Long term observations of CDOM absorption in the Baltic Sea. From discrete samples to remote sensing.

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CDOM – why bother?

More than 40 years has passed since Kalle has published a paper on CDOM optical properties

Kalle, K., 1966. The problem of the Gelbstoff in the sea. Oceanography and Marine Biolology Annual Review 4, 91–104.

CDOM is the part of DOM. The DOM cycling in the oceanic and marine waters should be studied for following reasons:

• DOM – the larges carbon pool in the ocean is unexploited and the knowledge on its cycling, sources and sinks and processes of its formation and degradation and their rates is still limited.

• Remineralization of DOM leads to formation of additional CO2 flux, which is enriches the oceanic waters and through air sea interactions is released to the atmosphere. This flux is adequately recognized and accounted in global carbon cycles and climate change models.

• Biotic and a-biotic remineralization of DOM leads to additional fluxes of inorganic nutrients in the coastal ocean, that could be utilized by phytoplankton communities and contribute to eutrophication of coastal areas and depletion of water quality.

Coloured (Chromophoric) Dissolved Organic Matter – CDOM – is a natural mixture of soluble in water organic compounds that absorbs light in the UV-VIS and thus affects both the availability and spectral quality of light.

Ocean colour remote sensing:

- error in Chl *a* estimates

- retrieval algorithms for DOM concentration

Optical properties:

- absorption, fluorescence and their spatial and temporal variability,

- specific absorption and fluorescence quantum yield

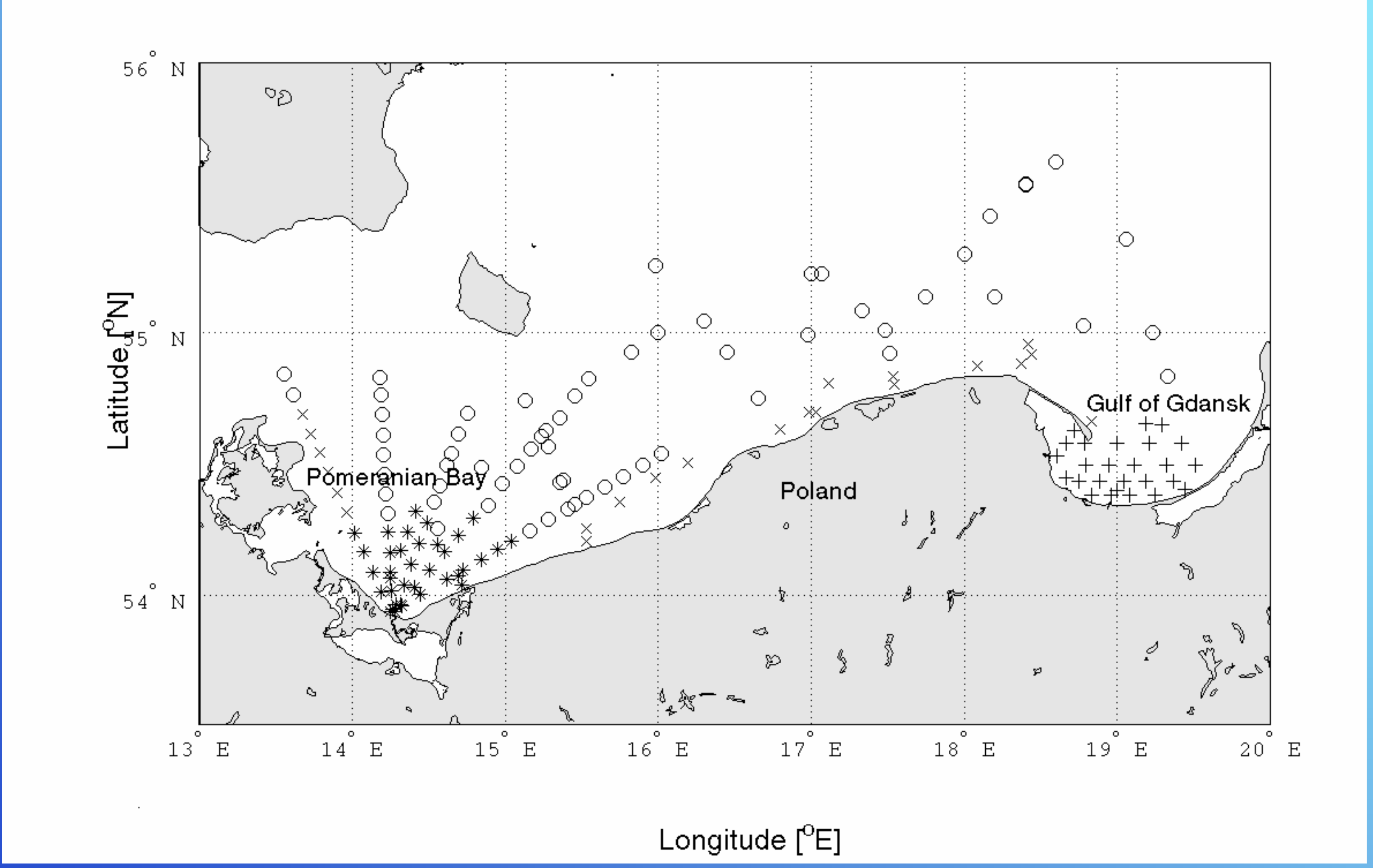
- qualitative and quantitative changes in CDOM composition

Bio-geochemistry of organic matter:

- CDOM is a substrate in photochemical reactions

- production of DON, DOP, LMW-DOM, O2, CO, SO

The study area



+ Gulf of Gdansk, * Pomeranian Bay, ° open Sea, ˣ coastal zone

Empirical data

During 16 years: in 1993 – 2009, that has been collected 2589 samples in the Baltic Sea for measurement of CDOM absorption spectrum

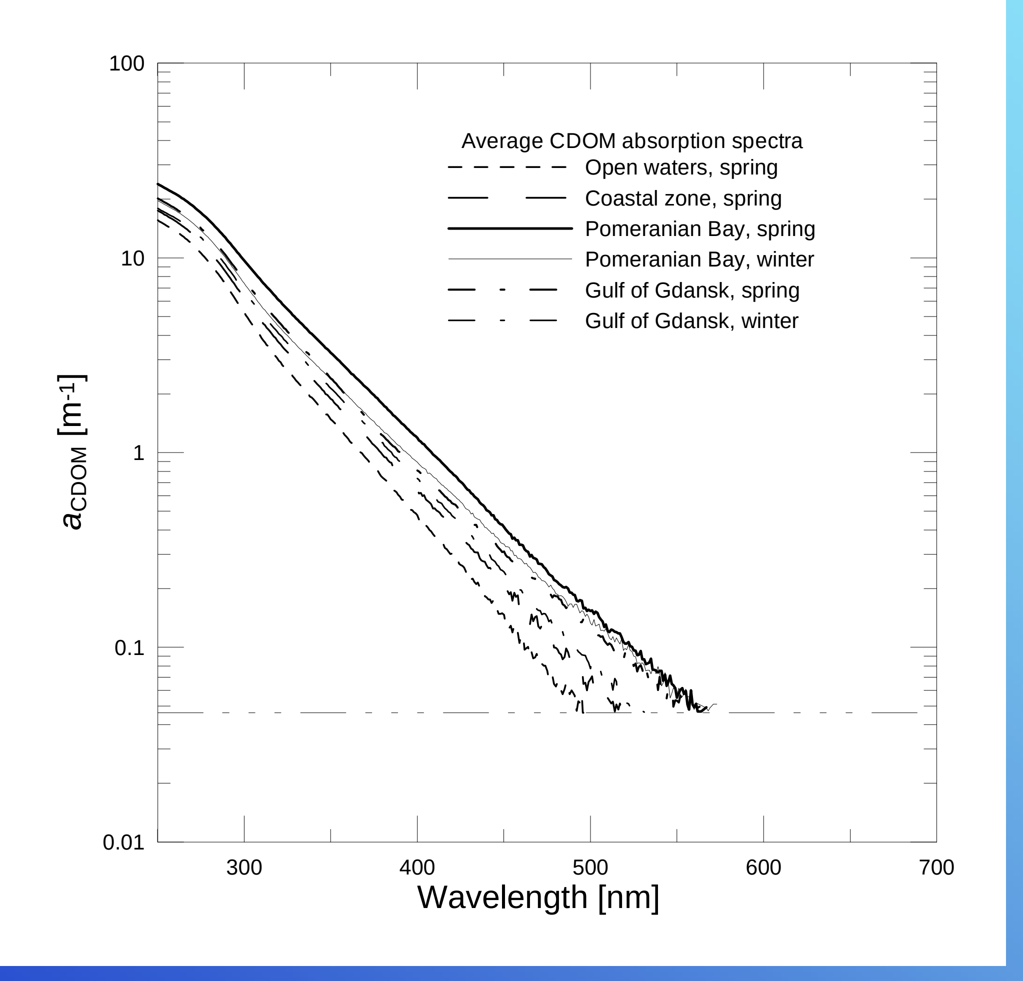
- 626 – spectrophotometer Perkin – Elmer in 1993 – 1996
- 192 – spectrophotometer Spekord in 1996 – 1997
- 1771 – spectrophotometer UNICAM in 1997 – 2009

The CDOM absorption coefficient $a_{\mathrm{CDOM}}(\lambda)$ and CDOM absorption slope coefficient S were estimated according to equation:

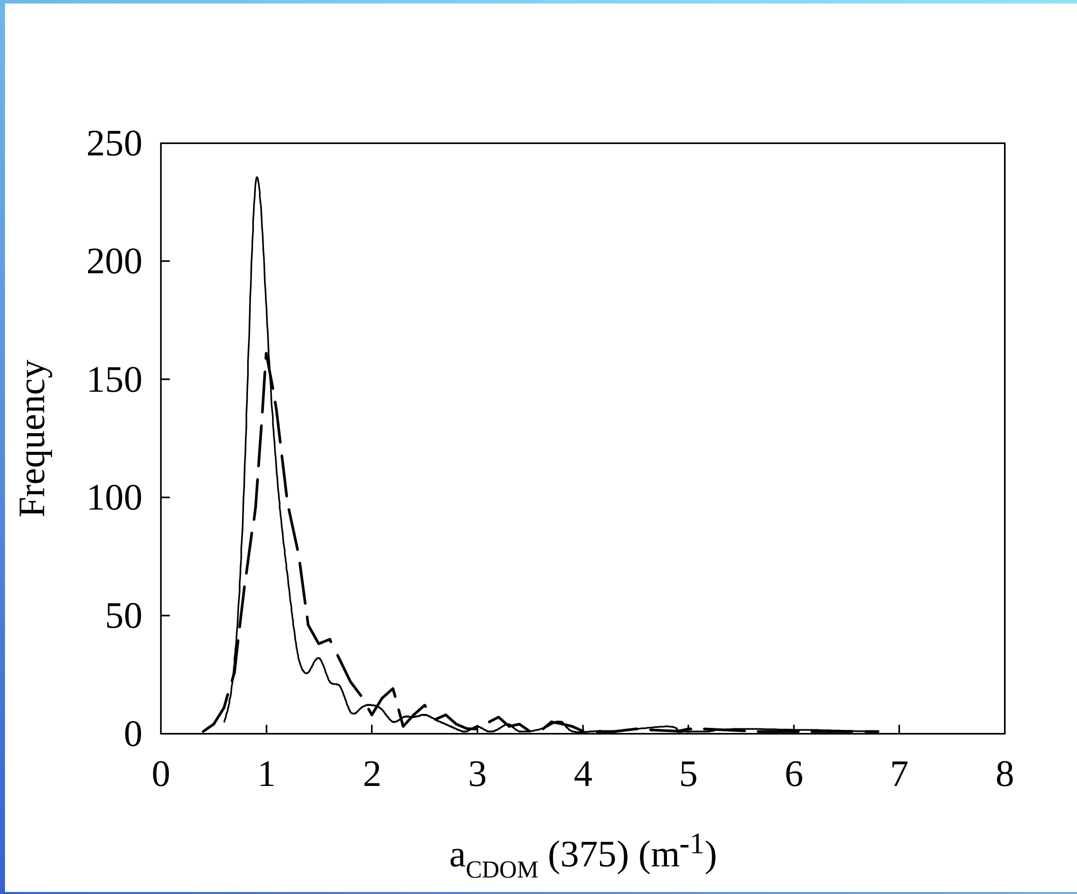
$$a_{CDOM}(\lambda) = a_{CDOM}(\lambda_0)e^{-S(\lambda_0-\lambda)} + K$$

The CDOM absorption spectrum slope coefficient was calculated using linear regression for log-transformed absorption and with use of non-linear fitting in two spectral regions 350÷550 nm i 300-650 nm.

Examples of measured CDOM absorption spectra

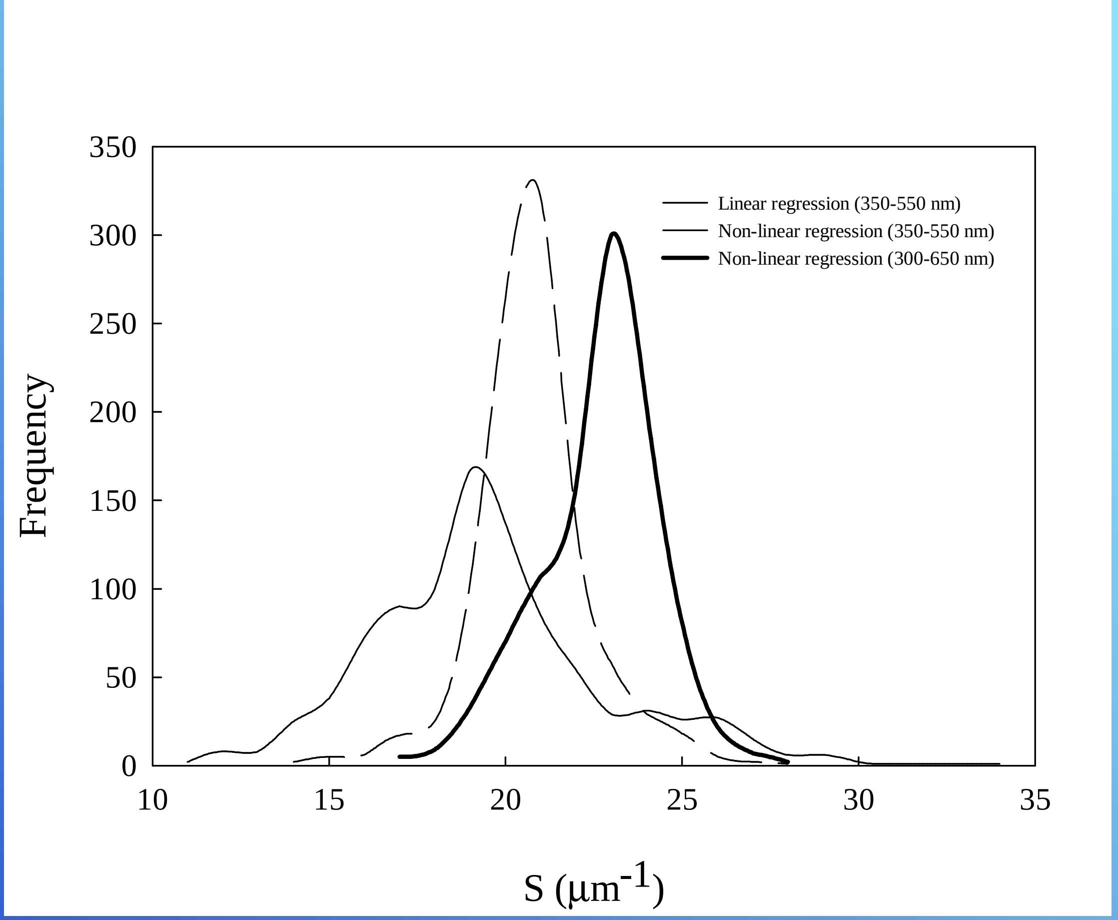


Statistical distribution of a_{CDOM}(375) values



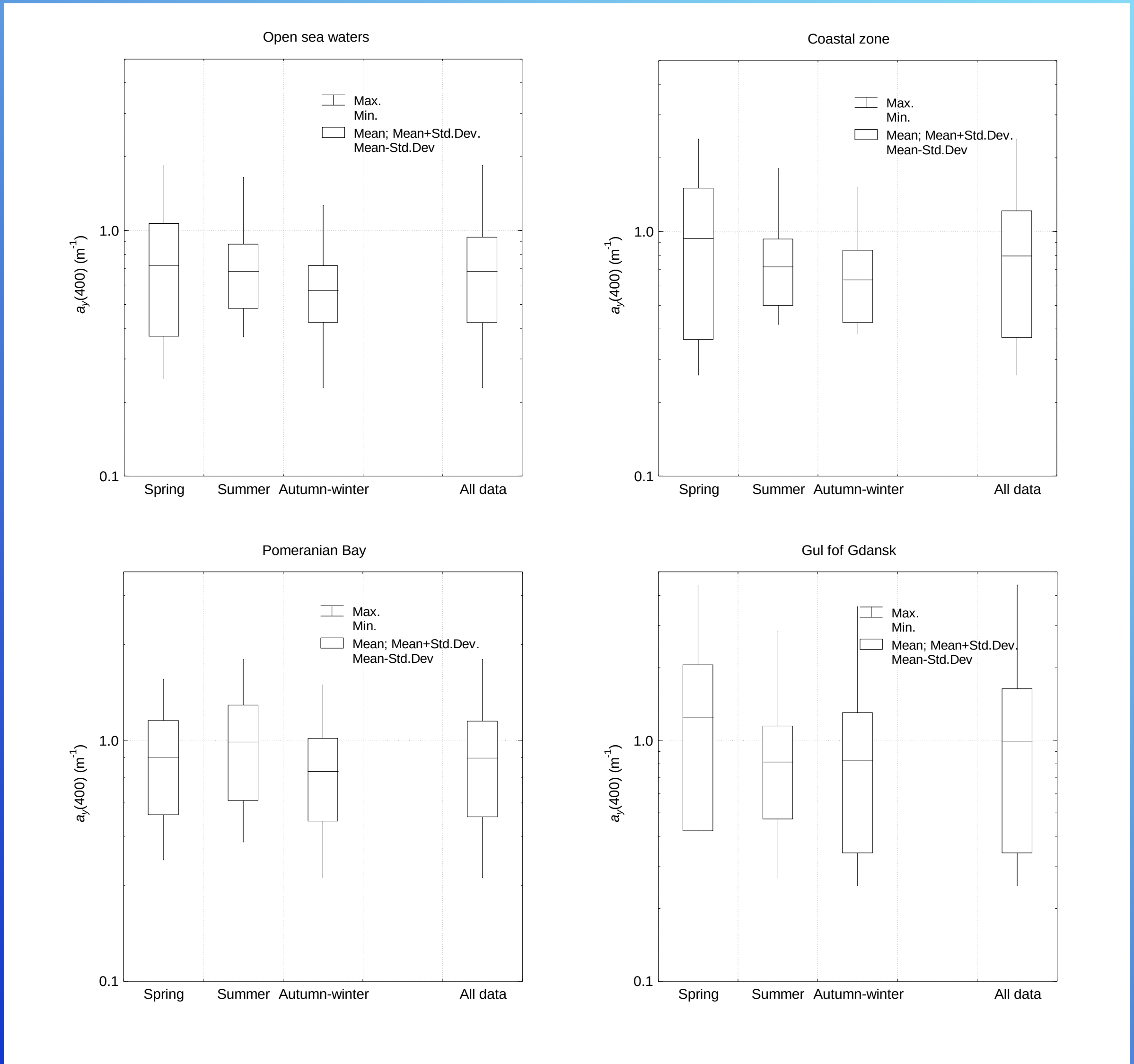
Distribution of a_{CDOM}(375) values calculated using two different baseline correction approaches; inclusion of constant “K” in a non-linear regression procedure (solid line) and subtraction of average absorption value between 650-700nm (dashed line).

Statistical distribution of the slope coefficient S



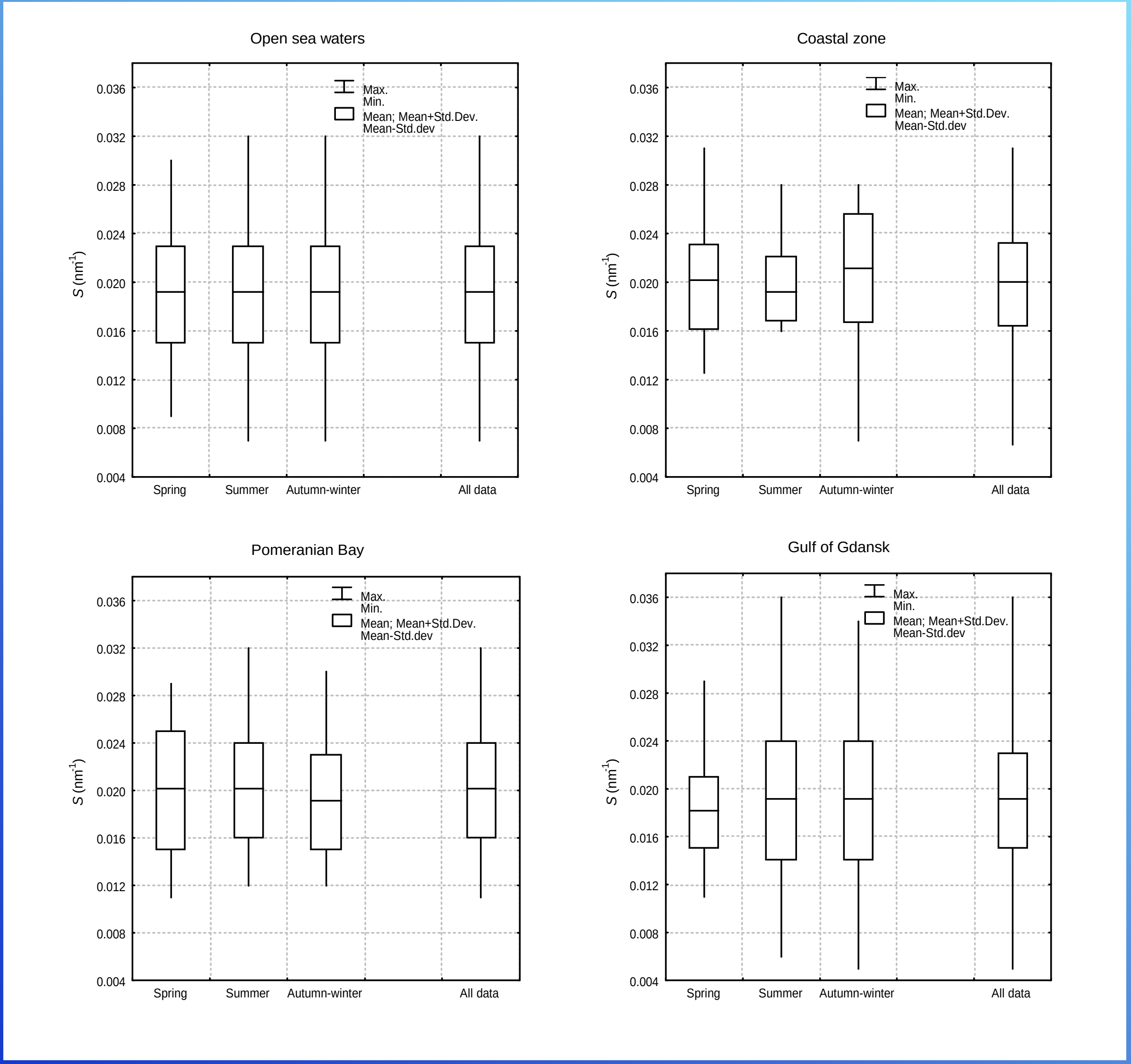
Distribution of *S* estimates from the three different approaches applied: linear regression in the spectral range 350-550 nm (thin solid line), non-linear regression, spectral range 350 – 550 nm (dashed line), non-linear regression in spectral range 300 – 650 nm (thick solid line).

Seasonal variability of $a_{CDOM}(400)$ values



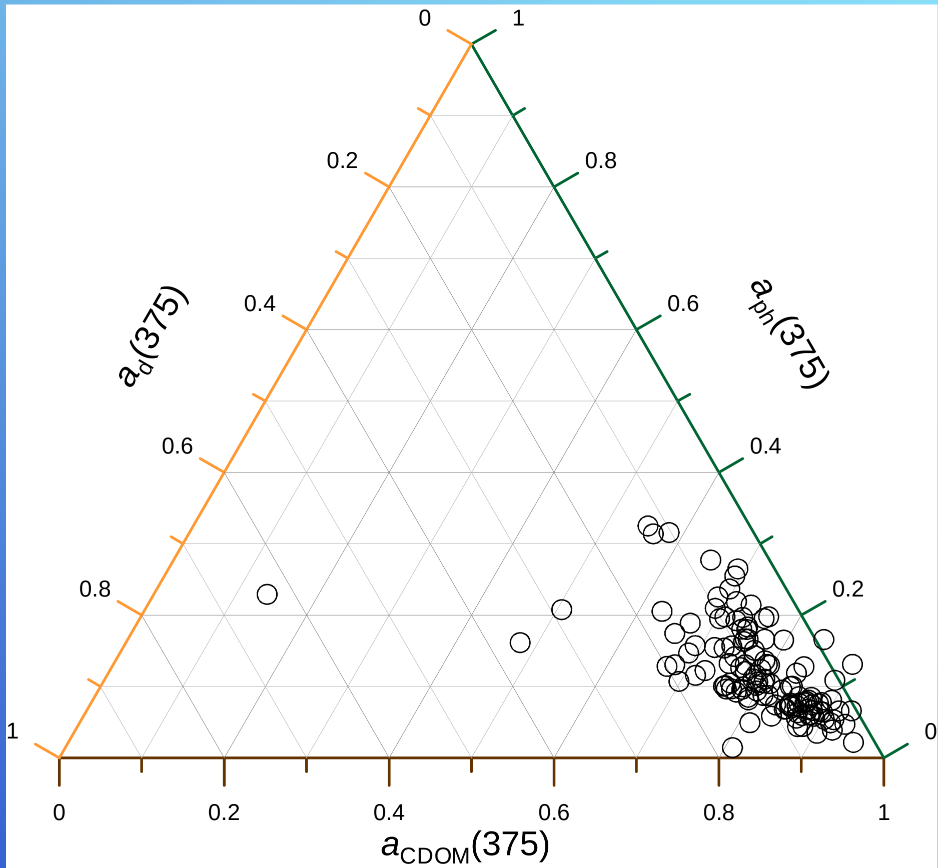
Seasonal changes of the statistical distribution of the value of CDOM absorption coefficient in open sea waters, costal zone, Pomeranian Bay and the Gulf of Gdansk.

Seasonal variability of *S* values



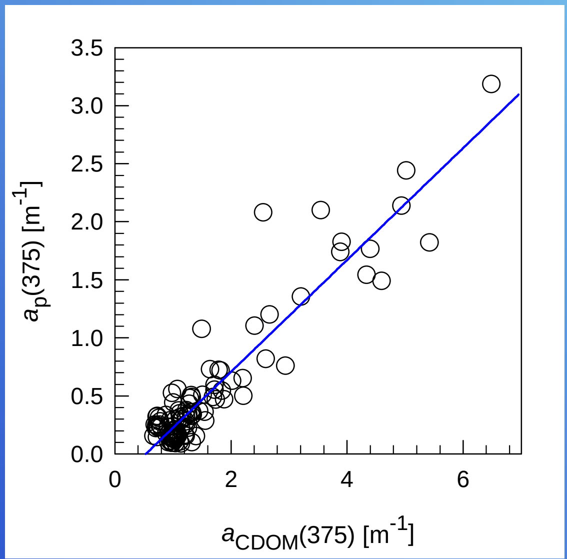
Seasonal changes of the statistical distribution of the value of CDOM absorption spectrum slope coefficient *S* in open sea waters, costal zone, Pomeranian Bay and the Gulf of Gdansk

Absorption budget in the Baltic Sea

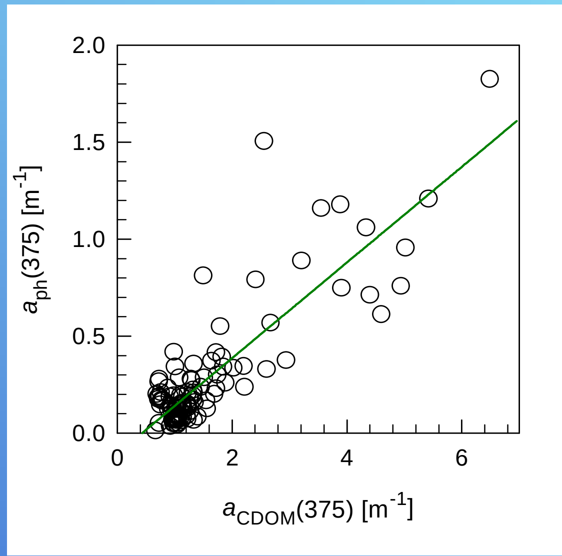


In 95% of cases the relative contribution of CDOM absorption in total absorption exceeds 80%.

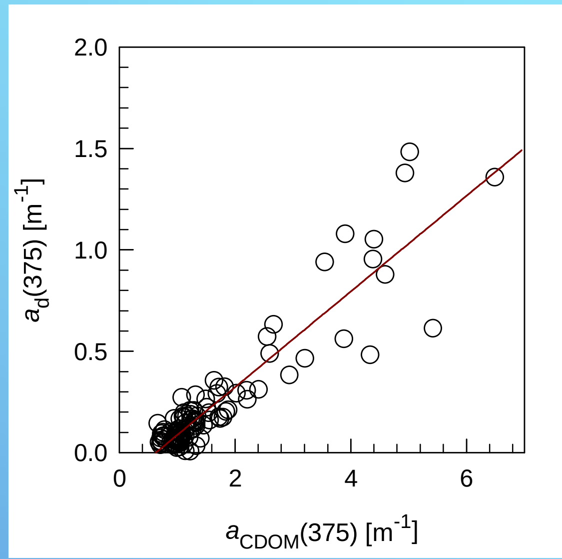
Covariance of main absorption components in the Baltic Sea



$a_p(375) = 0.482*a_{CDOM}(375) - 0.257$;
$R^2 = 0.87$;



$a_{ph}(375) = 0.247*a_{CDOM}(375) - 0.107$;
$R^2 = 0.73$;



$a_d(375) = 0.236*a_{CDOM}(375) - 0.149$;
$R^2 = 0.85$;

Absorption of light by CDOM, phytoplankton pigments and detrital particles are closely correlated suggesting a common forcing mechanism that drives variability of those components.

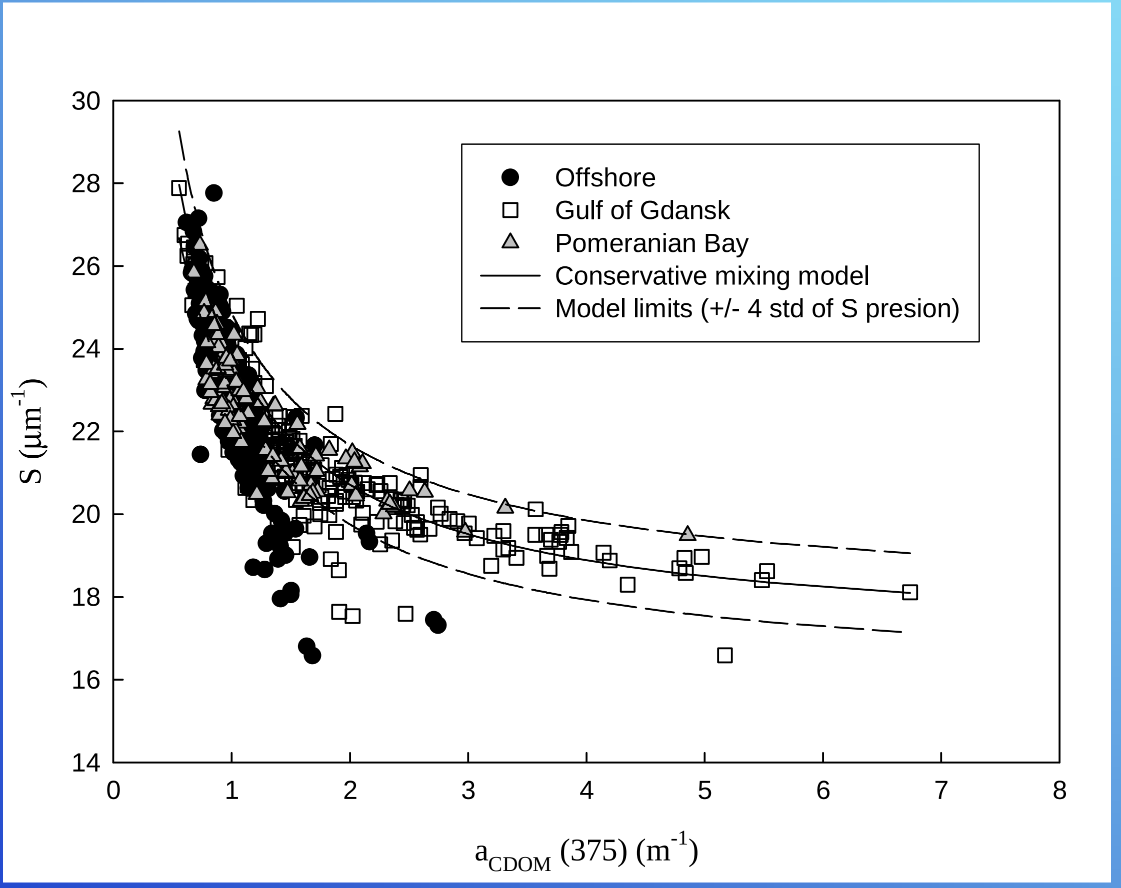
Modelling CDOM absorption from season, salinity and chlorophyll.

The effective optical properties of CDOM are shaped in a great extend by mixing of two water masses with distinctly different properties in conservative mixing (Stedmon and Markager, 2003).

$$a^{\Sigma}_{(\lambda)} = F^{\alpha} a^{\alpha}_{(\lambda)} + F^{\beta} a^{\beta}_{(\lambda)} = F^{\alpha} a^{\alpha}_{(\lambda_0)} \exp(S^{\alpha}(\lambda_0 - \lambda)) + F^{\beta} a^{\beta}_{\lambda_0} \exp(S^{\beta}(\lambda_0 - \lambda))$$

Input data: $a_{\mathrm{CDOM}}(375)$ in range of 0.3 do do 8 m^{-1}, slope coefficient S in range of 0.016 do 0.030 nm^{-1}, salinity from 1 to 12 , chlorophyll *a* concentration from 0.1 to 80 mgm^{-3}

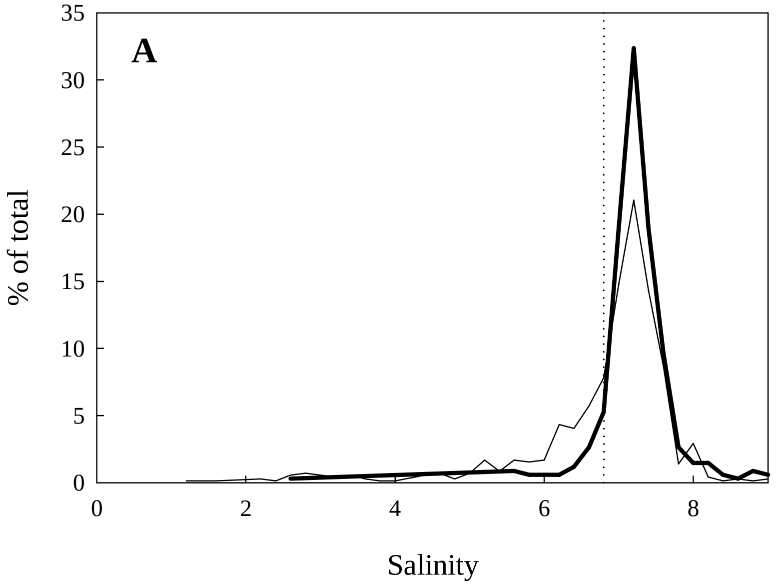
Relationship between $a_{CDOM}(375)$ and S



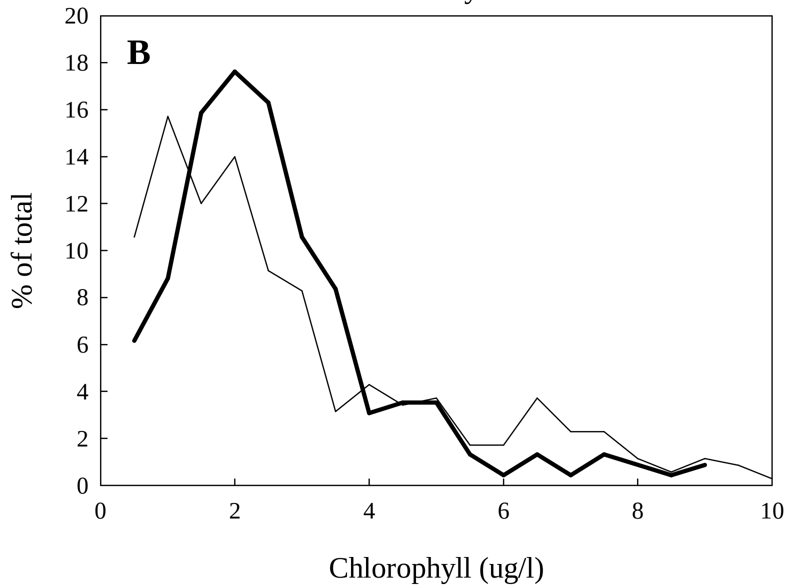
$$S = 16.8701 + \frac{40.4508 * 0.21}{0.21 + a_{CDOM}(375)}$$

Co-variation of $a_{CDOM}(375)$ and S in the dataset, indexed by sampling region. Superimposed is the modelled behaviour of $a_{CDOM}(375)$ and S under conservative mixing of the freshwater and off-shore CDOM end-members identified. Solid line represent the fitting equation. The dashed lines represent the +/- 4 standard deviations of the precision of the S estimate, taken from Stedmon & Markager 2001. Any points falling within this bracket (n=614) do not deviate significantly from the conservative mixing model of the two end members. Points falling outside the graph indicate samples where additional processes effects the optical properties of CDOM.

Deviation of S value from conservative mixing model



Heavy line: frequency distribution of salinity for the samples with *S* values below that predicted by the conservative mixing model. Thin line frequency distribution of all samples.



Heavy line: frequency distribution of chlorophyll concentrations for samples with S values below that predicted from the model and salinity greater than 6.8. Thin line: frequency distribution of all samples at salinities below 6.8.

Deviation of S value from conservative mixing model

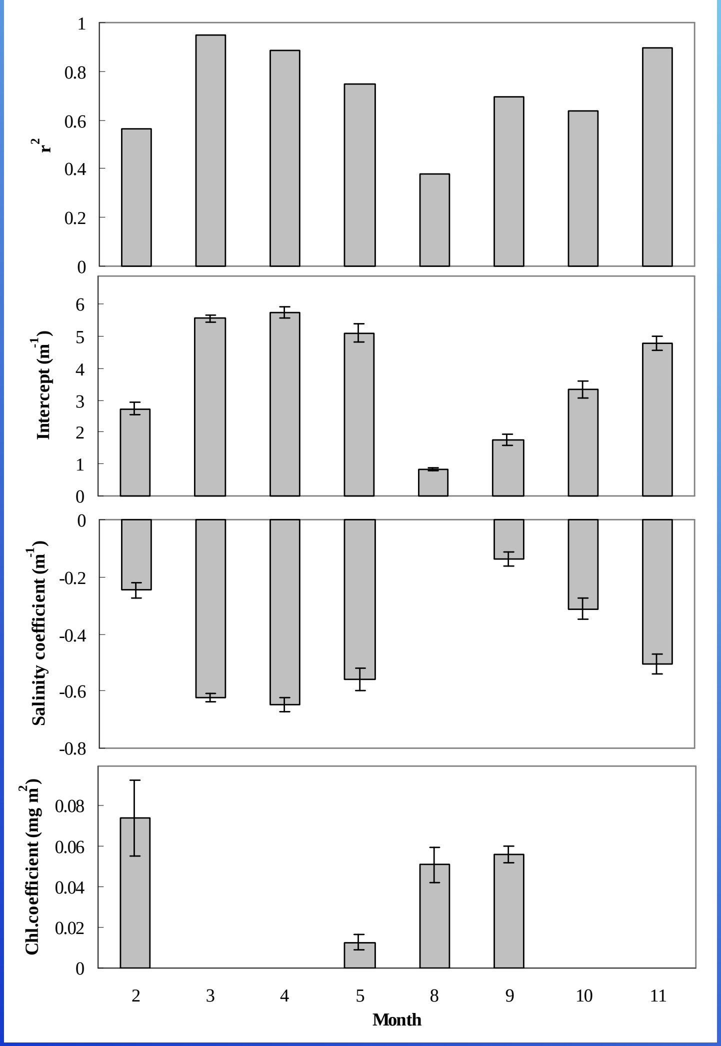
The likelihood of the *S* value for a CDOM sample with a salinity > 6.8 and a chlorophyll *a* concentration >1.5 mgm^{-3} to deviate significantly from the conservative mixing model in respective regions.

Region	% chance of lower *S*
Off-shore	50
Coastal zone	47
Gulf of Gdansk	34
Pomeranian Bay	57

The likelihood of the S value for a CDOM sample with a salinity > 6.8 and a chlorophyll *a* concentration >1.5 mgm^{-3} to deviate significantly from the conservative mixing model for each month.

Month	% chance of lower *S*
2	28
3	0
4	11
5	29
8	40
9	73

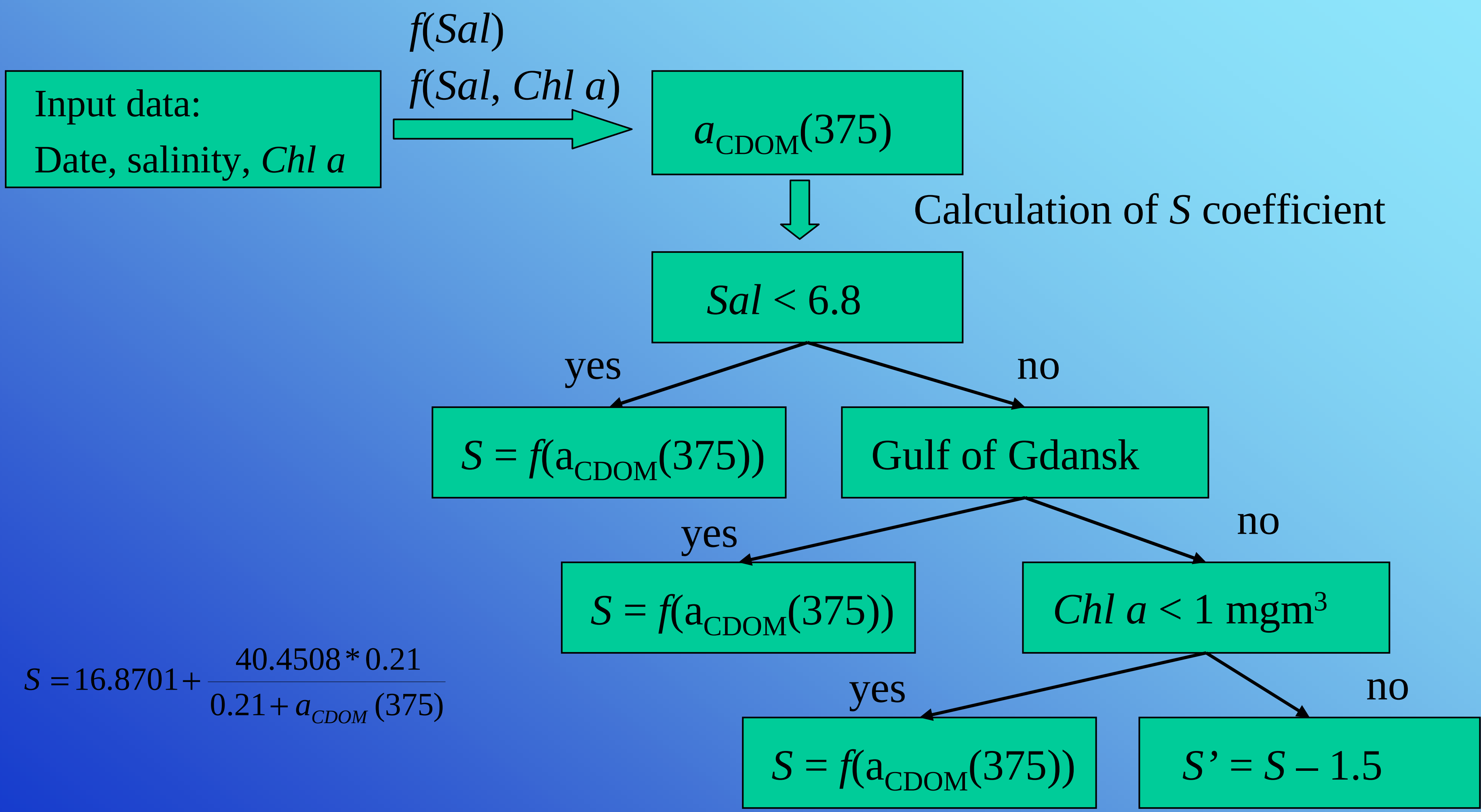
Modelling CDOM absorption from season, salinity and chlorophyll.



$$a_{CDOM}(375) = A \times Salinity + B \times [Chl] + C$$

Results from the linear regression of a_{CDOM}(375) versus salinity and chlorophyll *a* concentration with above equation. "N.S." the coefficient is not significantly different from zero. "N.D." data not available.

Algorithm for estimation of CDOM optical properties in the Baltic Sea.



$$S = 16.8701 + \frac{40.4508 * 0.21}{0.21 + a_{CDOM}(375)}$$

CDOM fluorescence

- Excitation-Emission Matrix fluorescence spectroscopy
  - SPEX Fluoromax 3 scanning spectrofluorometer – excitation range 250-550 nm, emission range 280-600 nm, spectral resolution 5 nm, results scaled in QSE units (quinine sulfonates equivalent)
  - EMM spectra were corrected for scattering with use Zepp et al., (2004) algorithm for Matlab

CDOM Fluorescence

A peak – terrestrial humic acids, Ex./Em. 265/460

C peak – terrestrial fulvic acids, Ex./Em. 345/460

M peak – marine fulvic acids, Ex./Em. 312/420

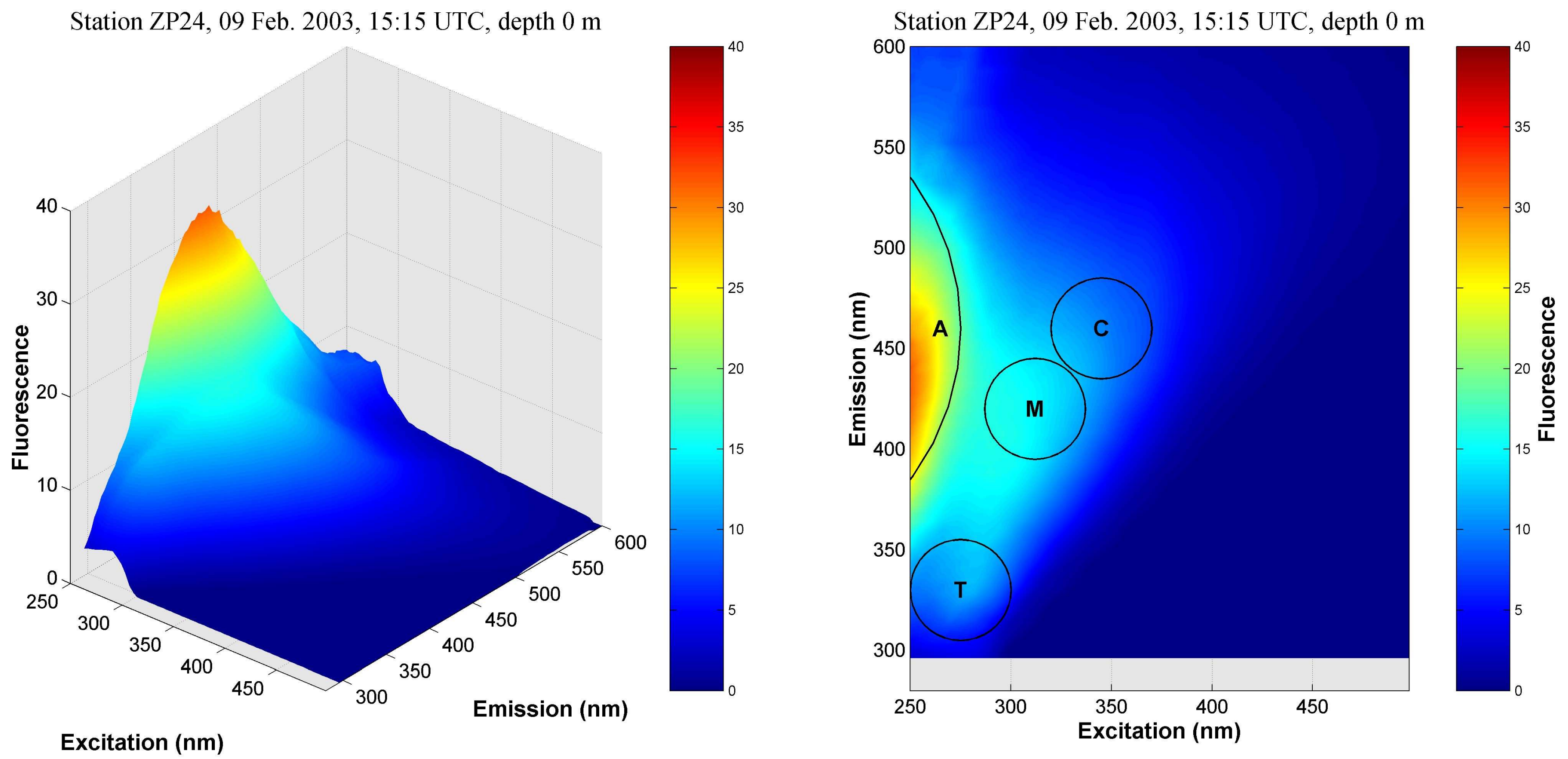
T peak – Proteinlike - tryptophan, Ex./Em. 275/330

Peak Excitation/Emission characteristics may be different for specific locations

For quantitative analysis we have chosen specific peak integral of EEM fluorescence spectrum

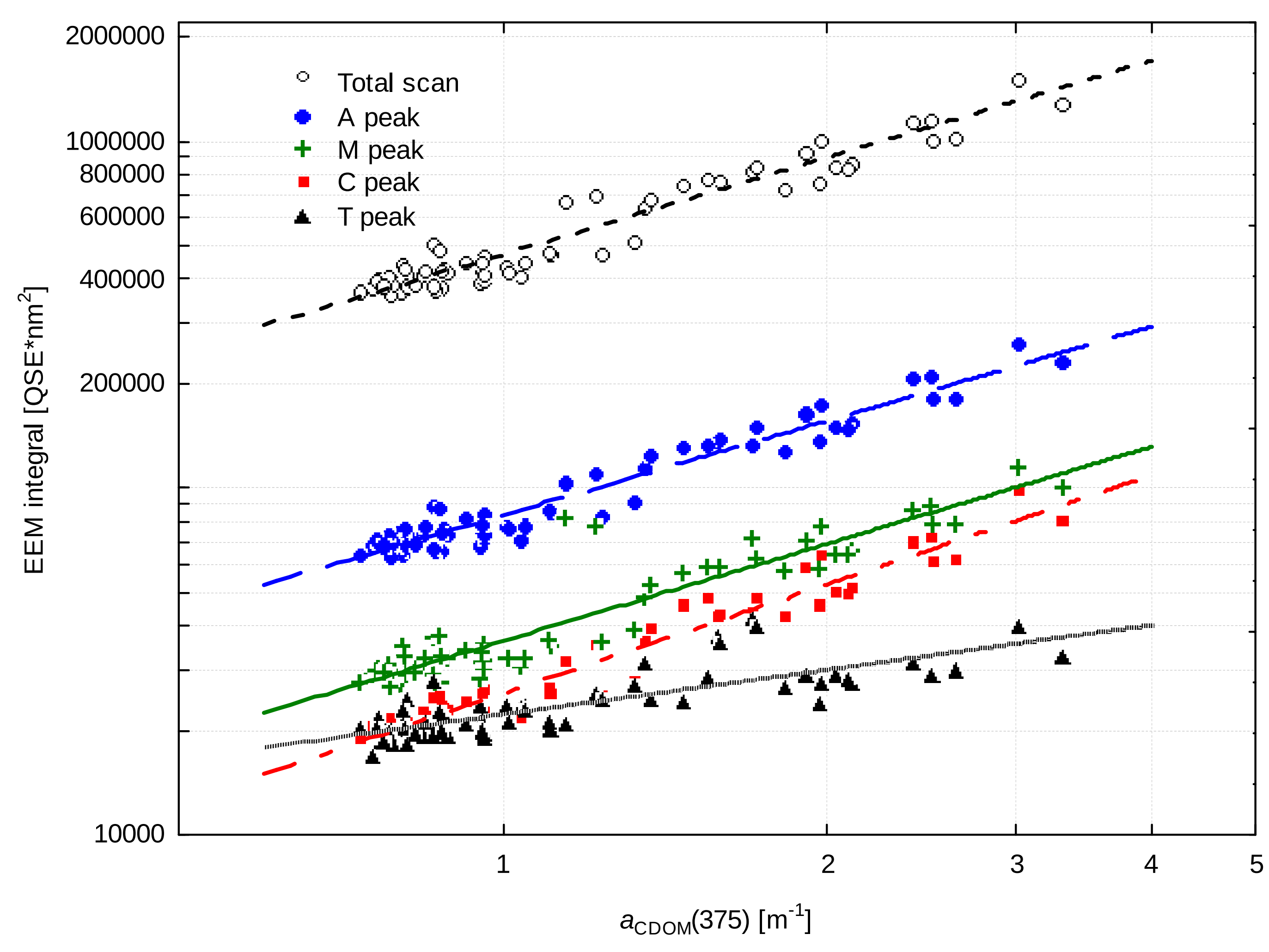
- Coble et al., 1996, Marine Chemistry 51:325-346.

CDOM EEM spectra - marine water end member

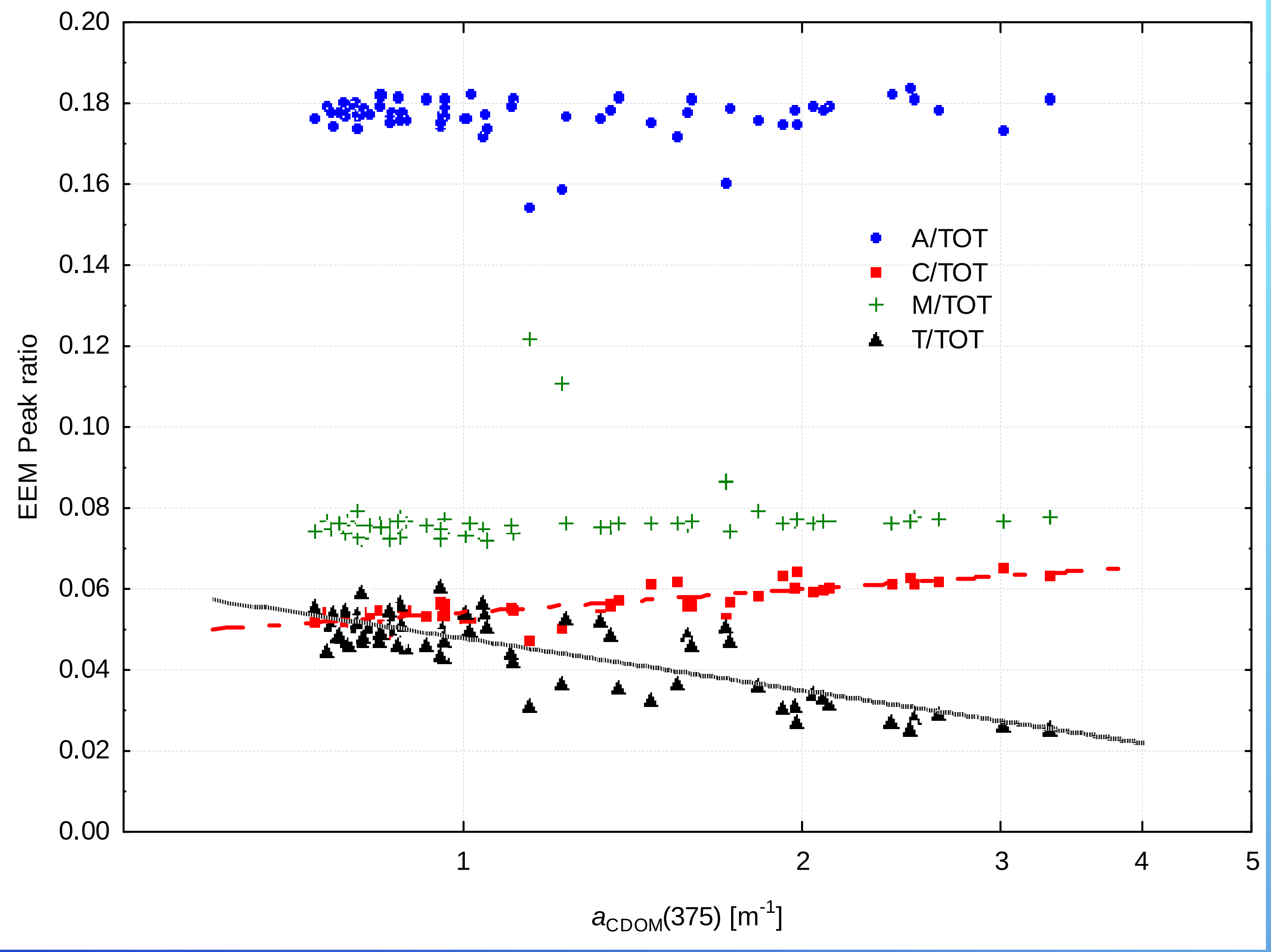


Baltic Sea, open sea waters - $a_{CDOM}(375) = 0.83\ m^{-1}$, $S = 0.0212\ nm^{-1}$, Salinity = 7.32

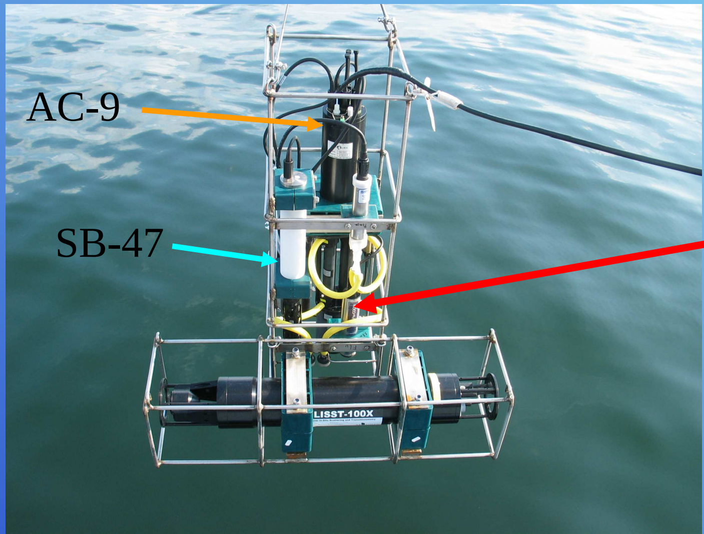
Relationship between CDOM absorption and fluorescence



Relationship between CDOM absorption and fluorescence peak ratios



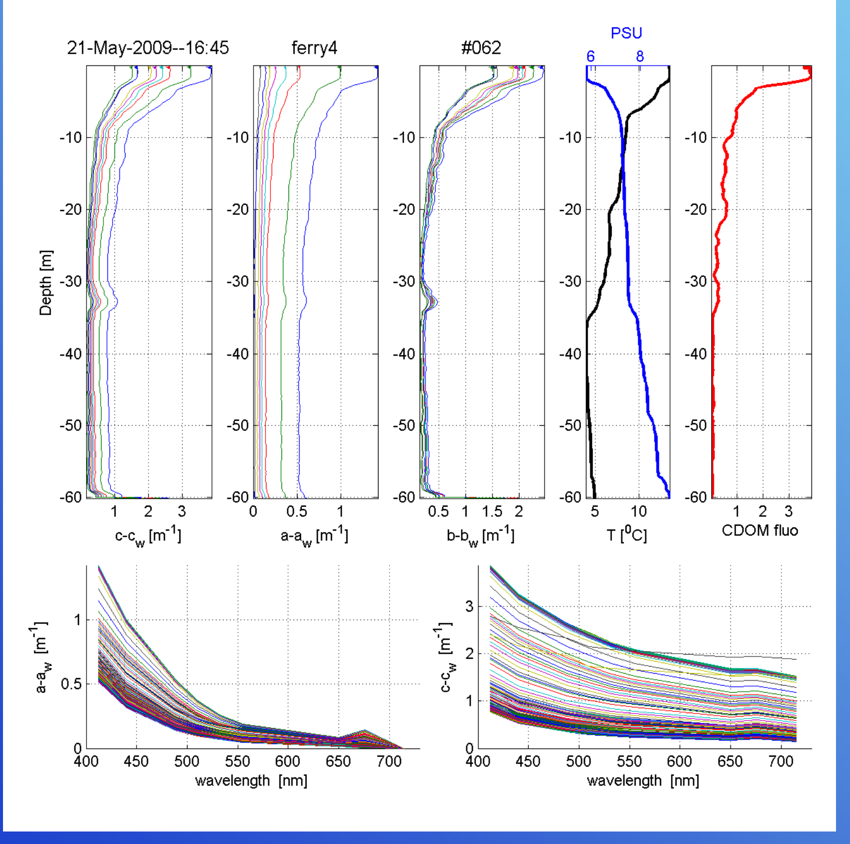
Application of in situ CDOM fluorescence measurement to study DOM distribution in space and time.

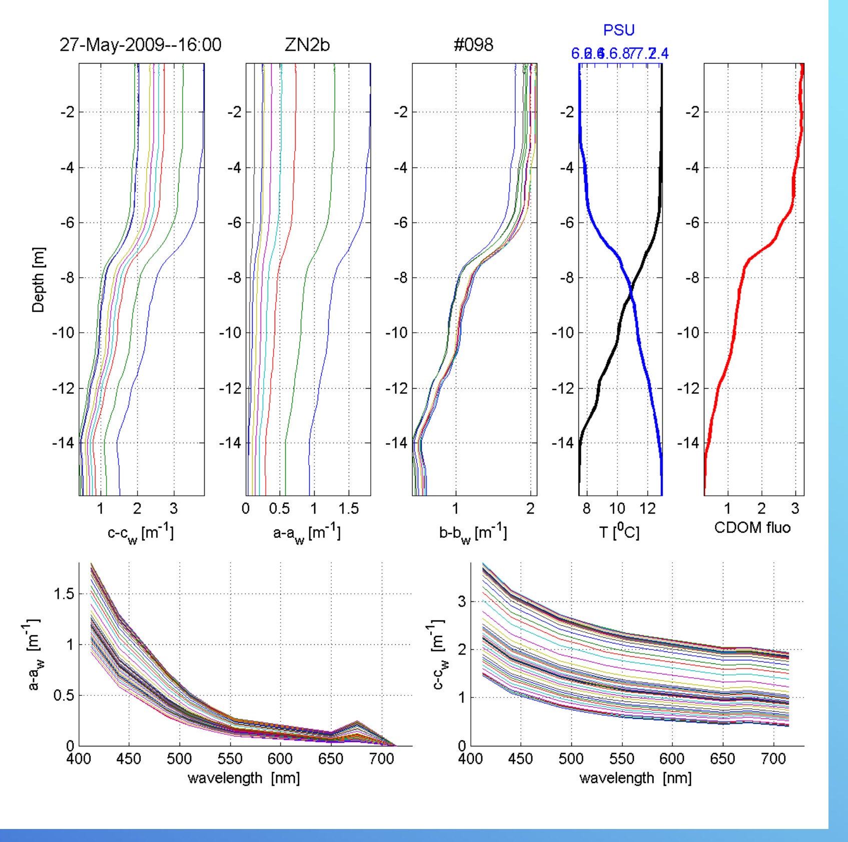


The TRIOS microFlu-CDOM fluorometer was integrated with AC-9 instrument and Seabird SB-47 CTD head. The AC-9 instrument is acting as signal integrator from optical and hydrological sensors. The IOPAS has developed a specifically designed power supply and data transmission and telemetry deck control unit and processing software. This new instrumental set up has been named Integrated Optical-Hydrological Probe, which could be deployed to acquire the vertical profiles as well as the surface distribution of optical and hydrological quantities in quasi flow-through system.

Application of in situ CDOM fluorescence measurement to study DOM distribution in space and time.

Preliminary results from test deployments – vertical profiles

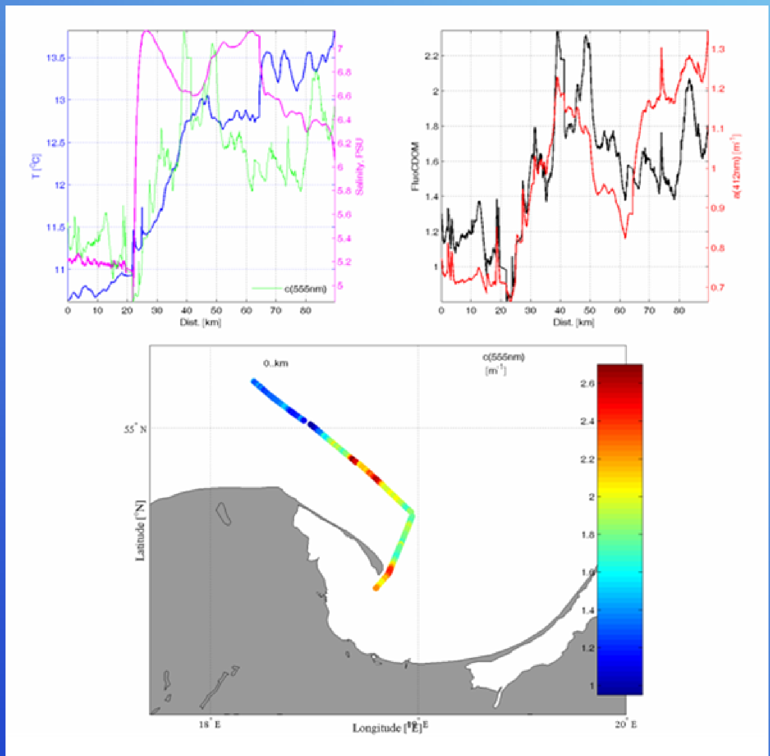


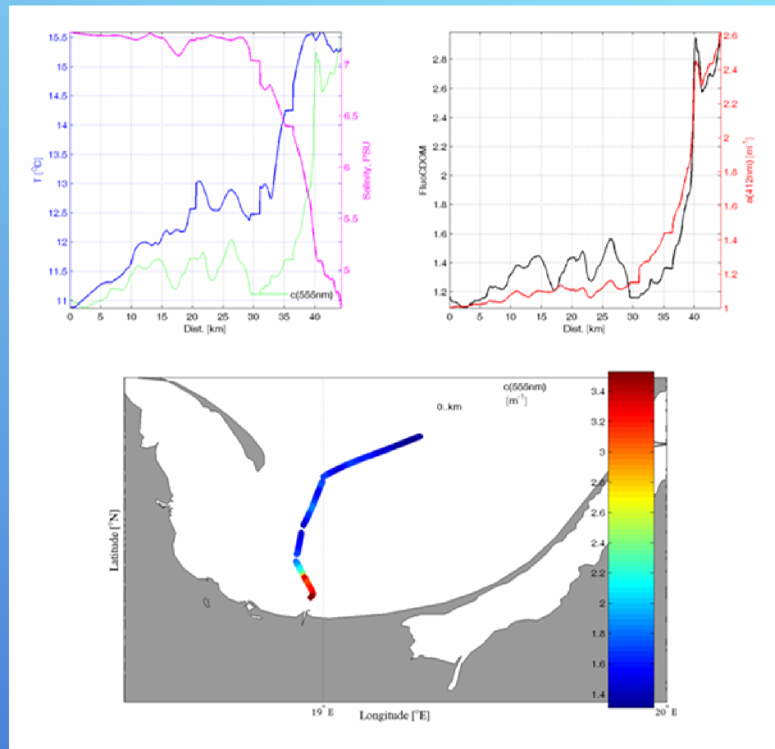


Examples of the vertical profile of salinity temperature, spectral absorption and attenuation coefficients and CDOM fluorescence (not calibrated, in DC fluorometer output)

Application of in situ CDOM fluorescence measurement to study DOM distribution in space and time.

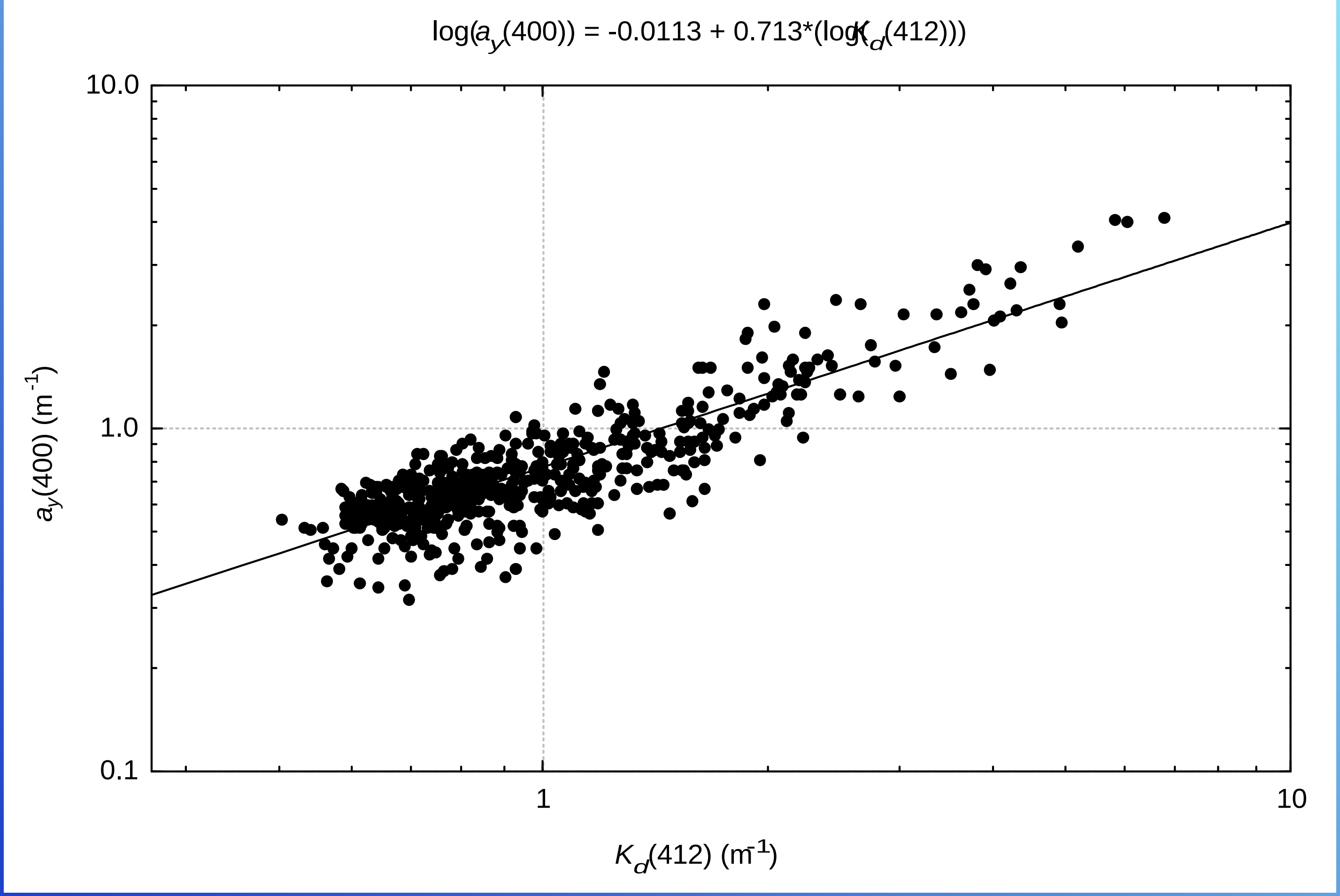
Preliminary results from test deployments – horizontal distributions acquired from quasi flow-through system.





Examples of the horizontal distribution of salinity temperature, spectral absorption and attenuation coefficients and CDOM fluorescence in the Gulf of Gdansk (not calibrated, in DC fluorometer output).

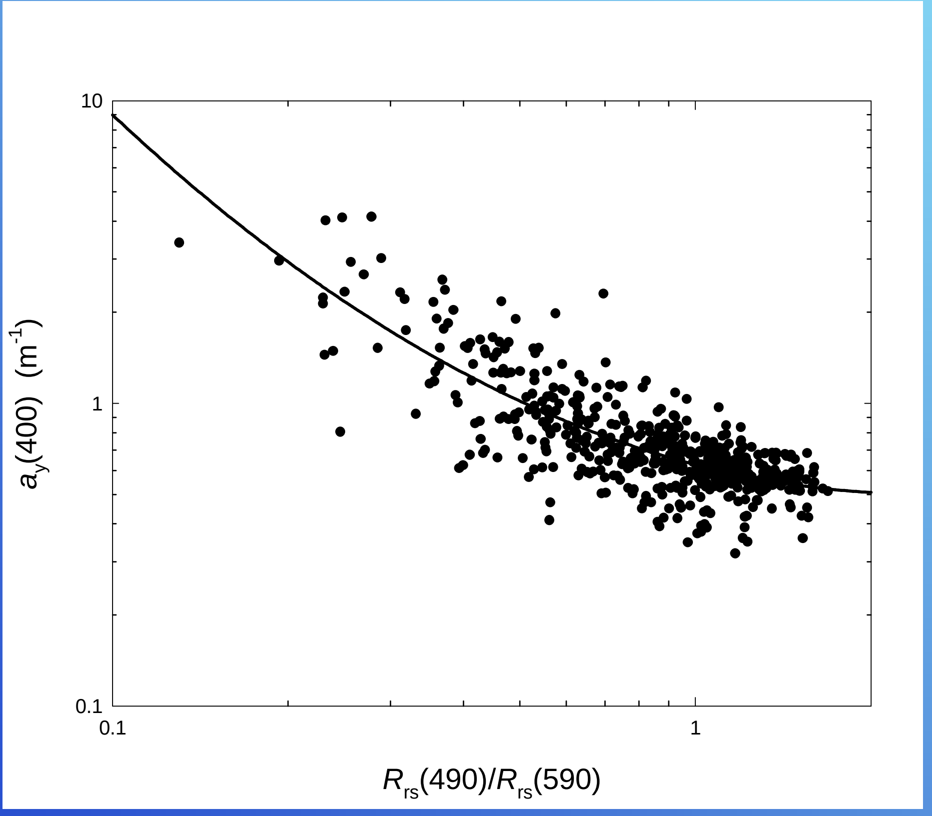
Relation of CDOM absorption with diffuse attenuation coefficient $K_d(412)$



Relative estimation errors are: systematic: 24.6%, random: 25.3%.

Calculated linear relationship between log-transformed values of $a_{CDOM}(400)$ and $K_d(412)$, correlation coefficient r =0.83, n = 580, p = 0.05.

Relation of CDOM absorption with spectral reflectance



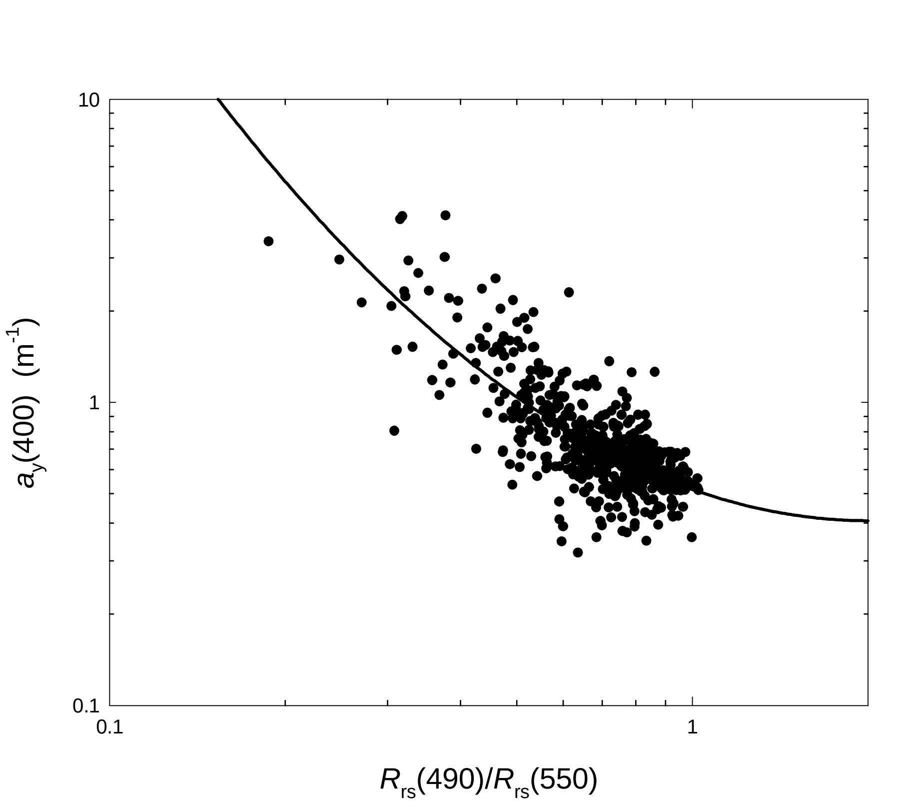
$$a_{CDOM}(400) = 10^{(-0.20-0.50X+0.62X^2)}$$

Where: X=log(Rrs(490)/Rrs(590)).

The error of $a_{CDOM}(400)$ estimation by above equation is: 4% for systematic error and 32% for random error.

Calculated second ordered polynomial approximation of relationship between log-transformed values of $a_{CDOM}(400)$ and spectral reflectance ratio in wavebands optimized for the Baltic Sea, correlation coefficient $r^2 = 0.63$, $n = 577$.

Relation of CDOM absorption with spectral reflectance



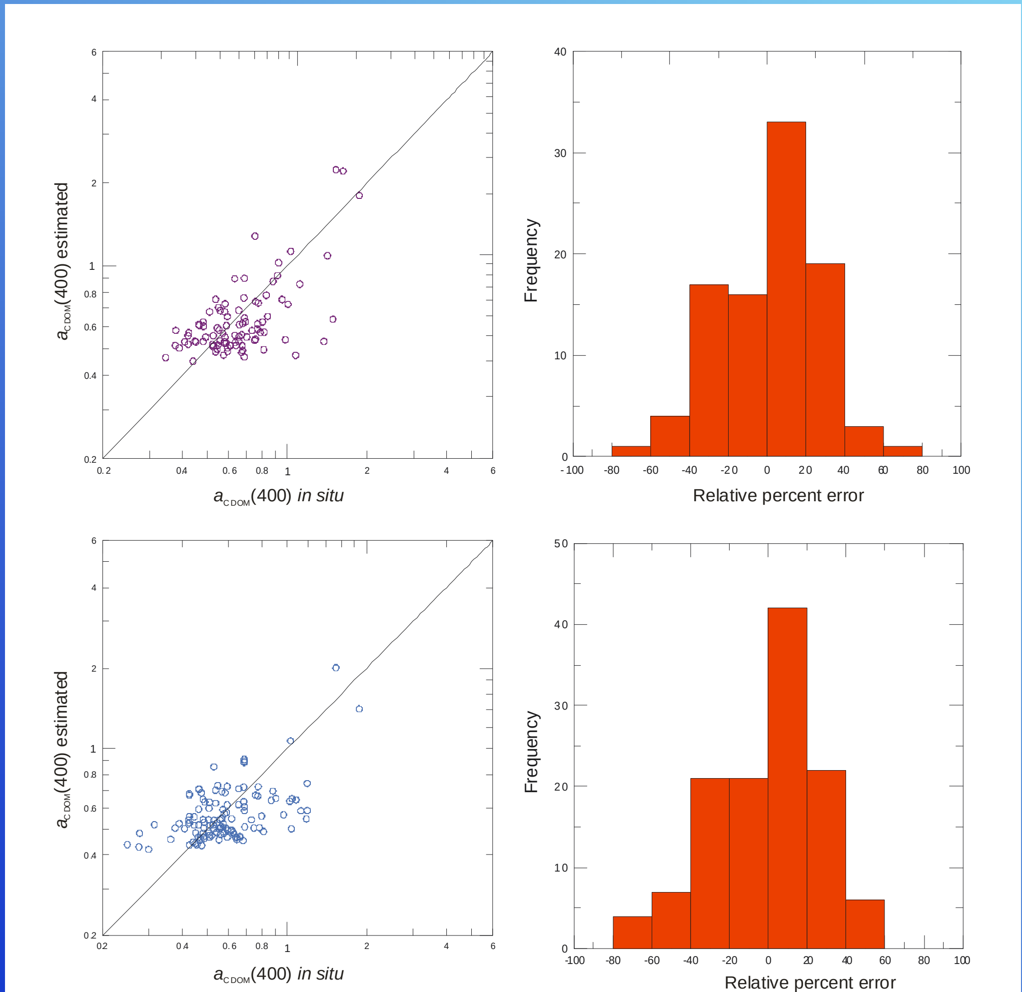
$$a_{CDOM}(400) = 10^{(-0.29-0.708X-1.12X^2)}$$

Where X=log(Rrs(490)/Rrs(550)).

The error of $a_{CDOM}(400)$ estimation by above equation is 5% for systematic error and 34% for random error.

Calculated second ordered polynomial approximation of relationship between log-transformed values of $a_{CDOM}(400)$ and spectral reflectance ratio in SeaWiFS and MODIS wavebands, correlation coefficient r^2 =0.59, n = 577.

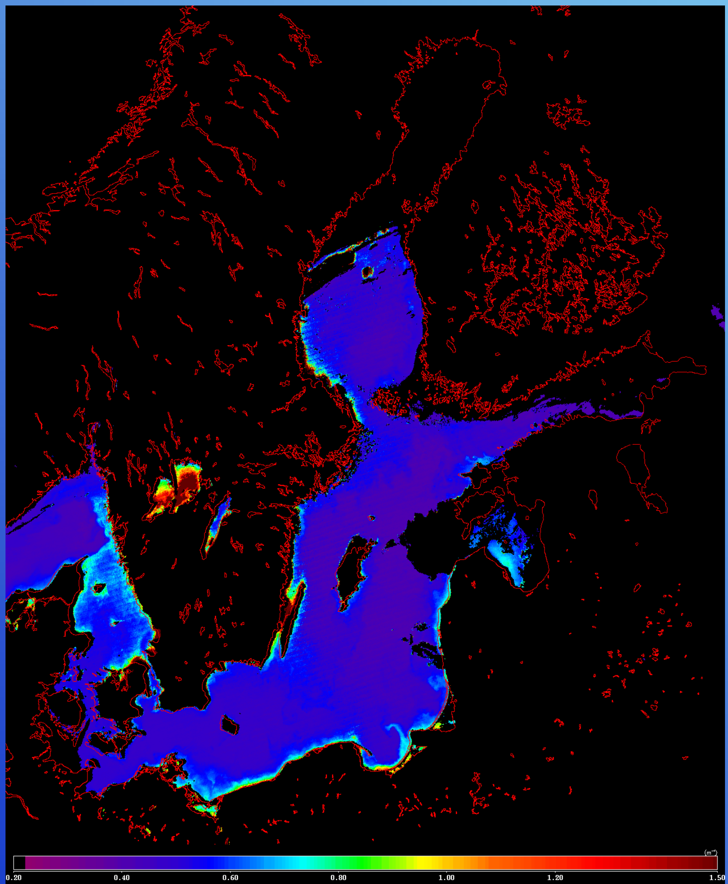
Validation of CDOM absorption coefficient algorithm in the Baltic Sea



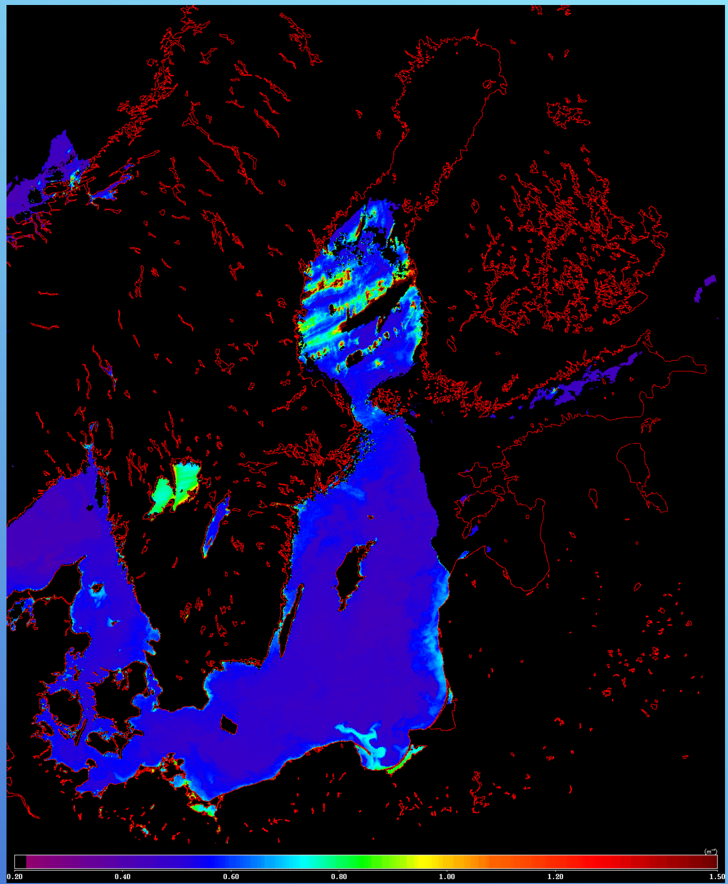
Upper panel: validation results of the Kowalczuk et al. (2005) algorithm using spectral reflectances derived from SeaWiFS ocean color imagery: Bias = 0.02, RMS = 0.23, R^2 = 0.50, n = 97. The lower panel validation results of the Kowalczuk et al. (2005) algorithm using spectral reflectances derived from MODIS ocean color imagery: Bias = 0.03, RMS = 0.19, R^2 = 0.38, n = 122.

CDOM mapping using satellite ocean colour imagery

Winter



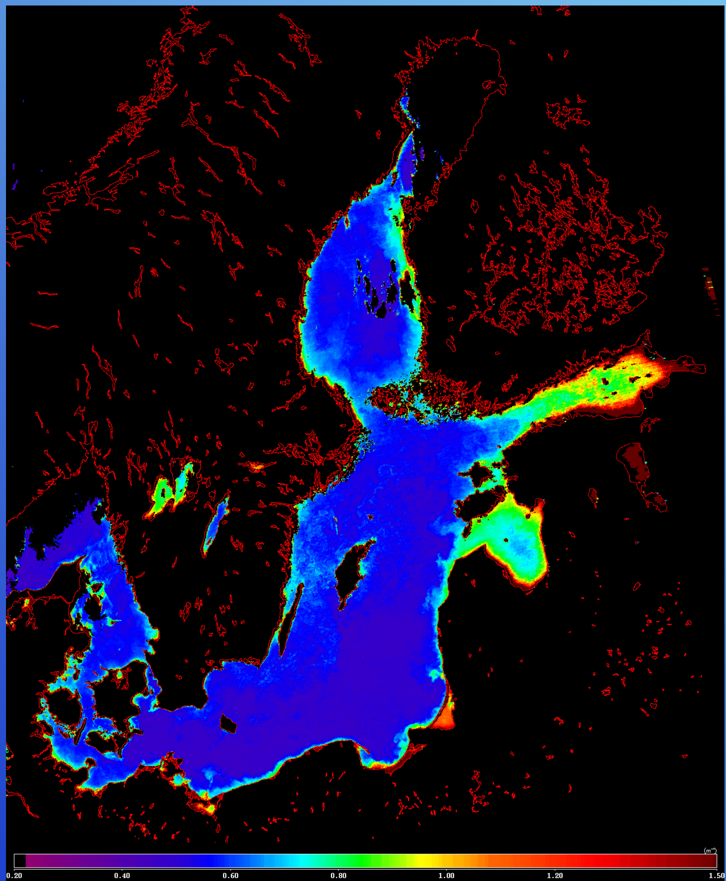
21 February 2004



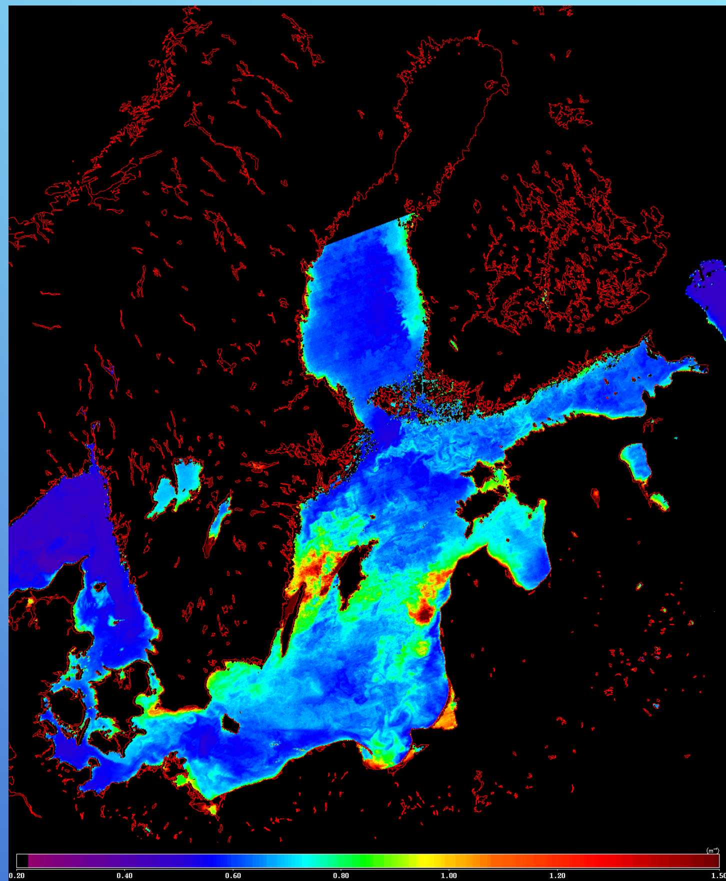
01 April 2005

CDOM mapping using satellite ocean colour imagery

Spring



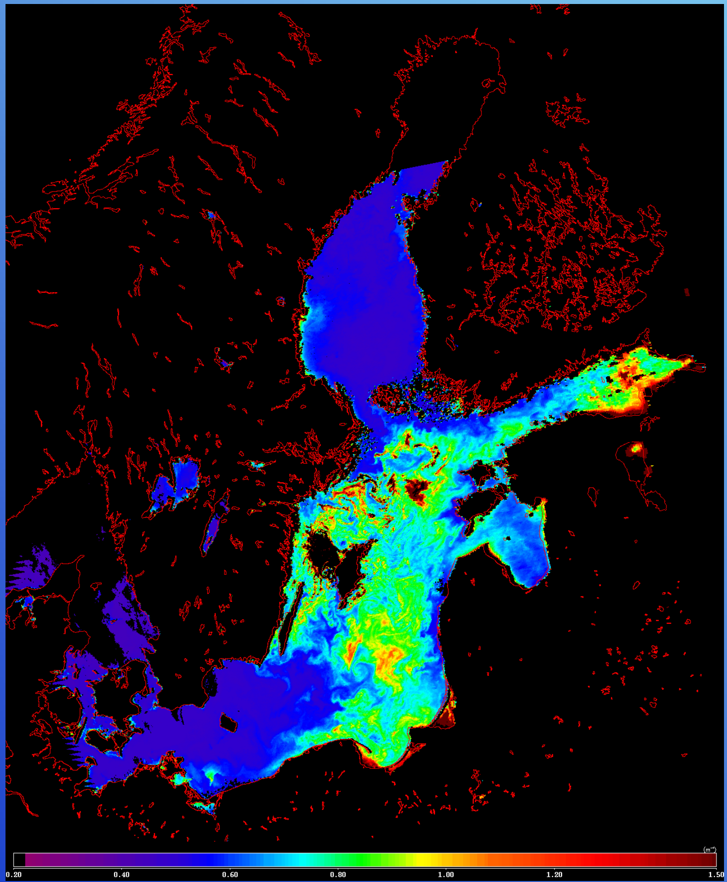
14 April 2007



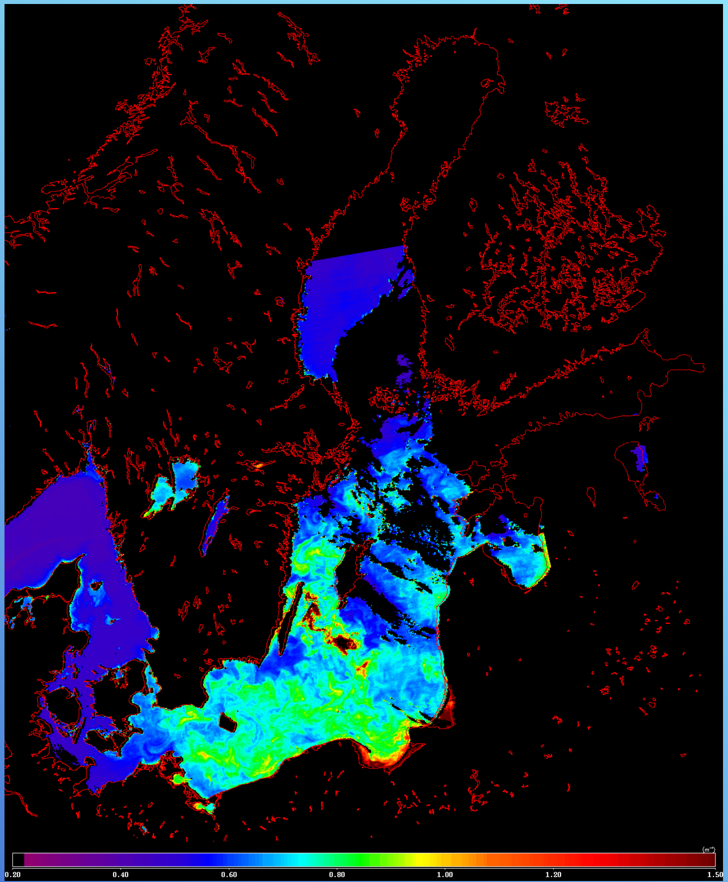
22 April 2008

CDOM mapping using satellite ocean colour imagery

Summer



4 July 2005



02 July 2008

What do we know about CDOM in the Baltic Sea

✓ The range of variability of $a_{CDOM}(\lambda)$ and *S*, and the pattern of seasonal and spatial distribution in the Baltic Sea.

✓ The conservative mixing of riverine CDOM with marine CDOM describes the majority of the variability in CDOM. Superimposed on this there is autochthonous production of CDOM occurring along the whole mixing gradient, causing the *S* values of CDOM to be less than predicted by the mixing model by approximately 1.5 mm^{-1}

✓The impact of the CDOM absorption on the spectral properties of diffuse attenuation coefficient and spectral reflectance.

✓ We can estimate CDOM absorption from irradiance measurements in the sea, or by use of remote sensing methods.

✓ Application of the fluorescence measurement in situ enables to study CDOM dynamics in greater spatial and temporal resolution.

What shall we learn more about CDOM in the Baltic Sea

- There is a need for better classification of CDOM components in the Baltic Sea – application of PARAFAC model to decompose EEM spectra. The relationships between CDOM optical properties and chemical composition need to be established.
- Through the systematic observations we need to select processes that control cycling of specific CDOM components in the Baltic Sea.
- We need to establish relationships between CDOM components and optical properties and DOC concentration – *under investigation, see poster Zabłocka et al.,.*
- Apply the optical methods to study the DOC dynamic with better spatial and temporal resolution – *under investigation, see poster Zabłocka et al.,.*

Acknowledgements

My collaborators:

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