Fluorescence and Reflectance for the *in-situ* Determination of Some Quality Parameters of Surface Waters

**Summary:** Ship-based experiments around Berlin and laboratory tests were carried out in order to develop spectroscopic methods for the *in-situ* determination of chlorophyll a (Chla) and chemical oxygen demand (COD$_{cd}$) of surface waters. The regression analysis of spectroscopic data (reflectance ($R$); laser-stimulated and conventional fluorescence ($I_p$)) and chemical-biological data yielded correlations of a relatively good quality.

**Introduction**

In the assessment of the state of surface waters the phytoplankton content and total (dissolved) organic load are of special interest. Usually, these parameters are determined in the laboratory with a considerable measuring effort. Rapid field methods are able to reduce the respective expenditure and can eliminate sample distortion which might occur in transport, storage, and analysis. Such a field method is, e.g., spectroscopy from ships or aircraft.

Ship-based experiments around Berlin and laboratory tests have been carried out for the development of such methods. The task was to find correlations between reflectance (measured in the field) and phytoplankton content (chlorophyll $a$) as well as between fluorescence, phytoplankton and the total dissolved organic load.

**Experiments and Methods**

Experiments were carried out in late September and early October 1988 on the river Spree and the lakes Müggelsee, Dämmeritzsee, Seddinsee, Zeuthener See and Langer See (river Dahme), comprising the following steps:

1. In the field:
   - water sampling at different points,
   - reflectance measurement ($R$).

2. In the laboratory:
   - determination of the chlorophyll $a$ concentration (Chla) according to NUSCH (1980),
   - measurement of the parameters chemical oxygen demand (COD$_{cd}$) and UV extinction at 254 nm (UV$_{254}$) of the filtered samples,
   - fluorescence measurement ($I_p$) by means of the fluorimeters „Quant 5“ and „Turner 111“ (of raw and filtered samples),
   - measurement of the spectral and time-resolved fluorescence by means of a laser fluorimeter (of raw and filtered samples).
Spectroscopy

This section describes the methods of measuring reflectance and fluorescence. The reflectance measurements will not be described in detail, as this has been done in some earlier publications (Gitelson et al. 1986, 1987, 1988; Mittenzwey et al. 1985, 1987, 1988; Garbusov et al.).

Reflectance Measurements

The spectral reflectance $R(\lambda)$ ($\lambda$: wavelength) is the ratio between the radiance ($L$) of a water body and the irradiance ($E$) of the global radiation. Thus, $R$ expresses the share of the global radiation that is scattered back by the water body. Reflectance and radiance both depend on the kind of optically active substances in the water and on their concentrations (Austin; Bukata et al.; Gordon et al.; Morel and Prieur).

The measurement of $R$ from a ship or an aircraft is relatively easy. If the correlations between $R$ and the phytoplankton content in the water are known, then it is possible to draw conclusions on the phytoplankton concentration from the measured $R$.

Fluorimetry

Conventional fluorimetry

Conventional fluorimetry means that the excitation of fluorescence is performed with broad-band short-wave radiation of conventional sources of light. Two fluorimeters of the types „Turner 111“ and „Quant 5“ were used for the excitation and measurement of fluorescence in water samples. Both devices measure fluorescence under an angle of 90° to the direction of incidence. The excitation and measurement of the algal fluorescence was performed with the Turner 111 fluorimeter in the following way (Schellenberger et al.): fluorescence was stimulated by means of a blue lamp and a blue filter with a maximum transmission at $\lambda = 423$ nm. Fluorescence intensity was measured in the range of $\lambda \geq 655$ nm.

With the Quant 5 device, the following measuring procedure was pursued: to stimulate algal fluorescence the excitation wavelengths 400, 515, and 540 nm were used and emission was measured in the range of $\lambda \geq 670$ nm. These wavelengths were recommended by Gold et al. in order to distinguish between green algae, blue-greens, and diatoms. Further measurements were made (filtered samples) in the ranges of 410 ... 450 nm (excitation at 330 ... 390 nm) and 510 ... 580 nm (excitation at 445 ... 495 nm). These wavelengths were proposed by Gitelson and Dubovitski (1986) to differentiate humic and fulvic acids.

Laser-stimulated fluorimetry

In the case of laser-stimulated fluorimetry the raw samples and filtered ones (filtration through glass-fibre paper, pore size approximately 2 ... 5 µm) were exposed to the radiation of a nitrogen laser IGT 50 (impulse power 50 KW, impulse duration 0.5 ns, wavelength 337.1 nm). The repetition rate was 5 ... 10 Hz. The intensity of fluorescence was measured at an angle of 90° to the direction of incidence.
At first, the spectral measurement was performed by means of a stepping-motor driven filter disk at 16 different wavelengths in the range of 448 ... 790 nm. The interference filters covered an average band width of approximately 8 ... 10 nm. A silicon receiver PEE 103 was used as an optoelectronical converter.

Then, the fluorescence intensity of the raw sample was measured at wavelengths of 500 nm < \lambda < 600 nm as well as \lambda \geq 600 nm as a function of time. A silicon receiver PDE 103 with a time response of the rise of 3 ns and a boxcar integrator BCI 280 registered the signals. The range of 500 ... 600 nm was chosen to examine the fluorescence decay process of dissolved organics, while the range \lambda \geq 600 nm covered the phytoplankton. For simplicity, it was assumed that fluorescence in the 500 ... 600 nm range is dominantly caused by dissolved organics and in the range \lambda \geq 600 nm by phytoplankton. According to international literature, this is a justified approximation (Günnerberg; Kondratjev et al.; Chappelle et al.).

The fluorescence measured by the receiving system was always corrected to eliminate the electronic background noise (baseline sampling) and related to the laser intensity.

*Measurement of chemical and biological control data*

The total load of dissolved organics in natural waters is often expressed in the parameters COD$_{c_r}$ (chemical oxygen demand — chromate) and UV$_{254}$ (ultraviolet extinction at the wavelength 254 nm). They were determined in the filtered samples by a special method (Vobach; Müller).

Phytoplankton is represented by the concentration of chlorophyll a (Chla) determined with a method by Nusch (1980).

**Results**

*Reflectance and chlorophyll a*

Following Gordon et al., Morel and Prieur and others, so-called colour indices (reflectance quotients) were established. Tab. 1 shows some results of the regression analysis (r$^2$: performance index). Fig. 1 illustrates the correlation between chlorophyll a

<table>
<thead>
<tr>
<th>colour index $x$</th>
<th>regression equation</th>
<th>$r^2$</th>
<th>$n$</th>
<th>range of Chla</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R(705)/R(670)$</td>
<td>$\text{Chla} = -186.0 + 324.5x - 64.8x^2$</td>
<td>0.87</td>
<td>51</td>
<td>26 ... 134 ( \mu \text{g/l} )</td>
</tr>
<tr>
<td>$R(705) - R(670)$</td>
<td>$R(550)$</td>
<td>$\text{Chla} = 71.9 + 483.1x + 910.9x^2$</td>
<td>0.90</td>
<td>51</td>
</tr>
<tr>
<td>$R(705) - R(670)$</td>
<td>$R(550)$</td>
<td>$\text{Chla} = 71.2 + 279.4x + 459.1x^2$</td>
<td>0.90</td>
<td>51</td>
</tr>
<tr>
<td>$R(705) - R(670)$</td>
<td>$R(550) - R(760)$</td>
<td>$\text{Chla} = 71.6 + 349.7x + 528.3x^2$</td>
<td>0.90</td>
<td>51</td>
</tr>
</tbody>
</table>

Table 1. Results of the regression analysis between colour indices and chlorophyll a

Tabelle 1. Ergebnisse der Regressionsanalyse zwischen Farbindizes und Chlorophyll a
and the colour index \( (R(705) - R(670))/R(550) \). The correlations found are of a relatively good quality (performance index \( r^2 > 0.87 \)) in the concentration range of 26 ... 134 µg/l chlorophyll a, i.e. the determination of Chla by means of the above mentioned colour indices is possible with sufficient accuracy.

Furthermore, it should be mentioned that for the 3- and 4-band indices (760 nm, 705 nm, and 550 nm) the performance index was \( r^2 = 0.9 \) and for the 2-band colour index (705 nm, 670 nm) it was \( r^2 = 0.87 \). This suggests that the use of more than two wavelengths may increase accuracy.

**Fluorescence, chlorophyll a, and total dissolved organics**

Fluorescence and chlorophyll a (Chla)

Table 2 shows the correlations between Chla and the intensity of fluorescence measured with the devices Turner 111 and Quant 5 (conventional fluorimetry, i.e. broad-band excitation of fluorescence) at different excitation wavelengths. Fig. 2 illustrates the correlation between Chla and the fluorescence intensity \( I_\lambda (540, \lambda \geq 670) \). (The first figure in the parentheses signifies the excitation wavelength and the second one the emission wavelength.) A comparison of the performance indices \( r^2 \) indicates that \( r^2 \) increases with increasing excitation wavelength (400 nm: \( r^2 = 0.8 \); 423 nm: \( r^2 = 0.84 \); 515 nm: \( r^2 = 0.92 \); 540 nm: \( r^2 = 0.92 \)), while there are no significant differences between \( r^2(515) \) and \( r^2(540) \). This phenomenon might be explained as follows: In the water
Table 2 Results of the regression analysis between the fluorescence intensity (conventional fluorimetry) and chlorophyll $a$

<table>
<thead>
<tr>
<th>Fluorescence $I_F$</th>
<th>Regression equation</th>
<th>$r^2$</th>
<th>$n$</th>
<th>Device</th>
<th>Range of Chla</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_F (400, \lambda \geq 670)$</td>
<td>Chla = $-24.9 + 2.9x - 0.004x^2$</td>
<td>0.80</td>
<td>55</td>
<td>Quant 5</td>
<td>26 ... 134µg/l</td>
</tr>
<tr>
<td>$I_F (423, \lambda \geq 670)$</td>
<td>Chla = $17.4 + 1.7x + 0.084x^2$</td>
<td>0.84</td>
<td>55</td>
<td>Turner</td>
<td></td>
</tr>
<tr>
<td>$I_F (515, \lambda \geq 670)$</td>
<td>Chla = $-9.83 + 1.34x - 0.0025x^2$</td>
<td>0.92</td>
<td>55</td>
<td>Quant 5</td>
<td></td>
</tr>
<tr>
<td>$I_F (540, \lambda \geq 670)$</td>
<td>Chla = $0.77 + 1.64x - 0.005x^2$</td>
<td>0.92</td>
<td>55</td>
<td>Quant 5</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2. Chlorophyll $a$ concentration (Chla) in dependence on the fluorescence $I_F (540, \lambda \geq 670)$ (conventional fluorescence spectroscopy).

Abb. 2. Chlorophyll $a$ Konzentration (Chla) in Abhängigkeit von der Fluoreszenz $I_F (540, \lambda \geq 670)$ (herkömmliche Fluoreszenzspektroskopie).

bodies under examination diatoms and blue-green algae were dominant. Both algal groups show greater differences in their quantum efficiency at shorter wavelengths (400 nm, 423 nm) than at longer ones (515 nm, 540 nm) (GOLD, 1986). This could result in a greater deviation of the measured values from the regression curves in the case of short-wave excitation.

The regression analysis of the correlation between Chla and fluorescence intensity stimulated by the nitrogen laser and measured at 687 nm ($I_F (337, 687)$) yields a performance index of $r^2 = 0.94$ (Tab. 3). This measurement was made with the receiver PEE 103. Fig. 3 shows the chlorophyll $a$ concentration as a function of fluorescence intensity stimulated by the nitrogen laser and measured at $\lambda \geq 660$ nm with the receiver PDE 103. The fluorescence intensity values shown are the maximum values for the
Table 3. Results of the regression analysis between the intensity of laser-induced fluorescence and chlorophyll a

<table>
<thead>
<tr>
<th>Fluorescence $I_F$ regression equation</th>
<th>$r^2$</th>
<th>n</th>
<th>device</th>
<th>range of Chla</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_F$ (337, 687) Chla $= -34 + 18.54x - 0.27x^2$</td>
<td>0.94</td>
<td>55</td>
<td>Laserfluorimeter (PEE 103)</td>
<td>26 ... 134 µg/l</td>
</tr>
<tr>
<td>$I_F$ (337, λ≥660) Chla $= -31.4 + 13.46x - 0.15x^2$</td>
<td>0.96</td>
<td>55</td>
<td>Laserfluorimeter (PDE 103)</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3. Chlorophyll a concentration (Chla) in dependence on the laser-induced fluorescence $I_F$ (337, λ≥660) as maximum value for the time decay function $I_F=f(t)$.

Abb. 3. Chlorophyll a Konzentration (Chla) in Abhängigkeit von der laser-erzeugten Fluoreszenz $I_F$ (337, λ≥660) als Maximumwert der Abklingkurve $I_F=f(t)$

time decay function. The performance index $r^2$ is 0.96. According to the explanation given above, the relatively high performance indices suggest that in the ultraviolet spectral range (here 337.1 nm) no great differences exist between the quantum efficiency of blue-green algae and diatoms.

It can be summarized that laser-induced (337 nm) fluorescence spectroscopy and conventional fluorescence spectroscopy with the excitation wavelengths in the ranges around 515 and 540 nm yield a relatively high accuracy in chlorophyll determination.
Fluorescence and dissolved organics (COD<sub>Cr</sub> and UV<sub>254</sub>)

A short theoretical consideration with very rough assumptions will be made here. We assume the following case: A sample contains, besides the fluorescent substance to be determined (here: dissolved organics with the concentration C<sub>1</sub>), another substance (here: phytoplankton with the concentration C<sub>2</sub>) absorbing in the same spectral range like component C<sub>1</sub> but without any fluorescence in the emission range of C<sub>1</sub>. According to WIBERG, ZANDER, SCHWEDT and FÖRSTER, the fluorescence intensity I<sub>f</sub> of a solution is proportional to the quantum yield Q<sub>f</sub> of the fluorescent substance (C<sub>1</sub>) and the intensity I<sub>a</sub> of the excitation radiation absorbed by C<sub>1</sub>. We can write it in a differential form:

\[
dI_f = Q_f \frac{dI_a}{dx}
\]

\[(x \leq d, d: \text{length of the cuvette})\]

The intensity dI<sub>a</sub> absorbed by C<sub>1</sub> can be expressed as the variation of the incident intensity caused by C<sub>1</sub>:

\[
\frac{dI_a(x)}{dx} = -\frac{dI(x)}{dx} = k_1 I(x)
\]

\[(k_1: \text{extinction coefficient of the substance C}_1 \text{ at the excitation wavelength})\]

In general I(x) can be described by

\[
I(x) = I_0 \exp \left[ - (k_1 + k_2)x \right]
\]

\[(I_0: \text{laser intensity, } k_2: \text{extinction coefficient of the substance C}_2 \text{ at the excitation wavelength})\]

Thus, the integration of equation (1) yields

\[
I_f = \int_0^d Q_f k_1 I_0 \exp \left[ - (k_1 + k_2)x \right] dx = Q_f I_0 \frac{k_1}{k_1 + k_2} \left( 1 - \exp \left[ - (k_1 + k_2)d \right] \right).
\]

If equation (4) is split into a series and if it is assumed that the extinction of the solution is lower than approximately 0.01, the higher terms of the series may be neglected resulting in:

\[
I_f = Q_f k_1 I_0 d.
\]

It is assumed that dissolved organics fluoresce in the bluegreen spectral range, whereas suspended organics (especially phytoplankton) do not show any noticeable fluorescence in this spectral range. A distinct algal fluorescence occurs in the red spectral range. In the blue-green spectral range algae show marked absorption bands. The blue-green fluorescence light emitted by the dissolved organics may consequently be weakened by algae on the way to the cuvette wall through absorption. Consequently, the measured fluorescence is lower than the actual fluorescence of the dissolved organics. Equation (5) needs „correction“ with respect to this phenomenon. Thus, the measured fluorescence is:

\[
I_f(\lambda_4) = I_f \exp \left( -k_2 d \right)
\]
with \( l \) standing for the distance between the place where fluorescence is generated and the cuvette wall and \( k_2 \) for the algal extinction coefficient. \( \lambda_1 \) lies in the blue-green spectral range.

Inserting (6) into (5) yields:

\[
I_p(\lambda_1) = Q_p k_1 l_0 d \exp(-k_2 l).
\]

(7)

As in the first approximation linear relations exist between algal concentration \((C_2 = \text{Chla})\) and fluorescence in the red spectral range (especially \( I_p(687) \)) — cf. section fluorescence and chlorophyll \( a \)—equation (7) can be written in the following form:

\[
\frac{I_p(\lambda_2)}{I_0} = I_p(\lambda_1) = \tilde{A} C_1 \exp(-\tilde{B} C_2) = \bar{A} C_1 \exp(-B I_p(\lambda_2)).
\]

(8)

The values \( \tilde{A} \), \( \tilde{B} \), and \( B \) are shortened forms. \( \lambda_2 \) lies in the red spectral range of algal fluorescence. If we separate the concentration of dissolved organics \((C_1)\) in equation (8), we obtain:

\[
C_1 = AI_p(\lambda_1) \exp(BI_p(\lambda_2)).
\]

(9)

Thus, formula (9) is the fundamental approximation to carry out regressions between the parameters COD\(_{Cr}\) and UV\(_{254}\) (which characterize the total dissolved organic load), on the one hand, and the measured values of fluorescence intensity, on the other hand. Formula (9) is based — as mentioned above — on strongly simplified assumptions. Furthermore, the absorption of the blue-green fluorescence radiation by the dissolved organics themselves (self-absorption) is not considered in (9).

In the following the results are presented, first of fluorescence measurements with the Quant 5 device (broad-band excitation) and secondly the measurements made with the laser fluorimeter (narrow-band excitation).

Table 4. Results of the regression analysis between the fluorescence intensity (conventional fluorimetry) and COD\(_{Cr}\), UV\(_{254}\) (device: Quant 5)

<table>
<thead>
<tr>
<th>regression equation</th>
<th>( r^2 )</th>
<th>( n )</th>
<th>range mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD(_{Cr}) = 2.73I(_p)(470, 550)( \times 0.44) ( \exp(0.0633I(_p)(540, \lambda \equiv 670)R) )</td>
<td>0.73</td>
<td>18</td>
<td>12.5 ... 20.4</td>
</tr>
<tr>
<td>UV(_{254}) = 0.072I(_p)(470, 550)( \times 0.15) ( \exp(0.0018I(_p)(515, \lambda \equiv 670)R) )</td>
<td>0.68</td>
<td>40</td>
<td>0.12 ... 0.16</td>
</tr>
</tbody>
</table>

Fluorimeter Quant 5: Tab. 4 shows relations between UV\(_{254}/\text{COD}_{Cr}\) and fluorescence data (conventional fluorimetry) on the basis of (9). (The letter "R" stands for raw sample and "F" for filtrate.) The magnitude of the performance index indicates the existence of a defined correlation between the fluorescence data of water samples and the total dissolved organic load, and thus the possibility to determine this total load by means of conventional fluorimeters.

Laser fluorimetry: Tab. 5 shows the relations between UV\(_{254}/\text{COD}_{Cr}\) and laser-induced fluorescence data on the basis of (9). Fig. 4 illustrates the relation between COD\(_{Cr}\) and \( I_p \) of the raw samples. The correlations between COD\(_{Cr}\), UV\(_{254}\) and laser-
Table 5. Results of the regression analysis between the intensity of laser-induced fluorescence and COD_{Cr}, UV_{254}
(device: Laser fluorimeter (receiver PEE 103))

<table>
<thead>
<tr>
<th>regression equation</th>
<th>r^2</th>
<th>n</th>
<th>range mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD_{Cr} = 3.64I_p(337, 538)R^{0.50} \text{exp}(0.043I_p(337, 658)R)</td>
<td>0.72</td>
<td>18</td>
<td>12.5–20.4</td>
</tr>
<tr>
<td>UV_{254} = 0.057I_p(337, 586)R^{0.29} \text{exp}(0.02I_p(337, 638)R)</td>
<td>0.69</td>
<td>40</td>
<td>0.12–0.16</td>
</tr>
</tbody>
</table>

Fig. 4. Chemical oxygen demand (COD_{Cr}) in dependence on \( A \cdot I_p(337/538)R^{41} \cdot \text{exp}(B \cdot I_p(337/658)R) \) (laser impulse spectroscopy).

Abb. 4. Chemischer Sauerstoffbedarf (CSB_{Cr}) in Abhängigkeit von \( A \cdot I_p(337/538)R^{41} \cdot \text{exp}(B \cdot I_p(337/658)R) \) (Laserimpulsspektroskopie)

induced fluorescence indicate the possibility to determine the total dissolved organics also by means of remote sensing or "no-contact" measurements. Here, one could think of laser systems on vehicles, boats, in automatic measuring stations, or in helicopters.

Here follows another brief and very simplified theoretical consideration on time-resolved laser fluorimetry: We consider a solution containing fluorescent molecules which are excited with short laser impulses. At every time \( t \) the number of molecules which make the step of disactivation in the time unit is proportional to the number of stimulated molecules \( C_a \) at the time \( t \) (Zander; Herrmann and Wilhelmi; Dahne et al.; Scholz et al.).
\[
\frac{dC_g}{dt} = K_p C_g.
\]

The integration of equation (10) results in:

\[
C_g(t) = C_g(t = 0) \exp \{- K_p t\}.
\]

The value \(K_p\) is the first-order rate constant for the decay process and indicates the number of disactivation processes per second. Besides fluorescence \((K_p)\) there are, as a rule, further possibilities of disactivation which can be described by the rate constant \(K_i\) (e.g. thermal disactivation). (In the case of disactivation of the considered molecules by other species, one must take into consideration also the concentration of these species, in addition to the respective rate constants.) In general, there holds:

\[
K_D = K_p + K_i.
\]

The “mean” life-time \(\tau_D\) of the state of excitation is defined as the time during which the number of molecules being in the state of excitation at the beginning of the disactivation process is reduced to 1/e. For \(\tau_D\) there holds:

\[
\tau_D = \frac{1}{K_D} = \frac{1}{K_p + K_i}.
\]

In other words: The higher the number of possibilities for disactivation, the shorter is the life-time of the state of excitation.

Because of the same time behaviour of \(C_g(t)\) as well as \(I_p(t)\), (11) can also be formulated as follows:

\[
I_p(t) = I_p(t = 0) \exp \{- K_p t\} = I_p(t = 0) \exp \{- t/\tau_D\}
\]

In case of using a “slow” silicon receiver PEE 103 (cf. section laser-stimulated fluorimetry) the value is an integration over the whole fluorescence impulse:

\[
\int_0^{\tau_D} \frac{r_D}{0} I_p(t) dt = \int_0^{\tau_D} [I_p(t = 0) \exp \{- K_p t\} dt = 0.63 I_p(t = 0) \tau_D
\]

i.e. the measured fluorescence \(\int_0^{\tau_D} I_p(t) dt\) is dependent on the life-time \(\tau_D\) of the disactivation process.

Considered under another aspect, equation (9) yields the following: Parameter \(A\) comprises, inter alia, the inverse value of the fluorescence quantum efficiency \(Q_F^{-1}\). \(Q_p\) is directly proportional to the observed decay time \(\tau_D\), i.e. \(A \sim \tau_D^{-1}\). (Remark: \(\tau_D\) is equal to the “real” life-time of radiation only if \(K_i < K_p\))

The value of \(\tau_D\) may vary for different samples with equal concentrations of dissolved organics because of different disactivation processes. This would falsly suggest different concentrations. In order to avoid this error, the fluorescence (measured with the receiver PEE 103) has to be “corrected” by a factor which should be introduced here as a relative value:

\[
F_r = \tau_{\text{max}} / \tau_D
\]

with \(\tau_{\text{max}}\) being the highest decay time measured. \(\tau_{\text{max}}\) and \(\tau_D\) were determined by means of (14) in the range of 500 ... 600 nm (raw sample).
Fig. 5. Chemical oxygen demand (COD₆₇) in dependence on \( A \cdot (F_r \cdot I_p(337/538)R)^4 \cdot \exp (B \cdot I_p(337/658)R) \) (laser impulse spectroscopy).

Abb. 5. Chemischer Sauerstoffbedarf (CSB₆₇) in Abhängigkeit von \( A \cdot (F_r \cdot I_p(337/538)R)^4 \cdot \exp (B \cdot I_p(337/658)R) \) (Laserimpulsspektroskopie)

Table 6. Results of the regression analysis between the “life-time-corrected” intensity of laser-induced fluorescence and COD₆₇. UV₂₅₄

Tabelle 6. Ergebnisse der Regressionsanalyse zwischen der „lebensdauer-korrigierten“ Intensität der laser-erzeugten Fluoreszenz und CSB₆₇, UV₂₅₄ (Gerät: Laserfluorimeter (Empfänger PEE 103 und PDE 103))

<table>
<thead>
<tr>
<th>regression equation</th>
<th>( r^2 )</th>
<th>( n )</th>
<th>range mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD₆₇ = 1.53 ( (F_r \cdot I_p(337, 538)R)^{0.42} \cdot \exp (0.043 \cdot I_p(337, 658)R) )</td>
<td>0.80</td>
<td>18</td>
<td>12.5 ... 20.4</td>
</tr>
<tr>
<td>UV₂₅₄ = 0.064 ( (F_r \cdot I_p(337, 586)R)^{0.21} \cdot \exp (0.02 \cdot I_p(337, 658)R) )</td>
<td>0.67</td>
<td>40</td>
<td>0.12 ... 0.16</td>
</tr>
</tbody>
</table>

Figure 5 illustrates the result of such a “correction” by means of the factor (16) for the correlation between COD₆₇ and laser-induced fluorescence of the raw sample according to formula (9). The performance index is 0.80 (Tab. 6). Without "F_r correction" \( r^2 \) for this correlation was 0.72. This may be an indication that the inclusion of the life-time for the determination of the total dissolved organic load (COD) from fluorescence data yields a higher accuracy. Similar "F_r corrections" with respect to UV₂₅₄ yielded only little or no increase in \( r^2 \).
Conclusions

(1) The applicability of fluorescence algorithms to the determination of the total dissolved organic load should be extended in further experiments to higher and lower concentrations.
(2) The possible influence of different types of water bodies on these fluorescence algorithms should be examined.
(3) Fundamentally, the statistical certainty should be increased through additional measurements.
(4) More theoretical considerations on fluorescence should be made which take account of the self-absorption of the total dissolved organics to be determined and of possible non-linearity in case of mean and higher concentrations as well as of “reduced fluorescence” due to a weakening of the stimulated radiation on the pathway through the cuvette.

References


GORDON, H. R., D. K. CLARK, J. W. BROWN, O. B. BROWN, R. H. EVANS and W. W. BROENKOW:


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