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## OIL SPILL RELATED HEAVY METAL: A REVIEW

(Logam Berat Berkaitan Tumpahan Minyak: Satu Ulasan)

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#### Abstract

Oil spill occurs every day worldwide and oil contamination is a significant contributor for the higher levels of heavy metals in the environment. This study is purposely to summarize the heavy metals which significant to major oil spill incidents around the world and effects of toxic metals to human health. The study performed a comprehensive review of relevant scientific journal articles and government documents concerning heavy metals contamination and oil spills. Overall, the heavy metals most frequently been detected in oil spill related study where Pb>Ni>V>Zn>Cd and caused many effects to human health especially cancer. In conclusion, the comparison of heavy metal level between the post - spill and baseline levels must be done, and implementation of continuous monitoring of heavy metal. In addition, the result based on the strategies must be transparent to public in order to maintaining human health.

Keywords: oil spill, heavy metal, human health, contaminants, water quality

## Abstrak

Kejadian tumpahan minyak berlaku setiap hari di seluruh dunia dan menjadi penyumbang yang signifikan terhadap tahap logam berat yang tinggi dalam persekitaran. Kajian ini bertujuan merumuskan spesies logam berat yang signifikan dengan kejadian tumpahan minyak utama di seluruh dunia dan kesan logam berbahaya ini terhadap kesihatan manusia. Kajian ini dijalankan dengan membuat ulasan yang menyeluruh melalui jurnal saintifik berkaitan dan dokumen rasmi kerajaan berkenaan pencemaran logam berat dan tumpahan minyak. Keseluruhannya,logam berat yang paling banyak dikesan adalah Pb>Ni>V>Zn>Cd dan menyebabkan banyak kesan kepada manusia terutamanya penyakit kanser. Secara konklusinya, perbandingan tahap logam berat selepas tumpahan minyak dengan tahap asal perlu dilakukan beserta pemantauan berterusan. Selain itu, keputusan daripada strategi di atas perlulah mudah diakses kepada orang awam dalam usaha mengekalkan kesihatan orang ramai.

Kata kunci: tumpahan minyak, logam berat, kesihatan manusia, bahan pencemar, kualiti air

## Introduction

Oil spill occurs every day worldwide. It has probably happened worldwide in many levels of environment such as on land, at sea and freshwater. Liquid petroleum is the major components involve in oil spills cases around the world. It is contribute by the development of petroleum as the world's main source of energy. Besides, the demand for better energy that is petroleum speeds up worldwide caused by the increasing population and industrialization of developing countries [1]. The rate of crude oil production has a significant relationship with the rate of development

in order to fulfill the industrial needed of modern community [2]. The demand of petroleum sources is increasing as industrialization developed massively around the world. These organic compounds occur in environment because of exploitation, transportation and storage of this resource due to rapid industrialization [3]. According to Schmidt-Etkin [4] oil industry start from oil exploration or production to distribution to the consumer is the main contributor to the spillage. Based on the report by the US Department of Energy [5], the worldwide demand and supply for liquid petroleum from 1970 to 2004 show some increasing trend to prove the high demand of petroleum recently. Massive industrialization around the world speed up the petroleum demand as shown by the graph on Figure 1. China is the most extensive growth country in the last decade and their GDP was increased by 40%. The growth led to a rapid increase in energy consumption in recent years. Based on the report, China moves ahead of US as the world's largest consumer of energy on 2009 [6]. From the statement above, we can conclude that rapid growth in industrialization has influenced the China's energy demand.

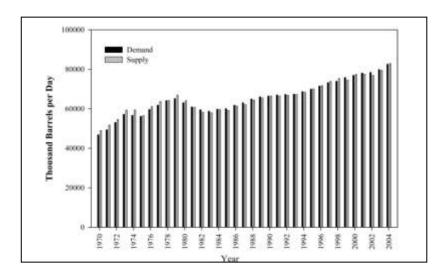


Figure 1. Worldwide demand and supply for liquid petroleum from 1970 to 2004

There are several devastating oil spill cases occur around the world that affect biodiversity massively. Start on the history of oil industry, Deepwater Horizon oil spill in the Gulf of Mexico is one of the largest crude oil spills in the history. This tragedy happen on between April 20, 2010 and July 15, 2010 with estimation crude oil released into Gulf of Mexico water about 170 million gallons [7]. The oil spill tragedy occurred at Gulf of Mexico (GOM) also was subjected to the largest offshore crude oil spill ever recorded in the western hemisphere [8]. Approximately 686,000 mT of crude oil was released caused by the incidents [9]. Based on Johnson et al. [10], the crude oil estimated release rate was ranging from 1,670 to 2,670 mT per day, very large amount of pollutant that restricted from present in marine environment. A studied by Michel et al. [11] summarized that the spillage of Deepwater Horizon spill spread extensively to 1,773 km of shoreline and the degree of oiling decreased to 847 km on first year after the tragedy following subsequently with 687 km two years later. To curb the problem, it is important to us to well understand the movement and transport of oil spill in marine ecology. Dubbed as one of the most largest occurred cases in the Gulf of Mexico, it is happen caused by the explosion of drilling platform at Macando exploration site (MC252) [12]. A study by Mulabagal et al. [13] suggests that the blowout cause the spillage of 4.4 million barrels crude oil into the shoreline. From the day incident happen, the Deepwater Horizon related oil undergo weathering process forms tar balls and deposited along Alabama beaches [14].

Exxon Valdez is one of the monumental marine oil spills ever happen around the world. On March 24, 1989, an oil tanker struck cause the spilled of 258,000 barrels of Alaska North Slope crude oil into Prince William Sound. On that year, monitoring to shoreline found that approximately out of 4,800 km, 783 km (16%) and 1,300 km out of

10,000 km in PWS and Gulf of Alaska respectively were covered by Exxon Valdez oil spill [15]. According to Wiens [16], the incident spilled 40 million liters of crude oil and a late winter storm surge in the area caused the oil were spread outward 2100 km of marine water. Based on the tragedy, until the last two decades, many researchers done field studies to briefly understand the movement or distribution of oil spill that still remain in shoreline [17-18]. That research activities were followed by another which come out with important finding such as research from the joint local government and responsible agencies undergo between 1990 to 1992 [19 – 22].

From 2001 to 2009, the subsequent studies taken by Exxon and National Oceanic and Atmospheric Administration (NOAA) to continue the monitoring programmes [11, 21 – 24]. Gulf War oil spill is another catastrophe tragedy which regarded as largest spillage ever in oil spill history. Eight tankers, a refinery, a tank field, and two terminals released more than 1 million barrels of crude oil [25, 26]. Shoreline of Saudi Arabia had been covered by oil 706 km extensively, with 366 km, 220 km, 34 km, and 86 km were classified as heavy, moderate, light, and very light respectively [27]. From 1992 to 1993, there are several research were carried out to study the distribution of the oil remained in Saudi Arabia, coastal and then come out with findings that intertidal habitats were greatly affected [28, 29]. Oil spill also regarded as high impact environmental pollution due to the large scale of habitats were greatly affected [30]. The different types of environmental were affected by oil spill caused by the release of heavy metal into ecosystems [2, 30, 31]. Basically, heavy metals such as Cadmium (Cd), Lead (Pb), Nickel (Ni), Chromium (Cr), Vanadium (V) and Zinc (Zn) present in crude oil and drilling fluid which widely used in oil field industries [31 – 35]. Oil contamination is a significant contributor for the higher levels of heavy metals in different types of environment such as on soil, in seawater and freshwater [36, 37]. The existence of heavy metal in the aquatic environment poses a significant threat as since the source of pollutants come from oil export facilities and petrochemical plant [38].

### **Materials and Methods**

The study began by collecting information from established and high impact scientific publications identified using an internet search engine such as Google Scholar [39], and variety of the following search terms: "oil spill" (including the individual names of major oil spills around the world), "human health", "heavy metals" (including individual metals), and "heavy metals in oil spill". The same terms also being applied to search in federal and international organization technical reports and databases from NOAA, the U.S. Environmental Protection Agency (EPA), the National Toxicology Program, World Health Organization (WHO), and the International Agency For Research on Cancer.

## **Results and Discussion**

## **Heavy Metal Related to Oil Spill**

The rapid development of crude oil exploration and transportation increase the tendency to oil spill incident which released heavy metals as the major contaminants in the worldwide environment. According to Fu et al. [35], summarized that the concentration of Zn, Cd, Ni, V and Mn in oil polluted soils were present in high level and surpass the permissible value of the region which is at Shengli Oilfield, China. The exceeded value of the contaminants is significance with the development of oil well, which shows that anthropogenic activities contribute to the situation. In United States of America, Exxon Valdez oil spill is the worst spillage ever occurred. Located nearby Kachemak Bay, Alaska, [40] performs a study of heavy metal concentrations in surficial sediment. The finding from this research shows that level of Cr, Ni, Pb and Zn were higher at the east part of bay compared to west strata and also the concentration still below permissible value. It is due to the fate of river flow which carries eroded contaminants to the area and proved by the varied presence of sediment form coarse sandy type to finer sandy mud. In addition, heavy metals such as Zn, Mn, As, CO, Cr, Se, Hg, Cd, Cu, Pb, Ni, Sn, Sb, V significantly present in different types of environment such as sediments and marine organisms origin from oil spill region. Heavy metals are common portions of crude oil and drilling fluid applied in oil exploration industries [41, 42]. Furthermore, a study by Wainipee et al. [43] comes out with finding that potential increased elemental As after the release of crude oil into ocean because of chemical reaction have taken place. In a study performed by [30] V and Ni show relatively higher concentration than background value. The Gulf of Thailand sediments being analysed and high value of the pollutants were caused by the release of petroleum or crude oil due to high traffic of water transportation.

There are several studies that conduct continous monitoring at Gulf of Mexico which can provide good baseline data which can be used to find out the impact of Deepwater Horizon oil spill to the concentration of heavy metals in seafood [44, 45, 46]. Another study reported that the level of V was higher in mussel after the Prestige oil spill incident compared to level before spillage has occurred and also non affected sites [47, 48]. In Lebanon, a study conducted by [49], Jiyeh oil spill in the Eastern Mediterranean Sea caused the concentration of Pb, Ni and V in oysters were higher than normal value and also suggested that the concentration directly proportional to size and length of the oysters.

Crab also a good bioaccumulator that can be as indicator to the concentration of heavy metal in environment [50, 51]. Accumulations of heavy metals naturally occur in marine sediments and can be as indicator the level of contamination for that area if any intrusions of contaminants occur [52 – 55]. One of study use crab as their sample by Al-Mohanna and Subrahmanyam [56] which identified high level of Zn, Cu, As, Pb, Mn, Mg, Se, and V in fatty tissue 10 years after 1991 Gulf War oil spill. Fish is an essential food for meet human nutrition [57, 58,59]. Minimized the risk of heart diseases and stroke were several advantages of consuming fish as their function in lowering the cholesterol levels in blood and also provides minerals and vitamins [60]. So, the present of heavy metal in fish give impact to the human health. Furthermore, fish also can be good bioindicators of heavy metal contamination due to its capability to accumulate contaminants in tissue [61, 62, 63]. According to study conducted by Nduka et al. [64], Fe recorded highest concentration in different parts of fish at Niger Delta. The study also related high level of the trace metal due to crude oil spill which is occurs regularly in the region. This occurrence is so harmful to human who may consume the fish as their daily nutrient sources. Nigeria is the sixth largest petroleum producer in the world. The industry contributes approximately 80% of nation income [64, 65]. Based on study by Obiajunwa et al. [2], enrichment factors for Sr, Zr, Pb, Ba, and Fe were very high for every sample. The study summarize that there is significant relationship between heavy metal pollution and crude-oil production industry which may be spillage have occurred in the process of production. This is very harmful because the high contamination of heavy metal is very dangerous to both aquatic environment and human health [66, 67, 68]. Hence it is important to determine concentrations of heavy metals in every difference level of environment in order to evaluate the possible risk of consumption. From the review conducted, Figure 2 simplifies the species of heavy metals which frequently detected after major oil spill incidents around the world. Based on the figure, Pb > Ni > V > Zn > Cd were the major heavy metals which significant to oil spill through review from many scientific studies around the world. From the graph, Pb occurs as most frequent heavy metal present in oil spill incidents followed by Ni, V, Zn and Cd. Table 1 shows several studies on heavy metal related to oil spill conducted around the world. Based on the table, researchers tend to study heavy metal in many medium such as sediment, water, seafood, plant, and crude oil itself to represent the level of contaminants in environment. The oil spill incident that involved in this study consists of major and large scale spillage which causes devastated effect on aquatic environment.

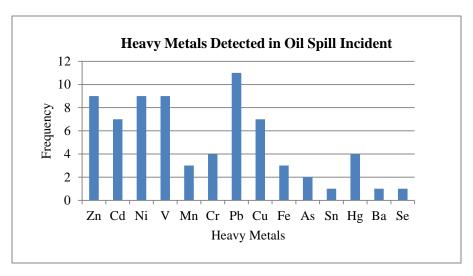


Figure 2. Frequencies of Heavy Metals Detected in Oil Spill Incident

Table 1. Significant Heavy Metal based on Oil Spill Studies

Heavy Metal	Medium	Oil Spill Area	References
Zn, Cd, Ni, V, and Mn	Soil	Shengli Oilfield, China	Fu et al. [35]
Cr, Ni, Pb, and Zn	Sediment	Kachemak Bay, Exxon Valdez	Apeti and Hartwell [40]
V	Sediment	Mina Al Fahal, Oman	Al Husaini et al.[69]
Cu and Zn	Water	Bohai Bay, China	Wang et al. [130]
Ni, Cd, Pb, and Cu	Mosses	Nigerian Petroleum Depot, Nigeria	Fatoba et al. [124]
Cd, Cr, Cu, Fe, Ni, and Pb	Water and Sediment	Niger Delta, Nigeria	Owamah, [72]
Ni and V	Crude oil	Gulf of Mexico	BP [126]
V	Mussel	Prestige Oil Spill	Bartolome et al. [127]
Hg	Air	West Coast Korea	Pandey et al. [125]
Zn, Cu, Cd, and Pb	Sediment	Gulf of Mexico	Ruelas-Inzunza et al. [70]
Pb, Ni, V	Oyster	Jiyeh Oil Spill	Barbour et al. [49]
As, Cd, Cu, Pb, Hg, Ni, Sn, and Zn	Mussel	National Coastal Zone, United States	Kimbrough et al. [44]
V	Mussel	Prestige Oil Spill	Villares et al. [48]
V and Ni	Sediment	Gulf of Thai	Censi et al. [30]
Pb, Zn, Cu, Ni, Cd, Co, Cr, Fe, and Mn	Fish	Niger Delta, Nigeria	Nduka et al. [64]
Hg	Seabird	Prestige Oil Spill	Perez Lopez et al.[128]
Sr, Zn, Pb, Ba, and Fe	Soil, sediment, solid waste	Niger Delta, Nigeria	Obiajunwa et al. [2]
Zn, Cu, As, Pb, Mn, Mg, Se and V	Marine blue crab	Gulf War Oil Spill	Al-Mohanna and Subrahmanyam [56]
Pb and Cd	Sediment	Gulf of Suez	El-Tokhi and Mostafa[71]
Zn, V, Pb, and Cr	Seawater	Gulf War Oil Spill	Olayan et al. [131]

## **Human Health Effect**

There are several studies conducted used different types of sediment to determine the level of heavy metal in the area [2, 30, 69 - 73]. Sediments would be as place for accumulation of heavy metals once entering the water body and following with undergo movement due to exchanges between water, sediment and biota through natural process. Sediments also contain high concentration of heavy metal can reach until 1000-100,000 times and 10,000-100,000 times higher than water and fish respectively [74 - 77]. Heavy metal in sediments also can be harmful to human health although not being consume directly by human. It is because heavy metal deposited in sediments which largely known as major sink for trace metal pollution and also contribute to high heavy metal uptake by fish [73, 78]. The uptake will be absorbed and stored in fish fatty tissues subsequently enter the food chain [79]. Generally, heavy metal can be categorized into two types which are essential metals and non-essential metals. Lead, mercury, and cadmium while nickel, copper and manganese were non-essential metals and essential metals respectively [80 - 84]. Heavy metals are naturally occur which present at low levels in environment and if larger amounts, it can impact human health [85]. Heavy metals in water can enter into human body through several pathways including food chain, dermal contact and inhalation [86].

Worker in industry exposed to heavy metals everyday in their work routine through inhalation while the main route of exposure of non-occupationally individuals is food consumption [87]. The accumulation of heavy metals in fish mainly caused by regular surface contact with the water, by breathing, and include in the food chain. Human exposed to the potential health risk by consuming commercial fish which contaminated with heavy metal [88, 89, 90]. Thus, the monitoring of the level of heavy metal content in fish is very important to ensure does not exceed permissible level and not expose any hazard to the human [91, 92, 93].

Generally, Lead (Pb) significantly appears as highest number of element determined throughout several studies related to oil spill conducted around the world. Pb become very harmful by enters into biota by several pathways such as the inhalation of element in air, oral intake or ingestion in contaminated water, and consume it from food and soil in polluted areas [94, 95]. Subsequently absorption, Pb is distributed evenly in human body via bloodstream and excreted it at very slow rate through faeces and urine [96]. Pb can be very dangerous to human health by cause multiple toxic effects. Higher than permissible level exposure to Pb may lead to abnormalities such as alteration in hematological, immune, reproductive, nervous and renal systems [95, 97, 98].

Vanadium (V) is an element which has been the topic of much research and significantly present in their study. V is widely distributed naturally in our environment and its prevalence higher than other familiar metals such as copper and lead [99, 100]. Severe vanadium found in human body caused nausea, weakness, vomiting, headache, transient coronary insufficiency, anaemia, dermatitis and lowering of cholesterol levels [99, 101]. Change in neurobehavioral abilities also one of the effect if expose to exceed permissible vanadium value [102, 103]. Nickel (Ni) is a toxic element which human exposure to it by several pathways such as via inhalation, ingestion and dermal absorption [104]. Nickel is present in different type of environment such as soils and waters in form of soluble and insoluble compound [105]. Many unique physical and chemical characteristics make this metal widely used in modern industry [106]. Continous exposure to high level of nickel cause increased the risk of lung cancer, nasal cancer, DNA damage, cell death, inflammation and impacts the cellular metabolism [104, 107, 108, 109].

Since the 1960s, Cadmium (Cd) was closely related to the 'itai-itai' painful bone disease due to high level in Japan environment. The contamination was caused by mining activities that caused contaminant transportation into river and remained in paddy fields before being consumed by local people. The element has also recently been shown to be an endocrine-disrupting chemical with estrogenic properties and a potential prostate carcinogen [110, 111]. Naturally, Cd accumulated with high level in the kidney which can be persistent and toxic to human body. According to 112, inorganic Cd is very toxic to humans and can enter to human body through inhalation and ingestion. The high concentration of Cd closely related to nausea, vomiting, diarrhea, headache, abdominal pain and also can resulted in death within 1-2 weeks subsequently by liver and kidney damage. A study conducted at Europe summarized that significant correlation between cancer incidence and Cd concentration in topsoil and stream water [113]. Excessive zinc intake can cause acute and chronic toxicity. Acute toxicity of high zinc intake cause several adverse effects such as nausea, loss of appetite, vomiting, diarrhea, headaches and abdominal cramps [114]. Zinc gluconate is one of the elemental zinc examples that caused nausea and vomiting if high intakes occur in human body [115]. High intakes of zinc also altered or reduce another process function such as iron function, immune function, and low copper status [116, 117].

## **Recommendation for Future Heavy Metal Research**

Based on the review from many published heavy metal studies, the statistical analyses have done quite simple and not comprehensive. The analyses covered only to determine the presence of heavy metal on the study area but not investigate the pollutant source apportionment. More complicated and comprehensive statistical analyses needed to be done in order to comply from sources to solution concept. The understanding of changing heavy metal concentration and distribution is essential for good environmental management [118]. The pollution control and monitoring of heavy metals in the environment becoming as most important aspect of pollution study [119]. In the effort to understand the trend of heavy metal, selection of the most suitable statistical methods is important in obtaining meaningful results, particularly in determining the significant impact of the heavy metal species on water quality. The application of environmetric, a branch of environmental analytical chemistry, uses multivariate statistical modeling and data treatment was reported to be the best method in analyzing a large complex environmental monitoring data [120]. Environmetric methods have been widely used in drawing meaningful

information from environmental data. These methods have often been used in exploratory data analysis tools for classification of variables and the identification of pollution sources [121, 122]. The most common environmetric methods for classification are cluster analysis (CA) and principal component analysis (PCA). The goal of CA is to identify the similarity, that is, homogeneous groups of the water quality variables, while PCA enables a reduction in data and description of a given multidimensional system by a small number of new variables. PCA analysis assists to find out in what respect one variable is different from another, which variables contribute most to this difference. Thus, PCA is a useful distinguishing which variables carry most significant impact. In addition, the results from environmetric analysis are able to extract information on the possible sources of pollutants. By using different methods of environmetric analysis, it helps to reduce the complexity of large data sets and also suggested better interpretation of the data [123]. The application of different environmetric statistical analysis for the interpretation of the complex databases offers a better understanding of heavy metal level in the study region.

### Conclusion

In summary, we studied about different significant heavy metal related to oil spill incidents around the world that show remarkably increasing pattern from day to day. Basically, heavy metal assessment in all research under oil spill incident are lack of statistical analysis such as multivariate analysis consist of Cluster Analysis and Principle Component Analysis can be apply for meaningful interpretation of the large set of environmental data. Detailed and systematic monitoring must be implement that includes heavy metal assessment to initiate effective risk communication in the future in order to minimize human health affect from incident. We believe that implementation of these recommendations will help ensure to maintain the quality of human health.

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