

Weathering Processes and Time Scales

The physical and chemical characteristics of petroleum change almost immediately when spilled in the marine environment due to evaporation, dispersion, emulsification, dissolution, oxidation, sedimentation, and biodegradation. All of these processes interact with each other and are collectively referred to as *oil weathering*. The table following describes some of the weathering processes and the time scales of those processes important for emergency response.

Weathering processes and time scales important for emergency response

| Weathering Process | What is It? | Why is it Important? | Time Scales |
|--|---|---|---|
| Evaporation | Conversion of liquid to a gaseous phase. The lighter fractions in the oil are lost first. | Major process that accounts for the loss of oil, particularly light oils. At 15°C, gasoline evaporates completely over a 2-day period, 80% of diesel fuel evaporates, 40% of light crude, 20% of heavy crude, and only about 5-10% of Bunker C. | < 5 days |
| Emulsification, or formation of mousse | Very small water droplets are mixed into the liquid oil. Water content often reaches 50-80%. Occurs on water, needs some wave action. | Can increase the amount of pollutant to be recovered by a factor of 2-4. Slows down other mixing processes. | Onset can be delayed for days but the emulsification process happens rapidly. |
| Natural dispersion | Breakup of an oil slick into small droplets that are mixed into the water by energy. | Removes the oil from the water surface. | < 5 days |
| Dissolution | Mixing of the water-soluble components of oil into the water. | The most water-soluble components of oil are most toxic. | < 5 days |
| Biodegradation | Breakdown of oil by microbes into smaller compounds, eventually to water and carbon dioxide. | Rate depends on oil type, temperature, nutrients, oxygen, and amount of oil. | weeks to months |
| Formation of tarballs | Breakup of slicks of heavy crudes and refined oils into small patches that persist for long distances. | Tarballs are hard to detect, so the slick appears to be going away though it is still a threat. | days to weeks |

Percent evaporated over time for an instantaneous release of 100 barrels with winds at 10 knots and water temperature at 20°C

| | % Evaporated | Hour |
|-----------------|---------------------|-------------|
| Gasoline | 94 | 1 |
| Lagomedio | 38 | 18 |
| Diesel fuel oil | 37 | 18 |
| Prudhoe Bay | 28 | 70 |

Evaporation

Evaporation can be a major mechanism for removing oil. The amount evaporated depends chiefly on the oil properties, the wind speed, and the water temperature.

Generally, light refined products, like gasoline or jet fuel, evaporate faster than heavier products, such as heavy crude oil. From the table, you can see that most of the gasoline evaporates within a few hours. Lagomedio and Prudhoe Bay crude oils are more persistent in the environment and have much lower evaporation rates, 38% and 28%, respectively. After 120 hours, much of the product would be expected to remain on the water surface.



Dispersion

Breaking waves can drive small droplets of oil into the water column. If the droplets are small enough (diameters less than 50-70 microns) natural turbulence in the water will prevent the oil from resurfacing, just as turbulence in the air keeps small dust particles afloat. The smaller droplets that stay in the water column are considered dispersed.

Dispersion can be a mechanism for removing oil from the water surface. The amount dispersed depends on the oil properties (the viscosity and surface tension, in particular) and water conditions.

Oil products with low viscosity, like gasoline or kerosene, are more likely to disperse into the water with breaking waves than a high-viscosity oil, like an IFO 380 or Oficina heavy crude. Therefore, the dispersed fractions of gasoline or kerosene can be relatively large in heavy seas.

A possible treatment of oil spills is to spray the slick with chemical dispersant. Chemical dispersants enhance natural dispersion by lowering surface tension. This guide does not address subsurface oil movement because of the difficulty in developing a trajectory analysis of dispersed oil.

Sample oil solubilities

| Oil | Aqueous Solubility (mg/L)* |
|-------------------|-----------------------------------|
| Unleaded gasoline | 260.9 |
| Diesel | 60.4 |
| Prudhoe Bay crude | 20.5 |
| Lagomedio | 10.0 |

*Jokuty, P., S. Whiticar, Z. Wang, M. Fingas, B. Fieldhouse, P. Lambert, and J. Mullin. 1999. *Properties of crude oils and oil products*. EE-165. Ottawa, Ontario: Environment Canada.

Dissolution

Dissolution begins immediately and is likely to continue throughout the weathering process.

The loss of petroleum product from dissolution is minor when compared to the other weathering processes.

Less than 0.1% (very heavy oil) to 2% (gasoline) of the spilled oil volume actually dissolves into the water column. However, the components of the oil that dissolve into the water column are often more toxic to the environment.

Sample viscosities

| Product | Viscosity at room temperature (cP) |
|--|------------------------------------|
| water | 1 |
| diesel fuel | 10 |
| Prudhoe Bay crude | 46 |
| Prudhoe Bay crude after emulsification | 250,000 |
| Lagomedio | 20 |
| Lagomedio after emulsification | 300,000 |
| honey | 10,000 |
| peanut butter | 1,000,000 |

Emulsification

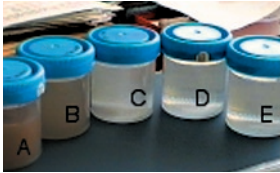
For many crude oils and some refined products, weathered oil is likely to reach a stage where water droplets are mixed into the oil, forming a water-in-oil emulsion, or “mousse.”

The ability to form an emulsion depends on water conditions and the chemical properties of the oil. For example, oils with high wax and asphaltene content, such as Prudhoe Bay crude, emulsify easily if there are breaking waves. Once the oil has emulsified, the viscosity can increase enormously (see table).

Generally, oils must weather a certain amount before forming an emulsion. Although the onset of emulsification may take several days, the emulsification itself can occur within a few hours.

The emulsion can be 70 to 90% water so that the combined volume of oil and water mixture may be much greater than the volume of the original spill.

Emulsions are often classified by their stability. In unstable emulsions, water and oil separate easily under calm conditions with warm temperatures. In stable emulsions, water remains in the oil for weeks to months.



Different concentrations of fine dust in water.

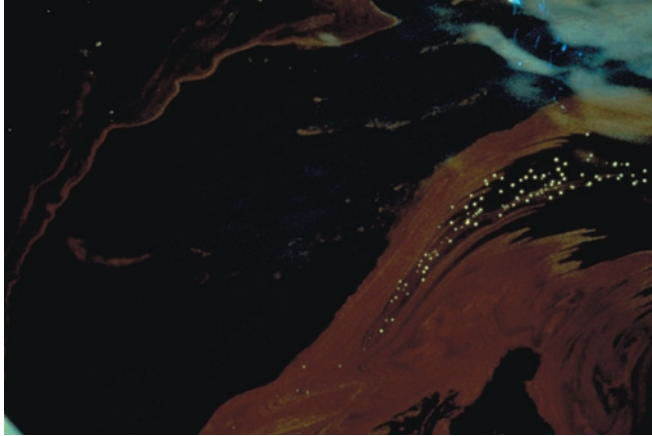
- A) $10,000 \text{ g/m}^3$
- B) 1000 g/m^3
- C) 100 g/m^3
- D) 10 g/m^3
- E) 1 g/m^3

Sedimentation

Sedimentation is defined as the adhesion of oil to solid particles in the water column. Oil can be sorbed onto sediments in the water column and may eventually be found in the bottom sediments.

Turbulent waters with high sediment load ($\sim 500 \text{ g/m}^3$), such as a fast-moving, muddy river, can move the oil through the water column within hours of the initial release.

Waters with low sediment load ($< 5 \text{ g/m}^3$), as in the open ocean, will allow oil to remain on the surface much longer (weeks), spreading the slick over a wider area.



Photograph showing a large patch of weathered oil with a crusty, “skin” layer on the surface. The white spots in the picture are 3-inch by 4-inch drift cards cast into the water to help track the movement of the oil.

Photo-oxidation

Sunlight changes the spilled oil’s chemical and physical properties.

This process is limited to the surface of the oil and can result in a thin, crusty “skin” on slicks and tarballs.

The “skinning” of the oil is thought to limit evaporation because the lighter oil components can no longer diffuse through the surface of the slick.

Photo-oxidation may increase the ease of emulsification and is considered a long-term weathering process taking weeks to months.



Kelp attached to weathered oil or "tarballs"

Biodegradation

The spill is finally removed when the oil biodegrades. The microbes that degrade oil occur naturally in the environment.

The rate at which the organisms degrade the oil depends on the properties of the water and the oil and microbial activity. This process is thought to occur over time scales of weeks to years.