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Laboratory measurements of IOPs

Rüdiger Röttgers

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- 1) CDOM/Gelbstoff absorption
- 2) particulate absorption (phytoplanktonic and non-phytoplanktonic absorption)

recent methodological developments and recommendations for protocol revision

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CDOM/Gelbstoff absorption, a_{cdom}

problematic issues:

- low sensitive (typical max. path length: 10 cm), measurements in oligotrophic waters difficult
- use of spectrophotometer on board of ships is difficult \rightarrow
- sample storage/conservation, (sample storage seems less problematic, e.g. Swan et al. 2012, 12 month at 4°C), enhanced particle scattering after storage → re-filtration necessary
- artifacts due to optical influences of temperature and salinity differences (sample vs. reference) or insufficient particle removal
- typically a null-point correction is applied to remove scattering errors

recommendations

- use of liquid core waveguide capillary cells (LWCC, UltraPath) in clear waters (path lengths: 0.5 – 2 m, Miller et al. 2002), can be used on ships, allows immediate sample measurements, avoids sample storage and conservation, T&S effects more severe due the measurement principle, (Nelson et al., 2007, 2010, Swan et al. 2009)
- correction of salinity effects necessary (using NaCl solution as reference or determine system-specific salinity correction coefficient)
- avoid conservation of samples (and storage if possible)
- work out recommendations for LWCC/Ultrapath methodology



2

1.5

0.5

1

0

GF/F (Whatman) filters

problematic issues:

 optical contamination of some filter patches (colour from the blue plastic trays?) see e.g. Mitchell et al. 2003: "Glass fiber filters should be avoided if possible because they have been shown to cause rather severe contamination of the filtrate in tests using purified water."

recommendations

- always, i.e. for any analysis, combust glass fiber filters (10 min 450°C is sufficient) or check each filter for contamination (not easy)



Fig. 1. (a) Optical density, OD_f , as a function of wavelength for different GF/F filters (Whatman) showing contamination (dirty filter) with an absorption maximum around 420 nm; (b) the OD_f of uncombusted and combusted GF-5 filters.

Röttgers & Gehnke, 2012, AO

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Methodology: (potential errors under ideal conditions, main error source)

- Quantitative filter technique (QFT), min. error ca. ±25% due to variations in the amplification factor
- PSICAM, error ca. ±5% due to uncertainties in the calibration
- WetLabs ACS/AC9, error ca. ±5-50% due to assumption of negligible NIR absorption for scatter correction and errors in the attenuation determination
- Hobilabs A-sphere, error ca. ±5-10% due to uncertainties in the calibration and small scattering errors

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problematic issues:

- low precision due to scattering errors, especially for simple QFT transmission measurements
- strong variations in the path length amplification for QFT
- significant NIR absorption in turbid waters precludes scatter correction by a null-point correction (using a signal at a NIR wavelength)
- pigment bleaching/extraction induces errors, bleaching might add absorption at shorter wavelengths, bleaching and extraction do often not remove pigments completely
- loss of water soluble pigments
- other techniques (e.g. A-sphere, PSICAM) more accurate but less sensitive than QFT

recommendations

- QFT preferably done by Transmittance-Reflectance (Tassan & Ferrari, 1995) or even direct absorptance measurements (Röttgers & Gehnke, 2012)
- individual determination of the sample amplification factor could be done by PSICAM, A-sphere, or improved ACS/AC9 measurements (poster David McKee et al.)
- null-point correction should be avoided (at least in coastal waters) to improve accuracy at red and NIR wavelengths



Fig. 3. Variation in optical density as a function of wavelength for filters from the same filter batch depicted as standard deviation, $\sigma_{\rm OD}$, for multiple measurements of (a) dry filters, (b) wet filters, and (c) filters prepared from an algal culture sample, measured as transmittance, T, as absorptance, A, and by the T-R method.

Röttgers & Gehnke, 2012, AO

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Fig. 8. Theoretical absorption coefficient, $a^{\beta=1}$, measured as absorptance, A, and by the T-R method, plotted against the real absorption coefficient, a, (a) for algal cultures (A: n = 23; T-R: n = 15) and (b) for natural samples (A: n = 31; T-R: n = 34). Indicated are the mean slopes (i.e., the mean amplification factor). The data are normalized to the maximum of a of each data set to compensate for differences in the maximum absorption of each sample.

Röttgers & Gehnke, 2012, AO

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particulate absorption, a_p

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Particulate absorption measured by improved QFT (Röttgers & Gehnke, 2012)

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Particulate absorption measured by T&R and PSCIAM, Atlantic Ocean



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- protocols for PSICAM, A-sphere measurements

suspended matter concentration

problematic issues:

- offset problems especially with glass fiber filters by salt retention in the rim of the filter (Stavn et al. 2009)
- recommendations
- follow Stavn et al. 2009



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