Optically effective area of particle ensembles in the sea

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Abstract

The optically effective area (OEA) concentration of particles was computed from measured size distributions and concentrations of particles in the upper 100 m of the Pacific Ocean off Baja California and is shown to correspond closely to direct measurements of the volume coefficient of light scattering at an angle of 20°, shown previously to be proportional to total scattering.

Plots of OEA as a function of particle diameter exhibit a maximum contribution at about 2 μm diameter at offshore stations and at 3.5 μm at nearshore stations. The roll-off at smaller particle diameters is attributed to diminished optical efficiency rather than to decreased concentrations of smaller particles.

Size distribution of particles in seawater and its effect on the optical character of the ocean have received increasing attention both as biological and as physical problem areas. A degree of confusion is apparent from previous work as to the size of particles which contribute most heavily to light scattering in the sea; I have tried to clarify this relationship by combining Coulter measurements of particle size distributions with light scattering measurements. By applying scattering theory to these measurements, I estimate the contribution of particle size fraction to the total light scattering.

The current confusion on this subject is due almost certainly to differences in methods used as well as to real variations in time and space. Burt (1955, 1958) inferred from selective attenuation characteristics a predominant effect of small particles (< 1 μm diameter) in Chesapeake Bay and in the eastern tropical Pacific. Sasaki et al. (1960, 1962) obtained similar results by fitting observed scattering functions of deep water samples to theoretically derived curves. Hinzpeter (1962) and Hishida (1966) inferred from color dispersion of scattered light that particles of 1–2 μm diameter predominate, though without regard to particle pigmentation. Also inferring particle characteristics from optical measurements, others (e.g. Joseph 1955; Hanaoka et al. 1960; Jerlov 1961; Duntley 1963) concluded that particles larger than 1–2 μm control optical characteristics.

A few investigators have worked with both optics and particle size characteristics; their conclusions also are somewhat conflicting. Jerlov (1955), Pickard and Giovando (1960), and Ochakovsky (1966) have made microscopic counts of particles in addition to optical measurements: they determined dominant optical effects of particles of, respectively, 16 μm, 7–17 μm, and < 1 μm diameter. Beardsley et al. (1970) and Carder (1970), using light scattering and electronic particle counting, concluded that the median particle diameter at eastern tropical Pacific stations was < 1 μm; size distributions were well described by a two-parameter exponential equation. Pak et al. (1971) computed scattering for a measured log-normal distribution of minerogenics, indicating that 90% of total scattering was due to particles in the diameter range 0.6–8.6 μm, in essential agreement with Tucker and his associates (e.g. Tucker et al. 1969) who found that 68% of particles that affect beam attenuation are less than 10 μm diameter, and 96% are less than 13 μm.

Working with particle size characteristics but without optical measurements, Lisitsin (1961) showed a predominance of particles with diameters around 1 μm, whereas the work of Krey and his associates (e.g. Krey 1961) indicates dominance of larger size fractions. Bader (1970),

working with electronic particle counts of nearshore water samples, described hyperbolic distributions of size. Zeitzschel (1970) presented electronic counts which indicated numerical dominance of small particles, but, in terms of volume, larger particles contributed nearly as much as small ones to the total.

The methods used to date to provide independent measures of particle size unfortunately have a lower limit of resolution of about 1 μm and a falling-off of accuracy as this limit is approached. Direct evidence of the dominance of particles of this size and smaller is thus lacking. Most of those who conclude that these small particles account for most of the scattering do so on the basis that their assessment of somewhat larger size fractions fails to account for the observed optical effects. Particle sizes above those measured may also contribute to variation of scatter, although preliminary experiments (Owen 1972) show that this is not the case where my measurements were made.

There is, on the other hand, agreement based on measurement that light scattering is predominantly due to particles that are large compared with the scattered wavelength: nearly every observation in natural waters exhibits an intense forward component of scattered light and independence of wavelength over much of the visible spectrum.

Theory

From the Mie (1908) solutions for scattering of a monochromatic plane wave incident on a homogeneous, isotropic sphere, van de Hulst (1957) derived an expression relating the volume scattering coefficient s to the total particle cross section $N\pi r^2$

$$s(\lambda, r, n) = \int_0^\infty Q(\lambda, r, n)N(r)\pi r^2 dr. \quad (1)$$

The term Q is the scattering efficiency, the ratio of the light flux scattered at wavelength λ by a particle of radius r and relative index of refraction n to the flux incident on the particle. The scattering efficiency of single particles is related by the Mie theory to wavelength, particle radius, and index of refraction (Fig. 1, curve a). In the presence of a range of particle sizes, the oscillatory character of Q is smoothed (curve b—van de Hulst 1957). This damping effect was confirmed experimentally by Hodkinson (1963), who worked with polydisperse suspensions of irregularly shaped particles (curve c). He also demonstrated that particles of irregular shape scatter as would spheres of equivalent volume. Hodkinson's results are of immediate interest because they confirm theory by the use of suspensions similar to those encountered in the sea in that both have a wide range of particle sizes and shapes.

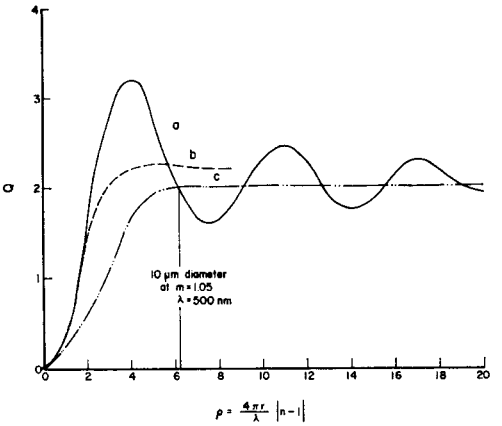

Fig. 1. Scattering efficiency Q as a function of the particle size parameter ρ. a—Function for single spherical particles; b—function for a polydisperse ensemble of spheres; c—experimental function observed for polydispersed ensembles of irregularly shaped particles.

Methods of measurement and data analysis

Measurements of particle size distribution and light scattering were made at 12 stations off the west coast of Baja California and of size distribution alone at two additional stations (Fig. 2). At stations where paired measurements were made, a submersible scattering meter was lowered slowly to 100 m to provide a continuous trace on a shipboard recorder of scatter vs. depth. Upon recovery of the scattering meter, cleansed polycarbonate sampling bottles were lowered to capture water for

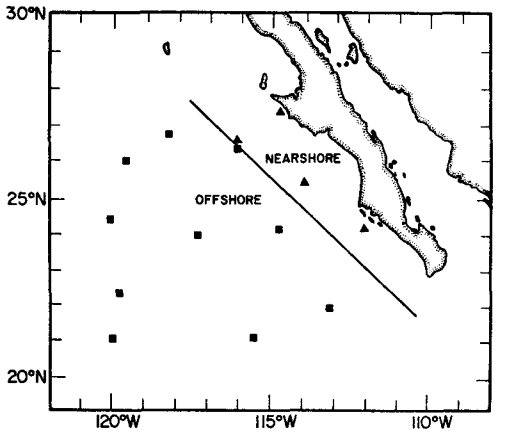

Fig. 2. Measurement locations off Baja California. Also shown is the separation of "nearshore" and "offshore" stations used (*see text*).

particle size analysis from one to four depths selected on the basis of the scatter record obtained minutes before; these were subsampled gently on recovery and particle size analyses performed within an hour. The scatter measurement was made at the single forward angle of 20°, chosen to maximize the light flux sensed by a multiplier phototube from a 0.6 cm^3 volume irradiated by a collimated light beam while still maintaining a well defined forward angle (*see* Owen 1972).

Particle size analyses were made with a Coulter counter (model B, Coulter Electronics) using general procedures given by Sheldon and Parsons (1967) for calibration and operation. Sensitivities and threshold settings were chosen to obtain particle counts in size categories that would yield numbers of particles in arithmetic and geometric progressions of particle cross-sectional areas for each sample. Numbers of particles were measured over intervals of 1.0 μm^2 from 2–16 μm^2 and over intervals of 2^n μm^2 from $n = 1$ through $n = 10$, i.e. from 2–1,000 μm^2 (1.6–36 μm equivalent diameters). A 50 μm diameter orifice was used to count particles up to 6.4 μm diameter and a 100 μm orifice thereafter. Counts made at sea were repeated when it was seen that the ship's motion caused back flushing of the sample or when clogging occurred. Counts in each size interval usually were replicated and repeated when differences exceeded roughly 5%. Methods of the particle size analysis are described elsewhere (Owen 1972).

One source of error was found by matching particle samples with values on the continuous vertical profile of scattering—vertical displacement of the pycnocline between measurements was occasionally apparent from measurement of temperature and salinity profiles obtained before and after scattering meter and sampling bottle casts and from comparison of the light scattering profile with computed water density structure. To reduce these matching errors, where they were obvious, alternate values of scattering were determined by shifting the scattering profile vertically to obtain closest consistent agreement between scattering and profiles of particle mass and carbon concentration in the pycnocline layer. A better fit could be found because the latter particle measurements were more closely spaced. These "best fit" values are shown separately and used for computation herein. Clearly, however, residual errors from this source of variation remain because not all profile pairs could be matched perfectly.

Scattering efficiency for each particle size interval analyzed in the Coulter counter was estimated graphically by finding the respective Q values from Hodkinson's (1963) experimentally determined curve (curve c, Fig. 1) which corresponds to each value of ρ. Values of ρ, in turn, were computed from the midpoint particle radius r of each size interval from the equation

$$\rho = (4\pi r/\lambda)|n - 1|,$$

using 500 nm for the wavelength λ, close to the peak sensitivity of the scattering meter used, and 1.05 for the relative refractive index of the particle ensembles measured.

The value 1.05 for the refractive index was chosen as the most likely one for particle ensembles in surface waters having

small sediment loads. The true value and variation of the index for surface layers are as yet only approximately known, but are converging to a value such as that used here with application of new methods (e.g. Gordon and Brown 1972; Carder et al. 1972; Zaneveld and Pak 1973). Values for individual components range widely (Jerlov 1968) but it is obvious that natural ensembles within specific areas and depths of the open sea have more nearly constant composite indices of refraction because the composition of such ensembles is not highly variable. The possibility that refractive index may be size dependent in surface layer waters cannot yet be evaluated. Differentiation of the composite refractive index into two components is desirable to the extent that the composite refractive index is size dependent. Gordon and Brown (1972) attempted to distinguish organic and inorganic fractions from their derived composite refractive index of 1.05 (for Sargasso Sea particles). They found that differences between each of their two-component models were, in fact, sensitive to whether size dependence of the refractive index was assumed, and that, in each case, organic particles dominated over inorganic. Brown and Gordon (1973), constructing two-component models, concluded that only models with organics predominating at small size ranges (<2.5 μm) and inorganics predominating at larger size ranges could account for observed scattering. Their argument would, however, be altered by using an index of refraction somewhat higher for the organic fraction than the 1.01–0.01i used.

From the values of scattering efficiency and of particle numbers measured in each size category (i), I computed the optically effective area (OEA_i) by a form of the integrand of equation 1

$$OEA_i = Q_i N_i A_i,$$

where A_i is the midpoint cross-sectional area of equivalent spheres in the size category.

To make the data from all samples comparable, I summed the OEA_i values for each sample over the observed range of sizes (1.6–36 μm diameter) to obtain a total measured OEA and computed the percent contribution to the total for each size category. These percentages were then averaged over all comparable stations within each size category for a composite of percentages as a function of diameter. Variation about these mean values was too small to plot geographically in the important small size categories. Individual station plots of OEA vs. particle diameter are available from me or may be computed from the individual plots of particle size distributions given elsewhere (Owen 1972). The final step was to remove the effect due to unequal size intervals from the percentage distribution: cumulative percentages were plotted as a function of diameter, a smooth line was drawn through the points and then differentiated by graphical methods to yield the distributions shown in Figs. 3 and 4.

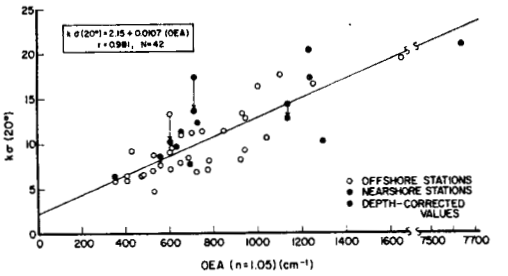

Fig. 3. Correspondence of forward light scattering at 20° off the beam axis with total measured optically effective area (OEA) from 42 paired observations. The relationship and correlation coefficient r, computed statistically, are shown in the inset. Values corrected for depth-matching error (cf. text) are shown as solid circles and are connected to the uncorrected plot.

Results

To demonstrate the correspondence of OEA computations to measured optical values, the relationship of 20° light scattering to OEA concentration of particles from 1.6–36 μm diameter, the size range indicated by Morel (1973) to contribute about 80% to scattering at this angle, is shown in Fig. 3. The correlation coefficient of 0.98,

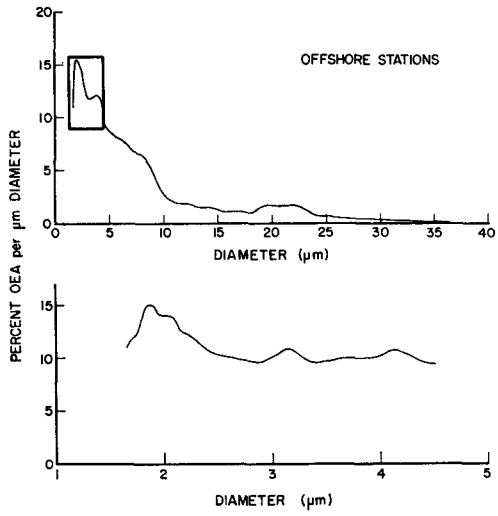

Fig. 4. Composite percent contribution to total measured optically effective area (OEA) per unit particle diameter as a function of particle diameter from 35 samples at offshore stations. Upper panel presents an independently determined subsection of the function shown in the lower panel.

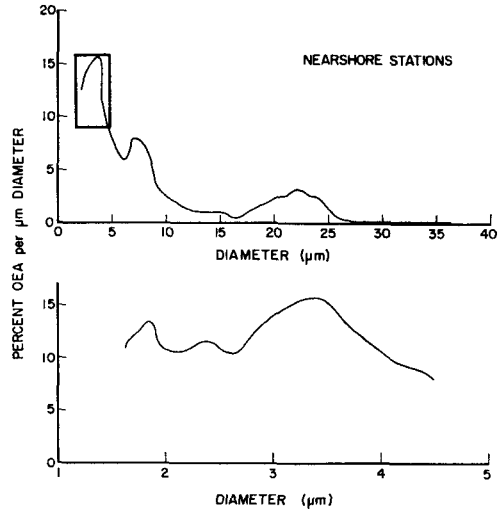

Fig. 5. Same as Fig. 4 except from 11 samples at nearshore stations.

computed using depth-corrected data pairs shown in the figure, can be considered good in view of the sources of error. These sources include variation of particle size distribution beyond the stated limits of measurement; possible variation between samples of the composite refractive index; variation of the relationship of 20° scatter to total scatter; error not already accounted for in the depth matching of discrete samples with scattering profiles. The last two sources are likely to contribute more to the residual variance than the others, although it is obviously desirable to obtain measurements of size distribution of particles below 1.6 μm and above 36 μm diameter.

The contribution by particles of given size to total OEA, determined as described above, is shown in Fig. 4 (offshore stations) and Fig. 5 (nearshore stations). This separation of offshore and nearshore stations was made on the basis of the consistent differences between particle size distributions and physical oceanographic characterstics (*see* Owen 1972). Stations were divisible by these criteria into two discrete groups, one located in an upwelling-influenced area off the west coast of Baja California and the other contiguous and seaward of the first. The difference between these areas also is apparent from the OEA percentages: contributions from particles in the vicinity of 7 μm diameter and 22 μm diameter, relatively pronounced in the nearshore group, are much attenuated offshore. Identification of these particles was not done although it is reasonable to consider them a biological expression of upwelling.

Perhaps the most significant feature of these curves is the maximum OEA contribution that occurs at about 2 μm diameter offshore and 3.5 μm diameter nearshore. This denotes that particles smaller than 2 μm make a decreasing contribution to light scattering with decreasing diameter, even though they are increasingly numerous (Carder et al. 1971; Owen 1972; Sheldon et al. 1972). This maximum and the subsequent decrease occur because the scattering efficiency of particles decreases (cf. Fig. 1) although it has not previously been demonstrated that the scattering efficiency decreases faster with decreasing

particle size than the corresponding increase in particle cross-section concentration in seawater.

The curves lend support to those workers who have inferred that particles < 5 μm diameter dominate light scattering in natural waters. They do not, however, support the contention that particles with diameters less than 1 μm contribute most heavily to light scattering in the euphotic zone of waters without heavy sediment loads. A growing body of evidence (Carder et al. 1971; Owen 1972; Sheldon et al. 1972) suggests a general constancy over a wide range of particle sizes of the size distribution of particles in the upper layers of the open sea. Even though particles < 1.6 μm diameter were not measured here, the roll-off below 2–3 μm is an indication that the OEA contribution from particles < 1.6 μm continues to decrease with decreasing size.

The tendency to dominance by smaller particles in clear oceanic waters, noted by Kullenberg (1969) in comparing three widely separated areas, is confirmed here in comparing contiguous rich and poor waters. Kullenberg's finding that a predominance of particles at 3.5 μm diameter occurs in the Baltic, however, is only fortuitously close to the nearshore value shown here, because Kullenberg assumed normal distribution of particle sizes.

The quasi-stationary distribution of particle size referred to above also suggests generality of the form of the contribution to OEA from various particle sizes shown in Fig. 4. The location of the maximum contribution to OEA is sensitive to the composite refractive index of the particle ensembles. Subsequent work may show a value different from that used in the calculations presented here (1.05) or a variation of values. Refractive indices larger than 1.05 would shift the contribution maximum to smaller particle diameters: this would be expected in the deep ocean where small inorganic particles predominate. The point remains, however, that a maximum likely exists in the important upper 100 m of the sea, and that it is probably located at diameters of particles that can be measured conveniently in unpreserved whole water samples in the field.

Particles in the upper layers of the sea, as pointed out by K. Carder (personal communication), could have size-dependent refractive indices. Partly because this would affect the size of maximum contribution to light scattering, independent measurements of refractive indices are needed for natural particles, especially at the poorly understood small size fractions. Work with two-component models such as that of Brown and Gordon (1973), together with firmer estimates of refractive indices, should be helpful.

References

BADER, H. 1970. The hyperbolic distribution of particle size. J. Geophys. Res. **75**: 2822–2830.

BEARDSLEY, G. F., JR., H. PAK, AND K. L. CARDER. 1970. Light scattering and suspended particles in the eastern equatorial Pacific Ocean. J. Geophys. Res. **75**: 2837–2845.

BROWN, O. B., AND H. R. GORDON. 1973. Two component Mie scattering models of Sargasso Sea particles. Appl. Optics **12**: 2461–2465.

BURT, W. V. 1955. Interpretation of spectrophotometer readings on Chesapeake Bay waters. J. Mar. Res. **14**: 33–46.

———. 1958. Selective transmission of light in tropical Pacific waters. Deep-Sea Res. **5**: 51–61.

CARDER, K. L. 1970. Particles in the eastern Pacific Ocean: their distribution and effect upon optical parameters. Ph.D. thesis, Oregon State Univ. 140 p.

———, G. F. BEARDSLEY, JR., AND H. PAK. 1971. Particle size distribution in the eastern equatorial Pacific. J. Geophys. Res. **76**: 5070–5077.

———, R. D. TOMLINSON, AND G. F. BEARDSLEY, JR. 1972. A technique for the estimation of indices of refraction of marine phytoplankters. Limnol. Oceanogr. **17**: 833–839.

DUNTLEY, S. Q. 1963. Light in the sea. J. Opt. Soc. Am. **53**: 214–233.

GORDON, H. R., AND O. B. BROWN. 1972. A theoretical model of light scattering by Sargasso Sea particulates. Limnol. Oceanogr. **17**: 826–832.

HANAOKA, T., A. FURUKAWA, AND K. NAGAMI. 1960. Studies on suspended matter in the sea. 4. On the relation between suspension factor, extinction coefficient and turbidity. Bull. Jap. Soc. Sci. Fish. **26**: 469–471.

HINZPETER, H. 1962. Messungen der Streu-

funktion und der Polarisation des Meerwassers. Kieler Meeresforsch. **18**: 36–41.

HISHIDA, K. 1966. On the scattering and the attenuation of light in the sea water. J. Oceanogr. Soc. Jap. **22**: 1–6.

HODKINSON, J. R. 1963. Light scattering and extinction by irregular particles larger than the wavelength, p. 87–100. *In* M. Kerker [ed.], Electromagnetic scattering. Macmillan.

JERLOV, N. G. 1955. Factors influencing the transparency of the Baltic waters. Medd. Oceanogr. Inst. Goteborg **25**: 1–19.

———. 1961. Optical measurements in the eastern North Atlantic. Medd. Oceanogr. Inst. Goteborg, Ser. B 8. 40 p.

———. 1968. Optical oceanography. Elsevier.

JOSEPH, J. 1955. Extinction measurements to indicate distribution and transport of water masses. Proc. UNESCO Symp. Phys. Oceanogr., Tokyo, 1955, p. 59–75.

KREY, J. 1961. Der Detritrus im Meere. J. Cons., Cons. Int. Explor. Mer **26**: 263–280.

KULLENBERG, G. 1969. Light scattering in the central Baltic. Copenhagen Univ., Inst. Phys. Oceanogr. Rep. 5. 12 p. + 6 Figs.

LISITSIN, A. P. 1961. Distribution and composition of suspended materials in seas and oceans, p. 175–231. *In* Recent sediments of the seas and oceans [transl. S. S. Rodolfo]. USSR Acad. Sci., Comm. Sediments, Div. Geol. Geogr. Sci.

MIE, G. 1908. Beiträge zur Optik trüber Medien, speziell kolloidalen Metallösungen. Ann. Phys. **25**: 377.

MOREL, A. 1973. Diffusion de la lumiere par les eaux de mer. Resultats experimentaux et approche theorique. NATO-AGARD Lecture Ser. 61, Sect. 3.1. 76 p.

OCHAKOVSKY, Y. E. 1966. On the dependence of the total attenuation coefficient upon suspensions in the sea. U.S. Dep. Comm. Jt. Publ. Res. Serv. Rep. 36, 8165, p. 16–24.

OWEN, R. W., JR. 1972. The scattering of light by particulate substances in the sea. Ph.D. thesis, Univ. Calif., San Diego. 235 p.

PAK, H., J. R. V. ZANEVELD, AND G. F. BEARDSLEY, JR. 1971. Mie scattering by suspended clay particles. J. Geophys. Res. **76**: 5065–5069.

PICKARD, G. L., AND L. F. GIOVANDO. 1960. Some observations of turbidity in British Columbia inlets. Limnol. Oceanogr. **5**: 162–170.

SASAKI, T., N. OKAMI, G. OSHIBA, AND S. WATANABE. 1960. Angular distribution of scattered light in deep sea water. Rec. Oceanogr. Works Jap. **5**: 1–10.

———, ———, ———, AND ———. 1962. Studies on suspended particles in deep sea water. Sci. Pap. Inst. Phys. Chem. Res. (Tokyo) **56**: 77–83.

SHELDON, R. W., AND T. R. PARSONS. 1967. A practical manual on the use of the Coulter counter in marine science. Coulter Electronics, Toronto. 66 p.

———, A. PRAKASH, AND W. H. SUTCLIFFE, JR. 1972. The size distribution of particles in the ocean. Limnol. Oceanogr. **17**: 327–340.

TUCKER, S. P., R. D. WAER, AND L. A. YESKE. 1969. The correlation of oceanic parameters with light transmissivity in Monterey Bay, California. (Abstr.) Opt. Soc. Am., 1969 Spring Meeting Program, p. 9.

VAN DE HULST, H. C. 1957. Light scattering by small particles. Wiley.

ZANEVELD, J. R. V., AND H. PAK. 1973. Method for the determination of the index of refraction of marine particles suspended in the ocean. J. Opt. Soc. Am. **63**: 321–324.

ZEITZSCHEL, B. 1970. The quantity, composition and distribution of suspended particulate matter in the Gulf of California. Mar. Biol. **7**: 305–318.

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