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Comparison of the spectral-angular properties of light scattered in the Baltic Sea and oil emulsions

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Angular distributions of scattered light, which are described by one of two forms, i.e. the Volume Scattering Function (VSF) or the phase function, are the least-known optical properties of seawater. This is because there is currently no commercially available instrument commonly used for such measurements. In particular, little is known about the spectral variability of VSF. The spectral properties of VSF can be presented by linear slopes of a scattering spectrum separately for all scattering angles. Through research conducted using a prototype Volume Scattering Meter (VSM), the linear slopes were determined for three Baltic Sea marine regions: open Baltic Sea waters, the Gulf of Gdańsk and the mouth of the Vistula River. In this paper, the spectral slopes of VSFs of those waters are compared with VSFs of oil-in-water emulsions. The optical properties of crude oil extracted from the Baltic seabed, called *Petrobaltic*, were taken for calculations. The results show that VSFs of oil emulsions differ from those of natural waters, especially close to the perpendicular direction of scattering. For scattering angles between 70° and 120° there is an increase observed for oil emulsions which distinguishes them from VSFs of Baltic waters. While the spectral slopes of VSFs of oil emulsions differ from those of Baltic water across almost the entire angular range, excluding backward directions close to 180°.

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1 INTRODUCTION

Inherent Optical Properties (IOPs) play an essential role in the spreading of light in the sea water column which describe the interaction between the light and water with dissolved and suspended constituents. The set of IOPs include absorption and scattering properties. The absorption is fully described by the spectrum of absorption coefficient $a(\lambda)$. However for a complete description of light scattering, the scattering coefficient and the angular distribution of scattered light are needed. Full information on the ability of water to scatter light is included in the Volume Scattering Function (VSF) defined as:

$$\beta(\theta,\lambda) = \frac{dI(\theta,\lambda)}{E(\lambda)\cdot dV}, \tag{1}$$

where dI is the radiant intensity scattered into given direction θ, and E is the irradiance illuminating the element of scattering volume dV.

Integration of the VSF over a full solid angle gives the scattering coefficient $b(\lambda)$ and normalization of the VSF by the scattering coefficient gives the phase function $p(\theta) = \beta(\theta)/b$, which describes only the relative angular distribution of scattered light. Another useful quantity in operational ocean optics is the backward scattering coefficient b_b, which is the integral of the VSF over all angles of the rear hemisphere (90°–180°).

Optical methods used to determine the type and concentration of seawater constituents are often focused on the impact of suspended particles on the VSF. Therefore, in this paper (although not marked), both the VSF and the phase function refer to the particle VSF and the particle phase function.

Spectral changes of absorption coefficient are measured regularly by many research teams and they are a source of knowledge of the components of seawater. Spectral absorption for the Baltic Sea water is examined, for example, by Kowalczuk et al. (2010) [1] and and Woźniak et al. (2011) [2]. On the other hand, the volume scattering function is rarely measured and its spectral variation across a wide range of angles is little-known for seawater.

Since the 1990s, a correlation between the VSF for specific scattering angles and the backward scattering coefficient has been sought. It was started by Oishi [3] who, based on computations of Mie scattering, concluded that scattering into 120° provides the best correlation. He also claimed that this correlation can be easily used to estimate the depth profiles of backscattering coefficient by measurements. Work on the construction of measuring instruments has developed in two directions. Maffione et al. [4, 5] chose the scattering into 140° as better for this purpose, while Boss and Pegau [6] argued that the VSF for 117° is more useful because of its spectral independence. As a result, commercially available meters for determining the b_b for several wavelengths on the basis of the VSF measurement for selected angles were created.

A comparison of these two approaches made on the basis of precise measurements prepared in the waters of the Baltic Sea was made by the author [7], who appreciates the importance

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of spectral studies of light scattered in a marine environment. This paper presents results which show that the spectral measurements of VSF for several selected scattering angles close to perpendicular (much smaller than 117°) would provide information on the type of suspensions in sea depths on the basis of both shapes of VSF and its spectral variability. Another recent paper presenting the spectral–angular properties of scattered light (for selected cultures of phytoplankton) is that of Tan et al. [8], who presented a new method for VSF measurements. They describe the instrument which allows quick data acquisition with high angular resolution and additionally in spectral bands covering visible wavelength range with 20 nm steps. The above–mentioned citations are connected with the spectral-angular properties of seawater. Because they do not exhaust the topic of marine optics, I would refer interested readers to recent textbooks, such as Kirk's "Light and Photosynthesis" [9] or Watson and Zielinski's "Subsea Optics and Imaging" [10].

The following section of the paper describes the measurements of Baltic water VSFs [11] and also new, non-published parameterization results, which makes those previous results reproducible. The third section presents a simple way to show the angular variability of spectral slopes of VSFs. Section Four describes the new results of Mie scattering calculations prepared for the known refractive indices of oil. The Discussion section contains a comparison of both VSFs and their scattering spectral slopes for natural seawater and oil emulsion.

2 PARAMATERIZATION OF THE VSF MEASURED IN BALTIC SEA WATERS

Due to complicated designs, there is currently no commercially-available scattering function meter for a wide range of scattering angles. That is why the measurements of the VSFs made in the Baltic Sea waters [11] (carried out for wavelengths 443, 490, 555 and 620 nm) were unique and important. The measurements were prepared for a wide range of scattering angles (from 0.5° to 179° with high angular resolution of 0.25°). Such a large range of angles, and measurements made at four wavelengths, were possible through the use of a prototype Volume Scattering Meter (VSM) described by Lee and Lewis [12]. This instrument contains both a stationary light source and a photomultiplier, while a stepper motor-controlled rotating periscope prism transmits the scattered light from the scattering cell to the receiver. The compact size of the instrument allows for it to be used both *in situ* and in a laboratory. The VSM covers a wider angular range than the instrument described by Tan et al. [8] although their spectral possibilities are better.

Measured VSFs were averaged for three types of water separately. These included open Baltic Sea water, water from the Gulf of Gdańsk and from the mouth of the Vistula river. The averaged VSFs plotted for four wavelengths are presented in Figure 1.

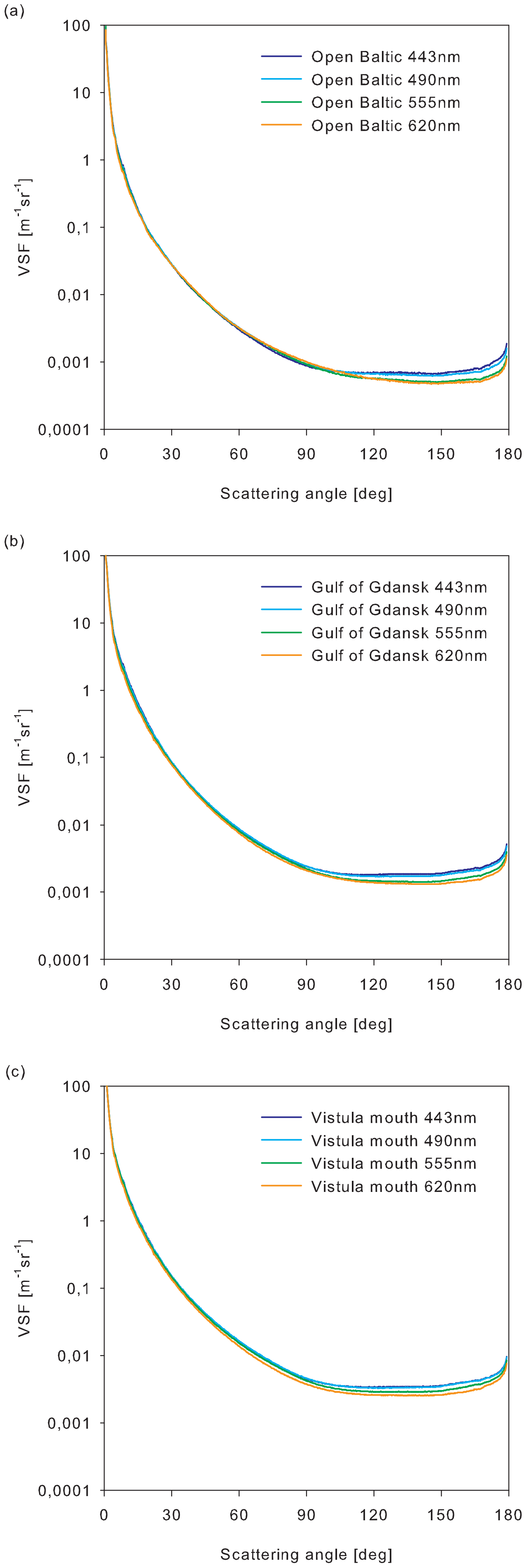

FIG. 1 Average VSFs of open Baltic waters (a), Gulf of Gdańsk (b) and Vistula river mouth (c) plotted for four wavelengths.

Data obtained from a similar prototype were previously parameterized by a 7–parameter function [13]:

$$p_p(\theta) = \exp\left(\sum_{n=0}^{6} c_n \cdot \theta^{\frac{n}{2}}\right) \tag{2}$$

where p_p is the parameterized approximation of the measured phase function. And $c_0 \ldots c_6$ are the best–fit parameters obtained with the polynomial least square method for relation of the natural logarithms of the phase function to the square root of scattering angle θ. The use of natural logarithms and square roots allow the relative variability of fitted quantities to be limited, which is essential for obtaining correct matching results.

Parameters $c_0 \ldots c_6$ of averaged phase functions in three types of Baltic water are presented in Table 1. Errors of the fit depend on scattering angle θ and are the highest for both 0.5° and 179°. However, the relative error does not exceed 21%, even for these individual angles. For the following spectral considerations, the accurate non-parameterized values of the measured VSFs are taken.

Probably the first discussion about spectral variation of VSF for a wide range of scattering angles was that of Chami et al. (2006) [14], based on measurements made in the Black Sea for only three wavelengths. In turn, using a prototype instrument allowed the spectral variation of the VSF measured in the Baltic Sea to be obtained, as presented by Freda (2012) [7]. These measurements were also the basis of parametrisation of analytic Fournier-Forand phase function of Baltic water [15], which were used for consideration of the phase function shape impact on the water-leaving radiance [16].

3 SLOPES OF THE SPECTRA OF NORMALIZED VSFS

As shown in Figure 1 and previously for different measurements by Freda et al. (2007) [11] (Figure 2), the angular characteristics of VSFs for four wavelengths have different shapes. The functions measured in some areas are characterized by a fixed sequence, i.e. for the shortest wavelength they receive the highest values and increasing wavelengths have decreasing VSF values. Such an arrangement is qualitatively consistent with the theoretical scattering on particles much smaller than a wavelength (the so-called "Rayleigh scattering"). But for other stations, some intersections and inverted orders of spectral VSFs are observed, especially for mid–range angles (perpendicular scattering), or the sequence is clearly visible only for high scattering angles (higher than about 120°). Hence, for each scattering angle, one can obtain a different spectrum.

To show the angular variation of the VSF spectra for each scattering angle, they were normalized by the VSF value for 443 nm. These spectra are plotted in Figure 2, for selected scattering angles between 1° and 175°, for the measurement made at the station P1 (open Baltic Sea area, see [11]). Additionally, the spectral variability of molecular scattering (Rayleigh scattering), that do not depend on scattering direction, is shown in Figure 2. As shown there, normalized spectra measured in the seawater can be both increasing, for some scattering angles θ, or decreasing, unlike Rayleigh scattering which is constantly decreasing for all directions. That is why the normalized spectra were then approximated by linear functions [7], with the least squares method, to receive slopes A_{443} for each of the scattering angles:

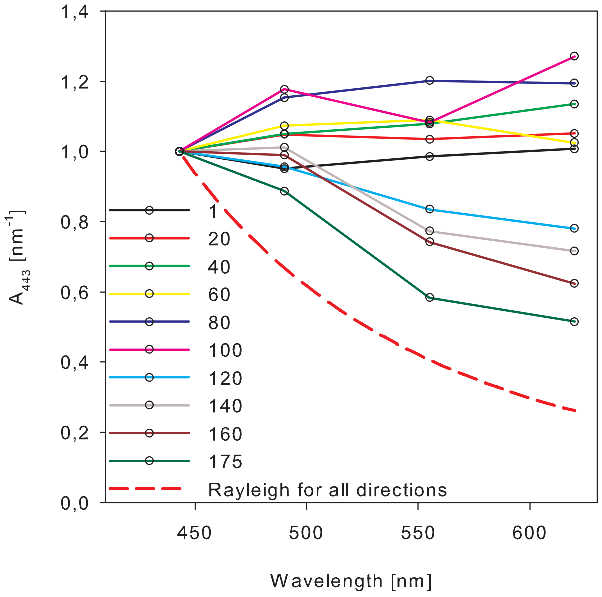

FIG. 2 Spectra of VSF normalized by VSF of 443 nm for selected scattering angles between 1° and 175°, measured for the same water sample (station P1 at the Baltic Sea) - colored lines with circles, and for molecular Rayleigh scattering - single red dashed line which applies for all directions.

$$\frac{\beta(\theta,\lambda)}{\beta(\theta, 443\ \mathrm{nm})} = A_{443}(\theta)\cdot\lambda + B_{443}(\theta), \tag{3}$$

Recently, it was shown that such angular variation in slope depends on the type of water (the location where the measurements were made). Freda (2012) [7] analyses the relationship between the spectral backscattering coefficient and the VSF measured at angles of about 117° and 140° and also contains a comparison of the angular variation of the slopes of the normalized VSFs spectra for open Baltic Sea water, the Gulf of Gdańsk and the mouth of the Vistula River (Figure 1 in Freda, 2012 [7]).

4 MODELLING OF LIGHT SCATTERING BY OIL EMULSIONS

Modelling was performed to compare the spectral variability of light scattered in both natural seawater and oil emulsions. *Petrobaltic* crude oil was chosen because this oil is mined from the Baltic seabed and its emulsion may be present in the Baltic depths. Calculations were made with the Mie theory, using measurements of the complex light refractive index in *Petrobaltic* crude [17]. The spectral variation of the refractive indexes was determined with 10 nm resolution.

Particle Size Distributions (PSD) of oil droplets, in equations denoted as $n(r)$, were taken from microscopic measurements made by [18]. They were approximated with log-

Water body	λ [nm]	c_6	c_5	c_4	c_3	c_2	c_1	c_0
Open Baltic	443	7.440	-45.42	110.94	-136.1	90.85	-41.15	8.758
	490	7.041	-42.85	104.82	-129.7	88.05	-40.68	8.733
	555	6.880	-41.21	99.71	-123.1	84.49	-39.98	8.703
	620	8.331	-49.08	116.17	-140.1	93.45	-42.10	8.839
Gulf of Gdańsk	443	9.020	-54.90	132.06	-156.5	97.42	-39.85	8.218
	490	8.723	-52.93	127.53	-152.3	96.19	-39.95	8.261
	555	8.543	-51.50	123.74	-148.1	94.27	-39.71	8.270
	620	9.668	-58.38	140.04	-167.0	105.2	-42.52	8.483
Vistula river mouth	443	7.699	-46.70	112.29	-133.3	83.66	-35.89	7.781
	490	7.018	-42.58	103.01	-123.7	79.24	-35.11	7.750
	555	7.085	-42.39	101.35	-120.8	77.17	-34.60	7.729
	620	7.899	-47.22	112.52	-133.5	84.37	-36.48	7.881

TABLE 1 Best-fit parameters for the phase functions of three types of seawater.

normal shaped functions defined as:

$$n(r) = C \cdot exp\left(-\frac{ln^2(r/r_0)}{2\sigma^2}\right), \tag{4}$$

where C is a quantity parameter, r_0 is a radius for maximum of distribution, and σ is a shape parameter of size distribution.

For further calculations, two distributions were used. They correspond to the fresh oil emulsion of $r_0 = 0.25$ µm and $\sigma = 1.02$ as well as the emulsion aged for 14 days of $r_0 = 0.08$ µm and $\sigma = 0.87$. The VSFs of *Petrobaltic* oil emulsion of two size distributions marked by $r_0 = 0.08$ µm and $r_0 = 0.25$ µm calculated for wavelengths 440 nm, 490 nm, 550 nm and 620 nm are presented in Figure 3. Calculations were made for pure seawater, i.e. for a medium whose refractive index changes from 1.3421 (for 440 nm) to 1.3341 (for 620 nm). The VSFs were obtained separately for 19 wavelengths from 440 nm to 620 nm with a 10 nm step, corresponding to the range of VSFs measured in Baltic waters. Although the data allow spectral slopes A_{440} congruent to A_{443} (see Eq. (3)) to be obtained, VSFs were normalized by its value for 440 nm.

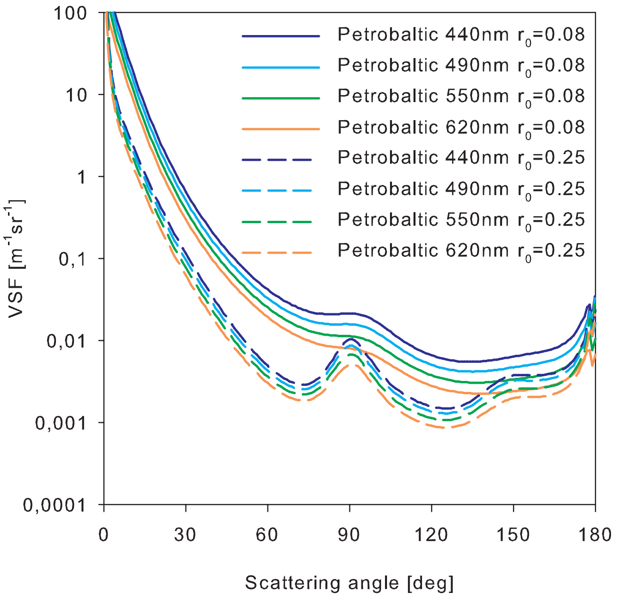

FIG. 3 VSF of *Petrobaltic* oil emulsions of two size distributions plotted for wavelengths 440 nm, 490 nm, 550 nm and 620 nm.

The obtained VSFs do not include the impact of any other particles present in natural seawater. That is why the oil emulsion VSF can be treated as an additional component to the background of natural water particle VSF in radiative transfer calculations. The concentration of oil emulsion was not specified, although a single scattering regime is assumed. A multiple scattering was not considered. Recently, oil content has been involved in radiative transfer studies and light scattering data would provide a useful input to such a study (see [19]–[22]). These papers include a discussion on the impact of the presence of oil emulsions on water leaving the light field.

5 DISCUSSION

The differences between the shapes of the Baltic VSF presented for each measured wavelength in Figure 1 are caused by the presence of various types of suspensions. Each type of suspension, which includes mineral particles, various kinds of phytoplankton and zooplankton cells, non-living organic particles and others, has a different spectral absorption characteristic. The part of the spectrum which has not been absorbed, undergoes scattering and the angular distribution of scattered light depends on many factors. These include: size, complex refractive index of light, shape of particles, internal structures and concentration (which, if high enough, can lead to multiple scattering). The influence of particle size and their complex light refractive index of the phase function can be easily checked, for example, using Mie theory [3, 23, 24]. Showing the influence of particle shape and internal structure on the VSF requires the use of numerical methods, for example Mishchenko et al. [25] and Yang et al. [26], while the effect of multiple scattering on the shape of the angular distribution of scattered light was examined by Piskozub and McKee [27].

The VSF obtained in the Baltic Sea was compared with the calculated VSF of oil-in-water emulsion. In Figure 1, the VSFs of the average types of Baltic Sea water are presented for each measured wavelength. Moreover, the VSFs of fresh oil emulsions, plotted for the nearest wavelengths (e.g. 440 nm, 490 nm, 550 nm and 620 nm) are shown in Figure 3. The colors in these graphs correspond approximately to the spectral colors of recording channels. The comparison of function shapes shows the peak of oil-in-water emulsions VSFs for angles close to 90° and a high increase for backward-direction angles. A similar view of the oil emulsion VSF was presented previously by Otremba and Piskozub (2004) [24].

In order to show the spectral variation, the VSF values were normalized by its value for the smallest wavelength $\lambda = 443$ nm (or $\lambda = 440$ nm for emulsions), for each angle separately. The comparison of the slopes, presented in Figure 4, shows that for oil-in-water emulsions, the slope values slightly depend on the scattering angle. It is like the Rayleigh scattering for which the slopes of VSF do not depend on the scattering direction. For fresh oil emulsion, these values are between -0.002 and -0.003 for almost the entire angular range, while for weathered emulsion (smaller droplets) the slopes are lower, between -0.003 and -0.004. This means that spectra have a uniform decreasing character. The Rayleigh scattering gives a constant value of -0.0041 for all scattering angles (the value depend on the considered spectral range). The smaller particle sizes of the oil droplets made the spectral light scattering in the emulsion converge with the molecular scattering.

In contrast, the Baltic Sea water VSF slopes depend heavily on the scattering angle (see Figure 4). As mentioned by Freda (2012) [7] they depend on the water type. Both for water of the Gulf of Gdańsk and for the Vistula river mouth, the slopes of normalized VSFs decrease steeply from 0 to about -0.002 except for scattering angles smaller than 30°, unlike the waters of the open Baltic Sea, where an increase in the value of A_{443} is observed in angular ranges from about 30° to 120° and for backward directions (angles higher than 160°). This means that the spectra of these types of Baltic VSFs are almost flat for small scattering angles ($\theta < 3°$) and the higher the scattering angle θ, the steeper the decrease in the spectrum of VSF. An exception is mentioned above in the range of $\theta < 30°$. Moreover, for open sea waters, flat spectra (slopes around 0) are also observed for scattering angles close to 33° and 100° as well as between 53° and 63°. Additionally, increasing spectra are observed for scattering angles θ from 33° to 53° and between 63° and about 100° for open sea water only.

6 CONCLUSIONS

This paper compares the light scattering properties of natural waters of Baltic Sea and the emulsions of crude oil extracted from the Baltic Sea bottom. This comparison shows the difference in both the angular shape of VSFs (for angles of about 90° and for high angles of backward directions) as well as differences in angular characteristics of spectral slopes of the VSFs. These spectral slopes for measured Baltic Sea waters generally decrease for increasing scattering angles. However, for angles $\theta < 30°$ a local minimum of slope is observed for three kinds of Baltic waters. Moreover, open waters are characterized with two maxima, for which the slopes are positive – normalized spectrum increases. In contrast, the slopes of oil emulsions only slightly depend on scattering angle. The spectra decrease across the entire range of angles and the slopes depend on the size distribution of emulsion droplets.

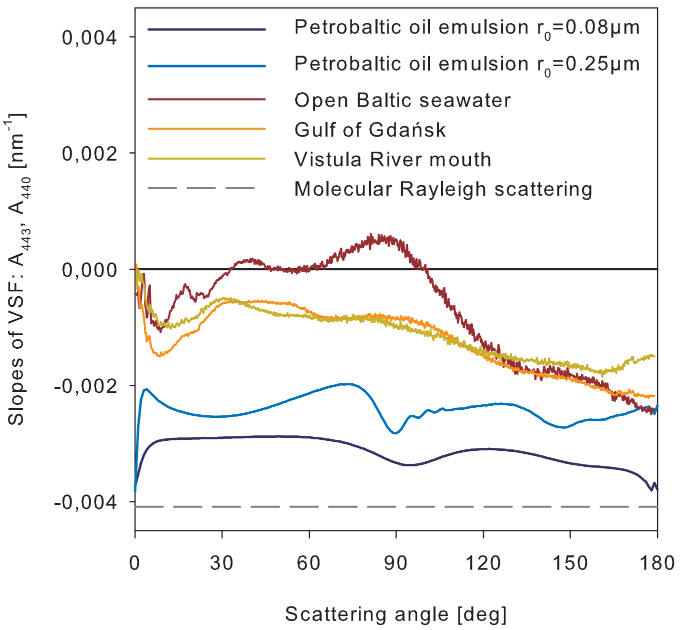

FIG. 4 Linear slopes of VSF spectra of three average types of Baltic waters A_{443} and two emulsions of *Petrobaltic* oil A_{440} plotted against scattering angle.

The analysis of the measured spectra of the natural slope of the sea would probably obtain information about the suspension composition contained in the water. However, several measurements taken separately for different types of suspensions are needed to carry out such an analysis.

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