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Comparison of measured and computed light scattering in the Baltic

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ABSTRACT

Mie theory was used to calculate the average scattering functions of suspended particles from the surface layer of the Baltic in summer and winter. Good agreement with data has been achieved in the angle range of ~15° to ~165°. Corresponding average particle size distributions measured using a Coulter counter in the diameter range of 2.5 to 20 μm were used in the calculations. The size distribution of smaller particles and the refractive indices of particles in the entire optically important diameter range were determined using the trial and error method.

A refractive index of 1.1 was obtained for both summer and winter particles in the diameter range of 0.1 to 2 μm. The size distributions of these particles, also determined from light scattering, were hyperbolic with a slope of 4.1. The concentration of particles with diameters between 0.1 and 2 μm in summer was about twice that in winter. Refractive indices: 1.05–0.005*i* and 1.03–0.01*i* were obtained for summer particles with diameters between 2 and ~10 μm and over ~10 μm respectively. A refractive index of 1.1 was obtained for winter particles larger than 2 μm.

Only particles with diameters in the range of 0.1 to 10 μm contributed significantly to the volume scattering function measured. Particles smaller than ~2 μm dominated light scattering at angles > 10° and larger particles at smaller angles.

The calculated volume scattering function at angles smaller than ~15° for the summer particles agreed with the experimental data. Values of the scattering function in this angular range for the winter particles were about half of those measured. This is explained as a consequence of an underestimation of the projected areas of particles when using Coulter counter data in the computation of light scattering. It can be compensated for in the case of summer particles, with a small refractive index and slope of the size distribution, by selecting a higher than actual refractive index of the particles. Such a compensation is not possible in winter for mostly mineral particles whose refractive index and the slope of the size distribution are already high.

1. Introduction

It is generally known that suspended particles dominate the scattering of light in sea water and thus affect the conditions of the transfer of light energy in the sea. It is therefore of prime importance in studies of photosynthesis and remote sensing to be able to predict the effect of a given ensemble of particles on the scattering of light in sea water. On the other hand, light scattering can be used to characterize suspended particles. Since it can be measured continuously and rapidly in space and time in a water mass, its use to determine physical properties of suspended particles is an attractive alternative to discrete and laborious chemical analyses.

Both uses of light scattering depend on the availability of an adequate numerical model. In addition, the determination of physical properties of the particles from light scattering depends on

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the existence of a reliable inversion algorithm. A numerical model for homogeneous spheres is provided by the Mie theory of light scattering (Mie, 1908; later reviews, e.g., in van de Hulst, 1957; Born and Wolf, 1976). It relates the scattering pattern of a homogeneous sphere to its diameter and refractive index. The latter is determined by the chemical composition of a particle. Organic particles suspended in sea water have low refractive index relative to water from 1.01 (phytoplankton—Carder et al. (1972)) to 1.05 (bacteria—Ross and Billing (1957)). Minerals are characterized by higher refractive indices from about 1.08 (amorphous silicon) to 1.23 (aragonite). An approximate relationship exists between the refractive index and the density of the particles (biological particles—Ross and Billing (1957) and references therein; minerals—Carder et al. (1974)).

Suspended marine particles are nonspherical. They exhibit wide variety of shapes and internal structures. Their light scattering pattern as an ensemble, however, agrees roughly with patterns computed using Mie theory (Kullenberg, 1970; Kullenberg and Olsen, 1972; Brown and Gordon, 1974; Reuter, 1980; Jonasz, 1980). Thus it appears possible to select an ensemble of spheres that simulates the actual scattering pattern of suspended marine particles.

The general problem of the determination of physical properties of particles from their light scattering is complex (Rozenberg, 1976) and has not yet been given much attention. Limited cases have been considered, e.g., when the refractive index of the particles is known a priori and only the particle size distribution is being sought (Chow and Tiou, 1976). Real situations, with no a priori information about particles, have been approached so far using the trial and error method (Kullenberg, 1970; Kullenberg and Olsen, 1972; Brown and Gordon, 1974; Jonasz, 1980). In this approach, scattering patterns computed for a number of size distributions and refractive indices are matched to experimental data: the size distribution and refractive index providing the best fit are assumed to be closest to the actual characteristics of the particles.

Physical properties of suspended Baltic particles were determined from light scattering by Kullenberg (1969, 1970) and Kullenberg and Olsen (1972). No independent determinations of these properties were made. It is thus difficult to assess the validity of their results. Measurements of scattering of polarized light (Kadyshevich, 1977) suggest that light scattering by the Baltic particles is more similar to that by spheres than is scattering by oceanic particles. Reuter (1980) simulated light scattering of suspended organic particles in the coastal waters of the Baltic using spheres with equal volumes. However, he reports that the absolute value of scattering by mineral particles in these waters differs significantly from calculated scattering for spheres with equal volumes. Similar conclusions for forward scattering were reached by Jonasz (1980). We postulate that this discrepancy is due to combined effects of underestimation of the projected areas of large particles and the form of the dependency of the scattering efficiency of these particles on their size.

The aim of this paper is to present a quantitative evidence for that hypothesis. Another aim is to determine the size distribution and refractive indices of particles in the size range inaccessible to the Coulter counter.

The data discussed in the present paper were obtained during two oceanographic expeditions on research vessel "Prof. A. Penck" of the Academy of Sciences of GDR (Gohs et al., 1978)

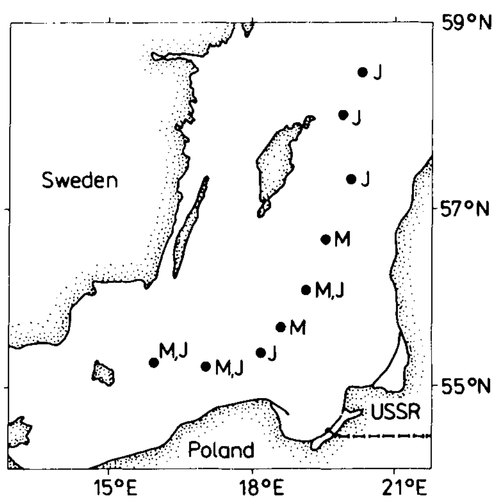

Fig. 1. The sampling stations in the Baltic for particle size distributions and volume scattering function. Capital letters denote the period of sampling as follows: M—March 1976, J—June 1977.

in the central Baltic. The measurements were made at locations shown in Fig. 1.

2. Methods

2.1. Sampling and storage of samples

Sea water was sampled using a remotely controlled rosette with PTFE samplers of van Dorn type. Measurements were usually completed within 4 hours after collection of the samples. In order to minimize changes taking place during storage large quantities of sea water (~ 10 l) were sampled and stored in polyethylene containers for particle size analysis. Samples for light scattering measurements were stored in 0.5 l dark glass bottles.

2.2. Particle size distributions

A Coulter counter model ZBI with a 100 μm orifice was used to measure cumulative size distributions CD(D) of particles suspended in sea water following the standard procedure (Sheldon and Parsons, 1967; Jonasz and Zalewski, 1978; Jonasz, 1983). The cumulative particle size distribution relates number concentration of particles with diameters larger than D to particle diameter, D. This concentration was determined for about 20 values of D in the range of 2.5–20 μm. The upper limit was sometimes lowered to keep counts not smaller than ~ 1 particle/cm^3.

The error of cumulative number of particles, CD(D), is proportional to square root of CD(D) for a single count (Jonasz, 1983). Two or more counts, depending on the number concentration of particles, were made as a rule. Errors due to the nonsphericity of particles (Golibersuch, 1973) and the way the particle crosses the orifice (Kachel et al., 1970) are difficult to estimate for the particles we analysed and were not accounted for.

Cumulative particle size distributions were then converted to frequency particle size distributions, FD(D), related to CD(D) through the equation

$$\mathrm{CD}(D) = \int_D^\infty \mathrm{FD}(D)\,\mathrm{d}D \qquad (1)$$

using a piecewise numerical differentiation scheme (Jonasz, 1983). The frequency size distribution will be referred to as the particle size distribution (PSD) in the following.

2.3. Light scattering

The volume scattering functions, $\beta(\theta)$, of sea water (for definition, see, e.g., Jerlov (1976)) were measured for 15 to 30 different scattering angles, θ, in the range of 5–165° using a laboratory light scattering meter PSP 75 (Fig. 2). The instrument, described in detail by Prandke (1980) has been designed for oceanographic use. The light source is a He–Ne 1 mW laser (wavelength 0.633 μm in air). The calibration of the instrument is similar to that of in situ scattering meters (Kullenberg, 1968) and eliminates errors caused by drift of laser power output, sensitivity of the detector, measuring electronics and varying attenuation of the sea water.

Fluctuations of the scattering intensity caused by variations of the number of scatterers in a relatively small scattering volume (10 mm^3 at scattering angle of 90°) were smoothed using an electronic integrator. The estimated error of the measurement is normally 5%, increasing up to 10% for extremely high fluctuations of the intensity of scattered light.

The volume scattering functions, $\beta_p(\theta)$, of suspended particles were computed by subtracting

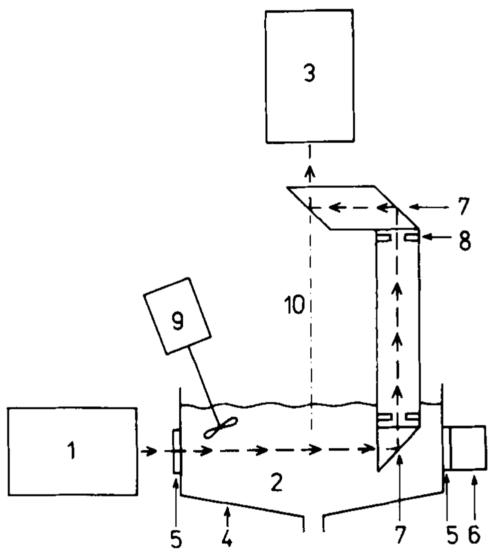

Fig. 2. The design of the laboratory scattering meter: (1) light source, (2) sample, (3) detector (photomultiplier), (4) sample container, (5) glass window, (6) light trap, (7) prism, (8) stop, (9) mixer, (10) axis of rotation of a system of two prisms (7) and two stops (8). Light path is indicated by arrows.

the volume scattering function of clear sea water (Jerlov, 1976)

$$\beta_w(\theta) = 8.74 \times 10^{-6}\, \lambda^{-4}(1 + 0.835 \cos^2 \theta) \quad [\mathrm{m}^{-1}\ \mathrm{srd}^{-1}] \qquad (2)$$

where λ is the wavelength of light (μm), from $\beta(\theta)$'s.

2.4. Mie scattering computations

Mie scattering functions, $\beta_1(\theta, x, n)$, of individual uniform spheres for scattering angles $\theta = 0, 0.2, 0.7, 3, 5, 10, 20, 30\ (15)\ 150, 160\ (5)\ 180$ degrees, where increment is given in parentheses, and relative particle size $x = 0.1\ (0.1)\ 1\ (0.2)\ 10\ (0.5)\ 50\ (1)\ 100\ (2)\ 220$ were computed on an ELWRO ODRA 1305 computer for 30 complex refractive indices, n, with real parts 1.01 (0.02) 1.07, 1.10, 1.15, 1.20 and imaginary parts -0.01, -0.005, -0.001, -0.0001 and 0. The relative dimension, x, of a sphere of diameter D, is defined as $\pi D/\lambda_w$ where λ_w is the wavelength of light in water. Generation of one set of functions for a given refractive index took about 12 min. All computed functions were stored on magnetic tape. Computations were performed according to a modified numerical scheme of Dermendijan (Dermendijan, 1969; Jonasz, 1980). Numerical problems arising in such computations and optimized computer programs in FORTRAN are described in detail elsewhere (Jonasz, 1980).

Scattering functions $\beta_p(\theta)$ of suspended particles characterized by size distribution $\mathrm{FD}_x(x) = \mathrm{FD}(D(x))$ and refractive index $n(D)$ were obtained by numerical integration of $\beta_1(\theta, x, n)$ weighted by $\mathrm{FD}_x(x)$ over the range of x indicated previously, using trapezoidal rule of integration. This range of x assures convergence of integrals at all angles θ, except $\theta = 0°$ and angles in its vicinity, and corresponds to diameter, D, range of 0.015–33 μm for the wavelength of light used in our light scattering measurements.

3. Experimental results

3.1. Oceanographic conditions

Depth profiles of light scattering (Prandke, 1978) and particle size distribution (Zalewski, 1977; Jonasz, 1980; Jonasz, 1983) reveal the existence of well-defined winter mixed layer and summer top layer in the open Baltic waters with distinct sets of particles. The winter mixed layer extends from the surface to the permanent halocline at about 60–70 m. Increased solar heating of its upper part in spring and summer results in the formation of a summer top layer which extends from the surface to the seasonal picnocline at about 20–30 m.

3.2. Particle size distributions

Particle size distributions characteristic for the two layers differ substantially in the particle diameter range of 2–30 μm (Jonasz, 1983). The concentration of particles is higher in the summer top layer than in the winter mixed layer, and the shape of the PSD changes also (Fig. 8).

21 size distributions from March 1976 were used to calculate the average PSD typical for the winter mixed layer and 12 distributions from June 1977 yielded the average PSD typical for the early summer top layer. In each case, data from the top 30 m of the water column were used. The early summer PSD varies more within the summer top layer than the winter PSD varies within the winter mixed layer (Jonasz, 1983). The PSD typical for the early summer is not representative for the late summer when the concentration increases and the peak at 6 μm disappears (Jonasz, 1983). We will nevertheless refer to the early summer PSD as summer PSD for brevity.

The least squares approximations for the PSD's, using hyperbolic and Gaussian functions (Jonasz, 1983), are:

$$\mathrm{FD}(D) = \begin{cases} 3.47 \times 10^4\, D^{-3.41} & 2\ \mu\mathrm{m} < D < 8.6\ \mu\mathrm{m} \\ 4.06 \times 10^5\, D^{-4.56} & 8.6\ \mu\mathrm{m} < D < 33\ \mu\mathrm{m} \end{cases} \qquad (3)$$

for the winter mixed layer, and

$$\mathrm{FD}(D) = 410 \exp[-0.6(D - 6.2)^2] + \begin{cases} 3.72 \times 10^4\, D^{-2.73} & 2\ \mu\mathrm{m} < D < 9.6\ \mu\mathrm{m} \\ 4.45 \times 10^5\, D^{-4.86} & 9.6\ \mu\mathrm{m} < D < 33\ \mu\mathrm{m}, \end{cases} \qquad (4)$$

for the summer top layer, both in units of $\mathrm{cm}^{-3}\ \mu\mathrm{m}^{-1}$. Although there is no direct evidence, the Gaussian term in (4) may be caused by a phytoplankton population (Jonasz, 1983).

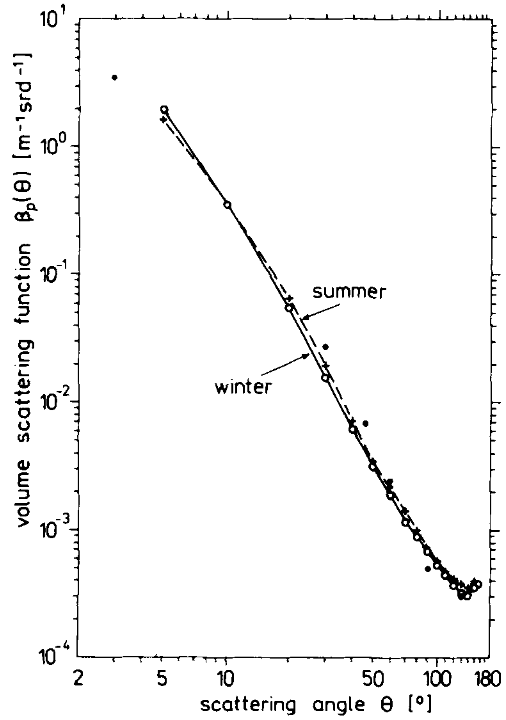

Fig. 3. Average volume scattering functions of suspended particles. Wavelength of light 0.633 μm in air. Full points represent the data of Kullenberg (1969) measured in June at a depth of 5 m at a location near the most western station of Fig. 1 for light of the same wavelength.

Table 1. *Average volume scattering functions of particles $\beta_p(\theta)$ from surface layer of the Baltic in winter (March 1977, 13 samples) and early summer (June 1977, 12 samples); wavelength of light 0.633 μm*

Scattering angle θ [°]	Volume scattering function [m^{-1} srd^{-1}] Winter	Summer
5	1.85×10^0	1.68×10^0
10	3.61×10^{-1}	3.47×10^{-1}
20	5.37×10^{-2}	6.60×10^{-2}
30	1.58×10^{-2}	1.93×10^{-2}
40	6.31×10^{-3}	7.30×10^{-3}
50	3.27×10^{-3}	3.51×10^{-3}
60	1.90×10^{-3}	2.20×10^{-3}
70	1.25×10^{-3}	1.46×10^{-3}
80	8.88×10^{-4}	1.00×10^{-3}
90	6.80×10^{-4}	7.42×10^{-4}
100	5.42×10^{-4}	5.88×10^{-4}
110	4.35×10^{-4}	4.68×10^{-4}
120	3.66×10^{-4}	4.21×10^{-4}
130	3.20×10^{-4}	3.83×10^{-4}
140	3.09×10^{-4}	3.50×10^{-4}
150	3.65×10^{-4}	4.08×10^{-4}
160	3.80×10^{-4}	—

3.3. Volume scattering functions

Average volume scattering functions, $\beta_p(\theta)$, of suspended marine particles corresponding to winter and summer sampling periods are similar to each other (Fig. 3, Table 1). The winter volume scattering function is a little steeper than the summer one. The functions are typical for polydisperse particles. As shown in Fig. 3, they correspond well to earlier results for the same area in summer (Kullenberg, 1969). We know of no other data from the Baltic area in winter which we could compare with our data.

4. The method of derivation of the complete size distribution and refractive index of suspended particles

The volume scattering function β_p, of a population of homogeneous spheres with a size distribution FD(D) and refractive index $n(D)$, relative to water, generally can be expressed as:

$$\beta_p(\theta, \lambda, n(D)) = \int_{D_{min}}^{D_{max}} \beta_1(\theta, n(D), \lambda, D)\, \mathrm{FD}(D)\, \mathrm{d}D, \tag{5}$$

where β_1 is the scattering function of a single particle, and D_{min} and D_{max} are limits of the range of diameters of particles which contribute significantly to β_p. Both limits depend on the scattering angle, θ, and the particle size distribution. The lower limit, D_{min}, is expected to be of the order of magnitude of 0.1 μm (Brown and Gordon, 1974) while D_{max} about 30 μm (Kullenberg, 1970). Therefore PSD's obtained using a Coulter counter fall into the upper subrange of (D_{min}, D_{max}). PSD's in the small size range and refractive indices of particles in the entire particle diameter range of (D_{min}, D_{max}) are unknown.

For PSD's of the hyperbolic type

$$\mathrm{FD}(D) = kD^{-m}, \tag{6}$$

one can easily identify from (5) the concentration factor, k, the slope, m, of the PSD and the refractive index, n, as three major factors influencing β_p for a specified wavelength λ of light. The latter will be omitted assuming $\lambda = 0.633$ μm (in air). The volume scattering function depends linearly on the concentration factor, k, but nonlinearly on the slope, m, and the refractive index, n. Some general features of this nonlinear dependency for particles with relative size, x, in the range of 0.1–220 can be formulated on the basis of Mie computations (Jonasz, 1980). We assume that the refractive index and the slope of the PSD are constant in the entire size range.

For a given refractive index, n, an increase of the slope, m, in the range of 2–5 results generally in the flattening of the volume scattering function (Fig. 4). The majority of PSD's of marine suspended particles have slopes in this range (Jonasz, 1983). A greater slope indicates higher relative concentration of small particles, with scattering functions flatter than those of large particles. Their increased contribution to the volume scattering function causes the latter to flatten. This effect is less pronounced for higher refractive indices.

For a given slope, m, of the PSD, an increase of the refractive index also flattens the volume scattering function. This is caused by a shift of the maximum efficiency of light scattering by the particles towards smaller sizes as the refractive index increases. This effect is less pronounced than that of the slope of the PSD, and for slope $m = 5$ is not significant for scattering angles, θ, larger than about 10° (Fig. 5). The refractive index, however, can substantially change absolute values of the volume scattering function at a given angle (Fig. 6).

The above relationships provided the basis of the trial and error method. We used this method to derive the fractions of the PSD's which were not measured using the Coulter counter and the refractive indices of particles. We will briefly demonstrate this method using the winter mixed layer as an example.

In order to simplify calculations, we followed the approach of Brown and Gordon (1974) assuming that different hyperbolic fractions of the PSD refer to populations of particles with the same refractive index. Accordingly the PSD (eq. 3) measured using the Coulter counter has been divided into:

a mid fraction including particles with diameters $D = 2$–8.6 μm, and
a large fraction for $D = 8.6$–33 μm.

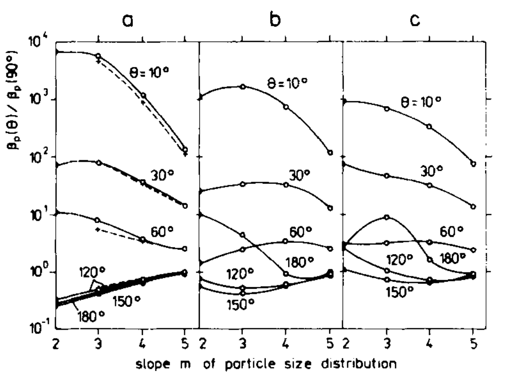

Fig. 4. The effect of slope m of the particle size distribution, D^{-m}, on the volume scattering function of homogeneous spherical particles for selected scattering angles and refractive indices. The computed volume scattering function (circles) is normalized to 1 at $\theta = 90°$. Slope m and refractive index n are constant in the entire diameter range of 0.01 to 33 μm. Wavelength 0.633 μm in air: (a) continuous line and circles, $n = 1.03$–$0i$, broken line and crosses: $n = 1.03$–$0.01i$, (b) $n = 1.07$–$0i$, (c) $n = 1.15$–$0i$.

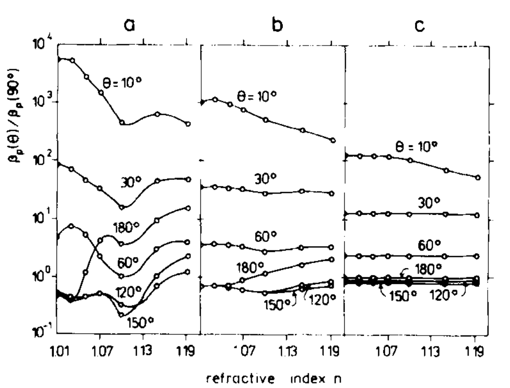

Fig. 5. The effect of real refractive index of homogeneous spherical particles on their volume scattering function for selected angles and slopes m of their size distribution. The other information as in Fig. 5. (a) $m = 3$, (b) $m = 4$, (c) $m = 5$.

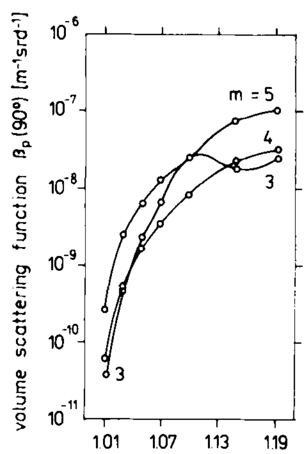

Fig. 6. The effect of real refractive index on the absolute value of volume scattering function at 90°. Slope m of the particle size distribution D^{-m} cm^{-3} μm^{-1} is indicated by the curves. Points denote computed values. Particle diameter range 0.01–33 μm. Slope m and refractive index n are constant in this diameter range. Wavelength 0.633 μm in air.

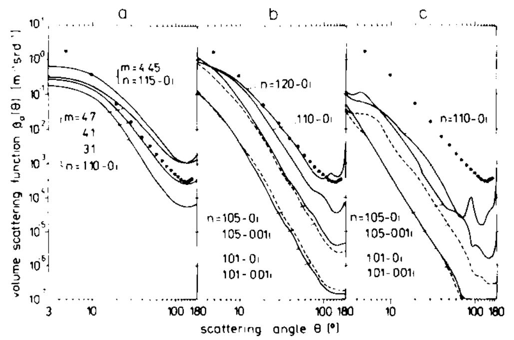

Fig. 7. Volume scattering functions of various size fractions of the average particle size distribution of suspended particles in the surface waters of the Baltic in winter. Wavelength of light 0.633 μm. The average measured scattering function for these waters is shown with circles of diameter equal to the error of measurement (10%). (a) Extrapolated small fraction: diameter $D\in[0.1\text{–}2\ \mu\text{m}]$; slope m of the hyperbolic size distribution, unknown in this case, is indicated by the curves; (b) mid fraction, $D\in[2\text{–}8.6\ \mu\text{m}]$; (c) large fraction, $D\in[8.6\text{–}33\ \mu\text{m}]$.

Particles smaller than 2 μm, not sensed by the Coulter counter, formed the small fraction. We assumed that its size distribution is also hyperbolic. The lower size limit of this fraction was originally set at $D = 0.01$ μm. Volume scattering functions β_p for each fraction were then calculated for various refractive indices with the real part in the range of 1.01 to 1.20 and the imaginary part in the range from -0.01 to 0 (Fig. 7).

It is clear from results presented in Fig. 7 that only the small and mid fractions are likely to influence light scattering in the range of scattering angles from about 5 to 180°. The large fraction has very little effect on light scattering in this angular range, except at angles between 80 and 90° and at angles larger than about 130°, where its values can be comparable with or greater than that of the mid fraction. The small fraction starts to dominate light scattering for angles larger than about 10–20°, the mid fraction dominates for smaller angles. The largest contribution of particles smaller than $\sim$0.1 μm to the scattering function was found to be of the order of 1%. Therefore, the lower limit of the small fraction has been increased to 0.1 μm.

Accordingly, the slope, m, of the size distribution and refractive index, n, of particles from the small fraction have been selected so to provide the first approximation of the experimental volume scattering function at angles larger than 10°. The concentration factor, k, of the PSD of the small fraction was determined from the condition that $FD_s(2\ \mu\text{m}) = FD_m(2\ \mu\text{m})$, where subscripts s and m stand for small and mid fraction. According to Fig. 7 one can expect that the small fraction should be characterized by a slope $m \simeq 4$ and a refractive index $n \simeq 1.1$. Light scattering by small spheres is independent of the value of the imaginary part of the refractive index provided that this part is small enough (Kattawar and Plass, 1967; Jonasz, 1980). Acceptable values of the imaginary part of the refractive index of suspended marine particles fulfill this condition. Therefore, only real refractive indices were tried for the small fraction.

The measured light scattering at small angles cannot be accounted for by particles from the small fraction. This contribution must come from the mid and large fractions. As seen in Fig. 7, the refractive index of the mid and large fractions should be around 1.1. The addition of β_p due to the mid and large fractions to that of the small fraction increased the calculated scattering at angles larger than 10° as well. Therefore, the slope and the refractive index of the small fraction had to be adjusted. This procedure was repeated until further adjustments in the slope of the size distribution of the small fraction and the refractive indices of particles from all fractions did not bring the calculated scattering function any closer to the experimental one. Such a procedure required computation of about 100 scattering functions to be completed.

5. The complete size distribution and refractive indices of suspended particles

The complete PSD's of the winter and summer particles are shown in Fig. 8. The slopes of the

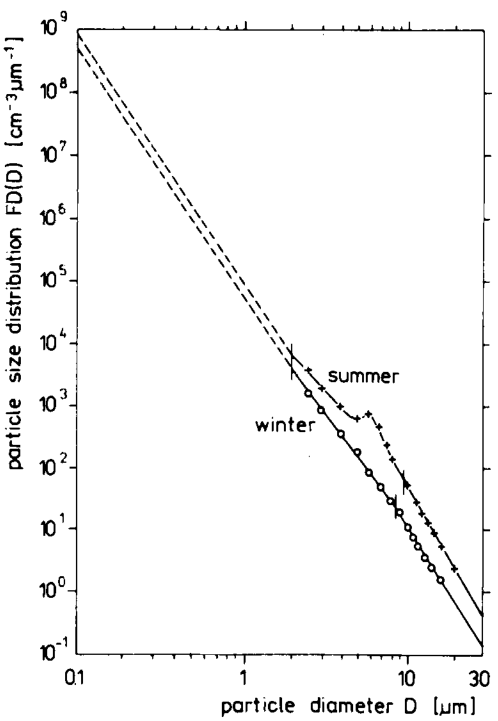

Fig. 8. Average particle size distributions of surface waters of the Baltic in winter and summer. Coulter counter data are indicated by circles and crosses. Full lines are their least squares approximations. Broken lines indicate sections of the PSD's derived from light scattering. Vertical bars indicate size limits of fractions of particle size distribution characterized by different slope and refractive index of particles.

small fractions, the same in both PSD's, are equal to 4.1. The concentration factor of the PSD of the small fraction was 5.6×10^4 in winter and 9.6×10^4 in summer.

The refractive indices are: 1.1 for all fractions in winter and the small fraction in summer, 1.05–0.005i for the mid fraction and 1.03–0.01i for the large fraction in summer. This is equivalent to more organic particles in summer than in winter. Chlorophyll *a* data from the same cruises (Gohs et al., 1978), which indicate significantly more phytoplankton in summer than in winter, agree with this assignment of refractive indices.

6. Comparison with other results

Kullenberg (1974) summarizes the earlier results for the Baltic (Kullenberg, 1969; Kullenberg, 1970; Kullenberg and Olsen, 1972): "A reasonable average [refractive] index seems to be 1.04. The size distribution [...] is poorly known, and the assumed hyperbolic distribution is at best a crude approximation. The exponent [our slope, *m*] is varied between 1.25 and 1.5. [...] Only the general trends of computed and observed functions conform. It is evident that (1) both the exponent and the index of refraction are lower than in the ocean, and that (2) more refined size distributions and several index values covering a range larger than so far used should be applied in coastal waters."

Jonasz (1983) found that the hyperbolic function provides good approximation of the PSD of Baltic particles in the diameter range of 2 to 30 μm. He compared slopes of size distributions measured with Coulter counters in various seas and oceans. Using those data we conclude that the slope of the PSD of our mid fraction in summer is slightly smaller than the slopes reported for most areas. The slope of the PSD of the mid fraction in winter is comparable to slopes found for other areas. These values are about twice higher than those obtained by Kullenberg.

Contradicting results can be found in the literature about the form of particle size distribution in our small fraction size range. Transmission microscopy yielded hyperbolic PSD (Harris, 1977) with a slope of 3.44 down to 0.02 μm. Coulter counter data (Brown and Gordon, 1974) yield a slope of about 6 for diameter down to 0.65 μm. Log-normal PSD's for oceanic particles, with concentration of particles decreasing below ~0.5 μm are reported by Lambert et al. (1981), who used a Scanning Electron Microscope. The diameter of 0.5 μm is about the lower limit of the diameter range of a Coulter counter. Unfortunately no data on the PSD for diameters smaller than 2 μm are available for the Baltic.

Particles with diameters smaller than 0.5 μm contribute significantly to the volume scattering function at angles greater than 10°. Their contribution is about 55% at 45° and reaches a maximum of about 80% at 150°. These particles are therefore significant for light scattering. The present results thus support the hyperbolic PSD for small particles, or a log-normal PSD with its maximum shifted toward smaller sizes, since the large-particle tail of log-normal PSD can be approximated by the hyperbolic function.

The refractive index of 1.04 used by Kullenberg and Olsen (1972) to simulate light scattering by summer particles with diameters between 2 and 39 μm, is close to our value of $n = 1.05\text{–}0.005i$ for the mid fraction in summer. However, their slope, $m = 1.25$, is about half of that of the mid fraction.

The scattering function they calculated agrees with their experimental data but only for angles smaller than about 100° (their Fig. 25). The shape of the volume scattering function depends weakly on the slope of the PSD for small slopes and refractive indices (Fig. 4a). For angles from the range of ~10 to ~100° this shape is also weakly dependent on the upper limit of the integral (5) provided that this limit is greater than ~10 μm for light of wavelength ~0.5 μm (Jonasz, 1980). This is probably the reason why their and our values of the refractive index of particles in the diameter range of 2 to 10 μm are similar.

However, the values of their calculated scattering function for angles larger than about 100° are about half of their experimental values. Their calculated function also exhibits oscillations not found in our data (obtained at 5° resolution for the Baltic, Gohs et al., 1978). Kullenberg and Olsen start integration (5) at the diameter $D_{\min} = 2$ μm and neglect smaller particles. The latter have a scattering function that is much smoother than that of larger particles (Fig. 7). Thus, the small particles better explain the scattering function of suspended particles at large angles. The shape of the scattering function in this angular range depends weakly on the lower limit of integral (5) for low refractive indices and small slopes (Jonasz, 1980). Thus, a simple inclusion of small particles, assuming that their size distribution and the refractive index is the same as that of larger particles, would probably not remove the disagreement between the calculated and measured scattering functions. In our calculations we had to increase both the slope of the size distribution and the refractive index of small particles in order to match the experimental volume scattering function at large angles.

Reuter (1980) compared volume scattering functions of suspended particles from coastal waters of the Baltic (his Fig. 18). The PSD of particles larger than 2 μm in diameter was determined using a Coulter counter. Large number of phytoplankton cells were present in this size fraction. Unfortunately, he did not specify the refractive index adopted for these particles. He assumed a hyperbolic PSD with a slope of 3.8 for particles smaller than 2 μm. A refractive index of $1.15\text{–}0.001i$ has been assumed for 20% of these particles and 1.05 for the rest of them. His computed scattering function is significantly smaller than that measured for angles greater than about 70°. According to the results of the present work this can be a consequence of an underestimate of the contribution made by small particles.

Brown and Gordon (1974) determined the refractive index of coastal oceanic particles in a diameter range equivalent to our small fraction. They obtained two sets of values that reproduce the experimental scattering function similarly well: $n = 1.01$ for the slope of 5 of the PSD and $n = 1.15$ for the slope of 3. The refractive index of particles and the slope of the PSD of our small fraction ($n = 1.1$, $m = 4.1$) thus lie between these two sets of values. These authors also determined the refractive index of particles in a diameter range corresponding to our mid fraction to be in the range from 1.01 to $1.03\text{–}0.01i$. The refractive index of particles from the mid fraction in summer is thus similar to their values.

Our optically effective range of particle diameters agrees approximately with other results obtained for the Baltic waters. Prandke (1980) gives the range of $D = 2\text{–}15$ μm based on the analysis of contribution of particles of various sizes to the scattering coefficient. The latter is simply the integral of the volume scattering function over 4π solid angle. That diameter range corresponds to our 2–10 μm diameter range since light scattered within the angle θ range of 0 to 20°, i.e. by particles with diameters withn 2–10 μm, constitutes ~80% of light scattered into the entire sphere in our case. Kullenberg (1970) gives a diameter range of 2–28 μm based on computations similar to ours, but not supported by Coulter counter data. His upper limit appears to be too large. The postulate that particles larger than 40 μm would significantly contribute to light scattering in the Baltic (Kullenberg and Olsen, 1972) is not reasonable in view of the present results. This problem is discussed further in Section 8. Reuter (1980) calculates his scattering functions for coastal Baltic particles in a particle diameter range from ~0.02 to ~20 μm.

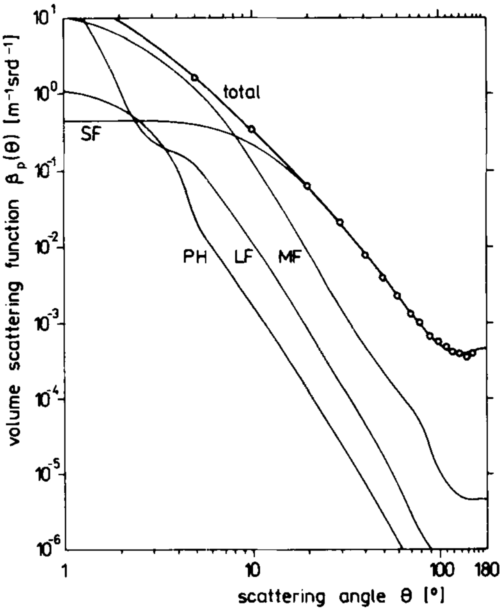

Fig. 9. Comparison of the average experimental volume scattering function of suspended particles in surface waters of the Baltic in summer (points) and the best fit computed function (total) with its components due to small (SF), mid (MF), large (LF) and phytoplankton (PH) fraction.

7. Applicability of the PSD measured using a Coulter counter to modelling of light scattering by suspended marine particles

The combined volume scattering functions of the small and mid-fractions matched quite well with the experimental volume scattering function for the summer top layer in June (Fig. 9). The large fraction contributed virtually nothing to the volume scattering function. Therefore, the refractive index of particles from this fraction should be treated as a rough approximation of the upper limit allowable. Also the small "phytoplankton" term (Gaussian term of eq. (4)) was not found to introduce substantial corrections to this volume scattering function for the refractive indices in the range appropriate for biological particles. This indicates that light scattering in the angle range of 5 to 180° may be of little use for phytoplankton research in the Baltic.

The computed volume scattering function for winter also agreed with the experimental one, except for angles smaller than about 15° (Fig. 10). The calculated scattering was significantly smaller than the experimental data for this angular range. The only particles which could influence light scattering in that angular range are those from the mid and large fractions. Given the PSD, determined using the Coulter counter,

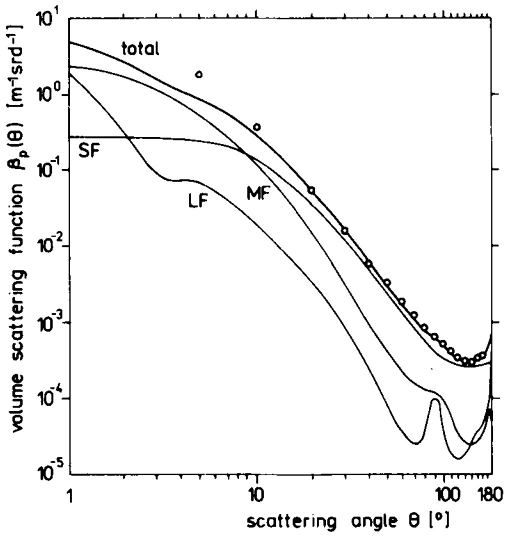

Fig. 10. Comparison of the average experimental volume scattering function of suspended particles in surface waters of the Baltic in winter (points) and the best fit computed function (total) with its components due to small fraction (SF), mid fraction (MF) and large fraction (LF).

one can increase computed scattering in the angular range of ~10–180° only by increasing the refractive index of particles (Fig. 6). The effect of this increase, however, diminishes with increasing refractive index and for indices with a real part larger than about 1.07 the β_p actually begins to decrease for scattering angle $\theta = <5°$ (Fig. 7b). Therefore, adjustment of the refractive index cannot improve the fit. The poor fit for small angles could also have been due to limiting the PSD at $D = 33$ μm. However, an extrapolation of PSD up to $D = 66$ μm gave negligible corrections to the shape of the volume scattering function in the range of $\theta = 5$–180°.

A similar problem of a poor fit for small angle scattering was encountered by Brown and Gordon (1974) in their modelling of light scattering by particles from clear coastal waters of the Atlantic ocean. They solved it by allowing the calculated scattering function to assume values greater than the experimental ones in the range of angles of 5 to 15°.

The measured and calculated scattering function in the small angle range for winter particles corresponded much more closely when the PSD measured using the Coulter counter, was replaced by a PSD determined only from light scattering (Jonasz, 1980). The latter had smaller slopes ($m = 2.7$ and 4.2) than those of the measured PSD in the diameter ranges of the mid and large fraction. The new PSD was used in conjunction with a refractive index of 1.07, smaller than that used with the PSD obtained using the Coulter counter. The concentration of particles of those two fractions, according to the new PSD was significantly higher than that measured.

Light scattering in the angular range of 0 to 20° contributes about 80% to the scattering coefficient of suspended particles, b_p, in the present case. It is thus reasonable to treat the forward scattering, where the discrepancies occurred, integrally, by means of the scattering coefficient. The latter can be expressed as follows:

$$b_p(\lambda, n(D)) = \int_{D_{min}}^{D_{max}} Q_b(n(D), \lambda, D)\, P(D)\, \mathrm{FD}(D)\, \mathrm{d}D \qquad (7)$$

where Q_b is the scattering efficiency of a particle, $P(D)$ is the projected area of the particle. Limits D_{min} and D_{max} determine the diameter range from which particles contribute significantly to the scattering coefficient. The scattering efficiency is the ratio of the light flux scattered by the particle to the light flux incident on its projected area.

Kullenberg (1974) pointed out that the PSD obtained using the Coulter counter may result in an underestimation of the projected area of suspended particles. A Coulter counter senses the volume of a particle. The size of the particle is then represented by the size of a sphere of equal volume. For a nonspherical particle, the projected area of this sphere is smaller than that of the particle, averaged over all its orientations. According to eq. (7), given a scattering efficiency, this underestimation of the projected area can be compensated for by increasing the particle concentration.

Measurements of Proctor and Barker (1974) indicate that the efficiency, Q_b, of nonspherical particles is reasonably approximated by that of spheres (e.g., van de Hulst, 1957, p. 137). The scattering efficiency passes through a maximum followed by a series of oscillations with decreasing amplitude before approaching a limiting value for large particles. The particle size corresponding to the maximum of the scattering efficiency becomes smaller with increasing refractive index. The value of Q_b at the maximum remains practically constant for small refractive indices, appropriate for suspended marine particles.

The contribution, b_p^{MF}, to the scattering coefficient of particles from the mid fraction increases with the refractive index (Fig. 11). Three ranges can be distinguished. For refractive indices small enough to place the maximum of the scattering efficiency at diameters larger than the upper limit of the mid-fraction, the contribution b_p^{MF}, increases steeply with the refractive index. Larger refractive indices cause this contribution to increase only slightly as the maximum of the efficiency enters the diameter range of the mid-fraction. With the refractive index increasing further, the maximum of the scattering efficiency shifts towards diameters smaller than the lower limit of the mid fraction. This initially decreases the scattering since the maximum of Q_b moves out of the mid fraction. Then the scattering tends to a limit since the efficiency itself approaches the limiting value for large particles within the diameter range of the mid fraction.

The magnitude of the contribution, b_p^{MF}, of

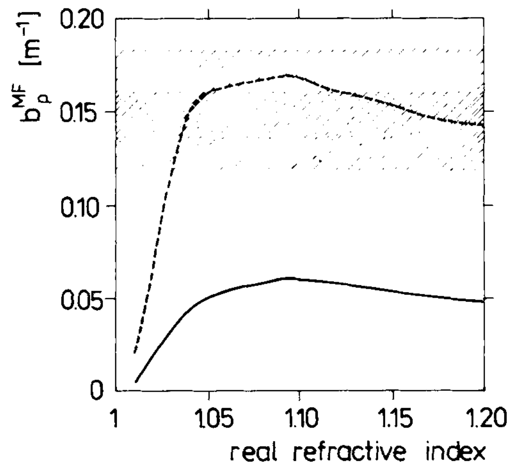

Fig. 11. The dependency of the contribution, b_p^{MF}, of the mid-fraction to the scattering coefficient, b_p, versus the refractive index of particles in winter (full curve) and summer (broken curve). Hatched areas denote ranges of experimental value of b_p ($\pm 15\%$ error) less the contribution of the small and large fractions in winter (full line) and summer (broken line). The curves were obtained using an approximate expression of van de Hulst (1957), p. 137, for the scattering efficiency of spheres.

particles from the mid fraction to the scattering coefficient depends on the combined effect of the forms of the scattering efficiency and the size distribution (Fig. 11). It is apparent that an underestimation of the projected areas of particles by a factor from 2 to 3 easily can be compensated for by varying the refractive index in case of the summer mid fraction. This cannot be done for the mid fraction in winter and requires the concentration of particles to be increased in order to match calculated and experimental scattering coefficient.

Thus the refractive indices of large suspended particles, derived in this work using the PSD determined with the Coulter counter, are overestimated. Values of the refractive index obtained earlier from light scattering with the use of the Coulter counter data on the PSD of marine particles, are most likely overestimated as well.

In summer, the contribution b_p^{MF}, of the mid fraction to the scattering coefficient, b_p, is close to that expected both for small and large refractive indices (Fig. 11). The large refractive index of these particles, however, results in a calculated scattering function that disagrees with the experimental one. This illustrates the inadequacy of using only the scattering (or attenuation) coefficient to deduce the refractive index of suspended particles.

8. Particle size range versus scattering angle range

The volume scattering function at 45° for the winter mixed layer and summer top layer is fairly well correlated with the number concentration of particles larger than 3 μm, i.e., CD(3 μm) (Prandke and Jonasz, 1981). The correlation coefficients were 0.90 and 0.87 respectively for extended data sets (52 and 33 data points respectively) for these layers. Upon expanding the particle size distribution as follows,

$$FD(D) = CD(3\ \mu m)\ FD_{norm}(D) \tag{8}$$

the linear relationship of $\beta_p(45°)$ on CD(3 μm) is apparent from eq. (5), provided that $FD_{norm}(D)$ and refractive index distribution $n(D)$ have constant forms in the diameter D range of particles that are likely to control $\beta_p(45°)$.

Though high correlation between $\beta(45°)$ and CD(3 μm) is reported for extended data sets, the data subsets analysed presently are characterized by a low correlation between $\beta_p(45°)$ and CD(3 μm). The correlation coefficient is ~0.11 for March 1976 data and ~0.34 for June 1977 data. This appears to be a consequence of the smaller concentration range considered here as compared to our earlier paper and suggests that coupling between variations of PSD for diameters below and above 2 μm is rather poor. It is worthwhile to stress that variations of the refractive index of particles larger than 2 μm have little significance here since these particles contribute very little to $\beta_p(45°)$ (Figs. 9 and 10).

According to the present study, a better correlation should be expected between CD(3 μm) or CD(2 μm) and say $\beta_p(5°)$ or even $\beta_p(10°)$. This is observed for the summer top layer data, where the correlation coefficient between $\beta_p(5°)$ and CD(2 μm) rises from 0.34 to 0.74. This is not so for the winter mixed layer, where the correlation coefficient between $\beta_p(10°)$ and CD(2 μm) stays at a low value of ~0.15. However, the concentration range in winter is reduced almost 4 times as compared to the summer top layer, and apparently even ~50% contribution of particles larger than 2 μm to $\beta_p(10^\circ)$ (Fig. 10) cannot improve the correlation.

These facts agree with an earlier study on correlations between values of volume scattering function at different angles for ocean waters by Kopelevich and Burenkov (1972). They found that the values of the volume scattering function at angles smaller than ~6° are poorly correlated with those at larger angles, though still reasonably well correlated within both angular ranges.

9. Conclusions

Mie theory was successfully used to model the average volume scattering functions of suspended particles from the surface waters of the Baltic in winter and summer. These functions were approximated to within experimental error in the scattering angle range from ~15 to 165° using the average measured particle size distributions in the diameter range of 2.5–20 μm. The approximation is much better than those obtained in the past for suspended particles from the Baltic. Unlikely to previous results for the Baltic, it was found that particles with diameters in the range of 0.1 to 10 μm contributed significantly to light scattering in the angle range of 5 to 165°. Particles smaller than 2 μm dominated light scattering at angles larger than about 10° while those with diameters larger than 2 μm controlled scattering at smaller angles.

Forward scattering in the range of 5 to 15° of particles from the surface layer in summer was also approximated well. However calculated scattering in this angular range for winter particles was about half of the experimental value at scattering angle 5°. This is explained by the underestimation of the projected areas of the suspended particles determined from PSD's obtained with the Coulter counter. Most likely, the calculations for the summer top layer are affected as well. However, a compensation was then possible. The light scattering by particles is determined by the product of their scattering efficiency, projected areas and size distribution. The underestimated projected areas of summer particles with low refractive index and a small slope of the PSD can be compensated for by adjusting the scattering efficiency, through the selection of a higher refractive index. This is not possible in winter, when the refractive index of particles and the slope of their PSD was high.

The overestimation of the refractive index of the particles to compensate for the underestimation of their projected area is most likely the case also in computations of other authors where the PSD measured with a Coulter counter was used to aid the modelling of light scattering by suspended marine particles.

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