
7 Fluxes of Particles to the Interior of the Open Oceans

SUSUMU HONJO

7.1 INTRODUCTION

It must have been more of a shock than we can now imagine when the Azoic theory was disproved with Charles Wyville Thompson's discovery during his 1868 expedition in the North Atlantic Ocean (re-cited from Mills, 1983) that there are live organisms on the abyssal seafloor of the North Atlantic. However a simple but critical question was, until recently, never answered and remained in speculation: How are energy and nutrients supplied to the animals who live on the deep seafloor where no plants can possibly grow?

About a century later, Osterberg et al. (1963) were among the first researchers who suspected an efficient and direct linkage between euphotic production and bathypelagic ecosystems. They analyzed radionuclides in deep-ocean benthic feeders such as sea urchins collected from the 2800-m seafloor off the coast of Oregon. Among the nuclides they found was ^{95}Zr the half-life of which was only 65 days; therefore the time required for radionuclides to be transferred from atmospheric sources to the ocean bottom would have to be constrained. Thus, these authors concluded that ocean particles which carry radionuclides to the ocean's floor should settle far more quickly (in a few weeks' time) through this water column than individual fine particles whose settling time would be on the order of years - as estimated from Stokes Law. They speculated that radionuclides at this site were delivered to the ocean's floor by rapidly settling particles such as fecal pellets of surface-living zooplankton.

Another example to be reiterated is the so-called "Coccolith Riddle" (Honjo, 1976). This 20-year-old problem involves fundamental aspects of ocean biogeochemical cycles and has provided, for me at least, stimulation for further research regarding ocean particles and their role in the global geochemical cycle. Though the process of attacking this riddle was an impetus to develop modern time-series sediment trap technologies, the results have been findings regarding many crucial aspects of ocean particles and their fluxes, particularly bringing to light the linkage between upper ocean ecology and bottom sediment.

Particle Flux in the Ocean

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The discovery of a transport link between the atmosphere, upper ocean and the ocean's interior with the deep seafloor was not trivial, but promised leaping progress in many other fields of ocean science. All particles and materials that arrive on the ocean's bottom still carry a memory imprint of the air and upper layer environments in which they were produced. Unloading this memory is critically important for understanding the past environment of the ocean and atmosphere. In order to decode environmental information from a microfossil in the sediment sequences, such as ocean temperature, salinity and nutrient concentration, etc., we must know the environmental relationship between the living counterpart of the fossil species and the present-day ocean environments which support them; many of these relationships have been missing from our knowledge. To establish the environmental relationship between a living and fossil assemblage using a trap-collected counterpart (biocoenosis) as the key, the "paleoproximity study" is one of the crucial and exciting ramifications of recent efforts to understand global change. As a token of our progress in this direction, the range of sea surface temperatures interpreted from our global, settling particle collection program using moored sediment traps is illustrated in Figure 7.1.

Beside the contamination of our planet's oceans by a long list of hazardous materials beginning with anthropogenic radionuclides (e.g., Fowler et al., 1983; Kempe et al., 1987), another burning issue has emerged which demands serious attention: the alarming rate of increase of atmospheric carbon dioxide due to the combustion of fossil fuels that upsets the global environment (e.g., Kellogg, 1991), resulting in the rise of earth's atmospheric temperature by the greenhouse effect (e.g., IPCC, 1990; Jones, et al., 1987).

The majority of CO₂ that is fixed by photosynthesis in the euphotic layer returns to the atmosphere within a short period, on the order of days. Some removed organic matter penetrates through the bottom of the euphotic layer with settling particles or in dissolved form. Much of this matter is regenerated throughout the middle or mesopelagic layer by heterotrophs and microbial activity, and a part of the resulting CO₂ also returns to the atmosphere. The deeper the layer where organic carbon is remineralized, the longer it takes to recycle the carbon to the upper ocean layers and the atmosphere. Only a small percent of particulate carbon continues settling to the bathypelagic layer and to the deep ocean floor.

The main role of the deep ocean in maintaining the efficiency of biogeochemical cycles of carbon, the biological pump, is to absorb atmospheric CO₂ and to hold a portion of the excess in the ocean's layers where the depth is too great for regenerated CO₂ to return to the atmosphere within our tangible time scale. A molecule of carbon from CO₂ which reaches the bathypelagic layer would take as long as the period of the ocean's general circulation, several hundreds to a thousand years, until it re-appears in the upper ocean and, ultimately, returns to the atmosphere. Some carbon molecules take hundreds of million years to be re-injected into the atmosphere, going through tectonic processes of the oceanic crust, after being subducted to the mantle and ejected back into atmosphere as

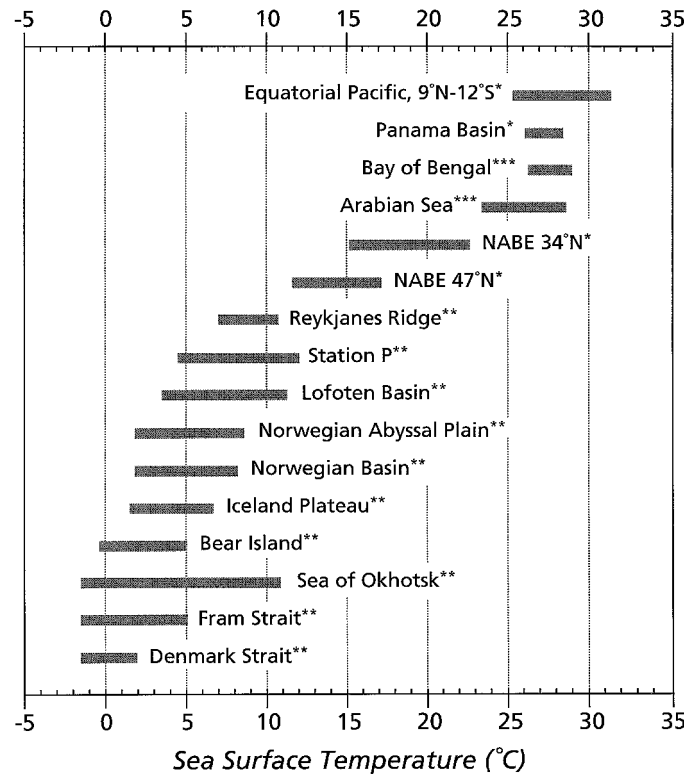


Figure 7.1 A partial list of global planktonic foraminifera sample sets for carbonate isotope measurements collected by time-series sediment trap experiments operated in a wide variety of global open ocean environments with sea surface temperatures ranging from freezing (-1.7°C) to as high as 29°C for ongoing paleoproximity investigations. Each sample set covers a minimum of all seasons of one year and are often of interannual duration. At most sediment trap stations, 2 to 3 traps were deployed in depth series and their open/close timing was synchronized (based on the talk by Dr. W. Curry, SCOPE/ UNEP Symposium, 1993). This work is supported by *the National Science Foundation through the Joint Global Ocean Flux Study (JGOFS), **the High Latitude Ocean Flux Studies of the Office of Naval Research, and ***the University of Hamburg's Biogeochemistry of the Oceans Program.

volcanic CO₂. Therefore the carbon molecule which arrives in the ocean's interior can be treated as a dropout from active recycling. It is critical to understand that this "export carbon" ("transit carbon" of Berger et al., 1989) arrives in the layers of the ocean which are deep enough so that it does not recycle within the time scale of deep-ocean turnover. One of the objectives of particle flux studies is to constrain the quantity and quality of carbon and other materials, as well as anthropogenic pollutants which are exported to this global sink.

This chapter summarizes in a descriptive and narrative manner the results of particle flux experiments using time-series sediment traps during the last 2 decades highlighting questions on the use of sediment traps such as the definitions, units and methods involved, and discussing the performance of sediment traps in various oceanic environments. Hypotheses are proposed on geographic distribution in order to search for the most effective direction of tomorrow's ocean particle flux research.

7.2 OCEAN PARTICLE FLUX: DEFINITION, UNITS AND ATTRIBUTES

The term "flux" ("*flow*" in Latin) is defined as a measure of the rate of transfer of material from one reservoir to another, and one physical or chemical state to another. Another general definition of flux is

Flux = (Proportionality Factor) X (Driving Force).

The dimension of flux is $M L^{-2} T^{-1}$, where M is a measure of the quantity of material carried by the flux (in our case this is a mass term such as grams), L is a linear dimension (such as meters) and T is time (such as hours).

In the early period of particle flux research, researchers used a variety of practical dimensional units including geological mass units: $g\ cm^{-2}\ ky^{-1}$. The particle flux unit that is now most commonly used is $mg\ m^{-2}\ d^{-1}$; this unit reflects the size of a sediment trap commonly used (between 0.2 and 1 m^2 aperture size), the seasonal variability of particle fluxes (a year or more), resolution of time-series trap openings/closings (minimum of 10–15 days), and the fact that particle fluxes observed in the ocean are normally within the order of $mg\ m^{-2}\ d^{-1}$.

Unless there is either advective or vertical movement of particles, there is no measurable flux. For example, labile organic material is often lighter than seawater and therefore never settles. If we apply Stokes Law, the sinking speed of most of the biomineralized particles produced in the euphotic layer, including coccoliths and diatom frustules, is on the order of $cm\ d^{-1}$ (Honjo, 1977); thus the residence time would be on the order of a hundred years in a deep ocean basin. The theoretical residence time of individual clay particles which are supplied to the open ocean as aerosols is even on an order of magnitude longer than that of these biogenic particles (Lerman, 1979). Such long residence times of ocean particles in water are, in effect, a state of suspension; therefore their vertical flux is negligible. Only particles which are "licensed" to settle can reach the ocean's interior and the deep seafloor (or be caught by a sediment trap). Therefore, the term *particle flux* can only be applied to *settling particles* and not to suspended particles.

7.3 METHODS OF STUDYING OCEAN PARTICLES

Settling particles can be separated from a known volume of bottle-cast or pumped water and, in theory, the flux of particles can be estimated if their mass and settling velocity are known. However estimation of settling velocity involves assumptions, and the estimated flux does not represent a continuous time span (e.g., Bishop et al., 1977). Other noble methods, such as measuring the size and settling speed with time-lapse photography (Asper, 1987) or *in situ* laser holography, for example, have only been used for specific purposes, not world-wide applications (this volume, Chapter 5).

7.3.1 SEDIMENT TRAPS

A sediment trap not only provides a quantity of mass flux but also collects actual material that is settling through the water column. When using a sediment trap, the volume of sample which can be obtained is determined by the size of the trap's aperture and the length of deployment. Depending on the size of trap that can be handled easily onboard, on the order of 100 mg to 1 g of samples can be collected per day from the interior of the oceans (e.g., Honjo and Doherty, 1988). These particles can be examined not only to measure the total mass flux but also their characteristics with chemical and microscopic analyses to establish the mass balance of compounds and find tracers to depict the ocean processes. By applying destructive and non-destructive analyses, research through an extremely wide range of disciplines is possible on a single sediment trap-collected sample. These ramifications include biogeochemistry, radiochemistry, paleoceanography, anthropogenic pollutants and even cosmic dust.

Settling particles which are caught by sediment traps are buffered in time and space; fine-scale events in the upper oceans such as individual diurnal events are averaged in time and space. The optimum time resolution for determining upper ocean events has not been well established but should be related to the residence time of settling particles in the water column. Settling particles are advected by a Lagrangian motion of turbulent flow, and the virtual volume of water from which a sediment trap receives particles can be expressed as an inverted cone relative to a source of particles at the surface (this volume, Chapter 9).

7.3.2 TIME-SERIES ARRAY AND SYNCHRONIZATION

The time-series trap mechanism, which sets the opening and closing of traps according to a pre-programmed schedule, makes it possible to observe the variability of particle flux with time. One deployment of modern sediment traps allows continuous collection of flux and its separation into a set of more than 20 time-series samples (Honjo and Doherty, 1988). An open-close time schedule (a

"period") can be set at regular intervals or with a complex schedule of uneven time spacing, hours to a month, but always allows continuous measurement of particle flux, typically six months to a year. Such intervals provided, for example, measurements of the flux associated with the evolution of blooms in the North Atlantic from their onset to end (e.g., Honjo and Manganini, 1993). If the amplitude of a concurrent oceanographic or meteorological event is known, an ideal minimum sediment trap collection interval is one quarter of that amplitude. The majority of time-series experiments in the deep ocean so far have used uniform 14- to 17-day open/close intervals for deployment of deep ocean traps. In practice, experiments with 17-day intervals have been able to identify tropical instability waves with approximately 3 to 4 weeks of wavelength in the equatorial Pacific (JGOFS - EqPac: Joint Global Ocean Flux Study - Equatorial Pacific; Honjo et al., 1995).

An open-close schedule can be synchronized between two or more sediment traps (sediment-trap "arrays"). Not only can all traps on a bottom-tethered mooring be synchronized, but many traps on many moorings in an area or transect can also be synchronized; an example is shown in Figure 7.2. Synchronization of open-close periods provides an advantage which enables understanding of the vertical and horizontal propagation rate of an oceanographic event. Researchers have found that a synchronized sediment-trap array provides information critical to the understanding, through the variability of particle fluxes, of meso- and large-scale oceanographic variables of ocean and atmospheric cycles of the earth.

7.3.3 CONSTRAINTS IN MEASURING PARTICLE FLUXES WITH SEDIMENT TRAPS

Laboratory plume simulation indicated a significant difference in trapping efficiency due to both the general configuration of the trap and design of the aperture baffle (e.g., Gardner, 1980a, b; Blomqvist and Kofoed, 1981; Butman, 1986; Baker et al., 1988). Complex water movement *within* a sediment trap may enhance the unreliability of particle flux data collected with the sediment trap method (e.g., Gust et al., 1992).

The sediment-trap measurement of particle flux in high-energy environments such as the euphotic layer and upper ocean do not agree with other estimates such as thorium isotope removal rates (e.g., Buesseler, 1991; this volume, Chapter 6). Researchers suspect that there are a number of reasons for this disagreement, including: 1) stable settling particles are not yet well formed in the shallow water; *in situ* marine snow cameras show a great difference in the morphological nature between the aggregates in the upper ocean and the ocean's interior; 2) violent shear usually exists between a sediment trap and the surrounding water; 3)

vigorous *in situ* biological activities strongly modify trap-collected samples in warm and sun-lit environments unless strong preservatives are added.

7.3.4 SAMPLE INTEGRITY

7.3.4.1 Swimmers

There are two major biological problems related to maintaining the integrity of samples which are collected by sediment traps: "swimmers" and sample degradation (e.g., Lee et al., 1988; Michaels et al., 1990). "Swimmers" are autotrophs which are attracted by the fresh samples collected and stored in the sampling bottle (cylinder-type traps such as VERTEX traps collect samples on their floor). The presence of swimmers changes the nature of the particles that are already collected, or adds to the apparent flux remaining as part of the sample after they die (often due to the effect of preservatives). In more complex cases, zooplankton or nekton visit the sample bottle, uptake the sample, leave feces and then swim away from the trap, or hatch eggs after they are trapped. The swimmer problem occurs more frequently in the upper ocean simply because of its large and active ecosystem. In the mesopelagic layer a sediment trap attracts metazoans which make scheduled vertical migrations. Researchers often find that the "majority" of the particles collected in traps deployed in the upper oceans are accompanied by swimmers (e.g., Harbison and Gilmer, 1986). They can be manually removed, but the inevitable result would be flux strongly biased for two reasons: uncertainty in identifying genuine settling particles *vs.* swimmers, and the possibility of small swimmer fragments remaining during the picking process, particularly when the sample is not chemically fixed. Many methods to prevent swimmers such as using nets (Karl and Knauer, 1989) or mechanically rotating indented ball valves (Peterson et al., 1993) have been proposed, with successful initial field tests (this volume, Chapter 5).

In the bathypelagic layers, the zones deeper than 1 to 1.5 km, the ocean's interior, this situation changes to the advantage of export production measurement, escaping the serious problems mentioned above; the population of living zooplankton drastically decreases below the mesopelagic layer; the particles are not as fresh as in the upper layers so are probably less attractive to many metazoans. Bathypelagic fish often disturb samples (Honjo and Manganini, 1993). This problem has been solved by placing a thin, 1-cm-mesh nylon net underneath the baffle (Honjo et al., 1995). In some areas, the near-bottom traps (several hundred meters above the seafloor) collect bathypelagic zooplankton as swimmers (Honjo, 1978). In practice, when dealing with deep-ocean trap samples, particles which remain after being sieved through 5-mm mesh need to be examined for freshness. Swimmers are only a small percent of the total flux, and their mis-identification usually falls within analytical error (Honjo and Manganini, 1992; Honjo et al., 1995).

7.3.4.2 Microbial growth and degradation of samples

In situ bacterial degradation of settling particles (e.g., Knauer et al., 1984; Lee et al., 1992; Pfannkuche and Lochte, 1993) could also bias the measurement of

organic matter export. In the upper ocean where temperatures are generally high, the rate of degradation accelerates. For example, in a laboratory incubation when the water temperature was as high as 18°C, the membranes covering a freshly produced copepod fecal pellet were largely degraded within the time it would have taken to settle through the euphotic layer (Honjo and Roman, 1978). In deep layers, fresh organic matter degraded quickly during an experiment due to exposure along a mooring (Gardner et al., 1983). An *in situ* experiment using fresh-cultured phytoplankton at the 4-km ocean bottom showed a rapid degradation rate. However, the same experiment showed particles collected in deep layers were far less susceptible to degradation than fresh organic matter (Cole et al., 1987).

Unless a sediment trap is deployed in low-temperature water such as the polar oceans (Fischer et al., 1988; Honjo, 1990a; Wefer, 1989; 1991), collected samples must be treated with a preservative (e.g., Knauer et al., 1984). Relatively small concentrations of HgCl₂ are universally effective in preventing the growth of bacteria and other protists. Compared to other preservatives, HgCl₂ remains in the sampling bottle of a trap without diffusing rapidly. However, it does not chemically fix the tissue, as formaldehyde does; thereby labile organic matter often disintegrates before being recovered, and swimmers often become indistinguishable from settling particles. The extreme dominance of Hg molecules in a sample makes many non-destructive chemical analyses, such as X-ray fluorescence analyses, difficult to impossible.

On the other hand, sodium azide offers some advantages. The greatest advantage of using sodium azide is that this preservative does not add any significant alien molecules to the sample (it consists of hydrogen and nitrogen) as Hg does, yet it prevents the growth of a dominant group of bacteria in the seawater. Diffusion can be slowed down by using a diffusion chamber and slightly raising the salinity of water in the sample bottle (Honjo et al., 1979). However, sodium azide does not prevent all microbes and, like HgCl₂, does not fix organic tissues. Both HgCl₂ and sodium azide are highly hazardous.

Formaldehyde or formalin fixes the tissue and also prevents growth of most protists and microbes. A diffusion of formalin can be retarded by slightly raising salinity in the sampler bottle. The hazard-preventive laboratory protocol for handling a sample containing formaldehyde has been well established. Although re-distilled formalin adds no metals, the addition of alien carbon modules (formalin is a petroleum product) to a sample makes it difficult to measure the amount of dissolved carbon in the supernatant of the sample, and leaves doubt about the reliability of the ¹³C measurement in organic matter (Manganini et al., 1994).

As is explained more fully in a later section, during a time-series array experiment in the equatorial Pacific, three identical traps were deployed on a mooring approximately 100 m apart at a depth of about 2 km (Figures 7.2 and 7.3). The 21 sampling bottles of each trap were pre-filled with 3 different solu-

tions of preservatives commonly used by researchers: sodium azide, formaldehyde (buffered NaBO_3) and HgCl_2 . All samples were collected during synchronized open periods over the span of about one year in 1992. The total flux of each corresponding period of the 3 traps differed only a few percent. The Na, P, Al, Ti, Fe and Ba content among the 3 traps were within analytical error. However, Mn

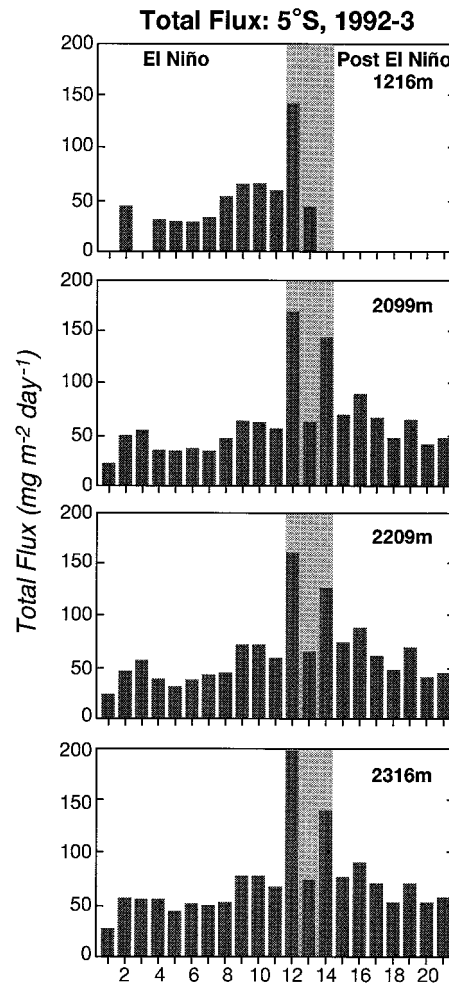


Figure 7.3 For the entire year of 1992, the particle flux collected by 3 sediment traps 100 m apart at 5°S 140°W at a depth of around 2.1 km in 1992 did not change significantly with regard to total fluxes or constituents of particles. A different preservative was added to each trap to test and compare the effect. Also the partially available flux at 1.2 km, showed no difference from the deeper samples (Honjo et al., 1995).

fluxes calculated from samples which were treated by sodium azide were significantly less than fluxes of other elements in all periods; this indicates greater oxygen depletion. The percentage of > 1 mm particle flux in the total flux was largest in the formaldehyde-treated sample, followed by the HgCl₂-treated sample, and smallest in the sodium-azide-treated sample, as predicted. DOC measured in the supernatant of the sodium-azide-treated sample indicated that about 10% of the trapped organic carbon was dissolved in the supernatant (Manganini et al., 1994). The pH level in the samples' supernatant which is treated by formaldehyde with an appropriate buffer usually is kept close to the ambient water until recovery in a sealed sample bottle; also no significant elevation of Ca concentration in the supernatant, compared to ambient water, was found, indicating no significant carbonate dissolution. Five to 10% of the biogenic SiO₂ dissolved from formaldehyde-treated samples into the supernatant. The "flux" observed by recent researchers is usually a combination of the solid and dissolved portions which are found in the supernatant. During storage, a sample bottle of any time-series trap must be sealed from the ambient water so that the dissolved phase can be preserved.

7.3.5 *IN SITU* SEDIMENT TRAP INTERCOMPARISON IN THE DEEP WATER COLUMN

A number of sediment trap intercomparison experiments have been performed in deep-ocean layers. For example, an intercomparison experiment in the Santa Barbara Basin indicated that particle flux measured by traps with significant differences in configuration were comparable (e.g., Dymond et al., 1981); in addition the trap-measured flux was generally smaller, not catching the advection near bottom, but matching reasonably well with the general sediment-accumulation rate of the basin.

A large-scale comparison experiment at a Panama Basin location showed that traps with a wide range of opening or aperture size (0.004 m² to 1.5 m²) and with cylinder- or funnel-type configurations collected similar fluxes that included a wide range of particle size and classes during 4 months of deployment along ridged bottom-tethered moorings (supported by strong upward tension to the taut-line by applying a large amount of buoyancy to the mooring) (Honjo et al., 1992).

Samples collected from deep traps which were deployed in typical deep-ocean conditions in a deep basin of the Nordic Sea with less than 10 cm s⁻¹ advection and indistinct directionality showed no statistical relationship between the flux, size fraction and kind of particles studied (Honjo and Wefer, unpublished data). When water advection was slower than 12 cm s⁻¹, Baker et al. (1988) found no difference in trapping efficiency between a trap which followed the water flow and a trap which was tethered at the bottom. These observations indicated that collection of settling particles by a sediment trap deployed in the deep ocean was not likely to be affected by the physical environment. In contrast, a strong,

unidirectional deep current of about 30 cm s^{-1} influenced the quality and quantity of sediment collected by a bottom-tethered sediment trap which was placed near the slope of the Panama Basin (Honjo, 1982).

7.3.6 SELF CALIBRATION OF PARTICLE FLUXES BY RADIONUCLIDES

The behavior of radionuclides offers an independent estimation of settling particle fluxes. Some radionuclides are chemically reactive, strongly absorbed by ocean particles and are supplied to the water column at rates which are known exactly by the decay of their parent nuclides in decay series (e.g., Bacon et al., 1976; 1988; this volume; Nozaki, 1987). In practice, a calibration is based on a determination of the degree of radioactive disequilibrium (deficiency of a daughter nuclide relative to a parent nuclide) in the water above the trap to be calibrated. Because of its favorable vertical flux balance, a trans-uranium nuclide with a relatively long half-life, ^{230}Th (7.52×10^4 year) has been used for the tracer to calibrate particle fluxes to the ocean's interior (Brewer et al., 1980; Anderson et al., 1983). This method can be better applied to a longer and continuous flux record such as one year (Bacon et al., 1985; this volume). A number of self-calibration efforts using radionuclide tracers on the deep-ocean samples in long-term deployments supports the measured mass flux, matching the disequilibrium model of ^{230}Th within a reasonable error, such as $\pm 15\%$ (e.g., Bacon et al., 1985; this volume). In contrast, radionuclide calibration applied to mass flux measured with floating sediment traps in the euphotic layer and upper ocean differs from the disequilibrium model (Buessler, 1991). Researchers agree a sediment trap tethered to the seafloor produces persistent and explainable results, and particles collected by such a sediment trap represent the vertical flux of settling particles in these deep-ocean layers.

The major alteration of particles including the dissolution of CaCO_3 and biogenic SiO_2 occurs within a thin, less than one centimeter thick, boundary layer where seawater and sediment interface (benthic transition layer; Cole et al., 1987). Therefore burial rate can only be estimated on refractory material (such as Al) or by using radioactive tracers (Dymond, 1984; Dymond and Lyle, 1985). At present it is usually not possible to compare a simple accumulation rate to, or calibrate it with, particle flux itself. Sedimentation rates estimated from ^{210}Pb , for example, are often high because they occur at a site where the slope gradient is relatively large, such as trench walls (Nozaki, 1989a) and slopes (e.g., Butman and Folger, 1979), or where there is a source of high energy re-suspension of sediment nearby (Gardner et al., 1985), advectively transported to a layer between the deepest sediment trap and the sea floor. Varved sediments of the Black Sea are thought to provide natural calibration of sediment-trap-measured annual fluxes. However, both studies of particles collected by time-series sediment traps and

analyses of varves on the seafloor in the Gulf of California and the Black Sea shed light on a new hypothesis: that a pair of bands in varves does not necessarily represent a year of particle sedimentation (Hay et al., 1990); on the other hand, the ratio between terrigenous and biogenic matter in the varves of the Gulf of California are well matched with the annual sequence of settling particles measured by time-series sediment traps (Thunell et al., 1993).

7.4 SAMPLE SHARING AND LABORATORY ANALYSES

A significant advantage of investigating the settling particles collected by a large sediment trap is that this process supports multi-disciplinary studies. A time-series sediment trap with a 0.5 m² aperture is capable of collecting 50 mg per period (e.g., an annual per-period average at the Fram Strait) to about 400 mg per period (e.g., Bering Sea) and much more in a neritic environment (Wefer et al., 1988; Thunell et al., 1994a); these amounts are usually sufficient to support several research groups simultaneously working on the sample from one collection period. The inside of a modern sediment trap is coated with or made of analytical-grade polyethylene or its equivalent, and the structural frame is composed of titanium; therefore there is minimal contamination of the collected samples from the trap (Manganini, in preparation).

In order to share a sample among interdisciplinary projects such as listed in Table 7.1, it must be split into a number of aliquots. Samples collected with a VERTEX-type sediment trap (Knauer et al., 1979), which consists of a cluster of several independent collectors, would not require further splitting. All large-aperture, funnel-shaped time-series sediment traps (Honjo and Doherty, 1988) require a controlled sample splitting process. Biocoenosis investigations require the sample not be dehydrated, otherwise foraminifera tests and radiolarian shells would be unidentifiable, so it is mandatory that the sample be split with seawater collected with the sample. A wet-splitter can separate a one-cup sample into 10 equal aliquots with a better than 3.7% precision for typical > 1 mm samples (Honjo et al., 1995).

As explained below in more detail, the basic 5 biogeochemical properties of settling particles, converted to flux terminology (mg m⁻² d⁻¹), are the total flux, and CaCO₃, organic carbon (nitrogen), biogenic opal and the lithogenic constituent fluxes. A typical procedure to analyze these 5 properties is illustrated in Figure 7.4. Although the operation needs improvement, laboratory intercalibration must be practiced frequently and continuously on basic laboratory procedures. Previous comparisons of results show relatively small deviations, less than ±10%, from the norm (Nozaki, 1989; Honjo et al., 1992; 1995). Usually these basic biogeochemical analyses consume 3/10 of the sample, or 3 1/10 aliquots (Figure 7.4).

Table 7.1 A typical sharing plan of a time-series-trap-collected sample using a wet sample splitter which divides the sample and cup water into 10 equal aliquots with known precision for the < 1 mm fractions. The > 1 mm fractions are usually divided by the "wet-cake" method (e.g., Honjo and Manganini, 1993). Basic biogeochemical constituent analyses and biocoenosis investigations usually require further splitting of a 1/10 aliquot.

1.	3 aliquots	Total flux and basic biogeochemical constituents: CaCO ₃ , biogenic SiO ₂ (opal); organic elements (carbon, nitrogen and phosphorous); and lithogenic components
2.	2 aliquots	Radiochemistry
3.	1 aliquot	Trace metals and rare earth elements
4.	1 aliquot	Biocoenosis (coccoliths, diatoms, radiolaria and silicoflagellates)
5.	2 aliquots	Organic geochemistry
6.	1 aliquot	Archive (wet samples), to be dehydrated after a few years for dry/cold storage
7.	(1 aliquot)	Emergency supply

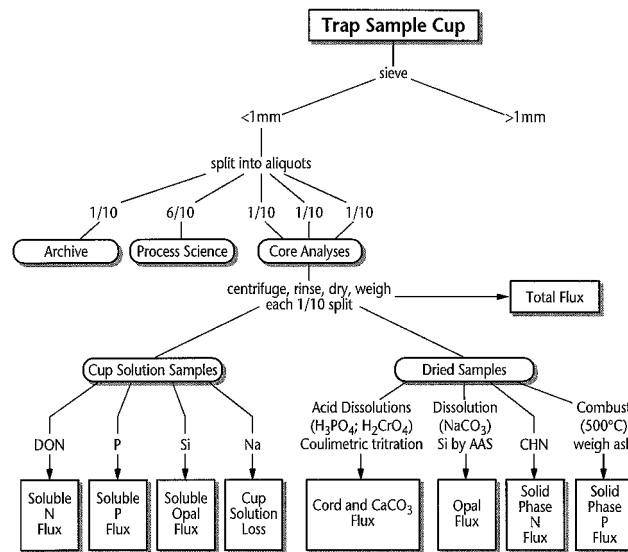


Figure 7.4 A diagram showing an analytical process for basic biogeochemical constituents of settling particle samples collected by a time-series sediment trap practiced by the majority of laboratories.

Since Spencer et al., (1978), many researchers have investigated radionuclides, including ²³⁴Th, ²³²Th, ²³⁰Th, ²²⁸Th, ²¹⁰Po and ²¹⁰Pb, effective tracers to constrain the time scale of the biogeochemical cycle. Typically, 1/5 of the sample is used for these analyses, but counting is a non-destructive process so the left-over samples

may be used for other types of analyses. A 1/10 aliquot is dried, analyzed and digested for trace elements including Ba (Francois et al., 1995), Cd, Ti, Cu, Mn, and many others (e.g., Brewer et al., 1980; Bruland et al., 1981; Tsunogai et al., 1982; Nozaki, 1989b; Jickells et al., 1990 and Thunell et al., 1994b). Organic compound studies usually require 1 or 2 aliquots.

Paleoceanography/paleoproximity research requires 1 aliquot for stable isotope analyses of ^{18}O and ^{13}C . In order to investigate independent taxonomic groups, further splitting of samples is required. For example, diatom or coccolithophorid research requires preparation of a number of 1/100 to 1/1000 aliquots for optical microscopy and SEM investigation. Lithogenic particle flux is usually estimated from the Al (and Ti) content (Dymond and Collier, 1988). Although clay mineral species are excellent tracers of settling particles, (Honjo et al., 1982b; Ramaswamy et al., 1991), X-ray diffraction studies require large amounts of trapped material. One 1/10 aliquot is archived with seawater for a few years then dehydrated for long-term storage. Another 1/10 aliquot is kept refrigerated as an emergency supply (Table 7.1).

7.5 WHAT ARE SETTLING PARTICLES?

7.5.1 ORIGIN OF SETTLING PARTICLES

Later research has indicated that fecal pellets are not the only form of vertical transport to bring ocean particles and organic matter downward (PilskaIn and Honjo, 1987), but that natural aggregates such as amorphous aggregates (often referred to as "marine snow"; Suzuki and Kato, 1953) have been found to be an important and often dominant mode of settling particles (e.g., Silver and Alldredge, 1981). In upper oceans, particularly in more productive areas such as upwelling coastal oceans, amorphous aggregates are abundant and individual aggregates are as large as a centimeter in diameter. Alldredge and Gotschalk (1988) reported a large aggregate with the diameter of about 22.5 mm and 75 mm long from the San Pedro Basin. The agglutinate labile matter suspended in surrounding seawater (Silver and Bruland, 1981), offer microcosms to host microbial activity and are a possibly significant food resource (Gowing and Silver, 1983). Fecal pellets are often attached to large aggregates and settle with them. In any case, the majority of settling particles are biogenic; lithogenic particles which are always heavier than sea water are a minor part - not more than several percent - of open-ocean particles.

As will be explained later, both fecal pellets and marine snow are produced as a reflection of the dominant ecosystems in the upper ocean at a given time. For example, the sediment which settled to deep layers of the northern Weddell Sea right after the retreat of the ice edge was dominated by marine snow which

consisted of flaky aggregates containing diatoms. However, such amorphous particles were later replaced by fecal pellets, and the peak flux consisted of mono-specific fecal pellets (Fischer et al., 1988). In lower latitudinal, neritic stations it has been reported that the entire particle flux is made up of fecal pellets (e.g., Dunbar and Berger, 1981; von Bodungen et al., 1987), but this does not necessarily mean the area does not produce amorphous aggregates throughout the year.

The common structure of marine snow is, as Tsujita (1953a, b) originally observed, an agglutination of marine detritus on a "sticky" amorphous matrix. In the upper oceans, the configurations of aggregates are often variable, suggesting different origins. Discarded larvacean (Appendicularians) houses, often abundant in the open ocean (Alldredge, 1976), decaying gelatinous zooplankton such as *Doliolum*, salps, and medosae, and other unknown sources may supply the material to form substance for the late stage of a bloom which offers abundant material to form a matrix. Bacterial growth (Gowing and Silver, 1983) would enhance the matrix's ability to produce a sticky surface by bacterial extracellular biopolymers (e.g., Robb, 1984). The mass settling of living diatoms due to their apparent ecological needs (Smetacek, 1985) or the mass settling of coccolithophores during their "palmeroid" state (Smayda, 1970; Honjo, 1982) are examples of "pseudo-active" settling. The valves and girdles of common open-ocean diatoms such as *Chaetoceros* form into a long chain with protrusions of setae which interlock with each other as well as with other detritus. Also the common diatom *Rhizosolenia* with very fibrous frustules often form lint-ball aggregates by themselves.

Marine snow also occurs in the ocean's interior (Silver and Alldredge, 1981), and the distribution has been quantified, mainly by applying light-scattering photo-optics (Honjo et al., 1984; this volume, Chapter 5). The relationship between abundance of aggregates and particle flux in the deep open oceans has begun to be clarified (Asper et al., 1992; this volume, Chapter 5).

The distribution of aggregates in the ocean's interior is quasi-uniform, suggesting consistent downward settling; if aggregates were supplied constantly from the surface, the steady state of vertical distribution could not be kept. In the deep Panama Basin, however, many zones of higher concentration were found (Figure 7.5). This zoning is explained by marine snow which had accumulated on the near-by shelf, and which was occasionally resuspended by the strong boundary current and advected in an off-shore direction (Asper et al., 1992). A similar re-transportation of marine snow from a shoal to a deep basin by internal wave was observed recently by Tuji using a time-interval scattering camera in Sagami Bay, Japan (Tuji, 1993).

In situ camera observations indicate that individual marine snow particles in the ocean's interior are of lesser volume and more uniform than the aggregates in the upper layers (Honjo et al., 1984). A speculative explanation is that aggregates are shaved into a smaller size as a result of the hydraulic shear of seawater caused by settling through the water column. The resulting size is the product of the balance

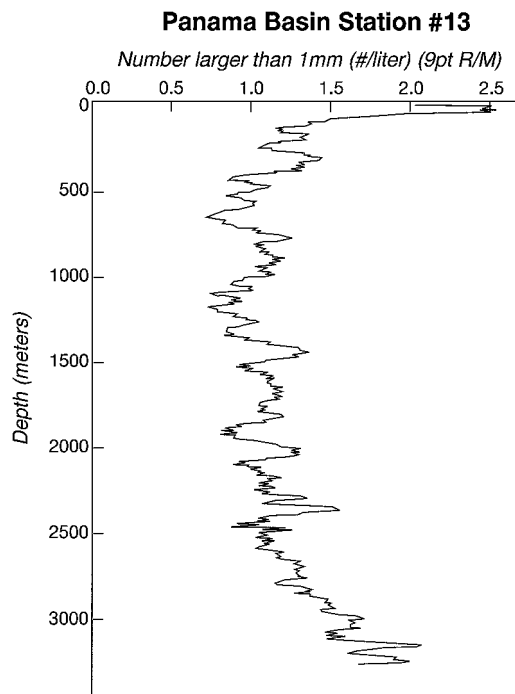


Figure 7.5 The distribution of large amorphous aggregates (> 1 mm diameter) per liter through a water column in Panama Basin using a "marine snow camera" (data collected by Asper and Honjo in 1987, a point flying average).

between the speed and the degree of agglutination which holds fine particles together in one-piece of aggregate. Particles thus sloughed off the hosts become suspended; this is the only process to produce suspended particles in the deep layer, as explained below.

7.5.2 THE CONSTITUENTS OF SETTLING PARTICLES

The process of particle export from the upper ocean to the interior is a complex interplay of the participants in the ocean's ecosystem which involves hundreds of species of animals, plants and microbes as well as land-based material such as pollen and aerosol particles. A flake of marine snow or a piece of pellet is a micro-cosmos that represents the complexity of the ocean. These complicated products of the ecosystem can be divided into four principal particle components: organic matter, CaCO_3 , biogenic SiO_2 particles and lithogenic particles. The annual constituents of settling particles gained from some locations is presented in Table 7.2. More information is available in Wefer (1989), Tsunogai et al. (1991)

and Milliman (1993). Vertical variability of each of the constituents will be discussed in a later section.

7.5.2.1 The CaCO₃ component

CaCO₃ particles consist of two major classes. One is phytoplankton-produced exoskeletons, the vast majority of which are coccoliths and coccospheres (Steinmetz, 1991) (here they are referred to as coccoliths). The other is zooplankton-produced shells of planktonic foraminifera. In some areas and seasons, pteropod shells (aragonite) occupy significant portions of the CaCO₃ flux, but not consistently (e.g., Betzer et al., 1984; Fabry, 1989). The ratio between phytoplankton-produced and zooplankton-produced calcium carbonates is estimated to be about 6 to 4 (Honjo, 1977; Deuser and Ross, 1989; Fabry, 1989), but this warrants more detailed study. Although aragonitic pteropod ooze is distributed over a relatively large area of the Atlantic, Mediterranean and northern Indian oceans and is important in adjusting the ocean's alkalinity (Milliman, 1974; Berner, 1977; Betzer et al., 1984), the flux of these shells is found to occur sporadically, indicating patchy distribution (Harbison and Gilmer, 1986). However, Meinecke and Wefer (1990) found that the Lofoten Basin may have been an ideal location to grow shell-forming pteropods such as *Limaacina helicina* and *L. retroversa*; they observed a constant flux of shells in the late summer to autumn. Production of Mg-rich CaCO₃ is limited to the coral reef phase and produced by plankton (Milliman, 1974). However, Berner and Honjo (1981) reported Mg-rich CaCO₃ collected from a deep trap station in the Panama Basin 280 n. miles from the shore line, indicating lateral transport of reef carbonate.

7.5.2.2 The SiO₂ component

Oceanic biogenic SiO₂ mostly consists of poorly crystallized polymorphs of silica classified as *Opal-AC* (Calvert, 1983). In terms of mass, biogenic SiO₂ is largely diatom frustules. Compared to planktonic foraminifera, radiolarian shells arriving at the ocean's interior consist of far more diversified species (e.g., Takahashi, 1991). However, the contribution of radiolarian shells to biogenic SiO₂ fluxes is usually not more than 10%. Despite abundance, silicoflagellates in low-latitude, open-sea water are not significant in mass, but are an important paleoproximeter (Lisitzin, 1972; Takahashi, 1989).

7.5.2.3 Organic matter

Organic compounds in settling particles are used as valuable environmental tracers. For example, it was found that arabinose sugar is enriched in the particles which settled during a calcareous phytoplankton bloom (coccolithophorids), though more fucose is included in siliceous frustules (Ittekkot et al., 1984a). From a Black Sea sediment-trap experiment, Michaelis et al. (1987) reported that sterol

markers can be used to trace the origin of the settling particles. In general, the ratio of glucose to ribose in the land-derived organic matter is larger than 50 (Mopper and Degens, 1972); the ratio is less than 10 in marine-phytoplankton-derived particles (Tanoué and Handa, 1986). Using this relationship in simple saccharide contents found in settling particles in the Japan Trench, Handa (1989) observed that the glucose/ribose ratio in the settling particles was 5 to 6 in the Japan trench and that a large portion of particles in the deep trap was advectively transported, suggesting that land organic matter does not reach the trench environment despite the relatively short distance between the shore line and the trench axis. On the other hand, using ^{13}C as a tracer, Druffel et al. (1986) observed that a significant portion of land-originating organic carbon was delivered to Ocean Station P, Gulf of Alaska which is located far from a land mass. Hinga et al. (1979) found that a significant portion of organic carbon flux at a deep slope station south of Cape Hatteras consisted of pine and cedar pollen; however, this observation was made during only a part of a year.

Rich information regarding the organic compounds in settling particles has been produced (e.g., Wakeham et al., 1980; Lee et al., 1983; Ittekkot et al., 1984a, b). Beside hard-tissue-producing organisms, there are significant "naked" plankton and microbial masses produced in the upper oceans, but often they are grazed and so are not microscopically isolatable in a sediment-trap sample. In an open-sea trap experiment, organic carbon does not form a flux peak by itself like other particle components. In many cases a large organic carbon flux is more likely to be associated with a biogenic- SiO_2 bloom than with a calcium-carbonate bloom. As an exception, in the Arabian Sea an organic carbon peak during the summer monsoon is associated with a CaCO_3 flux maximum (Haake et al., 1993). One reason for this coupling between the fluxes of organic carbon and biogenic SiO_2 is that amorphous opal contains a significant amount of organic carbon as the structural compound, up to 30% (Heath et al., 1976), while, on the other hand, coccoliths consist of pure calcite crystallites and foraminifera shells and contain no significant organic matter compared to diatom frustules.

Organic matter contains water in variable situations which are difficult to constrain by our present analytical methods. Therefore, organic carbon and/or nitrogen are independently analyzed to represent organic matter.

7.5.2.4 The lithogenic component

Lithogenic particles are always being transported from distant land sources to the surface of the ocean, and their distribution pattern reflects the earth's general atmospheric advection. The density of lithogenic particles in the air, which is related to their fallout rate over the sea, differs in several orders of magnitudes depending on the distance from the source (Duce et al., 1991). Three areas supply most of the lithogenic aerosol to the open ocean (this volume, Chapter 3).

