APP4SEA

ARCTIC PREPAREDNESS PLATFORM

FOR OIL SPILL AND OTHER ENVIRONMENTAL ACCIDENTS

APP4SEA Climatic zones in the NPA region March 2020

University of Oulu/Water, Energy and Environmental Research & **Norwegian Meteorological Institute**/Oceanography & Marine Meteorology

Existing oil weathering databases for Arctic marine conditions

Project report

Victor Pavlov, Lars R. Hole, Niko Hänninen

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The 21st century brought unprecedented interest in the Arctic resources, turning the region from the world's unknown periphery into the centre of global attention.

Within the next 50 years, local coastal communities, their habitual environment and traditional lifestyle is expected to undergo severe changes, caused by climatic perturbations, petroleum industrial intervention and increased shipping presence.

The APP4SEA project, financed by the Northern Periphery and Arctic Programme will contribute to environmental protection of the Arctic waters and saving the habitual lifestyle of the local communities. It will improve oil spill preparedness of local authorities and public awareness about potential oil tanker accidents at sea.

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Summary

This report introduces oil weathering processes, and states why knowledge of those in case of oil spill response is important. An example study of crude oil from the northern part of the North Sea is demonstrated. Its physical and chemical properties are listed in an extract from the study, giving an understand which ones are the most crucial for oil behaviour in water. The properties also serve as input material to software tools developed in order to forecast oil spill drifting scenarios and showcase oil mass balance. The tools provide visual materials such as graphs and maps, where oil spill response authorities can observe the incident and prepare all necessary equipment to respond it. One example of such tool is described in the report. The tool is open access and can be used worldwide.

Introduction

As it originates from the core of the word, "weathering" is all possible climatic processes and phenomena, which can happen to oil spill at sea to transform it to one or another form. It is not only weather as we deal with usually – precipitation, wind, sunshine, and temperature, but also several other processes of mostly physical and chemical nature, related to the sea and its inhabitants. It has two main components: one being the biological component, for example, bacteria, plankton, larger marine organisms; and the other - lifeless component mostly represented by purely physical substances such as air, water, and mineral solids. The complete set of weathering processes considered in the oil spill response field are spreading, evaporation, dispersion, emulsification, dissolution, oxidation, sedimentation and biodegradation. This report will give an overview of all of them: one by one. It will also demonstrate with a concrete example how important it is to understand what happens with oil slick in water, and how it can possibly transform during time. There are multiple collections of such weathering studies available worldwide. Each of them has a set of tabled data that includes such parameters as physical and chemical properties of oil. In addition, there is also computer software processing those properties as inputs and producing results with visible weathering characteristics and oil behaviour. The last section of the report will include description of one of them – being an open access oil weathering tool developed by the US National Oceanic and Atmospheric Administration.

This work has been carried out as part of the Arctic Preparedness Platform for Oil Spill and other Environmental Accidents (APP4SEA) project financed by the Northern Periphery and Arctic Programme (NPA) during 2014-2020. NPA is a European Regional Development Funding instrument and it involves remote communities of Northern Europe and aims to facilitate its sustainable development with related social, economic and environmental benefits. Fig. 1 shows the partners and the four countries which are represented in the project by them. The partnership consists of University of Oulu & Finnish Environment Institute (Oulu & Helsinki, Finland); Norwegian Meteorological Institute & Norwegian Coastal Administration (Bergen & Tromso, Norway); University of Iceland (Reykjavik, Iceland); North Highland College, Scottish Natural Heritage & Marine Scotland (Thurso, Inverness, & Aberdeen, Scotland). The lead partner is the University of Oulu (Finland).

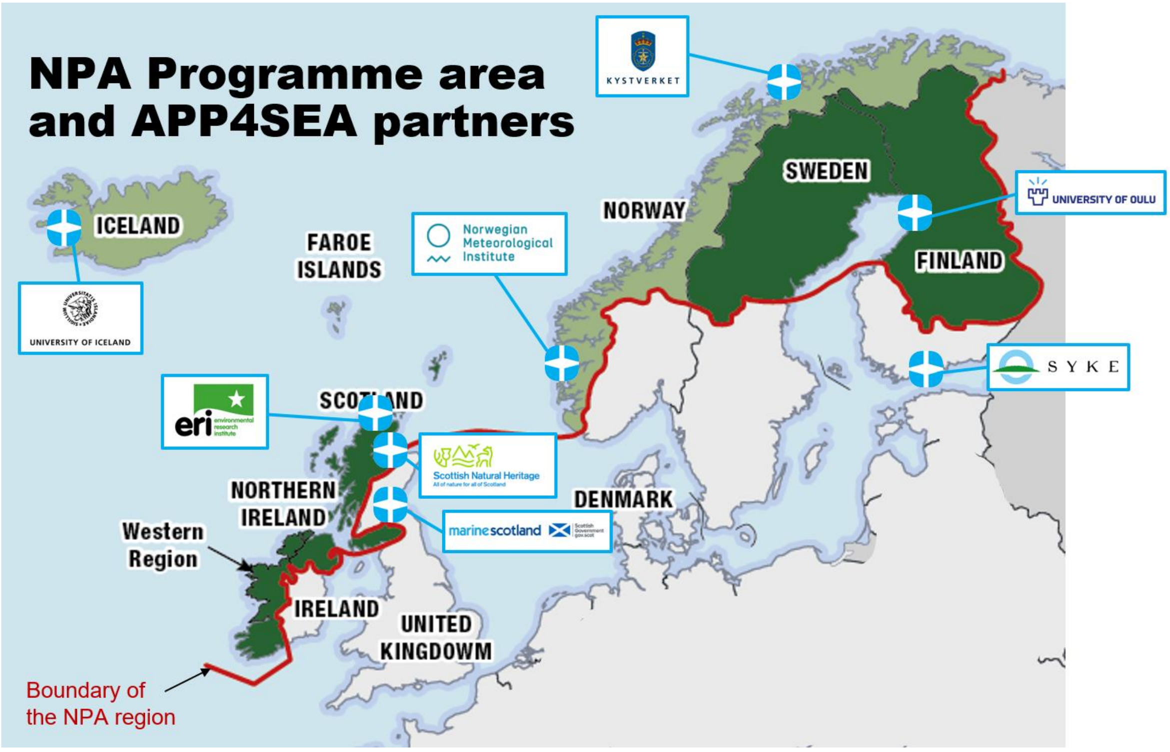

Fig. 1 - NPA programme area and APP4SEA project partners.

Oil weathering

Main weathering processes

Weathering, as a sum of processes, can be put in the following abbreviation: SEDEDOBS. In the description below, we will go letter by letter with elaboration on each (ITOPF, 2018). Fig. 2 helps in demonstration of those processes.

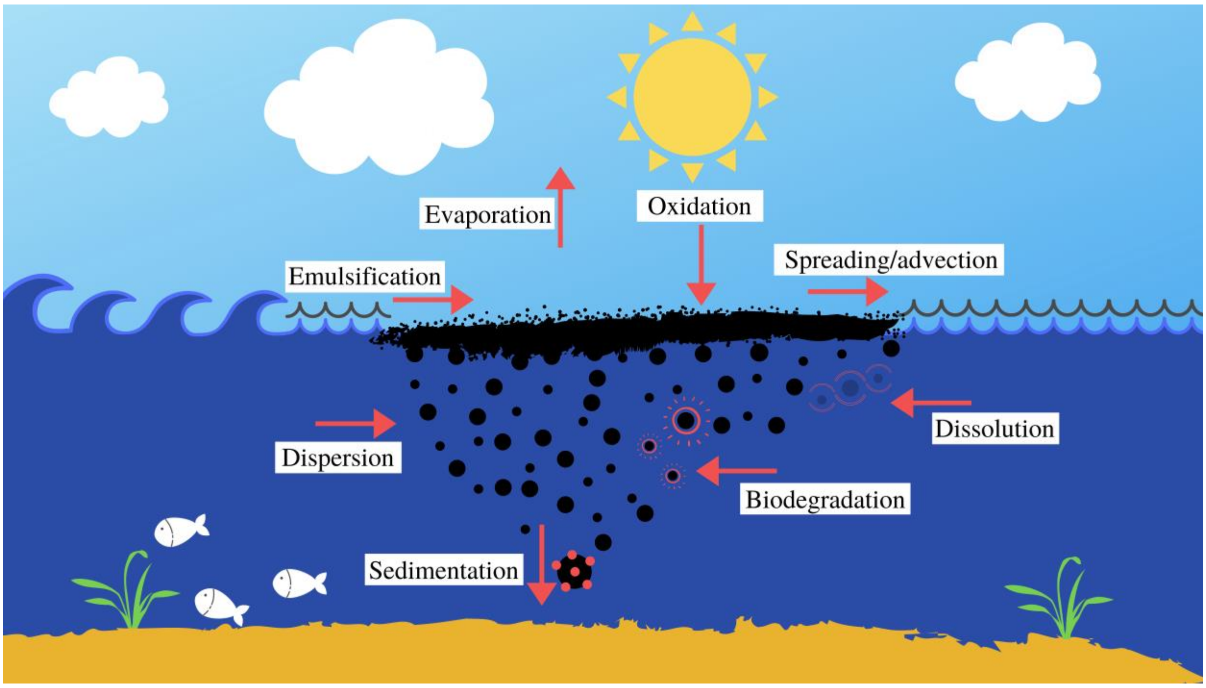

Fig. 2 - Physical and chemical processes known as weathering of oil.

S-*spreading*. This is the very first process that starts immediately when oil reaches any surface: be it water, or any solid form. Depending on oil type, it can spread fast or slow. This has to do with oil physical properties such as density or viscosity. For instance, oil of light density spreads faster, the one that is highly dense – slower. If we give a visual illustration, compare two examples: vegetable oil and fresh honey. Both have the state of liquid, but the way they flaw on the flat surface of plate are different. The same happens with petroleum substances. At sea this process depends on water temperature. The warmer the ambient medium where oil spreads, the faster, easier and broader oil flaws, moves and travels around its surface. The spreading pattern of oil at sea is rarely ideal or has certain standard type of shape, as it could be on the plate example with honey and vegetable oil. In nature, it is rather atypical, unique and varies in thickness, forms and unity. One slick can break in pieces, drift apart or it can stay as one slick body. This mostly depends on influence of surrounding wind and sea currents conditions.

E-*evaporation*. This feature of oil behavior is defined by its volatile ability. The more of volatile components are in the chemical compound of oil, the better it evaporates at the location of the accident. As a general rule, the lighter (with low density) oils and oil products, such as car fuel – benzene or diesel, and aircraft fuel – kerosene, are more prone to evaporate than the heavy ones: for example, heavy fuel oil. When dealing with lighter oils, you can easily recognize them by smell. Those are the volatile substances you feel immediately at the gas station. In fact, in some oil spill response operations where in situ burning is involved, it is strictly forbidden to be close to the spill of lighter oil products. Usually highly volatile products are also highly ignitable. This is also why smoking is not allowed at gas stations. When we talk about evaporation, it starts at the same time as spreading of oil. Both processes are 90% completed within the first day of the accident. After 24 hours only minor parts of the oil slick continue to spread and evaporate. The correlation with spreading is also connected to the available surface area of slick. Rougher seas, higher outdoor temperatures and windy conditions also tend to contribute to the evaporation process.

D-*dispersion*. Mostly driven by wave energy and sea turbulence, this weathering process is about whole oil slick being torn apart into droplets of various sizes. If we consider a water column of 50 m at sea, some of those oil droplets remain on surface, some – will be suspended. The state or their position depend on size of the droplets. The larger ones tend to resurface and reform the slick, whereas small ones stay suspended in the water column, being disperse in its body. Calm seas precondition less dispersion to occur, rough seas – more. If we come back to examples from evaporation sub-section, car fuels will disperse much easier than ship fuel. The heavier the oil, the more likely it stays as a one piece in water, being persistent and hard to break part.

E-*emulsification*. The most common example of emulsion is the mixture of vegetable oil and water. When stirring it together, oil becomes dispersed, but it will never mix with water. The same happens at sea during oil spills. This phenomenon is described as oil-in-water (o/w) emulsion. When oil incorporates water in its body, water-in-oil (w/o) emulsions are created. Those are highly viscose and persistent, almost as heavy fuel oils, and make oil slicks larger in size due to additional volume of water. Formation of emulsions is mostly caused by mixing wave energy at sea. At stormy conditions, emulsification in both directions (w/o and o/w) are highly probable.

D-*dissolution*. Some oil chemical chains dissolve organically in the sea water. When oil becomes highly available in the form of droplets providing high surface area, it is easily dissolved, especially if the droplets have soluble components. This process is however known as a rather weak weathering process. Evaporation and dissolution usually dissolve or evaporate exactly the same volatile/soluble compounds as the other process of both. Evaporation is 10 to 1000 times faster than dissolution.

O-*oxidation*. This process is highly dependent on solar UV-radiation, or solar light. But even in tropical regions oxidation can only break down 0.1% of the oil film into soluble compounds. When 1 kg out of 10 tons is solidified, dissolution takes places in turn.

B-*biodegradation*. When the oil is dispersed in the water, it becomes available for bacteria that feeds on hydrocarbon molecules. The availability is enhanced by increased surface area of oil. For higher organisms, it is cloud of toxic "spray". Those oleophilic micro-organisms now take their role in oil weathering and digest its parts as a source of energy. They biologically turn toxic compounds into water soluble ones, eventually producing carbon dioxide and water. Heavy oil types biodegrade more slowly and sometimes do not degrade at all rather than light or medium oils and oil products. One factor is that oil type should match oil-feeding bacteria "taste". There is no unique species that can feeds on all oil types. Also, besides oxygen, oil degraders need well-balanced amounts of nitrogen and phosphorus. According to Vergeynst, *et al*., 2018, their levels should correlate as 16-to-1, N-to-P. Temperature is also important factor but not limiting. Biodegradation appears in both temperate and polar environments, as natural oil seeps occur in all oceans, the Arctic Ocean included.

S-*sedimentation/sinking*. After the oil has spread, emulsified and weathered, it is a very dense and viscose substance. This generally means that there are heavy, persistent, and chemically complicated components of oil left in spill residue. This dense material can either connect with shoreline sediments and be attached with sand particles and stay there, or they can sink in the ocean, when its density becomes much larger than the seawater around it.

SEDEDOBS occurs with any known oils and oil products. Therefore, each of those substances, which may potentially appear at sea is studied in advance with the following focus: how the weathering will take place in certain marine environments. In the oil spill response industry, the terms "oil behavior" or "oil fate" are also used.

Natural sea pollution with oil happens regularly and globally, about 600,000 m^3 or 47% of all crude oil entering the global marine environment. It is in the form of oil seeps from the ocean bottom caused by certain geological formations, which create favorable conditions for such leakages. Examples of such formations can be continental margins or bottom sites with overpressure conditions in the sedimentary basin. (Kvenvolden & Cooper, 2003) The remaining 53% of marine contamination cases with oil is man-made. These are related to industrial stages of extraction, transportation, refining, storage, and utilization of petroleum. One of the most famous examples of pollution disaster is from 2010 and the Gulf of Mexico – Deepwater Horizon platform blowout. One of the first major oil spill accidents with oil carrying vessels is from 1967 and the Celtic Sea - Torrey Canyon grounding. Luckily, there was no major oil spill yet in the Arctic Ocean.

Example of an oil weathering study

To give an example, imagine the following situation. A new oil is discovered in the North Sea. Before the industry actually starts the extraction and its transport overseas, it has to first carry out a series of laboratory analysis with the crude oil. Its weathering properties must be studied in advance to be prepared for a contingency. This is a requirement from the Norwegian Environment Agency and the government of the country.

Among known conditions for the study are type of oil and its properties, and environmental data of the sea it might end up: in this case – the North Sea. The only thing that is left is to input the known physical and chemical oil properties (density, pour point, asphaltene content, etc) into a specially designed software and observe how the oil will behave in those conditions. In short, this is a story how each oil sample is studied and documented to help oil spill response operations.

As an example of such a study, let us consider Oseberg Øst crude oil, found in the northern part of the North Sea. It was tested by SINTEF (Vadla & Sörheim, 2013). Weathering properties were studied at 5 and 13^{o}C. Here are some conclusions:

"Oseberg Øst is a medium density (0.842 g/ml) paraffinic crude oil, with medium asphaltene (0.5 wt. %) and medium wax content (4.9 wt. %), resulting in a relatively high evaporative loss. The evaporation after an oil spill will cause an increase in the relative amount of wax and asphaltene. As the relative concentration of heavy end components increases, the physical properties of the oil will change. Some vessels engaged in oil recovery operations may not be classified to carry liquids with flash point <60°C (e.g. towing vessels, smaller cargo or vessels available in the emergency situation). At low wind speed (2 m/s) this limit will be reached in approximately 6 hours in winter conditions and 3 hours in summer

condition for Oseberg Øst crude. The flash point limit will be reached considerably faster at higher winds.

As oil is spilled on the sea surface, the temperature of the oil will be cooled to ambient water temperature within a short period of time. The fire hazard will be at its greatest as long as the flash point of the oil is below the sea temperature. For Oseberg Øst crude the flash point will be above the sea temperature within a few minutes at winter temperature, and earlier at higher wind speeds. In summer condition, at low wind speed of 2 m/s, within 15-30 minutes. Experiences from Norwegian field trials have shown that the efficiency of different mechanical clean-up operations is reduced due to high degree of leakage of the confined oil or w/o-emulsion from the oil spill boom. This leakage is particularly pronounced if the viscosity of the oil or the w/o emulsion is lower than 1000 mPas. It should be emphasized that boom leakage is also influenced by other factors as e.g. the operational speed of recovery vessel and weather conditions. The viscosity of Oseberg Øst remains beneath this limit for approximately <1 hour under winter conditions and 6-7 hours in summer conditions at calm weather conditions (2 m/s wind speed). At higher sea states, this limit is reached considerably faster.

Studies have shown that both weir skimmers and adsorption skimmers may have reduced recovery effectiveness at viscosities above 15-20 000 mPas. This viscosity limit is predicted to reach its limit in winter condition after 9 hours weathering at the sea surface at 15 m/s wind speed. In summer condition this limit is reached after 4 days weathering at high wind speed (15 m/s). Oseberg Øst forms stable w/o- emulsions (approx. 72 vol. % at 5°C and 80 % at 13 °C) and will lose nearly no water in 24 hours settling, even after several days at sea. Emulsion breaker will, however, be effective and more effective at 2000 ppm compared to 500 ppm. The highest concentration of emulsion breaker will settle out approximately 40 % of the water emulsion, even several days weathering at sea in summer conditions. When high viscosity of the oil/emulsion is not the limiting factor, high pour point could cause solidification of the oil on the sea surface. Oseberg Øst's relatively high pour point could possibly imply solidification at the sea surface.

Oseberg Øst is expected to have a high potential for chemical dispersion, particularly in summer condition. The oil/emulsion is chemically dispersible up to 1-2 days at 10 m/s at 5 °C, and chemically dispersible more than 5 days at 10 m/s at 13 °C. When the oil is expected to have reduced dispersibility (between 3 000 mPas and 35 000 mPas), additional energy by use of e.g. thrusters, fire fighting systems or man over board boats, or use of a higher dosage rate (dispersant to oil ratio) and/or repeated dispersant application, may increase the effectiveness."

Such studies provide sufficient information and improve preparedness for maritime oil spill incidents. Usually the time required to conduct the study is in scale of days. When dealing with real case, provided there is a lack of weathering data and descriptive information about oil properties, it is more difficult to react and operate efficiently during the emergency.

Database of oil weathering studies

Once oil is tested, the data are provided to a database of similarly studied samples. This is an approach used in Norway. The US Automated Data Inquiry for Oil Spills (ADIOS) database contains data of well-described physical and chemical properties of more than a thousand different crude oils and refined products. More info on ADIOS is available at NOAA web pages. In this report, we only mention the database it uses for its calculations and what visual weathering data it provides.

Only a few of all weathering processes are currently visualized with ADIOS or other computer programs. The latter is explained by current scientific development and existing technological limitations of the applied software. As a result, we have graphs similar to one presented in Fig. 3, based on simulations by OpenDrift. (GitHub, 2020)

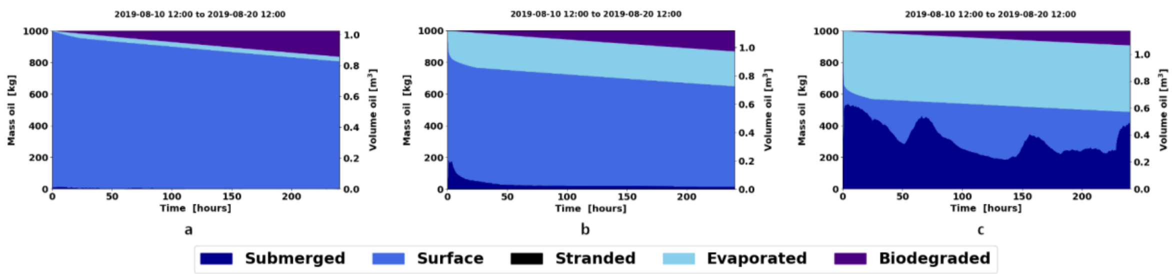

Fig. 3 – Mass balance from OpenDrift simulation of three different oil types.

It shows three types of oil. Heavy crude is represented by IFO-180LS [2014] (diagram "a" on the left), medium crude – by VOLVE [2006] (diagram "b" in the middle), and light oil – by MARINE DIESEL [ESSO] (diagram "c" on the right). They are compared by their weathering properties mentioned at the bottom of the figure with colour code. This helps to see how much of initial oil mass was submerged, surfaced, stranded, evaporated or biodegraded. The figures illustrate hypothetical 10-day spill incident of 1,000 tons of oil, which took place in August 2019, from 10th to 20th of the month. For example, on day 5 or 120 h, approximately 3% of heavy oil evaporated, one tenth – biodegraded, and the rest, which is more than 85% - surfaced. In contrast, marine diesel on day 5 is about 56% evaporated, 30% surfaced, 20% submerged and 4% biodegraded. This means that due to evaporation, for instance, heavy oil lost from the initial 1,000 t only 30 t, whereas marine diesel lost 560 t. Thus, data on oil behaviour in water is essential.

Conclusion

This report gives an overview of oil weathering processes and demonstrates their importance with example on Oseberg Øst crude oil from the North Sea. Knowledge of oil physical and chemical properties and its behaviour in water is crucial and required when developing operations on oil spill response at sea. Supported by oil weathering studies and visualized graphs of oil behaviour at sea, it is possible to conduct operations in time, with adequate forces and carrying suitable response equipment.

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Contact:

Niko Hänninen

Energy and Environmental Engineering Research Unit

University of Oulu

OULU

FINLAND

Tel: +358 40 704 5512

niko.hanninen@oulu.fi

http://app4sea.interreg-npa.eu

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