Long path length liquid waveguide capillary cell (LWCC) systems using simple spectrometers to determine the spectral absorption by colored dissolved organic matter (CDOM) have previously been shown to have better measurement sensitivity compared to high-end spectrophotometers using 10 cm cuvettes. Information on the magnitude of measurement uncertainties for LWCC systems, however, has remained scarce. Cross-comparison of three different LWCC systems with three different path lengths (50, 100, and 250 cm) and two different cladding materials enabled quantification of measurement precision and accuracy, revealing strong wavelength dependency in both parameters. Stable pumping of the sample through the capillary cell was found to improve measurement precision over measurements made with the sample kept stationary. Results from the 50 and 100 cm LWCC systems, with higher refractive index cladding, showed systematic artifacts including small but unphysical negative offsets and high-frequency spectral perturbations due to limited performance of the salinity correction. In comparison, the newer 250 cm LWCC with lower refractive index cladding returned small positive offsets that may be physically correct. After null correction of measurements at 700 nm, overall agreement of CDOM absorption data at 440 nm was found to be within 5% root mean square percentage error.

1. INTRODUCTION

The spectral absorption of light yields information on the presence and concentration of absorbing constituents within a natural water sample. While water itself absorbs strongly in the near-infrared (NIR) region of the spectrum, nonwater constituents typically absorb most strongly at visible and ultraviolet (UV) wavelengths, with only limited signals in the NIR [1]. For example, phytoplankton have a characteristic absorption spectrum that is composed of the absorption by different pigments present in the cells, with typically two absorption peaks in the blue and red spectral region and negligible absorption in the NIR. The absorption of other organic components such as particulate detrital material and colored dissolved organic matter (CDOM), increases continuously with decreasing wavelength, with maximum absorption in the UV (<300 nm) [2].

Light absorption by CDOM is well known to play an important role in aquatic environments, contributing to a variety of biogeochemical processes and the light propagation underwater [3–5]. For example, CDOM absorption might protect phytoplankton from damaging UV radiation [6,7], and, at the same time, limits the amount of light available for photosynthesis, and hence, hinders primary production [8,9]. Knowledge on CDOM absorption spectra is relevant for the correct interpretation of ocean color remote sensing signals, such as for the retrieval of chlorophyll a concentrations [10,11], and the parameterization of primary production models [7]. The spectral slope can provide additional information on the origin of the material (e.g., marine or terrestrial), which can be used for monitoring of river discharge processes, and on the chemical composition [12]. CDOM absorption is highly variable and typically highest in fresh water systems and rivers, generally decreasing with distance from shore [13]. In the past, a strong link between CDOM concentration and salinity has been demonstrated in coastal waters, where conservative mixing of river and oceanic water is likely to influence CDOM absorption [14–16]. CDOM has also been utilized as tracer for changes in biogeochemistry and circulation of water masses [11,17,18]. Some recent studies have investigated CDOM absorption and its influence on solar heating of the upper ocean, in particular for Arctic regions [19,20].
CDOM light absorption coefficients, \(a_{\text{CDOM}}\), are determined spectrophotometrically from natural water samples that have been filtered through a 0.2 \(\mu\)m pore-size filter. This has traditionally been done using bench-top spectrophotometers equipped with quartz-glass cuvettes and a typical path length of 10 cm [2]. However, this method is not sensitive enough, particularly in the visible spectral region, to measure absorption by CDOM in oceanic waters where concentrations are extremely low. More recent studies have therefore used measurement systems with longer optical path lengths such as liquid core waveguide cells [21] or point-source integrating cavity absorption meters (PSICAMs) [22]. The latter are complex, require large sample volumes, have a relatively limited spectral range, and have therefore not been routinely used. Liquid core waveguide systems, however, are compact, fairly simple to operate, and have found increased application in aquatic studies.

There are currently two different types of cells used for the determination of absorption by natural water samples: (1) the multiple path length UltraPath system manufactured by World Precision Instruments Inc. (WPI), U.S., [23,24] and (2) single path length liquid waveguide capillary cells (LWCC, also WPI) [21]. In both cell types light is guided through the cell containing the sample using internal reflections at the cell walls. The main difference between the two types is the capillary’s optical construction (see [25]). The UltraPath is a Type I cell with a large inner diameter, made from a very low refractive index (less than water) polymer (Teflon) allowing total internal reflection of light directly at the water to cell surface. LWCCs are Type II small inner diameter cells, where low refractive index material is used as a cladding around a transparent quartz-glass tubing. This construction reduces contamination issues and minimizes problems due to adhesion of air bubbles [26]. Light penetrating the quartz-glass tubing before being reflected on the outer Teflon cladding leads to a visible high-frequency pattern (when using spectrometers with high optical resolution) which changes with the refractive index of water, i.e., with salinity. The exact mechanism for this high-frequency pattern remains essentially unknown. For both types of cells, the quality of the capillary performance depends on the absolute refractive index of the polymer, i.e., the absolute difference to the refractive index of (sea-)water. Available LWCC path lengths range from 50 to 500 cm, while an UltraPath system allows choice from multiple path lengths between 2 and 200 cm to be used with a single instrument.

Liquid waveguide measurement systems typically consist of a cell, a stable light source, and a spectral detector. These systems are compact, without any moving parts, and thus are less susceptible to ship movement than traditional cuvette measurements in spectrophotometers. Waveguide cells only require small sample volumes, 125 \(\mu\)L–2.5 mL for LWCCs and <10 mL for UltraPath cells. However, small volumes of samples can heat up very quickly inside the cell, leading to a higher susceptibility to temperature changes that influence light absorption at NIR wavelengths. Heating of the sample can further result in degassing and buildup of gas bubbles. The presence of bubbles inside the cell results in increased scattering and potential overestimation of absorption. In addition, air bubbles inside the cell are a major issue because air has a higher compressibility relative to water and measurements become extremely sensitive to the sample injection pressure, which can be observed as relatively large negative offsets (\(\sim -0.02\) m\(^{-1}\)). This is a considerable disadvantage compared to other spectrophotometric systems like a cuvette spectrophotometer or a PSICAM where samples do not have to be injected. Given the smaller sample volume required and the lower risk of contamination and adhesion of air bubbles, the LWCC is potentially preferable over an UltraPath cell.

UltraPath systems have found application in seawater studies [17,18]. LWCC systems have predominantly been used for opto-chemical analysis with non-saline waters and only in very few marine studies [27,28]. A remaining concern is the lack of information on the magnitude of measurement uncertainties and information on the performance of these systems. Some work has been done in the past, predominantly focusing on UltraPath systems [29], and, to our knowledge, no comparable investigation has been carried out for the Type II LWCC systems. This work will present an optimized procedure to reduce the influence of scattering by particles and small bubbles on CDOM absorption coefficient determinations and compare absorption measurements from three different path length LWCCs (50, 100, and 250 cm). The investigation will include a comparison of the precision and accuracy for different path lengths and look at the effects of applying pressure versus not applying pressure to the sample during measurement recording.

2. METHODS

A. Sampling

Absorption data were collected during a cruise on RV Heincke, circumnavigating Great Britain, in spring 2015. The 62 sample sites included the English Channel, Bristol Channel, several Scottish sea lochs, the east coast of Scotland close to the River Tay and River Forth estuaries, as well as the central North Sea (Fig. 1). A variety of water types was sampled, including sediment-dominated estuaries, various coastal waters, and the onset of the phytoplankton spring bloom in Loch Fyne. Water samples were collected using Niskin bottles, mainly at depths close to the surface (top 10 m) but data sets also include a few samples from greater depths, up to 85 m. On board, samples were divided into two subsamples that were

![Fig. 1. Sampling sites during a 20-day cruise in April 2015.](Image)
processed independently by two different groups from (1) the Helmholtz–Zentrum Geesthacht (HZG) and (2) the University of Strathclyde (Strath). Both groups used their own filtration systems to prepare CDOM samples by two-step vacuum filtration. First, samples were filtered through a 47 mm GF/F filter (Whatman, Germany) with a typical pore size of 0.5 μm [30] and then through 47 mm nitrocellulose membrane filters with a 0.22 μm pore size (GSWP, Merck Millipore Ltd., Ireland). After filtration, the samples were stored in a water bath to stabilize at room temperature (same as the purified water reference) and measured within a few hours of collection.

B. Absorption Determination
CDOM absorption spectra were determined from measurements using Type II liquid waveguide capillary cells (World Precision Instruments Inc., U.S.) connected to Deuterium Halogen UV/VIS light sources (DH-2000-BAL, Ocean Optics Inc., U.S.) and photodiode array spectrometers (AvaSpec ULS2048XL, Avantes, Netherlands) using optical fibers. Samples were measured by the two groups using two slightly different setups. The Strath measurement system used a 100 cm LWCC (LWCC-2100) and a VIS to NIR spectrometer; the HZG group used LWCCs of two path lengths, 50 cm (LWCC-2050) and 250 cm (LWCC-3250), and the UV to VIS version of the spectrometer. The setup control, measurement recording, and data storage were done using a Python routine developed in the HZG group. The absorption by CDOM was determined in triplicate from 300–750 nm against purified water (Milli-Q, water purification system: Millipore, Ireland) and used to calculate absorption coefficients using the Beer–Lambert law with nominal path lengths provided by the manufacturer for each LWCC. Data with optical densities greater than 1.5 were found to be subject to problems associated with detector nonlinearity and stray light, and were therefore excluded from further analysis.

C. Salinity Correction
The presence of salt ions in seawater introduces a change in absorption relative to pure water that is significant at red/NIR wavelengths [31]. LWCC measurements are further affected by changes in the refractive index caused by variations in the salinity of the sample, resulting in the formation of high-frequency structures in recorded spectra when using detectors with high sensitivity and fine spectral resolution (Fig. 2). This high-frequency pattern is not typically observed with lower spectral resolution detectors (<5 nm), and is slightly variable, typically changing with each (dis)assembly of the kit. Salinity correction coefficients are system-specific (combining water and LWCC effects) and were determined by measuring the absorption of a freshly prepared sodium chloride (NaCl) solution multiple times during the 20-day cruise (5 times for the 50 cm and 100 cm cell and 3 times for the 250 cm cell) following the suggestions in Ref. [32]. The NaCl solution was prepared by adding 100 mL of purified water to 10 g of NaCl (>99.5%; Sigma-Aldrich, Germany), resulting in a concentration of approximately 90.9 g/kg⁻¹.

This relatively strong, single concentration was used to minimize the effort going into the determination of correction coefficients whilst increasing the signal-to-noise ratio compared to using a concentration closer to the sample salinity. It has been shown in the past that the optical effect of an NaCl solution increases linearly with concentration [31]. Therefore, final correction coefficient, as shown in Fig. 2, can be derived by

![Fig. 2. Mean (black) and corresponding standard deviation (gray) spectra of salinity (where salinity is expressed as salt concentration in g/kg) correction coefficients derived for the three LWCC systems.](image-url)
dividing the measured NaCl absorption spectra by the concentration. To correct CDOM absorption spectra for salinity effects, correction coefficients were scaled to the corresponding sample salinity (in g/kg) and subtracted according to Eq. (1).

\[ a_{\text{corrected}}(\lambda) = a_{\text{measured}}(\lambda) - S \times \psi_S(\lambda), \]

where \( a_{\text{corrected}} \) is the absorption coefficient corrected for salinity effects, \( a_{\text{measured}} \) is the uncorrected absorption coefficients, \( S \) is the sample salinity and \( \psi_S \) is the salinity correction coefficient.

Röttgers et al. [32] showed that salinity correction coefficients determined using either a NaCl solution or artificial seawater are comparable in the visible range. They also found that artificial seawater salts suffer more strongly from contamination issues due to the presence of other salts containing optically impure halogen ions. Contamination cannot easily be removed by combustion and artificial seawater therefore gives less reliable results at wavelengths <500 nm. Salinity correction coefficients are expected to become increasingly negative into the blue/UV following the trend in absolute differences in refractive indices of pure water and salt solutions. Although measurements were stable over the course of the cruise, at UV/blue wavelengths (<450 nm) there was increased variability and measured spectra did not follow the expected negative trend but tended to be artificially high which is assumed to be due to impurities of the sodium chloride solution. The effect of salinity on absorption was smallest for the longest path length and increased with shorter path lengths. The salinity of each sample was recorded, and CDOM spectra were corrected using the average of all NaCl spectra of each LWCC scaled to the salinity of the sample.

D. Assessment and Statistic Descriptors
Geometric mean linear regressions were applied to find best-fit slopes and offsets with corresponding 95% confidence intervals in order to assess the performance of the two longer path lengths in comparison to the 50 cm LWCC cell. Additionally, root mean square errors (RMSEs) [Eq. (2)] and root mean square percentage errors (RMS%Es) [Eq. (3)] calculated for the whole data set provided information on the absolute and relative deviation between data determined using the longer capillary cells, \( a_i \), (with \( i \) being either 100 cm or 250 cm) and absorption measured with the 50 cm path length, \( a_{50\, \text{cm}} \).

\[ \text{RMSE} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (a_i - a_{50\, \text{cm}})^2}, \]

\[ \text{RMS}\% = \sqrt{\frac{1}{n} \sum_{i=1}^{n} \left( \frac{a_i - a_{50\, \text{cm}}}{a_{50\, \text{cm}}} \times 100 \right)^2}. \]

3. RESULTS
A. Absorption Spectra
The performance of CDOM absorption determinations with different path length LWCC systems was assessed from 300–750 nm at 2 nm resolution. Figure 3(a) shows an example spectrum for a selected station and highlights some of the features observed at the edges of the spectrum. Measurements with the 250 cm path length cell show features associated with limited signal-to-noise ratio at both edges of the spectrum. In the NIR, strong water absorption reduces the transmitted signal significantly, whereas strong sample absorption in combination with reduced detector sensitivity and low lamp output reduces signals at UV/blue wavelengths toward the signal-to-noise limit. This results in nonlinear behavior that can be observed.

\[ \text{RMS}\% = \sqrt{\frac{1}{n} \sum_{i=1}^{n} \left( \frac{a_i - a_{50\, \text{cm}}}{a_{50\, \text{cm}}} \times 100 \right)^2}. \]
as systematic curving off and underestimation of the absorption spectra when sample absorption is high [>1.1 m⁻¹; Figs. 3(b) and 4].

In the two shorter path lengths, 50 and 100 cm, signals are not attenuated as strongly, and no systematic curve-off was observed in the wavelength range used for this work [Fig. 3(b)]. For the following analysis, data measured with the 250 cm capillary were therefore limited to absorption values <1.1 m⁻¹ to avoid artifacts due to sensitivity limitations. Despite the imposition of this restriction, remaining spectra extended at least down to 334 nm.

Absorption spectra measured with the 50 and 100 cm LWCCs showed consistently significant negative offsets at red/NIR wavelengths even after the correction for salinity effects [Fig. 3(c)]. Therefore, an offset correction was applied before subsequent analysis using averages calculated from 690–710 nm, with overall average offsets of −0.0074 m⁻¹ and −0.0103 m⁻¹ for the 50 and 100 cm path lengths, respectively. Data obtained using the 250 cm LWCC did not exhibit negative offsets once measurements were corrected for salinity effects. This is presumably due to the fact that the LWCC-3250 capillary cell has a cladding of a material with lower refractive index than the two shorter cells of the LWCC-2000 series [33]. The lower refractive index of the cladding leads to a higher optical transmission through the capillary and much lower refractive index effects by seawater when compared to purified water. Positive NIR absorption signals from the newer LWCC-3250 capillary cell may represent genuine nonzero CDOM absorption. However, the necessity to offset-correct the shorter path length data resulted in a methodological inconsistency between data sets that could only be resolved by also offset-correcting the 250 cm data.

Furthermore, the absorption in the NIR is strongly affected by the temperature dependency of pure water absorption which occurs when reference and sample temperature differ. These effects were not corrected as they are a result of small sample volumes being rapidly warmed during passage of the sample through the LWCC. There is no practical means to measure the temperature of samples inside the LWCC but the effects, as observed in spectral features around 750 nm, were generally low. The magnitude of the effect was greatest for the longest cell (250 cm) due to strong amplification of temperature-induced signal changes along the path length. The comparison of the performance of the different setups was limited to wavelengths <720 nm to avoid bias due to temperature artifacts (Fig. 4).

When comparing the performance of the three different capillary cells, it became apparent that the signal-to-noise ratio (observed as fine scale structure in measured spectra) improved with path length (Fig. 5). The signal-to-noise ratio was influenced by the sensitivity of the system and the strength of the high-frequency pattern caused by the high refractive index of the saline sample, which often remains even after applying a salinity correction. Remaining features of this high-frequency pattern postsalinity correction presumably originated from differences in the refractive index of a high-concentration NaCl solution compared to natural seawater and can generally be fully removed during postprocessing by smoothing (not applied in this work).

B. Precision

Measurement precision and its dependence on the path length of a LWCC were assessed by looking at the standard deviation of triplicate measurements. Figure 6 shows histograms of the standard deviation determined at 440 nm for each of the LWCCs. The standard deviation determined for the 250 cm cell showed lowest spread in the data and overall highest precision [Fig. 6(c)]. Measurements with the 100 cm path length showed highest standard deviation and widest spread [Fig. 6(b)]. Absorption data measured with the 50 cm cell exhibited overall lower
standard deviation compared to the 100 cm LWCC [Fig. 6(a)], despite the shorter path length limiting its sensitivity. This was presumably due to the advantages of inflow measurements compared to stationary flow conditions. The comparison of measurements made with the 50 and 250 cm LWCCs, using the same approach of continuous manual sample pumping demonstrates how the increase in path length improves sensitivity, precision, and repeatability of LWCC absorption measurements.

The average spectral standard deviation showed the same pattern (Fig. 7) with regard to precision level, with lowest precision for measurements made in the nonpressurized 100 cm cell. Lowest standard deviations were achieved using the 250 cm LWCC, except at wavelengths greater than 720 nm, where elevated standard deviations were observed. Results also show that the precision is wavelength dependent, relatively flat from 450–700 nm but strongly increasing toward both edges of the spectrum, where light intensity levels drop toward the detection limit. No correlation between magnitude of the standard deviation and the absorption signal could be observed (data not shown). Measurements made with the 250 cm LWCC showed the most rapid decline of the precision at wavelengths >720 nm caused by high sensitivity to temperature changes, which is enhanced by the long path length. This confirms the necessity to constrain the comparison of NIR data to wavelengths <720 nm. In the blue/UV spectral region, average standard deviations increase exponentially for all three LWCCs. However, this systematic reduction in measurement precision is relatively small compared to the sample absorption at these wavelengths.

Fig. 6. Measurement precision of three LWCC systems with three different path lengths. (a) 50 cm; (b) 100 cm; (c) 250 cm. Measurements for (a) and (c) were recorded while sample was pumped through the cell, data shown in (b) were recorded under stationary conditions. Histograms show standard deviations derived from triplicates of absorption measured at 440 nm.

Fig. 7. Average spectral standard deviation of all samples collected, measured with three different path lengths. Measurements with the 50 and 250 cm path lengths were performed while the sample was in-flow, whereas measurements in the 100 cm capillary cell were recorded when no pressure was applied to the syringe.

Fig. 8. Comparison of absorption data measured with the 100 and 250 cm LWCC against measurements with the 50 cm path length, from 300–720 nm. Data measured with the 250 cm LWCC system were limited to absorption <1.1 m$^{-1}$ to avoid nonlinearity artifacts at UV wavelengths.
C. Accuracy-Instrument Comparison

Absorption data measured with the three different LWCCs were compared against each other to assess the consistency of the method. Results can provide a first indication of the accuracy of LWCC absorption coefficient measurements. Figures 8 and 9 show data obtained with the two longer path lengths plotted against data measured with the 50 cm path length LWCC, following a linear relationship with an $R^2$ of 0.9970 for the 100 cm and 0.9983 for the 250 cm path length (Table 1). Slopes derived from geometric mean linear regressions applied to the data were close to unity, 0.981 ± 0.0006 (100 cm) and 1.007 ± 0.0006 (250 cm). Regression offsets were insignificant, i.e., below the typically observed detection limit. Data were centered around the 1:1 line for both comparisons. Absorption data measured with the 100 cm cell showed slightly

![Graph](image1)

**Fig. 9.** Comparison of absorption measured with a (a) 100 cm and (b) 250 cm LWCC system against the 50 cm LWCC for wavelengths 300–720 nm on a log-log scale. Data measured with the 250 cm LWCC system were limited to absorption <1.1 m$^{-1}$ to avoid detector related artifacts at UV wavelengths.

<table>
<thead>
<tr>
<th></th>
<th>100 cm LWCC</th>
<th>250 cm LWCC</th>
</tr>
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<tbody>
<tr>
<td>No. of samples</td>
<td>59</td>
<td>44</td>
</tr>
<tr>
<td>Wavelength range</td>
<td>300–720 nm</td>
<td>variable–720 nm</td>
</tr>
<tr>
<td>Slope [nm$^{-1}$ m$^{-1}$]</td>
<td>0.981 ± 0.001</td>
<td>1.007 ± 0.001</td>
</tr>
<tr>
<td>Offset [m$^{-1}$]</td>
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<td>-0.0009 ± 0.0002</td>
</tr>
<tr>
<td>$R^2$ [-]</td>
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<td>0.9983</td>
</tr>
<tr>
<td>RMSE [m$^{-1}$]</td>
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<td>0.0040</td>
</tr>
<tr>
<td>RMS%E [%]</td>
<td>13.7%</td>
<td>11.2%</td>
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**Table 1.** Statistical Descriptors, Slope, Offset, $R^2$ (All Obtained from Geometric Mean Linear Regression), RMSE, and RMS%E, of Absorption Spectra Measured with the 100 cm LWCC and 250 cm LWCC against Measurements with the 50 cm LWCC

![Graph](image2)

**Fig. 10.** Wavelength dependency of (a) RMSE [Eq. (2)] and (b) RMS%E [Eq. (3)] derived from comparison of absorption measured with the 100 cm LWCC and 250 cm LWCC against the 50 cm LWCC.
wider spread with overall RMS%E of 14% compared to 11% for the comparison 250 cm versus 50 cm (Table 1). Data spread (i.e., deviation between measurements) increased toward the edges of the spectrum as deviation from 1:1 line (Figs. 8 and 9).

D. Spectral Analysis of Deviation

For a better understanding of the nature of the deviation and its wavelengths dependence, the RMSE and RMS%E were determined spectrally (Fig. 10). Both mean absolute (RMSE) and mean relative (RMS%E) deviations were found to be strongly wavelength dependent. RMS%E values ranged from a few percent in the UV to >100% at NIR wavelengths [Fig. 10(b)]. The RMSE derived for both the 100 and 250 cm LWCCs varied over 1 order of magnitude across the spectrum, with smallest values of 0.001 m⁻¹ at NIR wavelengths. Both 100 and 250 cm path lengths showed comparable agreement with the 50 cm cell with RMSE at 440 nm of about 0.004 m⁻¹ and RMS%E <5%, with the 250 cm LWCC showing closer agreement than the 100 cm for wavelengths <350 nm. Figure 10 demonstrates that the overall error is wavelength dependent and shows some variation between different LWCC systems. Unfortunately, it is not possible to provide a single, simple statistic to describe the error of this type of measurement, as there are a number of features contributing to the overall error (some possibly unknown) and do so in combinations of both absolute and fractional terms. As a result, the error in any individual measurement will vary depending on the optical setup, the strength of the absorption signal, and other factors such as the temperature and salinity of the sample. However, the data presented in Fig. 10 may be considered as a rough indicator of the magnitude of errors that might be anticipated for a data set collected in coastal waters with the magnitude of errors that might be anticipated for a data set presented in Fig. 10 may be considered as a rough indicator of the temperature and salinity of the sample. However, the data measurement will vary depending on the optical setup, the and fractional terms. As a result, the error in any individual setup. The precision was found to be wavelength dependent and strongly increasing toward the edges of the spectrum. This reflects the underlying wavelength dependency of (1) the lamp output, which is low at UV and blue wavelengths, and (2) sample absorption, which is particularly high in the UV/blue due to the absorption by CDOM and in the NIR due to strong absorption by water itself. Given the preponderance of \( a_{\text{CDOM}} \) (440 nm) values in the literature, it probably makes sense to provide 440 nm statistics as representative values, but this work emphasizes that the true uncertainty requires a more robust expression that is likely to be wavelength dependent.

At NIR wavelengths, the sensitivity of water absorption to changes in sample temperature has an additional adverse effect on the measurement precision in this spectral region. The effect is most dominant in spectra measured with the 250 cm LWCC, presumably because it takes longer for a sample to pass through the longer cell, allowing it to heat up more strongly. Monitoring or control of the sample temperature inside the cell is not feasible. Temperature effects, however, are fairly constant, and can be corrected manually during post-processing using absorption coefficients for the temperature dependence of water absorption [31,32], in an iterative approach to establish minimal residual spectral structure in the NIR.

Even after correcting measurements for salinity dependency, two systematic artifacts were observed in the spectra that were associated with increased refractive index of saline samples: (1) a high-frequency oscillation pattern and (2) negative offsets observed for the 50 and 100 cm LWCCs. Using the same high spectral resolution detector, high-frequency patterns are not observed in measurements of freshwater absorption (not shown) but always occurred for the samples measured for this work (salinities >32 psu). If necessary, spectra can be smoothed using a moving average to minimize this oscillation feature. No smoothing was done for the analysis in this work in order to minimize bias in the comparison due to data processing.

The observed negative offsets for the two shorter path length cells are relatively small, compared to typical offsets caused by light scattering due to the presence of (micro-)bubbles inside the cells when using vacuum-filtered samples rather than pressure-filtered [29]. These small negative offsets were only detectable after optimizing the measurement procedure, including significant reduction of scattering effects and improvement of measurement stability (by filtering the sample directly into the LWCC). Insufficient correction of salinity effects could be explained by limitations in the derivation of correction coefficients from a measurement of a weakly absorbing NaCl solution, especially with the shorter path lengths. Another potential source of error is the use of NaCl solutions instead of artificial seawater [32], which might not be a sufficient representative of seawater absorption and refractive index. An offset correction was applied to the data, forcing spectra through zero at 700 nm. This correction is based on the assumption that the error originating from insufficient salinity correction is constant with wavelength, which potentially
introduces a systematic error of unknown magnitude to the data. The assumption of zero NIR absorption for null corrections might not hold in all waters. PSICAM measurements that are not susceptible to scattering errors have shown that CDOM absorption at wavelengths >700 nm can be nonnegligible but is usually very low [22]. Therefore, if available, LWCC spectra can also be corrected to match PSICAM data at 700 nm. For the cross-comparison attempted in this study, the magnitude of a flat offset correction is consistent and provides a more meaningful result than would be the case otherwise. Mutual self-correction does not alter the results presented here.

Despite remaining issues regarding the correction of salinity effects, comparison of CDOM absorption data (350–750 nm) obtained with the 100 cm cell with corresponding PSICAM data showed an RMSE of 0.0078 m$^{-1}$ at 440 nm and an overall RMS% of $\sim$15% (data not shown). A total of 58 CDOM absorption spectra were available from both instruments, covering a range of absorption at 440 nm from 0.011 m$^{-1}$ to 0.157 m$^{-1}$. This level of consistency between two independent data sets is a very encouraging endorsement of the performance of the LWCC approach.

The 50 and 250 cm LWCCs were part of the same setup using identical light source, detector, and flow conditions during measurements. The comparison of measurements made with these two capillaries allows an assessment of the effects of different path lengths on the measurement. Due to the five times longer path length and the higher transmission of the new LWCC-3000 series cell, the spectra measured with the 250 cm LWCC are less noisy. However, the combination of low lamp output, sensor sensitivity, and high CDOM absorption results in very low light levels close to the detection limit being transmitted through the cell in the UV/blue. This effect can be observed as underestimation of absorption in the longer path length cell. Due to these limitations in the optical setup, the LWCC path length used has to be carefully adapted to the wavelength range of interest and the level of the absorption coefficient of the sample.

The comparison of 50 cm and the 100 cm LWCC setups provides information on the combined effects of different detectors, different flow conditions, and the overall consistency of the method. As increasing the pressure on the sample inside the cell can result in relatively large negative offsets in measured absorption, it is extremely important to record all sample and reference spectra under the same pressure conditions. Continuously pressurizing the system, i.e., recording measurements of sample inflow, was found to increase measurement repeatability significantly, and continuous pumping is highly recommended for high-precision absorption determinations. Integrating a peristaltic pump in the setup to inject a sample with a constant pressure is likely to further improve the measurement stability. Future work is required to assess the benefits of automated sample pumping on the precision of LWCC-based determinations of the absorption coefficient of CDOM.

When the light intensity is generally low, the detector’s internal stray light and nonlinearity can cause artifacts and lead to a strong underestimation of the absorption coefficient. Analysis of raw intensity spectra showed that the Avantes UV/VIS sensor (used for the 50 and 250 cm system) measured a signal of 20–50 counts at wavelengths outside the lamp’s emission spectrum, i.e., <180 nm (data not shown). This signal is presumably caused by stray light inside the spectrometer. Tests of a simple stray light correction approach, subtracting the detected signal at 180 nm as a flat offset across the spectrum showed a rather good compensation of the underestimation in measurements with the 250 cm cell. Application of the same correction to data measured with the 50 cm cell showed a smaller effect due to generally higher intensity signals in the shorter cell. The effect of a (constant) stray light correction depends on the path length, intensity level, and CDOM concentration, and further work is required to develop a suitably robust stray light correction, for example, following the suggestion presented in Refs. [35] and [36]. The impact of a simple, constant offset stray light correction was fairly small in the visible spectrum. A revised comparison after stray light correction (both 50 and 250 cm LWCCs), including all data from 300–720 nm, showed comparable agreement (Table 1), with an RMS% of 10.5%, RMSE of 0.0042 m$^{-1}$, and a slight trend for the 250 cm to overestimate 50 cm LWCC absorption: 1.021 ± 0.001 (slope), −0.00148 ± 0.0002 (offset), with an $R^2$ of 0.999. The VIS/NIR detector used with the 100 cm LWCC system did not have any pixels that could be considered outside the lamp’s emission spectrum and, hence, no stray light correction was attempted for this setup.

The assessment of measurement performance of waveguide systems presented here does not cover a comparison of the different cell types, LWCC versus UltraPath. Previously published studies developing and analyzing the UltraPath methodology [18,34,37] suggest that determination of CDOM spectra with UltraPath systems can be expected to show a comparable level of performance with the advantages and disadvantages discussed above.

5. CONCLUSIONS

The comparison of three different LWCCs with three different path lengths enabled the assessment of measurement uncertainties and data consistency. Results showed good agreement of determined spectral CDOM absorption coefficient data with RMS% within 5% at 440 nm. The cross-comparison also revealed that it is difficult to come up with meaningful single value statistics to describe the performance of these measurements. Precision and accuracy are both wavelength dependent, reflecting underlying wavelength dependencies in lamp output, sensor sensitivity, internal detector stray light, and CDOM absorption characteristics. At the same time, they depend on the path length used. Salinity correction for absorption measurements inside a LWCC, derived from a single highly concentrated NaCl solution appeared to have some limitations, and further work is required to minimize remaining systematic measurement errors. Not pressurizing the sample inside the cells introduces additional uncertainty to observations compared to constant pressurization, i.e., in-flow conditions. Artifacts associated with temperature dependence of seawater absorption are significant beyond 720 nm and are not easily controlled or corrected directly but can be addressed in post-processing to some extent. Finally, the requirement for null correction in the NIR is probably a real limitation that is currently
only directly addressed by making alternative measurements, e.g., PSICAM. This, however, is only important for applications where CDOM absorption rather than total absorption (absorption by water itself is dominating) needs to be known with high accuracy at these wavelengths.

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