Comparison of hyperspectral measurements of the attenuation and scattering coefficients spectra with modeling results in the north-eastern Baltic Sea

Liis Sipelgas*, Urmas Raudsepp

Marine Systems Institute at Tallinn University of Technology, Akadeemia tee 15a, Tallinn 12618, Estonia

A R T I C L E   I N F O

Article history:
Received 23 January 2014
Received in revised form 17 July 2015
Accepted 10 August 2015
Available online 19 August 2015

Keywords:
Attenuation spectra
Scattering spectra
Total suspended matter
Chlorophyll a
Baltic Sea

A B S T R A C T

The spectral variations in the attenuation and scattering coefficients measured with a hyperspectral ac-spectra (Wetlabs) instrument were analyzed from a dataset collected in the vicinity of commercial harbors on the Estonian coast of the Gulf of Finland, Baltic Sea. In total, the measured TSM concentration varied from 0.4 to 30 mg L⁻¹ and the concentration of Chl a varied from values below the detection limit (0.05) to 23 mg m⁻³. The reliability of the power law describing the particle attenuation coefficient \( c_a(\lambda) \) and scattering \( b_p(\lambda) \) coefficients was evaluated by means of a determination coefficient \( R^2 \). The power law described the particle attenuation spectra with high accuracy \( (R^2 > 0.67) \), giving the dataset an average \( c_a(\lambda) \) slope of 1.3. In the case of particle scattering coefficients, the power law did not represent the whole dataset. Depending on a particular spectrum, the \( R^2 \) varied from 0 to 1.0 and the slope varied from 1.15 to –0.56. Decomposition of \( b_p(\lambda) \) into dominant modes using principal component analyses resulted in the first principal mode accounting for the power law dependence of \( b_p(\lambda) \), i.e. the “mineral-type” spectrum, and the second and third mode representing the characteristic \( b_p(\lambda) \) of dominant algal particles, i.e. the “algae-type” spectrum. From our dataset we estimated that if Chl a concentration is above 10 mg m⁻³ or below 5 mg m⁻³ then most likely the “algae-type” or the “mineral-type” spectrum is dominant, respectively. There was strong linear relationship \( (R^2 > 0.92) \) between TSM concentration and \( c_a(555) \) and \( b_p(555) \), irrespective of the dominant shape of the particle scattering spectra. The estimated TSM-specific attenuation and scattering coefficients at 555 nm were \( 0.8 \) m² g⁻¹ and \( 0.68 \) m² g⁻¹, respectively. Corresponding values for water samples with a dominant “mineral-type” spectrum were \( 0.85 \) m² g⁻¹ and \( 0.73 \) m² g⁻¹, respectively and for water samples with a dominant “algae-type” spectrum were \( 0.64 \) m² g⁻¹ and \( 0.52 \) m² g⁻¹, respectively.

© 2015 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1. Introduction

Penetration of light in coastal waters is influenced by a wide range of dissolved and suspended materials (Kirk, 1994). Of these constituents in the water mass, phytoplankton, colored dissolved organic matter (CDOM), and suspended mineral particles have received significant attention from the remote sensing and optical modeling communities (Babin et al., 2003). Optical measurements of coastal waters have also gained broad utility in coastal management and engineering (Coble et al., 2004; Trees et al., 2005; Sipelgas, 2011). Inherent optical properties (IOP) – absorption, scattering and attenuation coefficients – are the result of additive contributions of light absorption and scattering by the optically significant constituents in water: phytoplankton, CDOM, and suspended mineral particles. Absorption and scattering coefficients display specific spectral features or a dependency that may be used to estimate the concentration of each constituent. Several studies have shown that inherent optical properties can be used to describe the composition of suspended particles in the water column (Oubelkheir et al., 2005; Bowers and Binding, 2006; McKee and Cunningham, 2006; Oubelkheir and Sciandra, 2008; Woźniak et al., 2011; Astoreca et al., 2012). These relationships rely on numerical or experimental methods and have been necessary for the development of remote-sensing algorithms, ecological modeling of marine environments and establishing practical marine research methods.

* Corresponding author.
E-mail address: liis.sipelgas@msi.ttu.ee (L. Sipelgas).

http://dx.doi.org/10.1016/j.ecss.2015.08.008
0272-7714/© 2015 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).
Recent advances in bio-optical instrumentation that enable the measurement of high-resolution spectral data on absorption, attenuation and scattering coefficients open new possibilities for monitoring biogeochemical parameters and their dynamics in estuaries (Oubelkheir and Sciandra, 2008), and for characterizing the loading of particles into the water column during dredging operations (Sipelgas, 2011). Also, the spectral variations of IOPs have been shown to provide information about particle size distribution (Oubelkheir et al., 2005; Boss et al., 2001a,b; Bowers et al., 2011). In studies by Oubelkheir et al. (2005) and Boss et al. (2001a,b), the authors have found that either the beam attenuation spectral slope or the scattering coefficient spectral slope is a proxy for average particle size distribution. This relation between the particle attenuation/scattering coefficients and particle size distribution relies upon the assumption that particle attenuation/scattering coefficients can be modeled by the power law. In bio-optical modeling and in remote-sensing algorithms spectral dependency of the particle attenuation/scattering coefficients is also mainly described by the power law.

The aim of this study is to evaluate the reliability of the power function in describing the spectra of the particle attenuation and scattering coefficients in the eastern Baltic Sea. Coastal waters of the Baltic Sea are optically complex due to the variability of the concentration and the composition of the constituents. The changing composition of water constituents in coastal waters can be caused by natural phenomena (phytoplankton bloom and its degradation, substances from land transported in by rivers, wind-induced re-suspension in shallow regions) and also by human activities (dredging operations in harbors and re-suspension caused by shipping). Therefore, our collected dataset covers both all the seasons with different natural variations of water constituents as well as anthropogenic effects caused by harbor dredging. According to several previous studies, the power law may not adequately reproduce absorption (scattering) coefficient spectra if the contribution from algal particles is significant (e.g. Doxaran et al., 2009; Shi et al., 2014). Therefore, we seek an alternative approach for representing the particle scattering spectra, one that is based on the principal component analyses (PCA) of the measured scattering coefficient spectra. The parameterization of particle-specific attenuation/scattering coefficients could help remote sensing applications designed for TSM monitoring in coastal seas. In addition we also evaluate the variability of the TSM-specific attenuation and scattering coefficients for waters dominated by different particle types under different natural and anthropogenic conditions. The current study is based on hyperspectral measurements (WetLabs, ac-spectra) which give high-resolution spectral insights to the variability of attenuation/scattering spectra in the Baltic Sea.

2. Study site and methods

The dataset of inherent optical properties has been collected with the goal of monitoring suspended matter load in the coastal sea during dredging operations, in order to evaluate their environmental impact in two harbors at Muuga (Muuga Bay) and Paldiski (Pakri Bay) (Fig. 1). The dataset contains 135 measurements from twelve days, covering a wide range of environmental conditions with different dredging intensities and resulting in varied TSM concentrations. The locations of the sampling stations and the dredging area are shown in Fig. 1.

2.1. Laboratory analysis

Concentration of chlorophyll a (Chl a, in mg m\(^{-3}\)) was determined by filtering the water samples through Whatman GF/C glass microfibre filters (pore size 1.2 \(\mu\)m, diameter 47 mm, Whatman International Ltd., Mainstone, England), extracting the pigments with hot ethanol (90%, 75 °C) and measuring absorption at wavelengths of 665 nm and 750 nm. The values of Chl a were calculated with the Lorenzen (1967) formula. The detection limits of the method used the spectrophotometer were 0.05 mg \(m^{-3}\).

In order to determine the total suspended matter (TSM) concentrations, the water samples were filtered through pre-weighted Millipore membrane filters (pore size 0.45 \(\mu\)m, diameter 47 mm, Millipore Corporation, Bedford, MA), and the filters were dried to a constant weight at a fixed temperature (103–105 °C). The increase of filter weight indicates the suspended matter concentration in the water sample.

2.2. In situ measurements of inherent optical properties

Inherent optical properties of water were measured using a hyperspectral ac-spectra instrument (attenuation and absorption meter manufactured by WetLabs Inc.), which allows measurements of attenuation (\(c\)) and absorption (\(a\)) coefficients between the wavelengths (\(l\)) of 402–732 nm. The instrument was deployed together with the rosette and lowered from the surface to the bottom, along with a SeaBird CTD instrument. The manufacturer’s calibration was checked before each day of measurement, and the data was acquired with WetView 7 software. Correction for the temperature and salinity effects was done using Compass post-processing software provided by WetLabs. The software makes corrections for the temperature and salinity effects according to the ac protocol document (http://www.wetlabs.com/ac-s). Correction of scattering residuals in near-infrared was also performed using the Compass software by subtracting the data at a reference wavelength where the absorption is assumed to be zero. We chose an absorption value of 720 nm as a reference. Pure water attenuation and absorption were subtracted from the measured \(c(l)\) and \(a(l)\) before the data analysis. The corresponding particle scattering coefficient \((b_p)\) was calculated as follows:

\[
b_p(l) = c(l) - a(l) \tag{1}\]

Measurements at a depth of 1 m were used for data analysis.

3. Results

3.1. TSM and Chl a determined from water samples

In Pakri Bay, field campaigns were performed on 25.07.2008, 27.08.2008, 5.09.2008, 25.09.2008, 28.10.2008, 21.11.2008, 28.04.2009, and 10.09.2009. Daily minimum, maximum and mean concentrations of TSM (mg L\(^{-1}\)) and Chl a (mg m\(^{-3}\)), as well as the daily dredging amount (m\(^3\)) in Pakri Bay, are shown in Table 1. Dredging works in Pakri Bay started on 21.07.2008, and at the time of the field campaigns on 25.07.2008 and 27.08.08 we could not see a plume caused by dredged sediments near the dredging site by visual observation. However, a slightly higher TSM concentration was measured at the station closest to the dredging inside the harbor anchorage. During both field campaigns, high values of Chl a were measured and on 25.07.2008 some residuals of cyanobacterial scum were also visible at the entrance to Pakri Bay. Dredging works were on-going at the highest intensity during September. On 5.09.2008 the dredging amount was at its highest, reaching 10 000 m\(^3\) per day. The TSM concentration reached 30 mg L\(^{-1}\) inside the dredged sediments plume and ranged from 0.8 to 3.2 mg L\(^{-1}\) in the surrounding area.

During the second field campaign in September 2008 the TSM plume caused by dredging had settled and the TSM varied from 0.5 to 5.2 mg L\(^{-1}\). The next field campaigns were performed on
...on 21.11.2008, when the dredging intensity was lower, around 1500 m$^3$ per day. The TSM concentration varied from 2 to 9.6 mg L$^{-1}$. Higher values were measured near the harbor on both days the measurements were taken.

The last two field campaigns were performed on 28.04.2009 and on 10.09.2009, several months after dredging operations had stopped. In April 2009 the concentration of TSM varied from 1.8 to 4.2 mg L$^{-1}$ and the concentration of Chl$\alpha$ was between 1.9 and 7.8 mg m$^{-3}$. In September 2009 the TSM varied from 0.9 to 2.8 mg L$^{-1}$ and the concentration of Chl$\alpha$ was between 0.7 and 4.2 mg m$^{-3}$.

Field campaigns in Muuga Bay were performed on 20.02.2009, 09.09.2009, 23.04.2010 and 28.04.2010. Daily minimum, maximum and mean concentrations of TSM and Chl$\alpha$, as well as the daily dredging amount in Muuga Bay, are shown in Table 2.

Most of the TSM concentrations were between 1 and 4 mg L$^{-1}$ and Chl$\alpha$ concentrations were high, varying from 7.4 to 16.9 mg m$^{-3}$, indicating spring bloom. Fig. 2a, b shows histograms of concentrations of TSM and Chl$\alpha$ for the surface samples of all 135 measurements in Pakri and Muuga Bay. In total, the measured TSM concentration varied from 0.4 to 30 mg L$^{-1}$ and the concentration of Chl$\alpha$ varied from values below the detection limit (0.05) to 23 mg m$^{-3}$. Most of the TSM concentrations were between 1 and 4 mg L$^{-1}$. Measurements where the concentration of TSM exceeded 4 mg L$^{-1}$ were quite rare (Fig. 2a). In only one case, when intensive dredging activities were being conducted, was the TSM concentration over 30 mg L$^{-1}$ at the station near the harbor. Most Chl$\alpha$ concentrations varied between 0 and 8 mg m$^{-3}$, but moderate concentrations of Chl$\alpha$ from 8 to 16 mg m$^{-3}$ were also determined in 35 cases (Fig. 2b). In 27 cases the Chl$\alpha$ content was below the detection limit.

3.2. Analysis of attenuation coefficient spectra $c(\lambda)$

In all cases described in the previous section simultaneous measurement with ac-spectra was performed. We excluded the measurement performed inside the very heavy dredged sediment

### Table 1

<table>
<thead>
<tr>
<th>Date</th>
<th>No of samples</th>
<th>TSM min mg L$^{-1}$</th>
<th>TSM max mg L$^{-1}$</th>
<th>Daily mean TSM mg L$^{-1}$</th>
<th>SD</th>
<th>Chl$\alpha$ min mg m$^{-3}$</th>
<th>Chl$\alpha$ max mg m$^{-3}$</th>
<th>Daily mean Chl$\alpha$ mg m$^{-3}$</th>
<th>SD</th>
<th>Daily dredging amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.07.08</td>
<td>10</td>
<td>2</td>
<td>3.6</td>
<td>2.9</td>
<td>0.5</td>
<td>1.6</td>
<td>11.4</td>
<td>6.4</td>
<td>2.9</td>
<td>~2500</td>
</tr>
<tr>
<td>27.08.08</td>
<td>15</td>
<td>1.6</td>
<td>4.2</td>
<td>2.5</td>
<td>0.9</td>
<td>5</td>
<td>23</td>
<td>10.4</td>
<td>4.7</td>
<td>no dredging</td>
</tr>
<tr>
<td>5.09.08</td>
<td>15</td>
<td>0.8</td>
<td>30</td>
<td>3.8</td>
<td>6.8</td>
<td>1.2</td>
<td>6.8</td>
<td>7.1</td>
<td>2.7</td>
<td>~10 000</td>
</tr>
<tr>
<td>25.09.08</td>
<td>13</td>
<td>0.5</td>
<td>5.2</td>
<td>1.4</td>
<td>0.6</td>
<td>&lt;DL</td>
<td>5.2</td>
<td>2.3</td>
<td>1.9</td>
<td>~1500</td>
</tr>
<tr>
<td>28.10.08</td>
<td>6</td>
<td>2</td>
<td>4.6</td>
<td>2.6</td>
<td>1</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>0</td>
<td>~1500</td>
</tr>
<tr>
<td>21.11.08</td>
<td>9</td>
<td>4.8</td>
<td>9.6</td>
<td>7.2</td>
<td>1.6</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>0</td>
<td>~1500</td>
</tr>
<tr>
<td>28.04.09</td>
<td>11</td>
<td>1.8</td>
<td>4.2</td>
<td>3</td>
<td>0.9</td>
<td>1.9</td>
<td>7.8</td>
<td>4.7</td>
<td>1.9</td>
<td>no dredging</td>
</tr>
<tr>
<td>10.09.09</td>
<td>11</td>
<td>0.9</td>
<td>2.8</td>
<td>1.6</td>
<td>0.6</td>
<td>0.7</td>
<td>4.2</td>
<td>2.9</td>
<td>1</td>
<td>no dredging</td>
</tr>
</tbody>
</table>

<DL indicates that the measured values were below the detection limit.
the absorption coefficient of dissolved organic material \( \alpha_{\text{CDOM}}(\lambda) \), which can be modeled with the exponential function as follows:

\[
\alpha_{\text{CDOM}}(\lambda) = c'_l(380) \exp(-S_{\text{CDOM}}(\lambda - 380))
\]  

(Sipelgas et al., 2004). We did not measure \( c'_l(380) \) with the laboratory spectrophotometer this time. We relied on our earlier work, (Sipelgas et al., 2004) where we used the following relationship between \( a(440) \) measured by ac-9 and the attenuation of filtered water \( (c'_l) \) at 380 nm measured with the laboratory spectrophotometer:

\[
a(440) = 1.65c'_l(380) + 0.095.
\]

Thus, expressing \( c'_l(380) \) from (3) and, according to the results of the previous experimental measurements, taking \( S_{\text{CDOM}} \) equal to 0.013 in Pakri Bay (Sipelgas et al., 2009), we can calculate the spectra of \( \alpha_{\text{CDOM}}(\lambda) \) using \( a(440) \) measured by the ac-spectra during the current experiment.

By applying the last two equations, we calculated the CDOM absorption spectra for each measurement. The absorption of CDOM at 440 varied from 0.14 to 0.73 m\(^{-1}\), being 0.33 (SD 0.12) m\(^{-1}\) on average. The contribution of \( \alpha_{\text{CDOM}} \) in total attenuation at 440 nm was on average 12.35% (SD 2.79).

Finally, after subtracting the contribution of dissolved organic matter from the total attenuation coefficient, we obtained the \( c_p(\lambda) \) values. The spectra of \( c_p(\lambda) \) are shown on Fig. 3b. In theory, the spectral dependence of \( c_p(\lambda) \) can be modeled according to the power function (Boss et al., 2001a,b)

\[
c_p(\lambda) = a\lambda^{-\gamma_c}
\]

where \( \gamma_c \) is the spectral slope in log–log space and \( a \) is the scaling factor. In several recent studies, variations in the spectral slope of the \( c_p(\lambda) \) has been related to particle size distribution (Boss et al., 2001a,b; Oubelkheir et al., 2005; Astoreca et al., 2012). These relations rely on the Mie theory, which states that under well-constrained conditions (i.e. non-absorbing spherical particles with a spectrally constant index of refraction) \( \gamma_c \) is linked to the Junge exponent of the particle size distribution.

Next, we calculated the slope of measured \( c(\lambda) \) and the slope of calculated \( c_p(\lambda) \) from our dataset we concluded that slope \( \gamma \) of the \( c(\lambda) \) varied from 0.73 to 3.95, being 1.64 (SD 0.61) on average. The slope \( \gamma_c \) of \( c_p(\lambda) \) varied from 0.44 to 3.48, being 1.30 (SD 0.57) on average. We also calculated the difference between the measured \( c(\lambda) \) and the modeled \( c_p(\lambda) \) by calculating the coefficient of determination \( R^2 \). The \( R^2 \) ranged from 0.8 to 0.99, indicating that the power function described the \( c(\lambda) \) with high accuracy. Again, the reliability of the power law function in representing the \( c_p(\lambda) \) was evaluated by calculating \( R^2 \) between the measured \( c_p(\lambda) \) and modeled \( c_p(\lambda) \). The coefficient of determination varied from 0.67 to 1, indicating that the power function describes the \( c_p(\lambda) \) with high accuracy. In the case of our dataset, there was no reliable correlation between TSM or Chl \( a \) concentrations and the slope \( \gamma_c \).

The TSM-specific attenuation coefficient \( c_p^T(\lambda) \) was calculated by
normalizing $c_p(\lambda)$ to TSM. The spectra of calculated $c_p(\lambda)$ are shown in Fig. 3c. Absolute variability of $c_p(555)$ for all data was extremely large, varying from 0.29 to 3.84 m$^2$ g$^{-1}$ and being 0.87 (SD 0.52) m$^2$ g$^{-1}$ on average. All very high values ($c_p(555) > 2$ m$^2$ g$^{-1}$) were obtained from measurements made inside and near the dredged sediment plume in Muuga Bay on 9.09.2009. The shape of the $c_p(\lambda)$ spectra were similar by following the power law and decreasing towards longer wavelengths. TSM concentration and $c_p(555)$ were related by a significant linear relationship ($R^2 = 0.93$) with the corresponding regression formulas:

$$TSM = 1.25 \cdot c_p(555)$$

(5)

3.3. Analysis of scattering coefficient spectra $b(\lambda)$

The particle scattering coefficient at 440 nm varied from 0.37 to 7.9 m$^{-1}$. Spectral variations of the scattering coefficient are often described by the power law (Morel, 1988; Graver and Siegel, 1997), although the power law is only valid for a population of non-absorbing particles following a Junge-type size distribution (Babin et al., 2003). We analyzed the spectral slope of the scattering coefficient in the visible range of wavelengths of 400–705 nm. The spectral dependence of $b_p(\lambda)$ was fitted to the power law:

$$b_p(\lambda) = a \lambda^{-\gamma_b}$$

(6)

where $\gamma_b$ is the slope of the scattering spectrum in a log–log space and $a$ is the scaling factor. The reliability of the power law function in representing the scattering spectrum was evaluated by calculating the determination coefficient $R^2$ between the modeled $b_p(\lambda)$ and measured $b_p(\lambda)$. The $R^2$ varied from 0 to 1.0.

Slope $\gamma_b$ of $b_p(\lambda)$ varied over a very wide range, from 1.15 to $-0.56$. Even negative slope values were obtained, which means that the scattering spectrum increased towards longer wavelengths. There was also interdependency between the $\gamma_b$ and the $R^2$ (Fig. 4). From Fig. 4 we can well observe the tendency for the $R^2$ to decrease when $\gamma_b$ approaches 0, indicating that the difference between the modeled $b_p(\lambda)$ and the measured $b_p(\lambda)$ is considerable.

The shape of particle scattering spectra (slope $\gamma_b$) was analyzed in respect to particle concentrations (TSM and Chl a). There was no dependency between slope $\gamma_b$ and the TSM concentration in our dataset. However, there was a significant relationship between the slope of $\gamma_b$ and Chl a concentration (Fig. 5). The slope of $\gamma_b$ decreased or even became negative when Chl a concentration increased. The linear relationship between $\gamma_b$ and Chl a concentration was

$$\gamma_b = -0.048 \cdot \text{Chl a} + 0.59, \quad R^2 = 0.57.$$  

(7)
3.4. Decomposition of scattering spectra

Measured TSM and Chl $a$ concentrations showed that some samples were dominated by TSM and some samples by Chl $a$. The slope values of scattering spectra and $R^2$ show that the power law may not describe the measured scattering spectra adequately, especially when Chl $a$ concentration is high. The attenuation spectra were well modeled by the power law.

We used principal component analyses (PCA) to find dominant types of scattering spectra. The PCA were performed in a logarithmic space, i.e. $\log_{10}(b_p)$. First we subtracted the mean value of each spectrum and then applied PCA. The shape of the three spectra and the corresponding amplitudes, which explain 86.1%, 9.6% and 2.7% of the total variability respectively, are presented in Fig. 6.

The spectrum of the first mode decreases monotonically with increasing wavelength (Fig. 6a). We call the first mode a “mineral-type” spectrum. The spectrum of the second mode has low values in the blue part of the spectrum, then increases towards intermediate wavelengths and then decreases towards the red part of the spectrum. A local minimum at 672 nm caused by algal particles is clearly visible. We call the second mode an “algae-type” spectrum. The third mode also has a local minimum at 672 nm, which indicates the effect of algal particles. The main difference between the second and third mode spectrum is that the third mode spectrum decreases sharply between 400 and 430 nm and has a broad minimum between 430 and 490 nm.

The amplitude values are mainly positive (Fig. 6b), which means that the shapes of the spectra are preserved. Negative amplitude values mean that shapes of corresponding spectra are reversed relative to the $x$-axis (on Fig. 6b). We would like to highlight two groups of measurements from the amplitude values. The first 24 stations were visited in Muuga Bay on 23rd and 28th April 2010 during spring phytoplankton bloom when dredging work was not being performed. The stations 98–112 were visited in Pakri Bay on 28th October and 21st November 2008 when dredging intensity was around 1500 m$^3$ and biological activity was low.

The TSM-specific scattering coefficient ($b_p(\lambda)$) was calculated as the ratio of $b_p(\lambda)$ to the TSM concentration. The calculated $b_p(555)$ from our dataset showed a large degree of variability, from 0.2 to 3.14 m$^2$ g$^{-1}$. All 11 cases when $b_p(555)$ was >1.02 m$^2$ g$^{-1}$ were observed from measurements made near and inside the dredged sediment plume in Muuga Bay on 9.09.2009. TSM concentration and $b_p(555)$ were related by a significant linear relationship ($R^2 = 0.91$) with the corresponding regression formulas:

$$TSM = 1.47*b_p(555)$$  (8)

$$Slope_{b_p} = 0.91$$

$$C_0 = 1.02 m^2 g^{-1}$$

$$b = 3.14 m^2 g^{-1}$$

$$g = 0.2$$

The scatterplot of the amplitude values of the first and second mode (Fig. 7) shows strong linear relationship ($R^2 = 0.79$) where low values of the amplitudes of the first mode correspond to the high values of the amplitude of the second mode and vice versa. From this scatter, we cannot separate different groups of stations, as the transfer from “algae-type” spectra to “mineral-type” spectra is smooth. There is no statistically significant linear relationship

**Fig. 5.** Scatterplot (crosses) and linear regression relationship (bold line) of Chl $a$ vs. the slope $\gamma$ of $b_p(\lambda)$ as modeled according to (6).

**Fig. 6.** The shapes of the first three principal modes of scattering coefficient spectra (a) and corresponding amplitudes (b). Dotted lines separate the two groups of measurements. The first 24 stations were visited in Muuga Bay on 23rd and 28th April 2010 during spring phytoplankton bloom, when dredging work was not being performed. The stations 98–112 were visited in Pakri Bay on 28th October and 21st November 2008 when dredging intensity was around 1500 m$^3$ and biological activity was low.
between the amplitudes of the first and third mode spectra and the amplitudes of the second and third mode spectra. The shape of the first mode spectrum matches the power function (Fig. 6a). Therefore, it is justified to seek a relationship between the amplitudes of the first mode and the slopes of the modeled scattering spectra, $\gamma_b$. The strong linear relationship ($R^2 = 0.999$) shows that the first principal component accounts for the power law dependence of the measured scattering spectra (Fig. 8). There is strong linear relationship between $\gamma_b$, and the amplitude of the second mode spectra ($R^2 = 0.82$), but this is due to co-linearity of the amplitudes of the first and second mode spectra.

The spectra explained by the first principal component and the sum of the second and third principal component were fitted separately to the measured scattering spectra. The match of the fitted spectra and the measured spectra were counted by calculating $R^2$ values. We use the threshold value of $R^2 = 0.5$ for the separation of the two types of spectra. Using these criteria, we found that 88 spectra belong to the “mineral-type” spectrum (Fig. 9a) and 43 to the “algae-type” spectrum (Fig. 9b). Three spectra did not belong to either type. In comparison, if we use a threshold value of $R^2 = 0.8$, then the corresponding numbers of the spectra are: 76, 13 and 35.

To analyze the relationship between the TSM and Chl $a$ concentrations and the dominant type of the spectrum, the scatter of TSM vs. Chl $a$ concentration is plotted for different types of spectra (Fig. 10). It is obvious from Fig. 10 that we cannot draw solid conclusions about Chl $a$ (or TSM) concentrations and the types of spectra. Relying on the current dataset, we may say that if Chl $a$ concentration is $\geq 15$ mg m$^{-3}$ then we have an “algae-type” scattering spectrum. If Chl $a$ concentration is below the detection limit, then we have a “mineral-type” spectrum. We may weaken the constraint and assume that if Chl $a$ concentration is above 10 mg m$^{-3}$ or below 5 mg m$^{-3}$, then most likely we have an “algae-type” or a “mineral-type” spectrum, respectively.

4. Discussion

The measurements were carried out in the coastal sea of the southern part of the Gulf of Finland during all seasons. The Chl $a$ values varied from a negligible concentration during late autumn and winter to 23 mg m$^{-3}$ in spring. We missed the peaks of intensive phytoplankton blooms in spring and summer when Chl $a$

---

**Fig. 7.** Scatterplot of the amplitude values of the first and second principal mode of measured scattering coefficient spectra.

**Fig. 8.** Scatterplot of the amplitudes of the first principal mode and the slopes of the scattering coefficient spectra, $\gamma_b$, modeled by power law.

**Fig. 9.** The measured scattering spectra belonging to a) “mineral-type” spectrum and b) “algae-type” spectrum with mean (solid bold) and SD (dashed bold). The criteria for the separation of different types of spectra is explained in the text.
concentrations may exceed 100 mg m\(^{-3}\) (Rantajärvi et al., 1998). Most of the TSM concentrations varied between 1 and 4 mg L\(^{-1}\), i.e. in the range of natural variability. The TSM concentrations which rose above 5 mg L\(^{-1}\) on a few occasions can be attributed to the effect of dredging. Still, there are no solid criteria which would help define the dominant constituent in the water based on the ratio of TSM and Chl a concentrations.

In this study, we used decomposition of the measured scattering spectra into dominant modes by applying PCA. The first mode represented the power law dependence of the particle scattering coefficient spectrum on wavelength. The amplitudes of the first mode and the slope values \(\gamma_b\) of modeled \(b_p(\lambda)\) showed strong linear relationship. As this spectrum did not show a significant absorption peak at 672 nm due to algal particles, we named this mode the “mineral-type” spectrum. The second mode or the composition of the second and third mode was named the “algae-type” spectrum, as in both cases there was an obvious minimum at 672 nm in the scattering spectrum. Stramski et al. (2001); Babin et al. (2003); and McKee and Cunningham (2006) have shown the clear minima in the scattering spectrum within the main phytoplankton pigment absorption bands. This spectral shape of the scattering coefficient is typical for particle populations dominated by phytoplankton.

We fitted the spectra reproduced by the first principal component and the sum of the second and third component separately to the measured spectra. We defined the criteria as follows: if the determination coefficient is above 0.5 in the first case, then we have the “mineral-type”, and if the determination coefficient is above 0.5 in the second case, then we have the “algae-type” spectrum. There was no obvious relationship between the TSM or Chl a concentrations (or their ratio) and the type of the dominant scattering spectrum. We established that if the chlorophyll concentration is either high or low, then the “algae-type” or “mineral-type” scattering spectrum is dominant, respectively. Based on our database, we chose that if Chl a concentrations are above 10 mg m\(^{-3}\), then the “algae-type” spectrum is dominant and if Chl a concentrations are below 5 mg m\(^{-3}\), then the “mineral-type” spectrum is dominant. The selection of threshold values was done by visual inspection of the TSM and Chl a concentration scatterplot for different types of spectra (Fig. 10).

In accordance with our analyses, it is meaningful to fit a power function to the samples that were defined to have “mineral-type” spectra and for Chl a concentrations that were below 5 mg m\(^{-3}\). In the first case, the mean \(\gamma_b\) of modeled \(b_p(\lambda)\) was 0.50 (SD = 0.22) and in the second case it was 0.52 (SD = 0.2). For the water samples of the “algae-type” scattering spectrum, mean \(\gamma_b\) of modeled \(b_p(\lambda)\) was –0.07 (SD = 0.14). Shi et al. (2014) also found that the power law describes the particle scattering coefficient spectra accurately in waters dominated by inorganic particles. In their study, mean average percent error (MAPE) was <0.07 in waters dominated by inorganic particles. In our case, MAPE was <0.05 over the entire spectral range for the “mineral-type” spectra. Babin et al. (2003) compared the \(b_p(\lambda)\) collected in different regions and showed that the scattering spectrum for the Baltic Sea had the steepest ascending slope towards short wavelengths.

A simple power law function closely reproduced the \(c_p(\lambda)\) and \(c_p(\lambda)\) spectra. An argument could be made against how we managed to determine the \(a_{\text{CDOM}}(\lambda)\) spectra, considering that we did not measure them directly. Indeed, \(a_{\text{CDOM}}\) parameterization influences the shape of the power law function fitted to \(c_p\), but not \(b_p\). In the case of high values of \(\text{CDOM}\) in (2) the particle attenuation spectrum approaches the attenuation spectrum. The impact of \(a_{\text{CDOM}}(\lambda)\) parameterization on slope factor \(\gamma_c\) for \(\text{CDOM} \rightarrow 0\) is not so straightforward. We did tests with different \(\text{CDOM}\) values (test 1 with different \(\text{CDOM}\) values (0.011, 0.013, 0.015)). The maximum difference from \(\text{CDOM} = 0.013\) was 5%, while the mean difference for the entire dataset was 1%. Thus, the changes of \(c_p(\lambda)\) and \(c_p(\lambda)\) are negligible if \(\text{CDOM}\) is kept in a reasonable range.

The slopes of the \(c(\lambda)\) and \(c_p(\lambda)\) spectra varied in a wide range, from 0.73 to 3.95 and from 0.44 to 3.48 for the \(c(\lambda)\) and \(c_p(\lambda)\) spectra, respectively. This is to be expected when the measurements cover different seasons and include harbor dredging activity. For example in the Mediterranean, Oubelkheir et al., 2005 found the slope of \(c_p(\lambda)\) to be 2.8 in deep water and 0.34 in the upper mixed layer, where the dominant particles were phytoplankton. In comparison, the \(\gamma_c\) of \(c_p(\lambda)\) in the North Sea varied from −0.3 to 0.7 (Astoreca et al., 2012). Both results were obtained from WetLabs ac-9 data. We got lower slope values of \(c_p(\lambda)\) for the samples belonging to “algae-type” scattering spectra than from those belonging to the “mineral-type” scattering spectra. Mean values of \(\gamma_c\) were 1.0 (SD = 0.3) and 1.5 (SD = 0.6) for “algae-type” and “mineral-type” scattering spectra, respectively. Median values of \(\gamma_c\) were lower for both types of spectra, being 0.8 and 1.3, respectively. The results did not change significantly when we used Chl a concentrations (Chl a >10 mg m\(^{-3}\) or Chl a <5 mg m\(^{-3}\)) to separate the algae- and mineral-dominated samples.

The variability of \(b_p(555)\) and \(c_p(555)\) for all data was extremely large, but all large values were obtained from measurements made inside and near the dredged sediment plume in Muuga Bay on 9.09.2009. At that time, very fine whitish sediments were visible via visual observation, although the concentration of TSM was rather low. This situation was exceptional. Its exceptional nature was confirmed when we calculated the linear regression relationship between \(b_p(555)\) and \(c_p(555)\) and TSM concentrations. The linear relationship was rather strong in both cases (see (8) and (5)), which shows that TSM-specific attenuation and scattering coefficients at \(\lambda = 555\) nm were quite stable. From (8) and (5) we obtain that \(b_p(555) = 0.68\) m\(^2\) g\(^{-1}\) and \(c_p(555) = 0.8\) m\(^2\) g\(^{-1}\). According to a study by Babin et al. (2003), the average \(b_p(555)\) varied from 0.42 m\(^2\) g\(^{-1}\) in the Mediterranean to 0.97 m\(^2\) g\(^{-1}\) in the Atlantic, being 0.49 m\(^2\) g\(^{-1}\) in the Baltic Sea.

We applied linear regression analyses between \(c_p(555)\) and TSM concentrations and \(b_p(555)\) and TSM concentrations for the samples of “mineral-type” and “algae-type” scattering spectra separately. All \(R^2\) values were in excess of 0.92. The \(c_p(555) = 0.85\) m\(^2\) g\(^{-1}\) and \(c_p(555) = 0.64\) m\(^2\) g\(^{-1}\), the
The average scattering spectra into the sum of the 10 mg m\(^{-3}\) estimate from our dataset that if Chl and higher values at intermediate wavelengths. We may roughly estimate from b\(_p\)(532) was higher for inorganic particles (0.71 m\(^2\) g\(^{-1}\)) than for organic particles (0.45 m\(^2\) g\(^{-1}\)). Several previous studies (Baker and Lavelle, 1984; Babin et al., 2003) have reported an increase in b\(_p\)(555) moving from coastal (case II) to open waters (case I). In a study by Doxaran et al. (2009), the calculated b\(_p\)(555) was 0.41 m\(^2\) g\(^{-1}\) (SD 0.09) for the Baltic Sea. Wozniak et al. (2011) found the average b\(_p\)(555) to be 0.64 m\(^2\) g\(^{-1}\) (SD 0.22) for the southern Baltic Sea.

5. Conclusions

Hyperspectral ac-spectra measurements in Estonian coastal waters were analyzed for the attenuation and scattering spectra. The power law described the attenuation and particle attenuation spectra with high accuracy, and the R\(^2\) was 0.8–0.99 and 0.67–1, respectively. The dataset average c(\(\lambda\)) and c\(_p\)(\(\lambda\)) slopes were 1.6 and 1.3, respectively. There was no significant linear relationship between the spectral slopes of c(\(\lambda\)) and c\(_p\)(\(\lambda\)) and TSM or Chl a concentrations.

Although the power law did not describe particle scattering spectra for the whole dataset, there was relatively strong linear relationship between Chl a concentration and the spectral slope of b\(_p\)(\(\lambda\)).

Principal component analyses enabled to decompose particle scattering spectra into the sum of the “mineral-type” and “algae-type” spectra. The “mineral-type” spectrum matches the power law dependence of the particle scattering coefficient spectrum on wavelength. The “algae-type” spectrum has a prominent local minimum at 672 nm, low values in the blue part of the spectrum and high values at intermediate wavelengths. We may roughly estimate from our dataset that if Chl a concentration is above 10 mg m\(^{-3}\) or below 5 mg m\(^{-3}\), then most likely the “algae-type” or “mineral-type” spectrum dominates, respectively. Taking into account the separation of scattering spectra into a “mineral-type” and an “algae-type” spectrum, we may conclude that “algae-type” water samples have 1) lower slope of attenuation and scattering spectra; 2) lower variability of attenuation and scattering spectra than “mineral-type” water samples.

There was strong linear relationship (R\(^2\) > 0.92) between TSM concentration and c\(_p\)(555) and b\(_p\)(555), regardless of the shape of the particle scattering spectra. The estimated TSM-specific attenuation and scattering coefficients at 555 nm were 0.8 m\(^2\) g\(^{-1}\) and 0.68 m\(^2\) g\(^{-1}\), respectively. Corresponding values for water samples with a dominant “mineral-type” spectrum were 0.85 m\(^2\) g\(^{-1}\) and 0.73 m\(^2\) g\(^{-1}\), respectively. Lower values were obtained for water samples with a dominant “algae-type” spectrum, being 0.64 m\(^2\) g\(^{-1}\) and 0.52 m\(^2\) g\(^{-1}\), respectively. Therefore, a separate parameterization for different water types is suggested when converting scattering into TSM concentration.

In general, based on our results, we suggest the following procedure for the modeling of particle scattering spectra. First, principal component analyses should be applied to the region-specific database of hyperspectral in situ measurements, in order to obtain 2–3 dominant types of scattering spectra. Second, a linear combination of these types of spectra should be fitted to an independent database for validation and improvement of the model. A validation of the current model for the eastern Baltic Sea is the aim of a future study.

References


