



# Transmissometer measurement of POC

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## Abstract

The relationships between beam attenuation coefficient,  $c$ , at 660 nm, measured using a Sea Tech transmissometer, and particulate matter concentrations, size distributions, and chemistry determined by the Multiple Unit Large Volume in situ Filtration System (MULVFS) were investigated in the central equatorial Pacific during 1992 US-JGOFS cruises TT007 and TT011. Results from 24 pairs of simultaneous casts to 1000 m from the two 3000 km long transects showed highest correlation between beam attenuation coefficient and particulate organic carbon (POC) when POC was summed over all size classes sampled. Regression of  $c$  vs in situ POC data from TT007 and TT011 yields slopes of  $6.34 \pm 0.03$  and  $6.09 \pm 0.03 \times 10^{-5} \text{ m}^{-1} (\text{nmol C l}^{-1})^{-1}$ , intercepts of  $0.366 \pm 0.002$  and  $0.368 \pm 0.003 \text{ m}^{-1}$  and  $r^2$  values of 0.97 and 0.95. A reanalysis of 1982 data from the NW Atlantic and 1996 results from sub-polar NE Pacific waters indicate that the calibration specifics of  $c$  vs POC are largely independent of ocean environment, season, or depth sampled. Our results suggest that the transmissometer can provide a quantitatively useful estimate of POC over a diverse suite of oceanographic environments. This opens the opportunity for deploying transmissometers from platforms other than ships to characterize the high-frequency (diurnal and longer time scales) variability of particulate organic carbon within the upper kilometer of the ocean. A framework for interpreting the vast body of beam attenuation coefficient measurements made in the oceans over the past two decades is provided. © 1999 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

Transmissometers have been used to optically characterize distributions and variability of suspended particulate matter in the marine environment since the 1970s (Zaneveld, 1973; Bartz et al., 1978). The relationship between transmittance,  $T_r$ ,

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measured by a beam transmissometer of path length,  $r$ , and beam attenuation coefficient,  $c$ , is

$$c = \ln(T_r)/r \quad (\text{m}^{-1}), \quad (1)$$

where  $c$  is the sum of the effects of absorption and scattering losses from the transmissometer light beam caused by particles, water, and dissolved substances (Zaneveld, 1994). At 660 nm beam attenuation coefficient,  $c$ , has two dominant components: (1) absorption and scattering of light by particles,  $c_p$ , and (2) absorption by water,  $c_w$ ;  $c_w$  is widely accepted to be constant at  $0.364 \text{ m}^{-1}$ . A third component, absorption by dissolved organic matter, is assumed to be negligible at 660 nm (Jerlov, 1976).

Beam attenuation coefficient should be related to total cross-sectional area of particles in the beam (Van de Hulst, 1957); however, the variations of beam attenuation coefficient of natural populations of particles are poorly understood. This is not due to a lack of understanding of the physics of scattering and absorption of particles of a given size and refractive index, but rather is due to a lack of means to measure the optical properties of complex assemblages of marine particulate phases in situ and how they change in response to variations in particle size distribution and chemistry. This in turn has limited application of transmissometer data either to systematic descriptions of  $c$  only, or to localized quantitative studies of particle distributions characterized by bulk particulate measurable properties such as total particle volume (PV) and suspended mass concentration (SPM) (e.g. Pak et al., 1980; Spinrad, 1982; Baker and Lavelle, 1984; Bishop and Joyce, 1986; Pak et al., 1988; Siegel et al., 1989; Bishop et al., 1992; Joyce et al., 1992; Dickey et al., 1993, 1994; Gardner et al., 1993, 1995; Stramska et al., 1995; Walsh et al., 1995).

Investigations between  $c$  and particle volume (PV) measured by coulter counter (e.g. Peterson, 1977; Kitchen et al., 1982; Spinrad, 1982; and Pak et al., 1988) yielded correlation ( $r^2$ ) values for near-surface samples ranging between 0.92 (Peterson, 1977;  $n = 13$ , selected data values) and 0.65 (Kitchen et al., 1982;  $n = 131$ ); excellent results were found in the deep nepheloid layer (Spinrad, 1982). Kitchen et al. (1982) showed that variability of  $c$  (at 660 nm) vs PV is primarily a function of particle concentration and size distribution. Unless particle size distribution remains constant, one would not expect a simple relationship between any bulk particulate property and  $c$ . In other studies (reviewed below),  $c$  was calibrated against the dry-weight concentration of suspended particulate matter (SPM) determined by either bottle sample filtration or by in situ filtration techniques. In a few cases, particulate organic carbon (POC) concentrations were estimated by application of a constant SPM/POC ratio to SPM calculated from  $c$  (e.g. Siegel et al., 1989; Cullen et al., 1992; Walsh et al., 1995). Direct calibration of  $c$  vs POC from bottle filtration methods has not yielded useful or consistent results (Gardner et al., 1993; Walsh et al., 1995).

Bishop (1986) and Bishop et al. (1992) described the calibration of  $c$  against SPM using data from the NW Atlantic collected as part of the Warm Core Rings Experiment (WCRE). Regressions of  $c$  against SPM data from three seasons and a variety of hydrographic environments ranging from productive Slope Water to the oligotrophic waters of the Sargasso Sea showed that calibration slopes and intercepts were different, depending on whether or not samples originated in the euphotic zone or

deeper waters, and whether or not samples were obtained in oligotrophic or productive waters. Because  $c$  and particulate matter chemistry were measured from different ships at different times, significant scatter in the data compared was found. Regression slopes for  $c$  vs SPM varied by nearly a factor of two for open ocean waters (Fig. 1), and  $r^2$  values never exceeded 0.8. The springtime data from Bishop et al. (1992) fall along the “productive waters” trend, whereas the Bishop (1986) data spans productive to oligotrophic environments sampled later in the year. All the WCRE results were for samples obtained shallower than 1000 m; when the ocean bottom is approached in active nepheloid layers, the calibration slopes can vary by nearly a factor of 10 (Baker and Lavelle, 1984).

We demonstrate below that  $c$  is best correlated with particulate organic carbon (POC) concentration. POC is measured directly from samples collected by Large Volume in situ Filtration System (LVFS; Bishop and Edmond, 1976) and Multiple Unit Large Volume in situ Filtration System (MULVFS; Bishop et al., 1985). Because of the large quantities (100’s of mg) of particulate matter captured by the LVFS and MULVFS, the determination of POC is accurate not only for particle-rich euphotic

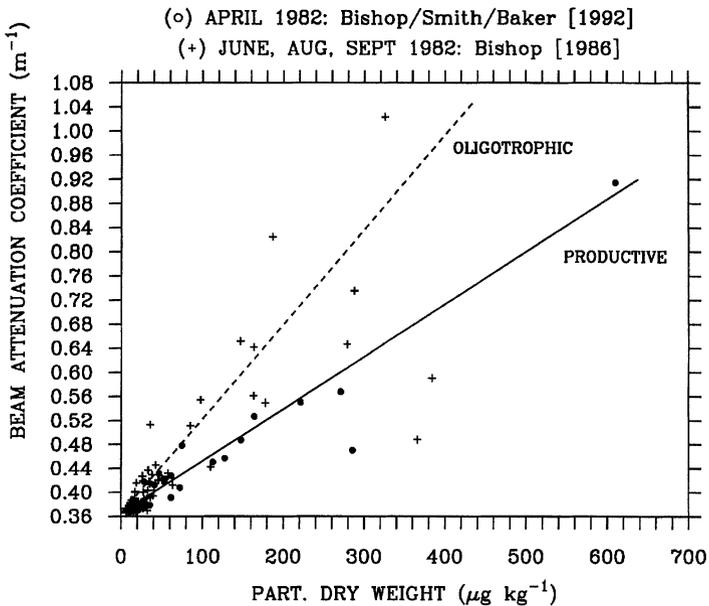


Fig. 1. Comparison of particulate dry weight (SPM) vs beam attenuation coefficient ( $c$ ) at 660 nm. Particulate matter samples were collected by large volume in situ filtration during April, June, August and October 1982 as part of WCRE.  $c$  measurements were made using a Sea Tech transmissometer from a different ship and were matched with MULVFS profiles taken within 10 km distance and on the same day. Filled symbols are data from springtime bloom conditions (Bishop et al., 1992). Plus symbols, data from productive and oligotrophic environments June, August and October 1982 (Bishop, 1986). The lines “productive” and “oligotrophic” are based on Bishop (1986) and have slopes of  $0.00087$  and  $0.00157 \text{ m}^{-1} (\mu\text{g kg}^{-1})^{-1}$ , respectively.

zone waters, but also for particle-poor deeper waters. We will also demonstrate that *c* vs POC calibrations are largely independent of ocean (Atlantic vs Pacific), whether or not samples are collected in the euphotic zone or deeper, whether or not the waters are productive or oligotrophic, and are independent of season sampled.

## 2. Methods

The transmissometer data described in this study have been mostly obtained by a single Sea Tech 1-m path length transmissometer used by our group since 1982. Likewise, particulate matter observations have been made with identical in situ filtration methodology (LVFS, Bishop et al., 1977; MULVFS, Bishop et al., 1985). Each LVFS and MULVFS sample represents the collections of particles filtered from 1000 to 20,000 l volumes of seawater (lowest near the surface) over several hours. Samples are split in situ into  $< 1$ , 1–53 and  $> 53$   $\mu\text{m}$  size fractions. One significant difference between LVFS (which dominates the WCRE data sets) and MULVFS is the time required to obtain a profile of samples from the water column: a complete profile of 12 samples to 1000 m obtained with LVFS would take 2–3 days of ship time, whereas MULVFS sampling is completed in only 8–9 h.

Calibration details and data reduction protocols used to improve precision and accuracy of the Sea Tech measurements of beam attenuation coefficient have been described by Bishop (1986). Briefly, the instruments of this type suffer from thermal hysteresis, which renders unusable data from waters below the euphotic zone; the paper describes a solution to this problem.

Particulate matter data sets used by Bishop (1986) and Bishop et al. (1992) have been described by Bishop et al. (1986). They are part of the Warm Core Rings data base archives and are available from NODC or the author.

In the WCR experiment in 1982, the transmissometers were deployed from a ship different from the one used for LVFS or MULVFS sampling, hence data were matched when the ships were within 10 km of each other during a 24 h period. This spatial/ temporal mismatch contributed significantly to the scatter shown in Fig. 1.

The different ship/different time problem was eliminated beginning with the 1992 US Joint Global Ocean Flux Study cruises to the equatorial Pacific ocean (EqPac). In this case the transmissometer was interfaced to an autonomously operating Applied Microsystems STD-12 logging CTD attached to the end of the electromechanical cable of the MULVFS. For best temporal match, down-cast transmissometer data were compared with the MULVFS particulate matter values, since most filtration of shallow samples occurs during the early part of the cast (Bishop et al., 1985). We would still expect some scatter of results in the upper pycnocline, where strong particulate matter concentration gradients are found, due to the effects of internal waves being averaged in MULVFS samples but not in the transmissometer data. A total of 24 MULVFS casts to 1000 m (approximately 240 samples) were obtained between 12°N and 12°S along 140°W during EqPac cruises TT007 (February–March 1992) and TT011 (August–September 1992). The transmissometer and MULVFS data

sets are available via the US-Joint Global Ocean Flux Study (JGOFS) data system (<http://www1.who.edu/jgofs.html>).

When we describe POC or SPM data from LVFS or MULVFS samples below, we mean the sum of the concentrations of material collected in  $< 1$ ,  $1$ – $53$ , and  $> 53$   $\mu\text{m}$  size classes; the three size fractions were collected using a filter series consisting of  $53$   $\mu\text{m}$  Polyester mesh, and two identical Whatman QMA quartz fiber filters. The  $< 1$   $\mu\text{m}$  class is representative of only a fraction of the material smaller than  $1$   $\mu\text{m}$ , since it is the material that passes through the first QMA filter but is retained by the second. As will be shown below, regression statistics are better when all three particle size classes are included.

In the MULVFS configuration in use beginning with the EqPac cruises, both transmissometer voltage and transmissometer temperature channel outputs were digitized to better than 1 part in 20,000 (14 bits). The stability of the logging device, verified by thermal cycling of the logging unit in a cold room, showed both digitizing channels to be stable at 1 part in 20,000 over  $2$ – $25^\circ\text{C}$ .

Thermal cycling of the transmissometer attached to the logging unit revealed a hitherto unrecognized change in the blocked beam “zero” voltage. Since the calculation of transmittance from transmissometer output voltages depends on the “zero” value being known, correction for this effect is crucial in waters having low particulate matter loadings. The effect of the correction was to increase the value for beam attenuation coefficient of colder deep waters by as much as  $0.007\text{ m}^{-1}$ . Air calibration specifics as a function of temperature did not materially change from those documented by Sea Tech.

The “zero” voltage correction, linearly proportional to in situ temperature, has been retroactively applied to data sets previously described by Bishop (1986) shown in Fig. 1. The Bishop et al. (1992) data, also shown in Fig. 1, were obtained by a 25 cm path length Sea Tech transmissometer and have not been corrected. These data were obtained from waters shallower than 200 m and generally in productive particle-rich environments; thus the correction of the data would have a minor effect on the values.

A benefit of the compact configuration of the MULVFS transmissometer and CTD logging system was that the package could be stored in the ship’s laboratory between deployments. Cleaning of the optics and measurement of transmittance values in air (air calibration) and with a blocked beam (zero) were performed prior to each deployment. Such procedures are typically not performed with rosette mounted CTD/transmissometers due to inconvenience of instrument location and the impossibility of obtaining a reliable “air calibration” under most on-deck conditions. A further benefit of the MULVFS package was that it could be mounted on the ship’s rosette system for direct comparison with the rosette’s CTD/transmissometer during special casts.

When comparing our earlier published results with results from 1992 onwards, we ascribe improvements in order of importance: (1) transmissometer data and MULVFS particulate matter samples were obtained during the same cast, (2) better cleaning of transmissometer optics was possible, and (3) we have an improved knowledge of “zero” voltages. Comparison of results from near 1000 m from TT007

and TT011 EqPac cruises shows that  $c$  values are repeatable to better than  $0.001 \text{ m}^{-1}$  in deep water.

### 3. Results and discussion

#### 3.1. Equatorial Pacific 1992

As mentioned earlier, the different-ship, different-cast problem was eliminated for the 1992 US-JGOFS program cruises in the equatorial Pacific (EqPac), and we were able to obtain  $c$  data for comparison with POC and SPM data from in situ collected particulate matter samples during the same MULVFS cast (Fig. 2A and B). With the improvements in our ability to compare the two techniques, the correlation between POC concentration and  $c$  data turns out to be much better than found for  $c$  vs SPM. Pooled data from the multiple casts for each of the two US-JGOFS cruises (TT007: El Niño and TT011: normal conditions) showed less than 5% difference in  $c$  vs. POC regressions, with slopes of  $0.63 \times 10^{-4}$  and  $0.61 \times 10^{-4} \text{ m}^{-1} (\text{nmol C l}^{-1})^{-1}$ , and  $r^2$  values of 0.97 and 0.95 for TT007 and TT011 (Fig. 2A). Intercept values agreed with the accepted  $0.364 \text{ m}^{-1}$  value for particle-free water. In contrast,  $c$  vs SPM slopes were different by 20%, with values of  $0.185 \times 10^{-2}$  and  $0.153 \times 10^{-2} \text{ m}^{-1} (\mu\text{g l}^{-1})^{-1}$  for the two cruises (Fig. 2B); intercepts fell significantly below the clear water value. If we pool the EqPac data sets into depth intervals shallower and deeper than 200 m, then the  $c$  vs POC regression statistics show little difference, whereas the  $c$  vs SPM slope changes by over a factor of two (Table 1).

#### 3.2. Effect of particle size class on $c$ vs POC regression statistics

Recently, in response to the finding of significant diurnal variability in the  $c$  profiles (e.g. Siegel et al., 1989) more attention has been focused on the biological contributions to the signal (Chung et al., 1996; Durand and Olson, 1996). Both efforts concluded that heterotrophic bacteria, prochlorophytes, cyanobacteria, and small autotrophic eucaryotes contribute significantly to the signal; total scattering cross section of these four groups (stained and measured by flow cytometry) vs  $c_p$  gave  $r^2$  values of 0.91 and 0.78, respectively, for data from the upper 200 m of US-JGOFS cruises TT007 and TT011. Size filtration experiments showed that 41–89% of the  $c_p$  signal could be explained by particles in the  $< 8 \mu\text{m}$  size class. Chung et al. (1996) concluded that the  $c_p$  signal is dominated by small particles.

We have found that inclusion of the  $>53 \mu\text{m}$  size class, improperly sampled by bottle filtration methods, significantly improves the correlation of the data. To illustrate this, we pooled the data from the two EqPac cruises (Table 2);  $c$  vs total ( $<1$ ,  $1$ – $53$ ,  $>53 \mu\text{m}$ ) POC yields  $r^2$  of 0.951. If we eliminate the contributions of the  $>53 \mu\text{m}$  particle size fraction (row 2), the  $r^2$  value drops to 0.89; considering only the  $1$ – $53 \mu\text{m}$  size fraction leads to an  $r^2$  of 0.87. Thus, the large size fraction contributes to  $c$ . The comparison of  $r^2$  values is a valid estimator of “goodness” of fit, especially since exactly the same 119 samples were used in the analysis.

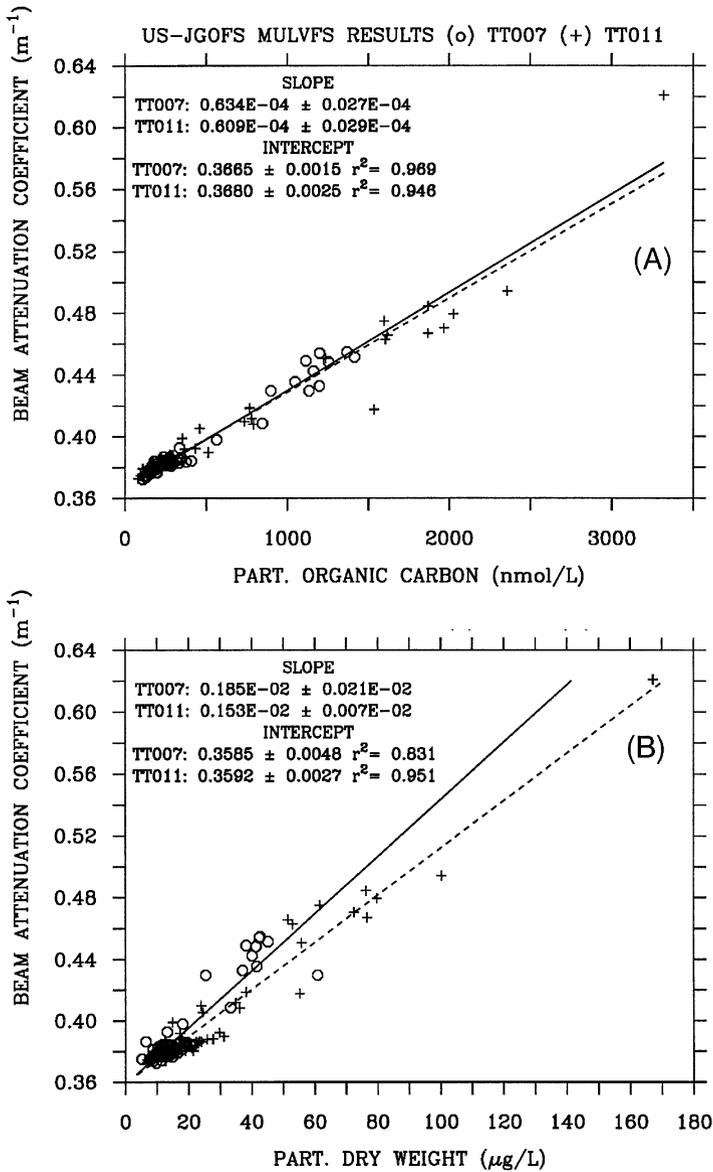


Fig. 2. (A) Regression of MULVFS beam attenuation coefficient ( $c$ ) vs POC from MULVFS samples collected during TT007 and TT011 JGOFS EqPac cruises. The slopes of the regression data differ by less than 4%, and intercepts are indistinguishable from clear water values. (B) Regression of MULVFS total particulate dry weight vs  $c$  for the same two cruises. Close inspection of the data in the lower left-hand corner of the figure reveals a kink in the  $c$  vs SPM trend for samples below 150 m, which is not found in the  $c$  vs POC relationship (Fig. 2A).

Table 1

| Data set                    | c vs POC                  |                           |       | c vs SPM                  |                           |       | $n^a$ |
|-----------------------------|---------------------------|---------------------------|-------|---------------------------|---------------------------|-------|-------|
|                             | Slope<br>$\times 10^{-4}$ | Intercept<br>( $m^{-1}$ ) | $r^2$ | Slope<br>$\times 10^{-2}$ | Intercept<br>( $m^{-1}$ ) | $r^2$ |       |
| TT007 + TT011               | 0.614 $\pm$<br>0.021      | 0.368 $\pm$<br>0.002      | 0.951 | 0.155 $\pm$<br>0.029      | 0.360 $\pm$<br>0.002      | 0.914 | 119   |
| TT007 + TT011<br>0–200 m    | 0.633 $\pm$<br>0.042      | 0.365 $\pm$<br>0.005      | 0.930 | 0.148 $\pm$<br>0.012      | 0.367 $\pm$<br>0.005      | 0.903 | 49    |
| TT007 + TT011<br>200–1000 m | 0.675 $\pm$<br>0.078      | 0.367 $\pm$<br>0.002      | 0.752 | 0.067 $\pm$<br>0.011      | 0.371 $\pm$<br>0.002      | 0.599 | 70    |

<sup>a</sup>Only half of the 240 MULVFS samples collected were used in this analysis because sub-sampling of the other half of the samples for  $> 53 \mu m$  material for other EqPac investigators resulted in these samples not yielding quantitative  $> 53 \mu m$  POC values through gravimetric analysis.  $\pm$  value indicates 95% confidence limits.

Table 2

| Data set  | Notes  | Slope<br>$\times 10^{-4}$ | Intercept<br>( $m^{-1}$ ) | $r^2$ | $n$ |
|---|--|---------------------------|---------------------------|-------|-----|
| 1 TT007 + TT011<br>< 1 + 1–53 + > 53              | All MULVFS size fractions included   | 0.614 $\pm$<br>0.021      | 0.368 $\pm$<br>0.002      | 0.951 | 119 |
| 2 TT007 + TT011<br>< 1 + 1–53                     | Excludes largest size class  | 0.905 $\pm$<br>0.048      | 0.365 $\pm$<br>0.002      | 0.894 | 119 |
| 3 TT007 + TT011<br>1–53                           | Excludes largest and smallest size classes   | 1.140 $\pm$<br>0.067      | 0.363 $\pm$<br>0.003      | 0.873 | 119 |
| 4 TT007 + TT011<br>1.6 $\times$ < 1 + 1–53 + > 53 | Simulates the change if a 0.7 $\mu m$ GFF filter was substituted for the 1.0 $\mu m$ QMA used for < 1 $\mu m$ fraction. Based on M. Bacon data | 0.566 $\pm$<br>0.020      | 0.368 $\pm$<br>0.002      | 0.952 | 119 |
| 5 TT007 + TT011<br>1.6 $\times$ < 1 + 1–53        | As in (4), excluding the > 53 $\mu m$ fraction   | 0.804 $\pm$<br>0.041      | 0.366 $\pm$<br>0.002      | 0.902 | 119 |

What is the effect of including more particles in the smallest size class? Our  $< 1 \mu m$  material is the organic carbon retained by the second of two identical 1.0  $\mu m$  Whatman QMA quartz fiber filters in series. It is well known that glass and quartz fiber filters collect more material the deeper the filter used (Bishop and Edmond, 1976). During EqPac cruises TT008 and TT012, a different in-situ filtration system was deployed using a filter series (53  $\mu m$  polyester screen, 1  $\mu m$  Whatman QMA filter, and 0.7  $\mu m$  Whatman GFF) that was nearly identical to MULVFS except for the filter used to collect the  $< 1 \mu m$  size fraction (Bacon et al., 1996). Regression of our 1–53  $\mu m$  vs  $< 1 \mu m$  POC compared with the Bacon et al. (1996) results showed that the second GFF fiber filter collects approximately 60% more POC than our second

QMA. Row 4 in Table 2 approximates the collection of this extra small material and shows that the slope decreases by about 10% while  $r^2$  values are relatively unaffected. If we exclude the  $> 53 \mu\text{m}$  fraction from the regression, the  $r^2$  values are again worse. Thus, our results show that the best correlations are obtained when all size fractions are included. This holds whether the  $< 1 \mu\text{m}$  size class is sampled using Whatman QMA or GFF filters. We support the conclusions of Chung et al. (1996) that small particles are a major contributor to  $c_p$ ; however, including the largest size fraction is important to improve the fit.

### 3.3. Rosette $c$ vs Bottle POC and Bottle SPM

While temporally coincident  $c$  vs large volume in situ POC data showed excellent agreement, temporally coincident rosette/CTD derived  $c$  vs bottle-filtered POC showed poor correlation and a factor of two difference in the slope of the  $c$  vs POC relationship for the same two cruises (Fig. 3; POC data from Murray et al., (1996)). It is paradoxical that the large volume filtration POC data (representing particles filtered from 1000's of l) should compare well with a 1 m transmissometer with an effective sampling volume of 200 ml (a water volume equivalent to 4 l when data are averaged over 2 m depth bins assuming a typical  $1 \text{ m s}^{-1}$  lowering rate and 100 ms transmissometer time constant). If anything, rosette bottle samples and CTD-transmissometer measurements should be superior to those obtained by in situ filtration

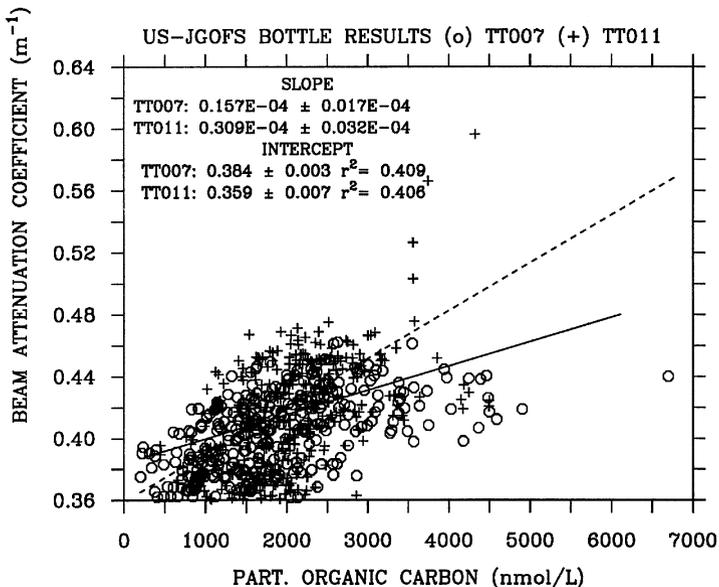


Fig. 3.  $c$  vs POC from analysis of samples filtered from small volume rosette-mounted 10 L PVC bottles during US-JGOFS EqPac cruises TT007 and TT011. MULVFS and rosette transmissometer data compared well at the same stations, suggesting that much of the scatter in POC is due to sample processing methodology (see also e.g. Altabet et al., 1992).

because they sample similar volumes of water, and their samplings are temporally and spatially coincident to within a few seconds and a meter. The similar range of beam attenuation coefficient values measured by MULVFS and CTD transmissometers (cf. Figs. 2 and 3), and the good agreement between the rosette and MULVFS beam attenuation coefficients found during special simultaneous casts of the two transmissometer assemblies suggests that the problem must lie with the POC data determined using shipboard filtration methods. There is also lack of consistency in  $c$  vs bottle POC calibrations for EqPac cruises TT008 and TT012 (Walsh et al., 1995). At the same time Walsh et al. (1995) reported SPM vs  $c$  slope values ranging between  $0.16 \times 10^{-2}$  and  $0.22 \times 10^{-2}$ , close to those shown in Fig. 2B. The higher slope values of Walsh et al. (1995) are consistent with the loss of large particles by sedimentation within the water samplers prior to filtration (Bishop and Edmond, 1976; Gardner, 1977).

The bottle SPM values were obtained using methodology that minimized sample handling, whereas the POC processing involved multiple handling steps. This may explain the relatively good agreement (barring sedimentation biases) of bottle and in situ SPM values and the poor agreement between bottle and in situ POC results (see also Altabet et al., 1992). Given the large scatter of POC values from various shipboard filtration measurements, it is no surprise that the relationship of  $c$  vs POC had not been previously noted. The good agreement between MULVFS POC and  $c$  further indicates that POC variability is small on a given isopycnal surface in the open ocean.

#### 3.4. *Depth variations*

Systematics of the depth profiles of MULVFS POC and SPM data and Sea Tech  $c$  data gives further insight into the regression relationships amongst these quantities. Unlike shipboard small volume filtration methodology using bottle-collected samples, in situ large volume filtration methodology allows the determination of POC and SPM concentrations in the same samples, thus eliminating differences due to different sample handling methods (Bishop et al., 1977). Consistent with the findings of Bishop (1986) and by others previously,  $c$  data could be fitted to the SPM profile in the upper 150 m but are seen to diverge sharply in deeper waters (Fig. 4). Conversely, one can match the deeper profile, but not surface values simultaneously. The divergence occurs at the depth where organic matter percentages shifted from shallow values near 90% of dry weight to approximately 50% of dry weight. The chemistry of the samples shows that the inorganic component is dominated by calcium carbonate and biogenic silica phases. Our results therefore suggest that carbonate and opal do not contribute significantly to  $c$ . In contrast, POC from all depths overlaid  $c$  nearly exactly (Fig. 4). Similar excellent agreement in profile between  $c$  and POC from the surface to 1000 m was found at the other 23 stations sampled (Fig. 2).

#### 3.5. *Productive and oligotrophic waters in the NW Atlantic 1982*

A reexamination of data from the 1982 Warm Core Rings experiment (from different ships; Bishop, 1986; Bishop et al., 1992) shows that  $c$  vs POC results are

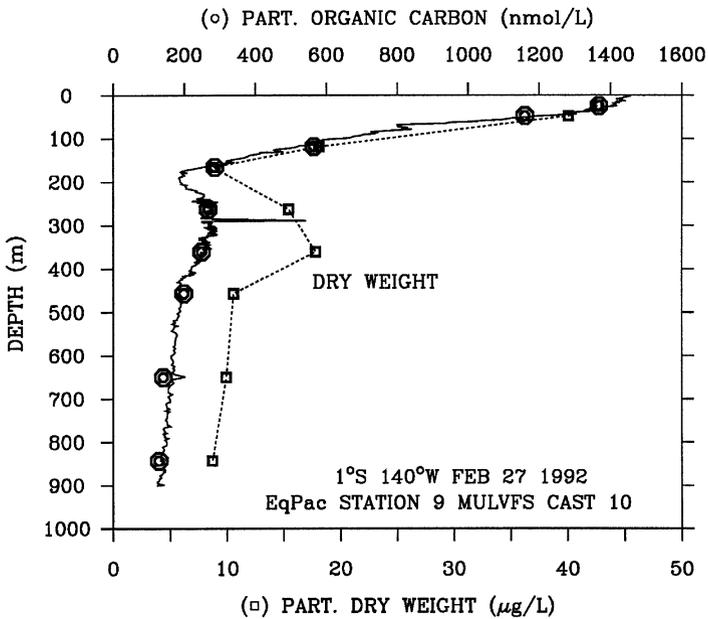


Fig. 4. Profiles of particulate organic carbon and particulate dry-weight concentration from a MULVFS cast on 27 February 1992 at 1°S 140°W during the equatorial Pacific US-JGOFS study. The solid line denotes particulate carbon concentration computed from beam attenuation coefficient ( $c$ ) data and the regression formula for TT007 data shown in Fig. 2. The  $c$  data were obtained during the MULVFS deployment phase on the same cast.

clearly better correlated than  $c$  vs SPM (Fig. 1 vs Fig. 5; Table 3). The regression slope for the entire data set is  $0.54 \pm 0.04 \times 10^{-4}$  and is little different statistically from  $0.62 \times 10^{-4}$  found in the equatorial Pacific in 1992. Similar slopes were found for productive and oligotrophic waters. There is thus little change in calibration slope between the euphotic zone and sub-euphotic zone waters. The April 1982 WCRE data suggest a 25% difference in slope ( $0.43 \times 10^{-4}$ ) compared with EqPac; given that the in situ samples were collected with the much slower LVFS and that bloom conditions prevailed, it is impossible to determine if the 25% difference is real.

### 3.6. Sub-arctic waters of the NE Pacific 1996

Figure 6 shows preliminary results from CGS Tully cruise 9609 in May 1996, one of four C-JGOFS occupations of six stations from southern Vancouver Island to Ocean Weather Station Papa (OWS P) in the southern Alaska Gyre. Preliminary results based on POC analyses of 1–53  $\mu\text{m}$  MULVFS samples, estimation of the  $<1 \mu\text{m}$  POC and preliminary gravimetric analyses of the  $>53 \mu\text{m}$  size fraction indicate that the regression of  $c$  vs POC is not likely to be different from EqPac or WCRE, since these data fall near the EqPac regression lines.

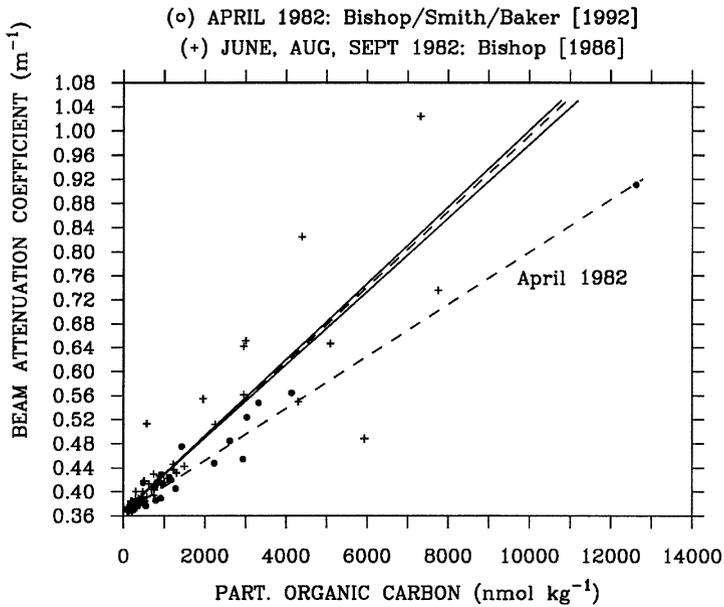


Fig. 5. Comparison of POC vs  $c$  at 660 nm. Particulate matter samples were collected by large volume in situ filtration during April, June, August and October 1982 as part of WCRE.  $c$  measurements were made using a 1-m pathlength Sea Tech transmissometer deployed from a different ship and were matched with MU(LVFS) profiles taken within 10 km distance and on the same day. Solid lines are from the EqPac regression; dashed from regressions of WCRE data. The different ship – different place – different time matching process introduces considerable scatter and possible slope biases into the comparison (see for comparison, Fig. 2). Whether or not the 25% difference in slope values shown in Table 3 for April 1982 vs June, August and September 1982 is an artifact of such biases cannot be determined.

Table 3

| Data set           | $c$ vs POC                |                                  |       | $c$ vs SPM                |                                  |       | $n$ |
|--------------------|---------------------------|----------------------------------|-------|---------------------------|----------------------------------|-------|-----|
|                    | Slope<br>$\times 10^{-4}$ | Intercept<br>( $\text{m}^{-1}$ ) | $r^2$ | Slope<br>$\times 10^{-2}$ | Intercept<br>( $\text{m}^{-1}$ ) | $r^2$ |     |
| All WCRE data      | $0.536 \pm$               | $0.369 \pm$                      | 0.810 | $0.101 \pm$               | $0.367 \pm$                      | 0.711 | 114 |
| Bishop 86<br>(all) | 0.040                     | 0.009                            |       | 0.010                     | 0.011                            |       |     |
| BSB 92 (all)       | $0.627 \pm$               | $0.365 \pm$                      | 0.799 | $0.127 \pm$               | $0.361 \pm$                      | 0.710 | 94  |
| 0–200 m            | $0.434 \pm$               | $0.372 \pm$                      | 0.967 | $0.080 \pm$               | $0.367 \pm$                      | 0.900 | 20  |
| Bishop 86          | 0.034                     | 0.011                            |       | 0.011                     | 0.020                            |       |     |
| 0–200 m            | $0.611 \pm$               | $0.372 \pm$                      | 0.749 | $0.120 \pm$               | $0.376 \pm$                      | 0.650 | 45  |
| Bishop 86          | 0.091                     | 0.022                            |       | 0.023                     | 0.026                            |       |     |
| 200–1000 m         | $0.369 \pm$               | $0.366 \pm$                      | 0.344 | $0.043 \pm$               | $0.366 \pm$                      | 0.310 | 49  |
|                    | 0.125                     | 0.003                            |       | 0.016                     | 0.003                            |       |     |

All: Bishop (1986) and Bishop et al. (1992); BSB 92: Bishop et al. (1992) – data only obtained from upper 200 m.

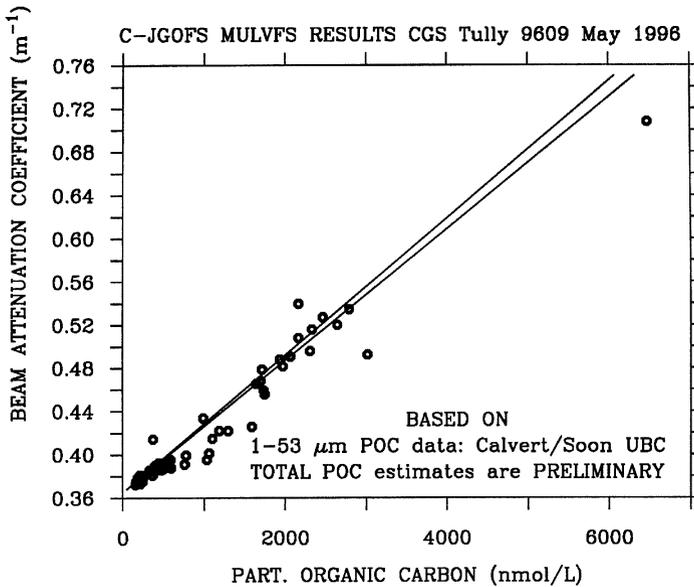


Fig. 6. Preliminary results for  $c$  vs POC calibration. CGS Tully 9609 eastern sub-arctic Pacific Ocean, May 1996. Data for all size classes derived from preliminary gravimetric analysis of  $>53 \mu\text{m}$  particles, CN analysis of  $1-53 \mu\text{m}$  size class, and interpolation of  $<1 \mu\text{m}$  size class from analysis at other stations. Lines drawn are the EqPac regressions.

Finally, we include finalized data from the February 1996 occupation of station PAPA (Fig. 7). In this case both  $<53 \mu\text{m}$  fractions were measured for POC, and the gravimetric estimate of  $>53 \mu\text{m}$  POC included corrections for  $\text{CaCO}_3$ , opal, and sea salt (Bishop et al., 1977). These samples are important in that they represent a case where 35% of the POC was found in the  $>53 \mu\text{m}$  particle size fraction in shallow waters and because they represent mid-winter conditions unsampled here-to-fore. The line shown is transmissometer  $c$  values predicted using the EqPac relationship (slope =  $0.62 \times 10^{-4}$ ). That the regression of the actual  $c$  data vs POC gives a slope of  $0.64 \pm 0.06 \times 10^{-4}$  and  $r^2 = 0.97$  confirms agreement with EqPac results. More work is necessary on existing C-JGOFS samples and in more extreme environments to confirm this promising result.

#### 4. Conclusion

Suspended particulate matter consists of a large variety of particles of different size and composition and hence optical properties. We have shown that transmissometer beam attenuation coefficient,  $c$ , is much better correlated with POC than with other bulk particulate matter properties such as SPM. One explanation goes back to underlying optics theory (Van de Hulst, 1957), which predicts that  $c$  and total particle

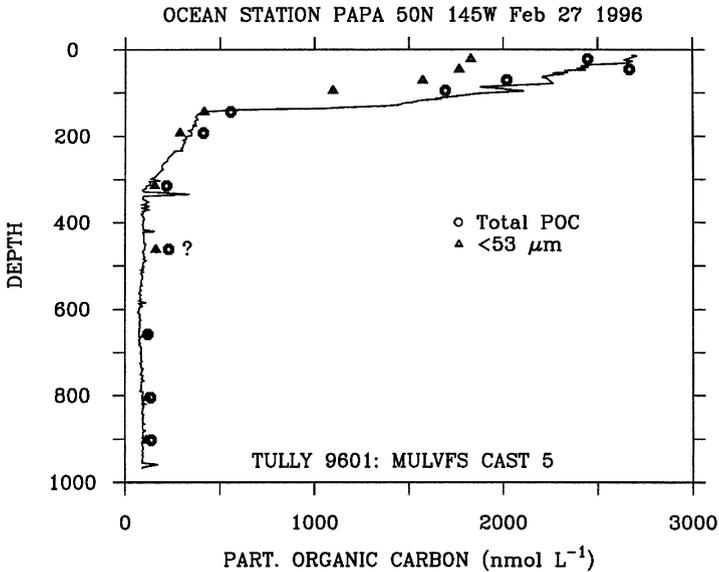


Fig. 7. Finalized POC and transmissometer data from a 1996 wintertime MULVFS deployment at Ocean Weather Station PAPA (50N, 145W). The transmissometer  $c$  profile (solid line) is converted to POC using the EqPac calibration data. Circles – total POC. Triangles <53  $\mu\text{m}$  POC. The line could be matched exactly to the deeper sample POC by adjusting  $c$  values upwards by only  $0.002 \text{ m}^{-1}$ . Sample identified by (?) near 450 m has a 10–20% uncertainty of concentration due to a flow metering problem during sampling. The >53  $\mu\text{m}$  POC contributes approximately 35% to the total POC in shallow waters, decreasing to 15% in deeper waters. In the euphotic zone much of the material in the larger size fraction was phytoplankton.

cross-sectional area should be correlated. What has been missed is the fact that organic particles are hydrated in the water column (living organisms contain water) and, therefore, present a much bigger scattering cross section than predicted by the contribution of POC to total dry weight. Returning to the case represented by Fig. 4, if organic particles were 90% water by weight (inorganic particles contain no water), their contribution to total particulate wet weight would be 99% in shallow waters and 91% deeper rather than the 90 and 50% dry-weight contributions to SPM found. Thus, the  $c$  signal would mostly be derived from organic matter.

Changes of particle size distribution, scattering, and absorptive properties are substantial going from the euphotic zone to the intermediate water column, and among environments sampled in this study. Although we have offered a first-order explanation of why POC concentration is so well correlated with  $c$ , the details cannot be answered with available data. We also have not had the opportunity to examine  $c$  vs POC relationships in shelf environments or in strong nepheloid layers, both of which can be strongly depleted in organic particles. The fundamentally new result here is that POC on a dry-weight to dry-weight basis has a much stronger contribution to  $c$  than other inorganic particle phases (e.g. calcium carbonate and biogenic silica).

Our results show that the relationship between beam attenuation coefficient and POC appears to be largely independent of ocean environment, season, or depth

sampled. They demonstrate that the transmissometer can provide a quantitatively useful first estimate of POC. Data collected over a distance of nearly 3000 km in the Equatorial Pacific in two different phases of ENSO show less than 4% difference in  $c$  vs POC calibration specifics. Comparable quality data from the sub-arctic Pacific in the winter time produced an identical result. These results, together with a reanalysis of data from WCRE in the NW Atlantic and other preliminary results from the subarctic NE Pacific show that POC can be easily quantified to better than 25% accuracy (probably much better) in the upper 1000 m and systematically on a day-to-day basis to better than a few percent. This is a huge improvement over the Bishop (1986) and other more recent results comparing  $c$  vs SPM, since the method applies to a highly diverse set of oceanographic environments and conditions.

In summary, we have provided an improved basis for interpretation of the vast body of beam attenuation coefficient measurements made in the oceans over the past two decades. More importantly, our findings open the opportunity for deploying transmissometers from platforms other than ships to characterize the high-frequency (diurnal and longer time scales) variability of particulate organic carbon within the upper layer of the ocean. The fact that bottle POC results can be so variable in their relationship with  $c$  suggests that shipboard methodology must be critically reexamined. The universality of the  $c$  vs in situ POC relationship is not yet fully understood and will be explored further in ongoing analysis of MULVFS samples and data and as part of efforts to collect new MULVFS samples from contrasting environments.

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