), the RIB 'Tuimelaar' (acting as monitoring workboat), and the Belgian remote sensing aircraft. Within this NEBAJEX-monitoring part of POLEX 2002, the following limited objectives were successfully executed by MUMM personnel:

- To train observers in making aerial monitoring observations of an oil slick (location, time, dimensions and coverage, colour/appearance, behaviour and central position of slick) and to report the observations in a standardized way to the overall monitoring coordinator on board the Belgica;
- To deploy the bottom- and hull-mounted ADCP (Acoustic Doppler Current Profiler), for current measurements at sea, and for evaluation of the possibilities offered with these instruments for mathematical model validations;
- Testing sampling of surface slick under guidance of aircraft;
- Testing of subsurface oil monitoring strategy (tracking along the length axis of a slick, while zigzagging) as described by SINTEF;
- Testing and training of various communication procedures: air-sea (aircraft-Belgica), sea-land (Belgica-Modellers at MUMM Brussels), sea-sea (On Scene Commander- central monitoring coordinator; Belgica-small workboat).

The experience and lessons learned were use in the discussions during the NEBAJEX workshop (see below) and in the development of procedures and strategies.

### 3.2. NEBAJEX workshop, Brussels, 25-27 Sept. '02

On 25-27 September 2002 a workshop was organised by MUMM in Brussels, with participants from MUMM, CEDRE, SINTEF (research institutes involved in NEBAJEX), and also from TNO and Rijkswaterstaat (Dutch institutions responsible for the NEEBA project). The workshop resulted in:

- (1) A common understanding of NEBA and of the added value of real-time *in situ* monitoring in support of NEBA (see 1.).
- (2) A better understanding of the relevant experience of each of the three 'NEBAJEX' institutes in crisis management, in pollution response, in the application of NEBA, in the real-time monitoring at sea of oil spills (field trials and/or accidents), and in the application of assessment tools.

- (3) A set of clear objectives for the NEBAJEX exercise.
- (4) A basis for a common monitoring and NEBA approach: it was decided what oil properties should be monitored (in the field + in lab), what monitoring procedures, strategies and methods should be developed and tested, for surface and subsurface oil. The following elements were also thoroughly discussed: a possible exercise scenario, the role of remote sensing aircraft in the exercise, the application of mathematical models, and finally, the use of monitoring and modelling results as an input for the NEBA evaluation and decision-making Refe**procesis** made to the detailed workshop report drafted by MUMM (Schallier, 2003a), of which the main parts and conclusions are further discussed in this report.

## 3.3. Preparatory work – meeting in Brest (France), 2-3 april '03

After the workshop of September 2002, preparations for the organisation of the joint (NEBAJEX) exercise were initiated by the three institutes. An experimental oil pollution monitoring exercise was scheduled for the first week of June 2003 (2-6 June 03). The following aspects were developed, and discussed in a preparatory meeting in Brest on 2-3 April '03:

- Day-to-day planning of operations in consultation with the French Navy (CEPPOL); drafting of exercise scenario and additional (optional) scenarios in case of extremely bad or good weather.
- Logistical organisation: organisation and coordination of naval and aerial means, and other (combating) means; dispersant supply and way of application for exercise (French Navy, CEDRE and MUMM).
- Choice of type and quantity of oil to be used in the exercise, to be supplied by Total S.A., and agreement on pre-treatment (pre-weathering, by evaporation of light ends) at CEDRE, for safety reasons; pre-study of the chosen 'NEBAJEX-DEPOL 03' crude oil in Polludrome at CEDRE.
- Defining operational limitations on the basis of environmental criteria (working limits); Security and safety requirements (mainly CEDRE).
- Discussion on method for release of oil in respect of the objectives of the NEBAJEX exercise.
- Detailed planning of monitoring and sampling strategy and frequency (taking the hours of daylight into account that are available in June).
- Ground-truth monitoring and sampling procedures (initiative: SINTEF (Melbye, 2003); hereby assisted by MUMM and CEDRE); listing and collection of necessary instruments and monitoring/analysis equipment and purchase of additional equipment (coordination MUMM).
- Aerial monitoring: definition of tasks and development of procedures and strategy, coordination of remote sensing aircraft that acknowledged participation in the exercise. This was mainly done by MUMM, with the participation from the French customs, and input from CEDRE and SINTEF.
- Developing communication procedures between the different monitoring teams (mainly MUMM, in consultation with CEDRE and SINTEF).
- Coordination of NEBAJEX objectives in exercise, with other, additional scientific experiments (dispersant effectiveness on emulsified oils, testing of new remote sensing systems, testing of new aerial dispersant spraying system (POD dispersant application system), Bonn Agreement Oil Appearance Code validation).

Due to new, significant stranding of tar balls of oil from the Prestige along the western coastline of France (coast of Finistère and Morbihan) at the end of May 2003, the French Navy decided to postpone the NEBAJEX-DEPOL 03 exercise, until the beaching along the Brittany coast of any remaining Prestige oil would cease. MUMM therefore decided to carry out an alternative scenario in Belgian waters during the week of 2-6 June '03.

## 3.4. Belgica campaign in Belgian waters, 3 June '03

Due to the last-minute cancellation of the June '03 NEBAJEX-DEPOL exercise in French waters, MUMM decided to test to the best possible extent the various monitoring procedures already developed in a smaller scale exercise in Belgian waters (Schallier, 2003b). In this exercise, two minor DIESTER oil slicks were created and monitored at the sea surface. DIESTER is a non-toxic vegetable oil that was applied to simulate the behaviour of mineral oil at sea. The following objectives were met in this exercise:

- Collecting information on environmental conditions on the exercise location (via research vessel Belgica that continuously measures the relevant oceanographic and meteorological data; cf. ODAS system, see 2.5.1.).
- Training of aerial monitoring of an oil spill and reporting procedures (see 2.5.2.).
- Testing ground-truth monitoring procedures and instruments (such as sampling of surface slick, further testing of Aquatracka fluorometer, MiniBAT undulator, Winchester bottle; see 2.5.3. and 2.5.4.).
- Training of communication links and co-ordination between small ground-truth work boats, the research vessel acting as central monitoring platform, the Belgian remote sensing aircraft and the modellers on land.
- Training of aerial guidance of a dispersant spraying vessel and of ground-truth monitoring teams.
- Training of environmental impact evaluation and Net Environmental Benefit Analysis (NEBA) on the basis of information collected during monitoring, modelling, and ecological sensitivity of threatened area.

This exercise proved to be an excellent training opportunity for the scientific staff of MUMM, in terms of co-ordination, communication, monitoring, and guidance procedures and in the application of NEBA. It was also demonstrated that the research vessel Belgica is an ideal vessel for the role of central monitoring platform in case of a major oil spill, mainly owing to the following elements:

- The numerous communication facilities on the bridge,
- The large laboratory facilities,
- The large working deck,
- The possibility to collect the most important environmental parameters, mainly via the ODAS system,
- The fact that the Belgica can act as an official government vessel representing the Coastal State on the location of a marine pollution incident (The Belgica is a Belgian military oceanographic vessel managed by MUMM).

## 3.5. Laboratory and field work with Aquatracka fluorometer and MiniBAT undulator (MUMM)

In 2002-2003, MUMM purchased an Aquatracka fluorometer and a MiniBAT undulator (see 2.5.4.). After the small-scale field trial during the Belgica campaign of 3 June 2003, where the Aquatracka-MiniBAT system was deployed for the first time in a small-scale sea trial, it was decided that:

- The operational range of the Aquatracka instrument should be further determined, for different types of oils, via bench calibration in the chemical lab of MUMM.
- Because of the high background fluorescence values measured with the Aquatracka during previous test tracks, with a Rigid Inflatable Boat (RIB) at sea, or during the Belgica campaign of 3 June '03, Spatial and seasonal variations of background fluorescence values at sea and in shallow and turbid coastal waters should be determined.

Both important aspects were further dealt with in 2003 (Di Marcantonio, in prep).

In MUMM's chemical lab, a series of oil concentrations of different oil types (gas oil, diesel, crude oil, jet fuel, gasoline, heavy fuel and bunker fuel) were tested with the Aquatracka. The concentration range varied from 0 ppb till 10 ppm, or from 0 ppb till the maximum detection concentration (*i.e.* instrument's saturation point for this type of oil). All oil types were calibrated with the one reference product, carbazole (Aquatracka reference product for fluorometry of mineral oil).

The laboratory bench-calibrations showed that the maximum concentration or saturation point that can be detected by the Aquatracka can vary significantly for different oil types. For marine diesel, the saturation point is merely 100 ppb in seawater; for bunker fuel, the saturation point is 1200 ppb (= 1.2 ppm) in sea water; the NEBAJEX-DEPOL 03 crude oil (oil supplied by TotalFinaElf for the initially planned NEBAJEX exercise) has the same saturation point of 1200 ppb.

MUMM also investigated why relatively high background fluorescence values were measured with the Aquatracka in the Belgian coastal waters as well as further offshore. The company argumented that the high turbidity in the Belgian marine areas was the cause of this. This was tested in lab by filtering of all SPM of seawater and coastal water samples. However, even filtered sea- and coastal water did not show a significant decrease of fluorescence signals. A second step was to extract dissolved components in seawater, but also in this case no decrease of the UVF background signal was observed. These results indicate that the high background UVF signals in the Belgian marine areas are caused by (one or several) unidentified polar substances in seawater.

The three major conclusions of the lab calibration tests with different oil types and water types, were:

- The oil detection interval and saturation point were very dependent on the type of oil
- The oil detection interval is dependent on the (surrounding) water.
- The high background value has no influence on the oil detection interval: because of the logarithmic course of the UVF signal, the measured values go gradually slower towards the maximum.

MUMM's platform for deployment of the Aquatracka-MiniBAT integrated system is the 'Tuimelaar', a RIB which can operate independently from any larger, sea-going vessel. The testing of and training with the Aquatracka-MiniBAT system on board the Tuimelaar took place on several occasions. The Aquatracka-MiniBAT was not only used during the Belgica campaign of 3 June '03, but test tracks and training sessions with this UVF system were also done during independent Tuimelaar campaigns in the Belgian marine areas:

- Tuimelaar campaigns of 15 and 18 April 2003 (first testing/training stage);
- Tuimelaar campaigns of 11, 16 July '03 (detecting spatial variations in background UVF signals, mainly along the coastline);
- Tuimelaar campaign of 5 September '03 (further detecting of background UVF signals; Aquatracka fluorometer tracking at 5 knots perpendicular on the coast, towards the open sea).

## 3.6. Preparatory work for postponed NEBAJEX exercise – meeting in Brest (France), 27 August '03

The NEBAJEX-DEPOL 03 exercise, which was initially planned in the first week of June '03, and had been cancelled, was again scheduled to take place in French waters off Brittany in week 38, from 15-19 September 2003. Due to the important decrease of daylight hours in September, the detailed scenario of the initial sea trial needed to be redrafted (ground-truth monitoring), including the succession and role of each remote sensing aircraft (aerial monitoring), the time after weathering of dispersant spraying, etc. Because of the need to adapt the exercise scenario to the different seasonal situation, a meeting was organised at CEDRE in Brest on 27 August 2003, where the different abovementioned points already discussed in the first preparatory meeting in Brest in April 2003, were examined re-adapted whenever necessary.

As it turned out, the exercise off Brittany had to be cancelled by the French Navy merely one week before 15 September, because major oil releases from the Tricolor during wreck removal operations (see 4.1.) required re-directing naval resources to this shipwreck site off Dunkirk. This notwithstanding, **the work invested by MUMM, CEDRE and SINTEF in the preparation of this sea trial was far from futile**. On the contrary, it enabled a quick and efficient change of plans in September, as it was decided at the last minute to hold the main NEBAJEX exercise around the wreck of the Tricolor in French (and nearby Belgian) waters, off Dunkirk.

## 4. NEBAJEX exercise 15-18 Sept. 2003: operations & results

#### 4.1. Introduction

### 4.1.1. A last minute shift of exercise plans

This chapter presents the monitoring activities during the main NEBAJEX exercise in September 2003. All three scientific institutes (MUMM, CEDRE and SINTEF) participated in this central exercise of the NEBAJEX pilot project. Much of the information of this chapter is derived from Schallier (2003b) and Schallier *et al.* (subm.).

The NEBAJEX main exercise had been planned to take place in French waters off Brittany in week 38 of 2003 (15-19 Sept.03). This NEBAJEX-DEPOL 03 exercise had been prepared to the last detail (with amongst others a final preparatory meeting in Brest (France) on 27 August '03 with participation of the three scientific institutes, the French Navy and Customs) (see 3.6.).

Unexpectedly, in the weekend of 06-07 September a major amount of oil (cf. reported by Dutch authorities) was released from the TRICOLOR wreck in French waters off Dunkirk due to intense cutting operations. On Monday 08 September, a Belgian remote sensing aircraft observed a spill of magnitude greater than 100 m³ (see 4.1.2.). Because of this major pollution at the TRICOLOR site in the beginning of week 37, a general oil pollution response was initiated. Significant French, Belgian and Dutch means, assisted by British means, were activated *inter alia* for regular aerial surveillance of the oil pollution, and for mechanical recovery operations. Other means were placed on standby. MUMM and CEDRE personnel were involved in the response operations and in incident management.

In view of these developments, the French authorities (PREMAR) decided to cancel the NEBAJEX – DEPOL 03 exercise in Brittany, because:

- (1) the French BSHM vessel, which was scheduled for participation in NEBAJEX-DEPOL03 as On Scene Commanding and central operations vessel, was sent to Dunkirk in the northern part of France to reinforce the French oil recovery means,
- (2) significant oil releases could still be expected during forthcoming Tricolor cutting and hoisting operations in week 38 (*i.e.* week of NEBAJEX-DEPOL 03 exercise),
- (3) MUMM and CEDRE personnel were involved in the follow-up of this new TRICOLOR pollution incident of mid-September,
- (4) it became very difficult to keep on justifying an experimental release of additional oil after the recurrent and recent sea and shoreline pollutions caused by both the TRICOLOR and the PRESTIGE oil spills in 2003.

After consultation with its partners to the NEBAJEX project and with the European Commission, MUMM decided that the NEBAJEX-DEPOL 03 experimental exercise in Brittany waters could adequately be replaced with a full scale oil monitoring exercise held at the TRICOLOR site. A scientific monitoring of further oil releases from the TRICOLOR wreck would be performed in real-time at sea, the research vessel 'Belgica' remaining the central pollution monitoring platform.

#### 4.1.2. Overview of the TRICOLOR incident

On 14 December 2002 the car carrier 'Tricolor' collided with the containership 'Kariba' in French Exclusive Economic Zone off Dunkirk in the Dover Strait, near UK and Belgian waters. The oil pollution resulting from this initial collision was

limited. The Kariba, which was only slightly damaged, sails to the port of Antwerp (Belgium). The Tricolor however sank on the spot, in the middle of an important navigation route, at location 51°22′ N and 02°12′ E. The wreck sank at a depth of ca. 35 m, and one side was visible at the sea surface at low tide. It represented an imminent danger for further collisions, and for the marine environment. The Tricolor carried 1988 tons of at least four different heavy fuel oils (HFO), 167 tons of marine diesel oil (MDO), some 50 tons of lubricating oil, and several tons of gas oil and gasoline (automotive fuel of cargo). The French authorities ordered the oil to be pumped out and the wreck to be removed. The ship owner and company agreed. The removable oil volumes were pumped out by the end of February 2003. A salvage consortium "Combinatie Berging Tricolor" started with the difficult task of salvage of the more than 200 m long car carrier. Although several safety measures were taken, such as navigation warnings, placing of warning buoys and positioning guard vessels, other collisions and pollution incidents took place, apart from numerous near-collisions:

- (1) On 16 December 2002, the small vessel 'Nicola' collided with the Tricolor wreck. Owing to the fact that the Nicola was empty, the damage to the Tricolor and resulting oil pollution was minimal.
- (2) The tanker 'Vicky', carrying 66.000 m³ of diesel, collided with the wreck on January 1, 2003. Again an amount of HFO escaped from the Tricolor, whereas the Vicky lost at least 200 m³ of oil (mainly fuel, gas-oil). Several hundreds of oiled seabirds stranded along the Belgian [and French?] coast.
- (3) On 22 January 2003, the hull of the wreck got damaged during salvage operations and resulted in a major oil spill incident at sea. At least 200 m³ of (mainly) HFO escaped from the cracked and partially collapsing hull. The oil spill had a huge impact on wildlife. Because of periods of strong onshore winds, more than 18.000 seabirds stranded along the North-French, Belgian and Southwest-Dutch coastline. Along the Belgian coast 9.177 birds of 32 different species were collected.

Although further collisions or incidents were avoided in 2003, the surrounding coastal states were fully aware of the fact that oil spillages could not be avoided during the salvage operations. The wreck was to be cut in nine pieces, and each hull section hoisted on a pontoon and transported to the port of Zeebrugge (Belgium). During these cutting and hoisting operations, it was expected that the oil remaining in the wreck could escape into the sea. This residual oil consisted of up to 200 m<sup>3</sup> HFO, up to 20 m³ MDO, up to 10 m³ of lubes, and a couple of tons of automotive fuel (i.e. estimates from salvage consortium). In the weekend of 6-7 September 2003 a significant amount of oil escaped from the wreck due to intense cutting operations, and drifted towards and within the Belgian EEZ. The oil spill was spotted by Dutch authorities, who sent a dedicated oil pollution combating vessel on site, which recovered ca. 50 m<sup>3</sup> of w/o emulsion in two days. The 'Union Beaver', a mechanical recovery vessel from the salvage consortium that was on continuous standby at the Tricolor wreck, also started recovery operations. Early on Monday 8 September, the Belgian and Dutch remote sensing aircraft observed a major oil pollution spread out in the Belgian EEZ, with an estimated volume of more than 100 m<sup>3</sup>. Later that day, the British and French remote sensing aircraft also spotted the oil spill, reporting however a drastic decrease in estimated volumes and dimensions. The aerial observers also reported the presence of debris and macro-algae floating in the oil

slick. The next morning, when the Belgian aircraft was surveying the Belgian EEZ, the 'major' oil spill observed the day before had entirely disappeared from the sea surface. No immediate explanation could be found for this strange oil behaviour.

Although the major oil pollution had partly been combated and had disappeared from the surface, significant oil releases could still be expected during planned cutting and hoisting operations in week 38 (15-19 September 2003). The NEBAJEX exercise, which was originally planned off the Brittany coast that week, got cancelled. After agreement with CEDRE, SINTEF and the European Commission, and with the kind permission of the French Maritime Prefect, MUMM decided to hold the NEBAJEX exercise at the Tricolor site. This 'adapted' NEBAJEX exercise aimed at monitoring and evaluating oil pollution that would accidentally escape from the wreck during week 38. It was considered beneficial that an intense monitoring campaign for the purpose of NEBA could be performed in the light of the Tricolor incident, because the weathering properties of the oils from the Tricolor were hardly known before the exercise. The three scientific institutes also hoped that useful information would be obtained that could explain the unusual behaviour of the oil spill the week before.

The NEBAJEX exercise started on Monday 15 September and the oil pollution monitoring activities lasted till Thursday 18 September. At Thursday noon, the weather conditions got worse and as the working limits for the exercise were exceeded, the exercise was stopped.

Apart from the BELGICA, two small boats (the Belgica's rigid inflatable boat (RIB 1) and MUMM's "Tuimelaar" (RIB 2)) participated in this altered NEBAJEX exercise, operating at the sea surface to perform oil sampling and sub-surface oil monitoring, as well as the Belgian remote sensing aircraft B-02 (Belgian Army 402). The aircraft perform aerial monitoring of the TRICOLOR incident and offered guidance to the monitoring platforms at the sea surface. The Belgian Navy vessel VALCKE was also on standby that week in Zeebrugge and could be called upon if it was decided by the BELGICA (after agreement with the French On Scene Commander (OSC) in case the oil was still in French waters) to chemically disperse the drifting oil.

### 4.2. Overview of operations during the NEBAJEX exercise

## 4.2.1. Planned operations

Contrary to the first plans, the NEBAJEX exercise did not take place with controlled slicks, but with uncontrolled oil releases from the Tricolor wreck. The BELGICA was to offer a scientific support to the Belgian authorities and to the French On Scene Commander at the TRICOLOR site (position 51°21′90 N 002°12′.65 E; in French EEZ) through the intensive monitoring of oil spills originating from the ship wreck during that campaign week.

Although monitoring results could not be obtained in a controlled experiment, they

did advantageously serve as a real-time input during this pollution incident. The NEBAJEX exercise at the TRICOLOR site (BELGICA campaign 2003-14C) met the following objectives:

- To test the abovementioned monitoring procedures, strategies, instruments and the oil spill models, as planned in the NEBAJEX project (**Objectives 2-3-4**);
- To feed the NEBA evaluation process with real-time monitoring of oil escaping from the TRICOLOR (**Objective 5**);
- To try and find an explanation for the drastic changes (very quick weathering and disappearing) of the extensive spillage observed on 08 September '03 by several remote sensing aircraft.

The BELGICA acted as central monitoring platform and its role were diverse. The vessel served as:

- overall co-ordinating platform for monitoring activities;
- central communications platform: sea-air (with Belgian remote sensing aircraft B-O2); sea-sea (with RIB's); communications with French authorities and salvage consortium, sea-land (with MUMM, SINTEF, CEDRE, COMOPSNAV, ...);
- floating marine chemistry lab where several oil parameters were analysed immediately after sampling in the oil slick(s);
- oceanographic platform that continuously measured relevant oceanographic and meteorological data (ODAS system; hull-mounted ADCP), *inter alia* for validation of mathematical models.

### 4.2.2. Course of operations from 15-18 September 2003

#### (1) Day 1 - Monday 15 September 2003

In <u>Table 12</u>, an overview can be found of the activities and operations of Monday 15 September. Due to the sudden change of plans, the CEDRE personnel had to collect all equipment that was prepared and gathered for the NEBAJEX – DEPOL 03 exercise, and leave from Brest (Brittany, France) to Zeebrugge (Belgium). That was the reason why the scientists from CEDRE could only embark on Monday evening. However, it was decided that the scientists from MUMM and SINTEF would already start with monitoring operations on Monday - if weather permitting, which was the case - and with only a limited amount of equipment. The major reason for this decision was that important cutting and hoisting operations at the TRICOLOR site were scheduled around week 38, but is was unknown at what moment these operations were actually going to happen (depending on the success of technical and operational preparations).

The Belgica left the naval base of Zeebrugge in the morning and arrived on the northeast side of the TRICOLOR wreck at ca. 13 h. The remote sensing aircraft, Belgian Army 402 (B-02) arrived on scene round the same time, and made a first rapid evaluation of the oil pollution present in the area at that moment. That Monday afternoon, a significant oil pollution originating from the TRICOLOR could repeatedly be observed from the air. The accidental oil spill caused by the salvage operations at the TRICOLOR was of a sufficient order of magnitude to test the different aerial and ground-truth monitoring procedures as envisaged within the NEBAJEX project (see table 2). That day, several bulk samples were taken of highly

viscous heavy fuel oil or fuel oil lumps, and also water samples with MUMM's Winchester bottle. Furthermore mathematical model simulations were performed by MUMM in the office in Brussels, and by SINTEF on board the BELGICA. All these elements served as a basis for a NEBA evaluation.

Apart from the NEBAJEX monitoring aspects, this pollution incident was also taken seriously by the authorities: the Belgian aircraft B-02 guided the Union Beaver during the mechanical recovery operations that afternoon, and the oil spill evaluation led to a higher state of alert. This was justified given the earlier major pollution incident in the foregoing week, and the planned salvage operations in week 38.

The ground-truth and aerial monitoring operations were interrupted that day at ca. 17:30 h and the Belgica returned to Zeebrugge for a touch and go to pick up the scientists from CEDRE with their equipment (equipment from CEDRE <u>and</u> from SINTEF, which had already been sent to Brest for the initially planned NEBAJEX exercise off the Brittany coast).

### (2) Day 2-3-4: Tuesday 16 till Thursday 18 September 2003

Over the whole period of the TRICOLOR incident, the Belgian remote sensing aircraft has been observing oil slicks on a regular basis around the wreck. These oil pollutions consist of volumes of various orders of magnitude and originate from the wreck:

- (1) At low tides (minor oil pollutions), or
- (2) During cutting and lifting operations (major oil pollutions)

In week 38 important cutting operations of the TRICOLOR wreck were planned by the salvage consortium. Therefore, from Tuesday till Thursday, the Belgica remained on scene, waiting for oil escaping from the TRICOLOR during salvage operations, or for oil escaping at low tide.

On Tuesday 16/09 (see <u>table 13</u>), a minor but very widespread oil slick was observed in the early morning by the B-02. Most of the oil slick consisted of sheen, only a minor part (less than 1%) consisted of continuous true oil colour. Nevertheless, bulk sampling operations that were performed that day were quite successful, with seven oil samples taken, as well as two pad samples, owing to the excellent guiding of the small platform RIB1 by the aircraft. Also subsurface oil monitoring was performed that day with the Aquatracka on board the RIB2, but no marked dispersed oil concentrations were detected in the water column. In the afternoon, scientists from the Belgica visited the recovery vessel 'Union Beaver' to collect bulk samples of the oil in its tanks. Two bulk samples were taken and analysemik sample of fuel oil pumped out of a tank of the TRICOLOR during fuel lightening operations last winter;

A bulk sample of oil that had been recovered by the Union Beaver from the sea

surface near the TRICOLOR wreck since the beginning of the incident.

Later that day, the Belgica was informed by the liaison officer of the salvage operations that cutting operations on the wreck would not start before Wednesday.

operations that cutting operations on the wreck would not start before Wednesday 17/09 in the afternoon.

In the morning of Wednesday 17/09 (see table 14), a minor oil slick was again

observed around the Tricolor wreck, this time however with minimal amounts of true oil colour at the sea surface. An attempt was made by the monitoring team in RIB1 to perform bulk sampling, but without success. A subsurface oil monitoring team mounted two Turner fluorometers on board of the RIB2 and was on standby in case of more significant oil releases that day. Since no pollution was observed in the early afternoon, a training session was organised by SINTEF on board the BELGICA on how to perform oil slick thickness monitoring with a thickness cylinder and pad sample. In the late afternoon (ca. 16:30), the aircraft B-02 again reported oil pollution in the immediate vicinity of the wreck, and the monitoring team in RIB1 pad samples were taken in that area (in co-ordination with aircraft). The team in RIB2 performed subsurface oil monitoring with the Turner, again no dispersed or dissolved oil was measured in the water column. At the end of that day, the Belgica was informed by the liaison officer of the salvage operations that the cutting of section 6 of the Tricolor had stopped because the sawing chain got broken, and that further cutting operations would not start before Thursday afternoon.

On Thursday 18/09 (see <u>table 15</u>), only a minor oil slick was observed at the Tricolor site in the morning. As for Wednesday, the monitoring team on board RIB1 started with bulk and pad sampling, whereas RIB2 started with subsurface oil monitoring with the two Turner fluorometers mounted on board. Unfortunately, the weather conditions got worse that morning and the working limits for ground-truth monitoring were soon reached. At the same time the Belgica was informed by the salvors' liaison officer on board the 'Norma' (salvage consortium vessel) that difficulties had been encountered and cutting operations would not start before Friday. Finally, when returning to the Belgica, the RIB2 (Tuimelaar) reports serious engine problems.

Due to the fact that the end of the Belgica's NEBAJEX campaign was scheduled on Friday 19 September, the weather conditions got above working limits, one of the two small monitoring platforms (Tuimelaar) suffered engine problems that could not be solved at sea, and most of the aims of the NEBAJEX exercise had been met, it was decided on Thursday at 12:00 h to stop this NEBAJEX exercise and to return to Zeebrugge. The Belgica arrived in the naval base of Zeebrugge at 17:00h.

Table 12: Overview of operations on Day 1 – Monday 15-09.03 (logbook Belgica).

Time	Platform/	Activity/remarks	
(LT)	service		
08:30	BELGICA	Embarking of MUMM and SINTEF personnel + part of monitoring/sampling equipment	
10:30	BELGICA	Belgica leaves Navy base Zeebrugge, start transit to TRICOLOR site	
13:05	B-02	Aircraft B-02 airborne, but has communication problems when trying to contact the Belgica (read 1 by 5)	
13:15	BELGICA	Belgica is arriving on NE side of TRICOLOR; thin oil trails are observed.	
13:25	B-02	Good communication between aircraft and Belgica is established. B-02 is requested to perform a first observation and evaluation of the pollution around the TRICOLOR, and to report	

		to Belgica.
13:30	BELGICA	Belgica contacts AILETTE (French OSC vessel) to report arrival on site; OK from Ailette, that requests Belgica to contact the F guard vessel CORMORANT for further contacts with F authorities.
13:35	MUMM BXL	Fax from Salvage consortium received at MUMM BXL, forwarded to Belgica: the consortium informs MUMM that due to unforeseen circumstances, cutting operations are interrupted, and that hoisting of Section 2 of wreck is com-
14:07	B-02	Bitstesserial monitoring report of 13:57 LT to Belgica (see table 18).  Because the position of the slick is SW of Tricolor, the Belgica decides to sail to the vicinity of that location before starting ground-truth monitoring with small boats.  B-02 reports it has to return to airport for refuelling.
15:10	BELGICA	Belgica on site of location of thicker parts of oil slick; two RIBs are launched at sea; Rib 1 → start surface oil sampling; in total 6 oil samples + 2 water samples (with Winchester bottle) are taken. (see Annex A, table 1) Rib 2 → start subsurface oil monitoring, with Aqua-tracka fluorometer.
	BELGICA	<u>First model simulation</u> based on aerial observations, received from MUMM BXL; simulation indicates that oil slick will remain drifting for the next 48 h in the vicinity of the TRICOLOR, no coastal waters threatened.
16:30	BELGICA	Belgica observes ca. 20 distinct, thicker oil patches, and gives indications to RIB 1 & RIB 2. The consortium's recovery vessel Union Beaver is contacted and informed about these combatable parts.
16:45	Union Beaver B-02	Recovery vessel Union Beaver on the spot, is preparing for mechanical recovery.  Second aerial monitoring report of 16:30, to Belgica (see table
16:58	B-02 + RIB 1	18).  B-02 guides RIB 1 towards thicker patches of oil slick, for the purpose of surface oil sampling. Due to communication problems o/b B-02, guidance communications happen with Belgica as intermediate.
17:02	B-02 + RIB2	B-02 guides RIB 2 for correct tracking with the purpose of subsurface oil monitoring with Aquatracka. Because of communication problems B-02, Belgica ensures a
17:20	RIB 1 + RIB 2	BothrRlBsiættiamstörtkelgica. After embarkement of RIBs, Belgica returns to Zeebrugge for touch & go.  Bulk samples from sea surface are being analysed on board the Belgica.
17:23	BELGICA	Request to MUMM-BXL to perform model simulations: (1) starting with a discharge at 07:00 on 15.09, with trajectory simulation for the next 32 h, and (2) starting with spill at 16:30h, with trajectory simulation for the

		next 48 h.
17:25	B-02	Gives guidance to UNION BEAVER (= recovery vessel from
		salvage consortium at TRICOLOR site), for recovery of oil
20:10	BELGICA	Doutches Go at Zeebrugge: two scientists from CEDRE +
		equipment coming from CEDRE are being embarked. One
		person from MUMM disembarks. Belgica returns to TRICOLOR

site.

<u>Table 13</u>: Overview of operations on Day 2 – Tuesday 16.09.03 (logbook Belgica)

Time (LT)	Platform/ service	Activity/remarks		
08:50	BELGICA	Anchor up (51°21.70′ 002°17.83′ E at 08:58)		
09:29	B-02	Remote sensing aircraft B-02 arrives on scene; start of aerial		
		monitoring of oil pollution around TRICOLOR.		
09:50	B-02	First aerial monitoring report of 16/09, of 09:30, communicated to		
		Belgica (see table 18).		
10:30	BELGICA	Arrival at location T2.		
10:47	RIB 1	RIB 1 starts oil sampling in T2. the RIB is hereby guided by aircraft		
		B-02.		
		In total 7 oil samples taken, with guidance from aircraft, as well		
		as 2 pad samples; pad sampling is documented, i.e. taken in co-		
		ordination with aircraft (comparison of pad sample + aerial		
		observation; cf. BAOAC validation)).		
11:00	BELGICA	Contact with MUMM BXL and COMOPSNAV (Belgian Naval		
		Operations Command); it is estimated that a 180 m³ of oil is still		
		on board of the TRICOLOR, and that during cutting of section 6		
		and section 4 of the wreck, an estimated volume of 45 m³ and		
		70 m³ resp. can be released if cutting operations start on 17.09.		
		Belgium is in third line of pollution response in case of significant		
<u> </u>	DID O	spillage.		
	RIB 2	RIB 2 is ready and on standby for measurements with 2 Turner		
11.15	D 00	fluorometers.		
11:15	B-02	Aircraft leaves site.		
12:00	RIB 1	bulk sampling stops, because no 'thick' oil trails remain at surface.		
14:40	Union	After a request from the Belgica, the UNION BEAVER welcomes		
14.40	Beaver	scientists on board. The aim is to take oil samples:		
	BCGVCI	(1) from fuel oil pumped out of the TRICOLOR wreck shortly after		
		the initial collision, and		
		(2) from tank with oil recovered from the sea surface that got		
		released during the whole period of salvage operations.		
15:20	BELGICA	Belgica demands MUMM BXL to perform a oil spill trajectory		
		simulation starting at 07:00h in the morning of Wednesday 17.09.		
(p.m.)	BELGICA	Bulk samples from sea surface and from Union Beaver are		
		being analysed in the labs of the Belgica.		
		No further oil release observed from TRICOLOR wreck.		
17:00	BELGICA	Scientists returned from Union Beaver, with several oil		
		samples taken and received from the recovery vessel		
		Belgica contacts salvage co-ordinator on board of Salvage		
		vessel NORMA, with request for information concerning the		
		start of cutting operations. The co-ordinator answers that		
		cutting will not start before Wednesday noon.		
		In lab on board Belgica, scientists start with diff. analyses on		
<u> </u>		bulk samples.		
I	All	End of operations Day 2.		

<u>Table 14</u>: Overview of operations on Day 3 – Wednesday 17.09.03 (logbook Belgica)

Time (LT)	Platform/ service	Activity/remarks	
09:30	BELGICA	Smell of diesel oil around Belgica; light trails visible at sea surface on the starboard side of the Belgica, in the vicinity of the TRICOLOR.	
09:55	RIB 1	RIB 1 launched at sea; on standby for immediate bulk sampling after info from aircraft	
	B-02	Aircraft on scene; performs aerial monitoring observations. Reports to Belgica that only a very light trail of oil (colours only sheen) is visible coming from the TRICOLOR and following the currents.	
10:00	B-02	First aerial monitoring report of 17/09, of 09:55, communicated to Belgica (see table 18).	
	BELGICA	It is decided that the aircraft returns on scene at ca. 15:30-16:00 LT and that RIB 1 returns to Belgica.	
10:00- 16:00	BELGICA	<ul> <li>Mathematical modelling (SINTEF);</li> <li>Further analyses + discussion on methodology; training of bulk sampling techniques &amp; film thickness measurements.</li> </ul>	
16:05	B-02 RIB 1 + RIB 2	Aircraft on scene; starts aerial monitoring of TRICOLOR site.  RIB 1 on standby for bulk sampling; RIB 2 on standby for subsurface oil monitoring with two Turner fluorometers.	
16:25	B-02	<u>Second aerial monitoring report</u> of 17/09, of 16:10, communicated to Belgica (see table 18).	
16:55	RIB 1	RIB 1 performs documented pad sampling in metallic-brown parts of slick east of TRICOLOR wreck (taken in co-ordination with aircraft). Three pads are taken.	
	RIB 2	RIB2 performs subsurface oil monitoring tracks.	
	B-02	Aerial guidance of RIB 1 and RIB 2.	
17:37	RIB 2 + B- 02	While tracking, RIB 2 observes limited parts of brown emulsion; aircraft above RIB 2 confirms. RIB 2 informs bulk sampling team of RIB 1. They collect black oil lumps.	
17:45	BELGICA	After contact with representative of salvage consortium, Belgica is informed that cutting operations have not been started because the cable at cutting section 6 has broken. The salvors will make an attempt to cut section 4 from Thursday on.	
18:00	All	End of operations Day 3.	

<u>Table 15</u>: Overview of operations on Day 4 – Thursday 18.09.03 (logbook Belgica)

Time	Platform/	Activity/remarks
(LT)	service	
08:45	BELGICA	Observation of broken, discontinuous oil trail connected with TRICOLOR. Sea state got worse: 2-3.
09:20	RIB 1+ RIB 2	Both RIB's launched at sea surface. RIB's are heading towards oil trail visible from Belgica.
09:30	B-02	Radio contact Belgica – remote sensing aircraft. Aircraft will be on scene within 30 min.
09:45	RIB 1 + RIB 2	RIB 1 in sheen area (rainbow colour) of oil trail.  RIB 2 starts with subsurface oil monitoring tracks, with Aquatracka/two Turners mounted on board.
09:57	B-02	Aircraft on scene; reports findings to BELGICA.  First aerial monitoring report of 18/09, of 09:57, communicated to Belgica (see table 18).  Aircraft starts guidance of RIB 1 for bulk sampling, + coordination with RIB 1 for pad sampling.
	RIB 1	Guided by the aircraft, the RIB 1 takes two pad samples and one sample of smaller oil lumps.
10:05	BELGICA	Belgica receives information from salvage co-ordinator on board of the NORMA that difficulties have been encountered and cutting will not start before Friday.
10:42	BELGICA	Weather is getting worse, wind force 6-7 Bft and sea state = 4. Working limits have been reached and RIB's return to Belgica. RIB2 reports engine problems
11:30	BELGICA	Final briefing; it is decided that after termination of field work, the Belgica will lift anchor up and return to Zeebrugge.
12:55	BELGICA	Radio contact with Norma, Union Beaver and French Guard vessel to thank them for their co-operation.
13:00	BELGICA	Anchor up + return to Zeebrugge.
17:00	BELGICA	Arrival Zeebrugge + disembarking of scientists and equipment.

### 4.3. Results

## 4.3.1. Results from the initial characterisation of NEBAJEX-DEPOL 03 oil

Before the change of exercise plans, CEDRE had already received and prepared 3 x 30 m<sup>3</sup> of crude oil (supplied by Total S.A.) that was to be used during the NEBAJEX-DEPOL 03 exercise off the coast of Brittany. The oil had already been pre-weathered: in order to work more safely on location and to reduce the time needed for the oil to emulsify, the oil pre-evaporated before the experiment, to get rid of the light end.

The chemical composition of that prepared crude oil was already determined before the NEBAJEX-DEPOL 03 exercise was cancelled. The results of this chemical characterisation are summarized in <u>table 16</u>. The percentage of aromatic HC mounts to ca. 25 % of the total amount of crude oil. When looking at the detailed composition of the toxic PAHs and NSO compounds, it can be concluded that the aromatic fraction of the NEBAJEX-DEPOL 03 oil mainly contains acutely toxic LMW PAHs and LMW S compounds, and significantly less carcinogenic HMW PAHs. The percentage of resins, and especially of asphaltenes is low, which is an indication that this oil type will most probably not form stable w/o emulsions. This was exactly what the NEBAJEX team wanted to achieve during the planned experimental oil spill (see also 2.2.).

The NEBAJEX-DEPOL 03 oil was also tested in the Polludrome at CEDRE. This test showed that the oil formed unstable emulsions, and that natural dispersion was an important weathering factor. Due to the cancellation of the NEBAJEX-DEPOL 03 exercise, the oil has not been released into the sea. There is still lack of validation testing in the field, so it is difficult to draw hard conclusions on the exact behaviour of this oil in the marine environment based on the Polludrome findings. Without validation, the Polludrome results only give an extra indication on the probable behaviour of that oil at sea.

<u>Table 16</u>: results of chemical characterisation of NEBAJEX-DEPOL 03 pre-weathered crude oil, and of the one TRICOLOR reference HFO (only toxic compounds).

Composition of oil	TRICOLOR ref. HFO	NEBAJEX-DEPOL 03
Major HC groups	(Wt%)	<u>oil</u>
Major no groops	(11170)	(Wt% )
Saturated HC	14,8	68,7
Aromatic HC	31,5	25,8
Resins	39,8	4,6
Asphaltenes	13,9	0,9
Detailed composition of toxic	Concentration	Concentration <sup>7</sup>
compounds:	(µg/g; = ppm)	(µg/g; = ppm)
Analysed PAHs & NSO compounds		
Benzo(b)thiophene	82	-
C1- Benzo(b)thiophenes	312	-
C2- Benzo(b)thiophenes	475	-
C3- Benzo(b)thiophenes	456	-
Naphtalenes	772	1097
C1- Naphtalenes	4820	3861
C2- Naphtalenes	6822	6238
C3- Naphtaleness	4706	5554
Biphenyl	5	145
Acenaphthylene	13	0
Acenaphtene	70	69
Fluorene	238	89
C1-Fluorenes	542	200
C2-Fluorenes	728	290
C3-Fluorenes	560	252
Phenanthrene	786	237
Anthracene	85	31
C1-Phenanthrenes/anthracenes	1954	819
C2-Phenanthrenes/anthracenes	1986	1073
C3-Phenanthrenes/anthracenes	1120	767
Dibenzothiophene	140	84
C1-Dibenzothiophenes	390	319
C2-Dibenzothiophenes	513	521
C3-Dibenzothiophenes	362	407
Fluoranthene	43	6
Pyrene	126	25
C1-fluoranthenes/pyrenes	288	92
C2-fluoranthenes/pyrenes	180	158
C3-fluoranthenes/pyrenes	89	212
Benzo[a]anthracene	13	8
Chrysene	27	38
C1-Chrysenes	46	72
C2-Chrysenes	53	107
C3-Chrysenes	49	153
Benzo[b+k]fluoranthene	5	-
Benzo[e]pyrene	9	-
Benzo[a]pyrene	59	-
Perylene	4	-
Indeno(1,2,3-cd)pyrene	2	2
Dibenz(a,h)anthracene	2	5
Dibenz(g,h,i)perylene	7	5

<sup>&</sup>lt;sup>7</sup> An indication of '-' means: not determined.

## 4.3.2. Results from the initial characterisation of one TRICOLOR reference heavy fuel oil

### Physical properties and dispersibility

<u>Table 17</u>: Results from characterisation of physical properties and dispersibility of TRICOLOR reference oil in lab.

Physical properties	Value	Lab which performed analysis
Viscosity	23.000 mPas at 10°C	CEDRE
(shear rate 10 s <sup>-1</sup> )	6.500 mPas at 20°C	
	11.000 mPas at 19°C8	SINTEF
Density	0,985 g/ml at 10°C	CEDRE
	0,984 g/ml at 20°C	
	0,989 g/ml at 15,5°C°	SINTEF
Water content	0 %	SINTEF
Pour point	<0°C	SINTEF
Dispersibility	80%, high	SINTEF
(ratio 1:20, at 20°C, using		
Corexit 9500)		

Apart from minor quantities of MDO, lubes, gas oil and gasoline, the Tricolor carried almost 2000 m³ of HFO, of which an estimated volume of 200 m³ remained in the wreck after the pumping operations. This HFO is in fact a sum of at least four different HFO oils. CEDRE disposed of a reference sample of only one of the HFO oils (directly taken from one of the fuel tanks in the beginning of the incident), with sufficient oil volume to perform the most important initial characterisation analyses. The analysis results of the most important physical properties of this Tricolor reference HFO, and its dispersibility, are shown in table 17. CEDRE already measured the viscosity and density of the one reference HFO before the exercise. The analyses at SINTEF were only performed after the exercise, due to the last minute decision to hold the NEBAJEX exercise at the Tricolor site.

The initial characterisation results indicate that both density and viscosity are high for the initial (reference) HFO. At SINTEF, the viscosity of the Tricolor oil was measured at a shear rate of  $10s^{-1}$  from 0 to  $50^{\circ}$ C. The obtained viscosity curve indicated that the intermediate fuel oil (IFO) grade of the one reference Tricolor oil is between 500 and 540 cSt. The density approached 0,99 g/ml. This confirms that the one reference Tricolor fuel is an extra heavy fuel oil (HFO) (Lewis, 2002; Dicks *et al.*, 2002). The reference HFO contained no water and the pour point was below 0°C. The dispersibility of this 'fresh' Tricolor HFO was tested with an IFP test using the dispersant Corexit 9500. The measured efficiency was high (approximately 80%). This indicates that chemical dispersion could have been effective if applied on 'fresh' HFO oil immediately after release. The potential of certain dispersants (such as

<sup>&</sup>lt;sup>8</sup> Viscosity was measured by SINTEF after the exercise at 19°C, because this was the sea temperature at the time of the exercise.

<sup>&</sup>lt;sup>9</sup> Density was measured by SINTEF at 15,5°C (ASTM standard).

Corexit 9500) for effectively dispersing HFO oils has been shown in systematic dispersibility studies and field trials at SINTEF (Daling, 1998).

#### Chemical composition + toxic compounds

After the NEBAJEX exercise, the major HC groups of the one TRICOLOR reference HFO oil has been determined by MUMM (using the CEDRE methodology; see 2.2.2.), whereas the toxic PAHs and NSO compounds of this oil have been analysed oil by CEDRE (see table 16). The differences in weight percentages between the major HC groups of the one Tricolor reference HFO and the DEPOL 03 crude is striking. The Tricolor HFO oil has a much higher asphaltene and resins content, which is a clear 'chemical' indication that stable w/o emulsions will be formed with this type of oil.

The Tricolor reference HFO oil also has a relatively high aromatic compounds percentage (31,5 %); it mainly contains LMW toxic PAHs and LMW S compounds, and considerably less carcinogene HMW PAHs. The analysis of PAH concentrations in the Tricolor reference HFO and the NEBAJEX-DEPOL 03 oil give quite parallel results; the Tricolor HFO however contains relatively more parent and alkylated phenanthrenes, and more parent and alkylated fluorenes. This quantitative information on the toxic components of the oil can be useful in the evaluation of the probable overall environmental impact of a spill, and in particular of the ecological (species and habitat) sensitivity of the marine and coastal environment threatened or impacted by the spill. The real toxic effect of the oil depends of course on several other important impact factors such as dilution rate, exposure time, and degree of contamination (see 1.1.).

### 4.3.3. Results from aerial monitoring and guidance

The oil spills originating from the Tricolor wreck during the exercise were monitored by a remote sensing aircraft. The observations and evaluation of the aerial monitoring are listed in <u>table 18</u>. The aircraft and the central monitoring platform 'Belgica' arrived at the Tricolor site on Monday 15 September at noon. At that moment, the salvors were just finishing the hoisting of two sections of the Tricolor wreck on a large pontoon. It was most probably as a result of these lifting operations and the calm weather, that a combatable oil spill was observed that day.

At ca. 14 h local time (LT), a polluted area of 9 km long and 500 m wide was observed and documented by the aircraft, with low oil coverage. A minor part of the oil slick consisted of discontinuous true oil colour and water-in-oil (w/o) emulsion (5% and 1% of total oil coverage respectively). The observers made a distinction between true oil colours and w/o emulsion, because the latter seemed thicker, had a brighter, granular-like appearance, and consisted of a distinct patch or trail, with a sharp border towards other appearances such as 'metallic'. The w/o emulsions were detected by IR in a very unusual way: except for some small white dots, the visually observed w/o emulsion patches were seen as black patches on a 'white hot' IR image, indicating that the emulsions were not hotter than the surrounding water surface (as w/o emulsions usually are), but colder. The order of magnitude of the oil volume of that slick was estimated at 1 to 10 m³. The Union Beaver started with a

mechanical recovery of the slick, on the basis of the information obtained from the aircraft. The observers reported that the oil slick seemed to change and disappear rapidly: some thicker parts of the slick seemed to become covered by a small water layer, as if the oil was floating just under the surface.

At 16:30 LT, the aircraft flew a second time over the Tricolor area, and the observers found a very different square-like oil slick of 3 km long and 3 km wide, with a lot more patches and trails of discontinuous true oil colour spread over the entire slick. The w/o emulsion was described in the same way as earlier that day, and was again not detected by IR as white patches, indicating that the w/o emulsion was not heated by sunlight. They observed more w/o emulsion (5 % of the total oil coverage) than a couple of hours earlier. The oil observation was reported to the Belgica, the RIBs and the Union Beaver. The latter started again with recovery operations, with extra guidance from the aircraft. From Tuesday 16 September till Thursday 18 September, no further significant oil pollution was observed. This was mainly due to the fact that, although important cutting operations were planned that could lead to new oil releases, the salvage consortium encountered several technical difficulties that week and continuously had to postpone the cutting operations. The oil pollutions observed by the aircraft during the rest of the week were therefore of a minor order of magnitude (below 1 m<sup>3</sup>). The slicks consisted mainly of sheen and metallic appearances, with some sporadic traces of true oil colour. These slicks were too small to be combated, but there were small areas with oil/emulsion patches to perform bulk sampling of the oil and to continue ground-truth monitoring operations. At the last day of the exercise, on Thursday 18 September, the minor oil slick that was observed from the air in the morning disappeared rapidly when weather conditions got worse, with wind speeds increasing from 3-4 Bft in the morning to 6 Bft at noon.

Good communications between aircraft and RIBs, and good aerial guidance of the ground-truth monitoring teams were shown to be key elements for effective ground-truth oil pollution monitoring at sea. Three kinds of guidance were given by the aircraft:

- For large distances: via slick positions reported to the Belgica, using the aerial monitoring reporting format. Then the Belgica, with the two RIBs embarked on deck, sails towards this location.
- Absolute directions: when the Belgica arrived on the location of the observed oil slick, the two RIBs were launched at the sea surface, and they received absolute directions, e.g. northern course, or a heading in degrees (e.g. 270°).
- Relative directions: these were finally given when necessary, to adjust the direction of the RIBs (finetuning). For example: 10° to the left; 20° more to the right; the thick patch is at two o'clock...

<u>Table 18</u>: Aerial monitoring results obtained during NEBAJEX exercise.

Parameter	1 <sup>st</sup> observation 15 September 03	2 <sup>nd</sup> observation 15 September 03	Observation 16 September 03
Time (LT)	13:57	16:30	09:30
Location slick	51°22.0'N 002°10.0'E	51°18.5'N 002°09.5'E	from Tricolor wreck <u>till</u>
(Begin-End)	<u>fill</u> 51°18.2'N 002°07.4'E	<u>till</u> 51°19.5'N 002°11.4' E	51°26.2'N 002°03.7'E
Length	9 km	3 km	15 km
Width	0.5 km (20m at begin, 500m at end)	3 km	10 km
Coverage %	10 %	30 %	Very low, widespread
Est. volume	< 10 m³	Between 10 and 50 m³	< 1 m³
Thicker parts	true oil colour + w/o emulsion, at: - 51°19.0'N 002°08.0'E - 51°21.0'N 002°11.2'E - 51°20.6'N 002°10.8'E	More patches and trails of true oil colour + w/o emulsion	Trail of 3 km on 50m, with < 1% true oil colour, till 51°26.8'N 002°19.0'E (NE part of slick)
w/o emulsion	Detected in 1 % of slick	Detected in 5 % of slick	Not detected
Form of slick	Fragmented, but changing and disappearing rapidly	Square, with fragmented thicker patches	Small oil trails
Combatable	Yes	Yes	No
Weather cond.	1 Bft, N wind, sunny	2 Bft, NW wind, sunny	2 Bft, NW wind, sunny
Parameter	1st Observation 17 September 03	2 <sup>nd</sup> Observation 17 September 03	Observation 18 September 03
Time, LT	09:55	16:10	09:57
Location slick	From Tricolor wreck <u>till</u> 51°23.5'N 002°13.0'E	Spreading from Tricolor wreck in east- west axis	From Tricolor wreck in NE direction
Length	(small trail)	2 km	3 km
Width	(-)	20 m	20 m
Coverage %	(-)	(-)	(-)
Est. volume	<<< 1 m³	<<< 1 m³	<<< 1 m³
Thicker parts	No (mostly sheen, some metallic, sporadically true oil colour)	No (mostly sheen, some metallic)	No (mostly sheen, some metallic, few true oil colour patches close to wreck)
w/o emulsion	Not detected	Not detected	Not detected
Form of slick	Small trail	Small trail	Small trail
Combatable	No	No	No
Weather cond.	2 Bft, SW wind, sunny	2 Bft, W-SW wind, sunny	3 to 4 Bft, SW wind, low clouds

Both RIBs had a portable marine VHF on board. The first surface bulk sampling RIB was regularly guided by the aircraft to find the patches of thicker oil films. The second RIB, that performed subsurface oil monitoring, was also guided by the aircraft. In the latter case, the aircraft gave information on the location and dimensions of the slicks, and gave directions to the RIB to orient or correct its tracking. From the above it is evident that guidance of the RIBs by the aircraft requires a guidance strategy: the aircraft must be informed about the monitoring tasks of the small monitoring platforms in order to reply in a prompt but correct

way to the requests for guidance coming from the ground-truth monitoring teams.

### 4.3.4. Results from ground-truth monitoring

### (1) Surface oil monitoring

During the NEBAJEX exercise the surface oil sampling teams collected 14 bulk samples in the area for further analysis on board of the Belgica (code: *D1-TRIEX-xx*). The oil in these bulk samples varied from very viscous w/o emulsions, to mouldable, semi-solid oil lumps. Four bulk samples were also taken from two different tanks of the mechanical recovery vessel 'Union Beaver' (code: *UB-triex-xx*): two bulk samples (UB-triex-1 and UB-triex-2) were taken from a tank containing Tricolor HFO that was pumped out of the Tricolor in the beginning of the Tricolor incident in the winter of 2003; two other bulk samples (UB-triex-3 and UB-triex-4) were taken from a tank where oil was collected that was recovered at sea over the whole incident period. On board of the Belgica, a team of scientists was ready to receive the bulk samples, and to start with the real-time analysis of density, viscosity, water content, emulsion properties and dispersibility testing.

The analysis results obtained in real time on board of the Belgica are summarized in Table 19. SINTEF further determined the viscosity and water content of surface oil bulk samples after the exercise, in a specialised lab. These results are also added in table 19. Just a few measurements of viscosity and density could be performed in real time on board the Belgica. The viscosity of the surface samples exceeded the limits of both the Haake Rhotovisco VT 550 (bob and cup) and the combined Anton Paar density/viscosity meter. A few samples were measured at sea temperature and some samples were measured at higher temperature. Although the obtained data were interesting for the purpose of NEBA, these results are of limited use for modelling purposes. The few *density* measurements that could be performed with the Anton Paar density meter were done on an oil sub-sample after water content extraction from the original w/o emulsion sample. The density measured at 19°C of water-free surface oil from one sample (D1-triex-1) was 1.017 g/ml. Only with one sub-sample of oil taken from the Union Beaver, UB-triex-1, the density could also be measured starting from the original w/o emulsion, without water separation. Because of the problems encountered in the field, the viscosity and density of some of the samples were measured at the SINTEF laboratory after the exercise. The lab results show that viscosity of the surface samples ranged from 110.000-4.000.000 mPas at sea temperature (19°C). The viscosity of the samples taken on board of the Union Beaver, of oil pumped from the wreck in the winter of 2003 and of oil recovered from the sea surface during past salvage operations, had lower viscosity and density values due the lower degree of weathering. The water content of the samples was measured in the field by use of the emulsion breaker Alcopol O 60 %. The water content of the surface samples ranged from 30-50 vol.%. Also oil samples coming from the Union Beaver were measured in the field. The obtained results were 6 to 17 vol. %. The water content measured by Karl Fisher titration in the SINTEF lab after the exercise was in the order of 50 vol. % for surface oil samples, and 50 to 65 vol. % for oil samples from the Union Beaver. These differences between field and lab results show that breaking of emulsion by use of Alcopol O 60 % was not effective. In other words, the Alcopol O 60% method for water content analysis in the field can become unreliable for heavy bunker fuel spills and highly

viscous, asphalthenic crude oils. The few *emulsion stability* and *emulsion breaker effect* tests illustrated that the surface w/o emulsions were very stable. The *dispersibility* tests showed that the w/o emulsions sampled at the sea surface were not chemically dispersible with Dasic NS, nor with Corexit 9500. Only the UB-triex-1 oil sample, coming from the Union Beaver, showed a slight or reduced dispersibility with Corexit 9500. Finally, interesting information was obtained from some visible and/or qualitative aspects of the sampled oil. Some oil samples contained a considerable amount of organic matter and fine mud particles; some others contained air-filled, berry-like vesicles of Japweed (*Sargassum muticum*; macroalgae). Some contained mud tubes of small, colonizing crustaceans of the genus *Jassa* (Isopoda), whereas others contained living crustaceans of the genus *Idotea* (Amphipoda) (pers.comm. F.Kerckhof, MUMM).

### (2) Sub-surface oil monitoring

A second RIB dedicated to subsurface oil monitoring, was on turn equipped with two Turner UVF instruments or with the Aquatracka-MiniBAT UVF system.

Several UVF tracks were performed under the oil slicks observed that week. With the Aquatracka-MiniBAT UVF system several test tracks were performed at 2-10 m depth. Minor fluorescence peaks were observed over a very short period on Monday 15 September, under the thickest parts of the major oil slick that afternoon, after guidance from the aircraft (see Figure 7). After calibration of the instrument with Tricolor HFO, the concentration values deduced from these UVF peaks amounted to max. 78 ppb. These concentration data however have a high degree of uncertainty, because (1) the instrument is still in a testing phase, (2) no validation samples were taken during this short period of peak measurements and (3) the calibration in lab was performed with dissolved oil only, whereas subsurface oil at sea consists not only of dissolved oil components but also of dispersed oil droplets.

The fluorescence measured by two Turner UVF instruments at two different depths (at 1 and 2 meter) that were used the following days could not confirm the initial Aquatracka measurements. The Turner UVF instruments showed no significant variations from background levels, even below thicker, true oil colour parts of the slicks. The very low, hardly detectable concentrations of dispersed or dissolved oil in the water column were confirmed by GC-MS analysis of several water samples taken at sea to validate the UVF measurements. Natural dispersion of oil depends on factors as film thickness, viscosity of oil and w/o emulsions, interfacial tension and presence of breaking waves. Heavy fuel oils normally have a high viscosity and thicker layers of oil on the sea surface, resulting in a very low natural dispersion rate.

<u>Table 19</u>: Analysis results of several important oil properties, obtained in real-time in the field, or later in the SINTEF laboratory. In a.: density, viscosity and water content; in b. emulsion stability, emulsion breaking and dispersibility.

a.

Sample	Real-time a	nalysis results obt	SINTEF lab results				
	Density <sup>10</sup> (g/ml)	Viscosity, Haake Rhotovisco RV20 (mPas <sup>11</sup> , 10-s <sup>-1</sup> )	Temp (°C)	Water content Alcopol O 60% (vol.%)	Water content, Karl Ficher titration (vol. %)	Viscosity, Physica rheometer (mPas, 10s <sup>-1</sup> )	
D1-triex-1	1.017	np	19	39	-	-	
D1-triex-5	np	np	19	52	-	-	
D1-triex-9	np	89.900	40	33	-	-	
D1-triex-12	np	np	!	-	50	110.000	
D1-triex-13	np	np	19	44	-	-	
D1-triex-14	np	np	19	-	-	>1.000.000	
D1-triex-15	np	np	19	-	-	4.000.000	
D1-triex-16	np	np	19	31	-	-	
D2-triex-FL	np	np	19	-	50	700.000	
UB-triex-1	1.003	np	10	6	-	-	
	(0.977)12	24.000	19	ĺ			
UB-triex-2	np	np	19	-	50	27.200	
UB-triex-3	1.011	44.500	19	17	-	-	
UB-triex-4	np	np	19	-	65	49.400	

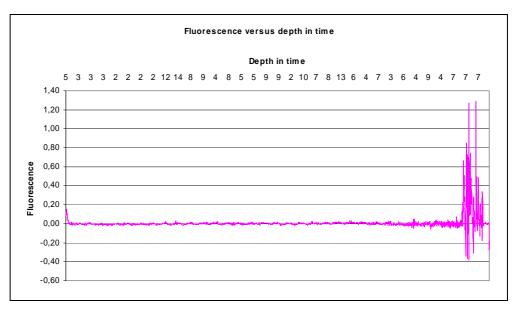
b.

Sample	Real-time analysis results obtained at sea												
	Emulsion Stability (%)			Effect of emulsion breaker (%)		Dispersability test Dasic NS Field test (Concawe,1988)			Dispersability test Corexit 9500 Field test (Concawe,1988)				
	30'	1h	4h	24h	2'	1h	24h	goo d	red.	bad	good	red.	bad
D1-triex-9	0	0	6	19	0	0	24		 	XX		 	XX
D1-triex-13	26	32	35	47	0	12	35		! ! ! !	XX		1 1 1 1	XX
D1-triex-16	0	0	12	19	0	0	26		! ! ! !	XX		 	XX
UB-triex-1		0 afte	r 24 h		0 0	after 2	24 h		Х	Χ	Х	Χ	: ! !

 $<sup>^{10}</sup>$  'np' = not possible for density measurements because oil was too viscous.

<sup>&</sup>lt;sup>11</sup> 'np' = not possible for viscosity measurements because oil was too viscous.

<sup>&</sup>lt;sup>12</sup> Density measured of w/o emulsion (without water extraction), after heating to 60°C.



<u>Figure 7</u>: Illustration of Aquatracka fluorescence peak values (with background fluorescence substracted), as measured on Monday 15 September 2003.

### (3) Currents monitoring (for modelling purposes)

The hull-mounted ADCP (*Acoustic Doppler Current Profiler*) of the Belgica has also been activated several times during the campaign (e.g. position of ADCP on 17.09.03 in <u>Figure 8</u>). While operating, the transducers of such an instrument continuously send out four acoustic beams which are in turn reflected on the particles suspended in the water column. The returning signals are processed at various intervals, providing measurements of the current speeds and directions prevailing at several depth levels beneath the ship. The purpose of the trial was to assess the usefulness of such measurements for predicting the fate of subsurface oil.

Examples of rough outputs are shown in <u>Figure 9</u> (courtesy of J. Backers and V. Pison, MUMM). The main problems for interpreting such results arise from:

- the need for correcting the measurements for depth changes due to tide and swell and for the possible reflection on the sea-bottom;
- the fact that the sensor is mounted on the keel of the ship and, thus, doesn't 'see' the first few meters under the water surface (ship's draught).

The latter problem is the most annoying for the modellers' purpose, as oil mostly drifts at a small depth under the water surface. It could be theoretically bypassed in shallow waters by using an ADCP on the sea floor and 'looking' upside (bottom-mounted ADCP). This however is a false good solution, as the instrument would be fixed while the oil is moving and, also, because mooring the instrument is a heavy and delicate task. So far, it is thought that using the absolute velocity computed from the measurements ("velocity magnitude" in Fig.9) gives useful information on the possible drift of oil that would be drifting under the surface. The picture could be completed in the future by operationally aggregating these measurements with results of 3D modelling of the currents.

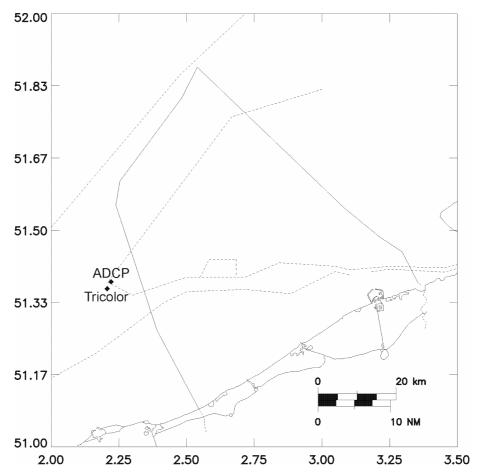
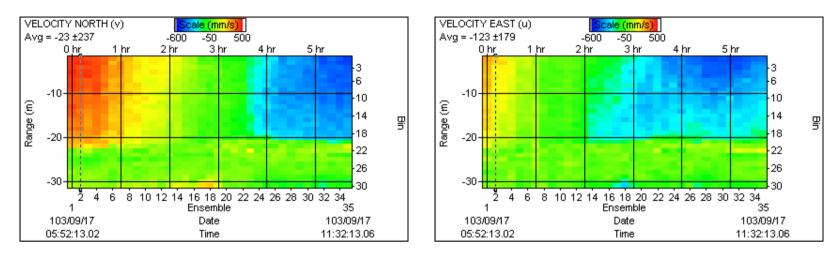


Figure 8: Location of the hull-mounted ADCP measurement on September 17th, 2003.



<u>Figure 9.a:</u> Measured S-N component of the current velocity over the depth ("range") and in time ("ensemble"). Fig.9.b: Measured W-E components of the current velocity over the depth ("range") and in time ("ensemble").

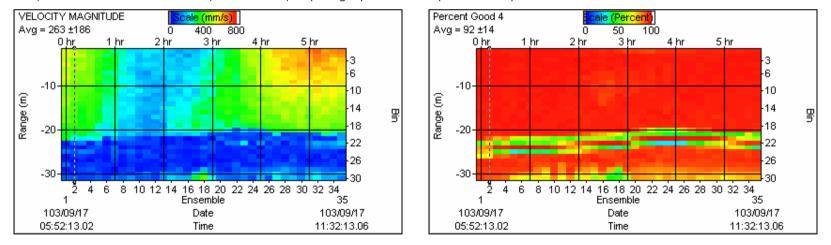


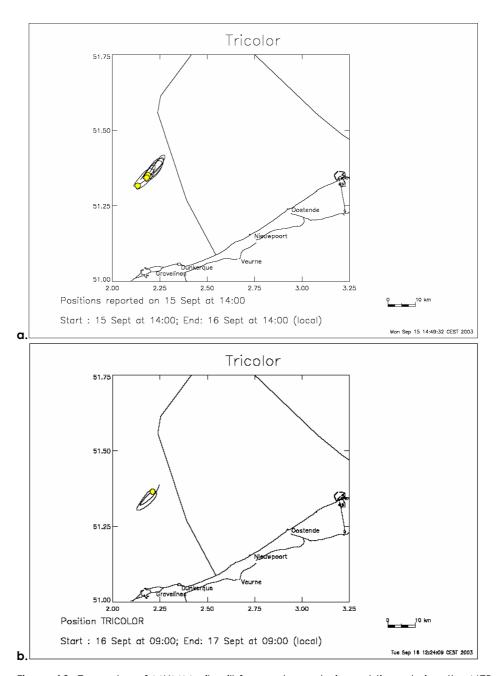
Fig.9.c: Absolute current velocity, derived from the measured S–N and E–W components. Fig.9.d: Estimate of the relative reliability of the measurements. The doubtful zone corresponds to the reflection of the signal on the bottom, combined with the local depth variation due to the tide.

### 4.3.5. Oil spill model results

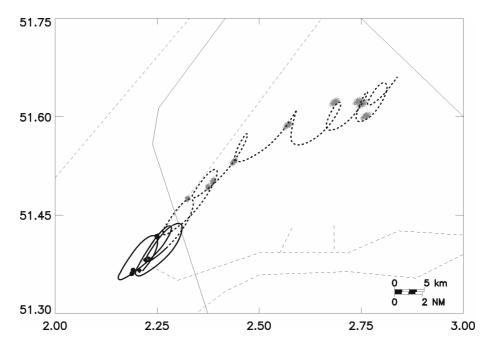
The oil spill simulations performed in real time during the exercise with Mu-Slick and Mu-Slicklets (MUMM) and with OSCAR (SINTEF) as shown in <u>Figure 10</u>, <u>Figure 11</u> and <u>Figure 12</u> respectively, all indicated that, taking into account the small volumes involved, the observed oil spills were never a direct threat for the more sensitive coastlines of the Dover Strait and the adjacent southern North Sea area. Due to the low wind speeds that week, the slicks remain in the vicinity of the Tricolor, drifting in an ellipsoid movement, mainly under influence of the local tidal currents.

Normally the results from the real-time monitoring of the oil at the surface, together with data on other oil types tested earlier at the SINTEF laboratory, were to be used to predict the weathering of the oil, both with the weathering module included in the Mu-slick(lets) model and with the OWM model from SINTEF. For the NEBAJEX exercise however the oil samples collected at the sea surface near the Tricolor were most probably a mixture of different types of HFO - as shown by the fingerprint analysis results from MUMM (Roose, in prep.) - with an unknown time and degree of weathering. The uncertainty of the predictions of weathering properties, on the basis of the analysis results from the complex oily mixture samples and initial characterization data of only one reference HFO, would be too high. For this reason, the possibilities of the various weathering models could not be demonstrated to their full extent during this exercise.

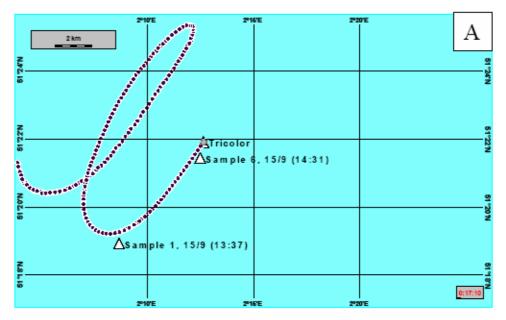
As an example however, the collected w/o emulsion samples have been plotted against predictions of viscosity of the Prestige oil at 19°C (see <u>Figure 13</u>). The reference heavy fuel oil from the Tricolor has a lower initial viscosity than the Prestige oil, but measured viscosities on some of the most weathered samples are higher than the viscosities predicted for the Prestige oil after 20 days of weathering. This comparative simulation indicates that the oil sampled in the immediate vicinity of the Tricolor during the exercise was probably already weathered to a large extent before it escaped from the wreck.



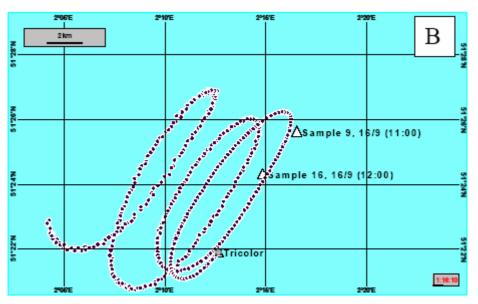
<u>Figure 10</u>: Examples of MUMM oil spill forecasts made in real time during the NEBAJEX exercise: a. Mu-SLICK trajectory simulation starting on September  $15^{th}$  2003, at 14:00 UTC; b. Mu-SLICK trajectory simulation starting on September  $16^{th}$  2003, at 09:00 h UTC.



<u>Figure 11:</u> Example of Mu-SLICKLETS oil spill forecasts made in real time during the NEBAJEX exercise. Simulation of trajectory and spreading starting on September 15th, 2003, at 16:00 UTC. The trajectory depicted with a solid line corresponds to the first 36 hours of drift and spreading. The dotted line (and the shadowed slicks) shows what would have happened until the 21st if some oil had been remaining at the surface. Slick extent is shown every 10 hours. For the purpose of this specific simulation an initial (and instantaneous) quantity of fifty tons fuel oil has been assumed.

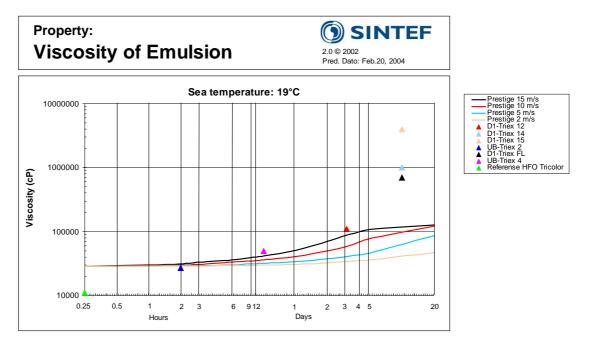


a.



b.

<u>Figure 12</u>: Examples of SINTEF oil spill trajectory simulations made in real time during the NEBAJEX exercise: a. OSCAR trajectory simulation on 15 Sept. 03 (13:00 LT); b. OSCAR trajectory simulation (SINTEF) on 16 Sept. 03 (12:00 LT) (Singsaas, 2004).



<u>Figure 13</u>: SINTEF OWM simulation of viscosity of w/o emulsion of Tricolor samples compared to Prestige oil at sea temperature of 19°C. (initial/terminal oil film thickness 20 mm/2mm; release rate: 1.33 MT/min).

#### 4.4. Results of validation of BAOAC

A limited number of pad samples were taken during the exercise. The slick thickness is calculated from the oil adsorbed to polypropylene and teflon pads. The adsorbed oil was inhomogenuously distributed on the pads, and thus the calculated thicknesses (see <u>table 20</u>) are somehow underestimated for pads sampled in thick oil. Samples taken in sheen and rainbow areas were influenced by millimetre sized patches of thicker oil on the surface, leading to an overestimation of the film thickness. The average concentrations throughout the pad will be correct for these samples. A water content of 50% and a density of 1 are used in the calculations for all samples.

The results in table 20 indicate that in general, the appearances observed and sampled at the sea surface coincide with the BAOAC intervals per appearance. The difficulty of estimating the total volume of w/o emulsions (even if they have a true oil colour appearance) is again illustrated with these results: the thickness calculated for the very limited pad samples taken in w/o emulsions varies from 279  $\mu$ m to 22 mm (which is a factor 100).

During the exercise, the aerial monitoring team was informed of the moment a pad sample was taken. In this way, the aircraft could check the appearance seen from a certain height, in comparison with the appearance observed by the ground-truth monitoring team in the small boat. For metallic and sheen slick parts, the observation was quite similar. From this small BAOAC validation part, it was evident that the scale of distinctions and variations of oil appearances is very different and less pronounced from the air in comparison with the observations at the sea surface. Because of this scaling effect, the aerial observers had a difficult task in trying to define the exact appearance in which a pad sample was taken.

A distinction between 'discontinuous true oil colour' and 'continuous true oil colour patches surrounded with metallic and sheen colours' was made in flight: the observers decided that the appearance of the thicker, distinct patches of the slicks would be defined as 'continuous true oil colour' floating in metallic or sheen films. They hesitated to use the code 'discontinuous true oil colour' to describe these distinct emulsion patches with metallic and sheen films around. The observers were of the opinion that the code 'discontinuous true oil colour' should rather be used for non-emulsified oil slicks with a film thickness between 'metallic' and 'continuous true oil colour', that have no such distinct, sharp edges (which is a visual indication of w/o emulsions).

Table 20: calculated thickness from surface pad samples (Resby et al., 2004).

Sample ID	Appearance of slick (as seen from small work boat; cf. logbook)	Calculated thickness (µm)	Conformity with BAOAC thicknesses
D1-triex-10	Continuous true oil colour (brown w/o emulsion)	5.175	Yes
D1-triex-11	Continuous true oil colour (brown emulsion)	21.950	Yes
D1-triex-18	Metallic	22	Yes
D1-triex-19	Discontinuous true oil colour	122	Yes
D1-triex-100	Rainbow	279	No
D1-triex-101	Continuous true oil colour (+ small lumps)	516	Yes
D1-triex-102	Continuous true oil colour (patchy brown slick)	15.600	Yes

### 5. Discussion and conclusions

# 5.1. Evaluation of monitoring procedures, instruments and models used

### 5.1.1. Objective 1: Initial characterization of oil

In the NEBAJEX project, priority was given to the real-time monitoring of an oil spill at sea. However, an initial characterization of the original or freshly spilt oil in the beginning of an incident by a specialized laboratory can already give valuable information on the probable behaviour and impact of a spill, and the probable effectiveness of response techniques. This is especially important if the various properties of the spilt oil are unknown, which is the case for most refined petroleum products such as intermediate and heavy fuel oils.

In this report, it is mentioned that a good knowledge of the chemical composition of the oil can lead to a better evaluation of the probable oil behaviour when spilt at sea (together with info on physical properties), and can give extra information on the probable toxicity of the oil.

<u>A subject for further research</u> could be the development of a standard protocol for the determination of the major hydrocarbon groups, and the selection of a list of PAH and other toxic oil compounds that need to be determined for the purpose of monitoring of marine oil pollution accidents and environmental monitoring.

### 5.1.2. Objective 2a: Real-time aerial monitoring

Aerial monitoring by trained observers on board a remote sensing aircraft remains essential to make a rapid evaluation of a large oil spill floating at the sea surface: information is rapidly obtained on the location and spreading of the spill, its forms, its thicker, combatable parts, presence of w/o emulsions, the spill dimensions, a first estimation of the oil volume, the weather conditions, and the position, dimensions and features of a dispersed oil plume (if present). The extra information obtained with the IR sensor for the evaluation of the w/o emulsions has shown the added value of sensors on board a remote sensing aircraft.

The aerial monitoring information is vital for an impact and response evaluation, and is valuable as input for mathematical models. The aerial monitoring reporting format developed during NEBAJEX proved an excellent format to report on oil spills to ground-truth monitoring teams. It has been demonstrated however that for in-flight reporting to ground-truth teams, the most important pieces of information are the location and the full description of the slick(s). The rest of the aerial monitoring reporting format remains useful for post-flight reporting to land-based authorities.

The information obtained by aerial monitoring remains essentially visual. Only limited information is obtained about the weathering degree, dispersibility and threat of the oil. Information from aerial monitoring should therefore ideally be combined with (semi-)quantitative information on the type of oil and its behaviour, obtained through different analyses performed in lab or in the field, and through mathematical modelling.

It has also been demonstrated that good communications between aerial and ground-truth monitoring teams is crucial for a successful ground-truth monitoring. A three-steps approach has been successfully tested for aerial guidance: a first one for guidance over large distances, a second one giving absolute directions towards a slick or thicker slick parts, and a third step for relative direction adjusting of the small work boats.

### 5.1.3. Objective 2b: Real-time ground-truth monitoring

Within this project, as well as during past incidents, it has been demonstrated that the initial characterisation of the (original) oil that is spilt at sea offers valuable quantitative information on various oil properties. However, making an evaluation of the weathering, evolution and behaviour of the oil at sea for the purpose of NEBA remains relatively uncertain, even with the best characterisation effort and with the most powerful mathematical models. With a real-time, ground-truth monitoring of the spilt oil at the sea surface and in the water column, and where several important physical and weathering properties are analyzed in the field, valuable quantitative or semi-quantitative information can be collected on important weathering properties such as water content, emulsion properties, changes in viscosity and density, dispersion, and dispersibility of the oil. These data are directly useful for NEBA evaluation and decision-making.

SINTEF's robust sampling arm with net, which was used during the exercise for bulk sampling of surface oil, functioned very well. Previous field trials have shown that it is not the bulk sampling of surface oil, but the analysis in the field that is the real bottle-neck in the whole ground-truth monitoring procedure. This was also the case during this NEBAJEX exercise, where the oil properties analyses on board the research vessel Belgica were even more time-consuming than initially thought, because of the high viscosity of the w/o emulsions. Of all the ground-truth monitoring methods and instruments used and tested, it was learned that highly viscous oils can pose serious problems to analytical instruments such as the Haake Rotovisco for viscosity measurements, the Anton Paar density meter, and the Alcopol O 60% for water content measurements. Viscosity measurements with a Haake Rotovisco normally take ca. 15 min., but during the exercise this was much more time-consuming or almost impossible because of the high viscosity of the w/o emulsion. The Haake Rotovisco used on board the Belgica also had some problems with the high temperature in the laboratories on board of the Belgica, but this problem could be solved. The Paar Physica Rheometer and Karl Fischer Titration

proved to be more effective for viscosity and water content measurements of the highly viscous w/o emulsions. Viscosity meters that are able to measure very high viscosity values and the Karl Fisher Titration method should in future exercises or incidents be used in the field.

Due to the presence of minor oil slicks with very fragmented, relatively thin and heterogenous w/o emulsion patches, the oil film thickness cylinder, for oil slick thicknesses > 3 mm, could not be used during the NEBAJEX exercise. The thickness cylinder has however been successfully tested in previous exercises in Norway and former oil pollution incidents (e.g. Strom-kristiansen *et al.*, 1997). SINTEF gave a demonstration to the scientists from MUMM and CEDRE on the use of the cylinder at the sea surface.

The dispersibility test used during the exercise (CONCAWE, 1988) gave expected results, indicating that the weathered HFO could not effectively be dispersed. However, for the samples taken on board the Union Beaver, the test showed a 'good to reduced' dispersibility with one of the dispersants, Corexit 9500. The difference in dispersant result when two different dispersants are applied shows that a criterion "dispersant performance" is to be taken into consideration when responding to an oil spill at sea. It was also mentioned that the test would benefit from a comparison with standard oil-in-water solutions or pictures of such solutions, for a better visual interpretation of a 'good', 'bad' or 'reduced' chemical dispersion (Le Guerroué and Duboscq, 2003).

For this exercise, the involved research institutes used their available analytical instruments and standardized methods. Further research could be invested in the development and validation of a field test kit for use in field monitoring operations during a major oil pollution incident. In the late 1970's, Fina developed a first Oil Spill Test Kit. This 'Fina' kit could measure 11 oil properties, but the measurements lacked accuracy because rough (non-standardized) empirical methods were used. In the 1990's, Environment Canada developed their own Portable Field Kit, using modern portable instruments and standardized methods for various properties measurements such as density, viscosity, water content, and flash point (Lambert *et al.* 1991; Lambert *et al.* 1994), but this field kit is probably too sophisticated for urgent operational field monitoring purposes.

<u>Further research</u> could thus be performed on the development of such an operational field kit, and could e.g. start by reconsidering and re-evaluating the existing kits in the light of the NEBAJEX exercise findings with very viscous HFO oils.

Another topic for <u>further research</u> is the development, and testing in the field, of an advanced and effective method for surface oil sampling from a helicopter. This has not dealt with in the NEBAJEX pilot project. However, in case a coastal state is confronted with a major oil spill incident at sea, and has no research vessel immediately available in the area (or any other vessel that could be suitable as monitoring platform) an attempt could be made to take samples from the oil spill

drifting at the sea surface via a helicopter.

# 5.1.4. Objective 3: Real-time monitoring of dispersant effectiveness

Due to the fact that the weathered oil from the TRICOLOR was not dispersible, no dispersants were applied on the slicks during the NEBAJEX exercise, and no dispersant effectiveness measurements with UVF instruments could be performed. The use of the Turner UVF however, as explained in detail in chapter 2.5.4., was successfully demonstrated in previous sea trials (e.g. Brandvik et al., 1995; Lunel et al., 1995). Turner UVF instruments were also successfully applied in the monitoring of the dispersant effectiveness during the Sea Empress incident in 1996 (Lunel et al., 1996, SEEEC, 1998). The possibilities of monitoring the dispersant effectiveness with the Aquatracka-MiniBAT system remain to be tested in an exercise (or incident). An element for concern however is the relatively low maximum detection range (depending on the type of oil being spilt), that leads to the careful, temporary conclusion that the Aquatracka is more adequate for the monitoring of lower oil concentrations deeper in the water column, or for determining the borders of an oil plume (in three dimensions), rather than concentrations in the centre of it. In this context it is worthwhile mentioning that MUMM was informed about the purchase of two Aquatracka fluorometers by Spanish and French authorities, for the purpose of monitoring of oil in the water column that possibly escapes from the Prestige wreck.

<u>Further research</u> is needed to study the possibilities and limitations of UVF instruments in dispersant effectiveness monitoring – this is especially the case for the Aquatracka fluorometer.

### 5.1.5. Objective 4: Application of assessment tools

Oil spill trajectory simulations were successfully obtained in real time during the exercise, enabling a better evaluation of the probable impact of the oil spill originating from the Tricolor wreck that week. Unfortunately, due to the very complex situation of the Tricolor, where a mixture of (at least) four different types of HFO escaped from the wreck, with unknown composition and properties (cf. only one reference HFO was characterized after the exercise), and with an unknown time and degree of weathering, the uncertainty of predictions with the SINTEF models OWM and OSCAR would be unacceptably high. Therefore, the possibilities of these models could not be demonstrated to their full extent.

The NEBAJEX exercise has shown that for sudden accidents with vessels carrying an unknown type of oil, important, limiting problems still arise when trying to reliably simulate the oil spill behaviour in support of NEBA, even with very powerful mathematical models.

Further research could be usefully done in evaluating the existing mathematical

models in the light of the reported findings, aiming at making them more operational in as many cases as possible.

- 5.2. Objective 5: using the obtained information for the purpose of NEBA: the example of the TRICOLOR incident.
- 5.2.1. Monitoring and modelling results as input for overall environmental impact evaluations

The NEBAJEX monitoring results suggest that the oil escaping from the wreck, which was in fact a complex mixture of several HFO oils, was most probably already weathered to a significant degree before it got released:

- (1) Analysis results show that the surface oil that was observed and sampled during the NEBAJEX exercise in the immediate vicinity from the Tricolor wreck:
  - was highly viscous, forming stable w/o emulsions,
  - had a high water content,
  - had a density close to that of seawater and
  - had a very low natural dispersion rate.
- (2) The drifting w/o emulsions were not detected as white but as black patches by the IR sensor on board of the remote sensing aircraft, indicating that the emulsions were not heated up, but were colder than the surface water.
- (3) When comparing the viscosity of the Tricolor emulsions to the HFO from the Prestige (with the SINTEF OWM model), it was found that the Tricolor emulsions had a very high viscosity as if the oil had been drifting at sea for weeks, which was not the case.
- (4) Moreover, the w/o emulsions sampled near the Tricolor had a high organic matter content and mud tubes of colonizing amphipods were observed at the surface of the stable, semi-solid w/o emulsions.
- (5) Finally, the oil spill observed from the air had a higher estimated volume several hours after the end of hoisting operations of two major hull parts on the first day of the exercise, than immediately after the hoisting operations.

The thesis that the oil escaping from the Tricolor was a complex mixture of several oil types, of at least four different HFO oils, and was already weathered significantly within the wreck, is not surprising. The wreck was severely damaged and collapsing. The wreck was directly affected by the waves, and the marine areas around the wreck are characterised by strong tidal currents (maxima in the order of 1 m/s) and a relatively high suspended particular matter load (average SPM of 10-20 mg/l in winter season (Van den Eynde *et al.*, 2004)) compared to deeper offshore areas.

Stable, highly viscous and dense w/o emulsions were most probably already formed within the severely damaged and collapsing wreck. As a result of this, the total oil pollution volume that was remaining in the wreck in September was probably significantly higher than estimated by the salvage consortium, due to w/o emulsion forming inside the wreck. The order of magnitude (> 100 m³) of the significant oil

spill observed on Monday 9 September by the Dutch and Belgian remote sensing aircraft, containing a high number thicker patches with features similar as those observed during the NEBAJEX exercise, was therefore not unrealistically high.

When the oil got released during salvage operations, it is supposed that it only slowly mounted towards the sea surface, while drifting away from the wreck by tidal currents. This result also explains why the Union Beaver, the recovery vessel that was on continuous standby in the immediate vicinity of the Tricolor, could not observe thicker patches and trails of oil originating from the wreck and that only appeared several kilometers further in the direction of the current.

Because of the high density and weathering degree of the oil at the surface, and due to small wave actions and turbulence, it is plausible that the surface oil could submerge for some time. This could also explain the disappearing of the oil spill observed at the sea surface the week before the exercise, with an estimated volume of more than 100 m³. It remains difficult however to explain why the large oil spills observed that month changed and disappeared so drastically, or why the thicker oil patches did not resurface later. Scientists from the ground-truth monitoring teams described the thicker oil parts around the Tricolor as wax-like continuous patches with sharp edges, but with rather thin film thicknesses for w/o emulsions - although the patches also contained thicker emulsion parts and oil lumps. The lack of a better description of these complex oil patches hampers a better understanding of the behaviour of the sub-surface oil.

# 5.2.2. Monitoring and modelling results as input for response effectiveness evaluations and final NEBA decision-making

The ground-truth monitoring results obtained in real time showed that the w/o emulsions were no longer dispersible, and were so viscous that only recovery means that could deal with highly viscous emulsions would still be effective. These results found and fully support the decision taken by the French Maritime Prefect to prohibit the use of dispersants when responding to oil spills originating from the Tricolor site.

Oil spill trajectory simulations indicated that the sensitive coastlines of the southern North Sea were under immediate threat by the observed oil slicks, due to the calm weather conditions. However, because the w/o emulsions were very stable and persistent, they could easily drift in the water column over a very long period before sedimenting or stranding ashore and polluting a coastline. The Union Beaver (i.e. the recovery vessel that was on standby near the wreck), has a LORI recovery system installed on board. Before the NEBAJEX exercise in September 2003, the vessel had already successfully recovered oil that had escaped from the Tricolor earlier that year. The overall monitoring coordinator on board the Belgica therefore immediately informed the Union Beaver about the combatable oil patches and trails on Monday 15 September 2003 and requested to start recovery operations under guidance from the Belgian remote sensing aircraft, before the oil slick would become too fragmented or would disappear from the surface.

# 5.2.3. Drafting a mass balance of the TRICOLOR oil releases of Sept.'03

From the results and discussion above, the following mass balance can be suggested:

- The total oil pollution volume that escaped from the Tricolor wreck during the month of September 2003 is estimated by remote sensing aircraft at a magnitude of more than 100 m³. Even if the exact volume remains unknown, the volume estimates give a reliable indication of the magnitude, because of the high emulsification rate of the released oil. In fact, the recorded degree of emulsification (w/o emulsions with 50% water content) leads to the conclusion that the 200 m³ HFO quantities probably remaining inside the Tricolor at the end of the pumping operations, could have doubled in volume within the wreck.
- Because of the low amount of LMW hydrocarbons in HFO oils, and the significant degree of weathering (high density values), the evaporation percentage of the spilt oil after release is considered to be very low, most
- phehabtyrak dispersion and dissolution rate of HFO oils is known to be low. The emulsification process of spilt oil hampers these processes even more. Several results and indications described within this project point to the thesis that the oil was most probably already significantly weathered within the wreck. It can therefore be logically concluded that the natural dispersion and dissolution rate of the oil mixture that escaped from the wreck in September must have been very low, most probably << 5%.
- The exact total amount of oil and/or w/o emulsion that got spilt during the month of September is unknown. therefore no distinction can be made in percentages between the amount of oil and w/o emulsion that was mechanically recovered by the Arca and the Union Beaver (which together recovered more than 50 m³ of oil and w/o emulsion from the surface), *versus* the amount of the very persistent oil that submerged and that was subject to a subsurface drift in the water column. This oil could then finally sediment or strand along a coastline.

### 5.3. Additional objective: validation of BAOAC

Following the request for further BAOAC validation of BONN 2003, a limited, further validation of the BAOAC has been executed during the exercise. This was done in two ways:

- A limited number of pad samples were taken, to calculate the thickness of several oil appearances seen from the sea surface. Most of the thicknesses coincide with the respective BAOAC intervals.
- When trying to couple the observation of appearances seen from a small work boat, with the appearances seen from a remote sensing aircraft, an important scaling effect was recognized: the level of detail for appearance observations from the air is remarkably lower. Elements for an enhanced definition of 'discontinuous true oil colour' are put forward.

### 5.4. General NEBAJEX conclusions

Scientific institutes such as CEDRE and SINTEF dispose of a large dataset of oil properties of various oil types. These oil properties datasets are very useful in support of NEBA in case of a major release of one of these oils in the marine environment. The characteristics of crude oils are better documented than those of some refined products. The NEBAJEX exercise has shown that in case a coastal state has to respond to a marine pollution incident with a major release of an unknown oil type (such as HFO oil), valuable extra information can be obtained quite rapidly on the oil behaviour and combatability at sea, through a strategic monitoring and modelling effort. This has been demonstrated in the NEBAJEX exercise at the Tricolor site in September 2003, where spills consisting of highly viscous, complex mixtures of (mainly) HFO oils were monitored. Valuable information was not only obtained via aerial monitoring of oil spills, but also from different analyses of important oil properties obtained in real-time in the field or performed in a specialized lab, and from oil spill models.

### The main conclusions of the NEBAJEX pilot project are the following:

## (1) Several oil spill assessment steps have been developed and tested in an exercise:

- the initial characterisation of oil in a specialized lab,
- the real-time monitoring of oil spilt at sea: monitoring of its behaviour, weathering and fate, and testing of its dispersibility (aerial and ground-truth monitoring),
- using the obtained results as input for mathematical models, whenever possible,
- using both monitoring and modelling results for a better understanding of the oil behaviour and as extra input for NEBA evaluations during an ongoing incident.
- (2) It has been demonstrated that an **initial characterisation** of the original or freshly spilt oil in the beginning of an incident by a specialized laboratory can give valuable information on the probable behaviour and impact of a spill, and the probable effectiveness of response techniques.
- (3) **Aerial monitoring** by trained observers on board a remote sensing aircraft remains essential to make a rapid evaluation of a large oil spill floating at the sea surface. The collected information is also vital for an impact and response evaluation, and is valuable as input for mathematical models.
- (4) It has also been demonstrated that **good communications between aerial and ground-truth monitoring teams** is crucial for a successful ground-truth monitoring.
- (5) With a real-time, ground-truth monitoring of the spilt oil at the sea surface and in the water column, and where several important physical and weathering properties are analyzed in the field, valuable quantitative or semi-quantitative information can be collected on important weathering properties such as water

- content, emulsion properties, changes in viscosity and density, dispersion, and dispersibility of the oil. These data are directly useful for NEBA evaluation and decision-making.
- (6) Due to the fact that the weathered oil from the TRICOLOR was not dispersible, no dispersants were applied on the slicks during the NEBAJEX exercise, and no dispersant effectiveness measurements with UVF instruments could be performed. The use of the Turner fluorometer has been successfully demonstrated however in previous sea trials and during the Sea Empress incident. The possibilities of monitoring the dispersant effectiveness with the Aquatracka-MiniBAT system remain to be tested.
- (7) Oil spill trajectory simulations were successfully obtained in real time during the exercise, enabling a better evaluation of the probable impact of the oil spill originating from the wreck. However, due to the very complex oily mixtures escaping from the wreck, with unknown composition and properties, and with an unknown time and degree of weathering, the uncertainty of other predictions from oil spill models would be unacceptably high. Limiting problems still arise when trying to reliably simulate the oil spill behaviour in support of NEBA, even with very powerful mathematical models.
- (8) The collected monitoring results lead to the conclusion that a **significant** weathering of the Tricolor HFO oils must have already taken place within the Tricolor wreck before it got released during wreck removal operations. The high density and weathering degree of the oil at the surface, and due to small wave actions and turbulence, probably explains why the surface oil patches submerged.
- (9) The ground-truth monitoring results obtained in real time showed that the **w/o emulsions were no longer dispersible**, and were so viscous that only recovery means that could deal with highly viscous emulsions would still be effective. Only the first day of the NEBAJEX exercise, mechanically combatable oil spills were observed. That day, the recovery vessel on standby at the Tricolor site has been informed by the overall monitoring co-ordinator about the thicker oil patches and trails observed and monitored at the sea surface, and has been advised to recover the oil with guidance from a remote sensing aircraft.
- (10) On the basis of general knowledge of the behaviour and weathering of heavy fuel oils, and on the various monitoring and modelling results, an attempt was made to draw a mass balance of the Tricolor oil pollution of September 2003:
  - The estimated 200 m³ HFO quantities, remaining inside the Tricolor at the end of the pumping operations, could in fact have doubled in volume within the wreck before most it got released in the summer or late summer of 2003.
  - It is assumed that the natural dispersion and evaporation rate of the released oily mixture was very low.
  - Because the exact amount of oil and/or w/o emulsion that got spilt during September is unknown, no reliable figure can be given of the amount of oil pollution volume that was mechanically recovered *versus* the amount that effectively submerged. Although 50 m³ of oily waste was mechanically recovered from the sea surface that month, the results indicate that most of

the weathered and persistent HFO must have submerged in the water column, being subject to subsurface drift. These very persistent submerged HFO emulsions could finally sediment or beach on the shores.

### The following main subjects for further research have been identified:

- Chemical composition of the oil: the development of a standard protocol for the
  definition and determination of the major hydrocarbon groups, and of a standard
  list of PAH and other toxic oil compounds (BTEX, NPDs, toxic NSO compounds)
  that need to be determined for the purpose of monitoring of marine oil pollution
  accidents and environmental monitoring.
- **Ground-truth monitoring of surface oil**: the development of a more operational field kit, starting by a reconsideration and re-evaluation of existing field kits, in the light of the NEBAJEX exercise findings.
- Ground-truth monitoring of sub-surface oil and of dispersant effectiveness: further study of the possibilities and limitations of different UVF instruments especially the Aquatracka fluorometer.
- **Assessment tools**: in the light of the modelling difficulties during this exercise (with releases of complex oily mixtures), further work is needed to make the existing oil spill models more operational in as many cases as possible.
- The developing and testing in the field, of an effective method for surface **oil sampling with aerial means** (helicopters).

### Acknowledgements

The authors want to thank all other scientists and personnel from MUMM, SINTEF and CEDRE who were involved in this project and exercise: E. Donnay, J.Haelters, J.P. De Blauwe, A. Pollentier, J. Ozer, V. Pison, M. Knockaert, D. Van Tuyckom, J. Tavernier, B.Loicq, L. Vigin, E. Monteyne, M. Neyts, J.P. Vogt, M. Reed, and E. De Nantueil. We want to express our gratitude to the French Navy, CEPPOL, and especially the French Maritime Prefect for his kind authorization to hold the exercise near the Tricolor wreck. We thank the Belgian Navy, and in particular commander P. Ramboer and the crew of the Belgica, for their motivating assistance during the exercise. We also wish to thank the Belgian School for Light Aviation of Brasschaat, for their flexibility in organizing the aerial surveillance around the Tricolor. The project was supported substantially by a pilot project grant from the European Commission.

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This report was issued by MUMM in March 2004.

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MANAGEMENT UNIT OF THE NORTH SEA MATHEMATICAL MODELS

SECTION 15 MARINE ECOSYSTEM MANAGEMENT



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