Kill•Spill

Integrated Biotechnological Solutions for Combating Marine Oil Spills

Deliverable D6.6

Protocol on performance of the boom in different climatic conditions

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1 Introduction

The need to minimize environmental damage from spilled oil makes it worth developing effective and easy-to-apply oil slick collection methods. The most common equipment used for controlling oil spills is the oil boom. Booms are used to contain the oil and keep it from spreading prior to various oil removal techniques. In an effort to achieve high oil collection efficiency, researchers have investigated boom arrangement [1, 2]. Booms are used to contain the oil and keep it from spreading prior to various oil removal techniques. In an effort to achieve high oil collection efficiency, researchers have investigated boom arrangement. Such studies are especially useful to oil spill recovery at inlets, rivers, and canals. Booms help to concentrate oil in thicker surface layers so that skimmers, vacuums, or other collection methods can be used more effectively. Often the first containment method to be used and the last equipment to be removed from the site of an oil spill, they are the most commonly used and most environmentally acceptable response technique to clean up oil spills in the United States. There are three main types of boom: ***hard boom*** is like a floating piece of plastic that has a cylindrical float at the top and is weighted at the bottom so that it has a "skirt" under the water; ***fire boom*** is like metal plates with a floating metal cylinder at the top and thin metal plates that make the "skirt" in the water to contain oil long enough that it can be lit on fire and burned up; ***sorbent boom*** looks like a long sausage made out of a material that absorbs oil. If you were to take the inside of a disposable diaper out and roll it into strips, it would act much like a sorbent boom. Sorbent booms don't have the "skirt" that hard booms have, so in case of heavy oil spills they can't contain oil for very long.

Each sorbent boom is usually constructed with a tough outer mesh skin that encases the super absorbent filler. A nylon rope runs through each boom and has carbon steel connectors so operator only uses the number of booms required to contain the spill. Retrieval is easy with the long lasting, durable linking system. The oil absorbent booms typically come in a bright white colour to make it easy to see when they are completely fully saturated. The oil absorbent booms commercially available from many distributors (see the links below as only few examples:

(i) http://www.oilspill-cleanup.com/oilabsorbentboom.html;
(ii) http://www.oilspill-cleanup.com/oilabsorbentboom.html;
(iii) http://www.chemtexinc.com/absorbents/booms-sweeps.html;
(iv) https://www.grainger.com/category/absorbent-socks-and-booms/spill-control-supplies/safety/ecatalog/N-k4k.

Sorbent booms are very effective in protecting environmental resources, beaches and off-shore aquaculture hatcheries from modest and low-scale oil spills. Although after saturation, the boom sorbents have to be replaced with novel material, which demand operational and waste treatments costs. To the best of our knowledge, self-regenerating boom sorbents with enhanced absorption & bioremediation capabilities are not currently market-developed.

2 Self-regenerating Bio-Boom oil-sorbent with enhanced absorption & bioremediation capabilities: the lab-scale proof-of-concept: the lab-scale proof-of-concept

Aiming at minimizing the above mentioned problems several sorbent booms have been developed and optimized within the **Kill•Spill Project**. Special emphasis was given on development of sorbent boom, when used in a combined way, which allows obtaining a very high adsorption capacity with simultaneous degradation of adsorbed oil by petroleum-degrading microbial consortia, stuffed inside sorbent boom sausage. Active biomass will thus regenerate the sorbent and increase its efficient life time. We named this product the **Bio-Boom**.

The design of the self-regenerating Bio-Boom oil-sorbent consisted of four basic system elements: reusable foam sorbent prepared in form of floatable sausage, immobilized petroleum-degrading microbial biomass served as sorbent regenerator, and oil emulsifier and slow nutrient-releasing particles served as agents stimulating the biodegradation.

The system concept is to place the Bio-Boom sorbent onto the floating oil. After residence time to allow the sorbent to absorb floating oil, the saturated sorbent can be either collected and removed from the seawater in handleable container (*ex situ* scenario) or left for the period necessary to complete the degradation of adsorbed oil (*in situ* scenario). In first case, , the Bio-Boom oil-sorbent will be extracted from the handleable container and transported to regenerator, which represents the incubation tank with regulated temperature/oxygenation. After regeneration, the sorbent could be transported back to the contaminated area and reapplied to the slick. The process cycle could then be repeated many times, using the same sorbent material, until the oil spill is recovered completely. Another, *in situ* scenario, would be an implication of the self-regenerating Bio-Boom oil-sorbent either in the area with permanently leaking contaminants (around docks and pilings) or in environmental resources area, beaches and off-shore aquaculture hatcheries to protect them from modest and low-scale oil spills. Broadcasting of the **Bio-Boom sorbent** would be done from the shore or from a small boat and monitored regularly for saturation and eventual replacement.

In brief, the parts of developed **Bio-Boom** are:

Efficient oil-absorbing non-toxic fabric used as the external part of Bio-Boom. Kill•Spill partner HeiQ with collaborators have developed an oil-absorbing, water-repelling, nonwoven fabric for oil relief efforts called Oilguard (www.oilguard.org). The product originally was intended for beach protection against oil spills to be applied to the shoreline. The Oilguard fabric can be prepared up to 5 m wide and several hundred meters long and can be used for preparation of Bio-Boom sausage. This allows for the fabric to absorb crude oil yet repelling the seawater. The company HeiQ Materials AG, located in Bad Zurzach, Switzerland participates in the Kill•Spill project and develops, produces and commercializes this sorbent.

Efficient petroleum-degrading consortia consisting of bacterial and fungal strains or enrichments characterized by high oxidative capacities are added. Before stuffed into the Bio-Boom sausage, the biomass is immobilized in chitosan or other carriers (kappa-carrageenan, alginates, etc.). Immobilization significantly facilitates the handling procedure and elongates the shelf-life of the whole product.

(a) **Optimized bio-surfactant characterizing by both high efficacy of emulsification and low toxicity. Application of emulsifying agent significantly enhance the bioavailability of otherwise recalcitrant heavy fraction of crude oil and thus improve the rates and degree the biodegradation.**

(b) **Optimized slow nitrogen- and phosphorus-releasing particles. The benchmark products are developed by Kill•Spill partner FHNW and described in details in corresponding deliverables.**

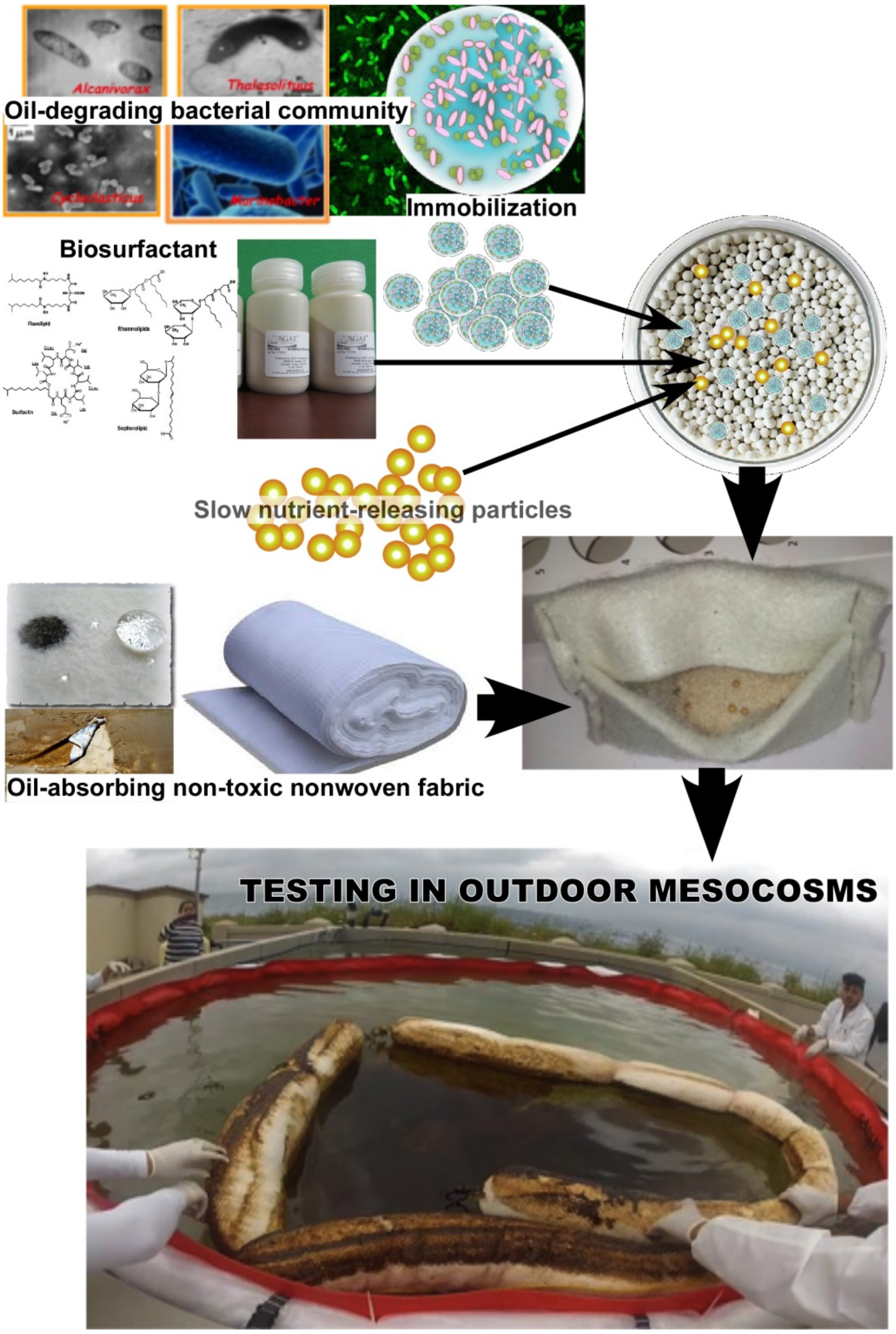

Figure 1 **A schematic representation of the preparation of self-regenerating Bio-Boom oil-sorbent and subsequent testing in outdoor mesocosms.**

3 Protocol on performance of the boom sorbent in different climatic conditions

3.1 Aims

Within the **Kill•Spill** project partner HeiQ assessed a variety of boom envelope materials including non-woven fabrics manufactured from cellulose-derived fibres. The non-woven fabric materials serve to both contain sorbent materials developed and also as a scaffold for surface treatments to assist in oil absorption, water repellence and nutrient delivery functions. We anticipated that the ideal booms for the respective oil types will be tested in partner institutes located in Mediterranean and North Sea testing how the booms can work in a broad variety of climate zones and in different seasons to prove universal applicability of the booms.

Following the promising results obtained at the laboratory scale (see Figure 3), the OilGuard oil sorbent was up-scaled and tested in the mesocosm facilities available at the laboratories of IAMC-CNR in Messina (Italy) under different temperatures, representing Mediterranean (18-25°C) and North Sea (4°C) conditions. The primary scopes of these experiments were the following:

- Assessing the Bio-Boom performance under experimental conditions more closely resembling those occurring at a real contaminated site in a broad variety of climate zones and in different seasons;
- Gaining a deeper understanding of the relative contribution of petroleum immobilization and biodegradation processes participating in the removal of petroleum hydrocarbons and bio-regeneration of Bio-Boom;
- Assessing the extents of adsorption and rate of biodegradation as function of ambient temperature.

3.2 Experimental, operational, and monitoring parameters

1. The mesocosm experiment consisted of 4 glass tanks (length: 100 cm, depth: 30 cm; height: 40 cm). Each tank was filled with 50 litres of seawater that was artificially contaminated with 45 mL of Dansk/Pier1 crude oil, to a final petroleum concentration of approximately 700 ppm. The wave maker was positioned inside each tank that kept seawater under a continuous-flow at a flow rate of approximately 3000 L h^{-1}. The tanks were separately maintained at +25°C, +20°C, +15°C and +4°C, respectively.

2. OilGuard sorbent, served as the basic structural component of Bio-Boom, was cut in circular pieces with 3g of weight each and placed in filter holder in triplicate as shown in Figure 2. We have used an upgraded version of this product, called Oilguard™ 2014.
A water pump was connected with filter holder, which received seawater and petroleum with inflow rate of 3 L min^{-1}. Absorption capacity of Oilguard™ 2014 was tested three times during one week of first phase of experiment (after 24, 48 and 158 hours, respectively). Verification of oil absorbance by HeiQ Oilguard™ 2014 in mesocosm tests was performed to estimate the amount of crude oil absorbed by sorbent per weight.

3. At fixed periods of time, 0.3-0.5 g pieces of the nonwoven Oilguard™ 2014 fabric was taken from the filter holder and placed in 100 mL Schott flask. 10 ml of hexane was added and extraction of petroleum, immobilized inside the sorbent, was performed during 1 h of vigorous shaking at 30°C. Hexane was separated and extraction was repeated two times more. All three hexane fractions were combined and after solvent evaporation, the amount of extracted petroleum was measured gravimetrically. Cleaned pieces of the nonwoven Oilguard™ 2014 fabric was weighted and adsorption capacities was estimated as $K_{abs} = N_{oil} / N_{sorbent}$, where N_{oil} and $N_{sorbent}$ are amount of extracted petroleum (in mg) and weight of piece of nonwoven Oilguard™ 2014 fabric (in grams), respectively.

Figure 2 Set-up of the first phase of oil sorbent performance estimation.
Mesocosms, contaminated with crude oil, were supplemented with filter holders filled with OilGuard 2014 discs. Discs were regularly monitored by adsorption capacities using both gravimetrical and GC-FID analyses.

4. After one week of saturation, the bio-regeneration of contaminated sorbent (5 g of total weight) was performed during consecutive 30 days under tested temperatures. The Oilguard™ 2014 fabric was liberated from filter holder and placed in 100L glass tanks (+25°C, +20°C, +15°C and +4°C). As in the first phase of experimentation, each tank was filled with 50 litres of seawater. The wave maker was positioned inside each tank that kept seawater under a continuous-flow at a flow rate of approximately 3000 L h^{-1}. Addition of 500 mL of active biomass (10^7 cells/ml) of hydrocarbon-degrading bacteria grown in artificial seawater [3] stimulated the degradation. Bacterial strains used in bio-regeneration experiments:

Temperature 25°C → *Marinobacter hydrocarbonoclasticus*;

Temperature 20°C → *Alcanivorax borkumensis*;

Temperature 10°C and 4°C → *Oleispira antarctica*.

After 30 days of exposition of chosen temperatures, the sorbent was taken from the flasks and petroleum was extracted with 50 ml of *n*-hexane. Extraction was repeated 3 times. 150 mL of combined solvent was evaporated and amount of remaining petroleum was measured gravimetrically.

4 Results

As it shown in Figure 3A, the capacity of oil absorbance by HeiQ Oilguard™ 2014 increased during first 48h likely due to evaporation/dissolution effect of light fraction of crude oil. With time, crude oil weathered and became more dense. In general, during the first phase of the mesocosm tests the HeiQ Oilguard™ 2014 sorbent demonstrated a very efficient capacity to tightly immobilize crude oil with adsorption capacities K_{abs} of 3,200 ± 400 at 20-25°C. The adsorption capacities K_{abs} of Oilguard™

2014 sorbent were slightly lower at cold conditions, namely 2,500 ± 370. This was most probably due to increased density of petroleum occurred under low temperatures.

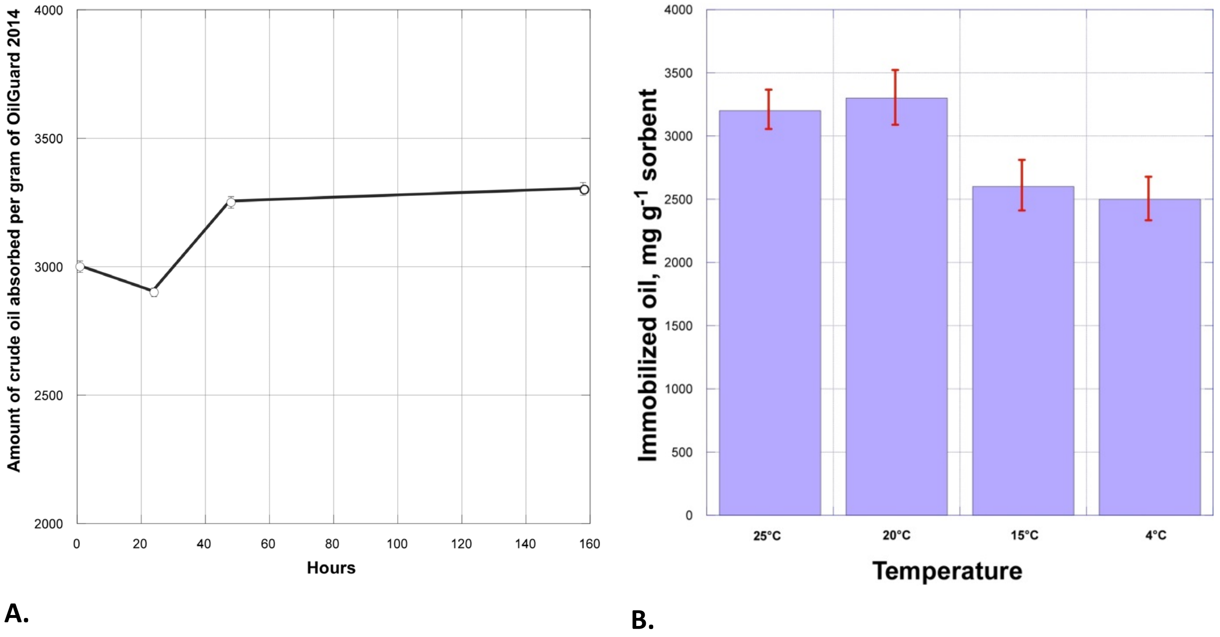

Figure 3 **Oil absorption experiment with HeiQ Oilguard 2014.**
A. Amount of crude oil, absorbed on the sorbent during first week of experiment at temperature of 20° and 25°C is shown as an average of six independent measurements. B. Dansk/PierE1 crude oil immobilized inside of the nonwoven Oilguard™ 2014 fabric, as measured after 48 hours of saturation at various temperatures.

Bio-regeneration experiments revealed high availability of immobilized petroleum towards used oil-degrading microorganisms. Less than one percent of initially adsorbed Dansk/PierE1 crude oil was extracted from the sorbent after one month of contact with *Marinobacter hydrocarbonoclasticus* (temperature of cultivation +25°C) and *Alcanivorax borkumensis* (temperature of cultivation +20°C) as is summarised in Table 1. Degradation levels at lower temperature were somehow behind the values obtained at 20-25°C. Nevertheless, *Oleispira antarctica* was able to regenerate of 75-80% of the adsorption capacities K_{abs} of Oilguard™ 2014 sorbent at temperatures, typical for the North Sea.

Table 1 **Bio-regeneration of HeiQ OilGuard 2014 nonwoven fabrics contaminated with Dansk/PierE1 petroleum. Marinobacter hydrocarbonoclasticus and Alcanivorax borkumensis were cultivated at 25°C and 20°C, respectively.**

	Percentage of oil remaining on sorbent after 30 day of bio-regeneration
Control (no bacterial strain added)	100 %
Marinobacter hydrocarbonoclasticus	1 %
Alcanivorax borkumensis SK2	1 %
Oleispira Antarctica (at 4°C)	21 %
Oleispira Antarctica (at 15°C)	24 %

5 Conclusive remarks

The main results of the experimentations described in this deliverable can be summarized as follows:

- The self-regenerating Bio-Boom oil-sorbent with enhanced absorption & bioremediation capabilities turned out to be suitable and effective technology to remove hydrocarbons from contaminated surface of the seawater in different climatic conditions.
- The self-regenerating Bio-Boom oil-sorbent with enhanced absorption & bioremediation capabilities allows effective adsorption of released petroleum, independently of the ambient temperature in the range of 4-25°C.
- Consistently with obtained data, the self-regenerating capacities of Bio-Boom resulted in a remarkable degradation of immobilized crude oil in the temperature range between 4°C and 25°C.
- Data deriving from our experiments have provided a clear confirmation of the positive effect of contaminants removal using Bio-Boom.
- The Bio-Boom technology can be applied in the sea at different geographic locations and under different climatic conditions occurred both in Mediterranean and North Seas.

6 References

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