DISPERSANT EFFECTIVENESS TESTING:
THE NEW ZEALAND EXPERIENCE

JULIAN ROBERTSAND LEIGH STEVENS

ABSTRACT

Oil spill response in New Zealand (NZ) relies in part on the appropriate use of oil dispersants to limit the adverse environmental impacts of the spilt oil. Recently the Maritime Safety Authority of NZ (MSA) tested the effectiveness of existing dispersants stockpiled in NZ for the first time.

Testing addressed two issues. Firstly, age-related degradation was assessed by comparing the efficacy of existing stocks to freshly manufactured dispersant using a standard test oil. Secondly, the response capacity of MSA owned dispersants was evaluated by testing existing dispersants against five crude oils and nine fresh IFO-380 fuel oils considered by the MSA to pose a high risk if spilled in NZ waters. Testing followed the Warren Springs Laboratory (WSL) LR 448 protocol.

Results identified that age-related degradation was apparent with some existing MSA dispersant stocks. The testing of response capacity showed that while most of the un-weathered crude oils and some un-weathered IFO-380 oils tested could be dispersed, dispersion rates for the IFO-380 oils were relatively low, and some IFO-380 oils were unable to be dispersed with existing MSA stocks.

Subsequently, two alternative high performance dispersants, Corexit 9500 and Slickgone EW, were tested on the same crude oils and IFO-380 oils, and across a range of temperatures and dispersant to oil ratios, to see if they offered a better response capability.

The results of these investigations are presented and discussed with particular reference to how they have been applied to enhance the overall response capability in NZ.

INTRODUCTION

Dispersant use is considered a primary response option in the New Zealand (NZ) National Marine Oil Spill Contingency Plan, alongside oil containment and recovery at sea, clean-up of oil from shorelines, bioremediation, and *in situ* burning (Stevens, 2001). The Maritime Safety Authority of NZ (MSA) has a general pre-approval for the appropriate use of dispersants in marine waters, subject to a site specific assessment of the net environmental benefit of their use.

For a dispersant to be used in NZ, it must first be evaluated and approved by the Director of Maritime Safety. This requirement is established under the enabling legislation of the Maritime Transport Act 1994, and specified in Marine Protection Rule - Part 132. The assessment requires, among other things, the evaluation of dispersant efficacy using the Warren Springs Laboratory (WSL) LR 448 protocol (Morris & Martinelli, 1983).

Following initial approval, there is currently no formal process to review, over time, the effectiveness of dispersants stockpiled in NZ. Consequently, most of the dispersants stockpiled by the MSA have not been tested for effectiveness since they were purchased. Recently, Merlin *et al.* (1997) reported on age-related variability in the effectiveness of selected concentrate dispersants stockpiled in France. Many of the NZ dispersant stocks have been held in storage for over 20 years, have been stored or handled under different conditions, or were obtained from different sources; all factors that may contribute to possible differences in effectiveness. Therefore, to test whether NZ dispersant stocks had variable or reduced effectiveness through ageing or storage, the MSA embarked on a testing programme to address the following key operational issues:

1. Determine whether differences existed between different batches of the same dispersants held by the MSA; and
2. Assess the relative efficacy of the range of dispersants held by the MSA and compare these with accepted international criteria.

The MSA also sought information on the effectiveness of dispersants on oils that pose a high risk of being spilt in NZ. The most recent NZ Marine Oil Spill Risk Assessment (Woodward Clyde (NZ) Ltd, 1998) clearly identifies spills of fuel oils from international cargo and passenger vessels as presenting the highest overall risk to NZ. In addition, Dicks *et al.* (2002) report that of all ship-sourced spills attended globally by ITOPF technical staff over the past 25 years, approximately 40% involve medium or heavy grades of fuel oil. Furthermore, over the past two years approximately 75% of spills attended involved medium and heavy grades of fuel oil. On this basis, the MSA sought to:

3. Assess which dispersants currently held by the MSA can effectively disperse a range of crude and heavy fuel oils considered to present a high risk in NZ waters; and
4. Evaluate whether more effective dispersants were required to augment the current response capability.

BATCH DIFFERENCES AND EFFECTIVENESS OF MSA DISPERSANT STOCKS

Representative samples of all the dispersant types currently held by the MSA were tested for effectiveness using the WSL LR 448 protocol. The protocol utilises a standard test oil defined as having a viscosity of 2000 millipascal seconds (mPas) at 10^{o}C at a shear rate of 10 reciprocal seconds (s^{-1}). This shear rate is thought to be typical of sea surface values and is commonly used for dispersant effectiveness testing (The Institute of Petroleum, 1986). The protocol provides a direct comparison of the relative effectiveness of different dispersants, and allows test results to be directly compared to international data or effectiveness thresholds. However, it must be stressed that no direct comparison with effectiveness on oil at sea can be inferred from this approach.

The acceptance criteria for Type 3 dispersant effectiveness in NZ using this approach is established at ≥ 60% (MSA, 1998).

Table 1 and Figure 1 show dispersant effectiveness results. Of the MSA stocked dispersants, Corexit 9527 and Slickgone LTSW exceeded the effectiveness criteria of ≥60%. Shell VDC, made to an identical formulation to Slickgone LTSW, fell below the acceptance criteria set for NZ, results independently confirmed by Dasic who, although not the original manufacturers of the Shell VDC samples, kindly retested the samples. Tergo R40, and Simple Green also fell below the acceptance criteria set for NZ with both the Shell VDC and Tergo R40 samples showing large between batch differences. The ≥60% criteria did not apply to Gamlen OSD LT which is approved only as a Type 2 dispersant in NZ and must be tested using a different method and compared to different effectiveness criteria.

The testing programme was not designed to distinguish between whether the reduced effectiveness identified was due to the age of the dispersant, or the manner in which it has been stored. However, older products were clearly correlated with lower efficacy values identified for some of the NZ stocked dispersants. The MSA has subsequently withdrawn from use those dispersant stocks that were below the effectiveness criteria, and is exploring whether poorly performing stocks can be cost effectively rejuvenated.

Table 1 Mean dispersant effectiveness at a dispersant to oil ratio (DOR) of 1:25 tested at 10°C using the WSL standard oil, viscosity 2000 mPas, $10\ s^{-1}$ shear rate.

Dispersant	Batch	Rep 1	Rep 2	Average %	SE
Corexit 9500[1]					
Benchmark 1998	CO9500	81.5	83.0	**82**	0.8
Corexit 9527					
Replaced stock (age unknown)	CO1	76.0	-	**76**	-
Replaced stock (age unknown)	CO2	78.1	-	**78**	-
New late 1970's	CO3	73.4	75.5	**74**	1.0
Benchmark 2000	CO4	81.9	82.4	**82**	0.3
Slickgone LTSW					
Benchmark 2000	DA1	69.1	71.3	**70**	1.1
New 1985	SH1	13.0	16.8	**15**	1.9
Replaced stock (age unknown)	SH2	50.2	46.4	**48**	1.9
Gamlen OSD LT					
Benchmark 2000	GA1	41.6	54.3	**48**	6.3
New late 1970's	GA2	34.8	-	**35**	-
Replaced stock (age unknown)	GA4	32.8	40.1	**36**	3.7
Simple Green					
Benchmark 2000	SG1	5.1	5.0	**5**	0.1
Tergo R40					
New 2000	TE1	42.9	44.6	**44**	0.8
New 1992	TE2	10.6	10.3	**10**	0.2
New 1992	TE(UK)	45.1	49.6	**47**	2.3

Shading indicates dispersant considered effective (threshold ≥60%)
- not tested

---

[1] Corexit 9500 is not currently approved for use or held in New Zealand. However, it was included in the testing programme for comparative purposes.

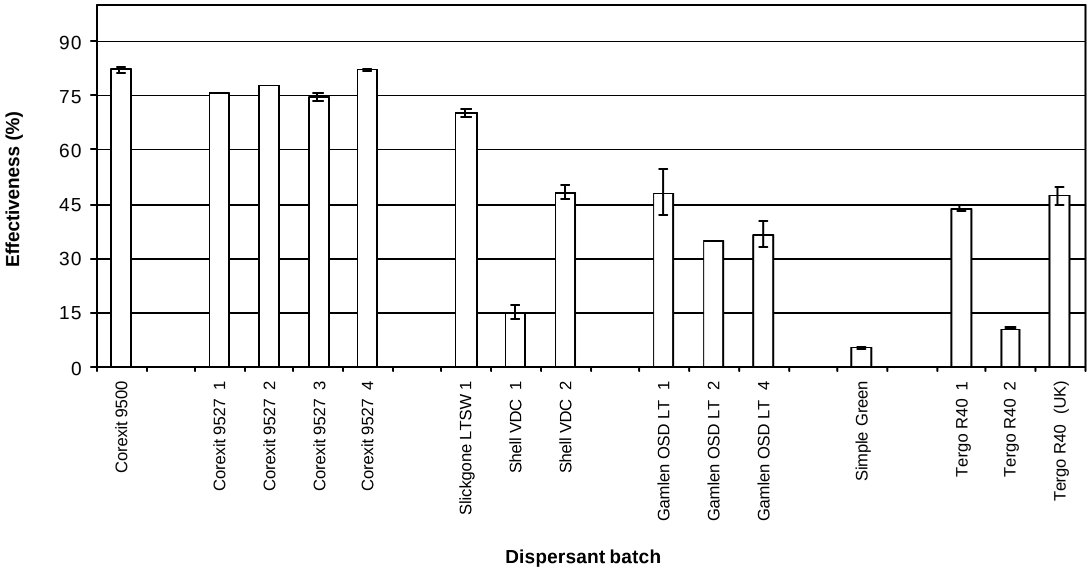

Figure 1 Mean dispersant effectiveness (± 1 standard error) at a dispersant to oil ratio (DOR) of 1:25 tested at 10°C using the WSL standard oil, viscosity 2000 mPas, 10 s^{-1} shear rate.

DISPERSIBILITY OF A NZ REFINED IFO-380 FUEL OIL

Fresh NZ refined IFO-380 is a difficult oil to clean-up and is near the threshold of likely dispersibility at most NZ water temperatures. To determine how temperature may limit the ability of MSA stocked dispersants to disperse this oil, and to define effectiveness at different dispersant to oil ratios (DOR's), tests were conducted at 5°C, 10°C, 15°C, and 20°C, and at a range of DOR's to:

- Identify which dispersants were the most effective over a range of temperatures.
- Determine if dispersant effectiveness could be increased when applied at higher dose rates.
- Determine if dispersants could be applied at lower dose rates without a significant loss in effectiveness.

The criteria used to define an effective dispersant on NZ refined IFO-380 was set at 15% based on the work of Lunel & Lewis (1999). The value was derived by comparison of laboratory WSL test results with measurements of dispersion made during steady-state, continuous oil release experiments at sea. The threshold has been proposed as an indicator of dispersant effectiveness at sea in wind speeds above 5 ms^{-1}.

Results presented in Table 2 show that at a DOR of 1:25, at ≤10°C, no dispersants stocked by the MSA effectively dispersed the fresh NZ refined IFO-380. Gamlen OSD LT, Tergo R40, and Simple Green were not effective on the oil at temperatures up to 20°C. Only Corexit 9527 and Slickgone LTSW exceeded the 15% effectiveness threshold at 15°C and 20°C. However, when the DOR was increased to 1:10 (Table 3), all of the MSA stocked dispersants with the exception of Simple Green were effective at 15°C.

Table 2 Mean dispersant effectiveness tested using fresh NZ IFO-380 at specified temperatures and viscosities, at a dispersant to oil ratio of 1:25.

		Mean % effectiveness at different temperatures (n=3-4)			
		5°C	**10°C**	**15°C**	**20°C**
Dispersant	**Viscosity** (mPas, $10s^{1}$ shear rate)	19,600	13,200	7,000	5,460
Corexit 9527		2	6	15	25
Slickgone LTSW		2	12	15	18
Gamlen OSD LT		1	2	4	-
Simple Green		1	2	1	-
Tergo R40		2	4	9	7
Control		0	0	0	0

Shading indicates dispersant considered effective (threshold ≥15%)
- not tested

Table 3 Mean dispersant effectiveness tested using fresh NZ IFO-380 at 15°C at specified dispersant to oil ratios (DOR's).

		Mean % effectiveness at different dose rates (n=3-4)				
Dispersant	**DOR:**	**1:5**	**1:10**	**1:25**	**1:50**	**1:100**
Corexit 9527		-	24	15	6	-
Slickgone LTSW		-	28	15	9	3
Gamlen OSD LT		-	17	4	-	-
Simple Green		2	2	1	-	-
Tergo R40		-	15	9	2	-

Shading indicates dispersant considered effective (threshold ≥15%)
- not tested

To assess the capacity of the MSA stocked dispersants to disperse the same NZ refined IFO-380 following emulsification (30% water in oil), additional testing was conducted at 15°C at dispersant emulsion ratios (DERs) of 1:10. None of the MSA dispersants were effective on the emulsified IFO-380 fuel oil, results confirmed by inter-laboratory testing conducted by AEA Technology in the UK (Table 4).

Table 4 Mean dispersant effectiveness at specified dispersant to emulsion ratios (DER's) tested at 15°C using emulsified NZ IFO-380.

		Mean % effectiveness at specified dose rates	
Dispersant	**Batch Code**	**DER 1:10 (n=3-5)**	**1:25 (n=2-3)**
Corexit 9500	C9500UK	6 (7)	4 (6)
Corexit 9527	CO3	7	-
Corexit 9527	CO4	8	-
Gamlen OSD LT	GA1	3 (7)	1 (4)
Simple Green	SG1	1	-
Slickgone LTSW	DA1	4	-
Shell VDC (now Slickgone LTSW)	SH1	2	-
Tergo R40	TE1	3	-
Tergo R40	TE2	1	-
Tergo R40	TEUK	9 (13)	2 (6)

Results in brackets indicate effectiveness of split samples tested by AEA Technology (UK)
- not tested

DISPERSIBILITY OF HIGH RISK CRUDE AND IFO-380 OILS

In contrast to the results showing low dispersant effectiveness on the NZ IFO-380, international data indicate that IFO-380 fuel oils sourced from Thailand, Norway and the UK were all dispersible (*e.g.* Crosbie *et al.*, 1999), and that there were dispersants more effective on IFO-380 fuel oils than those currently stocked in NZ (*e.g.* Lunel & Davies, 2001). Despite limitations in comparing oils from different sources, such data suggests that there are likely to be:

i. Dispersants not tested or stockpiled in NZ that are more effective at dispersing NZ IFO-380; and

ii. IFO-380 fuels used in NZ that are more readily dispersible than the NZ IFO-380 oil tested.

To better understand the potential for dispersant based response options in NZ, the MSA identified seven crude oils and nine fuel oils considered to pose a high risk if spilled in NZ waters. Oils were selected based on the following criteria:

i. persistence (*e.g.* specific gravity over 0.8);

ii. volume (large parcels carried as bunkers or cargo);

iii. frequency of transport; and

iv. availability of existing information about dispersion.

Testing was undertaken using the same dispersant stocks used in previous batch testing work (Corexit 9527, Gamlen OSD LT, Slickgone LTSW, and Tergo R40) on fresh (unweathered) oil at 15°C, at a DOR of 1:25. Results of effectiveness tests are presented in Table 5. In addition, two alternative dispersants well proven for their high performance but not currently part of MSA stocks, Corexit 9500 and Slickgone EW, were evaluated under the same test conditions and results are also included in Table 5.

The results indicate that existing MSA dispersant stocks have a reasonable capacity to disperse selected unweathered crude oils and some unweathered heavy fuel oils. Although the results on face value indicate that fresh crude oils are less dispersible than fresh heavy fuel oils for these dispersants, in reality, this is not the case. The results are demonstrating the relationship between oil density and a dispersants' preference to certain oil components, the more effective dispersants dispersing a higher proportion of light fractions in the crude oils that rapidly floats to the surface when the mixing energy in the test chamber is removed.

Corexit 9527 was clearly the most effective MSA stocked dispersant tested. However, dispersion rates with MSA dispersant stocks, particularly for the IFO-380 fuel oils, were relatively low, and two fresh fuel oils were unable to be dispersed. Test results for Slickgone EW and Corexit 9500 showed both dispersants were more effective than the MSA dispersants on the oils tested and were able to disperse the fresh fuel oils unable to be dispersed with existing MSA dispersant stocks. These findings prompted further work to examine the performance of Corexit 9500 and Slickgone EW on three of the test oils at varying dose rates and temperatures (Table 6).

Table 5 Mean dispersant effectiveness and oil viscosity for specified oils at 15°C, at a dispersant to oil ratio (DOR) of 1:25.

		Mean % effectiveness at 15°C (n=2)						
Oil	**Viscosity** (mPas, $10s^{-1}$ shear rate)	**Corexit 9500**	**Slickgone EW**	**Corexit 9527**	**Gamlen OSD LT**	**Slickgone LTSW**	**Tergo R40**	**Control**
Crude oil source								
Kuwait	38	45	34	52	16	38	17	4
Kutubu	11	11	15	11	22	13	25	3
Barrow Island	12	13	11	15	22	17	22	2
Oman	47	-	-	35	22	30	24	4
Arab Light	31	-	-	45	17	34	18	1
Labuan	14	10	15	8	22	11	26	2
Oman Residue	2058	46	25	38	25	18	30	1
IFO-380 fuel oil source								
Singapore	13268	62	59	35	8	22	6	0
Singapore (Jody F. Millennium)	-	30	12	4	7	13	4	0
Nagoya	12086	58	58	38	4	10	6	1
Tokyo	9155	66	61	48	17	16	19	0
KeeLung, Taiwan	2908	66	61	54	21	25	24	0
Antwerp	90325	39	41	14	1	3	1	0
Rotterdam/Flushing	15200	51	49	37	5	6	5	0
Santos, Brazil	6294	76	81	63	25	11	29	2
Cristobel	8000	59	62	56	17	7	15	0

Shading indicates dispersant considered effective (Threshold =15%)

\- Insufficient sample to test

The results presented in Table 6 show that overall there was generally ≤5% difference in the rates of effectiveness for the two dispersants. Corexit 9500 was slightly more effective on the NZ refined IFO-380 than Slickgone EW at lower dose rates and temperatures, while Slickgone EW was remarkably able to disperse the very viscous Singapore oil at 5°C. For both dispersants, effectiveness rates were lowest for the highest viscosity fuel oil.

Table 6 Mean dispersant effectiveness for Corexit 9500 and Slickgone EW for specified oils across a range of temperatures and dispersant to oil ratios (DOR).

IFO-380 fuel oil source	Temperature	15°C			10°C	5°C
	DOR	1:25	1:50	1:100	1:25	1:25
KeeLung, Taiwan	**Viscosity cP @ $10s^{-1}$**	**2,908**			**5,166**	**31,434**
	Corexit 9500	66%	40%	30%	59%	37%
	Slickgone EW	61%	34%	36%	48%	36%
Singapore	**Viscosity cP @ $10s^{-1}$**	**13,268**			**36,515**	**208,513**
	Corexit 9500	62%	40%	22%	49%	5%
	Slickgone EW	59%	22%	18%	46%	27%
Marsden Point, NZ	**Viscosity cP @ $10s^{-1}$**	**7,000**			**13,200**	**19,600**
	Corexit 9500	24%	22%	11%	29%	7%
	Slickgone EW	24%	13%	5%	19%	3%

Shading indicates dispersant considered effective (threshold =15%)
- Insufficient sample to test

DISCUSSION

The work undertaken has shown that obtaining a relative measure of effectiveness using a standard method is a cost effective and efficient way of defining the change in the status of dispersant stocks over time, and for defining whether the dispersant meets defined criteria for use.

Differences were apparent within batches of Tergo R40 and Shell VDC stocked by the MSA. While the testing programme did not allow the cause of batch effects to be specifically determined, effectiveness differences clearly corresponded with the age of the dispersant, older dispersants being less effective. Whether dispersant age or storage conditions contributes to reduced effectiveness is a logical aspect to investigate further and may be a useful consideration for any response agency with diverse stocks of dispersants.

Testing fresh crude oils and fresh heavy fuel oils identified by the MSA as having a high risk of being spilled in NZ showed existing MSA dispersant stocks have a reasonable capacity to disperse nearly all of the oils tested. As expected, the results showed that some dispersants were more effective than others, and that some dispersants worked better on specific oils. These findings confirm that access to a range of dispersants is likely to provide the most comprehensive response capacity.

However, although laboratory effectiveness tests under controlled conditions provide a good measure of relative differences between test samples, they do not necessarily indicate likely dispersion rates at sea. This is particularly important to bear in mind when testing only fresh oils. Oil spilled at sea will quickly start to weather with volatile components of the oil being lost primarily via evaporation, while oil and water emulsions may also form. A general consequence of weathering is an increase in oil viscosity with a corresponding decrease in dispersant effectiveness. As such, while the laboratory results indicate existing MSA dispersant stocks have a reasonable capacity to disperse fresh oil, effectiveness is expected to decrease once oils have become lightly weathered or emulsified (within a few hours of spillage).

In relation to the MSA's existing dispersant stocks, Corexit 9500 and Slickgone EW were more effective on fresh crude and fuel oils, and offer a better response capacity than the MSA's existing dispersants. Furthermore, test data show that both Corexit 9500 Slickgone EW are more effective across a range of dose rates, temperatures, and oil types. For Corexit 9500 these results corroborate previous laboratory results and field trials (*e.g.* Crosbie *et al.,* 1999). Similar comparative data for Slickgone EW are not currently available.

It is important to appreciate that the laboratory results this paper describes are specific to the test conditions used, and have not been verified by field trials. Field applications allow dispersant to be applied in ways that were beyond the scope of the present study to address. Multiple applications at lower doses may allow oil emulsions to be broken and successfully dispersed more efficiently than single applications at higher doses. It is widely accepted that wherever possible, laboratory studies should be used as a general guide to likely dispersant effectiveness, with actual dose rates and application regimes determined from specific monitoring of field trials.

OUTCOMES OF THE STUDY

It must be recognised that the results of such applied research will have little value unless the conclusions drawn from the research are integrated into operational policy for the use of dispersants in spill response.

In terms of the application of these results the MSA is addressing a number of issues highlighted by the studies:

1. The results indicate that a gap exists within the MSA's existing response capability. Accordingly, and based on the analysis results and a review of overseas experience, the purchase of new stocks of Corexit 9500 has been approved to augment the current dispersant response capability.

2. The results indicate that some existing stocks of dispersant fall below the acceptable criteria for efficacy in New Zealand. Accordingly, stocks of low efficacy or degraded dispersants are being withdrawn from use.

3. In the long term the MSA intends to implement a procurement and disposal plan for dispersants which will have regard to the following issues:

   i. total ongoing stock needs;
   ii. ageing issues;
   iii. warranties;
   iv. application requirements and capabilities; and
   v. likely oil types to be encountered

   In this regard, the MSA is seeking to clarify further the risks presented in NZ from a range of oils, and in particular those produced in NZ, and to assess suitable dispersants against each oil.

4. It is acknowledged that it would be impractical to hold sufficient stocks of dispersant to address every spill scenarios. In view of this the MSA is also to review the approvals of alternative stocks held by AMSA and AMOSC for deployment in New Zealand.

REFERENCES

Crosbie, A., Davies, L., Lunel, T. (1999). The Effectiveness of Tergo R40 and Ardrox 6120 on IFO-380. Restricted commercial report number AEAT-5734 prepared by AEA Technology for the Australian Maritime Safety Authority. 35 p. Released to the New Zealand Maritime Safety Authority as a member of the Australian Maritime Safety Authority National Plan Committee.

Dicks, B., Ansell, D.V., Guenette, C.C., Moller, T.H., Santner, R.S., White, I.C. (2002). A Review of the Problems Posed by Spills of Heavy Fuel Oils. In *Proceedings of 3rd Research and Development Forum on High Density Oil Spill Response*. International Maritime Organisation. 11-13 March, 2002. Brest, France. 11 p.

Lunel, T., Davies, L. (2001). Response to Bunker Fuel Oil: The Options. In *Proceedings of the 2001 International Oil Spill Conference on Global Strategies for Prevention, Preparedness, Response, and Restoration.* 26-29 March 2001. Tampa, Florida, USA.

Lunel, T., Lewis, A. (1999). Optimization of Oil Spill Dispersant Use. In *Proceedings of the 1999 International Oil Spill Conference, Beyond 2000 – Balancing Perspectives.* 8-11 March 1999. Seattle, Washington, USA. American Petroleum Institute, Washington, DC. pp 187–193.

MSA (1998). Marine Protection Rule Part 132 - Dispersants and Demulsifiers. Publ. Maritime Safety Authority of New Zealand, Wellington, NZ. July, 1998.

Merlin, F.X., Le Guerroue, P., Le Gall, A., Menot, L. (1997). Observations and Conclusions from 10 Years of Periodic Quality Controls on Operational Dispersant Stockpiles. In *Proceedings of the Twentieth Arctic and Marine Oilspill Program (AMOP) Technical Seminar*. June 11-13, 1997. Vancouver, BC, Canada. pp 551 –559.

Morris, P., Martinelli, F. (1983). A Specification for Oil Spill Dispersants. Report LR448. Warren Spring Laboratory, Stevenage, Hertfordshire, UK.

Stevens, L. M. (2001). Guidelines for Dispersant Use in New Zealand. In *Proceedings of the 17th Biennial International Oil Spill Conference on Global Strategies for Prevention, Preparedness, Response and Restoration.* 26-29 March 2001. Tampa, Florida, USA. pp 1185-1194.

The Institute of Petroleum (1986). Guidelines on the Use of Oil Spill Dispersants. London, Institute of Petroleum.

Woodward Clyde (NZ) Ltd (1998). Phase 2 of NZ Marine Oil Spill Risk Assessment. Prepared for The Director of Maritime Safety. December 1998.