Measurement of the spectral attenuation to support biological research in a "plankton tube" experiment

Light attenuation
Size distribution
Marine particle suspensions
Yellow substance
Atténuation de la lumière
Distribution de dimension
Suspensions particulaires marines
Substance jaune

P. Diehl, H. Haardt

Institut für Angewandte Physik der Universität Kiel, Olshausenstr. 40/60, 2300 Kiel 1, GFR.

ABSTRACT

For particulate suspensions with sizes statistically distributed according to a Junge (power law) distribution, there is evidence that the optical attenution due to particles alone follows a wavelength dependence proportional to λ^{3-c_j} where c_j is the Junge coefficient. A theoretical derivation based on Mie theory in the van de Hulst approximation proves this wavelength dependence. A further derivation yields the volume concentration of particles having diameters between given limits in terms of measured attenuation. During a "plankton tube experiment", total optical attenuation was measured, every two days within two closed-off volumes of seawater at Eckernfoerde Bay, Baltic Sea. During this period, no plankton bloom took place. Attenuation data pertaining to particulate matter alone indicate that the particles obey a Junge distribution with good accuracy. Absolute values of particle density inferred from optical measurements are in agreement with, and seem more accurate than, values obtained by filtration and weighing.

In addition, the contribution to attenuation due to dissolved matter was evaluated. These data support the suggestion that the plot of logarithm of attenuation versus wavelength on linear scale contains two straigth line sections in the blue range. In the red range three absorption bands associated with yellow substance were found consistently.

Oceanol. Acta, 1980, **3**, 1, 89-96.

RÉSUMÉ

Contribution à la recherche biologique par la mesure de l'atténuation spectrale au cours d'une expérience de développement planctonique *in vitro*

Si l'on considère des suspensions de particules dont les dimensions sont distribuées statistiquement selon la loi de distribution de Junge, il apparait que l'atténuation optique due aux particules seules dépend de la longueur d'onde proportionnellement à λ^{3-c_j}, c_j étant le coefficient de Junge. Une démonstration théorique fondée sur la théorie de Mie avec l'approximation de van de Hulst établit cette dépendance par rapport à la longueur d'onde. Une démonstration plus élaborée fournit la concentration en volume des particules ayant des diamètres donnés en fonction de l'atténuation mesurée.

Au cours d'une expérience de développement planctonique *in vitro*, on a mesuré, tous les 2 jours, l'atténuation optique totale, pour des volumes confinés d'eau de mer, provenant de la Baie d'Eckernfoerde dans la Baltique. Pendant cette période, aucune poussée planctonique ne fut observée.

Les mesures d'atténuation effectuées concernant la matière particulaire seule indiquent que les particules suivent avec une bonne concordance la loi de distribution de Junge.

Les valeurs absolues de la densité particulaire déduites des mesures optiques concordent bien avec les données obtenues par filtration et pesée, voire même sont plus précises. De plus, la part revenant à la matière dissoute dans l'atténuation a été évaluée. Les données appuient l'hypothèse selon laquelle la courbe logarithmique de l'atténuation en fonction de la longueur d'onde, en échelle linéaire, présente deux segments de droites dans le bleu. Dans le rouge, on a trouvé aussi trois bandes d'absorption associées avec de la substance jaune.

THE PLANKTON TUBE EXPERIMENT

For several years the "Joint Research Programme at Kiel University" (SFB 95) has been carrying out experiments with, artificially enclosed water bodies in the Eckernförde bay. Transparent synthetic tubing was hung up in a tower and embedded in the sea floor so that enclosed water columns were created. It was the aim of the experiment to study and record the interactions between the sediment and the water column (Bodungen et al., 1976). On June 28, 1978 two tubes of diameter 2 m (named sacks I and II) were installed at the plankton tower. Sack II was opaque at the upper end, sack I was transparent troughout. At two- day intervals water samples were taken from sack II from a depth of 2.5 m, whose spectral attenuation was measured in the laboratory. Starting from July 14, water samples from the same depth also were taken from sack I.

As far as possible, the samples were analysed on the same day.

Up to July 13, a distinct plankton bloom had not set in. Since a nutriment shortage was assumed at first, the water column was intentionally mixed. When that had no effect, the surface water was exchanged and nutrient salts were added to the water column on July 19. Very likely the surface water was again exchanged through a strong easterly gale on July 26. Finally, the experiment was stopped on July 28.

There was no plankton bloom throughout the measuring period.

METHOD OF MEASUREMENT AND QUANTI- TIES MEASURED

Measurements were made with a dual- beam spectral photometer developed for this purpose by Haardt and Diehl (in prep.) sample cuvette has a length of 1 m and, in order to prevent settling of particulate matter, its contents can be circulated by pumping. Usually measurements were made in the range 400 to 800 nm in increments of 10 nm. The monochromator was adjusted for passing a bandwidth of 3 nm and the reproducibility of a wavelength setting was about 0.2 nm. To exclude forward scattered ligth as much as possible, the total aperture was kept to a small value of 0.2 degrees (half angle). This apperatus permits the absolute measurement of attenuation coefficients with a resolution of 0.001 m^{-1}.

The measured attenuation coefficient c comprises three additive contributions.

$$c = c_w + c_p + c_d,$$

where c_w is the attenuation due to pure water, c_p due to particulate matter and c_d due to dissolved matter. These contributions are separated by subtraction.

In preliminary measurements the attenuation coefficient of pure water, c_w, was determined. Several runs were made and showed satisfactory agreement with published data, e. g. by Sullivan (1963). The largest deviation of 10 per cent was considered tolerable for present purposes. For a determination of the value c_d by subtraction, the c_w data measured in this work were used.

In measurements of the combined attenuation coefficient c, the slow settling of particulate matter and the ensuing decrease of c_p present a problem. To eliminate this effect as much as possible, the water sample was circulated within the cuvette by pumping. Still, settling caused some fluctuation of c_p values although these never exceeded 5 per cent. This source of error was checked regulary in every run.

In order to determine c_p and c_d separately, it is necessary to remove the particulate matter. This was achieved by filtering. For practical reasons, this was done in two steps. First a glass fiber filter was used to remove the bulk of the particles, i. e. those of large and medium sizes. Second, a Sartorius membrane filter was used to quantitatively remove particles down to the nominal filter mesh size of 0.1 μm. This two- step process prevents premature clogging of the final filter and thus ensures uniform properties of the filtrate for extended measurements runs.

CALCULATION OF c_p FOR HYPERBOLIC DISTRIBUTION

For monodisperse systems of spherical particles of radius r one has

$$c_p = NQ\,(\rho)\,\pi\,r^2, \tag{1}$$

N being the number of particles per unit volume, and $Q\,(\rho)$ the efficiency factor. For polydisperse particle systems (1) changes into

$$c_p = \int_{r_{min}}^{r_{max}} n\,(r)\,Q\,(r/\lambda)\,\pi\,r^2\,dr, \tag{2}$$

As many measurements with the Coulter counter have shown, particles in seawater often obey a Junge distribution

$$n(r) = ar^{-c_j}, \qquad r_{min} < r < r_{max}, \tag{3}$$

with good accuracy; c_j is the Junge coefficient. This is not the case, however during a plankton bloom (Bader, 1970; Klotz, 1978). For simplicity the following discussion is restricted to particles having a real index of refraction. The efficiency factor within the framework of Mie theory is, to good approximation, given by the van de Hulst formula (van de Hulst, 1957):

$$Q(\rho) = 2 - 4/\rho \sin \rho + 4/\rho^2 (1 - \cos \rho),$$

with

$$\rho = 2\alpha(m-1) \qquad \text{and} \qquad \alpha = 2\pi r/\lambda.$$

m relative index of refraction.

In seawater, there may be particles of organic and inorganic nature. Gordon and Brown (1972) and Brown and Gordon (1974) obtained a relative index of refraction of $m = 1.05 - 0.01\,i$ for organic particles. Work by Klotz-Reuter and in this laboratory Haardt and Diehl (in prep.) has shown that a real index $m = 1.05$ suffices except near the chlorophyll and carotenoid absorption bands around 670, 440 and 480 nm where a finite imaginary part should be taken into account. The relative index of many minerals lies between $m = 1.15$ and 1.20. Such small indices permit a sufficiently accurate description of attenuation within the van de Hulst approximation, which tends to be better for organic particles (Penndorf, 1958). In this approximation the integral (2) can be carried out. The error caused by the assumption of spherical particles cannot be estimated *a priori*. In order to solve the integral, $Q(\rho)$ is expanded into a series

$$Q(\rho) = \sum_{i=1}^{\infty} (-1)^{i+1} \frac{4(2i+1)}{(2i+2)!} \rho^{2i}. \tag{4}$$

For $\rho \to \infty$ this series converges towards 2. Replacing ρ by $2\alpha(m-1)$, equation (4) becomes

$$Q(\alpha) = \sum_{i=1}^{\infty} (-1)^{i+1} \frac{4(2i+1)\,[2(m-1)]^{2i}}{(2i+2)!} \alpha^{2i}. \tag{5}$$

Substituting (5) and (3) into (2) yields

$$c_p = \frac{a}{2(2\pi)^{2-c_j}} \lambda^{3-c_j}$$

$$\times \int_{\alpha_{min}}^{\alpha_{max}} \sum (-1)^{i+1} \frac{4(2i+1)\,[2(m-1)]^{2i}}{(2i+2)!}$$

$$\times \alpha^{2i+1-c_j} d\alpha. \tag{6}$$

This integral can be done without difficulty, leading to

$$c_p = \frac{a}{2(2\pi)^{2-c_j}}$$

$$\times \lambda^{3-c_j} \left[H(\alpha_{max}, c_j, m) - H(\alpha_{min}, c_j, m) \right], \tag{7}$$

where

$$H(\alpha, c_j, m)$$

$$= \sum (-1)^{i+1} \frac{4(2i+1)\,[2(m-1)]^{2i}}{(2i+2)!\,(2i+3-c_j)} \alpha^{2i+3-c_j}. \tag{8}$$

Here the choice $c_j = 5$ leads to a formal singularity, hence should be excluded. By a limiting process it can be shown, however, that the resulting attenuation is finite and similar to that for neighboring values.

Formula (7) does not yet prove the proportionality of c_p and λ^{3-c_j} since both α_{max} and α_{min} are wavelength dependent. The proportionality arises, however, if limiting processes

$$\alpha_{max} \to \infty, \qquad \alpha_{min} \to 0 \tag{9}$$

may be carried out which do not alter the result significantly. Experience has shown that Junge distributions for particles in seawater are characterized by a Junge coefficient in the range $3 < c_j < 5$. Further they usually have a smallest particle diameter of about 25 nm corresponding to $\alpha_{min} = 0.2$ for a typical optical wavelength (Morel, 1973). Similarly, plankton particles having an equivalent spherical diameter larger than 20 μm are rare. This is taken into account by the choice $r_{max} = 25$ μm and $\alpha_{max} = 400$. Computer calculations show that the choice of α_{min} influences the coefficient of c_p to a greater extent than that of α_{max}.

The limiting processes (9) were tested empirically by computer calculation. For the choice of $m = 1.05$ and the range $3.5 < c_j < 5$ they show convergence. As a result, there the proportionality between c_p and λ^{3-c_j} is assured. For c_j near 3, however, convergence is not obtained. This indicates that in this case a wavelength independent c_p — as one would expect from λ^{3-c_j} — is not obtained.

Next we wish to determine the volume concentration of particles with radii between given lower and upper limits. This concentration is defined as total volume occupied by particles per unite volume. Thus

$$v = \frac{4\pi}{3} \int_{r_{lower}}^{r_{upper}} n(r) r^3 dr, \tag{10}$$

Assuming a Junge distribution (3), one obtains

$$v = \frac{4\pi a}{3(4-c_j)} (r_{upper}^{4-c_j} - r_{lower}^{4-c_j}) \tag{11}$$

Here the case $c_j = 4$ is excluded; it leads to the corresponding logarithmic result. Eliminating a in (7) through (11) one finds

$$c_p = v \frac{3(4-c_j)\pi}{2(\alpha_{upper}^{4-c_j} - \alpha_{lower}^{4-c_j})\lambda}$$

$$\times \left\{ H(\alpha_{max}, c_j, m) - H(\alpha_{min}, c_j, m) \right\}. \tag{12}$$

Note that in this formula:

α_{max} refers to the largest particles actually present;

α_{upper} refers to the largest particles to be included in the concentration determination;

α_{min} refers to the smallest particles actually present;

α_{lower} refers to the smallest particles to be included in the concentration determination;

by necessity, $\alpha_{max} > \alpha_{upper} > \alpha_{lower} > \alpha_{min}$.

Thus formula (12) permits the determination of the volume concentration of particles having radii $r_{lower} < r < r_{upper}$ corresponding to $\alpha_{lower} < \alpha < \alpha_{upper}$ from measured c_p provided a Junge distribution with known c_j is present in the range $\alpha_{min} < \alpha < \alpha_{max}$.
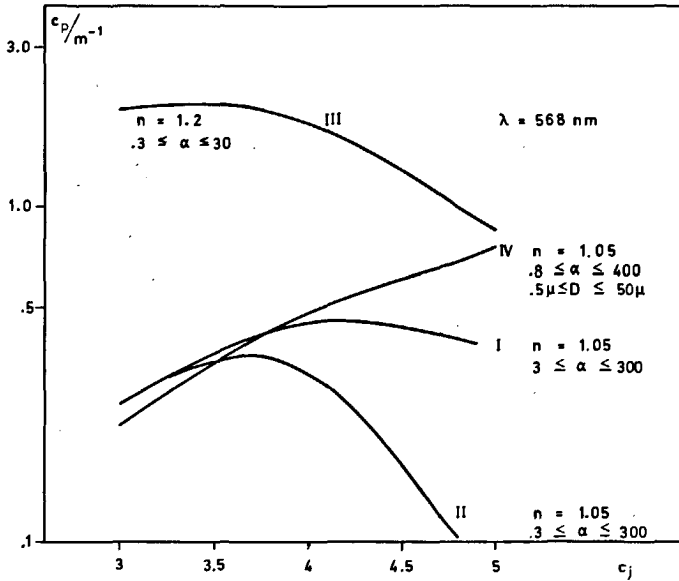
Figure 1

The attenuation coefficients for particulate matter c_p against the Junge coefficient c_j. The volume concentration is 1 μl/l in the limits of the size parameter α given in the Figure.

For $v = 1$ μl/l, c_p has been plotted as a function of c_j for different conditions in Figure 1. Curve I and II refer to organic particles ($m = 1.05$), curve I with particle diameters 0.4 μm < 2 $r < 40$ μm and curve II with 0.04 μm $< 2r < 40$ μm. For Junge coefficients $3 < c_j < 3.8$ deviations between both curves are small. For larger c_j the predominance of small particles causes a significant difference between both curves. Curve III shows the c_j dependence of c_p for sediment particles ($m = 1.2$) with diameters 0.04 μm < 2 $r < 4$ μm. Owing to the larger index the attenuation is larger, too.

For the evaluation of the plankton tube data, organic particles with $m = 1.05$ and the validity of a Junge

distribution between the limits $\alpha_{min} = 0.8$ and $\alpha_{max} = 400$ were assumed. For a typical wavelength of 500 nm this implies diameters between $2 r_{min} = 0.1$ μm and $2 r_{max} = 50$ μm. The former diameter $2 r_{min}$ is given by the mesh size of the membrane filter used to separate particulate matter from the remaining water. Parallel to present investigation, a determination of seston from the plankton sack was carried out. Water samples were filtered by glass fiber filters and seston was determined by weight. Assuming the filters may be characterized by pore diameter 0.5 μm, these weight measurements yield concentration data for particles with limiting diameters of $2 r_{lower} = 0.5$ μm and $2 r_{upper} = 50$ μm. For purposes of comparison with optical data, the c_p value to be expected at $\lambda = 568$ nm is plotted in curve IV as a function of c_j for a volume concentration of 1 μl/l of particles with diameters between $2 r_{lower} = 0.5$ μm and $2 r_{upper} = 50$ μm, while the presence of smaller particles down to $2 r_{min} = 0.1$ μm is taken into account.

THE DETERMINATION OF THE VOLUME CONCENTRATION

According to the theory put forward in the preceding sections it should be possible to determine the c_j value on the basis of the c_p (λ) data, provided there is a Junge distribution. For if c_p is plotted as a function of λ, one will get the hyperbolic function

$$c_p = a' \lambda^{3-c_j}.$$

As there was no plankton bloom in the plankton tube experiment, the assumed Junge distribution turned out to be a good approximation. Two typical wavelength dependencies of c_p are shown in Figure 2. They are representative of results during the entire measuring period. By using logarithmic scales, the equation can be reduced to the straight line equation

$$\ln (c_p) = (3 - c_j) \ln (\lambda) + \ln (a').$$
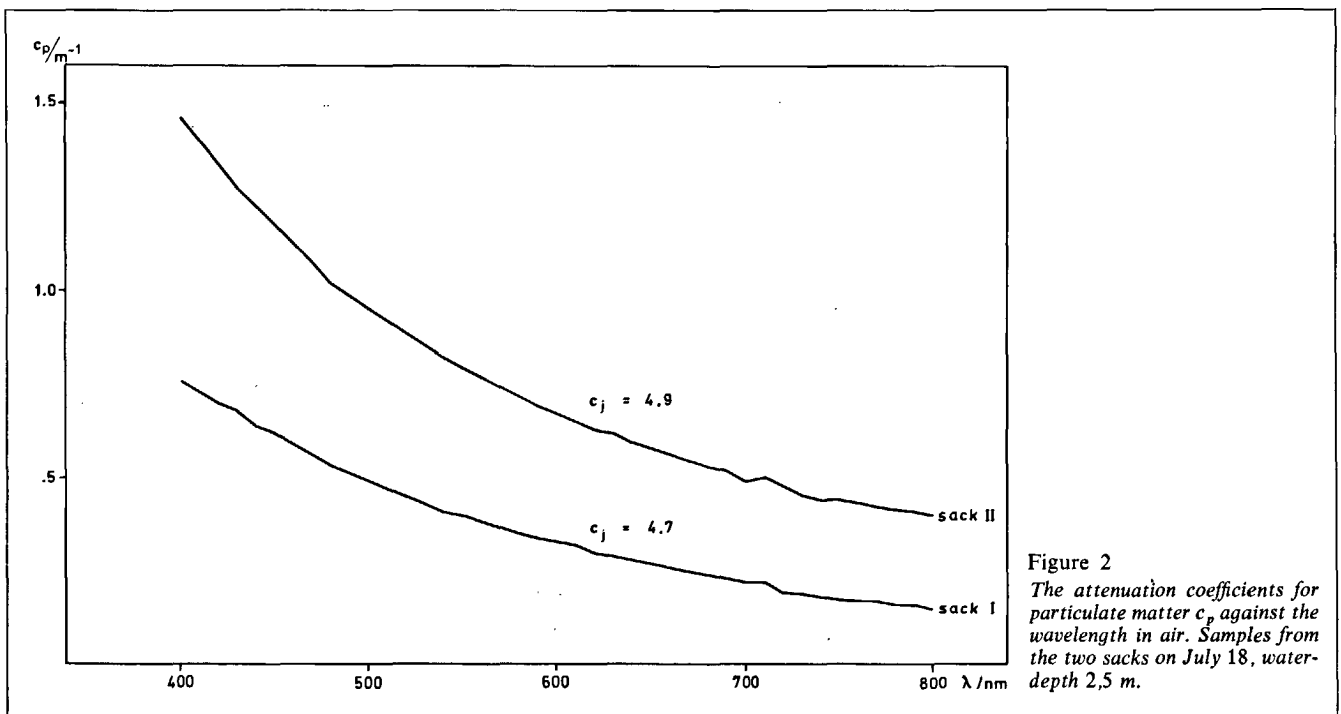

Figure 2

The attenuation coefficients for particulate matter c_p against the wavelength in air. Samples from the two sacks on July 18, water-depth 2,5 m.
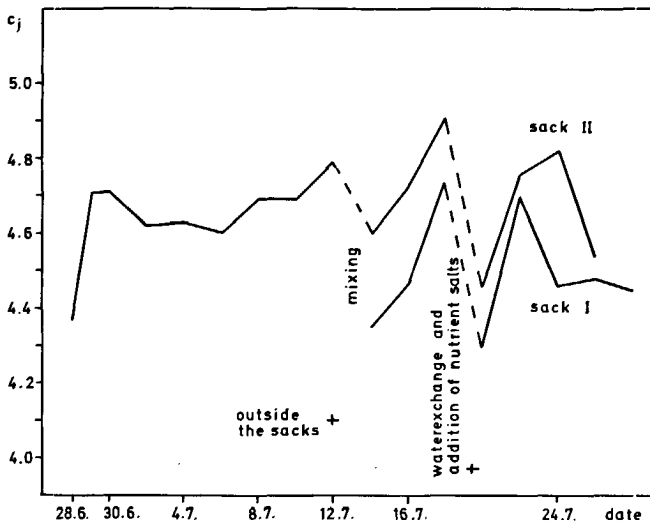
Figure 3

The coefficient of the Junge particle size distribution during the experiment.

Through linear regression, values a', c_j, and r^2 (square of correlation coefficient) can be determined. The value of r^2 indicates the degree of validity of the Junge distribution. Table shows the results from sack II.

The Junge coefficient c_j was determined from wavelength dependencies of c_p as typically shown in Figure 2. For the evaluation, however, only wavelength up to 650 nm were used since near 700 nm there are often deviations caused by strong increase of c_w associated with the first IR absorption band of water. As can be seen from the correlation coefficient, data support the power law very well. In Figure 3, c_j has been plotted for both tubes during the measuring period. From the rather high values for c_j a predominance of small particles (in this case probably bacteria) may be inferred. The strong decline on July 12 and 18 (continued line) should be explained by water exchange within the tubes, during which greater particles were carried upwards. Through settling processes, however, the

former trend set in; small particles begin to predominate again. It was not before July 22 (sack II: July 24), that the reverse trend set in, apparently without any influence from outside. On June 12 a sample from outside the tubes was taken. Its c_j was 4.1, a value within the typically expected range. A value of $c_j=4$ means equal volumina for particles within equal logarithmic size ranges.

The high values of c_j for surface water in comparison to low values from the outside samples indicate a development in the plankton tubes which is different from that outside.

For determination of the volume concentration the refractive index m is needed. If the majority of the particles is of organic nature, a refractive index of $m=1.05$ may be assumed (Gordon, Brown, 1972; Brown, Gordon, 1974). For a meaningful comparison of particle concentration data from seston weight and from optical attenuation measurements, both should refer to the same lower limit of particle diameters that are taken into account. For seston determination by weight, Whatman GF/C filters were used. Their mean mesh diameter is around 1 µm. But, owing to being plugged up by extended filtering operation, the mean diameter gradually decreases. Therefore an effective diameter of $2\,r_{lower}=0.5$ µm is considered representative for the seston determination. Figure 4 shows the seston weight data for sack II. The values obtained range between 1 and 2 mg/l with large scatter. The high values found on July 2 and 18 are believed to be unreliable. The large scatter makes it impossible to recognize any systematic trend in the data.

The volume concentration obtained from optical attenuation data for sack II is presented in the table. As explained before, the evaluation considers only particles with diameters between $2\,r_{lower}=0.5$ µm and

Figure 4

The volume concentration v from optical measurements and the seston weight data during the experiment.

Table
a', c_j, r^2 and v computed for sack II.

| Date	a'	c_j	r^2	v (µl/l)
28.6.78	5460	4.37	.999	1.6
29.6.78	37557	4.71	1.000	1.1
30.6.78	38785	4.71	1.000	1.2
2.7.78	24809	4.62	1.000	1.4
4.7.78	25933	4.63	1.000	1.3
6.7.78	18432	4.60	.999	1.2
8.7.78	26588	4.69	1.000	0.9
10.7.78	27379	4.69	.998	0.9
12.7.78	47550	4.79	.998	0.8
14.7.78	33130	4.60	1.000	2.1
16.7.78	54186	4.73	.999	1.5
18.7.78	135802	4.91	1.000	1.0
20.7.78	12743	4.46	1.000	2.0
22.7.78	57676	4.76	1.000	1.2
24.7.78	73421	4.82	1.000	1.0
26.7.78	17875	4.54	1.000	1.7
28.7.78	36645	4.66	1.000	–
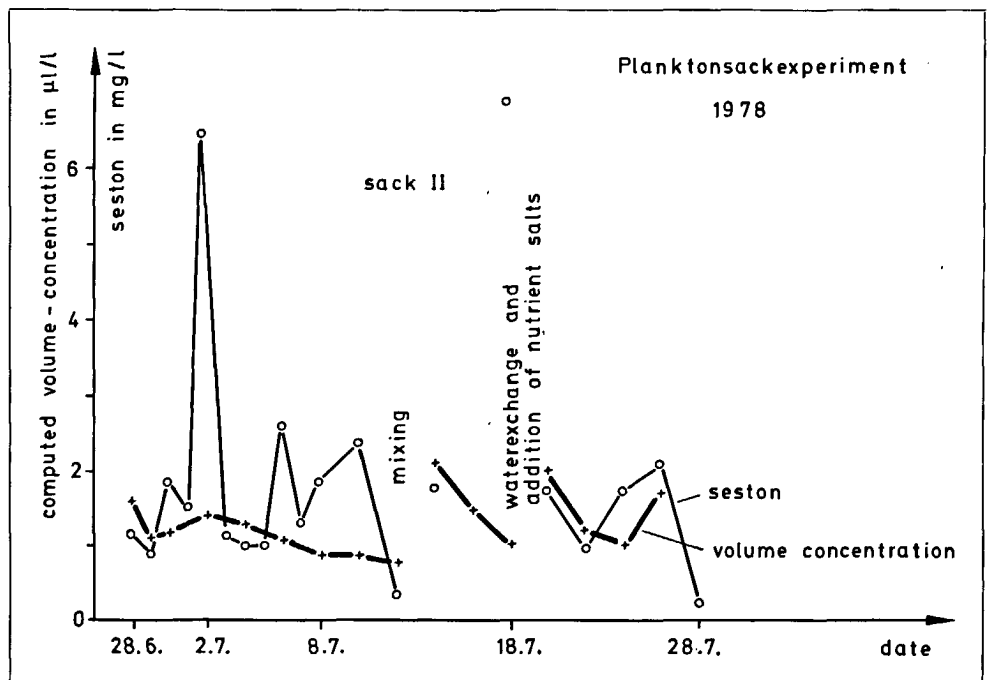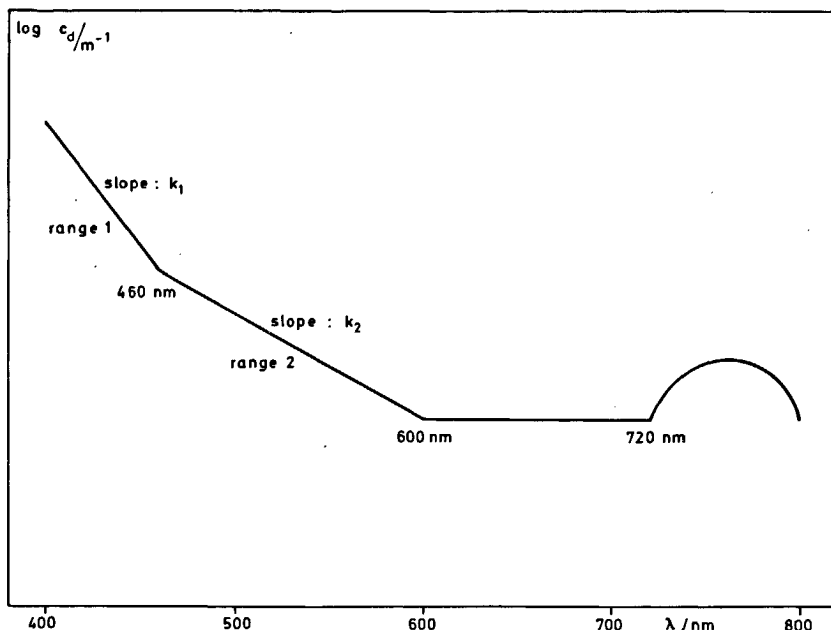
Figure 5
Schematic curve of the attenuation coefficient for dissolved substances c_d (logarithmic scale) against the wavelength in air.

$2 r_{upper} = 50$ μm. If the density of particles is 1 g.cm^{-3}, the concentration data in units of mg/1 and μl/1 are numerically the same. Using this simplification, the concentration data from optical measurements for sack II are also plotted in Figure 4. The weight data and optical data are in coarse agreement with the optical data having less fluctuations. The steep increases on July 14 and 20, which hardly can be recognized in the seston weight data, were caused by intentional mixing of the water within the sacks on July 13 and by exchanging water from within and without on July 19. The further increase on July 26 is a consequence of a gale which similarly caused the influx of outside water.

For an assessment of the accuracy of concentration data from optical attenuation data, it should be appreciated that the refractive index actually has a small imaginary part which was neglected in the present formulas. It can be shown that this neglect is of little consequence for larger particles since there Q does not depend much, in the mean, on α. This, however, is a significant effect with smaller particles where Q increases with the imaginary part of the index. A second point to consider is the fact that in the present analysis only organic particles were included. A small admixture of anorganic sediment particles (with $m = 1.2''$) will lead to noticeably higher c_p (see Fig. 1).

YELLOW SUBSTANCES

The suggestion, put forward in various publications, that c_d will result in a straight line if logarithmically plotted versus (Jerlov, 1976, p. 56), could not be verified. All measurements show the pattern shown in Figure 5.
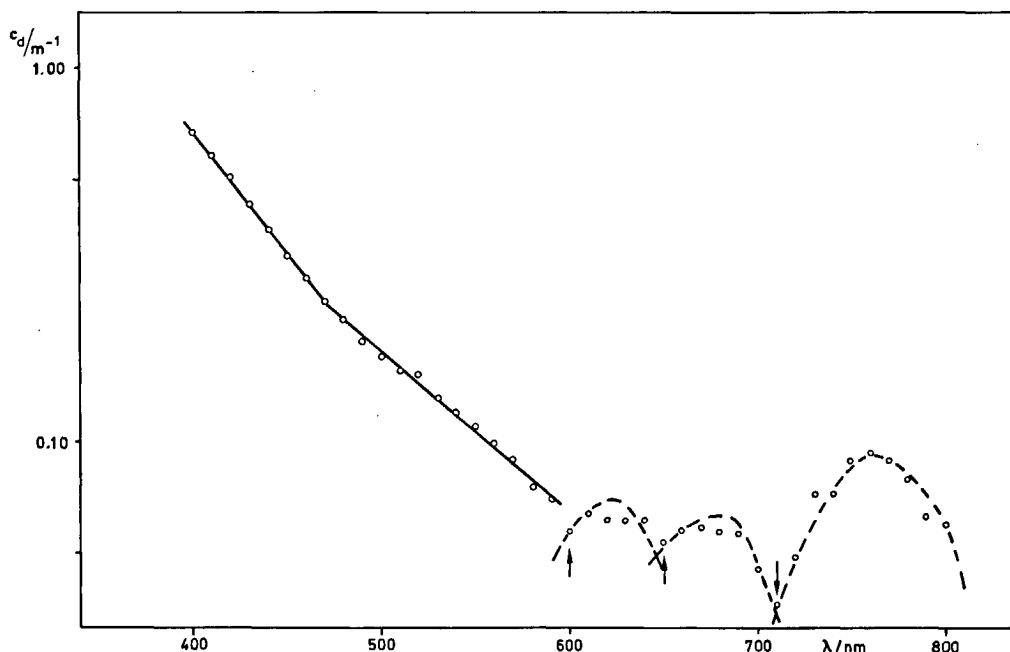

Figure 6
The attenuation coefficient for dissolved matter c_d against the wavelength. Sample from Eckernförde bay, Baltic Sea, waterdepth 2,5 m, July 12.
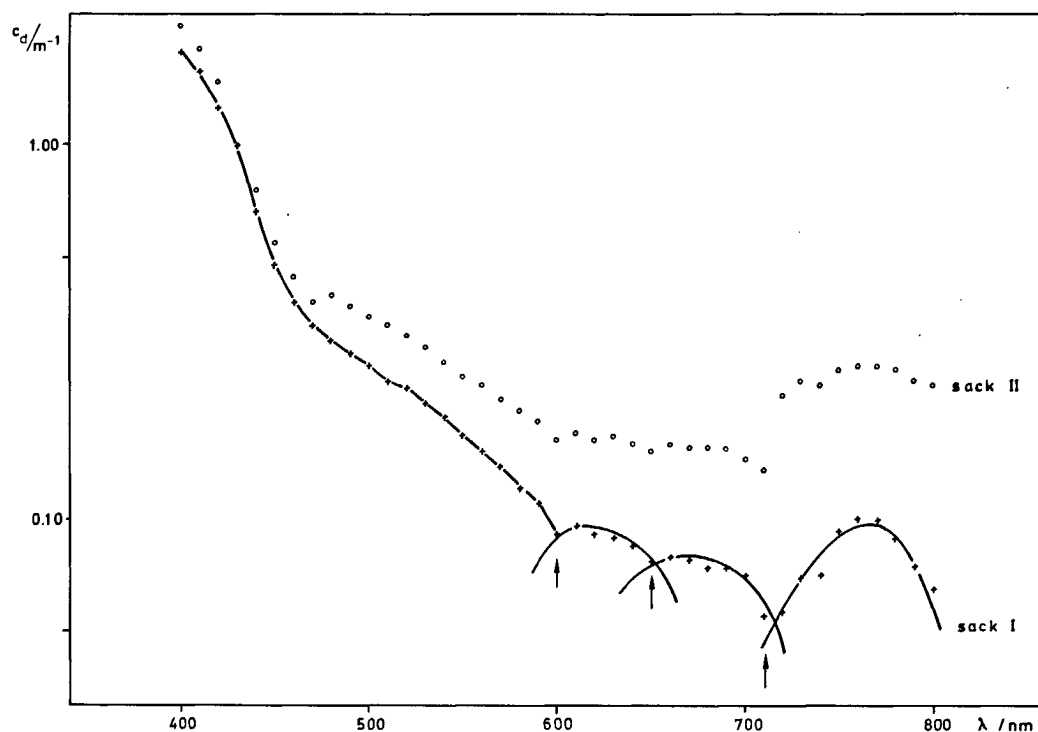
Figure 7
The attenuation coefficient for dissolved matter c_d against the wavelength. Samples from sacks I and II, waterdepth 2,5 m, July 14.

A logarithmic plot of c_d versus wavelength on linear scale shows straight lines in the wave length ranges of 400-460 and 460-600 nm; those lines, however, differ in their slopes. Above 600 nm c_d remains almost constant. A closer inspection reveals three minima (600, 650 and 710 nm) in this range. Figures 6 and 7 show these minima very clearly. Between 720 and 820 nm there is a weak absorption band.

Ultimately, these phenomena must be explained by the fact that here at least five absorption bands overlap each other. Three of their maxima are at 610, 670 and 760 nm approximately. The maxima of the remaining two bands cannot be determined from the measurements,

but they are in the near UV range. Characterizing these bands by the differing slopes associated with them (see Fig. 5):

$$k_i = d \left(\log \left(c_d \left(\lambda\right)\right)\right)/ d\lambda,$$

$i = 1$ for λ around 430 nm; $i = 2$ for λ around 530 nm; it was found that during the plankton sack experiment slope k_2 changed little whereas k_1 showed significant changes. This is shown in Figure 8. Furthermore, when high concentration of yellow substances is present as indicated by high values of c_d. such as on July 14, the dependence of $\log (c_d)$ upon λ in the neighborhood of 430 nm is not a straight line (see Fig. 7). Taking the
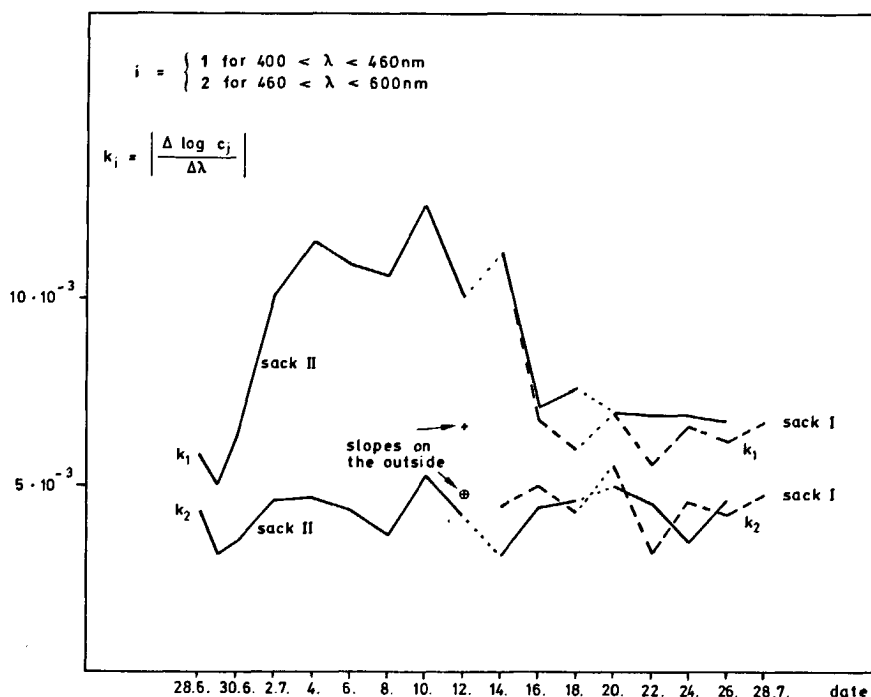

Figure 8
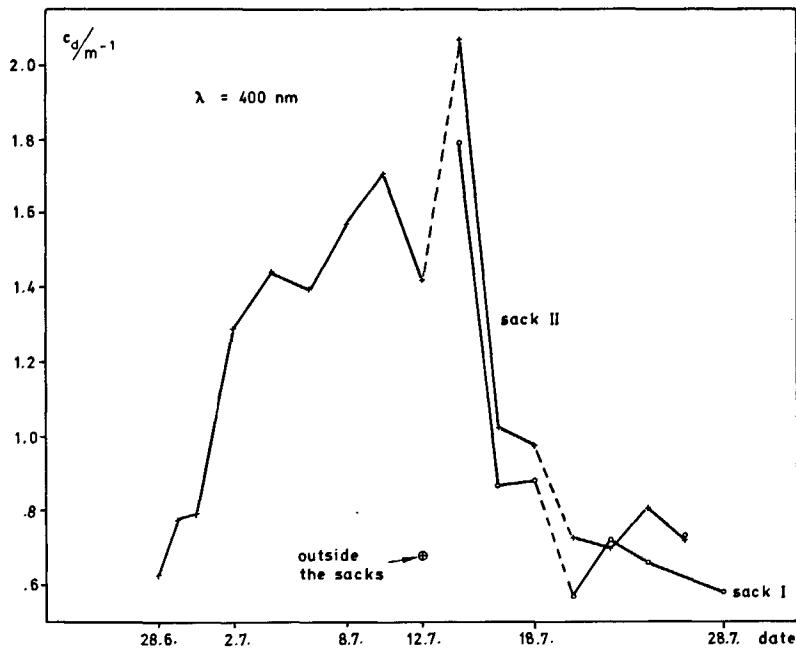*The slopes k_1 and k_2 during the experiment.*

Figure 9

The attenuation coefficient c_d ($\lambda = 400$ nm) characterizing the concentration of yellow substances.

value of c_d at 400 nm as an indicator for concentration of yellow substance, its time dependence for the duration of the experiment is shown in Figure 9 for both sacks. After the beginning of the experiment, production of yellow substance lead to a maximum on July 14. The maximum, however, was preceded by mixing of water in the sack on July 13, so that these high values reflect processes that very likely took place in the deeper layers of the tube. It is probably more correct to assume that the decrease of concentration of yellow substance began as early as July 10 and continued up to the end of the measuring period. Thus the maximum concentration representative of the measuring depth was most likely on July 10. Reference measurements outside the sacks indeed showed that production of yellow substance took place only inside the sacks.

Acknowledgements

REFERENCES

Bader H., 1970. The hyperbolic distribution of particle size, *Geophys. Res. Pap.,* **75,** 15, 2822.

v. Bodungen, v. Bröckel K., Smetacek V., Zeitzschel B., 1976. The Planktontower. A structure to study water/sediment interaction in enclosed water columns, *Mar. Biol.,* **34,** 369-372.

Brown O. B., Gordon H. R., 1974. Size-refractive index distribution of clear coastal water particulates from light scattering, *Appl. Opt.,* **13,** 12, 2874.

Gordon H. R., Brown O. B., 1972. A theoretical model of light scattering by Sargasso sea, *Limnol. Oceanog.,* **17,** 826.

Haardt H., Diehl H. P. Messungen des spektralen Attenuations-koeffizienten an Künstlichen und natürlichen Meerwasserproben aus der Ostsee (in preparation).

van de Hulst H. C., 1957. *Light Scattering by small Particles,* Wiley, New York.

Jerlov N. G., 1976. *Marine Optics,* Elsevier, N. Y., p. 231.

Klotz R., 1978. Untersuchungen über Streufunktionen im optischen Spektralbereich an künstlichen und natürlichen marinen Partikel-suspensionen mit Beispielen aus der Kieler Bucht, Report No. 46, SFB 95, Kiel University.

Morel A., 1973. Diffusion de la lumière par les eaux de mer. Résultats expérimentaux et approche théorique, *AGARD Lect. Ser.,* **61,** Optics of the Sea.

Penndorf, 1958. An approximation method to the Mie theory for colloidal spheres, *J. Phys. Chem.,* **62,** 1537.

Sullivan J. P., 1963. Experimental study of absorption in distilled water, artificial sea water, and heavy water in visible region of spectrum, *J. Opt. Soc. Amer.,* **53,** 962-967.