TOWARD A FRENCH APPROVAL PROCEDURE FOR THE USE OF DISPERSANTS IN INLAND WATERS

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ABSTRACT: *The use of dispersant at sea has been well defined in many studies. For inland waters the situation is not the same. At the request of the French authorities, a study was performed to assess the use of dispersants in fresh water. This study leads to the conclusion that dispersant use in fresh water is possible only in running and turbulent waters. The toxicity of a light crude oil and a diesel oil to some freshwater animals was assessed, leading to preliminary recommendations. In other respects, too, the effectiveness of dispersants has been tested; many products that are effective in seawater give poor results in fresh water. Consequently, dispersants must be controlled prior to their use in rivers. As it has for dispersant use at sea, France is establishing a procedure for approving use of dispersants in fresh water. This procedure involves specific laboratory tests to test their effectiveness, toxicity, and biodegradability in fresh water.*

Numerous dispersant studies have been made in France to optimize the use of these products for oil spill responses at sea.[7] These studies have led to a series of recommendations for dispersant use, with written guides; an approval procedure for dispersants that relies on trustworthy laboratory testing; and well adapted dispersant application equipment. However, it appears that very few studies have been made of the use of dispersants in inland waters. Since no recommendations or regulations have been formulated, dispersants are often used poorly in inland waters (for example, without a good understanding of their toxicity or effectiveness; under poor dispersion conditions, such as an absence of turbulence; or in areas that are particularly sensitive.

This state of affairs is even more unsettling since, due to their limited sizes (in both extent and depth), inland waters are often more sensitive than the open sea.

In light of these facts, French authorities have requested CEDRE, in association with its scientific partners, to evaluate the possibilities for using dispersants in fresh water.

A multidisciplinary working group was established, with members from the Research and Documentation Center for Accidental Water Pollution (CEDRE), the Center for Agricultural Mechanization and the Forest and Water Service (CEMAGREF), the French Petroleum Institute (IFP), the Institute for Applied Chemistry Research (IRCHA), and the National Natural History Museum of Paris (MNHN).

Background on the use of dispersants

Objective of dispersants. Dispersants were perfected for use at sea to achieve two main objectives:

- Preventing an oil slick from approaching ecologically sensitive areas (when oil is dispersed in the water column the influence of the wind on a treated slick is diminished)
- Preparing the slicks for biodegradation

If mechanical means of confining and recovery (skimming) are ineffective, it is often preferable to "dilute" the oil in water. This breakdown of oil can be accomplished with dispersants. Dispersants should not be used unless natural degradation processes will be sufficient to eliminate dispersed oil without major threats to the marine environment's equilibrium.

Natural degradation processes are more effective with increased surface contact between the oil and the surrounding environment. Thus, it is preferable to break up oil slicks into small droplets, thereby increasing the surface contact between the oil and the environment. Using dispersants in this manner will simultaneously promote the breakdown of a slick into tiny droplets and a slowdown in the process of recoalescing of droplets. The ultimate goal of dispersant use at sea is to break down the oil so that natural degradation processes will be enhanced.

Toxicity of dispersants and treated oil. One of the main criticisms of the use of dispersants is the increased toxicity to pelagic species in the water column. The toxicity of a nondispersed crude oil (as well as the intrinsic toxicity of the recent dispersants) is usually low in comparison with the apparent toxicity of an emulsion of crude oil and dispersant.[1] It has been stated that emulsification enhances the rate and extent of the more soluble oil components, which are often the more toxic ones.[8]

Moreover, the dispersion process makes oil bioavailable: the more efficient the dispersion (the smaller the droplets) the more bioavailable is the oil. This bioavailability is required to increase biodegradability; some toxicity may be judged acceptable if this toxicity doesn't rise over well defined limits.

The definition of these limits must take into account the time of exposure, which is usually rather brief.

Recommendations for dispersant use and approval procedures. Keeping in mind the two aspects of the problem (increased biodegradation and/or increased toxicity), recommendations for using dispersants at sea have been developed, especially in terms of the dissemination of the pollutant within the water mass and in terms of ecological criteria. The recommended limitations on using dispersants take into account the geographic location of a spill (distance from the coast, depth, currents, environmental sensitivity of an area). An approval procedure for dispersants has been established to guarantee that the chemicals used are acceptable in terms of their effectiveness and environmental impacts.

French approval procedures include the following tests:[6]

- Evaluating the dispersant's effectiveness (by a dynamic-dilution "flow-through" test, AFNOR[1] No. 90.345)
- Evaluating the dispersant's toxicity and the toxicity of a dispersant/oil emulsion (in tests on shrimps exposed for six hours, under procedures in standardization projects AFNOR No. 90.348 and No. 349
- Evaluating the dispersant's biodegradability (in a procedure derived from the sturm method, AFNOR No. 90.346)
- Verifying that the dispersant in no way inhibits biodegradation of oil (AFNOR No. 90.347)

Possibility of using dispersants in inland waters

This study was concerned with three aspects of the problem: the hydrological conditions necessary for dispersion, the sensitivity of freshwater organisms to dispersed oil, and the effectiveness of dispersants in fresh water.

Determining the hydrological conditions necessary for dispersion. The use of dispersants is feasible only in moving waters (rivers and streams) should not be undertaken in poorly renewed water bodies such as lakes or pools. Flowing water provides the necessary turbulence to maintain dispersed oil in suspension, and the water flow enables the dispersed pollutant to be diluted and disseminated.

Using a mathematical model developed by sedimentologists, the minimum flow rate of a waterway was defined as 0.3 m/s. It should be noted that waterways that flow more slowly than this minimum rate are better cleaned using confining and skimming methods.

In other respects, even using several hydrological mathematical models, it was not possible to evaluate the kinetics involved in the decreasing of the concentration of a pollutant in a river.[5]

Laboratory tests were made by the IFP to evaluate the interaction between sediment particles (always present in inland waterways) and dispersed oil. Various kinds of clay particles were placed in contact with a dispersed crude oil for two hours in a tank equipped with a wave beater. At the conclusion of each test period, a mass analysis was made, to determine the quantity of oil attached to the sediment; the sediment particles trapped 20 to 80 percent of oil (Table 1).

Therefore, it can be predicted that most of a pollutant dispersed in an inland watery will, if it remains in suspension, rapidly attach itself to the sediment. Sooner or later, the water currents and flow will transport the oil-coated sediment to a calmer area, where it will be deposited. The dispersion of a limited amount of oil should result in the pollutant's being spread over a large distance along the waterway (where it will be deposited when the sediment settles on the river bottom).

This process will transfer an oil slick from the water surface to the river bottom, but spread over a large area. In most cases, this process is favorable to biodegradation of the hydrocarbons. However, this would not be true if the deposit areas had low oxygen contents; this point will need further study and will probably limit the use of dispersants in some situations.

Table 1. Laboratory test results for oil-sediment attachment

	Proportion of oil fixed to sediment particles
Initial oil-to-sediment ratio, 1; 400 ppm oil	
Illite	20
Bentonite	44
Kaolinite	37
Talc	83
Initial oil-to-sediment ratio, 8; 800 ppm oil	
Illite	5
Bentonite	4
Kaolinite	10

Evaluating the sensitivity of freshwater organisms to dispersed oil. The usual ecotoxicological tests are too long (24 to 96 hours) to give an idea of the acute toxicity of dispersed oil in a waterway. As a matter of fact, in such a situation the exposure times are short, since continuous dilution of a polluted water mass is to be expected in a flowing water body (with an exposure time of up to a few hours in slow dilution conditions).

Two types of tests were conceived at CEMAGREF and CEDRE, using an Arabian Light crude oil and a domestic fuel oil. The first type of test involved zebrafish (*Brachiderio rerio*), and the second involved young trout (*Salmo gairdneri*) and water fleas (*Daphnia magna*).

The zebrafish were exposed to oil emulsions in aquariums equipped with clean water inflow pipes and overflow runoffs. This setup was intended to produce dilutions similar to those in a natural river environment. The chosen rate of dilution ($3\ h^{-1}$) permitted a rapid decrease in oil concentrations.[2]

Under these laboratory conditions, the zebrafish tolerated very high initial pollutant concentrations (several thousand ppm of Arabian light).

The tests on the young trout and water fleas were done with a constant pollutant concentration (in a closed environment), but for relatively short periods (1.3 and 6 hours). It appears that the domestic fuel oil employed in these tests is at least twice as toxic as the light crude oil. Also, these two species of organisms are more sensitive than the zebrafish, since the lethal concentrations for 50 percent of subjects in three-hour exposures are 200 and 800 ppm of dispersed domestic fuel oil for the water flea and young trout respectively (Figure 1).

In light of these results, and without knowing the rate at which a dispersed oil concentration decreases in a given waterway, it has been recommended that, preliminarily, dispersants should be used only when initial oil concentrations are not greater than 100 ppm; this criterion will be a function of the flow rate of the water body and the volume of the oil spill.

This value, 100 ppm, should be confirmed (or modified) following additional laboratory tests in the toxicity of a larger series of oils, especially diesel oil.

Evaluating dispersant effectiveness in fresh water. It is necessary to know if the dispersants currently on the market are sufficiently effective in fresh water. A series of laboratory tests were done at CEDRE and at the IFP on 17 different dispersants.

Dispersant effectiveness was evaluated using the French "flow-through" test (AFNOR No. 90.345), but with fresh tap water in the test tank instead of seawater.[2]

The tests were made using several oil types (an oil mixture with a viscosity of 1,000 centistokes at 20° C and a domestic fuel oil).

These tests have shown that several dispersants, especially those previously approved for use at sea (effectiveness ≥60) were relatively ineffective in fresh water (effectiveness ≤20). (Effectiveness is measured from 0 to 100, where 100 equals the theoretical maximum amount that could be eliminated should a substance be totally dissolved.)

Test results confirm the results of many studies made in other

1. AFNOR is the French association for standardization of testing methods.

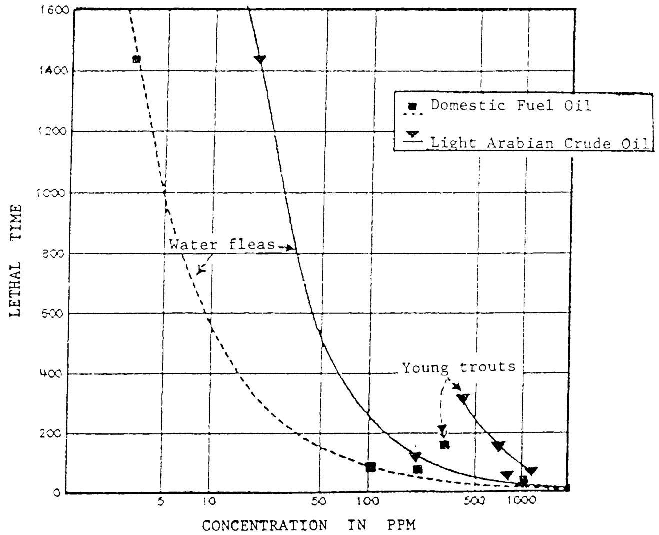

Figure 1. Lethal concentrations (ppm) for 50 percent of water fleas and young trout as a function of time (minutes)

laboratories.[4] However, it appears that some products have been designed to have acceptable effectiveness in both salt and fresh water (Table 2).

There is no way to predict the effectiveness of a dispersant in fresh water, and it will be necessary to verify the effectiveness of any available dispersant before it can be used in inland waters.

In other respects, a comparison of results obtained in fresh water on the same product at the IFP and the CEDRE laboratories has revealed a significant difference in results (see Table 2, results for dispersant A). This confirms the fact that the quality of fresh water will affect the effectiveness of a given product—especially the water's calcium and magnesium carbonate content (the TH—"Title Hydrotimetric"). In the test above, CEDRE's fresh water TH was 7, while IFP's fresh water TH was 30.

Recommendations on the use of dispersants in inland waters.

This study has enabled us to determine the main conditions for using dispersants in inland waters in terms of situation (dispersants should be used exclusively in free-flowing waterways); in terms of the volume of pollutant in relation to the flow rate of the river; and in terms of the type of pollutant.

Nevertheless, these first recommendations should be the object of additional ecotoxicological testing and will need confirmation under real conditions in a river, to better define the specific equipment and application procedures.

Finally, it has been shown that not all dispersants should be used in fresh water. Any dispersants that are to be used should be previously tested. It will be necessary to establish a procedure for approving dispersants for use in inland waterways.

Developing an approval procedure for dispersants to be used in inland waters

An approval procedure is being developed. As is true for dispersants to be used at sea, the approval procedure will rely on laboratory tests to assess the dispersants in terms of effectiveness, toxicity, and biodegradability. So far as a dispersant's effectiveness and toxicity are concerned, it will not be possible to apply results previously obtained from dispersant use at sea to dispersant use on inland waters (due to the physicochemical behavior of the dispersants and the different

Table 2. Results of flow-through test of dispersants' effectiveness in seawater and fresh tap water (test oil, 1,000 cs at 20° C)

Dispersant	Laboratory	Seawater	Fresh tap water
Dispersant A	IFP	63	77
	CEDRE	67	85
Dispersant 0	CEDRE	57	64

sensitivities of freshwater organisms. Work is being done to define trustworthy and appropriate laboratory methods.

Effectiveness. The effectiveness of a dispersant will be evaluated according to the same principles as for the use of dispersants at sea.

The test referred to is the "flow-through" test (AFNOR No. 90-345): it takes place in a 5-liter tank equipped with inflow and outflow (overflow) pipes, which create a flow current, enabling dilution in the tank. The tank is also equipped with a wave beater, which creates a moderate agitation or turbulence (Figure 2). At the beginning of the test, oil is poured in the surface water, and dispersant is added onto the oil. Effectiveness is determined by the quantity of oil dispersed and eliminated through the overflow pipe during a one hour period.

On the basis of comparative tests done at the IFP and CEDRE facilities, a few modifications were made for the following parameters:

- The fresh water has a standardized mineral content (hardness of water TH = 25).
- The wave beater action is reduced by half to simulate the lower turbulence usually encountered in rivers.
- Diesel fuel from atmospheric distillation is used as the reference oil pollutant, since this type of petroleum product is most similar to what is commonly encountered in inland water oil spills (diesel oil, domestic fuel oil, and kerosene).

Toxicity. The most important procedure developed involves tests for dispersant toxicity.

In principle, the procedure should include an evaluation of the intrinsic toxicity of a dispersant and a test for the toxicity of the oil/dispersant emulsion. The emulsion's toxicity should not be greater than that of a pure oil emulsion with the same physical characteristics.

The species of animal chosen for testing is the water flea (*Daphnia magnia*) due to the ease of using the organism and its relative sensitivity.

The test procedure, derived from the standard AFNOR No. 90.301 method designed for testing the toxicity of soluble substances, is being adapted for use with emulsions (oil/dispersant emulsion and pure oil emulsion).

The remaining problem was creating oil emulsions with and without dispersants, similar in term of toxicity and thin enough that the emulsions are stable during the test period.

A laboratory study carried out mainly by the IFP revealed that the use of a very powerful agitation system (an ultrasound beam) was able

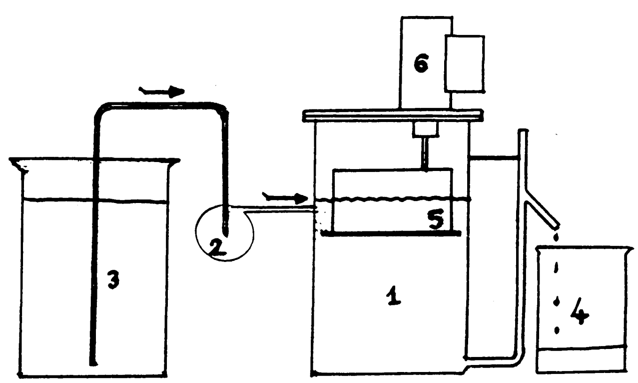

Figure 2. Experimental apparatus for French flow-through dispersion test AFNOR 90-345–1 = test tank, 2 = peristaltic pump, 3 = water tank, 4 = overflow reservoir, 5 = beater, 6 = electromagnet

to create a fine droplet emulsion in which the droplet size is similar whether or not a dispersant is part of the emulsion (diesel fuel alone, droplet size 2.1 μm; diesel fuel plus dispersant, droplet size 1.9 μm).

Calibration tests are currently being made at CEMAGREF that will develop the final version of a laboratory toxicity test for the water flea.

Aspects related to biodegradation. The fresh water dispersant approval procedure will include an evaluation of a dispersant's biodegradability and a complementary test to verify that the dispersant in no way inhibits the biodegradation of a particular oil.

These tests will employ the methods previously perfected by IRCHA and the MNHN, currently being used for approving dispersants for use at sea.

Conclusions

The use of dispersants can be considered as a method of responding to oil spills in inland waters. It appears that when confining and skimming a spill is impossible, dispersants may be appropriate for certain spills in flowing waterways, but not in stagnant or poorly renewed bodies of water.

An untreated slick will remain on the water surface and may be a serious source of pollution for the banks of rivers or streams. In many cases, long and costly cleanup and restoration may be required.

However, dispersing a slick will at first disseminate the oil within the water mass, which may increase the pollutant's toxicity to fauna and flora. Following this breakdown of the pollutant, the effects of turbulence and of oil attaching to sediment particles will "dilute" the pollutant over a long distance in a river, and the subsequent sediment deposit will cause the pollutant to be progressively deposited along the river bottom. This type of dissemination is seen as favorable for a pollutant's biodegradation and elimination by the natural environment.

Despite the ease of using dispersants, compared to other means of pollution response, chemical dispersants should not be considered a panacea for all spills. The use of dispersants should be limited to situations where it is possible to obtain a good emulsion of the oil/dispersant, and where the toxicity of such an emulsion will not be too dangerous for the environment.

Some initial recommendations have been developed. They will be completed with additional tests, to develop a coherent philosophy for the use of dispersants in inland waters.

Attaining this goal requires experiments in a real situation in a river in France, to confirm laboratory test results. These field tests will enable us to define and improve equipment and procedures for applying dispersants in rivers.

It is important that fresh water dispersants be approved, as are those designed for use at sea. At the request of the French authorities, a specific approval procedure for fresh water dispersants is being developed and will be operational by 1991.

As is true for dispersants approved for use at sea, the fresh water approval procedure will include tests for effectiveness, toxicity, and biodegradability.

Finally, since inland rivers know no political boundaries, it will be necessary to harmonize the recommendations and procedures with those of neighboring countries, especially between European nations.

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