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## Yellow Matters

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## 11. Synthesis

### 11.1 Summary and conclusions

The amount and type of dissolved organic matter (DOM) that is present in natural waters is regarded as an important measure of physico-chemical water quality. This DOM has been identified as a source of organic pollution, as an energy source for microbe-based aquatic food webs, as a factor in the cycling of trace elements and also as a factor in the biological activity of phytoplankton and bacteria. Because of its large organic complexes DOM usually acts as a buffer, thereby regulating the phyto- and zooplankton ecosystem and immobilising xenobiotic compounds such as heavy metals (Kramer, Jak, Stroomberg, Hooftman, and Mayer 2002). By binding contaminants, their bioavailability is reduced. At the same time, the oceanic DOM pool is identified as a major reservoir of organic carbon for the global carbon cycle.

As DOM cannot be measured directly, the determination of the dissolved organic carbon (DOC) concentration is therefore included in many Dutch and international water monitoring programmes (Anonymus 2000). DOC measurements involve point sampling and laboratory analysis. The coloured fraction of DOM, called Coloured Dissolved Organic Matter (CDOM), is proposed as an alternative proxy for DOM. It has been postulated that CDOM may be accurately determined from remotely sensed data. In that case it would be more cost-effective than traditional in-situ methods in most cases and the remote sensing method would, in addition, provide a wealth of spatial and temporal information.

Amongst others, spatial CDOM maps may provide an insight in the extension of river water plumes in coastal waters and the spatial effects on water- and ecosystem quality. Because of the high absorption in the UV CDOM can act as a protecting agent for the ecosystem in shallow waters

The goal of this research, as stated in chapter 1, is to improve the accuracy of the concentration of coloured dissolved organic matter retrieved from remote sensing spectra in shallow eutrophic inland waters. This is pursued in three complementary ways: by deriving a more accurate CDOM algorithm using new techniques in optical modelling, by using a Point-Source Integrating-Cavity Absorption Meter (PSICAM) device for more accurate CDOM absorption measurements in the laboratory and by decomposing CDOM into its major groups of humic and fulvic acids and modelling the measured absorption spectra separately. In addition the prerequisites for accurate CDOM concentration detection using remote sensing are determined.

#### 11.1.1 Part A: Background on Coloured Dissolved Organic Matter

Before starting with optical modelling of remotely sensed data, I first performed a literature study on the chemical and ecological background of CDOM (chapter 2). This was necessary to understand the optical properties of CDOM (that are determined by the molecular structures of CDOM) and relationships with other water quality parameters and the abundance of CDOM and variation therein that are determined by the formation and degradation processes. From the available literature I found that CDOM has spectral characteristics in the visible wavelength region that are significantly different than the spectral characteristics of chlorophyll and suspended matter. In theory it should therefore be possible to retrieve CDOM concentrations from remote sensing. Next to this, I learned that CDOM comprises roughly of two very broad groups of molecules: humic and fulvic

acids (HA and FA for short). Although the naming of these groups can cause confusion because of the weak and aged definitions of HA and FA, I chose to stick to them to make my work more compatible with other publications on this subject. Because HA and FA have different absorption spectrum slopes I suspected that by modelling HA and FA separately, the accuracy of CDOM retrieval as a whole would increase. Another possible advantage of modelling HA and FA separately arising from the literature study was that the ratio between HA and FA present in a water body could provide valuable information to water managers about the origin of the organic matter of that water body, as HA are mostly of terrestrious or allochthonous origin while FA are mostly produced locally by the algae (autochthonous).

A small case study at the end of chapter 2 that I performed on CDOM data collected in the Vecht Wetlands research area during this study showed that CDOM concentrations and slope parameters varied during the summer season. Although insufficient data was available to allow solid conclusions, I found that the CDOM appears to be consumed by blooming algae populations in spring and autumn, and is released in early summer.

### 11.1.2 Part B: Optical modelling theory

After establishing that CDOM is indeed distinguishable from remote sensing data, I had to select a suitable optical modelling approach from literature (chapter 3). Because of optical interference with ever present chlorophyll and suspended matter in Dutch inland waters, (semi-)empirical models would not suffice. Neural networks do not operate transparently so the insight in the relationships between the optically active parameters which I was looking for could not be gained this way. True analytical models were not feasible for my research because no operational model code was available at that time. Moreover, these models require extensive input data which could not be gathered during this study. By elimination I chose to use semi-analytical models, which are physically based but simplified, and have proven their worth in many other water remote sensing studies.

The next step was to select which simplifications, or which semi-analytical model, should be used (chapter 4). Considering the parameters that could be determined within this research, a further simplification of the optical model was needed as provided by the Gordon-Walker (GW) semi-analytical model (Gordon, Brown, and Jacobs 1975). This GW-model is known for its good performance in general; it has the least assumptions, its parameters could be obtained within this research and it can easily be linearised for inverse modelling. At the end of this chapter I selected two commonly used state-of-art inversion techniques: Matrix Inversion Methods (MIM) and Levenberg-Marquardt optimisation (LM). The reason for also selecting a non-linear method like LM is that it is less sensitive to small spectral errors, which are often present in the measured spectra.

At this stage, I knew exactly what model I would be using, so it was time to consider the exact parameterisation before running the model. The GW-model requires Inherent Optical Properties (IOP), concentrations and Apparent Optical Properties (AOP). The IOPs I selected are discussed in chapter 5:

1. The absorption and scattering of pure water
2. The absorption and (normalized) concentration of Coloured Dissolved Organic Matter, the only optically active dissolved constituent
3. The absorption and concentration of tripton
4. The scattering and concentration of seston
5. The absorption and concentration of phytoplankton pigments

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These SIOPs both fulfil the requirements of the GW-model and could be measured within the framework of my research.

Besides the SIOPs I also needed matching AOP measurements during my field works. AOPs can be measured in a variety of ways (chapter 6), but because of the encouraging results reported individually by Gons (Gons 1999; Gons, Rijkeboer, and Ruddick 2002), and Rijkeboer (Rijkeboer, Dekker, and Hoogenboom 1998; Rijkeboer 2000) and the availability of the necessary instrument, I chose to use the Gons method (Gons 1999) for above water subsurface irradiance reflectance measurements. Here too a number of choices were made for its parameterisation, concerning for instance the  $Q$ -factor, the  $\rho_{sky}$  and the nadir and azimuthal angles for measurement. Consequences of these choices were analysed and discussed; it should however be noted that the scatter to backscatter ratio  $B$  was optimised for each sample station prior to inversion, largely neutralising the effects of errors in  $Q$  and  $\rho_{sky}$ .

In chapter 7 the model and its parametrisation were selected and I performed a sensitivity analysis to check whether the model was robust enough to cope with small errors in the AOP and SIOP inputs that are commonly present in measured data. I selected the following types of potential errors to be examined:

1. Errors in scaling factors (introduced by e.g.  $Q$ ,  $g$ ,  $\bar{\mu}_d$  and  $\bar{\mu}_u$ )
2. Offset errors in the spectrum (introduced by e.g.  $L_{sky}$ )
3. Spectral errors that increase towards the blue wavelength region (introduced by e.g.  $\rho_{sky}$ )
4. Spectral errors caused by not knowing the exact spectral shape of some parameters (including the  $a_{ph}^*$  and  $a_{tr}^*$ )
5. Errors in the reference SIOP set

The sensitivity analysis was performed using a simulated dataset. Simulated TCHL, TSM and CDOM concentrations (based on the distribution characteristics found in my measured data) and the measured median SIOP dataset of this research were used to generate a total of 1,000 subsurface irradiance reflectance spectra (based on the GW-model).

When no error is implemented, all three inversion methods are capable of (near) perfect retrieval of TCHL, TSM and CDOM concentrations for both MIM and LM, indicating that the parameterisation of the GW-model was correct for my research. When all spectral errors are combined, the  $R^2$  values between the modelled and simulated concentrations generally decrease, especially for CDOM (from 0.99 to 0.75), but this performance is still acceptable. The LM method, unsurprisingly, scored slightly better agreements than MIM in this case. I further found that the GW-model was most sensitive to errors in the SIOP reference set used. This finding backed my initial goal of improving CDOM retrieval by improving CDOM reference measurements.

### 11.1.3 Part C: Improving CDOM retrieval accuracy analyses

After having determined the performance of the GW-model and its parameterisation I could start running the model fed with actually measured data testing the first proposed CDOM retrieval accuracy improvement by using state-of-art algorithms (chapter 8). My measured data however needed to be quality controlled first, as only sample stations of sufficient quality can be accurately inverted. The quality control procedure, always performed but often omitted in publications, consisted in this research of four checks: comparison with literature

values, comparison of optimised  $B$  values, comparison of normalized  $\chi^2$  differences between measured and forward modelled  $R(0-)$  spectra and the occurrence of masking TCHL concentrations. Only sample stations that passed all checks were selected for inversion (24 out of 52 stations for my research, an average score I have learned through personal communications).

Two rounds of inversions were carried out. In the first round the per-sample SIOP sets were used as references, in the second round a constructed median SIOP was used for all stations. As a consequence of using the median SIOP set, the accuracy of TSM retrieval decreased significantly (0.9 to 0.5), as scaling problems due to errors in measured spectra are not fully compensated for. The accuracies for TCHL and CDOM decreased only slightly (10%). The LM method yielded slightly better results. For Dutch inland waters the use of a single median SIOP set has apparently only a dramatic effect on the TSM retrieval accuracy. As this study focuses on CDOM it was decided to use the median SIOP set, determining the CDOM retrieval potential in the least favourable condition, as perfectly matching SIOPs are generally not available for inversion, leaving at best regional or water type based lumped SIOP sets.

The second proposed CDOM retrieval accuracy improvement involved the use of better CDOM reference measurements. This was tested by me in chapter 9 by using a Point-Source Integrating-Cavity Absorption Meter (PSICAM), which has 2 important advantages over using a standard spectrometer with a cuvette:

1. There is no loss of light due to scattering effects in the PSICAM, so it measures the true absorption.
2. The average path length of the PSICAM is much higher (in the case of this research about 3 m) than in a standard 10 cm cuvette, allowing for accurate measurements of very low concentrations.

Before the PSICAM available for this research could be used, I developed a successful calibration method through the use of three independent dilution series of Aldrich humic acid standard in the absorption range around  $1 \text{ m}^{-1}$ . The absorption spectra of the dilution series were measured in a bench spectrometer with a 10 cm cuvette, and because there were three independent series, the calculation of an accurate concentration-absorption relation was possible. With this concentration-absorption relation reference absorptions needed for the PSICAM calibration could be derived. This sound approach, which is common in chemistry, has not been applied at other published PSICAM calibrations to date. The best cavity reflectivity of the PSICAM, which best approached the concentration-absorption relation, was obtained by applying the transmittance ratio calibration method. After calibration, I found that the absorption measurements of the dilution series made with the PSICAM and a bench spectrometer are within 1% of each other (over the absorption range  $0.1 - 2 \text{ m}^{-1}$ )

The calibration experiment brought to light one limitation of the PSICAM: The accuracy of absorption measurements with the PSICAM rapidly declines when the absorption coefficient of the sample exceeds  $3 \text{ m}^{-1}$ , due to the size of the cavity and the cavity reflectivity. As Kirk (Kirk 1995) already suggested, different cavities dependent on the absorption range of the water type of interest can be used. Another possibility is the dilution of samples prior to measurement in the PSICAM, which was applied in this research.

In a subsequent PSICAM case study I showed that absorption measurements in a cuvette are likely to be affected with scattering effects when a  $0.7 \mu\text{m}$  filter is used, as CDOM absorption coefficients at 440 nm values between the PSICAM and cuvette differ significantly. After filtration over a  $0.2 \mu\text{m}$  filter there is no

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significant difference in  $C_{CDOM}$  between both methods. The difference of PSICAM absorption values between the two filtration steps is also significant. Therefore, the fraction between 0.7 and 0.2  $\mu\text{m}$  does significantly contribute to the absorption and scattering of a sample and should not be discarded in my opinion. This finding is in contrast with the SEAWiFS and MERIS sampling protocols and the general opinion in the water remote sensing community.

My final conclusion is that the theoretical advantages of a PSICAM over a bench spectrometer (absorption measurement not affected by scattering and capable of measuring lower concentrations due to a longer path length) is supported by actual measurements performed in this study. By using a PSICAM more accurate CDOM absorption spectra can thus be measured, improving the SIOP that are required for optical modelling.

When validating retrieved CDOM concentrations after inversions of the optical model with PSICAM reference absorption measurements in this research rather than cuvette references, the structural underestimation of CDOM was reduced by 10 – 15%, while the correlations increased by 10 – 20 %. This is a significant finding indicating that PSICAM CDOM absorptions are more accurate than cuvette CDOM absorptions.

The last of the three proposed CDOM retrieval accuracy improvements is discussed in chapter 10: the decomposition of CDOM into HA and FA. First I selected the most appropriate exponential HA and FA fit model, based on the CDOM fit models of Carder *et al.* (Carder, Steward, Harvey, and Ortner 1989) and Stedmon *et al.* (Stedmon, Markager, and Kaas 2000):

$$a_{CDOM}(\lambda) = \text{Offset} + a_{HA} \exp^{(S_{HA}(\lambda_0 - \lambda))} + a_{FA} \exp^{(S_{FA}(\lambda_0 - \lambda))} \quad 11.1$$

Next, two CDOM decomposition methods were tested in this research: linear and non-linear regression techniques. Linear regression requires the use of fixed slope parameters, called end-members. The end-members should be chosen with great care as spectral characteristics of humic and fulvic acids may vary in time and space. A number of suitable end-member pairs were proposed. Non-linear regression techniques allow the slope parameters to be modelled as well, but a unique solution was not be reached with this type of modelling and it was further discarded

A CDOM decomposition case study showed that the CDOM absorption spectrum modelling *Offset* parameter is significantly reduced (by 50%). It was also found that by using a linear two-component exponential model and well-chosen end-members the goodness of fit between the measured and modelled CDOM absorption spectrum does improve, on average with some 7% over the wavelength range between 400 and 700 nm. This provides evidence that the two-component CDOM absorption model is valid.

An inversion of the optical model was performed in this research using the normalised CDOM absorption spectrum in the SIOP set modelled with the two-component model. The same 24 selected and quality controlled sample locations as in chapter 8 and the same median SIOP set, with the exception of the normalised CDOM absorption spectrum that was remodelled using the two-component approach were used. The observed differences in correlation coefficients were very small, but the slope parameter may improve by some 10% using LM methods. Due to the outlier stations and the very small changes it could, however, not be established whether the two-component model leads to CDOM retrieval accuracy improvements. An additional study, including a larger dataset, is advised to establish the effect of two-component CDOM modelling.