



A literature review of portable fluorescence-based oil-in-water monitors

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Abstract

The results of a literature search on fluorescence-based portable detectors to measure the real-time concentration of oil are reported. For more than two decades, fluorimeters have been commonly employed to monitor dispersed oil levels at oil spills on water. The focus of this paper has been to extract specific information from references about how the instruments were used, including set up and calibration procedures, the oil and dispersant measured, the approximate concentration range of the oil in the water column, and how the real-time data compared to traditional laboratory techniques. Crown Copyright © 2003 Published by Elsevier B.V. All rights reserved.

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1. Introduction

One of the countermeasures available to the oil spill responder is the use of chemical dispersants. However, the use of chemical dispersants as an oil spill countermeasure has had its detractors. Much of the negative bias stems from the lack of certainty regarding the effectiveness of the dispersant at transferring the oil off the surface of the water, and the resulting increase in the concentration of the oil in the water column [1]. In recognition of this, determining the amount of oil dispersed or dissolved in water has been an ever present concern at oil spills. Many different methodologies exist for measuring oil-in-water concentration. For more than two decades, portable instruments have been used in the field to obtain timely information on the concentration of oil in the water.

2. Objective

The objective of this project was to review the historical use of portable fluorimeters for providing real-time oil-in-water data. More specifically, the intention was to examine how

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the instruments were set-up, calibrated and operated, the oil type, data generated as well as how the real-time results compared to subsequent laboratory analysis.

3. Literature search

A literature search was undertaken to collect information related to the operation of these instruments. A summary of the search is provided in the following paragraphs. The findings of the search have been presented predominantly based on the geographical location of the country or agency undertaking the work.

3.1. Canadian programs

The authors Green et al. [2] reports on a total of three experimental spills conducted at Royal Roads in Victoria, British Columbia, in 1978. The field trials were part of a larger program to look at the fate of chemically dispersed oil. This portion of the field program used 3 l of Prudhoe Bay crude oil (sometimes called North Slope crude oil in the report) and Corexit 9527 dispersant contained in, and then slowly released from a submerged bag. It was noted in the report that two systems employing fluorescent spectroscopy were employed, a flow-through system and a laboratory system. The instrument was the Turner model 130 unit equipped with a no. 110-811 excitation filter (300–400 nm wavelength), 10% neutral density filter, a no. 110-816 emission filter (415 nm wavelength), a no. 110-855 UV lamp and a no. 110-880 flow-through cuvette. A garden hose and a peristaltic pump with a flow rate of 5 l/min were used to draw the sample through the unit. As a check, samples of the effluent were collected at noted times, extracted using hexane and measured later on the same fluorometer, except, the cuvette had been changed to a discrete sample-type. The laboratory fluorometer was calibrated using prepared standards of Prudhoe Bay crude oil in hexane. The flow-through results, recorded on a chart recorder, were calibrated against the lab results. After calibration, the flow-through results were numerically similar, or in other words the same order of magnitude as the laboratory extracted samples. The laboratory fluorescence results were also compared to gravimetric total petroleum hydrocarbon methods using pentane solvent. Results show that for the limited sample set there was a satisfactory numerical comparison. Differences were very apparent for water samples collected days after the oil and dispersant were used. The reason given for this trend is that evaporation and biodegradation had removed some of the saturate chemical compounds from the oil however the more stable polyaromatic hydrocarbons remained. It is the polyaromatic components in oil that are detected by the fluorometer.

Along with the previous tests, a second group of three trials were conducted by releasing 200–400 l of oil into a boom. Two flow-through fluorometers were used on site as well as one underwater fluorometer. The sampling depths for the three trials were 1, 3.5 and 1 m respectively. The output voltage of the fluorometers was tracked and converted to concentration values using a calibration procedure determined in the laboratory. A Turner model 403 spectrophotometer employing a 308 nm excitation wavelength and a 383 nm emission wavelength was used for the laboratory analysis. Samples collected from the effluent of the flow-through fluorometers were used to calibrate the units. In addition, a

portion of these samples were analyzed by directly reading the fluorescence of the oily water followed by hexane extraction and fluorescence analysis on the same samples. The data shows that the flow-through fluorometer was capable of detecting the presence of the dispersed oil. The correlation between the flow-through fluorometer and laboratory values was not high (0.50) and the correlation between the extraction and direct reading methods of the selected oily water samples even less (0.19). The reason for this might be that the oil slick and sub-surface plume are in a dynamic state and that the sampling is being undertaken on a platform traversing the test zone. The explanation given for the poor correlation was the patchy nature of both the surface oil and the dispersed sub-surface plume. This patchiness works its way into the flow-through system and in combination with the time delay of a few seconds between the displayed reading and the output of the effluent, it is believed that the sample collected from the output may not have been representative of the oily water passing through at the time of the direct reading from the instrument.

In October of 1981, a sea trail was conducted off the coast of St. John's, Newfoundland. The program used Venezuelan, Lagomedio crude oil and Corexit 9527 dispersant. It was noted in the reports that 2 Turner model 10-005 flow-through fluorometers were used to monitor oil-in-water concentration. This information was obtained from the reference Gill and Ross [3,4].

Gill et al. [5] and Swiss and Gill [6] reported on a test that took place off Halifax, Nova Scotia in September of 1983. The program used Alberta Sweet Mixed Blend crude oil and the dispersants Corexit 9527, 9550 and a prototype product MA700. An extensive sample collection procedure was instituted. Following the trial, the samples were extracted with methylene chloride and hydrocarbon content determined by fluorescence spectroscopy. Calibration was carried out using prepared oil-in-solvent standards. In the report by Myers and Corry [7] more detailed information is given on the instrumentation. The bench top fluorometer was a Turner model 112 equipped with a Turner 2A (>410 nm) emission filter, 7-60 (320–390 nm) excitation filter and a general purpose UV lamp. Two Turner model 10-005 flow-through instruments were also used. During the trial, they were set to sample at 2 m; however due to low readings, the sampling depth was switched to 1 m. They were calibrated using a 10% solution of dispersant in 20% (wt.%) weathered ASMB crude oil in artificial seawater over 0.05–38.9 ppm. Included in the report was an estimate of the sources of error for the analytical instruments. The bench top unit was said to have a 5% instrumental error while the flow-through units had a 10% error, due mostly to air bubbles and particulate being drawn through the sample cell. The remainder of the discussion focussed on the concentration of dispersed oil in the water as opposed to analytical protocols.

A number of wave basin and field trials sponsored by Esso Resources wave basin facility in Calgary were conducted in the 1980s. The November 1984 program is reported in Brown [8] and Brown et al. [9] while the April of 1985 program is reported in Brown [10]. The program's objective was to evaluate the effectiveness of dispersant in cold water. Sub-surface monitoring was employed for all programs using continuous in situ fluorometers. A summary containing significant information on the instrumentation can be found in the reference Brown et al. [11].

In the 11/84 trials, there were three Turner model 10-005 units equipped with a short wavelength kit (excitation at 254 nm wavelength and emission at 350 nm wavelength). The fourth unit was a Sequoia-Turner model 112, continuous flow cell and a long wavelength

kit (excitation at 350 nm wavelength and emission at 450 nm wavelength). All of the units were located outside of the basin and piping was installed throughout the basin to draw in water samples. To calibrate the flow-through fluorometers, a closed system consisting of 40 l of uncontaminated water, taken from the basin to ensure consistently, was pumped from a drum. The water was continuously pumped through the tubing and fluorometer and returned to the drum. Known amounts of an oil and dispersant mixture (1:1) were added to the water. After each successive addition, the system was allowed to come to an equilibrium and then the reading on the instrument recorded. The data was stored on data loggers and later processed by computer. Also, the flow-through fluorometers were connected to a chart recorder. As a check, during the experiment samples were collected from the output of the fluorometers and subsequently extracted with methylene chloride. The Sequoia-Turner model 112 fluorometer was used to determine the oil content of the solvent extracted samples. Calibration of the 112 unit was achieved by preparing oil-in-solvent standards of known concentration. The test program used Alberta sweet mixed crude oil (also referred to as Federated crude oil) and two dispersants Corexit 9527 and a prototype product CRX-8.

Five Turner model 10-005 fluorometers were used in the 04/85 basin trials [10]. Like the earlier basin tests, the objective was dispersant in cold water studies. Test reagents were Norman Wells crude oil and the dispersants Corexit 9527, 9550 and CRX-8.

In July of 1985, a field trial was conducted in a freshwater fen lake in north central Alberta [12,13]. The objective was to study the impact of oil and dispersant in a freshwater environment. Norman Wells crude oil and Corexit 9550 were used. The reference by Quaife [13], describes a piping system constructed throughout the fen to draw water over to a workstation where flow-through fluorometers (two units) were set up and samples were collected from the units' output for additional analysis. One fluorometer was the Turner model 10-005 and the other a Sequoia-Turner model 112. It was stated that both were equipped with a short wavelength (254 nm excitation and 350 nm emission) kit and standard calibration procedures were employed. The reports from both the 04/85 basin trials and the 07/85 field trials contain plots of fluorometer concentration values versus time as well as some laboratory oil content data obtained from the extracted water samples and benchtop fluorescence analysis as described previously in this section.

The 1981 Baffin Island, NWT project, commonly referred to as BIOS, was a large scale effort undertaken by a consortium of international participants from both industry and government. The project looked at dispersant issues as part of several oil spill studies. A detailed summary of the studies can be found in Sergy and Blackall [14]. The test program used Lagomedio crude oil that was premixed with the dispersant Corexit 9527 at a 10:1 oil to dispersant ratio. In turn, the oil and dispersant mixture was blended with sea water at a ratio of 5 parts seawater to 1 part mixture and released out of a pipe placed a short distance offshore. A comprehensive system was set up to monitor the experiment. Details regarding the apparatus used to monitor the dispersed oil concentration are found in Green et al. [15,16] and Humphrey et al. [17]. The references state that a total of five fluorometers were used to monitor the dispersed oil concentration. Four were the Turner model 10-005 flow-through type and the fifth was a submersible unit called the Endeco Petrotrack also containing a Turner model 10-005. A floating platform held several pumps which brought the water samples to the four flow-through units located at the shore. The instruments were

equipped with the short wavelength optical kit (254 nm excitation, SG and 760 secondary filters). All instruments were calibrated simultaneously by adding known volumes of the oil and dispersant mixture to a volume of seawater in a large vessel. The contents of the vessel were vigorously agitated and then passed through the instruments. Steps were taken to adjust the instruments to give similar calibration curves. During the experiment, the data was logged and processed following the field work to obtain oil-in-water concentration results. It was stated that the linear range for this oil and dispersant combination was in the ppb range to 1 ppm. However, there was useful response up to 55 ppm which, with the use of calibration curves, could provide concentration results. Calibration curves were set for three concentration ranges, 0–3 mg/l, 3–15 mg/l and 15–40 mg/l. Numerous water samples were collected. A portion of these were extracted with Freon 113 solvent and the concentration determined using infrared (IR) spectroscopy. The concentration of the extracted water samples was determined by comparing their absorbance to those of a series of oil-in-solvent solutions prepared to known concentrations and also measured on the IR at 2930 cm^{-1} . Other samples were treated using a solvent exchange process over to hexane. A cuvette sampling system was installed in a Turner model 10 fluorometer and the hexane extracts were quantified. Like the IR process, the fluorometer absorbance values were compared to those of prepared Lagomedio crude oil-in-hexane standards in order to obtain oil-in-water concentrations. The agreement between the field and laboratory fluorescent data (Pearson correlation coefficient of 0.946) as well as the IR and laboratory fluorescent data was strong (0.944). Most of the water samples which underwent gas chromatographic analysis were used to note the change in composition of the dispersed oil. There was no information provided on any effort to compare the field fluorometer data to water samples analyzed by GC techniques.

3.2. American programs

The USCG has long been involved in developing the capability to measure petroleum hydrocarbon concentrations in water. In the report by Hiltabrand [18], information was provided on field trials of the Endeco towed fluorometer. The trials took place during March 1978 off the coast of Louisiana in the Gulf of Mexico. Designed as a submersible unit, it contains a Turner fluorometer for continuous monitoring. It was calibrated with Empire mix crude oil prior to deployment. Over the duration of the trial a significant distance was covered, the sampling depth ranged from 3 to 9 m and the real-time results ranged from 30 to 300 ppb, which was in good agreement with the results from the analysis of several grab-type water samples collected concurrently.

Recent efforts over the past number of years have resulted in the development of the SMART protocol. This is an operational plan developed for the Turner model 10AU fluorometer primarily for use at oil spills-of-opportunity in which dispersants are a potential countermeasure. The primary objective of the plan is to provide a means of monitoring the dispersed plume of oil. A general overview of the SMART program can be found in the report by Barnea and Laferriere [19], and a report by Gugg et al. [20] briefly discusses the findings from the use of the SMART protocol during two oil spills in the Gulf of Mexico. The oils spilled and dispersant employed were Gulf sweet crude oil with Corexit 9527 and Medium Arabian crude oil with Corexit 9500. The USCG SMART document [21] is

a comprehensive document containing both a summary of the need to monitor the fate of dispersed oil as well as the operational procedures. A paper by Henry et al. [22] provides much of the background information which lead to the decisions establishing the final protocol. In the SMART protocol, the degree of monitoring has increasing levels, or “tiers” as they are referred to in the report, and the selection of level is depended upon the needs at that specific incident. In tier III, the highest level, two instruments are deployed to monitor concentration at 1 and 5 m depths. The Turner fluorometer is equipped with the long wavelength kit for crude oils (350 nm excitation and 410–550 nm emission). Specific steps are listed to set up the instrument such as using the manufacturer’s default calibration, display “Raw” fluorescent data, concentration range set to manual/high and the time constant to 2 s. The instrument is calibrated on-site using an oil surrogate of 90 ppb fluorescein dye. While undertaking the monitoring operation, the following steps are recommended: (1) obtain background reading of the water from areas well outside the slick, (2) background readings of naturally dispersed oil prior to addition of the treating agents, (3) fluorometer readings beneath the slick after treatment, and (4) collect water samples from the outflow of the instrument for subsequent laboratory analysis. The final comparison of the real-time fluorometer data to laboratory analysis is at the discretion of the on-scene scientific personnel. Finally, while working on the SMART program, the USEPA carried out an internal program whose objective was to examine various calibration procedures for the Turner fluorometer. In a draft report obtained from the USEPA [23], information was provided on their evaluation of some novel calibration procedures. Examples include enhancing the solubility of the oil in water through sonication to developing calibration surrogates by dissolving an oil in a water soluble solvent (2-propanol) and then dissolving that solvent in water. Varying and limited success was achieved however no final report was found.

A report by Hillman et al. [24] outlines a proposed dispersant field monitoring procedure developed by the Alyeska Pipeline Service Company and EMCON Inc., Alaska, in order to meet Alaskan regulations. A unique feature of the protocol is the inclusion of a number of statements listing what the monitoring program was not intended to do. It is not intended to measure dispersant effectiveness, give real-time oil-in-water concentration results or be used to obtain estimates of the oil’s mass balance. The objective of the real-time monitoring is to have qualitative information showing the influence of the dispersant on the oil. The procedure specified a flow-through Turner model 10 fluorometer equipped with a short wavelength optical kit and quartz cuvette. The fluorometer is to be connected to an external data logger, with a logging interval of 2 min, and a sampling depth of 2 m. When in the field, the instrument is calibrated both before and after each survey while set up in flow-through mode. The procedure also calls for one to, first, record initial real-time background fluorescent readings of the water daily and second, real-time readings are taken immediately prior to entering the oil contaminated area. It is suggested that grab samples for subsequent laboratory analysis be collected. A laboratory test employed three types of calibration solutions prepared over the range of 0.5–100 ppm. Although specific ratios are not provided, the calibration solutions were as follows: (1) Alaska North Slope crude oil mixed with dispersant (Corexit 9527) which was then serially diluted into sea water to give individual oil and dispersant in sea water standards, (2) crude oil-in hexane standards, and (3) crude oil-in-hexane with fixed amounts of dispersants in each. All sets of standards were measured with the fluorometer set up for cuvette samples as opposed to flow-through configuration.

Steps are then given describing how to adjust the sensitivity controls of the instrument so that the displayed value correspond with a known concentration of a standard. Measuring the remaining standards leads to the creation of a calibration curve. The instrument has three sensitivity ranges. Calibration on one range is suitable for all ranges and calibration curves developed with the cuvette sampler can be used with the flow-through sample cell. There was little data in the report describing the laboratory or field experiments results.

3.3. Programs in France

A number of sea trials titled Protecmar, were conducted off the coast of France between the years 1979 and 1985. The program's objectives were to evaluate numerous aspects related to the use of dispersants. A summary of the program can be found in the reference Bocard [25] and Bocard et al. [26,27]. Sub-surface monitoring was carried out by dedicated vessels traversing along the x and y axis of the oil slicks. In the later trials, Protecmar 3 in 1981 through Protecmar 6 in 1985, the sub-surface monitoring of the dispersed oil included an in situ fluorometer and turbidimeter as well as a comprehensive water sample collection protocol. The water samples were subsequently analyzed to determine oil content. It was stated in Bocard [25] that there was a "rough correlation" between the real-time concentration measurements and the subsequent laboratory analysis of the water samples. The lack of accuracy was attributed to the impact of the distribution or size of the dispersed oil droplets during calibration. During Protecmar 3, the concentrations measured by the UV spectrofluorometer at a depth of 2.5 m was 7 ppm [25,28,29]. It was stated in Bocard et al. [28] that the instrument was calibrated for this trial using a stable emulsion of the same oil. There is a summary of the operational set up of the fluorometer instrument in the report by Bocard et al. [30]. The summary states that the Turner model 10-005 instrument was used and equipped with the short wavelength optical kit (254 nm excitation and 350 nm emission filter). The response of the instrument was tested in the laboratory without using dispersants. A test solution of fuel in DIFLUX (protisol DOS, Phosfac 6TDK Surfisorb TD20) at 1000 mg/l was prepared. This was diluted in water to a upper concentration of 3 mg/l. This was determined to be the approximate maximum concentration in which the calibration curve is linear. Four standards with concentrations of 3, 1, 0.3 and 0.1 mg/l were used to track the sensitivity of the instruments. The initial blank fluorescent value of the water was subtracted from subsequent readings thus correcting the real-time data to account for dispersed oil concentrations only. The flow rate of water through the fluorometer was 24 l/h.

A similar sub-surface water monitoring and sampling system was used at another field trial in France and was described in Desmarquest et al. [31,32]. Oily water samples were collected from the discharge outlet of the fluorometer and placed in bottles containing carbon tetrachloride solvent. The solvent was later analyzed by colorimetry, or more specifically IR analysis, to determine the hydrocarbon and surfactant content of the water. No information is given comparing the real-time fluorometer values to the IR results.

3.4. United Kingdom program

The agency AEA Technology of the National Environmental Technology Centre in Abington, United Kingdom, formerly referred to as Warren Springs Laboratory, has carried

out a number of field trials in the North Sea. Their recent field trials have regularly employed a Turner flow-through fluorometer. A summary is given of the information relevant to the Turner flow-through fluorometers gained through their operational use during the field trials and spills-of-opportunity.

The 1992 North Sea trials were outlined in the report by Lunel and Lewis [33]. The spilled product consisted of a 30% water-in-oil emulsion made from Forties blend crude oil and sea water. This emulsion was treated with the demulsifier solution of LA 1834 in Surdyne X113 solvent in a ratio of 60:40 by volume, respectively, and Dasic LTSW dispersant. Reports by Lunel [34,35] present dispersant findings from a 1993 sea trial employing a medium fuel oil and gas oil mixture (50:50) along with the dispersant Dasic Slickgone NS. Reference is made to calibration of the fluorometers using discrete samples. The authors Walker and Lunel [36] describe the 1994 North Sea trials in which Forties blend crude oil, a demulsifier solution (50:50 mixture of LA 1834:Surdyne X113) and Slickgone dispersant were used. At the 1994 trials, a total of eight Turner 10AU flow-through fluorometers were deployed to measure the oil-in-water concentration between 0.5 and 5 m depth. Another field trial employing continuous flow fluorometers was also conducted in conjunction with the 1994 North Sea trials and reported in Lunel et al. [37]. A medium fuel oil/gas oil mix (50:50) and the dispersant Corexit 9527 were used. Again, reference is made in this case to the instruments being calibrated using discrete water samples (Hurford et al. [38]). In Lunel et al. [39], the paper also discusses dispersed oil concentration results collected during the 1994 field trials using eight continuous flow Turner fluorometers; however, it is further added that the concentration was determined by subtracting out background water fluorometer values and using extracted discrete samples to calibrate. Information about the 1995 North Sea trials is found in Lunel and Davis [40]. The experimental methods were reported to be similar to the previous year's trials. Again, eight Turner 10AU fluorometers measured concentrations at various depths of 0.5–5 m. The data from the fluorometer was corrected for background signal and then they were calibrated via water samples extracted and then spectrophotometrically compared to a calibration curve developed from weathered oil-in-solvent standards. The oil type was Forties blend crude oil and MFO with the dispersants OSR-5, Slickgone NS, and 1100X. The Sea Empress spill of 1996 (Lunel et al. [41,42]) was a spill-of-opportunity in which much of the knowledge gained during the previous sea trials was applied. The mixture of Forties blend crude oil and heavy fuel oil (HFO) was treated with demulsifier (a 50:50 mixture of Shell LA1834 and Surdyne) and the dispersants Dasic LTSW, Finasol OSR-51, Dasic Slickgone NS, Dispolene 34S, Superdispersant 25, Enersperse 1583 and Corexit 9500. The 1997 field trial is described in Lewis et al. [43]. Forties blend crude oil, Alaskan North Slope crude oil and IFO-180 were tested using the dispersant Corexit 9500 and Dasic Slickgone NS. A total of six Turner model 10AU fluorometers were used to measure oil-in-water concentrations at 0.5, 1–5 m depths. The units were all equipped with the short wavelength optical kit (254 nm excitation and 350 nm emission); the calibration was carried out via the collection of water samples from the output of the instruments and then treated in a manner similar to that described earlier.

Research undertaken in the mid 1980s by Hurford and Buchanan [44] and Hurford et al. [38,45] for Warren Spring Laboratory was regularly referenced in the previous papers of this section. This work forms the foundation of its flow-through fluorometer operational

procedure. In [44], a report was presented comparing the capability of the Turner model 10 unit equipped with a short wavelength optical kit, a model 10 equipped with a long wavelength kit (350 nm excitation, 410–550 nm emission) and nephelometry for determining oil-in-water concentrations. A mixture of medium fuel oil and diesel oil at a ratio of 1:1 was used in the field test. The real-time results of the fluorometers were recorded on chart recorders. A calibration procedure using discrete samples is described. The 1 l samples were collected from the outflow of the instruments. In the laboratory, these samples were extracted with methylene chloride as preliminary work indicated that the solvent carbon tetrachloride and pentane were unsatisfactory. The sampling system in the Turner fluorometer was changed from the flow-through type to the individual cuvette type. Subsequently, each of the extracted samples were measured and the oil concentration determined by comparison to the spectrofluorometer signal of prepared oil-in-solvent standards. In turn, the results from the extracted samples were used to convert the recorded real-time response of the fluorometer to oil-in-water values. The results stated that only the fluorometer equipped with the short wavelength optical kit was capable of detecting the oil in the water. Hurford et al. [45] go on to state that the detection limit of the combination of fluorometer and short wavelength kit is between 10 and 50 ppb of oil.

In the papers by Hurford et al. [38,45], he compares the performance during a sea trial of the Turner flow-through fluorometer to a submersible unit called the Aquatracka by Chelsea Environmental Instruments. To calibrate the Aquatracka, mixtures with known amounts of oil-in-water are prepared and then directly measured on the instrument using a special quartz sample cell. Three test oils were used and included a 1:1 medium fuel oil and diesel oil mixture, diesel oil and 1:1:0.1 mixture of medium fuel oil, diesel oil and Corexit 9527 dispersant. It was mentioned that both instruments had similar responses. Nevertheless, the correlation of the Aquatracka results to the results from extracted samples was low. The explanation given is that the oily water mixtures used to calibrate the instrument contain dispersed droplets with very small diameters whereas beneath the oil slick, at the 0.5 m sampling depth used in this field trial, the droplets have larger diameters. The smaller droplets of the calibration mixtures would in theory maximize the fluorescence energy emitted from the oil hence the calibrations mixtures are not representative of the field samples. So, the larger droplets of the field samples would in theory generate higher concentration results because they interfere with the absorption/emission of the energy.

An operational protocol has been developed incorporating much of the experience gained from the aforementioned work. It is titled “Procedures for Monitoring Dispersant Operations” and was presented in the report by Wilde [46]. In the report it is stated that, using the oil same as that has been spilled, a 2 ppm oil and dispersant mixture is prepared in a 10 l bucket of salt water and used to calibrate the instrument in situ. The primary purpose of this step is to ensure the proper operation of the instrument. A detailed description is given for the operational portion of the procedure where it describes how to traverse across a slick collecting data and samples. Also the instructions call for one, to collect background data and samples outside the affected area for the correction of naturally occurring fluorescence, and to collect data and samples from the slick area before and after the dispersant application. The monitoring program recommends using several instruments simultaneously to monitor water drawn from multiple depths of up to 5 m. Throughout the monitoring program, the data is logged and 1 l water samples are collected from the output of the instrument at noted

times and locations using a global positioning systems. The water is placed in suitable bottles containing solvent for the initial extraction. The immediate success of the application of dispersant can be assessed based on the change in the fluorometer data from before and after the dispersant use as well as by observing the color of the solvent extract in the sample bottles. Oil would darken the color of the solvent. Following the program, the water samples are completely extracted. Oil in solvent standards are prepared over a desired concentration range with the same extraction solvent. The fluorescence of the standards and extracted water samples is measured by the fluorometer after it has been converted from a flow-through to cuvette-style sample system. From the calibration curve of the oil in solvent standards, the concentrations of the extracted water are determined. One then retrieves the fluorometer data recorded when that specific sample was collected. A calibration factor is obtained by dividing the laboratory oil-in-water concentration value by the difference in the fluorescence data for that sample and the background values. Once the data is transferred to an appropriate type of computer software file, the recorded fluorometer data can be processed using the correction factor to give continuous oil in water profile.

3.5. Norwegian programs

The agencies IKU Petroleum Research and Sintef in Trondheim, Norway have carried out a number of field trials in the North Sea. Like the AEA group, their recent field trials have regularly employed a Turner flow-through fluorometer. A summary is given of the information relevant to the Turner flow-through fluorometers gained through their operational use during the field trials and spills-of-opportunity.

In a report prepared by Sorstrom [47], information is provided on initial work in Norway to set up a method to obtain real-time values of the concentration of oil dispersed in the water column beneath a slick. Two different fluorometers, both designed for underwater use, were tested. Water samples were collected from the outflow of the fluorometers as well as individually during program. These were analyzed by gas chromatography techniques and the results compared favorably to the fluorometer data. However, limited information is given with respect to the type and set up of the instruments. Another report by Sorstrom [48] mentions the use of a prototype in situ fluorometer used during the 1985 Haltenbanken field trial. In this field trial, a topped Statfjord crude oil premixed with dispersant was used. A figure in the reports gives a depth profile for concentration with concentration reported in millivolts. Reports by Brandvik et al. [49] and Lewis et al. [50] presents findings from a 1994 North Sea trial employing a Sture blend crude oil and the dispersant Corexit 9500. In this trial, three Turner model 10AU instruments were employed to monitor oil-in-water concentrations at 1, 2, and 5 m depth. In the field, the units were calibrated using prepared dispersed oil-in-water mixtures containing the same Sture blend crude oil and Corexit 9500. In order to overcome the sensitivity of the instruments to temperature variation, after the field trials this same calibration procedure was repeated in the laboratory under controlled environmental conditions. Also, water samples were collected during the sea trial were extracted and the petroleum hydrocarbon content determined by gas chromatography techniques. It was stated that these results were compared to the real-time values but there was no further discussion in this paper. The 1995 North Sea trials were outlined in the report by Brandvik et al. [51]. The spilled product consisted of oil from the Troll field and the

dispersant Corexit 9500. The concentration of the oil-in-water was monitored and sampled at depths of 1, 3 and 8 m. Peak concentration of oil in the water under the dispersant treated slick ranged from 10 to 20 ppm while that under the untreated slick was 0.03–0.05 ppm.

3.6. Miscellaneous programs

During the literature search, a number of reports were obtained that briefly mentioned using fluorimeters to monitor oil-in-water concentration. Little further information was given outlining how the equipment was set up, calibrated, etc. Those reports specifically mentioning the in situ fluorimeters have been presented here.

The manufacturer of the instruments, Turner Designs Inc. of California, USA, has undertaken some development work on procedures to quantify oil-in-water concentration. The findings are available in two technical brochures by Turner Instruments [52,53].

In a report authored by Page et al. [54], a discussion is presented on a field trial undertaken nearshore to Long Cove, Maine. Murban crude oil premixed at a 10:1 ratio with Corexit 9527 was released. An elaborate system of tubing was used to draw water to a Turner model 10 instrument, which monitored real-time concentration, and also permitted the collection of individual samples for subsequent analysis. The discussion of the field fluorometer was limited to stating that the instrument was used to monitor the dispersed oil concentration along the bottom of the study areas, and it was reported that initial concentrations of 30–40 ppm were observed but decreased to non-detectable limits after two tidal cycles. An outline for an experimental monitoring plan was a report by Railsback et al. [55]. Its preparation was in response to recent spills in the San Francisco Bay area and called for the use of field fluorometric samples to monitor total oil concentration as well as sample collection followed by laboratory analysis using EPA method 413.1 or 418.1. No information was found related to a follow-up report. The authors Payne et al. [56] used in situ ultraviolet fluorescence measurements and water sampling to monitor the concentration of oil in water following a spill off the coast of California. A mixture of 20% diesel fuel and 80% IFO-180 was released. The dispersant used was not reported. The instrument was calibrated using mixtures of the seawater, dispersant and the IFO-180 from the tanks of the ship. Water samples were extracted and analyzed in the laboratory by gas chromatography (GC/FID and GC/MS) techniques to note the changes in the oil composition; however there was minimal concentration information either from the in situ fluorescence or grab samples other than to state that there was no indication of enhanced concentrations of dispersed oil. Again, the author Payne et al. [57] reported that in situ ultraviolet fluorescence was used at a spill-of-opportunity to monitor the oil-in-water concentration following the application of Corexit 9527 dispersant to a release of Angola Planca crude oil in the Gulf of Mexico. The fluorescent sampling along with a discrete sampling program was carried out with samples obtained from a depth of 4 m. The maximum concentration of dispersed oil measured was 22 ppm for total aliphatics and 5.6 ppb for total aromatics. A report by Sommerville et al. [58] stated the successful use of the Turner model 10 fluorimeters to detect Orimulsion. Orimulsion, described in Jokuty et al. [59], is an oil-in-water emulsion marketed as a fuel for power plants.

Finally, a report prepared by Fingas [60] and Nichols and Parker [61] were useful tools as they provided a list of offshore experimental spills used to determine the effectiveness

of dispersants. Summary tables in the reports includes information on the technique used to measure effectiveness, environmental conditions as well as the reference source.

4. Discussion

The use of the Turner instruments to measure oil-in-water concentrations began in the late 1970s and are still being carried out at present. Although there has been a clear evolution with the instrumentation over that time, there is a surprising number of similarities between the way operations were conducted initially and those being used presently. Prior to the 1980s, several varieties of Turner instruments were noted. These were often bench top units fitted with a flow-through cuvette and brought to the field. Specific references to the Turner model 10 field unit consistently appeared in projects undertaken around the year 1982.

During this same period and extending into the late 1980s, the references list several different names describing the excitation and emission filters used in the instruments. This can be misleading because they are often describing filters which cover the same excitation and emission wavelengths. During this time, the Turner Instrument Company undertook some development work in this area and introduced the “short wavelength kit” for oils. The kit includes an excitation filter at 254 nm and an emission filter at 350 nm. Subsequently, a “long wavelength kit” was released with an excitation filter at 350 nm and emission filter at 410–550 nm. Technical notes from Turner Instrument [52,53] state that the short wavelength kit is suitable for light and refined fuel oils while the long wavelength kit is better suited for heavy or crude oils. The choice of the wavelength kit is one of the significant differences in the operational procedures developed over the years. Some of the reasons which may have lead to the selection of a particular kit are the time period in which the work was conducted, the type of oil used and the intended requirement of the procedure. For example, much of Environment Canada’s work was conducted in the early to mid 1980s. The long wavelength kit was not as well known and the procedure had to be capable of dealing with any oil type. It was stated by Lambert et al. [62] that the short wavelength kit can be used with refined oils and crude oils; it just sacrifices sensitivity with respect to the fuel oils. Hence, the short wavelength kit is cited in Environment Canada’s work. The English programs also employed the short wavelength kit. A potential reason for this is that in the early work by Hurford et al. [45], it was stated that only the short wavelength kit was capable of detecting oil. However, a mixture of medium fuel oil and diesel fuel was being used in this research work and may be an explanation as to why only the short wavelength kit could detect the oil. Most recently, the SMART protocol developed by a consortium of US government agencies, stipulates the use of the long wavelength kit. Again, a kit specific for crude and heavy oils. The SMART protocol was initially designed for use by USCG strike teams to monitor dispersant effectiveness at actual oil spills. The majority of spills in which they would be involved with monitoring dispersant impact would be with spills of crude oil and not fuels; thus the long wavelength kit is preferred.

Sampling depths were relatively similar ranging from 0.5 to 7 m. A towed field unit call the Endeco Petrotrack had a Turner model 10 instrument mounted in a submersible casing and could potentially reach depths of tens of meters. Little information was available on extensive use of this unit. The general consensus was that 1 m was the most common

sampling depth. Sampling at depths of less than 0.5 m was difficult because the buoyancy of the unstable dispersed droplets resulted in highly variable readings. Sampling at depths below 3 m to 5 m had diminishing returns as the dispersed oil does not often reach that depth immediately after the dispersant is applied; hence the concentration in the water is near detection limits.

Oil types and dispersants employed in the experimental portion of the programs were highly variable. Some of the oils included medium fuel oil, medium fuel oils mixed with diesel fuel, ASMB crude, North Slope and Prudhoe Bay crude, Lagomedio crude, Forties blend crude, Sture blend crude oil and more. These oils have very different chemical composition and behavior with dispersants in water. The number of different dispersants and dispersant combinations used was also high. Corexit 9527 dispersant was often cited in early work while Corexit 9500 was more prominent in the late 1990s. Few field trials used the same combination of oil and dispersant making a direct comparison of results from different trials difficult.

One area generating debate has been with the calibration and operational procedures for the fluorometer. Many different protocols have been attempted. Once again, there are certain similarities between the procedures dictated by the requirements of the instrument itself. In order for the instrument to provide real-time results a procedure has to be developed to relate the real-time values to known oil concentration values. Usually attempts were made to develop a calibration solution of oil-in-water. Various approaches were taken to create the calibration solutions however, the calibration solution was usually obtained by combining the oil and dispersant into a premix. Oil to dispersant ratios regularly documented for the premix were 1:1, 4:1 and 10:1. Environment Canada's procedures called for an initial addition of dispersant only (up to 5 ml) to the test vessel, whose purpose was to blank out the fluorescent signal of the dispersant in the calibration solution and coat the interior surfaces of the apparatus thereby minimizing adhesion of the oil. The 5 ml volume was likely based on the behavior of the oil and dispersant combination used at the time; however results in Lambert et al. [62,63] show that using 5 ml of dispersant could have significant detrimental effects on the drift of the fluorometer values and a compromise of 1 ml was proposed. Collecting samples for subsequent laboratory analysis was consistently recommended. Examples of extraction solvents included pentane, hexane, Freon and dichloromethane. Employing the same Turner fluorometer with a change to a single sample type cuvette, along with prepared oil-in-solvent standards, was often the choice method to quantify the oil in the water samples. Gravimetric, IR spectroscopy and gas chromatography techniques were also used. How the laboratory data was employed was not universal. Sometimes, the subsequent laboratory analysis was used merely to confirm the real-time data while other times it was used to correct it. However, in most reports the research topic was something other than the analysis procedure and the procedure itself was there as a means to achieve an end. Thus, the reports provided only minimal details in regard to the analysis.

5. Conclusions

Findings have been presented on a literature search to document the historical use of fluorescence-based portable instruments capable of giving real-time oil-in-water

concentrations. It was found that various models of fluorometers manufactured by Turner instruments were most commonly employed to monitor oil and dispersed oil levels at spills on water. Originally, bench top units were adapted and used in the field, however over time dedicated equipment was developed by the manufacturer for this purpose.

References

- [1] M. Fingas, in: *The Basics of Oil Spill Cleanup*, 2nd ed., Lewis Publishers, New York, 2001, p. 121.
- [2] D. Green, J. Buckley, B. Humphrey, in: *Fate of Chemically Dispersed Oil in the Sea. A Report of Two Field Experiments*, Environmental Protection Service Report EPS 4-EC-82-5, Environment Canada, 1982, p. 150.
- [3] S. Gill, C. Ross, 1981 dispersant application field trial—St. John's Newfoundland, in: *Proceedings of the Fifth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ont., 1982, pp. 255–263.
- [4] S. Gill, C. Ross, Aerial application of oil spill dispersants, in: *Proceedings of the Third Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ont., 1980, pp. 328–340.
- [5] S. Gill, R. Goodman, J. Swiss, Halifax '83 sea trials of oil spill dispersant concentrates, in: *Proceedings of the 1985 International Oil Spill Conference*, American Petroleum Institute, Washington, DC, 1985, pp. 479–482.
- [6] J. Swiss, S. Gill, Planning, Development and execution of the 1983 East Coast dispersant trials, in: *Proceedings of the Seventh Arctic and Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ont., 1984, pp. 443–453.
- [7] R. Myers, K. Corry, Surface and sub-surface hydrocarbon concentrations measured during an offshore dispersant trial, in: *Proceedings of the Seventh Arctic and Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ont., 1984, pp. 454–470.
- [8] H. Brown, Dispersant Effectiveness in Cold Water, Proprietary Report ERCL.RS.85.10, Esso Resources Canada Limited Research Department, Calgary, AB, 1985, p. 45.
- [9] H. Brown, R. Goodman, G. Caneari, Dispersant effectiveness in cold water, in: *Proceedings of the Eighth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ont., 1985, pp. 245–259.
- [10] H. Brown, Dispersant Effectiveness in Cold Water 1985 Wave Basin Trials, Proprietary Report ERCL.RS.86.04, Esso Resources Canada Limited Research Department, Calgary, AB, 1986, p. 49.
- [11] H. Brown, R. Goodman, G. Caneari, Where has all the oil gone? Dispersed oil detection in a wave basin and at sea, in: *Proceedings of the 1987 International Oil Spill Conference*, American Petroleum Institute, Washington, DC, 1987, pp. 307–312.
- [12] H. Brown, R. Goodman, A. Holoboff, C. Peabody, L. Quaife, D. Shaw, Freshwater Oil Spill Research Program Field Trial Final Report, Physical/Chemical, Report ERCL.RS.86.22, Esso Resources Canada Limited Research Department, Calgary, AB, 1986, p. 108.
- [13] L. Quaife, Field Report for the Freshwater Oil Spill Research Program Field Trial, Proprietary Report ERCL.RS.86.02, Esso Resources Canada Limited Research Department, Calgary, AB, 1986, p. 103.
- [14] G. Sergy, P. Blackall, Design and Conclusions of the Baffin Island Oil Spill Project, Arctic, vol. 40, Suppl. 1, Arctic Institute of North America, University of Calgary, Calgary AB, 1987, pp. 1–10.
- [15] D. Green, B. Humphrey, B. Fowler, The use of flow-through fluorometry for tracking dispersed oil, in: *Proceedings of the Fifth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ont., 1982, pp. 435–444.
- [16] D. Green, B. Humphrey, B. Fowler, The use of flow-through fluorometry for tracking dispersed oil, in: *Proceedings of the 1983 International Oil Spill Conference*, American Petroleum Institute, Washington, DC, 1983, pp. 473–475.
- [17] B. Humphrey, D. Green, B. Fowler, D. Hope, P. Boehm, The Fate of Oil in the Water Column Following Experimental Oil Spills in the Arctic Marine Nearshore, Arctic, University of Calgary, Calgary, Canada, J. Arctic Inst. North America 40 (Suppl. 1) (1987) 124–132.
- [18] R.R. Hiltabrand, Continuous oil-in-water measurements by fluorometry, in: *Oceans'79 Proceedings*, The Institute of Electrical and Electronic Engineers (IEEE), Piscataway, NJ, 1979, pp. 566–588.
- [19] N. Barnea, R. Laferriere, Smart: scientific monitoring of advanced response technologies, in: *Proceedings of the 1999 International Oil Spill Conference*, American Petroleum Institute, Washington, DC, 1999, pp. 1265–1267.

- [20] P. Gugg, C. Henry, T. Bridgeman, S. Glenn, G. Buie, M. Austin, Proving dispersants work, in: *Proceedings of the 1999 International Oil Spill Conference*, American Petroleum Institute, Washington, DC, 1999, pp. 1007–1010.
- [21] United States Coast Guard (USCG), National Oceanic and Atmospheric Administration (NOAA), United States Environmental Protection Agency (USEPA), Centers for Disease Control and Prevention (CDC), SMART—Special Monitoring of Applied Response Technologies, Report <http://www.response.restoration.noaa.gov/oilaid/SMART/SMART.html>, 2000, p. 52.
- [22] C. Henry, P. Roberts, E. Overton, A primer on in-situ fluorometry to monitor dispersed oil, in: *Proceedings of the 1999 International Oil Spill Conference*, American Petroleum Institute, Washington, DC, 1999, pp. 225–228.
- [23] R. Nadeau, personal communication, Internal Progress Report, USEPA Environmental Response Team, Edison NJ, 1996, 30 pp.
- [24] S.O. Hillman, S.D. Hood, M.T. Bronson, Dispersant field monitoring procedures, in: *Proceedings of the Twentieth Arctic and Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ont., 1997, pp. 521–540.
- [25] C. Bocard, Summary of the protecmar experiments, the French dispersant offshore trials program, in: *Proceedings of the 1986 Dispersion of Oil on Sea Seminar*, Oceanographic Center Sintef Group, Norway, 1986, p. 20.
- [26] C. Bocard, C. Gatellier, J. Croquette, F. Merlin, Operation Protecmar, Environment Canada, Ottawa, Ont., *Spill Technol. Newslett.* 6 (2) (1981) 54–85.
- [27] C. Bocard, G. Castaing, J. Ducreux, C. Gatellier, J. Croquette, F. Merlin, Protecmar: The French experience from a seven-year dispersant offshore trials program, in: *Proceedings of the 1987 International Oil Spill Conference*, American Petroleum Institute, Washington, DC, 1987, pp. 225–229.
- [28] C. Bocard, G. Castaing, C. Gatellier, Chemical Oil Dispersion in trials at sea and in laboratory tests: the key role of dilution process, in: T.E. Allen (Ed.), *Oil Spill Chemical Dispersants: Research, Experience, and Recommendations*, STP 840, American Society for Testing and Materials, Philadelphia, 1984, pp. 125–142.
- [29] C. Bocard, C. Gatellier, Protecmar 3, Rapport IFP No 30482, Institut Francais du Petrole, Cedex, France, 1982, p. 41.
- [30] C. Bocard, J. Ducreux, C. Gatellier, J. Croquette, F. Merlin, Protecmar 4, Rapport IFP No 31478, Institut Francais du Petrole, Cedex, France, 1983, p. 51.
- [31] J. Desmarquest, J. Croquette, F. Merlin, C. Bocard, G. Castaing, C. Gatellier, Recent advances in dispersant effectiveness evaluation: experimental and field aspects, in: *Proceedings of the 1985 International Oil Spill Conference*, American Petroleum Institute, Washington, DC, 1985, pp. 445–452.
- [32] J. Desmarquest, J. Croquette, F. Merlin, C. Bocard, C. Gatellier, A field test and assessment of oil dispersant efficiency, in: *Proceedings of the 1983 International Oil Spill Conference*, American Petroleum Institute, Washington, DC, 1983, p. 574.
- [33] T. Lunel, A. Lewis, Effectiveness of demulsifiers in sea trials: the use of fluorometry, surface sampling and remote sensing to determine effectiveness, in: *Formation and Breaking of Water-In-Oil Emulsions Workshop*, Technical Report Series 93-018, Marine Spill Response Corporation, Washington, DC, 1993, pp. 179–202.
- [34] T. Lunel, Dispersant effectiveness at sea, in: *Proceedings of the 1995 International Oil Spill Conference*, American Petroleum Institute, Washington, DC, 1995, pp. 147–155.
- [35] T. Lunel, Dispersion of a large experimental slick by aerial application of dispersant, in: *Proceedings of the Seventeenth Arctic and Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ont., 1994, pp. 951–978.
- [36] M. Walker, T. Lunel, Response to oil spills at sea using both demulsifiers and dispersants, in: *Proceedings of the Eighteenth Arctic and Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ont., 1995, pp. 537–558.
- [37] T. Lunel, L. Davis, A. Chen, R. Major, Field test of dispersant application by fire monitor, in: *Proceedings of the Eighteenth Arctic and Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ont., 1995, pp. 559–602.
- [38] N. Hurford, I. Buchanan, R.J. Law, P.M. Hudson, Comparison of two fluorometers for measuring oil concentrations in the sea, *Oil Chem. Pollut.* 5 (1989) 379–389.
- [39] T. Lunel, L. Davis, P. Brandvik, Field trials to determine dispersant effectiveness at sea, in: *Proceedings of the Eighteenth Arctic and Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ont., 1995, pp. 603–628.

- [40] T. Lunel, L. Davis, Dispersant effectiveness in the field on fresh oils and emulsions, in: Proceedings of the Nineteenth Arctic and Marine Oilspill Program Technical Seminar, Environment Canada, Ottawa, Ont., 1996, pp. 1355–1394.
- [41] T. Lunel, J. Rusin, N. Bailey, C. Halliwell, L. Davies, A successful at sea response to the sea empress spill, in: Proceedings of the Nineteenth Arctic and Marine Oilspill Program Technical Seminar, Environment Canada, Ottawa, Ont., 1996, pp. 1499–1520.
- [42] T. Lunel, J. Rusin, N. Bailey, C. Halliwell, L. Davies, The net environmental benefit of a successful dispersant operation at the sea empress incident, in: Proceedings of the 1997 International Oil Spill Conference, American Petroleum Institute, Washington, DC, 1997, pp. 185–194.
- [43] A. Lewis, A. Crosbie, L. Davis, T. Lunel, Large scale field experiments into oil weathering at sea and aerial application of dispersant, in: Proceedings of the Twenty-first Arctic and Marine Oilspill Program Technical Seminar, Environment Canada, Ottawa, Ont., 1998, pp. 319–344.
- [44] N. Hurford, I. Buchanan, The Use of Flow-Through Techniques to Determine Sub-Surface Concentrations of Oil, LR 552 (OP)M, Warren Spring Laboratory, Stevenage, 1986, p. 25.
- [45] N. Hurford, I. Buchanan, R.J. Law, P.M. Hudson, Comparison of Flow-Through and Towed Fluorimeters For Measuring Oil Concentrations in the Sea, LR 621 (OP)M, Warren Spring Laboratory, Stevenage, 1987, p. 13.
- [46] S. Wilde, Procedures for monitoring dispersant operations, in: Proceedings of the 10th Environmental and Scientific Coordinators Workshop, Austrian Maritime Safety Authority, Queenscliff, Australia, 2001, pp. 163–177.
- [47] S.E. Sorstrom, Experiences with the use of in situ fluorescence for detection of petroleum hydrocarbons in sea water, in: Proceedings of the Seventh Annual Arctic Marine Oilspill Program Technical Seminar, Environment Canada, Ottawa, Ont., 1984, pp. 306–326.
- [48] S.E. Sorstrom, The 1985 Full scale experimental oil spill at Haltenbanken, Norway, in: Proceedings of the International Seminar on Chemical and Natural Dispersion of Oil on Sea, Center for Industrial Research, SINTEF, Trondheim, Norway, 1986, p. 19.
- [49] P. Brandvik, T. Lunel, P. Daling, A. Lewis, Measurements of dispersed oil concentrations by in situ UV fluorescence during the Norwegian experimental oil spill 1994 with Sture blend, in: Proceedings of the Eighteenth Arctic and Marine Oilspill Program Technical Seminar, Environment Canada, Ottawa, Ont., 1995, pp. 519–536.
- [50] A. Lewis, P. Daling, T. Strom-Kristiansen, A. Nordvik, R. Fiocco, Weathering and chemical dispersion of oil at sea, in: Proceedings of the 1995 International Oil Spill Conference, American Petroleum Institute, Washington, DC, 1995, pp. 157–164.
- [51] P. Brandvik, T. Strom-Kristiansen, A. Lewis, P. Daling, M. Reed, H. Rye, H. Jensen, The Norwegian Sea trial 1995 offshore testing of two dispersant application systems and simulation of an underwater pipeline leakage a summary paper, in: Proceedings of the Nineteenth Arctic and Marine Oilspill Program Technical Seminar, Environment Canada, Ottawa, Ont., 1996, pp. 1395–1415.
- [52] Turner Instruments, On-line Monitoring of Oil in Water using Fluorescence, Technical Brochure from Turner Designs Inc., Sunnyvale, CA, 1989, p. 7.
- [53] Turner Instruments, Oil in the Environment, Technical Brochure from Turner Designs Inc., Sunnyvale, CA, 1989, p. 16.
- [54] D. Page, J. Foster, J. Hotham, E. Pendergast, S. Hebert, L. Gonzalez, E. Gilfillan, S. Hanson, R. Gerber, D. Vallas, Long-term fate of dispersed and undispersed crude oil in two nearshore test spills, in: Proceedings of the 1983 International Oil Spill Conference, American Petroleum Institute, Washington, DC, 1983, pp. 465–471.
- [55] S. Railsback, G. Robilliard, J. Mortenson, Strategy for monitoring the short-term distribution of dispersed oils, in: Proceedings of the 1987 International Oil Spill Conference, American Petroleum Institute, Washington, DC, 1987, pp. 321–324.
- [56] J. Payne, J. Clayton Jr., C. Phillips, J. Robinson, D. Kennedy, Lt. J. Talbot, Lt. G. Petrae, J. Michel, T. Ballou, S. Onstad, Dispersant trials using the PAC baroness, a spill of opportunity, in: Proceedings of the 1991 International Oil Spill Conference, American Petroleum Institute, Washington, DC, 1991, pp. 427–433.
- [57] J. Payne, T. Reilly, R. Martrano, G. Lindblom, M. Kennicutt II, J. Brooks, Spill-of-opportunity testing of dispersant effectiveness at the Mega Borg oil spill, in: Proceedings of the 1993 International Oil Spill Conference, American Petroleum Institute, Washington, DC, 1993, pp. 791–793.

- [58] M. Sommerville, T. Lunel, N. Bailey, D. Oland, C. Mile, P. Gunter, T. Waldhoff, Orimulsion, in: Proceedings of the 1997 International Oil Spill Conference, American Petroleum Institute, Washington, DC, 1997, pp. 479–484.
- [59] P. Jokuty, S. Whitar, M. Fingas, Z. Wang, K. Doe, D. Kyle, P. Lambert, B. Fieldhouse, Orimulsion: Physical Properties, Chemical Composition, Dispersibility, and Toxicity, Environment Canada Report Number EE-154, Ottawa, Ont., 1995, 37 p.
- [60] M. Fingas, Field measurements of effectiveness: historical review and examination of analytical methods, in: L. Michael Flaherty (Ed.), Oil Dispersants: New Ecological Approaches, ASTM STP 1018, American Society for Testing and Materials, Philadelphia, 1989, pp. 157–178.
- [61] J. Nichols, H. Parker, Dispersants: comparison of laboratory tests and field trials with practical experience at spills, in: Proceedings of the 1985 International Oil Spill Conference, American Petroleum Institute, Washington, DC, 1985, pp. 421–427.
- [62] P. Lambert, B. Fieldhouse, Z. Wang, M. Fingas, M. Goldthorp, L. Pearson, E. Collazzi, Preliminary results from the laboratory study of a flow-through fluorometer for measuring oil-in-water levels, in: Proceedings of the Twenty-third Arctic and Marine Oilspill Program Technical Seminar, Environment Canada, Ottawa, Ont., 2000, pp. 69–98.
- [63] P. Lambert, M. Goldthorp, B. Fieldhouse, Z. Wang, M. Fingas, L. Pearson, E. Collazzi, A review of oil-in-water monitoring techniques, in: Proceedings of the 2001 International Oil Spill Conference, American Petroleum Institute, Washington, DC, 2001, pp. 1375–1380.