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15. Supplementary Notes

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16. Abstract (MAXIMUM 200 WORDS)

Many crude oils and fuel oils are flammable and pose a significant fire hazard if not handled properly. When an oil is accidentally spilled and exposed to the environment, the flammability characteristics of the oil can change significantly as it evaporates. A numerical weathering model that simulates the weathering and consequent changes in flammability was developed. The time required for a representative group of flammable oils to weather to a non-flammable state under various spill conditions was estimated. The effects of the level of mixing caused by environmental factors were closely examined.

Results of simulations indicate that flammable crude oils weather very slowly when there are no natural mixing mechanisms at work. In these cases weathering times are very sensitive to the thickness of the oil. In contrast, if there are effective mechanisms for mixing the oil, it weathers much more quickly and the weathering time is less sensitive to thickness.

Simulations indicate that flammable fuel oils are less likely to become non-flammable during weathering. Weathered gasoline remains flammable until it is almost completely evaporated.

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EXECUTIVE SUMMARY

When a common petroleum product spills in the marine environment, it begins to evaporate and a flammable atmosphere can form over the spill. U.S. Coast Guard (USCG) Vessel Response Plans (33 CFR 155) require responding vessels to be on site at a spill within two hours after detection and that booms are deployed within one hour. While this rapid response time is needed to minimize the spread of the spill, there is an inherent danger of explosion and fire due to the natural volatility and flammability of the spilled oil and petroleum products. This effort focused on developing a weathering tool which would benefit the Coast Guard by providing the technical foundation and guidance in these situations, and could be used to support a rule-making project for oil spill response vessels, ensuring the safety of response personnel.

Exposure to the marine environment can result in rapid changes to the oil's composition and, consequently, the oil's flammability. An oil slick will remain flammable until it weathers and loses its volatile components. Evaporation is the dominant weathering process responsible for changes in composition during the first few days following a spill. This study employed numerical modeling to examine how the evaporation and flammability characteristics of some representative flammable oils change after a spill in a confined area, such as a boomed area in a harbor. The model results predict how much time must pass from the time of an oil spill until the oil slick is no longer flammable.

The flash point of an oil is the temperature at which there is sufficient airborne concentration of the oil to be ignited by a spark or other ignition source. Flash points are commonly used to assess flammability hazards associated with oils that are transported. The Code of Federal Regulations uses flash points as the basis for grading liquids that are transported. Grade D and E liquids have flash points greater than 26.7°C (80°F) and are not considered flammable (U.S. Coast Guard, 1997). The flash point alone is not adequate to describe the flammability hazard associated with an oil in the environment, since the effects of wind and oil thickness can reduce the flammability hazard for oils while on the water. However, flash points are useful indicators of the dangers inherent in handling oils recovered from a spill. If the flash point of an oil is below the ambient temperature, the vapors in a vessel containing the oil may form a fuel-air mixture that can be ignited by a spark or other ignition source.

The numerical model developed for this study was specially constructed for oil slicks confined by booms and in fairly calm waters (i.e., in a harbor.) This model was used to simulate oil evaporation and flash point changes for cases where sufficient mixing from wind and sea occurs to keep the oil homogeneous (well-mixed oils), and for cases where there was no mixing and the conditions are calm. These represent the extremes of mixing that possibly occur in a spill and bound the operational conditions. The time required for some representative flammable oils to weather to Grade D, flash point reaching or exceeding 26.7°C (80°F), were computed for various conditions of mixing, temperature, and slick thickness. The weathering of five flammable crude oils and gasoline were modeled. It was not necessary to model diesel fuel since it is not a flammable liquid in an unweathered state. The weathering times were generally very sensitive to the thickness and to the level of mixing.

All five stratified crude oils thicker than one centimeter, except Avalon at 30°C, were predicted to take over 100 hours to weather to Grade D. In contrast, the same five crude oils under well-mixed conditions weathered to Grade D in less than three hours. This study indicated that flammable crude oils in thick slicks under calm conditions lose their volatile components very slowly and remain flammable for days following a spill. Crude oils that spread thin in open-water spills, or those effectively mixed by wave action, lose their volatile components in a matter of hours.

For gasoline, this study predicted that even after most of the gasoline evaporates, it remains a flammable mixture. Given the uncertainties in the models and the variability of gasolines, it seems prudent to treat all weathered gasolines as flammable liquids.
The results of the information obtained in this study will be used to write standards for classifying oil spill response vessels that work in flammable atmospheres during various types of fuel or oil spills. This information indicates how long various crude oils, diesel

and gasoline are flammable or explosive after the spill, and therefore, how much precaution must be taken in vessel design to preclude explosions, ignition or fire when the vessel is exposed to vapors.