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Flow-through-PSICAM: A new approach for determining water constituents absorption continuously

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Abstract

Determination of spectral absorption coefficients in seawater is of interest for biologic oceanographers for various reasons, but faces also several problems, especially if continuous measurements are required. We introduce the flow-through-point source integrating cavity absorption meter (ft-PSICAM) as a new tool for the continuous measurement of spectral absorption coefficients in a range of 400-710 nm. A description of the system is given and its performance in comparison with a conventional PSICAM has been evaluated on two cruises in 2011 in the southern part of the North Sea (German Bight). Furthermore, factors influencing the measurement are discussed. When comparing the data of both systems, a good linear correlation has been found for all wavelengths ($r^2 > 0.91$). Deviations between systems were different with respect to the wavelength examined with slopes of linear fits between 1.1 and 1.65 and offsets between -0.1 and 0.01, with the higher values at shorter wavelengths. They were caused mainly due to contamination of the flow-through system during operation by phytoplankton particles.

Focus was also laid on the measurement of chlorophyll-*a* concentrations ([chl-*a*]) and total suspended matter concentrations ([TSM]) on the basis of absorption coefficient determination. For this, appropriate relationships were established and [chl-*a*]- and [TSM]-values were calculated from the relevant ft-PSICAM absorption coefficients. Their progression matches well with the progression of fluorescence and turbidity measurements made in parallel. In conclusion, the ft-PSICAM is successful in measuring spectral absorption coefficients continuously and resolving relative changes in seawater optical properties.

Keywords: *Point-source integrating cavity absorption meter (PSICAM), absorption, continuous measurement, chlorophyll-a, total suspended matter, North Sea*

1. Introduction

Materials in seawater which absorb light in the visible part of the light spectrum are, apart from the water itself, the chromophoric dissolved organic matter (CDOM or gelbstoff) as well as living and non-living particles, i.e. phytoplankton particles containing different kinds of pigments and non-phytoplankton particles (detritus, mineral particles and heterotrophic organisms) (Babin et al. 2003; Bricaud et al. 1998). The corresponding spectral absorption coefficients are called a_{cdom} (CDOM) and a_p (particles), the latter subdivided into a_ϕ for phytoplankton pigments and a_{nap} for the non-phytoplankton part of particle absorption. Thus, determination of the spectral absorption coefficients of seawater is of importance, because they contain information about all these constituents. For example, a_ϕ can be used for the calculation of phytoplankton productivity as it allows to draw conclusions about the concentration of chlorophyll-*a* in a sample (Bricaud et al. 1998; Sathyendranath et al. 1987). Eventually, it can also provide information about phytoplankton taxonomy and size classes based on the different absorption properties of pigments abundant in different groups (Millie et al. 2002; Sathyendranath et al. 1987; Devred et al. 2011). Concentration and distribution of CDOM and non-phytoplankton particles (provided by a_{cdom} and a_{nap}) are important factors governing the light regime in the water (Bowers and Binding 2006; Nelson and Siegel 2013) and therefore influencing photosynthetic activity of the phytoplankton. Furthermore, information about a_{cdom} and a_{nap} are of interest for validation and calibration of remote sensing data or for comparison with model calculations. This is especially important in coastal regions, where both parameters do not necessarily covary with chlorophyll-*a* concentration (Babin et al. 2003; Tilstone et al. 2012). Concerning the measurement of spectral absorption coefficients there are two major issues: On the one hand, the measurements should be as exact as possible. On the other hand, they should be provided in a high temporal and spatial resolution, since trends and relative changes can only be inadequately resolved by point measurements. Furthermore, data obtained during operational measurements are considered to be useful for detecting long-time changes in phytoplankton biomass and composition, respectively, as well as single events like harmful algae blooms (HABs) (Cullen et al. 1997).

The measurement of spectral absorption coefficients in seawater deals with several difficulties, and different measurement techniques have evolved to encounter these problems: Simple photometric measurements of seawater are normally not useful, because of the usually low concentration of absorbing material in the sample. Additionally, loss of photons due to scattering on particles in the sample resembles a higher absorption than there actually is (Kirk 1994). A more elaborated, commonly used, and often modified measurement technique is the filter pad method (Yentsch 1962). Particles in a sample are concentrated on a glass fiber filter and filter and filtrate are measured separately to get a_p and a_{cdom} , respectively. The use of an integrating sphere even allows the collection of scattered photons (Maske and Haardt 1987). Nevertheless, using this method the optical path length is increased due to light reflections in the filter, and the absorption values have to be corrected to correspond to the absorption of the same amount of phytoplankton being in solution. The used correction factor (β) is still a source of uncertainty and controversy (Roesler 1998; Finkel and Irwin 2001). Finally, the different variants of the filter pad technique are laboratory-based methods which are not suitable for continuous or *in situ* measurement of absorption coefficients in seawater. For this purpose, different devices have been

developed in the last years: Reflective tube absorption meters (RTAMs) like the ac-9 and ac-s from WETLabs (Slade et al. 2010; Twardowski et al. 1999; Pegau et al. 1995), tethered optical profiling systems (TOPS), isotropic point sources (IPS), and compound radiometers. A comparison between these different systems is given by Pegau et al. (1995). A flaw concerning these methods is the remaining need for scattering correction.

Laboratory integrating cavity measurement systems like the ICAM (Elterman 1970; Fry et al. 1992; Pope and Fry 1997) and the technically simpler PSICAM (Kirk 1997; Leathers et al. 2000; Lerebourg et al. 2002; Röttgers et al. 2005) overcome the problem of particle scattering by introducing the sample in a diffuse light field set up in an integrating tube or sphere, respectively.

Scattered photons cannot go lost, but are reflected from the cavity wall until they are absorbed or reach the detector. Additionally, the optical path length is increased drastically by the reflective walls allowing the measurement of very clear waters with a relatively small device. Theoretical considerations and first experimental results concerning the construction of a flow-through device on the basis of an ICAM are given by Gray et al. (2006) and Musser et al. (2009), but the device has -to our knowledge- not been tested in the field yet.

In this contribution, we present a flow-through device designed on the basis of the PSICAM (ft-PSICAM) which combines the ability of measuring spectral absorption coefficients without the influence from particle scattering with the possibility of obtaining high-resolution data on a temporal and spatial scale. It is designed to be connected to a FerryBox (Petersen et al. 2011) which collects other parameters important for the correction of the absorption coefficients like salt and temperature.

Continuous, on-line measurements of total light absorption by all water constituents are performed with the ft-PSICAM in the field with a focus on the determination of [chl-*a*] as concentration of chlorophyll-*a* and [TSM] as concentration of total suspended matter. First, the performance of the ft-PSICAM is assessed by a comparison with measurements of discrete samples taken during stations using a controlled and continuously calibrated conventional PSICAM. Second, the necessary factors to convert the measured absorption coefficients to [chl-*a*] and [TSM] are determined by discrete measurements of these parameters in parallel to the continuous measurements.

2. Materials and methods

2.1 Study area

All data were collected during two ship cruises with the R/V “Heincke” conducted in April and June 2011 (Fig. 1). The German Bight is affected by different water masses: (i) The southern and eastern part along the coasts is influenced by runoff from the major rivers Ems, Weser, and Elbe as well as by freshwater discharge from the hinterland via the Wadden Sea, while (ii) the offshore areas have more open ocean characteristics. Therefore, the study area provides a broad spectrum with strong inshore - offshore gradients of relevant parameters like TSM and CDOM. According to HPLC and gravimetric measurements conducted in this study (see below), concentrations of chl-*a* reached from 0.004 to 16 $\mu\text{g L}^{-1}$, those

for TSM were in a range from nearly 0 to 34 g m^{-3} , just to give an impression of the diversity of the conditions.

2.2 Discrete measurements of chlorophyll, TSM, and absorption

During stations water samples were taken from the surface at a depth close to that of the water intake of the FerryBox system (ca. 4 m) by using a carousel water sampler (SBE 32, Sea-Bird Electronic, Inc.) equipped with seven 9-L sampling bottles (Hydrobios, Germany). The water samples were transferred from the sampling bottles into 10 L-PE containers and processed immediately for salinity (measured with WTW portable conductivity sensor), [chl-*a*], [TSM], and conventional PSICAM measurements.

2.2.1 Chlorophyll- *a*

Samples (1-5 L) for an analysis of [chl-*a*] were filtered onto 47 mm pre-combusted GF/F filters (Whatman, USA), flash-frozen in liquid nitrogen and stored at -80°C . Later in the laboratory the pigments in these sample filters were extracted with 100 % acetone at -30°C for 24 h. The extract was cleaned by passing it through $0.2 \mu\text{m}$ syringe filters (Spartan, A13) and transferred into 2-ml glass-vials. The pigments were separated and analyzed by high performance liquid chromatography (HPLC) using a HPLC system from JASCO (Japan) and the method described in Zapata et al. (2000).

2.2.2 Suspended matter

The particle mass concentration was determined by filtration of large volumes (1-8 L) of the samples on pre-combusted, pre-washed and pre-weighted GF/F filter ($\varnothing$ 47 mm, Whatman) as described by Van der Linde (1998). Some additional precautions were taken to reduce the influence of remaining salt in the filter (Stavn et al. 2009): (i) Before filtration, the filters were wetted with purified water to fill the rim of the filter, reducing the amount of salt that cannot be washed out after filtration by subsequently applied purified water. (ii) For each sample, three filters with different sample volumes were prepared. This was used to determine the salt offset from a linear correlation of the particle mass on the filter and the sample volume. A constant salt offset (0.1-0.5 mg) that is independent on the sample volume was observed by a bias of the linear regression line. This offset was subtracted from the measured mass and the mass concentration (in mg L^{-1}) calculated afterwards.

2.2.3 Single-point absorption measurements (PSICAM)

At the different stations, absorption measurements of surface seawater were made by a conventional PSICAM as described at Röttgers et al. (2005) and Röttgers et al. (2007). The only change was the usage of a Hamamatsu C10083CA mini spectrometer (Hamamatsu Photonics, Japan). For details of the theoretical principles of a PSICAM and the equations for the calculation of reflectivity and

absorption coefficients we refer to Kirk (1997), Leathers et al. (2000) and Lerebourg et al. (2002).

The PSICAM was calibrated once a day in triplicate using purified water (>18.2 MOhm) and nigrosine solution (an azine- and azo dye with relatively homogenous absorption coefficients over the visible spectrum) as described in Röttgers et al. (2005). The cavity was cleaned using a 0.1 % NaOCl (Riedel de Haën, Germany) solution for 15 min followed by rinsing of the cavity with purified water. The spectral absorption coefficients of the nigrosine solutions were measured in a liquid waveguide capillary cell (LWCC, path lengths: 0.5 and 2 m, WPI, USA) against purified water as a reference. All solutions with exception of those used for cleaning were adapted to the same (ambient air) temperature in a water bath prior to the measurements. Because the nigrosine solution is not stable over a longer period of time, for each calibration a fresh solution has been prepared. All PSICAM measurements were performed in triplicate. Previous to each sample, a reference measurement was made using purified water. Subsequent to the sample measurement the PSICAM was rinsed with purified water to remove the residues of the sample from the cavity and the reference was measured again. Temperatures of both reference and sample were recorded and used together with the determined salinity of the sample to correct their influence on the pure water absorption as described in Röttgers & Doerffer (2007).

2.3 Continuous measurements

During the entire cruises (i.e. both at stations and during transects), continuous measurements of chlorophyll-*a* fluorescence and turbidity have been performed by the use of a FerryBox system like it is described in Petersen et al. (2011). Its water intake was in the moon pool of the research vessel in around 4 m depth. Furthermore, continuous determinations of spectral absorption coefficients were performed in parallel using the ft-PSICAM. Sample water was supplied via a bypass from the FerryBox.

2.3.1 Continuous absorption measurements (ft-PSICAM)

The design of the ft-PSICAM is similar to the design of the conventional PSICAM used by Röttgers et al. (2005), but with a cavity made from PTFE which has been equipped with water in- and outlets to enable flow-through operation. It was installed into a setup of pumps, valves and tubes for water supply, drainage and supply of other fluids needed for the experiments. A detailed overview of the assembly is given in figure 2. For illumination of the cavity a 150 W IT 3900 lamp (Illumination Technologies, USA) was used. Light leaving the cavity was detected by a Ramses UV/VIS-spectrometer (TriOs, Germany) in a range from 400 - 710 nm. Thus, the detector was different from the one used for the conventional PSICAM. Other fluids besides the sample were supplied from separate containers: (i) Deionized water, (ii) purified water (> 18.2 MOhm), (iii) nigrosine solution, (iv) cleaning solution, a mixture of 1 % Extran[®] (Merck, Germany) plus 10 % Ethanol, and (v) 0.5 % NaOCl (Riedel de Haën, Germany) solution. The entire system was operated by a custom-made control software programmed in LabVIEW (National Instruments, Germany), which provided the opportunity either to run the system automatically in a pre-defined instruction

flow or to operate it manually by switching on the different pumps and valves. For the experiments performed for this study, the latter mode was used.

Due to the design as a flow-through device, all fluids were pumped into the cavity by activating the corresponding valves and pumps. No manual handling or opening of the cavity was necessary.

The principle of calibration and the equations for the calculation of spectral absorption coefficients are the same for both the ft-PSICAM and the conventional PSICAM. Calibration of the device was performed once a day in the same manner as for the conventional PSICAM, but with a modified cleaning step: In order to clean the system after each calibration measurement, first the cleaning solution was cycled from its container through the cavity for 2 min, afterwards the same was done with the bleaching solution for 5 min. Subsequently, the cavity was rinsed first with deionized water, then with purified water.

Sample measurement in ft-PSICAM and conventional PSICAM differed from each other. In the latter case, a reference measurement was made right before each sample. In contrast, as the flow-through system measured water samples continuously every five seconds during the time of the cruise (6 - 7 days), purified water as reference was only measured a few times a day, commonly at the stations (see below). To get artificial reference data for absorption coefficient calculation in the time between the stations, measured reference data were interpolated linearly. The calculated spectral absorption coefficients were corrected for the influence of salt and temperature in the same manner as described for the conventional PSICAM, but using the values measured by the FerryBox instead of manual measurements. Afterwards, the data were averaged in a one minute interval.

Measurements during the stations were used to assess the performance of the ft-PSICAM in comparison to the conventional one as well as to check the stability of the system under field conditions. Discrete sample measurements (1 min duration), were performed at the beginning and the end of every station. Each of the sample measurements were accompanied by a reference measurement. After the measurements at the beginning, the ft-PSICAM was cleaned and the measurements were repeated. The detailed measurement sequence at the stations was as follows: Sample measurement, reference measurement, cleaning, reference measurement, sample measurement. Sample data from the beginning and the end of each station were used to estimate the effect due to contamination of the system on the measurements.

2.3.2 Fluorescence and turbidity measurements

Chlorophyll-*a* fluorescence and turbidity have been continuously measured with a SCUFA-II-sensor (Turner Design, USA) mounted in the FerryBox system. It uses a prompt fluorescence method for chlorophyll-fluorescence. Turbidity is determined by measuring light scattering at 90°. Calibration of the sensor has been performed by the manufacturer and was checked before the cruise by using a solid fluorescence standard provided by the manufacturer.

3. Results and discussion

3.1 Assessment of the flow-through-PSICAM

Automatic absorption measurements with the ft-PSICAM were compared to measurements of discrete samples with the conventional PSICAM in the on-board laboratory. The conventional PSICAM was cleaned and calibrated very regularly, thereby it provided data with a measurement error $< 3 \%$ for the spectral range of 400 – 700 nm (Röttgers et al. 2005) and was used as reference method.

Figure 3 shows examples of spectral absorption coefficients of the seawater constituents (a_{p+cdom} , for the sum of particulate and dissolved fraction) from both cruises (April and June 2011) measured with both PSICAM versions. The data presented for the ft-PSICAM are from measurements at the beginning of each station, before the system had been cleaned. Samples are exemplarily shown from locations that strongly differ in the absolute light absorption, from values as low as 0.05 m^{-1} to up to 1 m^{-1} (Fig. 3). Both PSICAM systems showed a progression of the spectral absorption coefficients with wavelengths that is typical for marine waters: Highest absorption was observed in the blue portion of the light spectrum, mainly caused by phytoplankton pigments and CDOM, and the absorption decreased with increasing wavelength, with exception in the red part of the spectrum where an absorption peak around 675 nm related to chl-*a* was visible. Here, absorption is dominated by phytoplankton pigments and, to a lower extend, by non-phytoplankton particles, while CDOM absorbs only weakly (Roesler et al. 1989; Kirk 1994). As it can be seen from figure 3, the spectral absorption coefficients determined by both the ft-PSICAM and the conventional one were not identical in their values, but were similar in their progression. In the next section, the differences in the absolute values are quantified and the reasons are discussed.

3.1 Deviations of spectral absorption coefficients

It can be observed that the deviations - both on absolute and relative basis - varied on one hand between the cruise stations and, thus, with time and space, and on the other hand they were wavelength-dependent (Fig. 4). On average, the ft-PSICAM generated higher absorption coefficients than the conventional PSICAM; lower values for the whole spectrum were only measured for some stations, as well as for most of the stations in the red spectral region, predominantly above 700 nm. Because of the low absolute values at longer wavelengths, there was a tendency of higher relative deviations with increasing wavelength. Generally, the deviations were higher for the cruise in April than in June. Measurements at the beginning of the station were repeated after the ft-PSICAM had been cleaned. The aim was to evaluate the effect of the cleaning procedure that should remove possible contaminations of the instrument. It can be seen that the values measured at begin of the stations (uncleaned; Fig. 4A) differed more from the conventional PSICAM than those measured at the end (cleaned; Fig. 4B).

These deviations are the result of a composition of different factors affecting the ft-PSICAM measurements. In the following section, the deviations are explained in the context of factors influencing the measurement and calculation of the spectral absorption coefficients:

(i) Imprecision in the calibration procedure

Determining the PSICAM's cavity wall reflectivity during the calibration measurements is a critical factor for the retrieval of the spectral absorption coefficients. An error of 1 % in wall reflectivity induces an error in the absorption determination by ca. 10 % (Leathers et al. 2000).

Calibration of the ft-PSICAM has been performed once a day and several reflectivity spectra were obtained during both cruises. The reflectivity varied by 0.4 - 1.3 %, depending on the wavelength (Fig. 5). Besides actual measurement errors during calibration, the variations resulted mainly from contaminations inside the cavity. The differences in the spectral shape of the reflectivity between both cruises could not be readily explained, but they are likely related to the composition of contaminations remaining in the cavity. Because reflectivity determination has been performed irregularly and the ft-PSICAM has not been cleaned in advance, the observed variation is considered to cover the total range of wall reflectivity values for both cruises. A certain bias was introduced in the data by using a mean reflectivity value for the calculation of the spectral absorption coefficients instead of the (not known) true reflectivity at the time of the sample measurement. In order to estimate this effect, the absorption coefficients were recalculated with the mean reflectivity of each particular cruise and with reflectivity values of mean $\pm$ standard deviation. Comparing the results, the spectral absorption coefficients varied between $\pm$ 6 % in the blue spectral region and $\pm$ 4 % in the red region for the cruise in April; for the cruise in June, the values were $\pm$ 11 % and $\pm$ 2 %, respectively.

Hence, on a relative basis, these variations were generally lowest at longer wavelengths. This is expected as contamination by particles inside the cavity would lead to an influence proportional to their absorption which is typically low at longer and high at shorter wavelengths. Especially at the construction parts of the openings of the cavity it was observed that residues of particles were not always completely removed by water flow or the cleaning procedure and thus could have affected the reflectivity measurement. In addition, the design of the ft-PSICAM as an automated device without manual handling might also have had an influence on the calibration: When filling the cavity automatically, it is possible that a certain amount of air remained in the cavity during calibration measurements which could have biased the results. Furthermore, after draining the system, small leftovers of the previous measured liquid (nigrosine, purified water, cleaning or NaOCl solution) might have remained in the tubes and valves. This could have altered the absorption properties of the reference or the nigrosine solution in the subsequent measurement.

(ii) Degradation of the wall reflectivity by contamination

As shown in figure 4, the deviations between the conventional and ft-PSICAM measurements were smaller at the end of a station (Fig. 4B) than at the beginning (Fig. 4A). Because the two measurements were separated by two reference measurements and cleaning of the cavity, this change was most likely caused by contaminations that had accumulated at the cavity wall during the flow-through operation and that were removed by the cleaning procedure. To determine the effect of cleaning and to identify the type of particles contaminating the cavity, we examined the ratio of light

intensity of the reference measurements before and after the cleaning as a function of wavelength. The value would be 1 at a given wavelength, if no contamination was present in the cavity before cleaning, and decrease with amount of contamination. Depending on station and wavelength, we obtained values between 1 and 0.9. They were subtracted from 1 to get the relative light loss caused by removable contamination. In figure 6A, typical examples are given. As it can be seen, the progressions of the curves resemble phytoplankton absorption spectra, indicating that the contaminants that accumulated in the cavity were predominantly phytoplankton cells. In order to give a scale for the effect of this contamination-induced light loss, figure 6B shows the loss of light which occurs during normal sample measurements at the same stations for comparison. It is calculated from light intensity of a sample measurement divided by light intensity of the according reference measurement. This ratio is subtracted from 1 to get the light loss. Roughly, the loss of light due to contaminations was about 20 % of that one during the according sample measurements.

It is important to note that these effects are limited to that part of the contamination that was removable by cleaning: Thus, the cleaning was likely not exhaustive, since we still had differences between both PSICAM systems afterwards (Fig. 4B). Hence, there was probably a persistent contamination which has not been removed by the cleaning procedure.

(iii) Temperature effects

The sample measurements of the ft-PSICAM were corrected for the effect of temperature differences between sample and reference. For this purpose, temperature values obtained by the FerryBox as well as by hand-made temperature measurements (in case of the reference measurement with purified water) were used (Röttgers and Doerffer 2007).

Nevertheless, high values for relative deviation between both PSICAMs above 590 nm with distinct features at 606 nm, 660 nm as well as above 690 nm (Fig. 4) indicated substantial errors in this correction due to a wrong determination of temperature, as at these wavelengths water absorption is especially influenced by temperature (Buiteveld et al. 1994; Röttgers and Doerffer 2007). A potential temperature change of 1 °C can alter the absorption by 0.00106 m^{-1} at 606 nm and 0.00085 m^{-1} at 710 nm, for example, which is in average about 3 % of the total absorption measured at these wavelengths.

The major source of errors regarding temperature was that it has not been directly measured inside the cavity, but in the FerryBox or – in case of the reference – in the storage container. On their way from the point of measurement to the cavity, one or both of the solutions probably changed their temperatures. In that case, the effective discrepancy in temperature between sample and reference were different from the measured one, which led to an improper correction of the data. This is also an explanation why deviations from the conventional PSICAM at the beginning of the station were higher in April than in June. In April, the average temperature over the whole cruise was ca. 6 °C for the samples and ca. 18 °C for the references, respectively. Thus, at the beginning of the station, the reference temperature has been determined in its container, but then the reference was pumped into the (due to the previous continuous measurement) relatively cool flow through-system and might also have cooled down. In

this case, the temperature difference between sample and reference would have been smaller in comparison to the previous determined difference. This led to an overcompensation of the temperature difference in the calculations. After the cleaning, the ft-PSICAM system was probably warmer and the reference has not been cooled down so much. Therefore, the real temperature difference was closer to the measured one and the differences between both PSICAMs were smaller. In contrast, the temperature difference between sample (average 14 °C) and reference (average 17 °C) were generally smaller in June. Consequently, this effect can be neglected for this cruise. In order to avoid such problems in the future, a temperature sensor should be installed directly in the cavity or at its inlet. This would also eliminate the need of manual temperature measurement of the reference water in its container.

(iv) Instability of light intensity

This paragraph discusses errors introduced in the measurements by instabilities in the optical setup of the ft-PSICAM. While fluctuations in overall light intensity of the lamp itself (e.g. due to aging) were detected via a sensor and corrected in our calculations, the light intensity within the cavity is also variable. It can vary due to contamination of the central light source's surface or due to shifts of the glow filament within the lamp, which alter the amount of light getting into the fiber optic to the central light source. Both effects cause changes in light intensity observed by the detector, although the true absorption properties of the sample remain unchanged. Additionally, aging of the lamp could also have an effect on the spectral composition of the emitted light besides its overall intensity. The reference measurement of purified water corrects for these instabilities, thus, they are not crucial for the absorption coefficients measured at the stations. But they might play a role for the continuous measurements, where no references have been made over a longer period of time. Our approach was to assume a linear development of light instability related to setup-variations and therefore interpolate the values between the reference measurements made at the stations in a linear way. In reality, this development is unlikely, because there are probably short-time fluctuations in the light regime of the cavity (caused by the above named factors) in both ways. This is a problem inherent in the principle of continuous measurements performed with the ft-PSICAM. Thus, a determination of the error of the continuous measurement in relation to a certain time cannot be given in the context of this work, but we can assume that the error shortly after each station, when the system has been cleaned and a reference measurement was made, is relatively small but increases with time due to contaminations. However, a possible correction for setup-related light instabilities during the continuous measurements could be achieved by a permanent, direct determination of light leaving the central light source. For this, a direct connection from the light source's surface to a photospectrometer is needed. But this would probably alter the optical properties of the cavity and would require further testing. Moreover, changes caused by contamination of the light source's surface would not be detected in this way, because the light source would not contaminate at the point of measurement.

(v) Variance in the detector response

During the cruise, also the light detection by the spectrometer used might have varied to a little extend. The detector signal can be influenced by changes in internal stray light, the nonlinearity response, and the dark offset due to changes in temperature. The influences of these parameters have not been investigated in particular during this study, but are considered as negligible.

(vi) Setups and sampling procedures

At last, factors related to the setup and the different sampling procedures of both PSICAMs likely contributed to the differences in measured spectral absorption coefficients. Different detectors have been used for the conventional and the ft-PSICAM. The slight increase observed at a_{p+cdom} above 700 nm for the conventional PSICAM (compare Fig. 3) is probably an artifact related to a stronger internal stray light error of the used Hamamatsu-detector (Röttgers, unpublished). Additionally to the temperature-related effects, this contributes also to the deviations above 700 nm. Furthermore, the differences in the sampling procedure can also have a certain influence on the measurements. Water for the conventional PSICAM was sampled in Niskin bottles, while the FerryBox and the associated ft-PSICAM got their water via an impeller pump. For the conventional PSICAM there might have been subsampling effects, even if the samples used have been mixed very carefully. On the other side, shear effects caused by pumping the sample into the ft-PSICAM could also altered the optical properties in the sample, inasmuch as phytoplankton chains or cells might have been damaged. Furthermore, it should be mentioned that time and place of both sampling methods were not necessarily completely identical because of the different sampling procedure of both systems. It is possible that the water mass had changed during the time span of the station (10-25 minutes) due to ship movement, so that the ft-PSICAM indeed measured two slightly different water bodies at the beginning and the end of the particular station. An obvious example of a deviation between ft-PSICAM and conventional PSICAM resulting from a change in water mass can be seen at the station shown in brackets in figure 7B. As it can be seen, the station lies at the edge of an absorption peak. This results in a high deviation when the ft-PSICAM data for the beginning of the station are used; if the data from the end are used, the deviation is in the range of the fit shown in the inlay graphic. That this is not entirely due to the effect of the cleaning can be seen from the fluorescence data (not shown), where the same strong gradient for this station is visible. Thus, if a gradient is present, minor differences in the time of the sampling can result in high differences between both measurement systems. But this should be the exception; normally, differences according to changes in water properties during the measurements are considered to be of minor importance compared to those resulting from contamination and calibration imprecisions. For verification of this assumption, the issue of the effect of different sampling procedures on the results should be incorporated in future tests of the ft-PSICAM.

Several of these factors are interacting with each other, thus, it is difficult to separate their exact contribution to an observed deviation between conventional and ft-PSICAM at a certain station. Despite all potential sources of errors, the general progression of the continuous measured data is in good agreement with

the point measurements of the conventional PSICAM (exemplarily shown for a_{p+cdom} at 676 nm in Fig. 7). The inlay in figure 7 shows the correlation between the data of both systems at the stations for this wavelength. The applied linear fit has a small offset, but the relative deviation represented by the slope of the fit of 14 % in April and 20 % in June is of more importance.

For other wavelengths, we also found good linear correlations with $r^2 > 0.91$ in all cases; slopes vary between 1.1 and 1.65, offsets between -0.1 and 0.01, depending on cruise and wavelength (Fig. 8). It can be seen that features related to the temperature effects and pure water absorption were visible in the progression of the slope over wavelengths, and, to a lower extent, in the progression of the offsets. This is an indication for a combined influence of relative (e.g. cavity wall reflectivity) and absolute (e.g. temperature effects) errors on the spectral absorption coefficients determined with the ft-PSICAM, whereupon the relative error is the major one.

3.2 Determination of chlorophyll-a and TSM based on absorption measurements

3.2.1 Chlorophyll-a determination

To determine [chl-*a*] on the basis of the phytoplankton spectral absorption coefficient (a_ϕ), often particular absorption (a_p) of a water sample is measured by the quantitative filter techniques according to Yentsch (1962). Subsequently, the proportion of non-algal particulate matter (a_{nap}) on a_p is determined by extracting the pigments with organic solvents e.g. (Kishino et al. 1985) or by bleaching the sample (Tassan and Ferrari 1995). The difference between both results in a_ϕ . When using the ft-PSICAM, the absorption of the different water constituents cannot be separated. Therefore, to establish a relationship between absorption measurements and [chl-*a*] in a sample, we have to use the absorption coefficient at the red chl-*a* absorption maximum at 676 nm. At this wavelength, the absorption associated with CDOM is negligible, and the measured absorption of water constituents is only related to due to a_p . However, to get a_ϕ at this wavelength, still a_{nap} has to be subtracted.

As methods for a_{nap} determination like bleaching or extraction of pigments are not suitable in our case, a_{nap} at 676 nm had to be estimated. Since a_{nap} is increasing with decreasing wavelength in a nonlinear manner, its values can theoretically be calculated using the appropriate slope and equations given e.g. in Bowers and Binding (2006) and Bricaud et al. (1998). The basis of such calculations would be measurements of a_{nap} virtually free of the influence from phytoplankton pigment absorption. But such values would only be obtained at wavelengths considerably higher than 710 nm, the limit of reliable ft-PSICAM-measurements, because water absorption increases strongly in this region (Pope and Fry 1997). Since calculation of a_{nap} at 676 nm is not applicable, we used an alternative approach to get a reliable value for a_ϕ at 676 nm: The value of a_{nap} at 676 nm was estimated by assuming that a_p at 700 nm (composed of a_{nap} and a little portion of a_ϕ) is a reasonable representative of a_{nap} at 676 nm, because its portion of a_ϕ is equivalent to the real increase of a_{nap} from this wavelength to 676 nm. In order to test this approach, we subtracted a_p at 700 from a_p at 676 nm to get estimated values for a_ϕ at 676 nm. The latter ones were correlated with HPLC-measured [chl-*a*] and fitted in a linear way (Fig. 9A), assuming a linear relationship according to

Lambert-Beers law. The basis for these considerations was the absorption coefficients obtained with the conventional PSICAM, because of its higher accuracy compared to the ft-PSICAM. The coefficient of determination was $r^2=0.84$, with a slope of 0.018 and an offset of 0.005. Thus, the absorption at 700 nm is a good estimation of a_{nap} at 676 nm and we get a reasonable estimation for a_ϕ at 676 nm, when we subtract it from a_p at 676 nm. A direct correlation of a_p at 676 nm with [chl-*a*] would result in a much weaker correlation ($r^2=0.63$) with a higher offset (0.019) and a different slope (0.026). This demonstrates the influence of a_{nap} in the region of the red chl-*a* absorption maximum.

The variability in the linear relationship between a_ϕ at 676 nm and [chl-*a*] observable in figure 9A is caused only to a minor degree by measurement errors of [chl-*a*] and absorption coefficients, because both HPLC and conventional PSICAM measurements have a high accuracy. Instead, the main factor is the natural variability of the *in vivo* chlorophyll-specific absorption coefficient. It is depended on the relationship between cell size and intracellular pigment concentration, the so called ‘pigment packaging effect’ (Kirk 1976; Morel and Bricaud 1981). Therefore, the same amount of pigment can result in different absorption coefficient values at a given wavelength. In addition, the *in vivo* chlorophyll-specific absorption coefficient can be altered due to changes in pigment composition (Hoepffner and Sathyendranath 1992). This affects predominantly the blue region of the spectrum, as most of phytoplankton pigments absorb to a considerable amount there. In the red region, pigment composition virtually affects the chlorophyll-specific absorption coefficient only in the presence of chlorophyll-*b* or phycocyanin. But as both pigments do not have an absorption maximum in this region, only high amounts of these pigments are expected to have an effect. According to our HPLC measurements, the concentration of chlorophyll-*b* is (with exception of one station) never higher than 20 % of [chl-*a*] during the cruises (data not shown). Concentration of phycocyanin has not been determined. For our data, the values for the *in vivo* chlorophyll-specific absorption coefficient at 676 nm were in a range of 0.01 – 0.04 m² mg⁻¹. Since the maximal value caused by pigment packaging is considered to be 0.033 m² mg⁻¹ at this wavelength (Johnsen and Sakshaug 2007), the higher values indicate in fact an influence by pigment composition in addition to the packaging effect.

The high variability of the chlorophyll-specific absorption coefficient is probably linked to the broad spectrum of life conditions in our sampling area, which reached from almost oceanic to very turbid coastal and brackish waters. This results in a high diversity in phytoplankton community, including different species, pigment compositions and size classes. A regional variability of the chlorophyll-specific absorption coefficient according to different phytoplankton communities has been previously found by e.g. (Hoepffner and Sathyendranath 1992) in the western North Atlantic and by Staehr et al. (2004) in a transect from Danish coast to Greenland Sea. Bricaud et al. (1995) found a variability of the chlorophyll-specific absorption coefficient with a range from 0.01 to 0.06 m² mg⁻¹ at 675 nm in samples from different regions of the world, which is similar to our observations for the North Sea.

3.2.2 Total suspended matter determination

In order to derive also a proxy for [TSM] from our absorption measurements, a similar simple approach as for [chl-*a*] was used: We correlated the absorption coefficient at 700 nm with gravimetrically determined [TSM] data. The resulting correlation was quite strong with $r^2 = 0.95$, a slope of 0.014 and an offset of 0.006 (Fig. 9B). Thus, a linear relationship between a_p at 700 nm and [TSM] in the water is approved, while the influence due to CDOM and pigments is negligible at this wavelength. Wavelengths above 700 nm could in principle also be used to establish a linear correlation with [TSM], but they were not used because of the stray light error of the Hamamatsu spectrometer in this region mentioned above. A correlation between [TSM] and [chl-*a*] (not shown) exhibited no linear relationship between both parameters. This indicates a considerable contribution of other particles than phytoplankton to the [TSM] in the water. This is not surprising, as a relatively large proportion of our study area is located close to the shore or is influenced by riverine input.

3.2.3 Comparison of [chl-*a*] to both fluorescence and turbidity measurements

The established relationships between absorption coefficients, [chl-*a*] and [TSM] (Fig. 9) can now be applied to derive continuous [chl-*a*] and [TSM] data from our ft-PSICAM measurements. However, for calculation purposes, we decided to force the appropriate fits through zero, because it is physically true. Additionally, this avoids getting negative values when dealing with absorption coefficient values smaller than the offsets. This resulted in slightly altered slopes of 0.019 (formerly 0.018) for [chl-*a*] and of 0.015 (formerly 0.014) for [TSM] calculation, respectively.

Furthermore, the obtained spectral absorption coefficients from the ft-PSICAM were corrected with the data of the conventional PSICAM measurements. For a_p at 700 nm, the slope and offset of the fit between both PSICAMs at the particular cruise for this wavelength was used (Fig. 8). In order to get corrected values also for a_ϕ at 676 nm, we estimated them for the ft-PSICAM station measurements as described above for the conventional PSICAM. In a second step, they were correlated with the corresponding values obtained with the conventional PSICAM (Fig. 10). The offsets in the linear fits for both cruises are insignificantly small, thus the fits were again forced through zero; the final slopes used for the correction of a_ϕ at 676 nm were 1.17 for April and 1.13 for June, respectively. This means that even the uncorrected ft-PSICAM data have only an error regarding [chl-*a*]-determination of max. 17 %.

The resulting progression of the calculated values for [chl-*a*] and [TSM] are in good agreement with chl-*a* fluorescence and turbidity measured by the FerryBox (Fig. 10). Although the values for fluorescence and turbidity are not calibrated for [chl-*a*] and [TSM] and the data are therefore not directly comparable, the similarities in the curves indicate that our measurements as well as our correction approaches were sufficient. Small fluctuations, as can be seen during the April cruise for ft-PSICAM-[TSM] at low concentrations, cannot be identified as real or artifacts due to temperature effects or reference interpolation. They have to be further investigated, especially as they did not appear during the cruise in June at similar concentrations.

3.3 Conclusion and outlook

In summary, absolute spectral absorption coefficients continuously measured with the ft-PSICAM differ from those obtained with the conventional PSICAM under laboratory conditions. Main factors influencing the determinations of the spectral absorption coefficients are: (i) Imprecision according to the calibration procedure, (ii) contamination-induced degradation of the cavity wall reflectivity during operation, (iii) instability in the reference light intensity (not at the station measurements), and (iv) improper temperature correction. The differences between conventional and ft-PSICAM vary with time and wavelength, but are primarily important on a relative basis, and can therefore be corrected to a large degree by some discrete validation measurements with the conventional PSICAM. But as such comparison measurements are not possible if the system is used as unattended device in the FerryBox, for example, effort should be made to improve the system in order to reduce the observed deviation between ft-PSICAM and conventional PSICAM. This concerns setup modifications as well as changes in the measurement process. A major improvement would be the use of a solid object for calibration, because it would eliminate the need to prepare and handle the nigrosine solution. The duration of the calibration would be reduced, because the cleaning step after the use of the nigrosine solution could be omitted, which would allow a more frequent calibration. However, this would be a difficult technical challenge; a possible solution would be the installation of a small retractable bolt in the cavity wall. Furthermore, temperature should be measured directly in or close to the cavity, to avoid discrepancies between the measured and the real temperature in the cavity. Completing the automation of the system would allow a more regular measurement routine concerning regular cleaning intervals, reference measurements and calibrations, even during the night time. Furthermore, experiments should be made to invent a more effective cleaning procedure to prevent contamination of the cavity wall and the central light source. Nevertheless, in conclusion and despite all possible improvements of the system, the general approach to develop a system for the continuous measurement of seawater absorption was already successful: The obtained continuous data are consistent with the pattern shown by the point measurements. Furthermore, when converting the appropriate absorption coefficients to [chl-*a*] and [TSM], the resulting curves are also confirmed by fluorescence- and turbidity-measurements of the FerryBox. Hence, the ft-PSICAM offers the possibility to determine relative changes of water constituent absorption in a very high temporal resolution. Fronts and trends in the optical properties of seawater can be observed in this way, which is not possible with single-point measurements. Because a whole absorption spectrum is measured instead of single absorption coefficients at defined wavelengths, the obtained data can be used not only for [chl-*a*] or [TSM] determination, but also for other purposes like the discrimination of phytoplankton groups due to their specific pigment absorption properties. Furthermore, as with absorption a direct physical property of chl-*a* is measured, the determination of [chl-*a*] based on this method is not biased by quenching effects resulting from the physiologic state of the photosynthetic apparatus, as it is the case when measuring chl-*a* fluorescence. The only variation is caused by the natural variability of the chlorophyll-specific absorption coefficient. In contrast to fluorimetric determinations, scattering effects are negligible using the ft-PSICAM at low chl-*a* concentrations even in high turbid waters and is supposed to be the preferred probe for investigations regarding [TSM] and [chl-*a*].

Appendix

Tab.1 Abbreviations used in the text

a_p	absorption coefficient of particulate matter [m^{-1}]
a_{cdom}	absorption coefficient of dissolved matter [m^{-1}]
a_ϕ	absorption coefficient of phytoplankton pigments [m^{-1}]
a_{nap}	absorption coefficient of nonalgal particulate matter [m^{-1}]
CDOM	chromophoric dissolved organic matter
chl- <i>a</i>	chlorophyll- <i>a</i>
[chl- <i>a</i>]	concentration of chlorophyll- <i>a</i> [mg m^{-3}]
TSM	total suspended matter
[TSM]	concentration of total suspended matter [g m^{-3}]

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Figure captions

Fig. 1 Map of standard cruise tracks and sampling sites in the German Bight

BE=Belgium, DK=Denmark, DE=Germany, IE=Ireland, NO=Norway, NL=Netherlands, SE=Sweden, UK=United Kingdom. The depth profile is represented by the different shades of grey (from light for shallow to dark for deep areas). Named stations are referring to the examples shown in figure 3. The map was created with Ocean Data View Software (Schlitzer 2011)

Fig. 2 Flowchart of the ft-PSICAM. V= valve

Fig. 3 Spectral absorption coefficients obtained with both conventional (black line) and ft-PSICAM (grey line) in the range of 400 to 710 nm at different stations in the German Bight during cruises in April and June 2011. Note the different scale of ordinates for the stations

Fig. 4 Deviation of the ft-PSICAM from the conventional PSICAM for the different stations of both cruises (April and June) depending on wavelength. Absolute values are displayed at the left side, relative values at the right side. (a) Deviations at the begin of the station (uncleaned system), (b) deviations at the end of the station (cleaned system)

Fig. 5 Measurements of the cavity-wall reflectivity for both cruises in April and June 2011. Single measurements are pictured in grey, the mean value in black with the standard deviation as error bars

Fig. 6 Effect of cavity wall contamination on the measured light intensity. (a) Light loss caused by contaminations on the cavity wall, calculated from the reference measurements of purified water

made before and after the cleaning (b) For comparison, light loss occurring during sample measurements on the same stations, calculated from the sample and the reference measurement before the cleaning. Note the different scales of both graphs.

Fig. 7 Values for a_{p+cdom} at 676nm derived from ft-PSICAM (grey dots) and conventional PSICAM (black dots) in (a) April and (b) June 2011. Gaps in the timeline are due to maintenance work, calibrations or deletion of data points with obviously incorrect spectra. Inlay graphics show the correlation between the values from both systems at the cruise stations. The value in brackets was omitted

Fig. 8 Results of linear fits applied to the station data of both PSICAMs. The fits were done for each wavelength separately. (a) Slope and (b) offset were plotted in dependence of wavelength

Fig. 9 Linear fit between (a) a_ϕ at 676 nm and HPLC-measured [chl- a], (b) between a_p at 700 nm and gravimetrically determined [TSM]. Both absorption coefficients were measured with the conventional PSICAM. n= number of samples

Fig. 10 Correlations with linear fits between estimated a_ϕ at 676 nm derived from conventional and ft-PSICAM for both cruises in April and June, respectively. Fits are quite similar; therefore the lines of the fits are hardly distinguishable

Fig. 11 Calculated values for (a) [chl- a] and (b) [TSM] on the basis of a_ϕ at 676 nm and a_p at 700 nm, respectively, measured by the ft-PSICAM. Calculations were done for both cruises and compared with chlorophyll-fluorescence and turbidity measurements, respectively

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