SETTLING OF POROUS SPHERES, AS A PROXY FOR MARINE SNOW, THROUGH DENSITY STRATIFICATION

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Abstract

SUNGDUK YU: Settling of porous spheres, as a proxy for marine snow, through density stratification
(Under the direction of Brian L. White.)

The settling of marine snow, which is a dominant form of settling particulate organic carbon (POC), is a major pathway for carbon transport from the surface to the deep ocean. Although there have been many studies to estimate the global POC flux, the physical settling behavior of POC at an individual level has not been well investigated. Because marine snow is a hotspot for microbial activity, most POC is remineralized while sinking through the upper water column, limiting the total carbon export to the deep ocean. Thus, an understanding of the competing timescales of physical sinking vs. remineralization can lead to a better understanding of vertical carbon flux. Accordingly, the time scale of delayed settling of porous particles at the stratified region (residence time, $\tau_r$) is the key variable in this study. Here we present experimental results for the settling of a single and a cloud of porous spheres, as a proxy for marine snow, through water columns with various stratification regimes, e.g. homogeneous, 2-layered, and linearly stratified. In addition, the experimental results were compared with the results from numerical models formulated both for a single and a cloud of spheres. We found that the settling of porous spheres can be characterized by two regimes depending on their sizes—when sphere sizes are small, their settling behavior at a density interface is governed by their settling rate (settling regime), and when sphere sizes are large, their settling behavior at a density interface is governed by molecular diffusion (diffusion regime). In the settling regime, $\tau_r$ decreases with sphere size, while in the diffusion regime, $\tau_r$ increases with sphere size. The numerical models could predict the overall tendency of $\tau_r$ over the sphere sizes (e.g. the settling and diffusion regimes), but the $\tau_r$ from the numerical models were underestimated compared to the laboratory experimental results. However, the modified numerical model, which included the entrained fluid shell around a sphere, was able to return $\tau_r$ similar to the laboratory experimental results. Considering that the thin layers in the ocean are usually observed near density discontinuities, the prolonged retention of porous spheres within density stratification we observed could be a possible mechanism of thin layer formation.
Many people have helped me along the way of my research. First of all, I should like to convey my big thanks to Brian White, my advisor, who gave me an opportunity to be here together with UNC’s Marine Sciences department and complete my master’s research and who I discussed with about my research the most. I also had invaluable feedbacks on my research from my committee members (most of them were my class teachers, too)—Carol Arnosti, John Bane, Richard McLaughlin, and Harvey Seim—and from CMG project team—Roberto Camassa, Claudia Falcon, Emma He, Shilpa Khatri, Jenny Prairie, Chung-nan Tzou, and Bailey Watson. Also, Rachel Copeland and Lindsay Leonard helped me not miss the important time line. I also want to thank all my friends at UNC, who made this land home. I owe you more than I can return. To name a few, Elaine Monburu, Anna Jalowska, Tingting Yang, Jenny Prairie, Ivana Vu, Winnie Yu, Jihyuk Kim, Luke McKay, JP Balmonte, Popo, Jamie Browne, Sarah Underwood, Jesse Bikman, Natalie Cohen, Lisa Nigro, Ben Von Korff, Caroline Lowcher, Luke Dodd, Dan Hoer, and Mike Muglia (he surfs). Also, I thank my friends at home for moral support. Eunkyu Park, EJ Choi, Now He Sung, Juhngwha Lee, Byungho Cha, and Byungjun Song. Ultimately, my family. Thank you always for your unconditional support and love. (This work has been financially supported by National Science Foundation CMG Program ARC-1025523 and the Department of Marine Sciences at UNC Chapel Hill)
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Chapter 1

Background

Settling of marine snow, organic aggregates larger than 0.5 mm in diameter (Alldredge & Silver 1988) and a dominant form of settling particulate organic carbon (POC) (Fowler & Knauer 1986), has a central role in transporting organic carbon from the surface ocean to the interior ocean (Turner 2002). This has a direct linkage to the climate, for example, Falkowski (2000) estimated the annual export of 11–16 Gt of organic carbon from the surface to the deep ocean makes atmospheric carbon dioxide concentration 150–200 ppmv lower than the case with no primary production in the ocean. However, estimating how much organic carbon is exported is uncertain due to imperfect existing methodologies and limited sampled data (Burd et al. 2010). Studies using sediment traps, the only tool which can directly measure POC flux, gave 5.36 GtC/yr of global export production (Honjo et al. 2008). The model calculation based on the empirical relationship between sea surface temperature (SST), net primary production, and export production gave 11.1–20.9 GtC/yr depending on the model algorithms (Laws et al. 2000). An alternative approach using relationship between $^{234}$Th–$^{238}$U and SST yielded about 5 GtC/yr (Henson et al. 2011). In contrast to many efforts to estimate the global POC flux, the physical settling process of individual POCs has been left largely unstudied. The better understanding of the physical settling processes mechanistically will contribute the better incorporation of field data and important biogeochemical processes to the model. Accordingly, it will lead to the better estimation of the global POC flux.

A handful of studies in the lab as well as the field have been done on the settling rate of marine particulates such as fecal pellets, marine snows, and phytoplankton. Turner (2002) authored a review on the topic, and a summary of his review is given in table 1. The settling velocity of marine snow spans a wide range (16–368 m/day) because of variation in its density, size, and morphology. The settling velocity of marine snow has been found to increase with its size by lab experiments and in situ measurements (Kajihaera 1971; Alldredge & Gotschalk 1988; Iversen & Ploug 2010), and porosity also increases with the size (Kajihaera 1971; Alldredge &
Gotschalk 1988). Iversen & Ploug (2010) found the excess density of marine snow to the ambient water decreases with its size, while Alldredge & Gotschalk (1988) found no correlation between them. Besides the experimental studies, models to predict settling velocity and excess density of flocculated sediment in the river and coastal environment were proposed (Kranenburg 1994; Khelifa & Hill 2006).

<table>
<thead>
<tr>
<th>Particles</th>
<th>Sinking rate (m d⁻¹)</th>
<th>Source</th>
</tr>
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<tbody>
<tr>
<td>Euphausiids</td>
<td>16–862</td>
<td>Fowler &amp; Small (1972), Youngbluth et al. (1989), Yoon et al. (2001)</td>
</tr>
<tr>
<td>Appendicularians</td>
<td>25–166</td>
<td>Gorsky et al. (1984)</td>
</tr>
<tr>
<td>Chaetognaths</td>
<td>27–1313</td>
<td>Dilling &amp; Alldredge (1983)</td>
</tr>
<tr>
<td>Heteropods</td>
<td>120–646</td>
<td>Yoon et al. (2001)</td>
</tr>
<tr>
<td>Saips</td>
<td>43–2700</td>
<td>Madin (1982), Yoon et al. (2001)</td>
</tr>
<tr>
<td>Phytodetritus</td>
<td>100–150</td>
<td>Billett et al. (1983), Lampitt (1985)</td>
</tr>
</tbody>
</table>

Table 1: Sinking rates of zooplankton fecal pellets, marine snow and phytodetritus (adapted from Turner 2002).

Regardless of whether they were experimental or in situ observational studies, the previous studies were not able to actively control the important parameters of marine snows including size, density, porosity, and shape. Considering the various origins of marine snow, ones with an identical size and shape do not necessarily have same properties. Accordingly, a systematic approach is desired to elucidate the underlying physical processes.

Another limitation of the previous studies is that the majority of them examined settling velocities in a homogeneous density water column, not in a stratified environment, which is an ubiquitous feature of the ocean. In the tropics and temperate regions, the thermocline is a permanent feature of water column. The polar region generally lacks a permanent thermocline, but a seasonal thermocline often exists, and density stratification is also driven by salinity difference due to ice melting and formation. In addition to the bulk stratification, multiple pycnoclines at a meter scale in the surface ocean exist (Prairie et al. 2010). These density discontinuities have a significant correlation with marine snow’s vertical distribution (MacIntyre et al. 1995;
Lastly, the studies based on an individual particle overlook possible interactions between particles. This issue will be especially important for the episodic settling of large numbers of particles, e.g. algal blooms.

Only a very few studies have investigated the effect of stratification on the settling of real marine particles or porous particles. MacIntyre et al. (1995) studied the vertical distribution of marine snow and its correlation with density discontinuities by analyzing observational data and using models. Kindler et al. (2010) used manufactured porous particles and they found the porous particles are trapped for some period of time at the density transition layer to exchange the interstitial and the ambient fluids by molecular diffusion. Prairie et al. (2012) conducted similar research to Kindler et al. (2010) but with natural aggregates and proposed two possible mechanisms which reduce the settling velocity of particles in the density interface: 1) by diffusion, which is also observed by Kindler et al. (2010), and 2) by entrainment of lighter fluid from the upper layer.

In this study, the settling behavior of a single and a cloud of porous spheres, which resembles the highly porous nature of marine snow, was investigated. By using manufactured porous spheres, the key factors could be studied systematically because of the exclusion of the variability and uncertainty of physical characteristics including porosity, solid matrix density, and shape. In Theory, the governing physics will be discussed. In Methods, the experimental procedure and the formulation of the numerical model will be introduced. In Results and Discussion, the results from laboratory experiment and numerical simulation will be presented and discussed. Finally, in Conclusions, the findings of this study will be summarized, and future work will be suggested.

Theory

The porosity of spheres and the presence of density stratification distinguish this study from previous studies. The initial density of porous particles in this study is always lighter than the bottom layer (BL) fluid, while it is heavier than the top layer (TL) fluid. Once a porous particle reaches the depth of its neutral density, its settling speed is significantly reduced, and it gains further negative buoyancy by diffusive exchange of lighter interstitial fluid with denser ambient fluid. This density adjustment is unique to porous particles.
Settling of a single porous sphere in a stratified water column

The settling of a low Reynolds number sphere is governed by the Basset-Boussinesq-Oseen (BBO) equation. When no ambient fluid motion exists, the BBO equation is expressed as

\[
\frac{\pi}{6} \rho_s d^3 \frac{dU}{dt} = -\frac{\pi}{8} \rho_f U^2 C_D d^2 - \frac{\pi}{12} \rho_f d^3 \frac{dU}{dt} - \frac{3}{2} d^2 \sqrt{\pi \rho_f \mu} \int_{t_0}^{t} \frac{1}{\sqrt{t - \tau}} \frac{dU}{d\tau} d\tau + \frac{\pi}{6} (\rho_s - \rho_f) d^3 g
\]  

(1)

where \( \rho_s \) is the density of the sphere, \( d \) is the diameter of the sphere, \( U \) is the settling velocity of the sphere, \( \rho_f \) is the density of the ambient fluid, \( t \) is time, \( C_D \) is drag coefficient, \( \mu \) is dynamic viscosity of a fluid, and \( g \) is gravity (modified from Johnson 1998, chapter 18). The term on the left hand side is inertia, and the terms on the right hand side are drag force, added mass effect, basset force, and reduced gravity, respectively. In this study, the added mass effect and basset force are negligible (Khatri, 2012, unpublished data). Hence, equation (1) is simplified to

\[
\frac{\pi}{6} \rho_s d^3 \frac{dU}{dt} = -\frac{\pi}{8} \rho_f U^2 C_D d^2 + \frac{\pi}{6} (\rho_s - \rho_f) d^3 g.
\]  

(2)

As the Reynolds numbers of the spheres ranges from 0.1 to 10 in this study, a corrected Stokes drag law was used (White 1974):

\[
C_D = \frac{24}{Re} + \frac{6}{1 + \sqrt{Re}} + 0.4
\]  

(3)

\( (Re = \frac{\rho_f U d}{\mu}) \).

For a stratified water column, \( \rho_f \) is not a constant but a function of depth, \( z \),

\[
\rho_f = \rho_f(z).
\]

Accordingly, while a sphere is sinking, \( \rho_s \) also changes over time since diffusive exchange occurs whenever a density difference exists between ambient fluid and the interstitial fluid of a porous sphere. The density of a porous sphere with a porosity, \( P \), which is a volume fraction of the interstitial fluid out of the total volume of the sphere, can be defined as

\[
\rho_s = P \rho_{f'} + (1 - P) \rho_m
\]  

(4)

where \( \rho_{f'} \) is the average density of interstitial fluid, and \( \rho_m \) is the solid matrix density. Here, \( \rho_{f'} \) is theoretically a function of temperature, the concentration of salt inside a sphere, and pressure. Assuming the fluid is incompressible and temperature is constant, \( \rho_{f'} \) becomes a function of only
salt concentration, $C$:

$$\rho_f' = \rho_f'(C).$$

$C$ of the interstitial fluid of a sphere can change in a stratified water column, whenever a concentration difference exists between the ambient fluid and the interstitial fluid of the sphere. The salt concentration of the ambient fluid, $C_f$ at the surface of a sphere, which changes over time while a sphere is settling through stratification, drives molecular diffusion of salt into the sphere. Also, the gradient of salt inside a sphere usually exists because diffusion is a slow process compared to sinking of a sphere:

$$C = C(r,t)$$

where $r$ is the distance from the center to a point in a sphere.

The diffusive process can be described by Fick’s second law, assuming diffusion coefficient, $D$, is a constant.

$$\frac{\partial C}{\partial t} = D \frac{\partial}{r^2} \left( r^2 \frac{\partial C}{\partial r} \right) \quad (5)$$

Initial condition: $C(r,0) = 0$

Boundary conditions: $\frac{\partial C}{\partial r} = 0$ at $r = 0$, and $C = C_f$ at $r = d/2$

Then, the average concentration of interstitial fluid inside a sphere can be calculated.

$$C_{avg}(t) = \frac{\int_0^{d/2} C(r,t) \pi r^2 dr}{\frac{1}{6} \pi d^3} \quad (6)$$

$$\rho_f' = \rho_f'(C_{avg})$$

In this study, sodium chloride (NaCl) was used to stratify a water column. The conversion between $\rho_f'$ and [NaCl] was interpolated using a density-concentration table at 20°C (in appendix, Mettler Toledo).

**Settling of a cloud of porous spheres in a stratified water column**

If multiple particles settle simultaneously, the settling behavior of each particle might be different from the case of a single particle settling. For example, a particle cloud—a mixture of particles and fluid, the total density of which is higher than that of water column to be released—released instantaneously at the top of water column of homogeneous fluid descend in a form of thermal (hereafter, a negatively buoyant fluid mass will be called a thermal). Due to turbulent entrainment, the width of the thermal increases and the settling speed decreases as it sinks and incorporates the ambient fluid (Scorer 1957). Accordingly, the control factors determining the growth of a thermal can be described by its vertical location from the origin.
and the total buoyancy, $Q$,

$$Q = g'V_0,$$

where $Q$ is the released total buoyancy, $g'$ ($= \frac{\rho - \rho_f}{\rho}g$) is the reduced gravity, $\rho$ and $V_0$ are the initial density and the volume of the thermal, $\rho_f$ is the density of the ambient fluid, and $V$ is the volume of the thermal. Then, dimensional study shows

$$b = c_1z, \quad W = c_2Q^{1/2}/z, \quad g' = c_3Q/z^3,$$

where $b$ is the half horizontal length of the thermal, $z$ is the vertical length of the front from the release point, and $W$ is the settling speed of the thermal (Noh & Fernando 1993; Bush et al. 2003). The constants ($c_1$, $c_2$, and $c_3$) can be obtained empirically.

In a homogeneous column, theoretically the thermal, which consists only of a fluid denser than the water column, can sink indefinitely satisfying the above similarity condition because it has excess negative buoyancy at any moment. However, a particle cloud, which consists of heavy particles and a fluid with density identical to that of the water column, initially forms a thermal but does not propagate indefinitely. At a certain point, the particles in the thermal will fall out, and the separated particles form a bowl-shaped cluster, which settles as a group of independent individual particle, not as a thermal (Slack 1963; Rahimipour & Wilkinson 1992; Bühler & Papantonioiu 2001; Noh & Fernando 1993; Bush et al. 2003). Accordingly, two different regimes exist: the so called thermal regime and the particle settling regime (Noh & Fernando 1993). Noh & Fernando’s (1993) experiment found the critical depth measured from a virtual origin, $z_c$, where the transition between the two regimes happens, follows the relationship, $z_c w_s/\nu \sim (q/\nu w_s)^\alpha$ with $\alpha \approx 0.3$, where $w_s$ is the terminal settling velocity of an individual particle, $\nu$ is kinematic viscosity, and $q$ ($= \frac{4}{3}\pi a^3g'N$ where $a$ and $\rho_p$ are the radius and the density of a particle, respectively, $g'$ is the reduced gravity of the particles, $\frac{\rho - \rho_f}{\rho_p}g$, and $N$ is the number of the released particles per unit length) is the total buoyancy of the released particles per unit length. Later, Bush et al. (2003) found another empirical relationship: $z_c/a = (11 \pm 2)(Q^{1/2}/w_s)^{5/6}$.

Compared to a cloud of particles in a homogeneous environment, the settling of a cloud of particles in a stratified environment is not well investigated. Noh (2000) studied settling of a cloud of particles through a 2-layered environment. He found a cloud of particles settles uniformly keeping its cloud shape if it is in the particle settling regime ($X = q/lw_s^2 \ll 1$), where $l$ is the depth of the density interface; however, when the front of the cloud of particles hit the density interface, the cloud of particles spreads horizontally along the density interface forming a turbidity current—which is a fast-moving, sediment-laden fluid—if it is in the thermal regime ($X \gg 1$). In the latter case, the turbidity current can last as long as its virtual density is
lighter than that of the bottom layer, but it disappears soon because the particles escape while propagating and accordingly the turbidity current loses its momentum.

Bush et al. (2003) studied a cloud of particles in a linearly stratified column. They found when the stratified cloud number, $N_s = w_s Q^{-1/4} N^{-1/2}$ (Luketina & Wilkinson 1994), is bigger than unity, the cloud initially sinks as a thermal, then particles in the cloud fall out as a bowl-shaped swarm at a certain depth and the rest of fluid associated in the cloud ascends to the depth which matches its density. A vertical oscillation of the remaining fluid was observed at a frequency close to $N$, the buoyancy frequency of the ambient stratification. When $N_s < 1$, the cloud initially sinks as a thermal; however, the whole cloud overshoots the neutral depth, bounces back, and intrudes at the depth of its neutral buoyancy forming a gravity current. The particles in the cloud fall out between the maximum penetration depth and the neutral depth in an irregular shape.

To the author’s knowledge, no work has been done with clouds of porous spheres, the density of which is initially lower than that of the BL fluid but higher than that of the TL fluid. If the porous sphere is large enough that the diffusive uptake of salt from the ambient fluid takes for a certain period of time until it gains an excess negative buoyancy, the porous spheres in the cloud would be temporarily trapped at their neutral depth regardless of $X$ or $N_s$. On the other hand, if the porous spheres are so small that the diffusive fluid exchange occurs instantly, the settling behavior of the porous sphere cloud may be similar to the case of the solid (or non-porous) particle settling.

**Methods**

**Experimental scheme**

*Porous spheres*

The spheres used in this study were made of agarose. Smaller spheres (diameter: 50–300 μm) were supplied from a commercial supplier (ABT), and larger spheres were made in the laboratory according to Kiørboe et al. (2002). Agarose solution was prepared by microwaving agarose powder (Sigma Aldrich) and deionized (DI) water in a flask. Then, it was dripped into a beaker containing cooler DI water with a 1.5–2 cm thick mineral oil layer on the top. A pipette was used to drip the agarose solution, and the end of the pipette tip was cut to widen its mouth. The size of manufactured spheres ranged from 0.8 to 3 mm (figure 1).
Water column stratification

An acrylic water tank (28 cm L x 28 cm W x 60 cm H, inner dimension) was used to set up three kinds of water columns: 1) homogeneous water column, 2) sharp 2-layer stratified water column, and 3) linearly stratified water column. For a 2-layer stratification, BL fluid with a higher density was poured first, and TL fluid, which was always DI water, was introduced slowly using a diffuser, a sponge with a styrofoam rim which floats on water. For linear stratification, BL fluid was poured to a certain height, then Oster’s (1965) two vessel technique was applied to make a linearly stratified region, and finally TL fluid was introduced at the top using the diffuser. For some experiments, a same 2-layered water column sit for an extended period of time to make its stratification thicker (figure 21 (c)).

After setting up a stratified water column, temperature and conductivity were profiled every 1 cm or 0.5 cm around the density interface from the bottom to the top using a sensor (MSCTI Model 125, PME Inc.), then converted to density using Gibbs-SeaWater (GSW) Oceanographic Toolbox (McDougall & Barker 2011). However, due to the discrepancy of the composition between the real seawater and a NaCl solution, GSW Oceanographic Toolbox does not return the actual density of the NaCl solution. Accordingly, it was scaled using the actual densities of BL and TL fluids, which were measured by a density meter (DMA 35, Anton Paar).

Video imaging

A monochrome camera (Pike F-100C, AVT) with computer imaging acquisition software (SmartView, AVT GmbH and StreamPix, NorPix Inc.) was used. An LED light panel was placed on each of two opposite side walls of the water tank during experiment, and images were
taken at about 8 or 16 frames per second (figure 2). The frame size was 1,000 x 1,000 pixels at maximum with bit depth of 8 or 16 bit/pixel. The timestamp function on the software did not return the right time information due to an unknown computer error, so time information was reconstructed using an average time interval (the total number of images / [the oretime the last image was taken - the time the first image was taken]).

Experiments

Single sphere experiment. Water columns with different stratification were made, then the water tank was covered with a specially designed lid to prevent effects from any free surface disturbance, which was submerged to a depth of about 2 cm. The lid had a 4 mm diameter hole at its center, where a sphere was released. Another hole, wider than the center hole, for a conductivity and temperature measuring probe was located at each of the four corners. After the diameter of a sphere was measured using a gridded slide with a digital microscope (26700-300, Aven Inc.), the sphere was taken gently by a pipette, and released to the water column through the center hole of the lid. Images were acquired while the sphere was settling. At the end of each experiment, an image of a ruler in the tank was captured to scale the pixel size. The spheres were collected to use in other experiments. All spheres were always hydrated in TL fluids before experiment.
Fig. 2: Experimental setup. The water tank with inner dimensions of 28 cm L x 28 cm W x 60 cm H was built of acrylic. LED lighting apparatuses were placed on each side of the tank. The water column was homogeneous or stratified according to the purpose of the experiment. A single sphere or a cloud of spheres was released from the top of the tank. For single sphere releasing experiments, an acrylic lid with a center hole sat just below the water surface in order to eliminate disturbances due to the free surface.

Cloud of spheres experiment. Experimental procedures were identical to that of the single sphere experiment, except for the sphere preparation stage and the presence of a lid. The lid was not used, since the free surface disturbance was not as significant as in the case of the single sphere experiments. The spheres were sorted by using sieves with different mesh sizes (0.053, 0.100, 0.150, 0.180, 0.250, 0.300, 1.00, 1.40, 1.70, 2.00, 2.36, 2.80 mm, Cole-Parmer). Then, each was weighed on a balance and made into a cloud solution with a certain concentration of spheres (known weight of spheres to a total weight of the spheres and DI water). Large-sphere clouds, with the total weight of 9.2 or 10 g, were released using a stemless funnel and a plunger as described in Bush et al. (2003). However, clouds of small spheres, with total volume of 1 cm³, was released by a pipette slowly. The concentration of spheres in a cloud was always 25% (25% of spheres and 75% of DI water by weight).

Image processing

Preconditioning. Images were processed using MATLAB (MathWorks) and DataTank (Visual Data Tools Inc.). First, the size of an image was cropped to exclude the non-working area, and
the background image, which was usually set to be the image at \( t = 0 \), was subtracted from the cropped image. Then, low-value signals under a threshold (1–2 % of the saturated value of a pixel) were removed from all pixels in each image.

**Single sphere tracking.** The initial location of a sphere at \( t = 0 \) was picked manually, and then the sphere was tracked automatically with the following algorithm: 1) set a small region around the sphere, 2) identify all dots in the region, 3) pick dots bigger than a certain area, which is a number of connected pixels, 4) find a dot with the largest area, which is assumed to be the sphere, and 5) if the number of dots with the largest area are more than two, find a dot which is the closest to the previous sphere position. The centroid of the connected pixels in a dot was set as a position of the sphere. Finally, the trajectory was smoothed using a Butterworth filter in order to remove fluctuations due to a fairly large pixel size that is comparable to the size of the sphere.

**Cloud of spheres tracking.** The centroid of the whole cloud was tracked for each image using the following equation,

\[
Z_c(t) = \int_0^{z_n} \left( z \frac{\int_0^{x_n} \int_0^{z_n} i(x, z, t) dx}{\int_0^{x_n} \int_0^{z_n} i(x, z, t) dx dz} \right) dz
\]

where \( Z_c \) is the vertical location of centroid, \( z_n \) is the vertical length of the image in pixels, \( x_n \) is the horizontal length of the image in pixels, and \( i(x, z, t) \) is the signal intensity at \((x, z)\) at time \( t \). Also, 2nd, 3rd, and 4th moments were calculated to investigate the shape of a cloud:

**Standard deviation, \( SD(t) \)**

\[
SD(t) = \sqrt{\int_0^{z_n} (z - Z_c(t))^2 \frac{\int_0^{x_n} \int_0^{z_n} i(x, z, t) dx}{\int_0^{x_n} \int_0^{z_n} i(x, z, t) dx dz} dz}
\]

**Skewness**

\[
Skewness(t) = \frac{1}{SD(t)^3} \int_0^{z_n} (z - Z_c(t))^3 \frac{\int_0^{x_n} \int_0^{z_n} i(x, z, t) dx}{\int_0^{x_n} \int_0^{z_n} i(x, z, t) dx dz} dz
\]

**Kurtosis**

\[
Kurtosis(t) = \frac{1}{SD(t)^4} \int_0^{z_n} (z - Z_c(t))^4 \frac{\int_0^{x_n} \int_0^{z_n} i(x, z, t) dx}{\int_0^{x_n} \int_0^{z_n} i(x, z, t) dx dz} dz
\]

**Numerical models**

**Single sphere model**

The model calculates the location of a porous sphere at each time step (schematic diagram of the model is shown in figure 3). Letting the center of ambient stratification be at \( z = 0 \) and \( z \) increases toward the direction of gravity, the settling velocity of the sphere is

\[
U(t) = \frac{dz_p}{dt}
\]
where \(z_p\) is the position of the sphere. Then, it is discretized with a forward time scheme,

\[
z_{p_{t+1}} = z_{p_t} + \Delta t \cdot U_t.
\]

\(\frac{dU}{dt}\) was discretized from equation (2) with forward time scheme,

\[
U_{t+1} = U_t + \Delta t \left( -\frac{3\rho_f C_D U^2}{8\rho_s a} + \frac{\rho_s - \rho_f}{\rho_s} g \right)
\]

where \(a\) is the radius of a sphere. The initial velocity, \(U_0\), is an arbitrarily assigned small number since \(C_D\) cannot be defined when \(U = 0\).

![Schematic diagram of the numerical model](image)

\[
\begin{align*}
dw_s &= \sqrt{\frac{4}{3} g} \frac{d\Delta\rho}{C_D \rho_f} \\
\rho &= \rho(s, T, p) \\
&= \rho([\text{NaCl}])
\end{align*}
\]

(Fig. 3: Schematic diagram of the numerical model. The left shows a density profile of a stratified water column. When a porous sphere settles in a stratified water column, it experiences a change in \(\Delta\rho\), the density difference between the sphere and the ambient fluid. \(\Delta\rho\) is a key control factor of settling speed. Because all experiments were performed at room temperature and the water column height was only 60 cm, density of fluid becomes a function of the concentration of salt (NaCl) in this study. As the sphere was porous, salt molecules are diffused from the ambient fluid to into the sphere since the settling sphere has lighter interstitial fluid than the ambient fluid at depth. The diffusion equation was adapted to our model with an initial condition that the salt concentration ([NaCl]) is initially zero and two boundary conditions: 1) [NaCl] of the interstitial fluid on the sphere’s surface is identical to that of the surrounding ambient fluid and 2) the gradient of [NaCl] at the center of sphere is zero.

In the presence of ambient stratification, a porous particle changes its density until equilibrium as long as the density of interstitial fluid of a sphere \(\left(\rho_f'\right)\) is different than that of ambient fluid \(\left(\rho_f\right)\). Diffusion equation (equation (5)) was discretized with forward time and central space schemes,

\[
C_{r,t+1} = C_{r,t} + \Delta t[k_1 C_{r+1,t} + k_2 C_{r,t} + k_3 C_{r-1,t}],
\]

on a grid.

12
\[ k_1 = \frac{D}{r\Delta r} + \frac{D}{\Delta r^2}, \quad k_2 = -\frac{2D}{\Delta r^2}, \quad k_3 = -\frac{D}{r\Delta r} + \frac{D}{\Delta r^2}, \]

where \( C_{r,t} \) is a concentration of salt at a point with a distance of \( r \) from center and at time of \( t \), \( \Delta r \) is a spatial grid spacing, and \( \Delta t \) is a time step spacing. The initial salt concentration of the interstitial fluid was assumed to be zero. For each time step, the boundary conditions change. To calculate the \( C_{r,t+1} \), \( C_{0,t} \) and \( C_{a,t} \) were substituted with \( C_{dr,t} \) and \( C_f(z_p(t)) \), respectively.

The average concentration of salt of the interstitial fluid, \( C_{avg} \), was calculated using equation (6),

\[
C_{avg}(t) = \sum_{i=0}^{nr-2} \frac{4}{3\pi}[ (dr \cdot (i+1))^3 - (dr \cdot i)^3 ] \frac{C_{dr,(i+1),t} - C_{dr,i,t}}{2}
\]

where \( nr \) is the number of spatial grid points along the radial axis, and \( dr \) is the spatial grid spacing. Then, \( C_{avg} \) was converted to \( \rho_f' \). Then, \( \rho_s \) was calculated using equation (4).

White’s (1974) empirical drag law (equation (3)) was used for \( C_D \). The ambient density profile \( \rho_f \) was approximated to a fitted curve from each experiment. An error function fit was used for 2-layered stratification,

\[
\rho_f(z/\sqrt{4Dt^*}) = \rho_f + \frac{\Delta \rho_f}{2} erf(z/\sqrt{4Dt^*})
\]

where \( t^* \) is the characteristic time which best fits the measured density profile. Also, a piecewise cubic Hermite interpolating polynomial function fit was used for linear stratification.

**Cloud model**

Assuming no interparticle effects, a cloud of spheres was modeled as a histogram of the vertical positions of \( n \) single spheres with different sizes. Also, all particles were assumed to be at rest at \( t = 0 \), and accordingly, the model did not demonstrate a thermal phase which occurred upon the release of a cloud of spheres in experiment. First, the single sphere model described above was simulated to obtain the vertical location, \( z_p \), at each time for spheres with the range of sizes \( (z_{a_1}, z_{a_2}, z_{a_3}, \cdots, z_{a_n} \) where \( a_n \) is the radius of sphere and \( a_n - a_{n-1} = constant \)). Then, assuming the size distribution of spheres in the cloud is a normal distribution, each sphere was weighted according to its size frequency by multiplying by its probability density function, \( p = p(a) \). This was again multiplied by an arbitrary intensity function \( (I(a) \propto a^3) \), a function of the scattered light intensity according to sphere size, to demonstrate the actual experimental condition. At each time step, all spheres’ locations were binned to a gridded vertical axis. In this manner, the vertical distribution of spheres was tracked at each time point.
**Results**

Three main sets of laboratory experiment were conducted to investigate the settling behavior of porous spheres in the present of stratification: 1) settling of single spheres in homogeneous water columns, 2) settling of single spheres in stratified water columns, and 3) settling of sphere clouds in stratified water column. Porous spheres made of agarose were used as a proxy for marine snow, and sodium chloride was used as a stratifying agent. By using these laboratory-manufactured spheres, the potential uncertainties caused by the irregular shape, porosity, and solid matrix density of real marine snow could be excluded while maintaining key parameters (e.g. porosity and stratification type). The parameters utilized in the experiments were sphere size, type of density stratification, and porosity (table 2). In addition, numerical simulation was conducted to demonstrate both settling of a single sphere and of a cloud of spheres. Then, results from the lab experiments were compared with that from the numerical simulation.

<table>
<thead>
<tr>
<th>ID</th>
<th>Radius (mm)</th>
<th>(\rho_{TL}) (g/cm(^3))</th>
<th>(\rho_{BL}) (g/cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1†</td>
<td>—</td>
<td>0.9982</td>
<td>—</td>
</tr>
<tr>
<td>2†</td>
<td>—</td>
<td>1.0108</td>
<td>—</td>
</tr>
<tr>
<td>3†</td>
<td>—</td>
<td>1.0216</td>
<td>—</td>
</tr>
<tr>
<td>4†</td>
<td>—</td>
<td>1.0300</td>
<td>—</td>
</tr>
<tr>
<td>5†</td>
<td>—</td>
<td>1.0407</td>
<td>—</td>
</tr>
</tbody>
</table>

**Homogeneous Column**

<table>
<thead>
<tr>
<th>ID</th>
<th>Diameter (mm)</th>
<th>Releasing Amount</th>
<th>Sphere Concentration (%)</th>
<th>(\rho_{TL}) (g/cm(^3))</th>
<th>(\rho_{BL}) (g/cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1.00–1.40, 1.40–1.70, 1.70–2.00</td>
<td>10 g</td>
<td>25% spheres</td>
<td>0.9979</td>
<td>1.0225</td>
</tr>
<tr>
<td>11</td>
<td>2.00–2.36, 2.36–2.80</td>
<td>10 g</td>
<td>+</td>
<td>0.998</td>
<td>1.02</td>
</tr>
<tr>
<td>12†</td>
<td>0.150–0.106, 1.40–1.70</td>
<td>1ml, 9.2g</td>
<td>75% TL fluid</td>
<td>0.9983</td>
<td>1.0220</td>
</tr>
<tr>
<td>13</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.9980</td>
<td>1.040</td>
</tr>
<tr>
<td>14</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.9980</td>
<td>1.0201</td>
</tr>
<tr>
<td>15</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.9980</td>
<td>1.0101</td>
</tr>
</tbody>
</table>

(a) Single sphere experiment list. (†: the experiment were repeated three times.)

(b) Cloud experiment list. (†: the experiment was conducted with five different density interface thicknesses.)

**Table 2:** List of experiments.

**Homogeneous column experiment**

The eight agarose (1%) spheres in table 3 were released in five different homogeneous water columns—0.9981, 1.0102, 1.0216, 1.0300, and 1.0406 g/cm\(^3\). For each column, three sets of
repetitive experiments were done.

<table>
<thead>
<tr>
<th>Sphere ID</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius (mm)</td>
<td>0.4266</td>
<td>0.4451</td>
<td>0.5380</td>
<td>0.6260</td>
<td>0.6576</td>
<td>0.7826</td>
<td>0.8512</td>
<td>0.9413</td>
</tr>
<tr>
<td>(Re) in Fresh Water</td>
<td>1.3246</td>
<td>1.5287</td>
<td>2.3631</td>
<td>3.4739</td>
<td>3.8325</td>
<td>5.6344</td>
<td>6.9021</td>
<td>8.5932</td>
</tr>
</tbody>
</table>

Table 3: Agarose spheres used for a single sphere experiment. The ID, radius, and Reynolds number of each sphere are shown in the first, second, and third rows, respectively.

The vertical position of a sphere was plotted for the entire time domain. However, in some cases, fluctuation existed near the bottom. Accordingly, the top 50 pixels and the bottom 300 pixels were cropped (figure 4). The trajectories in the cropped region were each fit with a line by the least squares method, and the slope of each curve was the terminal settling velocity, \(w_s\). As each experiment was repeated three times, the mean value of the three became the final settling velocity used for further analysis.

![Fig. 4](image)

Fig. 4: Vertical trajectories of the eight agarose spheres (table 3) in a homogeneous column with 1.0406 g/cm\(^3\). Each different color marks a different sphere whose ID number is shown in the box at the top right corner. Only the middle section between the two dashed lines was used to calculate the settling velocity of each sphere.

Equation (2) with \(dU/dt = 0\) and \(U = w_s\) is rearranged to

\[
\rho_s = \left( \frac{3CDw_s^2}{4dg} + 1 \right) \rho_f.
\]

The total density of each sphere was calculated with the above equation using \(w_s\) from experiment.

Then, the porosity, \(P\), and the solid matrix density, \(\rho_m\), were calculated by linear regression.
between $\rho_f'$ and $\rho_s$ using equation (4). As the spheres were hydrated in the same fluid of the water column before experiment, $\rho_f'$ was identical to $\rho_f$. The porosity was 0.9916 and the matrix density was 1.5215 g/cm$^3$ (figure 4). These values were used for the numerical model simulation.

![Diagram](image)

Fig. 5: Linear regression between the water column density and the sphere density. According to equation (4), the slope of the linear regression line is the porosity ($P$) of agarose spheres, and the y-intersect is the product of $(1 - P)$ and the density of matrix, $\rho_m$. $P = 0.9916$ with 95% confidence interval [0.9886, 0.9947], $\rho_m = 1.5215$ with 95% confidence interval [0.8624, 2.1806], $R^2 = 0.9997$.

**2-Layer stratification experiment**

In the presence of stratification, regardless of its type and the strength (figure 6), all spheres show delayed settling around and inside the stratification (figure 7). A larger sphere reaches the entrance of the stratified region earlier but escapes later than a smaller one (e.g. compare the results of sphere 1 and 8 in figure 7). Also, we can observe the sphere’s speed gain when it escapes the stratification region is slower than its speed loss when it enters the region (e.g. compare the first and second kinks of each line in figure 7). This is because the sphere needs only a slight negative buoyancy to escape the stratification and to settle through BL water.
Fig. 6: Density profiles of water columns used for a single sphere settling experiment. The blue circles are the measured densities using a CT probe, and the red lines are the fitted curves—an error function was used for a and b, and a piecewise cubic Hermite interpolating polynomial function was used for c and d. $\rho_{\text{top}}$ was always fresh water, while $\rho_{\text{bottom}}$ was 1.0216 g/cm$^3$ (a and c) and 1.0406 g/cm$^3$ (b and d). Experiments were done in both sharp 2-layered stratification (a and b) and linear stratification (c and d).
Fig. 7: Vertical trajectories of the eight agarose spheres (in table 3). The first two figures (a and b) are in the sharp 2-layer stratification (as in figure 6 (a) and (b)), and the last two figures (c and d) are in the linear stratification (as in figure 6 (c) and (d)).
The single most important parameter is a time scale of delayed settling due to stratification, because it has important ecological implications—e.g. the amount of POC remineralized or consumed by microbes and zooplankton is related to the time that POC spends in the water column. To measure the time scale, residence time, $\tau_r$, was introduced (figure 8). $\tau_r$ was defined as the time taken to settle through a stratified region. The stratified region was defined as the region where the local density gradient is equal to or greater than one thousandth the maximum local density gradient ($z$ where $\frac{d\rho}{dz} \geq 0.001 \max(\frac{d\rho}{dz})$, figure 8 (c)). In addition, residence time normalized by settling time scale, $\tau_r/\tau_s$, was used when necessary. The settling time scale, $\tau_s$ was defined as

$$\tau_s = \frac{1}{2} \left( \frac{l_{box}}{w_{TL}} + \frac{l_{box}}{w_{BL}} \right)$$

(11)

where $l_{box}$ is the vertical length of the stratified region as defined in figure 8 (b), and $w_{TL}$ and $w_{BL}$ are the terminal settling velocities of the sphere in TL and BL fluids, respectively.
Fig. 8: The definition of residence time, $\tau_r$. The vertical position of a sphere over time (from the numerical simulation using profile of figure 6 (a), where the center of stratification is located at the zero depth) is shown in (a). The vertical length of the density region is defined as the region where $d\rho_f/dz$ is equal to or higher than 0.1% of the maximum $d\rho_f/dz$ (b). The residence time is the difference in two time points when a sphere passes the upper boundary and the lower boundary of the density interface (c).

The result shows a trend that a larger sphere has a longer $\tau_r$ in both 2-layered and linear stratifications (figure 9). A larger sphere had a larger interstitial volume initially containing TL fluid, which was always fresh water. Accordingly, compared to a smaller sphere, a larger sphere takes a longer time to exchange the lighter interstitial fluid with the denser ambient fluid. Also, it is observed that a stronger density stratification delays the settling of a sphere longer than a weaker one, because a sphere should take more salt by molecular diffusion to be denser than BL fluid. The $\tau_r$ in a linear stratification is longer than that in a 2-layer stratification (figure 10), although in a linear stratification the settling speed of a sphere does not approach zero. This would be because linear stratification has a longer vertical length scale of stratification for a given $\Delta \rho_f$ than a 2-layer stratification. Therefore, settling through a longer length in linear stratification takes more time, while the time scale for diffusive process would be similar.
Fig. 9: $\tau_r$ of a settling single sphere from experiments in 2-layer stratification (a) and in linear stratification (b). The density difference between top and bottom layers ($\Delta \rho_f$) was $\sim 0.04 \text{ g/cm}^3$ (blue) and $\sim 0.02 \text{ g/cm}^3$ (red). The spheres in table 3 were used.

Fig. 10: $\tau_r$ of a settling single sphere from experiments in $\Delta \rho_f \approx 0.02$ (a), $\Delta \rho_f \approx 0.04$ (b). Water column stratification was linear (blue) and 2-layered (red). This figure and figure 9 share same data, but organized differently. The spheres in table 3 were used.

As shown in figure 11, the numerical model did not reproduce the experimental result per-
fectly. However, it seems to predict the tendency well, although the $\tau_r$ was significantly lower in the numerical simulation result than the experimental result (figure 13). The main reason is likely to be the entrainment of the buoyant TL fluid (Srdic-Mitrovic et al. 1999; Abaid et al. 2004; Camassa et al. 2009, 2010). The entrained fluid from the TL forms a shell of lighter fluid (figure 12) around a sphere, which acts as a barrier to molecular diffusion. Because the [NaCl] of the entrained fluid is lower than that of the ambient fluid, it slows down the diffusive exchange process.

![Diagram showing vertical trajectories](image)

Fig. 11: Comparison of vertical trajectories between experimental (blue) and numerical (red) results in 2-layer stratification (top) and linear stratification (bottom) with $\Delta \rho_f \approx 0.04 g/cm^3$. Left figures are the result of the agarose sphere with 1.0760 mm diameter, and right figures are the result of the agarose sphere with 1.8825 mm diameter.
Fig. 12: Entrainment of fluid (adapted from Camassa et al. 2009). A sphere with 0.635 cm radius and a density heavier than BL fluid was released from the top in a stratified fluid column in a acrylic cylinder with 9.45 cm radius. The pictures were taken every 10 seconds. The TL fluid was the mixture of pure corn syrup and dye with the density of 1.37661 g/cm$^3$, while the BL fluid was the mixture of pure corn syrup and salt with the density of 1.38384 g/cm$^3$.

2-Layer

<table>
<thead>
<tr>
<th>Sphere Size, a (mm)</th>
<th>Residence Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>0</td>
</tr>
<tr>
<td>0.6</td>
<td>200</td>
</tr>
<tr>
<td>0.8</td>
<td>400</td>
</tr>
<tr>
<td>1</td>
<td>600</td>
</tr>
</tbody>
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<td>400</td>
</tr>
<tr>
<td>1</td>
<td>600</td>
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</tr>
<tr>
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<td>200</td>
</tr>
<tr>
<td>0.8</td>
<td>400</td>
</tr>
<tr>
<td>1</td>
<td>600</td>
</tr>
</tbody>
</table>

BL: $\cong 1.02$ g/cm$^3$

BL: $\cong 1.04$ g/cm$^3$

2-Layer

Linear

<table>
<thead>
<tr>
<th>Sphere Size, a (mm)</th>
<th>Residence Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>0</td>
</tr>
<tr>
<td>0.6</td>
<td>200</td>
</tr>
<tr>
<td>0.8</td>
<td>400</td>
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<tr>
<td>1</td>
<td>600</td>
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<th>Residence Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>0</td>
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<tr>
<td>0.6</td>
<td>200</td>
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<tr>
<td>0.8</td>
<td>400</td>
</tr>
<tr>
<td>1</td>
<td>600</td>
</tr>
</tbody>
</table>

Fig. 13: Comparison of $\tau_r$ between experimental (blue) and numerical (red) results in 2-layer stratification (top) and linear stratification (bottom). The density difference between top and bottom layers ($\Delta \rho_f$) is $\sim 0.02$ g/cm$^3$ (left) and $\sim 0.04$ g/cm$^3$ (right). The spheres in table 3 were used.

The settling behavior of smaller spheres ($< 0.4$ mm radius) was investigated only through numerical model simulation because of the limitation of experimental technique. Imaging such a
small particle was not implementable with the current experimental setup. In addition, porous spheres in this size range could not be manufactured with the same method in the laboratory. When a sphere is smaller than a certain size, $\tau_r$ decreases with the size of the sphere (figure 14 (a) and (c)). On the other hand, the opposite is true for a sphere that is larger than a certain size. When a porous sphere is smaller than a certain size, it seems that a diffusive process is less important for a smaller sphere than a larger sphere that because equilibration occurs relatively faster due to a lesser volume of interstitial fluid. In such a case, physical settling rates would be more important. A smaller sphere has a smaller settling velocity, and accordingly, it has a longer time to settle through the stratified region. This can be also seen using $\tau_r/\tau_s$ (figure 14 (b) and (d))—for smaller spheres, $\tau_r/\tau_s$ is $\sim 1$.

It seems that two main regimes exist for settling of a single porous sphere through stratification. When a porous sphere is smaller than a certain size, settling process is governed by settling process (settling regime). On the other hand, when a porous sphere is larger than a certain size, settling process is governed by diffusion process (diffusion regime). The transition size range between the two regimes might be around the size, with which a sphere has the lowest $\tau_r$. 
Fig. 14: $\tau_r$ and $\tau_r/\tau_s$ from the numerical simulation. The water column density profile of experiment #6–9 in table 2 was used (figure 6). The vertical lengths of density interface region was 3.09 (blue) and 3.97 (red) cm for 2-layer stratifications (top) and 26.00 (blue) and 29.00 (red) cm for linear stratifications (bottom).

**Settling of a cloud of porous spheres**

Centroids were used to track the position of clouds for both experiment and numerical simulation, using equation (7). In general, the settling of a porous sphere cloud showed a similar behavior to that of an individual porous sphere. A cloud with larger spheres (a large-sphere cloud) nearly stopped settling in the stratified region (figure 15 (d) and (e)), while a cloud with smaller spheres (a small-sphere cloud) sharply decelerated its settling rate, but not stopped, in the stratified region (figure 15 (a), (b), and (c)). Accordingly, $\tau_r$ of clouds of spheres would also have a v-shaped trend similar to the settling of an individual sphere (figure 14)—$\tau_r$ of a cloud with spheres smaller than a certain size decreases with the sphere size (settling regime), while
that with spheres larger than a certain size increases with the sphere size (diffusion regime)—
(figure 16, figure 17, and figure 18). This can be also inferred from $\tau_r/\tau_s$ (figure 19). For
small-sphere clouds, $\tau_r/\tau_s$ is $\sim 1$, which indicates that $\tau_r$ is governed by settling process. On the
other hand, for large-sphere clouds, $\tau_r/\tau_s$ is an order(s) of magnitude larger than 1 and increases
with the sphere size range of a sphere cloud. It indicates that $\tau_r$ of large-sphere clouds is not
governed by settling process but involves other processes, among which molecular diffusion seems
most important.
Fig. 15: Cloud centroid vs. time. $\Delta \rho_f$ was $\sim 0.02g/cm^3$ in both experiments. The total releasing amount was 1 cm$^3$ (a, b, and c) and 8–10 g (d and e), while the sphere concentration was same in all experiments (25% w/w). The spheres were made of 4% agarose (a, b, and c), 1% agarose (d), and 2% agarose (e). All graphs were smoothed using the Butterworth filter.
Fig. 16: $\tau_r$ of different clouds of spheres. $\tau_r$ of single sphere experiment are also plotted for comparison (yellow and dark grey). More details are in figure 17 and figure 18.

Fig. 17: $\tau_r$ of clouds of small spheres (53–300 µm) in different $\Delta \rho_f$. The total volume of each cloud was 1 cm$^3$ (25% of spheres and 75% of TL fluid (w/w)). The size range of each cloud was 53–106, 106–150, 180–250, 250–300 µm in diameter. Different colors show different $\Delta \rho_f$. The concentration of agarose of spheres was 4% in all experiments.
For large-sphere clouds, $\tau_r/\tau_s$ has a power law relationship with the median size of spheres in the clouds (figure 19). It is also true for $\tau_r/\tau_s$ of single spheres, and it seems that the relationship between $\tau_r/\tau_s$ and sphere size is similar among the single sphere settling and the sphere cloud settling. The exponents ($\alpha$, $\tau_r/\tau_s \sim \text{size}^{\alpha}$) lie between 2.427 and 2.699. Considering that diffusion time scale is proportional to size$^2$ ($\tau_d = \text{size}^2/2D$), the experimental results shows that unknown processes, which further prolong $\tau_r$, in addition to molecular diffusion might be involved. It is likely to be an influence of the entrained shell of TL fluid around a sphere, because it works as a barrier which slows down the diffusive exchange of salt by decreasing the gradient of salt at the surface of a sphere. Kindler et al. (2010) found the empirical relationship between residence time ($\tau_r^*$) and sphere size is $\tau_r^* \sim \text{size}^{2.1}$ ($\tau_r^*$ is Kindler et al.’s (2010) normalized residence time, $(\tau_r - \tau_s)/\tau_s$). Their $\alpha$ does not match with ours, and it would be due to the different experimental set up, e.g. the porosity and the solid matrix density of porous sphere and $\Delta \rho_f$. Nonetheless, their result still indicates processes other than diffusion would be involved in the settling of a porous particle.
Both large- and small-sphere clouds seemed sensitive to the density slope of stratification, \( d\rho_f/dz \), (figure 21), while small-sphere clouds were more sensitive. When \( \Delta \rho_f \) was constant, \( \tau_r \) was higher with smaller \( N^2 \). This might be due to the different thickness of the stratified region. When the stratification has a wider density interface or a smaller \( N^2 \), the time to settle through the stratified region is longer. Accordingly, small-sphere clouds, which are in the settling regime (\( \tau_r/\tau_s \sim 1 \) in figure 21 (b)), are more sensitive to the vertical extent of stratification than large-sphere clouds, which are in the diffusion regime.
The numerical model of a porous sphere cloud was an ensemble of numerical simulation results of individual spheres (figure 22). The settling of individual spheres of various sizes with a uniform increment was simulated, and a sphere of each different size was weighted using a hypothetical size distribution. Then, the distribution of all spheres were recorded at every time step.

The cloud model result did not exactly match the experimental result (figure 22 (c)). First, the settling rate of the centroid in the actual experiment was initially faster than that of the model and decelerated in the top layer. This is due to turbulent entrainment (Scorer 1957; Noh & Fernando 1993; Bush et al. 2003). A cloud released with sufficient momentum gains a high velocity and accordingly generates turbulence, which eventually enhances mixing with ambient fluid. Through turbulent entrainment, the cloud grows while sinking, and its settling velocity
decreases since the initial momentum is diluted with entrained ambient fluid over time. However, the numerical model assumes every sphere in a cloud was initially at rest and accordingly had zero momentum. Hence, the numerical model result did not reproduce the same evolution of the sinking process.

Second, $\tau_r$ is significantly shorter in the numerical simulation result than in the experimental result (figure 23). The numerical model is an ensemble of results from single sphere settling model simulations, so it inherently has the same problem as the single sphere model—the absence of entrainment of lighter fluid from the top layer. However, it predicted the overall tendency of $\tau_r$ over the sphere size in clouds (figure 23).

![Graph showing depth vs. time and radius vs. probability density](image)

**Fig. 22:** Numerical simulation of a cloud of spheres. (a) Trajectories of individual spheres (d: 1.71–2.00 mm with 0.01 mm increment) from numerical simulation. The size distribution is shown on the right graph. Color scheme corresponds. (b) Size distribution (pdf) of spheres in a cloud. Normal distribution was assumed with $d_{\text{mean}} = d_{\text{median}}$ and $2\sigma = d_{\text{median}} - d_{\text{min}}$. (c) Comparison between experiment and numerical simulation. Experiment conditions were $\Delta \rho_f \approx 0.02 g/cm^3$, sphere size range: 1.70–1.20 mm, and releasing amount 10g (2.5g sphere + 7.5g TL water) as found in #10 in table 2.
In addition to the residence time of clouds, the evolution of cloud shapes over time was different between a small-sphere cloud and a large-sphere cloud (figure 24). Upon release, both clouds formed a turbulent thermal, but a small-sphere cloud seemed as if its thermal phase was terminated before reaching the density interface, while a large-sphere cloud was in a thermal phase when it hit the density interface. Accordingly, a large-sphere cloud arrives at the density interface faster than a small-sphere cloud (figure 27 (a-c)). Another big difference is the cloud shape at the density interface. Large-sphere clouds became very thin like a pancake, but small-sphere clouds were comparatively thicker at the density interface (figure 27 (d)).
(a) $Z_c = 8\text{ (cm)}$, $t_L = 2.15\text{s}$, $t_R = 23.5\text{s}$

(b) $Z_c = 13\text{ (cm)}$, $t_L = 5.57\text{s}$, $t_R = 51.5\text{s}$

(c) $Z_c = 24\text{ (cm)}$, $t_L = 27.2\text{s}$, $t_R = 436\text{s}$

(d) $Z_c = 26\text{ (cm)}$, $t_L = 140\text{s}$, $t_R = 617\text{s}$

(e) $Z_c = 26\text{ (cm)}$, $t_L = 712\text{s}$, $t_R = 808\text{s}$

(f) $Z_c = 31\text{ (cm)}$, $t_L = 838\text{s}$, $t_R = 1210\text{s}$

Fig. 24: The comparison between a large-sphere cloud and a small-sphere cloud. $Z_c$: position of centroid, $t_L$: the record time for left pictures, and $t_R$: the record time for right pictures. In each pair of pictures, the left one is a cloud with 1.70–2.00 mm spheres, and the right one is a cloud with 0.106–0.150 mm spheres (more details are in table 2 #10 and #15). For better visualization, the intensity was amplified 1.5 and 3 respectively for large-sphere cloud and small-sphere cloud pictures.

To quantitatively investigate the evolution of cloud shapes, the standard deviation for vertical spread, the third standardized moment for vertical skewness, and the forth standardized moment for vertical kurtosis were calculated using equations (7–10) (figure 25). The vertical migration rate of a large-sphere cloud became nearly zero and it resided for a significant period of time at the density interface, while that of a small-sphere cloud decreased sharply at the density
interface, but not to zero. This is because the spheres in small- and large-sphere clouds are in different regimes—settling regime and diffusion regime, respectively.

Fig. 25: Centroid (in the first column), standard deviation (in the second column), skewness (in the third column), and kurtosis (in the fourth column) of the clouds of spheres. (a) Small-sphere clouds (#14 in table 2). (b) Large-sphere clouds (#10 in table 2). (c) Large-sphere clouds (numerical simulation based on #10 in table 2).
The sphere clouds in different regimes show different spread, skewness, and kurtosis patterns. Both the small-sphere clouds and the large-sphere clouds show a tendency for their standard deviation to decrease until the centroid of the clouds reaches the density interfaces, then the standard deviation increases. However, the standard deviation of the large-sphere clouds decreases more sharply around the density interface and recovers faster in the bottom layer (figure 26), because the spheres in large-sphere clouds are pancaking with an extremely limited spread due to a prolonged diffusion time scale. This extreme pancaking causes the highest kurtosis and the smallest standard deviation at the density interface in figure 25. The pancaking can also explain the pattern of skewness of large-sphere clouds. In the TL, the frontmost spheres in a cloud start to be packed as soon as they reach the density interface; accordingly, they slow down while the rest of the spheres in the cloud is still sinking behind. This will make a negative tail or a negative skewness. Contrary to this, when the spheres escape the density interface, the frontmost spheres will accelerate to their terminal velocity in the bottom layer and sink faster while the rest of spheres are still trapped in the density interface. This will make a positive tail or a positive skewness.
Fig. 26: Centroid and standard deviation of a cloud with 0.106–0.150 mm spheres (a) and 1.70–2.00 mm spheres (b) in 2-layer stratification ($\Delta \rho_f = 0.02$ g/cm$^3$). The stratified regions are within the two dotted lines. The red line is the centroid, and the green region shows the ± one standard deviation of the cloud.

On the other hand, the same pattern of the different moments was not observed in the small-sphere clouds, although their standard deviation was minimum around the density interface (figure 25 (a)). This is likely to be due to the absence of pancaking at the density interface. However, the slight decrease of standard deviation and the small increase of kurtosis around the density interface would indicate that the diffusive exchange of lighter interstitial fluid and denser ambient fluid still happens, although it is in a settling regime. The skewness of the small-sphere clouds generally decreases over depth.

The moments of a large-sphere cloud from the numerical model showed patterns similar to the experimental result although the magnitude of the higher moments were not captured well (figure 25 (c)). Both clouds show the extreme pancaking at the density interface (figure 27 (c) and (d)). This causes the smallest standard deviation and the largest kurtosis for the entire period of cloud growth. In addition, when both clouds leave the density interface, the clouds becomes positively skewed as smaller spheres start to settle earlier than larger ones (figure 27 (d)).
((e) and (f)). However, a main difference is their behavior at the early stage. The cloud model does not demonstrate the thermal phase (figure 27 (a) and (b)). Due to the thermal phase, the large-sphere cloud from experiment stretches over a wide depth quickly upon its release, and this ultimately leads to a larger standard deviation than in the numerical simulations.
The comparison of the cloud growth between the experiment and the numerical simulation.

(a) $Z_c = 13\,(cm)$, $t_m = 26.9\,(s)$, $t_{exp} = 5.6\,(s)$

(b) $Z_c = 13\,(cm)$, $t_m = 41.8\,(s)$, $t_{exp} = 7.97\,(s)$

(c) $Z_c = 26\,(cm)$, $t_m = 105.3\,(s)$, $t_{exp} = 140.1\,(s)$

(d) $Z_c = 26\,(cm)$, $t_m = 91.0\,(s)$, $t_{exp} = 139.2\,(s)$

(e) $Z_c = 31\,(cm)$, $t_m = 218.6\,(s)$, $t_{exp} = 808.1\,(s)$

(f) $Z_c = 31\,(cm)$, $t_m = 109.8\,(s)$, $t_{exp} = 1147\,(s)$

Fig. 27: The comparison of the cloud growth between the experiment and the numerical simulation. The results from experiment and numerical simulation were compared when both had same centroids. Accordingly, the time points of both do not match as they have different growth. The picture on the lefthand side is post-processed and the pseudo-color shows the normalized brightness. The graph on the righthand side is the horizontally summed intensity profiles, and the values were normalized to make the area under the curve unity. The size range of sphere in the cloud was 1.70–2.00 mm (a, c, e) and 2.36–2.80 mm (b, d, f) in diameter. Further details of the experimental setting can be found in #10 in table 2.
Discussion

Entrainment of fluid around a sphere

To test if entrainment can prolong the residence time of a settling sphere in stratified environment, numerical simulation was performed with a modified momentum equation. Assuming the thickness of entrained fluid shell is fixed during the settling of a sphere, the entrained fluid shell was added in inertia and reduced gravity terms in equation (2):

\[ M^* \frac{dU}{dt} = -\frac{\pi}{8} \rho_f U^2 C_D d^2 + M^* g - \rho_f V^* g \tag{12} \]

where \( M^* \) is the total mass of sphere and entrained fluid, \( \frac{\pi}{6} \rho_s d^3 + \frac{\pi}{6} \rho_f (d^*^3 - d^3) \), \( V^* \) is the total volume of sphere and entrained fluid, \( \frac{\pi}{6} \rho_f d^* \), and \( d^* \) is the outer diameter of entrained fluid shell (figure 28).

In the modified numerical simulation, a porous sphere with an entrained fluid shell stayed longer within a stratified zone (figure 29 and figure 31). A larger entrained shell made \( \tau_r \) larger for all spheres; however, the normalized thickness of an entrained fluid shell \( (d^* - d)/d) \), which matches \( \tau_r \) from laboratory experiment, decreases with the size of a sphere in the 2-layered stratification (e.g. \( \tau_r \) of the smallest sphere from laboratory experiment lies between that from numerical simulation with \( d^* = 1.4d \) and \( d^* = 1.5d \), while \( \tau_r \) of the largest sphere from laboratory experiment lies between that from numerical simulation with \( d^* = 1.2d \) and \( d^* = 1.3d \) in figure 30). However, in the linear stratification, it does not decrease monotonically with a sphere size, but increase with a sphere size and then decrease beyond a certain sphere size (figure 32).

It seems that size of a sphere is an important parameter to determine the thickness of an entrained fluid shell. It is possibly due to the fact that a faster flow around a larger sphere lessens the thickness of a boundary layer. Accordingly, the settling velocity of a sphere, not the
size of sphere which is one of important variables determining settling velocity, can be directly related to the thickness of the entrained fluid shell. In such a case, the thickness of an entrained fluid shell will be adjusted according to the settling velocity of the sphere. This needs further investigation since it contradicts the assumption of the fixed thickness of the entrained fluid shell.

Fig. 29: Vertical trajectories of a agarose sphere with diameter, 0.1076 cm, from laboratory experiment (black) and numerical simulation with different entrained fluid shell thicknesses (colored). The experiment was performed in the 2-layered water column ($\Delta \rho_f = 0.02$ g/cm$^3$, #6 in table 2). The numerical simulation was performed with a stratification and a sphere size identical to the experiment condition.

Fig. 30: $\tau_r$ of a agarose sphere from laboratory experiment (black) and numerical simulation with different entrained fluid shell thicknesses (colored). The experiment was performed with eight agarose spheres (table 3) in the 2-layered water column ($\Delta \rho_f = 0.02$ g/cm$^3$, #6 in table 2). The numerical simulation was performed with a stratification and a sphere size identical to the experiment condition.
Fig. 31: Vertical trajectories of a agarose sphere with diameter, 0.1076 cm, from laboratory experiment (black) and numerical simulation with different entrained fluid shell thicknesses (colored). The experiment was performed in the linear water column ($\Delta \rho_f = 0.02 \text{ g/cm}^3$, #8 in table 2). The numerical simulation was performed with a stratification and a sphere size identical to the experiment condition.

Fig. 32: $\tau_r$ of a agarose sphere from laboratory experiment (black) and numerical simulation (colored). The experiment was performed with eight agarose spheres (table 3) in the linear water column ($\Delta \rho_f = 0.02 \text{ g/cm}^3$, #8 in table 2). The numerical simulation was performed with a stratification and a sphere size identical to the experiment condition.

The settling velocity in both the top and bottom layers increases when the entrainment of a fluid shell is included (e.g. compare the black and blue lines in figure 29). This would be resulted from our rough assumption about entrainment, but it might be attributed to the way that the entrainment was incorporated in the momentum equation. In equation (12), the entrainment was introduced to the inertia and buoyancy terms, but not to the drag term.

V-shaped trend of $\tau_r$

The v-shaped trend of $\tau_r$ was observed in numerical simulation of a single sphere settling (figure 14) and laboratory experiment of a sphere cloud settling (figure 16). This is because $\tau_r$
can be roughly interpreted as the sum of the settling time scale, $\tau_s$ and the diffusion time scale, $\tau_d$ (defined as $a^2/2D$) (figure 33). In the numerical simulation with zero entrainment, when the spheres were very small, the $\tau_r$ was exactly identical to $\tau_s$ because $\tau_d$ was comparatively negligible. However, when the spheres were large, the trend of $\tau_r$ was dictated by that of $\tau_d$, but the values of $\tau_r$ and ($\tau_d + \tau_s$) did not match. This would be due to the simple representation of $\tau_d$ and the exclusion of the entrainment of lighter fluid in the vicinity of a sphere (Srdic-Mitrovic et al. 1999; Abaid et al. 2004; Camassa et al. 2009; Yick et al. 2009; Camassa et al. 2010). Nonetheless, the shift in dominant physical phenomena controlling $\tau_r$ over the sphere size range can be observed. The transition point between the settling regime ($\tau_r \sim \tau_s$) and the diffusion regime ($\tau_r \sim \tau_d$) lies somewhere around the sizes where $\tau_s = \tau_d$. It seems that, in a given water column depth and a given stratification, neither a very small nor very large particle stays the shortest time in the ocean, but some particle size in the middle does.

Fig. 33: Comparison between $\tau_r$, diffusion time scale ($\tau_d$), and settling time scale ($\tau_s$) in 2-layer stratification (top) and linear stratification (bottom). The density difference between top and bottom layers ($\Delta\rho_f$) is $\sim 0.02$ g/cm$^3$ (left) and $\sim 0.04$ g/cm$^3$ (right). $\tau_d = \frac{a^2}{2D}$ and $\tau_s = \frac{l_{box}}{w_s}$. 
\( \tau_r/\tau_s \) of a clouds of spheres from the laboratory experiment generally increases with the size range of spheres in the cloud (figure 19). The trend agrees well with the result of the single sphere numerical simulation (see red dots in figure 33). However, while \( \tau_r/\tau_s \) of a single sphere from numerical simulation is always larger than 1 (> 1.007), that of small-sphere clouds from laboratory experiment are in the range of 0.54–1.85. The value of smaller-than-unity \( \tau_r/\tau_s \) would be artifact due to the normalization using a settling time of a single sphere—\( \tau_r \) of a cloud of spheres was calculated using its centroid, although that of a single sphere was calculated using its actual position. In addition, the value of smaller-than-unity \( \tau_r/\tau_s \) might be partly attributed to the overly simplified scaling of \( \tau_s \), just using two terminal velocities in the top and bottom layers.

**Thin layer formation**

Thin layers are the patches of marine particles including phytoplankton and marine snow within a limited vertical extent (e.g. less than 5 meters) above a certain concentration of particles (e.g. 2–3 times higher than the background concentration) (Dekshenieks et al. 2001; Sullivan et al. 2010). The fine-scale phenomena has been observed in various locations thanks to the recent progress in detection instruments and techniques, and the mechanisms of thin layer formation has been suggested (Durham & Stocker 2012). Considering thin layers are often associated with pycnocline in the ocean (Dekshenieks et al. 2001; Alldredge et al. 2002; Prairie et al. 2010), the delayed settling of porous spheres at stratification in this study can be one of possible scenarios related to the formation and dissipation of thin layers.

We found that a cloud of spheres are packed within a density interface for both small- and large-sphere clouds (figure 24). While the large-sphere clouds showed very thin layers within an extremely limited vertical range, the small spheres showed relatively thicker layers at the density interface. However, in both cases, the smallest vertical standard deviations of the sphere distributions were observed around density interfaces (figure 25). For large-sphere clouds, molecular diffusion of salt between the ambient and interstitial fluids drives the retention of spheres at density interfaces, and the entrained lighter fluid around sphere enhances the retention. However, for small-sphere clouds, molecular diffusion seems to be less important than the entrainment of lighter fluid. MacIntyre et al. (1995) hypothesized that marine aggregates would, at density stratification, accumulate due to the time to equilibrate the interstitial fluid density with the ambient fluid density. Although, Kindler et al. (2010); Prairie et al. (2012) demonstrated the prolonged retention of porous spheres and real aggregates, respectively, by laboratory experiment, this study showed the prolonged retention of multiple particles, which is more similar to the oceanic situation of thin layer formation.
The laboratory experiments and numerical simulations in this study were conducted in stratifications with $\Delta \rho_f = O(10^{-2} g/cm^3)$, which is an order of magnitude higher than stratification of open sea. Accordingly, the retention of spheres within such a weak stratification would be different from that of this study. However, environment similar to the experimental condition in this study can be found in stratified estuaries (MacDonald & Horner Devine 2008; Kasai et al. 2010). Even more extreme stratifications are also found in the ocean. The density interface of brine pools have stratification with $\Delta \rho_f = O(10^{-1} g/cm^3)$ (Shokes et al. 1977; Eder et al. 2001). In these cases, the settling behavior of marine porous particles might be comparable to the result of this study.

Conclusions

Through experimental and computational work, the settling behavior of both an individual porous sphere and a cloud of porous spheres in different stratified environments was investigated. The porosity of spheres and the presence of density stratification introduce unique settling behavior compared to a non-porous sphere settling. For example, if the density of a non-porous sphere is between those of TL fluid and BL fluid, it will be stuck in the density interface as long as the stratification persists. However, if it is a porous sphere, it will eventually escape the density interface after gaining excess density through diffusive exchange between the sphere’s lighter interstitial fluid and the denser ambient fluid. Therefore, the time scale of delayed settling in the stratified region is of key interest in this study. Residence time ($\tau_r$) was used to measure the delayed settling. $\tau_r$ is defined as the time taken to settle through a stratified region, which is defined by density gradient $\frac{d\rho_f}{dz} \geq 0.001 \left( \frac{d\rho_f}{dz} \right)_{max}$, (figure 8 (c) and (d)).

The $\tau_r$ of a single sphere decreases with its size when the sphere is smaller than a certain size (settling regime). However, when the sphere is larger than that size, $\tau_r$ increases with its size (diffusion regime). Accordingly, it forms a v-shaped curve if $\tau_r$ to the size of sphere is plotted (figure 14). This is because the time scale of delayed settling, $\tau_r$, is mainly governed by settling processes and molecular diffusion. Therefore, these time scales can be considered roughly as a sum of the settling time scale ($\tau_s$) and the diffusion time scale ($\tau_d$) (figure 33). If the size of the sphere is the same, $\tau_r$ increases with $\Delta \rho_f$ (figure 9). If $\Delta \rho_f$ is the same, $\tau_r$ was longer in a linear stratification than in a sharp 2-layered stratification (figure 10).

A similar v-shaped trend was observed in the settling of a cloud of porous spheres (figure 16). Also, $\tau_r$ increased with $\Delta \rho_f$ and porosity (figure 17 and figure 18). In a 2-layer environment, $\tau_r$
of small-sphere clouds was longer with smaller \( N^2 \) (figure 21). In addition to \( \tau_r \), the evolution of cloud shapes was studied (figure 24–27).

Before including the entrainment of a fluid shell, the numerical simulation results for both a single sphere and a sphere cloud did not exactly match the experimental results (figure 11 and 22 (c)). The \( \tau_r \) from the numerical model were smaller than the experimental result in all cases (figure 13 and 23). However, the model could predict the tendency of \( \tau_r \), e.g. the v-shaped trend (figure 14). Specifically for a cloud of spheres, the vertical migration rate of the centroid of a cloud in the top layer was slower in the numerical model than in the experiments, since the initial turbulent thermal phase was not included in the model (figure 22(c)).

The modified numerical model, which included the shell of entrained fluid in our model (figure 28), predicted \( \tau_r \) better than the original model for a single sphere settling. The thickness of entrained fluid shell seemed to vary over the size of spheres (figure 30 and figure 32). However, our assumption that the entrained fluid shell thickness does not change during settling needs to be investigated further. Although the cloud model simulation with entrainment was not conducted, it is very likely that \( \tau_r \) of sphere clouds will also increase in the numerical model with entrainment because the cloud model is the ensemble of single sphere model simulation results.

The delayed settling of porous spheres in the stratified region would be a possible mechanism of thin layer formation in the ocean. Previously, a hypothesis was proposed that marine porous aggregates might accumulate at the stratified region due to the time taken for density equilibration (MacIntyre et al. 1995). Also, some laboratory experiments, which can support the hypothesis, were performed using porous spheres and real aggregates (Kindler et al. 2010; Prairie et al. 2012). However, we showed the prolonged accumulation of a cloud of porous spheres at the density interface, which is more similar to thin layers in nature.

In order to understand the settling problem better, the following work needs to be done. First, further laboratory experiments, which were not conducted due to the technical issues, will enhance our knowledge. Single sphere settling experiments for very small spheres (< 0.8 mm diameter) will let us find the transition point where the dominant regime (diffusion vs. settling) changes. Also, cloud settling experiments in a linear stratification will let us know if \( \tau_r \) is longer in a linear stratification than in a 2-layer stratification. Third, the numerical model needs to be improved especially for the estimation of the entrained fluid shell thickness and the incorporation of the entrainment fluid shell into the numerical model.

Most importantly, the outcome of this study must be compared to the real marine snow. Although the agarose spheres in this study had a high porosity (> 99 %), as marine snow does, real marine snow characteristics, including porosity, solid matrix density, and shape, are highly
variable. In addition, the stratification in most parts of the ocean is orders of magnitude smaller than that in our study, although a certain environment, which our study result can be directly applied to, exists (e.g. stratified estuaries and brine pools). Accordingly, experimentation with real marine snow will give us a better idea how this study can be calibrated so that it can be further used to investigate the settling behavior of marine snow.
Appendix

A. Skewness and kurtosis

Skewness is a measure of asymmetry of a distribution. If a distribution has a positive skewness, it has a longer tail on the right side than that on the left side, and its mass lies more on the left side. On the other hand, if a distribution has a negative skewness, it has a longer tail on the left side than that on the right side, and its mass lies more on the right side. The third standardized moment is commonly used for a measure of skewness:

$$\text{Skewness} = \frac{\sum_{i=1}^{N} (x_i - \mu)^3}{(N - 1)\sigma^3}$$

where $N$ is the sample size, $x_i$ is the value of the $i$th sample, $\mu$ is the mean, and $\sigma$ is the standard deviation.

Kurtosis is a measure of how peaked a distribution is compared to a normal distribution. If a distribution has a high kurtosis, it has a sharper peak around its mean with a fatter tail compared to a normal distribution. On the other hand, if a distribution has a low kurtosis, it has a blunter peak around its mean with a thinner tail compared to a normal distribution. The fourth standardized moment is commonly used for a measure of kurtosis:

$$\text{Kurtosis} = \frac{\sum_{i=1}^{N} (x_i - \mu)^4}{(N - 1)\sigma^4}$$
A normal distribution has a kurtosis of 3; therefore, a distribution with a kurtosis higher (or lower) than 3 is more peaked (or less peaked) than a normal distribution.

![Fig. 35: Probability distributions with a kurtosis of 3 (green), a kurtosis smaller than 3 (red), and a kurtosis higher than 3 (blue).](image)

### B. NaCl concentration–density conversion table


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