Type of the Paper (Review)

Title

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**Abstract:** A single paragraph of about 300 words maximum. For research articles, abstracts should give a pertinent overview of the work. We strongly encourage authors to use the following style of structured abstracts, but without headings: (1) Background: Place the question addressed in a broad context and highlight the purpose of the study; (2) Methods: Describe briefly the main methods or treatments applied; (3) Results: Summarize the article's main findings; and (4) Conclusions: Indicate the main conclusions or interpretations. The abstract should be an objective representation of the article, it must not contain results which are not presented and substantiated in the main text and should not exaggerate the main conclusions.

**Keywords:** keyword 1; keyword 2; keyword 3. List three to ten pertinent keywords specific to the article; yet reasonably common within the subject discipline.

1. Introduction and Background

Oil and petroleum products, such as gasoline, are nonrenewable, important commodities that are a major component in the everyday life of people worldwide. Originating mostly from Alberta and Saskatchewan, 450, 000 tons of oil and products are consumed daily in Canada, most of which is used for transportation (Fringas, capp). Crude oil is naturally formed over millions of years from decayed organic bodies of marine organisms combined with intense heat and pressure (national). Varying in compositions, crude oil and products are composed of thousands of distinct compounds, such as hydrocarbons and metals, which give it unique characteristics that will influence how it will behave in specific environments (national research council).

As the demand for energy has increased globally, the consumption of oil has been steadily increasing since the beginning of the 20th century (Ledenko 2018). Future demands for oil, as a non-renewable source, may cause overexploitation of the Earth’s oil reserves as well as economic unrest with fluctuating oil prices (Own 2010).

Two ways in which crude oil can enter marine environments is through anthropogenic activities and crude oil seeps, the latter having occurred naturally throughout Earth’s history (hunt 1996). However, with the high demands faced by the oil and gas industries, it comes to no surprise that pollution, via oil spills, has occurred during transport and extract of crude oil in marine environments. It is estimated that up to 50% of spills are caused directly or indirectly by human error or equipment malfunction (Fingas). Just in the past century, several large-scale oil spills have occurred, one of which became the largest to date. In April 2010, over 200 million gallons of oil was spilled during the *Deepwater Horizon* oil spill in the Gulf of Mexico, which was 19 times more than the pervious large-scale *Exxon Valdez* oil spill in 1989 (pop mechanics). Although there has been a decline in oil spills since 1992, studies focusing on large-scale spills have reported major environmental changes in marine ecosystems, such as disruption of photosynthesis by marine vegetation, increases in mortality rates of benthic organisms and changes in marine biogeochemical cycles (Musk, Mendelssohn, bae).

In terms of remediation of large-scale oil spills, several physical, chemical and biological methods are available. However, with global climate and pollution issues rising, recent emphasis has been placed on the development of environmentally sustainable clean-up methods that follow green chemistry standards. Green chemistry is the use of sustainable, safe and non-polluting practices in chemical science, with the overall goal creating minimal waste while using the least amounts of energy and materials (Manahan). For example, one of the most common chemical and environmentally controversial tools used in large-scale oil spills are dispersants. When released, dispersants dilute large oil spills and disperse tiny oil droplets throughout marine environments, which can facilitate microbial biodegradation by providing them with a rich source of hydrocarbons (butler). On the other hand,

Numerous studies have taken place to understand the short and long-term impacts of large-scale oil spills in aquatic communities, such as the Deepwater Horizon Oil Spill. Only by fully understanding the impacts of oil in marine environments, advancements in effective, fast and economically feasible remediation methods can occur. This paper aims to summarize reported environments impacts of large-scale oil spills, review current clean-up methods and discuss current advancements in sustainable physical clean-up methods.

2. Results and Discussion

2.1. Environmental Impacts of Oil Spills

Large-scale oil spills have the potential to affect many aquatic communities and species.

2.1.1. Impacts in Coast Regions

Due to movement by winds and ocean currents, oil spills can alter a variety of aquatic communities by affecting the plant and wildlife species that live within them. Through examination of coastal benthic community changes before and after the *Deepwater Horizon* spill, major impacts have been reported regarding the community structure across the Gulf of Mexico (Bik et. all). Although the presence of oil is visibly absent, shifts from high species richness to low richness following the oil spill was found in fungal and nematode populations (bik). Changes in the benthic community structure could impact higher tropic levels, leading to alterations in food webs (bik). Another example needed to fully understand the impacts of oil spills on intertidal coastal regions is through evaluation of valuable mangrove wetlands. As oil is washed up into costal regions, it readily binds onto the oleophilic surfaces of mangrove vegetation, subsequently smothering, poisoning and killing them (Duke). Severity of the oil spill plays a large role in the likeliness of recovery in mangrove communities since oil impacts vary between species, in some cases communities can recover while others may not (Duke). Although environmental impacts have been found, it is not always the case that dramatic impacts in costal regions are reported following oils spill. For example, a study by Edgar and colleagues, that analyzed the environmental impacts of the *Jessica* oil spill on shore communities in the Galápagos Islands, found no detectable oil effects. The effects of oil spills depend heavily on the amount of oil spilled, weather conditions, prevailing winds and the composition of the shoreline community itself (Edgar 2003, Lin 2012).

2.1.2 Impacts of Mammalian Species

Large-scale oil spills can directly or indirectly impact mammals that live within or depend on aquatic environments. Direct effects include degradation of habitat and physical alterations resulting from direct contact with oil; while indirect effects include behavioral alterations and changes in prey availability (fingas, Ridoux ). However, the effects of oil spills on mammals heavily depends on species sensitivity, life stage, mobility and recovery potential (fingas).

Similar to other pollutants, there may be a risk of oil bioaccumulation in lower trophic levels that could indirectly affect mammalian food sources. For example, by feeding heavily contaminated mussel species from the *Erika* oil spill of the French Atlantic coast, DNA damage in the liver and bone marrow of rats was observed (lemiere). However, Lemiere’s study could not clearly assume that only the hydrocarbons found in the oil caused the DNA damage. Other contaminants, such as methyl chrysenes and thiophenes may have played a role in the damage observed in rats. On the other hand, some mammal species appear to be virtually unaffected by the *Erika* oil spill. Through assessment of mortality rates, trace elements and diet, no effects were observed in dolphin and seal populations along the coast of France (Ridoux). It is possible that this difference in oil spill affects can be related to the mobility of species. Mussels are relatively immobile, therefore facing the most effects from oil spills in aquatic environments.

2.2. Oil Remediation Methods and their Effects

When selecting appropriate clean-up methods that will remove the most amount of oil possible, the properties of oil must be considered in order to understand its behavior in aquatic ecosystems. As discussed earlier, the composition of oil plays a large role in its physical characteristics, such as viscosity, density and solubility (national research centre). For example, oils with high or low viscosity, do not readily form water-in-oil emulsions, which are known to drastically increase the volume of oil spills (Fingas 2012 not book). Composition and type are not the only challenging factors in oil spill clean-ups; additionally, weather and sea conditions should also be considered to select fast and effective methods (Hoang). Once the factors influencing the behaviour of oil in aquatic environments are identified, selection of appropriate physical, chemical and biological clean-up methods can be made.

2.2.1. Preventative Measures

Although they do not directly remove oil from aquatic environments, booms are typically the first step in oil spill remediation. Booms, resembling curtains that extend below and above waterlines, serve as a mechanical tool that contains and prevents spread of oil on water (Fingas). Blooms consist of several distinct sections which can be made from a variety of materials, such as nylon and polyester (fingas). There are generally three categories of blooms: fence, curtain and shoreline, with their effectiveness heavily depending on water currents, wind and waves.

2.2.2. In-situ Burning

In-situ burning is a time-efficient, one-step method that involves controlled burning of oil on water surfaces (fingas). Using fire-resistant booms, oil can be contained in a specific area and undergo repeated burnings (Betts). In-situ burning allows for less equipment, less labour and no secondary processing of oil tools, such as sorbents, to take place (fingas). In order for in-situ burning to be efficient, oil slick thickness was determined to be most affective between 10-22 mm, however, oil composition may play a role in maximum efficiency (Geldnen). Problems associated with in-situ burning is the production of large toxic smoke plumes and residues that can negatively affect surrounding wildlife and benthic environments (office of, fingas). For example, a study on seabird plumage found that along with fresh oil, in situ burning residues have a similar or even more negative effects (Rasmussen).

2.2.3. Skimmers

The first true physical method of oil remediation to be discussed is the use of skimmers on surface water. Similar to booms, the effectiveness of skimmers not only depends on weather and wind conditions, but oil heaviness and the amount of debris present also plays a large role (fingas). Several types of skimmers are available, such as oleophilic, weir and vacuum. Oleophilic skimmers are available in a variety of forms, such as belt, disk, and drum, however all essentially function in a similar way. The rotating surface of skimmers has adsorbent properties in which oil adheres to and is separated from surface waters (keller). Although oleophilic skimmers perform well in debris-filled and ice water, the process can be very time consuming and expensive (keller). Generally, the water-in-take of oleophilic processes are minimal since only the oil itself is bound the device (fingas). Unlike oleophilic skimmers, that depend on adsorbent characteristics of oil, weir skimmers use gravity to facilitate oil separation instead (cite?). In this form of oil remediation, oil on the surface of water is pulled and collected into storage tanks (hammoud). In most cases, weir skinners require calm waters and light to medium weight oils for maximum efficiency (fingas). Finally, vacuum skimmers are floating devices that suck oil from water surfaces and deposit it into a storage tank (epa). In most cases, vacuum skimmers perform better in calm waters, but can easily become clogged from debris in shallow waters (epa, fingas).

2.2.4. Sorbents

Through adsorption and absorption properties, sorbents are a form of physical and chemical methods that facilitate the change from liquid to semi-solid phases in oil spills, making contaminants easier to remove from aquatic environments (Saskikala). The goal of sorbent use is to remove oil from surface waters quickly and efficiently, to prevent oil accumulation in aquatic environments (Paulauskiene). Oil recovery and water in-take are two main factors that determine the efficiency, and therefore the use of specific sorbents in oil spill clean-ups (fingas). Generally, sorbents can be divided into three categories: organic, inorganic and synthetic, each with their own advantages and disadvantages. For example, synthetic sorbents are often used in oil spill clean-ups due to their oleophilic and hydrophobic properties (adebajo). In fact, synthetic sorbents often outperform organic and inorganic sorbents in oil recovery percentage, as shown in Table 1. Even with various oil types differing in weight, synthetic sorbents had oil recovery percentages of 90+, while inorganic and organic only reached 80+. Although naturally less efficient, many inorganic and organic sorbents can be treated to increase their oleophilic and hydrophobic properties (fingas). However, some problems are associated with sorbent use, such as post-processing of sorbent materials, reusability, sinking and durability (saskikala).

2.2.5. Dispersants

Dispersants are a form of chemical oil spill remediation, in which it’s effectiveness and environmental impacts are highly debated. Through injection into aquatic environments, dispersants reduce oil-size and stabilize small-sized droplets, enhancing the rate of oil biodegradation by bacteria (Respar). During the *Deepwater Horizon* oil-spill, more than 7 million liters of Corexit dispersants were released into the Gulf of Mexico (respare, kleindienst).

Many argue that the release of such large amounts of dispersants was unnecessary because of their lack of biodegradation stimulation and potential environmental effects. Under laboratory settings, Kleindienst and collogues examined the effects of dispersants on microbial communities and their degradation rates. Through measurement of alkane and aromatic hydrocarbon oxidation rates in crude oil, the researchers determined that the highest levels of degradation occurred without the use of dispersants. In fact, it was noted that dispersants negatively altered the microbial community by selecting against the most effective degrading organisms. Through assessment of degradation by alkane and aromatic bacterial cultures in crude and weathered oil, an experiment by Rahsepar supported Kleindienst. By using various dispersant to oil ratios, Rahsepar determined that increased aromatic solubility, facilitated by application of dispersants, led to higher aromatic concentration in water. Inhibition in degradation of these aromatic compounds took place when aromatic degrading organisms were not present, leading to inhibition of oil degradation. Rahsepar concluded the composition of the bacterial community in aquatic environments is the main factor in oil degradation and that addition of oil dispersants can inhibit degradation.

Conversely, Kleindienst’s experimental method was criticized for testing degradation only by using oil floating on water surfaces, since this is rarely the case in aquatic environments (prince1). In terms of other studies, Prince also argued that many, are not carried out long enough and that the oil used are in such low concentrations that it can be easily dispersed, thus allowing rapid degradation without using dispersants. Prince argued that in order to accurately test the effects of dispersants on oil degradation, experiments should compare degrading between dispersed oil in the water column and oil floating on water surfaces. By comparing untreated oil floating on surface waters and dispersant-treated oil in the water column, Prince concluded that dispersants highly stimulate the rate of biodegradation with additions of dispersants.

2.3. Sustainable Advancements in Oil Spill Remediation

Of the available remediation methods for large-scale oil spills that could, sorbents seem to be the most promising in terms of green chemistry. The research and development of many reusable sorbents appears to be on the rise and will be discussed in this section.

2.3.1. Synthetic and Natural Sorbents

Recently, the use of natural, renewable sorbents has been highly studied in green chemistry literature. Cork, being one of the more recently studied and promising sorbents, has been found to be a successful alternative for sustainable oil clean-up. Cork, that is heat and pressure treated to increase its hydrophobic and absorption properties, is derived naturally from the bark of the Cork Oak (Fonseca). By comparing the sorption of corks cells with oils varying in viscosity, Todescato et al. determined that as viscosity increased, so did the capacity of cork recovery, making it suitable for heavy oil clean-ups, such as lubricating oil. The researchers also determined that even when mechanically compressed and reused up to 30 times, the oil recovery in the cork cells remained high at approximately 80%. However, when compared to cotton and polypropylene sorbents, cork was outperformed in both sorption rate and capacity, but had better oil retention and floatability (Abreu). Other natural sorbents of interest which have been involved in recent research include peat, straw, wool and moss. When comparing the sorption capacity of these various natural sorbents and their composites in different oil-type spills, Paulauskiene and Jucike determined that each behaved very differently. While in crude oil, wool had the highest sorption capacity, compared to peat having the highest sorption capacity in diesel oil (cite?). When composites were evaluated, the straw/peat sorbent, with a ratio of 1:4, absorbed approximately 65% of both crude and diesel oil. From the research of natural sorbents, it can be concluded that their use is heavily dependent on oil type, their behaviour in water and availability of materials.

Perhaps, another method to clean-up oil spills in an environmentally sustainable manner, is through alteration of existing sorbents. As stated earlier, synthetic sorbents tend to be selected over inorganic and organic sorbents because of their oleophilic and hydrophobic properties. Through bulk polymerization of glycerol propoxylate and ICS monomer cross-linkers, a more efficient sorbent gel, in terms of sorption capacity, sorption time, specificity and reusability, was created (kizil). What makes this research significant in a green chemistry perspective, is that Kizil and Sonmez synthesized this highly efficient sorbent without the use of initiators, activators, solvents or catalysts. Another example of sorbent alteration is the through successive treatment with silica sol and gasoline to create a highly efficient sorbent from inexpensive and readily available polyurethane sponges (Wu). Wu and collogues found this new sorbent to have high sorption capacity in various oil-types, while absorbing negligible amounts of waters. The modified polyurethane was also found to be reusable up to 15 times, with approximately 70% sorption capacity remaining. Finally, synthetic sorbents developed from industrial wastes has also been explored. In 2018, a polysulfide polymer sorbent was created from sulfur waste and unsaturated cooking oils (Worthington). Worthington and collogues determined this new sorbent to have high sorption rates, high sorption time and easy reusability. Of the synthesized sorbents available, the polysulfide sorbent appears to be the most promising in sustainable chemistry, due to its low-cost, high efficiency and origination from industrial wastes (cite?).

Finally, sorbent booms, similar to regular booms, are used to contain large-scale oil spills while also absorbing or adsorbing contaminants through the use of sorbent materials on their surface (fingas). Although there has been a recent interest of organic/natural sorbents, there appears to be a lack of literature regarding the use of sorbents in mechanical booms. For example, an experiment by Pagnucco and Phillips found that hair used in sorbent booms were more efficient and had a higher sorption capacity than several sorbents, including the synthetic and popular sorbent, polypropylene. On the other hand, the experiment also confirmed the beneficial hydrophobic properties of synthetic materials, as polypropylene was found to absorb less water compared to the hair boom. In terms of green chemistry, this study confirms the comparability of natural sorbent booms as a sustainable alternative to synthetic booms, therefore more research in this area should be take place

When making environmentally conscious decisions, trade-offs, such as oil sorption rate, capacity, and retention, can influence the selection of synthetic and natural sorbents in oil spill remediation. In some situations when oil spills need immediate remediation, natural sorbents may be better suited compared to synthetic sorbents, that may need to be synthesized. On the other hand, highly efficient and reusable sorbents may only be achieved through synthetization. Nevertheless, development of sustainable clean-up materials seems to be well underway with potential in making selection between sustainable and non-sustainable methods obsolete.

4. Conclusions

As discussed, numerous oil spill remediation methods exist, such as skimmers, sorbents and dispersants. With recent global emphasis on environmentally sustainable procedures in all forms of chemical processing, the improvement of physical methods seems the most feasible and acceptable for large-scale oil spills. However, several variables apply that determines which sorbent material can be used, such as water conditions, oil type and local rules and regulations. There seems to be many trade offs associated with sustainable methods, such as reduced oil sorption vs. better oil retention in cork sorbents, that can influence the selection of materials.

This section is not mandatory, but can be added to the manuscript if the discussion is unusually long or complex.

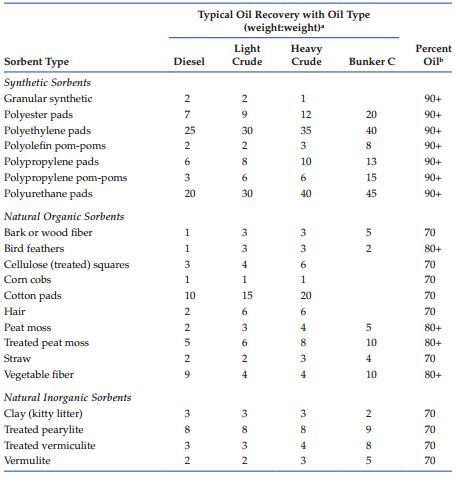
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In the text, reference numbers should be placed in square brackets [ ], and placed before the punctuation; for example [1], [1–3] or [1,3]. For embedded citations in the text with pagination, use both parentheses and brackets to indicate the reference number and page numbers; for example [5] (p. 10), or [6] (pp. 101–105).

1. Author 1, A.B.; Author 2, C.D. Title of the article. *Abbreviated Journal Name* **Year**, *Volume*, page range.
2. Author 1, A.; Author 2, B. Title of the chapter. In *Book Title*, 2nd ed.; Editor 1, A., Editor 2, B., Eds.; Publisher: Publisher Location, Country, 2007; Volume 3, pp. 154–196.
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   (under review; accepted; in press).
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32. rasmussen <https://www.sciencedirect.com/science/article/pii/S0025326X16303307>
33. keller<https://pubs.acs.org/doi/pdf/10.1021/es061842m>
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45. Kleindienst <https://www.pnas.org/content/112/48/14900>
46. Prince<https://www.jstor.org/stable/pdf/26468706.pdf?refreqid=excelsior%3A61fa8989815309349dd0d73162930413>
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Appendix

Table 1. Oil recovery of different types of sorbents.



There is no page limit for the Appendix section. The appendix is an optional section that can contain details and data supplemental to the main text. For example, explanations of experimental details that would disrupt the flow of the main text, but nonetheless remain crucial to understanding and reproducing the research shown; figures of replicates for experiments of which representative data is shown in the main text can be added here if brief, or as Supplementary data. Mathematical proofs of results not central to the paper can be added as an appendix.

2.2. Figures, Tables and Schemes

All figures and tables should be cited in the main text as Figure 1, Table 1, etc.

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**Figure 1.** This is a figure, Schemes follow the same formatting. If there are multiple panels, they should be listed as: (**a**) Description of what is contained in the first panel; (**b**) Description of what is contained in the second panel. Figures should be placed in the main text near to the first time they are cited. A caption on a single line should be centered.

**Table 1.** This is a table. Tables should be placed in the main text near to the first time they are cited.

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| --- | --- | --- |
| **Title 1** | **Title 2** | **Title 3** |
| entry 1 | data | data |
| entry 2 | data | data 1 |

1 Tables may have a footer.

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**Table 2.** Parameters for chemical structures.

|  |  |
| --- | --- |
| **Item** | **Parameter** |
| **Drawing Settings** | |
| chain angle | 120 degrees |
| bond spacing | 18% of length |
| fixed length | 14.4 pt (0.2 in.) |
| bold width | 2.0 pt (0.0278 in.) |
| line width | 0.6 pt (0.0083 in.) |
| margin width | 1.6 pt (0.0222 in.) |
| hash spacing | 2.5 pt (0.0345 in.) |
| **Text Settings** | |
| page setup | US/Letter/Paper |
| scale | 100% |
| font | Helvetica (Mac), Arial (PC) |
| size | 10 pt |
| **Preferences** | |
| units | points |
| tolerances | 3 pixels |

2.4. Formatting of Mathematical Components

This is an example of an equation:

|  |  |
| --- | --- |
| a = 1, | (1) |

the text following an equation need not be a new paragraph. Please punctuate equations as regular text.

Theorem-type environments (including propositions, lemmas, corollaries etc.) can be formatted as follows:

**Theorem 1.** Example text of a theorem. Theorems, propositions, lemmas, etc. should be numbered sequentially (i.e., Proposition 2 follows Theorem 1). Examples or Remarks use the same formatting, but should be numbered separately, so a document may contain Theorem 1, Remark 1 and Example 1.

The text continues here. Proofs must be formatted as follows:

**Proof of Theorem 1.** Text of the proof. Note that the phrase ‘of Theorem 1’ is optional if it is clear which theorem is being referred to. Always finish a proof with the following symbol. □

The text continues here.