

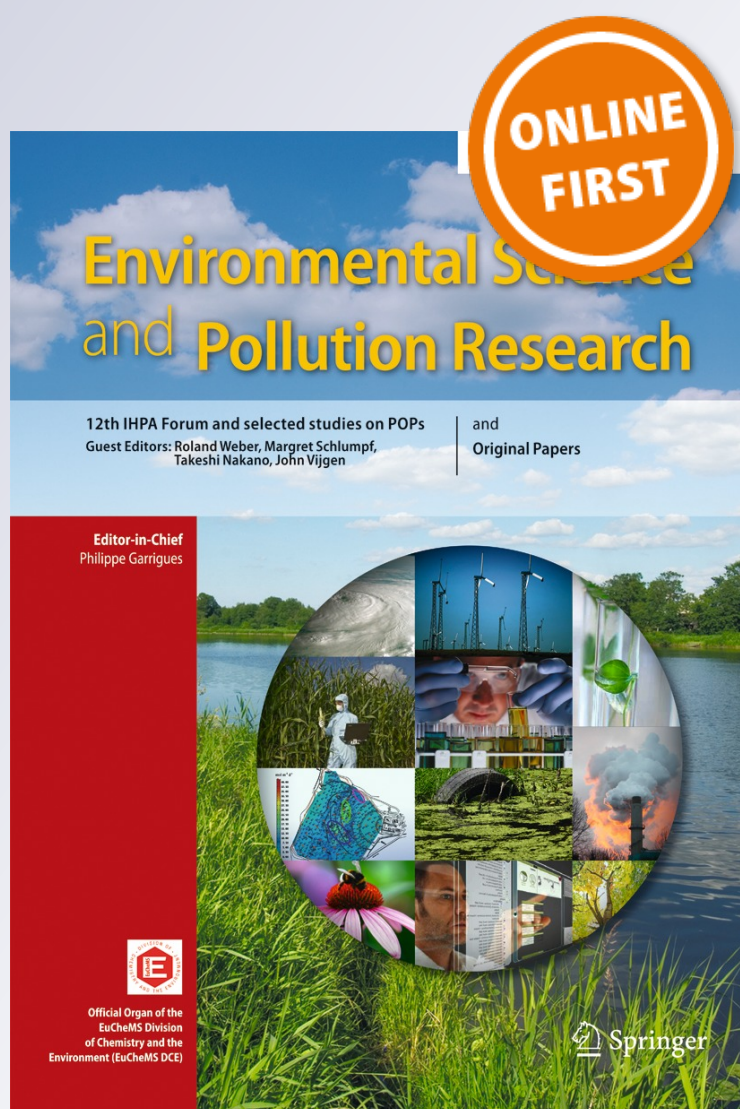
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Best available techniques (BATs) for oil spill response in the Mediterranean Sea: calm sea and presence of economic activities

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Abstract An oil spill is the accidental or intentional discharge of petroleum products into the environment due to human activities. Although oil spills are actually just a little percent of the total world oil pollution problem, they represent the most visible form of it. The impact on the ecosystems can be severe as well as the impact on economic activities. Oil spill cleanup is a very difficult and expensive activity, and many techniques are available for it. In previous works, a methodology based on different kinds of criteria in order to come to the most satisfactory technique was proposed and the relative importance of each impact criterion on the basis of the Saaty's Analytic Hierarchy Process (AHP) was also evaluated. After a review of the best available techniques (BATs) available for oil spill response, this work suggests criteria for BATs' selection when oil spills occur in the Mediterranean Sea under well-defined circumstances: calm sea and presence of economic activities in the affected area. A group of experts with different specializations evaluated the alternative BATs by means of AHP method taking into account their respective advantages and disadvantages.

Keywords Oil spills · BATs · Remediation techniques · Analytic Hierarchy Process · Mediterranean Sea · Calm sea

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Introduction

In the last 10 years, a review has been carried out on best available techniques (BATs) currently used for oil spills response (Cumo et al. 2007). Containment and cleanup techniques must be put into action when a marine oil spill occurs in order to limit its spreading on water surface. It is of utmost importance to contain the spill as quickly as possible in order to minimize danger to human beings, environment, and property. The most exploited containment technique is based upon floating barriers called *booms*. They are used for concentrating oil in thicker surface layers, making its recovery easier, as well as for keeping oil out of sensitive areas or for diverting oil into collection areas. There are many kind of booms, but all of them are greatly affected by conditions at sea: the higher the waves swell, the less effective booms become. Usually, booms are less effective with waves higher than 1 m or currents faster than 1 knot per hour. New technologies, such as submergence plane booms and entrainment inhibitors, have been developed with the aim of allowing booms to operate at higher speeds while retaining more oil (U.S. Environmental Protection Agency 1999). Straight after oil spill containment, oil removing operations can start. Seven types of techniques are currently used to recover oil from water surface:

- (1) booms;
- (2) skimmers;
- (3) sorbents;
- (4) dispersants;
- (5) in situ burning;
- (6) bioremediation;
- (7) magnetic nanocomposites.

Skimmers are mechanical devices used to remove floating oil from water surface. They may be employed from shore or

operated from vessels. The skimmer's efficiency hinges on weather conditions: in moderately rough or choppy water, skimmers tend to recover more water than oil (U.S. Environmental Protection Agency 1999). They are generally effective in calm seas and prone to clogging by floating debris.

Sorbents are insoluble materials or mixtures of materials used to soak up liquids by means of the mechanism of absorption, adsorption, or both. To be useful in facing oil spills, sorbents need to be both oleophilic and water-repellent. Even though sorbents may be used as the only cleanup technique in small spills, they are most often used to remove final traces of oil after skimming operation or in areas hardly reached by skimmers. Although sorbents are relatively cheap and very environmentally friendly, they still have several limitations. Sorbents are claimed to be inappropriate technology for use in the open sea and inefficient with heavy fuel oil. Besides, they are bulky to store and transport.

Dispersing agents, also called *dispersants*, are a group of chemical products designed to be sprayed onto oil slicks with the aim of accelerating the process of natural dispersion (International Tanker Owner Pollution Federation 2011). They contain surfactants or compounds acting to break oil into small droplets. These droplets disperse into the water column, where they are subjected to natural processes, such as waves, currents, and wind that help to break them down further. Dispersants are often used when mechanical recovery is not feasible. Their effectiveness hinge on the oil composition and on the method and rate at which the dispersant is applied. Heavy crude oils do not disperse as well as light to medium ones. Dispersants are most effective if applied straight after a spill before the lightest oil components have evaporated (U.S. Environmental Protection Agency 1999). Factors such as water salinity, temperature, and conditions at sea influence the effectiveness of dispersants. Even if dispersants can work in cold water, they work best in warm water. While some countries hinge almost exclusively on dispersants to face oil spills, because rather frequently rough or choppy conditions at sea make mechanical containment and cleanup difficult, some other countries do not use them because of concerns about the toxicity of the dispersed mixture. Dispersant used today are definitely much less toxic than those used in the past. Dispersants proved their capabilities to treat up to 90 % of spilled oil and are cheaper than the physical methods (Holakoo and Mulligan 2002). The inflammable nature of most dispersants can produce human health hazards during applications and potential damage to marine life.

In situ burning of oil requires the ignition and controlled combustion of oil slicks. It is typically used in conjunction with mechanical recovery on open sea (U.S. Environmental Protection Agency 1999). Fire-resistant booms are often used to collect and concentrate the oil into a slick that is thick enough to burn. Factors such as water temperature, wind direction and speed, wave amplitude, oil type, and slick

thickness influence the decision to use or not in situ burning. This technique is effective in calm wind conditions and spills of fresh oils or light refined products which quickly burns. However, the residue may sink. Removal of the residue can be achieved through mechanical means (Davidson et al. 2008). This technique enables to remove great amounts of oil from water surface, but there are a number of problems limiting its feasibility such as the generation of huge quantities of black smoke and possible sinking of viscous and dense residues. Even though it can be effective in some situations, in situ burning is not often used on marine spills because of widespread concern over atmospheric emissions and uncertainty about its impacts on human and environmental health. Despite its drawbacks, in situ burning could be an efficient cleanup technique when there are few negative effects on human populations or the environment such as remote areas and water covered with snow or ice. Under these conditions, burning can quickly prevent the movement of oil to other areas and provide a cleanup means for affected areas with restricted access for mechanical or physical removal methods or provide an additional level of cleanup when other methods become ineffective. When oil is spilled into water containing a layer or chunks of ice, burning can often remove much more oil than other techniques.

Oil as well as many natural substances biodegrade over some period into simple compound such as carbon dioxide, water, and biomass. *Bioremediation* is the term referred to the use of microorganisms to detoxify or remove pollutants owing to their diverse metabolic capabilities (Das and Chandran 2011) in order to accelerate natural biodegradation. Biodegradation of oil is a natural process that slowly removes oil from the environment. It is mainly affected by the bioavailability of nutrients and the concentration of oil, time, and the extent to which the natural biodegradation had already taken place (Zahed et al. 2010). Nutrients are necessary for the growth of hydrocarbon degraders such as nitrogen and phosphorus, but they are always in low concentrations in marine environment (Dave and Ghaly 2011). The high initial concentration of spilled oil has a negative effect on the biodegradation process causing a significant lag phase in the order of 2–4 weeks (Zahed et al. 2010). Bioremediation typically involves biostimulation, which means the addition of the rate-limiting nutrients in order to accelerate the biodegradation of the oil. Even after biostimulation, at least a week is needed for microorganisms to acclimate to the environment and the entire bioremediation process may require months and even years to complete (Zahed et al. 2010). Bioremediation is considered environmentally friendly and cost-effective (Macaulay and Rees 2014). As it is affected by environmental factors and nature of the oil (limitations on heavy fuel oils), bioremediation is not an oil spill response method suitable for all scenarios (International Maritime Organization 2004). A potentially significant problem at sea may be the difficulty to provide

proper nutrient concentration to the oil degrading microorganism (Zhu et al. 2001).

Researchers have been working for years to find out a new way to clean oil spills efficiently. A promising method for oil spill cleanup is based on the use of *magnetic nanocomposite* materials. Although the use of these materials is not yet widespread, they seem to have substantial growth perspectives. Just as an example, Nicolaides et al. (1998) proposed a magnetic separation technique using the material “CleanMag”. It is a nanocomposite magnetic non-toxic, recyclable, and environmental friendly material, with oleophilic and porous characteristics and has an apparent density lower than water. The material is magnetic, so the oil can be collected from boats equipped with magnetic collection means. The main environmental benefits of this material are

- full recovery of oil without leaving any residual oil pollution;
- development of an environmental friendly technology, since the material is non-toxic and can be also recycled;
- alternative option to the use of chemical dispersants.

Chemical analyses of water samples, taken from the area where experimental investigation have been carried out, showed that the residual oil pollution, which was left into the sea after using the CleanMag technology, was less than 8 ppb. The result is even more noteworthy when compared with MARPOL 1973/1978 regulated limits. As a matter of fact, MARPOL 1973/1978 states that in order for a boat's functional disposal water to be released into the sea, it has to contain no more than 15 ppm of oil (MARPOL 1973/1978). Also, MIT researchers have developed a technique for magnetically separating oil and water that could be used to cleanup oil spills. MIT's new technique would mix water-repellent ferrous nanoparticles (that contain iron) into the oil plume and then utilize a magnet to simply lift the oil out of the water (Khushrushahi et al. 2013). The researchers envision that the process could take place aboard an oil recovery vessel to prevent the nanoparticles from contaminating the environment. Seawater polluted with oil would be pumped onto a boat treatment facility. Once on board, the magnetic nanoparticles would be added and attach themselves to the oil. The liquid would then be filtered with the magnets to separate the oil and water, with the water returned to the sea and the oil carried back to shore to an oil refinery. Afterward, the nanoparticles could be magnetically removed from the oil and reused. The use of tiny nanoparticles is seen by some as controversial. They may have negative impact on human health if these particles are inhaled, ingested, or absorbed into the body through the skin. As well as being complex and difficult to use on a large scale, there are concerns that they could damage marine life, if accidentally released. In comparison to the other conventional methods, the new technology has two outstanding advantages:

1. it could remove oil spill in large scale and can be really efficient;
2. the materials could be reused and have no chemical effects on environment (Bush 2014).

One of the biggest advantages of this technology (besides high efficiency of separation claimed by the scientists) is very little need in electrical power and maintenance. The system can be manufactured on a large scale. However, following real-scale experiments and analysis are needed to make reliable conclusions (McCall and Pennings 2012). Another technology using magnets was developed at the Italian Institute of Technology (Center for Biomolecular Nanotechnologies). The core of the separation method is a novel composite material based on commercially available polyurethane foams functionalized with colloidal superparamagnetic iron oxide nanoparticles and submicrometre-terpolytetrafluoroethylene particles, which can efficiently separate oil from water. It was found that combined functionalization of the polytetrafluoroethylene-treated foam surfaces with colloidal iron oxide nanoparticles significantly increases the speed of oil absorption. Finally, due to their light weight, they float easily on water. Hence, by simply moving them around oil-polluted waters using a magnet, they can absorb the floating oil from the polluted regions, thereby purifying the water underneath. This low-cost process can easily be scaled up to clean large-area oil spills in water (Calcagnile et al. 2012). In the Chinese Technological University, a fast and selective removal of oils from water surface through core-shell Fe₂O₃@C nanoparticles under magnetic field was recently introduced. These nanoparticles combined with unsinkable, highly hydrophobic (water-repelling) and superoleophilic (attracted by oil) properties could selectively absorb oil up to 3.8 times of the particles weight while completely repelling water. The oil-absorbed nanoparticles are quickly collected in seconds by applying an external magnetic field, and the oil could be readily removed from the surfaces of nanoparticles by a simple ultrasonic treatment. Experiment results showed that the highly hydrophobic Fe₂O₃@C nanoparticles could be reused in water-oil separation for many cycles. This approach has the advantages of easy production and storage, fast distribution and collection, low cost, good recyclability, high resistance to corrosion, thermal stability, and environmental friendliness (Zhu et al. 2010).

Materials and methods

Proposed criteria for BAT selection

Many techniques can be used in order to reduce oil spill damages. Current remediation techniques are physical, chemical, thermal, biological, and nanotechnological (Mahajan 2011) (Table 1).

Table 1 Remediation techniques for oil spill cleanup

Remediation techniques			Chemical	Thermal	Biological
Physical			Dispersants	In situ burning	Microorganisms
Booms	Skimmers	Sorbents	Solidifiers		
Fence	Weir	Natural			
Curtain	Oleophilic	Organic			
Fire-resistant	Suction	Natural			
		Inorganic			
		Synthetic			
Nanotechnological—superoleophilic and superhydrophobic nanomaterials					
Aerogels					
Nanodispersants					
Magnetic nanocomposites					
Membranes, filters, foams, meshes, sponges					
Others					

When an oil spill occurs and lots of techniques are available, it is worthwhile to choose the technique, which turns out to be the most suitable in the context situation, keeping in mind that all oil spill response techniques have some environmental impacts. Simple and user-friendly criteria will be helpful in making this choice.

Cumo et al. (2007) proposed a methodology based on three different kinds of criteria, to be applied in sequence, in order to come to the most satisfactory technique. Parameters such as time of intervention (prompt or next), typology of the spilled oil (light, medium, or heavy), and conditions at sea (calm, choppy, or icy) are assumed as main criteria in the BAT selecting process. A very important factor when choosing the best available techniques to face an oil spill is the time of intervention. In situ burning, for example, should be used straight after a spill before the lighter volatile and inflammable fraction in the oil has evaporated. Other important factor is the typology of spilled oil (light, medium, and heavy oils). Some techniques, such as those based upon the use of dispersants have small effect on heavy oils. The third factor is represented by the conditions at sea where the spill occurred: calm sea, choppy sea, water covered with snow, or ice. For example, when a spill occurs in water containing a layer or chunks of ice, in situ burning can often remove much more oil than conventional techniques. In rough and choppy sea, the use of dispersant is not recommended because the oil will be submerged by breaking waves, preventing direct contact between the dispersant and the oil. BATs should also meet with the impact criteria, for instance, the impact on human health, on environment, and the economic one. These criteria consider

- the proximity of built-up areas;
- the presence of economic activities (such as fishery and tourism);

- the presence of environmental protected areas and submerged archeological sites;
- the loss of biodiversity;
- the cost of the technique.

Oil spill response into the Mediterranean Sea

Despite the number of techniques available for oil spill cleanup, when the accident occurs, the selection of the best suitable technique under given circumstances is still not easy. In previous works (Cumó et al. 2007; Guidi et al. 2009), the authors tried to define the criteria under which the chosen technique would be most effective. They also evaluated the relative importance of each impact criterion on the basis of the Saaty's Analytic Hierarchy Process (AHP).

In this work, first of all, it is assumed that the oil spill occurs into the Mediterranean Sea. Nearly 25 % of the world's sea-transported oil transits Mediterranean Sea (RAOP MED Project 2014). According to recent studies carried out by the United Nations Environment Programme (UNEP), although the Mediterranean Sea constitutes 0.7 % of the global water surface, it receives 17 % of global marine oil pollution (ARLEM 2013). Currently, the risk of a big scale oil spill accident is greater than ever due to the deployment of a series of offshore installations across the Mediterranean Sea. According to a recent study made by the Mediterranean Oil Industry Group (MOIG), there are approximately 100 facilities handling oil in the Mediterranean Sea. Among them, 40 % are refineries, 24 % are ports, 26 % are oil terminals, and 10 % are offshore platforms (RAOP MED Project 2014). These facilities pose a great risk to the sea and coastal environment, and the consequences of a big scale incident can be devastating not only at a local but also at regional level as well, affecting the economies of many countries at Mediterranean Basin level.

This work aims at selecting the best available technique under certain circumstances:

- calm sea;
- presence of economic activities in area affected by oil spill.

Figure 1 schematized the aim of the work, the main criterion, and the alternative BATs.

All seven cleanup techniques, previously described in the introduction section, could be used in calm sea conditions. Vicinity of the area of economic activities needs quick action before the oil spill reaches shoreline or fishery cages and shellfish beds. The chosen technique also must not threaten touristic and fishery resources. The authors decide to exclude bioremediation because it is a slow process as it can take months to years in areas of high oil concentrations (Atlas and Hazen 2011) and because it is much more effective if used after some other techniques. Aggressive techniques such as dispersants and in situ burning should not be generally used under these circumstances. Dispersants are toxic for undersea life especially in the sea depth less than 10 m (MEMAC Fact Sheet 2015) and must not be used near fishery resources; however, they can be used near touristic resources at a localized area. It is a quick and cheap technique. In situ burning is dangerous for human health, and it is suitable for open sea. Otherwise, it is a very effective and quick technique. It can be used as “minor damage” if oil spill cannot be faced otherwise. This technique is totally inappropriate near fishery resources. Dispersants and in situ burning are not excluded because sometimes they can be used. The booms are the oldest and the most popular technique for oil response but they are not a cleanup method. They are used to contain the spreading of oil slick, providing barrier to oil movement, and are a very quick and effective technique under calm seas (Dave and Ghaly 2011). Booms are necessarily combined with other techniques, such as skimmers, and are expensive. The skimmers

are also not autonomic and are almost ineffective without booms. Even in situ burning sometimes needs booms to make the oil spill slick thick enough to burn up. The skimmers save the oil covering part of the costs with it. They are an effective but slow and expensive cleanup technique. Classic sorbents are slightly less expensive materials (compared with other mechanical techniques) but potentially toxic (inorganic). They are very useful, especially when the cost of labour is low, high effective, and save the oil. In the last few years, many solutions to cleanup oil spills by means of nanomaterials: aerogels, nanodispersants, magnetic nanocomposites, membranes, and carbon nanostructures, by way of example, have been developed. A very recent review of up-to-date methods aiming at facing oil spills using nanotechnology-based techniques (Kharisov et al. 2014) showed that nanomaterials have enormous potential to provide innovative solutions for oil spill cleanup because of their unique structure, superior properties, and outstanding performance. The nanotechnological remediation of oil spill, including nanocomposite sorbents and magnetic nanocomposites, is autonomic, quick, high effective, and with full oil recovery. Ultimately, only six of the seven abovementioned techniques could be taken into account: booms, skimmers, sorbents, dispersants, in situ burning, and magnetic nanocomposites. Advantages and disadvantages of these BATs are shown in Table 2.

Cost of the BATs

The cost of the techniques has been taken into account in listing the advantages and disadvantages of BATs. Oil spill response costs depend on numerous factors such as location, oil type, spill size, and cleanup strategy, making it difficult to develop a universal per-unit cost factor (Etkin 2001). No modeling method can ever accurately define or predict the costs of an oil spill. A lot of models have been developed, for example, the EPA Basic Oil Spill Cost Estimation Model (BOSCEM) and the Oil Spill Response Cost-Effectiveness

Fig. 1 Aim, main criterion, and alternative BATs for oil spill response

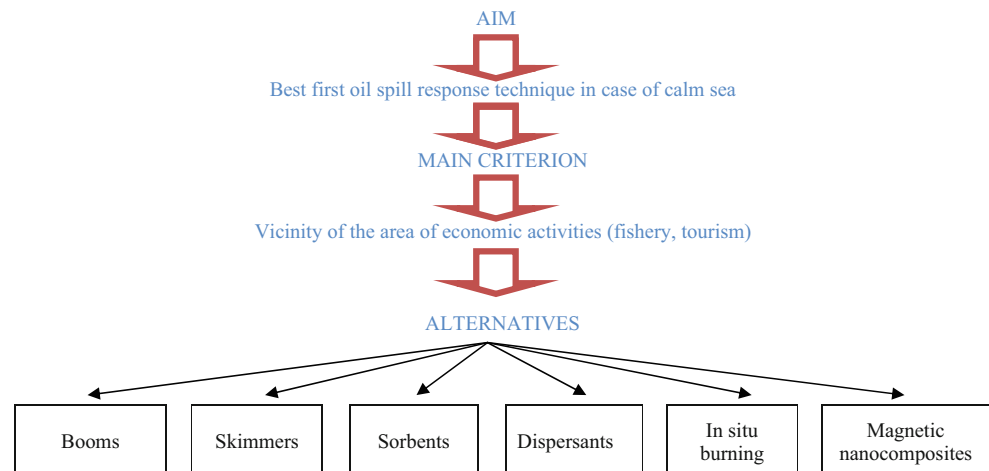


Table 3 Oil spill cleanup costs by primary cleanup methodology (2015 US \$)

Primary method	US \$/t
Mechanical	13,769.12
Dispersants	8070.37
In situ burning	4480.66

Analytical Tool (OSRCEAT). The first one was developed by Etkin for the US Environmental Protection Agency and provides a methodology for estimating oil spill costs, including response costs and environmental and socioeconomic damages for actual or hypothetical spills (Etkin 2004). The second one was developed to compare costs of response to benefits of response for hypothetical or actual oil spills (Etkin and Welch 2005). When an oil spill occurs near a potentially sensitive resource, the most cost-effective approach to a cleanup operation is to devote as much equipment and personnel into keeping oil away from the sensitive resource. As far as costs of the six BATs taken into account in this work are concerned, studies carried out by Etkin showed that cost factors are particularly affected by the use of dispersants. While costs vary broadly within each response technique category depending on logistical and other factors, oil spill responses involving dispersants only, or dispersants as the primary response technique are less expensive than those involving a variety of techniques. The cost reduction can be attributed to the lower labour costs (fewer personnel for a shorter period of time) and even lesser overall equipment costs that are required with dispersant application compared to mechanical containment and recovery operations (Etkin 2000). This trend is influenced by the fact that an offshore oil spill, which is treatable by dispersants only or by dispersants with minimal backup of manual and other methods, is generally less complicated to cleanup than one which occurs near shore. Etkin analyzed the cost data on over 200 spill cases that occurred outside the USA and summarized it in a table where costs are calculated in 1999 US \$. Authors adapted these values to 2015 US \$, taking into account the latest US government CPI (Consumer Price Index) data to adjust for inflation and calculate the cumulative inflation rate through July 2015 (Table 3).

Mechanical methods (including booms, skimmers, and sorbents) have been evaluated as the most expensive, followed

Table 4 Ranking of the methodologies according to their cost (adapted from Dave and Ghaly 2011)

Method	Score
Booms	7
Skimmers	7
Sorbents	8
Dispersants	8
In situ burning	10

Table 5 Semantic scale of Saaty

Value	Definition
1	Equal importance
3	Moderate importance
5	Strong importance
7	Very strong importance
9	Extreme importance
2,4,6,8	Intermediate values

by dispersant and in situ burning. Dave and Ghaly (2011) made a comparative analysis of oil spill response techniques taking into account ten evaluation criteria, one of which was cost. They gave the definition of the criteria and assigned a score to each of them on the basis of the advantages and disadvantages of these methods as they are related to criteria. As far as the criterion “cost” is concerned, the definition was “relatively inexpensive” and the highest score was 15, corresponding to the less expensive, that is, the higher the score, the lower the cost. The highest score (corresponding to the less expensive technique) was assigned to “in situ burning”, followed by dispersants and sorbents, while the most expensive techniques were the mechanical ones, booms, and skimmers (Table 4). These findings are in agreement with Etkin’s ones.

It was very difficult to find data about the cost of magnetic nanocomposites. Nicolaides et al. (1998) claim that CleanMag is 20–30 % cheaper than conventional methods. On the other hand, data were found on the cost of the following nanomaterials, mainly based on carbon nanotubes and graphene:

- Thermally reduced graphene (TRG) is priced at 20–30 \$/kg (Chen (2015));
- Multiwall carbon nanotubes (MWCNT) are priced at 100–150\$/kg, without logistics, and expected to reduce to 10–20\$/kg in the near future (Mahajan 2011). Chen (2015) for this material reports a decidedly higher cost of around 300\$/kg.

Iqbal and Abdala (2013) reported that 1 g of TRG removes approximately 300 g of crude oil, thereby leading to a cost in the range 67–100\$/t without logistics. It needs about 10–15 kg of MWCNT for a ton of oil spill (Mahajan 2011), thereby leading to a cost in the range 1000–2250\$/t. This cost would be in the range 3000–4500\$/t if we take into account

Table 6 Average consistencies of random matrices (RI values)

	1	2	3	4	5	6	7	8	9	10
RI	0.00	0.00	0.52	0.89	1.11	1.25	1.35	1.40	1.45	1.49

Table 7 Comparison matrix

	Booms	Skimmers	Sorbents	Dispersants	In situ burning	Magnetic nanocomposites
Booms	1	0.68	0.18	4.75	3.83	0.21
Skimmers	2.24	1	0.24	5.32	4.52	0.31
Sorbents	5.21	4.32	1	6.93	7.04	0.88
Dispersants	0.24	0.21	0.15	1	1.54	0.14
In situ burning	0.22	0.18	0.14	1.14	1	0.11
Magnetic nanocomposites	5.45	3.45	1.54	7.83	7.36	1
Total	14.36	9.84	3.25	26.97	25.29	2.65

the higher cost of Chen (2015). The price of MWCNT is expected to decrease to about 10–20\$/kg in a few years, and therefore, these materials could become commercially feasible solutions for oil spill cleanup in the next future (Mahajan 2011).

Analytic hierarchy process method

BATs accomplishing main and technical criteria should also satisfy impact criteria. Guidi et al. (2009) evaluated the relative importance of impact criteria according to AHP method, a well-known mathematical technique for prioritizing and ranking alternatives (Saaty 1980). This method has been developed by Thomas Saaty in the 1970s, at the University of Pittsburgh in Pennsylvania; it is regarded as one of the most successful techniques to solve decision-making problems involving multiple criteria (Saaty 1987). It has incomparable advantages when important elements of the decision are difficult to quantify or compare or when communication among team members is hindered by their different specializations, terminologies, or perspectives. AHP is a theory of measurement through pair-wise comparisons and relies on the judgments of experts to derive priority scales. The comparisons are made using a scale of absolute judgments that represents, how much more, one element dominates another with respect to a given attribute (Saaty 2008). This method has been widely used in many and various contexts to make decisions. The core of Saaty's method is an ordinal pair-wise comparison of all criteria. In other words, it addresses in particular preference

statements and allows to convert the qualitative judgments into numerical values. Per pair of criteria, the decision maker is asked to which degree a criterion is of more importance than the other. By means of these comparisons, the method defines the relative position of one criterion in relation to all other criteria. By using an eigenvalue matrix technique, quantitative weights can be assigned to the criteria. The Saaty method employs a semantic 9-point scale (Table 5) for the assignment of priority values. This scale relates numbers to judgements, which express the possible results of the comparison in qualitative terms. In this way, different elements can be weighted with a homogeneous measurement scale.

Through this method, the weight assigned to each single criterion reflects the importance which every party involved in the project attaches to the objectives. Moreover, the method verifies the fit between the components of the weight vector and the original judgements. From the pair-wise comparison, a “comparison matrix” is derived out of which, through the eigenvector approach, it is possible to calculate the weight vector to be used for a subsequent evaluation and investigation. Finally, the method is able to check the consistency of the matrix through the calculation of the eigenvalues. AHP allows inconsistency, but provides a measure of the inconsistency in each set of judgements. The consistency of the judgemental matrix can be determined by a measure called the consistency ratio (CR) defined as:

$$CR = \frac{CI}{RI} \quad (1)$$

where CI is the consistency index and RI the random index. Saaty provided average consistencies (RI values) of randomly generated matrices (Table 6) (Saaty 1980).

Table 8 Geometric mean, weight, and K eigenvalues

	Geometric mean	Weight	K eigenvalues
Booms	0.88	0.09	1.35
Skimmers	1.26	0.13	1.32
Sorbents	3.14	0.34	1.09
Dispersants	0.34	0.04	0.99
In situ burning	0.30	0.03	0.80
Magnetic nanocomposites	3.44	0.37	0.97
Total	9.37	1.00	6.53

Table 9 Index values

No. of components	Consistency index	RI	CR
6	0.11	1.25	0.085

Normally, a consistency ratio of 0.1 or less is considered acceptable. If the value is higher, the judgment may not be reliable and should be elicited again.

Results and discussion

A group of 15 experts with different specializations (applied physics, architecture, biology, chemical engineering, environmental engineering, mechanical engineering, nuclear engineering, geology, maritime studies) evaluated the six alternatives techniques by means of AHP method. The experts were informed about the aim of investigation (to choose the best technique for oil spill response in the Mediterranean Sea in calm sea conditions) as well as the notes about excluded and included alternatives. The experts were also given Table 2, summarizing the main advantages and disadvantages of the aforementioned techniques. Using Saaty's scale, they compared pair-wise each alternative to the others giving numerical advantage to the technique for which they thought it was better under the assigned criterion: presence of economic activities in the area affected by oil spill. The priorities expressed by experts have been combined using the arithmetic mean. The results are shown in Tables 7 and 8.

Each weight value is obtained by dividing the geometric mean of each line by the local sum of the geometric means. K eigenvalues are deduced by multiplying each weight, calculated for each technique, by the corresponding total: for example, the first K eigenvalue is obtained by multiplying the weight 0.09 by 14.36. The value does not seem to match exactly only because the weight value has been rounded to two decimal places.

Once the K eigenvalues are known, it was possible to define the consistency index (CI):

$$CI = \frac{K_{\text{tot}} - n}{n - 1} \quad (2)$$

where n is the number of components (Table 9). The consistency ratio (CR) is calculated by the ratio of the consistency index to the random consistency index (RI). RI is the random index representing the consistency of a randomly generated pair-wise comparison matrix. It is derived as average random consistency index calculated from a sample of 500 randomly generated matrices based on the AHP scale. In our case (six components), RI has 1.25 value.

It is interesting to note that the consistency ratio is <0.1 , so the pair-wise comparison matrix should be regarded as consistent enough. The expert group gave the highest weight to the magnetic nanocomposites (0.37), followed by sorbents (0.34), skimmers (0.13), and booms (0.09). In situ burning was judged to be the worst technique (0.03) followed by dispersants (0.04).

Conclusions

Despite the number of techniques available for oil spill clean-up, when the accident occurs, the selection of the best available one, under given circumstances, is still not easy. AHP is an extremely widespread and useful method on such occasions. In this work, AHP method was applied in order to select the best available technique for oil spill response in the Mediterranean Sea under well-defined circumstances: calm sea and presence of economic activities in the area affected by oil spill. Experts with different specializations, after being informed about advantages and disadvantages of the aforementioned BATs, were asked to choose the best technique between these ones: booms, skimmers, sorbents, dispersants, in situ burning, and magnetic nanocomposites. All of these techniques could be used under the condition "calm sea". The closeness of the area of economic activities was the criterion affecting their choice. Findings from the use of AHP method highlighted the preference given by the experts to magnetic nanocomposites and to sorbents, followed by skimmers and booms, while in situ burning and dispersants were deemed the less suitable techniques under the above defined circumstances. In the light of the fact that the value of the consistency ratio is 0.085 (<0.1), the pair-wise comparison matrix can be regarded as consistent enough. This work aims at providing a helpful, user friendly, and quick tool also to competent authorities in charge of facing the response to oil spills in the Mediterranean Sea. In a further development, AHP method could be applied in order to choose the best available technique under different circumstances, for example, selecting other impact criteria.

References

- ARLEM (2013), Work programme, <http://cor.europa.eu/en/activities/arlem/Documents/2013work-programme-en.pdf>
- Atlas RM, Hazen TC (2011) Oil biodegradation and bioremediation: a tale of the two worst spills in U.S. history. *Environ Sci Technol* 45: 6709–6715
- Bush S (2014) A new technology to cleaning oil spills with magnet, <http://www.renewableenergyworld.com/rea/blog/post/print/2014/01/a-new-technology-to-cleaning-oil-spills-with-magnets/>
- Calcagnile P, Fragouli D, Bayer IS, Anyfantis GC, Martiradonna L, Cozzoli PD, Cingolani R, Athanassiou A (2012) Magnetically driven floating foams for the removal of oil contaminants from water. *ACS Nano* 26:5413–5419
- Chen Y (ed) (2015) Nanotubes and nanosheets: functionalization and applications of boron nitride and other nanomaterials. CRC Press - Taylor & Francis Group, Boca Raton, USA
- Cumo F, Gugliermetti F, Guidi G (2007) Best available techniques for oil spill containment and cleanup in the Mediterranean Sea. *WIT Trans Ecol Environ* 103:527–535. doi:10.2495/WRM070491

- Das N, Chandran P (2011) Microbial degradation of petroleum hydrocarbon contaminants: an overview. *Biotechnology Research International*, Article ID 941810. doi: [10.4061/2011/941810](https://doi.org/10.4061/2011/941810)
- Dave D, Ghaly AE (2011) Remediation technologies for marine oil spills: a critical review and comparative analysis. *Am J Environ Sci* 7:423–440
- Davidson WF, Lee K, Cogswell A (eds) (2008) *Oil spill response: a global perspective*. Springer, Dordrecht, The Netherlands
- Etkin DS (2000) Worldwide analysis of marine oil spill cleanup cost factors. In: *Proceedings of the 23rd Arctic and marine oil spill program technical seminar*, Ottawa, Canada, 14–16 June, p. 161–174
- Etkin DS (2001) Comparative methodologies for estimating on-water response costs for marine oil spills. In: *Proceedings of the 2001 International Oil Spill Conference*, Tampa, USA, 26–29 March, p. 1281–1289
- Etkin DS (2004) Modeling oil spill response and damage costs. In: *Proceedings of the 5th Biennial Freshwater Spills Symposium*, St. Louis, USA, April 6–8
- Etkin DS, Welch J (2005) Development of an oil spill response cost-effectiveness analytical tool. In: *Proceedings of the 28th Arctic and Marine Oilspill Program Technical Seminar*, Ottawa, Canada, 7–9 June, p. 889–922
- Guidi G, Gugliemetti F, Violante AC (2009) Proposed criteria to select best available techniques (BATs) for oil spill response. *Chem Eng Trans* 17:367–372. doi:[10.3303/CET0917062](https://doi.org/10.3303/CET0917062)
- Holakoo L, Mulligan CN (2002) On the capability of rhamnolipids for oil spill control of surface water. In: *Proceedings of the Annual Conference of the Canadian Society for Civil Engineering*, Montreal, Canada, 5–8 June
- International Maritime Organization (2004) *Bioremediation in marine oil spills*. IMO, London, UK
- International Tanker Owner Pollution Federation Limited (2011) Use of dispersants to treat oil spills. Technical Information Paper, <http://www.itopf.com/tip4.pdf>
- Iqbal MZ, Abdala AA (2013) Oil spill cleanup using graphene. *Environ Sci Pollut Res* 20:3271–3279
- Kharisov BI, Rasika Dias HV, Kharisova OV (2014) Nanotechnology-based remediation of petroleum impurities from water. *J Petrol Sci Eng* 122:705–718
- Khushrushahi S, Zahn M, Hatton TA (2013) Magnetic separation method for oil spill cleanup. *Magneto hydrodynamics* 49:546–551
- Macaulay BM, Rees D (2014) Bioremediation of oil spills: a review of challenges for research advancement. *Ann Environ Sci* 8:9–37
- Mahajan YR (2011) Nanotechnology-based solutions for oil spills. *Nanotechnol Insights* 2(1):1–19
- MARPOL (1973/1978) International Convention for the prevention of pollution from ships
- McCall BD, Pennings SC (2012) Disturbance and recovery of salt marsh arthropod communities following BP deepwater horizon oil spill. *PLoS One* 7(3):e32735. doi:[10.1371/journal.pone.0032735](https://doi.org/10.1371/journal.pone.0032735)
- MEMAC Fact Sheet, 2015, Application of dispersants in the ROPME sea area, circular, approved dispersant and application, Bahrain, www.memac-rsa.org
- Nicolaidis GK, Skountzos P, Atanassova Y, Koutroumbas K (1998) CLEANMAG®: the magnetic cleanup of waterborne oil spills—a new approach in the battle of oil spill cleanups. In: *EUROMAT'98, Conference of the Portuguese-European Material Society on Materials in Oceanic Environment*, Lisbon, 22–24 July, vol. 1, p. 709–717
- RAOP MED Project (2014) <http://www.raop.eu/index.php/the-project/project-background>
- Saaty RW (1987) The analytic hierarchy process—what it is and how it is used. *Math Mod* 9:161–176
- Saaty TL (1980) *The analytic hierarchy process—planning. Priority Setting, Resource Allocation*, McGraw-Hill Inc., New York
- Saaty TL (2008) Decision making with the analytic hierarchy process. *Int J Serv Sci* 1:83–98
- U.S. Environmental Protection Agency (1999) Understanding oil spills and oil spill response, <http://www.hsdl.org/?view&did=25688>
- Zahed MA, Aziz HA, Isa MH, Mohajeri L, Mohajeri S (2010) Optimal conditions for bioremediation of oily seawater. *Bioresource Technol* 101:9455–9460
- Zhu Q, Tao F, Pan Q (2010) Fast and selective removal of oils from water surface via highly hydrophobic core-shell Fe₂O₃@C nanoparticles under magnetic field. *ACS Appl Mater Interfaces* 2:3141–3146
- Zhu X, Venosa AD, Suidan MT, Lee K (2001) Guidelines for the bioremediation of marine shorelines and freshwater wetlands. U.S. Environmental Protection Agency, Cincinnati, USA