Lab 4: Scattering, back scattering and the beam attenuation

**Equipment and Supplies**
1 x ac-s
LISST-100X type B (may have issues…)
C-Star - 10cm
Bb3-VSF three wavelengths three angle backscattering sensors
Eco-FLNTU – one angle backscattering sensor
Sample chamber for LISST
Two bench-top turbidity sensors (NIR and visible)

Dock water (+filtrate), 2 x Culture (+filtrate) and Arizona dust in tap water (+ tap water).
Power supplies for all instruments
Multi-meter to measure the C-star voltage
Containers to hold samples with hoses to supply water to and through instruments.
Computers.

**Laboratory Safety Issues**— General laboratory safety.

**Goals for Scattering and Attenuation Lab** – Be able to discuss

**Optical properties of particles:**
- Is the particulate scattering spectra influenced by absorption?
- Is the particulate attenuation spectra influenced by absorption (do you observe absorption peaks and valleys in the attenuation spectra)?
- Are different scattering properties correlated?
- Is the backscattering ratio influenced by the composition of material (i.e., organic vs. mineral)? Does it vary spectrally in a significant way?

**Instruments:**
- Is the particulate attenuation coefficient a function of acceptance angle?
- What can you learn by checking your instrument’s specs prior to using it, or do you rely on the manufacturer?

**Calculation:**
- Obtain temperature, salinity and scattering-corrected scattering spectra for 4 types of samples (2 x phytoplankton cultures, dock water, and dust suspension) using the difference between total beam attenuation and absorption spectra.

Determine spectral backscattering coefficients from measurements of scattering at three angles in the back direct as well as measurements with a single angle in the back direction.
Compute spectrally the particulate backscattering to total scattering ratio.
Compute the beam attenuation in the red near 660nm with three different instruments.
If time permits (e.g. before 12pm): obtain the particulate VSF (LISST + EcoVSF) and fit an analytical function to it. Next week, once samples for POC and SPM are analyzed, compute mass specific scattering for algae, inorganic clay and dock waters and compare to literature values.

**SKILLS:**

Learn to filtrate water for POC and SPM measurements.

**BONUS:**

Learn about the flowcam from an expert

**INTRODUCTION**

The volume scattering function, VSF or $\beta$, is a fundamental IOP that together with absorption, $a$, (and assuming no inelastic scattering) uniquely determines the subsurface light field for given boundary conditions (e.g. incoming light, bottom reflectance, etc.).

In this lab we will focus on the beam attenuation ($c$), the scattering coefficient ($b$), and the backscattering coefficient ($b_b$) which relate to $a$ (absorption) and $\beta$ as follows:

$$b = 2\pi \int_{\theta_\phi}^{\pi} \beta \sin \theta d\theta$$

$$b_b = 2\pi \int_{\pi/2}^{\pi} \beta \sin \theta d\theta$$

$$c = a + b$$

Where $\theta_\phi$ is the acceptance angle of the instrument used (e.g. $0.93^\circ$ for the ac-9).

As we learned for absorption, scattering can also be decomposed to the sum of scattering by different components of the medium under investigation. For seawater, its components – pure water, salts, dissolved materials, particles (inorganic particles, living and nonliving organic particles, bubbles) – all have important influences on scattering for a given condition. In general it has been found that pure water, salts, organic and inorganic material dominate scattering with bubbles being important during rough seas and where waves break.

In previous lectures you learned that the beam attenuation (excluding the contribution by water) has, to a large degree, a smooth spectrum because it is comprised of 1) CDOM with its characteristic smooth exponentially decreasing absorption and attenuation as function of wavelength and 2) particulate attenuation that in most oceanic conditions is well represented as a power-law function of wavelength:

$$c_{pg}(\lambda) = c_p + c_{p} \sim c_{pg}(\lambda_a) \sim (\frac{\lambda}{\lambda_a})^{-\gamma} + c_p (\lambda_a) \left( \frac{\lambda}{\lambda_a} \right)^{-\gamma p g}. $$
where \(c_{pg}\) is the total beam attenuation coefficient (less water), \(c_p\) is the beam attenuation of the dissolved material, \(c_p\) is the particulate beam attenuation, \(s\) is the spectral slope of dissolved attenuation, and \(\gamma\) is the spectral slope of particulate beam attenuation.

Since an absorbed photon is not scattered, the scattering coefficient of materials other than water \((b=c-a)\) does not have a smooth spectrum as function of wavelength and has a shape whose local maxima and minima mirrors that of the particulate absorption spectrum (in reality, there exist some mismatch, termed ‘anomalous dispersion’, that can be seen in instruments with high spectral resolution, due to a change in the real part of the index of refraction near absorption maxima).

The full angular VSF is not measured routinely due to unavailability of commercial instrumentation to measure it. Following the studies of Oishi, 1994, Maffione and Dana, 1997, and Boss and Pegau, 2001, the backscattering coefficient of particles is commonly estimated from measurement of scattering at a single angle in the backward hemisphere \((\beta(\theta)):\)

\[
b_{bp} = 2\pi \beta_p(\theta_1),
\]

or by interpolating between three measured angles of VSF in the back direction using an ECO-VSF (Mueller et al., 2003).

The ratio between the particulate backscattering coefficient and the particulate scattering coefficient, \(\tilde{b} = \frac{b_{bp}}{b_p}\), the particulate backscattering ratio, has been found to be most sensitive to the particulate composition, compared to changes in size distribution (e.g Twardowski et al., 2001, Boss et al., 2004). For water-filled organic particles \(\tilde{b} \approx 0.005\), while for inorganic minerals \(\tilde{b} \approx 0.02 – 0.03\).

Particulate organic carbon (POC) is operationally defined as carbon content of the particles collected on the GF/F (or other) filter, defined as mg m\(^{-3}\) or \(\mu\)mol L\(^{-1}\). Although POC is only a small fraction of the total organic carbon in the upper ocean (~ 3%), due to its composition (phytoplankton + detrital matter, including bacteria) and its role in the carbon cycle, is one of the key biogeochemical parameters. The most common approach for measuring POC in natural waters involves the collection of suspended particles from a known volume of water onto a C-free, glass fiber filter. The material collected is dried and treated with acid to remove inorganic C, and combusted at temperatures near 1000 °C in an elemental analyzer, where the resulting CO\(_2\) is measured.

Suspended particulate matter (SPM) is operationally defined through a filtration of seawater as the material retained on a GF/F filter, that includes both organic (autotrophic and heterotrophic plankton, bacteria, viruses, and detritus) and mineral particles. SPM is defined in units of mg L\(^{-1}\), or as g m\(^{-3}\), and it is determined by passing a known volume of the seawater through a pre-weighted filter. Same filter is then reweighted and SPM is calculated as a difference between the weight of the filter before the filtration, and after a filtration, by the volume of the filtrate. In case the blank filter has been collected (see in Station 2 write up), and changes of the weight are
significant, then the correction should be applied so the weight of the adsorbed material onto the filter blank is taken into consideration.

The class should divide in four: Students will measure \( b \) in Station 1, \( b_b \) in Station and backward VSF in station 2, will measure \( c \) and forward VSF at Station 3 and will learn to filter water samples for Particulate Organic Carbon (POC) and Suspended Particulate Mass (SPM) in station 4. Students will also see how the flowcam operates.

Each group will measure these properties for one type of suspension (2 x phytoplankton culture, DRE waters and a sediment suspension), so that at the end we should have a total of 4 samples on file for each instrument.

**Station 1**

The class should divide in four: Students will measure \( b \) in Station 1, \( b_b \) in Station and backward VSF in station 2, will measure \( c \) and forward VSF at Station 3 and will learn to filter water samples for Particulate Organic Carbon (POC) and Suspended Particulate Mass (SPM). Students will also see how the flowcam operates.

**Scattering Coefficient**

1. Calibrate an ac-s with Milli-Q water.
2. Measure the following:
   a. Absorption and attenuation with ac-s of filtrate and sample.
   b. Don’t forget to measure temperature and salinity (refractometer) for needed corrections.

**Station 2**

**Measurement of Backscattering at One Angle in the Back Direction**

Measure the dark current of the Eco-FLbb by covering it with black tape in water.

1. Using a radiometer, determine the wavelength of one head of the backscattering sensor (to the spectral resolution of the radiometer).
2. Measure the following:
   a. Backscattering at one angles and of filtrate and sample.
   b. Don’t forget to measure temperature and salinity for needed corrections.
   c. Turbidity of sample using two portable turbidity Hach meters (one with NIR the other with visible light source).

**Measurement of Backscattering at Three Angles in the Back Direction**

1. Measure the dark current of the Eco-VSF-3 by covering it with black tape in water.
2. Using a radiometer, determine the wavelength of one head of the backscattering sensor (to the spectral resolution of the radiometer).
3. Measure the following:
   a. Backscattering at three angles and 3 wavelengths of filtrate and sample.
   b. Don’t forget to measure temperature and salinity for needed corrections.
STATION 3
BEAM ATTENUATION COEFFICIENT
LISST-100X-B

1. Following a short introduction to the LISST, calibrate the LISST by obtaining a ‘zscat’ file with the LISST chamber being filled with Milli-Q water. Compare to manufacturer’s zscat file.
2. Make measurements of both filtrate and sample.

C-Star

1. Following a short introduction to the C-Star analogue transmissometer, calibrate the C-Star by obtaining its dark current (in air) and a reading with Milli-Q water in the tube.
2. Measure the attenuation of the filtrate and your sample.

Data for homework:
Acceptance angles (from manufacturers, in water):
ac-9/ac-s: 0.93°
C-Star: 1.2°
LISST-B: 0.026°

STATION 4

POC, SPM AND FLOWCAM

POC/SPM filtration
For POC filtration, method is slightly modified from Cetinic et al 2012. For SPM filtration, method is modified from Neukermans et al, 2012.

Preparation:
Whatman GF/F filters (25 mm) were placed in individual, heavy-duty aluminum foil packets (see “how to make alu foil packages.ppt”). Filters were then pre-combusted at 450ºC for 4 hours. Sheets of aluminum foil, that will be used as working area, were pre-combusted following the same procedure. Filters that will be used for collection of SPM, immediately after the combustion were stored into the desiccator, weighted on the high-precision scale, and then stored back into the same packages. The cooled POC packets were transferred to zip-lock bags. All plastic ware was washed with diluted RBS-35 solution. Nitrile gloves should be worn throughout the entire preparation, sampling and analysis process.

Procedure:
Each group will filter:
200 mL of “sample” onto a POC filter and onto a SPM filter
200 mL of filtrate onto a POC filter and onto a SPM filter.
1. Using the pre-combusted aluminum sheet, make a clean working space on which you will be assembling the filtration set.
2. Using the tweezers that are kept in the small container, immersed in low concentration of RBS and Milli-Q water, and then rinsed with Milli-Q, remove filter from the aluminum foil package and load it into the swinex filter holder.
3. Assemble the filtration set, and attach it to the bottle with filtrate. Mind to set the longer (air feeding tube) all the way to the bottom of the bottle. Filtration should be done on low vacuum (up to 5 inch Hg) to prevent cell breakage.
4. Store the filter:
   a. For POC: After all the water has passed through the filter, fold the filter, and store it into its alu foil pack. Write the number, and store it into freezer or liquid N2. No rinsing.
   b. For SPM; After all the water has passed through the filter, rinse the filter with Milli-Q water. Store the filter in a same way as POC one.
5. For every sample, or (at least) sample group, make sure you collect filtrate/DOC blank. These are pre-combusted filter through which only filtrate has been filtered. They are needed to account for the adsorption of DOC onto the filter matrix during sample filtration.
6. For every 6 samples, collect Lab/Cruise dry blank. These filters were pre-combusted with all others used before and were untouched, unopened, included with every samples and sample blanks. They are used to estimate the impact of the storage on filter (potential contamination).

Analysis (to be done by your lovely instructors or certified laboratory): POC samples, with associated filters should be dried immediately after the removal from the fridge, and exposed to the hydrochloric acid fumes, so the particulate inorganic portion of the particulate is removed. Following, filters will be dried, and analyzed in standardized methods in CHN-type analyzer, that is continuously standardized with community approved standards (e.g. Sulfanilamide standards(Elementar analysysysteme GMBH, 16.25%N, 41.81%C) and reference material (Buffalo River Sediment (BRS) NIST reference material NIST RM 8704; 3.348 ± 0.016 % Carbon)). SPM samples, with associated filters should be dried immediately after the removal from the fridge, on 75°C for 24 hours, stored in desiccator, and weighted.

Flow-CAM
Samples will be run on the FlowCAM (Fluid Imaging Technologies) imaging-in-flow system (Sieracki et al. 1998). The instrument is equipped with a 4X objective and a 300 µm flow cell, and was operated in fluorescence trigger mode at a flow rate of about 2.5 mL min⁻¹.
Table 1. Sources of error in POC measurements (NASA POC protocol, super early draft 2017):

<table>
<thead>
<tr>
<th>METHOD SUB-STEP</th>
<th>DIFFERENCE / ERROR / BIAS</th>
<th>REFERENCES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filter pore size / Material</td>
<td>Underestimation of POC / Overestimation of POC</td>
<td>(Gordon and Sutchiffe 1974; Moran et al. 1999)</td>
</tr>
<tr>
<td>Filter packaging (cross/air contamination)</td>
<td>Overestimation of POC</td>
<td></td>
</tr>
<tr>
<td>Contamination (collection bottles/ inappropriate filtration systems)</td>
<td>Overestimation of POC</td>
<td></td>
</tr>
<tr>
<td>In-situ filtration vs. bottle</td>
<td>Underestimation of POC</td>
<td>(Bishop et al. 2012a; Gardner et al. 2003b; Goldman and Dennett 1985; Liu et al. 2005; Moran et al. 1999)</td>
</tr>
<tr>
<td>Exposure to airborne particles during collection</td>
<td>Overestimation of POC</td>
<td>(Cetinić et al. 2012)</td>
</tr>
<tr>
<td>Volume filtered</td>
<td>Variable error (Signal to Noise issue)</td>
<td>(Bishop et al. 2004; Moran et al. 1999; Stramski et al. 2008)</td>
</tr>
<tr>
<td>Vacuum pressure (filtration)</td>
<td>Underestimation of POC</td>
<td>(Gardner et al. 2003b; Goldman and Dennett 1985; Liu et al. 2005)</td>
</tr>
<tr>
<td>Exposure to airborne particles during filtration</td>
<td>Overestimation of POC</td>
<td></td>
</tr>
<tr>
<td>Artificial creation of POC from DOC</td>
<td>Variable overestimation, depended on the type of the DOC (colloidal) + particles</td>
<td>(Batoosingh et al. 1969; Gardner et al. 2003b)</td>
</tr>
<tr>
<td>Large particles on the filter (puffs of trichio, copepods)</td>
<td>High variability in replicate samples</td>
<td></td>
</tr>
<tr>
<td>DOC adsorption on the filter</td>
<td>Overestimation of POC</td>
<td>(Gardner et al. 2003b; Gordon and Sutchiffe 1974; Menzel 1967a; Moran et al. 1999)</td>
</tr>
<tr>
<td>Sample storage - Temperature, media and longevity</td>
<td>Underestimation of POC</td>
<td></td>
</tr>
<tr>
<td>Analysis</td>
<td>Overestimation of POC</td>
<td>(Knapp et al. 1994)</td>
</tr>
</tbody>
</table>

ASSIGNMENTS (for instructions on how to analyze the data see below)
Coordinate with the other group with whom you simultaneously worked and make sure that the following questions are answered:

1. Are all scattering measurement correlated among them for a specific sample and with the turbidity measurement (in other words, is the sample that scatter the most also the most turbid and backscattering?)?
2. How are the scattering and attenuation spectra of phytoplankton affected by phytoplankton absorption? How are they different for the DRE and inorganic sample?
3. Does the total scattering to backscattering ratio change with particle composition?

4. Is the spectral particulate attenuation coefficient for the data collected well fitted by a power-law function? Is the particulate scattering coefficient well fitted by such a function (a code to fit such function is provided below)?

5. Are there significant differences in the beam attenuation in a red wavelength (670nm) measured by the three instruments for culture? For the dock waters? If there are differences, are they consistent with the reported acceptance angles of these instruments?

6. Are the reported wavelengths measured by the instruments consistent with what you measured with the radiometer?

7. Attempt to assign uncertainties to the values you are getting. What are the sources for uncertainties?

8. Extra credit, only if you have time (before 11pm): using the LISST-B data, obtain the VSF in the near forward (ask Nils for code). Use the Eco VSF output to add three angles in the back direction. Try to fit all this data to a Fournier-Forand function to it (Codes are in resources folder).

9. Once you get POC and SPM values from Nils (next week) compute mass and carbon specific IOPs.

DATA ANALYSIS FOR SCATTERING AND BACKSCATTERING COEFFICIENT AND GUIDING QUESTIONS:
(e.g. Boss and Pegau, 2001, Boss et al., 2004, Mueller et al., 2003, McKee et al., 2008, Zhang et al., 2009, Sullivan and Twardowski, 2009 and Leymarie et al., 2010, Sullivan et al., 2013)

Using the calibration constants provided by the manufacturer convert the counts measurements to values of the VSF at one angle.

$$\beta(\theta) = (\text{signal measured} - \text{dark}) \times \text{conversion-factor}$$

Because the VSF of salt-water and particles are very different, we first remove from the signal the VSF of salt water (or 0.2µm filtered background):

$$\beta_p(\theta) = \beta(\theta) - \beta_{sw}(\theta)$$

Where $\beta_{sw}(\theta)$ is obtained from Zhang et al., 2009 (Optics Express, 5698-5710, m-file on class folder, and also as text at the end of this handout). How big (in %) is this correction for your sample?

Correct VSF for absorption along the path.

$$\beta_p(\theta) = \beta_p(\theta)e^{L(a+eb)}$$

Where $L$ is the pathlength (from manufacturer), $a$ is the total (including water) absorption coefficient, $b$ total scattering coefficient and $e$, the fraction of scattering that is collected by the detector. Hydroscat manufacturer use $e=0.4$ based on the Petzold VSF. WET Labs recommends using $a$ only). How big (in %) is this corrections for your sample?

Convert particulate VSF to particulate backscattering using conversion from a single angle.

$$b_{bp} = 2\pi\chi\beta_p(\theta_1),$$
Table 1 from Boss and Pegau, 2001. A more recent table (with similar values at the angles used for backscattering instruments) can be found in Sullivan et al., 2013.

Compute the particulate scattering coefficient from the ac-9 as the difference between total attenuation (corrected for temperature and salinity) and the total absorption (corrected for temperature, salinity and scattering).

Compute the particulate backscattering ratio at the wavelength of the VSF device for the three samples. How do they compare with Figure 9 of Twardowski et al. 2001?

![Figure 9](image_url)

**Figure 9.** Estimated bulk refractive indices \( \eta_p(\beta_{bp}, \gamma) \) for four specific regions of the water column from the Gulf of California: (1) the case I stations below 100 m (Ia), (2) the case I stations at the chlorophyll maximum (Ic), (3) the case II stations south of the sill (Ila), and (4) the bottom water at the case II stations north of the sill (IId). All data are meter-averaged except the IId group, where data were averaged to 5 m.

Using the ac-9 (ac-s) data compute the spectral particulate attenuation and scattering coefficient of the dock waters and the culture. Do you see the absorption features in the attenuation spectra? Do you see it in the scattering spectra?

**DATA ANALYSIS FOR BEAM ATTENUATION COEFFICIENT:**

For all the transmissometers compute the mean and median beam attenuation coefficient near 660nm of the 0.2-µm filtered seawater sample and the dock data.

For the C-Star, compute the beam attenuation using the equation:
$c_{pg}(\lambda_o) = \frac{1}{Path\ length\ [m]} \ln \left( \frac{V_{\text{sample}} - V_{\text{dark}}}{V_{\text{DIW}} - V_{\text{sample}}} \right).$

To compute the particulate attenuation only you should use the dissolved for $V_{\text{DIW}}$.

**REFERENCES**


CODES (MATLAB):
X. Zhang’s code to measure salt-water scattering at any angle:

```matlab
function [betasw,beta90sw,bsw]= betasw_ZHH2009(lambda,Tc,theta,S,delta)
% Xiaodong Zhang, Lianbo Hu, and Ming-Xia He (2009), Scattering by pure
% seawater: Effect of salinity, Optics Express, Vol. 17, No. 7, 5690-5710
% lambda (nm): wavelength
% Tc: temperauter in degree Celsius, must be a scalar
% S: salinity, must be scalar
% delta: depolarization ratio, if not provided, default = 0.039 will be used.
% betasw: volume scattering at angles defined by theta. Its size is [x y],
% where x is the number of angles (x = length(theta)) and y is the number
% of wavelengths in lambda (y = length(lambda))
% beta90sw: volume scattering at 90 degree. Its size is [1 y]
% bw: total scattering coefficient. Its size is [1 y]
% for backscattering coefficients, divide total scattering by 2
% Xiaodong Zhang, March 10, 2009

% values of the constants
Na = 6.0221417930e23 ;  % Avogadro's constant
Kbz = 1.3806503e-23 ;  % Boltzmann constant
Tk = Tc+273.15 ;   % Absolute temperarture
M0 = 18e-3;  % Molecular weight of water in kg/mol

error(nargchk(4, 5, nargin));
if nargin == 4
    delta = 0.039;  % Farinato and Roswell (1976)
end
```
if ~isscalar(Tc) || ~isscalar(S)
    error('Both Tc and S need to be scalar variable');
end

lambda = lambda(:)'; % a row variable
rad = theta(:)*pi/180; % angle in radian as a column variable

% nsw: absolute refractive index of seawater
% dnds: partial derivative of seawater refractive index w.r.t. salinity
[nsw dnds] = RInw(lambda,Tc,S);

% isothermal compressibility is from Lepple & Millero (1971, Deep
% Sea-Research), pages 10-11
% The error ~ +/– 0.004e-6 bar^-1
IsoComp = BetaT(Tc,S);

% density of water and seawater, unit is Kg/m^3, from UNESCO,38,1981
density_sw = rhou_sw(Tc, S);

% water activity data of seawater is from Millero and Leung (1976, American
% Journal of Science,276,1035-1077). Table 19 was reproduced using
% Eq.(14,22,23,88,107) then were fitted to polynomial equation.
% dlnawds is partial derivative of natural logarithm of water activity
% w.r.t. salinity
dlnawds = dlnasw_ds(Tc, S);

% density derivative of refractive index from PMH model
DFRI = PMH(nsw); % PMH model

% volume scattering at 90 degree due to the density fluctuation
beta_df = pi*pi/2*((lambda*1e-9).^(-4))*Kbz*Tk*IsoComp.*DFRI.^2*(6+6*delta)/(6-7*delta);
% volume scattering at 90 degree due to the concentration fluctuation
flu_con = S*M0*dnds.^2/density_sw/(-dlnawds)/Na;
beta_cf = 2*pi*pi*((lambda*1e-9).^(-4)).*nsw.^2.*(flu_con)*(6+6*delta)/(6-7*delta);
% total volume scattering at 90 degree
beta90sw = beta_df+beta_cf;
bsw=8*pi/3*beta90sw*(2+delta)/(1+delta);
for i=1:length(lambda)
    betasw(:,i)=beta90sw(i)*(1+((cos(rad)).^2).*(1-delta)/(1+delta));
end

function [nsw dnswds]= RInw(lambda,Tc,S)
% refractive index of air is from Ciddor (1996, Applied Optics)
n_air = 1.0+(5792105.0./(238.0185-1./(lambda/1e3).^2)+167917.0./(57.362-1.7/(lambda/1e3).^2))/1e8;

% refractive index of seawater is from Quan and Fry (1994, Applied Optics)
n0 = 1.31405; n1 = 1.779e-4 ; n2 = -1.05e-6 ; n3 = 1.6e-8 ; n4 = -2.02e-6 ;
n5 = 15.868; n6 = 0.01155; n7 = -0.00423; n8 = -4382 ; n9 = 1.1455e6;
$$nsw = n0+(n1+n2*Tc+n3*Tc^2)*S+n4*Tc^2+(n5+n6*S+n7*Tc)./lambda+n8./lambda.^2+n9./lambda.^3; \quad \% \text{pure seawater}$$

$$nsw = nsw.*n_{air};$$

$$dnswds = (n1+n2*Tc+n3*Tc^2+n6./lambda).*n_{air};$$

**function** IsoComp = BetaT(Tc, S)

\% pure water secant bulk Millero (1980, Deep-sea Research)

$$kw = 19652.21+148.4206*Tc-2.327105*Tc.^2+1.360477e-2*Tc.^3-5.155288e-5*Tc.^4;$$

$$Btw_cal = 1./kw;$$

\% isothermal compressibility from Kell sound measurement in pure water

$$Btw = (50.886300.717582*Tc+0.7819867e-3*Tc.^2+31.62214e-6*Tc.^3-0.1323594e-6*Tc.^4+0.634575e-9*Tc.^5)./(1+21.65928e-3*Tc)*1e-6;$$

**seawater secant bulk**

$$a0 = 54.6746-0.603459*Tc+1.09987e-2*Tc.^2-6.167e-5*Tc.^3;$$

$$b0 = 7.944e-2+1.6483e-2*Tc-5.3009e-4*Tc.^2;$$

$$Ks = kw + a0*S + b0*S.^1.5;$$

\% calculate seawater isothermal compressibility from the secant bulk

$$\text{IsoComp} = 1./Ks*1e-5; \quad \% \text{unit is pa}$$

**function** density_sw = rhou_sw(Tc, S)

\% density of water and seawater, unit is Kg/m^3, from UNESCO,38,1981

$$a0 = 8.24493e-1; \quad a1 = -4.0899e-3; \quad a2 = 7.6438e-5; \quad a3 = -8.2467e-7; \quad a4 = 5.3875e-9;$$

$$a5 = -5.72466e-3; \quad a6 = 1.0227e-4; \quad a7 = -1.6546e-6; \quad a8 = 4.8314e-4;$$

$$b0 = 999.842594; \quad b1 = 6.793952e-2; \quad b2 = -9.09529e-3; \quad b3 = 1.001685e-4;$$

$$b4 = -1.120083e-6; \quad b5 = 6.536332e-9;$$

\% density for pure water

$$\text{density}_w = b0+b1*Tc+b2*Tc^2+b3*Tc^3+b4*Tc^4+b5*Tc^5;$$

\% density for pure seawater

$$\text{density}_sw = \text{density}_w + ((a0+a1*Tc+a2*Tc^2+a3*Tc^3+a4*Tc^4)*S+(a5+a6*Tc+a7*Tc^2)*S.^1.5+a8*S.^2);$$

**function** dlnawds = dlnasw_ds(Tc, S)

\% water activity data of seawater is from Millero and Leung (1976, American Journal of Science,276,1035-1077). Table 19 was reproduced using Eqs.(14,22,23,88,107) then were fitted to polynomial equation.

\% dlnawds is partial derivative of natural logarithm of water activity w.r.t. salinity

$$\ln aw = (-1.64555e-6-1.34779e-7*Tc+1.85392e-9*Tc.^2-1.40702e-11*Tc.^3)+......$$

$$\% (\text{-5.58651e-4+2.40452e-7*Tc-3.12165e-9*Tc.^2+2.40808e-11*Tc.^3})*S+......$$

$$\% (1.79613e-5-9.9422e-8*Tc+2.08919e-9*Tc.^2-1.39872e-11*Tc.^3)*S.^1.5+......$$

$$\% (-2.31065e-6-1.37674e-9*Tc-1.93316e-11*Tc.^2)*S.^2;$$

$$\text{dlnawds} = (-5.58651e-4+2.40452e-7*Tc-3.12165e-9*Tc.^2+2.40808e-11*Tc.^3)+......$$
\[ 1.5 \times (1.79613 \times 10^{-5} - 9.9422 \times 10^{-8} \times Tc + 2.08919 \times 10^{-9} \times Tc^2 - 1.39872 \times 10^{-11} \times Tc^3)^{0.5} + \ldots \times S \times 2 \times (-2.31065 \times 10^{-6} - 1.37674 \times 10^{-9} \times Tc - 1.93316 \times 10^{-11} \times Tc^2)^{0.5} \times S; \]

% density derivative of refractive index from PMH model

\[ \text{function } n\_density\_derivative = PMH(n\_wat) \]

\[ n\_wat2 = n\_wat \times n\_wat; \]

\[ n\_density\_derivative = (n\_wat2 - 1)^{0.5} \times \left( (1 + 2/3 \times (n\_wat2 + 2) \times (n\_wat/3 - 1/3/n\_wat)^2) \right); \]

E. Boss’s code to fit spectra to a power-law function:

driver_cp_fit.m is a driver program to fit a power function to a particulate attenuation spectra. It calls least_squares_cp.m which is where the function to minimize \( y \) is defined.

If the uncertainties in the attenuation values vary with wavelength, one should add the variance as a weight in the \( y \)-function of least_squares.m.

If you are afraid that outliers are affecting your slopes, use a robust minimization: rather than minimizing the square difference minimize the absolute values of the differences in \( y \).

To calculate the uncertainties in the fit parameters you could use a Monte-Carlo technique: add randomly noise to the data (based on your knowledge of the uncertainties and their statistics) to the spectra and recompute the fit. After you have done so sufficiently (~1000 times) compute the statistics of the fit parameters. These are your uncertainties.

%This is the driver used to find the best fit power-law function
%Assumes ac-9 like data

\[ \text{cp} = [1.50, 1.40, 1.26, 1.22, 1.16, 1.11, 0.95, 0.92, 0.85]; \]

\[ \text{wl} = [412, 440, 488, 510, 532, 555, 650, 676, 715]; \]

%setting options for fminsearch
\[ \text{opts} = \text{optimset('fminsearch');} \]
\[ \text{opts} = \text{optimset(opts,'MaxIter',4000);} \]
\[ \text{opts} = \text{optimset(opts,'MaxFunEvals',2000); } \] % usually 100*number of params
\[ \text{opts} = \text{optimset(opts,'TolFun',1e-9);} \]
\[ \text{opts} = \text{optimset('LevenbergMarquardt','on');} \]

%guess for parameters (amplitude at 532 and slope)
\[ \text{x0} = [1.22, 1]; \]

%minimization routine
\[ \text{x1} = \text{fminsearch(@least_squares_cp,x0,opts,cp,wl)} \]

%plot data and fit
\[ \text{plot(wl, cp, '.k', wl, x1(1)*(532./wl).^x1(2), 'b')} \]

\[ \text{function } y = \text{least_square_cp(x0,spec,1);} \]
\[ \text{fits a power-law function to a spectra. Assume uncertainties are the same for all wavelengths.} \]
\[ \text{y} = \text{sum((spec-x0(1).*(532./1).^x0(2)).^2)}; \]