

Variability of the amplification factor of light absorption by filter-retained aquatic particles in the coastal environment

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Abstract. The amplification of light absorption by aquatic particles retained on glass-fiber filters, the so-called β factor, has been measured for 29 stations located in the varying coastal environment of the northern basin of the Adriatic Sea. The spectral values of the optical density of particles have been determined on glass-fiber filters by the standard transmittance (T) method as well as by the transmittance-reflectance (T-R) method, which performs an accurate correction for light backscattering by the particles, and on glass slides by the modified filter-transfer-freeze (FTF) method, which eliminates the pathlength amplification. It has been shown that the relationships between the optical densities of particles on glass slides (OD_{sus}) and on glass-fiber filters (OD_f) have a low dispersion when OD_f is measured by the T-R method: in this case, the use of a single expression for all stations adds an error that does not exceed the typical uncertainty of the measurement of the filter-retained particle absorption. On the contrary, the OD_{sus} versus OD_f plots obtained by the T method exhibit considerable variability, apparently due to the approximate correction for light backscattering performed by this method, and do not permit the use of a single equation for all stations.

Introduction

The light absorption spectrum of aquatic particles is mostly determined by a method initiated by Yentsch (Yentsch, 1962) [in the following referred to as 'standard transmittance' (T) method], which consists of concentrating the particles on a glass-fiber filter and comparing light transmitted through the particle-retaining filter and through an unused 'reference' filter. The measurement is generally performed by dual-beam spectrophotometers, and the raw data are expressed in terms of the dimensionless optical density (= OD), which is equal to the base 10 logarithm of the inverse transmittance. The light fraction scattered by the particles outside the acceptance angle of the detector optics, mainly because of backscattering, contributes a spurious optical density term that is approximately corrected for by subtracting the optical density measured in the near-IR (usually 750 nm) from the measured optical density spectrum (Mitchell and Kiefer, 1988).

The absorption, and thus the measured optical density, OD_f , of the particles retained on the filter is amplified by multiple scattering in the glass-fiber medium. The measured OD_f is converted to the optical density of the particle suspension with the same geometrical pathlength, OD_{sus} , using empirical relationships. The ratio OD_f/OD_{sus} is often called the β factor, following the terminology of Butler (Butler, 1962). The volume absorption coefficient of the particle suspension, a (in m^{-1}), is obtained from the equation $a = 2.3 OD_{\text{sus}}/X$, where X is the ratio of the filtered volume to the clearance area of the filter, i.e. the geometrical pathlength.

Several empirical determinations of the OD_{sus} versus OD_f relationship have been performed, using the standard transmittance method and suspension samples taken from concentrated phytoplankton cultures [e.g. (Bricaud and

Stramski, 1990; Mitchell, 1990; Cleveland and Weidemann, 1993; Arbones *et al.*, 1996)]. The relationships obtained are currently applied to natural phytoplankton populations with varying algal composition and amount of detritus. Recent results, however, have shown considerably higher absorption amplification with some cultured picoplankton species (Moore *et al.*, 1995). This result suggests a dependence of the OD_{sus} versus OD_{f} relationship on particle size. Nevertheless, one must be aware that there are potentially large errors in measuring optical densities of very small phytoplankton cells with the T method because their size is similar to the wavelength of visible light, so that their volume scattering function will have relatively more scattering at large angles which is not collected by the instrument measuring optics. Thus, the observed variation of the OD_{sus} versus OD_{f} relationship could have been due, at least partly, to the approximate correction for light scattering operated by the T method.

In natural samples, mixing of various phytoplankton species is likely to reduce the cell size effect on the OD_{sus} versus OD_{f} relationship. Instead, an important source of variability for the OD_{sus} versus OD_{f} relationship, as measured by the T method, can be the presence of detritus, with size distribution usually including a significant fraction of sub-micron particles scattering at wide angles. Of particular concern are mineral particles, which are characterized by high refractive indices, and therefore high backscattering coefficients [(Gallie and Murtha, 1992; Tassan and Ferrari, 1995b); see also (Morel and Bricaud, 1981)]. Large concentrations of mineral particles are characteristic of coastal (case 2) waters, mainly due to river outflow and bottom resuspension.

Essentially because aquatic particles are naturally too dilute for a sufficiently accurate measurement of OD_{sus} by standard spectrophotometers, the variability of the OD_{sus} versus OD_{f} relationship in natural environments could not be investigated easily until recently. This difficulty can now be overcome through the use of the modified 'filter-transfer-freeze' (FTF) method (Allali *et al.*, 1995).

The present paper reports the results of a study of the variability of the OD_{sus} versus OD_{f} relationship in the northern basin of the Adriatic Sea, based on measurements carried out in summer 1997 within the framework of the EC Project *COASTIOOC*.

Method

The modified FTF method (Allali *et al.*, 1995) consists of concentrating particles onto a 0.4 μm polycarbonate membrane filter, transferring the filtered material to a glass microscope slide using liquid nitrogen freezing and, finally, measuring the particle optical density by the standard transmittance method on the slide mounted at the entrance port of an integrating sphere attached to the spectrophotometer. Since the particles are not embedded in a highly scattering medium, but retained on transparent glass, there is no absorption amplification, so that the measured optical density is identical to that of the particle suspension. The variability of the OD_{sus} versus OD_{f} relationship was investigated by this method in prochlorophyte-rich waters of the Equatorial Pacific (Allali *et al.*, 1997), and results were consistent with those of Moore *et al.* (Moore *et al.*, 1995).

However, this study also involved the standard T method, so that its results may also be affected by scattering errors.

A method for measuring optical density of particles retained on filters, including accurate correction for the effect of light scattering, has recently been set up by Tassan and Ferrari (Tassan and Ferrari, 1995a). This method, referred to as the ‘transmittance-reflectance’ (T-R) method, includes the additional measurement of the light reflected by the filter-retained particles, which is carried out using an integrating sphere attachment to the dual-beam spectrophotometer. The data analysis is performed by a theoretical model that eliminates the effect of light backscattering by the particles.

By combining measurements carried out by the modified FTF method and by the T and T-R methods, we determined the natural variability of the OD_{sus} versus OD_{f} relationship in the coastal waters of the northern basin of the Adriatic Sea, and tested the role of the experimental error due to light scattering in determining such variability.

The basin considered is characterized by mineral particle concentrations varying over a wide range, due to river discharge, open lagoons and bottom resuspension, and thus is a valuable test zone for assessing the impact of light scattering on the experimental error of optical density measurements.

Water samples were collected from a helicopter at 39 stations, located near and off-shore Venice Lido, at the outlets of the rivers Piave, Tagliamento, Livenza, Brenta and Adige, as well as of the various branches of the River Po delta (Figure 1). Simultaneous measurements by FTF, T and T-R methods were performed for 29 stations (6–8, 10–24, 26–27, 29–32, 34 and 36–39).

The T and T-R measurements on the filter-retained particles were carried out by a Perkin-Elmer Lambda 19 dual-beam spectrophotometer, using GF/F glass-fiber filters and the procedure detailed in Tassan and Ferrari (Tassan and Ferrari, 1995a), with minor modifications as specified in Tassan and Ferrari (Tassan and Ferrari, 1998) and Ferrari and Tassan (Ferrari and Tassan, 1999). The measurements yielded the $OD_{\text{f,T}}(\lambda)$ and $OD_{\text{f,T-R}}(\lambda)$ spectra, respectively.

The measurements of $OD_{\text{sus}}(\lambda)$ were performed with a spectrophotometer of the same model, using the modified FTF method, according to the procedure detailed in Allali *et al.* (Allali *et al.*, 1995). The measured spectra were normalized to the geometrical pathlength, X , of the corresponding measurement on the filter-retained particles [= $OD_{\text{sus,FTF}}(\lambda)$]. The wavelength range of all measurements extended from 400 to 750 nm.

Results

Two typical plots of $OD_{\text{sus,FTF}}$ versus $OD_{\text{f,T}}$ and $OD_{\text{sus,FTF}}$ versus $OD_{\text{f,T-R}}$ are presented in Figure 2A and B, respectively (stations 14 and 32 in Figure 1); the corresponding spectra $OD_{\text{sus,FTF}}(\lambda)$, $OD_{\text{f,T}}(\lambda)$ and $OD_{\text{f,T-R}}(\lambda)$ are shown in Figure 3A (station 14) and 3B (station 32). Slight spectral differences within the red absorption band account for the ‘loops’ apparent at low optical densities in Figure 2 [see (Bricaud and Stramski, 1990)]. Also displayed in Figure 2 are the curves (solid lines) corresponding to the OD_{sus} versus OD_{f} relationships obtained

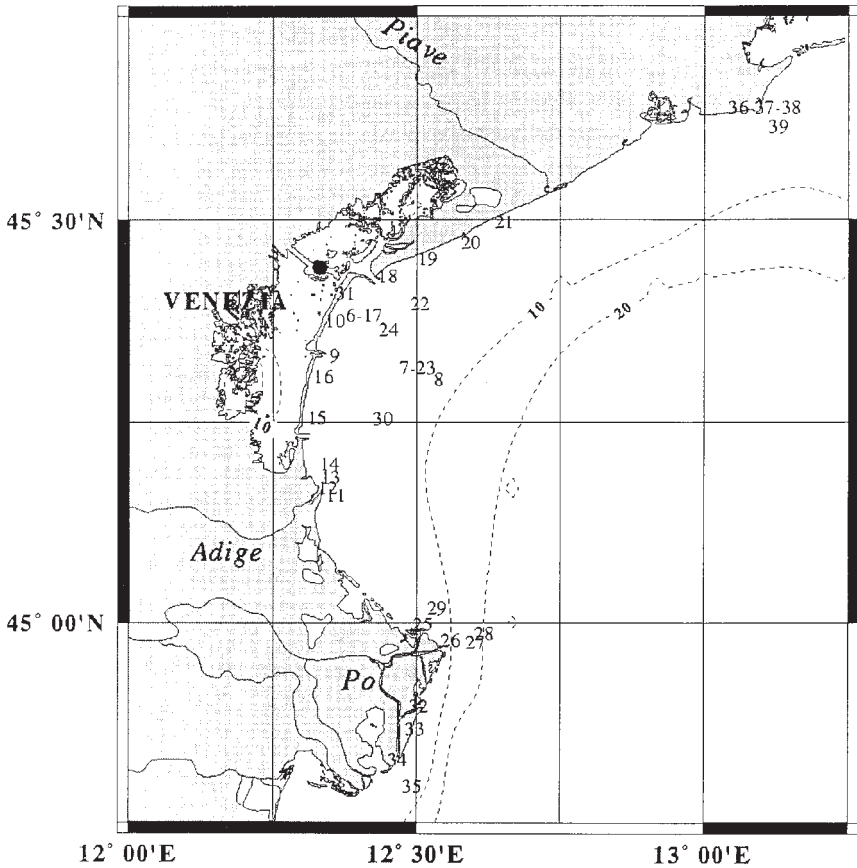


Fig. 1. Location of the stations in the northern basin of the Adriatic Sea during the 1997 *COAST-IOOC* experiment.

from T and T-R measurements performed on a laboratory culture of the fresh-water alga *Scenedesmus obliquus* (Tassan and Ferrari, 1995a), and successively used for a variety of applications, i.e.:

$$OD_{sus,T}(\lambda) = (0.406 \pm 0.010) OD_{f,T}(\lambda) + (0.519 \pm 0.05) OD_{f,T}^2(\lambda) \quad (1)$$

$$OD_{sus,T-R}(\lambda) = (0.423 \pm 0.012) OD_{f,T-R}(\lambda) + (0.479 \pm 0.06) OD_{f,T-R}^2(\lambda) \quad (2)$$

The quoted errors are standard deviations (SDs). Equations (1) and (2) (actually very close to each other) are intermediate between the relationships obtained by Mitchell (Mitchell, 1990) and Cleveland and Weidemann (Cleveland and Weidemann, 1993).

The data of each station were initially fitted by the standard equation used to represent the empirical OD_{sus} versus OD_f relationship, i.e. the quadratic form

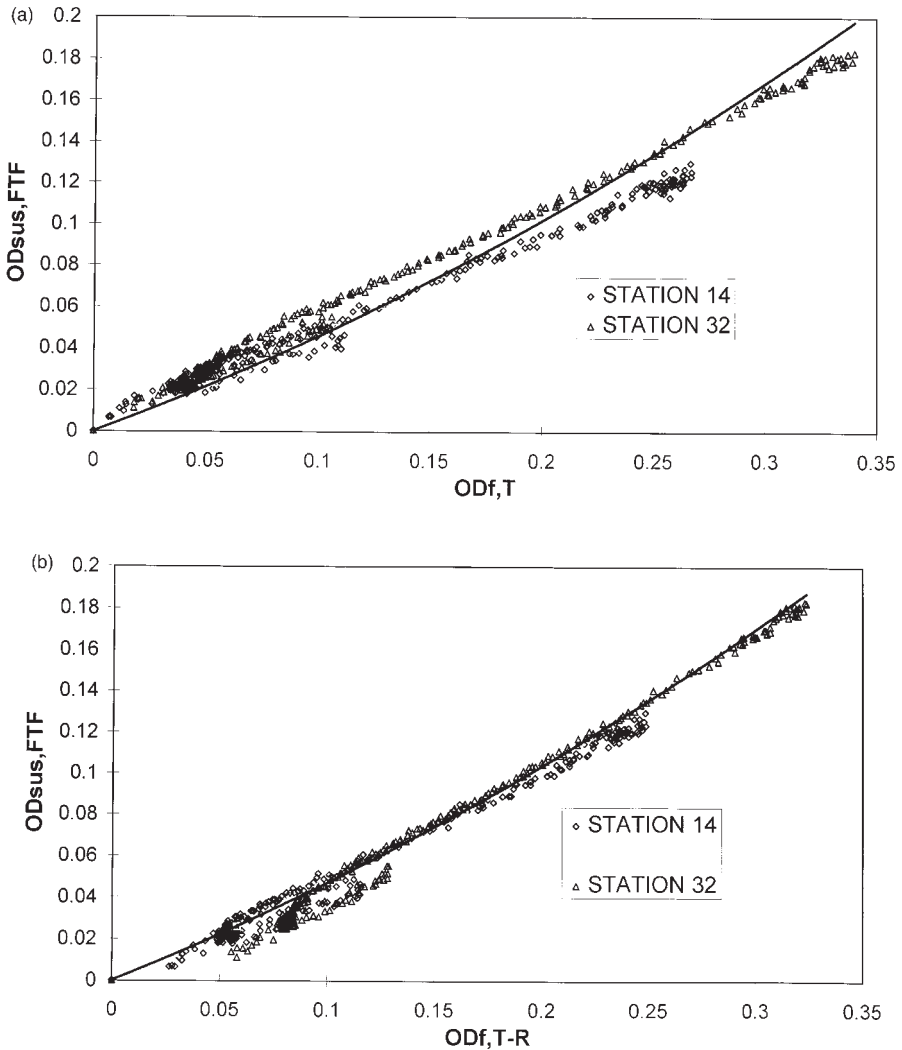


Fig. 2. Plot of the optical density of particles measured by the FTF method ($= OD_{sus,FTF}$) versus the optical density measured on the filter-retained particles by (A) the transmittance method ($= OD_{f,T}$) and (B) the transmittance-reflectance method ($= OD_{f,T-R}$), for stations 14 and 32. The $OD_{sus,FTF}$ values have been scaled to the geometrical pathlength corresponding to OD_f measurements. The solid lines are the curves of the OD_{sus} versus OD_f relationships, measured for *S. obliquus* [equations (1) and (2), respectively].

$y = k_1x + k_2x^2$ with k_1 and k_2 positive numerical constants. If the fit yielded a negative value for k_2 (which may occur when the curvature of the plot is very small and the measured optical density is low), the data were fitted with a linear form through the axis origin. The OD_{sus} versus OD_f curves obtained for the 29 analyzed

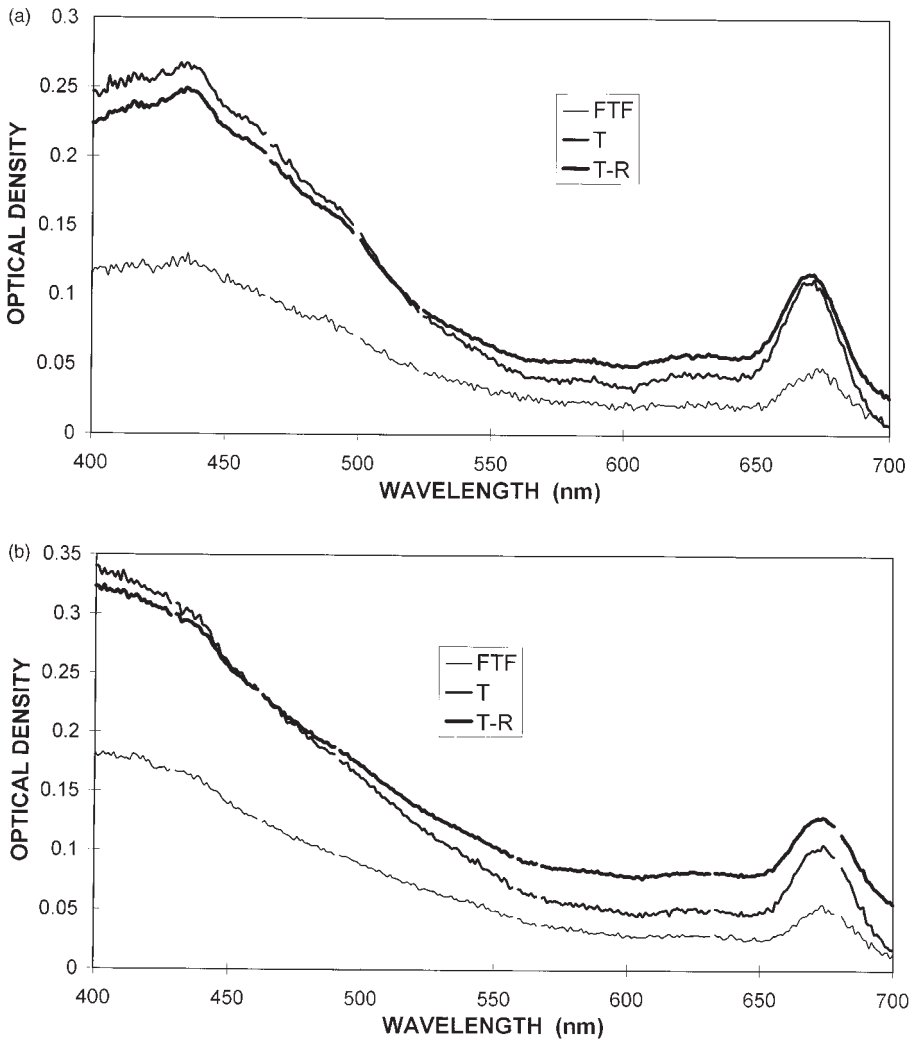


Fig. 3. Optical density spectra measured for stations 14 (**A**) and 32 (**B**) of Figure 1. Thin lines, $OD_{sus,FTF}$; medium lines, $OD_{f,T}$; thick lines, $OD_{f,T-R}$.

stations are grouped in Figure 4A (T method) and 4B (T-R method); each fitted curve is limited to the corresponding experimental range. The figure includes the OD_{sus} versus OD_f curves measured for *S.obliquus* [equations (1) and (2)], as thick lines.

Discussion and conclusion

Consideration of Figure 4A and B shows that: (i) the dispersion of the curves obtained by the T-R method is much lower than that of the OD_{sus} versus OD_f

curves obtained by the T method; (ii) the majority of the curves obtained by the T-R method are consistent with the curve measured for *S.obliquus*; (iii) the majority of the curves obtained by the T method lie well below the curve measured for *S.obliquus*. These observations were made in a coastal environment characterized by large variations in concentrations of mineral or detrital particles, as shown by the variability of the measured non-algal absorption, from 2 to 40% of total absorption at 440 nm [measurements performed after removing pigment absorption by the NaClO oxidation procedure (Tassan and Ferrari, 1995a)].

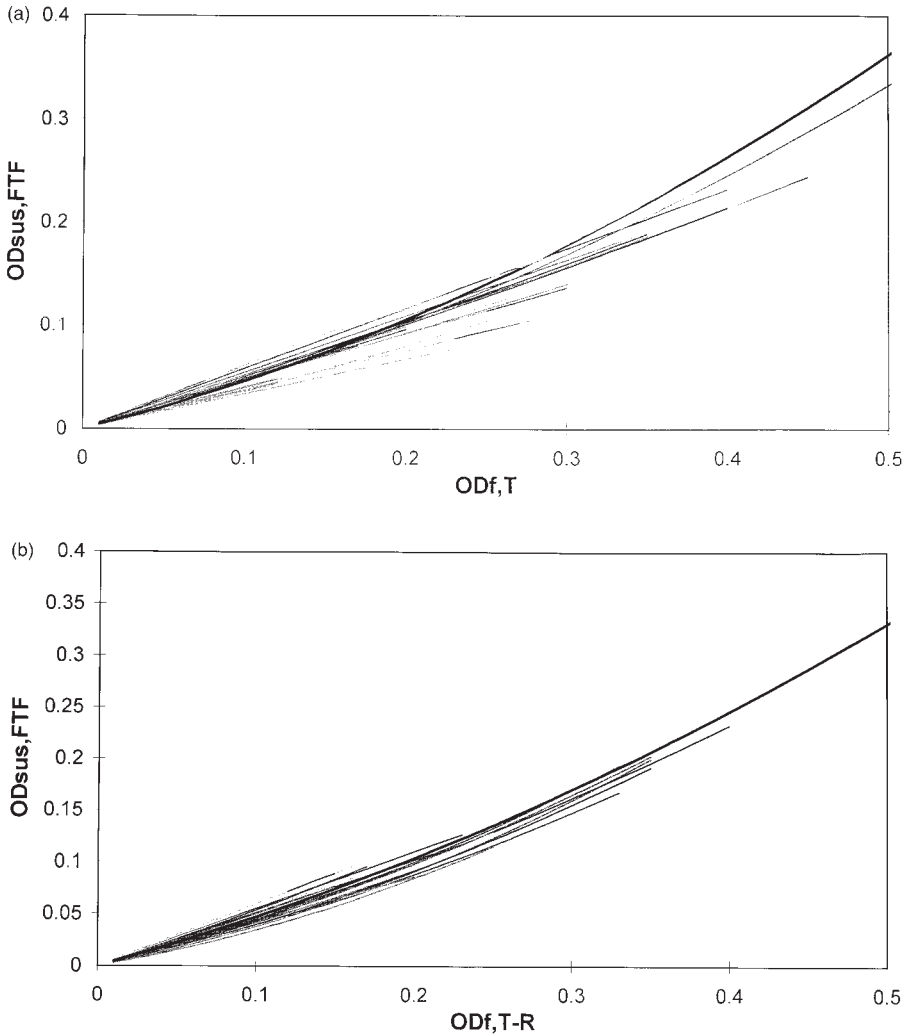


Fig. 4. $OD_{\text{sus,FTF}}$ versus OD_f curves fitted to the data of 29 stations of the Adriatic Sea *COASTIOOC* campaign, as obtained by (A) the T method and (B) the T-R method. The thick solid lines are the *S.obliquus* curves [equations (1) and (2), respectively].

The stability of the OD_{sus} versus OD_{f} relationship shown in Figure 4B also suggests that the modified FTF method is much less sensitive to backscattering errors than the GF/F filter technique. Although we do not have a theoretical justification for this lower sensitivity, this has been confirmed experimentally by comparing T and T-R measurements of particles on glass slides (K.Allali and S.Tassan, unpublished results).

In order to obtain a statistical estimate of the dispersion of the OD_{sus} versus OD_{f} curves obtained by the T-R method, the maximum and mid-range values of $OD_{\text{f,T-R}}$ measured for each analyzed station (roughly corresponding to the optical densities of the 440 and 675 nm chlorophyll *a* absorption peaks, respectively) were converted to $OD_{\text{sus,eq2}}$ using equation (2), and compared with the corresponding $OD_{\text{sus,fit}}$ values, as provided by the $OD_{\text{sus,FTF}}$ versus $OD_{\text{f,T-R}}$ fitted curve for the same station. Figure 5 shows the plots of $(OD_{\text{sus,eq2}} - OD_{\text{sus,fit}})$ versus station number for the maximum and mid-range optical density values. The $(OD_{\text{sus,eq2}} - OD_{\text{sus,fit}})$ mean value is +0.005 (SD 0.009) for the maximum OD values and +0.0026 (SD 0.0068) for the mid-range OD values. These results indicate that the use of equation (2) instead of the equation that fits the bulk of the collected experimental data causes on average an overestimate (i.e. +0.005 and +0.0026) of the suspension optical density. The computed SDs (i.e. 0.009 and 0.0068) are an estimate of the dispersion of the suspension optical density values caused by the use of equation (2) instead of the $OD_{\text{sus,FTF}}$ versus $OD_{\text{f,T-R}}$ relationship appropriate for each station.

The appreciation of these statistical data requires consideration of the errors (as SDs) of the FTF and T-R measurements. The $OD_{\text{sus,FTF}}$ error was assumed to equal the 0.005 error estimated for $OD_{\text{f,T-R}}$ (Tassan and Ferrari, 1998). By differentiating equation (2) and combining quadratically the $OD_{\text{f,T-R}}$ error with the errors of the numerical constants of the equation, the $OD_{\text{sus,T-R}}$ error was computed to vary from 0.002 to 0.008 as $OD_{\text{f,T-R}}$ increases in the range from 0.05 to 0.4. Adding quadratically this varying $OD_{\text{sus,T-R}}$ error to the fixed 0.005 error assumed for $OD_{\text{sus,FTF}}$ yielded a 0.005–0.0095 error for the difference $(OD_{\text{sus,FTF}} - OD_{\text{sus,T-R}})$. Such an error range is comparable with the range of the errors expressed by the mean values (+0.005 and +0.0026) and SDs (0.009 and 0.0068) previously computed for the difference $(OD_{\text{sus,eq2}} - OD_{\text{sus,fit}})$. This means that using equation (2) to convert to $OD_{\text{sus,FTF}}$ the $OD_{\text{f,T-R}}$ values measured for all considered Adriatic Sea stations, instead of converting the data of each station by the $OD_{\text{sus,FTF}}$ versus $OD_{\text{f,T-R}}$ relationship pertaining to the same station, does not cause a significant increase of the experimental error.

Since the T and T-R methods differ in the correction for light scattering by particulate material, the evidence presented in Figure 4 suggests that, in the northern basin of the Adriatic Sea, a considerable contribution to the variability of the measured OD_{sus} versus OD_{f} relationships is the light scattering error. The importance of this error source has already been demonstrated by a test performed on laboratory cultures of phytoplankton species with cell diameters in the 1–5 μm range and varying light-scattering properties (Tassan and Ferrari, 1998); the test did not show any evidence that the OD_{sus} versus OD_{f} relationship determined by the T-R method was dependent on particle size, while that

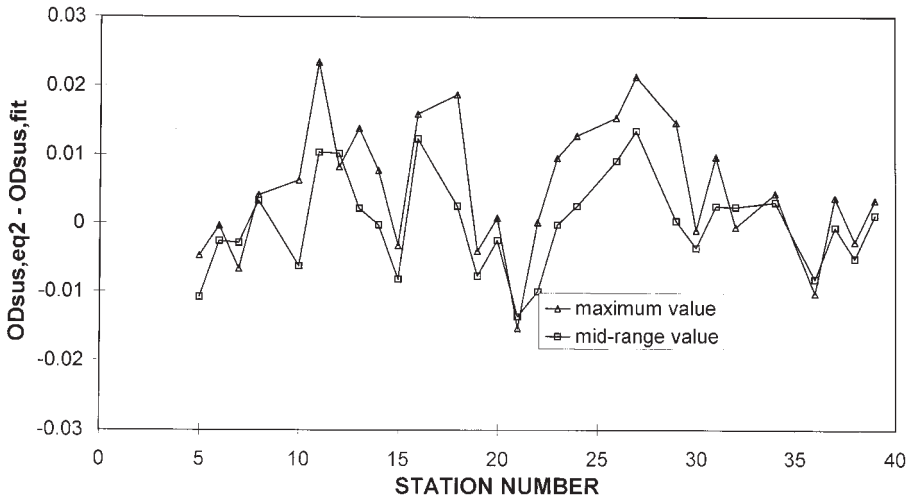


Fig. 5. Plot of ($OD_{\text{sus,eq2}} - OD_{\text{sus,fit}}$) versus station number, for the maximum and the mid-range optical density values. $OD_{\text{sus,fit}}$ is obtained from the $OD_{f,T-R}$ value using the OD_{sus} versus OD_f curve fitted for each station, whereas $OD_{\text{sus,eq2}}$ is obtained from the same $OD_{f,T-R}$ value using equation (2).

measured by the T method exhibited a dependence consistent with the results of Moore *et al.* (Moore *et al.*, 1995).

It can be concluded that in coastal waters with large and varying contents of highly scattering mineral particles, the OD_{sus} versus OD_f relationship obtained by the T-R method is likely to be more stable than that obtained by the T method. Thus, in these waters, the current practice of using a single expression for the β amplification factor would cause a smaller source of error if the measurement is carried out by the T-R method. For very accurate determinations of the particle absorption from measurements performed on filter-retained samples by the T and T-R methods, site-specific OD_{sus} versus OD_f relationships can be obtained by the experimental approach used in the present study.

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