

EXPERIMENTAL STUDY OF CHEMICAL BEHAVIOUR AT SEA :
POLLUTMAR I AND II TRIALS

by

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SUMMARY

In order to better understand the physico-chemical behaviour of chemicals when accidentally released at sea, two sea trials were conducted by CEDRE during 1989.

During the first series of trials off Brittany (POLLUTMAR I), 3 tons of chemicals were released (ethyl-2 hexanol, butyl methacrylate, acetone, ethylene glycol) and the diffusion of the chemicals in air and within the water column was observed and measured.

During the second series of trials in the Mediterranean sea (POLLUTMAR II), a gas tracer, sulfur hexafluoride, was released just above sea level and was followed and observed for several kilometers.

These two trials allowed us to compare the result predicted by forecast models with those obtained from "in situ" measurements.

INTRODUCTION

Chemical spill response at sea requires a good understanding of the chemical's behaviour in sea water.

Up to now, our knowledge of the physico-chemical behaviour of chemicals accidentally spilled have been based on laboratory tests, in tanks, or in a "controlled natural environment".

The first objective of the two "POLLUTMAR" trials which were undertaken by CEDRE in 1989 was to better define the behaviour of chemicals (spreading, dispersion in water, and in air) under conditions which are more realistic ; the second objective was to validate results provided by risk assessment prediction models.

Two sea trials took place with surface ship and air craft:

- "POLLUTMAR I" July 3-6, 1989, off the coast of Brest, where a total of approximately 3 tons of chemicals were released (ethyl-2 hexanol, butyl methacrylate, acetone, ethylene glycol),
- "POLLUTMAR II" October 23-25, 1989, off the coast of Toulon, in the Mediterranean, where a gas tracer (sulfur hexafluoride) was released and followed for several kilometers.

I. POLLUTMAR I TRIALSI.1. Description of the trials

During these series of trials the chemicals, chosen among those most often transported and representative of the different behaviour families, were released at sea. Quantities of 200 and 400 liters of each of the 4 chemicals were released.

The characteristics of the chemicals are presented in table 1.

Table 1Chemical characteristics

: Characteristics	: European classification	: Density		: Solubility	: Vapor pressure	: Dye
		: Liq.	: Vap/air			
: Chemical	:	: Liq.	: Vap/air	:	: AMB.T.	:
: Ethyl-2 hexanol	: FD	: 0.834	: 5.790	: 0.1	: 0.024	: RED ORGANOL
: N-Butyl methacrylate	: FED	: 0.8975	: 6.192	: 0.6	: 0.53	: RED ORGANOL
: Acetone	: DE	: 0.791	: 2.58	: 78	: 24.75	: BLACK SAVINYL
: Ethylene glycol*	: SD	: 1.115	: 2.761	: All	: 0.008	: PINK SAVINYL

: * During the trials, the chemical was used in a 30% solution in fresh water to obtain a density of 1.03.

Dyes which are specific for use with the chemicals and which are insoluble in water (see Table 1) were pre-mixed with the chemicals in amounts equal to 10g/l (mixing occurred before release). The slicks were also marked using buoys.

A certain number of water sample analyses were made on board (using colorimetry and infra red spectrometry) ; additional analyses were done in a laboratory after the trials were completed (using Gas Chromatography). Measurements of organic vapor in air were made using an HNU photoionizer. An oceanographic and meteorological station continually recorded the following parameters : surface current, subsurface current (down to 10 m), temperature, salinity, swell (height and direction), wind (speed and direction).

The slicks were also photographed and filmed from aircraft. In addition, we also attempted to use sensing techniques with the aircraft of the French customs authority which is specifically equipped for this job.

During the trials, several prediction models (CHEMSPIL, HACS, EFFECTS, EXAMS) were run in order to determine :

- the slick's spreading,
- chemical evaporation and dispersion in air,
- dissolution and dispersion in the water column.

I.2. Main results

a) Remote sensing

These flights enabled the following conclusions :

- no detection was possible using side SCAN radar,
- the presence of ethyl-2 hexanol and n-butyl methacrylate was detected using an infra-red scanner, but the presence of acetone was not determined (tests using the infra-red scanner to detect ethylene glycol were not made),
- the best results in remote sensing detection were obtained in the trials involving the methacrylate with a flight at 500 feet (the surface which can be swept is larger at 1 000 feet but results are less precise), and even these results are significantly poorer than those obtained for a test slick of diesel fuel.

Results obtained during the sea trials suggest the possibility of detection using an infra-red scanner for floating chemical slicks. On the other hand, an absence of detection for the acetone is logical since this very soluble chemical rapidly disappeared from the surface.

Even if the results obtained are poorer than those for oil slicks, they can still be interpreted and enable us to detect the presence of chemical slicks as well as determine the varying thicknesses of a slick.

However, we still have questions concerning the influence of the chemical dyes which were mixed with the test

chemicals before they were released. It is advisable to conduct trials using non-dyed floating chemicals.

b) Prediction models

On the whole, the predictions obtained using the various models are very similar : all agree that the four chemicals should be totally dispersed within the water and/or evaporated and dispersed in the air several minutes after release.

c) Comparison of field measurements and prediction models

The predictions provided by the various models differ from the "in situ" observations during the trials. The differences concern the following points :

- persistance of the slick on the water surface (ethyl-2 hexanol and N-butyl methacrylate)

The "in-situ" observations and measurements have shown that the slick persists for a longer time period than was predicted since when the observation period was terminated (after 30 minutes or 1 hour according to the case), the slick or patches of slick were still present. The slick of ethyl-2 hexanol was probably persistant for several hours ; since no longer observation time had not been scheduled during the trials, it is difficult to estimate the actual length of time the slicks remained on the surface. This persistance of surface slicks shows that the kinetics of dissolution for chemicals in the water mass as well as the kinetics of evaporation are longer than predicted.

- Diffusion of chemicals in water

In the same manner, the kinetics of a diffusion of chemicals in water are slower than predicted by the models.

* for ethyl-2 hexanol (solubility 0.1%), the dispersion in water was much slower than what the models predicted which was that the amounts of ethyl hexanol should rapidly decrease to an amount much lower than 1 ppm 10 minutes after the initial release. In fact, after the initial release, the chemical concentrations were about 10 ppm under the slick but they remained persistant (< 1 ppm) during the entire observation period (30 minutes) which shows the slow dissolution of the slick from the water surface.

* for n-butyl methacrylate (solubility 0.6%), the dispersion in water was also slower than what was predicted by the models ; the models estimated that all the n-butyl methacrylate would be dispersed in the water mass after 3 minutes, however the detectable amounts were again on the order of 1 ppm 30 minutes after release, with a maximum of more than 10 ppm.

* For acetone (78% solubility) the prediction models estimated that the release would dissolve very rapidly and provide zero concentration levels after 3 minutes. However, the results of the water analyses revealed that the concentrations of acetone were as high as 4 ppm (in the water level between 0-4 m deep) 15 minutes after release with a maximum of 30 ppm just below the slick surface.

As was the case for the two previous chemicals (floaters), the actual process of diffusion is slower than what was predicted.

* For ethylene glycol (total solubility, heavier than water), the models predicted that the concentration of ethylene glycol would rapidly diminish and zero concentrations in the water mass would be obtained within 2 minutes.

The trials have shown that after 15 minutes the concentrations varied between 0 and 100 ppm and at the conclusion of the observation period (30 minutes), the concentrations were still at approximately 40 ppm.

It should be remembered that this chemical was pre-diluted in fresh water in order to obtain a density which is the same as sea water, and this has probably modified the chemical's expected behaviour.

- Diffusion of chemicals in air

The results obtained have shown that the concentrations above the slick are very low for ethyl-2 hexanol (maximum concentration of 6 ppm just above the slick). For the butyl methacrylate, the maximum concentration of vapor above the slick is higher : a value of 70 ppm was recorded just after the release, which is normal in light of the higher evaporation rate for the chemical (vapor pressure 0.5 kPa for butyl methacrylate, classification FED, while ethyl-2 hexanol is considered as a floater and dissolver, FD).

However, the amounts of concentration in air are much lower than those predicted by the models, which were on the order of thousands of ppm (that is, on the order of 1 part/thousand) during several seconds or minutes following the release. In fact, the recorded concentrations are much lower (about 100 times lower), however the vapors persists for a longer time, apparently for the length of time that the slick is present on the water surface. The kinetics of a disappearance of these chemicals in air have shown a slow evaporation which may also explain the slicks persistence on the water surface.

The results observed for acetone or ethylene glycol are similar to what was observed for the two chemicals : the concentrations observed in the field (less

than 5 ppm) are much lower than what was predicted by the HACS (Hazard Assessment Computer System) model immediately after release.

I.3. CONCLUSION OF "POLLUTMAR I" SEA TRIAL

The differences observed between the predictions proposed by mathematical models and the actual field observations are as follows :

- the phenomena of evaporation and spreading are slower than what was predicted by the models ;
- the concentrations of chemicals in the water are lower than what was predicted.

From an operational point of view, this confirms the fact that :

- chemicals, even those considered to be evaporators or dissolvers, could persist for a long period on the water surface. This may justify using pollution response methods which might at first be limited by an absence of color for most chemicals,
- the models can be perfected and should be used with caution until they have been improved,
- remote sensing seems to give interesting results in some cases.

II. POLLUTMAR II TRIALS

This series of trials had the objective of :

- studying the dispersion of a gas cloud above the sea surface by releasing a non-toxic gas tracer : sulfur hexafluoride (SF₆),
- to compare observations in the field with the predictions of several mathematical models.

II.1. Description of the trials

A spray system was installed at the rear of a ship and puffs of a gas tracer were released at various intervals. Previously positioned surface craft recorded gas concentration at the surface and about 10 meters above the water (measured using gas phase chromatography).

- Installing the system

The spray system was intended to simulate the evaporation of a chemical from a chemical slick about 150 m in diameter ; in order to install such a set up, several anchored buoys were necessary as well as about 1000 m of hose, twenty spray heads, several bottles of gas tracer and a compressor.

- Trials

Several trials took place with various release rates in order to simulate the evaporation of chemicals which are more or less volatile. The gas tracer was measured up to a distance of 4 km down wind using 3 small sea crafts (zodiacs), one of which was equipped with a system for measuring at a low altitude. Two additional trials took place in order to simulate the movement of a gas cloud. The non-toxic tracer was captured in a 10 m long plastic bag which was then pierced and the pre-positioned surface crafts were able to observe the cloud's subsequent movement.

- Measuring different parameters

During the trials, the meteorological factors were measured by a weather station and positioning the surface craft for taking measurements was assisted by use of the radar on board the support ship.

II.2. Main results

The three main conclusions of this study are as follows :

- the diffusion of gas at sea is slower than that predicted by the models (and is also slower than what we observe on land) due to the absence of air turbulence caused by terrestrial relief,
- since meteorological conditions are relatively variable at sea, it is difficult to correctly predict the evolution of a toxic plume since the plume will coil and twist at the water surface,
- due to the lack of wind stability and to the lack of air turbulence, the gas cloud is observed as being larger (40°) and four times more extensive (spread out) than the value predicted by the models.

In fact, atmospheric diffusion is a function of a certain number of parameters, notably wind speed and direction, but also turbulence which could enhance a chemical's dispersion. On land, turbulence is caused by relief (trees, buildings, mountains). If we study atmospheric dispersion at sea, we are dealing with a flat surface that is devoid of relief which could result in supplementary turbulence. Thus, the diffusion of a pollutant is slower at sea since there is less mixing. This fact could explain the gap between the measured concentrations and those predicted by the models. In fact, at a given moment and at a given point, with less turbulence, there will be less diffusion of a pollutant and therefore a more homogeneous plume with a consequently higher chemical concentration.

In order to take into consideration this lack of turbulence, it is necessary to modify the mathematical formulas in order to correct the factor 4 which was experimentally proposed as compensation between the measured value and the predicted value.

The differences between diffusion at sea and on land can be summarized in the following table :

Table 2

	Diffusion at sea	Diffusion on land
Wind direction	Very variable 40° angle	In function of wind speed 60°, 40°, 30° and 20° angles
Turbulence	Poor	Significant

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