

Improved determination of particulate absorption from combined filter pad and PSICAM measurements

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Abstract: Filter pad light absorption measurements are subject to two major sources of experimental uncertainty: the so-called pathlength amplification factor, β , and scattering offsets, o , for which previous null-correction approaches are limited by recent observations of non-zero absorption in the near infrared (NIR). A new filter pad absorption correction method is presented here which uses linear regression against point-source integrating cavity absorption meter (PSICAM) absorption data to simultaneously resolve both β and the scattering offset. The PSICAM has previously been shown to provide accurate absorption data, even in highly scattering waters. Comparisons of PSICAM and filter pad particulate absorption data reveal linear relationships that vary on a sample by sample basis. This regression approach provides significantly improved agreement with PSICAM data (3.2% RMS%E) than previously published filter pad absorption corrections. Results show that direct transmittance (T-method) filter pad absorption measurements perform effectively at the same level as more complex geometrical configurations based on integrating cavity measurements (IS-method and QFT-ICAM) because the linear regression correction compensates for the sensitivity to scattering errors in the T-method. This approach produces accurate filter pad particulate absorption data for wavelengths in the blue/UV and in the NIR where sensitivity issues with PSICAM measurements limit performance. The combination of the filter pad absorption and PSICAM is therefore recommended for generating full spectral, best quality particulate absorption data as it enables correction of multiple errors sources across both measurements.

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1. Introduction

The light absorption and scattering properties of marine particles are important for the parameterisation of radiative transfer models [1] and the interpretation of ocean colour remote sensing signals [2, 3]. Spectral absorption data can be used to assess the composition of inorganic and organic material [4]. Light absorption by phytoplankton, in particular, is of interest in many biological studies as it can yield information on pigment composition and concentration [5, 6] and the size structure of phytoplankton communities [7] which can be used to populate models of primary production and photosynthesis [8].

The most common method to determine the spectral absorption of light by particles, a_p , is to collect the particulate matter on a glass fibre filter and measure its absorption in a spectrophotometer. This so-called filter pad technique or quantitative filter technique (QFT) [9] benefits from having a controllable sensitivity because signal strength can be modified by the amount of material concentrated on the filter paper. The filter pad technique therefore has sufficient sensitivity even in oligotrophic waters with very low suspended particle concentrations. The filter pad technique, additionally, allows the partitioning of particulate absorption into absorption associated with phytoplankton pigments and non-algal particulate matter, by removing light absorbing pigments from the filter paper with either an organic solvent [10] or an oxidising agent [11]. Particulate spectral absorption coefficients can also be partitioned through numerical decomposition [12, 13].

Alternatively, a_p can be determined from measurements of particles in suspension after subtraction of absorption by the dissolved components. Cuvette measurements in a standard spectrophotometer, however, suffer from scattering losses that can potentially cause systematic overestimation of absorption coefficients even for optically thin suspensions.

Recently developed methods to improve the measurement of absorption by suspensions are based on integrating sphere approaches [14]. One example is measurement with a point-source integrating cavity absorption meter (PSICAM), which has been shown to be virtually insensitive to the presence of scattering by particulate material and to have a reasonably high sensitivity (though some limitations have been identified – see Section 2.4) [15]. This makes the PSICAM well-suited for the determination of absorption by natural water samples. The operation of a PSICAM, however, is laborious and, to date, only very few studies using PSICAM absorption data have been published. For the determination of particulate absorption coefficients, current limitations of the PSICAM are (1) inability to separate algal and non-algal particulate absorption, and (2) lower sensitivity compared to the filter pad technique. Filter pad absorption measurements are therefore expected to be widely used for the determination of particulate absorption coefficients in the foreseeable future [16, 17].

Great effort has gone into the identification and quantification of measurement uncertainties and subsequent improvement of the filter pad absorption methodology. Error sources include wetness of the filter, different filter types [18], filter-to-filter variation even for filters of the same type [19], storage and freezing of filters [20, 21], sample loading [22], improper filtration, and temperature and salinity effects. The major sources of uncertainty, however, are the unknown extent of scattering offsets and limitations in the correction for pathlength amplification [13, 19, 22]. Light loss due to sample scattering can result in a systematic error by introducing a positive offset of unknown magnitude to measured absorption data. In practise, negative offsets due to imperfections in the experimental procedure can also be observed. This is problematic in both filter pad absorption and cuvette measurements. Scattering effects are commonly corrected by applying a null-point correction (subtracting the signal measured at wavelengths > 750 nm from the rest of the spectrum) assuming negligible NIR absorption. This assumption, however, does not hold in coastal or mineral-rich waters [23-25] and can lead to a systematic underestimation of particulate absorption coefficients across the entire spectrum.

Pathlength amplification occurs when the pathlength of a photon travelling through the sample filter is increased due to multiple scattering events within the filter/sample matrix. Pathlength amplification will result in apparent increased sample absorption and data have to be corrected to obtain quantitative absorption coefficients. Measurements are commonly corrected by applying a predetermined pathlength amplification factor, β , which is defined as the ratio of optical to geometrical pathlength. Accurate determination of β is crucial to convert the optical density, OD , of the sample on the filter as measured in a spectrophotometer into quantitative particulate absorption coefficients using

$$a_p(\lambda) = \frac{2.303OD_f(\lambda)A}{V\beta} \quad (1)$$

where a_p is the particulate absorption coefficient (m^{-1}) at a given wavelength (λ , nm), OD_f is the optical density of the sample on the filter (dimensionless), A is the filter clearance area (m^2), and V is the volume of sample filtered (m^3). The factor, β , has typically been derived from experiments with algal cultures and calculated as the ratio between the optical density of a filter, OD_f , and the optical density of the same sample in a dilute suspension, OD_s [13], with a functional relationship established that can later be applied to field samples.

An alternative, widely used approach to correct for pathlength amplification uses a predetermined function, $OD_s=f(OD_f)$, to directly convert OD_f into OD_s . a_p is then calculated using

$$a_p(\lambda) = \frac{2.303OD_s(\lambda)A}{V} \quad (2)$$

This approach was first proposed by Mitchell [9] who identified a second order

polynomial as best descriptor for the relationship. Many studies have since adapted this approach and observed variability in the pathlength amplification correction dependent on phytoplankton species, cell size and shape, OD or wavelength [9, 26-28]. The function $OD_s=f(OD_f)$ indirectly accounts for the β -factor.

In order to determine an accurate correction for pathlength amplification, it is necessary to minimise uncertainties in the determination of OD_f and OD_s . Over the past few decades, several geometric configurations for the measurements of OD_f and OD_s have been proposed and tested. Recent literature suggests four different set-ups currently being used to determine OD_f : the transmittance method (T-method), the transmittance-reflectance method (T-R-method) and two different set-ups measuring filters inside an integrating sphere (IS-method and QFT-ICAM). The IS-method uses scanning monochromatic illumination of a dual-beam spectrophotometer equipped with an integrating cavity whereas the QFT-ICAM set-up includes a broadband white light source [29]. Trüper and Yentsch [30] first suggested measuring the transmittance through a wet glass fibre filter relative to an empty, wet reference filter. The T-method is the simplest and fastest approach and has been used as a standard method for decades [see NASA protocols; 31]. It has been suggested, however, that it suffers from limited control over measurement parameters, such as scattering errors and filter-to-filter variation and a high sensitivity to changing wetness of the filter [e.g. 18, 22, 26, 27]. As glass fibre filters effectively act as diffusors, measurements are potentially susceptible to large scattering errors. Scattering errors can be reduced by placing the filters at the entrance of an integrating sphere or close to the detector window.

The transmittance-reflectance method proposed by Tassan and Ferrari [32, 33] was designed to reduce errors when minerogenic material changes the filter backscattering and to help overcome some geometric limitations associated with the T-method. It can partially correct for measurement errors due to backscattering losses and filter-to-filter differences. In theory, the T-R method does not require null-point correction but it might be applied in practice to reduce uncertainties originating from imperfections in the measurement set-up. Despite its apparent benefits over the T-method, the T-R-method has not been widely used in the past mainly because of its complex and laborious measurement protocol and the requirement for additional experimental apparatus (an integrating sphere).

Measuring the absorbance of a sample on a filter inside an integrating sphere (IS-method and QFT-ICAM) benefits from a significantly reduced scattering error, high sensitivity and improved signal-to-noise ratio [16, 17, 34] but has only been used in a limited number of studies [e.g. 35]. Measurements made with a QFT-ICAM or the IS-method do not require null-correction.

Röttgers and Gehnke [16] showed that average β -factors vary systematically between geometric configurations. They examined the relationship for three different configurations (T, T-R and IS-method) and showed significant differences, with median values for IS being two times higher than for T-R. This means that there is no universal β -factor and values determined for one measurement geometry cannot be simply ported onto another. All other factors being equal (e.g. availability of relevant equipment), the most favourable method is therefore the one with the smallest associated uncertainty in the determination of β and a quantifiable scattering correction.

Of course, determination of β requires an associated measurement of OD_s . Accurate determination of OD_s using a cuvette inside a spectrophotometer is extremely difficult and can be significantly affected by scattering losses. Scattering errors can be reduced, but not completely eliminated, when placing the cuvette inside an integrating sphere [36]. There remains, however, a concern about potential pathlength amplification effects for transmitted and scattered photons subsequently re-entering the sample. At this time, the most effective measurement set-up uses a PSICAM to determine the absorption of a sample, effectively without any scattering errors, and provides a standard against which filter pad absorption measurements can be validated. It should be noted that PSICAM measurements do not return

OD_s but rather a_p directly (after subtraction of CDOM absorption). Empirical relationships for $a_p=f(OD_f)$ can be derived, similar to $OD_s=f(OD_f)$, and used to directly convert OD_f into particulate absorption coefficients [37].

Accuracy of the filter pad method as a quantitative technique has remained controversial, at least partly because of the variety of protocols in use. As a result of improvements in instrumentation and methodology, uncertainties in the determination of particulate absorption coefficients were the subject of a number of recent publications. Stramski et al. [17] derived individual functional relationship between OD_s and OD_f for three different geometrical configurations (T-method, T-R method and IS-method) using samples with a variety of optically relevant particle characteristics. They recommended the use of a power law function for conversion of OD_f into OD_s for future and historic datasets. The study relied on OD_s measurements from cuvettes placed inside an integrating sphere. Neeley et al. [38] performed a multi-analytical approach to get robust estimates of uncertainties in a_p for selected ocean colour remote sensing wavelengths. They incorporated different experimental and analytical methods to derive a_p and found a large variability between the different approaches for different water types.

PSICAM data with minimal scattering error and baseline artefacts enables investigation of the impact of different error sources in filter pad absorption measurements and can help to establish a protocol for the correction for pathlength amplification and scattering offset. To date, three studies have used PSICAM data to assess the performance of traditional pathlength amplification corrections. All of them found that the relationships between particulate absorption coefficients and OD_f are well described using a linear function for individual samples using the T- method [37] and the IS-method [16, 29]. This suggests that previous significantly non-linear relationships might have been affected by errors in the determination of OD_s due to scattering errors in cuvette measurements. McKee et al. [37] established a linear regression scheme to correct filter pad absorption measurements (T-method). The slope of the linear function effectively represents a wavelength-independent, OD-independent β -factor. The intercept enables correction for scattering offsets without assuming zero NIR absorption.

The aim of this work is to investigate uncertainties in filter pad absorption techniques in comparison with PSICAM data. Three datasets will be used to quantify the variability in β -factors determined using a linear regression approach including samples with a variety of optical properties. This linear method will be compared to historic approaches to correct pathlength amplification and scattering effects in quantitative filter pad absorption measurements. This work will predominantly focus on the T-method as it is still the most commonly used technique and draw comparisons with more involved methods, such as IS and QFT-ICAM. The overall goal is to establish an optimised methodology for experimentally determining a_p drawing on the strengths of both PSICAM and filter pad absorption techniques.

2. Methods

2.1 Datasets

Variability in corrected filter pad absorption measurements was assessed using three datasets: (1) algal cultures (AC), (2) data from the Ligurian Sea (BP09) and (3) data from UK coastal waters (UKCW). All datasets contained at least one PSICAM measurement and a filter pad measurement (T-method) for each sample.

AC data were gathered during a series of laboratory experiments at the Scottish Association for Marine Science (SAMS) in June 2014. The dataset contains 14 samples which were dilutions from cultures of 8 different algal species (Table 1). The BP09 dataset contains 62 samples collected in coastal and oceanic waters in the Ligurian Sea in 2009. A detailed description of the sampling location, methods and data can be found in [37]. For 51 samples collected on the UKCW cruise in 2015, a more extensive dataset is available, including 3 different filter pad measurement approaches and 2 sets of independently measured PSICAM

absorption spectra. Filter pad data measured with the T-method plus one set of PSICAM data were collected by the University of Strathclyde ('Strath'). A second set of PSICAM measurements and 2 additional filter pad absorption were made by the Helmholtz-Zentrum Geesthacht ('HZG'). The latter were based on the integrating cavity approach: (1) using an integrating sphere with a spectrophotometer (IS) and (2) using the recently developed QFT-ICAM. Details on methods and data were recently published in [40].

Table 1. Summary of cultured algal species, type, size and location of isolation.

species (reference)	type	size	isolation
<i>Alexandrium minutum</i> (CCAP, 1119/50)	dinoflagellate	30 µm	2008, Scapa, Orkney (58° 55'N 003° 06' W)
<i>Alexandrium temarense</i> (CCAP, 1119/28)	dinoflagellate	50 µm	2008, Scapa, Orkney (58° 55'N 003° 06' W)
<i>Heterocapsa spp.</i> (CCAP, 1125/4)	dinoflagellate	8 µm	2011, Argyllshire
<i>Karenia mikimotoi</i> (SCCAP, K-0260)	dinoflagellate	34 µm	1977, Oslofjorden Norway
<i>Microcystis aeruginosa</i> (CCAP, 1450/2)	cyanobacteria	5 µm	1954, Little Rideau Lake, Ontario, Canada
<i>Pseudonitzschia seriata</i> (CCAP, 1061/42)	diatom	100 µm	2012, Loch Creran, Argyll
<i>Scripsiella sp.</i> (CCAP, 1134/8)	dinoflagellate	25 µm	2003, LY5 sampling site (SAMS)
<i>Skeletonema marinoi</i> (CCAP, 1077/5)	diatom	20 µm	1956, Long Island Sound, Milford Harbour, Connecticut
<i>Synechococcus sp.</i> (CCAP, 1479/9)	cyanobacteria	1 µm	1989, South Basin, Windermere, Cumbria, England, UK

2.2 PSICAM absorption measurements

The absorption by non-water constituents in an untreated sample (all dissolved and suspended material) was determined in triplicate against purified water (Milli-Q; water purification system: Simplicity UV, Millipore) as a reference (for details on calibration and measurement protocol see [39, 40]. The temperature and salinity of each sample were recorded and absorption spectra were corrected for temperature and salinity effects using instrument specific correction factors [40]. For separation of suspended and dissolved material, each sample was filtered through a 0.22 µm pore size membrane filter (GSWP, Merck Millipore Ltd., Ireland) using a low vacuum <0.2 bar (to avoid cell breakage and loss of pigments) and the absorption by the filtrate, i.e. that of chromophoric organic matter (CDOM), was measured following the same protocol. The absorption by particulate matter was calculated by subtracting the CDOM absorption from the total absorption coefficient.

Data from two independent PSICAM measurements were available for samples collected on the UKCW cruise which were used to test the overall performance of the method. To avoid artefacts due to differences in the calibration solution, 5L of the calibration solution, Nigrosine, were prepared every morning and two fresh sub-samples were used for each calibration (3-5 times a day) of the two different PSICAMs. The required corresponding measurements of Nigrosine absorption spectra were also made independently by the two groups, using two long pathlength systems (LWCC, World Precision Instruments Inc.). Particulate absorption spectra from natural samples measured using both PSICAMs were found to agree within 7.3% RMedianS%E in the visible spectrum (Fig. 1). The relative deviation between the two instruments increased towards the NIR (typically within 30%, maximum of 95%) where absorption coefficients were generally low. Separate comparison of CDOM absorption coefficients against data measured with the two liquid waveguide systems showed agreement within 15% (data not shown). This level of consistency between two independent datasets is a very encouraging endorsement of the performance of the PSICAM

approach.

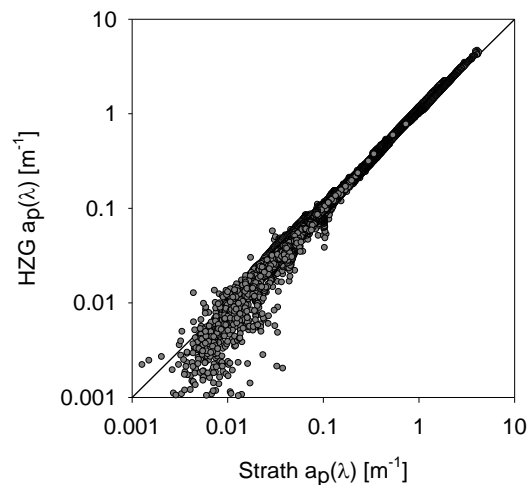


Fig. 1. Comparison of particulate absorption spectra (400-700 nm) of all samples collected on the UKCW cruise using two independent PSICAMs – one operated by the Helmholtz-Zentrum Geesthacht (HZG) and one by the University of Strathclyde (Strath).

2.3 Filter pad absorption measurements

The OD of particulate matter collected on a filter paper was measured in a dual-beam spectrophotometer (UV2501-PC, Shimadzu Corp., Japan) using the T-method for all three datasets. The spectrophotometer was allowed to warm up for an hour before the first measurement was taken. Two reference filters were prepared by running 300 mL of 0.2 μm filtered seawater through 47 mm GF/F filter paper (Whatman) under a low vacuum. A baseline was recorded without filters in place and a reference measurement was taken with two reference filters attached to the alcohol-cleaned glass windows, placed directly against the exit ports inside the spectrophotometer. Sample filters were prepared by filtering a specific volume (0.05 L to 5 L) through a 47 mm GF/F filter [$<0.5 \mu\text{m}$; 41] using a low vacuum. The volume filtered was adjusted for each sample so that the maximum OD measured was close to, but did not exceed, 0.4 OD. Funnel and filter paper were kept covered at all times to avoid contamination and filters were measured directly after filtration. Filters were hydrated with drops of filtered seawater in between measurements when necessary. The OD of each filter was determined in a single scan to minimise artefacts due to heating or bleaching of the filter inside the spectrophotometer (alteration of the filter absorption by the measurement itself were observed for multiple scans). Each filter was bleached by adding a few drops of dilute sodium hypochlorite to the filter paper, exposing it until pigment loss was observed. The bleach was removed by rinsing the filter with approx. 300 mL of filtered seawater and the OD spectrum of the bleached filter determined against the Milli-Q reference filter. A reference measurement was measured before and after each set of sample filter/bleached filter to monitor drifts in the baseline. Observed shifts were usually smaller than the measurement error.

Additional filter pad absorption data measured using the IS-method and the QFT-ICAM were available from the UKCW cruise. Measurements were performed following the procedure described in [16]. All data collected by HZG has been published together with a detailed description of set-up and measurement protocols for the new QFT-ICAM by Röttgers et al. [29].

Table 2. Summary of literature pathlength amplification as functional relationships $OD_s=f(OD_f)$ and scattering offset corrections for the T-method.

reference	pathlength amplification correction	null-correction	samples
Stramski et al. (2015) [17]	$OD_s = 0.679 OD_f^{1.2804}$	at 750 nm	'artificial samples'
Stramska et al. (2003) [42]	$OD_s = 0.33 OD_f + 0.983 OD_f^2$	at 750 nm	field samples
Finkel and Irwin (2001) [28]	$OD_s = 0.446 OD_f + 0.122 OD_f^2$	-	field samples, cultures
Roesler (1998) [19]	$OD_s = 1/2 OD_f$	wavelength dependent correction	
Nelson et al. (1998) [43]	species specific	at 750 nm	cultures
Allali et al. (1997) [44]	$OD_s = 0.264 OD_f + 0.322 OD_f^2$	at 750 nm	field samples
Arbones et al. (1996) [27]	$OD_s = 0.38 OD_f + 0.42 OD_f^2$	at 750 nm	field samples, cultures
Tassan and Ferrari (1995) [32]	$OD_s = 0.406 OD_f + 0.519 OD_f^2$	at 750 nm	cultures
Moore et al. (1995) [45]	species specific		cultures
Cleveland and Weidemann (1993) [26]	$OD_s = 0.378 OD_f + 0.523 OD_f^2$	at 750 nm	cultures
Hoepffner and Sathyendranath (1992) [46]	$OD_s = 0.31 OD_f + 0.57 OD_f^2$	-	cultures
Bricaud and Stramski (1990) [13]	$OD_s = 1/1.63 OD_f (\lambda)^{-1.22}$	empirical relationship	field samples, cultures
Mitchell (1990) [9]	$OD_s = 0.392 OD_f + 0.655 OD_f^2$	at 750 nm	cultures

2.4 Alternative approaches to correction of filter pad measurements

Numerous studies have investigated the performance of quantitative filter pad absorption measurements and acknowledge the susceptibility to errors in the correction for pathlength amplification and scattering offsets. Various factors have been identified to affect the magnitude of pathlength amplification (see above) and proposed correction methods vary strongly. Some studies suggest a dependency of β on OD_f [22, 34]. Bricaud and Stramski [13] described this relationship using a power function. Mitchell [9] proposed use of a second order polynomial to describe the relationship between OD_f and OD_s . This approach was adopted in many subsequent studies in which alternative coefficients for this model were derived. Stramski et al. [17] recently found that a power law function is the best descriptor for the relationship between OD_f and OD_s , based on extensive lab work using samples with a wide range of different optical properties.

Most investigations used algal cultures to determine a function for the correction of pathlength amplification which can then be applied to field samples [19, 27, 28, 32]. Some studies suggested that a single correction for pathlength amplification might be sufficient if its determination is based on a large number of samples with different particle characteristics [17, 19, 26]. Others, however, point towards a potential dependency on particle characteristics or phytoplankton species. The selection of an inappropriate correction for pathlength amplification could therefore result in systematic errors when applied to field samples. So far, no consensus on an appropriate method has been achieved. An overview over the different approaches used to correct filter pad absorption measurements is given in Table 2.

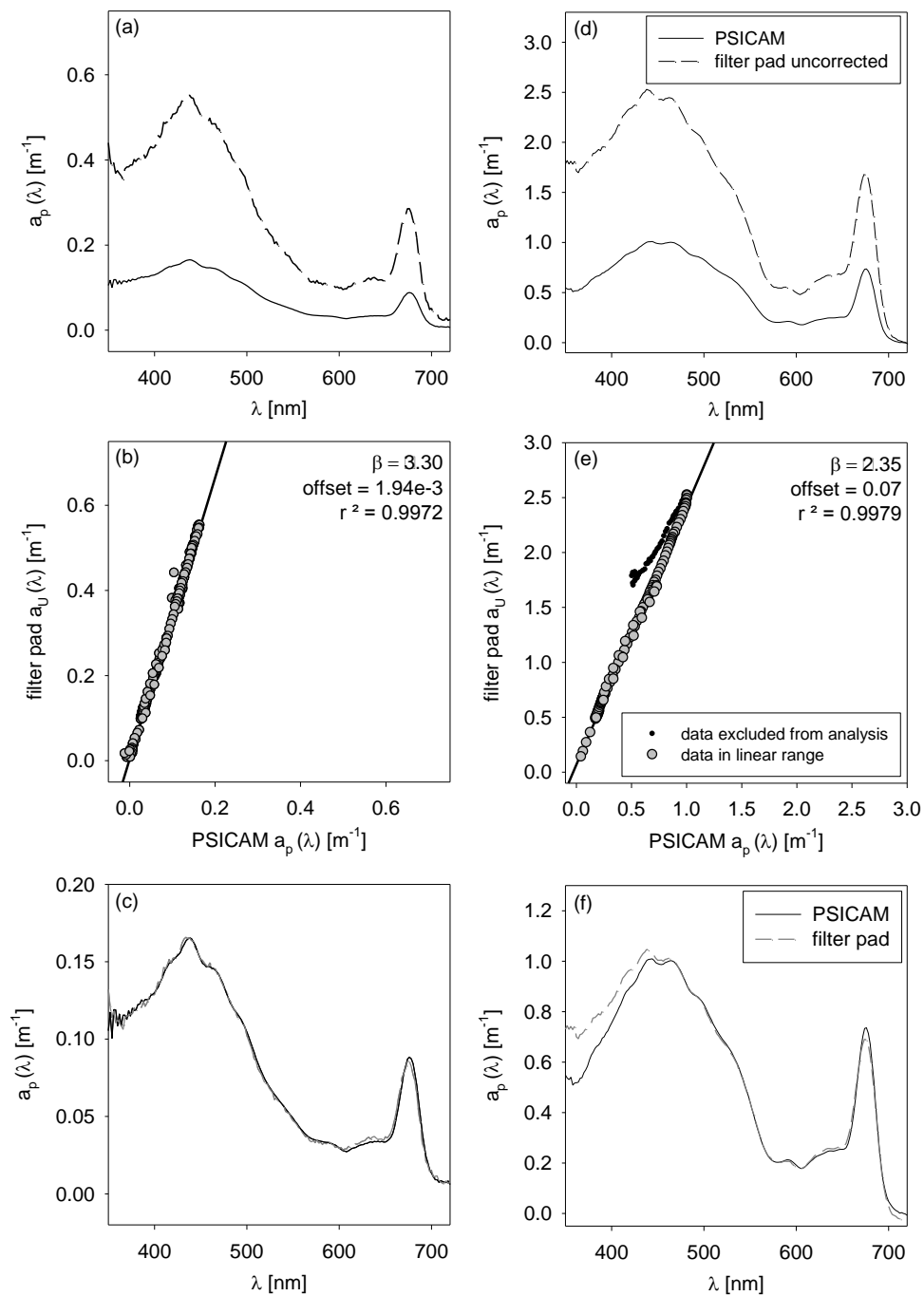


Fig. 2. (a) and (d) PSICAM data, a_p , and uncorrected ($\beta = 1$) filter pad data, a_u , of two different samples. (b) and (e) linear regression, coefficients and R^2 for the same samples. Data ranges for the linear regression were limited to 400 – 700 nm for (b) and 440 – 700 nm for (e). (c) and (f) show final particulate absorption spectra measured with PSICAM and T-method. Filter pad data have been offset corrected and re-scaled using Eq. (3) and the coefficients derived in (b) and (e) respectively.

Only a few studies investigating pathlength amplification in filter pad absorption measurements have had access to PSICAM data for validation. Röttgers and Gehnke [16] studied the variability in β for filter pad measurements using the T, T-R and IS method. For low OD (<0.4 for the T-method, <0.1 for the integrating cavity methods), they observed a linear relationship between OD_f and a_p for all configurations which showed no significant dependency on wavelength or OD. Their results suggest that availability of PSICAM data is highly advantageous as it enables performance of sample-by-sample correction and cross-validation.

McKee et al. [37] introduced a regression based approach to correct filter pad absorption measurements made for the determination of chlorophyll specific absorption coefficients using the T-method. Their analysis also showed linear relationships between PSICAM absorption and uncorrected filter pad absorption coefficients. Fig. 2 shows the different stages of the linear regression filter pad absorption correction. In a first step, the uncorrected filter pad absorption coefficient, a_u , is calculated using Eq. (1) and $\beta = 1.0$ (Figs. 2(a) and 2(d)). a_u is plotted against corresponding PSICAM particulate absorption coefficients (Figs. 2(b) and 2(e)) and a linear function is fitted through the data, returning a slope, i.e. the pathlength amplification correction factor, β , and an intercept, o , which can be used to correct for scattering offsets without assuming zero NIR absorption. Regressions were limited to the linear range of the data (deviations from linearity as shown in Figure 2(e) are discussed in the next section). a_u can then be converted into quantitative filter pad absorption coefficients, a_p , using Eq. (3) (Figs. 2(c) and 2(f)).

$$a_p(\lambda) = \frac{a_u(\lambda) - o}{\beta} \quad (3)$$

Röttgers et al. [29] recently introduced a field instrument to determine the OD of a sample collected on a filter pad, the QFT-ICAM. They analysed the performance of this new instrument in comparison to the IS-method used in [16] and estimated an average β -factor for both methods. They found comparable mean β values for the different techniques but observed much lower variability in β for the determinations with the QFT-ICAM.

A common feature of these recent studies is apparent sample-by-sample dependency in β and a linear relationship between a_p and a_u for low OD_f . Results suggest that the OD dependency of β that was previously observed might be due to insufficient accuracy in measurements of OD_s due to scattering and/or pathlength amplification effects for cuvette based measurements. The comparison with PSICAM data enables the correction of measurements on a sample-by-sample basis for both β -factor and scattering artefacts.

2.5 Limitations of PSICAM

PSICAM measurements outside the visible spectrum have proven to be challenging due to very low intensity levels inside the cavity with artefacts regularly observed in both the UV and NIR. Fig. 2 shows that, particularly in the blue/UV, the current set-up using a Tungsten lamp as a broadband light source reaches its limits. Observed underestimations at blue/UV wavelengths are due to a combination of low lamp output, lower reflectivity of the cavity material, low sensitivity of the photo-diode detector at shorter wavelengths and high sample absorption. These in turn lead to a potentially higher sensitivity to internal detector stray light issues or baseline drifts. As this effect can occur in both total absorption and CDOM absorption determinations, it can result in large uncertainties in the blue/UV spectral region when propagated into final particulate absorption coefficients. In the absence of additional measurements, it is very difficult to determine the exact wavelength at which absorption coefficients are affected by this systematic error as it changes with constituent concentration and measurement configurations. As filter pad absorption is measured in a scanning, monochromatic dual beam spectrometer and gain setting can be adjusted with wavelength,

measurements are less susceptible to issues due to low intensity levels in the blue/UV. Fig. 2 shows data for two samples, only one of which exhibits PSICAM underestimation in the UV. Plotting PSICAM and uncorrected filter pad absorption (Figs. 2(b) and 2(e)), there is a clear point of deviation in one of the plots (Fig. 2(e)) where the effect of PSICAM underestimation becomes obvious. The linear regression slope and offset is generated using only the undeviating parts of the PSICAM data, but can be applied to the entire filter pad spectrum. The approach presented here can therefore help extend the range of accurate particulate absorption coefficients into the UV (Figs. 2(c) and 2(f)) and at the same time provide a quality control mechanism for PSICAM measurements.

3. Results

3.1 Differences in β -factors between geometric configurations

Using the linear regression approach, distributions of β -factors were derived for three different geometrical configurations (T-method, IS-method and QFT-ICAM), used during the UKCW cruise in 2015. The coefficient of determination against PSICAM data was > 0.92 for all samples. Observed mean β values varied strongly between the different methods and were over 60% larger for the integrating sphere methods with 4.5 for the IS-method and 3.9 for the QFT-ICAM compared to 2.5 for the T-method (Table 3). Mean β -factors vary only very slightly from the values (4.56 and 4.06 for IS-method and QFT-ICAM, respectively) presented in [29] because here the HZG filter pad data is compared against ‘Strath’ rather than ‘HZG’ PSICAM absorption data. Measurements made inside integrating spheres tend to amplify the pathlength more strongly, and hence result in larger β , than the T-method. The apparent variability in β (95% PI, Table 3) was similar across all geometries, which suggests that the integrating cavity methods might not have a significant advantage over the T-configuration.

Table 3. Mean and 95% prediction intervals for β -distributions derived for three different geometrical configurations used during the UKCW cruise in 2015.

Method	Median	95% prediction intervals
T-Method	2.5	± 1.3
QFT-ICAM	3.9	± 1.0
IS-method	4.5	± 1.7

3.2 Variability in β within the T-method

Across the three different datasets, median β values derived for the T-method ranged from 2.2 for the AC dataset to 3.2 for the BP09 cruise with 95% prediction intervals (PI) of ± 1.0 to ± 1.7 , respectively (Table 4). The mean value determined for measurements made with the T-method on the UKCW cruise was 2.5 ± 1.3 (Fig. 3). Filter pad absorption data generally underestimated PSICAM absorption in the NIR which results in small negative intercepts (positive offset correction) in the linear regression. 69% of all intercepts, o , were within $\pm 0.025 \text{ m}^{-1}$. Largest intercepts ($< -0.2 \text{ m}^{-1}$) were observed for samples with high NIR absorption, e.g. in the Bristol Channel or for bottom water samples.

Table 4. Mean and 95% prediction intervals for β -distributions derived for three different datasets and measurements with the T-method.

Dataset	Median	95% prediction intervals
Algal cultures	2.2	± 1.0
BP09	3.2	± 1.7
UKCW	2.5	± 1.3

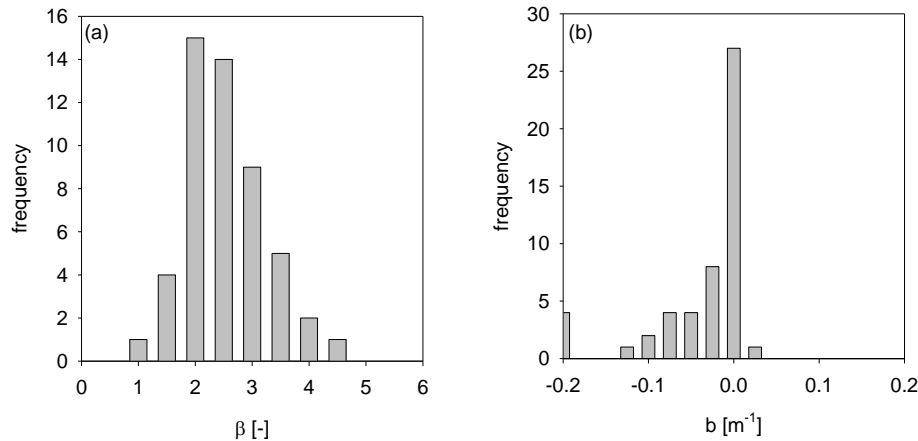


Fig. 3. Distributions of (a) β -factors (regression slopes) and (b) scattering offsets (o , regression intercepts) determined for filter pad absorption measurements made using the T-method on the UKCW cruise.

3.3 The effects of filter-to-filter variation and natural variability of the sample

A small experiment was conducted to investigate the magnitude of differences between β -factors determined for a single sample subsampled onto multiple filter papers. The aim was to assess if the variability within measurements made with the same configuration (Table 4) can potentially be explained by natural variability or variation between individual filter papers. Two 5L samples, one natural sample collected from a stream in the Scottish Highlands and one from a diluted culture (*D. maritima*), were divided into five 1L sub-samples and the particulate absorption was measured with the PSICAM and T-method filter pad absorption technique. For the natural sample, high CDOM concentration, $a_{CDOM}(440\text{ nm}) = 0.95\text{ m}^{-1}$, resulted in low PSICAM signal levels in the blue, and the linear range was limited to data from 480 – 700 nm for the natural sub-samples in this experiment.

Fig. 4 shows the regression plots and determined β -factors for the different subsamples. Observed mean β values were (by chance) similar, approx. 2.75, for both the natural sample and the algal culture sample. The variability in β of ± 0.25 observed here, which is assumed to be due to differences between filter pads, does not fully explain the overall variability of $> \pm 1.0$ in β in the T-method for natural sample datasets. This suggests that variability in β is due to both filter pads and some aspect of sample variability acting in combination.

During the AC experiments, samples from 4 cultures were measured 2 - 3 times within a 2 week period. β -factors determined for samples of the same species varied strongly and showed a tendency to increase over time (Fig. 5), suggesting that stable species-specific β values are not easily reproduced. Potential explanation for the observed tendency in β to increase could be increasing concentrations of bacteria and detrital material due to aging of the cultures which might affect the packaging of cells on the filter paper. Results, however, remain inconclusive due to the limited amount of data available.

3.4 Impact of alternative correction approaches

The performance of different correction methods for filter pad absorption measurements with the T-method was tested on data collected on the UKCW cruise in 2015. Results show excellent agreement between measurements corrected with the linear regression approach and a_p measured with a PSICAM (Fig. 6(a), Table 5). The corresponding root mean square percentage error, RMS%E, of 3.2% was calculated using Eq. (4). This value, however, masks

remaining large individual errors of up to >100% for particulate absorption values < 0.5 m⁻¹. Any deviation from the sample-by-sample approach, such as applying an average slope (Fig. 6(b)) or a null-correction (Fig. 6(c)), led to larger differences greater than 19.6%, between the two measurements.

$$RMS\% E = \sqrt{\frac{1}{n} \sum_1^n \left(\frac{x_{model} - x_{meas}}{x_{meas}} \times 100 \right)^2} \quad (4)$$

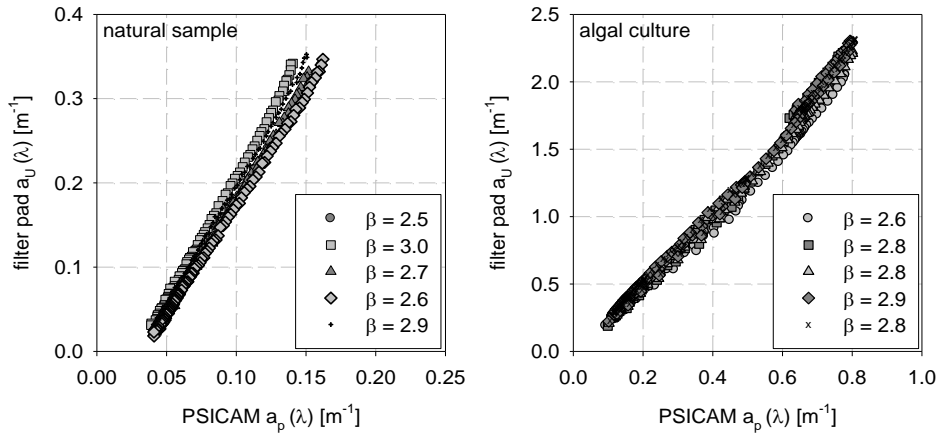


Fig. 4. Slopes of linear regression applied to theoretical filter pad absorption, a_u , (calculated using Eq. (1) and $\beta = 1.0$) vs. particulate absorption, a_p , measured in a PSICAM for 5 subsamples of the same (a) natural sample and (b) sample of *D. maritima*. Data in (a) is limited to the linear range from 480 – 700 nm.

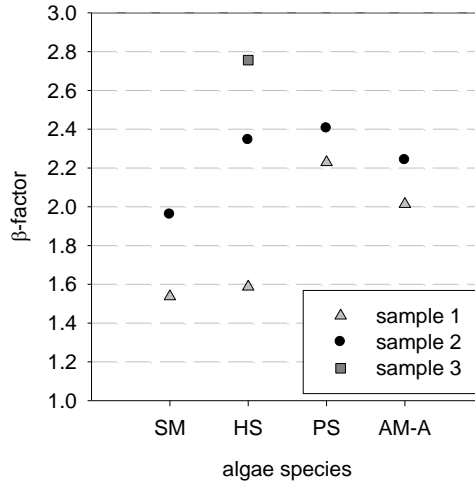


Fig. 5. Multiple determinations of β -factors for 4 algal culture samples within a 2 week time period. SM – *Skeletonema marinoi*, HS – *Heterocapsa spp.*, PS – *Pseudonitzschia seriata*, AM – *Alexandrium minutum*

The linear regression approach improves the agreement of filter pad data with PSICAM data in 2 ways: (1) sample-specific β -factors have a positive effect by accounting for filter and sample artefacts discussed above and (2) the application of offsets account for sample dependent scattering artefacts. Figure 6 also shows examples of performance of two previously published corrections, the earliest [9] and most recent work [17]. Data correction with historic correction methods (Table 5) showed lower agreement with PSICAM data, with a minimum RMS%E of 20.7% ranging to almost 46%. The regression approach to correct NIR scattering offsets resulted in one order of magnitude smaller intercepts for subsequent linear regression applied to the comparison with PSICAM data (Table 5) and high R^2 (>0.96) even when approximated β -factors were applied. Null-correcting filter pad absorption data consistently resulted in negative intercepts when compared to PSICAM measurements which means that NIR absorption values are systematically underestimated. Inappropriate correction of NIR-offsets therefore clearly has a strong impact on the overall performance of the quantitative filter pad technique.

Table 5. Slope, intercept and coefficient of determination (R^2) for linear regression (362 or PSICAM cut off wavelength) – 726 nm) of corrected T-method filter pad absorption data vs. PSICAM data. Overall agreement is given as RMS%E.

reference	slope [-]	intercept [m ⁻¹]	R^2	RMS%E [%]
regression slope + offset	0.99	0.000	0.999	3.2
regression slope + null correction	1.38	-0.012	0.913	19.7
average slope + regression offset	0.72	-0.001	0.954	19.6
average slope + null correction	1.00	-0.012	0.877	20.8
Stramski et al. 2015	0.77	-0.017	0.801	42.6
Stramska et al. 2003	0.94	-0.018	0.814	29.6
Finkel and Irwin 2001	0.96	-0.012	0.871	22.4
Roesler 1998	1.04	-0.013	0.877	20.7
Allali et al. 1997	0.63	-0.010	0.849	45.7
Arbones et al. 1996	0.90	-0.014	0.851	26.9
Tassan and Ferrari 1995	0.98	-0.015	0.847	24.4
Cleveland and Weidemann 1993	0.92	-0.015	0.845	26.6
Hoepffner and Sathyendranath 1992/1993	0.79	-0.013	0.836	34.5
Bricaud and Stramski 1990	0.79	-0.016	0.818	38.7
Mitchell 1990	0.98	-0.016	0.839	25.2

3.5 The linear regression approach for different configurations

Restricting analysis to historic pathlength corrections only [16, 17], the QFT-ICAM and IS-method filter pad data showed better agreement with a_p derived from PSICAM measurements than T-method data (Tables 5 and 6). The correction proposed in [16] was developed using PSICAM data which can potentially explain the lower RMS%E of 10.4% for the QFT-ICAM corrected using [16] compared to 18.1% for IS data corrected using [17]. In all cases, however, further improvement was achieved when the linear regression correction approach was used with any of the geometrical configurations.

Table 6 and Figure 7 show the comparison of corrected filter pad data made with the T-method, the IS method and the QFT-ICAM with particulate absorption coefficients measured in a PSICAM, limited to data in the visible spectrum. Data from all four measurements were available for a total of 51 samples. RMS%Es were broadly comparable for all three methods (1.7 - 3.2%) and regression slopes against PSICAM data were all within 1.5% of unity. Given

the comparable levels of performance, there appears to be no significant disadvantage to the relatively simple and widely available T-method.

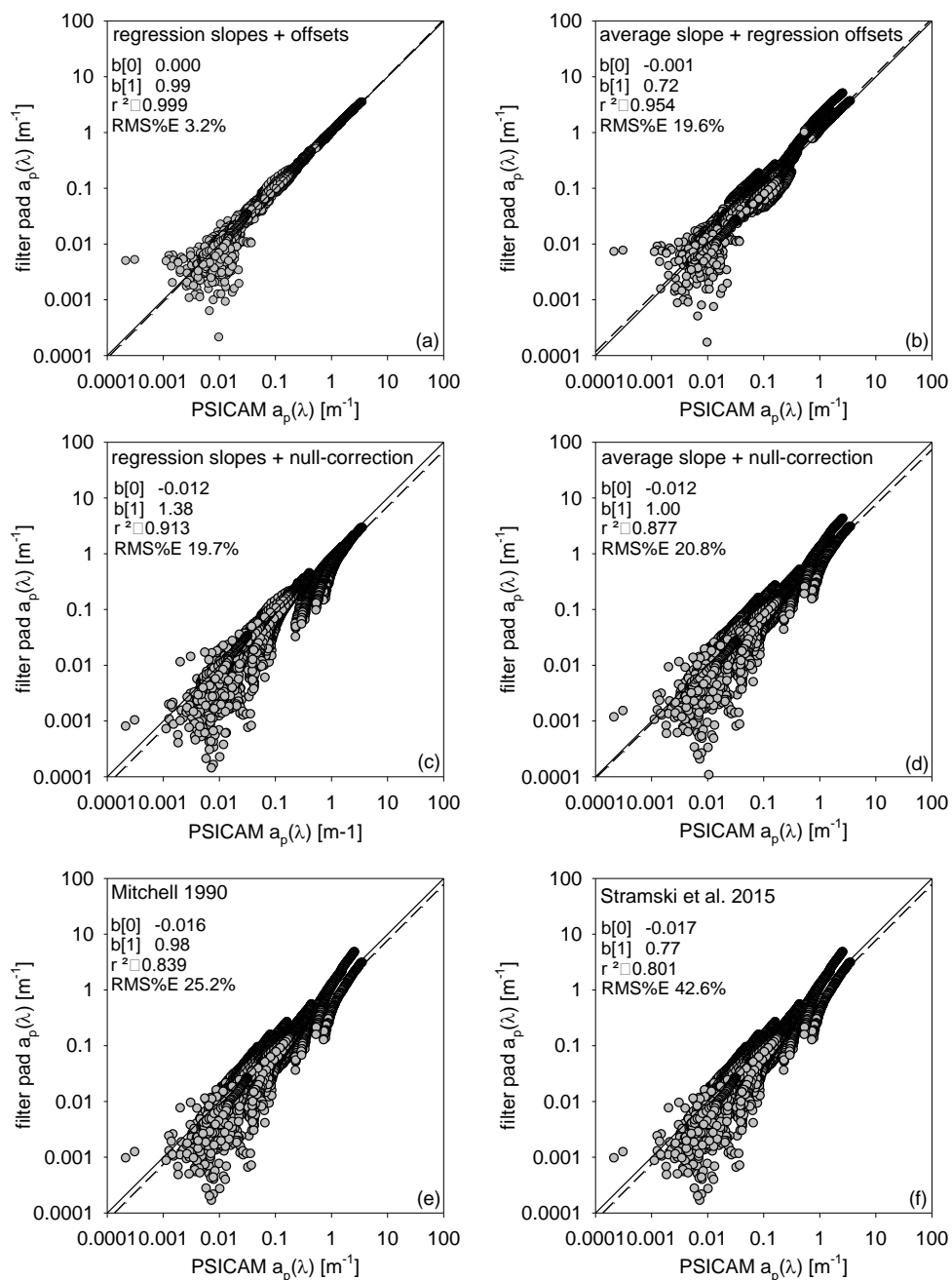


Fig. 6. The effect of different filter pad absorption correction methods on the agreement between a_p derived from PSICAM and filter pad measurements from 362 – 726 nm (except where PSICAM data was limited in the blue to eliminate artefacts due to very low signal levels), made on the UKCW cruise in 2015. (a)-(d) show variations of the linear regression correction in comparison to two previously published corrections by (e) Mitchell (1990) and (f) Stramski et al. (2015). Solid lines: 1:1 line, dashed lines: linear fit through data.

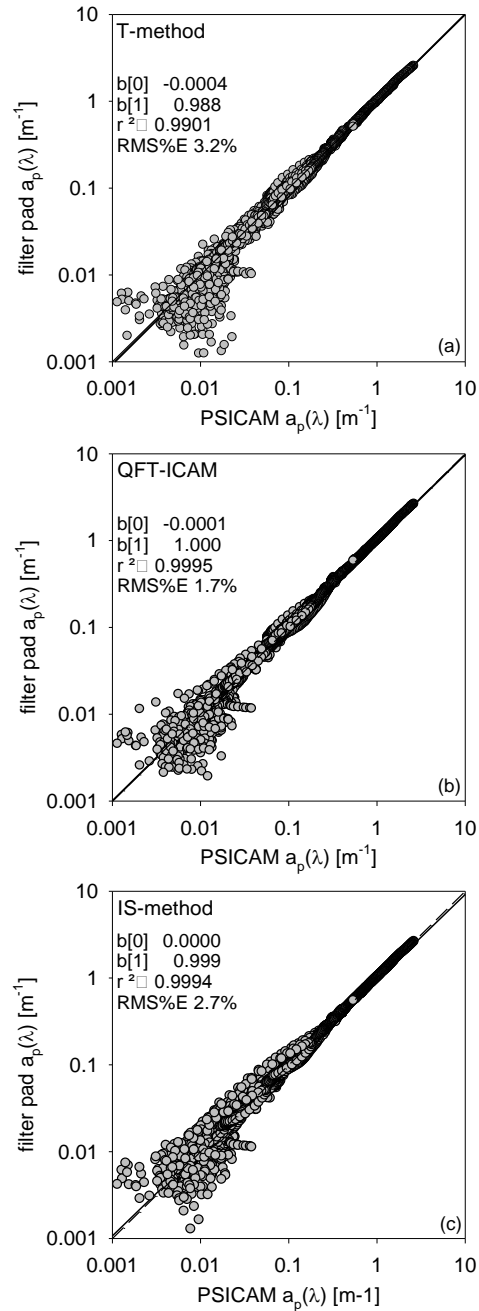


Fig. 7. The effect of the linear regression filter pad absorption correction methods on the agreement a_p derived from PSICAM and filter pad measurements using different geometric configurations: (a) T-method, (b) QFT-ICAM and (c) IS-method. Data presented is a subset of 51 stations sampled during the UKCW cruise in May 2015, from 362 – 726 nm (except where PSICAM data was limited in the blue to eliminate artefacts due to very low signal levels). Solid lines: 1:1 line, dashed lines: linear fit through data.

Table 6. Performance of geometrical configurations to measure filter pad absorption, when corrected with different correction approaches, and compared to PSICAM data. The analysis was performed for a subset of 51 stations sampled during the UKCW cruise in 2015 for which data from all three filter pad measurements was available. The spectral range was limited to 362 – 726 nm. Data where PSICAM sensitivity issues in the blue were observed were excluded from this comparison.

method	slope [-]	intercept [m ⁻¹]	R ²	RMS%E [%]
T-method	0.988	-0.0004	0.9991	3.2
QFT-ICAM	1.000	-0.0001	0.9995	1.7
QFT-ICAM (corrected using [16])	1.013	-0.0101	0.9914	10.4
IS-method	0.999	0.0000	0.9994	2.7
IS-method (corrected using [17])	1.322	-0.0168	0.9925	18.1

4. Discussion

The PSICAM, like other integrating cavity absorption meters [47], has been shown to be virtually insensitive to the presence of scattering material [15] and enables the determination of accurate absorption coefficients of natural water samples. In the past, however, it has rarely been used because calibration and measurement protocols are labour intensive and sensitive to sample handling artefacts. This work highlights a different problem due to limitations when signal levels are particularly low, as can be the case in the blue/UV. Here it has been shown that cross-validation with filter pad absorption data can provide a quality control mechanism which is useful to identify low signal measurement artefacts and improves the overall quality of measured IOPs.

In the past, non-linear relationships between suspension and filter pad absorption data were observed. The comparison with PSICAM data performed here and previously by Röttgers and co-workers suggests that non-linear effects could be due to either (a) imperfections in the determinations of absorption from suspensions in a cuvette, which are susceptible to scattering effects, (b) incorrect baseline correction of individual samples, introducing non-linear bias to the entire dataset or (c) intrinsic sample variability being misidentified as a non-linear effect when trying to fit a single relationship through multiple samples. PSICAM data enables the derivation of linear regression coefficients for individual samples which can be used to correct for pathlength amplification, (slope) and offsets due to sample scattering losses compared to that of the reference filter (intercept).

The agreement within 3.2% of corrected filter pad absorption data and PSICAM data demonstrates the excellent performance of the linear regression correction approach. This approach clearly distinguishes between pathlength amplification and scattering offset artefacts and potentially has the advantage that it can be extrapolated to wavelengths where the PSICAM data is either suspect or otherwise unavailable, e.g. filter pad data beyond the spectral range of the PSICAM data. The performance of different correction methods to correct measurements of bleached filter pads remains inconclusive due to a lack of validation data as there is currently no method to partition pigmented and non-pigmented absorption in PSICAM measurements.

Comparison of β -factors between different filter pad absorption methods showed no clear benefit to more complex approaches over the relatively simple T-method. Correction for scattering effects using the regression approach effectively compensates the T-method for the intrinsic insensitivity to scattering error for the two integrating cavity approaches. It is clear that the combination of the T-method and PSICAM is capable of producing higher quality a_p data than either technique on its own, and as good as any of the other filter pad techniques in combination with the PSICAM. Very importantly, none of the filter pad techniques offers a satisfactory standalone solution.

5. Conclusion

The availability of PSICAM data enabled significant progress in the development of the methodology to determine quantitative particulate absorption coefficients from filter pad measurements. The comparison of filter pad and PSICAM data confirmed previous observations of a linear relationship [16, 29, 37]. Fitting a linear function through the data provides regression coefficients (slope and intercept) which can be used to correct filter pad absorption measurements and match them with PSICAM data on a sample-by-sample basis, resulting in agreement within 3.2% RMS%E.

It has been demonstrated here that filter pad absorption measurements benefit from complementary PSICAM measurements to derive appropriate correction coefficients. At the same time, PSICAM data has been shown to benefit from the availability of corresponding filter pad data as this enables identification of wavelengths at which sensitivity issues occur. The traditional T-method, despite its theoretically higher measurement uncertainties, is broadly comparable in performance with more complex configurations. The simplicity of the measurement protocol makes the T-method favourable for future field work campaigns where time and labour are limited when ICAM-type determinations of a_p are made in parallel.

The linear correction outperforms previously proposed correction methods (RMS%E > 20%) but is dependent on the availability of PSICAM data. Unfortunately, this eliminates its application to historic datasets and imposes a significant additional experimental burden on future work. However, new commercially available integrating cavity absorption meters, such as the Trios OSCAR, the HOBI Labs a-Sphere and the Turner Designs flow through ICAM, may help to make these types of measurements more accessible for the wider community in the near future.

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