Chemicals In Combating Oil Spills

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Abstract

This paper presents the usefulness of chemical aids in oil spill combatment. The studied product types are: (1) dispersants, (2) demulsifiers, (3) bioremediation agents, (4) Solidifiers (gel agents and viscofiers), (5) herders, (6) cleaning agents for objects and flora, (7) cleaning agents for fauna, (8) synthetic sorbents, (9) in-situ burning agents and (10) elasticity agents. A description of the use of these agents is given and the steps to be taken to decide on the use of these products in case of an actual spill.
For approval it is necessary to assess the risks involved in the use of oil spill chemicals. Risk assessment of oil spill chemicals is a complicated process, since not only the chemical itself, but also the spilled oil is of concern. The complete assessment for the approval of oil spill chemicals can be separated into three stages:
Firstly approval of products, prior to oil spill response e.g. testing of products on effectiveness and hazardousness (toxicity, bioaccumulation and persistency).
Secondly, approval of use prior to actual oil spill response on the basis of location specific parameters, type and size of the oil spill, environmental benefit, etc.
Thirdly, during response, information is required on application and safety aspects to enable an effective and safe treatment.

Introduction

Spilled oil can cause damage to a variety of resources: ecological resources, such as seabirds, marine organisms or sensitive habitats; economic resources, such as fisheries and amenity resources, such as tourist beaches and facilities.
The type of damage varies according to the particular circumstances of the spill. The purpose of any oil spill response should be to reduce the observed or expected damage.
Oil spill chemicals are chemical substances, added to spilled oil in order to change its physical and/or chemical properties, so the oil is easier to control. Each treatment agent has its own window of opportunity and specific spill conditions in which it can be used.

Ten types of agents each with a different mode of action are distinguished. In Table 1 an overview of these chemical agents is presented. A specific type of oil spill chemical can be selected on the basis of the aim of application and the location of the oil spill.

	Type of agent	Aim of application
1	Dispersants	Remove oil from water surface by rapidly dispersing it into the water column
2	Demulsifiers	(1) Prevent formation of water-in-oil emulsions or(2) break existing emulsions back into separate oil and water phases (e.g. to improve pumpcapacity)
3	Bioremediation agents	Accelerate oil degradation by bacteria
4	Solidifiers	Turn the oil into a solid coherent mass
5	Herders	(1) Prevent oil from spreading or (2) move it to another area
6	Cleaning agents for objects and flora	Enhances the amount of oil washed of objects in 'open' environment compared to water alone
7	Cleaning agents for fauna	Substantial removal of oil without disturbance of natural processes
8	Synthetic sorbents	Substantial sorption of oil which can then be removed without substantial oil loss
9	In-situ burning agents	Removes free oil or oily debris from water surface by burning oil in place
10	Elasticity agents	Increasing the cohesiveness of the oil thereby improving skimmers effectiveness

Table 1 Overview of the aim of application of agents for oil spill response

The present paper is a summary of an extensive literature study that has been performed, aimed to answer the question whether certain chemical agents for treatment of oil spills have potential for use (Jongbloed e.a. 2002). The results of that study, concerning every chemical agent category separately, were translated in more operational documents. These operational documents are published in a series of 10 booklets (one for each type of oil spill chemical) and are intended for oil spill responders (surface water quality managers/controllers) and for producers/suppliers of oil spill chemicals (Tamis, J.E, Koops, W and Jongbloed, J.H., 2003).

This paper is not a statement of the Dutch Ministry of Transport, Public Works and Water Management or current policy in the Netherlands. The information is required to determine if chemical agents may be used in Dutch waters.
At present the use of oil spill chemicals is not allowed without approval by the relevant authorities. For approval it is necessary to assess the risks involved in the use of oil spill chemicals. Risk assessment of oil spill chemicals is a complicated process, since not only the chemical itself, but also the spilled oil is of concern.

The complete assessment for the approval of oil spill chemicals can be separated into three stages

(1) Approval of products, prior to oil spill response. Testing of products on their effectiveness and hazardousness (toxicity, bioaccumulation, persistency);
(2) Approval of use, immediately after an oil spill occurred but prior to actual oil spill response. On the basis of location specific parameters, type and size of the oil spill, environmental benefit, etc;
(3) During response information is required on application and safety aspects to enable an effective and safe treatment.

The format of this paper is also based on these three steps and covers the following topics (thereby indicating for whom it is intended):

Topic

Approval of products (pre-approval) intended for Suppliers/decision makers
- o Data requirements
  - – *General information*
  - – *Ecotoxicological information*
  - – *Effectiveness*
  - – *General safety*
  - – *Instructions for use*

Approval of use intended for decision makers
- o Selection of chemical categories
- o Selection of products
  - – *Factors determining the effectiveness*
  - – *Effectiveness tests*
- o Environmental aspects

Response intended for responders
- o Application
- o Safety aspects

Figure 1 The three evaluation steps required before using a chemical in oil spill response

Approval of products

This chapter describes the first stage of the assessment for the potential approval of oil spill chemicals: (pre-) approval of products. Within this stage, a selection of products can be made with potential use for oil spill response. The selected products can be put on a 'pre-approval list' for potential use. All relevant product information, which is described below, should be reviewed in this stage.

In order to pre-approve chemicals for oil spill response, the following package of information should be supplied to the authorities responsible for decisions on the approval for use:

1. general information on substances and preparations;
2. eco-toxicological data;
3. effectiveness of the product;
4. general safety;
5. instructions for use.

General information on substances and preparations should be generated and submitted according to the guidelines described in the following. These guidelines are based on Appendix 2 of the OSPAR Recommendation 2000/5 on a Harmonised Offshore Chemical Notification Format (HOCNF), OSPAR 00/20/1-E, Annex 17, available on the OSPAR website: www.ospar.org.

Products should be screened according to the schedule presented in Figure 2. Eco-toxicological data should be generated and submitted according to the guidelines.

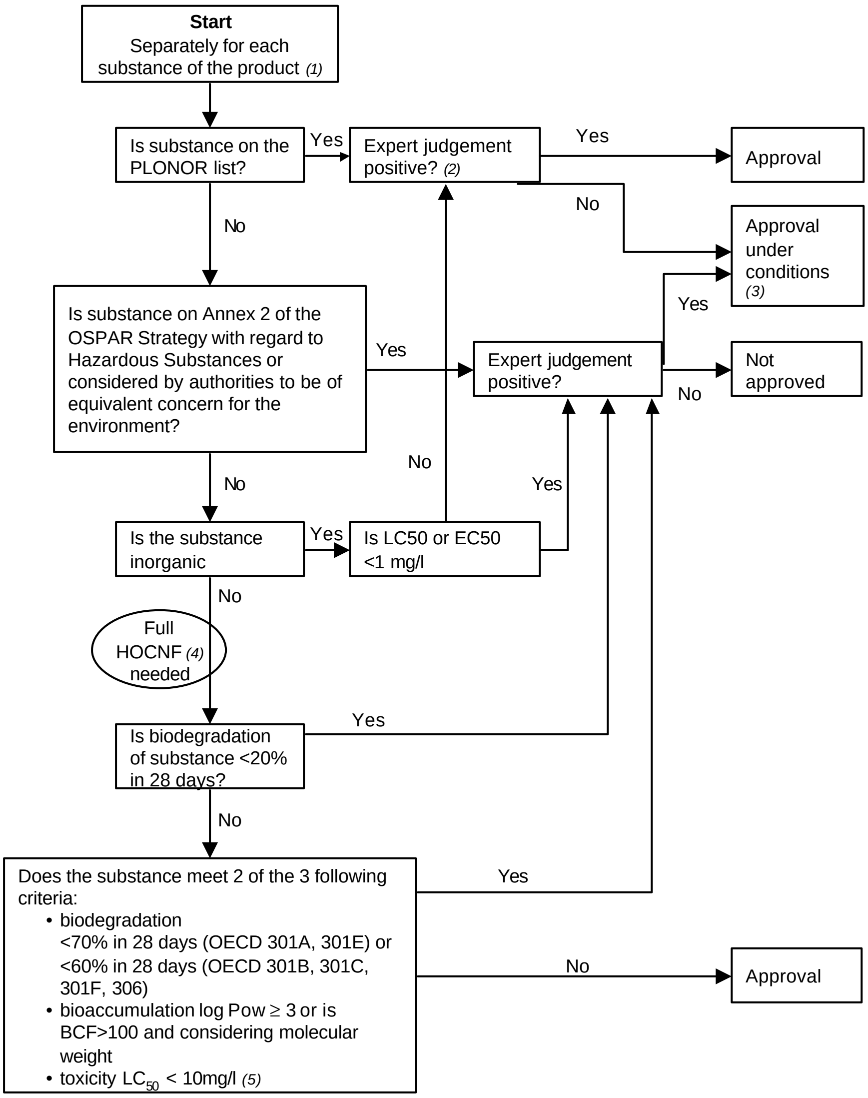

Figure 2 **Pre-screening scheme for the assessment of oil spill chemicals, based on OSPAR Recommendation 2000/4 on a Harmonised Pre-screening scheme for Offshore Chemicals**

(1) A product should be tested according to approved effectiveness test(s) described for each individual chemical category. Test results should be submitted to the authorities.

A Safety Data Sheet, according to EC Commission Directive 91/155/EC of 5 March 1991 defining and laying down the detailed arrangements for the system of specific information relating to dangerous preparations in implementation of Article 10 of Directive 88/379/EEC, is required and should be submitted to the relevant authorities.

Instructions for use of the product are required and should be submitted to the relevant authorities. This should include method(s) of application and application dose(s).

The full chemical composition of the product should be known. The pre-screening should be performed on all substances. Product can only be approved if all separate substances in the product are approved.

In accordance with the precautionary principle, expert judgement on a PLONOR substance should take into account sensitive areas, where the discharge of certain amounts of such a PLONOR substance may have unacceptable effects on the receiving environment. In such a case, the product should not be approved.

(2, 3) Expert judgement on substances should take into account sensitive areas, where the discharge of certain amounts of such a substance may have unacceptable effects on the receiving environment. Specific circumstances for approval or disapproval of the product on basis of the substance should be noted.

(4) When a full HOCNF (Harmonised Offshore Chemical Notification Format) is required, information should be generated and submitted according to the guidelines presented in of this document. These guidelines describe a HOCNF based on OSPAR 00/20/1-E, Annex 17 and adapted for oil spill chemicals.
If toxicity data are available only for the preparation, the authority should, on a case by case basis:
(a) seek further information from the supplier to identify that substance, which is the major contributor to the overall toxicity of the preparation; or
(b) use the toxicity data of the preparation to estimate the toxicity of a substance contained in it, taking into account the concentration of the substance in the preparation.

Approval of use

This section, the approval of use, describes the stage in oil spill response immediately after an actual spill has occurred. There are several steps in the approval of use of oil spill chemicals, see Table 2.

Step	Subject
1	Selection of chemical categories
2	Selection of products
3	Assessment of potential (environmental) effects

Table 2 Steps in the approval of using oil spill chemicals

The first step is the selection of chemical categories that could potentially be used under the given circumstances. Table 3 describes the overall applicability of oil spill chemicals for oil combat activities. It is intended for oil spill responders and it aims to provide an overview of available chemical response options and a guide to decision making in oil spill response.

The next step is to select an approved product, which is effective under the given circumstances. The final step for approval of using a product in oil spill response, is an assessment of the potential effects.

Oil spills may have serious impacts upon ecological, economic and/or amenity resources. Economic effects are mainly related to dispersed oil in the water column and sediment, which could affect (shell)fisheries by toxicity and/or tainting. Therefore, the decision how to protect economic resources should be based on preventing/reducing the amount of dispersed oil. Amenity effects are mainly caused by stranded oil, which could affect tourist beaches and facilities by covering relevant areas. The decision how to protect amenity resources should, therefore, be based on preventing/reducing the amount of oil reaching the shoreline/coast. Ecological effects are related to different forms of spilled oil (floating oil layer on the water surface, dispersed oil in the water column, stranded oil and oil in the sediment). The decision on how to respond to protect ecological resources is, therefore, much more complicated, compared to economic and amenity resources.

Applicability of oil spill chemicals

The applicability of oil spill chemicals for oil combat activities is summarised in a series of Tables and decision trees. The applicability depends on the limitations for use and the importance of the application of the chemical. This paragraph aims to provide a short decision scheme on the applicability of oil spill chemicals for oil combat activities. It does not aim to provide complete information on all chemical categories of oil spill chemicals. First of all the location of the oil (top of Table 3) has to be determined and the purpose of treatment and the activity needed (left side of Table 3).

Purpose of treatment	Activity	Location of the oil					
		In ship/truck	On water surface	On coast or bank	In soil	On object/ road/plants	On birds/animals
Source-strength reduction	1. Reduce /restrict outflow	**Sorbents Solidifiers Elasticity agents**					
Removal of the oil	2. Enhance effectiveness of mechanical removal		**Demulsifiers Elasticity agents Sorbents**	**Sorbents Elasticity agents Solidifiers**		**Sorbents**	
	3. Remove from water surface to water column		**Dispersants Demulsifiers**				
	4. Burn		**Burning agents (demulsifiers)**	**Burning agents (demulsifiers)**			
	5. Enhance biodegradation			**Bioremediation agents**	**Bioremediation agents**	**Bioremediation agents**	
	6. Remove from hard substrate to water			**Dispersants Cleaning agents**		**Dispersants Cleaning agents**	
	7. Clean object/vegetation	**Dispersant Sorbents Cleaning agents**		**Dispersants Sorbents Cleaning agents**		**Dispersants Sorbents Cleaning agents**	
	8. Clean fauna (birds)						**Cleaning agents**
Reduce/ Limit spreading	9. Reduction of spreading	**Sorbents Solidifiers**	**Sorbents Herders Solidifiers**	**Sorbents**		**Sorbents**	
	10. Prohibit adhesion (preventive)			**Herders Sorbents**		**Herders Sorbents**	
	11. Prohibit penetrating in soil			**Herders Sorbents Elasticity agents**			
	12. Move the oil to a more favourable place			**Herders**			

Table 3 **Selection of category or categories of chemical treatment agents, dependent on the location of the oil pollution, the purpose of the treatment and the activity involved.**

Based on purpose of treatment and the activity needed, a chemical category is recommended.

1. There could be a need to **reduce/restrict outflow** when the oil is contained in an enclosed environment (for example, a tanker) and there is a potential that the oil will enter the open environment. In such a case, measures can be taken in order to prevent/reduce this outflow, which will reduce the potential exposure of oil to the marine environment..
2. There could be a need to **enhance the effectiveness of mechanical removal** when the oil cannot be (effectively) removed without altering the physical form of the oil. In such a case, measures can be taken, prior to- or during mechanical removal, which will increase the amount of oil removed and/or decrease the time needed for removal.
3. There could be a need to **remove the oil from the water surface to the water column** when there is a (high) risk that birds will be affected by the floating oil slick and/or there is a (high) risk that the floating slick will reach a sensitive area and mechanical recovery is not a feasible option.
4. There could be a need to **burn the oil** when there is a (high) risk that birds will be affected by the floating oil slick and/or there is a (high) risk that the floating slick will reach a sensitive area and mechanical recovery is not a feasible option. A special case, in which there is a need to burn the oil spill, is when the water surface is (partly) covered with ice. The ice makes it not- or hardly possible to reach the polluted area for oil spill response. *In-situ* burning of oil can be achieved by simply lighting the oil from an aircraft. There could also be a need to burn oil when oil is located on coast or bank and other options (mechanical recovery or leaving the oil untreated) are not feasible.
5. There could be a need to **enhance biodegradation** when oil is located on coast, bank, in soil and other areas (for example, vegetation covered areas) and other options (mechanical recovery or leaving the oil untreated) are not feasible.
6. There could be a need to **remove oil from hard substrate to water** when oil has covered hard substrates (such as docks) and other options (mechanical recovery or leaving the oil untreated) are not feasible.
7. There could be a need to **clean objects/ship/truck** when oil has covered certain objects or parts of a ship/truck. These objects/parts will have to be cleaned. There could be a need to **clean objects/ vegetation** when oil has covered objects and/or vegetation on coast or banks and leaving the oil untreated is not an option. In such a case, measures can be taken which will decrease the potential exposure of oil for intertidal resources. There could be a need to remove oil from hard substrate to water when oil has covered hard substrates (such as docks) and other options (mechanical recovery or leaving the oil untreated) are not feasible.
8. There could be a need to **clean birds** when they are found, covered with oil. In such a case, measures can be taken which will increase the chance for survival of the bird.
9. There could be a need to **reduce spreading** when oil is spilled on a ship/truck and there is a potential that the oil will spread to cover and pollute a greater area. In such a case, measures can be taken in order to prevent/reduce this spreading. There could also be a need to reduce spreading when oil is floating on the water surface and: the oil has a potential to spread and cover a larger area (increasing the potential exposure for birds), and/or the oil has a potential to reach the shoreline. There is also a need to reduce spreading when oil is located on coast or bank, on object/road/plants and the oil has a potential to spread and cover a larger area. In such a case, measures can be taken that will decrease the potential exposure of resources

10. There could be a need to **prohibit adhesion (preventive)** when there is a threat that oil will pollute a coast or bank or an object/road/plants (for example, in case a floating oil slick is heading for a dam or the shoreline). In this case measures can be taken (preventative treatment of the area that is threatened by an oil spill) that will prohibit the oil adhesion.
11. There could be a need to **prohibit penetration in soil (preventive)** when there is a threat that oil will pollute a coast or bank (for example, in case a floating oil slick is heading for the shoreline). In this case measures can be taken (preventative treatment of the area that is threatened by an oil spill) that will prohibit the oil penetrating in soil.
12. There is a need **move the oil to a more favourable place** on the water surface when the floating oil slick is located at a place that is difficult to reach (for example, underneath a dock) and needs to be pushed away to a place where it can be (mechanically) removed.

Based on purpose of treatment and activity required a selection of recommended category or categories of chemical treatment agents can be made (see Table 3) For each category a decision tree has been developed to determine if a product from the recommended category can be used. In the following each category of chemical treatment agents will be discussed. The product types are: (1) dispersants, (2) demulsifiers, (3) bioremediation agents, (4) Solidifiers (gel agents and viscofiers), (5) herders, (6) cleaning agents for objects and flora, (7) cleaning agents for fauna/birds, (8) synthetic sorbents, (9) in-situ burning agents and (10) elasticity agents**.**

Dispersants

The use of dispersants enhances natural dispersion and by that also the biodegradation rate. Dispersants reduce the effects of oil layers on floating organisms (birds) and may reduce the amount of stranding oil on shorelines

Dispersants should not be used for very thin layers (“sheen”, “rainbow” and “metallic”) of oil, since dispersant droplets could ‘fall through’ the thin oil layer (also depending on the droplet size of the dispersant spray. The net environmental benefit of using dispersants to thin layers may even be negative or counter productive. Always consider the effectiveness of the product under the given circumstances

Dispersants increase the concentration of dispersed oil in the water column and consequently the risk on ecological effects in the water column; most modern dispersants however are much less toxic than the hydrocarbons they disperse. Acute toxic effects due to the use of dispersants have been observed on sites offering low dilution possibilities, such as shallow bays or coral reefs close to the surface. Providing enough water for dilution, toxic effects are not expected following oil dispersion;

The concentration of dispersed oil in water can be predicted on basis of the dilution factor. The dilution factor is, however, not the most important factor for predicting the environmental concentration. The spill dimension (surface area polluted and layer thickness before application of the dispersants) plays a more important role.

In Koops e a (2004) recommendations on the use of dispersants are described depending on the layer thickness of the oil slick, the concentration of dispersed oil and the water depth. Based on these results, it can be concluded that large spills (>200 m^3) normally with a layer thickness of 100 – 200 µm (0.1 – 0.2 mm) should not be treated with dispersants unless the water depth is more than 20 meters. Medium spills could be treated with dispersants in case the water depth is more than 5 meters, assuming a layer thickness of less than 200 micron (0.2 mm). Small spills (< 2,000 litres) could be treated with dispersants regardless of the water depth.

In summary, the use of dispersants in oil spill response should be based on the following decisions (see Figure 3 and assuming response is necessary and mechanical recovery is not feasible):

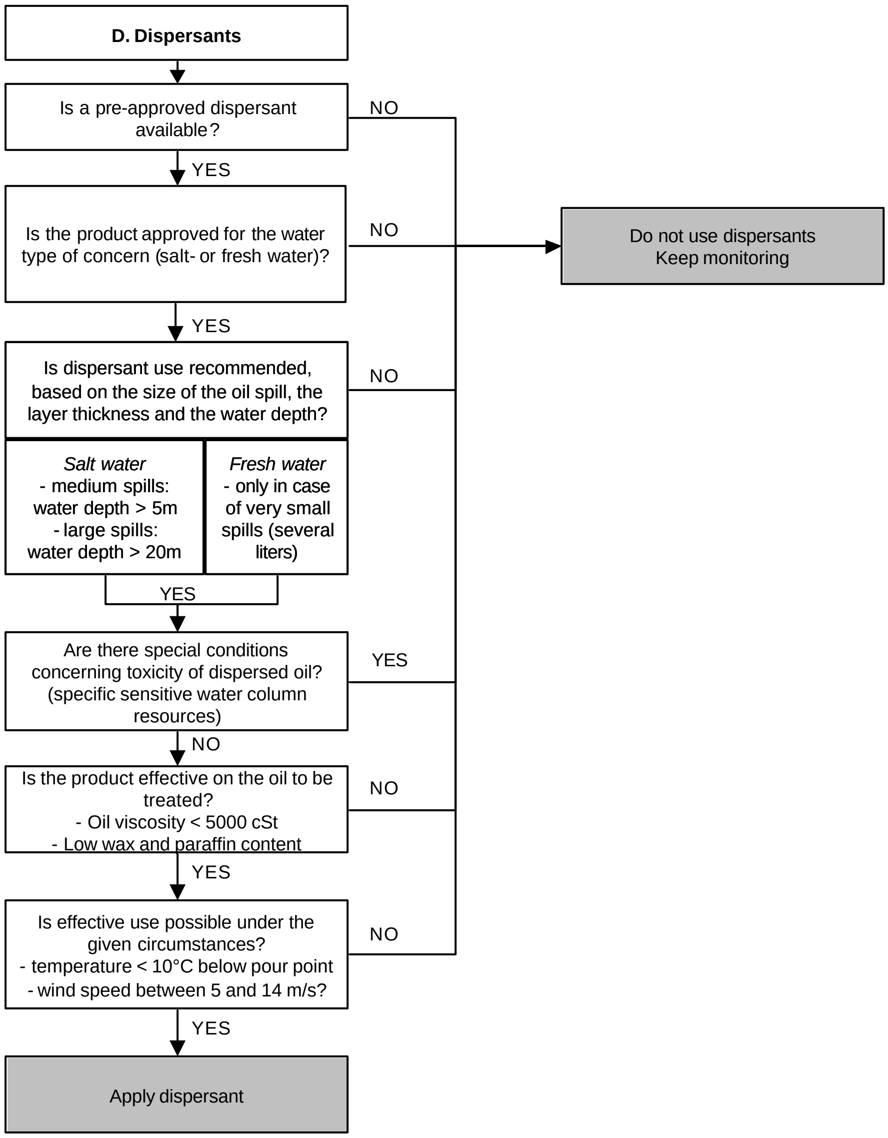

Figure 3 Decision tree for the use of dispersants

The use of the dispersion method should be selected only if environmental profits are likely to occur. Dispersion of oil into the water column is not likely to result in acute toxic effects on aquatic organisms in deep well mixed waters. In other types of water the effects of dispersed oil on aquatic organisms can be considerable. At sea, in coastal waters and large rivers, treatment with dispersants of small to medium spills leads to a reduction in risk for birds, while the dispersion of oil into the water column is not likely to result in limited acute toxic effects on aquatic organisms. For inland waterways the use of dispersants should only be considered in case of very small spillages. Special fresh water dispersants should be used.

Alternative response methods, that could remove the oil from the environment, should always be considered; the use of dispersants from an aircraft is a fast response method compared to the other response methods that need a vessel to apply. If time is important this could enhance the possibility of the use of the dispersant method;

Demulsifiers

The benefit of using demulsifiers, is reduction of the viscosity of the spilled oil, thereby increasing the effectiveness of mechanical recovery. In countries, where mechanical recovery at sea is considered to be the main approach in oil spill response, the use of demulsifiers is an option for treatment of a water-in-oil emulsion aiming at decreasing the volume of the recovered "oil", thereby increasing the capacity of mechanical recovery. The results strongly depend on the nature of the oil, degree of weathering and aging of the oil.. Matching a product with an oil type is an empirical process.
Available information suggests that the toxicity of the product alone for water organisms may be acceptable for some products. It can be assumed that most of the used demulsifiers will be recovered with the oil and, therefore, environmental risks of remaining demulsifiers are not likely to occur, especially in combination with the fast dilution in the open sea conditions.
It can be concluded that the application of demulsifiers to an oil spill is not likely to result in acute toxic effects on aquatic organisms in deep well mixed waters. The ecological benefit could be considerable in combination with a follow up treatment like mechanical removal
In summary, the use of demulsifiers in oil spill response should be based on the following decisions (Figure 4 assuming response is necessary and mechanical recovery will be enhanced by the use of demulsifiers):

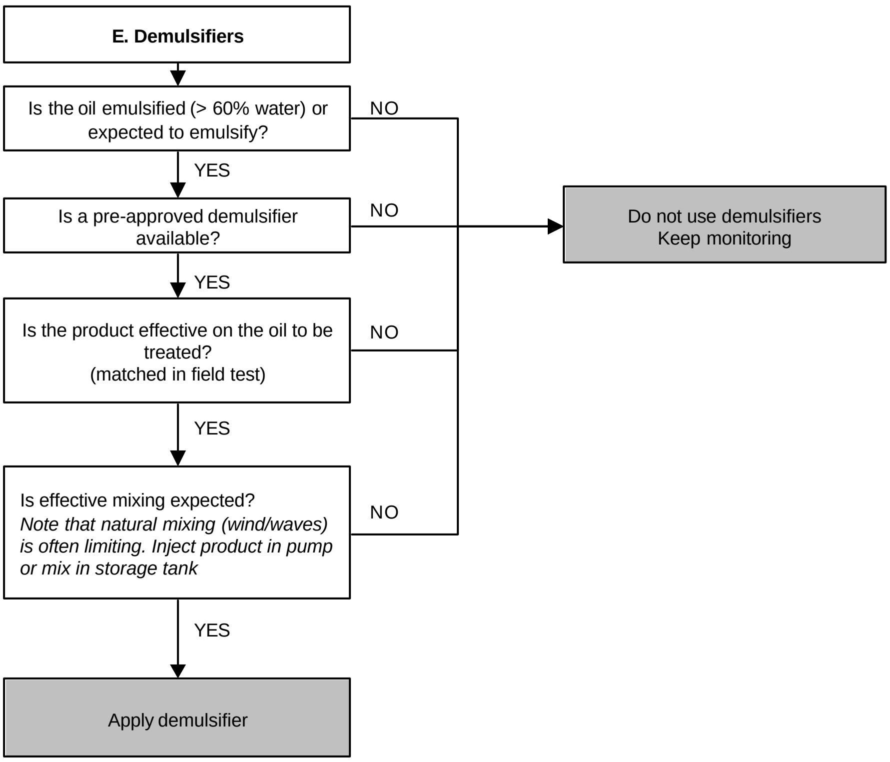

Figure 4 **Decision tree to determine if demulsifiers can be used**

Bioremediation agents

Bioremediation agents are to be used to enhance oil biodegradation. Bioremediation agents are potentially applicable when the oil is located on the coast or bank, in soil, or in case of residual oil when oil is spilled on a road(side).

Bioremediation is only useful in case mechanical removal is not possible, in case residual oil after mechanical removal, or when natural biodegradation processes are limited, due to, for example, low nutrient concentrations. Bioremediation is not useful on open waters. For use on open waters the bacteria and stimulating product should be kept in contact with the oil in one way or the other. This doesn't seem a very practical method of performing bioremediation. Furthermore, this type of oil spill response is a slow process and floating oil on the water surface requires fast response. Bioremediation is not useful on firm sandy shorelines, because the oxygen level is often limited. When dealing with salt marshes and vegetation covered shorelines, bioremediation might be considered. Bioremediation is not an option for heavy, weathered or emulsified oil. Products are not effective on thick layers of oil..
Laboratory tests and field observations reveal that acute toxic effects of bioremediation agents are unlikely at locations with high dilution. Application of biodegradation agents may result in an increase of the acute toxicity of oil for aquatic species

In summary, assuming response is necessary and mechanical recovery is not feasible, the use of bioremediation agents in oil spill response, should be based on the following decisions (see

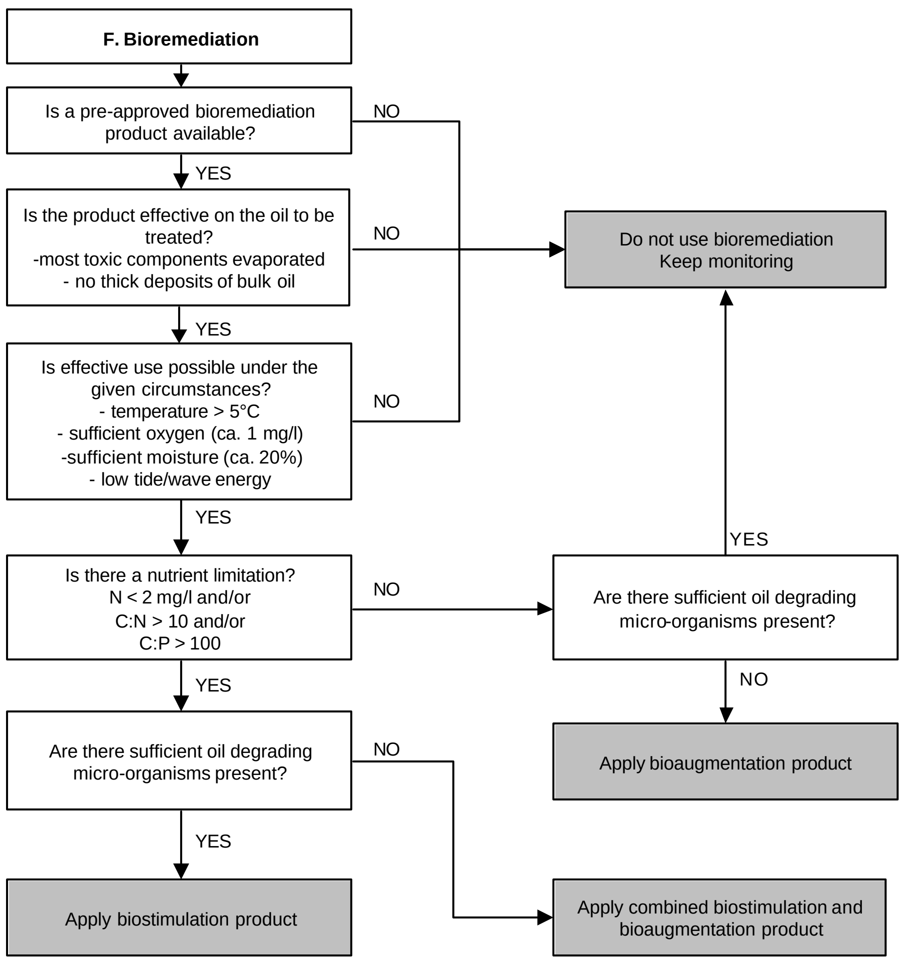

Figure 5 Decision tree to determine if bioremediation agents can be used

Environmental benefit of application of bioremediation agents may only be expected in salt marches or vegetation covered shorelines and where mechanical removal damages flora. This means that bioremediation is not useful on open waters and firm sandy shorelines. Bioremediation could also be an option in case the oil spill is located on shorelines with soft sediment (See Table 4).

Location	Feasible?	Reason
Shallow coastal waters	No	High rate of evaporation and spreading
Surface water	No	High nutrient levels, difficult application
Littoral zone	No	Oxygen limiting in sediments
Salt marshes	Yes	Mechanical removal damages flora
Shallow fresh water	No	Oxygen often limiting, nutrient levels sufficient
Rivers / Channels	No	Movement of oil faster than oil degradation
Rocky shores	No	Physical processes/removal
Vegetation covered shorelines	Yes	Mechanical removal damages flora
Not covered shorelines (soft sediment)	Yes*	
Firm sandy shorelines	No	Insufficient oxygen penetration into sediment

1. = natural attenuation (doing nothing, only monitoring) is often preferred, due to lower costs.

Table 4 Feasibility of bioremediation in various locations

Solidifiers

The need for using solidifiers in oil spill response could be in preventing the oil from entering the environment (reduction of outflow from a ship or tanker), reduce spreading of an oil slick on open water surfaces, or enhancing mechanical removal on coast/banks. However, application of solidifiers can only be effective under very limited circumstances.
The toxicity of the selected solidifiers for aquatic organisms is relatively low. The toxicity of No. 2 fuel oil for crustaceans and fish decreases, when treated with a solidifier. Effects of treated oil on birds could be increased due to the use of solidifiers.
In summary, the use of solidifiers in oil spill response should be based on the following decisions tree to determine if solidifiers can be used (see Figure 6)

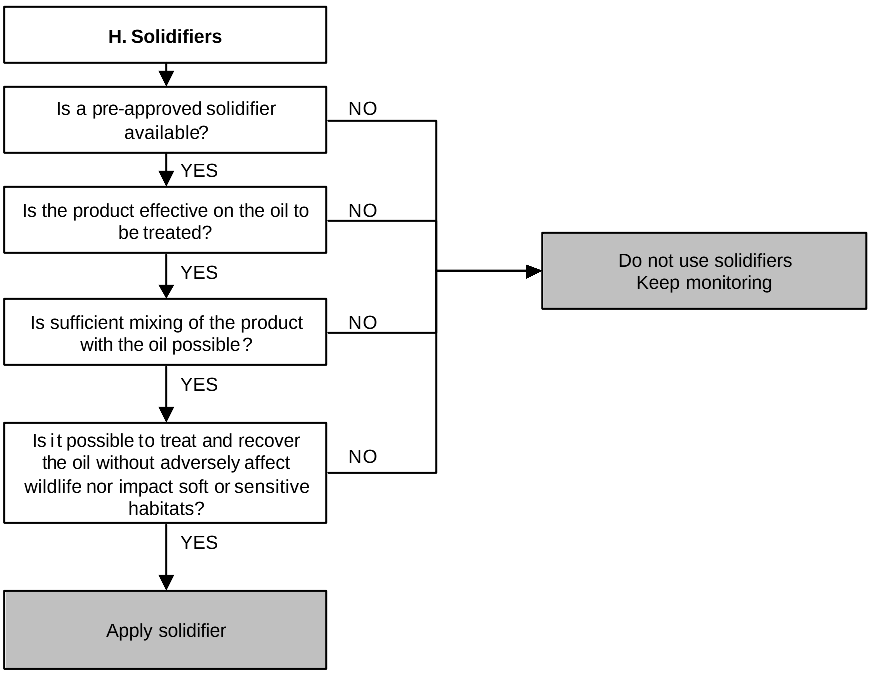

Figure 6 Decision tree to determine if solidifiers can be used

The use of solidifiers on open water is questionable, because the solidified oil is considered more as a problem than a solution. Solidifiers will inhibit the natural process of dispersion and evaporation, which act to remove oil from the surface of the water. Solidified material from each spill should be tested in order to determine if the material is characteristically hazardous or non-hazardous.

Herders

Herders are collecting agents, which reduce the spreading of an oil slick. The products should be applied as soon as possible after a spill release. Herders as chemical barrier are more effective on thin films and low to medium viscosity oils. Limiting factors include rain, high wind and moderate currents. Herders could also be used to prevent sticking of oil on objects and quay-walls.
Herders decrease the potential exposure to oil for water surface and intertidal resources. There is no increase in exposure to oil expected for resources, when using herders in oil spill response. However, exposure of resources to the herder itself is expected, since the chemicals are applied not directly to the oil but to the surrounding environment.
It can be assumed that potential adverse effects, caused by using herders in oil spill response, are related to the product. Based on eco-toxicological information of the reviewed products, significant adverse effects on the environment are not expected when using herders in oil spill response. However, the given circumstances of an oil spill, like a specific sensitive environment or limited dilution, should always be considered in the decision whether to use herders in oil spill response or not.
Note that herders have a very limited scope of application and have not been used at real oil spills for many years. The application of herders has important advantages, but also important disadvantages (considering the limited effectiveness and lack of experience).
In summary, the use of herders in oil spill response should be based on the following decisions see Figure 7 and Figure 8

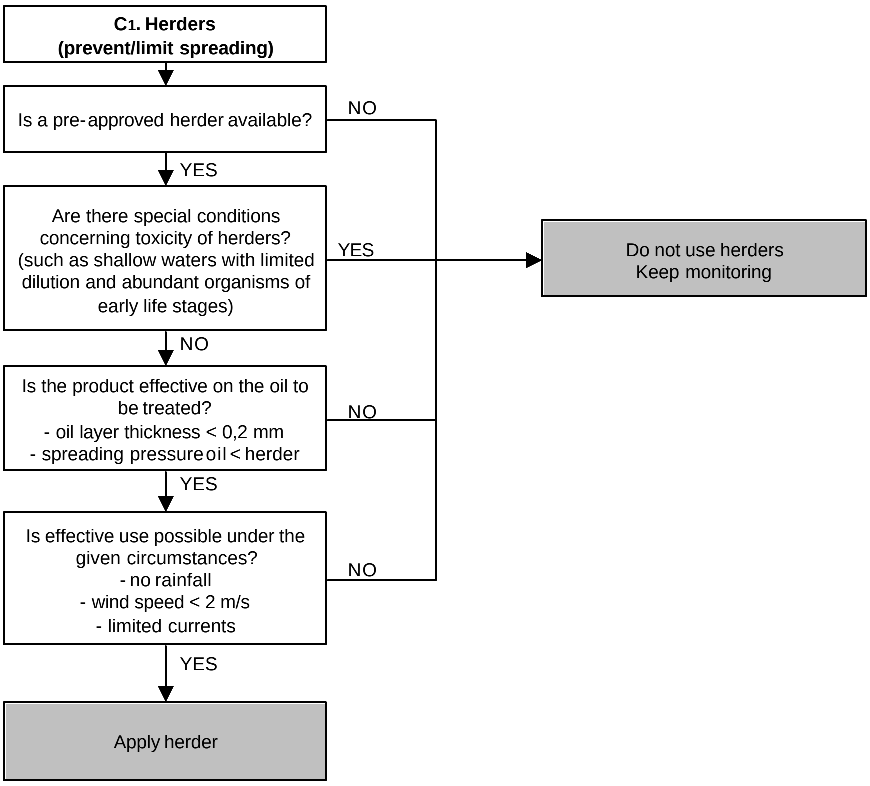

Figure 7 Decision tree to determine if herders can be used to prevent/limit spreading

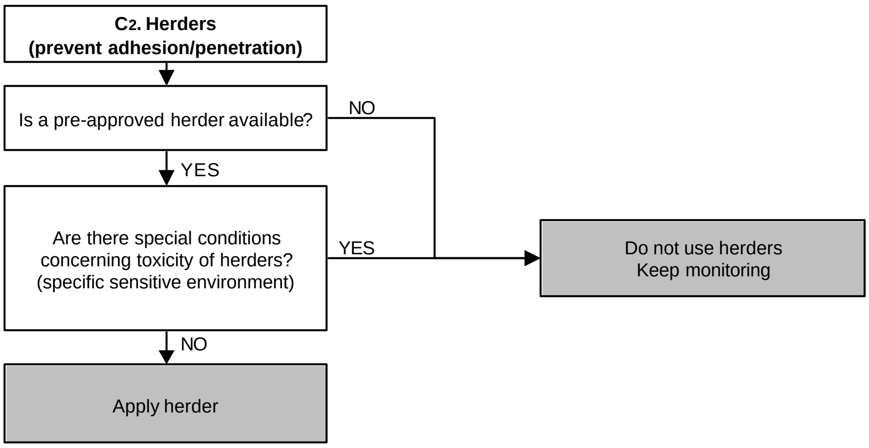

Figure 8 Decision tree to determine if herders can be used to prevent adhesion/penetration

Cleaning agents for objects and flora

The fate and effects of treated oil, using cleaning agents for objects and flora, varies considerably because of the different types of cleaning agents and applications. Treated oil could either be washed into the aquatic environment (by use of emulsifying products) or recovered (by use of non-emulsifying products).

When non-emulsifying cleaning products are used, clean-up operations do not cause substantial effects on the environment, provided that unstuck oil is actually recovered. When emulsifying cleaning agents are used, the removed oil will be released into the aquatic environment, possibly leading to important oil concentrations in coastal waters. Even worse, surface active agents may facilitate the oil's penetration into the sediment.

In summary, the use of cleaning agents for objects and flora in oil spill response should be based on the following decisions (see Figure 9)

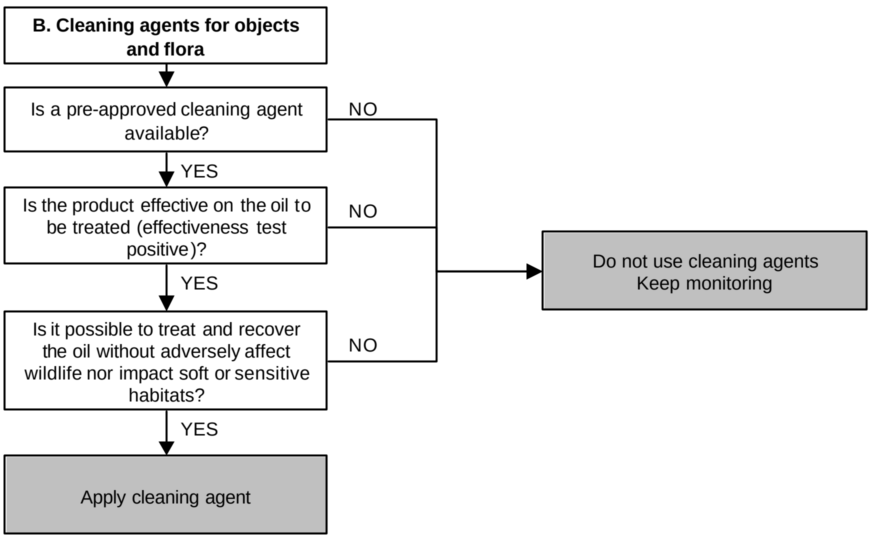

Figure 9 Decision tree to determine if cleaning agents can be used to clean objects and or flora

The intertidal zone is of great value both in amenity and ecological terms. Toxic effects of beached oil treatment with non-emulsifying cleaning agents are likely to have only limited impact on commercial fish or (shell)fisheries (e.g. cockles) since these products do not enhance oil dispersion and the treated oil will be recovered. Therefore, for this environment (sandy amenity beaches) it is assumed that a pre-approved product will be of an acceptably low risk. However, mechanical removal without the use of cleaning agents should always be considered first.

Sorbents (synthetic)

The use of sorbents is a temporary method to deal with an oil spill. It can prevent oil from spreading and facilitates its collection without presenting severe hazard to marine life. Application of synthetic sorbents efficiently limits the contamination of objects, birds and mammals. Synthetic sorbents are not efficient enough to secure a satisfying leachate quality from the various kinds of disposals. Attention should be focused on the physical risk instead of the chemical risk, but information is lacking for both. Activities for deploying and retrieving sorbents should not adversely affect wildlife, nor impact soft or sensitive habitats (marshes, sheltered tidal flats, etc.). Synthetic sorbents should not be used in a manner that might endanger or trap wildlife.
The following characteristics must be considered when choosing sorbents for cleaning up spills: spreading of the product and behaviour in windy conditions; mixing quantity of sorbent needed to allow collection; separation of the saturated sorbent from the underlying sand and behaviour of the saturated sorbent in water.
Re-use: some sorbents allow the sorbed liquid to be extracted via mechanical or chemical means enabling re-use. This could limit the amount of solid waste generated during a spill cleanup operation. The safety aspects of attempting re-use should be considered. Re-use has never been used in a real spill.
In summary, assuming response is necessary and mechanical recovery is not feasible, the use of synthetic sorbents in oil spill response should be based on the following decisions

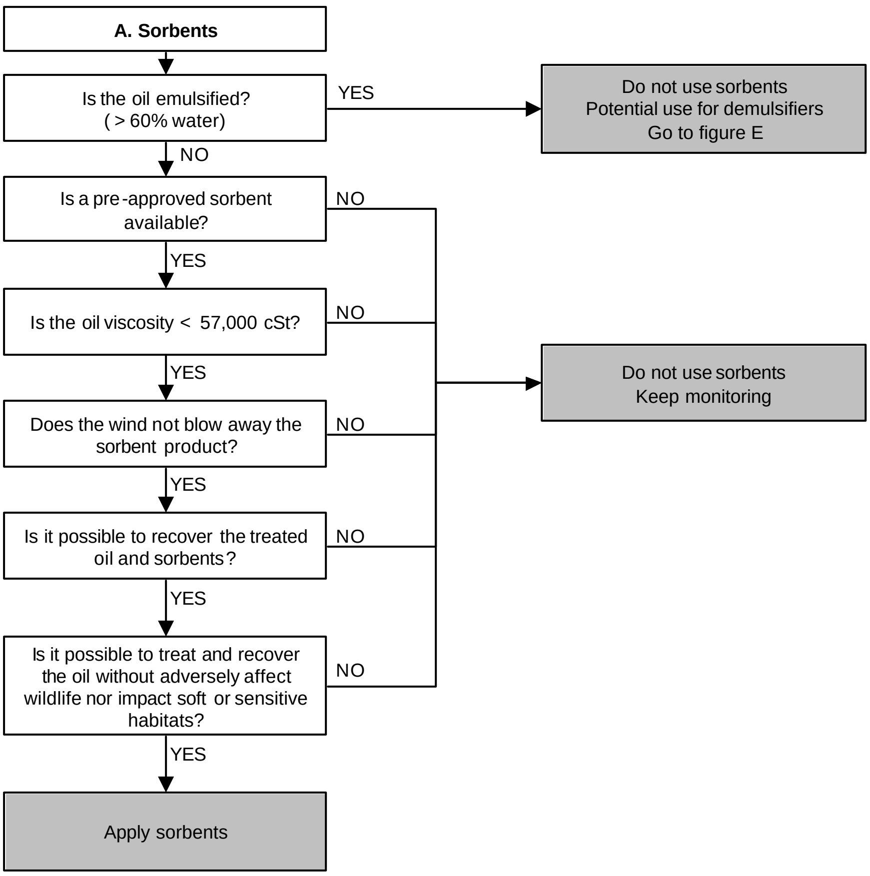

Figure 10 Decision tree to determine if synthetic sorbents can be used

Elasticity agents

Elasticity agents reduce natural dispersion of oil into water, so it can potentially be used in situations where the aquatic life is very sensitive to dispersed oil in the water column.
There is insufficient data for an evaluation of the real risk of these kind of products and the treated oil in the marine environment. Especially the impact on birds, mammals and shorelines should be investigated, since the effect on these resources are expected to be greater for oil that is treated with elasticity agents than for untreated oil. The unrecovered treated oil may also be more persistent.
There is considerable environmental concern for unrecovered treated oil, which may be more persistent. Treated oil can be very sticky and is more likely to adhere to fur, feathers, vegetation, and dry shorelines. Therefore, the impact of elasticity agents and oil treated with elasticity agents on birds, mammals and shorelines should be investigated.
Elasticity agents should only be applied to contained slicks, so that the treated oil is immediately recovered. They can be very helpful for treatment of light or medium oil types that are difficult to recover with mechanical equipment or sorbents. Limiting factors are low temperatures of water and air, when heavy oils are more viscous and mixing of the product into the oils is more difficult. Elasticity agents have a very limited scope of application.

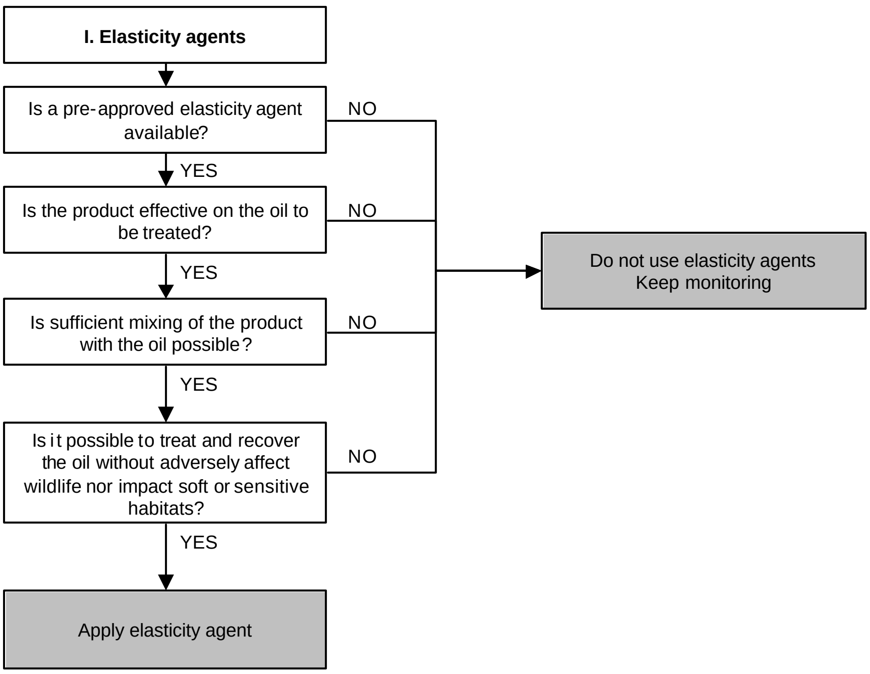

Figure 11 Decision tree to determine if elasticity agents can be used

Burning agents

In-situ burning has some advantages, such as rapid removal of oil. However, the disadvantages mostly outweigh the advantages. Important disadvantages are the creation of smoke plumes and the formation of residues of unburned oil. In-situ burning and igniters should not be applied to oil spills with small slick thickness, high evaporation, and high wind speed or high waves. Emulsification of an oil spill negatively affects in-situ ignition and burning.
It is not clear whether the overall risk for water-column inhabiting organisms and birds and mammals will be reduced or increased by application of in-situ burning agents in combination with the burning of oil slicks, as compared to the situation that the oil slick will not be burnt. The risks

for man and environment are difficult to be assessed and controlled. Therefore, in-situ burning is not commonly used.

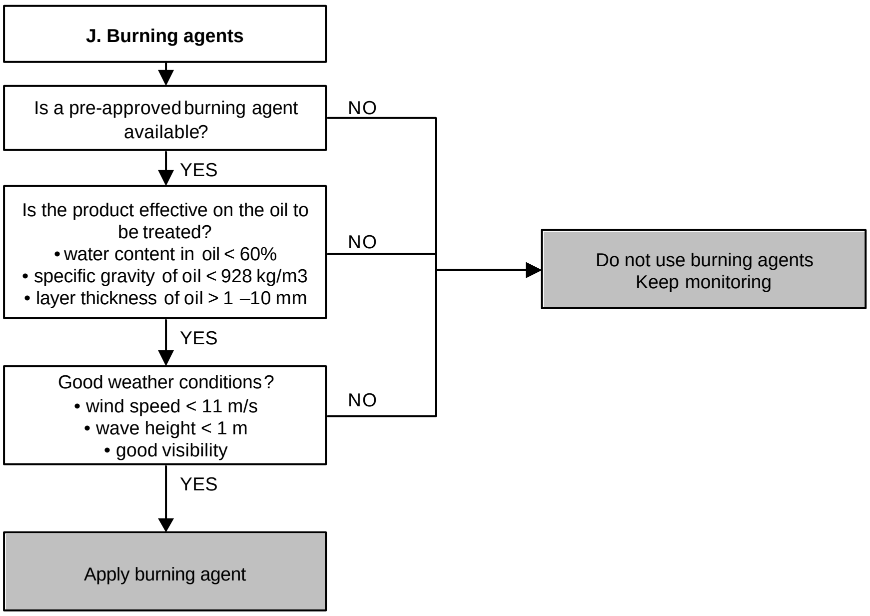

Figure 12 Decision tree to determine if burning agents can be used

Cleaning agents for oil polluted birds

It is assumed that cleaning with cleaning agents is necessary as cleaning with water alone will not be sufficient.
The decision whether the cleaning of birds will result in an environmental benefit is also not relevant in this case. The cleaning agent together with the treated oil could be collected after treatment so the use of these products will pose no additional risk to the environment. It has to be noted that washing away the treated oil together with the product in the sewage system, should be prevented.

In summary, assuming response is necessary, the use of cleaning agents for birds in oil spill response should be based on the following decisions (:

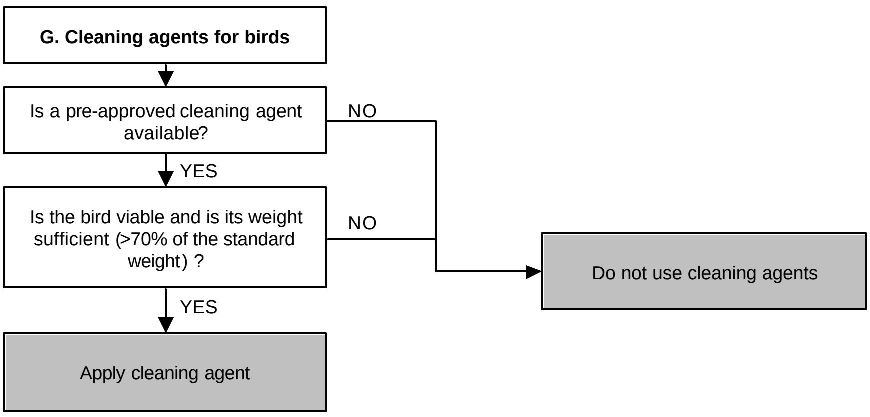

Figure 13 Decision tree to determine if cleaning agents can be used to clean birds

Discussion & Conclusions

For the selected chemical categories, sufficient information was found with regard to effectiveness, environmental factors influencing the effectiveness, test methods for effectiveness and general safety. However, insufficient information was available about composition, biodegradation, bioaccumulation and eco-toxicity of products and biodegradation and eco-toxicity of treated oil. This kind of information may be present in confidential product dossiers. However, this was not accessible for this study that was confined to the open literature. For the majority of the selected products, only limited information could be collected from Material Safety Data Sheets (MSDS). Persistence, Bioaccumulation and Toxicity (PBT) could often not be determined. A screening of the products was therefore not possible.

The most relevant conclusions for each selected chemical category are the following:

Dispersants can be very effective on certain oil types, but may only be acceptable on marine locations with high dilution rates due to the increase in toxicity of dispersed oil to water and sediment inhabiting organisms. Information on the influence of dispersants on the degradation and toxicity of oil is very important, but scarcely known. These are very important issues in the evaluation of dispersant product for approval..

D**emulsifiers** can be used on water in oil emulsions, facilitating the mechanical recovery of the spilled oil. Environmental effects of the demulsifier are not likely to occur because most of the demulsifier is contained within the oil and will be mechanically removed with it.

The use of **bioremediation** is very limited. It is only useful and recommended under specific circumstances such as contaminated salt marshes and vegetation covered shorelines where mechanical removal is not possible and natural biodegradation processes are reduced.

Solidifiers are only effective under very limited circumstances. They also have some important disadvantages, like inhibition of natural dissipation processes (dispersion and evaporation) and unknown risks for birds. Therefore, application of these chemicals is not considered relevant at present.

Herders can be very useful in reducing the spreading of thin slicks of low to medium viscosity oil, provided that they are applied in an early stage after a spill. Herders can also be used to prevent sticking of oil on objects and quay-walls. There is, however, a lack of experience with herders in practice.

Cleaning agents for objects are only specifically applicable for oiled solid surfaces like roads and quay-walls contaminated by supratidal or intertidal oiling. The effectiveness for cleaning vegetation will be limited. Discharge of oil and chemicals to the environment should be avoided by collection during and after treatment.

Cleaning agents for birds are already used word wide. The effectiveness of several products has been demonstrated, but survival of treated and released birds is not well known. Mixtures of oil and cleaning agents should be collected and treated, before discharge to sewage systems in order to avoid environmental contamination.

Synthetic sorbents can be effective and useful tools for the prevention of spreading and collection of light to medium viscous oil in specific conditions, like calm seas, near shore and on rocks and soil surfaces. The environmental effects of synthetic sorbents cannot be assessed adequately yet, due to missing information.

In-situ burning may be effective for the reduction of slicks of certain oil types at open sea, but this does not outbalance the disadvantages and uncertainties. The potential risks of

the formation of smoke plumes and burn residues for the economy, man and environment cannot be assessed and controlled.
Elasticity agents may be effective in the recovery of light and medium oil types present in slicks at sea or contained slicks. The effectiveness is reduced by low temperature hampering the mixing of the product with the oil. The scope of application is very limited. Treated oil may enhance the impact on birds and shorelines, but this is not investigated sufficiently.

In Table 5 the applicability of oil spill chemicals for oil combat activities is summarized. The recommendations depend on the limitations for use and the importance of the application of the chemical. The importance is determined by 3 aspects; (1) presence of a non-chemical alternative, (2) expected chance of application, and (3) the ecological impact. The recommendations that only apply for certain limited conditions are marked with an asterisk.

Activity	Category chemicals	Potentially applicable?
Reduce/stop leakage	Sorbents	Yes *
Increase effectiveness mechanical recovery	Demulsifiers Sorbents	Yes *
Remove floating oil from water surface to water column	Dispersants	Yes *
Burning	Burning agents	No
Enhance biodegradation	Bioremediation agents	No
Wash back	Dispersants Cleaning agents	No
Cleaning object/ vegetation	Cleaning agents	Yes *
Cleaning fauna (birds)	Cleaning agents	Yes *
Reduce spreading	Herders Sorbents	Yes
Reduce/prevent sticking	Herders Sorbents	Yes
Reduce/prevent penetration in soil	Herders Sorbents	Yes

Table 5 Potential use of the different chemicals in oil spill response

In case a responsible authority wishes to approve certain chemicals to combat oil spills, products have to be screened first. It is recommended to evaluate the following package of information:
- Composition of the product
- Effectiveness
- Environmental factors influencing effectiveness
- General safety
- Persistence of the product components
- Bioaccumulation of the product components
- Acute toxicity of the products
- Acute toxicity of the treated
- Degradation of the treated oil ((standard oil type) in water as well as in sediment).

Applicants of commercial products for combat of oil spills should supply this information to the authorities. It should be noted that a large amount of information on these chemicals is already available because some countries have already evaluated products for approval for use in their national waters.

This study revealed a fundamental lack of information on certain issues, namely:

1. A Net Economic Environmental Benefit Analysis (NEEBA) should be carried out as an extension of this study in order to incorporate other important resources of concern (for example birds and mammals). This analysis can be recommended for the products selected in the current study.
2. To predict potential effects of an oil spill, it should be known what resources are present at the location of the spill, for which sensitivity maps could be used. These maps could also be used to indicate zones where it is already clear that chemicals should not be used under certain (or no) circumstances. This would make the assessment whether to use chemicals or not in case of a real oil spill more easy.
3. Experiments should be conducted to determine the rate and extent of degradation of oil in seawater and sediment. The influence of different types of dispersion (natural, mechanical, chemical) and suspended matter should be included. A dynamic mesocosm system can be recommended for this purpose.

Information generated by the recommendations number 2 and 3 is necessary to tune the application of dispersants for combat of oil spills to the conditions like in Dutch waters (high suspended organic matter contents, moderate temperatures, etc).

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References

1. Jongbloed R.H., Tamis, J.E., Holthaus, K.I.E, Veen D.P.C. van der, Velde, I van der, Blankendaal, V.G., Goedhart, P.C., Jak, R.G, Koops, W. (2002) Chemicals in combating oil spills. A literature review in perspective of the Dutch situation. TNO Report 2002/640 (300 documents have been reviewed and referred and form the basis of this paper)
2. Tamis J.E., Koops, W., Jongbloed, R.H. (2003) Chemicals in combating oil spills: the use of dispersants, TNO report R 2003/221
3. Tamis J.E., Koops, W., Jongbloed, R.H. (2003) Chemicals in combating oil spills: the use of demulsifiers, TNO report R 2003/222
4. Tamis J.E., Koops, W., Jongbloed, R.H. (2003) Chemicals in combating oil spills: the use of Bioremediation agents, TNO report R 2003/223
5. Tamis J.E., Koops, W., Jongbloed, R.H. (2003) Chemicals in combating oil spills: the use of Solidifiers, TNO report R 2003/224
6. Tamis J.E., Koops, W., Jongbloed, R.H. (2003) Chemicals in combating oil spills: the use of Herders, TNO report R 2003/225
7. Tamis J.E., Koops, W., Jongbloed, R.H. (2003) Chemicals in combating oil spills: the use of cleaning agents for objects and flora, TNO report R 2003/226
8. Tamis J.E., Koops, W., Jongbloed, R.H. (2003) Chemicals in combating oil spills: the use of cleaning agents for birds, TNO report R 2003/227
9. Tamis J.E., Koops, W., Jongbloed, R.H. (2003) Chemicals in combating oil spills: the use of synthetic sorbents, TNO report R 2003/228
10. Tamis J.E., Koops, W., Jongbloed, R.H. (2003) Chemicals in combating oil spills: the use of in-situ burning agents, TNO report R 2003/229

11. Tamis J.E., Koops, W., Jongbloed, R.H. (2003) Chemicals in combating oil spills: the use of elasticity agents, TNO report R 2003/230
12. Koops W., Jak R.G. and Veen D.P.C.van der, (2004), Use of dispersants in oil spill response to minimize environmental damage to birds and aquatic organisms. Interspill 2004 Throndheim.