Deliverable 1.2

Report on Open Sea and Near Shore Emergency Response to Oil Spills

Kill●Spill

Integrated solutions for combating marine oil spills

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1 Introduction

This report provides comprehensive information on the available technologies and methods to respond to oil spills at sea and on the shoreline at a European scale. As various inventories are periodically released by the European Maritime Safety Agency (Inventory of EU member states Oil Pollution Response Vessels (2009), Network of Stand-by Oil Spill Response Vessels (2012), Oil Spill Dispersants Inventory (2012), Inventory of National Policies regarding the Use of Chemical Dispersants (2011), and other regional organizations aimed at presenting the state of emergency preparedness, the resources and other details of the national contingency planning in EU and EFTA member states, it was considered more advisable for this report to provide qualitative information on the abovementioned technologies and methods and reveal the existing technological and operational gaps that biotechnology as an emerging spill response and remediation method would potentially cover, displaying in parallel the applicable framework regulating its application in the context of the European and regional strategy.

2 Oil Spill Response and Cleanup Techniques

2.1 Conventional cleanup methods

2.1.1 Open Water Response Techniques

2.1.1.1 Mechanical cleanup methods

Physical containment and recovery of oil is the primary response option of choice globally as it can significantly mitigate the environmental damage and deal more effectively with the waste disposal challenges. Commonly used mechanical methods make use of the following equipment:

- Booms: Booms are mechanical barriers capable of controlling the movement and spreading of floating substances, that are used primarily to contain oil and secondly to deflect oil far from resources of socio-economic or environmental importance. When used for containment, booms are often arranged in a U, V, or J configuration and can be divided into four categories:
    - Curtain booms: often used in offshore situations with a good wave response;
    - Fence booms: used in high-current areas with no or limited wave profile;
    - Shore sealing booms: used as a barrier in inter-tidal zones; and
    - Fire-resistant booms: used in conjunction with in situ burning techniques.
- Skimmers: These are mechanical specialized devices to recover oil from the sea surface that incorporate an oil recovery element and a flotation or support element. In addition a pump or vacuum device is necessary to transfer oil to storage means. Almost all existing skimmers use one of the following oil recovery techniques:
    - Recovery by suction: This category includes vacuum skimmers, weir skimmers, vortex skimmers, and the dynamic inclined plane with belt known as DIP.
    - Recovery by adhesion (*Oleophilic surface skimmers*): This category includes drum skimmers, belt skimmers, disc skimmers, rope mop skimmers, and brush skimmers.
- Heavy oil skimmers: They are specifically designed to recover high viscosity oil and emulsified oil–water mixtures.
- Skimmer vessels: These are Special purpose ships designed to remove oil from the sea surface. These ships have been built with a hull that splits to form a V-shaped containment boom with

skimmers or have been built with holes in the hull to hold skimmers. Skimmer vessels can operate well in open sea and some designs can withstand severe weather conditions.

- Specialized response vessels: These vessels incorporate sweeping arms, skimming devices and onboard oil storage. One of the main advantages of sweeping arm oil recovery systems is that they are a combined containment and recovery system so negating the need for separate deployment of lengths of boom and skimmer. In addition, they are also less likely to fail in heavier weather conditions and their better sea-keeping behavior also enhances their performance. Due to the relatively narrow sweeping width, they are best suited to recovering oil in ribbons or windrows. Furthermore, they can operate with some success across a range of oils in more adverse weather conditions than towed boom systems.

- Sorbents: These materials are manufactured to recover oil from water using either absorption or surface adhesion. They are frequently used to clean up the final traces of oil spills on water or land, as a backup to other containment means, such as sorbent booms and as a primary recovery means for very small spills close to shores and ports. This type of cleanup method includes:
  - natural organic sorbent materials;
  - mineral or natural inorganic sorbent materials;
  - synthetic sorbent materials.

2.1.1.2 Chemical methods

Chemical methods, in particular dispersants, have been routinely used in many countries as a response option. For some countries, such as the United Kingdom, where rough coastal conditions may make mechanical response problematic, dispersants are the primary choice (Lessard and Demarco, 2000) while for Greece they are considered as the last refuge in an oil spill response operation. It must be noted that the usage of dispersants is a “sensitive” subject due to the ecological damage it may cause. However, chemical methods have not been extensively used in the United States due to the disagreement about their effectiveness and the concerns of their toxicity and long-term environmental effects (U.S. EPA, 1999). Major existing chemical agents include:

Dispersants: These are mixtures of surfactants and solvents, which reduce the interfacial tension between oil and water; thus oil breaks into fine droplets and is distributed in the water column. Oil spill dispersants need to be applied to spilled oil in a manner that allows the surfactants within the dispersants to soak into the oil and then allow wave action to disperse the dispersant-treated oil.
Since many modern dispersants are of the “concentrate type”, most – but not all - dispersants can be sprayed from both ships and aircraft, but it is essential that the correct spraying equipment is used in order to achieve the recommended treatment rate.

Other chemicals: These chemical combinations may include the following agents/additives:

- Demulsifiers: Used to break water-in-oil emulsions and to enhance natural dispersion.
- Solidifiers: Chemicals that enhance the polymerization of oil can be used to stabilize the oil, to minimize spreading, and to increase the effectiveness of physical recovery operations.
- Surface film chemicals: Film-forming agents can be used to prevent oil from adhering to shoreline substrates and to enhance the removal of oil adhering to surfaces in pressure washing operations.
- gelling agents;
- Bioremediation chemicals (they accomplish the acceleration of oil’s biological degradation);
- Burning agents;

- Neutralizing agents;
- Sinking agents;
- Other (e.g., viscoelastic additives, etc.).

2.1.1.3 In situ burning

It is suitable for massive spills and for remote areas. In-situ burning is an oil spill cleanup technique that involves controlled ignition of spilled oil. The major advantage of this technique is its potential for removing large amounts of oil over an extensive area in less time than other techniques. The technique has been used at actual spill sites for some time, especially in ice-covered waters where the oil is contained by the ice. The most obvious disadvantage of burning oil is concerns about toxic emissions from the large black smoke plume produced. The second disadvantage is that the oil will not ignite and burn unless it is thick enough. Most oils spread rapidly on water and the slick quickly becomes too thin for burning to be feasible, while sufficient volatile hydrocarbons must be present to sustain burning, so after initial weathering may be also more difficult to burn. Fire-resistant booms are used to concentrate the oil into thicker slicks so that the oil can be burned.

2.1.2 Shoreline Cleanup

The fate and behaviour of oil on shorelines is influenced by many factors, some of which relate to the oil itself, some to characteristics of the shoreline, and others to conditions at the time the oil is deposited on the shoreline, such as weather and waves (Fingas, 2000a). These factors include the type and amount of oil, the degree of weathering of the oil, both before it reaches the shoreline and while on the shoreline, the temperature, the state of the tide when the oil washes onshore, the type of beach substrate, i.e., its material composition, the type and sensitivity of biota on the beach, and the steepness of the shore. As it is almost impossible to fully prevent shoreline oiling during a spill, cleanup decisions at the shoreline are as important as containment and protection priorities. Several factors influence the selection of cleanup techniques. Types of shorelines impacted and degree of impact allow responders to develop a list of preferred response options by shoreline type, which include:

2.1.2.1 Physical Methods

Manual Removal: Removing surface oil and oily debris by manual means (hands, rakes, shovels, etc.) and placing in containers for removal from the shoreline. Generally can be used on shorelines (mostly all types) where the oil can be easily removed by this non mechanical means and is most appropriate for light to moderate oiling conditions.

Passive Collection (Sorbents): Sorbent material is placed on the surface of the shoreline substrate allowing it to absorb oil as it is released by tidal or wave action. Oil removal is dependent on the capacity of the particular sorbent, energy available for lifting oil off the shoreline, and degree of weathering. Thus oil must be of a viscosity and thickness to be released by the substrate and absorbed by the sorbent. Sorbents are often used as a secondary treatment method after gross oil removal, and along sensitive shorelines where access is restricted.

Debris Removal: debris is removed manually or mechanically from the upper beach face and the zone above high tide beyond the normal wash of waves. It can include cutting and removal of oiled logs and can be used on any shoreline type, where safe access is allowed.

Trenching: Remove subsurface oil from permeable substrates. Trenches are created to the depth of the oil and floating oil on the water table is removed by vacuum pump or super sucker. Water flooding or high-pressure spraying at ambient temperatures can be used to flush oil to the trench. It is applicable when large quantities of oil penetrate deeply into permeable sediments and cannot be removed by surface flooding. It can be used on beaches ranging in grain size from fine sand to gravel.

Sediment Removal: Oiled sediments are removed by either manually using hand tools or mechanically using various kinds of motorized equipment. It is applicable on any shoreline with surface sediments and the oiled material must be transported and disposed of off-site.

Cold-Water Flooding (Deluge): A flexible perforated header hose is used during deluge with seawater to wash surface oil and oil from crevices and rock interstices to water's edge for collection. Flow is maintained as long as necessary to remove the majority of free oil. Oil is trapped by booms and picked up with a skimmer or other suitable equipment. Generally it is applicable when the oil is still fluid and loosely adhering on beaches with sediments coarser than sand, and gently sloping rocky shorelines but not applicable to mud, sand, vegetated, or steep rocky shorelines. This method is frequently used in combination with other washing techniques (low or high pressure, cold or warm water).

> **Cold-Water/Low-Pressure Washing**: Low pressure washing with ambient seawater sprayed with hoses is used to flush oil to the water's edge for pickup. Oil is trapped by booms and picked up with skimmers or sorbents. It can be applied on heavily oiled gravel beaches, rocky coasts, riprap and seawalls where the oil is still fresh and liquid and Also, in marshes and mangroves where free oil is trapped.
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> **Cold-Water/High-Pressure Washing**: Similar to low pressure washing except that water pressure is up to 100 psi. High pressure spray will better remove oil that has adhered to rocks and due to low water volumes, it may require placement of sorbents directly below treatment areas. It can be used to flush floating oil or loose oil out of tide pools and between crevices on rocky shores, riprap, and seawalls.

Warm-Water/Moderate-to-High-Pressure Washing: Mobilize thick and weathered oil adhered to rock surfaces prior to flushing it to the water's edge for collection. Seawater heated up to 100°F (38°C) is applied at moderate to high pressure to mobilize weathered oil that has adhered to rocks. The warm water may be sufficient to flush the oil down the beach. If not, "deluge" flooding and additional low or high pressure washing can be used to float the oil to the water's edge for pickup. Oil is trapped by booms and picked up with skimmers or sorbents. It can be applied when the oil has weathered to the point that low pressure washing with cold water is not effective at removal of adhered oil from rocky shores, gravel beaches, riprap, and seawalls that are heavily oiled.

Hot-Water/High-Pressure Washing: Dislodge trapped and weathered oil from inaccessible locations and surfaces not amenable to mechanical removal. Water is heated up to 170°F (77°C), which is usually sprayed by hand with high pressure wands. Used without water flooding, this procedure requires immediate use of vacuum (vacuum trucks or super suckers) to remove the oil/water runoff. With a deluge system, the oil is flushed to the water surface for collection with skimmers or sorbents. It can be applied on rocky shores, gravel beaches, riprap, and seawalls that are heavily oiled.

Slurry Sand-Blasting: sandblasting equipment is used to remove heavy residual oil from sand in some cases seawalls and riprap. Equipment can be operated from boat or land.

Vacuum: Use of a vacuum unit with a suction head is used to recover free oil in sheltered areas. It can be used with water spray systems to flush the oil towards the suction head and May be mounted offshore on barges, onshore on trucks, or as individual units on boats or ashore at low tide.

Sediment Reworking: Rework oiled sediments to break up the oil deposits, increase its surface area, and mix deep subsurface oil layers that will expose the oil to natural removal processes and enhance the rate of oil degradation. Tilling-type activities work best on beaches with a significant sand fraction and on beaches exposed to significant wave activity.

Sediment Removal, Cleansing, and Replacement: Oiled sediments are excavated using heavy equipment on the beach at low tide. The sediments are loaded into a container for washing. Cleansing methods include hot-water wash or physical agitation with a cleansing solution. After the cleansing process, the rinsed materials are returned to the original area. Cleaning equipment must be placed close to beaches to reduce transportation problems. The beaches must be exposed to wave activity, so that the replaced sediments can be reworked into a natural distribution. Applicable on beaches (sand- to boulder-sized beaches, depending on the limitations of the cleanup equipment) with large amounts of subsurface oil, where permanent removal of sediment is undesired and other cleanup techniques are likely to be ineffective.

Cutting Vegetation: Manual cutting of oiled vegetation using weed eater, and removal of cut vegetation with rakes to prevent oiling of wildlife.

In-situ Burning: Oil on the shoreline is burned, usually when it is on a combustible substrate such as vegetation, logs, and other debris.

2.1.2.2 Chemical methods

Chemical Oil Stabilization with Elastomizers: Enhanced polymerization of hydrocarbon molecules resulting from the application of semi-liquid spray or dry chemical in proper dosages (broadly ranging from 13% to 44% by weight of the product to oil) can solidify oil and thus prevent it from spreading or escaping. Depending on the beach type and equipment used, recovery may be enhanced. It is suitable on shorelines of low permeability where heavy oil has pooled on the surface, except vegetated shorelines.

Chemical Protection of Beaches: Certain types of water-based chemicals, some of which are similar in composition to dispersants, are applied to beaches in advance of the oil to prevent oil from adhering to coarse- and fine-grained sand beaches, seawalls and piers (particularly piers or waterfront facilities that are of historical significance), eroding bluffs, wave-cut platforms, and riprap.

Chemical Cleaning of Beaches: Special formulations, which can be characterized as weak dispersants, are applied to the substrate, as a presoak and/or flushing solution to soften weathered or heavy oils to aid in the efficiency of flushing treatment methods. The intent is to be able to lower the temperature and pressure required to mobilize the oil from the substrate. This approach may be most applicable where flushing decreases in effectiveness as the oil weathers.

2.2 Alternative Technologies

Nutrient Enhancement: Aimed at accelerating the natural microbial degradation of oil by adding nutrients (specifically nitrogen and phosphorus). Microbial biodegradation is the conversion by microorganisms of dissolved and dispersed hydrocarbons into oxidized products via various enzymatic reactions. Some hydrocarbons and non-hydrocarbon components of the oil are converted to carbon dioxide and cell material, while others are partially oxidized and/or left unaltered as a residue. Nutrients are applied to the shoreline using one of several methods: soluble inorganic formulations that are dissolved in water and applied as a spray at low tide, requiring frequent applications; slow-release formulations that are applied as a solid to the intertidal zone and designed to slowly dissolve; and oleophilic formulations that adhere to the oil itself, thus they are sprayed directly on the oiled areas.

Microbial Addition: To increase the rates of natural microbial degradation of oil by the addition of nutrients and microbial products. Microbial biodegradation is the conversion by microorganisms of dissolved and dispersed hydrocarbons into oxidized products via various enzymatic reactions. Some hydrocarbons are converted to carbon dioxide and cell material, while others are partially oxidized and/or left untouched as a residue. Formulations containing hydrocarbon-degrading microbes and fertilizers are added to the oiled area. The argument is made that indigenous organisms will be killed by the oil, so new microbial species need to be added to begin the process of biodegradation. To date, microbial addition has not been shown to work better than fertilizer alone in field tests.

3 Oil Waste Separation and Disposal of Waste Materials

It is crucial to start removing oil promptly from contaminated shorelines because as time passes the oil weathers, spreads and becomes more difficult to recover and contain. Both at-sea oil recovery and particularly shoreline clean-up generate substantial amounts of oil and oily waste. It is important for employed vessels to respond rapidly in the event of an oil spill but also to be fully equipped (sweeping arms, booms and skimmers) in order to maximize the capacity of oil recovered. In this regard response vessels should have large recovered oil storage capacity and the required maneuverability and speed as demanded by the conditions. Oil collected from the sea will be the most suitable for processing since it will usually only be necessary to separate any water collected with the oil by gravity separation in tanks thus maximizing the utilization of the onboard storage capacity. The removal of water from water-in-oil emulsions is more difficult and often requires heat treatment or the use of chemicals known as 'emulsion breakers' or 'demulsifiers' mixed into the oil.

Solid and varied waste (contaminated soil, oiled organic debris, oiled equipment debris contaminated sorbent material and Personal Protective Equipment (PPE), etc.) is produced during land based shoreline clean-up operations.

Contaminated sediments or soil can be stockpiled in designated lay-down areas near cleanup activities. Stockpile areas are covered with geomembranes or other sheeting may be required to prevent rainfall infiltration and runoff. Stockpiling of contaminated soils should be viewed as a temporary measure, as the soil will eventually be containerized for off-site treatment and/or disposal. Soil will be characterized and stored as per direction from the responsible waste management authorities.

Oiled organic debris includes wood, grasses, aquatic vegetation, and similar organic matter that cannot be treated and restored. Oiled organic debris should be segregated from dissimilar debris and containerized in clear plastic bags so the contents inside can be viewed. This material typically is designated for disposal at an approved solid waste landfill.

Oiled equipment debris includes equipment and materials that are not deemed to be treatable or material that cannot be returned to its original service. This may include oiled wooden material from beaches, oiled nets, buoys, oiled trash collected from the beach, and oiled equipment. Oiled debris should be containerized in drums or roll-off boxes and/or dumpsters. This material typically is designated for disposal at an approved solid waste landfill.

Contaminated material (absorbent booms, pads, wipes, etc.) and PPE will be transferred from decontamination areas to the nearest waste storage area. Oiled sorbents and PPE will be containerized in plastic bags, drums, roll-off boxes, or dumpsters as appropriate. Plastic bags, taped closed and stored in roll-off boxes is the preferred technique.

Disposal of oil is a major problem, particularly following shoreline clean-up, when large amounts of oily debris can be collected. Contingency plans for major spills need to include details of all oil disposal techniques which can be utilised for the area covered by the plan, including details of legislative and regulatory requirements. With respect to materials recovered during shoreline clean-up operations, the lack of waste segregation is often a major issue. Preferably waste material should be separated into various waste streams to facilitate disposal. Unfortunately, this is often not the case and consequently shoreline waste material can be a mix of a wide range of substances including sand, beach debris, PPE and other oiled material. This type of waste should be transferred, stored temporarily and ultimately disposed of in an environmentally acceptable manner. More traditional disposal routes include incineration and landfill however recent EU Directives have strengthened the conditions under which these techniques can be utilized. In part due to the lack of waste segregation, waste disposal operations often continue long after the clean-up phase is over. It is worth noting that that for every ton of oil recovered at sea it is estimated that at least 10 tons of shoreline clean-up waste material is avoided. In extreme cases, up to 30 times more waste than the volume of oil originally spilt can be generated.

Storage facilities are indispensable to the proper spill-generated waste management. This requires appropriate storage areas in terms of the environment and human health and safety:

- local intermediate storage facilities near the shoreline, allowing rapid evacuation of collected waste on a daily basis generally in very sensitive coastal areas, and

- where necessary, final storage sites for the whole geographical area, which are temporary but longer term installations, prior to the final disposal or recycling.

The quality of spilled oil at the stage of recovery and storage onboard vessels, in particular its non-intrinsic properties including the presence of debris and emulsions, the viscosity and the flash point following the weathering of oil at sea should be considered when designing or determining in which storage facility recovered oil waste should be transported.

Oil collected from the surface of the sea tend to accumulate on debris that might float on the sea surface originating from the land such as seaweed, wood, plastic materials of various types, dead marine organisms, suspended sediments, or from the ship or installation involved in an accident and other sources. Fixed as well as floating facilities such as tankers or barges can be used. Fixed facilities are stationary facilities accessible from the sea which enable the direct, on-shore collection of oily wastes, while floating facilities allow spilled oil recovery at sea to proceed faster. Such facilities should provide the necessary equipment to handle different types of oil waste.

Debris can be removed from the flow stream of recovered oil by self-cleaning strainers/filters, hydrocyclones and vibrating screens. Debris removal equipment is intended to separate and remove the larger material which might interfere with the efficiency of the operations of oil receiving facilities and to protect downstream oil transfer pumps and the associated piping of vessels from hard and large debris in the recovered oil flow.

Water-in-oil emulsions mostly originate from oil spills at sea. In general, emulsions constitute a suspension of droplets, greater than about 10 μm, consisting of two completely immiscible liquids, one of which is dispersed throughout the other. Emulsification of oil is caused by the uptake of water by the oil which results in a substance with increased viscosity. Water-in-oil emulsions and viscosity are interrelated, as the presence of emulsions influences the viscosity of oil and the water content, while increasing the overall quantity to be discharged to a facility.

The most common method of emulsion breaking is the combination of heat and application of specific agents. Emulsion breaking agents are products used to break or prevent the formation of emulsions in the sea and in tanks. Emulsion breaking, as a combination of injecting and mixing proper demulsifiers with oil and heating was considered to be useful in case of stable water-in-oil emulsions. Heating of oil with the aim to reduce viscosity is effective in the absence of stable emulsions that prevent water and oil separation. The injection and mixing of emulsion breaking agents should be preceded by the removal of debris to enhance the efficiency of the emulsion breaking process. This is a standard practice in wastewater treatment to remove large or finer debris and solids that can interfere with the treatment process or cause undue mechanical wear and clogging to downstream equipment. The emulsion breaking unit consists of an emulsion breaking agent storage tank, a dosing pump and a static mixer all positioned between the discharging hose of the oil skimmer and the ship's manifolds.

4 Application of biotechnology in the context of a spill response strategy

Well known incidents such as the *Amoco Cadiz* (France, 1978), the *Exxon Valdez* (USA, 1989), the *Prestige* (Spain, 2002) but also other minor events such as *Seal Beach* (USA, California, 1990) and *Apex Barge* (USA, 1990) have stimulated the development and use of alternative techniques including bioremediation to fight oil pollution at sea and on the shoreline. As with other response techniques, bioremediation requires careful planning to help achieve the intended results, while the identification of potential spills or polluted sites for its application on an operational scale requires detailed analysis before being incorporated in a contingency plan.

The difficulty of conducting controlled experiments in the open sea to expand the existing knowledge base, the lack of widely accepted protocols for testing the efficacy and assessing any secondary environmental impacts, the advancement of biotechnology as an economic sector on the national level, the complex framework of spill response being subject to regulations on waste management, the sustainability of fisheries and aquaculture, etc., and other factors differentiate the extent and the way that biotechnology products and processes are reflected in regional or national contingency plans and the related response strategies.

Looking first at Europe, one of the key recommendations of the European Science Foundation in its Position Paper titled "*Marine Biotechnology: A new vision and strategy for Europe*" released in September 2010, is to incorporate novel marine biotechnology approaches in existing and new action plans for combating marine oil spills based on biotechnology products or processes. It further underlines the potential of biostimulation and bioremediation in reducing the recovery time of a severely impacted coastal ecosystem against one left untreated, which, if it will be further explored and demonstrated might show off biotechnology as a cost-effective component of a marine oil spill response strategy.

It must be noted that the Marine Board constitutes a pan-European platform consisting of 30 research organizations from 19 countries, aimed at advancing marine research and bridging the gap between science and policy to meet further marine science challenges and opportunities.

On 13 February 2012, the European Commission launched a new strategy on bioeconomy entitled "*Innovating for sustainable growth: Bioeconomy for growth*". Among other things, this strategy aims to improve the knowledge base of the biotechnology, support the implementation of ecosystem-based management and find better ways to mitigate the impacts of pollution to the environment.

It is also interesting that EU Directive 2004/35/CE on the Environmental Liability on the Prevention and Remedying of Environmental Damage considers the potential preventive (measures taken in response to an imminent or actual threat of environmental damage) and remedial measures (actions intended to restore or rehabilitate natural resources.

Primary measures for restoring the natural resources on an accelerated time frame might be covered by this Directive. Moreover, the Directive places the competent national authority in charge of prescribing the exact remedial method taking into account a number of factors including the length of time it will take for the restoration of the ecosystem, the likelihood of success, the cost of implementation and the extent to which an option will prevent future damage and avoid collateral damage as a result of its application.

The Helsinki Commission (HELCOM), an intergovernmental organisation of the Baltic coastal countries with a mandate to protect the marine environment from all sources of pollution, recommends that when authorizing the use of chemical agents and other non-mechanical means in oil spill response operations in the Baltic Sea, the responsible national authorities should ensure that any method is carried out with optimized efficiency and with acceptable effects to the marine environment. It also acknowledges that new response methods, such as bioremediation, fertilization techniques and biosorbents have been at a developmental stage. Russia for example, has identified the use of bioproducts in its national spill response strategy, as the third tier of defence, to follow after mechanical recovery and chemical dispersion, requiring written permission from the Federal Supervisory Natural Resources Management Service and the Federal Agencies for Fisheries and Consumer Protection.

With regard to the Mediterranean Sea, the Regional Marine Pollution Emergency Response Plan – REMPEC, through its Regional Information System which provides principles, recommendation and guidelines on the accidental pollution preparedness, response and mutual assistance, sets the objectives that a treatment product other than chemical dispersants should pursue when used:

- in operations at sea to facilitate the recovery of oil, to alter the properties of spilled oil (surface tension modifiers) or destroy it via burning, and
- on shore with the aim to facilitate the pumping and transfer of oil, to accelerate the clean-up or to increase the rate of the natural degradation by using proper biological agents.

No equivalent guidelines on the use of bioremediation are currently included in the general strategy and the specific policies on oil spill response of the Agreement for Co-operation in dealing with Pollution of North Sea by Oil and Other Harmful Substances (Bonn Agreement).

In the context of the Agreement on Cooperation on Marine Pollution, Preparedness and Response in the Arctic, bioremediation is identified as a potential response method aimed at enhancing the collection of oil and accelerating the natural weathering processes. Solid fertilizers such as pellets can be used by employing seed spreaders commonly used on lawns and fields, and liquid fertilizers can be sprayed on the impacted shoreline using various commercially types of equipment. The rate of biodegradation decreases with lower temperatures, so that nutrient enrichment is more effective during warmer summer months.

Moving to the other side of the Atlantic, the U.S. Environmental Protection Agency's (EPA) Office of Emergency Management Regulation and Policy Development Division has compiled the National Oil and Hazardous Substances Pollution Contingency Plan (NCP) Product Schedule, as required by the Clean Water Act, the Oil Pollution Act of 1990 (OPA 90), and the National Contingency Plan of the country.

This National Contingency Plan Product Schedule Technical Notebook provides information on a number of commercial products that might be used in spill response operations given certain prerequisites. It must be noted that in the most recently revision of this publication (August 2013), the abovementioned Notebook lists 26 bioremediation agents as shown in the following table:

Table 1: Listed products by category

Type of product	Number
Dispersants	18
Surface washing agents	52
Surface collecting agents	2
Bioremediation agents	26
Miscellaneous oil spill control agents	14

The listed bioremediation agents include: a) biological additives, b) microbiological cultures, c) enzyme additives, and d) nutrient additives. For each one of these products, codified information is provided on the following:

1) the special handling and workers precautions for storage and field application,
2) its shelf life,
3) the recommended application procedure (from vessels, aerial or land-based means, manually) and concentration required,
4) toxicity and effectiveness, and
5) physical properties and microbiological analysis.

The Bioremediation Agents listed are the following: ABR BI CHEM PETROLEUM BLEND, Advanced Bio Cultures L-103, L-104, AE-BIOSEA PROCESS, Bactozyme, Biogee HC, Biozyme 1000 HC, Biomax, BR, DBC Plus Type R-5 and Type L, EEC Biological Media, EN-2000 Concentrate, Enzyt, Hydrobac, KBC 100, LRC-1, LRC-4, MaxBac Customblen, Medina Microbial Activator, Microrpo (D, NOW Bac, Super Cee), Munox (212, 512, 112,), No-Scum, Nutri –bio, PES 31, Petrobag, Petrodeg (100, 200), Petrovore, Phenobag, PRP, Putidoil, Wooddace Briquettes, WST (Bioblends). The EPA NCP Product Schedule as per August 2013 can be found in the following link
http://www.epa.gov/oem/docs/oil/ncp/schedule.pdf

5 Available Spill Response Equipment in EU

5.1 Network of Stand-by Oil Spill Response Vessels

One of the tasks of the European Maritime Safety Agency (EMSA) is to support on request with additional means, in a cost efficient way, the pollution response mechanisms of EU Member States. Following public procurement procedures, EMSA has established contracts for at-sea oil recovery services around the European coastline with commercial vessel operators. The primary objective of the Stand-by Oil Spill Response Vessel service is to "top-up" the marine oil recovery capacity of Member States thus minimizing the potential impact to the European coastline.

EMSA currently maintains contracts for 17 fully equipped Stand-by Oil Spill Response Vessels, which are available, upon request, to assist coastal States in oil spill recovery operations. The current Network provides at-sea oil recovery services from vessels based in all the regional seas of Europe. It should be noted that all vessels are at the disposal of all Member States regardless of their actual area of operation. The map in the following page shows the distribution of vessels and equipment stockpiles around Europe. More technical and operational specifications of all the contracted services are available on the Agency website www.emsa.europa.eu.

The average individual oil storage capacity of the EMSA contracted vessels is in the region of 3800 m^3 and they provide a total storage capacity of more than 52,000 m^3. During an incident, the vessel and her crew will be under the operational command of the affected Member State. To maintain the quality of the at-sea oil recovery service, all vessels and crews undergo regular equipment drills under the supervision of the Agency. In order to work under an international command and control structure, which is the most likely scenario during a major spill, each vessel is available to participate in regular at-sea spill response exercises.

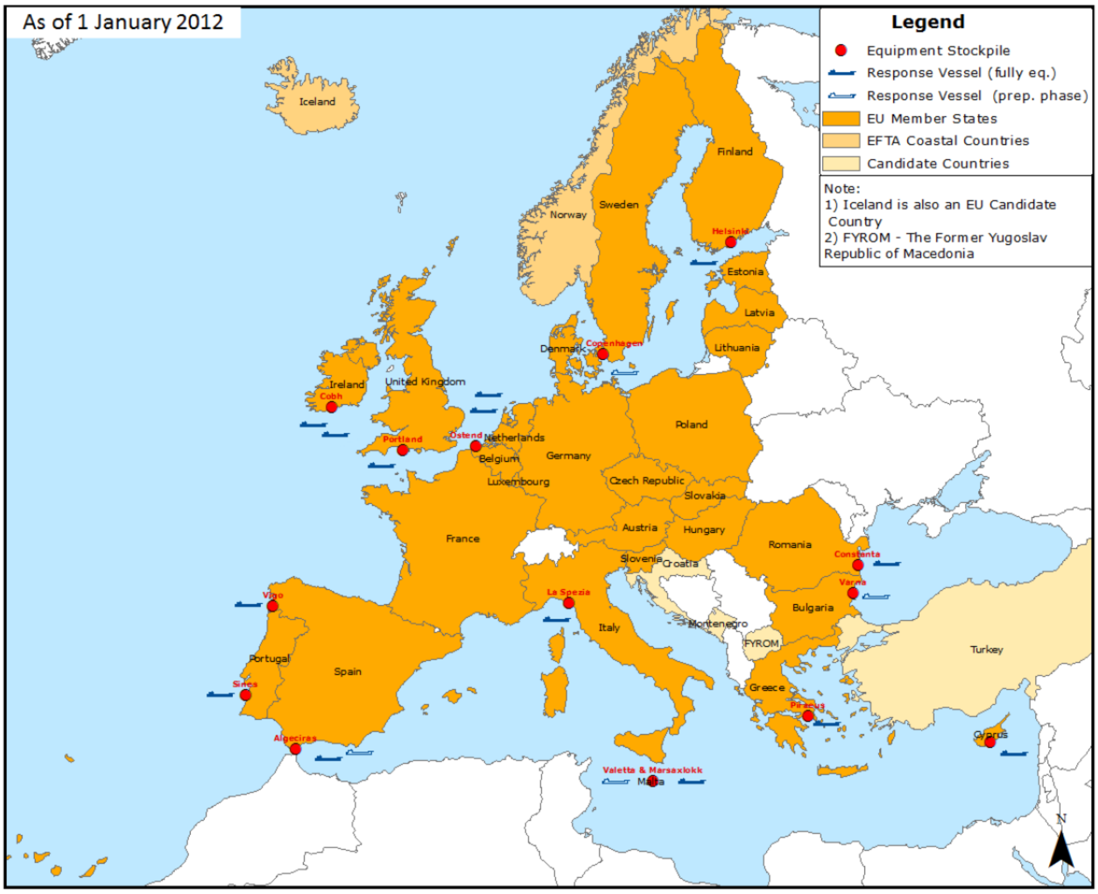

Figure 1: Network of Stand-by Oil Spill Response Vessels and Equipment

Each of the EMSA contracted vessels is equipped with oil pollution response equipment. The contracted vessels should have the following characteristics:

- Large recovered oil storage capacity.

- The primary oil recovery system is based around the 'sweeping arm' concept with an alternate 'ocean-going boom and skimmer' system also available. The requesting Member State can select the equipment in accordance with the incident characteristics.
- They must be fitted with a local radar based oil slick detection system to facilitate the positioning of the vessel in the thicker oil slicks, and to enable operations at night.
- The required maneuverability to carry out oil recovery operations.
- The ability to decant excess water thus maximising the utilisation of the onboard storage capacity.
- Each vessel has the ability to heat the recovered cargo and utilise high capacity pumps in order to facilitate the discharging of heavy viscous oil mixtures to shore side facilities as designated by the Member State concerned.

5.2 Discharge facilities for oil recovered at sea

Currently, 35 facilities suitable to accommodate EMSA's contracted vessels are available to receive recovered oil. As many as 9 of them can receive oil with a maximum viscosity of oil of 380 cSt at 10 to 50^{o}C, while only 6 of the total have either no restrictions at all or the maximum viscosity might be from 700 to 10,000 cSt at the same range of temperatures. With regard to the difficulties encountered due to the presence of water-in-oil emulsions, 17 facilities can receive emulsions without serious restrictions, for one facility only minor concentrations of emulsions in the recovered oil are acceptable (up to 1%), while 10 facilities can't receive oil containing emulsions.

The presence of debris in recovered oil was considered to be a prohibitive factor for the majority of the facilities. Only a limited number of facilities (it must be noted that they are all ship-generated waste treatment companies) replied that the presence of debris is irrelevant or causes no restrictions to the acceptance of oil while others (two facilities) indicated quantitatively the maximum permissible content (ranging from 1% to 3%).

5.3 Oil spill dispersants available in EU and EFTA countries

Most EU and EFTA countries have certain legal instruments in place to regulate the application of chemicals into the sea requiring in most cases a proper authorization from the relevant national authorities. The addition of oil spill dispersants to spilled oil at sea is normally considered to be a circumstance where specific authorization is required by a specified national authority.

Of the 24 coastal countries EU and EFTA members:

- 13 countries (Belgium, Denmark, Estonia, Finland, Germany, Ireland, Latvia, Lithuania, the Netherlands, Poland, Portugal, Slovenia and Sweden) currently have no formal, standard dispersant testing or approval schemes. In some countries, such as Finland, Portugal, Slovenia and Sweden, no dispersant approval scheme is in place because dispersant use is prohibited or it is considered dispersants will not be used in oil spill response. In other countries, for example Belgium, Denmark, Germany, Ireland, the Netherlands and Poland, dispersant use may be considered as a suitable response and dispersants approved in some other EU countries would be accepted.
- 7 countries (Cyprus, France, Greece, Malta, Norway, Spain and the United Kingdom) have testing schemes for dispersant toxicity and dispersant effectiveness and dispersant approval schemes.
- A total of just over 3,642 tons of modern "Concentrate" (UK Type 2, UK Type 3 and UK Type 2/3) dispersant are currently stockpiled in EU and EFTA countries, the vast majority contained in the UK and French stockpiles. This total quantity of dispersant is, in theory,

capable of dealing with a spill of 100,000 tons of oil at the generally recommended treatment rate of 1 part of dispersant to 20 or 30 parts of spilled oil.

- The majority of dispersants is stored in NW Europe; in the UK, in Norway and in the French stockpiles on the Atlantic and Channel coasts. A total of just over 3,000 tons of dispersant, theoretically capable of dispersing approximately 75,000 tons of spilled oil is close to the North Sea. The amount of dispersant available for rapid use within the Mediterranean Sea is dominated by the French government Mediterranean stockpile of 654 tons and the additional 60 tons from the oil industry in France. The quantity of 714 tons is supplemented by 248 tons of third generation dispersants in Greece and lesser amounts in Italy, Cyprus and Malta. Slightly over 1,000 tons of dispersant, theoretically capable of dispersing 25,000 tons of spilled oil, are potentially available for use in the Mediterranean Sea.

Dispersant spraying capability

- Ship-based dispersant spraying capability

Nine of the 22 EU and EFTA maritime countries have absolutely no dispersant spraying capability from boats or ships. The dispersant spraying capability in most countries is very limited with only a few 'stand-alone' spraying kits that can be fitted to 'vessels of opportunity'. France, Cyprus, Malta, Norway and Spain have some vessels with permanently installed dispersant spray systems.

- Aerial dispersant spraying capability

The UK, France, Norway and Malta each have an indigenous aerial dispersant spraying capability while Ireland and Spain rely on services that would be provided by private companies (OSRL).

The variety of chemical dispersants, the lack of internationally agreed testing protocols and the variability of test methods render difficult the comparison and the assessment of the potential toxicity of either the chemical dispersants or the dispersed oil. The majority of the responsible State Authorities in Europe as well as in USA and other countries have in place certain procedures to issue permits for the application and use of chemical dispersants in their jurisdictional waters in case of oil spill. Most of the studies published focused on measuring the lethal effects of chemical dispersants on certain marine organisms, while other impacts such as those on reproduction, endocrine disruption, etc are missing.

6 Limitations of Spill Response Methods and Equipment

6.1 Limitations of containment and recovery methods

Oil spill response is primarily based on the so-called conventional cleanup methods. The use of the appropriate equipment is limited by the following three basic parameters: wave height, current velocity and spilled oil properties.An attempt was made to identify/determine the limitations in applying mechanical containment and recovery (booms and skimmers) and chemical dispersants. A comprehensive framework for assessing the capabilities of the abovementioned equipment against the hydrodynamic conditions and the type of oil spilled to the marine environment is provided in a tabular format at the end of this document (tables 4, 5, 6 and 7). Using these tables one can easily and quickly decide whether a specific type of equipment can be functional and effective in certain sea conditions and with specific types of spilled oil, but at the same time to identify the gaps and the operational limitations of the equipment.

Effect of Weather Conditions

Oil spill countermeasures are affected by weather such that, in some cases, these countermeasures cannot continue under adverse weather conditions. A literature review was carried out to determine if there were data related to the performance of all countermeasure techniques under varying weather conditions. Wind and wave height are the most important factors influencing countermeasures. These two factors are related and, given sufficient time for the sea to become ‘fully-arisen’, can be inter-converted. These factors must sometimes be considered separately, however, so that specific weather effects can be examined. Other weather conditions affecting countermeasures include currents and temperature. Currents are the critical factor for certain countermeasures such as booms. Temperature primarily affects the performance of dispersants and has been shown to have only minimal effect on other countermeasures. Formation of ice, however, is a problem with most countermeasures. Booms are the type of countermeasures most susceptible to weather conditions. Conventional booms will fail at a current of 0.5 m/s (1 knot) regardless of the boom’s design or other conditions. This is due to inherent hydrodynamic limitations. There is wave-associated degradation of this value which is dependent on design. The basic limitations in using oil booms in spill response operations are summarized below:

Table 2: Basic limitations in the use of oil booms

Basic limitations in the use of oil booms
• Anchoring of booms in deep waters to be retained in the right position requires extensive lengths of anchor cable and logistical support (it is estimated that the length of the cable should be approximately 3 - 5 times the depth of the water column). • Oil booms if not used in combination with recovery devices might allow oil escape, when the quantity of oil contained exceeds the holding capacity of the boom. • Oil booms fail to be functional in surface current speeds greater than approximately 1 nautical mile per hour (this failure might be controlled to some extent by reducing the angle of the boom to the direction of the surface current). • It has been repeatedly demonstrated that the effectiveness of oil booms might be limited by the poor deployment and handling during an operation. • Changing hydrodynamic conditions during an oil spill might render an existing way of deployment of booms ineffective.

Weather conditions at a spill site have a major effect on the efficiency of skimmers. Most skimmers work best in calm waters. Depending on the type of skimmer, some will not work effectively in waves greater than 1 m or in currents exceeding 1 knot. Most skimmers do not operate effectively in waters with ice or debris such as branches, seaweed, and floating waste. Some skimmers have screens around the intake to prevent debris or ice from entering, conveyors or similar devices to remove or deflect debris, and cutters to deal with sea weed. Very viscous oils, tar balls, or oiled debris can clog the intake or entrance of skimmers and make it impossible to pump oil from the skimmer's recovery system. Advancing skimmers often recover more oil with increasing tow rate as this increases the encounter rate with the oil. On the other hand one of the main advantages of sweeping arm oil recovery systems is that they are a combined containment and recovery system so negating the need for separate deployment of lengths of boom and skimmer. In addition, they are also less likely to fail in heavier weather conditions and their better wave-following capability also enhances their performance. However they do have a relatively narrow sweeping width, but, they can operate with some success across a range of oils in more adverse weather conditions than towed boom systems. The environmental conditions constitute the overwhelming factor why containment and recovery at sea rarely results in the removal of more than a relatively small proportion of a large spill, at best only 10 - 15% and often considerably less. The limitations of skimmers are summarized below:

Table 3: Basic limitations in the use of skimmers

Basic limitations in the use of skimmers
• The recovery rate of a skimmer depends on rather a large number of factors including the thickness of oil, the type of oil being recovered, the viscosity of oil, the level of emulsification, the capacity of the skimmer to deal with debris and the sea state. • In waters not sheltered the efficiency of skimmers is affected. It is considered that the higher the height of waves at sea, the lower the efficiency of a skimmer in collecting oil. • The relatively small surface area of the skimming devices limits the overall recovery rate of skimmers. • Recovery of oil in cold climates is currently inefficient due to the lack of properly designed skimmers to collect oil – ice mixtures.

6.2 Limitations of chemical dispersants

The use of dispersants has in the past tended to provoke controversy since their application can be seen as a deliberate introduction into the sea of an additional pollutant into the water. Many of the first dispersants used in the 70s and 80s did show high toxicity to marine organisms. However, today there is a wealth of laboratory data indicating that modern dispersants and oil/dispersant mixtures exhibit relatively low toxicity to marine organisms. The variety of chemical dispersants, the variability in test methods, and the lack of distinct species overlap between studies make it difficult to compare and deduce which dispersant is most toxic and which is least. A comparative, acute toxicity testing of eight commercially available chemical dispersants (Corexit 9500A, Dispersit SPC 1000, JD-2000, Nokomis 3-AA, Nokomis 3-F4, Saf-Ron Gold, Sea Brat-4 and ZI-400) to two endemic aquatic species of the Gulf of Mexico (the invertebrate *Americamysis bahia* and an estuarine fish *Menidia beryllina*) conducted recently by USEPA (2010) showed that all the abovementioned products were found to be slightly toxic or practically non-toxic with one exception, as follows:

Table 4: Toxicity of eight commercially available chemical dispersants (Source: Comparative Toxicity of Eight Oil Dispersant Products on Two Gulf of Mexico Aquatic Test Species, USEPA, June 2010)

	96 hr acute toxicity test Menidia beryllina		*48 hr acute toxicity test Americamysis bahia*	
Dispersant	**LC50** (ppm)	**Toxicity Category**	**LC50** (ppm)	**Toxicity Category**
Dispersit SPC 1000	2.9	Moderately toxic	12	Slightly Toxic
Nokomis 3-F4	19	Slightly Toxic	42	Slightly Toxic
Nokomis 3-AA	19	Slightly Toxic	30	Slightly Toxic
ZI -400	21	Slightly Toxic	55	Slightly Toxic
Saf-Ron Gold	44	Slightly Toxic	118	Practically Non-Toxic
Sea Brat-4	55	Slightly Toxic	65	Slightly Toxic
Corexit 9500A	130	Practically Non-Toxic	42	Slightly Toxic
JD-2000	>5,600	Practically Non-Toxic	788	Practically Non-Toxic

Chemically dispersed oil, however, can be toxic in both the short and long term, and less oil on the surface means more elsewhere in the water, spread over a wider area. The rapid dilution of the dispersed oil, the proximity to sensitive areas as well as the direction of currents and the mixing depths of surface waters are all factors which should be considered when deciding upon dispersant use. In the open sea, dispersed oil concentrations after spraying are unlikely to remain high for more than a few hours and significant biological effects are therefore improbable. In shallow waters close to the shore, where water exchange is poor, higher concentrations may persist for long periods and may give rise to adverse effects. However, the controlled application of dispersants may, on occasions, be beneficial in that it may reduce damage to adjacent ecologically sensitive shorelines by oiling.

Furthermore, the Deepwater Horizon (DWH) oil spill initiated a large amount of research and regulatory developments focusing on dispersant usage and dispersant testing. Dispersant effectiveness in deep waters is still in question (dispersants may have had little effect on the amount of oil that ultimately surfaced) raising major concerns about its possible environmental impact on deep sea microbiota (oil–dispersant mixture is highly toxic to deep-sea soft corals and sea-floor animals).
The new trend of deep waters deposits exploration has raised concerns about operational aspects regarding sea surface and subsea dispersant use, including challenges and limitations linked to such large-scale dispersant applications with possible environmental impacts. Finally, there is no reason to suppose that all dispersants act in the same manner. They may, depending upon their chemical makeup, have strikingly dissimilar impacts. For example, some evidence indicates that the ionic surfactant in Corexit 9527 and 9500 inhibits biodegradation while their non-ionic surfactants increase biodegradation. The basic limitations in applying chemical dispersants are as follows:

Table 5: Basic limitations in the use of chemical dispersants

Basic limitations in the use of chemical dispersants
• Not always effective on all oil types. Less effective or ineffective on viscous oils (there is a general assumption that oils with a viscosity less than 2,000 centistokes at 15 – 20^0 C can be chemically dispersed). • Little or no effect on oils which have a pour point near to or above that of the ambient temperature. • Not recommended in shallow waters with poor water exchange and long renewal time. • Potential persistence and toxicity of dispersed oil. • The salinity of water is proportional to the effectiveness of dispersants. • The safety of application in high temperatures should be assessed due to the presence of solvents. • During beach clean-up activities, the use of dispersants might increase the penetration of oil into the sediments. • Natural biodegradation might be inhibited.

6.3 Limitations of shoreline cleanup methods

It is important to start removing oil promptly from contaminated shorelines because as time passes and the oil weathers, it will stick more and more firmly to rocks and sea walls, and may become mixed with or buried in sediments. Shoreline clean-up is usually straightforward, however, and does not normally require specialized equipment - it is not a 'high tech' business. Reliance is frequently placed on locally-available equipment and manpower, rather than specialized equipment. Good organisation and management are the key to effective clean-up. Poorly thought out and uncoordinated clean-up efforts usually result in inefficient use of resources and excessive quantities of waste for disposal.

The fate and behaviour of oil on shorelines is influenced by many factors, some of which relate to the oil itself, some to characteristics of the shoreline, and others to conditions at the time the oil is deposited on the shoreline, such as weather and waves (Fingas, 2000a). These factors include the type and amount of oil, the degree of weathering of the oil, both before it reaches the shoreline and while on the shoreline, the temperature, the state of the tide when the oil washes onshore, the type of beach substrate, i.e., its material composition, the type and sensitivity of biota on the beach, and the steepness of the shore. Two major factors such as oil volume and type and shoreline (as summarized below) highly influence the final selection of the technique that will be used at the site to be decontaminated.

Influence of oil volume and type
The type and quantity of the oil spilled must be determined. Oil types vary greatly and have a major influence on the degree of shoreline impact, oil persistence, and ease of cleanup. For example, lighter fuels (diesel, home heating fuel and light crude oils) will evaporate quickly, but tend to be more toxic and penetrate the shoreline sediments to a greater degree. Heavy oils (bunker C, #6 fuel and heavy crude oils) are less toxic to shoreline ecosystems and do not penetrate finer sediments, but they are very persistent, difficult to clean and may smother shoreline organisms.

Influence of Shoreline Type
Shorelines types greatly influence the impacts of oil and cleanup methods, and must be considered in each spill. State and federal mapping projects have categorized U.S. coastlines in terms of habitat sensitivity to oil. The NOAA Environmental Sensitivity Index, the most common scheme, ranks shorelines by sensitivity to oil spill impacts, predicted rates of removal of stranded oil by natural processes, and ease of cleanup.
The ESI shoreline ranks, from least to most sensitive:

1. Exposed rocky cliffs & seawalls
2. Wave cut rocky platforms
3. Fine to medium-grained sand beaches
4. Coarse-grained sand beaches
5. Mixed sand and gravel beaches
6. Gravel beaches/Riprap
7. Exposed tidal flats
8. Sheltered rocky shores/man-made structures
9. Sheltered tidal flats
10. Marshes

Preferred techniques for the spill are set based on shoreline type. For example, the method for treating exposed seawalls might be high-pressure, ambient temperature seawater flushing at mid-tide stages. Natural recovery is often misunderstood; in sensitive environments active cleanup

activity may cause more harm than allowing the oil to slowly degrade naturally, as disturbance by activity can drive oil below the surface causing significant damage. Cleanup teams are mobilized based to conduct shoreline surveys and develop recommendations for specific shorelines, based on the general options for each shoreline type. The survey teams include scientific and oil response expertise. Survey results include type, degree of oiling, location of specific sensitive resources to be avoided or protected, other logistical information, and the team's recommended cleanup method, selected from the agreed upon cleanup options for that shoreline type. Areas of specific concern are identified and are planned based on unique factors. Cleanup is monitored to ensure that continued response measures do not cause more harm than remaining oil.
Shoreline cleanup plans try to minimize the harm caused by spilled oil, not to clean up all oil. Responders must weigh the response priorities in determining the end point for shoreline cleanup actions.

6.4 Final disposal of recovered oil – Challenges

The technical limitations that might compromise the discharge of oil recovered by EMSA's vessels and in general from other navigable recovery means to available facilities relate to:

- the quality of spilled oil at the stage of recovery and storage onboard the vessels, in particular its non-intrinsic properties including the presence of debris and emulsions, the viscosity and the flash point following the weathering of oil at sea, and
- the berthing and discharging operations of pollution fighting vessels, in particular the suitability of berths and jetties, the connection of vessels' manifolds to the facility's cargo arms/receiving piping and various, operational requirements as the inerting of cargo tanks, (filling with inert gas to reduce explosion hazards), etc.

Engineering solutions aimed at overcoming the oil-related restrictions should be safe for the operating personnel onboard the vessels, proven, commercially available, and feasible for applying. In particular in Europe from a recently released study by EMSA and for various sizes of oil spills it was found that the area off the coast of Iceland, off the west coasts of Norway and part off the northern coasts of Turkey are not covered by facilities capable of receiving the collected oil.

As the size of the simulated spills increases more areas are left uncovered, e.g. the gulf of Biscay, the Mediterranean Sea, and the North Sea. A solution for these 'orphan' areas would be the adoption of dedicated ship to ship transfer operations so that the recovered oil is transferred to oil tankers that can be easily accommodated in the available facilities and perform the discharging operations.

The aforementioned 'orphan' areas comprise the following:
For oil spills of 1,000 m^3 in European waters:

- Off the west coasts of Norway;
- Off the coasts of Iceland;
- Part of the Biscay Gulf, France and off the north coasts of Spain;
- A limited part of the central Mediterranean Sea (i.e. the sea region south to Sardinia);
- Off part of the north coasts of Turkey.

For oil spills of 10,000 m^3 in European waters:

- Off the west coasts of Norway;
- Off the coasts of Iceland;
- Off the northern coasts of Great Britain;
- Off the western coasts of France and off the north coasts of Spain (European Atlantic);
- Almost the entire Mediterranean Sea (except the area off the coasts of Cyprus)

- The Black Sea.

For oil spills of 40,000 m^3 in European waters:

- Off the west coasts of Norway;
- Part of the Bothnian gulf;
- The North Sea;
- Off the coasts of Iceland;
- Off the northern and eastern coasts of Great Britain;
- The English Channel;
- Off the coasts of France, Spain and Portugal (European Atlantic);
- Almost the entire Mediterranean Sea (except the area off the coasts of Cyprus)
- The Black Sea.

The re-use/valorization of oil recovered during spill response operations at sea and on-shore is dependent on various parameters, with the applicable waste management framework in the country where the incident occurs, to often define whether collected oil and/or oil contaminated waste should be treated as hazardous waste and what would the preferable treatment, recycling and final disposal options in local or national level. Although, there might not be specific national strategy for the re-use of disposal of recovered oil, sustainable waste management options must be always sought taking into account the available locally treatment and disposal infrastructure. During a Workshop on Oil Spill Waste Treatment and Disposal from a Legislative and Technical Point of View" that was conducted as an action under the European Community co-operation framework against accidental or deliberate marine pollution (October 2002), the following re-use and disposal options were recorded in various EU countries.

Table 6: Re-use and disposal options in various EU countries

	Oil-water emulsions	High viscosity oily waste	Oil water mixtures
Land filling	Ireland, Spain	Spain, Ireland	Spain, Ireland
Incineration	Denmark, Italy, UK, Netherlands	Denmark, Italy, UK, Netherlands	Denmark, Italy, UK,
Co-incineration	UK	UK	UK
Biological treatment	UK	UK	UK
Recycling	Netherlands, Ireland	Ireland	Ireland

Table 7: Code Letters Nomenclature

skimmers (Bi)		heavy oil skimmers (Bii)		barriers/booms (A)	
Skimmer category	Skimmer type	Skimmer type	Skimmer name	Boom category	Boom type
Mechanical (b)	Vacuum (1)	Rot. drums (1)	LORI		
	Weir (2)	Incl. belt (2)	MARCO	Fence (1)	Flexible (a)
	Vortex (3)	Belt (3)	ERE		Semi-rigid (b)
	DIP (4)	H.O. belt (4)	AXION HOBS		Rigid (c)
Oleophilic (c)	Drum (2)	Incl. belt (5)	Tar Hawg	Curtain (2)	Flexible (a)
	Disc (3)	Rotating net drum	UNISEP		Semi-rigid

		(6)			(b)
	Belt (1)	Rot. drum (7)	KLK		Rigid (c)
	Rope mop (4)	Rot. disc (8)	Sea devil	Shore sealing (3)	
	Brush (5)			Fire resistant (4)	
		Rot. drums (1)	LORI		
Mechanical (b)	Vacuum (1)	Incl. belt (2)	MARCO		
	Weir (2)	Belt (3)	ERE		
	Vortex (3)	H.O. belt (4)	AXION HOBS		
	DIP (4)	Incl. belt (5)	Tar Hawg		
Oleophilic (c)	Drum (2)	Rotating net drum (6)	UNISEP		
	Disc (3)	Rot. drum (7)	KLK		
	Belt (1)	Rot. disc (8)	Sea devil		
	Rope mop (4)				
	Brush (5)				

Skimmer vessels (C)	**sorbent materials (D)**	**Dispersants (E)**
Vacuum system (C1)	Natural organic, Mineral (D1)	Conventional (E1)
DIP (C2)	Synthetic (D2)	Undiluted (E2)
Multi-type adapter (C3)	Towels , Pillows, Rolls (D3)	Diluted (E3)
Self-propelled barge (C4)	Booms (D4)	

Table 8: Compatibility framework of oil response means— sea state features

Sea state	**Booms**	**Skimmers**	**H.O. skimmers**	**Skimmer vessels**	**Sorbents**	**Dispersants**
0	A	Bi	Bii	C	D	
1	A	Bi	Bii	C	D	
2	A	Bi	Bii	C1, C2, C3	D	
3	A1, A2, A4	Bic2, Bic3, Bic4	Bii1, Bii3, Bii6	C1, C2, C3	D2, D3, D4	E1, E2, E3
3–4	A1a, A1b, A2a, A2b, A4	Bic5	Bii1	C1, C2, C3	D4	E1, E2, E3
4				C2, C3		E1, E2, E3
5				C2, C3		E1, E2, E3
6				C2		E1, E2, E3

Table 9: Compatibility framework of oil response means— current velocity limits

Current velocity (knots)	Booms	Skimmers	H.O. skimmers	Skimmer vessels	Sorbents	Dispersants
0.6	A	Bi	Bii	C	D	E1, E2, E3
0.6–0.7	A1, A2, A4	Bi	Bii	C	D	E1, E2, E3
0.7–1.0	A1, A2, A4	Bic	Bii	C	D	E1, E2, E3
1.0–1.5	A1, A2, A4			C	D	E1, E2, E3
1.5–2.0	A1c, A2c			C	D	E1, E2, E3

Table 10: Compatibility framework of oil response means—oil viscosity limits

Oil viscosity (cSt)	Booms	Skimmers	H.O. skimmers	Skimmer vessels	Sorbing materials	Dispersants
<1,000	A	Bib, Bic1, Bic2, Bic3, Bic4		C1, C2, C3	D3, D4 (maximum 250 cSt)	E1, E2, E3
1,000–2,000	A	Bib1, Bib2, Bib3, Bic2, Bic3, Bic4		C1, C2, C3	D1, D2 (minimum 1500 cSt)	E1, E2, E3
2,000–3,300	A	Bib1, Bib2, Bib3, Bic2, Bic3, Bic4		C1, C2, C3	D1, D2	
3,300–20,000	A	Bib1, Bib2, Bib4, Bic2, Bic4		C1, C2, C3	D1, D2	
20,000–30,000	A	Bib1, Bib2, Bib4, Bic2, Bic5		C1, C2, C3	D1, D2	
30,000–50,000	A	Bib1, Bib4, Bic5		C	D1, D2	
>50,000	A		Bii	C4	D1, D2	

7 Alternative Technologies to overcome potential limitations-Main goals of Kill Spill project

Although conventional response actions, such as physical removal with booms, skimmers and absorbent materials, are the first option, they rarely achieve complete cleanup of oil spills (10-15% of spilled oil is recovered) and must be deployed soon after the spill occurs. Chemical methods, particularly dispersants, although they have been routinely used in many countries as a response action, their use is restricted due to their toxicity and the toxicity of dispersed oil, and because they cannot be applied under certain circumstances (such us severe weather conditions, open sea -only allowed at coastline depth > 15 m). On the other hand biological methods have gained importance and acceptance mainly due to the low environmental impact, the costs and the capability to degrade a wide variety of organic contaminants. Bioremediation through its first successful application on the *Exxon Valdez* spill has motivated many researchers to investigate physical, chemical and biological factors that could produce favourable conditions for in-situ and ex-situ treatments.

The dominant compounds present in crude oil and refined products are biodegradable and they will eventually be removed from the environment as microbes consume them. Enhanced bioremediation aims to stimulate the rate of this process by the following two complementary approaches: bioaugmentation and biostimulation. In bioaugmentation, the addition of oil-degrading bacteria boosts biodegradation rates whereas in biostimulation, the growth of indigenous hydrocarbon degraders is stimulated by the addition of nutrients (mainly N & P) or other growth-limiting nutrients. Availability of hydrocarbons to microorganisms could be an important factor in oil bioremediation, since oil degradation occurs in the oil-water interface and novel biostimulants such as biosurfactants (instead of the more toxic dispersants) or other oleophilic nutrients that can emulsify oil and make it available to hydrocarbon degraders and cannot be washed by waves action are crucial and should be consider as a bioremediation strategy in the future.

Although the problem of combating marine oil spills has been studied extensively for several decades, there are several areas that could benefit from further research developments. These are:

- The development of low cost oxygenation systems for aerobic bioremediation of contaminated anoxic sediments and deep sea environment.
- The development of novel biostimulants that are non toxic to the marine environment for example by increasing in situ production of biosurfactants at the oil-water interface.
- The development of novel oleophilic amendments and slow release fertilizers with better transport characteristics for application in cold shoreline environments.

In this sense, bioremediation has gained importance and the development of new bioremediation formulations can exceed potential limitations as those previously described and thus bioremediation can be upgraded to one of the first response actions.

Considering the above issues rising from conventional cleanup technologies such as dispersant's inefficiency in deep water as well possible toxicity, in the current project Kill Spill emphasis is given on promoting alternative technologies and products that could counter oil spills in a more environmentally friendly way but sufficiently and efficiently as well.

Specifically Kill Spill is aimed at delivering innovative biotechnologies, which can be integrated to the real sequences of state-of-the-art actions used currently to cleanup oil spills. Kill●Spill is expected to test and validate chemicals & biochemicals to be used as the 1st tier of response actions to disperse/emulsify oil and materials enabling the containment and sorption of oil, preparing the field for the follow-up actions. In addition, the project examines biotechnologies aiming at intensified biodegradation processes by bioaugmentation/biostimulation as follow-up and longer term actions in aerobic/slight anoxic compartments. Kill Spill is also aimed at producing new knowledge on dispersion/sorption and biodegradation processes to help produce multifunctional products, which are suited for follow-up and longer term actions. The multifunctional products address the necessity for integrated bioremediation (bioavailability, metabolic requirements, etc.) and are efficient along the whole redox gradient from surface water to sediments.

Specifically the ability and availability of novel biosurfactants, dispersants and sorbent materials particularly those of biological origin for deployment on oil spills in marine and terrestrial environment as a means to accelerate dispersion and/or rate of degradation and removal of such compounds are explored in WP3 of Kill Spill project. Also the capabilities of microorganisms (MO) to breakdown petroleum hydrocarbons in diverse environments (deep sea, anoxic sediments) as well as to produce biosurfactants are investigated and further their incorporation into innovative formulations for bioaugmentation activities is examined in WP4. Development of low cost biostimulant additives such as oleophilic biostimulants for enhanced bioremediation is also one of the goals in this project. Delivery systems of nutrients, microorganisms or other co-substrates such as oleophilic nutrients or encapsulated nutrients and/or hydrocarbon degrading consortia in porous sorbents materials are also under investigation. Slow release fertilizer granules (e.g. Custonblen) and laterite minerals and high Ni and Co mineral by products (WP3) will be tested for delivery of macronutrients and Ni and Co respectively to enhance biodegradation in anoxic sediments. In addition low cost biogenic mobilizing agents (Quillayasaponin, a soya lecithin, randomly methylated β-cyclodextrins and humic substances), sorbents (activated carbon, organophilic clays, biochars, surfactant modified zeolites) and new microbial surfactants obtained within WP3 will be tested for their biodegradation potential in chronically contaminated and freshly contaminated sediments from sites with different environmental conditions (Mediterranean and Norwegian Seas). Novel sorbent materials will be developed and explored as a line of defence and protection against oil spills: polymer-based non-woven fabrics (HeiQ), mineral-based powders (OMYA), and porous granules (BIOREM) will support the incorporation of the novel biosurfactants into dispersant formulations.

Oxygen limitations in hydrocarbon biodegradation that arise in deep sea explorations but also in sediments can be dealt with special oxygen releasing compounds developed in WP3 and WP6 like - "Oxygen-releasing dispersant OXYGELTM" (formulated as an inorganic gel) and Porous granular sorbent AEROBEADSTM (formulations which carries nutrients and microorganisms while moving downward towards the sediment slowly releasing oxygen). Oxygen can also be generated from water electrolysis at different finely controlled voltages at the surface of carbon-based electrodes deployed in the contaminated sediments or sediment caps as part of novel bioelectrochemical remediation approaches.

Combinations of the above different formulations will promote the development of novel and innovative multifunctional remediation agents that have at least two modes of actions (e.g., dispersing oil and providing nutrients or microbes, or absorbent materials with encapsulated nutrients & hydrocarbon degrading microbes) or innovative devices with such agents for specific uses. These multifunctional remediation agents include:

Multifunctional bioremediation agents (combination of dispersants from WP3 with bioremediation agents) for deep sea hydrocarbon releases which are expected to enhance the bioremediation rates of the expected side-cloud of micro-droplets that was observed for the first time in the recent BP Gulf of Mexico incident (Hazen et al., 2010).

Mesoporous (nano)particles which can be included in formulations to intensify natural (biostimulation) and/or bioaugmentation processes and microparticles with co-immobilized HC-degrading microbes and slow-release fertilizers (SRF). Innovative “all-in-one” multifunctional carrier based on Oxygel™ and Aerobeads™ products that deliver oxygen combined with isolated hydrocarbon-degrading microbial consortia from WP4, nutrients (N & P) and oligo-elements (micronutrients) and different dispersants into active and reactive functional product formulation for combating oil spills suitable for use as a first response in an oil spill. Multifunctional sorbent materials (mineral based multifunctional sorbent material and Porous bio-carriers as natural sorbents) can be used as carriers for biostimulation and bioaugmentation agents.

Improved Biodegrading Boom for small oil spills: non-biodegradable and reusable (to reduce production costs) for use in coastal areas and harbors and an emergency boom made out of biodegradable material. Booms of this type primarily bind oil to prevent spreading and sedimentation. Slow-release fertilizers provide a localised zone of high nutrient concentrations on the surface and the immediate vicinity of the boom, thus providing naturally occurring oil degrading microbes to colonize absorbed oil. Both types of booms constructed in this WP will be supplied with commercial slow-release fertilizers available on the market as well as products developed within this project. The non-woven fabric materials will serve to both contain sorbent materials developed as part of the WP and also as a scaffold for surface treatments to assist in oil absorption, water repellence and nutrient delivery functions.