

# **Oil dispersant effectiveness and ecological consequences in San Juan County marine waters**

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## **Summary**

- We summarized current scientific knowledge on chemical dispersants to inform San Juan County decision makers.
- Mechanical response may be insufficient to respond to an oil spill because of low effectiveness or unfavorable sea conditions. Dispersants should be considered an alternate response option because they may reduce overall environmental harm, especially to sensitive shoreline habitats.
- There may be better (more effective and less toxic) dispersant options than Corexit 9500, which is the only one currently in stock in Washington state. Further evaluation of other dispersant types could be beneficial.
- Dispersant effectiveness will depend on real-time conditions; in particular, the type of oil, the state of the oil slick, and ocean mixing energy. Low sea water temperature and low salinity are unlikely to substantially decrease dispersant effectiveness in San Juan County marine waters.
- Both dispersants and chemically dispersed oil are toxic, but not necessarily more toxic than oil itself. Evidence is mixed on whether dispersants promote biodegradation.
- There remains considerable uncertainty about the best possible response to oil spills because the tradeoffs of different responses are site and spill specific. Based on the published literature, there is substantial uncertainty about both the costs and benefits of dispersants. There is a particular need for linked models of oil transport and fate, dispersant effectiveness, and ecological consequences on local habitats and taxa.

## 1. Introduction

If an oil spill occurs in San Juan County marine waters, responders may use dispersants to help deal with the spill. In this report, we review what scientists currently know about how well different kinds of dispersants work and how using dispersants may affect local marine organisms. There is a lot of published information on dispersants. We aimed to distill information relevant to San Juan County (SJC) into concise, plain language that informs the county's decision makers. We gathered most of the information for this review from books on dispersants (Fingas 2011; NRC 2005), government reports, and recent primary literature (papers published after 2012).

The scope of this report covers chemical dispersants that responders could use to deal with a major marine oil spill in SJC waters. While oil spills also happen on land, we focus on marine spills because most major spills (>10,000 gallons) happen in the ocean. From 1970 to 1997, spills from ocean vessels constituted 59% of the total volume of major oil spills in Washington (Neel et al. 1997). Furthermore, if a major spill does occur on the mainland, the oil would reach SJC by water. We also focus on surface spills because there are currently no deep-water oil wellheads near SJC. We structured this report to follow a flow chart that a decision maker might use when considering dispersants (Figure 2). This flowchart is for outlining thought process only; a formal decision process is outlined in the 2017 Northwest Area Contingency Plan (NWACP 4000-31). The science available does not give clear-cut answers to the questions in Figure 1 because all research studies have inherent uncertainty and are limited in application. For example, much information on dispersant efficacy is based on laboratory tests and may not apply precisely to real-world spills. This review is thus a somewhat simplified view of our current state of knowledge.

### *What are dispersants?*

Dispersants break up large oil slicks into tiny oil droplets by changing how oil interacts with water. On their own, oil and seawater mix poorly because their molecular structures give them opposing chemical properties. Oil tends to interact with itself (hydrophobic) and water tends to interact with itself (hydrophilic). Dispersants can interact with both oil and water because they contain surfactant (surface-active agents) molecules that are hydrophobic on one end and hydrophilic on another. Similar to laundry detergents, dispersants work at the oil-water interface and help break oil slicks into oil droplets surrounded by surfactants. Ideally, the droplets then become entrained in the water column, diluting their toxic effects, and become less likely to resurface and join the surface slick (CRRC 2017). A potential benefit of dispersants breaking oil into droplets is for microbes to consume the droplets. The idea is for marine microbes (such as bacteria) to biodegrade the oil—to “break down” oil droplets into less toxic substances (NRC 2005; Prendergast and Gschwend 2011). Microbes can access oil droplets more easily than large oil slicks because droplets have more surface area per volume.

How well a dispersant breaks up an oil spill depends on the dispersant's operational, hydrodynamic, and chemical effectiveness (NRC 2005). Operational effectiveness refers to how well the dispersant is applied to an oil spill (e.g., how much sprayed dispersant hits an oil slick). Hydrodynamic effectiveness refers to how well dispersed oil dilutes and moves away from the plume. See NRC (2005) and Fingas (2011) for information on operational and hydrodynamic effectiveness. Chemical effectiveness refers to how well a dispersant breaks up oil into droplets. A dispersant's chemical effectiveness depends on the chemical properties of the oil, the

properties of the dispersant, and the environmental conditions.

Dispersants have changed over time. First-generation dispersants (before 1970) were designed to clean engines and contained highly toxic solvents (Lyons and Castaneda 2005). Various reformulations led to the modern dispersants currently in use (second- and third-generation dispersants), which are designed to have lower toxicity (Bejarano et al. 2014); some have ingredients (and toxicities) similar to household cleaning products (Word et al. 2015).

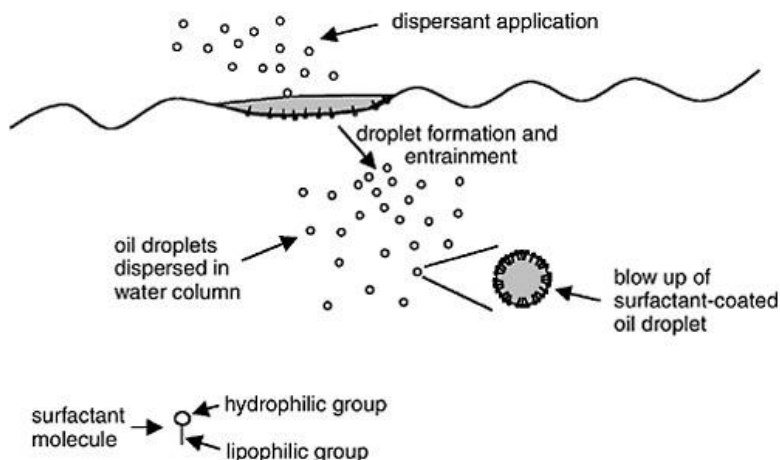


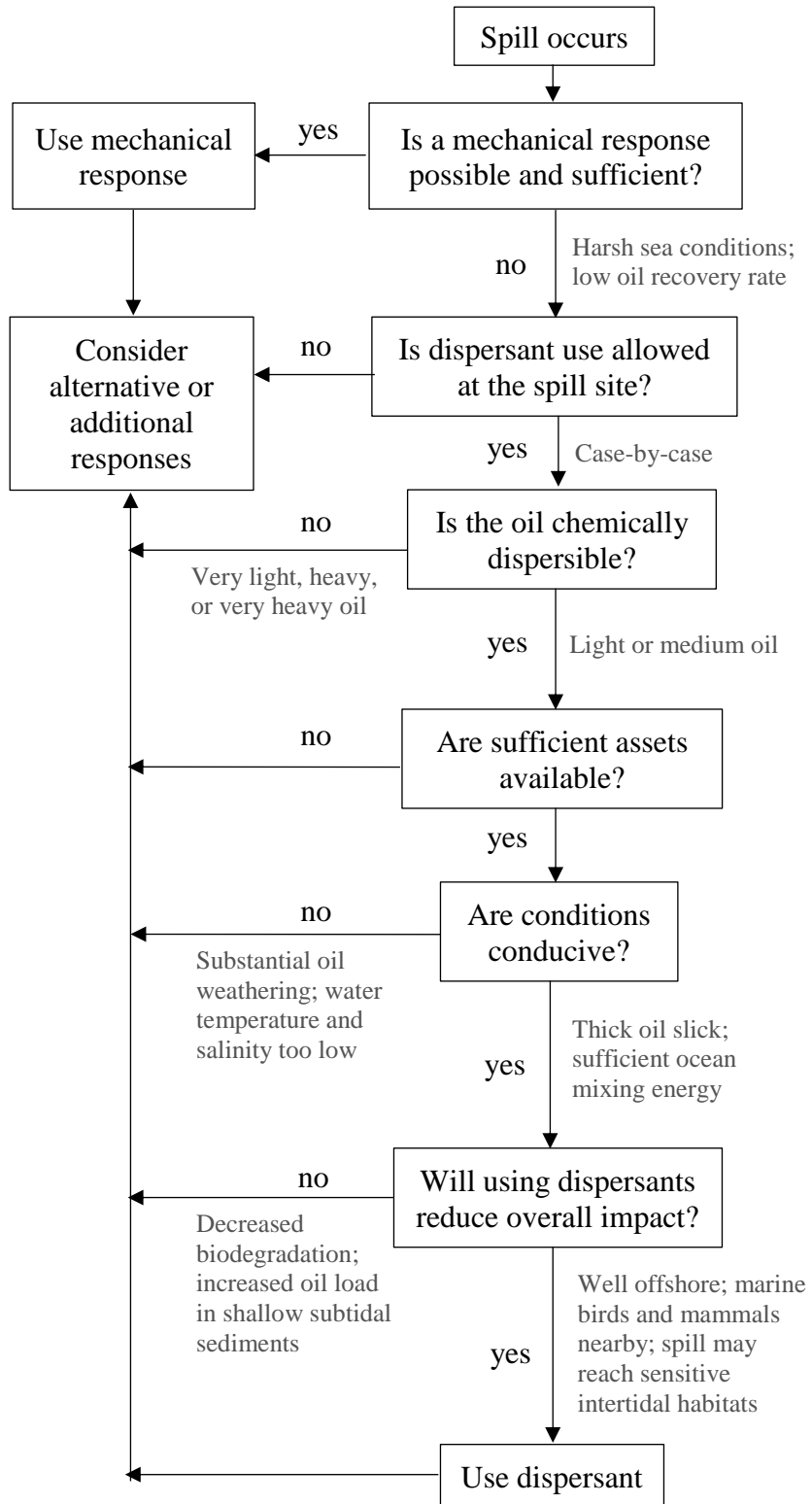
Figure 1. Chemical dispersants are designed to increase the formation of oil droplets that become entrained in the water column<sup>1</sup>. This is Figure 3-1 from NRC (2005).

## 2. Is mechanical response possible and sufficient? Is dispersant use allowed at this site?

The 2017 NWACP dictates that SJC responders consider mechanical methods “the initial and primary” response to oil spills (NWACP 4000-28). Responders prioritize mechanical responses because they likely have less environmental costs than chemical responses (NRC 2005). Mechanical responses refer to methods that physically contain or remove oil from the water (e.g., skimming, booming, absorbing pads). If mechanical responses are infeasible (due to rough ocean conditions; Fingas 2011; NRC 2005) or insufficient (due to low oil recovery rates; Coelho et al. 2013; NRC 2005), decision makers can consider chemical dispersants as a response strategy (NWACP 4000-28; Prince et al. 2015). An evaluation concluded that SJC ocean conditions “present a very difficult environment to contain and recover a major marine oil spill” and that maximum potential recovery capacity is 52% (Nuka Research & Planning Group, LLC 2015). Based on a qualitative comparison of costs and benefits of different response methods, Dave and Ghaly (2011) concluded that the most effective strategy is to recover oil mechanically and use chemical dispersants, then apply bioremediation<sup>2</sup>. Bioremediation refers to methods that attempt to increase biodegradation rate, such as adding oil degrading microbes or nutrients that those microbes need to degrade oil (Dave and Ghaly 2011). Which method or combination of methods responders in SJC use will depend on the spill and dispersant characteristics (Section 3, 4), environmental conditions (Section 5), ecological tradeoffs (Section 6), and whether dispersants are allowed.

<sup>1</sup> For the purposes of this report, lipophilic = hydrophobic.

<sup>2</sup> Note that the oil remaining after mechanical recovery may have weathered too much for effective dispersant use (see Section 5).



In this report:

Section 2

Section 2

Section 3

Table 1: Oil types and general chemical efficiency of dispersants

Section 4

Figures 3, 4: Comparison of different dispersants

Section 5

Table 2: Environmental conditions generally conducive to effective dispersant use

Section 6

Table 3: Potential environmental costs and benefits of using dispersants

Figure 2. Flowchart for deciding whether to use dispersants with some key parameters for each decision. Evidence is mixed on many of these parameters; see relevant parts in this report for more information. During an oil spill, decision makers should continuously re-evaluate each question based on real-time conditions. This flowchart is based on NRC (2005).

According to the 2017 NWACP, dispersant use in SJC marine waters, which are deeper than 10 fathoms (60 feet) and within 3 nautical miles (nm) of the shoreline, is currently allowed on a Case-by-Case basis (NWACP 4000-33). Local stakeholders have discussed<sup>3</sup> whether waters within 3 nm of shorelines should be changed to dispersant No-Use zones because dispersants and chemically dispersed oil may not have enough time to dilute sufficiently before reaching shorelines. While this is a valid concern to keep in mind, we did not find evidence that chemically dispersed oil harms nearshore organisms more than oil alone (see Section 6). Based on the lack of evidence that using dispersants nearshore would cause greater harm than untreated oil, we recommend keeping the Case-by-Case designation for SJC marine waters. Decision makers may prioritize other response methods but the Case-by-Case designation keeps dispersants open as an option.

### 3. Is the oil chemically dispersible?

Dispersant effectiveness depends partly on the oil’s chemical properties, such as viscosity, density, and boiling point (NRC 2005). One relatively simple way to classify oils is by grouping them into categories ranging from “Light” to “Extra Heavy” based on their API gravities<sup>4</sup>. API gravity is a scale developed by the American Petroleum Institute for how heavy an oil is compared to water. Generally, chemical dispersants can work well on “Light” and “Medium” oils but neither very light nor very heavy oils (Table 1).

All four types of oil are spill risks for SJC because they have all been spilled in Washington state previously (Neel et al. 1997) or are currently transported by vessels in Washington waters (Dagmar et al. 2015). Alaskan North Slope comprised ~50-90% of all crude oil imports to four of five refineries in Washington state in 2013 (see Table 33 and 34 in Dagmar et al. 2015).

Table 1. Oil types and general chemical efficiency of dispersants

Oil type	Examples	Chemically dispersible?	API gravity
Light	Very Light <sup>a</sup> : Jet fuel, gasoline	No <sup>a</sup>	>31.1
	No. 2 Fuel Oil, Louisiana Sweet,	Yes <sup>b</sup>	
Medium	Most crude oils, Prudhoe Bay, Alaskan North Slope	Yes <sup>b</sup>	22.3-31.1
Heavy	No. 6 Fuel Oil (a.k.a. Bunker C), diluted bitumen	Probably not <sup>a, b, c</sup>	<22.3
Extra Heavy	Tar, bitumen	No	<10

Note this table includes crude and refined oils while API gravity was designed for crude oils.

<sup>a</sup>NOAA Office of Response and Restoration website: <http://response.restoration.noaa.gov/oil-and-chemical-spills/oil-spills/oil-types.html>, accessed 5/9/17. <sup>b</sup>NRC (2005). <sup>c</sup>Dagmar et al. (2015).

<sup>3</sup> For example, at the San Juan County Department of Emergency Management Dispersant workshop, 6/13/17.

<sup>4</sup> An alternative classification method is by “persistence”; see Table 57 in Dagmar et al. 2014.

#### 4. Are sufficient assets available?

The outcome of using dispersants depends on the type of dispersant, which differ in their availability, effectiveness, and ecological consequences. Under current policy, decision makers can authorize dispersant use but the choice of dispersant type is left to industry<sup>5</sup>. According to the 2017 NWACP, spill responders must use one of the dispersants listed on the EPA National Contingency Plan Product Schedule. Of the dispersants on the Product Schedule, only Corexit 9500 is currently stocked in WA; more about this at the end of this section. The EPA Product Schedule currently lists 18 different dispersants with their respective effectiveness and toxicity values<sup>6</sup>. To compare dispersants, we plotted effectiveness vs. toxicity values for different dispersants (without oil; Figure 3) and for different dispersants combined with oil (Figure 4) using data from Hemmer et al. (2011) and the EPA Product Schedule. The x-axes, Effectiveness (%), indicate chemical effectiveness—the percentage of oil dispersed in laboratory swirling beaker tests. We calculated one effectiveness value for each dispersant by averaging how effective it was on a light (Prudhoe Bay) and a medium (South Louisiana Sweet) crude oil.

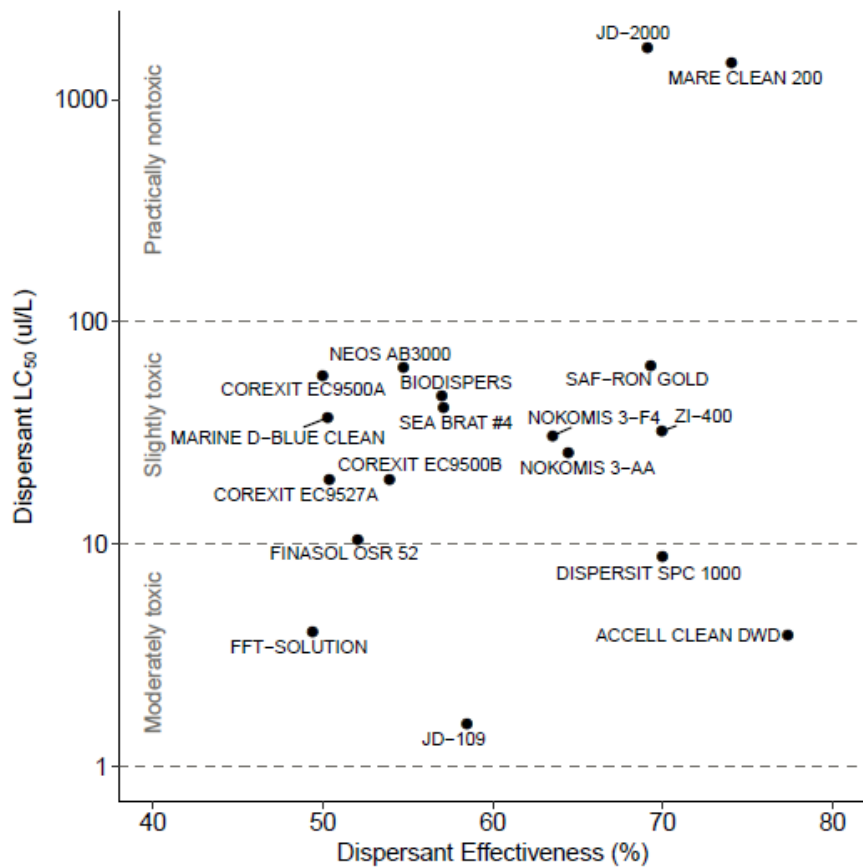


Figure 3. Toxicity and effectiveness for various dispersants (without oil). In laboratory tests on mysid shrimp and Atlantic silverside fish, most dispersants alone were slightly toxic. For toxicity and effectiveness of various dispersants combined with oil, see Figure 4. (1  $\mu\text{L/L} \approx 1 \text{ ppm}$ ).

<sup>5</sup> Brian MacDonald, Washington Department of Fish and Wildlife, personal communication.

<sup>6</sup> EPA Product Schedule: <https://www.epa.gov/emergency-response/national-contingency-plan-product-schedule-toxicity-and-effectiveness-summaries>, accessed 5/10/17.

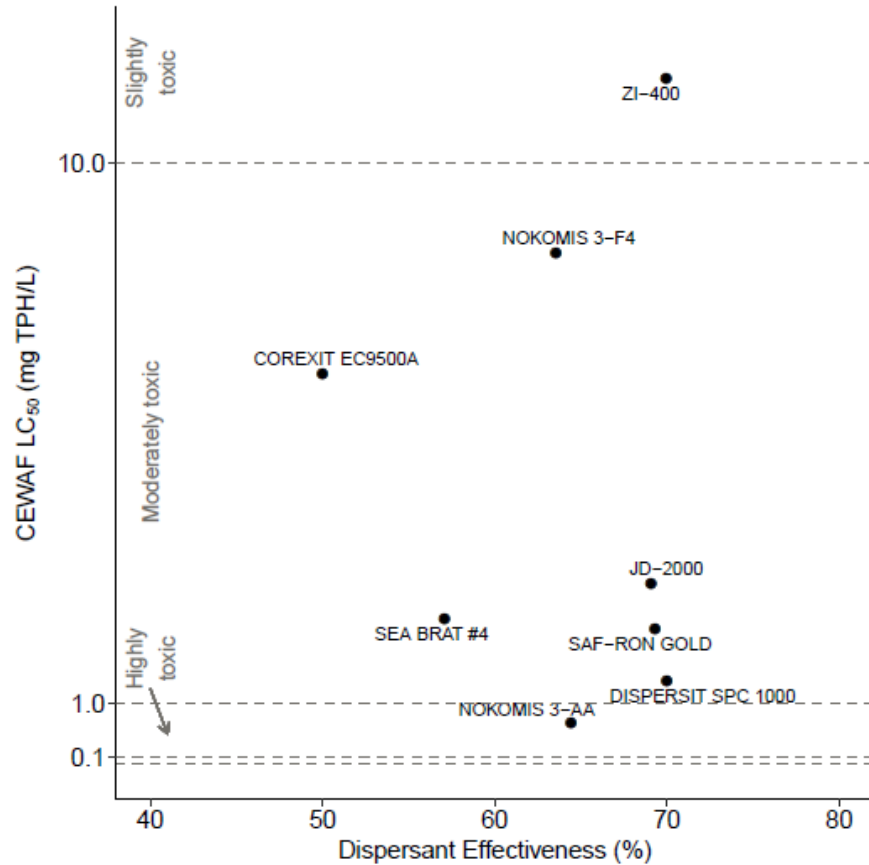


Figure 4. Toxicity and effectiveness for dispersants combined with oil (chemically enhanced water accommodated fraction; CEWAF). In laboratory tests on mysid shrimp and Atlantic silverside fish, most dispersants combined with oil were moderately toxic. (1 mg/L  $\approx$  1 ppm).

The y-axis, Toxicity (LC<sub>50</sub>), indicate the Lethal Concentration for 50% — the amount of a substance needed to kill 50% of individuals of a test organism in a certain amount of time. For example, if there were 100 goldfish in a 30 L tub, and adding 16 ml of a dispersant killed 50 goldfish after 2 hours, then the 2 hour LC<sub>50</sub> for that dispersant on goldfish would be 16 ml/30L. Figure 3 shows data for dispersant alone, so the toxicity units are volume of dispersant per volume of seawater (ul/L). Figure 4 shows data for dispersant combined with oil (chemically enhanced water accommodated fraction; CEWAF), so the toxicity units are amount of total petroleum hydrocarbons per liter of seawater (mg TPH/L). We will discuss CEWAF and TPH further in Section 6. Using data from the EPA Product Schedule and Hemmer et al. 2011, we calculated one toxicity value for each dispersant by averaging across test species, test durations (48 or 96 hours), and the two studies where possible. Both data sources provided LC<sub>50</sub> values for two common toxicology test species: the Atlantic silverside fish (*Menidia menidia*) and the opossum shrimp (*Mysidopsis bahia*). While other studies have also measured effectiveness and toxicity for some of these dispersants, we only included data from the EPA Product Schedule and Hemmer et al. 2011 because these two data sources used similar methods. Thus, Figures 3 and 4 are not affected by the much larger number of studies on Corexit 9500 compared to other dispersants. The EPA developed the qualitative toxicity categories (e.g., “slightly toxic”) shown in the figures (Hemmer et al. 2011).

The main message of Figure 3 is that most modern dispersants are only slightly toxic. Like the conclusion reached in NRC (2005), evidence from laboratory tests do not support the idea that dispersants themselves are extremely harmful to marine organisms. Based on their analysis, Hemmer et al. (2011) states that “second-generation dispersants such as Corexit 9500A are typically less toxic than oil alone or dispersed oil... suggesting that dispersant toxicity during a spill response is of secondary concern to the inherent toxicity of the oil or dispersed oil”. Some dispersants, such as JD-2000 and Mare Clean 200, may be practically nontoxic.

The main message of Figure 4 is that most dispersants combined with oil (CEWAF) are moderately toxic. Some dispersants, such as ZI-400, may be slightly toxic. Decision makers should be aware of CEWAF toxicity while remembering that all spill response strategies have costs. For chemical dispersants, protecting sensitive shorelines and marine birds and mammals comes at the cost of subjecting water column organisms to CEWAF, potentially at moderately toxic levels (Dave and Gahly 2011; Coelho et al. 2013). We will further discuss these tradeoffs in Section 6.

In using Figures 3 and 4 to compare dispersants, decision makers should consider that these effectiveness and toxicity values were measured in the laboratory and will differ in the field. Laboratory tests tend to overestimate both dispersant effectiveness (Fingas 2011) and toxicity (Bejarano et al. 2014) compared to in the field. For example, using data for five dispersant-oil combinations compiled in Table 15.6 of Fingas (2011), we found that effectiveness measured in lab tests were on average ~3 times higher than in field tests. Dispersant toxicities in the field may be lower than what laboratory tests suggest because organisms in the lab are exposed to CEWAF for longer durations (standard tests of 48 or 96 hours) or more constant concentrations (constant bath of CEWAF) than they would in the ocean (Bejarano et al 2014). We will further discuss issues in interpreting laboratory toxicity tests in Section 6.

Of the dispersants listed on the EPA Product Schedule, Washington state currently keeps Corexit 9500<sup>7</sup> in stock, with the closest stockpile to SJC in Everett, WA ([www.wrrl.us](http://www.wrrl.us), accessed 5/15/2017). Many dispersant toxicity studies use Corexit 9500. Although alternate dispersants may be difficult to obtain due to low availability<sup>8</sup>, we recommend that Washington state investigate and consider stockpiling other dispersants<sup>9</sup>, such as ZI-400, which may be less toxic and more effective than Corexit 9500 when combined with oil (Figure 4). It may also be worth investigating the availability of methods that improve Corexit 9500 performance. For example, a laboratory study suggests that “environmentally friendly” xanthum gum can increase Corexit 9500 effectiveness and biodegradation while decreasing the amount of dispersant needed (Wang et al. 2017). Researchers continue to explore other “natural” dispersant methods (e.g., substances from soybeans; Nyankson et al. 2015; Nyankson et al. 2016); these methods are not available yet

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<sup>7</sup> Corexit 9500 is a second-generation dispersant (Hemmer et al. 2011) developed by EXXON in 1992 (Lyons and Castaneda 2005). Corexit products are the main dispersants in the United States (Lyons and Castaneda 2005).

<sup>8</sup> Brandon Todd, U.S. Coast Guard, San Juan County Department of Emergency Management Dispersant workshop, 6/13/17.

<sup>9</sup> Under current NWACP policy, while Washington State can regulate facilities to ensure that responders have the capability to apply dispersants, industry and Oil Spill Removal Organizations decide which dispersants listed on the EPA product schedule to use (Brian MacDonald, Washington Department of Fish and Wildlife, personal communication).



but may be good options in the future. Note that changing dispersant type may also require changing and testing the various equipment and vessels used in dispersant application.

## 5. Are conditions conducive?

Dispersant effectiveness depends on the conditions of the oil and the environment. Responders should consider these conditions: degree of oil weathering, wind and wave energy, water temperature, water salinity, sediments, and rain<sup>10</sup>. We summarize how each condition affects dispersant effectiveness and provide data for SJC where possible. During an oil spill, responders should constantly evaluate real-time conditions to decide whether to use dispersants (NRC 2005). General conditions conducive to dispersant use are summarized in Table 2; conditions outside these parameters (e.g., a very thin or weathered slick) will lead to low dispersant effectiveness and thus poor cost/benefit tradeoffs.

Table 2. Environmental conditions most conducive to effective dispersant use in SJC waters.

Variable	Metric	Condition
Weathering <sup>a,b</sup>	Time since spill	< 24 hours (winter), < 72 hours (summer)
	Slick thickness	> 1 mm thick
Mixing energy <sup>a,c</sup>	Wind speed	5-12 m/s (9-23 kts)
	Wave height	≥ 15 cm (5.9 in)
	Rainfall	> 22 mm/h
Water temperature <sup>c</sup>	Sea surface temperature	≥ 10°C
Salinity <sup>c,d</sup>		~ 30 PSU

<sup>a</sup>NRC (2005); <sup>b</sup>Zeinstra-Helfrich et al. (2015); <sup>c</sup>Fingas (2011); <sup>d</sup>Chapman et al. (2007)

### *Degree of oil weathering*

Once oil is released into the ocean, it undergoes weathering—changes in its physical and chemical properties—that can decrease dispersant effectiveness (NRC 2005, Soloviev et al. 2016). As oil weathers, its lighter components evaporate or dissolve into the water column, leaving the oil slick heavier and more hydrophobic (Prendergast and Gschwend 2011). Water droplets also become trapped in the oil (emulsification<sup>11</sup>), increasing oil viscosity (Prendergast and Gschwend 2011). More viscous oil slicks are harder to disperse, so chemical dispersants should be applied before the oil has weathered substantially (NRC 2005). The NRC states that there is no hard cutoff of oil viscosity for using dispersants but the window of opportunity to apply dispersants is <72 hours in fall-summer and <24 hours in winter<sup>12</sup> (NRC 2005, p.65).

<sup>10</sup> Other operational factors, such as dispersant to oil ratio, are also important (CRRC 2017).

<sup>11</sup> Emulsification (water in oil) decreases effectiveness of dispersants and other response methods; entrainment (oil in water) is a desirable outcome of dispersant use. A potential benefit of using dispersants early on in a spill is that dispersants can prevent further emulsification.

<sup>12</sup> Some studies state a hard viscosity cutoff (4,000 mPa s) with much shorter windows of opportunity (5-10 hours; see data from Daling et al. 1997 in Figure 1 of Prendergast and Gschwend 2011). However, more recent studies (e.g., Daling et al. 2014) indicate effective chemical dispersion at higher viscosities (10,000 mPa s) and longer windows of opportunity (> 1

Winter has a shorter window of opportunity to apply dispersants because the water is colder, which increases oil viscosity. For example, a field study indicated that oil viscosity after 5 hours was twice as high in winter (~10°C) vs. summer (~15°C) seawater (see Figure 1 in Prendergast and Gschwend 2011). A recent modeling study suggests that chemical dispersants may still work on high viscosity oils if there is strong mixing energy over a long time (Pan et al. 2017). Note that while we provide general information relevant to dispersants here, oil weathering depends heavily on specific oil characteristics and environmental conditions (NRC 2005 p.155). NOAA maintains an oil weathering model (ADIOS) that responders can use to estimate characteristics and behavior of numerous oils under different environmental conditions<sup>13</sup>.

In addition to weathering, an oil slick becomes thinner as it spreads horizontally on the sea surface. For dispersants to work effectively, an oil slick should be at least 1 mm thick (Fingas 2011, p.586, 603). Based on laboratory tests, the amount of oil entrained may be proportional to the thickness of the slick (Zeinstra-Helfrich et al. 2015). How long a slick remains >1 mm thick will depend on the oil type and the environmental conditions; thickness of an oil slick can be estimated by modeling or aerial measurement. In general, dispersants should be applied as soon as possible over the thickest part of an oil slick (NRC 2005, p.137).

#### *Wave and wind energy*

Effective chemical dispersion requires mixing of dispersant and oil (NRC 2005). Unless responders artificially provide mixing energy (e.g., by using their boat propellers), mixing depends on wind and wave energy. Wind speed should be at least 5 m/s (NRC 2005, p.32) and ideally 12-13 m/s (Fingas 2011, p.406). Winds faster than 12-13 m/s will likely blow dispersants away from a target oil slick<sup>14</sup> (NRC 2005, p.32). Waves 15-20 cm or higher can generate sufficient mixing energy (NRC 2005, p.32). The NRC (2005) states that it is unknown whether dispersants applied in calm conditions can work if winds pick up later, and we have not found any studies addressing this issue. Note that while strong winds can temporarily entrain untreated oil, the resulting droplets may quickly resurface to rejoin the oil slick (NRC 2005, p.157). The effect of mixing energy on dispersing resurfaced chemically treated oil is unclear (CRRC 2017).

Winds in SJC range from 0-200 m/s in all months of the year (Figure 5). Thus, responders will have to judge real-time wind and wave conditions to determine if there is enough mixing energy to use dispersants effectively.

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week). The discrepancy is likely due to the different oils, dispersants, and conditions tested. Given the discrepancy, we defer to the NRC's recommendation (NRC 2005).

<sup>13</sup>Automated Data Inquiry for Oil Spills: <http://response.restoration.noaa.gov/adios>.

<sup>14</sup> Conditions conducive to chemical effectiveness may decrease operational effectiveness (NRC 2005; Fingas 2011). For example, high mixing energy may mean difficult operating conditions for responders, vehicles, and equipment.

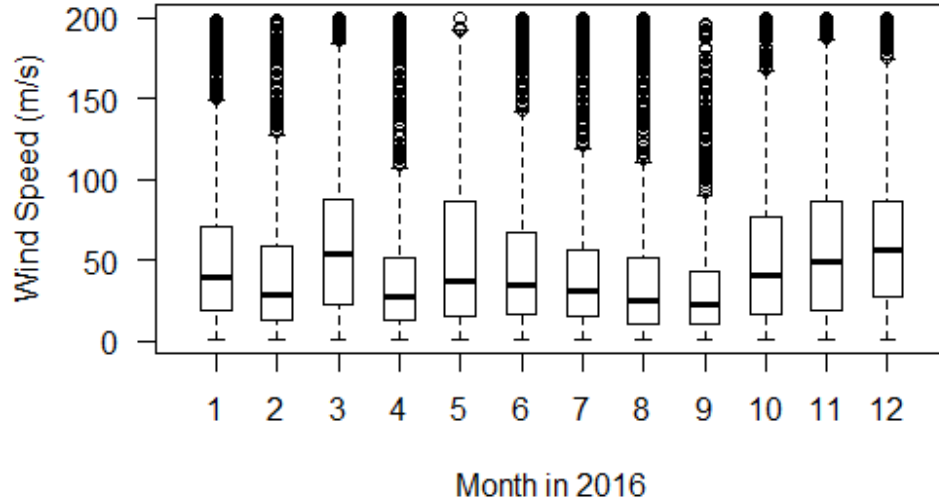


Figure 5. Wind speed varies widely throughout the year in SJC waters<sup>15</sup>. Data in Figures 5-7 are displayed using boxplots, which summarize how numbers are distributed. In each box, the thick horizontal line indicates the median of the data; box upper and lower edges indicate first and third quartiles respectively; horizontal dashes above and below boxes indicate maximum and minimum respectively; and circles indicate potential outliers.

#### *Water temperature*

Decreasing water temperature can decrease dispersant effectiveness by increasing oil viscosity or changing some other mechanism (Fingas 2011). Some studies reported that cold water ( $\leq 10^{\circ}\text{C}$ ) can decrease dispersant effectiveness to below 10% (Fingas 2011, p.512; Moles et al 2002). These studies, however, likely conducted tests in laboratory conditions with low mixing energy (Moles et al. 2002) and might have underestimated dispersant effectiveness in field conditions with higher mixing energy. Belore et al. (2009) tested dispersant effectiveness on fresh and weathered crude oils in cold water ( $< 10^{\circ}\text{C}$ ) using wave tanks that generated 20-50 cm waves. We averaged the effectiveness values reported in Figure 6 of Belore et al. (2009) for various oils and found that Corexit 9500 had ~78% effectiveness in these tests. Based on this evidence, dispersants seem to be able to work well in cold water if there is sufficient mixing energy to consider applying dispersants in the first place (see above).

Water temperature in SJC generally ranges 10-15°C from May to November and 8-10°C from December to April (Figure 6). In the latter period, water temperature is generally still above 8°C, so dispersant effectiveness probably will not decrease drastically due to water temperature, given sufficient mixing energy.

<sup>15</sup> Data for Figures 5-7 are from NOAA Friday Harbor buoy for 2016 only, [http://www.ndbc.noaa.gov/station\\_history.php?station=frdw1](http://www.ndbc.noaa.gov/station_history.php?station=frdw1), accessed 5/19/2017.

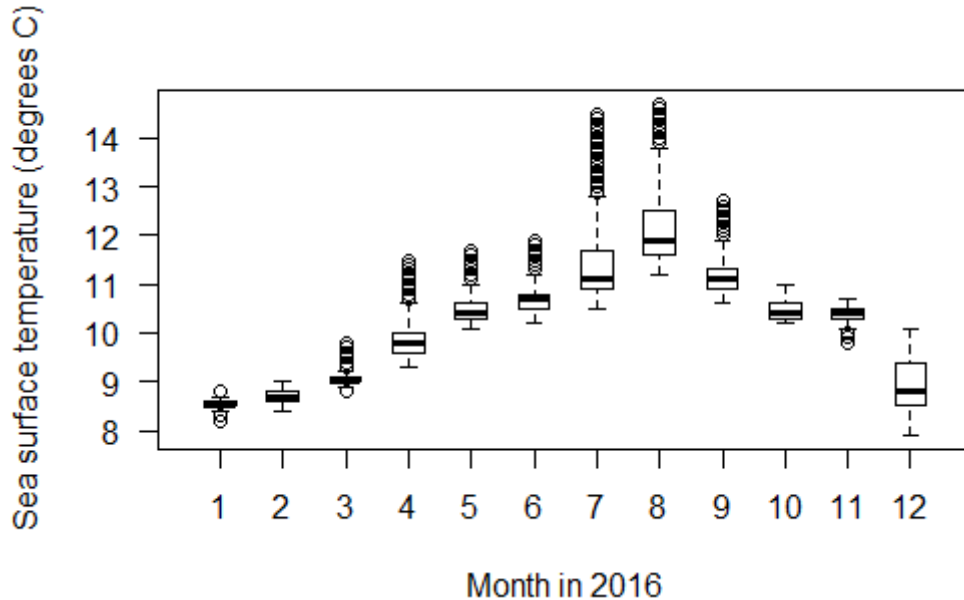


Figure 6. Water temperature in SJC decreases in the winter months but generally remains above 8°C.

### *Salinity*

Most commercially available dispersants are designed to work at “typical” ocean salinities (30 PSU) or higher (Chapman et al. 2007; but see Tansel et al. 2014). In principle, lower salinity can decrease dispersant effectiveness by increasing surfactant solubility in water. If surfactants become too soluble in water, they interact less with oil and form fewer oil droplets (Fingas 2011, p.516). Based on the summary provided by Fingas (2011), previous studies (> 20 years old) found that decreasing salinity decreased dispersant effectiveness dramatically. For example, Fingas (2011, p.514) shows a graph indicating that Corexit 9527 effectiveness drops from 50% at 30 PSU to 10% at 20 PSU. Other studies, however, found less dramatic declines. Chandrasekar et al. (2006) studied how salinity (10, 20, 34 PSU) affects the effectiveness of two dispersants on three kinds of oil using swirling flask tests. They did not find an effect of decreasing salinity alone, but that salinity affected how mixing energy (swirling speed) impacted one of the six oil-dispersant combinations tested (Chandrasekar et al. 2006). Kuhl et al. (2013) found that dispersant effectiveness decreased from 18 to 4 PSU. Some studies indicate that the negative effect of decreasing salinity on dispersant effectiveness is greater in cold water (Fingas 2011, p.512; Moles et al. 2002); however, these interaction effects seem to be important mostly in arctic conditions ( $\leq 10^{\circ}\text{C}$  seawater, ~20 PSU).

Salinity in SJC is controlled primarily by freshwater river inputs and tidal regimes<sup>16</sup>. SJC waters remain around 30 PSU except in June – August when salinity can drop to 24 PSU (Figure 7). The summer decrease in salinity is caused primarily by increased freshwater input from the Fraser River (Banas et al. 2015). Since low salinities generally occur during summer in SJC, interactive negative effects between low salinity and low water temperature on dispersant effectiveness (Fingas 2011, p.514) are probably irrelevant to SJC waters.

<sup>16</sup> Alex Lowe, University of Washington (UW) Department of Biology, personal communication.

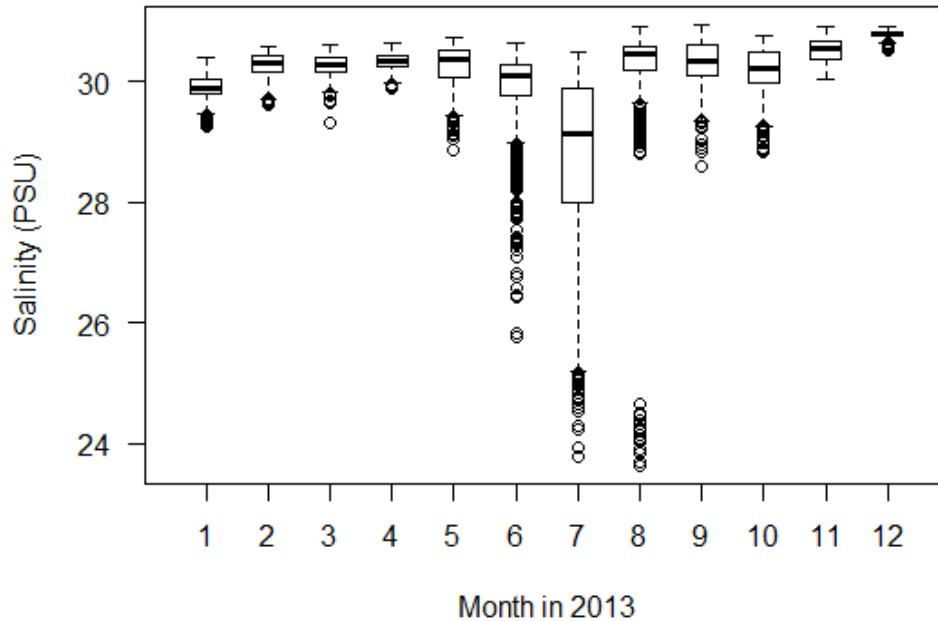


Figure 7. Salinity in SJC waters generally remains 30 PSU except during summer, when salinity decreases due to river inputs.

### *Sediments*

Oil sticks to both sediment particles in the water column and to sediments on the seafloor. Dispersants can influence how oil interacts with both kinds of sediments (Gong et al. 2014a). In the water column, dispersants can increase the number of small oil droplets that stick to suspended sediment particles, which may be less likely to resurface and rejoin the oil slick (Boglaenko and Tansel 2016; CRRC 2017; Gong et al. 2014; NRC 2005, p.180). One recent study, however, found that a dispersant strongly decreased how much oil droplets stick to suspended sediment particles (Sørensen et al. 2014). At the seafloor, dispersants can increase the amount of oil absorbed into the sediment (Gong et al. 2014a).

Sediment processes in SJC are influenced by input from nearby Fraser, Skagit, and other rivers; generalizing about sediment dispersal this area is difficult (Hill et al. 2008). We are not aware of any studies that predict sediment loads in the water column in SJC<sup>17</sup>. Due to the mixed evidence for dispersant effects on oil-sediment interactions in the scientific literature and lack of data on real-time sediment conditions in SJC, we think responders currently do not have enough scientific information to consider sediment influences on dispersant effectiveness in the decision process.

### *Rain*

A recent study suggests that rainfall can create enough mixing energy to increase dispersant effectiveness, especially for light oils (Wu et al. 2017). Using mathematical models, Wu et al. (2017) found that mixing energy generated by heavy rain (> 22 mm/h) is comparable to energy generated by wind induced waves in British Columbia. We did not find any other studies about the effects of mixing energy from rainfall on dispersants, but it seems worth considering in SJC.

<sup>17</sup> Emily Eidam, UW Department of Oceanography, personal communication.

## 6. Will using dispersants reduce overall impact?

Using dispersants will involve tradeoffs between decreasing oil spill impacts on some organisms, habitats, and ecological processes while increasing impacts on others (Moles 2001; NRC 2005). In some cases, dispersants may decrease overall harm to sensitive habitats in the long-term at the cost of increasing short-term damage to less sensitive habitats (Moles 2001). Dispersants should only be used if they decrease overall harm to the environment. The potential costs and benefits of using dispersants (Table 3) have often been assumed based on logic or anecdotal evidence (NRC 2005). In this section, we focus on summarizing recent research that examined some of those assumptions.

The information we present here is inadequate for decision makers to determine conclusively whether using dispersants would decrease the overall impact of an oil spill in SJC; based on the published literature, there is substantial uncertainty about both the costs and benefits of dispersants. To help inform decision makers about dispersant tradeoffs, scientists should develop linked models of oil transport and fate (including 3D models under various conditions), dispersant effectiveness, and ecological consequences on local habitats and taxa. As far as we are aware these models have not been built, although the basis for such models do exist (e.g., Bejarano and Mearns 2015). Such models can contribute scientific information that complements the experience and professional judgement of responders making time-sensitive decisions during a spill.

We did not find any existing analyses of the environmental tradeoffs of dispersant use for areas similar to SJC. However, tools that can help such an analysis are available, including the NOAA CAFE database<sup>18</sup> and the net environmental benefit analysis framework (Barron et al. 2013; Bejarano et al. 2015; Efroymsen et al. 2004). Coelho et al. (2013) stated that a net environmental benefit analysis “will often conclude that it is preferable to expose offshore water column organisms to a rapidly diluting dispersed oil plume rather than allowing a slick to remain on the water surface and potentially impact sensitive shorelines.” However, Coelho et al. (2013) did not provide supporting sources or evidence for that part of their paper.

Table 3. Potential ecological costs and benefits of dispersant use.

Potential benefits	Potential costs
Increase oil droplets in water column habitat <ul style="list-style-type: none"> <li>Oil dilution can decrease toxicity</li> <li>Oil droplets may be more readily biodegraded</li> </ul>	Increase oil load in water column habitat <ul style="list-style-type: none"> <li>Oil can harm plankton, fish, invertebrates directly and indirectly through foodweb</li> </ul>
Decrease oil load at ocean surface <ul style="list-style-type: none"> <li>Surface slicks may directly harm marine birds and mammals</li> </ul>	Increase oil load in ocean floor <ul style="list-style-type: none"> <li>Benthic habitats may be sensitive to oil</li> </ul>
Decrease oil load reaching intertidal habitats <ul style="list-style-type: none"> <li>Oil persists long term in intertidal</li> <li>Intertidal habitats may be especially sensitive to oil</li> </ul>	Increase toxic impacts of oil spill <ul style="list-style-type: none"> <li>Dispersants may be toxic</li> <li>Dispersant-oil combinations may be more toxic than oil alone</li> </ul>

<sup>18</sup> NOAA Office of Response and Restoration Chemical Aquatic Fate and Effects database: <http://response.restoration.noaa.gov/oil-and-chemical-spills/chemical-spills/response-tools/cafe.html>.

Scientists continue to debate how dispersants influence the toxic effects of oil on marine organisms (Coelho et al. 2013), although recent evidence indicates that oil-dispersant combinations are not necessarily more toxic than oil alone (Bejarano 2014; NRC 2005 p. 229). Most information available on dispersant and oil-dispersant toxicities were determined in laboratory tests, which presents two challenges for understanding the potential costs of using dispersants. First, estimations of dispersant toxicities likely differ in laboratory and field conditions (NRC 2005). We will further discuss this point below. Second, studies have used various methods, making it difficult to compare their results (Coelho et al. 2013). To address this issue, a research group known as CROSERF established standard methods for testing and reporting dispersant toxicities during the 1990s (Coelho et al. 2013; NRC 2005). Studies that follow CROSERF protocols can be synthesized, while those that do not (e.g., Rico-Martinez et al. 2013) may draw incomparable or misleading conclusions (Coelho et al. 2013).

Several CROSERF concepts are key to understanding dispersant toxicity studies. Scientists comparing the toxicities of oil, dispersants, and oil-dispersant combinations mix each of these chemicals in seawater, diluting them to simulate concentrations that would occur in the field. To make diluted oil in seawater mixtures, known as water accommodated fractions (WAF), the oil is usually mixed mechanically with seawater in swirling beakers. The same amount of oil added to a certain amount of seawater (oil loadings, or nominal oil concentrations) can differ in the concentrations of hydrocarbons released from the oil: Total Petroleum Hydrocarbons (TPH)<sup>19</sup>. It is the concentrations of TPH that determine toxicity of a WAF, not the nominal concentrations (Bejarano et al 2014; NRC 2005). CROSERF protocols require that studies report TPH concentrations to indicate how much toxic chemicals organisms were exposed to<sup>20</sup>. The same concepts apply to mixtures of oil and dispersant in seawater, known as chemically enhanced water accommodated fractions (CEWAF).

Is CEWAF more toxic than WAF? Recent studies examined whether the toxic effect of oil and dispersants together is greater than the sum of their separate toxicities (synergistic effects). Some found evidence of synergistic effects (e.g., Al-Jawasim et al. 2015; Rico-Martinez 2013) while others did not (e.g., Adams et al. 2014; Dussauze et al. 2015; Hemmer et al. 2011). Bejarano et al. (2014) reviewed dispersant toxicity studies and found that, for Corexit 9500, the LC<sub>50</sub> or EC<sub>50</sub><sup>21</sup> for CEWAF was  $\leq$  WAF in 78% of paired comparisons when based on measured TPH concentrations (Figure 8). The opposite pattern occurred when data were reported based on nominal oil concentrations (Bejarano et al. 2014). The NRC (2005) drew similar conclusions to Bejarano et al. (2014). This evidence suggests that 1) CEWAF is similar or less toxic than WAF and 2) studies claiming that toxicity of CEWAF > WAF based only on nominal oil concentrations are flawed and should not be used in decision making (Bejarano et al. 2014). Note that while studies may find that CEWAF can be more toxic than WAF, these results are caused by dispersants increasing exposure of organisms to hydrocarbons rather than dispersants chemically altering oil toxicity (Adams et al. 2014; Hemmer et al. 2011).

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<sup>19</sup> Studies report concentrations of Total Petroleum Hydrocarbons (TPH), Total Polycyclic Aromatic Hydrocarbons (TPAH), and Total Hydrocarbon Content (THC). They are different but we do not differentiate them in this report.

<sup>20</sup> In addition to TPH concentrations, it is valuable for studies to measure concentrations of target analytes (specific hydrocarbons that contribute to TPH concentrations) when possible (Bejarano et al. 2014; Coelho et al. 2013).

<sup>21</sup> EC<sub>50</sub> is the half maximal effective concentration, a measure of a toxicity comparable to LC<sub>50</sub>.

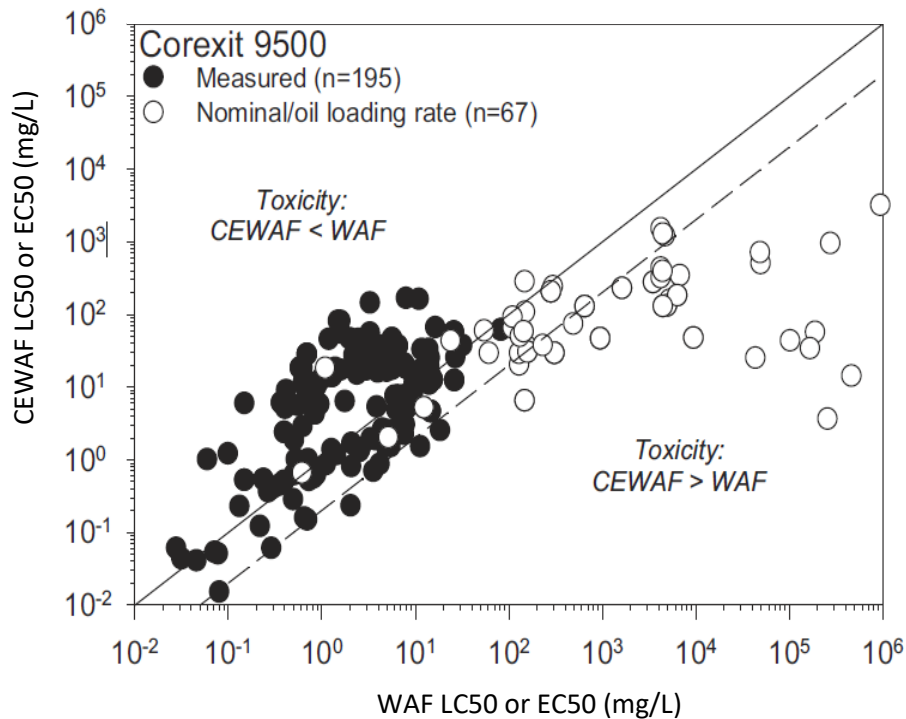


Figure 8. Based on measured TPH concentrations, toxicity of oil dispersed with Corexit 9500 is similar or less than oil without dispersant. This is a modified figure from Bejarano et al. 2014.

It is important to recognize that most studies have been conducted in the laboratory, and lab studies can over- or underestimate CEWAF toxicity relative to what organisms experience in the field (NRC 2005). Lab studies can overestimate CEWAF toxicity if they expose organisms to constant levels of CEWAF for long periods (Bejarano et al. 2014). For example, Adams et al. (2014) found that CEWAF (Corexit 9500 and medium crude oil) was toxic to fish embryos under chronic but not acute exposure. Even standard “acute” tests of 24-96 hours probably do not reflect the much shorter exposures of field conditions (Bejarano et al. 2014; Moles 2001). Studies that test toxicities under short (minutes to hours) and “spiked” or flow-through (as opposed to constant) exposure conditions are needed to provide information more applicable to field conditions (Bejarano et al. 2014). Note however, that the biological effects of short exposures may occur over longer time periods (e.g., delayed mortality) and may be missed by standard acute toxicity tests (CRRC 2017). Comparisons to field data (e.g., Bejarano et al. 2013) will help determine the applicability of laboratory toxicity values to open ocean spills.

Lab studies can underestimate CEWAF toxicity if they do not account for photoenhanced toxicity—an increase in toxicity due to UV radiation (Barron et al. 2003; NRC 2005). UV radiation present in natural sunlight (UVA and UVB) reacts with hydrocarbons that organisms absorb from oil, forming more toxic compounds (Barron et al. 2003; Finch et al. 2016). Dispersants can facilitate photoenhanced toxicity by increasing the amount of hydrocarbons that organisms are exposed to. Most existing studies do not account for photoenhanced toxicity because typical laboratory lights have minimal UV (Barron et al. 2003); however, some studies have tested photoenhanced toxicity directly. For example, Barron et al. (2003) found that, under natural sunlight, chemically dispersed oil was more toxic than oil alone to Pacific herring eggs



and larvae. Almeda et al. (2016) found that UVB radiation increased toxicity of oil dispersed by Corexit 9500 to marine zooplankton by 1.3 to 3.8 times. Similarly, Finch et al. (2017) found that dispersants increased the phototoxic effects of oil on shrimp and fish species. We did not find any studies comparing how much CEWAF toxicities have been over- vs. underestimated.

Although studies have examined the toxicity of chemically dispersed oil to various marine organisms, we lack quantitative comparisons between habitats and taxa. Offshore (> 3 nm) pelagic habitats are thought to be the ideal system to use dispersants (Fingas 2011; NRC 2005) because oil droplets can dilute and spread quickly without reaching subtidal benthic habitats. Subtidal benthic habitats deeper than 10 m will likely be unaffected by chemically dispersed oil (NRC 2005, p.250), which generally stay within the first few meters of the water column (Bejarano et al. 2014). Shallow subtidal benthic habitats, however, may be affected by dispersed oil. At the time of their review, NRC (2005) concluded that dispersed oil likely has similar toxicity to benthic and water-column organisms, but benthic sediments may trap untreated oil and cause chronic exposure to organisms (p. 251).

Recent studies have tested how toxic polyaromatic hydrocarbons from oil interact with subtidal benthic sediments, but no clear picture has emerged. Macías-Zamora et al. (2014) found that Corexit 9500 did not change the degradation of oil polyaromatic hydrocarbons in sediments under subtropical ocean conditions. Gong et al. (2014a) found that Corexit 9500 increased sediment uptake of polyaromatic hydrocarbons. Zhao et al. (2015) found that dispersants can increase or decrease sediment uptake of polyaromatic hydrocarbons depending on the dispersant concentration and properties of the hydrocarbons. In intertidal soft-sediment habitats, studies generally indicate that dispersants decrease oil retention (see reference 15 in Bejarano et al. 2014; mudflat, Cuny et al. 2015; sandy beach, Gong et al. 2014b; NRC 2005, p.251).

There is a body of work demonstrating the toxicity of chemically dispersed oil to various taxa, especially invertebrates and fishes (NRC 2005 Tables 5-6, 6-7; >50 published studies since 2012). Crustaceans seem to be more sensitive to chemically dispersed oil than fishes (Bejarano et al. 2014). For fishes, acute lethal toxicity of chemically dispersed oil will likely be due primarily to chemicals released from the oil rather than the dispersants (CRRC 2017). One study found that the acute effects of CEWAF on fish were temporary: European sea bass exposed to crude oil dispersed using Corexit 9500 for 96 hours had decreased performance one month after exposure, but the decrease did not affect long term survival and growth (10 months post exposure; Mauduit et al. 2016). In general, larval and juvenile stages of invertebrates and fish are more sensitive than adult stages (NRC 2005), although there is more evidence for early life stages of fishes than for invertebrate embryos (CRRC 2017).

Marine plants and algae are often assumed to be less sensitive than animals; however, a recent review indicates that it depends on the species compared (Lewis and Pryor 2013). Much of the information on marine plant and algal sensitivity to chemically dispersed oil may be outdated because they were conducted using first-generation dispersants (Lewis and Pryor 2013).

Interactions between chemically dispersed oil and marine plankton may be important. For example, using dispersants during phytoplankton blooms may increase the amount of hydrocarbons carried to subtidal benthic systems via “marine snow”<sup>22</sup>, although evidence on this is mixed (CRRC 2017). Ozhan and Bargu (2014) found that CEWAF increased the abundance of resistant compared to sensitive species in a Gulf of Mexico phytoplankton community. Similar

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<sup>22</sup> Susan Saupe, Cook Inlet Regional Citizens Advisory Council, San Juan County Department of Emergency Management Dispersant workshop, 6/13/17.

community shifts likely occur in other microbial and planktonic systems in response to CEWAF (e.g., Ortmann et al. 2012); these shifts may impact foodwebs, depending on the rates of plankton community transport and turnover.

Recent studies have also found negative effects of chemically dispersed oil on birds and mammals. Oil dispersed with Corexit 9500 is more toxic to mallard duck eggs than oil alone, although the effect may depend on the oil to dispersant ratio (Finch et al. 2012; Wooten et al. 2012). Fiorello et al. (2016) found that common murre develop pink eye when exposed for 90 seconds to oil, dispersant, or chemically dispersed oil, and that birds exposed to the latter may also develop eye ulcers. Preliminary evidence indicates that CEWAF (crude oil and Corexit 9500) changes the structure of common murre feathers, decreasing water repellency of feathers and buoyancy of birds, although not necessarily more so than untreated oil (Drayer et al. unpublished<sup>23</sup>; Duerr et al. 2011). A 1988 study found that chemically dispersed oil increased thermal conductance of sea otter pelts to levels similar to untreated oil (Williams et al. 1988), which means dispersants did not decrease the heat-loss effects of oil on otter pelts. We did not find studies testing dispersed oil effects on living mammals, but studies indicate that dispersants kill or harm sperm whale skin cells (Wise et al. 2014), human bronchial (airway) cells (Shi et al. 2013), and various other human and rat cells (Judson et al. 2010; Zheng et al. 2014). Note that untreated oil also harms marine birds and mammals (e.g., Peterson 2001; Peterson et al. 2003). Mammals that breathe at the air-water interface may be especially vulnerable to the toxic effects of inhaling volatile compounds from both dispersed and undispersed oil (CRRC 2017). The key issue is how the negative effects of dispersed oil on marine birds and mammals compare to the effects of untreated oil, which is lacking in the published scientific literature.

Aside from tradeoffs between habitats and taxa, it is also important to consider how dispersants affect oil biodegradation. Ideally, dispersants increase biodegradation by forming oil droplets that are more accessible to oil degrading microbes (Prince 2015). However, dispersants can also decrease biodegradation by being toxic to microbes or facilitating microbial degradation of dispersants rather than oil. Evidence is mixed on how dispersants affect oil biodegradation (Kleindienst et al. 2015a; NRC 2005, p.165, 257). King et al. (2015) concluded in a review of microbial responses to the Deepwater Horizon spill that Corexit 9500 likely increased oil biodegradation overall, although dispersants may have changed which microbes were present. Furthermore, studies that found that dispersants harmed microbes may have tested unrealistically high dispersant concentrations (King et al. 2015). Using laboratory tests, Prince et al. (2013) found that Corexit 9500 does not inhibit biodegradation. They argue that this supports dispersant use because dispersants are meant primarily to disperse thick oil slicks, not to increase biodegradation per se (Prince et al. 2013).

In contrast, Kleindienst et al. (2015b) found that dispersants (Corexit 9500) selected against microbes that degrade oil (pertaining to the Deepwater Horizon spill), instead selecting for microbes that degrade dispersants. Dispersants may inhibit certain oil degrading microbes and decrease overall biodegradation (Hamdan and Fulmer 2011; Rahsepar et al. 2016), except in diverse microbial communities where resistant species can help maintain biodegradation (Rahsepar et al. 2016). Note that studies comparing biodegradation rates of chemically dispersed oil and oil without dispersants often mechanically disperse the latter to much greater extents than would occur in the field (CRRC 2017). Thus, caution should be used in applying the findings of

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<sup>23</sup> [http://www.vetmed.ucdavis.edu/onehealth/local\\_resources/pdfs/whitmer-dispersed-oil.pdf](http://www.vetmed.ucdavis.edu/onehealth/local_resources/pdfs/whitmer-dispersed-oil.pdf), accessed 6/12/17.

these lab studies to comparing biodegradation rates of chemically dispersed oil vs. an untreated oil slick in the field (CRRC 2017). Overall, microbial community responses to oil and chemically dispersed oil are highly variable (Kleindienst et al. 2015a; Ortmann and Lu 2015; Overholt et al. 2016) and scientists are still debating the key question of whether dispersants help or harm biodegradation (e.g., Kleindienst et al. 2016 vs. Prince 2016).

## **7. Conclusions**

Responders need the right tools and information to decrease the environmental impacts of a major oil spill in SJC marine waters. No response method, whether mechanical, chemical, or biological, can totally negate the effects of an oil spill. Decision makers should realize that all response methods have tradeoffs and pick the method or combination of methods that best reduces overall environmental harm. Although mechanical responses have less environmental costs than chemical dispersants, dispersants should still be considered an alternate response option. This is because mechanical response alone may be insufficient (due to low oil recovery rates) or impossible (due to unfavorable sea conditions). Dispersant use may reduce overall long-term environmental harm by shifting oil impacts from sensitive shoreline habitats to water column habitats, which may be relatively more resilient, although quantitative comparisons are lacking. Washington state currently only stocks Corexit 9500—it may be beneficial to further evaluate other more effective and less toxic options. Regardless of the specific dispersant, dispersant effectiveness will depend on real-time conditions, especially the type and state of the oil and ocean mixing energy. Cold water conditions in SJC are unlikely to substantially decrease dispersant effectiveness. In addition to environmental conditions, decision makers must also consider the ecological costs and benefits of dispersants. Modern dispersants have low toxicity to marine organisms, and dispersant-oil combinations are not necessarily more toxic than oil itself. Evidence is mixed on whether dispersants promote the decomposition of oil by marine microbes. Overall, there remains considerable uncertainty about the best possible response to oil spills because the tradeoffs of different responses are site and spill specific. There is a particular need for linked models of oil transport and fate, dispersant effectiveness, and ecological consequences on local habitats and taxa.

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