DETECTION OF WAVY SEA SURFACE OIL-DERIVATIVE CONTAMINATION WITH FORWARD SPECULAR HIGH-FREQUENCY SCATTERING

Stanisław Pogorzelski
Paweł Rochowski
Maciej Grzegorczyk
Bogumił B. J. Linde
Institute of Experimental Physics, University of Gdańsk, Poland
Ewa Skrodzka
Faculty of Physics, Institute of Acoustics, A. Mickiewicz University, Poland
Łukasz Bielasiewicz
INFO-EKO Design-Consulting Office, Poland

ABSTRACT

A spectrum of low-frequency (20–30 Hz) amplitude fluctuations of the ultrasonic (10 MHz) signal specularly scattered from water surfaces covered with monomolecular and thicker crude oil origin films of well-defined, oceanographically relevant viscoelastic properties was examined in laboratory and at-sea conditions. The relationship between the surface water wave (30 Hz) damping coefficient and the oil layer thickness was established, and compared to the one predicted by the classical Stokes theory. The depression of the spectral energy density of wind-driven waves by surface films was inferred from the ratio of acoustic signal fluctuations spectra with/without films, and compared to that resulting from the Marangoni damping theory applicable to monolayers of particular surface viscoelasticity. The agreement between the theory and experimental data was satisfactory. As shown in at-sea experiments performed with a free-floating, buoy-like acoustic system, and an artificial oil slick spread over the Baltic Sea surface, the film’s rheological surface properties can be recovered from acoustic surface probing, as well as oil spill edge detection. Simultaneous statistical analyses of the scattered signal amplitude distribution parameters turned out to be unequivocally related to the oil substance fraction weight, oil layer thickness, and the form of oil contamination.

Keywords: crude oil contamination, capillary wave damping, acoustic surface scattering, statistical-frequency analyses, at-sea pollution detection

INTRODUCTION

A crude oil derivative introduced on a water surface may form a number of structural arrangements [4]. One of them can be a monomolecular layer with very diverse viscoelastic properties [10]. If the amount of petroleum derivatives is quite large, then their excess will form a lens-shaped layer in equilibrium, as shown in Fig. 1. The spreading coefficient is defined as $S_{o/w} = \gamma_{w} - \gamma_{o} - \gamma_{w/o}$. Oil spreads on the water surface (complete wetting), for $S_{o/w} > 1$ [11], where: $\gamma$ – surface tension of water ($w$), surface tension of oil substance ($o$), and interfacial tension of water–oil ($w/o$). For $S_{o/w} < 1$, a lens-shaped oil layer of particular thickness $d$ (a few millimetres [4]) is formed. The equilibrium thickness of the lens is strictly determined by the value of surface and interfacial tensions and the densities of both liquids [1]. The crude oil spreading phenomenon existing in the sea is much more complex to evaluate quantitatively. In particular, the steady-state signatures of oil contamination are affected by the presence of the sea surface’s natural surfactant films having 2D thermoelastic properties [2, 29], and the spreading coefficient is a quantity that is dependent on surfactant concentrations, surface activity and temperature. Moreover, the oil spreading kinetics is mediated by the viscoelasticity modules of all the interfaces (O/W/A) [3].
An intense undulation process will result in the formation of several other structural arrangements, in particular an emulsion, in which the fraction of the dispersed phase of the organic compound varies in time and space.

The attenuation coefficient of the sine surface capillary (frequency > 13 Hz) wave of low amplitude, propagated along such an oil-coated surface, cannot be described by the Stokes equation (1),

$$\alpha_m = \frac{4k^2\eta}{3\rho\omega}$$  \hspace{0.5cm} (1)

where:
- $k = 2\pi/\lambda$, $\lambda$ - wavelength,
- $\eta$ - liquid viscosity,
- $\rho$ - density,
- $\omega = 2\pi f$, and $f$ is the frequency.

Such a relation refers to the waves running on the surface of an ideal liquid [21]. The proximity of both interfacial surfaces creates different conditions of the liquid flow, and facilitates the exchange of energy between adjacent areas. The dependence of the surface wave attenuation coefficient as a function of the thickness of the layer consisting of various petroleum compounds was obtained by the ultrasonic pulse reflection method [23, 24]. The determined structural physico-chemical properties of the investigated liquids, obtained in an accompanying study, supplied interesting information on the damping process of water surface wave motion in a two-layer type system. In further studies, high-frequency scattering signal amplitude characteristics (spectral and statistical) were evaluated for the wind-driven surface of a clean (pollution-free) and affected by crude oil layer of water [20, 27, 28].

**EXPERIMENTAL CONDITIONS**

The influence of oil layers of different properties on the amplitude fluctuation of scattered ultrasonic signals from a wind-driven water surface was examined under natural conditions in Gdynia’s Naval Port [19]. The air and the sea water temperatures during the measurements were 285 and 287 K respectively. A high-frequency (10 MHz), two-transducer acoustic system based on a forward specular scattering geometry as a free-floating buoy-like arrangement was used in these investigations [18, 23, 25, 28] (Fig. 2).

The registered acoustic signal amplitude fluctuations were played back by a level tape recorder and analysed using a Bruel & Kjaer 1621 analogue tuneable band pass filter with a width of 1/3 octave (23%) and a V-543 digital multimeter over a frequency range of 1-50 Hz. The crude oil substances were used as an oil-film-slicks-forming mono-layer on the sea surface. The oils applied in these investigations were dissolved in hexane to make a volatile solution, and spread carefully on the sea surface. It should be noted that the intensity of high-frequency scattered signals $I_s$ is inversely proportional to the square of the slope of the surface,$$S/h/1 \sim I_s$$, and linearly related to the scattered signal amplitudes $A_s$. The damping ratio $D_s(f)$ of the oil films spread on the open sea surface can be measured on the basis of the following theoretical expression, for the spectral density proportional to the surface wave height $S(\omega) \sim h^2$, as described by Phillips [18, 22].

$$D_s(f) = \left[ \frac{S_0(\omega)}{S_o(\omega)} \right]^2 = \frac{h_s(\omega)}{h_o(\omega)} = \frac{I_s(\omega)}{I_o(\omega)} = \left( \frac{A_o}{A_s} \right)^2$$ \hspace{0.5cm} (2)
The physical and visco-elastic properties of an oil-covered sea surface were obtained for the selected oil substances from additional measurements performed using the Langmuir trough system [17].

The light oils were treated as monolayers exhibiting positive spreading coefficients. The Selectol plus oil had a negative spreading coefficient, and appeared on the sea water surface as floating lenses or spots with an equilibrium thickness of 0.39 cm.

The static and dynamic oil film 2D properties characterised by the elasticity modulus \( E_0 \), the film surface pressure \( \Pi \), and the relaxation time \( \tau \), were introduced in Eq. (3) over the frequency range of 1–35 Hz, for two oil substances (Gasoline 94, Gasoline 86) for a better comparison.

**RESULTS AND DISCUSSION**

The damping ratio results were obtained in the presence of oil substances under natural conditions at a constant wind velocity above the sea surface. The damping ratios within a frequency range of 1–35 Hz were analysed. The frequency relationships of the damping ratio \( k \) are illustrated in Fig. 3, where the theory predicted relation together with the scattered signals ratio experimentally determined are presented.

It is clear from the plots that the wave damping ratios appear to have low values (0.5‒1.5) in the frequency region of \( f >> 20 \text{ Hz} \). The theoretical damping ratio (contrast) values of \( D_r(f) \) were computed for Gasoline 94 and Gasoline 86, by means of Eq. (3).

The damping ratio of short surface waves in the presence of insoluble oil films [5, 6, 14‒16] is given by:

\[
D_r(f) = \alpha_0 / \alpha_0 = \frac{1 - 2\tau - 2\tau^2 - X_0 - Y_0(X_0 + \tau)}{1 - 2\tau + 2\tau^2 - 2X_0 + 2X_0^2}
\] (3)

where:

\[
X_0 = \frac{E_0K^2}{\rho^2 \eta^2 \omega^2}, \quad Y_0 = \frac{E_0K}{4\eta \rho}, \quad \tau = \left( \frac{2f}{\omega} \right)^{1/2},
\]

where:

\[
E_0 = -\frac{4 \pi A}{\Delta A} - \text{the dilatational elasticity modulus accounting for film-forming material adsorption or desorption variations during a compression-dilation film area cycle, } A - \text{ the film-covered area, } \eta - \text{ the viscosity of water, } \rho - \text{ density of water, } K = 2\pi/\lambda - \text{ wave number of surface water wave, } \omega = 2\pi f - \text{ angular frequency, } t_r - \text{ relaxation time.}
\]

We believe that the not close agreement between the theoretical and experimental curves could result from other environmental factors (temperature, currents, non-uniform slick deposition, etc.). This disagreement may have arisen from the fact that the static and dynamic oil film parameters, introduced in the theoretical relationship in Eq. (3), were taken from laboratory measurements made under different conditions. In the open sea investigation, the monolayer films were not completely and uniformly distributed over the sea surface. In addition, the elastic films spread on the sea surface with different physical properties may break any holes that occur, and the surface oil films will move slowly as a result of Stock’s wave drift and currents. The other responsible factor is the roughness of the sea water surface modified by an oil film at lower wind velocities. From the damping ratios obtained in the presence of the insoluble oil substances in situ, which are depicted in Fig. 4, it can be seen that a peak in the frequency region of 5‒10 Hz is observed in all cases.

The damping intensity (peak height) and peak frequency may be introduced, as the maximum of the damping ratio \( D_{r,\text{max}}(f) \) and the resonance frequency, \( f_{\text{m}} \) (in the so-called Marangoni damping phenomenon). From the theoretical relationship \( D_r(f) \), one can see that the respective maximum damping ratio values for Gasoline 94 and Gasoline 86 are 20 and 13, occurring at a maximum frequency of 5 Hz.

The similar peaks of the amplitude fluctuation spectra of scattered acoustic waves on capillary waves are easier to notice for both clean and polluted water and for different wind speeds. This process, some kind of relaxation, can be explained as a physico-chemical nature of the sea surface films, but to clarify the process it is necessary to have more experimental data from in situ measurements.

The amplitudes of the acoustic signal as a function of the surface capillary wave’s frequency are shown in Fig. 5 in the frequency range 1‒50 Hz. The measurements were performed for a clean surface and a surface covered with the oils. All the frequency dependencies of the amplitudes are similar in shape. They have a maximum at relatively low
frequencies, between 5–10 Hz, whereas the amplitude above these frequencies is rather low and constant. However, the measurements of the statistical parameters of the scattered signals are performed under the same surface conditions, and they are presented in the following chapter.

To sum up, it can be stated that the measurements of the first three liquids are positive, which suggests the ability to form on a water surface a layer with a thickness ranging from monomolecular to one resulting from the amount of the liquid and the surface area available.

Extra 15 and Marinoll 111 oils have negative values of \( S_{ow} \); introduced onto the water surface, they will form a lens with a thickness of 0.004242 and 0.005091 m, respectively.

In order to obtain intermediate values of an oil layer thickness, before spreading an oil film, a surface-active agent (Fotonal) was dissolved in water phase. Undergoing absorption, this substance reduced the interfacial water–oil tension, changing the value of wettability coefficient \( S_{ow} \) into a positive one. Thus, it was possible to form a permanent film of both oils with thicknesses ranging from 0.00001 m to the equilibrium thickness \( d_{\infty} \).

**EFFECT OF OIL LAYER THICKNESS ON THE ATTENUATION OF THE SURFACE WAVES ON WATER**

The model material used consisted of five crude oil derivatives; ethyl gasoline 78, lamp oil, Diesel oil, Extra 15 engine oil and Marinoll 111 gear oil. In order to characterise the materials used, the following additional measurements of structural parameters were performed: density, viscosity, surface and interfacial tensions in contact with water. The results are collected in Table 1. The two last columns in the table contain the wettability coefficient \( S_{ow} \) and equilibrium thickness \( d_{\infty} \). The values of \( S_{ow} \) for the first three liquids are positive, which suggests the ability to form on a water surface a layer with a thickness ranging from monomolecular to one resulting from the amount of the liquid and the surface area available.

Extra 15 and Marinoll 111 oils have negative values of \( S_{ow} \); introduced onto the water surface, they will form a lens with a thickness of 0.004242 and 0.005091 m, respectively.

In order to obtain intermediate values of an oil layer thickness, before spreading an oil film, a surface-active agent (Fotonal) was dissolved in water phase. Undergoing absorption, this substance reduced the interfacial water–oil tension, changing the value of wettability coefficient \( S_{ow} \) into a positive one. Thus, it was possible to form a permanent film of both oils with thicknesses ranging from 0.00001 m to the equilibrium thickness \( d_{\infty} \).

**RESULTS**

The attenuation coefficient of a surface wave with a frequency \( f = 30 \) Hz propagating on a water surface covered with a film of crude oil derivative, as a function of its thickness \( d \), is presented in Fig. 6. The value of the coefficient \( \alpha \) was determined by means of an instrument described in \([23, 24]\). Table 2 presents the theoretical values of \( \alpha_m \) (1) and the condition of applicability (4) of this expression, for \( p_d \) – the penetration depth of the eddy component [25] based on the measurement results from Table 1.

\[
p_d^2 = k^2 + \frac{i \omega \rho}{\eta} \tag{4}\]

when the following condition

\[
k^2 << \frac{\rho \omega}{\eta} \tag{5}\]

is met, then the flow is mainly laminar, and the attenuation of the wave may well be approximated by the Stokes equation.
DISCUSSION

The nature of function α(d) presented in Fig. 6, although complicated, has some common features for ethyl gasoline 78, lamp oil, Diesel oil and Extra 15 oil.

The values of α for the thinnest film (0.00001 m) are greater than those predicted by the theory, being equal to 2.44αm for ethyl gasoline, 1.573αm for lamp oil, 1.378αm for Diesel oil and 16.36αm for Extra 15 oil.

For larger thicknesses, the value of α decreases steadily and approaches the values predicted by theory, although they remain higher by several per cent: 1.04αm for ethyl gasoline, 1.015αm for lamp oil, 1.0004αm for Diesel oil and 1.028αm for Extra 15 oil.

Higher than theoretical values of α most likely result from the partially eddy-like, duct-similar flow of liquid in the vicinity of the undulating surface, as was suggested by the applicability condition of the Stokes expression (4) found in Table 2, for all the investigated liquids. It is fulfilled in the case of the first three liquids of low viscosity, while the values on both sides of inequality (5) for the remaining two liquids differ by not more than one order of magnitude. When the thickness of the film increases, the values of α decrease and pass through a well-pronounced maximum at d ≈ 0.0001 m.

Recently, several other methods have been used to determine the spatial, seasonal and temporal variability of the elastic and spreading characteristics of oil layers in contact with seawater [29, 30].

Tab. 2. Applicability condition of Stokes approximation (5)

| Petroleum derivative | αm x 10² [m⁻¹] | ηb < ρb0kₙ | λb x 10⁻² [m] | λb x 10⁻² [m] |
|----------------------|----------------|-------------|---------------|---------------|
| Ethyl gasoline 78    | 0.0602         | 0.00676 < 1.461 | 0.65          | 0.85          |
| Kerosene             | 0.1379         | 0.0164 < 1.5358 | 0.65          | 0.83          |
| Diesel oil           | 0.2155         | 0.0354 < 1.9827 | 0.7           | 0.7           |

Higher than theoretical values of α most likely result from the partially eddy-like, duct-similar flow of liquid in the vicinity of the undulating surface, as was suggested by the applicability condition of the Stokes expression (4) found in Table 2, for all the investigated liquids. It is fulfilled in the case of the first three liquids of low viscosity, while the values on both sides of inequality (5) for the remaining two liquids differ by not more than one order of magnitude. When the thickness of the film increases, the values of α decrease and pass through a well-pronounced maximum at d ≈ 0.0001 m.

Recently, several other methods have been used to determine the spatial, seasonal and temporal variability of the elastic and spreading characteristics of oil layers in contact with seawater [29, 30].

CONCLUSIONS

The attenuation of a surface wave propagated on the surface of water covered with an oil film attains higher values than those assumed by the classical hydrodynamic theory. When the thickness of the film approaches or exceeds the generally assumed value which determines the depth of penetration of the undulatory motion d ≥ lb/2, the values of the coefficient tend to approach the Stokes expression αm, exceeding it only by several per cent.

The observed instances of the departure of α from the theoretical value are probably caused by the short distance between interfacial surfaces and the excessive viscosity of heavier fractions of crude oil, which lead to violation of the applicability condition of the Stokes approximation for an ideal liquid.

The depression of the spectral energy density of wind-driven waves by surface films (the relative spectra, so-called contrast K) was inferred from the ratio of acoustic signal fluctuations spectra with/without films, and compared to that resulting from the Marangoni damping theory applicable to monolayers of particular surface viscoelasticity (determined in a separate measurement) and a moderate agreement was found.

The high-frequency two-transducer buoy-like free-drifting scattering system based on a specular forward scattering geometry was successfully applied in at-sea experiments to recover the viscoelastic oil film properties and turned out to be an effective oil pollution detection system.

REFERENCES

1. Adamson A.W. (1982): Physical chemistry of surfaces, Wiley, New York.
2. Boniewicz-Szmyt K., Pogorzelski S. J. (2018): Evolution of natural sea surface films: A new quantification formalism based on multidimensional space vector. Environ. Sci. Pollut. Res., 25, 4826-4836.
3. Boniewicz-Szmyt K., Pogorzelski S. J. (2008): Crude oil derivatives on sea water: Signatures of spreading dynamics. J. Mar. Syst., 74, S41-S51.
4. Boniewicz-Szmyt K., Pogorzelski S. J., Mazurek A. (2007): Hydrocarbons on sea water: steady-state spreading signatures determined by an optical method. Oceanologia, 49(3), 413-437.
5. Cini R., Lombardini P. P. (1978): Damping effect of monolayers on surface wave motion in a liquid. J. Coll. Int. Sci., 65, 387-389.
6. Cini R., Lombardini P. P., Fiscella B., Trivero P. (1985): Ripple damping on water surface covered by spreading film. Nuovo Cimento, 86, 491-500.
7. Ermakov S. A., Plinovsky E. A. (1984): Variation of the spectrum of wind ripple on coastal waters under the action of internal waves. Dyn. Atmos. Oceans, 8(1), 95-100.
8. Ermakov S. A., Zuykova A. M., Panchenko A. R., Salashin S. G., Talipova T. G., Titov V. I. (1986): Surface film effect on short wind waves. Dyn. Atmos. Oceans, 10, 31-50.
9. Ermakov S. A., Zuykova A. M., Salashin S. G. (1987): Transformation of spectra of short wind waves in spilled layers. Izv. AN USSR, Phisica Atmosfery i Okeana, 23(7), 707-15 (in Russian).
10. Harkins W. D. (1952): The physical chemistry of surface films, Reinhold Publ. Corp., New York.
11. Hoult D. (1969): Oil on the sea, Plenum Press, New York.
12. Hühnerfuss H., Alpers W., Lange P. A., Walter W. (1981): Attenuation of wind waves by artificial surface films of different chemical structure. J. Geophys. Res. Lett., 8, 1184-1186.
13. Hühnerfuss H., Garret W. (1981): Experimental sea slicks: their practical application and utilization for basic studies of air-sea interaction. J. Geophys. Res., 86(C1), 439-447.
14. Hühnerfuss H., Lange P. A., Walter W. (1985): Relaxation effects in monolayers and their contribution to water damping. I. Wave induced phase shifts. J. Colloid Interface Sci., 108, 430-441.
15. Hühnerfuss H., Lange P. A., Walter W. (1985): Relaxation effects in monolayers and their contribution to water wave damping. II. The Marangoni phenomenon and gravity wave attenuation. J. Colloid Int. Sci., 108, 442-450.
16. Hühnerfuss H., Walter W., Lange P. A., Alpers W. (1987): Attenuation of wind waves by monomolecular sea slicks and the Marangoni effect. J. Geophys. Res., 92, 3961-3963.
17. James A. M., Prichard F. E. (1974): Practical physical chemistry, Longman Group Ltd.
18. Khalifa S. (1990): An investigation of physical-chemical properties of polluted sea surface by an acoustical method, PhD Thesis, University of Gdańsk, 1990.
19. Khalifa S. S., Linde B., Pogorzelski S., Śliwiński A. (1992): Aspects of the physical properties and the visco-elastic features of the sea water - oil system. Oceanologia, 32, 19-28.
20. Khalifa S. S., Linde B., Pogorzelski S., Śliwiński A. (1992): Detection of derivative substances on a sea surface by statistical analysis of scattered acoustic signals. Oceanologia, 32, 29-40.
21. Lamb H. (1945): Hydrodynamics, Dover, New York.
22. Leonard F. (1970): Survey of literature on reflection and scattering of sound waves at the sea surface. J. Acoust. Soc. Am., 47(5), 1209-1228.
23. Linde B., Pogorzelski S., Śliwiński A. (1983): Determination of the surface wave amplitude on water surface by acoustic pulse method. Acoustics Letters, 7(6), 83-85.
24. Linde B., Pogorzelski S., Śliwiński A. (1984): Attenuation measurements on a water surface in the frequency range 20-60 Hz by the ultrasonic pulse method. Acoustics Letters, 7(7), 96-99.
25. Linde B. (1999): Acoustical Spectroscopy of Cyclic & Heterocyclic Compounds, Ketones and Polluted Water Surface, Wydawnictwo Uniwersytetu Gdańskiego, Gdańsk.
26. Lucassen-Reynders E. H., Lucassen J. (1969): Properties of capillary waves. Adv. Colloid Interface Sci., 2, 347-395.
27. Pogorzelski S. J. (1992): Characteristics of acoustic scattering from a wind-created water surface covered with monomolecular organic films. Dyn. Atmos. Oceans, 17, 63-78.
28. Pogorzelski S. J. (1991): The influence of crude oil spills on the sea surface on ultrasound scattering. Oceanologia, 31, 107-118.
29. Pogorzelski S. J., Boniewicz-Szmyt K. (2016): Thermoelectric surface properties of seawater in coastal areas of the Baltic Sea. Oceanologia, 58(1), 25-38.
30. Pogorzelski S. J., Mazurek A. Z., Szczepanska A. (2013): *In-situ surface wettability parameters of submerged in brackish water surfaces derived from captive bubble contact angle studies as indicators of surface condition level.* J. of Marine Systems, 119, 50-60.

**CONTACT WITH THE AUTHORS**

**Stanisław Pogorzelski**  
*e-mail: fizsp@ug.edu.pl*  
Institute of Experimental Physics, University of Gdańsk,  
Wita Stwosza 57, 80-308 Gdańsk,  
**POLAND**

**Paweł Rochowski**  
*e-mail: p.rochowski@ug.edu.pl*  
Institute of Experimental Physics, University of Gdańsk,  
Wita Stwosza 57, 80-308 Gdańsk,  
**POLAND**

**Maciej Grzegorczyk**  
*e-mail: maciej.grzegorczyk@ug.edu.pl*  
Institute of Experimental Physics, University of Gdańsk,  
Wita Stwosza 57, 80-308 Gdańsk,  
**POLAND**

**Ewa Skrodzka**  
*e-mail: afa@amu.edu.pl*  
Faculty of Physics, Institute of Acoustics,  
A. Mickiewicz University,  
Umultowska 85, 61-612 Poznań,  
**POLAND**

**Łukasz Bielasiewicz**  
*e-mail: lbielasiewicz@infoeko.com.pl*  
INFO-EKO Design-Consulting Office,  
Łódzka 50A/3, 80-180 Gdańsk,  
**POLAND**

**Bogumił B. J. Linde**  
*Adres e-mail: fizbl@ug.edu.pl*  
Institute of Experimental Physics, University of Gdańsk,  
Wita Stwosza 57, 80-308 Gdańsk,  
**POLAND**