Nº 027/2003

INFORMES CIENTÍFICOS Y TÉCNICOS

FACULTAD DE CIENCIAS DEL MAR

EVALUACIÓN DE LA TOXICIDAD Y EFECTIVIDAD DEL DISPERSANTE QUÍMICO PARA DERRAMES DE PETRÓLEO

MPCD

Prof. Fernando Alcázar González

♦ junio de 2003 ♦

EVALUATION OF THE EFFECTIVITY AND TOXICITY OF THE OIL DISPERSANT

MPCD

BACKGROUND

The detergent **MPCD** is a non flamable dispersant based on a dilution of surfactants in water, sodium bicarbonate and sodium metasilicate. The solution is provided in 55 gallon drums in a concentrate form.

MPCD is an acqueous solution, pink, presenting a density slightly heavier than water. This characteristic requires an inicial agitation of the product to dissolve in water.

The oil spill dispersant is applied in the field by means of a strong spraying apparatus, using a standard automatic dosing machine to disperse the adequate ratio water/dispersant. The dispersant can be dissolved and used indistinctly in fresh and sea water.

According to the instruction provided by the supplier (Annex 1) the Dispersant **MPCD** is environmentally safe for its application in presence of field crews. It is also safe for aquatic fowl, marine mammals and subaquatic species in general.

The product can be disolved in water in a ratio of one part of chemical in 64 parts of water (1,5 % solution). The field application may require pressure sprayers and nozzles, directly over the oil spills, in fresh and sea water.

METHODS AND RESULTS

Efficiency Test:

A 5% solution of the dispersant **MPCD** was used to test the stability of the emulsion formed by mixing the dispersant with a sample of Kuwait light crude oil. The mix was swirled in a 500 ml Erlenmeyer flask applying smooth circular movements to form a distinct emulsion. The emulsion was left standing for 10 minutes observing the capacity of the oil dropplets to be dispersed again after a gentle swirling. The dispersing effect was judged as adequate and satisfactory.

Toxicity Test

The biological toxicity of the dispersant was evaluated following the protocols established at the IX Session of the Marine Environment Protection Commitee of IMCO (IMCO/MEPC) (Annex 2). The mortalities were graphically plotted against discreet concentrations. The LC 50 after 96 hours was determined by a projection of the 50% survival against the concentration gradient.

BEHAVIOR OF THE DISPERSANT IN AQUEOUS SOLUTION

A master solution of the dispersant was prepared (1 part dispersant in 20 parts of sea water). This dilution is slightly higher than that suggested by the supplier, but it was recommended for the bioassay procedures after preliminary trials that indicated that at 1,5 % solution the curve was not resulting in a practical endpoint.

The solution is slightly pink, translucent and giving off a slight ammonia odour. The solution is clear, homogeneous and does not show any precipitates.

EVALUATION OF THE TOXICITY OF THE DISPERSANT **MPCD**

]Specimens of the fish *Girella laevifrons* (juveniles of 60 to 80 mm) and adults of the rock shrimp *Rhynchocinetes typus* (50 y 80 mm) were acclimated in 20 liter glass aquaria.

The specimens were obtained from the intertidal pools at the Marine Station of the Facultad de Ciencias del Mar , Universidad de Valparaíso.

The shrimp were captured using traps in the sublittoral areas of Caleta Higuerillas. Both species were adapted to laboratory conditions during one week prior to the bioassays.

A series of assays were conducted in a concentration range between 250 and 1.750 parts per million for both species. The glass aquaria were kept aerated by means of air pumps. The physical conditions and behavior of the specimens were observed during 96 hours in all concentrations, observing the opercular movements, the swimming movements and the branchial chamber movements and general attitude for the fish and shrimp. The mortality criteria was based on the cesation of all vital movements.

The results of the exposure of the specimens to the test dispersant after 96 hours is given in the following table.

	C**oncentration** / Mortality (10 specimens)					
Species (10 individuals)	**control**	**750**	**1000**	**1.250**	**1.500**	**1.750**
Rhynchocinetes typus	0/10	1/10	0/10	**5**/10	**10**/10	**10**/10
Doydixodon laevifrons	0/10	0/10	0/10	0/10	**4**/10	**10**/10

The graphic determination of the Lethal Concentration for 50% of the specimens of rock shrimp *Rhynchocinetes typus* is 1.250 mg/L .

For the specimens of the fish *Girella (Doydixodon) laevifrons*, the graphic reading of the CL50 96 hours is 1.450 mg/L.

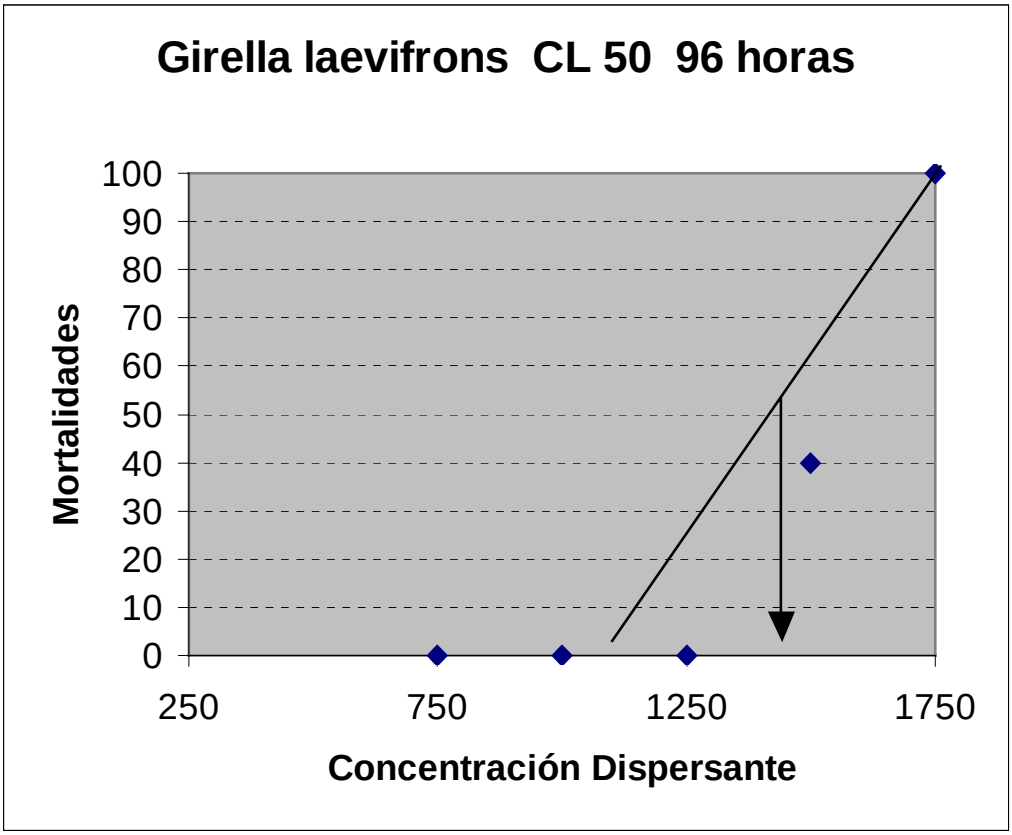
The IX th Sesión of the MEPC classifies as inocuous any solution that causes a CL50 96 hours above 1.000 mg/L, therefore environmental applications of dilutions of 5% or lower of the dispersante **MPCD** can be proven as inocuous for the test species and can be considered inocuous for other species in field applications.

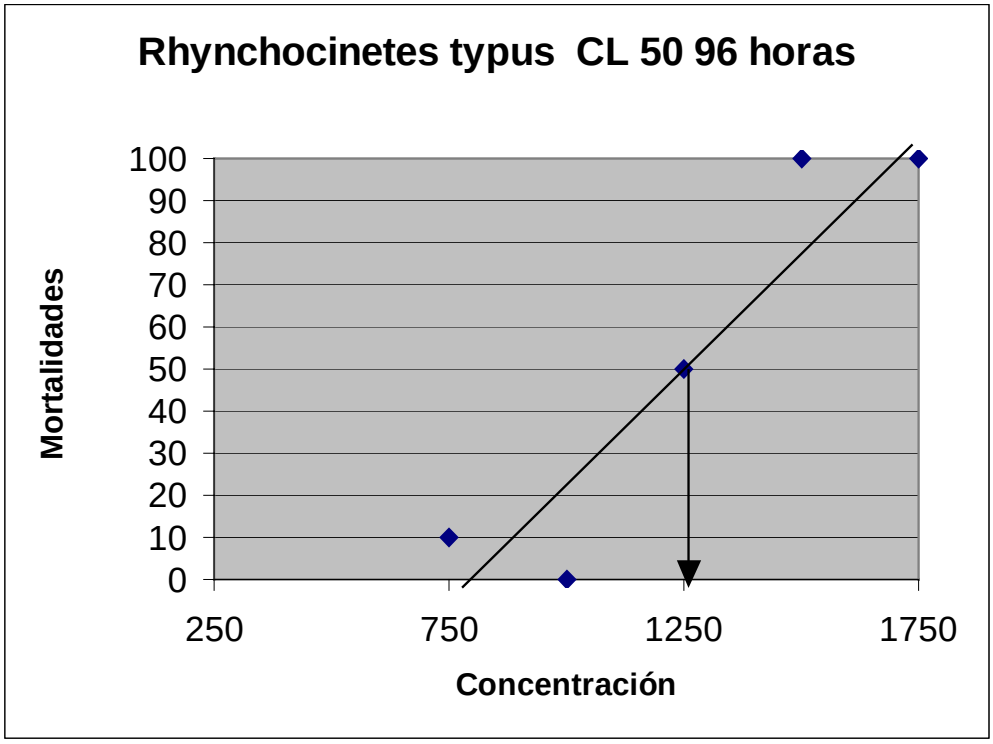
TESTING RESPONSIBILITIES

The bioassays and toxicity tests were performed in the laboratories of the Facultad de Ciencias de Mar, Universidad de Valparaíso, Chile, between April 20 and June 10, 2003, under the supervision of Prof. Fernando Alcázar González (Lic. Marine Biology) and the practical laboratory skills of Mr. Luis Rodríguez Siclari, Laboratory Assistant.

The specimens were captured and acclimated to laboratory condutions in the aquaria of the Marine facility by Mr. Juan Soto Cepeda, artisan fisherman. The logistics and administration of the assays was provided by Mr. Julio Jara, Administrative Officer at the Marine Station.

Fernando Alcázar González
Licenciado en Biología Marina
Viña del Mar, June 12, 2003


Girella laevifrons CL 50 96 horas
Mortalidades
100
90
80
70
60
50
40
30
20
10
0
250
750
1250
1750
Concentración Dispersante


Rhynchocinetes typus CL 50 96 horas
Mortalidades
100
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80
70
60
50
40
30
20
10
0
250
750
1250
1750
Concentración

A N E X O

TABILITY

he products shall have a store life of at least five years.

OXICITY

.1. General

.1.1. Principle of method

The method is based on determination of acute toxicity by determination of LC_{50} (Lethal Concentration 50 percent).
This is the concentration of the product at which 50 percent of the animals used in the test survive for a given time (24, 48 or 96 hours). The concentration is ascertained first by a preliminary test, followed by a final one. The preliminary test serves to bracket the approximate range of concentration of the LC_{50} value, while the final test enables the value to be pinpointed.
The "level of toxicity" of the product is derived from the 96 - hour LC_{50} value.

.1.2. Storage of samples

About 500 ml of product are required to run the test. The samples are stored in completely full, sealed containers.

2. Equipment

The toxicity tests are run in glass or plastic tanks. Six tanks each having a capacity of at least 10 litres are required for the preliminary test, and five, with a capacity of at least 25 litres, for the final one.
The shape of the tanks is not of great importance, provided that the depth of liquid is not less than 15 cm. Each tank must be complete with an air-bubbling system which ensures good oxygenation and uniform distribution of the liquids throughout the whole of the tank.
During the tests and the holding period prior to the tests, the water temperature must be kept at 20° C $\pm$ 1, by means of water bath or thermostatic chamber.
Tanks are also required in which to keep the animals prior to use. The water in these tanks must be brought gradually to the test temperature, care being taken to ensure that it remains clear (by recycling over carbon or by being continuously changed) and is adequately oxygenated (70 to 100 percent saturation) by bubbling air through it.
In the case of tanks working on the recycling principle, the frequency with which the water has to be replaced will depend on the num-

ber of animals kept and their needs. Some useful pointers on frequency can be obtained by analysis of certain physical characteristics of the water (e.g. N - NH_3) performed at given intervals. However, this system of holding animals prior to the test should only be used when there is no possibility at all of the water being continuously changed. Under such circumstances th holding period should be reduced to the absolute minimum requi red.

9.3. Experimental animals and solution

9.3.1. Experimental animals

The species selected for performance of the tests is Liza Aurata sin Mugil auratus RISSO 1810 (Golden-grey mullet), a kind of mullet common around the coasts of Italy and readily obtained from breeders. It adapts well to aquarium conditions.
The fish, whose overall average length will be 8 to 10 cm. must remain in the holding tanks for at least 15 days before the test is started. If, during this time the natural death rate exceeds 10 pe cent, the whole batch of fish must be put on one side until the rat drops.
During the holding period the fish are fed regularly until the day before the start of the test, during which time they must not be fed.

9.3.2. Number of animals and volume of liquid

In the preliminary test, four animals are used for each dilution the 10-litre tanks. In the final test, instead, ten animals are u per 25-litre tank. In both cases the tanks must be properly aera to ensure an oxygen-saturation level of not less than 70 percen and to keep the product under test evenly distributed throughout t mass of the dilution water.

9.3.3. Dilution water

This can be seawater taken from points offshore where it is cert there is no pollution, or "artificial" seawater, the salts for whic can be bought off the shelf already batched in the right proportio (see Para 10.3.1).

LC_{50}. Six 10-litre tanks are prepared with product concentrations (in seawater) of 1, 10, 100 and 10,000 ppm, and one containing only seawater to act as control. Twenty-four hours after, the fish are put into the tanks it will be possible to ascertain the dilution range in which all or many of the fish (more than half) have died, and that where none or only some of the fish (less than half) have died.

4.2. Final test

This test is designed to indicate the concentrations at which the percentage of survivors is below 50 percent (though not nil) or higher than 50 percent (but not all), after 24, 48 and 96 hours. Concentrations intermediate between the two bracketed by the preliminary test are prepared in 25 - litre tanks, using logarithmic intervals. For instance, if the preliminary test has indicated a range of between 100 and 10 ppm for the LC_{50}, the concentrations prepared for the final test will be 100, -50.1, - 22.4 and 10 ppm, plus the control.

The relevant survival percentages are noted after 24, 48 and 96 hours, care being taken to remove dead fish from the aquariums as soon as possible.

If the desired results are obtained after the times indicated, it is then possible to calculate the LC_{50}, otherwise it is necessary to repeat the test by selecting other dilution intervals.

5. Graphic determination of LC_{50}

The percentage of survivals observed at two successive concentrations (on the logarithmic scale) after 24 hours are plotted on log - normal paper. The two points (which should be located above and below the 50 percent level) are joined by a line and a perpendicular is dropped to the "concentration" axis from the points where the plotted line crosses the 50 percent level; this gives the 24-hours LC_{50} value.

The same procedure is adopted for the 48 and 96-hour survivial percentages, in order to obtain the relevant LC_{50} values.

6. Toxicity evaluation

The level of toxicity of the product is derived from the 96-hour LC_{50} value by reference to the following scale:

96-hour LC_{50}	Level of toxicity
<1 ppm	Highly toxic
1 - 10 ppm	Toxic
10 - 100 ppm	Slightly toxic
100 - 1000 ppm	Virtually nontoxic
>1000 ppm	Innocuous

Presentation of results

The results of the toxicological test are expressed in terms of 96-hour LC_{50} (in ppm). However, it is advisable to indicate the 24 and 48 - hour LC_{50} values too.

ARMADA DE CHILE
DIRECCION GENERAL DEL TERRITORIO MARITIMO
Y DE MARINA MERCANTE
DIRECCION DE INTERESES MARITIMOS
Y MEDIO AMBIENTE ACUATICO

DGTM. Y MM ORD. Nº 12.600/ 1937 / VRS.

AUTORIZA USO DE DISPERSANTE QUÍMICO PARA PETRÓLEO "MPCD"

VALPARAÍSO, 0 1 JUL. 2003

VISTO: la solicitud presentada por la empresa SERPROTEC LTDA.; el informe N°027/2003 de evaluación de la toxicidad y efectividad del dispersante químico para derrames de petróleo elaborado por el Instituto de Oceanología de la Universidad de Valparaíso de Marzo del 2002; y las facultades que me confieren la Ley N°. 2.222, Ley de Navegación, Título IX de fecha 21 de Mayo de 1978,

CONSIDERANDO:

Que el producto dispersante **MPCD**, con valores de CL50 96 horas sobre 1.000 mg/L es inocuo para las especies sometidas a ensayo y puede ser considerado para aplicaciones ambientales en las tasas de dilución recomendadas por el fabricante,

R E S U E L V O:

1.- **AUTORÍZASE,** el uso del dispersante denominado "**MPCD**", en las aguas sometidas a la jurisdicción nacional, sólo bajo condiciones de dilución al 5% (1 parte de dispersante en 20 de agua) o mayor.

2.- No se aprobará su uso en forma concentrada o bajo el límite de dilución señalado en el punto anterior.

3.- Su aplicación siempre deberá ser autorizada y supervisada por la Autoridad Marítima Local, conforme a que su uso debe ser "sólo eventual" y controlado al producirse un derrame o vertimiento.

4. La presente resolución tendrá una vigencia de cinco (5) años a contar de la fecha de aprobación del producto.

ANÓTESE y COMUNÍQUESE a quienes corresponda para su conocimiento y cumplimiento.

POR ORDEN DEL SR. DIRECTOR GENERAL

ARMADA DE CHILE D.G.T.M. Y M.M. DIRECTOR DIRECCION INTERESES MARITIMOS Y MEDIO AMBIENTE ACUATICO

CARLOS CANALES GUERRERO
CAPITÁN DE NAVÍO LT
DIRECTOR DE INTERESES MARÍTIMOS Y
MEDIO AMBIENTE ACUÁTICO

DISTRIBUCIÓN:
1.- SERPROTEC LTDA.
2.-17 GOBERNACIONES MARÍTIMAS

ARMADA DE CHILE
DIRECCION GENERAL DEL TERRITORIO MARITIMO
Y DE MARINA MERCANTE
DIRECCION DE INTERESES MARITIMOS
Y MEDIO AMBIENTE ACUATICO

DGTM. Y MM ORD. Nº 12.600/ 1934 / VRS.

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4. La presente resolución tendrá una vigencia de cinco (5) años a contar de la fecha de aprobación del producto.

ANÓTESE y COMUNÍQUESE a quienes corresponda para su conocimiento y cumplimiento.

POR ORDEN DEL SR. DIRECTOR GENERAL

CARLOS CANALES GUERRERO
CAPITÁN DE NAVÍO LT.
DIRECTOR DE INTERESES MARÍTIMOS Y
MEDIO AMBIENTE ACUÁTICO

DISTRIBUCIÓN:
1.- SERPROTEC LTDA.
2.-17.- GOBERNACIONES MARÍTIMAS
18.- BOLETIN DGTM Y MM. (Inf.)
19.- ARCHIVO

MINISTERIO DE DEFENSA NACIONAL
SUBSECRETARIA DE MARINA

Fecha 24 JUL. 2003

CONFORME CON LA(S) FIRMA(S)
DEL PRESENTE DOCUMENTO

CARLOS DE LA MAZA URRUTIA
Capitán de Navío
SUBJEFE SUBSECRETARIA DE MARINA

MINISTERIO DE DEFENSA NACIONAL - SUBSECRETARIA DE MARINA - Sub Jefe

Legalizada en el Ministerio
de Relaciones Exteriores de Chile
Firma del Señor

MIGUEL REYES VARGAS
Oficial de Legalizaciones
24 JUL 2003

CONSULADO GENERAL DE ESPAÑA
Santiago de Chile
Nº 9232/03

VISTO EN ESTE CONSULADO GENERAL DE ESPAÑA bueno para legalizar la firma de Don. MIGUEL REYES
Oficial de Legalizaciones del Ministerio de Relaciones Exteriores de Chile, por ser el parecer la suya, sin entrar en el contenido del documento ni ulterior destino que pueda dársele.

En Santiago de Chile a 30 JUL 2003

EL CONSUL GENERAL DE ESPAÑA
Ricardo Peldró Conde

CONSULADO GENERAL DE ESPAÑA - SANTIAGO DE CHILE

AMBASCIATA D'ITALIA - SANTIAGO

Si legalizza la firma del Funzionario del M.A.E. cileno Sig.(a)

Santiago, 06 AGO 2003

CONS. SUP. DELEGATO
FRANCESCA DELLI
(DECRETO Nº 05/2003)

AMBASCIATA D'ITALIA
ANTIAGO
06/08/2003 Num. Registro: 3.175
ARMADA DE CHILE
Articolo T.C.: 70a
Importo in Euro: 15,50
Importo in valuta: 12.791,840
Arrotondato a: 12.792,000

REPUBLIC OF CHILE)
PROVINCE AND CITY OF SANTIAGO) SS:
EMBASSY OF THE UNITED STATES OF AMERICA)

I, the undersigned consular officer of the United States of America at Santiago, Chile, duly commissioned and qualified, do hereby certify that Miguel Reyes Vargas **whose true signature and official seal are respectively subscribed and affixed to the foregoing document was, on the day of** JUN 24 2003 **the date thereof, an official of the Ministry of Foreign Affairs of the Republic of Chile duly commissioned and qualified, to whose official acts full faith and credit are due.**

IN WITNESS WHEREOF I have hereunto set my hand and affixed the official seal of this Embassy at Santiago, Chile, this
JUL 29 2003 .

Timothy L. Cipullo
Vice Cónsul
of the United States of America

ARMADA DE CHILE
DIRECCIÓN GENERAL DEL TERRITORIO MARÍTIMO
Y DE MARINA MERCANTE
DIRECCIÓN DE INTERESES MARÍTIMOS
Y MEDIO AMBIENTE ACUÁTICO

D.G.T.M. Y M.M. ORDINARIO N° 12600/ 836 /VRS.

AUTORIZA USO DE DISPERSANTE QUÍMICO "MPCD".

VALPARAÍSO, 13 JUN 2008

VISTO: la solicitud presentada por la Empresa INMOBILIARIA E INVERSIONES AUCHILÚ S.A.; el informe de evaluación de la toxicidad y efectividad del dispersante químico para derrames de petróleo, emitido por la Facultad de Ciencias del Mar de la Universidad de Valparaíso N° 027/2003, de Junio del 2003, y las facultades que me confieren la Ley N° 2.222, Título IX, de fecha 21 de Mayo de 1978,

R E S U E L V O:

1.- **AUTORÍZASE,** el uso del dispersante denominado "MPCD", en el litoral de la República, sólo bajo condiciones de dilución al 5% (1 parte de dispersante en 20 de agua) o mayor y en una concentración igual o menor a 1250 ppm.

2.- La aplicación del dispersante deberá ser siempre autorizada por la Autoridad Marítima Local, en atención a que su uso debe ser "sólo eventual" y controlado al producirse un derrame o vertimiento.

3.- La presente Resolución está sujeta a un cobro de US$ 41,02; conforme a lo dispuesto por el D.S. (M) N° 427, de fecha 25 de Junio de 1979, y tendrá una vigencia de cinco (5) años a contar de la fecha de aprobación.

4.- **DÉJESE SIN EFECTO**, la Resolución D.G.T.M. Y M.M. ORD. N° 12600/1937, del 01 de Julio del 2003, que autoriza el uso del dispersante químico "MPCD" en el litoral de la República.

5.- **ANÓTESE y COMUNÍQUESE** a quienes corresponda, para su conocimiento y cumplimiento.

POR ORDEN DEL SR. DIRECTOR GENERAL

LUIS BURGOS VELÁSQUEZ
CAPITÁN DE NAVÍO LT
DIRECTOR DE INTERESES MARÍTIMOS
Y MEDIO AMBIENTE ACUÁTICO SUBROGANTE

ARMADA DE CHILE D.G.T.M. Y M.M. DIRECTOR DIRECCION INTERESES MARITIMOS Y MEDIO AMBIENTE ACUATICO

ALBERTO VALENZUELA LEON NOTARIO SUPLENTE 61 SANTIAGO GUILLERMO

CERTIFICO: que la presente copia fotostática se encuentra conforme con el documento que he tenido a la vista.
15 JUL. 2008
IVAN TAMARGO BARROS
NOTARIO PUBLICO