

From: Fritz, David E.
Sent: Wed Apr 28 02:59:46 2010
To: Rainey, David I
Cc: Cavanagh, Ian
Subject: FW: visual obs paper
Importance: Normal
Attachments: AMOP2010.doc; ATT5977110.htm

Very relevant to your oil observation "studies".

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From: Ed Levine [mailto:Ed.Levine@noaa.gov]
Sent: Monday, April 26, 2010 12:11 PM
To: Fritz, David E.
Subject: Fwd: visual obs paper

Begin forwarded message:

From: Bill Lehr <Bill.Lehr@noaa.gov>

Date: April 26, 2010 11:45:11 AM EDT

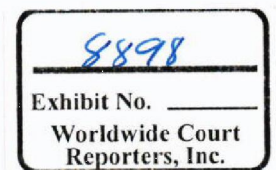
To: Ed Levine <Ed.Levine@noaa.gov>

Cc: Debbie Payton <Debbie.Payton@noaa.gov>, Doug Helton@noaa.gov, John Tarpley <john.tarpley@noaa.gov>, Glen Watabayashi <Glen.Watabayashi@noaa.gov>, William Conner <William.Conner@noaa.gov>

Subject: visual obs paper

Reply-To: Bill.Lehr@noaa.gov

Ed,



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Attached is a preprint of the paper I will present in June on why using BAASH is a bad idea for spill volume estimation.

Bill L

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VISUAL OBSERVATIONS AND THE BONN AGREEMENT

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Abstract

By far the most common remote sensing techniques for estimating spill thickness are systems based upon the visual spectrum (400-750 nm). Usually the 'system' is a trained observer who records with his/her eye and a simple camera the appearance of the slick. Various formulas have been built to link slick appearance with spill thickness. The Bonn Agreement Aerial Surveillance Handbook (BAASH) uses an appearance code based upon previously published scientific papers, small-scale laboratory experiments, mesoscale outdoor experiments and field trials. The author examines the theoretical and practical limitations of estimating thickness and volume using such visual appearance methods. These limitations include atmospheric visibility constraints, spatial and temporal inhomogeneity of the oil, irregularity of the water surface and optical characteristics of hydrocarbons. The expected limitations of BAASH and equivalent formulas for practical volume estimation are discussed. A possible modification, using separation into simple thick oil and sheen areas is presented.

1. Introduction

Wherever oil is produced, stored, or transported there will be a risk of oil spills. The size of the response is usually dependent upon the volume released but often this quantity is not known. Therefore, attempts have been made over the last four decades to develop technology or operating procedures that can quantify the spill by the size and visible appearance of the slick (Fingas and Brown, 2005). Unfortunately, there still does not exist a recognized method or equipment that can reliably provide the response team with an accurate answer. This paper reviews the difficulties, both theoretical and practical, that have prevented the advancement in this area.

2. Oil Spill Behavior and Properties

Oil spills provide an interesting challenge to the environmental scientist because oil is not a pure chemical but rather a mixture of thousands of different hydrocarbons. As it interacts with the environment, the properties of the material, including its optical properties, change. Oil begins to spread as soon as it is spilled, but it does not spread uniformly. Any shear in the surface current will cause stretching, and even a slight wind will cause a thickening of the slick in the downwind direction. Most spills quickly form a comet shape where a small, thick oil, region is trailed by a much larger sheen that can be of varying colors. Figure 1 shows such a situation for an experimental spill of 50 bbl of Arabian crude oil (Lehr et al., 1983). Competing theories exist to explain this phenomenon (Elliot, 1986; Mackay et al., 1980). It is unknown whether a vertical cross sectional profile of such a slick would be wedge-shaped, i.e. linear change in thickness as one moved away from the thick oil center, or be more non-linear, with a large thickness gradient at the

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thick-sheen boundary and a small gradient elsewhere. Personal experience of the authors from actual spills suggests the latter 'fried egg' model would be more appropriate but lack of rigorous experimental data leaves this question unresolved.

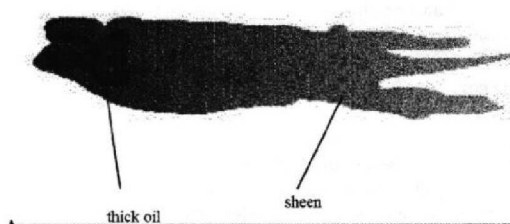


Figure 1 - Processed image of a 50-bbl test spill showing separation into thick part and sheen, plus the beginning of streamers.

As the slick spreads further, it is not uncommon to have it split into separate streamers due to wave action or Langmuir effects (Lehr and Simcock-Beatty, 2001). The latter refers to a pattern of repeating Langmuir cells below the surface that create a system of ridges and troughs on the surface. The troughs become natural collection areas for floating oil. The end result is lines of oil that may be spread over a large geographical area but effectively cover only a small percentage of the water surface.

As the slick spreads, it also weathers, i.e. changes its physical properties and composition, mainly due to evaporation of the more volatile hydrocarbons. Such chemical composition changes can affect the bulk physical properties of the slick. The viscosity of the slick can, for example, increase to such an extent that it is no longer a Newtonian fluid and its surface roughness is altered. Oil density may increase, reducing the slick buoyancy and increasing wave overwash. Organic matter and suspended particulates in the water column may become imbedded into the slick. Waves and turbulence can break highly viscous oil into small 'tar balls'. All these factors may affect spill detection. One final factor for some oil spills is water-in-oil emulsification. Many crude oils and some refined oils may form a stable emulsion where water droplets get bonded into the oil slick. Such emulsified oils are opaque, highly viscous, and quite thick, as much as several centimeters.

3 Measuring Oil Thickness

Mechanical thickness measurements of the surface slick in open water are prone to a high degree of uncertainty, particularly for thinner films. Usually they involve isolating a section of the oil slick and collecting all the oil in that section (Allan and Schlueter, 1969; Goodman and Fingas, 1988; Fazal and Milgram, 1979; Dahling et al., 1999) although alternative techniques are also used (Brown et al., 1998). Clingage to the sampler, failure to collect all the oil, leakage into the sampled area from surrounding regions, and slick disturbance from the sampling device are just some of the difficulties with these methods.

The author and other researchers performed a series of experimental crude oil spills with surface mechanical measurements in coordination with visual observations from a helicopter, the

standard platform for oil spill observations, and as well as a special aerial survey plane (Lehr et al., 1984). While there was a wide scattering in the data, the results indicate that oil thicker than 70-100 microns was opaque (black or brown). This was in agreement with the assessment of Lewis (2000), based upon a literature review. Lewis classified oil films between three and fifty microns as thickness that will absorb enough light to produce no overall rainbow affect caused by wave interference with reflected light. Fingas et al. (1999) report even more restrictive limits on dark oil appearance. According to them, oil thicker than 8 microns will appear brown. For diesel fuel the number is about 4 microns and for heavy fuel oils about 2 microns.

It is important to note that spill responders report actual oil thicknesses that are much greater than these minimum thicknesses and recovered volumes tend to support this observation. One common rule-of-thumb in the response community, based upon the studies of Hollinger and Mennella (1973), is that 90% of the oil spill volume is in the opaque 'thick' slick area, while, at least early in the spill, this same thick regime represents only 10% of the total slick surface area. Unfortunately Lehr et al (1983) found no reliable relationship for different spills between the ratio of thick oil/ sheen volume and thick oil/ sheen surface area. However, they did report that the major volume portion of the slick was in the opaque area.

4 Oil Spill Thickness Using Non-visual Methods/frequencies

Both the ocean and oil emit black body radiation that can be detected in the microwave region. Water has an emissivity that is higher than oil causing the latter to appear cooler even though the fluids are at the same temperature. Musseto et al (1994) showed that sensors using microwaves showed poor correlation with thickness. They are not widely used at present to detect oil. A more commonly utilized wavelength is the thermal IR band, 8 to 14 microns. In this band, oil emissivity is 0.94-0.97 compared to water emissivity of 0.988 so that oil appears slightly cooler than water, all else being equal. Unfortunately, all else is seldom equal. Oil may, for example, absorb solar radiation, dissipate heat more slowly, and be at an actual higher temperature than the surrounding water. Field instruments used to detect oil usually are calibrated for the specific field conditions. Brown et al. (1998) found no correlation between the thickness of oil and its infrared signal strength.

Brown and Fingas (2003) review various remote sensing techniques, using special equipment and/or frequencies outside the visual range. They found that laser fluorosensor signals are completely absorbed by any slick greater than 20 microns, and infrared bands suffer interference from thermal emission from the oil. Their suggested approach is to use a three-laser system that operates on certain acoustic properties of the slick. The system (Brown et al., 2005; Brown et al. 2006) has worked under controlled laboratory tests and field trials but has not been developed to the rigor required for actual field use made the transition from prototype to operational tool routinely used at spills.

5 Passive Systems in the visual Visual bands/Bands

By far the most common remote sensing techniques for estimating spill thickness are systems based upon the visual spectrum (400-750 nm). Usually the 'system' is a trained observer who records with his eye and a simple camera the appearance of the slick. Various formulas have been built to link slick appearance with spill thickness. The earliest reported system in the literature was a 1930 report to the U. S. Congress that listed six thickness categories from .04 microns to 2 microns. A

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Comment [JS1]: 8 microns for brown appearance is ridiculous. We have done extensive lab and on-ocean testing with various oils. The first slight hints of any true color first appear after about 10 microns and crudes don't appear truly brown until past 40-50 microns. We found most crudes to become opaque at about 120-150 microns - a bit thicker than your own findings from 1984 but still close.

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Comment [JS2]: I don't understand this sentence: Both dyed and undyed diesel appears colorless even at several millimeters thick. Fuel oils (IFOs) become black/brown at 70-100 microns from our experience.

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more widely circulated standard, done by API in 1963 closely followed this earlier report. Hornstein in 1972 developed a standard that was based upon actual experiments (Hornstein, 1972). Under controlled laboratory lighting, he spilled known quantities of different crude and refined oils into dishes and then documented their appearances. This standard is still widely used in response guidebooks. It divides oil thickness into five groups ranging from 0.15 microns to 3.0 microns. The European response community have produced their own set of standards, the most widely disseminated being those connected with the Bonn Agreement (Anon., 2007). The Bonn Agreement Aerial Surveillance Handbook (BAASH) uses an appearance code based upon previously published scientific papers, small-scale laboratory experiments, mesoscale outdoor experiments and field trials. However, its thickness codes below 1 micron are derived from Hornstein's work and the description of oils greater than 100 microns are taken from an earlier International Tanker Owner's Pollution Federation guide (ITOPF, 1981).

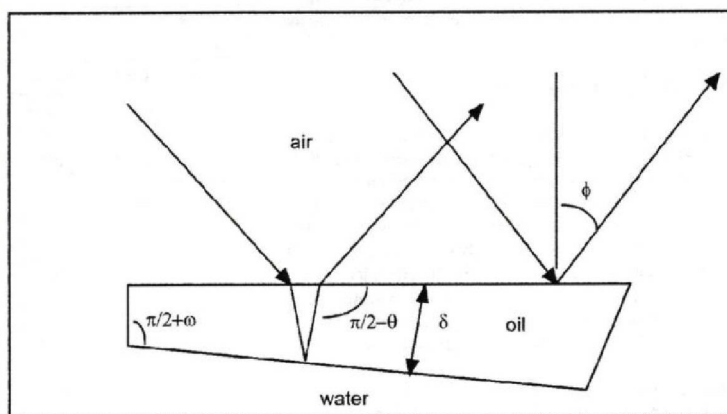


Figure 2 Geometrical diagram of light reflected from oil slick
FIGURE 1

Examination of the optical process involved in visual observation of oil films explains the physics and limitations behind this approach. For the very thinnest oils, the oil-water and oil-air interfaces operate as mirrors. As noted earlier, oil has a higher reflection coefficient than water. Fresnel Equations give the reflection coefficient R_r as

$$R = (R_s + R_p)/2$$

$$R_s = \left[\frac{n_o \cos(\phi) - n_e \cos(\theta)}{n_o \cos(\phi) + n_e \cos(\theta)} \right]^2 \quad (1)$$

$$R_p = \left[\frac{n_o \cos(\theta) - n_e \cos(\phi)}{n_o \cos(\theta) + n_e \cos(\phi)} \right]^2$$

where the angles are shown in Figure 1 and n_o is the refractive index of air and n_e is the refractive index for oil. The s and p subscripts refer to polarization. For normal incidence light ($\phi = 0$) and this yields for a typical crude oil ($n_o = 1.50$), $R = 4\%$ if we neglect the small correction due to light internally reflected from the oil-water interface. While this is twice what we would expect for reflection from seawater, the actual contrast seen by the observer for real spills is greater because the oil slick dampens capillary waves on the water surface, reducing light scatter.

As the viewing angle moves away from the vertical, a larger percentage of the light is reflected. This increase is highly non-linear with rapid increase in reflected percentage at angles greater than 60 degrees. The reflected light becomes more polarized with optimum polarization at the Brewster angle. The above calculation assumes that the seawater is pure but coastal waters often contain contaminants that reflect light much better than water, at least in certain frequencies. The author's experience indicates that it is the dampening of the capillary waves and the reduction in light scattering that makes the slick visible in thin sheen situations.

Light scattered by subsurface water can penetrate thin slicks from below. Otreombe and Piskozub (2001) have proposed using this reflected radiance as a mechanism for monitoring oil slicks.

If we include all multiply reflected light and neglect interference and absorption, the reflected energy ratio would increase by slightly more than a quarter of a per cent. Using an average absorption coefficient of $10,000 \text{ m}^{-1}$, assuming that the variation in slick thickness can be neglected ($\omega = 0$ in Figure 1), still ignoring interference, then, by Lambert's Law, the total radiant energy for normally incident light will show an order of magnitude drop in value every 230 microns. Table 1 shows the percent of normally incident radiant energy that would be expected to reflect off the oil-water interface to return to the air-oil interface for different color-defined film thicknesses, as specified by the Bonn Agreement and by the ASTM standard. It is interesting to note that the the ASTM standards generally specify a thinner oil slick limit for each color category, silver being the lone exception.

TABLE 1 Table 1 Returning radiant energy from oil-water interface

appearance	micron thickness (ASTM)	micron thickness (BAASH)	returning radiant energy (per cent)
silver	0.1 - 0.3	0.04 - 0.3	0.28 (0.25 microns thickness)
rainbow	0.2 - 3	0.3 - 5.0	0.26 (2.5 microns thickness)
metallic	~ 3	5.0 - 50	0.17 (25 microns thickness)

discontinuous true oil color to black	> 3	> 50	0.0019 (250 microns thickness)
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There is obviously a considerable drop off in returning radiant energy as the true appearance of the oil becomes apparent to the observer. There is very little difference between silver and rainbow sheen. For these two thicknesses, the key factor is wave interference. Light returning from the oil-water interface will be pi radians out of phase with light reflected from the oil-air interface. For normal incidence and continuing to neglect oil thickness variation, interference occurs at

$$\begin{aligned}\delta &= \frac{\lambda m}{2n_o} && \text{destructive} \\ \delta &= \frac{\lambda(2m-1)}{4n_o} && \text{constructive}\end{aligned}\quad (2)$$

where m is any positive integer representing the number of wavelengths, λ is the light wavelength, and δ is the oil film thickness. Because only a small amount of light impacting the oil-water interface is reflected, all but singly reflected light can be ignored. Moreover, there will be potential for more interference at the longer wavelengths than at the shorter wavelengths, due to increased absorption at the shorter wavelengths. Using $\lambda = 550$ nm, the energy available for destructive interference at $m = 1$ ($\delta = 0.18$ microns) thickness is 7% of the reflected light energy at the oil-air interface. According to the Bonn Agreement, rainbow sheen is replaced by metallic color at δ equal to 5 microns. This corresponds to approximately $m = 28$ (28 wavelengths), at which thickness the ratio of energies is about 6%. Hence, the implication is that even a small reduction in the number of returning photons from the oil-water interface can reduce the detectibility of interference patterns. The ASTM standards suggest an even more restrictive limit on the visibility of interference pattern since they place the transition from metallic (some remaining interference affects) to dark (true color according to BAASH) at 3 microns.

Of course, the observation platform, unless it is a satellite or high altitude aircraft, will not see a synoptic picture of the oil spill from a purely vertical angle. A typical spill observation helicopter overflight altitude is 300 m. Even a reasonably small spill can extend for tens of kilometers. Hence, the angle of observation may vary by eighty degrees or more. The Bonn Agreement aerial surveillance handbook recommends flying a racetrack with the sun behind the observer and the observer looking at the object from an angle of 45 degrees or less from a vertical direction.

The extension of Equation 2 to cases where the viewing angle is not normal and the oil film is not uniform is

$$\begin{aligned}\lambda &= \frac{4n_o\delta}{2m} \cos(\theta + \omega) && \text{destructive} \\ \lambda &= \frac{4n_o\delta}{2m-1} \cos(\theta + \omega) && \text{constructive}\end{aligned}\quad (3)$$

where $\sin(\theta) = \frac{\sin(\phi)}{n}$ by Snell's Law. Assuming that $\omega \approx 0$, we get interference equivalent to a perpendicular slick view whenever

$$\delta = \delta \cos[\arcsin(\sin(\phi)/n)] \quad (4)$$

where δ would be the equivalent slick thickness for the normal view, for interference purposes, to get the same result as an incident angle of ϕ with thickness δ . For the 40 degrees viewing angle recommended by the Bonn agreement, this corresponds to an apparent 10% equivalent increase in thickness, or 16% if the wave surface is tilted away from the observer. The path length of the light will be correspondingly larger, with increased dampening of light intensity. However, the biggest change occurs in the ratio of the reflected energies from the air-oil and oil-water interfaces. For vertical views, the author we found that the energy reflected from the oil-water surface was about 7% of the oil-air surface energy if we neglect internal absorption. However, if the view angle is 40 degrees, the percentage changes to 20%. If the oil slick surface is tilted so the angle is increased 45%, the percentage increases to 30%. Hence, rainbow appearance of the slick is conditional upon the viewing angle. The increased path length of the light through the oil will decrease these percentages somewhat, but the increase in ratio with increase in viewing angle will remain. This suggests that a key factor in assigning thickness based upon appearance is the viewing angle. Dahling et al (SINTEF report 1999) concluded that silver sheen and 'metallic' appearing oil may be difficult to distinguish, while the analysis above suggests that there is an ambiguity between 'metallic' and rainbow, depending upon viewing angle.

There are additional factors to consider. The water surface is not flat. Most wind-generated waves have a steepness of 3-6%. If we assume a maximum wave height of 1 m (Beaufort scale number 3), the corresponding (water) wave-length will be between 15-30 m. This means that incident viewing angles of the water surface will have an inherent uncertainty of ± 5 degrees or more.

As mentioned earlier, oil slicks are not uniformly thick. Some of the steepest thickness gradients will occur in windrows caused by the Langmuir affects mentioned earlier. Langmuir cells in the open ocean have widths of between 10-100 m with a typical width of 30 m (Rye, 20010-SST special issue). Thicker oil will collect in the troughs of these cells. An experimental spill of 100 tons in the North Sea reported thick parts of the slick reaching 8-9 mm (Rye, 20010). While this was due in large part to emulsification, even non-emulsified oils can easily exceed a mm: in thickness in the thicker part of the slick. Using 30 m as a Langmuir cell width, 1 mm as the thickness of the oil in the trough center and 1 micron as the thickness of the sheen, ω in Figure 2 is much less than a degree if the increase in thickness were linear across the cell. It almost certainly is not, however, so that estimating the impact of variable thickness becomes challenging. Unfortunately, there is no generally accepted algorithms that describe the cross sectional thickness variation of an oil slick. Most responders assume, based upon appearance, that the slick is relatively uniform in the sheen part with a rapid increase in thickness as the edge of the thick part. If this is true, then ω may be several degrees in the transitional regime from sheen to dark oil and the color boundary determination between the sheen and dark (or true color oil) may depend slightly upon viewing angle. This is, however, probably a small affect.

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When the slick is thick enough, light cannot make it through the slick and will not be reflected back to the surface. Instead, the photons are absorbed and partly re-emitted at longer wavelengths, primarily in the infrared but some in the visible range. These fluorescence properties of oil are commonly used to detect dispersed oil in the water column, and the greater emissivity of oil compared to water makes slicks appear warmer in IR images. The Bonn agreement classifies the thickness region between 5-50 microns as metallic appearance. In this region, photons emitted by the oil compete with the greatly reduced number of photons reflected from the oil-water interface and light reflected from the surface. The actual color of oil in this region then depends upon the type of oil and the incident light conditions.

The above discussions assume ideal viewing conditions and equipment. Real spill conditions are never ideal. Should the surface wind reach greater than seven to ten knots, whitecaps will form, breaking the oil sheen. As viewing angle increases, so does glitter from the water surface, making viewing very difficult. Very clear conditions require that the sun be behind the observer to prevent glare. Human eyes are variable in their sensitivities to color and acuity, causing different observers to see different patterns.

-A further complication is the increase in viscosity of the oil as it weathers on the water surface. Fresh crude oil typically has a kinematic viscosity of a few hundred cSt. However, weathered oil can easily have a viscosity of more than 100,000 cSt, giving it the characteristics of molasses. The surface of such a slick is no longer mirror smooth, resulting in an increase of light scattering from the surface due to a faceting condition.

The above discussion explains why the authors isare skeptical about sheen thickness measurements based upon appearance. Depending upon viewing angle and environmental conditions, the sheen may appear to be silver, rainbow, or metallic, regardless of its actual thickness. Moreover, as BAASH notes, roughly 90% of the oil will be contained within 10% of the overall slick area for fresh spills. This 10% is the usual part of the spill where the oil true colors are visible, i.e., the opaque part of the slick.

Since so little light is reflected from the oil-water surface for a thick film, it is impossible to estimate oil thickness by wavelength interference in the visual range. Beyond a certain thickness, increased thickness-oil depth does not contribute to change in surface appearance. One millimeter thick oil will visually look the same as one centimeter thick oil. Observers usually map the extent of the dark slick area and assign an estimated thickness value, based upon past experience or additional spill information. These estimates can sometimes vary by orders of magnitude. Since the majority of the oil is often in the thick, dark part of the slick, the error in estimating its volume is apt to be significantly larger than the entire sheen volume estimate. From a practical point of view, this makes sheen volume estimation of little value in total spill volume estimation. Barring alternative methods, an educated estimate of a spill expert of thick oil volume is probably the best operational choice for spillage amount. Hence, accuracy in estimating sheen thickness is often of little value in determining spill volume.

6 Conclusions

While the calculations will be uncertain, volume estimation of oil sheen to within an order of magnitude is possible. This is, however, of little value for total spill volume estimation in most

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cases since the majority of the oil will be in the optically thick portion, which cannot be accurately estimated by visual observation. Hence, accuracy in estimating sheen thickness is often of little value in determining total spill volume. Rather, careful mapping of the thick oil areal extent will usually prove more valuable to the response team, who should probably look to other methods to estimate spill volume, if available.

7 **Disclaimer**

The conclusions of this paper are solely those of the author and do not reflect any position of the US government or the National Oceanic and Atmospheric Administration.

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