Mass-specific light absorption coefficients of natural aquatic particles in the near-infrared spectral region

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Abstract

The extent of light absorption in the near-infrared spectral region (NIR; 700–900 nm) of natural suspended particles was investigated by determining the absorption and mass-specific absorption coefficients of samples from different environments: river, coastal waters, tropical lagoon, and oceanic waters. Large amounts of sample were collected onto glass-fiber filters and measured inside the integrating sphere of a spectrophotometer. The absorption coefficient of particle suspension was also determined for visible wavelengths with a point-source integrating cavity absorption meter. Measurable nonzero particulate absorption in the NIR was determined in all samples, even in algal cultures. It was highest in the river samples (e.g., 1.7 m^{-1} at 850 nm), reaching values similar to the NIR absorption of pure water—a strong NIR absorber. Lowest values were in oligotrophic waters and in algal cultures. Ratios of absorption at 750 nm to absorption at 442 and 672 nm varied between 2% to 30% and 3% to 80%, respectively. Mass-specific absorption in the NIR at 850 nm was also highest in the river (0.012 m^2 g^{-1}) and lowest in oligotrophic waters (0.002–0.003 m^2 g^{-1}). The observed NIR absorption can partly be explained by absorption of minerogenic particles, whereas the contribution of organic detritus to the NIR absorption is still mostly unknown.

Light absorption in natural waters in the ultraviolet (UV; wavelengths 280–400 nm) to visible (VIS; 400–700 nm) spectral range is dominated by absorption of dissolved and suspended matter. In the near-infrared spectral region (NIR; 700–3000 nm) it is generally thought that absorption by water is the dominant contribution. The strength of absorption by natural particles in the NIR region remains an open question (Babin and Stramski 2004; Woźniak and Dera 2007; Stramska et al. 2008).

For natural water samples, optical techniques are available that provide detection of certain classes of relevant absorbers in water, such as: chromophoric dissolved organic matter (CDOM), phytoplankton, and biogenic and minerogenic suspended detrital matter in the VIS region. With the exception of distinct absorption maxima by phytoplanktonic pigments, the light absorption of matter in natural waters continuously decreases with increasing wavelength, at least for the range of wavelengths at which measurements are usually conducted (i.e., 300–900 nm). Both dissolved and particulate non-algal matter exhibit a very strong absorption in the UV region and lower absorption in the VIS. The absorption in the NIR region is often thought to be negligible, and the signal measured here is used to compensate for scattering errors.

This common practice (referred to as null-point correction) often involves subtraction of a substantial observed signal (sometimes greater than the residual left after null-point correction) and directly affects final values of absorption across the entire spectrum. This null-point correction is based on assumptions that absorption by particles in the NIR is negligible and scattering by particles is wavelength independent.

The light absorption of CDOM and algal pigments dissolved in an organic solvent in the NIR is very low and can be neglected in most cases. Their absorption can be measured quite accurately because, when dissolved, scattering by these molecules is very low compared to that of water molecules. Suspended particulate matter does scatter light, and accurate absorption measurements for particles require a methodology without any scattering error.

The VIS to NIR light absorption by minerogenic particles has been investigated in studies to determine the influence of mineral particles on in situ optics in the ocean (Babin and Stramski 2004; Stramski et al. 2007; Stramska et al. 2008). NIR absorption by suspended particles in the ocean was investigated specifically in a few studies (Tassan and Ferrari 2003; Estapa et al. 2012; Moate et al. 2012). Most of this work on suspended particle absorption was performed with a method described first in Babin and Stramski (2002), where a sample inside a cuvette is placed in the center of a large integrating sphere of a spectrophotometer to reduce the scattering error to a minimum (Babin and Stramski 2004; Stramski et al. 2004; Estapa et al. 2012). Bowers and Binding (2006) used the quantitative filter

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technique (QFT) in the transmittance configuration (e.g., Mitchell 1990) and Tassan and Ferrari (2003) the QFT in the transmittance–reflectance (T-R) configuration (Tassan and Ferrari 1995) together with a similar (but different in some details) cuvette setup for measurement on particle suspensions as in Babin and Stramski (2002). The commonly used QFT technique generally needs corrections for scattering losses due to strong filter-to-filter variation of the filter's optical properties, whereas the T-R technique partly compensates for these losses (Röttgers and Gehnke 2012). On the other hand, measurements with a cuvette in the center of an integrating sphere showed low scattering losses, but revealed some additional scattering-related issues induced by reflections on the cuvette windows which need to be compensated (Babin and Stramski 2002, 2004). However, this method is limited by low sensitivity due to the short path length and the necessity to measure low optical densities to avoid multiple scattering events.

Tassan and Ferrari (2003) and Bowers and Binding (2006) reported measurable and reasonably strong NIR absorption up to 750 nm by marine particles. Estapa et al. (2012) showed significant absorption of particles from coastal waters up to 700 nm with the technique of Babin and Stramski (2002), providing indication of significant absorption at wavelengths > 700 nm, for which, however, no results were reported. Stramski and coworkers (Stramski et al. 2004, 2007; Stramska et al. 2008) reported NIR absorption up to 850 nm in many samples of minerogenic material (from dust, terrigeneous, and pure mineral particles) when suspended in seawater with the technique outlined in Babin and Stramski (2002) and improvements to correct for the remaining small scattering errors by using a mineral with an assumed negligible NIR absorption as the reference.

Our knowledge of NIR absorption by natural suspended particles in coastal and oceanic environments is still limited in either the extent (due to their normally low concentrations) or the wavelength range. The work presented is based on determination of NIR absorption of suspended particle samples with very high sensitivity and precision, in order to provide mass-specific absorption coefficients for NIR wavelengths, i.e., for wavelengths of 700–900 nm. By using techniques described above and by Röttgers and Gehnke (2012), the filters were measured inside a large integrating sphere of a spectrophotometer using high filter loads, to reduce the influence of the precision error and to increase accuracy especially in the NIR spectral region. The method showed insignificant influence of scattering, because even the strong scattering of the filters induced an optical density that was lower than that obtained from any examined particle sample. These measurements were validated in terms of absolute accuracy by independent (but in terms of the wavelength range restricted) measurements with a point-source integrating-cavity absorption meter (PSICAM; Röttgers et al. 2007). Water samples from different geographic areas, including water from a turbid river, coastal and oligotrophic areas, as well as from a few microalgal cultures, were measured, compared, and interpreted with respect to the possible sources of particulate NIR absorption.

Methods

Sample collection—Samples were collected with 12 liter water sampling bottles from just below the sea surface during five cruises: (1) on R/V *Prandtl* in the Elbe River estuary in July 2007, (2) on R/V *Oceania* in the Baltic Sea and the North Sea in September 2007, (3) on R/V *Polarstern* (ANT XXIV/1) in November 2007, (4) on R/V *L'Alis* in the New Caledonia lagoon in April 2008, and (5) on R/V *Heincke* in the German Bight in May 2010. Depending on the suspended matter concentration, 0.005–10 liters were filtered under low vacuum (maximum −200 hPa) onto pre-combusted 47 mm GF/F filters (Whatman) using a filtration unit equipped with an unused filter holder (avoiding inhomogeneity caused by a used, possibly partly clogged filter holder) to obtain a maximum optical density (OD) of around 0.1 in the spectral region of interest (500–900 nm). The samples were shock-frozen in liquid nitrogen, stored at −30°C to −80°C, and measured in the laboratory about 1 to 12 weeks later. Another 0.5 liter of water sample was used for an immediate determination of particulate absorption of particle suspension using a PSICAM (400–720 nm), and additional samples were taken for suspended matter concentration measurements as described below.

Particulate light absorption measurements—Light absorption of particles on filters was measured by placing the filter in the center of an integrating sphere attached to a dual-beam spectrophotometer (Lambda 800, Perkin Elmer) as described in Röttgers and Gehnke (2012). In short, each filter was cut in at least three pieces of about 1 × 2 cm. A single piece was placed in the center of the 150 mm integrating sphere using a clamp-style, center-mount sample holder. Occasionally, up to four pieces of one filter were measured to check the homogeneity of the particles on the filter and to determine a general measurement error.

The OD was measured from 900 to 300 nm with a resolution of 2 nm (slit width: 2 nm in the VIS, 2–4 nm at wavelengths > 860 nm); however, the data presented here are restricted to the range of 450–900 nm as the high filter loads used led to overly high OD values at shorter wavelengths which did not allow application of a constant amplification factor for correction. The baseline of the spectrophotometer was set with a dry piece of a blank filter. Filters wetted with purified water and measured regularly after every fifth sample filter served as references. The absorption was calculated after subtracting the OD of a reference filter and using filter-specific factors for the path length amplification correction. Use of a mean amplification factor would have led to an error of ± 15% for this quantitative filter technique due to strong variability of the amplification factor (Röttgers and Gehnke 2012). Röttgers and Gehnke (2012) showed that the precision and, hence, the sensitivity of this method is very high, with values of ± 0.0009 for σOD (valid for < 900 nm only).

In order to determine filter-specific amplification factors, the absorption was additionally measured on particle suspensions in the visible (400–720 nm) with a PSICAM as described previously in Röttgers et al. (2007) and

Röttgers and Doerffer (2007). The PSICAM was calibrated daily using a colored solution made from Nigrosine (Merck). The absorption of the solution was determined in a spectrophotometer using a cuvette with path length of 10 cm, or in a liquid waveguide capillary cell system with a path length of 50 cm as described in Miller et al. (2002). Nigrosine absorbs light at all relevant wavelengths, allowing a calibration for the complete spectral region in which the PSICAM can be used. Measurements of the sample in the PSICAM were done in triplicate using highly purified water as the reference. Temperature and salinity differences between sample and reference were corrected (Röttgers and Doerffer 2007).

Assuming that amplification in the NIR is constant and the same as at 500–700 nm (at all these wavelengths OD was < 0.1), we used the constant factor determined with the PSICAM measurements for all wavelengths > 500 nm. Determined amplification factors varied between 2.1 and 6.2, i.e., in the same range as reported earlier in Röttgers and Gehnke (2012). For the data from the Atlantic Ocean no PSICAM data were available and a general factor of 4.5 was used after Röttgers and Gehnke (2012).

For some sample sets the particulate absorption after bleaching the pigments was determined. Each piece of filter was bleached using a few drops of a 10% NaOCl (Riedel de Haen) solution dispensed onto the filter with a glass pipette in a glass petri slide. After 2–5 min the filter was put on a tissue to remove most of the free NaOCl solution. Afterwards the filter was placed back onto the petri dish and two drops of 10% H_2O_2 were dispensed onto the filter to oxidize the remaining NaOCl, which absorbs strongly at short visible wavelengths (< 450 nm; H_2O_2 only absorbs light at < 350 nm). The bleached filter was then measured as described above, and the absorption was calculated using the amplification factor determined earlier for the same but unbleached filter, assuming that bleaching does not change the optical path length amplification inside the filter, as it will mainly change the absorption not the scattering inside the filter. Absorption of bleached particles was not determined for the samples from the R/V *Oceania* cruise.

Suspended matter concentration—The dry mass concentration of suspended particulate matter (SPM) was determined by filtration of (if necessary) large volumes of the samples onto pre-combusted, prewashed, and pre-weighed GF/F filters (depending on cruise: diameter 47 mm or 25 mm, Whatman) as described in van der Linde (1998). Membrane filters (diameter 47 mm, pore size 0.45 μm, Nuclepore, Whatman) were used for the New Caledonia cruise. After filtration each filter was washed three times with ~ 50 mL deionized water to remove the salt water inside the filter. The filters were dried at 55°C for several hours and the mass difference to the blank filter determined. The suspended matter mass concentration, [SPM], was calculated by:

$$[\text{SPM}] = \frac{(w_s - w_i - m_i)}{V} \left[\text{g m}^{-3} \right]$$

where V is the filtered volume (m³), w_s and w_i are the masses (g) of the sample and the blank filter, respectively,

and m_i that of a constant which according to Stavn et al. (2009) compensates for the remaining salt mass in the filter. m_i was determined by filtering 500 mL of a < 0.2 μm filtered water sample through blank filters, and subsequently handling the filters as regular SPM filters. For seawater samples the masses of these "procedural control" filters ranged between 0.2 and 0.8 mg for 47 mm GF/F filters; here the mean value of 0.56 mg was taken for m_i. For river samples no subtraction of m_i was applied. For the membrane filters m_i was not determined, but considered to be lower due to the lower filter thickness. It was not taken to be zero (Banse et al. 1963); instead, an estimated value of 0.1 mg was used.

Results

As the mass-specific absorption is considered here, first some error analysis is given to differentiate variability in the mass-specific absorption due to natural variability induced by variation in the particle optical properties and that due to measurements error for the absorption coefficient and [SPM]. Thereafter, the NIR absorption and mass-specific NIR absorption are shown.

Error analysis—At half of the cruises 47 mm GF/F filters were used for [SPM] determinations and it was assured that large volumes were filtered. For samples from the Atlantic Ocean, when particle mass concentrations were lowest, 10–12 liters of sample water were filtered. In the cases of smaller filters (25 mm) and the membrane filters less volume was filtered, but the following description applies similarly on a relative basis as the mass of the filter as well as the salt offset are equally reduced with the diameter and the filter thickness, respectively. Absolute masses of the collected material ranged from 0.6 to 5 mg for Atlantic Ocean samples and up to 10 mg for the highest concentrations found in the River Elbe. The general errors related to weighing and volume determination are rather small ($\pm$ 0.006 mg and $\pm$ 0.4%, respectively, as determined from the balance and measuring cylinder descriptions) and can be ignored. Critical for the [SPM] determination is an offset induced by retention of sea salt in the filter despite washing the filters (Stavn et al. 2009). It was shown by Stavn et al. (2009) that ignoring the salt offset can lead to an error ≫ 10%. Stavn et al. (2009) reported values for this offset that ranged from 0.8 to 1.3 mg for a salinity of natural seawater. In our study a mean value of 0.56 $\pm$ 0.3 mg was determined. Including a correction for this offset is therefore necessary, but the $\pm$ 0.3 mg filter-to-filter or sample-to-sample variation of this offset presents a still significant error source. The observed variation of this offset would in extreme cases lead to errors between 10% and 50%.

Errors in the determination of particulate light absorption are smaller. The absolute error of the PSICAM determination depends mainly on the error of the photometric determination of the colored solution used for calibration. The error of the photometer used for this calibration was regularly controlled by a double-aperture setup and was < 0.1% (a nominal value of 0.06% is given

by the manufacturer [± 0.0003 OD at 0.5 OD]). Precision of the photometer measurement is influenced as well by cuvette positioning, cuvette wall optical changes, temperature-related changes in optics and water absorption, etc., but typically sum up to about ± 0.001 OD. Calibration was done with solutions of 0.05–0.15 OD, so the final error that is transferred to the PSICAM on a relative basis is in the range of ± 1–2%. Precision of the PSICAM was shown to be approximately ± 0.0008 m^{-1} by Röttgers and Doerffer (2007). Precision of the QFT used here is about ± 0.0009 OD and thus lower than for other QFT methods (Röttgers and Gehnke 2012). As high maximum ODs were used, the QFT error for absorption was 1–2% only when OD was very low, e.g., at longer wavelengths. This error and that related to variations of the path length amplification factor are small for the wavelengths of main interest (> 600 nm) as those were corrected by the PSICAM measurements. Remaining OD variations of this correction are still in the range of a few percent. In total, the averaged potential error for the absorption determination was between 3% and 5% depending on the absolute OD (for QFT) and absorption (for PSICAM) measured.

Lastly, the errors due to scattering are considered. The PSICAM was shown to have no significant response to scattering on a level of its precision (Röttgers et al. 2005) and, thus, scattering can be ignored in most cases. In extreme cases, i.e., when scattering is several orders of magnitude stronger than absorption, a significant influence of scattering on absorption is possible, but this situation only exists in suspensions of very strong scatterers that possess very low absorption. With natural samples this has not been observed yet for the spectral range of the PSICAM, 400–720 nm.

For the QFT measurements scattering can lead to artifacts in the observed OD. The strongest difference in scattering is induced by the filter itself. This scattering actually changes the light field inside the integrating sphere strongly and this change can be seen in partly positive and partly negative OD over the spectrum when a filter is measured against air. The scattering behavior of the filter changes strongly with filter wetness, but this effect was shown to be only of minor relevance (Röttgers and Gehnke 2012), and still can be corrected by an appropriate reference filter of roughly the same wetness. It is assumed that changes of the filter scattering behavior (e.g., the filter transmittance-to-reflectance ratio) by adding scattering particles is in the range of those induced by changes of filter wetness, as scattering by the filter is much larger than that by the retained particles, and, thus, are small compared to the precision. Hence, scattering errors were not significant on the level of ± 0.0009 OD.

NIR absorption—The methodology used here to determine particulate absorption was chosen to maximize accuracy and sensitivity and, simultaneously, minimize scattering errors as much as possible. This was achieved by combining accurate PSICAM measurements, that are not susceptible to scattering errors but restricted to visible wavelengths, with highly sensitive QFT measurements. Because of these very low scattering errors, a visible
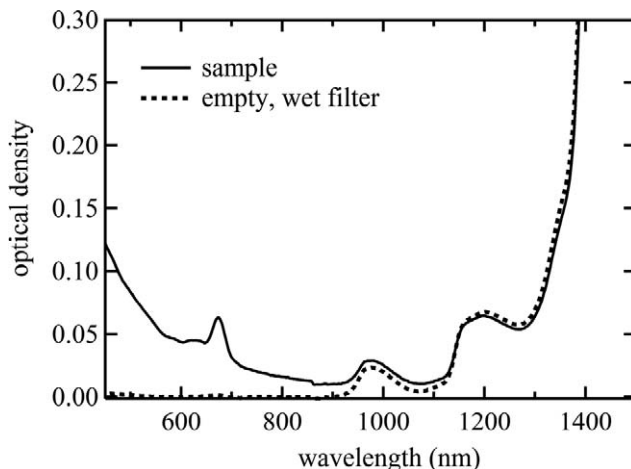

Fig. 1. Optical density as a function of wavelength in the range of 450–1500 nm of a wet filter from a random sample and a wet empty filter measured against a dry blank filter with the QFT method.

influence by absorption of water in the wet filters was expected and could clearly be seen in measurements of a wet filter against a dry filter blank (Fig. 1). Typical filter-to-filter variations in OD limit the precision at wavelengths > 900 nm, where water absorption is strong; therefore, measurements with wet filters are limited to wavelengths < 900 nm.

The substantial error related to the variation in the amplification factors (Röttgers and Gehnke 2012) was compensated by determining this factor individually for each filter using the concomitant PSICAM measurements. The necessary assumption is that the amplification factor is neither wavelength- nor OD-dependent, which was shown by Röttgers and Gehnke (2012) for the range of 400–720 nm when OD was below 0.1.

Figure 2 shows two examples of particulate absorption measurements with the PSICAM and the QFT when QFT results were corrected with a filter-specific amplification factor determined for > 500 nm. In most cases, the two spectra were very similar over all wavelengths (Fig. 2B) and, hence, the amplification factor was constant over the whole spectrum. As the objective was to obtain higher OD in the NIR to increase sensitivity in this region, the OD at shorter, visible wavelengths was sometimes too high, the real amplification lower, and thereby the absorption was underestimated (Fig. 2A). The relative differences between the two spectra showed values mostly below ± 10% at > 600 nm, but increased in the example shown in Fig. 2A to up to 20% for the shorter wavelengths. This effect was expected to be even stronger at even shorter wavelengths, which are not a focus of this paper; therefore, data are shown for > 450 nm only. However, at some wavelengths these differences in absorption between PSICAM and QFT (corrected with PSICAM) are about double than expected from the error analysis above. One explanation is the difference in the optical resolution of the two techniques (QFT: 2 nm vs. PSICAM: 7 nm) that can lead to differences in the spectral resolution of absorption structures.
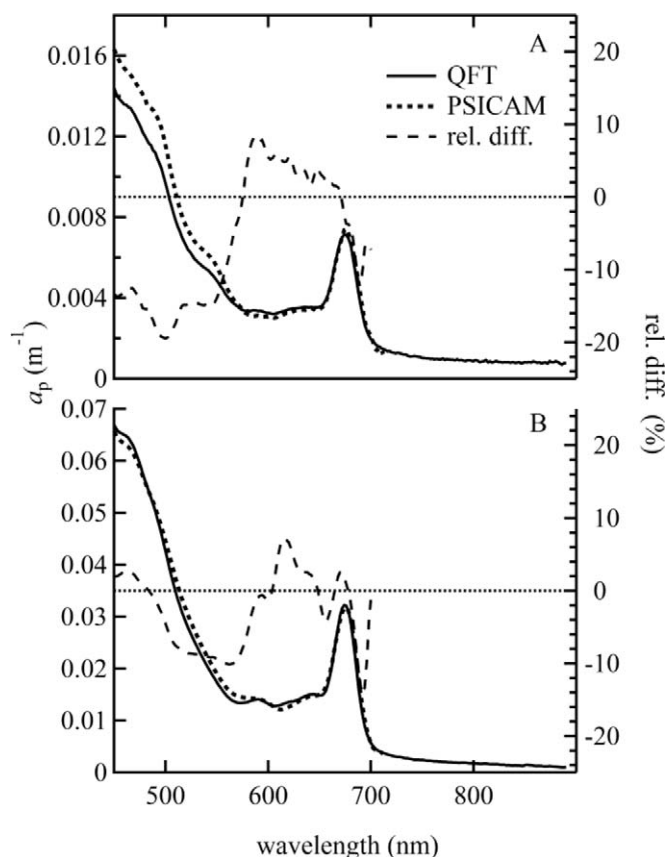
Fig. 2. Comparison of particulate absorption measurements using the QFT and the PSICAM method. Shown are two random examples (A and B) of QFT filter measurements that are individually corrected for path length amplification together with the absorption measured with the PSICAM (450–700 nm), and the relative difference (rel. diff.) between the two.

To validate the methodology in terms of a low scattering error, the particulate absorption of several algal cultures was measured, assuming very low absorption values in the NIR region. High filter loads were used such that ODs were as high as 1.0 in the VIS. The cultures were not axenic, but concentrations of bacteria and detritus were kept low by collecting samples in the exponential growth phase from cultures that had been grown directly from isolated single cells in bacteria-free medium. Used were several diatom species isolated from the North Sea (*Coscinodiscus* sp., *Biddulphia* sp., *Asterionella* sp.) and cultures of *Isochrysis galbana*, *Prymnesium* sp., and *Trichodesmium erythraeum*. For all cultures the raw OD of the sample filter was higher than that of a wet reference filter at all wavelengths measured. The observed minimum OD in the NIR was in the range of 0.001 to 0.005. The calculated maximum particulate absorption coefficient of the cultures was between 0.5 and 4 m^{-1}. The results showed measurable absorption coefficients of algal cultures in the NIR region with values at 750 nm of between 0.0003 and 0.0128 m^{-1}. As absorption coefficient of the different cultures varied strongly only normalized spectra of the cultures are shown (Fig. 3, "cultures").

The absorption of natural samples collected from different regions and different environments are shown in Fig. 3. In all cases the OD was above the detection limit at all wavelengths. The absolute particulate absorption at 850 nm varied from values as low as 0.0002 m^{-1} measured in the Atlantic Ocean to very high values measured in samples from the River Elbe of between 0.16 and 1.7 m^{-1}. The highest observed values at NIR wavelengths of 700–750 nm were similar to the absorption by pure water. In other regions the particulate NIR absorption was lower and correlated with the general particulate absorption of the sample at VIS wavelengths, e.g., values of 0.0029–0.21 m^{-1} were found in the North and Baltic Sea in autumn.

Visible inspection of the spectral distribution in Fig. 3 shows a clear relation between the extent of the algal pigment absorption peaks (e.g., at 442 and 672 nm) and the NIR absorption: when NIR absorption is high the pigment absorption peaks are less pronounced and vice versa. This is likely a result of a high contribution by detrital matter to the total particulate absorption. For verification the ratios of absorption at 750 nm to 442 nm, and 750 nm to 672 nm, were plotted against the absorption at 750 nm, a_p(750 nm) (Fig. 4)—here 750 nm is chosen as it is often used for the null-point correction. With increasing a_p(750 nm), there is a clear increase in the ratios showing that, when a_p(750 nm) is high, the peak at 672 nm and the increase in absorption towards 442 nm is less pronounced. Clearly, the lowest ratios were found for the culture samples for which absorption by detritus was expected to be very low. A small bias in this ratio may be expected as the spectral slope of the underlying detrital absorption might also be dependent on the absolute NIR absorption.

These spectral ratios were chosen as they can be used to evaluate the relative contribution of particulate absorption at NIR wavelengths. For cultures, a_p(750 nm) was between ~ 0.2% to 2% of a_p(442 nm) and ~ 0.3% to 3% of a_p(672 nm). For nearly all natural samples these factors are much higher; in the extreme case of the river samples a_p(750 nm) was 30% of a_p(442 nm) and 80% of a_p(672 nm). For samples from the Atlantic Ocean these contributions still ranged between 1.5–8% and 5–30%, respectively. For the same absolute value of a_p(750 nm), natural samples never reached ratios as low as those of cultures. On the other hand, some samples from the German Bight taken in spring reached rather low values even when a_p(750 nm) was relatively high, which might be a result of a high contribution of phytoplankton in spring bloom situations and relatively low contributions from other particles. Taking this into consideration, there might be general trends in these ratios that are independent of the geographic region or kind of environment (river, coastal, open sea).

The question whether the NIR absorption originates purely from detrital absorption was further investigated by bleaching the phytoplankton pigments and measuring the absorption of the bleached particles. There are methodological issues with this bleaching procedure that need some consideration. Figure 5 shows the particulate and bleached particulate absorption of one sample. It can be seen that
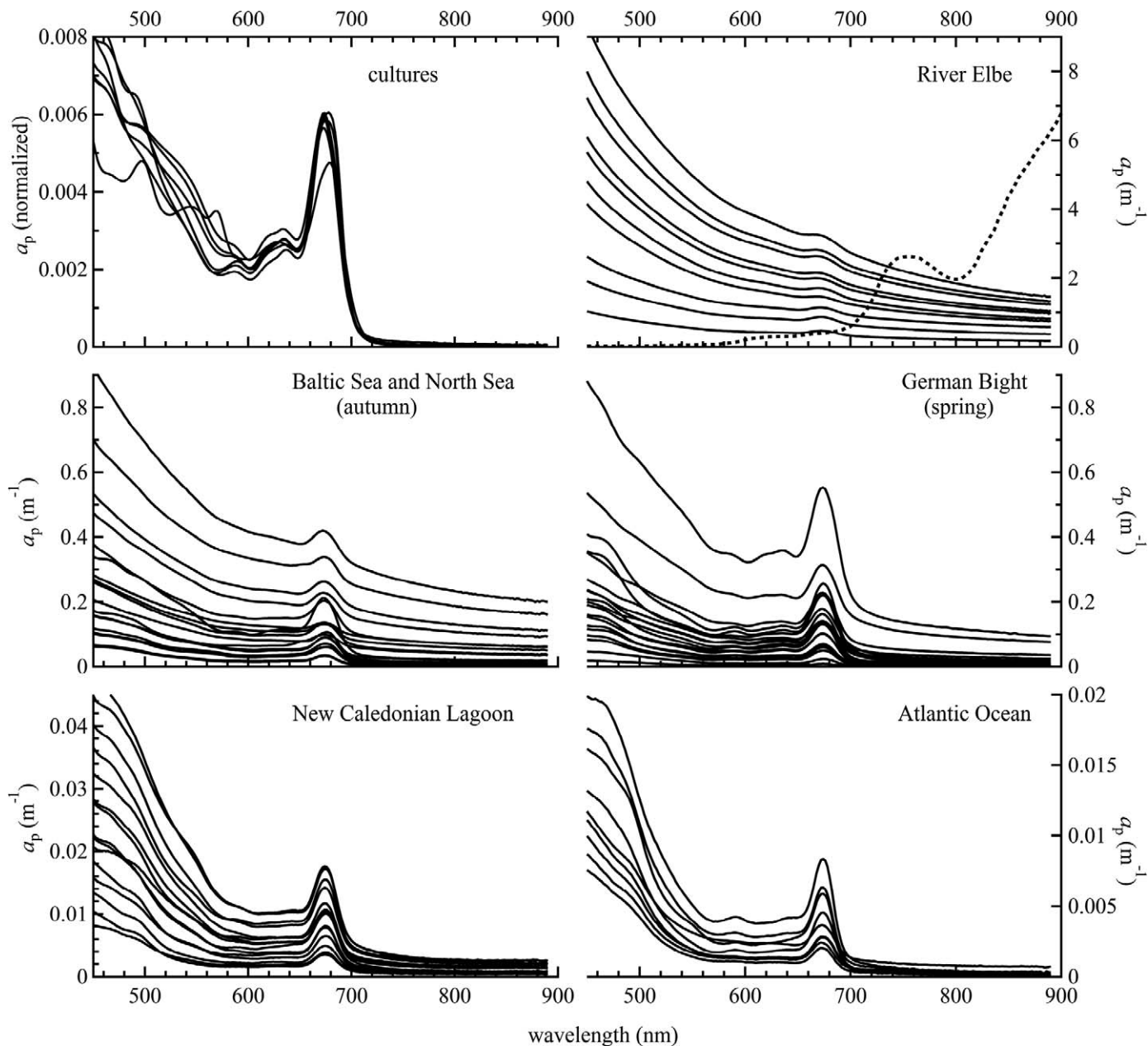
Fig. 3.   Particulate absorption coefficients (a_p, solid lines) as a function of wavelength for water samples from algal cultures and from the different geographic regions and environments. Additionally, the absorption coefficient of pure water (dotted line) taken from Pope and Fry (1997) and Hale and Querry (1973) was plotted in the "River Elbe" panel. Note that for cultures spectra are shown that were normalized to the area below the absorption spectrum.

bleaching mostly influences shorter wavelengths and leads to only small changes at NIR wavelengths. However, the procedure might on one hand not only bleach phytoplankton pigments but also some organic detrital matter, and on the other hand might disturb the particle distribution on the filter, thereby changing the measured OD and/or the path length amplification. In Fig. 6 the correlation between unbleached and bleached absorption of all measured samples at 800 nm is shown (800 nm is chosen here to avoid any influence by algal pigments that might still be detectable at 750 nm). Only a few points were above the

1:1-line when general absorption was low; these deviations were in the range of the general OD measurement error. For a few samples the bleached particle absorption at 800 nm was much lower, which might be due to problems during the bleaching procedure. For the majority of the samples the points were at or just below the 1:1-line and the bleached particle absorption at 800 nm reached values between 90% and 100% of the unbleached particle absorption. This small decrease in absorption was stronger than expected from OD measurement errors and might be due to a small influence of the bleaching procedure on the
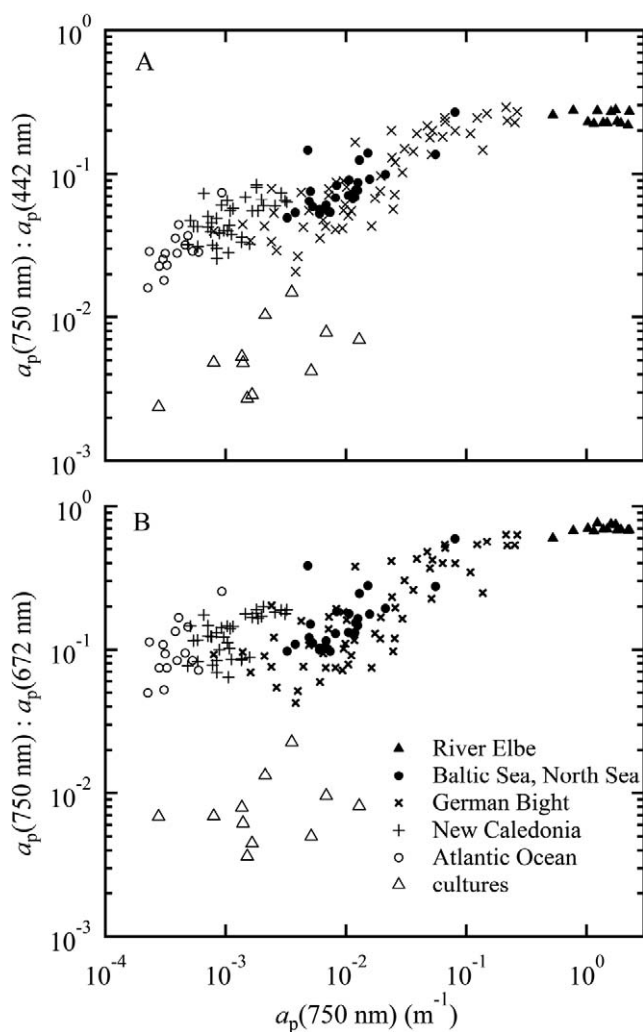
Fig. 4.   Spectral ratios of the particulate absorption at 750 nm to that (A) at 442 nm, $a_p(750 \text{ nm}) : a_p(442 \text{ nm})$, and (B) that at 672 nm, $a_p(750 \text{ nm}) : a_p(672 \text{ nm})$, as a function of particulate absorption at 750 nm, $a_p(750 \text{ nm})$, for algal cultures and samples from different geographic regions (*see* legend).

Fig. 5.   One example for the influence of pigment bleaching on particulate absorption. Particulate absorption coefficient (a_p) and the bleached particle absorption coefficient (a_{bp}) of the same random sample as a function of wavelength.

NIR mass-specific absorption—Figure 7 shows the correlation between [SPM] and particulate absorption at 750 nm, $a_p(750 \text{ nm})$. The observed relationship can be described over several orders of magnitude by a single nonlinear function. This general relationship is not given; instead, the mass-specific absorption was determined individually for each sample and is reported for each geographic region. Figure 7 shows a stronger variation for very low values, i.e., for samples from the Atlantic Ocean and the New Caledonian lagoon, which can be a combination of natural variability and noise due

absorbing material. On average, bleaching reduced the particulate absorption at 800 nm by only a few percent and these effects were not dependent on the type and origin of the samples. Assuming an error of a few percent induced by the bleaching procedure plus the error of the absorption determination would in the majority of the cases lead to no statistically significant differences of unbleached and bleached particulate absorption. Note that bleaching was not performed for samples taken in the Baltic and North Sea in autumn. For these data the particulate (unbleached) absorption at longer NIR wavelengths is taken as absorption of non-algal matter in the following. On the other hand, the results here indicate that there is no difference in the particulate absorption of unbleached and bleached material at NIR wavelengths. For the NIR spectral region particulate absorption of unbleached and bleached material is taken as being the same in the following.
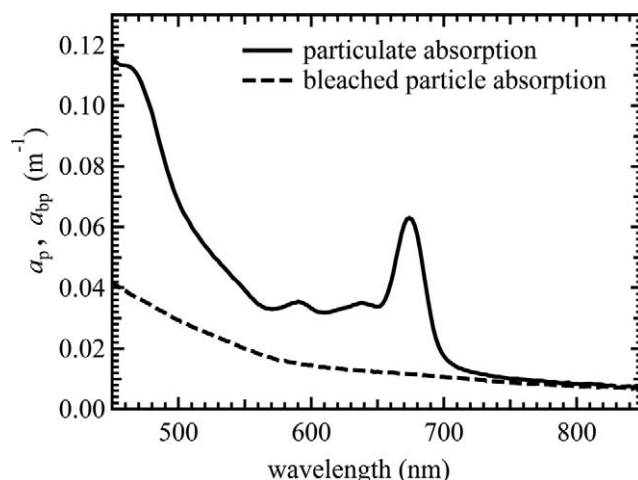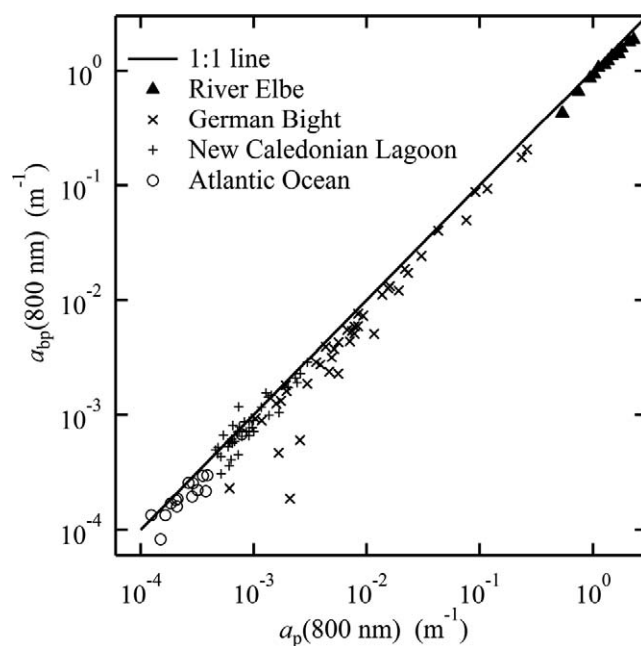

Fig. 6.   Particulate absorption at 800 nm, $a_p(800 \text{ nm})$, plotted against bleached particle absorption at the same wavelength, $a_{bp}(800 \text{ nm})$, for samples from different geographic regions as indicated in the legend.
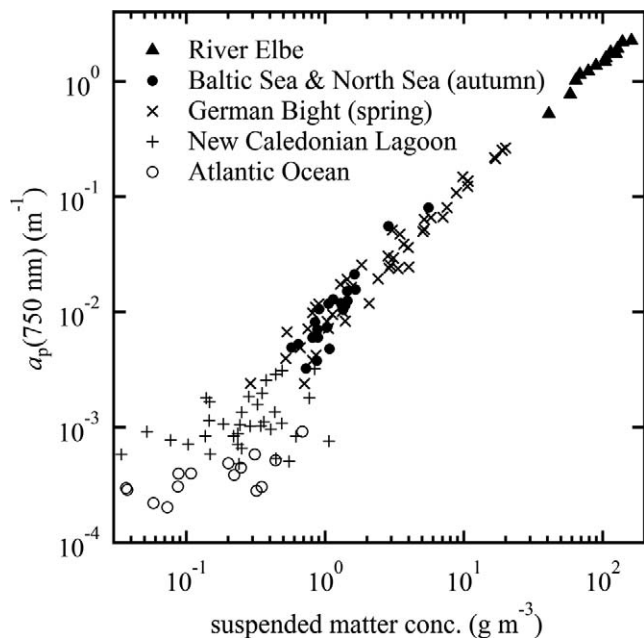
Fig. 7. Particulate absorption at 750 nm, a_p(750 nm), as a function of the suspended matter concentration, [SPM], for the different geographic regions as indicated in the legend.

to measurement uncertainties. Measurement errors for [SPM] can still be very substantial when concentrations are very low, despite the fact that large sample volumes were filtered. Based on the absolute masses of material on the filters and the general measurement error analysis described above, relative errors can be as high as 20–50% when [SPM] is below 0.5 g m^{-3}. Even when [SPM] is between 0.5 and 10 g m^{-3} the relative error can reach 10–20%, indicating that variations in mass-specific absorption are still partly due to measurement errors. This rather large error needs to be taken into account when mass-specific absorption is determined, as shown in Fig. 8.

Averaged values of the mass-specific absorption for each region are summarized in Table 1. The general mass-specific absorption spectra show some typical artifacts of bleached material, like a small visible remnant of the chlorophyll *a* absorption at $\sim$ 672 nm, indicating that bleaching of pigments was often not complete. However, this will induce a small error in the mass-specific absorption at these specific wavelengths only. Typically, the absorption decreased exponentially with increasing wavelengths. Some spectra from waters around New Caledonia showed a shoulder at $\sim$ 500 nm that indicated absorption from iron-rich minerals (Estapa et al. 2012). Those filters had a reddish color, which most probably originated from suspended laterites that are often observed in these waters. A similar shoulder was seen for most Atlantic Ocean samples.

The mass-specific absorption for bleached samples over all wavelengths was highest for the River Elbe samples, lower in the Baltic and North Sea (autumn) and the German Bight (spring), and lowest in the Atlantic Ocean and the New Caledonian lagoon. The respective averaged

values of a_{bp}^*(850 nm) were 0.012, 0.007, 0.007, 0.002, and 0.003 m^2 g^{-1}. The general trend was the same at all other wavelengths (Table 1). The range of values for the River Elbe was rather small: 0.011–0.013 m^2 g^{-1} at 850 nm. These samples were taken during the same season (within a few days), and at the same tide-influenced location. In the other regions the variations were larger, e.g., in the Baltic and North Sea (autumn) the value of a_{bp}^*(850 nm) ranged from 0.003 to 0.014 m^2 g^{-1}; however, a large part of this variation can be explained by errors in the [SPM] determination. It is noticeable that the maximum values at the shortest wavelength of each region were very similar (0.05–0.06 m^2 g^{-1} for a_{bp}^*(450 nm)).

Discussion

NIR absorption of phytoplanktonic algae—As the NIR absorption of phytoplankton has often been determined to be either below the detection limit or lower than the obtained offset error induced by scattering, it is generally assumed that absorption by phytoplanktonic pigments and by living phytoplanktonic cells in the NIR is very low and, thus, can be neglected. Hence, measurements with cultured microalgae have been used to verify optical methods and the related scattering errors (Babin and Stramski 2002). For the same reason, absorption of cultured microalgae was used in this study to verify the detection limit and to identify methodological artifacts and uncertainties. Our results show that NIR absorption by these algal cultures is measurable but very low, and that a measured signal stronger than the typical measurement precision in OD was due to absorption, as no significant scattering errors were expected. It was ensured that a detectable OD signal in the NIR was determined by concentrating the sample on the filter as much as possible by filtering several liters of a rather low concentrated culture. In some cases the obtained OD signal was still just above the level of precision. However, we did not observe any artificial signals, such as negative values or clear absorption maxima in the NIR, as observed in potentially degrading cultures by others (Babin and Stramski 2002). The relative proportion of NIR absorption to VIS absorption was also very low; absorption at 750 nm was between 0.2% and 2% of the absorption at 442 nm, with the lower values being one order of magnitude less than that of any natural sample (Fig. 4). NIR absorption by phytoplankton in the ocean can, hence, be neglected for most optical applications.

NIR absorption in natural samples—The results presented here showed that natural samples rarely possess NIR absorption coefficient as low as that of pure algal cultures, not even when phytoplankton is dominating the particle composition. These results indicate further that NIR absorption is measurable in all natural samples (even in samples from very clear, oligotrophic waters) and that it is always higher than that expected from phytoplankton alone due to significant contribution from detrital matter absorption. In clear waters (Atlantic Ocean) the proportion of the particulate absorption at 850 nm was low but still reached values of 2–8%, and 4–20% of the particulate
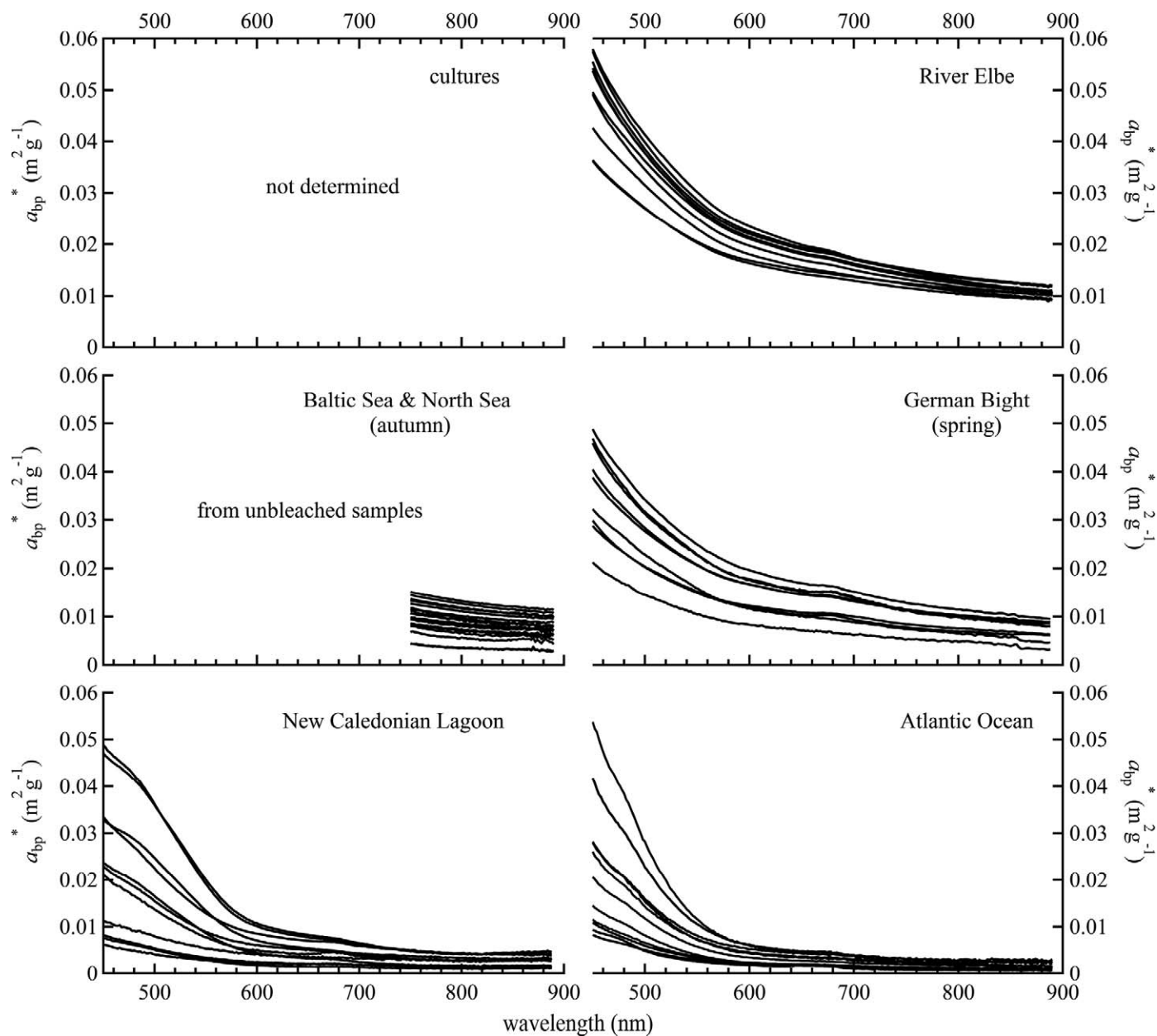
Fig. 8. Mass-specific particulate absorption of bleached particles ($a_{bp}^{*}(\lambda)$) as a function of wavelength of samples from different geographic regions.

Table 1. Values of mass-specific light absorption coefficients of bleached particles, $a_{bp}^{*}(\lambda)$, at chosen VIS and NIR wavelengths for the different regions. SD, standard deviation; nd, not determined.

Region	$a_{bp}^{*}(650\ nm)(m^2\ g^{-1})$		$a_{bp}^{*}(750\ nm)(m^2\ g^{-1})$		$a_{bp}^{*}(850\ nm)(m^2\ g^{-1})$	
	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range
Elbe River	0.018±0.001	0.016–0.020	0.014±0.001	0.013–0.015	0.012±0.001	0.011–0.013
German Bight	0.013±0.003	0.005–0.017	0.009±0.003	0.003–0.013	0.007±0.002	0.002–0.011
Baltic Sea, North Sea	nd	nd	0.009±0.003	0.004–0.019	0.007±0.003	0.003–0.014
New Caledonia lagoon	0.005±0.002	0.001–0.011	0.003±0.001	0.001–0.006	0.003±0.001	0.001–0.006
Atlantic Ocean	0.003±0.001	0.002–0.005	0.002±0.001	0.001–0.003	0.002±0.001	0.001–0.003

absorption at 442 and 672 nm, respectively. When absolute absorption and relative proportion of detrital matter (biogenic and minerogenic) was high, e.g., in the samples from the river, these values increased to up to 30% and 80%, respectively. In the river, NIR absorption in the range of 700–900 nm reached very high values that were of the same order of magnitude as absorption by pure water. Hence, it will have a strong influence on the total absorption in the water column at these wavelengths. The results clearly show an optically significant and occasionally very strong NIR absorption by natural non-algal particles in water, as it was earlier observed by Tassan and Ferrari (2003), Bowers and Binding (2006), and Moate et al. (2012). These results have implication for the often used null-point correction to compensate for scattering errors. Subtraction of the NIR signal will lead to underestimations in the determination of the particulate absorption of between 2% and 30% at 442 nm and between 4% and 80% at 672 nm, hence, often to inacceptable underestimations. This practice should generally be avoided, especially in turbid coastal waters or rivers. As our results for the NIR absorption by phytoplankton and of the bleaching procedure showed, when determining the absorption coefficient of phytoplankton alone the null-point correction is less critical. However, total particulate absorption coefficients from turbid water measured so far with a null-point correction applied might be strongly underestimated.

Origin of NIR absorption—The presented results show a nonlinear increasing trend in the relative NIR to VIS absorption with increasing absolute NIR absorption. The highest ratios are detected when NIR absorption is highest, and when the spectral distribution of the absorption indicates a high proportion of detritus (small pigment absorption peaks, and general increase in absorption with decreasing wavelength). With increasing contribution of detritus to the total particle concentration the absolute absorption and relative contribution of detritus absorption in the NIR are rising. Because of the nonlinearity of this trend it cannot be explained by detritus concentration differences alone, but also by qualitative differences in the detritus itself, i.e., by the type of detritus and its mass-specific absorption. As the contribution from phytoplankton to the NIR absorption is very low, the NIR absorption has to be caused by biogenic and minerogenic detrital matter.

Recently, an interest arose in measuring the absorption by minerals and minerogenic particles also for the NIR spectral region (Babin and Stramski 2004; Stramski et al. 2004; Stramska et al. 2008). Pure colorless minerals are thought to be very weak NIR absorbers and are not found to possess a measurable absorption in the NIR region (Babin and Stramski 2004). On the other hand, colored minerals, dust, and soil samples suspended in seawater possess a sizable NIR absorption (Babin and Stramski 2004; Stramski et al. 2004, 2007). Less is known about the NIR absorption of pure natural organic or biogenic detritus. There is probably no pure organic detritus in nature, as there will always be a significant contribution of minerogenic matter especially biogenic mineral matter, such as empty diatom shells. The data set presented here provides no information on the separation of organic and inorganic detrital NIR absorption.

Variation in mass-specific absorption detected in the presented study can be explained by, e.g., differences in the overall particle composition, but also by the particle size distribution, as mass-specific absorption decreases with increasing particle size due to the packaging effect (Woźniak and Dera 2007). Before these variations in the mass-specific absorption can be examined the accuracy of the determination of mass-specific absorption in seawater needs to be considered. Errors related to the absorption and mass determination are discussed above: there is always a major source of error for the [SPM] determination, which is the retention of sea salt in the filters despite washing with deionized water (Banse et al. 1963; Stavn et al. 2009). In our study the recommendations of Stavn et al. (2009) were followed. However, due to the sometimes still low particle mass on the filters and the large error in the determination of the salt offset with blank filters, the errors in mass concentration were still substantial and could reach > 50%, especially in oceanic waters where mass concentrations were quite low. Here, sample volumes of 50–100 liters would be needed (but are usually not used) for more accurate measurements. Thus, the strong variations in the mass-specific absorption measured among these samples can be explained in large part by errors in the determination of mass concentrations. For samples from the Elbe River these errors can be assumed to have been small (no salt water and high masses on the filter) and clearly the variations of the mass-specific absorption are small. However, one has to note that these samples were taken within a few days and represent probably a similar particle composition. Variations in mass-specific absorption over the year might be larger.

Despite these large errors, a trend towards lower mass-specific absorption coefficients in clearer waters was observed (Fig. 8). Highest mass-specific absorption coefficients were found in the river, lowest in oligotrophic oceanic waters. The mass-specific absorption of samples from the river and that of the highest values from the Baltic and North Sea at < 700 nm ($\sim$ 0.01–0.05 m^2 g^{-1}) were similar to those reported for Louisiana coastal waters around the Mississippi estuary by Estapa et al. (2012). Values reported by Bowers and Binding (2006) and Moate et al. (2012) for the Irish Sea ($\sim$ 0.02 and 0.1 m^2 g^{-1}, for 750 and 400 nm, respectively) are higher. Values reported for minerogenic particles in the VIS are typically up to one order of magnitude higher (Babin and Stramski 2004; Stramski et al. 2004, 2007). Low values are reported for noncolored and highest values for colored minerals, especially for iron-rich material (Babin and Stramski 2004; Stramski et al. 2007). Stramski et al. (2007) related the stronger mass-specific absorption to the smaller contribution of large particles in their samples. The question of the dependence of mass-specific absorption of particles on their size distribution is not often addressed in literature nor that of natural variations in the imaginary part of the refractive index of the particle material (*see* Stramski et al. 2007 for the results of laboratory experiments, or Woźniak and Stramski 2004 for a theoretical approach to these problems). Reported mass-specific

absorption of minerogenic matter in the NIR (800 nm) is, when not below the detection limit, in the range of 0.0107 to 0.034 m^2 g^{-1} (Stramski et al. 2004, 2007) and, hence, similar or even higher than reported here.

To what extent variations of the mass-specific NIR absorption are related to particle size distribution, the particle composition, and the imaginary part of the refractive index of the particle material cannot be concluded yet. Furthermore, not much is known about mass-specific NIR absorption of organic detritus. The lower values of NIR mass-specific absorption in open-ocean samples might equally be explained by the higher contribution of organic detritus which could have a general lower mass-specific absorption.

The results obtained here are based on the assumption of a constant path length amplification factor, such that the factor in the NIR is estimated from measurements in the VIS spectral region. Despite this limitation, it was shown that all natural particles might possess sizable (although sometimes low) light absorption in the NIR spectral region and that this absorption can be very high in turbid environments like coastal and river waters. The contribution by biogenic detritus to particulate NIR absorption and the spectral (mass-specific) optical properties of biogenic detritus in the aquatic environment are still largely unknown as no technique currently exists that adequately discriminates inorganic from organic (biogenic from minerogenic) particulate absorption, and as natural pure organic detrital matter is difficult to encounter in the aquatic environment. The high accuracy of the determination of NIR absorption as reported here will allow us in the future to gain better information on NIR absorption and mass-specific absorption. In combination with chemical techniques it might offer the possibility to separate more accurately the contribution of minerogenic and biogenic detritus to absorption by suspended matter in the sea.

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