Lab 4: Scattering, back scattering and the beam attenuation

EQUIPMENT AND SUPPLIES

1 x ac-s LISST-100X B C-Star - 25cm Bb9 nine wavelength backscattering sensors Sample chambers for LISSTs Eco-VSF at one wavelength Dock water (+filtrate), Culture (+filtrate) and sediment suspended in DIW (and DIW). Power supplies for all instruments Multi-meter to measure the C-star voltage Bench-top turbidity sensor 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 backscattering ratio influenced by the composition of material (i.e., organic vs. mineral)? Is the particulate scattering spectra influenced by absorption? Is the particulate attenuation spectra influenced by absorption? Are different scattering properties correlated?

INSTRUMENTS:

Is particulate attenuation 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 spectra for 3 types of samples (phytoplankton culture, dock water (if you have not done so in an earlier lab) and dust suspension) using the difference between total beam attenuation and absorption spectra.

Determine spectral backscattering coefficients from measurements of scattering at a single angle.

Determine backscattering at one wavelength from measurements of scattering at three angles in the back direction.

Compute spectrally the particulate backscattering to total scattering ratio. Compute the beam attenuation in the red near 660nm with four different instruments. <u>If time permits</u> (e.g. before 11pm): obtain the particulate VSF (LISST + EcoVSF) and find an analytical function that fits it.

INTRODUCTION

The volume scattering function, VSF or β , 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 β as follows:

$$b = 2\pi \int_{\theta_0}^{\pi} \beta \sin\theta d\theta$$
$$b_b = 2\pi \int_{\pi/2}^{\pi} \beta \sin\theta d\theta$$
$$c = a + b$$

Where θ_0 is the acceptance angle of the instrument used (e.g. 0.93° 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 today's lecture 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 it characteristic smooth exponentially decreasing absorption and attenuation as function of wavelength and 2) particulate attenuation that in most oceanic conditions can be well represented as a power-law function of wavelength:

$$c_{pg}(\lambda) = c_g + c_p \sim c_g(\lambda_0) e^{-s(\lambda - \lambda_0)} + c_p(\lambda_0) \left(\frac{\lambda}{\lambda_0}\right)^{-\gamma} \sim c_{pg}(\lambda_0) \left(\frac{\lambda}{\lambda_0}\right)^{-\gamma_{pg}}$$

where c_{pg} is the total beam attenuation coefficient (less water), c_g is the beam attenuation of the dissolved material, c_p is the particulate beam attenuation, *s* is the spectral slope of dissolved attenuation, and γ 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 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 ($\beta(\theta_l)$):

$$b_{bp} = 2\pi \chi \beta_p(\theta_1)$$

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 $\tilde{b} \sim 0.005$, while for inorganic minerals $\tilde{b} \sim 0.02 - 0.03$.

The class should divide in four: Students will measure b in Station 1, b_b in Station 2, backward VSF in station 3, and will measure c and forward VSF at Station 4. Each group will measure these properties for one type of water (2 x phytoplankton culture, dock waters or sediment suspension), but at the end we should have a total of 4 samples on file for each instrument.

STATION 1 SCATTERING COEFFICIENT

- 1. Calibrate an ac-s with Milli-Q water.
- 2. Measure the following:
 - a. Absorption and attenuation with ac9 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

- 1. Measure the dark current of the bb9 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 one angle and 9 wavelengths of filtrate and sample.
 - b. Don't forget to measure temperature and salinity for needed corrections.

STATION 3

MEASUREMENT OF BACKSCATTERING AT THREE ANGLES IN THE BACK DIRECTION

1. Measure the dark current of the Eco-VSF 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 of filtrate and sample.
 - b. Don't forget to measure temperature and salinity for needed corrections.
 - c. Turbidity of sample using a portable turbidity Hach meter

STATION 4

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: 0.9328°

C-Star:	1.1954°
LISST-B:	0.0262°

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 and with the turbidity measurement?
- 2. How are the scattering and attenuation spectra of phytoplankton affected by phytoplankton absorption? How are they different for the dock 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 Boss 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 (ask Boss for code).

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)

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

$$\beta(\theta)$$
=(signal measured - dark) x 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.

 $\beta_p(\theta) = \beta_p(\theta) e^{L(a+_{\varepsilon}b)}$

Where *L* is the pathlength (from manufacturer), *a* is the *total* (including water) absorption coefficient, *b* total scattering coefficient and ε , the fraction of scattering that is collected by the detector. Hydroscat manufacturer use ε =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. χ_p Based on 41 VSF Measurements ⁴											
		Angle (deg)									
	90	100	110	120	130	140	150	160	170		
X _p Percent error	0.71 4.3	0.9 2.6	1.03 3.1	1.12 4.2	1.17 3.3	1.18 3.5	1.13 4.2	1 6.4	0.62 34.8		

^ab_{bw} is less than 6% of b_b, and the estimated percent error is based on half of the difference between the 10th and 90th percentile. 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. Estimated bulk refractive indices $\hat{n}_p(\tilde{b}_{bp}, \gamma)$ for four specific regions of the water column from the Gulf of California: (1) the case I stations below 100 m (Id), (2) the case I stations at the chlorophyll maximum (Ic), (3) the case II stations south of the sill (IIa), and (4) the bottom water at the case II stations north of the sill (IId). All data were meter-averaged except the Id 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 I 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:

$$c_{pg}(\lambda_0) = \frac{1}{Pathlength[m]} ln \left(\frac{V_{sample} - V_{dark}}{V_{DIW} - V_{sample}} \right)$$

References

Boss E. and W. S. Pegau, 2001. The relationship of light scattering at an angle in the backward direction to the backscattering coefficient. *Applied Optics*, **40**, 5503-5507.

Boss E., W. S. Pegau, M. Lee, M. S. Twardowski, E. Shybanov, G. Korotaev, and F. Baratange, 2004. The particulate backscattering ratio at LEO 15 and its use to study particles composition and distribution. *J. Geophys. Res.*, **109**, C1, C0101410.1029/2002JC001514

Maffione R. A. and D. R. Dana, "Instruments and methods for measuring the backward-scattering coefficient of ocean waters," *Appl. Opt.* **36**, 6057–6067, 1997.

Mueller, L J. L., G. S. Fagion, C.R. McClain, W. S. Pegau, J. R. V. Zaneveld, B. G. Mitchell, M. Kahru, J. Wieland, and M. Stramska. 2003. Ocean optics protocols for satellite ocean color sensor validation. In: *Inherent Optical Properties: Instruments, Characterizations, Field Measurements and Data Analysis Protocols*. (NASA/TM-2003-211621/Rev4-Vol.IV.)

Sullivan, J. M., M. S. Twardowski, P.L. Donaghay & S. Freeman (2005). Using optical scattering to discriminate particle types in coastal waters. Applied Optics, Vol 44 (9): 1667-1680.

Sullivan, J. M. and M. S. Twardowski (2009). Angular shape of the oceanic particulate volume scattering function in the backward direction, Appl. Opt. **48**, 6811-6819.

Sullivan, J. M., M. S. Twardowski, J. Ronald, J. R. V. Zaneveld, and C. C. Moore (2013), Measuring optical backscattering in water, in Light Scattering Reviews 7, pp. 189–224, Springer.

Twardowski M., E. Boss, J. B. MacDonald, W. S. Pegau, A. H. Barnard, and J. R. V. Zaneveld, 2001. A model for estimating bulk refractive index from the optical backscattering ratio and the implications for understanding particle composition in case I and case II waters. *J. Geophysical Research*, **106**, 14, 129-14,142.

Oishi, T. "Significant relationship between the backward scattering coefficient of sea water and the scatterance at 120°," *Appl. Opt.***29**, 4658–4665, 1990.

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

```
function [betasw,beta90sw,bsw]= betasw_ZHH2009(lambda,Tc,theta,S,delta)
% Xiaodong Zhang, Lianbo Hu, and Ming-Xia He (2009), Scatteirng by pure
% seawater: Effect of salinity, Optics Express, Vol. 17, No. 7, 5698-5710
%
% 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 tempearture
M0 = 18e - 3;
                        % Molecular weigth 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 colum 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 Kq/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 polynominal 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/le3).^2)+167917.0./(57.362-
1./(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./lam
bda.^3; % 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 = (50.88630+0.717582*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
IsoComp = 1./Ks*1e-5; % 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; a1 = -4.0899e-3; a2 = 7.6438e-5; a3 = -8.2467e-7; a4 =
5.3875e-9;
a5 = -5.72466e-3; a6 = 1.0227e-4; a7 = -1.6546e-6; a8 = 4.8314e-4;
b0 = 999.842594; b1 = 6.793952e-2; b2 = -9.09529e-3; b3 = 1.001685e-4;
b4 = -1.120083e-6; b5 = 6.536332e-9;
% density for pure water
density w = b0+b1*Tc+b2*Tc^2+b3*Tc^3+b4*Tc^4+b5*Tc^5;
% density for pure seawater
density sw = 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 polynominal equation.
% dlnawds is partial derivative of natural logarithm of water activity
% w.r.t.salinity
% lnaw = (-1.64555e-6-1.34779e-7*Tc+1.85392e-9*Tc.^2-1.40702e-
11*Tc.^3)+....
            (-5.58651e-4+2.40452e-7*Tc-3.12165e-9*Tc.^2+2.40808e-
11*Tc.^3).*S+.....
2
            (1.79613e-5-9.9422e-8*Tc+2.08919e-9*Tc.^2-1.39872e-
11*Tc.^3).*S.^1.5+....
90
            (-2.31065e-6-1.37674e-9*Tc-1.93316e-11*Tc.^2).*S.^2;
dlnawds = (-5.58651e-4+2.40452e-7*Tc-3.12165e-9*Tc.^2+2.40808e-
11*Tc.^3)+.....
          1.5*(1.79613e-5-9.9422e-8*Tc+2.08919e-9*Tc.^2-1.39872e-
11*Tc.^3).*S.^0.5+....
          2*(-2.31065e-6-1.37674e-9*Tc-1.93316e-11*Tc.^2).*S;
% density derivative of refractive index from PMH model
function n density derivative=PMH(n wat)
n wat2 = n wat.^2;
n density derivative=(n wat2-1).*(1+2/3*(n wat2+2).*(n wat/3-1/3./n wat).^2);
```

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 aweight in the the y-funciton 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 paramters 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 suficiently (~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

cp=[1.50 1.40 1.26 1.22 1.16 1.11 0.95 0.92 0.85]; wl=[412 440 488 510 532 555 650 676 715];

%setting options for fmisearch
opts = optimset('fminsearch');
opts = optimset(opts,'MaxIter',4000);
opts = optimset(opts,'MaxFunEvals',2000); % usually 100*number of params

```
opts = optimset(opts,'TolFun',1e-9);
%opts = optimset('LevenbergMarquardt','on');
%guess for paramters (amplitude at 532 and slope)
x0=[1.22, 1];
%minimization routine
x1 = fminsearch(@least_squares_cp,x0,opts,cp,wl)
%plot data and fit
plot(wl, cp, '.k', wl, x1(1)*(532./wl).^x1(2),'b')
function y = least_square_cp(x0,spec,l);
% fits a power-law function to a spectra. Assume uncertainties are the same
% for all wavelengths.
```

```
y=sum((spec-x0(1).*(532./1).^x0(2)).^2);
```