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## **THE BEHAVIOUR AND EFFECTS OF OIL POLLUTION INTO MARINE ENVIRONMENT AND OCEANS**

### ***POSTUPAK I POSLJEDICE U SLUČAJU ONEČIŠĆENJA MORSKOG OKOLIŠA I OCEANA NAFTOM***

#### **SUMMARY**

*The main purpose of this paper is to analyse the latest developments in connection to the management of oil spills at sea. In this function, some of the most important elements such as behaviour, fate and effects that oil spills undergo when introduced into the marine environment, the possible impact that oil pollution may have on wild life and environment as well as the implications that oil weathering process has toward clean-up operation are discussed in his paper. In order to reveal the most substantial information regarding this issue some of the prestigious authors and organizations that deal with oil pollution at sea such as Brown, Parker, IPIECA and so forth are used in this paper. The authors are overall of the opinion that indeed the oil spills can heavily harm the marine environment and wild life and that the weathering process of oil may impact positively or negatively the clean-up operations.*

**Key words:** oil pollution, oil spills, marine environment, oil weathering process, oil clean-up, marine pollution

#### **SAŽETAK**

*U radu se analiziraju najnovija dostignuća vezana uz postupke koji se obavljaju prilikom izlivanja nafte u more. U tom su smislu razmatrana neka od najvažnijih elemenata kao što su postupak u slučaju uništenja morskog okoliša i živih organizama, a koja predstavljaju posljedicu za morski okoliš u slučaju izlivanja nafte, mogući utjecaj koji onečišćenje naftom može imati na okoliš i živa bića, kao i kako djeluje proces raspadanja i isparavanja nafte na postupak čišćenja od zagađenja naftom. Kako bi se objelodanile najnovije informacije iz toga područja, u radu su prikazana postignuća nekih od najvažnijih autora i institucija koji se bave onečišćenjem naftom. Svi su autori jednoglasni u mišljenju da izlivanje nafte može zaista jako oštetiti morski okoliš i žive organizme, te da proces raspadanja i isparavanja nafte može i na pozitivan i na negativan način djelovati na postupke skupljanja nafte.*

**Ključne riječi:** onečišćenje naftom, izlivanje nafte, morski okoliš, proces raspadanja i isparavanja nafte, postupak čišćenja od zagađenja naftom, onečišćenje morskog okoliša

## 1. INTRODUCTION

The marine environment is a key interrelated and complementary element, crucial for the existence of the biodiversity, ecosystem and human life on the planet. As such, the prevention and management of the oil spill effects towards the coasts and oceans are of a great significance. In this context, it is also paramount a comprehensive understanding and analyses of the weathering process of oil at sea and its related processes. Many studies have been carried out in order to clarify these important issues, but still, in the opinion of the authors, these issues need to be further studied and analysed in order to cope with the recent marine and technological developments.

In light of these considerations, this paper will seek to answer questions such as: what are the impacts of the oil spills at sea? What are the main processes influencing the weathering of oil? And how may the weathering process implicate clean-up operations? Therefore, the main effects of the oils spilled at sea will first be considered in this paper. Secondly, the physical, chemical, and biological processes affecting the behaviour and fate of oil spill at sea will be discussed. Finally, a brief analysis as to the implication of the weathering process in clean-up operations will conclude the paper.

## 2. THE EFFECTS OF MARINE OIL SPILLS

There are a number of factors which determine the precise nature and duration of a possible impact of an oil spill in a marine environment. The most significant factors are the category and quantity of oil and its behaviour once spilled; the physical features of the affected region, weather conditions and season; the nature and the efficiency of the clean-up operation, the biological and economical characteristics of the area and their vulnerability to oil pollution (ITOPF, 2002). Oil pollution may severely impact the ecosystem and the biodiversity of the ocean and coastal areas resulting thus in possible danger to the wild life and the human health. The most significant effects of oil spill in marine environment are as follows:

The principal effect of the oil spill is on marine environment within which the **seabed ecology** occupies a significant role. In this respect,

the **macro-fauna** such as the case of benthic fauna in offshore sediments are detritivores, feeding on organic particles either suspended in the water or deposited on the seabed and thus they are very sensitive to contaminants attached to particles which subsequently make it good indicators of the biological conditions of sediments (Ritchie, 1994 - Braer Environmental Impact). **Coral reefs** are also susceptible to oil spills because oil compounds can dissolve in water which exposes the corals to potentially toxic compounds (IPIECA, 2000).

**Fish and shellfish** can be severely affected by oil pollution and this can occur in three ways: a) direct lethal or sub-lethal effect on fish itself; b) direct effect on fisheries, and c) indirect effect via ecosystem disturbance (IPIECA 2000). The impact of an oil spill on marine life depends heavily on the physical and chemical characteristics of the particular oil and on the weathering process (ITOPF, 2002). Generally, the toxic effect of oil on marine life depends on the duration of exposure and oil concentration in the environment. Adult fish, squid, shrimps, wild stocks of important marine animals and plants seldom suffer long-term damage from oil spill exposure. The great impact is likely to be found on shorelines where animals and plants may be physically coated and smothered by oil or exposed directly to toxic components in the oil (ITOPF, 2002). Shellfish are more vulnerable than fish to the oil spills because of their close association with contaminated sediments and this goes also for captive fish. In addition, water column organisms such as **plankton** may be seriously impacted by oil pollution. Laboratory studies have revealed toxic and sub-lethal effects on the plankton (ITOPF, 2002).

**Sea and shore birds** such as shags, fulmars, kittiwakes, razorbills and guillemots are generally the group of birds mostly at risk from oil spills since they are easily harmed by floating water. Moreover, birds that submerge for their food or which gather on the sea surface are especially at peril. The most common cause of contaminated bird's death is from drowning, starvation and loss of body heat, and it must be noted that great mortality occurs during most spills which sometimes have even caused the entire breeding colonies to be seriously depleted (ITOPF, 2002). The effect on seabird supply such as *Ammodytes marinus* observed in Braer accident can also increase the mortality of birds (Ritchie, 1994).

With respect to **sea mammals**, the whales, dolphins and seals in the open sea do not appear to be particularly threatened from oil spill. However, marine mammals such as seal and otters that breed on shorelines are more prone to be affected by the oil pollution. The most endangered mammal species are those which rely on fur to regulate their body temperature because if the fur becomes contaminated with oil, the mammal may die from hyperthermia or overheating (ITOPF, 2002). In the Braer pollution the otters were the most affected animals in comparison with other mammals such as seals (Ritchie, 1994 - Braer Environmental Impact).

**Shorelines** are also vulnerable to the oil pollution and a study of the US Coast Guard has revealed that exposed rocky cliffs and seawalls, wave cut rocky platforms, fine to medium-grained sand beaches, coarse-grained sand beaches, mixed sand and gravel beaches, gravel beaches/riprap exposed tidal flats, sheltered rocky shores/man-made structures, sheltered tidal flats, and marshes may be susceptible to oil spills (U.S. Environmental Protection Agency Oil Program: Oil Learning center, 2008). On Braer accident the rocky shores were most heavily damaged from the oil spill and these was evident from the mortality *Patella vulgate* population and barnacle *Semibalanus* in shores near the wreck (Ritchie, 1994). Nevertheless, it appears that there is no long-term impact on rocky shores because the oil cannot be retained in large quantities and because most rocky shores species have considerable potential for re-establishing population (IPIECA, 2000)

**Air and fresh water** can be also among the effects caused by an oil spill which can seriously impact the **human health**. In the *Braer* case the oil spill had unexpected effects such as significant atmospheric pollution and subsequent contamination of inland waters, and the fresh water system (Ritchie, 1994). With regard to human health when individuals are exposed to oil pollution components of the oil such as polycyclic aromatic hydrocarbons (PAH), may be harmful because these elements are identified as carcinogens to humans (Clark, R.B, 2001,p.91). Even the contamination of supply food chain (fish) may have sometimes an impact on human health. In addition, oil spill can cause coughing, difficulties in breathing and nasal obstruction. (Olive Press, OP, 2007). **So-**

**ils, vegetation, grazing and mangroves** can also be affected from the oil pollution but these will also depend on weather conditions, physical characteristics of oil, amount of oil spilled and so forth.

### 3. PHYSICAL, CHEMICAL AND BIOLOGICAL PROCESSES INFLUENCING THE WEATHERING OF OIL

The physical and chemical changes that spilled oil undergoes when introduced into the marine environment are collectively known as weathering (Oceans Study Board at al, 2003). Although the individual processes causing these changes may act simultaneously, their relative importance varies with time and oil type (Christiansen, 2003). Rates at which these changes occur depend upon the amount of oil spilled, oil type and its properties such as gravity, distillation characteristics, viscosity and pour point, as well as the prevailing weather conditions and whether the oil remains at sea or is washed ashore (Butt, Duckworth & Perry, 1986). Following an event of oil spill into the marine environment, the weathering process begins immediately to transform the materials into substances with physical and chemical characteristics that differ from the original source material (Oceans Study Board at al, 2003). The spreading, evaporation and emulsification, dispersion and dissolution processes are most important during the early stage of a spill - whilst photo-oxidation, sedimentation and biodegradation are more important later; but all together these processes affect the behaviour of the oil and determine its final fate (Prof. Linden, 2008). Ultimately, the marine environment assimilates spilled oil through the long-term process of biodegradation (ITOPF, 2002).

When different kinds of oil enter into the sea, many physical, chemical and biological degradation processes commence acting on them. These processes change the property and the behaviour of the oil. **Spreading** is the first observable physical process that occurs when oil is spilled over the sea surface, and the speed in which this process takes place depends to a great extent on the viscosity of the oil and the amount spilled (Global Marine Oil Pollution Information Gateway, 2007). This process is

described as the action whereby, on deposition, oil spreads out to form a thin, ultimately monomolecular layer on the surface of calm waters (Robotham & Gill, 1989 p 44, at Green & Trett). Fluid, low viscosity oil spread more quickly than those with the high viscosity (ITOPF, 2002). Nevertheless, several authors have argued that the viscosity of the water is also an important driving mechanism in spreading process (Oceans Study Board at al, 2003). The rate at which oil spreads is also affected by tidal streams and currents as well as by the temperature of the water and wind speeds- the stronger the combined forces the faster the process, and in this regards, there are examples of spills spreading over several square kilometres in just a few hours (ITOPF, 2002). However, it must be noted that the spreading is rarely uniform and large variations in the thickness of the oil are typical (GMOPIG, 2007). Consequently, spreading assists all the processes of weathering, and natural dissipation is rapid once the oil has thinned to a silvery sheen (Butt, Duckworth & Perry, 1986).

The most significant initial weathering process for oil pills on the sea in terms of mass balance is **evaporation** (Oceans Study Board at al, 2003). This physical process involves the loss of the more volatile components of the oil mixture; estimates suggest that all n-< C15 compounds have evaporated in 10 days with slower rate for n-C15-C25 (Robotham & Gill, 1989, p 50). Under moderate conditions components with carbon numbers up to C10 are lost within 8 hours, while compounds boiling above 250 Degrees Celsius are lost over a week (Butt, Duckworth & Perry, 1986, p 17). In general terms, within a few days following a spill, light crude oil can lose up to 75% of its initial volume (Oceans Study Board at al, 2003). Nonetheless, the amount of evaporation and the rate at which it occurs depends mainly upon the volatile of the oil (GMOPIG, 2007), as well as from the ambient temperature, sea state and wind speed (ITOPF, 2002). Other factors influencing the evaporation of the oil may be the solar radiation, physical properties of the oil and wave action (Robotham & Gill, 1989). Crude oil products such as petrol, kerosene and diesel tend to evaporate completely within few days, and the evaporation process may increase on rough seas and high temperatures (GMOPIG, 2007). Because oil is a mixture of hundreds of compounds, and this mixture varies from source to so-

urce and overtime, the evaporation of oil is a particular difficult process to be studied and little work has been done in this respect (Fingas, 1995).

**Emulsification** is the term used for the formation of water in oil emulsions, which frequently results in the formation of mouse (Robotham & Gill, 1989). Emulsification is a physical process and is formed when two liquids combine, with one ending up suspended in the other; a physical mixture which is caused mainly by the turbulence at the sea surface (GMOPIG, 2007). These emulsions significantly change the properties and characteristics of spilled oil (Oceans Study Board at al, 2003). There are two types of emulsions: water-in-oil or as otherwise called 'chocolate mousse'; and oil-in-water which is a lighter mixture (GMOPIG, 2007). The formation of the emulsions may occur during the first 8 hours after the spillage, but normally the rate and extend to which these process take place depends upon the type of the oil involved and the sea state prevailing (Butt, Duckworth & Perry, 1986). Normally, the emulsification process occurs rapidly in sea states greater than Beaufort Force 3 involving wind speed 7-10 knots (ITOPF, 2002). The formation of these emulsions causes the volume of pollutant to increase between 3-4 times (GMOPIG, 2007) and the evaporation process slows spreading by orders of magnitude, which eventually causes the oil rides (Oceans Study Board at al, 2003). The emulsion formation affects evaporation, degradation, and dissolution.

**Dispersion** is also a significant physical process associated with the destruction of an oil spill and begins almost as soon as the spill occurs (Robotham & Gill, 1989). Waves and turbulence at the sea surface can cause all or part of a slick to break up into droplets a varying size which become mixed into the upper layers of the water column (ITOPF, 2002). The primary dispersions are unstable and separate easily by gravity alone, and in this case the average droplet size is normally taken as being larger than about 50  $\mu\text{m}$  (Parker & Pitt, 1987). On the other hand the secondary dispersions pose a severe separation problem since they do not separate by gravity, and the rates at which these very small droplets float to the surface are extremely low (Parker & Pitt, 1987). The increased surface area presented by dispersed oil can promote processes such as biodegradation,



dissolution and sedimentation (GMOPIG, 2007). The rate of dispersion is largely dependant upon the nature of the oil and the sea state, proceeding most rapidly with low viscosity oils in the presence of breaking waves (ITOPF, 2002). It must be noted that the biodegradation and chemo-degradation may also increase owing to increase dispersal (Green & Trett, 1989). Furthermore, the dispersal and disruption of oil particles and droplets are also calculated to increase weathering rates.

Another process which influences the weather of the oil is the dissolution which is the chemical stabilization of oil components in water. **Dissolution** accounts for only a small portion of oil loss but it appears that it is still considered an important behaviour parameter because the soluble components of oil, particularly the smaller aromatic compounds, are more toxic to aquatic species than the aliphatic components (Oceans Study Board at al, 2003). The rate and extend to which an oil dissolves depends upon its composition, spreading, water temperature, turbulence and degree of dispersion (ITOPF, 2002). Some components of oil such as Benzene, Toluene, Ethyl-benzene, P-xylene and Naphthalene are slightly soluble, whereas other heavy components of crude oil are virtually insoluble (Oceans Study Board at al, 2003). The most soluble components are volatile, low molecular weight hydrocarbons which can evaporate at rates of up to 100 times faster than they dissolve (Parker & Pitt, 1987). In practice, levels of dissolved hydrocarbons rarely exceed 1mg/litter in the sea water (Parker & Pitt, 1987, p. 187)

**Photo-oxidation** is a family of light-catalyzed reactions that oxidize the reduced carbon in petroleum hydrocarbons (Oceans Study Board at al, 2003). Photo-oxidation takes place at the sea surface and occurs most rapidly when the oil is spread as a thin film. This process is promoted by the sun light and its overall effect on dissipation appears to be minor compared to that of other weathering processes (ITOPF, 2002). Although the precise mechanism of photo-oxidation is not well understood its effect may result in the loss of about 1% of the oil volume per day (Butt, Duckworth & Perry, 1986). Other studies however have revealed that even under intense sunlight, thin oil film breaks down less than 0.1% per day (ITOPF, 2002). In comparison with the photo-oxidation of a variety of oils it was found that diesel oil was degraded fa-

stest, followed by synthetic coal oil and no degradation of crude oil could be detected (Robotham & Gill, 1989, p 73). The necessary ingredients for photo-oxidation are radiation and light absorbing molecules (chromophores), and because few petroleum hydrocarbons absorb sunlight efficiently, most photo-oxidation occurs via photo-reactions (Oceans Study Board at al, 2003).

**Sedimentation** occurs as a result of a number of processes which increase the specific gravity of the oil above that of the supportive water (Robotham & Gill, 1989). The adhesion of small amounts of dense particles to the large surface area can cause sedimentation. Evaporation and dissolution of low molecular weight hydrocarbons brings about an increase in the oil specific gravity and enhances sinking to the sediments where it will undergo a predominantly bio-degradative process provided that suitable dissolved oxygen and nutrient levels exist (Robotham & Gill, 1989). Most of the oil spilled will eventually enter the sediments and will degrade within them. Shallow waters are often laden with suspended solids providing favourable conditions for sedimentation. Oil stranded on sandy shores often mixes with sand and other sediments and when is washed off the beach into the sea and will eventually sink (Oceans Study Board at al, 2003)

Except from the physical and chemical processes that influence the weathering of the oil at sea, the **biodegradation** is another element which plays an essential role in this development. In this respect, the micro-organisms that are found in the sea water such as fungus, bacteria, algal genus and yeasts can attack the oil deposited on the surface as a substrate for growth converting it subsequently to microbial cells, carbon dioxide and water (Brown, 1989). The same other maintains that there are more than 100 species of micro-organisms that assist the biodegradation of oil which takes place at the oil-water interface since no oxygen is available within the oil itself. Shales (1989) argue that the micro-organisms are capable of degrading both the aliphatic and the aromatic hydrocarbons fractions in oil. It is important to note that from the various types of microbes that live at sea each one of them tends to degrade a particular group of compounds in crude oil. Heavy aromatics and asphaltenes may degrade very slowly whereas other compounds in oil can re-

sist this sort of attacks and escape degradation (ITOPF, 2002). The main factors affecting the efficiency of biodegradation are the levels of nutrients such as nitrogen and phosphorus in the water, salinity, as well as the temperature, the level of oxygen present and the physical properties of oil (Prof. Linden, 2008).

#### **4. THE IMPLICATIONS OF THE WEATHERING PROCESS TOWARDS OIL CLEAN-UP OPERATIONS**

The spreading process and fragmentation of the oil at, caused mainly by rough sea conditions, may place constraints on the efficiency of any response, and it may render the clean-up operation very difficult to carry out. Particularly, in low viscosity oil cases, which may spread just in few hours, the clean-up operation may rarely succeed to remove more than a fraction of a widely spread slick (ITOPF, 2002). Another related issue is that the weathering process may cause oil to sink at the sea-bottom. This process will subsequently prevent the clean-up operation from removing all this quantity of oil which ends up polluting the seabed ecology.

In addition, the weathering process can alter liquid petroleum to semi-solid or solid state, resulting thus in a possible re-evaluation and modification of the entire strategy and techniques of the response planning in order to cope with the new situation. Thus, the dispersants utilized at sea become less effective as the oil spreads and its viscosity reaches the 5 000-10 000 cSt level, and most cease to work completely when the viscosity rises above these figures (ITOPF, 2002). The dispersant effectiveness should also be checked frequently due to the rapid reaction and speed of oil viscosity when it interfaces

with water which eventually will shorten the time available for applying efficiently the dispersant. Similarly, if collection methods are employed to remove oil from the marine environment, the type of pumps and skimmers used may need to be changed as the oil weathers and the viscosity rises (IPIECA, 2000).

#### **5. CONCLUSIONS**

As a result, the oil spills at sea may result in severe effects towards the marine environment, on biodiversities, ecosystems of the ocean, wild life, and human health. This paper has revealed that macro-fauna, coral reefs, fish, shellfish, plankton, sea and shore birds, sea mammals, shorelines, air, fresh water system, mangroves, and soil may be exposed and dramatically affected by oil pollution.

In addition, as it was previously explained in the paper, the most significant physical, chemical and biological processes that influence the weathering of oil and its impacts are evaporation, emulsification, dispersion, dissolution, photo-oxidation, sedimentation, and biodegradation. Depending from several external factors, these processes, individually or interrelated, may alter the conditions of oil spilled when it interfaces with sea water, causing as a result the weathering process.

Finally, the process of weathering apart from the positive effects in connection to the marine environment may negatively influence the clean-up operation. In this respect, the paper revealed that the spreading process, emulsification, and the sinking of oil may render the clean-up operation very difficult and sometimes almost impossible. Moreover, the techniques, strategies and equipment must continuously undergo through changes as the weathering process proceeds.

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