Helmholtz-Zentrum Geesthacht
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Algorithm Theoretical Basis Document

The Water Optical Properties Processor (WOPP)

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

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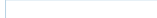|		**DOC:**	WR D6: Pure water spectral absorption and real part of refractive index model ATBD
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Overview

This document summarizes the necessary formulations to calculate inherent optical properties (IOPs) of pure 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. This formulations are included in a Water Optical Properties Processor (WOPP).

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 can be significant for large temperature changes or simply because seawater contains significant amounts 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 have just recently been determined with a good spectral resolution for temperature (Sullivan et al 2006, Langford 2002) and salinity (Sullivan et al 2006). Influences of salinity and temperature are also 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 wavelengths 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

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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 of T and S on the real part of the index of refraction by T and S is significant for calculating the specular reflectance of sun and sky light using the Fresnel formula. In the following sections 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.

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

OLCI (O); SLSTR (S)	Central wavelength in nm	Width in nm
O	400	15
O	412.5	10
O	442.5	10
O	490	10
O	510	10
S	555	20
O	560	10
O	620	10
S	659	20
O	665	10
O	673.75	7.5
O	681.25	7.5
O	708.75	10
O	753.75	7.5
O	761.25	2.5
O	764.375	3.75
O	765.5	2.5
O	778.75	15
O & S	865	20
O	885	10
O	900	10
O	940	20
O	1020	40
S	1375	15
S	1610	60
S	2250	50
S	3740	380

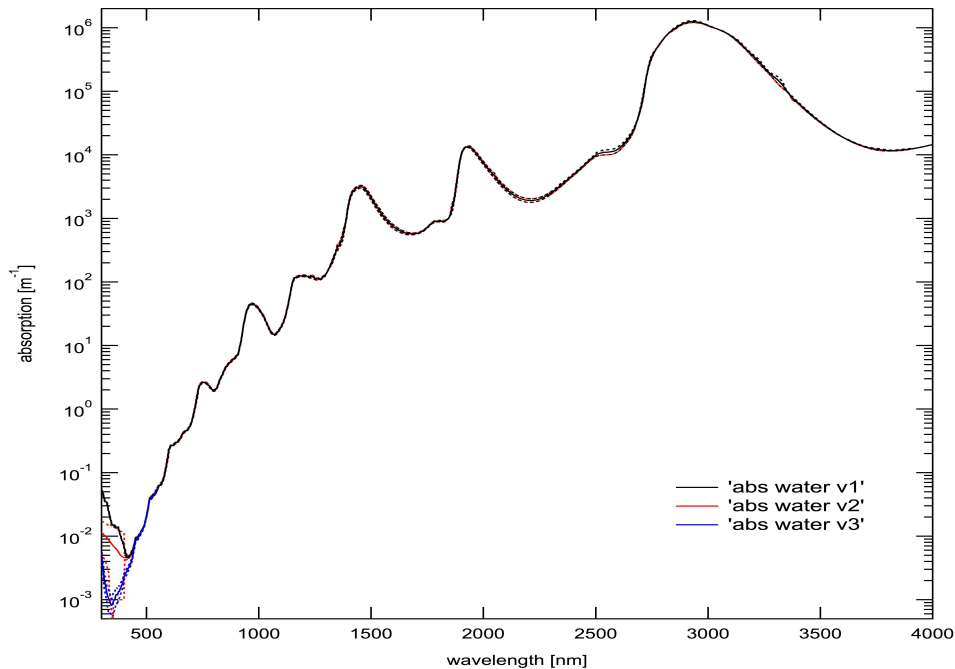|		**DOC:**	WR D6: Pure water spectral absorption and real part of refractive index model ATBD
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Fig. 1: Pure water absorption (± 1σ, dotted lines) in the UV/VIS to SWIR spectral region. Version 1 is based on measurements (see below); version 2 is based on further considerations by Morel et al. 2007 for <420 nm; version 3 is based on recent measurements by Mason et al. 2016 for <550 nm.
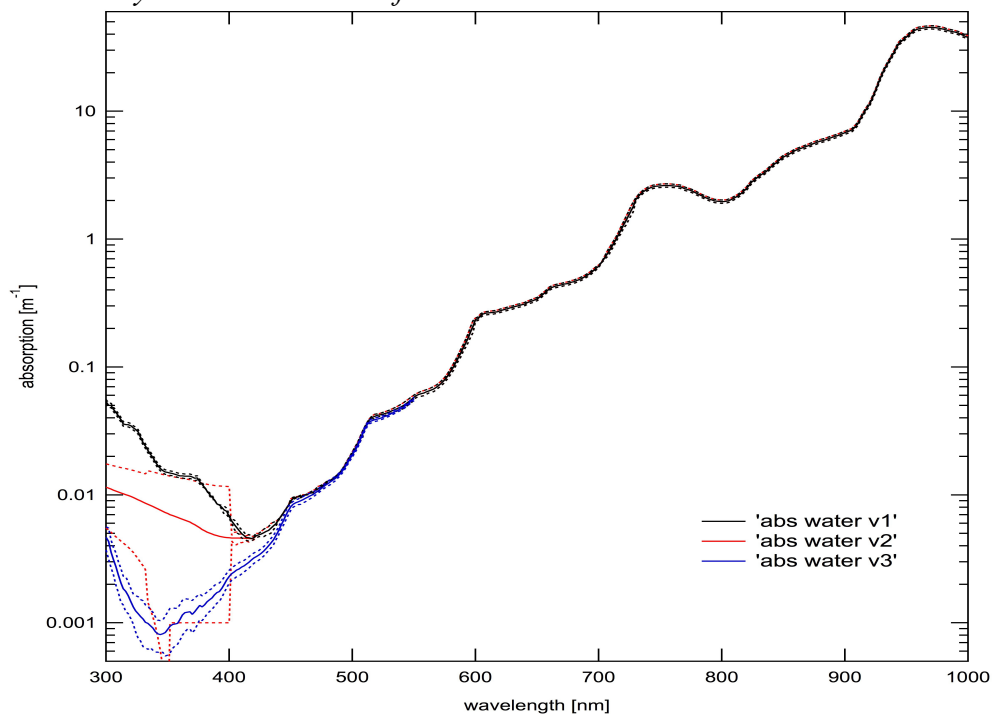

Fig. 2: Pure water absorption (± 1σ, dotted lines) in the UV/VIS spectral region. Version 1 is based on measurements (see below); version 2 is based on further considerations by Morel et al. 2007 for <420 nm; version 3 is based on recent measurements by Mason et al. 2016 for <550 nm.

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Absorption

The absorption of pure water (Fig.1 & 2) 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; thus, a single temperature-specific coefficient of pure water absorption $\Psi_T(\lambda)$ (Fig. 3) can be used to
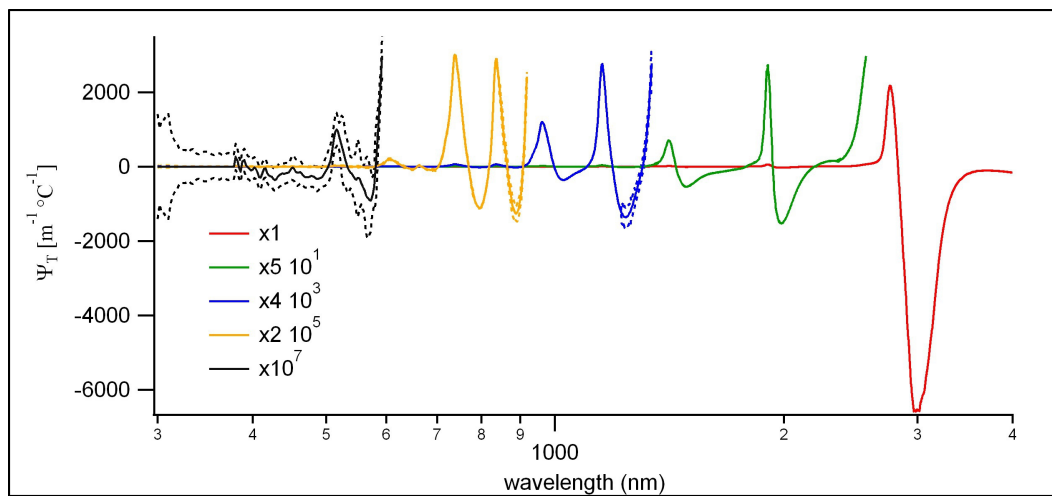

Fig. 3: The temperature coefficient of pure water absorption,Ψ_T (m^{-1} $°C^{-1}$), as a function of wavelength. The original data are shown in red. In addition, for specific spectral ranges the spectral features were enlarged by multiplying the values with different factor as indicated in the legend. The errors are shown as 2σ contour lines (dashed lines).
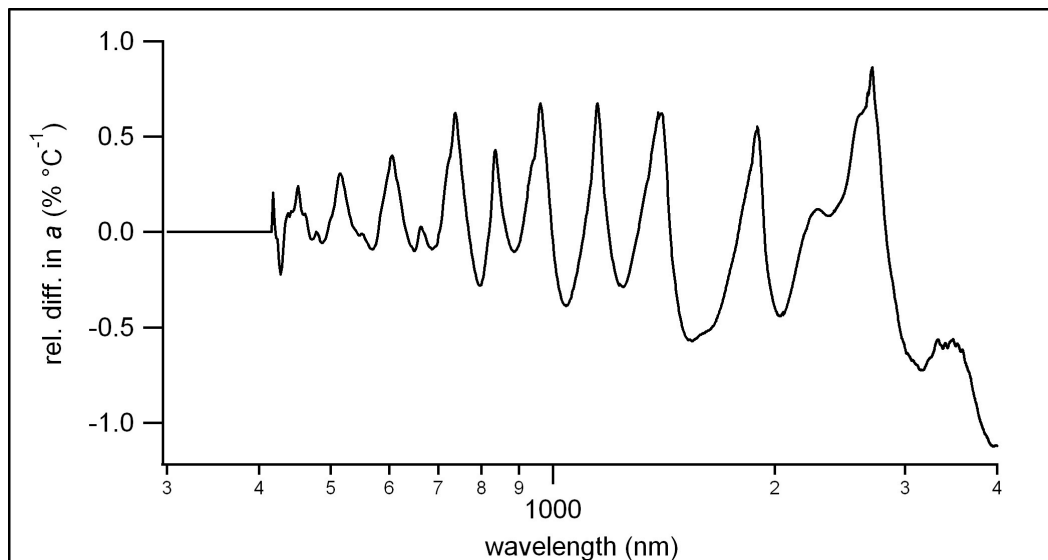

Fig. 4: Relative difference in % absorption per °C.

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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).
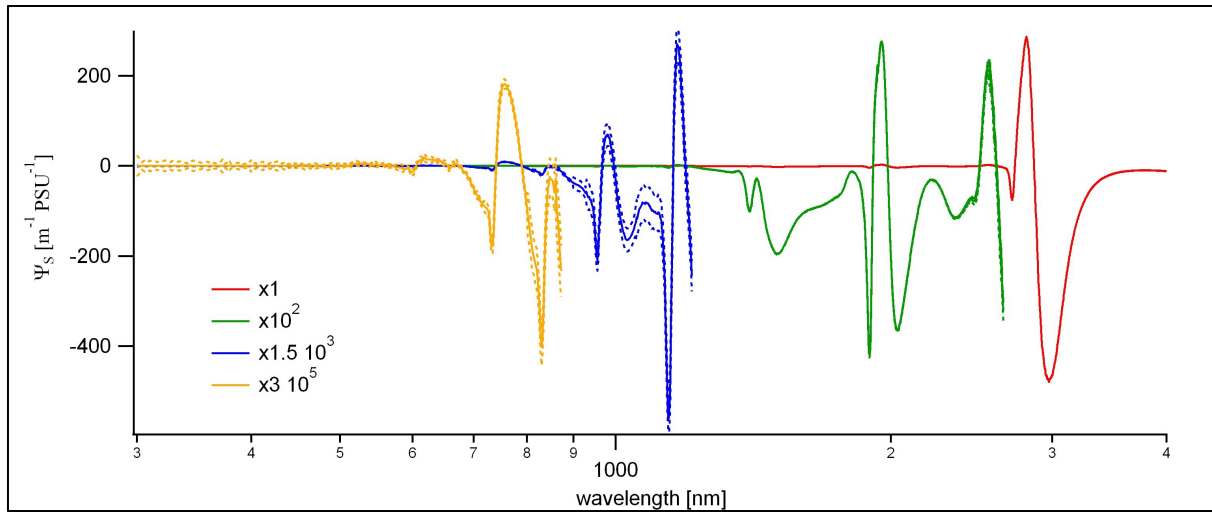

Fig. 5: The salinity coefficient of pure water absorption, Ψ_S (m^{-1} PSU^{-1}), as a function of wavelength. The errors are shown as 2σ contour lines (dashed lines).
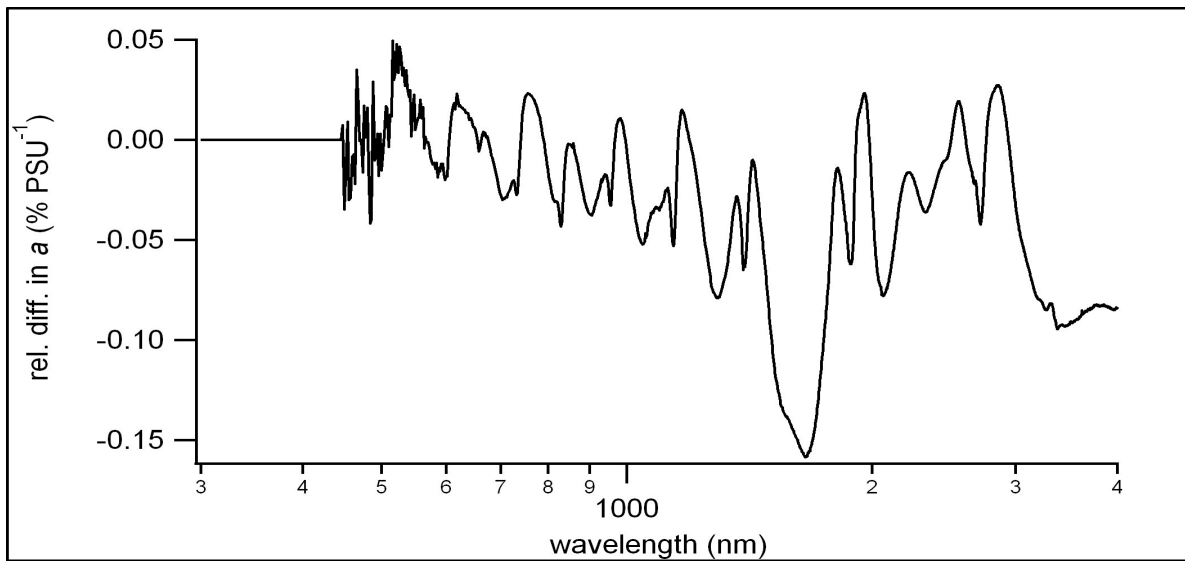

Fig. 6: Relative difference in % absorption per PSU calculated using Ψ_S and the pure water absorption at 0 PSU.

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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 related changes, 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, $\Psi_S(\lambda)$, (Fig. 5) can be used to calculate the water absorption at different salinities, when the water absorption at a specific salinity, S_0, is known, as

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

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

$$a_w(T,S,\lambda)=a_w(T_0,S_0,\lambda)+(T-T_0)\Psi_T(\lambda)+(S-S_0)\Psi_S(\lambda). \quad (3)$$

For the necessary water absorption at (T_0, S_0) the absorption of pure water at 20.0°C and without salt, $a_{w0}(\lambda) = a_w(20°C, 0\ PSU, \lambda)$ is used. Equation 3 is simplified to

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

The $a_{w0}(\lambda)$ spectrum is available in three versions (*v1, v2* and *v3*) to commit to different views of the UV absorption of water. For *v1* a combination of solely empirical measurements at different temperatures are used (Pope & Fry 1997, Lu 2006, Wang 2008, Segelstein 1981 (>700 nm), Wieliczka et al. 1989, and Max & Chapados 2009 (1850-2000 nm, > 2500 nm)), those were partly modified to get the absorption at the reference temperature of 20 °C using the spectrum of Ψ_T. For *v2* the consideration of Morel et al. 2007 are followed to give different values for wavelength <420 nm only. Data presenting lower absorption for <420 nm are used that where obtained by Morel et al. 2007 from interpolations of measurements at shorter wavelengths of Boivin et al. 1986 and Quickenden & Irvin 1980. For *v3* data of Mason et al. 2016 (measured at 23°C) were used for <510 nm after being transformed to $a_{w0}(\lambda)$, i.e. for 20°C. These three combined pure water absorption spectrum at 20.0 °C are shown in Fig 1 & 2. The relevant uncertainty, Δa_{w0}, at each wavelength is either taken from the experimental data or the standard deviation from the calculation of the mean in case several measurements were available for the same wavelength.

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 relative change in absorption varied from -0.4 – 0.7 % per

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°C (Fig. 4). The relevant uncertainty of the temperature coefficient, $\Delta\Psi_T$, is determined by the experimental error.

The spectrum of Ψ_S is is taken from Röttgers 2010 (300- 2700 nm) and combined with a spectrum calculated from data for the range 2700 – 40000 nm of Max & Chapados 2001 (Fig. 5). The relative change in absorption per PSU varied between -0.15 % and 0.05 % (see Fig. 6). The relevant uncertainty of the salinity coefficient, $\Delta\Psi_S$, is determined by the experimental error.

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

$$a_w \pm \Delta a_w \;=\; a_{w0} \;\pm\Delta a_{w0} \;\pm(T-20.0)*\Delta\psi_T \;\pm S*\Delta\psi_S \;.$$

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, ε_ω, as $\varepsilon_w = n_w{}^2$, 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_{sw}' 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_{sw} 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_{sw}' in the spectral range 400 – 700 nm. The formulation was used here for the range of 300 – 800 nm (see Huibers 1997). n_{sw}' (T, S, 300 – 800 nm) is calculated as

$$n_{sw}'(T,S,\lambda)=n_0+(n_1+n_2 T+n_3 T^2)*S+n_4 T^2+\frac{(n_5+n_6 S+n_7 T)}{\lambda}+\frac{n_8}{\lambda^2}+\frac{n_9}{\lambda^3}, \quad (5)$$

with $n_0 = 1.31405$, $n_1 = 1.779 \times 10^{-4}$, $n_2 = -1.05e^{-6}$, $n_3 = 1.6 \times 10^{-8}$, $n_4 = -2.02 \times 10^{-6}$, $n_5 = 15.868$, $n_6 = 0.01155$, $n_7 = -0.00423$, $n_8 = -4382$, $n_9 = 1.1455 \times 10^6$, T is the temperature in °C, and S the salinity in PSU.

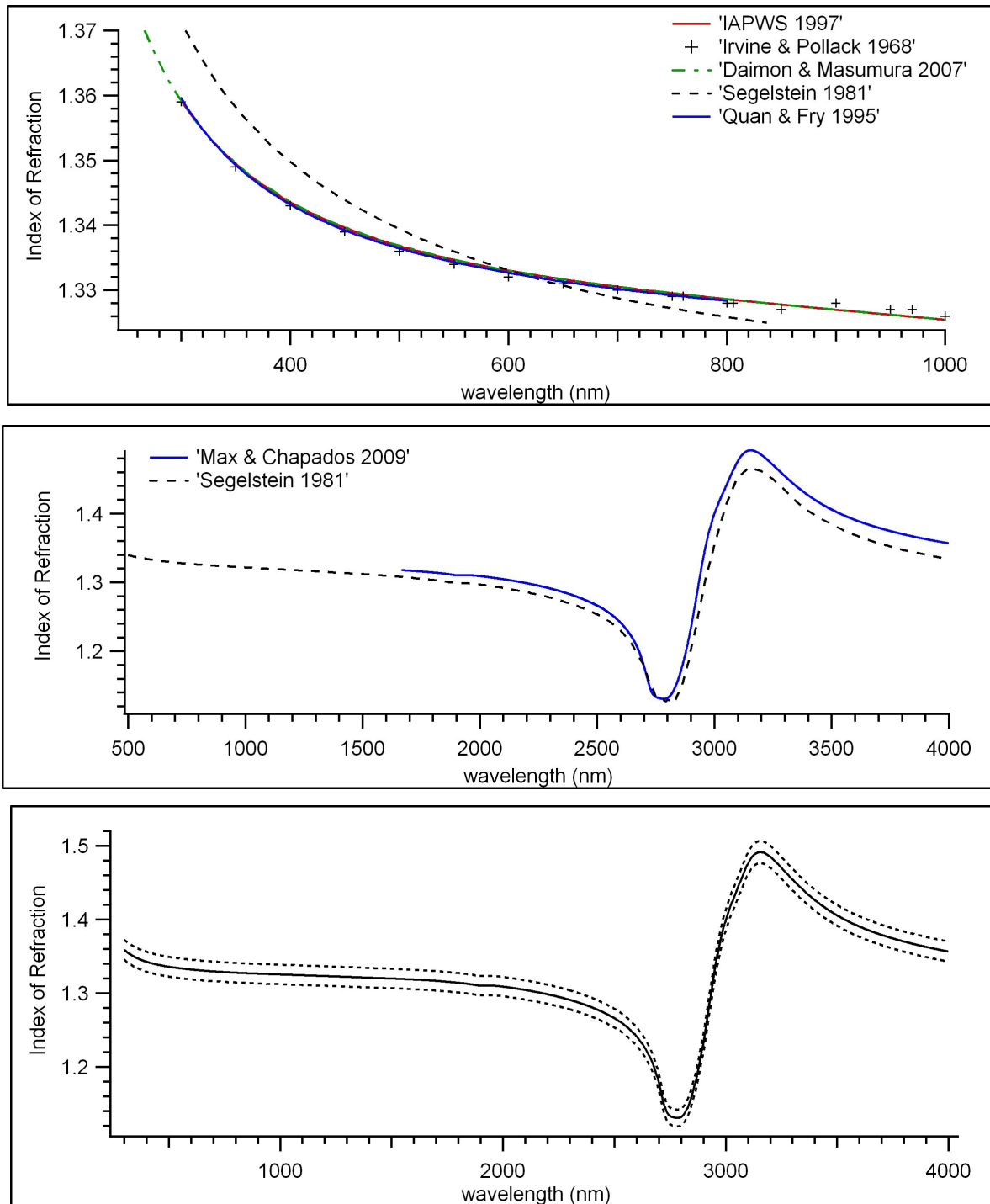|		**DOC:**	WR D6: Pure water spectral absorption and real part of refractive index model ATBD
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Fig. 7: The real part of the index of refraction of pure water and seawater. Upper panel: Different measurement in the UV/VIS spectral region. Middle panel: 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, the error is indicated as contour lines (±2σ, dashed lines).

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

$$n_{sw} = n_{sw}{}' * n_a, \quad (6)$$

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

$$n_a = 1 + [k_1/(k_0 - v^2) + k_3/(k_2 - v^2)]/10^8, \quad (7)$$

where v is the wavenumber in µm^{-1}, k_0 = 238.0185 µm^{-2}, k_1 = 5792105 µm^{-2}, k_2 = 57.362 µm^{-2}, k_3 = 167917 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_w 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 (lower panel).
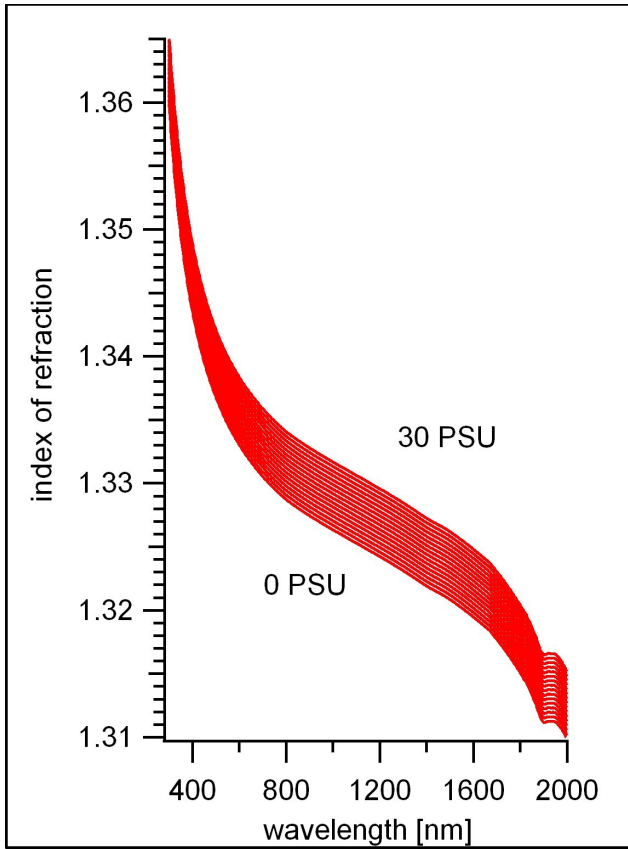

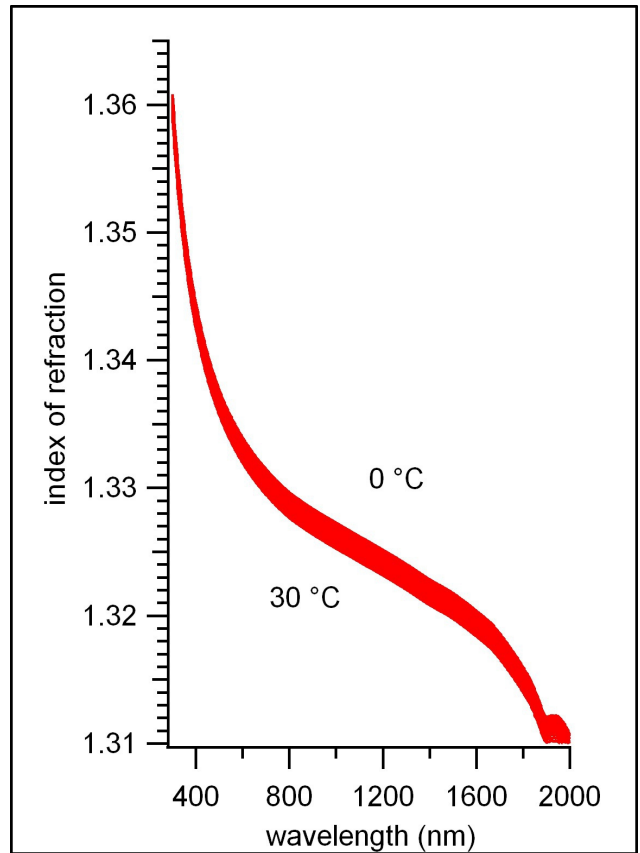Fig. 8: The real part of the index of refraction calculated for different salinities (0 – 30 PSU)

Fig. 9: The real part of the index of refraction calculated for different temperatures (0 - 30 °C).

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The complete spectra of n_{sw} (T, S, 300 – 4000 nm) is calculated by calculating first n_{sw}' (T, S, 300 – 800 nm) using the formulation of Quan & Fry 1995 and scaling it to n_a (using the formulation of Ciddor 1996 to calculate n_a). n_{sw} (T, S, 800 – 4000 nm) is calculated by adding the absolute difference at 800 nm between the standard spectrum n_{w0} (27 °C, 0 PSU) and n_{sw} (T, S), as

$$n_{sw}(T,S,300-800\,nm)=n_{sw}'(T,S,300-800\,nm)*n_a \quad (8)$$

$$n_{sw}(T,S,>800-4000\,nm)=n_{w0}(>800-4000\,nm)+[n_{sw}(T,S,800\,nm)-n_{w0}(800\,nm)]. \quad (9)$$

Spectra of the real part of the index of refraction for different temperature and salinities are shown in Fig. 8 & 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%. E.g. the absolute measurements error in the VIS spectral region was stated by Austin & Halikas 1976 to be 3 x 10^{-5}, the algorithm of Quan & Fry 1995 gives values which deviates less than this uncertainty of the original values. An uncertainty of >5 x10^{-8} is given for the refractive index of air by Ciddor 1996 and is neglected for the overall uncertainty of the refractive index of water. Uncertainties for wavelengths outside of the 400 to 700 range are no explicitly given but are generally higher. For example IAPWS 1997 stated an absolute uncertainty of 5 x 10^{-4} for the range of 200 – 400 nm.

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 Mobley (1994), Morel (1974), and Zhang & Hu (2009). The fluctuations are dependent on density and temperature, where the effect of temperature is < 1% of that of density (thus, the effect of temperature on density is neglected). 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 &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,

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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, δ, 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, β_w (λ, T, S), is calculated as the sum of scattering by density fluctuations, β_{wd} (T, λ) and that by concentration fluctuations, β_{wc} (S, λ), as

$$\beta_w(90°, \lambda, T, S) = \beta_{wd}(90°, \lambda, T) + \beta_{wc}(90°, \lambda, S). \quad (10)$$

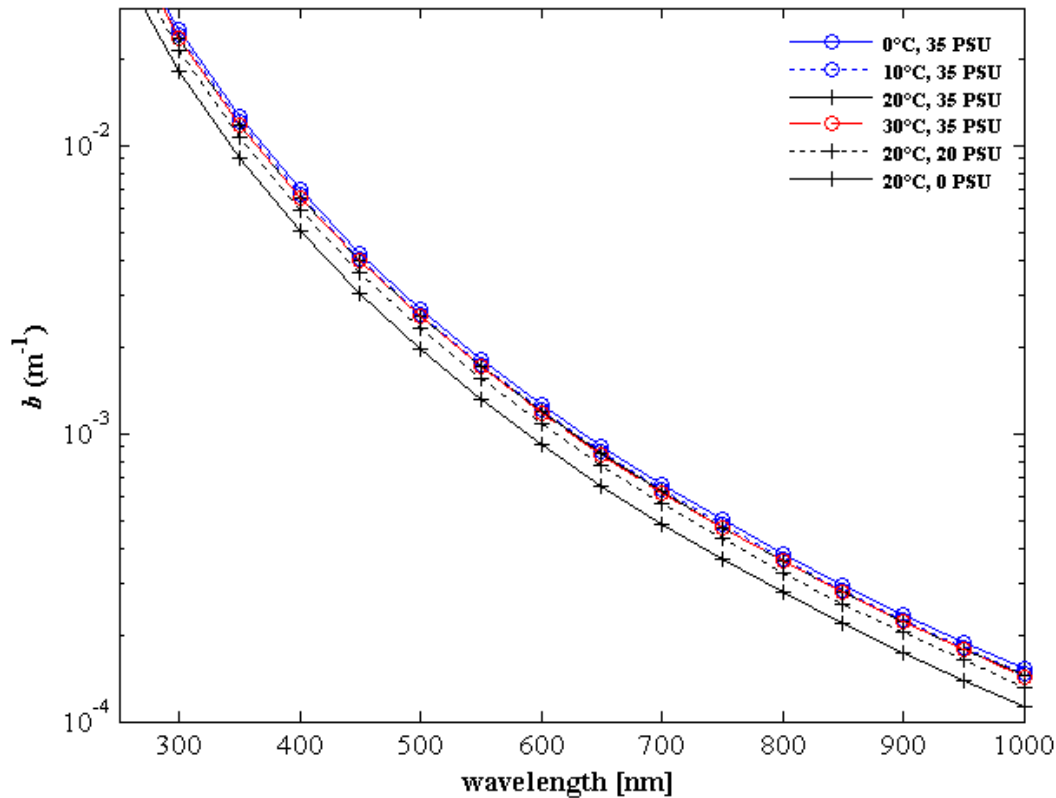Scattering of pure water is only due to density fluctuations and this is calculated according to Zhang & Hu 2009 as

Fig. 10: Scattering for different temperatures and salinities. The associated 2% error is much smaller than the size of the symbols.

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where k is the Boltzmann constant, and ρ, n, T_k, β_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 δ 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

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

where N_A is the Avogadro number, a_0 is the activity of seawater, and M_0 is the molecular weight of water. For more details and the necessary absolute values of these parameter see Zhang & Hu 2009 and Zhang et al. 2009.

The necessary formulation for the parameters needed are taken from Zhang et al. 2009. The salinity derivative of the seawater activity is calculated following Millero & Leung 1976 as
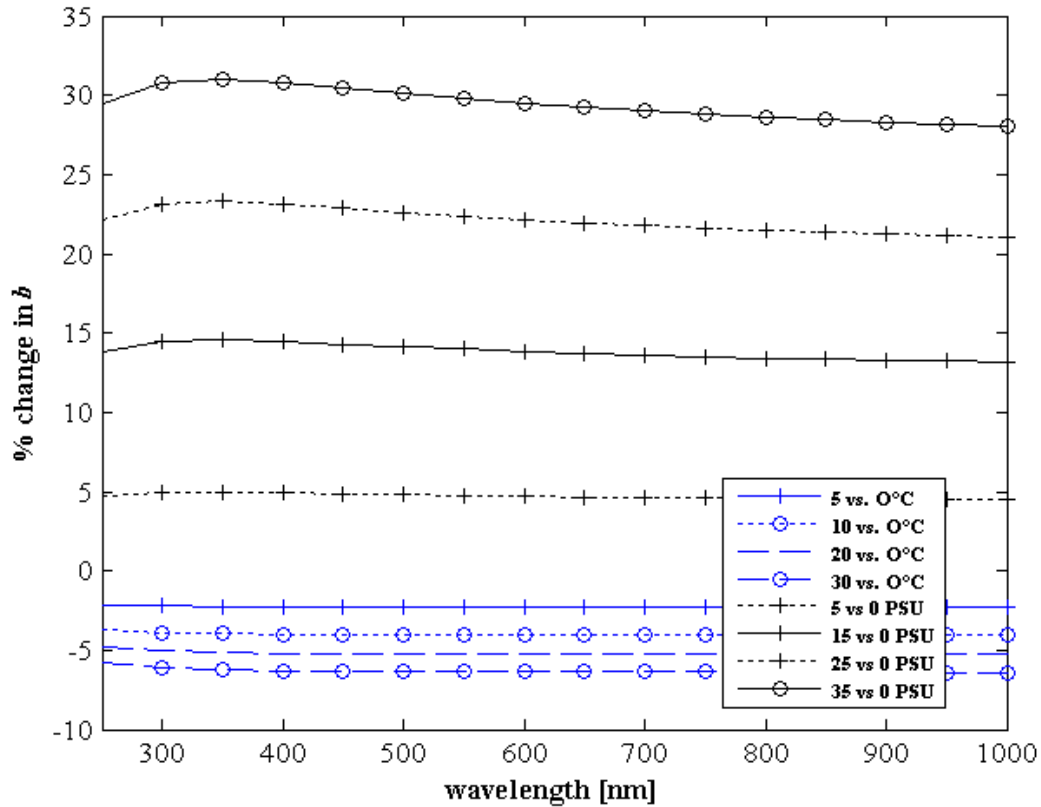

Fig. 11: Relative changes in scattering by water with respect to scattering at a temperature of 0 °C and a salinity of 0 PSU. Full strength oceanic water (~35 PSU) has ~33% greater scattering than fresh water (0 ppt) with bsw typically dropping between 5 - 6.5% over a 30 C temperature range from 0 C.

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with a_0 = -5.58651 x10^{-4}, a_1 = 2.40452 x 10^{-7}, a_2 = -3.12165 x10^{-9}, a_3 = 2.40808 x10^{-11}, a_4 = 1.79613 x10^{-5}, a_5 = -9.9422 x10^{-8}, a_6 = 2.08919 x10^{-9}, a_7 = -1.39872 x10^{-11}, a_8 0 -2.31065 x10^{-6}, a_9 = -1.37674 x10^{-9}, and a_{10} = -193316 x10^{-11}.

The density is calculated following UNESCO (1980) as

$$\rho\ [kg/m^3] = (b_0 + b_1 T + b_3 T^3 + b_4 T^4 + b_5 T^5) + (c_0 + c_1 T + c_2 T^2 + c_3 T^3 + c_4 T^4) S$$
$$+ (c_5 + c_6 T + c_7 T^2) S^{1.5} + c_8 S^2, \quad (14)$$

with b_0 = 999.842594, b_1 = 6.793952 x10^{-2}, b_2 = -9.09529 x10^{-3}, b_3 = 1.001685 x10^{-4}, b_4 = -1.120083 x10^{-6}, b_5 = 6.536332 x10^{-9}, c_0 = 8.24493 x10^{-1}, c_1 = -4.0899 x10^{-3}, c_2 = 7.6438x10^{-5}, c_3 = -8.2467 x10^{-7}, c_4 = 5.3875 x10^{-9}, c_5 = -5.72466 x10^{-3}, c_6 = 1.0227 x10^{-4}, c_7 = -1.6546 x10^{-6}, c_8 = 4.8314 x10^{-4}.

The density derivative of the refractive index is calculated after Proutiere et al. (1992) as

$$\rho\left(\frac{\partial n^2}{\partial \rho}\right)_T = (n^2 - 1)\left[1 + \frac{2}{3}(n^2 + 2)\left(\frac{n^2-1}{3n}\right)^2\right]. \quad (15)$$

The isothermal compressibility is given according to Millero et al. 1980 as

$$\beta_T\ [bar^{-1}] = 1/B$$

$$B = (b_0 + b_1 T + b_2 T^2 + b_3 T^3 + b_4 T^4) + (c_0 + c_1 T + c_2 T^2 + c_3 T^3) S$$
$$+ (c_4 + c_5 T + c_6 T^2) S^{1.5}, \quad (16)$$

with b_0 = 19652.21, b_1 = 148.4206, b_2 = -2.327105, b_3 = 1.360477 x10^{-2}, b_4 = -5.155288 x10^{-5}, c_0 = 54.6746, c_1 = -0.603459, c_2 = 1.09986 x10^{-2}, c_3 = -6.167 x10^{-5}, c_4 = 7.944 x10^{-2}, c_5 = 1.6483 x10^{-2}, c_6 = 5.3009 x10^{-4}.

The scattering at any other angle, $\beta_w(\psi, \lambda)$ is calculated (see e.g. Morel 1974) as

$$\beta_w(\psi, \lambda, T, S) = \beta_w(90°, \lambda, T, S)\left(1 + \frac{1-\delta}{1+\delta}\cos^2 \psi\right). \quad (17)$$

Since the VSF is symmetric around 90°, the total scattering coefficient is given by

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

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 1966, 1968 (see Zhang et al. 2009, Zhang & Hu 2009), therefore the experimental error of 2% is taken for the scattering data after Morel 1966, 1968.

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Conclusions

The above formulations can be used to calculate the inherent optical properties of pure water, i.e. the real index of refraction, absorption, and scattering (scattering coefficient for any angle, for back-, forward-, and total scattering), for different water temperatures and salinities in the range of 0 - 95°C, 0 - 100 PSU at wavelengths of 300 nm to 4000 nm. The formulations are included in the Water Optical Properties Processor (WOPP). The general structure of the WOPP is shown in Fig. 12. The output of the WOPP includes the uncertainties for each pure water IOP. Table 2 shows some exemplary results of this calculation for the relevant OLCI and SLSTR wavelengths. The relevant uncertainties are due to experimental errors when determining the pure water IOP and the necessary correction coefficients, and due to variations between different published results for each IOP.

The relative errors of the T and S coefficients of pure water absorption are relatively small in the VIS to SWIR spectral region, but large at shorter wavelengths. However the real coefficients at these shorter wavelengths are below the detection limit and were set to zero. It is suggested that relative changes at shorter wavelengths are in the same range as for the longer wavelengths. Hence, the absolute absorption and its changes with temperature and salinity at shorter wavelengths (<450 nm) remain uncertain, however under most conditions the contribution of pure water absorption to total absorption in natural water is relatively small. Scattering and the real index of refraction, n_w, of pure water and seawater are most accurately known for the VIS/NIR region. There is confidence that n_w of pure water at SWIR wavelengths is accurate as well, whereas there are no relevant data for the range of 800 to 1670 nm, (absolute data of Segelstein 1981 were considered as being wrong, and were only used to have information on the wavelength-dependence in the range of 800 to 1670 nm) nor is there any information of the change in n_w with temperature and salinity at wavelengths >1200 nm. The changes with salinity and temperature are simply extrapolated from the changes at shorter wavelengths.

There is no confidence that the calculation of scattering and its change with T and S is valid at wavelength >700 nm, as there are no experimental data available for this spectral region, but, compared to absorption, scattering at longer wavelengths is very low, and the calculation is mostly based on physical principles that are equally valid for longer wavelengths.

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Table 2. Exemplary values of the pure water temperature, Ψ_T, and salinity, Ψ_S, coefficient, and calculated values of pure water absorption (v1 and v2), total scattering and the real part of the refractive index, a_w, b_w, n_w, respectively, for OLCI and SLSTR wavelengths. Given are values for 20°C and two salinities (0 and 35 PSU).

wavelength [nm]	Ψ_T [m^{-1} degC^{-1}]	Ψ_S [m^{-1} PSU^{-1}]	n_w S=0 PSU, T=20degC	a_w [m^{-1}], v1 S=0 PSU, T=20degC	a_w [m^{-1}], v2 S=0 PSU, T=20degC	b_w [m^{-1}] S=0 PSU, T=20degC	n_w S=35 PSU, T=20degC	a_w [m^{-1}] S=35 PSU, T=20degC	b_w [m^{-1}] S=35 PSU, T=20degC
400	-0.000008	0.000000	1.343591	0.006770	0.004260	0.005039	1.350319	0.006770	0.006592
412	-0.000018	0.000000	1.342494	0.004805	0.004590	0.004439	1.349193	0.004805	0.005804
442	-0.000018	0.000000	1.340163	0.006773	0.006773	0.003291	1.346795	0.006773	0.004296
490	-0.000032	-0.000002	1.337312	0.015000	0.015000	0.002131	1.343855	0.014946	0.002774
510	0.000054	-0.000001	1.336350	0.033150	0.033150	0.001802	1.342860	0.033109	0.002343
556	-0.000044	0.000007	1.334489	0.061867	0.061867	0.001257	1.340934	0.062103	0.001631
560	-0.000059	0.000007	1.334347	0.063800	0.063800	0.001220	1.340786	0.064038	0.001583
620	0.000516	0.000054	1.332475	0.275500	0.275500	0.000800	1.338844	0.277404	0.001035
660	0.000054	-0.000015	1.331449	0.410000	0.410000	0.000618	1.337778	0.409472	0.000798
666	0.000039	0.000018	1.331307	0.431333	0.431333	0.000595	1.337631	0.431946	0.000769
674	-0.000192	0.000008	1.331122	0.448000	0.448000	0.000567	1.337439	0.448273	0.000732
682	-0.000406	-0.000036	1.330942	0.473667	0.473667	0.000540	1.337252	0.472393	0.000697
708	0.001140	-0.000232	1.330387	0.789754	0.789754	0.000463	1.336676	0.781620	0.000597
754	0.006439	0.000596	1.329505	2.626020	2.626020	0.000357	1.335759	2.646880	0.000460
762	0.002335	0.000579	1.329363	2.599933	2.599933	0.000342	1.335611	2.620185	0.000440
764	0.001406	0.000567	1.329328	2.588467	2.588467	0.000338	1.335574	2.608315	0.000436
766	0.000549	0.000542	1.329293	2.577000	2.577000	0.000335	1.335538	2.595974	0.000431
778	-0.003554	0.000323	1.329088	2.321600	2.321600	0.000314	1.335325	2.332913	0.000404
866	-0.001399	-0.000455	1.327857	5.194150	5.194150	0.000203	1.334080	5.178232	0.000260
886	-0.006299	-0.001745	1.327615	6.064075	6.064075	0.000185	1.333838	6.003011	0.000237
900	-0.003682	-0.002507	1.327450	6.792400	6.792400	0.000173	1.333673	6.704664	0.000222
940	0.118966	-0.005021	1.326993	29.005000	29.005000	0.000145	1.333216	28.829256	0.000186
1020	-0.087678	-0.009864	1.326129	29.325417	29.325417	0.000104	1.332352	28.980164	0.000133
1376	3.025518	-0.205858	1.322198	578.673472	578.673472	0.000030	1.328421	571.468456	0.000039
1610	-3.655445	-1.028382	1.319313	696.260577	696.260577	0.000016	1.325536	660.267218	0.000020
2250	1.995149	-0.401424	1.295900	2024.815446	2024.815446	0.000003	1.302123	2010.765596	0.000005
3740	-110.586643	-10.338122	1.376115	12411.980010	12411.980010	0.000001	1.382338	12050.145749	0.000001

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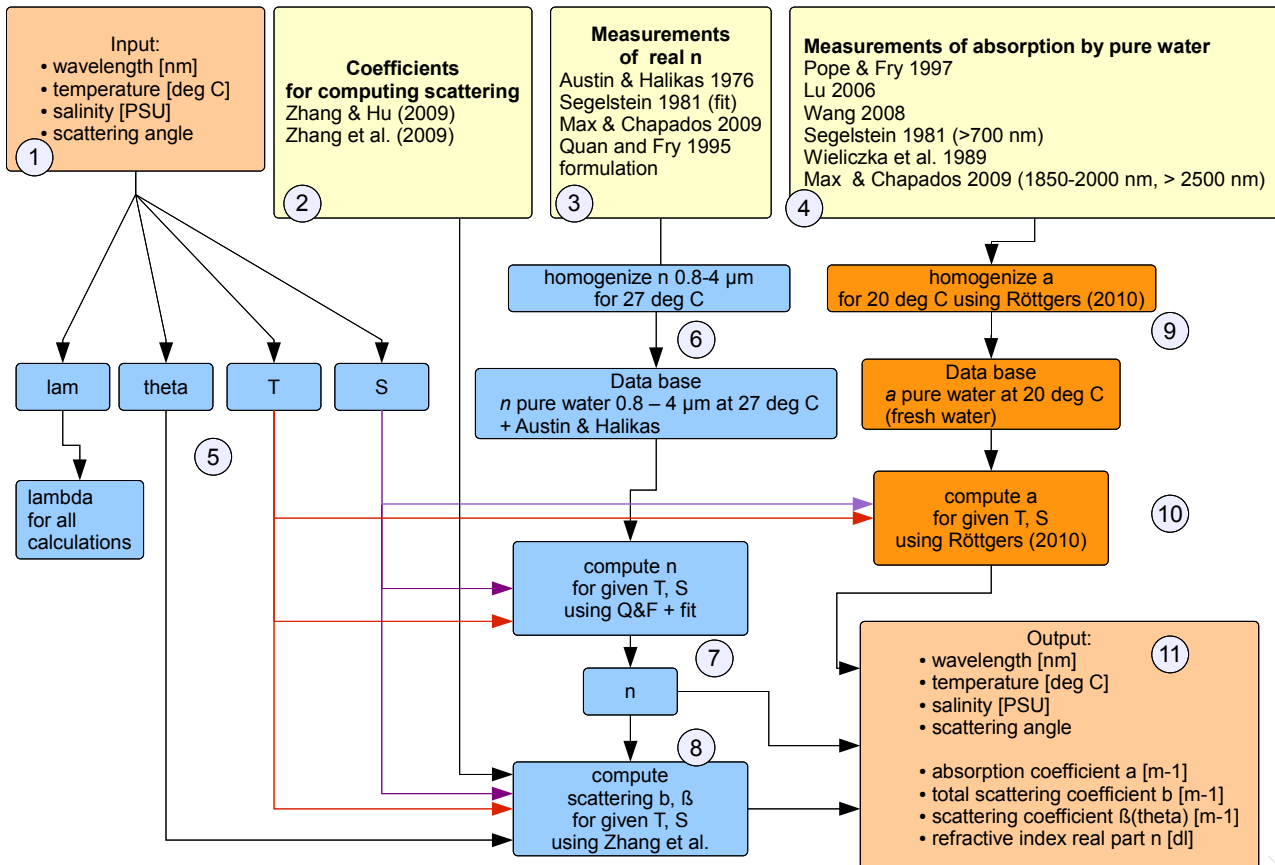## The Water Optical Properties Processor (WOPP)

Fig. 12: Structure of the water optical properties processor.

(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. A second version for pure water

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absorption can be used with considerations by Morel et al. 2007 that has different values in the spectral region of <420 nm; in a third version data of Mason et al. 2016 are used for <510 nm.

(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 $\beta(\theta)$ are computed using the formulation of Zhang et al. (2009). Input are n, T, and S. b and $\beta(\theta)$ 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.

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