Pure water spectral absorption, scattering, and real part of refractive index model

Algorithm Technical Basis Document
- Draft -

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Revisions:

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Overview

This document summarizes the necessary formulations to calculate inherent optical properties (IOPs) of water at atmospheric pressure and at a specific water temperature and salinity, namely absorption (absorption coefficient), scattering (scattering coefficient for any angle, for back-, forward-, and total scattering) and real part of the index of refraction. The obtained spectral data can be used for radiative transfer simulations or other application where knowledge of the temperature and salinity specific IOPs is necessary, e.g. for interpretation of surface reflection spectra in remote sensing applications or in measurements of other water constituents where changes in the reference water with temperature and salinity need to be corrected for.

Introduction

The inherent optical properties of pure liquid water and pure liquid seawater are fundamental for the interpretation of optical measurements of natural waters and its constituents. The sun light that is scattered backwards in water and hence can be measured from above the surface (e.g. by satellites)
contains information of absorption and scattering in the water body. A part of the light is reflected directly at the sea surface and, hence, is related to the real part of the index of refraction of seawater. As water itself absorbs and scatters light, the reflectance is influenced by the absorption, scattering and refractive index of pure water besides the IOPs of the other water constituents like that of dissolved and particulate matter. All three specific IOPs of pure water considered here (absorption, scattering and refractive index (real part) are dependent on the temperature and salinity of water. These changes with T and S are wavelength-dependent and lead to significant changes at specific wavelengths by large temperature changes or simply because seawater contains significant amount of salt compared to pure water. (sea salt itself does not absorb light in VIS-IR). These changes are known and are typically corrected in measurements of IOPs of water samples. However, some necessary correction coefficients are just recently determined with a good spectral resolution for

Table 1: The S-3 OLCI and SLSTR (shaded) band settings.

<table>
<thead>
<tr>
<th>OLCI (O); SLSTR (S)</th>
<th>Central wavelength in nm</th>
<th>Width in nm</th>
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<tr>
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<td>15</td>
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<tr>
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<tr>
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<tr>
<td>S 3740</td>
<td>380</td>
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temperature (Sullivan et al 2006, Langford 2002) and salinity (Sullivan et al 2006). Influences of salinity and temperature are as well known for the middle to far IR (Max & Chapados 2001a, 2007). New measurements for the UV and the near and short wavelength IR are necessary to allow sensitivity studies for these T and S related changes in the full spectral range of future satellite missions (400 - ~4000 nm).

Table 1 lists the wavelength of the instruments OLCI and SLSTR on Sentinel-3. Due to the strong absorption of pure water in the IR region and the very low scattering, the influence of T and S on absorption of pure water are considered to be limited to the mid VIS and NIR region. At shorter wavelength the absorption of water is low but that of other constituents (phytoplankton pigments, humic substances) is significantly larger. In the SWIR the influence on the real part of the index of refraction by T and S might be significant for calculating the specular reflectance of sun and sky light using the Fresnel formula.

In the following the calculation of these IOPs for different T and S values is described individually for absorption, the real part of the index of refraction, and for scattering.

Absorption

The absorption of pure water is influenced by water temperature, $T$, and salinity, $S$. Changes in $T$ seem to alter the frequency of the three main O-H vibrations and with it the frequencies of the related overtones and harmonics. This leads to characteristic increases and decreases in absorption at specific wavelengths. The exact physicochemical changes in the molecular composition and structure of water is not known (e.g. Marechal 2007, Larouche et al.2008). In the temperature range of liquid water these changes are linearly related to temperature and a single temperature-specific
coefficient of pure water absorption $\Psi_T(\lambda)$ can be used to calculate pure water absorption at different temperatures in case the absorption at a specific temperature, $T_0$, is known, as

$$a_w(T, \lambda) = a_w(T_0, \lambda) + (T - T_0) \Psi_T(\lambda) \quad (1)$$

Dissolving salt in water seems to lead to the formation of an additional type of water (in addition to pure water), the “pure salt-solvated water” that is part of a rather stable ion pair complex (Max & Chapados 2001). This type of water has the same basic absorption characteristics but the intensity of specific frequencies is altered leading to linear changes in the overall absorption spectrum with salt concentration. The obtained absorption at a specific salt concentration is the sum of absorption by pure water and that by the pure salt-solvated water (Max & Chapados 2001, Max et al. 2001). For the wavelength range considered here the absorption by salt itself is negligible. The absorption of pure salt-solvated water is dependent on the hydration number ($n = 2 - 5$), the number of water molecules organized in the salt ion complex and hence on the type of the salt due to the size ratio of the specific cation and anion (Max & Chapados 2001). However, for a specific salt the absorption of pure salt-solvated water is independent on the salt concentration, thus, the changes in total water absorption with salt concentration (salinity) is linear. Like for the temperature, the change in absorption at specific wavelengths can be positive or negative, as, when the concentration of pure salt-solvated water increases that of pure water decreases. A conceptual salinity coefficient of pure water absorption, $\Psi_S$, can be used to calculate the water absorption at different salinities, when the water absorption at a specific salinity, $S_0$, is known, as

$$a_w(S, \lambda) = a_w(S_0, \lambda) + (S - S_0) \Psi_S(\lambda). \quad (2)$$

Fig. 2: Pure water absorption ($\pm 2\sigma$) in the UV/VIS spectral region.
Ψ_S is considered to be valid for all seawaters as the salt composition of seawater is globally very similar. Besides salt ions several other ions are dissociated in seawater, hence, the water absorption is influenced also by organic ions and the pH. Due to relatively low concentration of these ions in natural waters the influence can be considered as being relatively small compared to that by inorganic salts. (But other constituents absorb light themselves in contrast to salt, which changes the absorption of the water).

The influence of temperature and salinity on pure water absorption are independent of each other and equation (1) and (2) can be combined to
\[ a_w(T, S, \lambda) = a_w(T_0, S_0, \lambda) + (T - T_0) \Psi_T(\lambda) + (S - S_0) \Psi_S(\lambda). \] (3)

For the necessary water absorption at \((T_0, S_0)\) the absorption of pure water at 20.0°C and without salt, \(a_w(\lambda) = a_w(20^\circ C, 0 \text{ PSU}, \lambda)\) is used. Equation 3 is simplified to

\[ a_w(T, S, \lambda) = a_{w0} + (T - 20.0) \Psi_T(\lambda) + S \Psi_S(\lambda). \] (4)

This \(a_{w0}(\lambda)\) spectrum is a combination of empirical measurements at different temperatures (Pope &}

![Fig. 6: The salinity coefficient of pure water absorption, \(\Psi_S (m^{-1} \text{ PSU}^{-1})\), as a function of wavelength.](image1)

![Fig. 5: Relative difference in % absorption per PSU calculated using \(\Psi_S\) and the pure water absorption at 0 PSU.](image2)
Fry 1997, Lu 2006, Wang 2008, Segelstein 1981 (>700 nm), Wieliczka et al. 1989, and Max & Chapados 2009 (1850-2000 nm, > 2500 nm)) that were partly modified to get the absorption at the reference temperature of 20 °C using the spectrum of Ψ_T. This combined pure water absorption spectrum at 20.0 °C is shown in Fig. 1 and 2. The relevant error at each wavelength was either taken from the experimental data are calculated from the calculation of the mean in case several measurements were available.

The spectrum of Ψ_T is that measured by Röttgers 2010 combined with measurements in the SWIR by Larouche et al. 2001 (see Fig. 3). The relevant errors of the temperature coefficient are the experimental errors calculated from several repetitions. The relative change in absorption varied from -0.4 – 0.7 % per °C (Fig. 4).

The spectrum of Ψ_S is is taken from Röttgers 2010 and the combination of new measurements in the UV to NIR and a spectrum calculated from data of Max & Chapados 2001 (Fig. 5). The relevant errors of the salinity coefficient are the experimental errors calculated from several repetitions. The relative change in absorption per PSU varied between -0.15 % and 0.05 % (see Fig. 5).

To determine the error for absorption at any temperature and salinity, the errors for the absorption, the temperature and salinity coefficient were combined using regular error propagation.

**Real part of the index of refraction**

The real part of the refractive index, \( n_w \), of pure water is determined by its dielectric constant, \( \varepsilon_\omega \), as \( \varepsilon_\omega = n_w^2 \), which depends on density and temperature. The real part of the refractive index of seawater, \( n_{sw} \), is the linear sum of \( n_w \) and the molar indices of the different salt ions dissolved in seawater. Molar indices for different ions are known only at single wavelengths, and empirical measurements of \( n_{sw} \) are rare especially in the IR region. Empirical data for refractive index of water and seawater measured against air, \( n_w' \) and \( n_{sw}' \), respectively, for different temperatures and salinities are given by Austin & Halikas 1976 but limited to the VIS spectral regions. Data of \( n_w \) for other wavelengths at a specific temperature are given in Segelstein 1981, Bertie & Lan 1996, Max & Chapados 2009, other data are reviewed by Irvine & Pollack 1968 and Schiebener et al. 1990. Measurements of \( n_{sw}' \) by Austin and Halikas 1976 for the range 400 – 700 nm were used by Quan & Fry 1995 for fitting a formulation to provide \( n_w' \) for different T and S. Huibers (1997) showed that the Quan & Fry 1995 formulation is valid for the spectral range of 200 – 1100 nm. Information on \( n_{sw} \) in the SWIR can only be gathered from measurements of NaCl solutions (e.g. Max & Chapados 1999). These measurements give evidence that \( n_w \) varies with wavelength in a constant manner, as the effect on the polarizability should lead to a rather constant shift in \( n \) over all wavelengths.

To have the full spectral information (300 - 4000 nm) a spectrum of \( n_w \) at 27 °C, \( n_{w0} \), was constructed from data of Austin & Halikas 1976 (using Quan and Fry 1995 formulation with correction for the refractive index of air, \( n_a \)), and the data of Max & Chapados 2009 (which were measured at 27 °C).

Quan & Fry 1995 provided accurate data of \( n_{w0}' \) in the spectral range 400 – 700 nm. The formulation was used here for the range of 300 – 800 nm (see Huibers 1997). \( n_{w0}' \) (T, S, 300 – 800 nm) is calculated as
with \( n_0 = 1.31405, n_1 = 1.779 \times 10^{-4}, n_2 = -1.05 \times 10^{-5}, n_3 = 1.6 \times 10^{-8}, n_4 = -2.02 \times 10^{-6}, n_5 = 15.868, \)
\( n_6 = 0.01155, n_7 = -0.00423, n_8 = -4382, n_9 = 1.1455 \times 10^6, T \) is the temperature in °C, and \( S \) the salinity in PSU.

The refractive index of seawater is calculated by scaling \( n_{sw}' \) to the refractive index of air, \( n_a \), as

\[
n_{sw} = n_{sw}' * n_a, \quad \text{(6)}
\]

where \( n_a \) is calculated for standard air after Ciddor 1996 (according to Zhang & Hu 2009), as

\[
n_a = 1 + \left[ k_1 \left( k_0 - \nu^2 \right) + k_2 \left( k_2 - \nu^2 \right) / 10^8 \right], \quad \text{(7)}
\]

where \( \nu \) is the wavenumber in \( \text{μm}^{-1}, k_0 = 238.0185 \text{μm}^{-2}, k_1 = 5792105 \text{μm}^{-2}, k_2 = 57.362 \text{μm}^{-2}, k_3 = 167917 \text{μm}^{-2}. \)

Quan & Fry (1995) provided accurate data for 300 – 800 nm, whereas Max & Chapados (2009) for > 1670 nm. The accuracy of this data is high as can be seen by comparison with other data (Fig. 7). The data of Max & Chapados 2009 are similar to those of Bertie & Lan 1996. Values for the region of 800 – 1670 nm are available from Segelstein 1981 but deviate from the other two data sets in the considered wavelength regions (see Fig. 7). Hence, data for \( n_{sw} \) (800 – 1670 nm) were constructed by linear interpolation of the data of Segelstein 1981 between 800 and 1670 nm, as these data showed another anomalous dispersion effect on \( n_a \) at about 1400 nm that would not have been resolved by a simple linear interpolation of the data of Austin & Halikas 1976 and Max & Chapados 2009 alone. The data and the constructed spectra are shown in Fig. 7.

The complete spectra of \( n_{sw} \) (T, S, 300 – 4000 nm) is calculated by calculating first \( n_{sw}'(T, S, 300 – 800 \text{ nm}) \) using the formulation of Quan & Fry 1995 and scaling it to \( n_a \) using the formulation of Ciddor 1996. \( n_{sw} \) (T, S, 800 – 4000 nm) is calculated by adding the absolute difference at 800 nm between the standard spectrum \( n_{sw0} \) (27 °C, 0 PSU) and \( n_{sw} \) (T, S), as

\[
n_{sw}(T, S, 300 – 800 \text{ nm}) = n_{sw}'(T, S, 300 – 800 \text{ nm}) / n_a \quad \text{(8)}
\]

\[
n_{sw}(T, S, > 800 – 4000 \text{ nm}) = n_{sw0}(T, S, > 800 – 4000 \text{ nm}) + [n_{sw}(T, S, 800 \text{ nm}) - n_{sw0}(800 \text{ nm})]. \quad \text{(9)}
\]

Spectra of the real part of the index of refraction for different temperature and salinities are shown in Fig. 8 and 9. The absolute error for the refractive index is taken as being 1% of the value throughout the spectrum. Measurements error in the UV/VIS spectral region are in the range of 0.0005 to 0.001 and, hence, more than an order of magnitude less than 1%. The errors for values at longer wavelengths are not given for the relevant data sets.

**Scattering**

Scattering by pure water is the result of fluctuations of molecule number density resulting in changes in refractive index and is described by the Einstein-Smoluchowski theory of scattering (Smoluchowski 1908, Einstein 1910). This kind of scattering was theoretical described e.g. by
Fig. 7: The real part of the index of refraction of pure water and seawater. Upper panel: Different measurement in the UV/VIS spectral region. Middle panel: Measurement in the NIR to SWIR spectral region. Lower panel: Combined spectrum at 27 °C using formulation of Quan & Fry 1995 and data of Max & Chapados 2009.
Mobley (1994), Morel (1974), and Zhang & Hu (2009). The fluctuation are dependent on density and temperature, where the effect of temperature is < 1% of that of density (not considering the effect of temperature on density). Different formulations have been developed to calculate scattering by pure liquid water, which uses approximations for some specific physical parameter, like the density derivative or the depolarization ratio (see Morel 1974, Shifrin 1988, Buiteveld et al. 1994). Recently Zhang & Hu (2009) reviewed these calculations and presented a new formulation using a physical description of the density fluctuation of the refractive index, \( n \) (as \( \varepsilon = n^2 \)). Measurements of the pure water scattering coefficient are rare, that of Morel (1966, 1968) for 5 wavelengths are widely accepted, as they showed the smallest values. Earlier measurements are reviewed by Morel 1974, together with a description of the technical difficulties in determining absolute values of scattering. The results of Zhang & Hu (2009) agreed with the measurements of Morel (1966, 1968) within the measurement errors of 2%. In sea water an additional scattering is caused by fluctuations of the concentration of the salt ions, which on the other side influences the total density fluctuations. Total scattering by sea water is the sum of scattering by density and concentration fluctuations and is, hence, a non-linear function of the total concentration of salt ions, i.e. salinity (Fig 10 and 11). Empirical studies on scattering by sea water are reviewed by Morel (1974) with those of Morel (1966, 1968) being widely accepted. The theoretical approaches for its calculation are recently
reviewed in Zhang et al. (2009). They presented a new calculation using again a physical description of the density and concentration fluctuations of the refractive index, which agree well with the measurements of Morel (1966, 1968). One last critical parameter is the depolarization factor of scattering, which is only roughly known and which varies in these formulation between 0.039 to 0.051. Scattering at different wavelengths by pure water and by seawater of different salinity and different temperature can be calculated from formulation given in Zhang et al. 2009, with a ~1% deviation from the empirical measurements of Morel (1974). The formulation of Zhang et al. 2009 is used to calculate scattering as a function of T and S. The depolarization factor, $\delta$, is 0.039 by default and necessary $n_{sw}$ data are calculated as described above. The calculation is extended to IR wavelengths by using the complete spectra of $n_{sw}(T, S)$. The results can be expressed in terms of the full phase function of scattering, total scattering, or backscattering.

The volume scattering function at 90° as a function of wavelength, temperature and salinity, $\beta_v(\lambda, T, S)$, is calculated as the sum of scattering by density fluctuations, $\beta_{wd}(T, \lambda)$ and that by concentration fluctuations, $\beta_{wc}(S, \lambda)$, as

$$\beta_w(90^\circ, \lambda, T, S) = \beta_{wd}(90^\circ, \lambda, T) + \beta_{wc}(90^\circ, \lambda, S). \quad (10)$$
Scattering of pure water is only due to density fluctuations and this is calculated according to Zhang & Hu 2009 as

$$\beta_{wd}(90^\circ, \lambda, T) = \frac{\pi^2}{2\lambda^4} \left( \rho \frac{\partial n^2}{\partial \rho} \right)_T kT \beta_T f(\delta), \quad (11)$$

where \(k\) is the Boltzmann constant, and \(\rho, n, T, \beta_T\) and \(f(\delta)\) are the density, the refractive index in vacuum, the absolute temperature, the isothermal compressibility, and the Cabbanes factor of water \((f(\delta) = (6+6\delta)/(6-7\delta))\), (where \(\delta\) is the depolarization factor of water), respectively.

Scattering due to concentration fluctuation is calculated as a function of salinity according to Zhang et al. 2009, as

$$\beta_{wc}(90^\circ, \lambda, S) = \frac{\pi^2}{2\lambda^4} N_A \left( \frac{\partial n^2}{\partial S} \right) \frac{M_0}{\rho - \partial \ln a_0/\partial S} f(\delta), \quad (12)$$

where \(N_A\) is the Avogadro number, \(a_0\) is the activity of seawater, and \(M_0\) is the molecular weight of water.
The scattering at any other angle, \( \beta_{\omega}(\psi, \lambda, T, S) \) is calculated (see e.g. Morel 1974) as

\[
\beta_{\omega}(\psi, \lambda, T, S) = \beta_{\omega}(90^\circ, \lambda, T, S) \left[ 1 + \frac{1 - \delta}{1 + \delta} \cos^2 \psi \right].
\]
Since the VSF is symmetric around 90°, the total scattering coefficient is given by

$$b_w(\lambda, T, S) = \left( \frac{8\pi}{3} \right) \beta_w(90^\circ, \lambda, T, S) \frac{2 + \delta}{1 + \delta},$$  \hspace{1cm} (18)

and backscattering is calculated as $b_{bw}(\lambda) = 0.5 b_w(\lambda)$. The absolute error for this calculation is considered to be less than the experimental error of the data of Morel (see Zhang et al 2009, Zhang & Hu 2009). An experimental error of 2% is taken for the scattering data.
The Water Optical Properties Processor (WOPP)

(1) User input to the water optical properties processor (WOPP) are the wavelength in the range 300 - 4000 nm, the temperature, the salinity and optional the scattering angle.

Three different type of data sets are used for the computations:

(2) the coefficients for computing scattering coefficients of water as provided by Zhang & Hu (2009) and Zhang et al. (2009),

(3) measurements of the real part of the refractive index as provided by Austin & Halikas (1976) for the visible spectral range, and Segelstein (1981) and Max & Chapados (2009) for different infrared sections. For the computation at different temperatures and salinities the coefficients as used in the formulation by Quan & Fry (1995) are stored.

(4) measurements of the absorption coefficients of pure water were taken from Pope & Fry (1997), Lu (2006), Wang (2008) for the UV, visible and NIR part of the spectrum. Here the mean was taken at overlapping regions of the spectrum. For different IR regions data of Segelstein (1981), Wieliczka et al. (1989) and Max & Chapados (2009) were taken.

(5) all calculations are performed as a function of the wavelength for the range 300 - 4000 nm.
(6) Data of the refractive index of the spectral range 0.8 - 4 µm are homogenized for a temperature of 27 deg C using the data Segelstein and Max & Chapados data. The data of Segelstein, which fill the spectral gap between the data of Austin & Halikas and Max & Chapados, had to be fitted to the other data because of their significant different offsets at both ends of its gap filling spectral range.

(7) The refractive index n for a certain temperature and salinity is computed using the Quan & Fry formulation for the spectral range < 0.8 µm using the Austin & Halikas data, then the infrared data are fitted by shifting to the Austin & Halikas spectrum for the requested T and S and provided as output.

(8) The total scattering coefficient b and the scattering coefficient at a certain angle β(θ) are computed using the formulation of Zhang et al. (2009). Input are n, T, and S. b and β(θ) are provided as output.

(9) The temperature measurements are homogenized for a temperature of 20.0 deg C and fresh water using the temperature coefficients as measured by Röttgers (2010).

(10) From this data base the absorption is computed for a given temperature and salinity using the coefficients of Röttgers (2010) and provided as output.
References


Röttgers, R. 2010. Technical note


