

Particle Aggregation

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Key Words

coagulation, marine snow, particle flux

Abstract

A basic problem in marine biogeochemistry is understanding material and elemental distributions and fluxes in the oceans, and a key part of this problem is understanding the processes that affect particulate material in the ocean. Aggregation of particulate material is a primary process because it alters the transport properties of particulate material and provides a mechanism for transferring material from the dissolved into the particulate pools. Aggregation theory not only provides a framework for understanding these processes, but it also provides a means for making predictions and has been successfully used to predict maximum particle concentrations in the oceans and the fate of diatom blooms (including those from iron fertilization), the size spectra of particles in the oceans, and the size distributions of trace metals. Here we review the basic theory involved, summarize recent developments, and explore unresolved issues.

Colloid: particulate material less than 1 μm in size

Marine snow: macroscopic aggregates millimeters or centimeters in size

INTRODUCTION

Particle aggregation is a major pathway for the formation and transformation of organic and inorganic material in the ocean. Changes in particulate concentration and size affect the fate and distribution of chemical elements within the water column, as well as light penetration into the water column. Similarly, changes in abundance of particles of different size affect their availability for zooplankton grazing and vertical flux.

Particulate material in aquatic systems ranges in length continuously from submicron (colloidal) scales (Wells & Goldberg 1992) to macroscopic particles (marine snow) that can be millimeters or centimeters in size (Alldredge & Silver 1988). The size of any individual particle in this range helps determine its characteristics and interactions with organisms, other particles, and its environment. The traditional division between particulate and dissolved material is an operational, size-dependent one: Traditionally, material that passes through a 0.4- μm filter is usually classified as dissolved. An example of the importance of size is that 1-nm particles are suspended in the water column, whereas cm-sized particles can sink. However, the fates of material at these two ends of the size distribution are related through aggregation and disaggregation processes that move material up and down the particle size range. Thus, aggregation can increase the removal rate of material in the form of small suspended particles by transforming them into large, rapidly settling particles.

The physical process of particle aggregation has not always been regarded as important in marine systems. Early studies demonstrated that particles had to somehow increase their settling velocity to explain patterns of benthic sedimentation (Rex & Goldberg 1958, Arrhenius 1963) and rapid sinking of diatoms at the end of a bloom (Smayda 1970). In both cases, physical aggregation processes, which could repackage material into faster-settling particles, were discounted because the concentrations of particles were regarded as being too low (Smayda 1970, McCave 1972). However, in some areas these processes were known to play a vital role. For example, a combination of aggregation (via Brownian motion) and sedimentation was argued to be important in controlling the fate of inorganic material delivered to the ocean (Hahn & Stumm 1970). Similarly, bubbles were found to enhance aggregation by forming organic aggregates from dissolved material (Riley 1963, Kepkay & Johnson 1989).

Measurements of the particle size distribution in the world's oceans showed that, to a first approximation, the distributions were well described by a power law (Sheldon et al. 1972). McCave (1975), reversing an earlier opinion, concluded that aggregation of particles is the norm and is sufficient to remove material rapidly from the surface waters, although he emphasized biological aggregation by zooplankton feeding and fecal pellet production. A combination of physical aggregation and sedimentation was later used to explain the observed shapes of the particle size distribution in the water column (Hunt 1980) and in nepheloid layers (McCave 1984).

Our understanding of aggregation processes, their roles, and factors that affect their efficiencies has improved in recent years (McCave 1984, Jackson & Burd 1998, Thornton 2002). Physical aggregation of particulate material has been successfully used to explain many phenomena in the oceans, including the sinking of diatom blooms (Jackson 1990, Thornton 2002), particle size distributions and fluxes in the midwater zone (Stemmann et al. 2004b, Kriest & Evans 2000), the scavenging of trace metals in the ocean (Honeyman & Santschi 1989, Burd et al. 2000), and the dynamics of nepheloid layers (McCave 1983, Hill & Nowell 1990). Physical aggregation of particulate material has also been used to study the fate of inorganic material in estuaries (Eisma 1986, Edzwald et al. 1974) and freshwater systems (Snodgrass & O'Melia 1975, O'Melia 1980, O'Melia & Bowman 1984, Weilenmann et al. 1989, Zimmermann-Timm 2002).

In this review, we concentrate on recent progress in our understanding of the physical processes of particle aggregation and the consequences for organic material in marine systems (**Figure 1**).

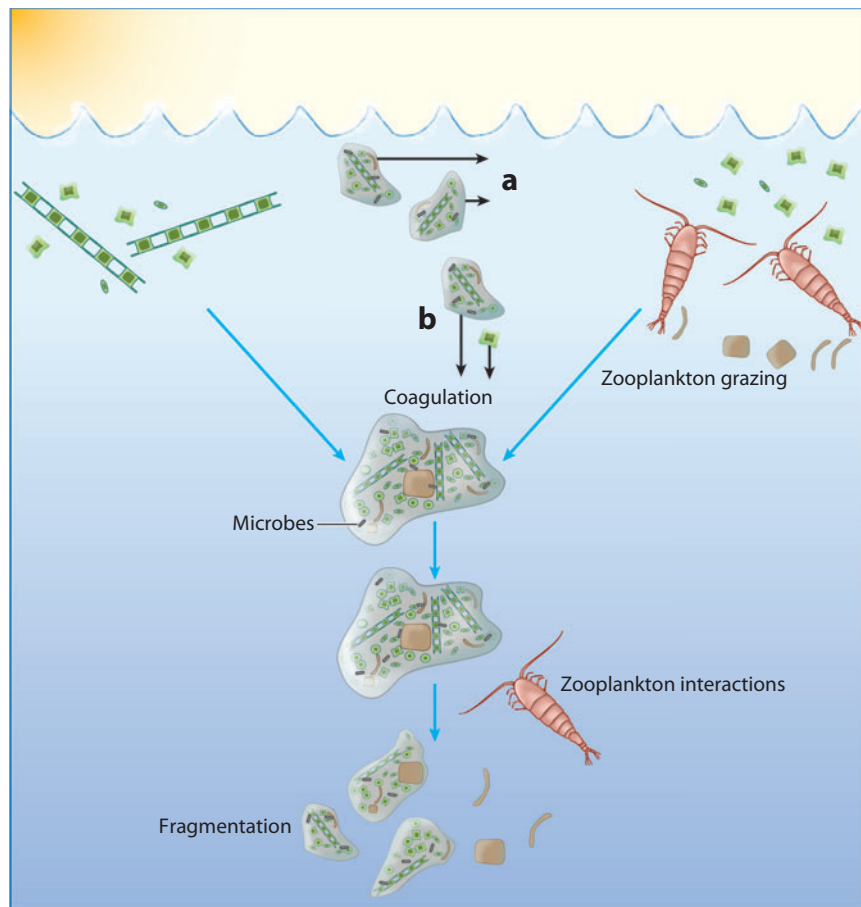


Figure 1

Particle aggregation processes and how they affect particles in the marine environment. Biological aggregation (e.g., fecal pellet production) and physical aggregation by (a) shear and (b) differential sedimentation form large, heterogeneous, rapidly settling particles in the surface waters. In deeper waters, fragmentation and repackaging of this material by zooplankton are the dominant processes that affect aggregate sizes and properties. Microbes decompose material throughout the water column.

Physical processes that bring particles into contact with each other are studied under the label of coagulation. Biological processes are also important in the formation and decomposition of particulate material, but are more complex and involve the formation of constituent particles and colonization (Simon et al. 2002, Kiørboe et al. 2003, Grossart et al. 2006).

We refer the reader to recent excellent reviews for more information on related topics such as diatom aggregation (Thornton 2002), transparent exopolymer particles (TEP) (Passow 2002), and the ecology of microbial communities on marine aggregates (Simon et al. 2002).

OBSERVATIONS OF AGGREGATION

Aggregates of detrital organic material have been observed in marine systems for many years (Riley 1963). This material was originally thought to consist of fecal matter and the remains of plankton

Coagulation: the physical processes that bring particles together

TEP: transparent exopolymer particles

Size spectrum: the differential particle size distribution

that were in various stages of dissolution. However, visual and photographic observations revealed the presence of abundant, large (>1 mm) marine snow aggregates (Suzuki & Kato 1953) that could remove a significant fraction of the organic material from surface waters (Shanks & Trent 1980).

The formation and sinking of aggregates are thought to be the mechanism by which diatom blooms terminate (Kranck & Milligan 1988, Jackson 1990, Riebesell 1991a, 1991b, Kiørboe et al. 1994). However, not all diatom blooms end in flocculation and sedimentation and the extent of aggregation varies with the diatom species, environmental conditions, and the production of extracellular polysaccharide material by the diatoms (Kiørboe et al. 1990, Passow 2002, Grossart et al. 2006).

Changes in average particle settling speed often signify the occurrence of aggregation. For example, typical sinking speeds of individual diatom cells range from 0.1–10 m d⁻¹ (Smayda 1970). However, diatoms have been observed on the deep-sea floor 2–3 weeks after a surface bloom, which requires vertical transport rates between 100 and 150 m d⁻¹ (Billett et al. 1983) and implies that individual cells must have been repackaged into faster-settling particles. Indeed, aggregates are observed in sedimenting material and have been photographed over time at different depths (Lampitt et al. 1993).

Laboratory and mesocosm experiments provide detailed observations of aggregate formation processes. The SIGMA program observed the coagulation of diatom aggregates in a mesocosm (Alldredge & Jackson 1995) and showed, among other things, that coagulation theory can explain changes in the particle size distribution (Jackson 1995a) and the importance of extracellular polysaccharides (Passow & Alldredge 1995, Dam & Drapeau 1995, Logan et al. 1995). Other recent experiments have examined the roles of particle stickiness (Engel 2000) and rates of aggregation (Prieto et al. 2002).

COAGULATION THEORY

Coagulation theory allows us to predict the changes in particle concentration and size that result from particles colliding and sticking. This process of colliding and sticking requires a relationship between particle size and concentration to form the basis of the equations that describe the aggregation dynamics. The particle size spectrum provides a simple, yet powerful way to represent that relationship.

The Particle Size Spectrum

Particulate material in marine systems is heterodisperse, with a diversity of particle sources that cover a wide range of particle sizes. As a result, the bulk properties of a population of particles change as these particles aggregate and disaggregate. The particle size spectrum [$n(s)$] is one way to characterize variations in the abundance of particles of different sizes and provides a means to calculate bulk properties of the particle population. The cumulative size distribution [$N(s)$] is the concentration of particles larger than a given size s and is related to $n(s)$ by

$$N(s) = \int_s^{\infty} n(s') ds', \quad n(s) = -\frac{dN}{ds}. \quad (1)$$

The size spectrum can be calculated with any measure of particle size, although particle diameter is most commonly used for observations and mass is most commonly used for theories. Spectra calculated via the use of different measures of particle size can be converted easily between one another using Equation 1. For example, to transform the particle size spectrum calculated with

respect to radius (r) to one with respect to particle mass (m) requires

$$\begin{aligned} dN &= -n(r) dr = -n(m) dm \\ n(m) &= n(r) \frac{dr}{dm}, \end{aligned} \quad (2)$$

where a relationship between the radius and mass of an individual particle must be known. Changing the measure of particle size also changes the units of the size spectrum. The dimensions of $n(r)$ are number length⁻⁴ whereas those for the spectrum with respect to mass [$n(m)$] are number length⁻³ mass⁻¹.

Useful properties of the particle population can be calculated by use of the moments of the particle size distribution. The i th moment (M_i) of a size distribution $n(s)$ calculated using a size parameter s is defined by

$$M_i = \int_0^\infty s^i n(s) ds. \quad (3)$$

Use of the particle size spectrum has the advantage that its moments are related to well-defined quantities of interest. For example, the zeroth moment of $n(d)$ is the total particle number concentration, and the second moment is proportional to the total surface area for spherical particles. Similarly, if some property of interest varies with particle size, the size spectrum can be used to calculate the bulk value of that property. The activity of the radio isotope ²³⁴Thorium (²³⁴Th) on particles with a radius larger than r_a can be expressed as (Burd et al. 2007)

$$^{234}\text{Th}(d_a) = \int_{d_a}^\infty \tau(d) n(d) dd, \quad (4)$$

where $\tau(d)$ represents the ²³⁴Th activity on a single particle of diameter d .

The differential size spectrum is particularly useful if all the important particle properties are simply related to one property, such as diameter, but observations show that this is not always true (Alldredge & Gotschalk 1988, Diercks & Asper 1997). In such cases, the size spectrum can be expanded to describe multiple particle properties, such as mass m and diameter d (Jackson 1998):

$$n(m, d) = \frac{\partial^2 N}{\partial m \partial d}. \quad (5)$$

Power laws are often used to represent marine particle size spectra. However, this practice can lead to inaccurate predictions. For example, large rare particles contribute most to mass flux, and apparently small deviations at large particle sizes from the power-law fit lead to inaccurate estimates of the mass flux (Figure 2).

The Coagulation Equations

Coagulation theory has long been used by atmospheric scientists to understand the dynamics of aerosol size distributions (Friedlander 2000). Hunt (1980) and McCave (1984) were among the first to rigorously apply this theory to marine aggregation and particle size distributions. The theory behind how coagulation affects a population of particles of different sizes was developed by Smoluchowski (1916) in the early part of the twentieth century. The rate of change of the particle size spectrum [$n(m, t)$] in a well-mixed layer of thickness z is given by an integrodifferential equation

$$\begin{aligned} \frac{dn(m, t)}{dt} &= \frac{\alpha}{2} \int_0^m \beta(m_j, m - m_j) n(m - m_j, t) n(m_j, t) dm_j \\ &\quad - \alpha n(m, t) \int_0^\infty \beta(m, m_j) n(m_j, t) dm_j \\ &\quad - n(m, t) \frac{w_s(m)}{Z} + I(m, t), \end{aligned} \quad (6)$$

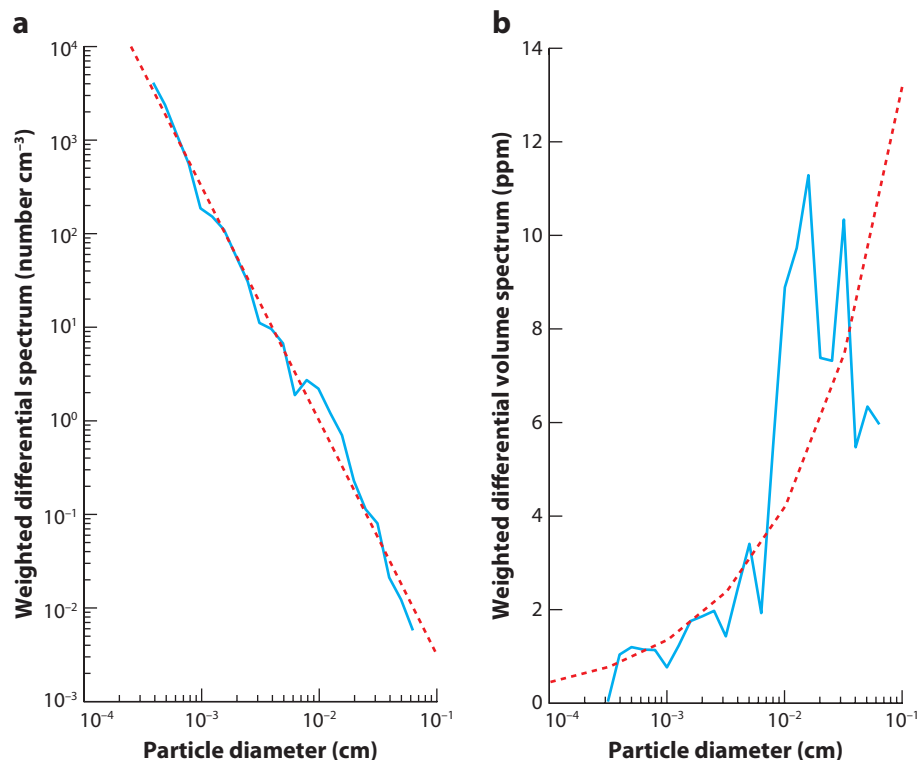


Figure 2

Different representations of particle size distributions: (a) the size-weighted particle size spectrum $[dn(d)]$ and (b) the weighted volume spectrum $[dV(d)m(d)]$. The advantage of the weighted spectrum is that the area under the curve of the weighted volume spectrum is proportional to the conserved volume for particles in that size range. The dashed line shows the best fit power-law spectrum in (a) and the weighted volume spectrum using that power law in (b). Data are from Monterey Bay (Jackson et al. 1997).

where m , $(m-m_j)$, and m_j are the masses of the particles involved in the collision, α is the stickiness (the probability that two particles will adhere once they have collided), Z is the depth of the water layer being considered, $w_s(m)$ is the settling velocity of a particle with mass m , $I(m,t)$ is the input rate of particles having a mass m , and $\beta(m_i, m_j)$ is called the coagulation kernel and determines the rate of collision between particles of masses m_i and m_j . The first term on the right-hand side of the equation represents all those collisions that add material in the size range m to $m + dm$, whereas the second term on the right-hand side represents those collisions that remove material from the same mass interval. The third and fourth terms represent the loss rate due to sedimentation and the input rate of new material, respectively. Importantly, Equation 6 deals only with physical coagulation and particle input processes and must be incorporated into a food-web model for biological coagulation to be included (Jackson 2001), and must be incorporated into an advective-diffusive framework to describe spatial variations.

The coagulation kernels contain information on the mechanisms that bring particles together. Traditionally, three broad categories of mechanism have been considered: Brownian motion, fluid shear, and differential sedimentation. A coagulation kernel can be formulated for each of these (Table 1), and the total kernel appearing in Equation 6 is their sum

$$\beta(m_1, m_2) = \beta_{Br}(m_1, m_2) + \beta_{sb}(m_1, m_2) + \beta_{ds}(m_1, m_2). \quad (7)$$

Table 1 Expressions for the coagulation kernels as functions of the particle radius (r). In these formulae, k is Boltzman's constant, T is the absolute temperature of the water, μ is the dynamic viscosity, γ is the shear gradient, ν is the kinematic viscosity, ε is the turbulent energy dissipation rate, and w_i is the settling velocity of a particle with radius r_i . Note that the fractal relationship (Equation 8) should be used to convert between the mass and radius for a given particle

Mechanism	Rectilinear kernel	Curvilinear kernel
Brownian motion	$\frac{2}{3} \frac{kT}{\mu} \frac{(r_i + r_j)^2}{r_i r_j}$	—
Laminar shear	$\frac{4}{3} \gamma (r_i + r_j)^3$	
Turbulent shear	$1.3 \left(\frac{\varepsilon}{\nu}\right)^{1/2} (r_i + r_j)^3$	$9.8 \frac{p^2}{1+2p^2} \left(\frac{\varepsilon}{\nu}\right)^{1/2} (r_i + r_j)^3$
Differential sedimentation	$\pi (r_i + r_j)^2 w_j - w_i $	$0.5 \pi r_i^2 w_i - w_j $

The relative importance of each of these mechanisms varies with particle size. For example, Brownian coagulation occurs when two particles are brought together by Brownian motion, and dominates the collision rate for small particles—in aquatic systems, this usually means particles with diameters less than 1 μm . As particle size increases, collisions arising from (turbulent or laminar) fluid shear, or faster-settling particles catching up with slower-settling ones, come to be more important (McCave 1984, Friedlander 2000). Differential sedimentation is an important aggregation process for particles of dissimilar size, and is therefore important for rapidly transporting material from small to large particles.

Expressions for some commonly used coagulation kernels are given in **Table 1**. The simplest expressions are the rectilinear kernels, which are derived from a consideration of the geometric collision cross section and the relative velocity of the particles. These expressions neglect hydrodynamic forces between the particles that act to decrease the particle collision rate. The curvilinear kernels take these forces into account and predict lower collision frequencies. A further complication arises from the increased porosity of fractal particles (Li & Logan 1997a, 1997b). Recent models of particle coagulation have included these effects (Jackson 2001).

Methods of Solving the Coagulation Equation

Unfortunately, Equation 6 admits a general analytical solution only under very restrictive assumptions about the form of the coagulation kernel (Drake 1972). Consequently, some form of approximation is required, which may take the form of a numerical solution to Equation 6 or may involve some assumptions about the form of the size spectrum or kernels that allow an analytic solution to Equation 6 to be found. Other assumptions, often motivated by a specific application, can be made that simplify Equation 6. We discuss some of these latter simplifications below in the section on applications of coagulation in aquatic systems.

Numerical methods. Researchers in colloidal and aerosol sciences (Zhang et al. 1999) have developed numerical algorithms to solve Equation 6. Sectional algorithms (Gelbard et al. 1980) are generally thought to produce the most accurate solutions and these have been used almost exclusively in studies of coagulation in marine sciences (Jackson & Lochman 1992, Ruiz 1997, Burd et al. 2000, Jackson 2001). This method approximates Equation 6 with a set of coupled, nonlinear ordinary differential equations by discretizing the particle size distribution, assuming an approximate form for the distribution within each interval.

Although accurate, the sectional approximation is ill suited to use in large-scale biogeochemical models because it is computationally expensive and can lead to significant numerical diffusion

Fractal dimension: the exponent in the mass-radius relationship for individual particles

(Seigneur et al. 1986). Faster, less accurate algorithms have been used to predict particle flux in one- and three-dimensional biogeochemical models (Kriest & Evans 1999, 2000; Gehlen et al. 2006). These methods rely on calculations of moments of the particle size distribution but require an assumed form for the particle size distribution. Moment-based algorithms have been used extensively in aerosol research and give results that agree within 5–10% of those obtained using more accurate algorithms. However, this might not be the case in marine systems because multiple particle sources, algal growth rates, and the interaction between multiple coagulation mechanisms must be considered.

Scaling and dimensional analysis methods. Some solutions of the coagulation equations can be obtained via the use of transformations with nondimensional scaling variables. The transformed coagulation equation can be solved assuming a steady state and if only one coagulation mechanism operates within a given range of particle size (Friedlander 2000). These asymptotic solutions are steady-state solutions that represent the particle size distribution that would be obtained after long periods of time and are independent of the initial conditions. Therefore, these solutions are only of academic use in marine systems where aggregation associated with phytoplankton blooms is important.

Dimensional arguments have been used to show that, in certain size ranges where a single aggregation process dominates, the size spectrum is a power law with a slope dependent on the aggregate fractal dimension (Hunt 1980, Jiang & Logan 1991). However, numerical simulations of steady state solutions of Equation 6 demonstrate that this assumption does not necessarily hold (Burd & Jackson 2002). What is more, naturally aggregating systems also involve particle disaggregation which can result in nonscaling (i.e., non-power-law) size distributions (Hansen & Ottino 1996, Burd & Jackson 2002).

IMPLICATIONS OF COAGULATION

The fact that particles are formed by coagulation has important consequences for the structure and properties of these particles. For example, the morphology of an aggregate is influenced by the processes that formed it, and the shape of the particle size spectrum is determined by the relative magnitudes of the source, sink, and aggregation terms in Equation 6.

Aggregate Morphology and Fractal Dimension

Aggregates formed by coagulation of identical source particles have a fractal geometry (Vicsek 1992) and can be characterized using a fractal dimension. For an aggregate formed from initially identical spheres having mass m_1 and radius r_1 , the relationship between the mass (m) and radius (r) of the aggregate is

$$\frac{m}{m_1} = \left(\frac{r}{r_1} \right)^D. \quad (8)$$

The fractal dimension (D) is the exponent in this relationship and gives an intuitive measure of how much the object fills the available space. Thus, a three-dimensional solid object would have an exponent of three. Fractal dimensions greater than three are physically impossible, and values of D less than three characterize objects that do not completely fill the three-dimensional space available to them. The fractal dimension of a particle formed by coagulation depends on both the collision mechanism that formed it and the stickiness (Jiang & Logan 1991).

The fractal nature of a particle affects its interactions with other particles and their environment. For example, the porosity of a fractal aggregate increases with the size of the particle, thereby affecting the density of the aggregate, its settling velocity, its collision frequency with other particles (Burd & Jackson 1997), and the advective transport within the particle as it moves through the water (Adler 1981, Veerapaneni & Wiesner 1996).

Fractal dimensions of marine aggregates have been estimated using particle size distributions (Li & Logan 1995, Jackson et al. 1995), size-porosity correlations (Logan & Wilkinson 1990), and photographic image analysis (Kilps et al. 1994). Reported values range from $D = 1.3$ to 2.3 . The particular method chosen to measure the size of a particle is not crucial for a determination of particle fractal dimensions, but must be chosen consistently (Bushell et al. 2002) and may not account for processes, such as restructuring of the aggregate, that alter D (Bushell et al. 2002). Indeed, a combination of measurements from different instruments requires a knowledge of what each is actually measuring (Jackson et al. 1995, 1997).

Ballast: mineral component of marine particles

Settling Speeds and Vertical Transformations

Directly measured settling speeds in the oceans vary from less than 1 m d^{-1} for single cells (Smayda 1970) to greater than 100 m d^{-1} for marine snow (Alldredge & Gotschalk 1988, Peterson et al. 2005). However, no universal relationship appears to exist between particle settling speed and particle diameter (Diercks & Asper 1997, Stemmann et al. 2004a), though such relationships may exist locally.

Accurate predictions of particle settling speeds in the oceans have remained elusive. Semi-empirical formulae give accurate predictions for the settling velocity of small, isolated impermeable spheres (Clift et al. 1978), but underestimate the settling velocities of fractal aggregates (Johnson et al. 1996). The settling rate of an aggregate depends upon its size and excess density—the difference between its average density and that of the surrounding water. However, the scaling of density with particle size differs between a solid and fractal particle and better estimates for settling speeds in the laboratory have been obtained by modeling the permeability of the particle using either Brinkman's or Happel's equations (Li & Logan 2001).

The density of a particle changes with its sinking speed. Chemical and biological processes alter the relative composition of aggregates as they sink through the water column, thereby altering their settling speed. At depths of approximately 2000 m, most of the organic material in the aggregate has been remineralized, leaving particles composed of largely mineral ballast (Armstrong et al. 2002). However, the precise relationship between organic and mineral material in aggregates remains unclear (Passow & De La Rocha 2006).

Sampling and Counting Statistics

The shape of the particle size spectrum predicted by Equation 6 implies that large particles are rarer than small ones. This has profound consequences for sampling and counting particles, depending on what is being measured. For example, large rapidly settling particles contribute significantly to the vertical flux of material. However, because they are relatively rare, large volumes of water need to be sampled to capture a representative number of these particles (McCave 1975, Burd et al. 2007). Undersampling large particles may not be a problem for estimates of total particulate abundance or mass. However, measurements related to particle flux will be underestimates.

Most measurements of particulate material in oceanography are bulk measurements of some property of interest. However, if the property of interest varies with particle size, then such measurements conflate two things: size variation of the property of interest and the particle size

POC: particulate
organic carbon

spectrum. For example, ^{234}Th is thought to be a surface-active radioisotope, and so the amount of ^{234}Th on a single particle should scale with surface area of that particle (Buesseler 1998) (or more accurately with the number of available surface binding sites, which we can assume to be proportional to the particle surface area). However, the available surface area for a given size class of particles also depends on the particle size spectrum (Equation 3). So measurements of the variation of ^{234}Th activity with particle size are actually measuring two things. This makes comparison of size-dependent particle properties prone to misinterpretation (Burd et al. 2007).

APPLICATIONS OF COAGULATION IN MARINE SCIENCES

Colloids and Adsorption

Small particles typically have a higher surface area to volume ratio, more effective transport from solution than larger particles, and are consequently more efficient at scavenging surface active elements from the water. However, measured trace element concentrations are typically far lower than those predicted from mineral solubility calculations (Honeyman & Santschi 1989). This observation can be explained by the colloidal (or Brownian) pumping model in which elements sorb onto colloidal particles (which are far more numerous than larger, rapidly sinking particles), which subsequently aggregate to form operationally defined particulate material (Honeyman & Santschi 1989). The apparent rate of sorption of the elements onto macroscopic aggregates will be controlled by the coagulation rate if sorption onto the colloids occurs on faster timescales than the coagulation of the colloids. Such a theory has been applied to the scavenging of various trace metals, in particular ^{234}Th (Honeyman & Santschi 1989, Burd et al. 2000). Honeyman & Santschi (1989) used a simplified coagulation model (Farley & Morel 1986) that predicted particle flux as a function of total particle concentration. Burd et al. (2000) solved a coupled adsorption-coagulation model numerically over a particle size range from 10 nm to 1 mm, making detailed predictions of the size-specific Th concentrations and size-specific particulate organic carbon (POC) to ^{234}Th ratios. The predicted POC/ ^{234}Th ratio decreased with increasing particle size in the colloidal size range, becoming approximately constant for particles larger than approximately 1 μm . This trend is similar to that seen at times in the ocean (Buesseler et al. 2006) and the predicted POC/ ^{234}Th values fell within observed ranges for all particle size classes. As a result, when particle flux is dominated by large aggregates, the POC/ ^{234}Th estimated on small particles is a good approximation for the POC/ ^{234}Th of large, sedimenting particles. This will not hold if the particles are not fractals, i.e., were not formed from physical aggregation processes such as shear and differential sedimentation (Burd et al. 2000, Buesseler et al. 2006).

Coagulation in Food Webs

Coagulation affects the evolution of food webs in ways that can be unexpected. Models of phytoplankton growth that incorporate nutrient and light limitation combined with coagulation demonstrate that coagulation is effective at limiting the concentration of algal cells by rapidly removing cells that are still capable of dividing (Jackson & Lochman 1992). What is more, as nutrients become limiting and the stickiness (α) changes, coagulation becomes more effective and removal of algal cells by sedimentation increases.

Food webs generate multiple sources of detrital material such as fecal pellets and dead algal cells. The coagulation of particles with such different properties requires an extension of the concept of the particle size spectrum to a two-dimensional spectrum, Equation 5 (Jackson 1998, 2001).

Such models demonstrate that there is no simple parameterization that relates particle flux and algal concentration, and even the relationship between flux and total particle concentration is a weak one. Different approaches have been used to incorporate mineral ballasting into aggregation models and indicate that both are required to drive an intense biological pump (Gehlen et al. 2006). Versions of the model that do not include mineral ballast overestimate particulate carbon fluxes in the mesopelagic; however, it is precisely this region where zooplankton grazing has a strong effect on particle flux and the particle size distribution (Stemmann et al. 2004b, Gehlen et al. 2006).

Combined food web–coagulation models provide insight into the links between physical and biological aggregation processes (Jackson 2001). These two processes are not strictly exclusive or competitive because fecal pellets can be incorporated into aggregates by physical processes. Consequently, one cannot assume that detritus and fresh algal material are distinct model compartments when zooplankton grazing controls the maximum detrital particle size. Conversely, when aggregation controls the vertical flux of material strong variability exists in both the average particle sinking velocity and the absolute particle flux. This phenomenon arises because of the occasional formation of large, rapidly sinking particles (Jackson 2001) and demonstrates that accurate model predictions of particle flux must incorporate both aggregation and a particle size distribution that resolves large particles.

Other aggregation models have been coupled to food web models and applied to data from the Arabian Sea (Kriest & Evans 2000). These models assume power laws for the particle size spectrum and so force the distribution of particle sizes to a particular form. However, these models demonstrate the importance of aggregation and particle stickiness for understanding particulate fluxes at depth. For example, if a high value of the stickiness is assumed ($\alpha = 0.5$), then peaks in flux occur at depths as great as 800 m.

Simple Solutions of the Coagulation Equations

Critical concentration. Coagulation occurs most readily under conditions of high particle concentration, such as occur at the end of a diatom bloom. Under these circumstances, simplified coagulation models can be combined with phytoplankton growth models to produce simple prognostic predictions, such as the existence of a maximum particle concentration, despite continued algal growth (Jackson 1990, 2005). The predicted maximum cell number concentration is (Jackson 2005)

$$C_{cr} = \frac{\mu}{1.3\alpha\gamma 8r_1^3}, \quad (9)$$

and the equivalent equation for volumetric concentration is

$$V_{cr} = \pi \frac{\mu}{8\alpha\gamma}, \quad (10)$$

where r_1 is the radius of a single algal cell, μ is the cell specific growth rate, γ is the shear rate, and α is the stickiness. This equation results from a balance between the formation of aggregates through cell growth and coagulation, and their loss from the system by sinking. Interestingly, the formulae for the critical concentration do not depend on the particle settling velocity.

The critical depth idea of Sverdrup effectively sets a maximum phytoplankton concentration that can be sustained by photosynthesis for a given mixed layer depth. Jackson (2008) combined a coagulation model with a photosynthesis model to explore how the two interact.

Change in particle concentration in a shear reactor. The standard method for estimating particle stickiness involves coagulating particles in a chamber with an imposed shear rate. For an

initially monodisperse system, coagulation theory predicts a simple result for the initial change in total particle number (Camp & Stein 1943, Birkner & Morgan 1968, Kiørboe et al. 1990). For appropriate simplifications, the coagulation equations can be solved for the total particle concentration

$$C_t = C_0 e^{-4\alpha\gamma t/\pi}, \quad (11)$$

where C_0 and C_t are total particle concentrations at times 0 and t , α is the stickiness, and γ is the average shear rate. Using Equation 11 with measurements made from shear reactors provides the dominant method used for estimating the stickiness (α). Although stickiness is theoretically a well-defined property, it needs to be borne in mind that quoted values are actually obtained from fits to Equation 11.

Vertical processes. To test the effect of particles falling through the water column, G. Jackson (unpublished data) examined the effect of multiple layers on particles formed by coagulation of growing algae in the surface layer. Particulate mass in deeper layers arrived by falling particles from the overlying layer and was lost to the next deeper layer.

Particle distributions near the surface were dominated by growing algae, the smallest particles of the simulations. Deeper layers shifted to larger particles, because the slower-settling velocities of small particles supplied fewer small particles and coagulation moved the mass of smaller particles from small to large. One result was an increase in the average settling rate of particle mass; the average velocity was 13 m d^{-1} from the surface layer and 175 m d^{-1} in the deepest layer (Figure 3).

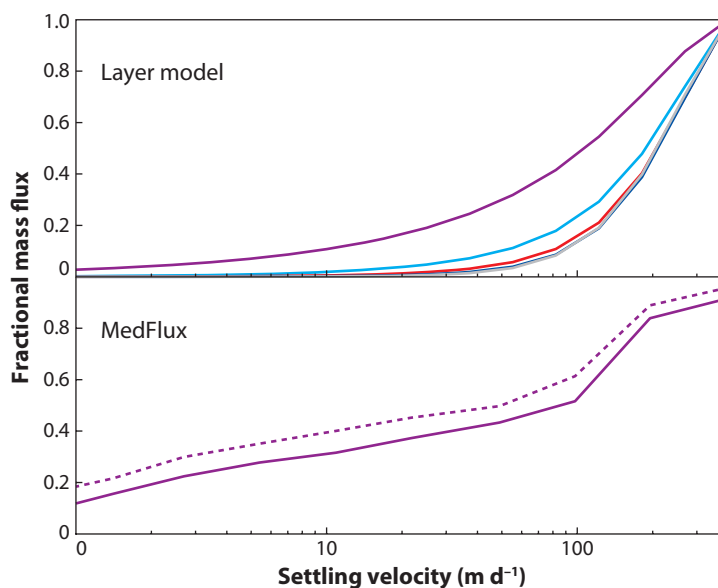


Figure 3

Particle flux as a function of settling velocity. The bottom panel shows the cumulative fraction of total flux as a function of settling velocity observed in Medflux at 200 m (Peterson et al. 2005); the top panel shows the cumulative fraction of total flux calculated using a 5 layer (each 50-m thick) coagulation model, with relative importance of particles with high sinking rates increasing with depth. Growth of single algal cells ($d = 10 \mu\text{m}$) occurs in the surface layer only. The maximum aggregate size is approximately 2 mm.

Stemmann et al. (2004a) described a series of processes that change particle concentrations and developed a series of expressions to describe how bacterial degradation and two types of zooplankton feeding affect the particle size spectrum. These researchers developed these expressions into a vertical model of particle size distributions that also included coagulation and settling. The particles came from an imposed particle size distribution in the surface layer. Resulting predicted distributions were compared with observations down to 900 m and the equations were solved (Stemmann et al. 2004b).

Representing coagulation in large-scale biogeochemical models. Large-scale biogeochemical models are used to calculate the vertical distributions of chemical elements and particle fluxes in the water column. However, these models usually calculate export using either highly parameterized relationships between production and export (Bacastow & Maier-Reimer 1990) or food web models of varying complexity (Fasham et al. 1993, Moore et al. 2004). The food web models in use have recently increased in complexity as a result of incorporating more components, such as multiple organism size classes and larger numbers of functional groups (Hood et al. 2006). Other export models have concentrated on using size-structured ecosystem models. A recent example is the model by Dunne and collaborators (2005), which also incorporates the features of an earlier deep-water ballast model (Armstrong et al. 2002). The increasing complexity of these models requires a corresponding increase in the constraints from appropriate observational data if they are to maintain or improve our predictive ability.

However, less attention has been paid to parameterizing the mechanisms that form large, rapidly sinking particles (Hood et al. 2006). Attempts have been made to parameterize the effects of coagulation on particle export in ecosystem models. This has been done by parameterizing particle export flux from the surface ocean as a quadratic function of production (Moore et al. 2002). Exported material is usually assumed to be remineralized instantaneously at depths immediately below those where the particles are produced. This is accomplished in practice by distributing the exported material with depth according to a Martin curve by using its depth derivative to obtain the remineralization rate of material.

Particle aggregation can also change the ecosystem dynamics. Jackson (2001) coupled a variation of an open ocean food web model (Fasham et al. 1990) to an aggregation model designed for heterogeneous particles (Jackson 1998). Modifications to the food web model included replacing the phytoplankton mortality with phytoplankton loss by aggregation and settling. Comparisons of model runs with and without aggregation demonstrated that, even at low particle concentrations observed in the oligotrophic gyres, this process could increase the average particle settling speed and increase the variability in flux throughout the year. By using a two-dimensional particle size spectrum to represent both aggregates and fecal pellets, Jackson was able to show that fecal pellet formation and aggregation both compete and interact with each other to remove algae and increase sinking particulate fluxes. This work indicated that there is no simple relationship between particle flux and algal concentration, such as those used in some biogeochemical models (Doney et al. 1996, Moore et al. 2002)—similar findings had been reported by Hill (1992). Jackson (2001) concludes that this result “suggests it is premature to use simple parameterizations to represent the effect of coagulation in planktonic food webs.”

Recently, attempts have been made to incorporate more realistic representations of particle aggregation into large-scale biogeochemical models (Kriest & Evans 1999, 2000; Gehlen et al. 2006). In these models, a moment method is used to solve the coagulation equations where it is assumed that the particle size spectrum can be parameterized by two parameters.

OBSERVATIONS AND APPLICATIONS OF COAGULATION

Critical Concentration Useful for High Concentration Regions

Predictions made using the critical concentration model have been successfully tested under various conditions. Kiørboe and colleagues (1994) observed the spring algal bloom in a Danish fjord and measured algal sizes, concentrations, and stickiness. These researchers successfully predicted the maximum algal concentration using the critical concentration despite changes in the dominant algal species. Riebesell (1991a, 1991b) observed the progress of the spring bloom in the North Sea and compared the maximum algal concentration to that predicted with Equation 9 for an assumed value of $\alpha = 0.1$. Riebesell found that the prediction overestimated the maximum concentration but Jackson (2005) was able to successfully predict the observed concentration by assuming a value of $\alpha = 1$.

Further tests of the critical concentration hypothesis are provided by iron addition experiments that stimulate the growth and accumulation of algal populations. In such experiments, iron is added to surface waters to stimulate phytoplankton growth and enhance the export of organic carbon as the diatoms aggregate and sink. Although these experiments show an increase in diatom production and biomass, not all produce a corresponding increase in particle flux out of the surface waters (Boyd et al. 2007). However, calculations of the critical concentration show that, in cases where increased export occurs, the observed maximum concentrations have been consistent with the predictions of the critical concentration hypothesis (Boyd et al. 2002, 2005).

More recently, Jackson & Kiørboe (2008) compared maximum particle concentrations in the Atlantic and Pacific Oceans and found them generally consistent with the prediction of Equation 10.

Reproduction of Observed Size Spectra

Coagulation theory provides a mechanism to predict changes to particle size spectra. Early measurements of the particle size distributions in the ocean revealed that distributions were well approximated by power laws (Sheldon et al. 1972, McCave 1975). The observed range of slopes of the particle size distributions can be explained using only coagulation theory and sedimentation (Hunt 1980). McCave (1984) later took this work further and showed how physical aggregation processes could be used to explain particle size distributions in the nepheloid layer.

Recent camera-based observations of changes in particle size distributions with depth have provided further tests of coagulation theory (Stemmann et al. 2004a, 2004b). The size distributions were measured between 60 and 1000 m depth at the Joint Global Ocean Flux Study (JGOFS) dynamique des flux de matière en Méditerranée (DYFAMED) site. This work showed that it is possible to predict particle size distributions at 1000 m given the size distributions at the surface. In addition, this work demonstrated the importance of biological processes in the mesopelagic that affect the particle size distributions.

Reproduction of Observed Vertical Particle Flux

Recently, Peterson and colleagues (2005) made elegant measurements of the size distribution of particle settling rates. These observations show that, for this site in the Mediterranean, most of the sedimenting material during high flux events settled at rates of 200–500 m d⁻¹. This measurement should be compared with assumed settling velocities of 50–150 m d⁻¹ used in models. The model

of coagulation in multiple layers discussed above had median settling velocities of 108 m d^{-1} in the surface layer and 210 m d^{-1} in the final layer (**Figure 3**).

Sediment traps with gels placed at the bottom of sample tubes can trap falling particles intact. The gels can then be scanned with automated imaging systems and the particles can be assigned lengths. The resulting observations can be used to calculate a number flux spectrum $w_s(d)n(d)$ for diameter d . These spectra can be compared with predictions from a coagulation model. Observations of the size-dependence of particle settling have also been consistent with predictions of simple coagulation models (Jackson et al. 2005).

UNRESOLVED ISSUES

Coagulation theories have successfully explained the occurrence of aggregates and predict particle size distributions and changes in the settling velocity of particles in the water column. However, some unresolved issues lead to an uncertainty when trying to make quantitative predictions using coagulation models.

Stickiness and the Role of Transparent Exopolymer Particles and Gels

An aggregate forms in two steps: particles are first brought together and then have to stick to each other. Processes that cause particles to collide have been well studied (Friedlander 2000, Elimelech et al. 1995), but the factors that cause marine particles to adhere have been less studied, even though the stickiness parameter (α in Equation 6) affects both the aggregation rate and the aggregate morphology (Vicsek 1992). Values for α are not directly measured, but inferred from measured changes in particle concentration combined with a coagulation model (Kjørboe et al. 1990, Kjørboe & Hansen 1993) and vary with phytoplankton species, cell age, and nutrient levels (Kjørboe et al. 1990, Kjørboe & Hansen 1993, Passow & Wassmann 1994, Engel 2000), as well as with the model being used (Prieto et al. 2006).

What causes variations in stickiness? Many species of diatom produce extracellular polysaccharides (EPS) (Decho 1990, Passow 2000) in the form of TEP (Gordon 1970, Alldredge et al. 1993), which can occur as discrete particles or gels (Chin et al. 1998, Verdugo et al. 2004). These particles are sticky ($\alpha > 0.1$) (Dam & Drapeau 1995, Engel 2000), partly through polymer bridging (Mopper et al. 1995), though steric and entropic effects may also play a role. TEP concentrations vary widely, with values as high as $2800 \mu\text{g L}^{-1}$ in the Ross Sea and subarctic Pacific (Hong et al. 1997), and decrease with depth in the water column (Prieto et al. 2006).

The production of TEP appears to depend on the intensity of turbulence (Beauvais et al. 2006) and nutrient concentration (Mari et al. 2005, Prieto et al. 2006) in the water column. TEP are thought to form from the coagulation of colloidal, fibrillar precursors (Passow 2000, Engel & Passow 2001, Passow et al. 2001, Leppard 1995, Santschi et al. 1998). The structure and chemical composition (Decho 1990, Leppard 1995) of the fibrillar material affect the morphology of the resulting aggregates (Stoll & Buffle 1998) and even challenge the concept of an “average stickiness” (Metcalf et al. 2006). If TEP are indeed responsible for enhancing aggregation, then these effects must be taken into account in models of phytoplankton aggregation and settling.

TEP can enhance aggregation rates by increasing either the average particle stickiness (Engel 2000) or the total particle concentration and hence the total number of collisions (Hill 1992), or both. Passow and colleagues (1994) argue that coagulation theory should be applied to TEP alone and not the aggregating cells. However, the aggregation properties of TEP are not straightforward (Jackson 1995b). The aggregation of TEP and cells that are not inherently sticky depends on the

dynamics of the two interacting populations (Mari & Burd 1998). It is also unclear what causes EPS to form discrete TEP as opposed to sheets or gels (Chin et al. 1998, Verdugo et al. 2004).

Estimates of Rates

In situ rates of particle aggregation and disaggregation are difficult to measure in the marine environment, partly because the formation of aggregates of a specific size depends on the interactions of particles across a wide range of size classes that all occur at different rates. However, aggregation and disaggregation rates have been estimated by dividing the particle size distribution into only two size classes: small, suspended particles and large settling particles (Clegg & Whitfield 1990, Murnane 1994). By measuring both the particle concentration and the activity of a radio isotope, such as ^{234}Th , in both size classes, aggregation and disaggregation rates have been estimated by fitting the data to a suitable model, usually assuming steady state. Importantly, the division between small and large particles is an operational one that depends on the filter sizes used in the data collection, which makes comparison of estimated rates difficult. For example, if P_S and P_L are the concentrations of small and large particles respectively, then the particle dynamics can be described by

$$\frac{\partial P_S}{\partial t} = P_r - P_S(\zeta + r_1) + r_{-1}P_L \quad (12)$$

$$\frac{\partial P_L}{\partial t} = r_1P_S - P_L(\zeta + r_{-1}) - \frac{\partial F}{\partial z} \quad (13)$$

$$F = P_LS, \quad (14)$$

with similar equations for the radioisotope. In these equations, P_r is the rate of production of small particles, ζ is the particle remineralization rate, r_1 and r_{-1} are the aggregation and disaggregation rates, respectively, S is the settling speed of large particles, and F is the vertical particle flux.

Such a model has the advantage of simplicity over Equation 6, but at the cost of assuming a steady-state distribution and a different interpretation of the rate constants. For example, the aggregation rate constant (r_1) is a first-order rate constant, whereas aggregation is a second-order process that involves the collision of two particles. The above model also assumes that aggregation occurs only between particles of the same size class (i.e., only small particles). Lastly, because aggregation rates, disaggregation rates, settling speed, and the particle size distribution all depend on particle size, the large particle group conflates several factors; aggregation of particles within the large size group will produce particles that are larger and sink faster and therefore contribute more to the flux than those that are smaller, but still within the particle size class. Without a knowledge of the particle size spectrum, the rates determined from this method cannot be related back to the coagulation kernels. Given these caveats, aggregation and disaggregation rates estimated using ^{234}Th show that disaggregation rates are typically as much as an order of magnitude greater than aggregation rates (Clegg & Whitfield 1990, Murnane 1994, Cochran et al. 2000, Lepore & Moran 2007) and that disaggregation can be more important than aggregation in the deep sea and surface waters. This result may not be too surprising given that particle concentrations decrease dramatically with depth (and so collision rates will decrease).

Disaggregation

Disaggregation is the converse process of aggregation and, like aggregation, can be the result of either physical or biological processes. Disaggregation in general redistributes material into the smaller size classes and physical disaggregation places limits on the size of the largest aggregate.

Fluid shear is the primary physical mechanism, although Hill (1998) has argued that shear forces from particle settling are the dominant force. If fluid shear is dominant, the size of the largest stable particle is given by the Kolmogorov length scale (η), which divides the inertial convection subrange and the viscous dissipation subrange,

$$\eta = \left(\frac{\nu^3}{\varepsilon} \right)^{1/4}, \quad (15)$$

where ν is the fluid kinematic viscosity and ε is the energy dissipation rate. Three mechanisms of particle breakup by physical disaggregation have been described (Parker et al. 1972): erosion from the particle surface, pressure fluctuations across the aggregate, and fracture. Each of these processes varies with ε such that the maximum size of a stable particle is

$$d_{\max} = C\varepsilon^{-\Gamma}, \quad (16)$$

with a different range of Γ for each of the processes.

Although disaggregation is an important process, few estimates have been made of the forces required to fragment a marine snow particle and few models explicitly include disaggregation. Energy dissipation rates required to break apart large marine snow aggregates vary between 10^{-7} and $10^{-4} \text{ m}^2 \text{ s}^{-3}$ (Alldredge et al. 1990), and aggregates composed of zooplankton feeding structures require more force than those composed of purely diatoms. These values should be compared with typical dissipation rates in the ocean, which vary between 10^{-10} and $10^{-1} \text{ m}^2 \text{ s}^{-3}$ (Thorpe 2005); the lower values are appropriate for the abyssal ocean and the larger values correspond to surface waters. This finding indicates that physical disaggregation is important in determining the particle size distribution in surface waters, which is consistent with field observations (Riebesell 1992, Jackson 1995a, Hill 1996).

Biological processes can also contribute to the breakup of particles, and might have particular significance for determining the particle size spectrum in the mesopelagic (Stemmann et al. 2004b). The fluid flow associated with zooplankton swimming and feeding can fragment large particles (Dilling & Alldredge 2000). The majority of daughter particles produced by this process are of a similar size to the parent particle, and can be still classified as marine snow (Goldthwait et al. 2004). Estimates that euphausiid swarms could interact with up to 50% of the marine snow particles in the surface waters indicate that such processes may have a significant, if local, effect on the particle size distribution. Zooplankton that vertically migrate and those that reside deeper in the water column could also have a significant effect on particle size distributions.

What is the relative importance of disaggregation? Estimates made using Th radio isotopes indicate that disaggregation can be more important than aggregation in deep and surface waters (Clegg & Whitfield 1990, Murnane 1994, Cochran et al. 2000, Lepore & Moran 2007). Models that incorporate particle processes have been used with profile data of particle abundances or size distributions to understand particle processes, though there is no agreement between these approaches. One-dimensional models of the northeast tropical Atlantic using two particle size classes (Dadou et al. 2001) indicate that particle remineralization and disaggregation are the dominant processes that affect particle flux below 150 m. However, models of changes in the particle size distribution with depth in the Mediterranean show that microbial activity and flux feeding are the important processes at depth (Stemmann et al. 2004b). This latter study does not include particle breakup by shear, but instead parameterizes particle breakup by zooplankton (Dilling & Alldredge 2000) and shows that mesozooplankton play an important role.

Aggregate Morphology and Fractal Dimension

The fractal relationship (Equation 8) is usually expressed as one between length and mass. However, it is also a relationship between length and the number of subunits that comprise the aggregate, or length and the porosity of an aggregate (Jackson 1998). This distinction is important for marine aggregates because they are formed from multiple particle sources, including algae, fecal pellets, and TEP. A fractal dimension that describes the relationship between mass and length for a diatom aggregate would be different if calculated in terms of porosity when much of the space is occupied by TEP.

Fractal dimensions of marine aggregates are often estimated by analyzing images. One potential problem with this method is that mass fractal dimensions are preserved under projection only if the fractal dimension is less than two. However, marine aggregates are not idealized fractals and so image analysis can be used for determination if the fractal dimension is somewhat greater than two, though by just how much is unclear (Bushell et al. 2002).

The fractal dimension is a useful tool, but should not be overinterpreted. Aggregates that are formed from a monodisperse source range in size from small clusters that contain two or three source particles to large particles that contain many more. The fractal dimension that characterizes the large particles obviously does not characterize the smaller ones. Therefore, natural aggregates can be characterized by a fractal dimension only over certain size ranges.

Best Kernels

The two types of kernel that are usually used, rectilinear and curvilinear, are theoretically derived. Because the curvilinear kernel incorporates hydrodynamic effects, the values it predicts for collision frequencies are smaller than those predicted by the rectilinear kernel. However, experiments using latex spheres indicate that the actual kernels for turbulent shear and differential sedimentation lie between these theoretical values (Li & Logan 1997a,b) because the fractal nature of the aggregate and the heterogeneity of the distribution within the particle produce high permeabilities.

Models of the fluid flow through aggregates make many assumptions (Adler 1981, Veerapaneni & Wiesner 1996). However, oxygen gradients exist within marine snow particles, and transport of oxygen within these particles is often dominated by diffusion (Ploug et al. 2002, Ploug & Passow 2007), indicating that advective velocities within the aggregate are very low, likely because TEP occupies a large fraction of the volume space within the particle, hindering advective velocities within the particle.

Ruiz and coworkers (2002) modeled diatom aggregate formation using only two size classes (small particles and aggregates). This produces simplifications in the coagulation kernel that allow for simpler numerical schemes. Ruiz and coworkers (2002) used an empirically derived kernel estimated from experimental data and found that the simulations are very sensitive to the initial conditions used, but this sensitivity is reduced when more particle sizes are used. They also found that theoretical kernels overpredicted aggregation.

Measurement Issues

Different instruments measure different physical properties, which are frequently designated with the same name. This is particularly true for particle “length.”

Measurements of individual marine aggregates and their properties most often involve optical methods, either photographic (e.g., Asper 1987, Stemmann et al. 2008) or other ocular methods (e.g., Alldredge & Gotschalk 1988, Ploug & Jørgensen 1999, Ploug & Passow 2007). Even with the

same physical technology, something as elementary as the length of a particle can cause problems. For example, the linear dimension of the aggregate can be measured in different orientations and from these measurements an estimate of the equivalent spherical diameter can be made. Alternatively, the diameter equivalent to the measured cross-sectional area can be calculated, either with or without internal voids.

When different physical principles are used, such as the conductivity, as used with the Coulter Counter, the reported diameter differs. The estimation of particle size from the voltage signal usually assumes that the measured impedance change is proportional to the conserved (i.e., solid) volume of the particle. However, for aggregated particles, the fluid within the particle can affect the changes in impedance and so the particle porosity must be taken into account (Treweek & Morgan 1977).

Particle settling velocity can also give a measure of particle size if one assumes that a relationship (such as Stokes' Law) exists between the settling speed and particle size (e.g., Asper 1987). Such techniques do offer the possibility of measuring multiple properties of the same particle.

The important point is that not all reported diameters are measurements of the same thing, because they use different physical properties and make assumptions about the nature of the particles.

An important, seldom-discussed issue is that instruments used to make automated determination of animal size and abundance also measure aggregates, and vice versa. The classical determinations of Sheldon and coworkers (1972) have been used to justify aggregate processes (Hunt 1980, McCave 1975) and biological size distributions (Platt & Denman 1977, Thiebaut & Dickie 1992).

SUMMARY POINTS

1. Particle aggregation is a key process affecting material fluxes and biogeochemical cycles in the marine environment. Aggregation and disaggregation repackage material into different sized aggregates, and affect the physical, chemical, and transport characteristics of this material.
2. Coagulation provides a useful framework for understanding the formation, transformation, and fate of particles in the marine environment. Coagulation can successfully explain maximum particle concentrations in the oceans, the rates and distribution of trace metal scavenging, the critical cell concentrations at the end of diatom blooms, and changes in particle size distribution and settling velocity.
3. Measurements of particulate material must be interpreted with caution, particularly when the particle properties of interest vary with particle size. Such measurements conflate changes of particle concentration with particle size and changes of the property of interest with particle size.

FUTURE ISSUES

1. Disaggregation is probably the greatest unknown of the physical processes that affect marine particles. Developing models of these processes is made difficult by the non-deterministic nature of particle disaggregation. We also have little understanding or knowledge of crucial pieces of information such as the size distribution of daughter particles and the forces required to break particles apart, though there has been some work to provide this information for marine snow.

2. The controls on particle stickiness are not well understood. Extracellular polysaccharides are known to play a role, but the relationship between cell-attached and free polysaccharides is not well understood. Is the use of a single parameter (particle stickiness, α) appropriate, or is a more complex parameterization required? Do different adhesion mechanisms operate for cells that are inherently sticky as opposed to those that rely on external factors such as transparent exopolymer particles (TEP)?
3. TEP undoubtedly play an important role in particle aggregation, but many particles aggregate without TEP. What is the process by which TEP enhance aggregation of other particles? The production, chemistry, and physics of these particles must be investigated further—for example, why do TEP sometimes form sheets, a structure that is not characteristic of coagulation? What other roles do TEP play in biogeochemical cycles in the oceans?
4. The formation and fate of marine particles play an important role in biogeochemical cycling, yet only recently have there been attempts to incorporate realistic aggregation models into large-scale biogeochemical models. The development of new, more efficient algorithms and parameterizations for aggregation will be needed for this approach to be successful.

DISCLOSURE STATEMENT

The authors are not aware of any biases that might be perceived as affecting the objectivity of this review.

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Errata

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