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LETTER TO THE EDITOR

FRACTAL ANALYSIS OF SUSPENDED PARTICLES IN SEAWATER

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Light-scattering data of suspended clusters of particles in seawater have been analysed to find some evidence for fractal structure of the scatterers. The behaviour of the scattering intensity $I(q)$ as a function of q suggests that the scattering medium consists of two kinds of particles, large ones, with fractal dimension 1.7 ± 0.1, resulting from a regular DLCA growing process, and smaller ones, with a considerably larger fractal dimension 2.7 ± 0.4, resulting from a more complex cluster-cluster aggregation process in which low sticking probabilities, restructuring and settling could be present. This conclusion is strongly supported by the $I(q)$ curve which, in a log-log plot, exhibits two well defined linear regions. In interpreting data, it is assumed that the polydispersity of the scatterers is described by a smooth two-component particle-size distribution. The fractal structure of the scatterers is described by the behaviour of the scattering intensity from clusters of different size.

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Apparent and inherent optical properties of all but the clearest natural waters are to a large extent determined by suspended particles. The optical properties of these particulates, especially those related to light scattering, are strongly influenced by the particle-size distribution (PSD) and composition.

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Particulate matter in the sea consists of two basic types: biogenic and terrigenous, characterized by different scattering properties. Abundances and relative concentrations of both vary considerably, and their dimensions can range from less than one micrometer to many micrometers [1]. Most terrigenous particles are small [2], whereas biogenic particles are usually large. Recent investigations also reveal the presence of a large number of biogenic particles in sub-micron range [3,4], which could be the source of aggregation.

To study the fractal structure of the seawater scatterers, we have analysed data from 34 static light scattering (SLS) experiments performed in various types of seawater [5,6,7].

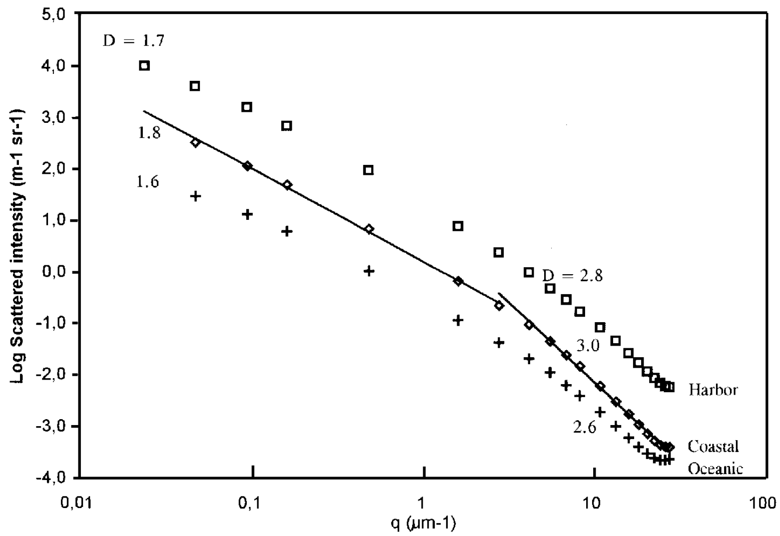

Fig. 1. Intensity of light scattering from suspended sea particles showing different q regions with the power-law behaviour. The data are from Ref. 7.

The log-log plot of typical data is shown in Fig. 1. It shows a dependence of the total scattering intensity $I(q)$ on the magnitude of the scattering vector q. We observe two different q regions in which $I(q)$ is likely to exhibit a power-law behaviour of the type $I(q) \sim q^{-D}$:

For $q \leq 2.5\ \mu\mathrm{m}^{-1}$, we find $1.6 \leq D \leq 1.8$.
For $2.5\ \mu\mathrm{m}^{-1} < q < 20\ \mu\mathrm{m}^{-1}$, we find $2.6 \leq D \leq 3.0$.

For q in the region between $19 - 23\ \mu\mathrm{m}^{-1}$, $I(q)$ goes through its minimum value. This region is dominated by the behaviour of the scattering intensity $I_0(q)$ of a single particle in the cluster.

Although the identification of two linear regimes in Fig. 1 may not be so obvious, a close look at Fig. 2, giving the $\log q$ dependence of

$$D(q) = -\frac{\mathrm{d} \log I(q)}{\mathrm{d} \log q},$$

clearly shows that there exist two different regions in which $D(q)$ behaves as a constant. We consider the power-law behaviour for $I(q)$ over the above indicated range of q as a possible signature of a fractal structure of suspended scatterers in seawater.

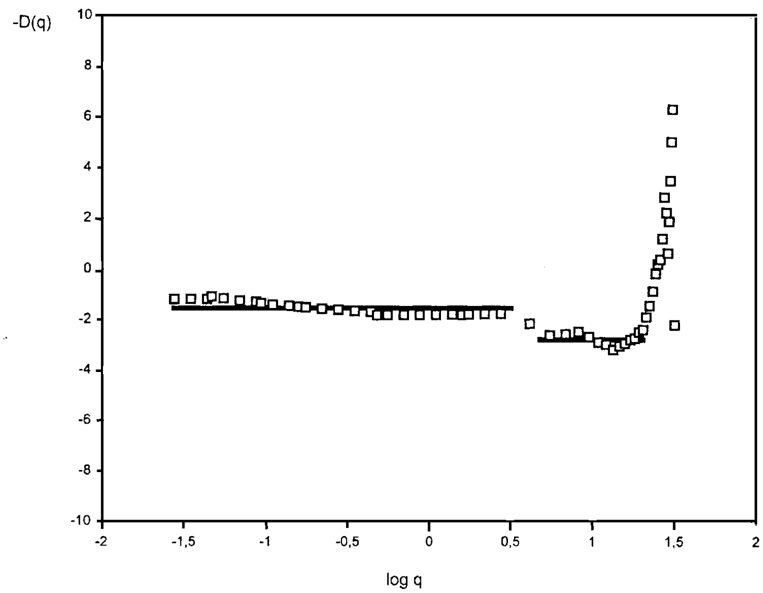

Fig. 2. Behaviour of the power-law exponent $D(q)$ as a function of $\log q$.

There is now substantial evidence that aggregates formed from coagulation processes possess fractal structures. Computer simulations of aggregate growth [8,9,10] and experimental studies [11,12,13] indicate that the magnitude of the fractal dimension is closely related to the mechanism of aggregate growth. Aggregates formed through particle-cluster aggregation have fractal dimensions in the range $D = 2.5 - 3.0$ [13], whereas cluster-cluster aggregation results in lower dimensions, typically $D = 1.6 - 2.2$ [14].

Depending on the particle stickiness, two different regimes of aggregation, resulting in different fractal dimensions, can be distinguished: diffusion-limited collodial aggregation (DLCA) [13] with a typical fractal dimension of around 1.8 and reaction-limited collodial aggregation (RLCA) with a fractal dimension of around 2.1 [15]. This suggests that the fractal dimension could be used to identify the aggregate formation mechanism as well as the stickiness (collision efficiency) of aggregating particles. However, the situation in seawater is far more complicated owing to the great polydispersity in sizes, shapes and properties of aggregating particles.

In this Letter, we show that the observed q dependence of the scattering intensity, $I(q)$, for suspended particles in seawater can be explained if the scattering medium consists of a mixture of two kinds of particles.

Let $N(R)\mathrm{d}R$ denote the number of clusters per unit scattering volume with radii between R and $R+\mathrm{d}R$. Then, in the dilute regime excluding multiple scattering, the total scattering intensity is given by

$$I(q) = \int I(q,R)N(R)\mathrm{d}R, \tag{1}$$

where $I(q,R)$ denotes the intensity of scattering from a cluster of size R. The total number of clusters per unit volume is

$$N_{tot} = \int N(R)\mathrm{d}R. \tag{2}$$

Integration over the size variable R is usually performed between R_{min} and R_{max}, where R_{min} (R_{max}) denotes the minimal (maximal) size of the clusters that contribute to light scattering. For suspended particles in seawater, the relevant range of R is 0.01 μm$\leq R <$ 100 μm [16].

Most authors model the sea-particle size distributions $N(R)$ by a one-parameter hyperbolic distribution [17,18] of the type

$$N(R) = CR^{-k}, \tag{3}$$

where C is a constant depending on the concentration, and $k \approx 3$ for big (biogenic) particles and $k \approx 2.5 - 5.0$ for smaller particles.

However, the method of dimensional analysis [19] predicts the polydispersity exponent k for a single coagulation mechanism to be 2.5 for Brownian coagulation, 4.0 for shear coagulation, 4.75 for differential-sedimentation coagulation and 4.75 for gravitational settling.

The real particle-size distribution over a range $R = (0.01 - 100)$ μm, which is relevant to light scattering, is certainly not possible to model using only a single-exponent hyperbolic-type distribution, because more then one coagulation mechanism may be important at the same time. For adequate description, it is usually necessary to employ several hyperbolic-type distributions

$$N(R) = \sum_i C_i R^{-k_i} = \sum_i N_i(R)$$

with various exponents k_i and constants C_i [19,20].

Recently, one of the present authors has proposed a smooth two-component model of the PSD over the size range $R = (0.01 - 100)$ μm, [16]:

$$N(R) = N_A(R) + N_B(R) = C_A R^2 \exp(-52R^{\gamma_A}) + C_B R^2 \exp(-17R^{\gamma_B}), \tag{4}$$

where γ_A and γ_B are the parameters of the distribution related to the average size of the cluster, and C_A and C_B are constants related to the concentration of the respective components. The model is in good agreement with all measured PSD data [16].

Although both components contribute in the whole considered size range, the A component is dominant for small sizes and the B component for large sizes, as shown in Fig. 3.

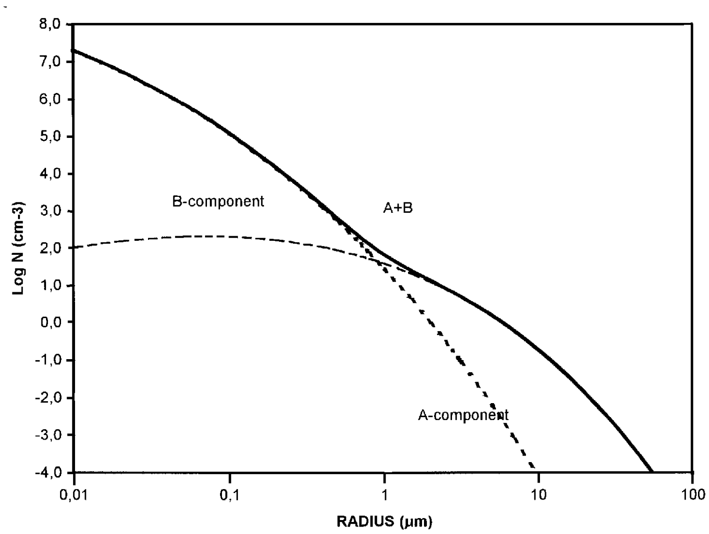

Fig. 3. Two-component model of sea-particle size distribution (schematic).

The total scattering intensity $I(q)$ receives contributions from both components A and B, so that

$$I(q) = I_A(q) + I_B(q), \tag{5}$$

where

$$I_{A,B}(q) = \int I(q,R) N_{A,B}(R) \mathrm{d}R. \tag{6}$$

A typical contribution of each component to the total light-scattering intensity $I(q)$ is shown in Fig. 4. Here $I(q)$ is calculated using a measured particle size distribution data and average relative indices of refraction for A- and B-component material (1.8 and 1.09, respectively) [16]. $I(q,R)$ is obtained from the Mie theory for a spherical scatterer of size R.

The B-component dominates at small scattering angles ($\theta < 10°$) or low q-values, whereas the A-component dominates at medium and large angles or large q-values. The crossover occurs at $q_c^{-1} \approx 0.3 - 1.0$ μm. The behaviour of these components implies that we can split the integration region in (1) in two parts

$$I(q) = \int_{R_{min}}^{R_b} I(q,R) N(R) \mathrm{d}R + \int_{R_b}^{\infty} I(q,R) N(R) \mathrm{d}R, \tag{7}$$

where $R_{min} = 0.01$ μm and the break point R_b is obtained from

$$N_A(R_b) = N_B(R_b).$$

The experimental data indicate that $R_b \approx (2-5)$ μm. Note that $q_c R_b \approx 1$.

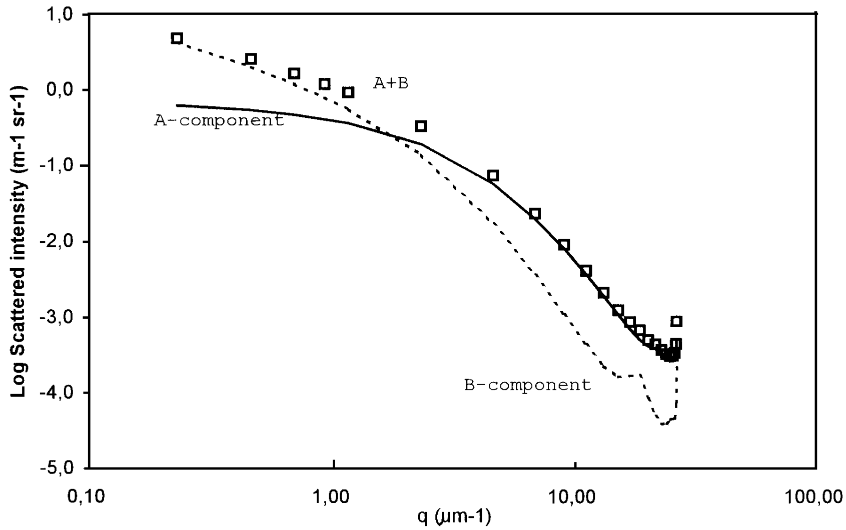

Fig. 4. Light-scattering contribution from the A and B components in the two-component model of Ref. 16.

In the regions 0.01 μm$< R < R_b$ and $R_b < R < 100$ μm, $N(R)$ can be replaced by $N_A(R)$ and $N_B(R)$, respectively. Since both $N_A(R)$ and $N_B(R)$ fall off very rapidly from the corresponding average size–radii [2] $\bar{R}_A$ and $\bar{R}_B$, respectively, we can approximate

$$I_A(q) \approx I(q, \bar{R}_A)$$

$$I_B(q) \approx I(q, \bar{R}_B).$$

Different power-law behaviour of $I_A(q)$ and $I_B(q)$ implies that in the approximation of smooth and very localized PSD, in the region $qR \geq 1$, we should expect the power-law behaviour of the type

$$I(q,R) \sim q^{-D(R)}, \tag{8}$$

with an R-dependent power-law exponent $D(R)$ [21].

In our model, the fractal dimension $D(R)$ of aggregates should slowly change from the value 3 for smallest particles ($R < 0.01$ μm) to about 1.2 for very large aggregates ($R > 200$ μm).

[2] Average size–radius is defined as

$$\bar{R} = \int_{R_1}^{R_2} RN(R)\mathrm{d}R \Big/ \int_{R_1}^{R_2} N(R)\mathrm{d}R.$$

In conclusion, by performing a fractal analysis of light-scattering data from various types of seawater, we have found that the smooth PSD implies the power-law behaviour of $I(q, R)$ in the region $qR \geq 1$, with an exponent $D(R)$ which is R-dependent. It is clear that in such a complicated system like the seawater, many corrections to scaling are possible, which we have not taken into account. The estimated average power-law exponents D of the measured scattering functions $I(q)$: 1.7 ± 0.1 for small q-values and 2.7 ± 0.4 for large q-values can be associated with cluster-cluster aggregation due to differential sedimentation and shear particle-cluster aggregation, respectively.

Since the measured $I(q)$ always depends on a product of $I(q, R)$ and $N(q)$, one of these two functions is usually arbitrary. Thus having the independent measurement of $N(R)$ in Eq. (1), we can in principle determine the $I(q, R)$ from the data using the method of deconvolution. However, owing to large uncertainties in the method of deconvolution and without a concrete physical model, it is difficult to see how the data alone could provide definitive evidence for fractal structure of scatterers in seawater.

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FRAKTALNA ANALIZA LEBDEĆIH ČESTICA U MORSKOJ VODI

Analizirali su se eksperimentalni podaci za raspršenje svjetlosti na grozdovima lebdećih čestica u morskoj vodi s ciljem otkrivanja fraktalne strukture raspršivača. Ovisnost intenziteta raspršenja $I(q)$ o q sugerira da se raspršivači sastoje od dvije vrste čestica, velikih s fraktalnom dimenzijom 1.7 ± 0.1, koje su posljedica DLCA procesa rasta, i manjih s većom fraktalnom dimenzijom od 2.7 ± 0.4, koje su posljedica složenijeg grozd-grozd procesa rasta. Pri objašnjenju eksperimentalnih podataka pretpostavljena je dvokomponentna raspodjela grozdovskih veličina.