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Evaluation of scatter corrections for ac-9 absorption measurements in coastal waters



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ABSTRACT

Determinations of inherent optical properties of natural waters are fundamental in marine optical research. In situ measurements of light absorption are mostly obtained with an instrument that uses a reflective tube design to reduce concomitant errors induced by light scattering (ac-9, WETLabs Inc.). The remaining, generally still substantial, error is commonly corrected using one of a number of different approaches, each of which is based on a set of assumptions. Until now, the errors in these measurements have only been theoretically examined using Monte Carlo modeling Leymarie et al. (2010). The study presented here used a lab-based point source integrating cavity absorption meter (PSICAM) which avoids scattering errors. The PSICAM data were used to evaluate the absorption determination with an ac-9 in coastal waters for each of the scattering correction approaches. The results showed that the assumption of negligible absorption at wavelengths >700 nm is not valid in coastal waters and that, as a result, ac-9 measurements strongly underestimate absorption at longer wavelengths (>600 nm). An empirical relationship between uncorrected (for scattering) ac-9 measurements and the true absorption at 715 nm was included in the correction scheme; this improved the quality of ac-9 data at longer wavelengths but showed overestimation at shorter wavelengths. However, additional inclusion of a scatter correction for the ac-9 attenuation measurement resulted in a significant improvement of the proportional scatter error correction across the spectrum. Despite these innovations, variations in scattering properties can, combined with low absorption at specific wavelengths,

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2211-1220/\$ - see front matter © 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.mio.2013.11.001 result in relatively large percentage errors for individual measurements.

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1. Introduction

Knowledge of the inherent optical properties (IOPs) of natural seawater is essential for satellite remote sensing of water constituents and for general optical research in aquatic science. These IOPs include absorption (a), scattering (b), and attenuation (c, with c = a + b) coefficients, which are generally difficult to measure accurately, and are especially difficult to measure in situ when, as is the case for oceanic waters, absolute values are low. The main reason for this is the difficulty in designing instruments that can totally separate absorbed from scattered photons or scattered from directly transmitted photons. A widely used instrument to measure two of these IOPs is the WET Labs Inc, ac-9 (or its hyper-spectral successor ac-S) (Moore et al., 1992; Zaneveld et al., 1992, 1994; Twardowski et al., 1999; Sullivan et al., 2006). The introduction of this instrument revolutionized in situ IOP measurement capabilities and it remains, almost two decades later, the industry standard. Over this period a massive amount of data has been collected using this instrument, by labs sampling natural waters across the planet. Ensuring and improving the quality of these data sets is a major motivation of this work and in doing so, we hope to further strengthen the legacy to the field of all those who worked towards the development of this instrument. The instrument measures beam attenuation with a lensaperture arrangement, and absorption using a reflective tube design and a large area detector. Both measurements are subject to significant scattering errors. With the reflective tube design the detector does not collect all scattered photons, and the beam attenuation detector fails to exclude photons that are scattered at angles smaller than the collecting angle of the detector. In general, attempts are made to correct the absorption measurement for this scattering error and afterwards calculate the scattering coefficient from uncorrected attenuation and corrected absorption (Zaneveld et al., 1994; Twardowski et al., 1999; Slade et al., 2010; Doxaran et al., 2007). Different methods are generally used for the scatter correction for absorption. The methods are described in the NASA Ocean Optics protocols (Müller et al., 2002) and are based on work of Zaneveld et al. (1994). A simple approach, that is also commonly used for other spectrophotometric methods, is to subtract the signal at a longer wavelength (>700 nm) from the values at all other wavelengths, such that the whole spectrum is shifted downwards to bring absorption at the longer wavelength to zero. There are two assumptions that would make this method valid: (1) the absorption is negligible at wavelengths >700 nm, and (2) the scattering error (and hence the absolute scattering) is wavelength-independent. A proportional scatter correction makes use of an additional attenuation measurement, which gives wavelength-dependent scattering signals, and therefore instead of (2) it is assumed that, in addition to assumption (1), (3)the shape of the volume scattering function (VSF) is wavelength-independent only, not the absolute scattering. A third, less often used method is to subtract a constant fraction of scattering from the absorption. This approach does not assume zero absorption >700 nm and attempts to account for variability in the magnitude of the VSF which is assumed to be wavelength independent. Factors between 0.14 and 0.18 are proposed for open ocean and turbid waters, respectively (see Müller et al., 2002).

The validity of each of these assumptions under natural conditions has been recognized as being questionable. For instance, natural waters contain significant amounts of detritus that shows absorption at wavelengths >700 nm (Tassan and Ferrari, 2003). Furthermore, both total scattering and VSF are sensitive to changes in both the composition and size distribution of the particle population. Recently, another method was proposed (McKee et al., 2008) and subsequently revised and validated (McKee et al., 2013) that uses additional backscatter measurements to estimate wavelength dependent VSF losses and does not require assumption (1). This method is not considered here in detail because we are interested in trying to establish a correction that does not require additional data and that could potentially be retrospectively applied to historic data sets for which backscattering data are not available. The theoretical extent and wavelength-dependence of possible errors have also been investigated with a Monte-Carlo simulation study (Leymarie et al., 2010).

An evaluation of these different scatter correction methods for absorption measurements with the ac-9 (or ac-S) is missing, as, until now, no other practical technique existed to determine particulate absorption that does not need the same kind of scatter correction and can be used at sea. Note that other techniques with a negligible scatter error do exist (e.g. Fry et al., 1992; Babin and Stramski, 2002; Tassan and Ferrari, 2003) but are rarely used for oceanographic measurements due to their relatively complex setup requirements (Pope et al., 2000) or their lack of sensitivity. An alternative approach has been proposed to measure absorption in the lab with a similar precision to the ac-9 but that, because of its integrating sphere design, is not affected by scatter losses (Kirk, 1997). This pointsource integrating-cavity absorption-meter (PSICAM) has been shown to provide accurate absorption measurements for particulate absorption (Röttgers et al., 2007). In this paper we present results from a large number of samples to perform error statistics, test different correction approaches, and compare them to theoretical predictions (Leymarie et al., 2010). The aim is to evaluate the performance of different scatter correction methods allowing us to (1) show the extent and range of typical errors, and (2) to develop an improved scatter correction that could be retrospectively applied to historical data without need for any additional measurements. A PSICAM was used to determine the 'true' absorption of all water constituents for algal cultures and a large set of natural samples from coastal waters, and these are compared with ac-9 measurements using different scatter correction methods. It is shown that absorption in the near infrared spectral region (>700 nm) is significant and has to be included in the scatter correction method, that the ac-9 attenuation measurement should be corrected before inclusion in the proportional correction method, and that variability in sample scattering properties induces significant errors.

2. Methods

2.1. General procedure

Different methods for scatter correction of ac-9 absorption measurements are evaluated by comparison with corresponding PSICAM absorption data which are not significantly affected by scatter losses (Röttgers et al., 2005). The results presented here for the ac-9 are generally applicable to the hyper-spectral version of the instrument (ac-S). Lab measurements were performed to measure the absorption and attenuation of suspensions of different microalgae. Then samples were taken for a range of different coastal waters (River Elbe, North Sea, German Bight, Baltic Sea). PSICAM measurements were made in the lab on board the ship and ac-9 measurements were either made in situ or in the ship's lab. Therefore two different experimental data sets are used: one comparing lab measurements of ac-9 and PSICAM data, and the second comparing in situ ac-9 data with lab PSICAM values. The lab-lab experimental set was expected to be more accurate for the following reasons: (1) samples and references (purified water blank) were measured several times in an alternating mode within a short time interval for both instruments, (2) temperature differences between samples and references were low (<1 °C) as the reference and sample were brought to the same temperature in a water bath before measurements, minimizing errors due to uncertainties in the temperature coefficient of pure water absorption and effects of drifts in ac-9 blank values over longer times, and (3) sub-samples for each instrument were drawn from the same batch, minimizing possible artifacts associated with fine-scale spatial heterogeneity affecting in situ measurements.

Leaving aside scattering errors, the main error sources for ac-9 measurements are random noise and uncertainty in the salinity and temperature coefficients of pure water absorption. The strongest influence of uncertainties in the T and S coefficients is expected for the 715 nm absorption channel of the ac-9 (due to large values of the coefficients and low absorption values). However, the 715 nm ac-9 absorption channel is used as a reference value for most scatter correction schemes and as a result, its error propagates to all other wavelengths. The potential errors can be estimated as follows: the water temperature during cruises in April and May in the North Sea were in the range 8–12 °C. Under typical lab calibration conditions the temperature difference (in situ sample to lab reference) could be in the range of >10 °C. The temperature correction coefficient at 715 nm is 0.0029 m⁻¹ °C⁻¹ with a standard deviation of 0.0001 m⁻¹ °C⁻¹ (Pegau et al., 1997). The correction for a 10 °C difference would be 0.029 m⁻¹ with a variation of 0.001 m⁻¹ (10 °C * 0.0001 m⁻¹ °C⁻¹). The corresponding salinity correction coefficient at 715 nm is $-0.00018 \text{ m}^{-1} \text{ S}^{-1}$ with an SD of $0.00005 \text{ m}^{-1} \text{ S}^{-1}$. For a salinity of 35 this would mean a correction value of -0.0063 m^{-1} with a variation of 0.0018 m^{-1} . Additionally, variations in repetitive blank measurements were in the range of $0.001-0.0015 \text{ m}^{-1}$. The lowest observed values in the ac-9 absorption channel (after all corrections, except for scattering, were performed) were 0.009 m^{-1} for cultures and 0.02 m^{-1} for natural samples. The lowest observed 'true' absorption was $< 0.002 \text{ m}^{-1}$. This suggests that temperature and salinity errors at 715 nm are sometimes larger than the true absorption at 715 nm, so particular care is required when large temperature and salinity differences exist between sample and reference. However, for the coastal waters studied here, the magnitude of the true absorption at 715 nm greatly reduces the importance of these errors.

2.2. Sampling and cultures

Cultures of different diatom species isolated from the North Sea were used. Additional cultures of *Trichodesmium erythreum* and *Prymnesium parvum* were provided by the Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, Germany. A culture of *Prochlorococcus marinus* was provided by the University of Freiburg, Germany. All cultures were maintained at 24 h light and 20 °C in the exponential growth phase by daily dilution with fresh medium.

A set of 113 surface samples was taken during several ship cruises. Cruises were conducted: on the R/V *Prandtl* in the estuary of the River Elbe in July 2007, on the R/V *Oceania* in August/September 2007 crossing the Baltic Sea from Gdansk going around Denmark into the German Bight, and on the R/V *Heincke* in the German Bight and the North Sea in May 2009. During the cruise in May 2009 ac-9 measurements were made in situ while the water sample bottles were closed. During the September 2007 cruise ac-9 measurements were made in situ and in the lab using two different instruments. Comparisons between these two different instruments and between in situ and lab measurements showed difference in the range of 1%–3% only. Following this result, no further distinction was made between lab–lab and lab–in situ results.

2.3. ac-9 measurements

Absorption and attenuation measurements with an ac-9 were performed with two instruments that had been serviced and calibrated shortly before the first cruise. Pure water data showed deviations from the manufacturer's calibration values and these blank values changed slightly over time for each wavelength channel but were constant over short time intervals, except for one channel (a630) of one instrument that showed slightly stronger variations after about one year of use. All measurements were carried out with 25 cm path length instruments according to the methodology described in the most recent ac-instrument manual (www.wetlabs.com), in Müller et al. (2002), and Twardowski et al. (1999). Lab measurements were performed with 5-l samples temporarily stored in 5-l glass bottles (Duran, Schott). The sample bottle and another 5 l bottle with freshly made purified water were placed in a water bath to adjust the temperature to be only slightly higher than the in situ water temperature. The 5-I samples and the reference water were passed through both channels of the ac-9 using a gravity-feed tubing arrangement, with the instrument mounted in a vertical position and sample passing upwards through the flow tubes. The instrument was flushed for approximately 30 s before measurements were taken over another 30 s period. Air bubbles were removed by shaking the tubing and gently shaking the instrument. Each sample was measured in this way at least five times alternating with measurements of purified water as a blank. Purified water was produced onboard by passing previously purified water through a Millipore water purification system (Gradient), about one hour before use. The source purified water had been prepared in the home lab using a Millipore MilliQ-185 system (after deionization of tap water), stored in acid cleaned 25 l plastic containers for degassing and taken on board.

Bubbles inside the cuvettes increase the measured attenuation and bubble-free measurements showed lower values for each sample of the purified water. Higher values due to bubbles were only occasionally observed and those measurements were rejected and repeated to have at least four repeat measurements with each sample and each blank. The ac-9 instrument used in the lab was switched

on 10 min before each measurement to warm up and switched off afterwards to keep its internal temperature within its required calibration range. The internal temperature was normally between 25 and 30 $^{\circ}$ C.

The data were collected, processed, and stored using WetView 5.0 (WetLabs) software; this included the instrument-specific internal temperature correction and the use of the latest pure water calibration data. These data were further corrected for the sample temperature and salinity as described in the manual using the temperature and salinity correction coefficients of Pegau et al. (1997). Measured and T-corrected values for purified water were subtracted from the sample values. The resulting data are the measured values of absorption a_m , and attenuation, c_m (the subscript 'm' indicates values not further corrected for either scatter losses of the absorption channel or underestimation of scattering in the attenuation channel).

2.4. PSICAM measurements

Measurements of what we shall assume to be 'true' absorption were taken using a point-source integrating-sphere absorption-meter (PSICAM) (Kirk, 1997; Röttgers et al., 2005, 2007). Briefly, each sample was measured with a calibrated instrument using purified water as the reference about 5 min after the ac-9 measurements were performed. The PSICAM cavity was filled with about 500 ml of the sample and the light intensity inside the cavity was measured with a spectroradiometer, before the reference light intensity was measured with the cavity filled with purified water. Alternating measurements were repeated at least 3 times to have triplicate determinations of the absorption of all water constituents (except water itself). The absorption was calculated from the "transmission" (sample/reference) and corrected for chlorophyll fluorescence, and for temperature and salinity differences between sample and reference using instrument-specific correction coefficients (Röttgers et al., 2007). The precision of the PSICAM is similar to or better than that of the ac-9 for the relatively high absorption values measured $(0.01 - > 5 \text{ m}^{-1})$. However, the overall error is also determined by the calibration against a spectrophotometric measurement of a dye solution. On a percentage basis this last error is between 1 and 2% at all relevant wavelengths when absorption is $>0.01 \text{ m}^{-1}$. The determination with a PSICAM is not sensitive to errors induced by bubbles or other sources of scattering.

2.5. Quality control of absorption measurements using colored solutions

Absorption determinations with the ac-9 and the PSICAM were validated in the lab with a commercial dual-beam spectrophotometer (Lambda 800, Perkin-Elmer) using colored solutions of Nigrosine (Merck) and a humic acids standard (Aldrich), to avoid particulate scattering adversely affecting the determinations. The absolute accuracy, linearity of response, and wavelength accuracy of the photometer was controlled using NIST neutral density absorption standards, a Holmium filter and a dilution series made from a Nigrosine solution. Due to the accuracy limits of the NIST standards the relative error of the spectrophotometer at the optical densities used is $\sim 2\%$.

The PSICAM was calibrated with the spectrophotometer using Nigrosine solutions. A direct comparison after calibration between the PSICAM, the ac-9, and the spectrophotometer was performed using solutions of Nigrosine and a humic acid standard. Differences in absorption between the ac-9, the PSICAM, and the spectrophotometer were not significant and <2.5% in the range of $0.1-5 \text{ m}^{-1}$. A 2% difference between PSICAM and ac-9 is in the error range for the PSICAM and just above the error range for the ac-9 for this range of absorption. All natural samples presented in this paper had absorption values >0.01 m⁻¹. These absorptions were much higher than the sensitivity limit of both instruments, and relative measurements errors were in the range of a few percent only.

2.6. ac-9 scatter correction for a_m

Two commonly used methods for scatter correction of a_m data are: (1) *flat*: a simple offset subtraction of the value at 715 nm, a_{m715} , and (2) *proportional*: a proportional scatter correction after Zaneveld

Table 1

ac-9 correction methods, showing the correction factor of the ac-9 attenuation measurement, e_c , and the offset used in Eqs. (1)–(4).

Name	ec	Offset	Remarks
flat	-	<i>a</i> _{m715}	
flat ⁺	-	$(a_{m715} - a_{715})$	a715, measured
flat ^e	-	$(a_{m715} - a_{715})$	a_{715} , estimated from a_{m715}
proportional	1	<i>a</i> _{m715}	
proportional _c	0.56	<i>a</i> _{m715}	
$proportional^+$	1	$(a_{m715} - a_{715})$	<i>a</i> ₇₁₅ , measured
$proportional_{c}^{+}$	0.56	$(a_{m715} - a_{715})$	a ₇₁₅ , measured
proportional ^e	1	$(a_{m715} - a_{715})$	a_{715} , estimated from a_{m715}
$proportional_{c}^{e}$	0.56	$(a_{m715} - a_{715})$	a_{715} , estimated from a_{m715}

et al. (1994). Using these corrections the absorption determined by an ac-9, a_{ac-9} , is calculated as:

$$a_{\rm ac-9}(\lambda) = a_m(\lambda) - a_{m715} \quad flat, \tag{1}$$

or

$$a_{ac-9}(\lambda) = a_m(\lambda) - a_{m715} \frac{[c_m(\lambda) - a_m(\lambda)]}{[c_{m715} - a_{m715}]} \quad proportional.$$
(2a)

A term for the correction of the attenuation measurement, $1/e_c$, can be introduced as follows:

$$a_{\rm ac-9}(\lambda) = a_m(\lambda) - a_{m715} \frac{\left[(1/e_c) c_m(\lambda) - a_m(\lambda) \right]}{\left[(1/e_c) c_{m715} - a_{m715} \right]}.$$
(2b)

Normally, the attenuation correction is used with $e_c = 1$ (i.e. no *c* correction) but here we introduce a rather simple approach with a value of $e_c = 0.56$ assuming a wavelength-independent correction. The value is based on results for turbid water at one wavelength presented by Boss et al. (2009). Potential wavelength-dependence of e_c was ignored for simplicity. Both methods assume (1) that absorption in the near infrared is negligible, and that a_{m715} is purely a result of the scattering error at 715 nm. The *flat* method assumes (2) that the A-channel scattering error, $f_a = (a_m - a)/(c_m - a)$, is wavelength-independent as the scattering is wavelength-independent. The *proportional* method assumes (3) that the volume scattering function is wavelength-independent and uses the attenuation measurements, c_m , to correct for wavelength-dependent differences in total scattering.

Two other methods were tested: the method proposed by Twardowski et al. (1999) in which a nonnegligible absorption at 715 nm due to the influence of the 676 nm pigment maximum is assumed, and another method described in early versions of the ac-9 manual (WETLabs, 2005) that uses a fixed portion of the scattering with values between 0.14 for clear and 0.18 for turbid waters (see Müller et al., 2002), but does not include an offset correction at 715 nm. Neither method performed as well as the other two methods described above and the results are therefore not shown.

It will be shown later that assumption (1) is generally not valid as significant absorption at 715 nm, a_{715} , was always observed for natural samples. A priori knowledge of the absorption at 715 nm (from PSICAM measurement) was used to test assumptions (2) and (3) by including 'true' values of a_{715} into the correction methods as follows

$$a_{ac-9}(\lambda) = a_m(\lambda) - (a_{m715} - a_{715}) \quad flat^+$$
(3)

and

$$a_{ac-9}(\lambda) = a_m(\lambda) - (a_{m715} - a_{715}) \frac{\left[(1/e_c) c_m(\lambda) - a_c(\lambda) \right]}{\left[(1/e_c) c_{m715} - a_{715} \right]} \quad proportional^+, \tag{4}$$

where a_c can be either a_m or a, and a_{715} is either the measured 'true' absorption or estimated from a_{m715} measurements (see later). Table 1 illustrates different combinations of parameters tested and the associated nomenclature of the correction schemes.



Fig. 1. Absorption coefficients, a (m⁻¹), as a function of wavelength for each sample set (*cultures, Elbe River, Baltic Sea and German Bight, North Sea*). Absorption measurements are done using a PSICAM (see text for details). For the sample set *Baltic Sea and German Bight* and *North Sea* only half of the spectra are depicted. Note the different *y*-axis scales.

3. Results and discussion

3.1. Absorption

Fig. 1 shows either all or half (for clarity) of the absorption spectra for each sample set. A first set of measurements was performed with batch cultures of different phytoplankton species under controlled lab conditions to allow highest precision absorption measurements. Freshly prepared cultures were used as it is widely believed that algal cultures do not exhibit significant absorption in the near infrared spectral region (NIR) as algal pigments do not significantly absorb in the NIR, and during their exponential growth phase the cultures do not induce production of significant concentrations of bacteria or organic detrital material. Each culture was diluted by two different factors to have a low and a high concentration of the same species. This results in two different total absorption to total scattering ratios, since there is a constant absorption of chromophoric dissolved organic matter (CDOM) in the culture medium. The resulting non-water absorption spectra (the sum of particulate and dissolved material) of all cultures are depicted in Fig. 1(a). The maximum values of each spectrum were between \sim 0.2 and 0.7 m⁻¹. The absorption at wavelengths >700 nm is not negligible but low, less than a few percent of a_{676} . Separating the absorption into particulate and dissolved fractions (data not shown) revealed that this absorption was mainly due to CDOM, as the cultures were maintained in medium made from natural seawater that contained relatively high concentrations of CDOM.

The next set of samples was taken from very turbid parts of the River Elbe. Based on the absorption spectra, the samples were considered to consist of reasonably homogeneous (mostly non-living) material but to vary in their absolute optical properties by concentration differences of the particulate matter above a relatively constant background of CDOM. The maximum absorption at 400 nm varied between 1 and 15 m⁻¹, and the absorption spectra showed an approximately exponential increase in absorption with decreasing wavelength, typical characteristics of CDOM/non-algal matter, and

only small pigment absorption maxima at ca. 676 nm (Fig. 1(b)). This data set exhibited substantial absorption at 715 nm with values between 0.05 and 2.2 m⁻¹. Absorption of CDOM (data not shown) was relatively low at 715 nm, so, $a_{715 nm}$ was mainly due to particulate matter.

The third set of samples was collected in late summer in the Baltic Sea and the inner German Bight. Sample spectra suggested mainly turbid waters with no indication of a phytoplankton bloom, typical for late summer in these regions. The absorption varied between 0.3 and 1.6 m⁻¹ at 400 nm and between 0.01 and 0.23 m⁻¹ at 715 nm (Fig. 1(c)). The shapes of the absorption spectra were similar to those from the River Elbe, with occasional examples of a pronounced pigment peak at ca. 676 nm, so it is assumed that CDOM and non-algal matter are the largest contributors to the total absorption. There were no systematic visible differences in spectral shapes between samples from the Baltic Sea and the German Bight, but highest absorptions were found in the German Bight.

The last set of samples was collected from the German part of the North Sea in spring, when phytoplankton blooms typically occur. The absorption spectra showed clear signals of phytoplankton contributing to the absorption (Fig. 1(d)). However, the highest values were always found at the shortest wavelengths indicating that no strong spring bloom situations were sampled and absorption was often strongly influenced by non-algal matter and CDOM. The absorption at 715 nm is significant but relatively small. However, some spectra were similar to samples from the River Elbe and showed a rather strong contribution by non-algal matter. The overall variability in spectral shapes is much larger compared to samples from the River Elbe and from the Baltic Sea/German Bight taken in late summer. Maximum absorption varied between 0.1 and 1.5 m⁻¹ at 400 nm (Fig. 1(d)).

3.2. Scattering

Particulate scattering was determined by subtracting the 'true' absorption from uncorrected attenuation measurements with the ac-9 ($b_p = c_m - a$). Scattering of the cultures was highly variable (<0.2–2.5 m⁻¹) depending on the cell concentration. It varied significantly between species in terms of strength and wavelength-dependence. The influence of anomalous dispersion was clearly visible in scattering spectra through reduced scattering near absorption maxima (van de Hulst, 1957). There is a tendency for higher cell concentrations to a decrease in scattering with shorter wavelengths.

The number of useful scattering measurements from the Elbe River was limited as the attenuation signal of the ac-9 (25 cm path length) was frequently saturated. The remaining spectra showed scattering between 2 and 35 m⁻¹, that rather linearly decreased with wavelength (not shown).

Scattering of samples from the Baltic Sea and German Bight varied between <0.4 and $\sim 7 \text{ m}^{-1}$, and generally decreased with increasing wavelengths. When scattering was high, this decrease was not linear but showed some influence of the absorption leading to a rather flat spectrum at shorter wavelengths. Again there were no visible differences in spectral shapes between samples from the Baltic Sea and the German Bight, but highest scattering was found in the German Bight.

For the North Sea samples the maximum scattering varied between 0.2 and 3 m⁻¹. The wavelengthdependence of scattering varied from increasing to decreasing with increasing wavelength, with pronounced absorption features in some scattering spectra. These variable spectral shapes sometimes resembled those of a non-algal matter dominated sample and sometimes those of an algal culture. Note that scatter correction of the attenuation (Boss et al., 2009), as discussed later, altered both the magnitude of the total scattering and its wavelength-dependence.

3.3. ac-9 absorption measurements

Typical results for ac-9 absorption measurements before and after scatter correction are shown in Fig. 2. ac-9 results uncorrected for scattering errors are considerably higher than the 'true' absorption. Plotting these uncorrected data against the real absorption for each wavelength (Fig. 3) shows a rather good linear correlation for the shortest wavelengths (412 nm) but greater spread at longer wavelengths, where absorption is generally lower. Each sample set can be differentiated due to differences in absolute absorption and mean deviation from the 1:1-line, especially at longer wavelengths. In this simple correlation plot it is already obvious that non-zero absorption at longer wavelengths has a strong effect on the deviation of ac-9 results, as the highest deviations are found



Fig. 2. One randomly chosen example for each data set of the 'true' absorption, a, the absorption measured by the ac-9, a_m , and the results of the two ac-9 scatter correction methods *flat* and *proportional*.

for samples with the highest absorption at 715 nm (Elbe River) and the lowest for samples with the lowest absorption at this wavelength (cultures).

Fig. 4 shows a rather good correlation between a_m and a at 715 nm for all of the natural samples. A best-fit power law relationship was found using non-linear least squares minimization. This relationship provides a simple way of estimating a_{715} from a_{m715} measurements, and is expected to be most useful when $a_{m715} > 0.1 \text{ m}^{-1}$. This empirical relationship has been found to give reasonable results for a more recently collected data set using a different ac-9 instrument and including data from other European shelf seas. This is an important observation as it facilitates attempts to derive scatter correction methods that do not require the assumption of zero NIR absorption.

3.4. ac-9 scatter correction

Typical results for the two scatter correction methods *flat* and *proportional* are shown in Fig. 2. Scatter-corrected ac-9 absorption values are close to the true absorption at many wavelengths. Due to significant non-zero absorption at 715 nm and the fact that both correction methods perform an offset subtraction at this wavelength, the absorption at longer wavelengths is typically and sometimes strongly underestimated.

Correlations for the *proportional*-correction for each wavelength are depicted in Fig. 5. As absorption at 715 nm is assumed to be zero for this method, there is no possible comparison for this wavelength. There are good linear relationships for shorter wavelengths (412, 440, and 488 nm), each of which shows a relatively small variation compared to a_m results, and all are near the 1:1 line. However, the *proportional* correction generally underestimates the absorption for wavelengths >488 nm. At the longest wavelengths this underestimation is significant and seems to be a function of the sample set. Strongest underestimations are found for samples from the Elbe River, and lowest for culture samples. The correlation of the results of the *flat* correction (data not shown) is not significantly different from those of the *proportional* correction, except for generally lower variability in the deviations from the 1:1 line.



Fig. 3. The measured ac-9 absorption (uncorrected for scatter losses), a_m , as a function of the 'true' absorption, a, for ac-9 wavelengths of 412–676 nm. The lines show the 1:1 relationship.

To check whether the origin of the samples or their individual optical properties were responsible for the deviations from the 1:1 line, individual differences between scatter-corrected ac-9 absorption measurements and the 'true' absorption for all samples and both scatter correction schemes (*flat* and *proportional*) were calculated. Error distributions (absolute errors and relative percentage errors) for the *proportional* correction for each wavelength are depicted in Fig. 6 as a function of a_{715} . The results of the *flat* correction (data not shown) were not significantly different from those of the *proportional* correction.



Fig. 4. Absorption at 715 nm, a_{715} , as a function of the absorption measured by the ac-9 (uncorrected for scatter losses), a_{m715} . Indicated is a potential function fitted through all data points (black line) but excluding those of the cultures, and the corresponding equation. The same data are shown in both plots, but on logarithmic (upper panel) and absolute (lower panel) scales.

The absolute difference and the relative error are clearly dependent on the absolute absorption at 715 nm for all wavelengths. There is a clear linear relationship in the relative percentage error with a_{715} for each wavelength. At longer wavelengths high absorption at 715 nm leads in extreme cases to an underestimation in the ac-9 determination of up to 1.2 m^{-1} that is equivalent to a relative underestimation of ca. -80%. The relative error ranges between ca. -80% to +30% and is less pronounced at the shortest wavelengths due to the higher absorption signals found at those wavelengths. The strongest overestimations are observed for a few culture samples. At longer wavelengths (555–650 nm) higher variation of the error with low $a_{715 \text{ nm}}$ might be due to relatively low signal levels leading to larger relative measurement errors. Error distributions are not significantly dependent on the sample set, beyond the dependence on a_{715} which in this case is effectively a proxy for turbidity or scattering. There are no significant differences in the general error distributions for the *flat* and *proportional* scatter correction methods, suggesting that neither adequately represents the wavelength-dependence of the scattering error. The most noticeable difference is greater overall variability of errors for the proportional correction. The fact that the proportional method shows higher variation could potentially be explained either by: (a) the *flat* correction uses fewer variables and there is less error propagation, or (b) there is some feature of the scattering error that is unintentionally being partially compensated for by the *flat* correction. Later results show that we are able to significantly reduce these errors using an improved version of the proportional correction method that uses even more variables, which suggests that point (b) is the more likely explanation in this case. The mean error at the shortest wavelengths (412-488 nm) is low in both cases and always in the range of $\pm 5\%$. For 75% of the samples the error at these wavelengths is in the range of $\pm 10\%$. At wavelengths >500 nm the error is generally negative and the magnitude increases linearly with increasing a_{715} , with extreme values at wavelengths of 630 and 676 nm.



Fig. 5. The result of the *proportional* scatter correction, a_{ac-9} , as a function of the 'true' absorption, *a*, for ac-9 wavelengths of 412–676 nm. The lines show the 1:1 relationship.

3.5. Analysis of scatter correction

We have shown that the main reason for errors in ac-9 absorption determination at longer wavelengths is significant non-zero absorption at 715 nm. This invalidates assumption (1). The wavelength-dependence and extent of the observed errors is very similar to theoretical calculations by Leymarie et al. (2010) for the same conditions (*proportional* and 715 nm as a reference wavelength) and a similar set of theoretical samples. However, that calculation showed underestimations of the absorption at all wavelengths and did not indicate any possible overestimation. Strong



Fig. 6. Absolute difference (m^{-1}) between the absorption results of the *proportional* correction and the 'true' absorption as a function of a_{715} . Relative percentage errors are depicted in the insets.

underestimations are not observed at the shortest wavelengths with field data even in situations where a_{715} is very high. In addition, the absolute underestimation at these wavelengths is relatively small compared to longer wavelengths for the same a_{715} , which suggests that there is compensation from an additional error that leads to an increased estimation of absorption at shorter wavelengths. In some individual cases a significant overestimation was observed, especially for some cultures. This indicates that the individual scattering properties of a sample influence the absorption measurements, and that in some cases there is a strong wavelength-dependence of the error that is not directly related to the wavelength-dependence of total scattering. The fact that Leymarie et al. (2010) restricted their analysis to a wavelength-independent VSF points to a possible source for this discrepancy.

Variations of the errors at shorter wavelengths are relatively small, but are highest for the cultures and the North Sea samples taken in spring when the influence of algae on absorption was greatest. Conversely, the samples with the highest relative concentration of non-algal particulate matter (River Elbe sample) showed the lowest variability. From this it may be concluded that the optical properties of algae are relatively variable whereas those of non-algal matter are rather conserved. Variability in the performance of scatter corrections will mainly be determined by variations in the wavelength-dependence of scattering as well as variations in the absorption to scattering ratio. However, the scatter correction that takes some measured spectral characteristics of scattering into account (*proportional*) does not seem to perform better than the simple *flat* correction. In some cases (e.g. cultures) the variation of the relative error is even higher for the *proportional* correction method, which suggests that perhaps there is an important aspect of the scattering that has not been adequately parameterized. Wavelength-dependence in the VSF is a potential candidate for the missing element.

To conclude, because of the non-zero absorption at 715 nm, a_{ac-9} at longer wavelengths is strongly underestimated with the two regular correction methods. The underestimation of absorption at shorter wavelengths is lower, again as a function of the absolute absorption, but in extreme cases the error can still reach ca. \pm 30%. The results of the *flat* and the *proportional* methods are generally comparable. Hence, the commonly used scatter correction methods for ac-9 absorption measurements give reasonably good results in coastal waters for the shorter wavelengths only, but underestimate absorption at longer wavelengths due to non-zero NIR absorption that invalidates assumption (1). There is no indication at this point that one of the methods is significantly superior to the other, indicating that for coastal waters the variation of the absorption at >700 nm is the main error source with only a small contribution from variation in the wavelength-dependence of the scattering error. This situation might be different in the case of phytoplankton dominated samples due to very low NIR absorption by algae. In addition the measurement error of the ac-9 attenuation determination will influence the *proportional* correction.

3.6. Testing assumptions about scattering

The results obtained above raise questions about the validity of assumptions of wavelength independent scattering and VSF. The above results showed that there can be strong variations in the wavelength-dependency of total scattering measured with the ac-9, e.g., for cultures. On the other hand, they also showed that it is possible to obtain rather constant wavelength-dependency of total scattering in certain environments (e.g. Elbe samples) even when there is strong variability in the magnitude of the total scattering signal. For this data set we have seen that low variation in the wavelength-dependency of total scattering coincides with (and possibly causes) low variation of the absorption error.

The assumptions that total scattering is wavelength-independent (2) or that only the volume scatter function is wavelength-independent (3) were tested by using the 'true' absorption at 715 nm in the two regular scatter correction methods (Eqs. (3) and (4)). This avoids errors introduced by an invalid assumption (1). The 'true' absorption at all wavelengths was used for the calculation of total scattering, however the differences between using 'true' absorption or a_m were found to be negligible for the resulting estimates of scattering. These correction methods, $flat^+$ and proportional⁺ (see Table 1) were used with all samples and the deviations from the 'true' absorption calculated as above. Using the correct offset ($a_{m715} - a_{715}$) and subtracting this from all measured a_m values will shift the whole spectrum downwards, such that the absorption at 715 nm obtained from ac-9 measurements is correct by definition. Compared to the results shown above the deviations should be improved for longer wavelengths but should also lead to overestimations at shorter wavelengths, with the overall result being dependent on the absorption.

Fig. 7 shows the results for all sample sets for the *proportional*⁺ method. The absolute differences are now relatively low for longer wavelengths (630–676 nm), but increase towards shorter



Fig. 7. Absolute difference in m^{-1} between the absorption results of the *proportional*⁺ correction and the 'true' absorption as a function of a_{715} . Relative errors are depicted in the insets.

wavelengths, and are a function of a_{715} . In the extreme case the absorption at 412 nm is overestimated by ca. 0.7 m⁻¹. The relative errors are clearly independent of a_{715} and rather constant for each wavelength, especially at the shortest wavelengths. At longer wavelengths the variation of the relative error was still high, though this reflects generally lower signal levels at these wavelengths. Again, no general difference in error trend is observed for subsets of data, however, higher variability is found for data sets in which sample absorption was dominated by algae (*cultures* and *North Sea*). Now the



Fig. 8. Variations of the relative error $([a_{ac-9} - a]/a * 100)$ for the different scatter correction schemes, *flat*⁺, and *proportional*⁺. The subscript 'c' indicates that the attenuation was corrected for measurement errors, and 'e' that a_{ac-9} at 715 nm was estimated using Eq. (5) (see Table 1). Indicated is the number of samples used.

relative errors are more independent of a_{715} and it is reasonable to combine the data sets and present the errors statistically as box plots. This was done for the different scatter correction approaches, $flat^+$ and proportional⁺ (Fig. 8(a) and (b)). In addition we tested whether a proposed correction of the ac-9 beam attenuation measurement error improved the absorption determination, proportional⁺ (Fig. 8(c)). In this case the attenuation was corrected by dividing it by 0.56 to corrected for acceptance angle effects such that $b_m = (1/0.56)c_m - a_m$ (see Eq. (4) and Table 1). This factor was determined by Boss et al. (2009) when comparing ac-9 attenuation measurements with those made with a LISST 100X Floc. The acceptance angle of the ac-9 transmissometer is 0.93° in water, while that of the LISST instrument is 0.006° (Boss et al., 2009, their Table 1). We tested a range of values (0.64–0.4), but the best results (i.e. mean errors close to 0) were obtained with the factor of 0.56.

Including the 'true' absorption at 715 nm in the *flat*⁺ correction led to a systematic overestimation of absorption at shorter wavelengths. At 412 nm the absorption was on average about 10% too high; at 555 nm it was about 20% too high. At most wavelengths 75% of the sample's absorption values were in a range of $\pm 10\%$ to $\pm 20\%$ around these median values. The *proportional*⁺ correction also led to overestimations at shorter wavelengths, but it performed better than the *flat*⁺ correction: the average overestimation was maximally 10%, and the variation range for 75% of the data was maximally $\pm 10\%$. Including the additional attenuation correction further reduced the mean deviations from the 'true' absorption and the variation of these deviations over all samples. In this case the median of the error at 412 nm was very close to zero and 75% of the values were in the range of $\pm 5\%$ (Fig. 8(c)). The proportional correction, which takes wavelength-dependence of the total scattering into account, now performed better than a simple offset correction that assumes total scattering to be wavelength-independent. Using corrected attenuation to determine total scattering further improved the correction for absorption. This suggests that the assumption of a wavelength-independent VSF (3) is not a major source of error in most cases. However, remaining large deviations which ranged from -70% to 70% (extreme outliers in Fig. 8) were observed and were found to be associated with cultures and samples that were dominated by phytoplankton (note that due to the scale these extreme values are not shown in Fig. 7). This again supports the finding that the scattering properties of non-algal matter are rather conservative, whereas those of cultured algae are more variable. This variability is not properly accounted for with the applied corrections. Assumption (3), wavelength-independent VSF, therefore appears to be invalid when algal particles dominate the scattering signal. Although results from algal culture measurements cannot be directly translated into interpretation of oceanographic data, they point towards a possible explanation of our observation of increased variability in the spectral distribution of scattering in waters where phytoplankton dominate the scattering signal.

3.7. Empirical approach for scatter correction

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We have previously observed an empirical relationship between the 'true' absorption at 715 nm and the ac-9 offset error a_{m715} . In coastal waters, large values of a_{715} are most likely to be associated with strong concentrations of non-algal particles, though CDOM can also make a contribution, e.g., from freshwater inflows. The contribution from phytoplankton to a_{715} is generally very small. Therefore we can reasonably assume that high values of a_{m715} can be associated with non-algal particles and we have seen that the scattering properties of this material class appear to be relatively invariant. We therefore propose to use the empirical relationship between the true absorption, a, and measured absorption, a_m , at 715 nm (see Fig. 4) to estimate a_{715} from a_{m715} :

$$a_{715} = 0.212 \times a_{m715}^{1.135} \quad (n = 85, r^2 = 0.930).$$
⁽⁵⁾

Estimated values of a_{715} were included in the proportional⁺ correction (Eq. (4)), and the total scattering was determined with acceptance-angle related attenuation errors corrected with $e_c = 0.56$ (Table 1). The error of this empirical correction is shown in Fig. 9 and the error statistics are shown in Fig. 8 (lower right panel). The results are very similar to those when the 'true' a_{715} was used in the correction, except that variability in errors at each wavelength is slightly larger. The error for the determination of the absorption at 715 nm can be calculated and is basically the variation of the sample absorption in the relationship shown in Fig. 4. As the absorption at this wavelength is sometimes very low the relative error in 75% of the samples ranged between -30% and +30% (see Fig. 9).

4. Conclusions

The most commonly used scatter correction schemes for absorption measurements with an ac-9 strongly underestimate absorption of natural samples at longer wavelengths, with a trend towards increasing underestimation in more turbid waters. At shorter wavelengths the relative error is smaller as usually the absorption is higher and the error is partly compensated by an error related to the wavelength-dependency of the scattering error or the error of the attenuation determination. ac-9 absorption measurements for algal cultures did not appear to be systematically underestimated at longer wavelengths, but variability between different cultured species was higher than between different natural samples. The algal cultures did not possess strong absorption in the NIR region and the low absorption observed for algal cultures in this spectral region originated from the dissolved fraction not from the algal cells. The assumption of low absorption in the NIR presumably holds for algal cultures. The observation of higher variability in errors for algal dominated samples must therefore be attributed to significant variability in the scattering properties of different algal species. Similarly, the lower variability for natural samples from coastal waters dominated by non-algal particles could be explained by a rather conservative wavelength-dependency of total scattering and of the scattering phase function in coastal waters. In this case the main reason for the observed errors in the determined absorption is significant NIR absorption of natural samples. A simple relationship between absorption at a NIR wavelength and the measurement error in the ac-9 A-channel, together with a simple correction for the attenuation measurement error, significantly improves results



Fig. 9. Absolute difference in m^{-1} between the absorption results of the *proportional*^e_c correction and the 'true' absorption as a function of a_{715} . Relative errors are depicted in the insets.

for longer wavelengths. However, large relative errors remain in cases where strongly varying scattering properties of phytoplankton negatively affect the performance of all of the proposed scatter correction methods. This situation can be improved when additional information on the wavelengths-dependence of the VSF is available (McKee et al., 2008, 2013). The revised proportional scatter correction, *proportional*⁺, combining Eqs. (5) and (2b), is proposed as an improvement upon previous methods and is expected to have significant impact on data collected in turbid coastal waters. Further

work is required to establish the general applicability of Eq. (5) and comparison with the revised iterative correction method (McKee et al., 2013) would help to establish ac-9 performance limits for algal dominated waters. The key advantage of the *proportional*⁺ scatter correction is that it appears to improve data quality whilst remaining independent of any requirement for additional data. This makes it potentially suitable for retrospective application to historic data sets, potentially greatly enhancing their value for future studies.

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