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REVIEW ARTICLE

The Toxicological Outcomes of Oil Spills and Oil Fires

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Summary
Oil may be a variety of materials, including crude oil, refined petroleum products or by-products, oily refuse or oil mixed in waste. With a high content of several organic compounds, oil may be the target of several terrorist attacks or may be spilt by accident. The term "oil spill" mainly refers to marine oil spills, where oil is released into the ocean or coastal waters. Oil spills must be taken into consideration seriously as sea organisms can either be poisoned by ingestion or can be affected by direct contact. On the other hand, oil well fires are oil gushers that have caught on fire and burn uncontrollably. These fires are more difficult to extinguish than regular fires due to the enormous fuel supply for the fire. Exposure to their dust and smoke can cause several short-term and long-term health effects as there comprise of several compounds like gases, acidic gases, polycyclic aromatic hydrocarbons, metals, volatile organic compounds and particulate matter. This review will mainly focus on oil spills, oil well fires and their environmental and health effects. Besides, measures to be taken are also covered by this contribution.

Key Words: *oil, oil spill, oil well fire, oil fire pollutants, health effects, environmental toxicity.*

Petrol Dökülmeleri ve Petrol Yangınlar

Özet
"Petrol", ham petrol, rafine petrol ürünleri veya yan ürünleri, petrol atıkları veya atıkların içindeki petrol gibi farklı anlamlara gelebilmektedir. Birçok organik bileşiği yüksek miktarda içerdiği için, petrol terörist saldırıların hedefi olabilir veya kazara dökülebilir. "Petrol dökülmesi" terimi çoğunlukla denize petrol dökülmesi anlamına gelmektedir, bu durumda genelde petrol okyanus ve kıyı sularına yayılır. Denizde yaşayan organizmaların petrolü yutmaları sonucu zehirlenebileceklerinden veya doğrudan temas ile maruz kalacaklarından petrol dökülmeleri dikkate alınmalıdır. Diğer taraftan, petrol kuyu yangınları alev almış olan ve kontrolsüzce yanan petrol kuyuları nedeniyle ortaya çıkar. Bu yangınların söndürülmesi, kuyularda inanılmaz bir yakıt kaynağı olduğu için normal yangınlardan çok daha zordur. Bu yangınlardan çıkan toz ve duman değişik gazlar, asidik gazlar, polisiklik aromatik hidrokarbonlar, metaller, uçucu organik bileşikler ve partiküle materyal içerdiği için birçok uzun dönem ve kısa dönem sağlık etkileri oluşturur. Bu derlemede petrol dökülmeleri ve petrol kuyu yangınlarının çevresel ve sağlık üzerine etkilerinden bahsedilecektir. Ayrıca, bunlara karşı alınması gereken önlemler anlatılacaktır.

Anahtar Kelimeler: *Petrol, petrol dökülmesi, petrol kuyu yangını, petrol yangın kirleticileri, sağlık etkileri, çevresel toksisite.*

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INTRODUCTION

Energy supply is vital for everyday life in the modern world. Supplying safe and reliable energy is the most important issue for the continuity of life for the nations and therefore, enabling the security of energy supplying plants, i.e. petroleum facilities, and safe transportation of petroleum and its' byproducts, must be at top priority.

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It is now evident that a new kind of warfare is taking place in the world. The conventional warfare and battlefields are left behind, in spite of the existence of various examples of unconventional warfare applications, particularly in the second half of the 20th century. Numerous chemical incidents have threatened civil populations and the environment in several parts of the world. While the contamination of public food or water supply with hazardous substances has been a readily and frequently used method of toxic war or terrorism over the centuries, threatening of military and public food and water resources, directly or indirectly is still possible at any time, therefore demands continuous and vigorous attention and protection (1).

Other than chemicals, oil with a high content of several organic compounds may be the target of several terrorist attacks or may be spilt by accident. In both cases, it will be causing serious series of problems with some of them still being unsolved. Evaluation of the potential and real threats for such companies that explore, produce, refine, transport (land and marine), distribute and market petroleum products has main importance in the prevention of future attacks. Since the infamous 9/11 events, measures to be taken in the petroleum industry have been changing dramatically. On the other hand, the world has experienced the largest offshore oil spill of U.S. The Deepwater Horizon oil spill, which started on April 20th, 2010 as a massive oil spill in the Gulf of Mexico. It is listed among the largest oil spills in the world with tens of millions of gallons spilled to date (2). However, American government could not prevent the spill entirely; only partial measures were taken for days. Later, the manufacturer company partially stopped the leak by capping the gushing wellhead, after it had released about 4.9 million barrels or 205.8 million gallons of crude oil. It was estimated that 53,000 barrels per day were escaping from the well just before it was capped (3).

Different kinds of strategies are changing according to the types of facilities and the threat that this facility could face. Risks cannot be totally prevented, but vulnerabilities can be assessed and the measures for the identification, analysis and reduction of such vulnerabilities can be suggested.

Oil Spills

An oil spill is the release of a liquid petroleum hydrocarbon into the environment due to human activity, and is a form of pollution of water. The term often refers to marine oil spills, where oil is released into the ocean or coastal waters. The oil may be a variety of materials, including crude oil, refined petroleum products (such as gasoline or diesel fuel) or by-products, ships' bunkers, oily refuse or oil mixed in waste. Spills take months or even years to clean up (4).

The Threat of Serious Accidents and Terrorist Attacks

The oil and gas industry should remain constantly alert against the threat of serious accidents and terrorist attacks (5). There are several reasons why oil is the target of terrorist attacks. Some of them are listed below:

i. The physical and chemical properties of oil and oil products have the potential to harm both lives and economy (6)
   - Pipelines are a traditional target for attack because they are difficult to protect and the effect of damage is immediate, i.e. cutting off supply of the product.
   - Oil well fires and oil refinery fires can cause serious health problems or fatalities if an attack / accident takes place. Attacks on personnel are often spontaneous and occur in places where expatriates gather or on transit roads where security is weak or non-existent.
   - Oil tankers can be a target for terrorist attacks and this can harm people and marine environment seriously.
   - Such an attack has long-term impacts and near-term effects on the world's economy.

ii. There is critical importance of the petroleum products, other than oil. Petroleum-based products are the major source of energy for industry and daily life. Petroleum is also the raw material for many chemical products such as fuel oil, gasoline, diesel, liquefied petroleum gas, lubricating oils, paraffin, kerosene, tar and asphalt plastics, paints, and cosmetics and these products have very important impacts on the world's economy. The transport of petroleum across the world is frequent, and the amounts of petroleum stocks in developed countries are enormous. Consequently, the potential for accidental oil spills or the ones caused by terrorist attacks, is significant, and the research on the fate of petroleum in a marine environment is important to evaluate the environmental threat of oil spills, and to develop biotechnology to cope with them (7).

There is no doubt that oil accidents or terrorist attacks on oil industry will cause a serious damage in the business world. The duration and the magnitude of overall effects are dependent on the flow of information and the public reaction to the event (8). Total recovery can take several months. Other than the short-term effects of the accident, long-term effects can cause serious problems both for the people and for the environment (9)

Oil Spill Accidents/Attacks

Only in 2000, there were 4000 accidents causing oil spills in seas worldwide. Oil spills caused by maritime transport of petroleum products are still an important source of ocean pollution, especially in main production areas and along major transport routes. The environmental and health impact of these spills is worsened by the inappropriate and inadequate environment and health impact assessment processes and policies. However, proper environmental and health impact assessment processes of petroleum drilling and transport projects is a major factor helping in the prediction and reduction of the health and environmental impacts of petroleum on the local environment (10). The major oil spills of the last 40 years are given in Table 1 (11-34).

The Gulf War oil spill is regarded as the worst oil spill in history, resulting from actions taken during the Gulf War in 1991 (11). It caused considerable damage to wildlife in the Persian Gulf. The biggest accident of all times is the Atlantic Empress spill in 1979 (12). The Exxon Valdez spill (1989), the

Table 1. Major Oil Spills of the Last Forty Years (11-34)

Spill/Tanker	Location	Date	Tons of crude oil spill
Atlantic Empress / Aegean Captain	Trinidad and Tobago	01979-01979	287,000
Exxon Valdez	Prince William Sound, Alaska, USA	1989	210,000
Gulf War oil spill	Kuwait	1991	136,000-205,000
Erika spill	Bay of Biscay, France	1999	15,000
Prestige spill	Galicia, Spain	2002	63,000
BP Exploration, Alaska (BPXA) spill (Prudhoe Bay oil spill)	Alaska North Pole, USA	2006	653
CITGO Refinery River Spill	Lake Charles, Louisiana, USA	2006	6,500
Jieh Coast Power Station Spill	Lebanon	2006	20,000
Guimaras Island, The Philippines Ship Oil Spill	Philippines	2006	172
South Korea Oil Spill	Daesan Port, Soth Korea	2007	10,800
New Orleans Oil Spill	New Orleans, Louisiana, USA	2008	8,800
West Cork Oil Spill	Southern Coast, Ireland	2009	300
Southeast Queensland Oil Spill	Queensland, Australia	2009	230
Lüderitz Oil Spill	Lüderitz, Namibia	2009	unknown
Full City Oil Spill	Langesund/Telemark, Norway	2009	200
Montara Oil Spill	Timor Sea, Western Australia	2009	4,000
Port Arthur Oil Spill	Port Arthur, Texas, USA	2010	1,500
Great Barrier Reef Oil Spill	Great Keppel Island, Australia	2010	3
MT Bunga Kelana 3 Tanker Collusion	Singapore Strait, Singapore	2010	2,000
Red Butte Creek Oil Spill	Salt Lake City, Utah, USA	2010	65
Deepwater Horizon oil spill	Gulf of Mexico near Mississippi River Delta, USA	2010	780

Erika spill (1999) and the Prestige spill (2002) have grabbed public attention and forced countries to take measures for such accidents (13-15). In 2005, nine oil spills happened because of Hurricane Katrina which affected the coasts of New Orleans, Louisiana (16).

In 2006, four major oil spills happened: BP Exploration, Alaska (BPXA) spill, CITGO Refinery on the Calcasieu River Spill, Jieh Coast Power Station Spill and Guimaras Island, The Philippines Ship Oil Spill (17-20).

Most Recent Oil Spills

Five big oil spills happened in 2009 (The West Cork Oil Spill, Southeast Queensland Oil Spill, Lüderitz Oil Spill, the Full City Oil Spill, the Montara Oil Spill). Furthermore, another five big oil spills happened in 2010 (Port Arthur Oil Spill, the Great Barrier Reef Oil Spill, MT Bunga Kelana 3 Tanker Collusion, the Red Butte Creek Oil and Deepwater Horizon oil spill) (27-34).

Ongoing Oil Spills

An oil platform by Taylor Energy Wells was destroyed by Hurricane Ivan in 2004, resulting in leaks from 26 wells near Louisiana. Oil spill started at September, 2004 and is still ongoing for more than 2500 days. 0.03-0.05 tones of oil per day are being released into the ocean (35).

Deepwater Horizon oil spill (also referred to as the BP oil spill or the Gulf of Mexico oil spill) is one of the most drastic environmental disasters of all times. The fiery destruction of an oil drilling platform of British Petroleum (BP) in the Gulf of Mexico was on 20 April 2010. The most important impacts are yet to be seen. The biggest biological impacts of the spill are expected to be on islands that host large colonies of breeding birds and in the rich coastal wetlands, which nourish young fish, shrimp, and shellfish. The many breeding seabirds on the barrier islands include some 2000 brown pelicans, which only last year had recovered enough to be removed from the federal list of endangered species (36).

Jebel al-Zayt oil spill started on June 15, 2010 and is still ongoing in the Red Sea, Egypt. It is considered to be the largest offshore spill in Egyptian history. The spill was reported to have polluted around 160 kilometers of coastline including tourist beach resorts (37).

Oil Spills and the Possible Toxicological Outcomes

For many decades, the seas and oceans have been under the threat of many accidents and attacks as most of the world's oil transportation is done by marine transportation. The safe and rapid transport of petroleum products from their source to their final destination is essential for a nation's growth, health and prosperity. The movement of vast quantities of petroleum products over great distances is usually over water (38, 39). Mishandling, accidents and attacks in the transport of large quantities are inevitable. As accidents and terrorist attacks are likely to happen, oil spills must be taken into consideration seriously (40). Though majority of operational spills are small, accidents can cause larger oil spills, about 20% of them having quantities of more than 700 tons of oil spilt (41). Aquatic spills can cause three kinds of stress factors -namely physical, physiological and toxicological- and they may bring a major problem to the well-being of aquatic life, ecosystem and human health (42).

Oil is a natural substance. Under favorable conditions, if it is spilt at sea, oil can disperse and eventually degrade through natural processes. However, crude oils and petroleum products are complex substances, and their different chemical compounds can react with sea life in a variety of ways. The sight of the seabirds' sinking into the oil during the Gulf War oil spill attracted world's attention to this problem (42).

Crude oil has thousands of components which are separated into saturates, aromatics, resins and asphaltenes (43, 44). Upon discharge into the sea, crude oil is subjected to weathering, the process caused by the combined effects of physical, chemical and biological modification. Saturates, especially those of smaller molecular weight, are readily biodegraded in marine environments (45). Aromatics with one, two or three aromatic rings are also efficiently biodegraded; however, those with four or more aromatic ring are quite resistant to biodegradation (46). The asphaltene and resin fractions include higher molecular weight compounds which has chemical structures yet to be resolved. The biodegradability of these compounds is not known yet (47). The concentrations of available nitrogen (N) and phosphorus (P) in seawater limit the growth and activities of hydrocarbon-degrading microorganisms in a marine environment (48). In other words, the addition of N and P fertilizers to an oil-contaminated marine environment can stimulate the biodegradation of spilled oil (49).

The effects of the spills on sea life may be summarized as below (50-59):

- Sea organisms can either be poisoned by ingestion or can be affected by direct contact.
- Some crude oils leave sticky residues as they weather and this may either float on the surface until they reach the shore, smothering animals and seaweeds, or form solid balls.
- Oil layer also clogs the feathers of the diver and swimmer birds, prevents their flying and reduces their resistance to cold.
- Marine mammals exposed to oil spills are affected in similar ways as seabirds. Oil coats the fur of sea otters and seals, reducing its insulation abilities and leading to body temperature fluctuations and hypothermia. Ingestion of the oil causes dehydration and impaired digestions.
- It should be considered that the hydrocarbon residues in water could affect different kind of enzyme systems (cytochrome P450 enzymes, i.e. CYP1A1/A2 activity) in fish and sea organisms and can be toxic and genotoxic.
- The area covered by petroleum shows the size of the pollution, but as the density of petroleum and its by-products are 10% lower than that of the seawater. The volatile portion will evaporate, some parts will form emulsion with seawater and they will be separated by photo-oxidation and oxidation and as a result 85% of the total volume will decrease and the 15% tarry part will sink or hit the coast.
- The negative effects of the oil spills on sea microorganisms, planktons, sea bottom dwelling organisms and for larvae fish can be poorly understood. Biodegradation of an oil spill in an aquatic environment, which is a massive heterotrophic event with rapid increase in oil-degrading bacteria and a concomitant demand for oxygen in the water column, cascades into potentially lethal anoxic environment for fish and invertebrates.
- Oil also prevents the photosynthesis of the sea plants by preventing the light passage through the water surface.
- The other issue is that fish ingest large amounts of oil through their gills and the effect of this ingestion can bring negative effects on their reproduction or result in a deformed offspring.
- Slow moving organisms such as shellfish are more vulnerable to the effects of oil as they cannot escape from the oil slick. Basic sources of oil spills are tanker accidents, tanker operations and shipping processes.

It is difficult to decide which changes in the ecosystem can be attributed to the oil spills and which changes stem from natural causes. The extent of the problem and the outcome has to be assessed properly and several measures have to be taken. Coordinated control is necessary in such a spill accident as toxic crude oil and degradation products can create a major problem.

Oil Well Fires

Oil well fires are oil gushers that have caught on fire and burn uncontrollably. Oil well fires are more difficult to extinguish than regular fires due to the enormous fuel supply for the fire. There are several techniques used to put out oil well fires, which vary by resources available and the characteristics of the fire itself (60).

Oil well fires can cause the loss of millions of barrels of crude oil per day (61). Combined with the ecological problems caused by the large amounts of smoke and unburned petroleum falling back to earth, oil well fires such as those seen in Kuwait can cause enormous economic losses (62). Not much has been learned from the Gulf War in 1990. The sheer magnitude of the gulf oil well fires caused concern about global effects, including alteration of worldwide weather patterns and drastic increase in the acid rain (62-65). Though the fear of these sudden and unwanted changes did not come into life as it was predicted and the global catastrophe did not occur, the smoke created by these oil fires was huge and it dispersed smoke plum that changed the air quality, because of the several hazardous gases and compounds generated. There are survivors who still have illness and serious complaints because of the exposure to these fires. This event can be a clue for what can happen if an attack is organized toward a plant that explores and produces oil (64).

Oil Well Fire Pollutants

The pollutants released to environment by oil well fires can be as follows (65):

a. **Gases** (ozone, sulfur dioxide, nitrogen dioxide, carbon monoxide, carbon dioxide, hydrogen sulfide)
b. **Acidic Gases** (sulfuric acid, nitric acid, hydrochloric acid)
c. **Polycyclic Aromatic Hydrocarbons** (PAHs) (acenapthene, antracene, carbazole, benzoanthracene, bipehnyls, benzo(f) fluoranthene, 2-methylnaphthalene, chrysene, fluoranthene, phenanthrene, pyrene, cumene, naphthlane, benzo(e)pyrene, benzo(a) pyrene, dibenzofurans, methylnaphthalene, benzo(g,h,i)perylene, dibenzo(a,h)anthracene, phenanthrene, 1-methylnaphthalene, ideno(1,2,3-cd)pyrene, fluoranthene, benzo(b)fluoranthene, 2,6-dimethylnaphthalene)
d. **Metals** (Cd, Fe, Hg, Cr, Ni, Pb, Va, Zn, As, Be, Mg)
e. **Volatile Organic Compounds (VOCs)** (benzene, toluene, ethane, butane, ethyl benzene, m-xylene, p-xylene, o-xylene)
f. **Particulate Matter (PM)**
   - Particulate matter 10 (<10 μm aerodynamic diameter, PM10)
   - Fine particles (<0.1 μm aerodynamic diameter)
   - Ultrafine particles (0.1-0.25 μm aerodynamic diameter)
   - Silica
   - Soot
g. **Others** (sodium, sulfate, Ca, Cl)

Oil Well Fire Health Effects

The crude oil itself is a health hazard because, in addition to other toxins, it contains benzene, which the US Public Health Service has determined is a cancer-causing compound (66). After the 1991 Gulf War, veterans of the conflict from the United States, United Kingdom, Canada, Australia and other nations described chronic idiopathic symptoms that became popularly known as "Gulf War Syndrome (GWS)" (67). The media, Gulf War Veterans and scientists suggested that illnesses observed among veterans after war could be attributable to deployment-related exposures (68). Nearly 15 years later, some 250 million dollars in United States medical research has failed to confirm a novel war-related syndrome and controversy over the existence and causes of idiopathic physical symptoms has persisted. Wartime exposures implicated as possible causes of subsequent symptoms include oil well fire smoke, infectious diseases, vaccines, chemical and biological warfare agents, depleted uranium munitions and post-traumatic stress disorder (67,69,70). Though some scientists believe this idiopathic symptom syndromes are associated with nearly every modern war with physical, emotional and fiscal consequences for veterans and for society, the exposure of the veterans to several chemicals associated with the oil well fires caused several outcomes in the short-term and long-term. Neither the excess morbidity reported in health surveys nor the experiences during deployment significantly influenced future mortality (71).

In order to understand the real health effect of the pollutants, the methodology that must be followed in an exposed population consists of four steps (64, 66, 72):

A. Data Collection and Evaluation
B. Toxicity Assessments
C. Exposure Analysis
D. Risk Characterization

Toxicity assessments were performed in two steps:

a. Hazard identification: It involves determining whether exposure to a pollutant could cause an increase in the incidence of an adverse effect.
b. Dose-response assessment: This process quantitatively evaluates the relationship between the dose of the pollutant exposed and the incidence of the adverse effects.

Following these steps, the short-term and long-term effects that are the result of the exposure to oil-well fires can be well-characterized.

The Short-Term Health Effects of Oil Well Fires

The short term health effects of oil well fires can be classified as follows (73-75):

- Respiratory Tract Disorders (shortness of breath, coughing, wheezing, runny nose, respiratory irritation, asthma, bronchitis, pneumonia)
- Cardiovascular System Disorders (heart disease)
- Gastrointestinal System Disorders (diarrhea)
- Immune System Disorders (immune suppression)
- Dermal Disorders (eye irritation, skin rashes, chemical sensitivity)
- Psychiatric Disorders (depression, memory loss)
- Nervous System Disorders (fatigue, headache)
- Other (weight loss)

The Long-Term Health Effects of Oil Well Fires

Several studies examined the relationship between the illnesses and Gulf War through the years. Common illnesses that have been associated with the Gulf War are persistent respiratory tract illnesses (asthma, bronchitis) and psychiatric disorders (major depression) (76). There is no current methodology for assessing carcinogenic risk from short-term exposures. Long-term effects can be estimated from the health problems and mortalities experienced from oil refinery workers or petroleum distribution workers. Though it is not appropriate to compare the occupational exposure and the exposure of the veterans and the population in the Gulf War, as total dose or body burdens differs, it can give an idea of the future outcome of the health problems are as follows (64).

The long-term health problems associated with oil well fire exposure can be classified as follows (77-80):

- Cancer (lung and bronchus cancers, skin cancers, prostate cancer, bladder cancers, esophagus and stomach cancers, pancreas cancer, large/small intestine cancers, leukemia, multiple mycelia, secondary cancers), genotoxicity, teratogenecity
- Respiratory Tract Disorders
- Gastrointestinal System Disorders
- Dermal Disorders
- Musculo-skeletal System Diseases
- Psychiatric Disorders
- Nervous System Disorders
- Endocrine / nutritional / metabolic Diseases
- Haematopoetic System Disorders
- Genitourinary System Disorders

Many studies have shown strong associations between PM levels and a variety of health outcomes, leading to changes in air quality standards in many regions, especially in the US and Europe. The most important pollutant that caused serious health problems was PM and the levels of PM was high in the region throughout the Gulf War, and there are reports saying that desert conditions (sand, weather), oil rain and smoke worsened the effects. The degrees to which airborne particulates impact human health depend on several factors including particulate mass, size distribution, composition (PAHs, Fe, Zn) and the presence of organic components (endotoxins, pollen, bacteria, viruses). The effects of silica and soot are on the lungs and on the cardiovascular system. When PM is found at high concentrations in an occupational environment and under conditions of extended exposure, changes in lung function, damage to lung tissue, and altered impaired respiratory defense mechanisms and cardiac arrhythmia can be the adverse effects (81-84). A recent study on PM levels in Kuwait showed that there was still PM in the air remaining from the oil well fires. A detailed particle characterization study was conducted over 12 months in 2004-2005 at three sites simultaneously with an additional 6 months at one of the sites. Two sites were in urban areas (central and southern) and one in a remote desert location (northern). The study reports the concentrations of particles less than 10 μm in diameter and fine PM, as well as fine particle nitrate, sulfate, elemental carbon, organic carbon, and elements measured at the three sites. Mean annual concentrations for PM10 ranged from 66 to 93 $\mu g/m^3$ across the three sites, exceeding the World Health Organization (WHO) air quality guidelines for PM10 of 20 $\mu g/m^3$. The mean PM2.5 concentrations varied from 38 and 37 $\mu g/m^3$ at the central and southern sites, respectively, to 31 $\mu g/m^3$ at the northern site. All sites had mean PM2.5 concentrations more than double the U.S. National Ambient Air Quality Standards

(NAAQS) for fine particles. Coarse particles comprised 50-60% of PM10. The high levels of PM10 and a large fraction of coarse particles comprising PM10 were partially explained by the resuspension of dust and soil from the desert crust. The researchers concluded that particulate levels in this study were high enough to generate substantial health impacts and present opportunities for improving public health by reducing airborne PM (85).

Petroleum inhalation is another important cause of long term toxicity and can lead to two forms of lipoid pneumonia. One form causes a lesion similar to a tumor within the lung and is called lipoid granuloma or paraffinoma. Extensive loss of pulmonary function can occur with this type of lesion. A second form of lipoid pneumonia is diffuse pneumonitis in which oil droplets are spread throughout the lung. This type of lipoid pneumonia can be accompanied by bacterial infection. Lipoid pneumonia symptoms can range from occasional cough to severe, debilitating breathlessness and pulmonary illness. Advanced lipoid pneumonia can lead to permanent loss of lung capacity from fibrosis. Lung damage from lipoid pneumonia can vary from slight to severe with necrosis and hemorrhage (86, 87).

Hydrogen sulfide (H_2S) and VOCs were also the causes of the health problems and the hot atmospheric conditions were effective in the adverse inhalation effects of such pollutants. The researchers also indicated that the synergic effect of multiple contaminants caused more stress on health than a single one acting alone (66).

Skin exposure to petroleum can cause skin cancer, rashes, eczema, acne, and dermatitis, as known for many years. The reaction of the skin to petroleum depends upon the composition, boiling range, viscosity and aromatic content of the oil. Aromatic content is a key toxicity parameter for petroleum; the higher the aromatic content is, the greater the toxicity is. Aromatic compounds boiling between 260-538^{o}C have been found highly carcinogenic. The potential for skin carcinogenicity and toxicity of the oil rain must be evaluated based upon its estimated boiling range, viscosity and aromatic content (88).

Considering all the adverse effects of the oil well air exposure, there are some studies conducted on the Gulf War veterans, but none of them shows the real effects of the exposure of soldiers to different substances mentioned above, because most of them were carried out by the US government and they underestimated the severity of the problems of the veterans and the exposed population (88).

What Should Be Done to Prevent Accidental or Intentional Oil Spills?

The most important issue is to prevent physical and environmental damage during oil transportation by sea. To provide protection and detection for hazards like fire, which may be accidental or intentional, security awareness education is necessary. Clarifying why security is necessary is the first step. Security awareness training and clarifying employee security responsibilities are the next steps. Making security controls and identifying the vulnerabilities is necessary for the maintenance of the security of the marine transportation.

A number of "clean-up" techniques can be employed for oil spills. These include (72):

- Spraying the oil with low toxicity dispersant chemicals from low-flying aircraft. The chemicals help break up the oil and disperse it into the sea where it can be broken down by naturally-occurring microorganisms.
- Using "skimmer-vessels"-specially adapted boats which skim the surface of the sea-removing floating oil.
- Placing floating booms across harbors and inlets to restrict oil movement physically.

International Maritime Organization (IMO), founded in 1948, is the United Nations (UN) specialized agency responsible for improving maritime safety and preventing pollution caused by the ships. IMO's Formal Safety Assessment (FSA) is a structured and systematic methodology aimed at enhancing maritime safety (protection of life, the marine environment and property) by using cost/benefit criteria. FSA consists of five steps (89):

1. Identification of hazards
2. Risk assessment

3. Risk control options
4. Cost/benefit assessment
5. Recommendations for decision making

As human reliability and mistakes are important issues in marine accidents, for incorporation of human factor, IMO offers an adoption of Human Reliability Analysis (HRA) that was developed and implanted for nuclear industry (90):
1. Identification of key tasks
2. Analysis of key tasks
3. Identification of human error
4. Analysis of human errors
5. Quantification of human reliability

Though several measures to be taken for the potential threat of massive and catastrophic spill accidents are identified, coordination between states is a big problem yet to be solved. Taking into account terrorist activities, handling issues for maritime safety is essential for a clean and safe marine environment.

Turkey and Oil Spills

As for Turkey, the Straits have always affected Turkish foreign policy. Throughout history, the Straits have been a problem between Ottoman Empire and other countries, then for Turkish governments. Thousands of tankers pass through Straits every year. Almost 160.000 tons of several products and 150.000 tons of oil are carried through the Straits every year. The oil shipped, may also be for domestic use as Turkey is being forced to import more oil and gas. This increased clogging has led to a growing number of accidents; between 1988 and 1992, there were 155 collisions in the Straits (91).

The risk the oil tankers may cause sometimes can be higher than the benefit they bring. Other than the risk of industrial pollution, trace metal contamination, eutrophication, and petroleum hydrocarbon contamination can cause serious problems both for human health and for the marine environment (91). However, Turkey's power to regulate commercial shipping through the Straits was limited by the 1936 Montreux Convention, which designates the Straits as an international waterway. Although some other international agreements gave Turkey the right to regulate the right of passage through the Straits for a safe flow of sea traffic, due to pressure from some Black Sea border countries, Turkey is not able to enforce the shipping laws and only a small number of ships report their cargo while passing through the Straits. As the number of ships through the Straits grows, the risk of accidents increase. Besides, traffic is likely to increases as the six countries surrounding the Black Sea are developing their economy very quickly (92, 93).

Several accidents took place in the Straits including the collusion of a Greek ship named "World Harmony" with "Peter Zoronic", a Yugoslavian ship in the Straits in 1960. 20 people died including the captain and sea pollution was higher than expected. In 1966 Lutsk (USSR) and Cransky Oktiabr (USSR) collided in the Straits and thousands of tons of oil spilt on the sea with a big fire. Independenta (Romanian) and Evriyali (Greek) ships collided strongly in November 1979, resulting in 43 deaths, fire and sea pollution. In March, 1990, Jambur (Iraqi) and Oatton Shang (Chinese) ships strongly collided and thousands of tons of oil spilt into the sea. The cleaning of the sea took several months and it was an environmental disaster. This danger was underscored in March 1994, when the Greek Cypriot tanker Nassia collided with another ship, killing 30 seamen and spilling 20,000 tons of oil into the Straits. The accident resulted in an oil slick over the waters of the Bosphorus, affected the urban life of North Istanbul and caused a disaster for five days. After the 1994 Nassia disaster, Turkey passed regulations requiring the ships carrying hazardous materials to report to the Turkish Environmental Protection Ministry (93). The tonnage of the ships is another issue in the threat of collision: on December 29, 1999, the Volgoneft-248, a 25-year old Russian tanker, carrying 4,300 tons of fuel oil on board ran aground and split in two in close proximity to the southwest shores of Istanbul. More than 800 tons of oil spilt into the Marmara Sea, covering the coast of Marmara with fuel oil and affecting about 5 square miles of the sea (94). Clean-up costs of the Straits and the Black Sea are estimated as high as 15 billion dollars, which is far beyond the six countries bordering the sea can afford and more international financial support is needed (95). As for the fishermen in the Marmara and in the Black Sea, they are about to face a big economic crisis, because nature's equilibrium is about to change because of overfishing and pollution. Pollution in the Straits contributed to a decline in fishing levels to 1/60th of the former levels. In the Black Sea, meanwhile, overfishing and pollution have changed the ecosystem enormously (95). On the other hand, apart from the major spills, gas-carrying ships in the Straits cause other problems, such as the day-to-day release of the load. To reduce the strain on the marine environment caused by ship traffic, Turkey has tried alternative means to transport oil and gas from Central Asia by installing the Caspian oil pipeline from Baku to the port of Ceyhan, as well as the Trans-Caspian gas pipeline from Turkmenistan across Azerbaijan and Georgia to Turkey. However, a recent Kazakh-Russian deal to ship more oil to the Russian Black Sea port of Novorossiisk guarantees that more oil will continue to flow through the Straits (95).

Turkey is a member of IMO since 1958, but as IMO is a technical organization rather than a political foundation, it cannot force the governments which use the Straits as a passage gate to world seas, to take serious measures for the prevention of accidents and for the pollution they cause. Finally, Turkey's State Planning Organization, together with the World Bank, is coordinating a project called the "Turkish National Environmental Strategy and Action Plan" to implement activities in Turkey. By establishing basic environmental standards and identifying environmental investment priorities, Turkey can integrate sustainable policies into its overall economic development, thereby safeguarding her environment well into the future (96).

Discussion

In every step of oil processes from exploration to marketing, there are several security requirements against the risks and the potential risks. A threat assessment is the key in evaluating the vulnerabilities and taking measures for the preparedness. In assessing threats:

1. Identification of potential threats and known threats
2. Analysis of the intention, method, strength and weapons of the threats
3. Discussing such an attack and brainstorming has to be made in order to assume the outcomes.

If the threat is credible and corroborated, the potential consequences must be evaluated. Creating a security plan for a company or company's facility is a hard, integrated and difficult process and creating a security plan while shipping is harder. In every step to be taken, the company has to:

- Characterize the potential of threat and identify the outcomes of threat
- Make a risk assessment
- Create a risk mitigation step

It should not be forgotten that threat assessment is a dynamic process and as conditions change, the measures to be taken have to change, so continuous evaluation is necessary.

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