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# Mass transfer to and from small particles in the sea[1,2]

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*Abstract*

Slowly sinking particles exchange mass with their liquid environment if dissolution processes within the particles maintain a surface concentration excess or deficiency $\chi_0$ of a soluble substance above background. If the exchange is controlled by diffusion in the liquid phase, the total mass loss is proportional to $\chi_0$, diffusivity $D$, and particle diameter $d$. If advection associated with the sinking of the particle dominates over diffusion, the exchange rate varies as $\chi_0 D^{2/3} d^2$ and is weakly affected by particle density and fluid viscosity. This is the case for spherical particles of a diameter $\gtrsim 70$ μm.

The resulting dissolution rate per unit depth of sinking is constant for large particles, but increases sharply once the particles are small and slow enough for mass exchange to be controlled by diffusion. With oxygen supply supposed the rate-controlling process of particle decomposition, a realistic depth of decomposition of order 1 km is calculated for 200-μm-diameter spherical particles. The generation of an oxygen minimum at such depths then requires the production near the sea surface of sufficiently large organic particles in sufficient numbers.

Small biogenic particles play an important role in the chemical balance of the ocean. Their decomposition produces a layer of oxygen minimum and layers of maxima of nitrate, phosphate, and silicate. In the Sargasso Sea the $O_2$ minimum layer lies at about 700-m depth, nutrient maximum layers somewhat deeper. In the Slope Sea (between the Gulf Stream and the continental shelf north of Cape Hatteras) the same layers are found some 500 m shallower. In a note supporting some ideas of Rossby (1936), Redfield (1936) suggested that the Slope Sea minimum and maximum layers must be maintained by along-isopycnal advection from the Sargasso Sea, rather than by in situ decomposition, because the sinking and decay of particles and mass exchange with the liquid phase must be roughly the same in the two locations and cannot result in such large differences between the layer depths in question. One could object that the physical properties of the water masses are also rather different, with colder (and denser and more viscous) layers lying at a much shallower depth in the Slope Sea than in the Sargasso Sea. This could conceivably retard the sinking of decomposing particles, so that they could exert their oxygen demand and release their decomposition products at a much shallower depth. To decide the question conclusively, it is necessary to examine the quantitative relationships between particle sinking rates and the supply of oxygen and the removal of decomposition products from particles.

Given the importance of this problem, it

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is surprising that only a few attempts have so far been made to develop a satisfactory quantitative theory. Munk and Riley (1952) discussed the absorption of nutrients by small organisms and, in their appendix, wrote down most of the equations on sinking rates and mass transfer necessary for dealing with the inverse problem of nutrient release. Munk and Riley's emphasis is on empirical relationships for mass transfer valid at relatively high Reynolds and Peclet numbers: they do not discuss the simpler and more illuminating physical relationships in the diffusion (small size) limit. Almost 20 years after Munk and Riley, Pond et al. (1971) considered the decomposition of particles while settling, including the effect of mass loss on the settling velocity. They again used an empirical mass transfer law valid for relatively large particles and focused on calcite loss from skeleton foraminifera after decay of organic matter. Lal and Lerman (1973) and Lerman et al. (1974) discussed the similar problem of calcite-silicate loss, assuming on the basis of some field studies that the rate of decrease of particle radius remains constant during the decomposition process. They did not relate this ad hoc mass transfer law to theory or laboratory studies.

Although Pond et al. (1971) made some illuminating general remarks, none of the quoted papers discusses systematically the fundamental physical aspects of particle-to-liquid-phase mass transfer. In order to judge the validity of arguments such as that of Redfield (1936), it is necessary to be aware what the key control variables are of the sinking particle decomposition process. To this end, the quantitative relationships applying to the problem are reviewed below and the interrelationship of the principal variables discussed. Following this, a very simple model of organic matter decomposition in settling particles is examined, in order to exhibit the physical factors that control the depth at which maximum oxygen demand or maximum nutrient release rate occur.

This article started out as a review of oceanic diffusion problems on the micrometer scale and up, on the invitation of Y. H. Edmondson. Because it seemed difficult to write a general review that would not be a series of quotes from textbooks, I chose to focus it on the nutrient release problem. This is certainly an important problem that requires more attention than has been paid to it in the past, and it also serves as a good vehicle for reviewing small-scale mass transfer problems.

*Mass exchange through diffusion*

In the problem of mass exchange between a fluid and an individual particle suspended in it a permissible idealization is to ignore how the exchanged mass, released to the fluid in a dissolved state, is ultimately disposed of (or where it originates from, if the exchange is fluid-to-particle). This is so because the spatial scale of concentration variations attendant upon the exchange is generally of the order of particle size, i.e. very much less than the scale associated with such replacement or removal processes as along-isopycnal advection, cross-isopycnal mixing, or biological uptake and release, the latter arising as the aggregate effect of all other suspended particles present. From the point of view of single particle-fluid mass exchange, any released material may be thought to escape to a sink at "infinity," while any uptake similarly comes from a distant source. Furthermore, only the time-independent, steady state exchange rate is of practical interest.

In any exchange problem, the flux $\mathbf{F}$ may be thought of as the primary variable, with properties akin to electrostatic force or fluid velocity: a vector, which in the absence of sources or sinks is "solenoidal," i.e. such that in the steady state, flux tubes may be constructed similar to stream tubes (Fig. 1). The axis of a flux tube is parallel to the direction of the local flux vector, while its cross-section is inversely proportional to the latter's magnitude, because the tube transports a constant amount of material:

$$|\mathbf{F}|\ \mathrm{d}A = |\mathbf{F}_0|\ \mathrm{d}A_0 \qquad (1)$$

where the right-hand side is what comes off a surface element $\mathrm{d}A_0$ of the particle, $\mathbf{F}_0$ being perpendicular to particle surface. The dimension of flux is mass per unit area per

unit time, $M L^{-2} T^{-1}$. The total mass leaving a particle's surface per unit time is therefore

$$E = \int_{A_0} |\mathbf{F}_0| \, dA_0. \tag{2}$$

The principal aim in the analysis of the particle-liquid mass transfer process is to determine $E$.

When the fluid is stagnant, mass flux occurs through diffusion alone. In this case the flux tubes diverge to infinity in all directions from the particle, because the diffusion process is isotropic. At a distance large enough so that any asymmetries of the release have been smoothed over, the flux tubes all become radial, the flux vector's magnitude a function of radius only (measured from a convenient origin within the particle, e.g. its center of mass), so that by Eq. 2:

$$|\mathbf{F}| = \frac{E}{4\pi r^2}. \tag{3}$$

Diffusion in a fluid is "driven" by concentration differences, which play a role akin to electrostatic or velocity potential, flux pointing "down" the local concentration gradient (in a stagnant fluid). Thus along a single stream tube:

$$|\mathbf{F}| = -D\frac{\partial \chi}{\partial s} \tag{4}$$

where $D$ is diffusivity, a scalar of dimension $L^2 T^{-1}$, $\chi$ is concentration, with units of $M L^{-3}$, and $s$ is distance along the stream tube. Far enough from the particle $s \cong r$ so that combining the last two equations and integrating one finds:

$$\chi = \chi_\infty + \frac{E}{4\pi r D} \tag{5}$$

where $\chi_\infty$ is the "background" concentration far from the particle. Because only concentration differences enter the problem, it is convenient to set $\chi_\infty = 0$, in which case $\chi$ becomes the concentration *excess* over background. This will be understood henceforth.

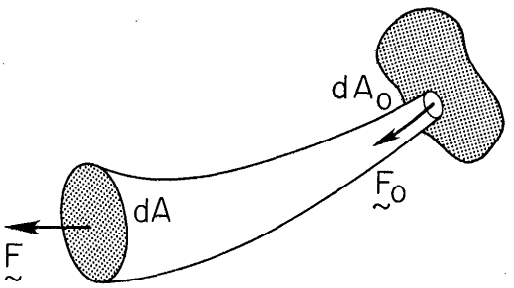


Fig. 1. Schematic illustration of a flux tube in material diffusion. The transport within the tube (flux × area) is everywhere the same, equal to the transport at the source, in this case a surface element of a suspended particle.

If a particle is spherical, no asymmetries arise in its near field, and the asymptotic results Eq. 3 and 5 remain valid to particle radius, $r = r_0$. Concentration and flux are then at the particle:

$$\chi_0 = \frac{E}{4\pi r_0 D}$$

and (6)

$$F_0 = \frac{E}{4\pi r_0^2}.$$

The concentration, $\chi_0$, of a given diffusing substance at the surface of a decomposing particle is determined by biochemical processes. In many cases $\chi_0$ depends only on what goes on within the particle, not on the diffusion in the liquid. $\chi_0$ is then an independent datum, and $E$ can be determined from the first half of Eq. 6. This will be supposed below.

In similar problems a mass exchange coefficient $m$ is often introduced by expressing the total transfer $E$ as a product of surface area, surface concentration (excess) $\chi_0$ and the coefficient $m$:

$$E = m\chi_0 A_0. \tag{7}$$

The dimension of $m$ is thus of velocity, $L T^{-1}$. By Eq. 6, for a spherical particle in the case of diffusion in a stagnant fluid the mass transfer coefficient is

$$m = \frac{D}{r_0} \tag{8}$$

showing that the mass transfer coefficient increases with decreasing particle size.

Rewriting Eq. 3 and 5 in terms of $\chi_0$ from Eq. 6 one has

$$\chi = \chi_0 \frac{r_0}{r}$$

and (9)

$$F = \chi_0 \frac{Dr_0}{r^2}.$$

These results illustrate that the "scale" of the concentration field is particle radius $r_0$, in the sense that the excess concentration $\chi$ becomes vanishingly small at large $r/r_0$. Similarly, the scale of $\chi$ is $\chi_0$, that of $F$ is $\chi_0 D r_0^{-1}$, in the sense that concentration and flux are nowhere greater than their scales.

For arbitrary particle shape, the pattern of flux tubes near a particle may be found by solving Eq. 1 and 4. Written in standard mathematical form these equations are

$$\Delta \mathbf{F} = 0$$

and (10)

$$\mathbf{F} = -D\,\Delta\chi.$$

Elimination of $\mathbf{F}$ yields

$$\Delta^2\chi = 0 \tag{11}$$

which is Laplace's equation. Equation 9 is a solution of this, with the boundary conditions:

$$\chi = \chi_0 \qquad (r = r_0)$$

and (12)

$$\chi = 0 \qquad (r \to \infty).$$

As noted above, these boundary conditions represent the case where biochemical processes within the particle maintain a fixed concentration excess or deficiency $\chi_0$ (and hence flux $F_0 = D\chi_0/r_0$) at the particle surface, e.g. a saturation value $\chi_0 = \chi_S$, or the negative of the background concentration, i.e. zero in absolute terms. Note, however, that the mass transfer velocity $m$ is fixed (Eq. 8) and cannot be specified independently of $D$ and $r_0$.

*Effect of advection*

The above relationships are considerably modified when the fluid is in motion. Because everything has to be referred to the suspended particle, it is the relative motion of fluid and particle that matters. The most important part of this relative motion is the settling of the particle through the fluid. For the small particles of interest in the present context, the settling velocity may be taken to be constant or varying slowly as the particle loses mass and encounters colder and therefore denser and more viscous fluid. Except for the relative motion associated with settling, the particle follows the regular or irregular motion of its immediate fluid environment. Some distance from the particle the fluid velocity may be different: the implied "shear," or spatial velocity gradient, modifies the flux vector.

In turbulent flow the shortest distance over which the fluid velocity varies appreciably is the "microscale":

$$l = \left(\frac{\upsilon^3}{\epsilon}\right)^{1/4} \tag{13}$$

where $\upsilon$ is viscosity, $\epsilon$ energy dissipation rate per unit mass, which is

$$\epsilon = \frac{u^3}{L_d}, \tag{14}$$

where $u$ is rms turbulent velocity, $L_d$ a dissipation (macro-) length scale, comparable to the size of the big eddies present. In the wind-driven surface shear layer of the sea $u$ is of order $u_*$, the friction velocity, or about 1 cm s$^{-1}$ under a wind of a speed of 7 m s$^{-1}$, and proportional to wind speed. $L_d$ is of the order of mixed-layer depth, say typically 10 m. Noting that $\upsilon$ is near $10^{-6}$ m$^2$ s$^{-1}$, one calculates $l \cong 1$ mm in moderate winds near the surface. Much lower values of $\epsilon$, and hence larger $l$, are found below the surface mixed layer, where the water is stratified. Even 1 mm is much larger than the typical organic particle size of 10–100 $\mu$m, however, so that shear associated with the smallest eddies does not distort diffusion processes in the immediate neighborhood of a particle. Small eddies do contort the wake of a settling particle and cause it to

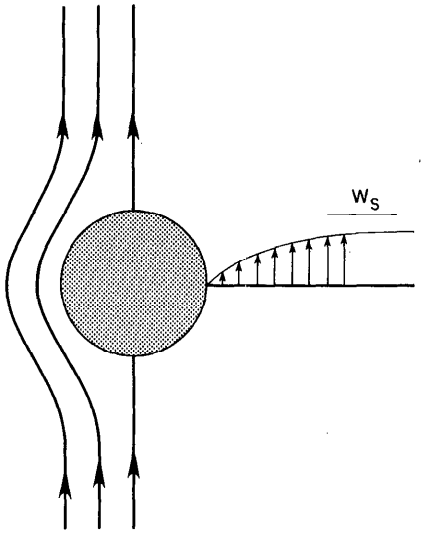


Fig. 2. Streamlines (left) and velocity distribution relative to a slowly sinking spherical particle. The motion is symmetrical about the vertical axis; the velocity distribution is shown in the plane perpendicular to the flow (*see Eq. 23 for the stream function*).

grow in width faster than molecular diffusion would.

Ignoring velocity variations on the scale of $l$ and larger for the time being, one is left with a steady upward motion of the fluid relative to the particle. The Reynolds number of this motion is low for typical particles: data of Hawley (1982) or Small et al. (1979) show that naturally occurring organic aggregates or fecal pellets have diameters $d$ of ten to a few hundred micrometers, settling velocities $w_s$ of $10^{-4}$–$10^{-2}$ m s$^{-1}$, giving a range of Reynolds numbers Re = $dw_s/\nu$ from $10^{-3}$ to order 1. At Re small compared to 1 the inertia of the fluid is unimportant, and viscosity controls the pattern of flow. The streamlines and velocity distribution of the flow relative to a slowly sinking spherical particle are illustrated in Fig. 2. At the surface the relative velocity is zero (no-slip condition). Along the diameter perpendicular to the flow the velocity increases slowly (within a few particle diameters) to the settling velocity. In the wake the streamlines close again and the velocity becomes nearly uniform.

Motion of the fluid transports ("advects") whatever material is dissolved in it, so that

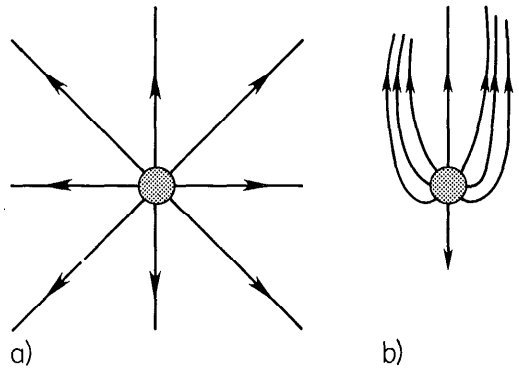


Fig. 3. Schematic drawing of flux lines (section through flux tubes) in a vertical plane through a sinking spherical particle: a—diffusion alone; b—diffusion and moderately fast advection.

the flux vector becomes, in place of Eq. 4 or the second part of 10:

$$\mathbf{F} = \mathbf{v}\chi - D\Delta\chi \qquad (15)$$

where $\mathbf{v}$ is the fluid velocity vector, and the term containing it describes the effect of fluid advection on flux. In the absence of sinks and sources the flux vector is still solenoidal (Eq. 1 and the first part of Eq. 10 hold), so that the differential equation for $\chi$ becomes, with $\Delta\cdot\mathbf{v} = 0$:

$$\mathbf{v}\cdot\Delta\chi - D\Delta^2\chi = 0. \qquad (16)$$

In a qualitative way, it is easy enough to envisage the effect of advection on the geometry of flux tubes (Fig. 3). According to Eq. 15, flux is the vector sum of advective and diffusive components. Right at the surface of a sinking spherical particle the relative velocity vanishes, so flux is as in the diffusion problem and flux tubes come out of the particle radially. A little distance away they are deflected by the streaming fluid and, given a not too small settling velocity, end up mostly vertical. In this case the mass released by the particle ends up mostly in its wake (or, for a depletion problem, the deficiency of a substance is confined to the wake).

The relative importance of advection vs. diffusion is measured by the ratio of what the slipstream can "flush away," against what can escape to infinity through diffusion alone. The slipstream may be thought to transport away a volume per unit time of

$\pi r_0^2 w_s$ (for a spherical particle), hence dissolved mass in the amount $\pi r_0^2 w_s \chi_0$. The ratio of this to $E$ from Eq. 6 is, except for factors of order, unity,

$$\mathrm{Pe} = \frac{w_s d}{D} \tag{17}$$

where $d$ is particle diameter, the nondimensional combination being known as Peclet number, as in the analogous heat transfer problem. At high Pe, most of the mass exchanged is contained in the narrow wake, while at vanishing Pe it is evenly distributed in the neighborhood of a particle.

The Peclet number (for diffusion) may also be written as the product

$$\mathrm{Pe} = \mathrm{ScRe} \tag{18}$$

where $\mathrm{Re} = w_s d/\upsilon$ is Reynolds number and $\mathrm{Sc} = \upsilon/D$ is Schmidt number. For most substances of interest in the present context $D$ is of order $10^{-9}$ m$^2$ s$^{-1}$, while $\upsilon$ is $10^{-6}$ m$^2$ s$^{-1}$, yielding Schmidt numbers of order $10^3$ and Peclet numbers 3 orders of magnitude above Reynolds numbers. The typical range of Peclet numbers is correspondingly 1–$10^3$, using earlier estimates of $w_s$ and $d$ for settling particles. Typically, therefore, advection dominates over diffusion.

*Mass transfer from a settling spherical particle*

In order to arrive at relationships equivalent to Eq. 6 for the case of advection-dominated mass transfer it is necessary to solve Eq. 16, with boundary conditions as stated previously (Eq. 12). The mathematical difficulties of this problem are considerable and analytical solutions can only be found for simple particle shapes, and then only for the large Pe limit, in which case there is a diffusive boundary layer at the surface of the particle. One should remember that low Re and high Pe are simultaneously possible for high enough Sc, and that this is precisely the range of Re and Pe characteristic of small biogenic particles.

The solution of the advection-diffusion equation at high Peclet number for a spherical particle is given in detail by Levich (1962). The concentration distribution is

$$\chi_0 - \chi = \frac{\chi_0}{1.15} \int_0^{\eta} \exp\left(-\frac{4}{9}\eta^3\right) d\eta \tag{19}$$

where $\eta = y/\delta$, with $y = r - r_0$ the distance above the surface of the spherical particle $\delta$, a diffusive boundary layer thickness:

$$\delta = r_0 \left(\frac{3}{8}\mathrm{Pe}\right)^{-1/3} \frac{\left(\theta - \dfrac{\sin 2\theta}{2}\right)^{1/3}}{\sin\theta}. \tag{20}$$

Here $\theta$ is the angular distance from the stagnation point at the bottom of the settling particle. At distances above the particle surface large compared to $\delta$, the concentration differs negligibly from $\chi_0$. The flux at the surface of the particle is

$$F_0 = \frac{D\chi_0}{1.15 r_0}\left(\frac{3}{8}\mathrm{Pe}\right)^{1/3} \frac{\sin\theta}{\left(\theta - \dfrac{\sin 2\theta}{2}\right)^{1/3}}$$

$$\equiv \frac{D\chi_0}{1.15\delta}. \tag{21}$$

The function of the angle $\theta$ contained in this expression is unity at $\theta = 0$ (the front stagnation point), 0.86 at $\theta = \pi/2$ (at the diameter perpendicular to the flow), and zero at $\theta = \pi$ (the rear stagnation point). Thus the flux is highest at the point of incidence, decreases with increasing $\theta$, and becomes zero at the rear stagnation point. The total mass transfer is

$$E = 6.33\chi_0 D r_0 \mathrm{Pe}^{1/3}. \tag{22}$$

The presence of $\mathrm{Pe}^{1/3}$ in this result has the consequence that the total mass transferred is not directly proportional to $D$ (but to $D^{2/3}$). The physical reason is, as Levich (1962) pointed out, that advection compensates to some extent for a smaller or larger value of the diffusivity. This is reflected by the thickness of the diffusive boundary layer: the surface concentration gradient varies as $\chi_0/\delta$, hence as $\mathrm{Pe}^{1/3}$, which is why this factor occurs in Eq. 22. In faster flow, the boundary layer becomes thinner, and more mass is exchanged than in a slower moving fluid.

Levich's analysis is based on the approximation that the thickness of the boundary layer, $\delta$, is small compared to particle radius

$r_0$. He approximated the stream function derived by Stokes for viscous flow around a sphere at small Reynolds numbers as follows:

$$\psi = -\frac{w_s}{2}\sin^2\theta \cdot \left(r^2 - \frac{3}{2}r_0 r + \frac{1}{2}\frac{r_0^3}{r}\right) \cong -\frac{3}{4}w_s y^2 \sin^2\theta. \qquad (23)$$

In an ingenious mathematical approach, he then transformed the advection-diffusion equation to $(\psi,\theta)$ coordinates and found the explicit solution given above. The presence of $\mathrm{Pe}^{-1/3}$ in the result has the unfortunate effect that the approximations are strictly only valid for $\mathrm{Pe} > 10^3$. A more accurate formula should not, however, differ more than by a factor of order 1.

In comparing the result of Eq. 22 with the diffusion limit, Eq. 6, one finds that the factor $4\pi$ has been replaced by $6.33\mathrm{Pe}^{1/3}$. The two are equal for $\mathrm{Pe} \cong 8$, characteristic of rather small organic particles. Expressed in terms of a nondimensional mass transfer coefficient (known in the analogous heat transfer problem as a Nusselt number) one has

$$\mathrm{Nu} \equiv \frac{md}{D} \equiv \frac{E}{4\pi r_0^2 \chi_0}\frac{d}{D} = 2 \qquad (\mathrm{Pe} \to 0)$$

and (24)

$$\mathrm{Nu} = \mathrm{Pe}^{1/3} \qquad (\mathrm{Pe} \to \infty).$$

The Nusselt number at low Pe approaches a constant, because $m$ varies as $d^{-1}$ (*see Eq. 8 above*). These results are in good accord with experimental data quoted by Spalding (1963), obtained at somewhat higher Reynolds numbers than supposed in Levich's analysis. Although some interpolation formula should strictly speaking be used for $1 < \mathrm{Pe} < 10^3$, in the following the two limiting results will be used, as an approximation, for the ranges $\mathrm{Pe} \lessgtr 8$.

*Particle settling*

Supposing low Reynolds number flow as before, the settling velocity of a spherical particle is given by Stokes' formula (which can be obtained from Eq. 23 above):

$$w_s = \frac{2g(\rho_s - \rho)}{9\nu\rho} r_0^2 \equiv B r_0^2 \qquad (25)$$

where $\rho_s$ is the density of the particle, $\rho$ that of the surrounding water. The quantity $B$ is introduced for convenience in writing down subsequent results and is defined by the above equation (dimension $L^{-1}\,T^{-1}$).

The validity of Stokes' formula for particles suspended in the sea has been questioned by Chase (1979). In presenting experimental data on the settling velocity of particles collected from Buzzards Bay and Lake Michigan, he claimed that such particles fall much faster (typically by a factor of two) than Stokes' Law (Eq. 25 above) predicts. This implies much reduced viscous drag or a systematic force aiding gravity, comparable to the latter in magnitude. Chase attributed the phenomenon to "electric forces," "of the same magnitude as the hydrodynamic forces," but has not shown that such forces are in fact present in the sea. His terminology of "drag reduction" hints vaguely at another known phenomenon, the reduction of viscous drag in a turbulent boundary layer by the introduction of a dilute polymer solution, the so-called Toms effect (Virk 1971). A third plausible explanation for Chase's result is that his particle density estimates were too low by 3–5%, about the supposed density excess of his particles: doubling the excess density, the settling velocity is doubled.

First the Toms effect. As Virk (1971) and others have shown, this effect consists of a thickening of the laminar sublayer below a turbulent boundary layer and can materially reduce the drag of a large, streamlined object such as a submarine. However, natural particles present in substantial numbers are neither streamlined, nor large enough to allow the development of a turbulent bound-

ary layer on their surface. Drag is mainly by the molecular viscosity of the surrounding liquid, the flow of which is already as laminar as it can get, certainly so in the model on which Stokes' Law is based (any turbulence reduces particle speed further).

Second, forces on a charged particle. If a vertical electric field pulled particles downward, their velocity would increase in the ratio

$$\frac{v_2}{v_1} = \frac{mg + Eq}{mg}$$

where $E$ is electric field strength, V m$^{-1}$, and $q$ is electric particle charge, $Q$ (coulombs). This formula is used in Millikan's method of determining charge, for example. Von Arx (1962) gave the strength of the electric field in the ocean as no more than $10^{-4}$ V m$^{-1}$. The mass of a 100-$\mu$m particle is about $4 \times 10^{-9}$ kg, hence its weight $mg$ is $4 \times 10^{-8}$ newtons. To generate an electrostatic force of the same magnitude requires a particle charge of at least $4 \times 10^{-4}$ $Q$. That is $2.5 \times 10^{15}$ times the electronic charge, $e$, or grossly in excess of what one encounters on deliberately charged oil-fog particles (order $10^3$ $e$, e.g. *see* Green and Lane 1964). It also implies a vertical current of density

$$J = Nw_s q \qquad (\text{A m}^{-2})$$

where $N$ is particle number density, number of particles per m$^3$. A typical mass concentration of 0.1 mg liter$^{-1}$ ($10^{-4}$ kg m$^{-3}$) of 100-$\mu$m particles has a number density of $2.5 \times 10^4$ m$^{-3}$, so that $J = 2.2 \times 10^{-2}$ A m$^{-2}$. According to Fleagle and Businger (1963) the current density flowing downward from the ionosphere to the earth is $4 \times 10^{-12}$ A m$^{-2}$, 10 orders of magnitude less than the charges on suspended particles would carry from the surface layer of the sea downward, if their charges were large enough to double their fall velocities.

The quantitative discrepancy is gross enough to reject any appeal to significant electric forces on particles, systematically acting vertically downward. What is left is that Chase's densities were wrong: settling velocity observations are indeed often used to determine unknown density, if shape and size of a particle are known.

*Particle dissolution in the course of settling*

Consider next the mass loss from a spherical particle to the liquid phase and the effect it has on settling velocity.

In their discussion of this problem, Lal and Lerman (1973) supposed that an outer layer of the particle dissolves, reducing its radius and that the mass loss of the particle is equal to the mass $E$ transferred to the liquid phase. A slightly more general formulation is more convenient: let $\alpha E$ be the mass loss of the particle, to allow for the release of other substances, or the case when $E$ represents oxygen supply, which controls the rate of dissolution:

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{4}{3}\pi\rho_s r_0^3\right) = -\alpha E. \qquad (26)$$

Take first the case of the low Pe limit, substituting Eq. 6 into 26:

$$r_0 \frac{\mathrm{d}r_0}{\mathrm{d}t} = -D\phi_0 \qquad (27)$$

where $\phi_0 = \alpha\chi_0/\rho_s$ is a "diffusion potential," given by the factor $\alpha$ times surface concentration normalized with *particle* density. This equation integrates to

$$r_0^2 = r_i^2 - 2D\phi_0 t \qquad (28)$$

where $r_i$ is the initial particle radius. The result is typical of diffusion problems, the square of the radius changing linearly in time. The particle disappears ($r_0 \to 0$) at time

$$t_d = \frac{r_0^2}{2D\phi_0}. \qquad (29)$$

Of greater practical interest is the depth reached by the particle at dissolution. This can be calculated from the settling velocity:

$$\frac{\mathrm{d}z}{\mathrm{d}t} = -w_s = -Br_0^2. \qquad (30)$$

Combining this expression with Eq. 27:

$$r_0^3 \frac{dr_0}{dz} = \frac{D\phi_0}{B}, \tag{31}$$

which integrates to

$$r_0^4 - r_i^4 = \frac{4D\phi_0}{B} z, \tag{32}$$

so that the depth of dissolution is

$$-z_d = \frac{Br_i^4}{4D\phi_0}. \tag{33}$$

The same calculations can be carried out in the high Peclet number limit. Substituting the settling velocity for Eq. 25, the Peclet number becomes

$$\mathrm{Pe} = \frac{Br_0^3}{D}. \tag{34}$$

Equations 22 and 26 now yield

$$\frac{dr_0}{dt} = -0.5\phi_0 D^{2/3} B^{1/3} = \text{constant} \tag{35}$$

where $\phi_0$ is again $\alpha\chi_0/\rho_s$. A constant rate of decrease of radius ("dissolution rate") was assumed in Lal and Lerman's (1973) analysis on an empirical basis. Here it is seen to conform to the analytical result at high Peclet number. It may also be noted that the mass transfer coefficient is proportional to $dr_0/dt$ and hence also constant in this limit:

$$\begin{aligned} m &= \frac{E}{4\pi r_0^2 \chi_0} \\ &= 0.5 B^{1/3} D^{2/3} \\ &\equiv -\phi_0^{-1} \frac{dr_0}{dt}. \end{aligned} \tag{36}$$

Upon integrating Eq. 35 one finds

$$r_0 = r_i - 0.5\phi_0 B^{1/3} D^{2/3} t \tag{37}$$

and therefore

$$t_d = \frac{r_i}{0.5\phi_0 B^{1/3} D^{2/3}}. \tag{38}$$

Similarly, from Eq. 35 and 30 one has

$$r_0^2 \frac{dr_0}{dz} = 0.5\phi_0 D^{2/3} B^{-2/3} \tag{39}$$

and

$$r_0^3 - r_i^3 = 1.5\phi_0 D^{2/3} B^{-2/3} z, \tag{40}$$

hence

$$-z_d = \frac{r_i^3 B^{2/3}}{1.5\phi_0 D^{2/3}}. \tag{41}$$

Of course the high Peclet limit ceases to apply at some small enough radius. If this is sufficiently below $r_i$, the result on $z_d$ is essentially unaffected: given the high power of radius occurring in this formula, the depth at which $r_l \ll r_i$ is reached is much the same as $z_d$.

The particle dissolution model just discussed is clearly oversimplified, and yet it yields one very clear conclusion: the primary variable determining the depth of dissolution is initial particle size. Doubling the initial radius increases the depth of dissolution by about an order of magnitude. By contrast, realistic variations of material properties—density excess, viscosity, diffusivity—result in much less drastic changes in $z_d$. The only other factor of real importance is $\phi_0 = \alpha\chi_0/\rho_s$, which can vary within a wider range than the material properties.

*Sink and source strength*

Although the mass released by a particle could legitimately be regarded as escaping to infinity, on the very small scale of a particle's immediate environment, from the point of view of large-scale processes each decomposing particle is a tiny mass source of nutrients and a sink of oxygen. The aggregate effect of many such particles can be described by distributed sources or sinks of strength $\sigma$ (mass per unit volume and unit time, $M\ L^{-3}\ T^{-1}$). It is of interest to relate this source/sink strength to particle properties.

Let the number of particles (of fixed size and other characteristics) falling through a given level be $n$ (number per unit area, per unit time, $L^{-2}\ T^{-1}$). The vertical mass flux is then $nM$, with $M$ the particle mass. The rate of change of this flux is the mass lost by particles falling, equal to the mass gained by the liquid phase, i.e. the desired source strength:

$$\sigma = \frac{d(nM)}{dz}. \tag{42}$$

For spherical particles of the same radius $r_0$, this becomes above their level of dissolution, where $n$ remains constant:

$$\sigma = n\frac{\mathrm{d}M}{\mathrm{d}z} = 4\pi n\rho_s r_0^2\frac{\mathrm{d}r_0}{\mathrm{d}z}. \qquad (43)$$

In the high Peclet number limit one may substitute from Eq. 39, also noting that $\rho_s\phi_0 = \alpha\chi_0$:

$$\sigma = 2\pi n\alpha\chi_0 D^{2/3}B^{-2/3}. \qquad (44)$$

A notable feature of this result is the absence of particle size: the source strength remains the same in the course of settling and decomposition, except for variations in material properties and the diffusion potential $\alpha\chi_0/\rho_s$.

At low Peclet numbers this is no longer true: with Eq. 31 one has

$$\sigma = 4\pi n\frac{D\alpha\chi_0}{Br_0}$$

$$= \frac{4\pi n\alpha D\chi_0}{B\left(r_i^4 + \frac{4D\chi_0}{B}z\right)^{1/4}}. \qquad (45)$$

This has a sharp peak at $z = -z_d$. One notes that the total mass released remains, of course, finite:

$$\int_{-z_d}^{0} \sigma\,\mathrm{d}z = nM_i \qquad (46)$$

where $M_i$ is initial particle mass.

A cloud of large particles released at the surface thus releases its mass at a constant rate per unit depth until particle size becomes small enough and settling velocity low enough for the diffusion limit to set in. At that point the rate of decomposition speeds up, as the particles sink only a small extra distance before complete dissolution.

As mentioned earlier, the source/sink effect of decomposing particles must be counteracted by some other large-scale process, such as advection of nutrient-poor and oxygen-rich water. This process was considered in some detail by Riley (1951) for the North Atlantic.

*Quantitative estimates*

Larger biogenic particles, as pointed out by McCave (1975), Hawley (1982), and others, have a density excess only of order $(\rho_s - \rho)/\rho = 0.1$. In warm near-surface waters the viscosity of seawater is near $\upsilon = 10^{-6}$ $\mathrm{m^2\ s^{-1}}$, hence the combined variable $B$ of Eq. 25 is typically

$$B = \frac{2(\rho_s - \rho)g}{9\upsilon\rho}$$

$$\cong 2 \times 10^5\ \mathrm{m^{-1}\ s^{-1}}.$$

The diffusivity of substances like $O_2$ or $NO_3^-$ in water is close to $D = 2 \times 10^{-9}$ $\mathrm{m^2\ s^{-1}}$, so that at the Peclet number separating "high" and "low" Pe (Pe = 8)

$$\mathrm{Pe} = \frac{2Br_0^3}{D} = 8,$$

from which one calculates $r_0 = r_l = 34$ $\mu$m, or $d = 68$ $\mu$m. It is interesting that this size coincides with the conventional limit of particles considered "fine."

As a crude model of the dissolution process, it will be supposed controlled by the availability of oxygen, supplied to the surface of a particle by diffusion. Bacterial activity will be supposed to establish an oxygen deficiency of $\chi_0/\rho_s = 10^{-6}$ (1 mg $\mathrm{kg^{-1}}$) at the particle surface. Oxygen supply is chosen as the rate-limiting process because the available diffusion potential for this substance is smaller than for nutrients. A more complete model would also take into account the oxygen utilization process within the particle itself, perhaps as Pasciak and Gavis (1974, 1975) have done for nutrient uptake. In terms of their work, the approach here corresponds to the diffusion-controlled limit, $P \ll 1$ ($P$: Pasciak and Gavis 1974, equation 11).

Mass loss from the particle will be taken to be due to reactions typified by

$$COH_2 + O_2 = CO_2 + H_2O$$

to which the oxygen has to be supplied at about the rate of mass loss, hence $\alpha \cong 1$ and $\phi_0 = \alpha\chi_0/\rho_s \cong 10^{-6}$.

Let a particle of initial size $r_0 = 10^{-4}$ m ($d = 200$ $\mu$m) be released at the sea surface.

It will decompose to a size corresponding to the Pe = 8 limit, $r_l = 34$ $\mu$m, in a period (Eq. 38):

$$t_l = \frac{r_i - r_l}{0.5\phi_0 B^{1/3} D^{2/3}}$$
$$= 14.4 \times 10^5 \text{ s}$$

(or about 15 days) by which time it reaches a depth of Eq. 41:

$$-z_l = \frac{(r_i^3 - r^3)B^{2/3}}{1.5\phi_0 D^{2/3}}$$
$$= 1{,}380 \text{ m.}$$

Subsequently, it sinks further only by (Eq. 32):

$$z_l - z_d = \frac{Br_l^4}{4D\phi_0} = 34 \text{ m.}$$

If the diffusion potential $\phi_0$ is twice as large as supposed, the dissolution depth is halved to about 700 m. Figure 4 shows particle size vs. depth for this case. On the other hand, a particle only half as large has a dissolution depth ⅛ of that calculated, i.e. <200 m.

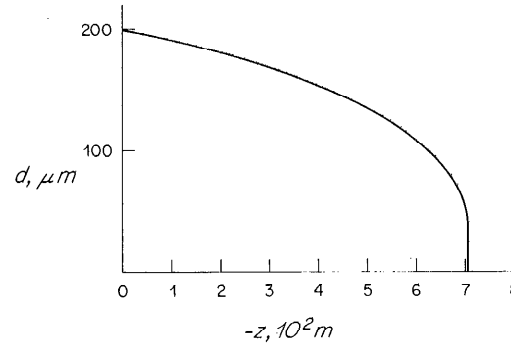


Fig. 4. Reduction of particle size with depth, for a spherical particle of initial size $d = 200$ $\mu$m, given a diffusion potential $\phi_0 = 2 \times 10^{-6}$ and typical material properties. Note sudden collapse of particle just above the dissolution depth of about 700 m.

*Discussion*

The particle dissolution model discussed here is clearly overidealized and no quantitative accuracy can be expected from it. In order of magnitude, it yields a realistic dissolution depth for large organic particles. While irregular particle shape and other complications clearly affect the actual depth of decomposition, the theoretical result regarding the dominant importance of particle size should be reliable. Similarly, the linear dependence of the mass exchanged on the diffusion potential $\phi_0$ is a fundamental property valid under a wide variety of circumstances. The material properties diffusivity and viscosity are intrinsically less important, and because they vary only within narrow limits in the sea (the diffusivity at least for $O_2$, $NO_3^-$, and similar ions) they should have little effect on $z_d$.

The net conclusion is that the development of an oxygen minimum, and nutrient maxima, at depths of order 1 km depends critically on the production of sufficiently large organic aggregates or fecal pellets in sufficient numbers.

Another result of the theoretical model is that large particles release their mass at about a constant rate down to almost their dissolution depth. Thus the appearance of an $O_2$ *maximum* layer also requires that in situ production or more efficient advection should counteract oxygen loss above the level of the minimum (and conversely for nutrients). This has been assumed in previous discussions of the problem (e.g. *see* Riley 1951).

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