Measurement of the Volume Scattering Function Using a Multi-Instrument Approach

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ABSTRACT

The spectral absorption coefficient and volume scattering function (VSF) are the fundamental inherent optical properties which govern the propagation of light in natural aquatic environments. Variability in seawater absorption has been extensively studied over the past decades, but owing to a lack of instrumentation measurements of the VSF are very limited. Instruments measuring discrete portions of the VSF over limited angular ranges are now available commercially. We present results of contemporaneous scattering measurements at 532 nm on particle suspensions using a Sequoia LISST-100X (32 angles, 0.08-13.5°), a Wyatt Technologies Dawn EOS (18 angles, 22.5-147°), a Wetlabs ECO-VSF (100, 125, and 150°), and a HobiLabs Hydroscat-6 (140°). The combination of these instruments provides the capability for measuring the VSF over a broad angular range. Experiments were conducted using suspensions of known particles (e.g. polystyrene microspheres) and natural seawater samples to evaluate the consistency among differing instrumentation. Utilizing this approach, we examine variability in the magnitude and shape of the VSF from samples of southern California coastal waters.

INTRODUCTION

The spectral volume scattering function, or VSF, describes the angular distribution of light scattered from an incident beam. Along with the spectral absorption coefficient, it is one of the two fundamental inherent optical properties which govern the propagation of light in aquatic environments. Variability in the absorption coefficient of the ocean and its relationship to seawater constituents has been extensively studied (e.g. Pegau et al. 1995, Bricaud et al. 1998). Despite its fundamental importance to radiative transfer modeling, however, relatively little is known about the variability of the VSF in the ocean.

For a monochromatic collimated incident beam of light with irradiance E at wavelength λ, the VSF is defined as

$$\beta(\psi,\lambda) = \frac{dI(\psi,\lambda)}{E(\lambda)\,dV} \quad [\mathrm{m}^{-1}\ \mathrm{sr}^{-1}], \tag{1}$$

where dI is the radiant intensity emanating from an elemental volume dV in a given direction ψ. Integration of the VSF yields the total scattering coefficient, $b(\lambda)$,

$$b(\lambda) = 2\pi \int_0^{\pi} \beta(\psi,\lambda)\sin(\psi)d\psi \quad [\mathrm{m}^{-1}]. \tag{2}$$

A convenient description of the shape of the VSF is the scattering phase function, defined as $\tilde{\beta}(\psi,\lambda) = \beta(\psi,\lambda)/b(\lambda)$. Both the VSF and the scattering coefficient can be considered as the additive sum of individual components which contribute to light scattering, such as seawater itself, turbulence, bubbles, and suspended particles. In most natural waters, particles represent the dominant contribution to the VSF. The measurements in the present study deal exclusively with the scattering of particles, and thus the optical quantities are denoted by the subscript p.

Direct measurement of the VSF over the entire angular range is challenging due to difficulties in instrument design and engineering, and no instrumentation is currently available which measures the entire VSF. The classic measurements of Petzold (1972), made more than 30 years ago with a custom-built instrument, are still widely-used in radiative transfer modeling applications despite the limited number of measurements comprising this data set. More recently, Lee and Lewis (2003) described a prototype instrument, utilizing a new design, for measuring the VSF over the angular range 0.6 – 177.3°. Their measurements in Atlantic coastal waters suggest the potential for significant variability in portions of the VSF, such as the near-forward and backward directions, that are not well-represented by the standard Petzold curves.

Instrumentation measuring angular scattering intensity has been commercially available for some time. Such instruments typically measure a limited portion of the VSF, such as a few fixed angles at a single wavelength, or multiple spectral bands measured at a single angle. By combining measurements from diverse instruments on the same suspension, a broader representation of the VSF can be discerned assuming that measurements among instruments are comparable. Here we present results comparing the VSF measured contempraneously with multiple instruments, and present preliminary observations on the variability of the VSF for natural water samples taken from San Diego coastal waters.

MATERIALS AND METHODS

VSF measurements and instrumentation

Four different instruments were used to measure the VSF. One is a laboratory instrument solely used for discrete samples, the other three have the capability for in situ deployment. Filtered seawater (0.2 μm filter) was used to determine the baseline for each instrument, and subsequently subtracted to yield the scattering coefficient of particles.

The LISST-100X (Laser In Situ Scattering and Transmissometer, Sequoia Scientific) measures the near-forward angular scattering pattern of a laser beam source using 32 detectors logarithmically spaced between 0.08 and 13.5 degrees. The LISST was originally designed for estimating the particle size distribution of sediments by inversion of the small angle scattering signal; however, the data can also be used to obtain estimates of the VSF (Agrawal 2005, Slade and Boss 2006). The instrument used in this study was modified by replacing the standard 670 nm red laser with a 532 nm laser. The instrument has a 5 cm pathlength, and can be used either in situ or outfitted with a sample chamber for analysis of discrete water samples in the laboratory. For a typical sample, 1500 measurements of the VSF were made at 1 Hz resolution, corrected for attenuation effects, and averaged.

A Dawn EOS (Wyatt Tech.) light scattering meter was used to measure scattering at 18 fixed angles (22.5–147°) from a 532 nm laser. This bench-top instrument is primarily marketed for characterizing macromolecular solutions, but has been used to estimate scattering characteristics of marine particles (e.g. Balch et al. 1999). Scattering measurements were made on discrete water samples (20 ml) contained within a cylindrical cuvette. A liquid crystal variable retarder was used to polarize the incident laser light in either a vertical or horizontal orientation. For each polarization state, triplicate measurements (each consisting of 1440 data points acquired by each detector over 3 minutes with a sampling rate of 8 Hz) were made on each suspension and averaged. The "unpolarized" VSF was calculated by averaging the results for these two polarization states. The 90° detector was calibrated by measurements of the VSF of pure toluene with a vertically polarized incident beam, as the value of the VSF for this solution is well known. The other detectors were intercalibrated (or normalized) relative to 90 degrees by measuring scattering on seawater filtered multiple times through a 0.2 um filter, and comparing the results with the theoretical values of scattering by pure seawater (Morel 1974).

Two additional instruments designed for in situ measurement of the VSF at fixed angles were used in selected experiments. An ECO-VSF (WET Labs, Inc.) was used to measure scattering at three angles in the backward direction (100, 125, and 150°) at 532 nm. A Hydroscat-6 backscattering meter (HS-6, HOBI Labs Inc.) provided measurement of the VSF at one angle (140°) in six different spectral bands (442, 470, 550, 589, 620, and 671 nm). The data from HS-6 were interpolated to 532 nm for comparison with other instruments.

Additional measurements

Spectral absorption and beam attenuation coefficients of particles were measured in a dual beam Perkin-Elmer Lambda 18 spectrophotometer equipped with an integrating sphere (Labsphere, RSA-PE-18). Beam attenuation, $c_p(\lambda)$, was measured on particle suspensions within a 1 cm cuvette by reducing the acceptance angle of the detector to <1° through the use of field stops. A baseline measured on filtered seawater (0.2 μm filter) was subtracted from the measurement of the particle suspension to yield the final beam attenuation due to particles only. Particle absorption, $a_p(\lambda)$, was measured on glass fiber filters using the transmittance-reflectance technique (Tassan and Ferrari 1995). The scattering coefficient of particles, $b_p(\lambda)$, was calculated as $c_p(\lambda) - a_p(\lambda)$.

The particle size distribution was determined on each suspension using an electronic particle counter (Multisizer III, Beckman-Coulter). The numerical concentration of particles, $N(D)$, in 256 discrete size classes of diameter D was obtained by averaging triplicate samples of 1-8 ml each. Filtered seawater was used as both the diluent and blank.

Particle suspensions

Standard microspheres– Scattering measurements in the laboratory were performed on suspensions of polystyrene microsphere size standards (Duke Scientific). Experiments included monodisperse suspensions consisting of single diameter standards (1, 2, 5, 10, 20, 50, and 100 μm), as well as polydisperse suspensions made by mixing microspheres of different sizes. All stock solutions of microspheres were first sonicated to minimize particle aggregation, then diluted in filtered seawater. The concentration of each suspension was adjusted to minimize multiple scattering effects, and serial dilutions of each suspension were measured to ensure signal linearity.

Mie scattering theory (Bohren and Huffman 1983) was used to calculate the theoretical VSF of the microsphere suspensions for comparison with measured scattering responses. The measured particle size distribution, $N(D)$, was used as an input to the calculation. Based upon the results of Ma et al.

(2003), the complex refractive index of polystyrene, relative to water, was assumed to be 1.18494 - 0.00035*i* at λ = 532 nm.

Field samples– Natural seawater samples were collected at Imperial Beach Pier in San Diego and transported back to the laboratory for analysis. Imperial Beach is located within the Tijuana River watershed, and can be influenced by outflow from this river. Sampling was conducted throughout the period January 2005 through June 2006.

Tank measurements– Experiments were also performed in the laboratory using natural seawater placed in a black cylindrical tank with a depth of 1.25 meters. For most experiments, this configuration resulted in an optical depth >1. To further minimize bottom reflections, an angled non-reflective plate was placed at the bottom of the vessel. The tank was filled with 70 liters of seawater collected at Scripps pier, and mixed continuously throughout the experiment. Measurements with the LISST, ECO-VSF, and HS-6 were made "in situ" by suspending the instruments within the tank and averaging data over a 5-10 minute period. A subsample of water was removed from the tank for measurements by benchtop instruments (e.g. Dawn, Coulter).

RESULTS AND DISCUSSION

Representative results from three experiments with differing size microspheres are illustrated in Figure 1. Coulter counter measurements of the bead suspensions indicated a relatively narrow distribution of particle size around the modal diameter, with low concentrations of particle aggregates (e.g. doublets) ocasionally observed in some experiments. The absence of other particles which could strongly influence the scattering signal was also confirmed.

Scattering intensity as a function of angle varied by as much as seven orders of magnitude for suspensions of large beads (Fig. 1). The behavior of the VSF measured with LISST and Dawn for individual bead suspensions generally agreed well with results predicted from Mie theory, with a tendency for the rate of increase in scattering intensity to decrease with decreasing angle at the smallest forward angles. Increasing particle size leads to a steeper VSF, with a narrower forward scattering lobe. In the case of the LISST, measurements at very small angles (<0.2°) were often problematic for the smaller microsphere suspensions. Natural particle assemblages are generally highly-peaked in the forward direction, and the instrument is designed with a variable detector area to maintain an approximately equal signal per detector. For monodisperse suspensions of small particles, the absence of the highly-peaked forward scattering lobe results in signals which are not signficantly higher than instrument noise in these detectors.

Figure 2 compares measured $\beta_p(\psi)$ with Mie calculated values for all microsphere experiments. All angles of measurements with LISST and Dawn are included. Overall, the results suggest a reasonable correlation between the magnitudes of measured and modeled values, with a large percentage of both the LISST measurements (90%) and Dawn measurements (75%) within 50% of the Mie calculated values. The frequency distributions of the relative error show that on average both instruments tend to underestimate the modeled values, with an average discrepancy of about 10%. For the LISST, this error was equally distributed among the different angular detectors. In the case of the DAWN instrument, however, larger errors were associated with the first few detectors (22.5–32°) and for detectors in the backward direction greater than 120°. Some portion of this variability may arise from sub-sampling error, and difficulties in keeping particles in a homogenous suspension during the time course of measurement (e.g. particle sinking). Other sources of discrepancies include measurement errors (for example, imperfect instrument calibration) and possible inadequacies in the Mie calculated values in terms of representing the actual particle suspension (for example, imperfect data on particle size distribution and refractive index used in Mie calculations).

Knowledge of the VSF in the backward directions is important to accurate determination of the backscattering coefficient, b_b, a critical parameter for interpretation of satellite remote sensing data. Currently, determinations of b_b are made by measurements at a few fixed angles between 100-150°, and utilizing a conversion factor which assumes a relationship between $\beta(\psi)$ and b_b (e.g. Chami et al. 2006). Examples of this type of instrument are the Hydroscat-6 (ψ=140) and the Eco-VSF (ψ= 100,125, and 150). The tank experiments allowed a direct comparison of the Dawn measurements in the backward direction with ECO-VSF and Hydroscat-6 (Figure 3). Results of these experiments indicate a reasonable agreement between the ECO-VSF and HS-6. However, the VSF values past 120 degrees from Dawn are significantly higher than those from the other instruments, and the shape of VSF from Dawn differs at these angles. One likely explanation is an issue with normalization factors for Dawn detectors, especially past 120 degrees.

Figure 4 illustrates results of VSF measurements made with LISST and Dawn on water samples collected at Imperial Beach Pier, CA. The general magnitude of the measured VSFs are consistent with the Petzold curve obtained from a turbid harbor. However, the data from Imperial Beach also show the potential for large temporal variability, with measured VSF varying more than two orders of magnitude throughout the year at this location. The highest values were recorded during a bloom of the red tide dinoflagellate *Lingulodinium polyedrum* on 07 July 2005, which dominated the particle assemblage on a volume basis (cell size of ~35 um, with cell concentrations in excess of 7×10^9 m^{-3}).

Using the LISST and Dawn measurements of VSF, we also calculated particle phase functions using b_p derived from independent measurements with a spectrophotometer. In the angular range 0.5–13.5°, the phase function based on LISST measurements is remarkably consistent (i.e. weakly variable), and agrees well with the average Petzold particle phase function. In the small angle region (<0.5 deg), however, significant variability in the shape of the VSF measured with the LISST is observed. At intermediate and large angles, the phase function from Dawn measurements show significant variability and is generally lower than the Petzold phase function.

Our preliminary results, based on combining data from these different measurements, suggest that significant variability from the Petzold phase function may exist in the near-forward (<0.5°) and in the near-backward directions. These findings are consistent with the observations of Lee and Lewis (2003), who observed similar behavior with a "hinge point" of low variability around 7-8 degrees. Such observations dictate the need for better understanding of the natural variance of the VSF, and its relation to environmental variability, for improved modeling of radiative transfer within the ocean.

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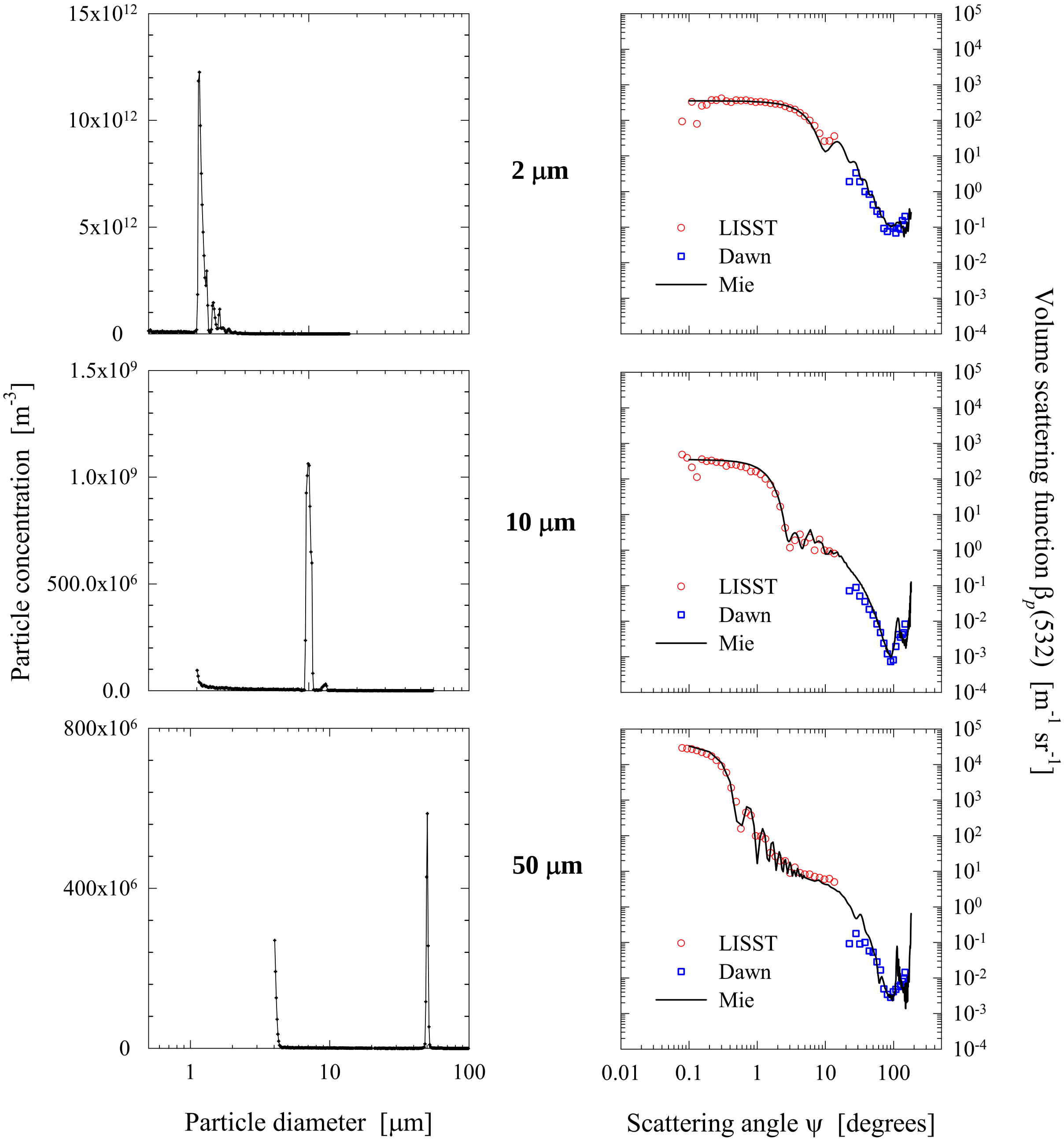

Figure 1. Representative results illustrating measured and modeled volume scattering functions for microsphere suspensions of varying size. The left panels depict the particle size distribution measured with a Coulter counter for each experiment. The right panels depict the measured VSF from the LISST and Dawn instruments, and the theoretical VSF calculated using Mie theory.

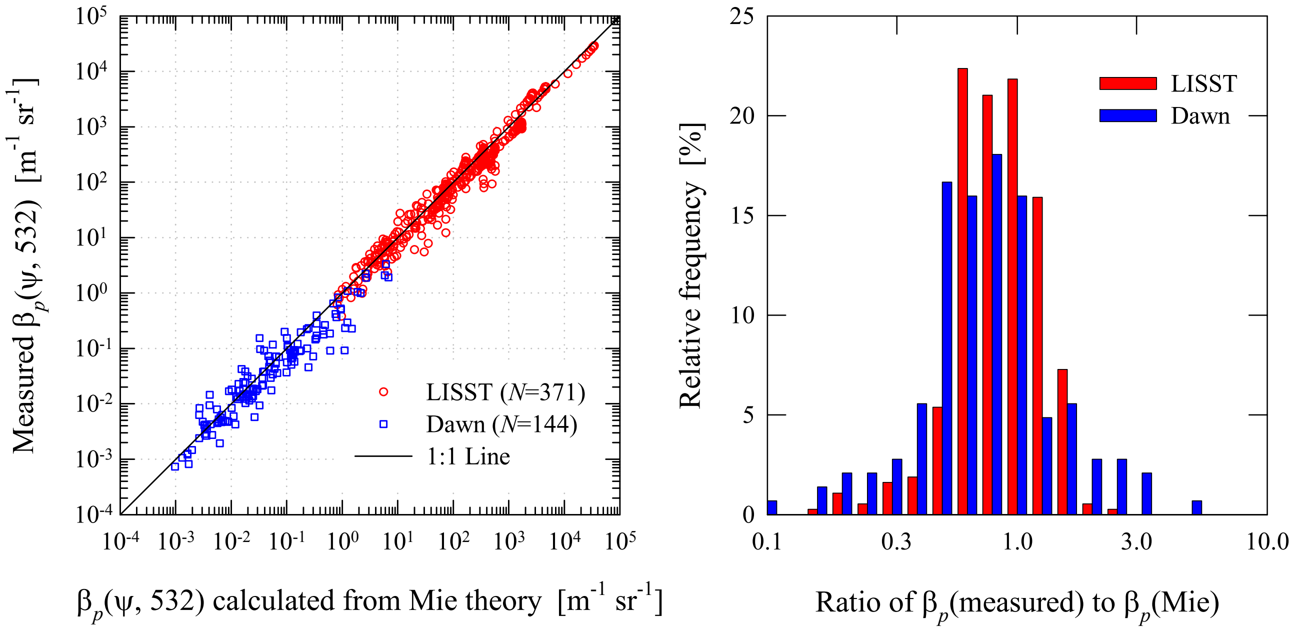

Figure 2. Comparison of the VSF measured with LISST and Dawn with Mie-derived values for experiments with polystyrene microspheres of various sizes and mixtures. The right panel illustrates the frequency distribution of the ratio between measured and modeled values.

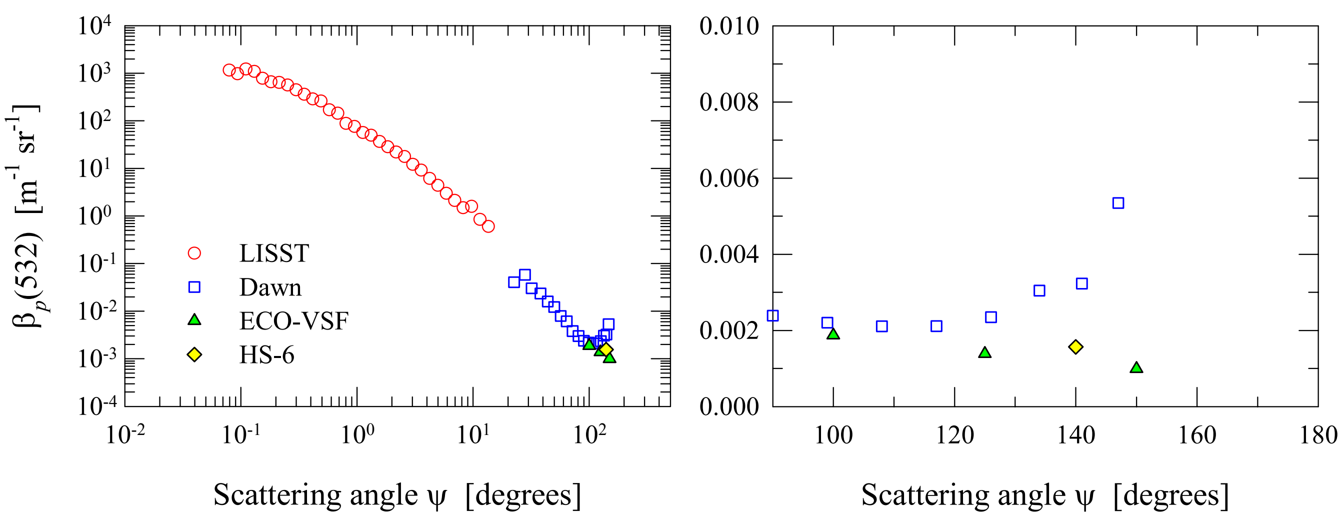

Figure 3. Volume scattering function measured with various instrumentation on a natural seawater sample collected from Scripps Pier on 05 July 2006. Seventy liters of seawater were used to fill a tank of sufficient depth to allow a simulated "in situ" measurement on the same water sample with the LISST, ECO-VSF, and HS-6 instruments. The measurement with Dawn was made on a water sample withdrawn from the tank. The right panel shows the backward scattering region of the same data with linear axes.

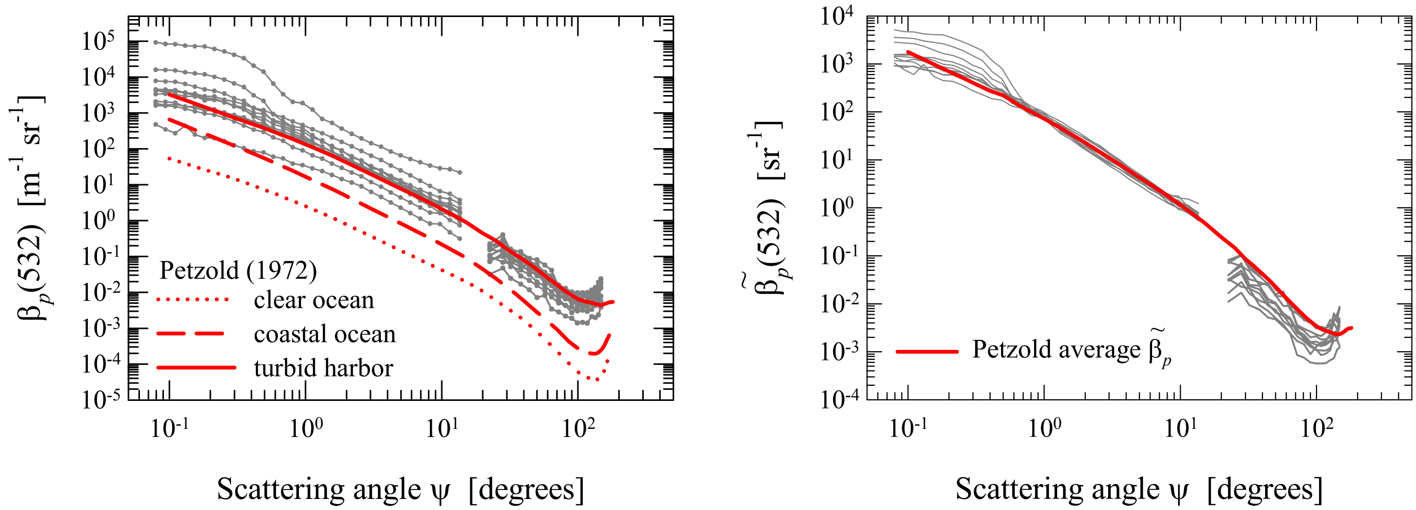

Figure 4. (Left panel) Volume scattering functions of particles measured with LISST (forward directions) and Dawn (intermediate and backward directions) on seawater samples from Imperial Beach Pier, California, during the period June 2005 to June 2006. The measurements of Petzold (1972) for three ocean environments are shown for comparison. The Petzold data were measured at 514 nm. (Right panel) Particle scattering phase functions corresponding to the data in the left panel. The Petzold average phase function is also depicted.