

**EXPERIMENTAL STUDY OF CHEMICAL
BEHAVIOUR AT SEA :
POLLUTMAR III SEA TRIALS**

**by : François Merlin
CEDRE**

ABSTRACT

In order to better understand the behaviour of chemical when accidentally released at sea, CEDRE has carried out offshore trials in October 1990 with the French Navy.

These experiments consisted in dumping different kinds of chemicals, dissolvers and floaters up to a volume of 1 m³ each.

The plumes of dissolved chemical were measured and recorded at 3 depths, while the vapor emission was followed using special sensor.

On floaters, the slick areas were assessed using aerial remote sensing device as the Infra-Red Thermographies.

All data collected were useful to check the reliability of predicting models for spreading, evaporation and diffusion.

I. INTRODUCTION

A great many studies have been carried out in order to determine the behaviour of chemical substances when they are released at sea. However, most of these studies have been theoretical such as the prediction of behaviour based on calculations using computerized models which were previously developed up to this time.

Unfortunately, there has been very little experimental work done in situ, at sea, which will permit us to verify the reliability of the prediction models. For this reason, the French authorities have undertaken the Pollutmar Experimental Program which consists of testing in the open sea. This program has been accomplished with the help of technical advice from CEDRE and with the logistic support of the French Navy. In 1989, the sea trials POLLUTMAR took place, in order to observe the behaviour of floating and soluble substances at

sea, and in 1989, POLLUTMAR II was concerned with the behaviour of gas clouds at sea.

In 1990, the sea trials (POLLUTMAR III) took place off the coast of Brittany (the Western coast of France) and consisted of releases between 400 l to 1 000 l of chemicals in order to specifically study :

- 1) The possibilities of using teledetection techniques in the event of chemical spills, especially the Infra-Red Scanner which is currently employed by French authorities.
- 2) The phenomena of Spreading, Evaporation and Dissolving for Floating and Soluble chemicals.

The observations made during this third phase of the study have also been compared with the predictions given by several computerized models in order to verify the models' reliability.

II. SEA TRIALS IN THE POLLUTMAR III PROGRAM

The sea trials took place in two distinct phases for this last chapter in the POLLUTMAR Experimental Program.

Phase 1 : Five releases of 1 m3 each (an oil, and two floating chemicals, which were both dyed and undyed) in order to study:

- a/ teledetection (responses compared for the various chemicals, especially when using Infra-Red detection methods)
- b/ evaporation/gas release

Phase 2 : Three releases of a colored soluble substance in order to observe its diffusion in water at various depths (1, 2, and 4 m).

III. TESTING METHODS

III. 1 - METHOD FOR RELEASING THE CHEMICALS

Each chemical slick was obtained by the instantaneous release of the substance to be studied, on the sea's surface. This release was possible since the substance was pumped into an open ended cylinder which, when raised, would instantly free the chemical. This method of release has the advantage of being able to be repeated in the same manner as often as necessary, and of creating slicks which are located exactly where desired.

III. 2 - PHASE 1 : COMPARISON AFTER RELEASE OF DIFFERENT FLOATING SUBSTANCES

Five slicks of 1 m³ each were successively released at very little distance from each other in order to compare their evolution (their slick formation and spreading), and the images obtained using teledetection devices, as well as to measure any vapor release in the air, for evaluation of the phenomenon of evaporation.

Three substances were chosen for this test phase :

- a) diesel fuel, as a reference substance
- b) ethyl-2-hexanol, a colorless floating chemical with a solubility of 0.1 % (classified as a floater/dissolver in the European Classification)
- c) N-butyl methacrylate, a colorless floating/volatile chemical with a solubility of 0.6 % (classified as a floater/dissolver/evaporator in the European Classification).

The two chemicals (Ethyl 2-hexanol and N-butyl Methacrylate) were released with and without a dye (Organol Red) in order to verify if the dye has a particular influence on detection when using remote sensing devices.

The measures used in the teledetection were done on board an airplane using an Infra-Red Scanner (thermography) and a side scan radar apparatus (SLAR).

Any gas released in the air was measured using an HNU photo ionization detector, and a Bruel Kaer detector (involving an Infra-Red photo-acoustic detection method).

The slick spreading was observed and evaluated on the basis of photographs (for the dyed slicks) and using the thermographic images obtained by means of the Infra-Red detector.

III.3 - PHASE 2 : OBSERVATION OF DIFFUSION DISSOLVING OF A SOLUBLE SUBSTANCE AT SEA

Three releases of 400 and 800 l of isopropanol took place. The isopropanol was traced with a water soluble dye (Rhodamine B, 8g/l).

The choice of this dye was made after laboratory testing, on a smaller scale, revealed that the behaviour of a mixture of isopropanol + Rhodamine B was identical to the behaviour of an undyed isopropanol.

The diffusion of the isopropanol at sea was continually measured using spectro fluorometric measurements for the content of colorant at depths of 1 m, 2 m, and 4 m.

Simultaneously to the spectro fluorometric measuring, water samples were recovered which enabled a later laboratory verification that the amount of colorants and isopropanol remained in the same original proportion during the entire test period.

All the measuring set-up (which included a submerged pump, and a spectro fluorometer connected to a recording device for each depth to be measured) was installed on a small craft, in order to cause the least disturbance to the chemical slick during the period necessary to complete the measurements.

During the entire test period, the small sea craft crossed the slick several times in order to obtain the necessary profiles of the Rhodamine B concentrations. As far as possible, these crossing were marked in relationship to the slick (on sketches and on the photographs taken from a helicopter) in order to locate the concentration profiles on the actual slick. An example of a concentration profile and slick crossing is shown on further Figure 2 .

IV. OBSERVATIONS AND RESULTS

IV.1 - TELEDETECTION

The Infra-Red thermographs have enabled us to detect releases of methacrylate, however the images have less distinct contrasts than those taken for the diesel oil. Nevertheless, the image is of a good quality, and the methacrylate images are similar despite whether the chemical is dyed or undyed.

No I.R. detection was possible for the release of Ethyl-2-Hexanol (either dyed or undyed).

For the side scan radar equipment (SLAR), no detection was revealed for any of the three types of substances released (diesel oil, methacrylate, or ethyl-2-hexanol) however, considering that this type of detection is more long range, the size of the spill, even if as much as 1 m³, may have been insufficient to be viewed by this type of large range imagery.

IV. 2 - SPREAD OF FLOATING SUBSTANCES

Observations have shown that :

1. The diesel oil slick is considerably spread in the wind direction (3000 m² five minutes after release) but becomes relatively more compact at the end of 1 h 30 to cover about 1,800 m² in the shape of a slick 80 x 250 m.
2. The slick of methacrylate without dye had a more stringy appearance and its surface diminished from the 2,200 m² observed 5 minutes after release to a surface of 1,400 m² at the end of 40 minutes (Figure 1).
3. The slick of dyed methacrylate is broken up and is also reduced from a surface of about 4,300 m² after 5 minutes following the release to about 1,200 m² after 40 minutes following the release.

Figure 1

Evolution of the Slick of Undyed N-butyl Methacrylate

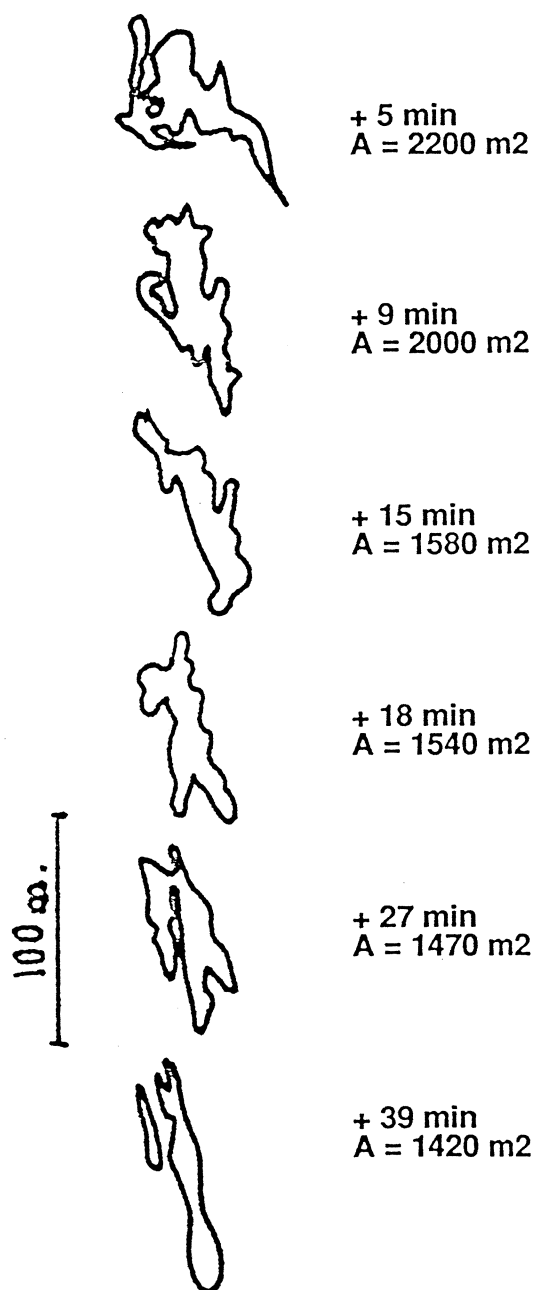
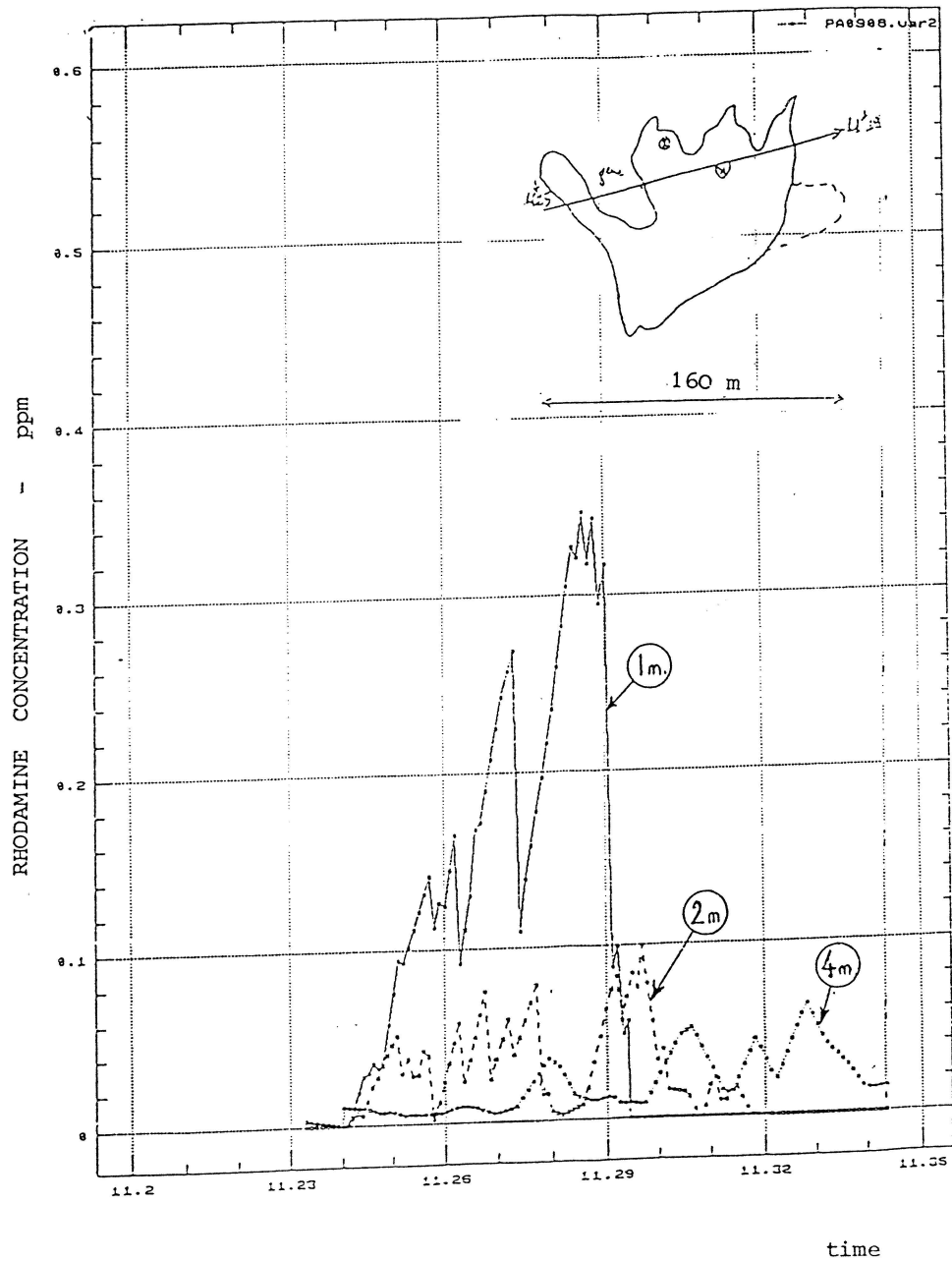


Figure 2
Evolution of the profile concentration Eight Crossing of Slick n°9



The fact that the slick of dyed methacrylate was half as much spread out in the first few minutes following the release as the slick of undyed chemical may be due to the difference in the two spreading coefficients which varied between 17 to 24 when previously measured in the laboratory.

For the slick No. 4 (dyed methacrylate), the aerial photographs confirm the images received by the I.R. thermographic imagery, and show a slick size which is reduced by half 40 minutes after release.

This reduction in the size of the slick for the two slicks of methacrylate is due to the chemical's evaporation rate.

IV.3 - EVAPORATION

♦ For the ethyl-2-hexanol the concentration of the gas released in the air down wind from the slick, shortly after the chemical slick release, was measured as being between 1 and 5 ppm, with a maximum concentration of 10-15 ppm. The evolution of the gas concentrations is not very regular and corresponds to the successive puffs of wind where the chemical concentrations were cut by passages of practically pure air.

After 53 minutes following the initial release, we can still measure a certain amount of evaporation. To give an idea of what we expected when comparing the real concentrations with those proposed by a prediction model, the model CHEMSPILL predicted that the slick would be completely evaporated after 23 minutes.

♦ For the methacrylate, gas concentration profiles were made at various distances from 50 meters down wind from the slick up to a distance of 250 meters. The slick disappears about 50 minutes after the release (the CHEMSPILL model predicted this would take place after 28 minutes). The following table shows the gas concentrations in function of the distance involved.

Dist. (m)	Profil 1 (10 mn)	Profil 2 (15 mn)	Profil 3 (25 mn)	Profil 4 (35 mn)
50	35.00	26.7	27.2	26.8
100	30.00	15.0	13.00	9.00
125	28.00	11.0	10.0	7.5
150	25.0	10.0	7.00	6.5
175		9.5	6.4	5.5
200		6.0	4.5	4.3
250	4.0	4.8	1.6	1.5

Table 1

Other gas concentration measurements were made for the release of isopropanol (phase 2 of the Sea Trials) and have shown that in the case of a soluble chemical, evaporation takes place much more slowly (gas concentrations in air of 1 to 4 ppm as much as 4 hours after the initial chemical release).

This observation is very different from what was predicted by the models (CHEMSPILL) where a rapid rate of evaporation (with concentrations from 40 to 50 ppm) were predicted for only the first three minutes.

The phenomenon of evaporation for soluble substances still needs to be evaluated.

IV. 4 - RATES OF DISSOLVING/DIFFUSION FOR SOLUBLE SUBSTANCES IN THE SEA

IV.4.1. Heterogeneity of the Dissolved Clouds Released by a Dissolving Chemical

An examination of the concentration profiles for the isopropanol when it is dissolved in seawater has shown that even though the slicks are compact very shortly after the isopropanol is released, within a few minutes the slicks begin to break up into several smaller, stringy slicks ; therefore the concentration profiles of dissolved chemical are very irregular (a succession of peaks) (see Figure 2).

IV.4.2. Rate of decreasing concentrations is a function of the sea surface agitation (Figure 3).

If the sea is relatively agitated (with waves 1.5 m high, for the release of 800 l of isopropanol slick n°10), after 45 minutes there is no more than a few ppm of isopropanol at a depth of 1 m.

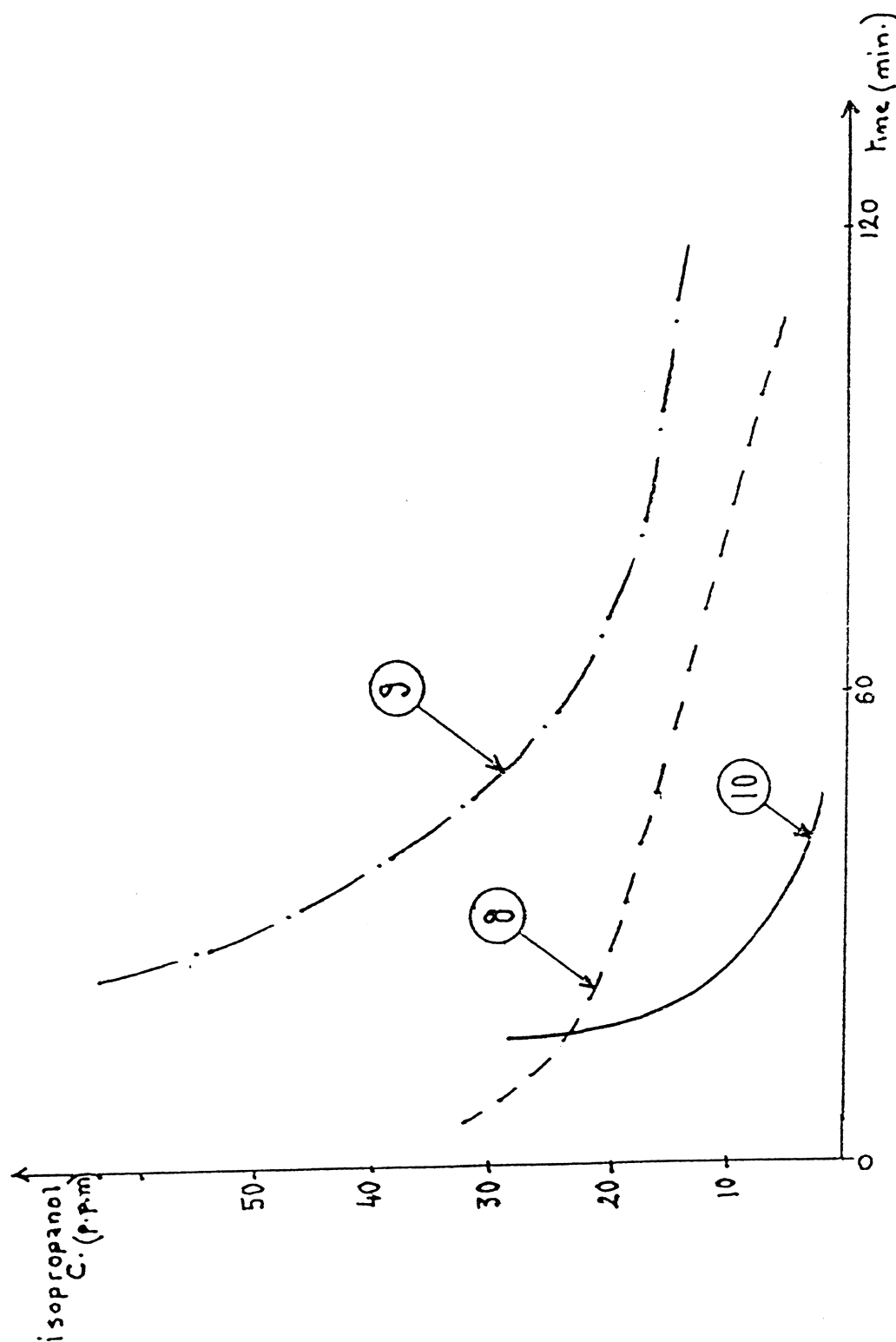
If the sea is calm (as was the case for the two other isopropanol releases of 400 l each slicks n°8 and 9), the dilution was much slower, and it was necessary to wait for 2 to 3 hours before a concentration of only a few ppm could be achieved.

A comparison of two different sea state agitations can be made by comparing the concentrations for slicks 9 and 10 where it can be seen that 30 minutes after release at a depth of 1 m, the concentrations of slick 10 are 10 times lower than those observed for slick 9.

IV.4.3. Evolution of a dissolved chemical depends on the state of the sea's agitation.

a/ on calm sea such as was present for the release of slick first isopropanol slick (400 l), the peaks of concentration at 2 m depth remained low and constant (few ppm) even when the

Figure 3
Evolution of the peaks of concentration at level 1 for Slick n° 8, 9 and 10



concentrations recorded on the surface showed large variation ; this shows that under these particular sea conditions, the diffusion of a chemical is more horizontal than vertical, and the chemical is more rapidly disseminated over the surface.

b/ for agitated sea such as the conditions at the time of release last isopropanol slick (800 l), the peaks of concentration at 2 and 4 m depths are only slightly different from the values obtained at 1 m depth ; this suggests that the vertical diffusion, at least up to a depth of 4 m, was much more significant than for the previous case, and had as much effect as the horizontal diffusion. The turbulence caused by 1.5 m waves has affected the diffusion for a depth of at least 4 m.

For a calm sea state, the predictions proposed by the CHEMSPILL model were very close to what was actually observed (see Figures 4 and 5).

V. CONCLUSIONS

The POLLUTMAR III sea trials have provided a great deal of information concerning the behaviour of chemicals released at sea. The objectives of the study were achieved, especially as far as :

1/ a teledetection of floating chemical substances : the significance of the equipment used by French authorities has been confirmed, but the limitations of this equipment have also been shown. In the future, it will be necessary to prepare a list of the floating chemicals which are able to be detected using this type of equipment.

2/ a better understanding of the behaviour of chemicals released at sea in terms of their evaporation and dissolving; one important aspect of this study concerns the numerous measurements that were made which have enabled us to verify the propositions of certain prediction models available at this time.

As far as the phenomenon of evaporation, the models need to be improved, especially in order to take into consideration the simultaneous actions of evaporation and dissolving.

As far as dissolving is concerned, the models seemed to be in agreement with the observations made in the field which is encouraging. Nevertheless, it will be necessary to confirm these findings under different conditions (more agitated sea state, or when testing other chemicals) in order to completely verify the reliability of the predictions calculated by the models.

Figure 4
 Slick n°8 : Evolution of the peaks of concentration observed (O) compared to the predicted peaks of concentration (P)

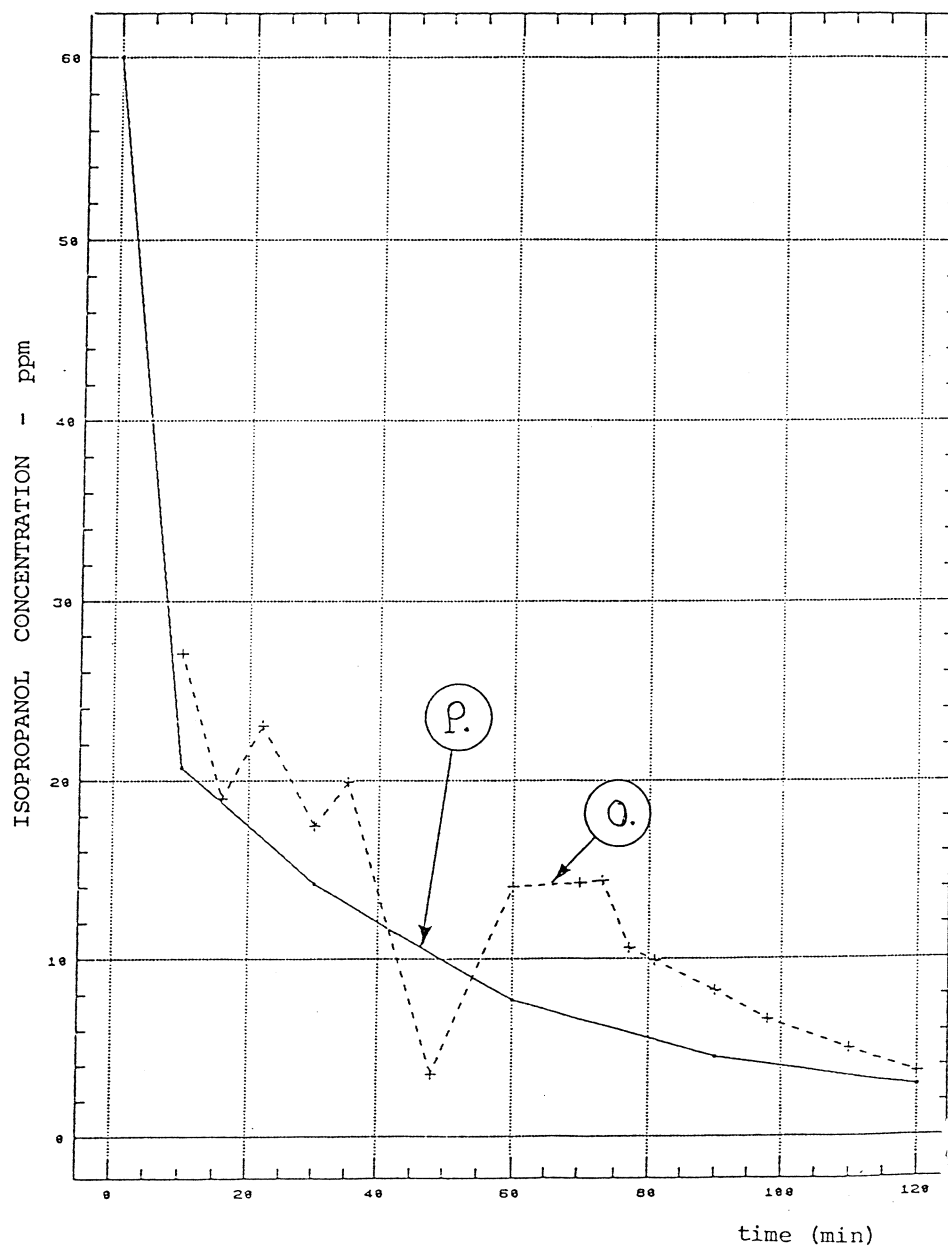


Figure 5
Slick n° 9 : Evolution of the peaks of concentration observed (O) compared to the predicted peaks of concentration (P)

