Correlations between COD, DOC, UV$_{254}$ and Fluorescence of Inland Waters Measured in the Laboratory

Kl.-H. Mittenzwey

Gesellschaft für Meß und Systemtechnik mbH, IGZ Rudower Chaussee 5, D12489 Berlin.
(telephone: (030) 63926238, telefax: (030) 63926245)

R. Reuter

Carl von Ossietzky University, Department of Physics, D26111 Oldenburg.
telephone: (0441) 7983522, telefax: (0441) 7983201

ABSTRACT

Experiments were carried out in the laboratory for investigation of correlations between organic load and fluorescence which can be applied to lidar remote sensing of inland waters. Spectral and time-resolved fluorescence of natural water samples generated by a nitrogen laser were measured in the range of 400-720nm. Synchronously, the sum parameters COD, DOC, and UV-absorption at 254nm of filtered samples were determined for characterization of the organic load. We investigated 6 different inland waters: Some waters around Berlin (lakes, rivers and little runs), Mittelland Canal, Elbe-Havel Canal and Elde.

In order to analyze correlations between organic load and fluorescence, regression calculations were performed. In a first step we used a simple quadratic fit. In a second step an approach was used, which is based on an optical model established for eutrophic waters around Berlin.

Different waters cause different relations between sum parameters and fluorescence. By means of the optical model the correlation coefficient r increases. Principally, it seems useful for the remote detection of yellow substances to know the behaviour of r(λ) for different sum parameters.

1. INTRODUCTION

Surface waters are able to fluoresce in the optical wavelength range, especially in the blue-green and red when excited with ultraviolet radiation. This is the basis for a fluorometric monitoring of some water quality parameters by Lidar. In some cases dissolved yellow substances (YS) are of special interest. YS is the sea major component of dissolved organic carbon, consisting mainly of lignin (L) and humic compounds (HC). L and HC show strong absorption in the blue and especially in the UV part of the spectrum and are able to fluoresce in a relatively wide wavelength range, (DUURSMA, GOERS, LAANE, MÄKINEN)

HC result from the decomposition of animal and vegetable organisms. Thus, HC should always occur in natural waters. HC play an important role in the water quality management, they can adsorb heavy metals and polycyclic aromatics, they can disturb the treatment of drinking water. (FRIMMEL, LIENIG, STROBEL)

Lignins are substances found in wood in amounts of up to 35%. They are primary substances for formation of humic compounds. Especially, we can find lignin or lignin-derivates in rivers, which travel through swamps and moist regions. So-called lignin-sulfonates occur in the waste water of paper industries. They are also important with respect to water quality, e.g. because of their ability to adsorb polycyclic aromatics. (KUKKONEN)

For simplification in our discussion we denote these substances as YS instead of L or HC.

Although YS have been investigated in detail, we think that there are lacks concerning the correlations between YS and fluorescence of natural inland waters, which could be used for a quantitative estimation of YS. We want to analyze how we can use relations between different sum parameters, e.g. COD, DOC, and UV$_{254}$, and fluorescence for water quality monitoring and under which conditions YS can be detected by simple fluorescence measurements.

According to these goals experiments in the laboratory and some statistical calculations were done for some inland waters in Germany.

2. SHORT DESCRIPTION OF WATERS INVESTI-GATED

We investigated six surface waters at different locations in Germany, which can be seen in Fig.1.
Tab.1 gives some information about the waters.

and to the spectral sensitivity of the photodiode. For this purpose spectral correction factors were determined on the basis of a known spectrum recorded with our equipment. Further, we determined the decay time of the blue-green fluorescence corrected with respect to the broadening of the decay function by the equipment. The decay time was

Table 1: Some information about waters investigated. n-number of samples.

WATER	COD mg/l	DOC mg/l	UV$_{254}$	n	Type
1	12.5-20.5			38	6 shallow lakes connected, 80km[**].
2	0.7-11.3[*]			63	2 little runs not connected in the same area, 20km[**].
3	2.5-14.2[*]			22	little run, 50km[**].
4	19.4-70.2	7.4-23.5	0.108-0.710	17	canal, 80km[**].
5	21.8-60.5	7.5-26.7	0.133-0.186	14	canal, 30km[**].
6	<15.0-55.1	3.0-18.0	0.015-0.280	15	little river, 70km[**]

[*] on the basis of potassium-permanganate.
[**] distance at which sampling was performed.

1 Spree-Water: Sept./Oct.88 and Nov./Dec. 89.
2 Dranse/Fließgraben: May-Aug. 90.
3 Mühlenfließ: May 91.
4 Mittelland-Canal: May 91.
5 ElbeHavel-Canal: May 91 and Dec.91.
6 Elde: Oct. 91.

The Chl-a concentration ranges from about 5 to 150µg/l.

3. EXPERIMENTS AND METHODS

A nitrogen laser beam (1) with a power of 50kW and a pulse length of 0.5ns emitting at 337nm is directed onto the cuvette (7) (Fig.2). The fluorescence signal of water samples is measured at an angle of 90°. The lenses (10,11) focus the signal onto a photodiode (13). A wheel (12) with 16 interference filters at selected wavelengths in a range of 400-750nm yields the spectral fluorescence. The bandwidths of the filters are around 10-15nm. Because the raman signal of the water occurs at 380nm raman contributions in the fluorescence spectra can be excluded. The mirrors (8,9) increase the signal-to-noise ratio. Plates (3,4) reflect a small part of the laser intensity to a reference photodiode (5) and a trigger photodiode (6). A boxcar integrator controls the measurement of spectral and time-resolved fluorescence. We performed a spectral correction of the measured fluorescence with respect to the spectral transmission of the optical part

determined in the blue (360-460nm) and in the green (500-600nm) spectral range.
The fluorescence was measured with natural and in some cases with filtered samples.

Sum parameters as dissolved organic carbon (DOC), chemical oxygen demand (COD$_{Cr}$ on the basis of potassium bichromate; in few cases potassium permanganate COD$_{Mn}$), and ultraviolet absorption (UV$_{254}$) were determined on filtered samples.
Filtration was performed with glass-fibre paper with pore sizes of 2-5µm for COD, and with membrane filters with pore sizes of 0.4µm for DOC and UV$_{254}$. The samples were cooled at around 10°C in the dark and analysed around 4-24 hours after sampling.

Synchronously, absorbances were measured, ranging from 0.08 to 1.5 at 337nm. In most cases the values fall in a range of 0.1 to 0.6.

In order to analyze correlations between the sum parameters and fluorescence, regression calculations were performed. In a first step we used a quadratic fit considering possible nonlinear effects.
In a second step an approach was used, which is based on an optical model established for eutrophic waters around Berlin.
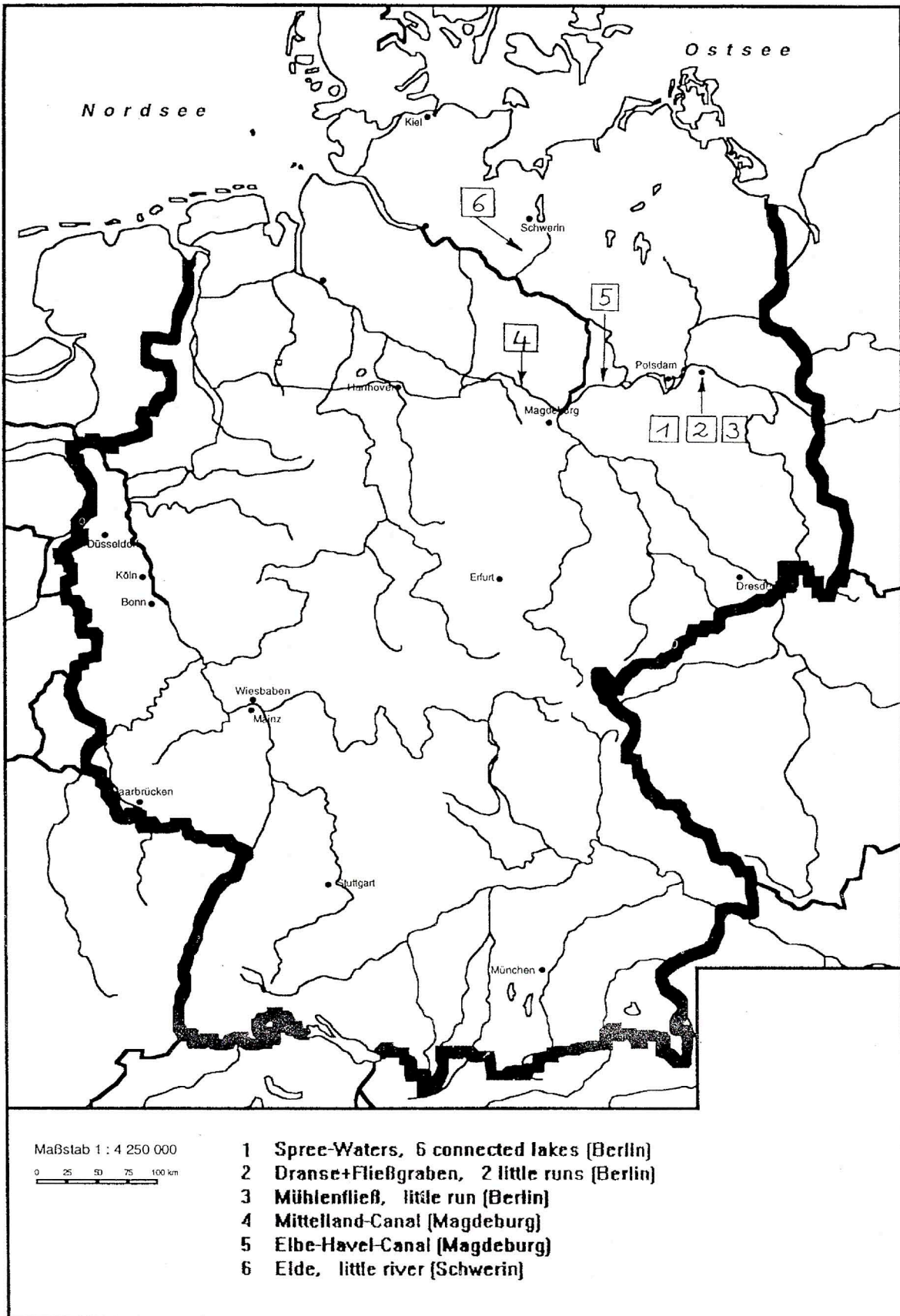Principally, we assume that the fluorescence intensity vary linearly with the laser power. It seems resonable, because

Fig. 1 - Location of investigated waters.

the laser power is 50kW and the pulse length 0.5ns leading to a photon number of around 10^{14}. The radiated volume of the sample is $0.5 \times 1 \times 1 cm^3$. Thus, the probability of nonlinear effects due to high photon numbers is relatively low.

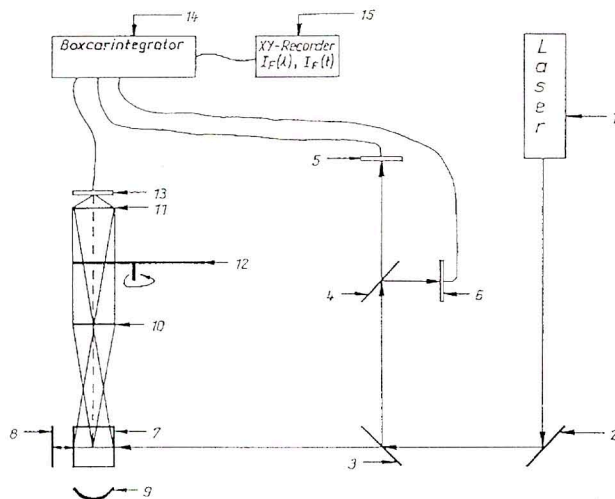Fig. 2 - Laser equipment.

4. RESULTS

4.1 Typical spectra

Fig.3 shows some typical spectra of the natural fluorescence. Principially, two different maxima can be seen. The higher blue maxima is dominated by dissolved YS in many cases. Of course, other substances like polycyclic aromatics, phenols etc. are also able to fluoresce. But because of their low concentration of ppb in contrast to YS concentration falling in the ppm range, we think that their influence to the natural fluorescence is relatively weak.

The lower red maximum is caused by phytoplankton.

The fluorescence maxima of the waters investigated are as follows (arb. units):

Spree-water: 11-23 at 448nm and 0.7-3.8 at 687nm.
Dranse/Fließgraben: 9-35 at 448nm and 0.3-2 at 687nm.
Mühlenfließ: 11-62 at 448nm and 0.8-4 at 687nm.
Mittelland-Canal: 10-71 at 448nm and 1.2-3.3 at 687nm.
Elbe-Havel-Canal: 12-35 at 448nm and 0.5-3.3 at 687nm.
Elde: 6-30 at 448nm and 0.4-1 at 687nm.

The fluorescence decay time ranges from about 2.4ns to 5.5ns.

The lower part of Fig.3 shows the fluorescence of a natural sample in comparison to its filtrate taken from the lake Müggelsee in Berlin. The filtered one shows a lower fluorescence at red wavelengths, and in contrast to this a higher fluorescence at blue-green wavelengths. Because the seston of lake Müggelsee is dominated by algae, this phenomenon is obviously caused by the absence of algae.

4.2 Regression Analyses

4.2.1 Quadratic fit

We perform a regression on the basis of a simple quadratic fit between the sum parameters COD, DOC, UV_{254} and the natural fluorescence in the range of 400-720nm. We want to analyse the squared correlation coefficient r^2 in dependence on the wavelengths. Fig.4 shows the results for the six waters investigated with respect to COD-values. According to the structure of $r^2(\lambda)$ four different classes can be defined:

Class 1: Lower values at short wavelengths and higher values at longer wavelengths.
Class 2: Higher values at short wavelengths and lower values at longer wavelengths.
Class 3: Higher values at short wavelengths, lower ones in the middle range, and higher values at longer wavelengths.
Class 4: Small values in the full spectral range.

Class 1 represents the waters Müggelsee, Dahme, Seddinsee and others, which we call Spree-waters. Because we found high Chlorophyll concentration of around 20-150µg/l as well as correlations of good quality between red fluorescence and chlorophyll a, we conclude that the red fluorescence is dominated by algae. Thus, the COD (of the filtered samples!) should be influenced by substances, which are covariant to the red fluorescence of algae. Such substances could be algae-borne or algae-covariant YS, carbon hydrates, amino- and fatty acids. r^2(red) falls in the medium range (0.5-0.6). A reason could be, that there are substances influencing the COD, which are not covariant to the red algae-fluorescence. The very low r^2-values in the blue-green range can be caused by the above discussed influence of phytoplankton on the YS fluorescence (Fig.3-below) and/or also by substances, which influence the COD but not the blue-green fluorescence.

According to this class 1-waters could be called "algae-controlled waters".

Class 2 represents the waters Dranse and Fließgraben, Neuenhagener Mühlenfließ, and Mittelland-Canal. The COD seems to be dominated by substances, e.g. YS, which are covariant to the natural fluorescence in the blue-green-orange range. The r^2-values in the red are relatively small.
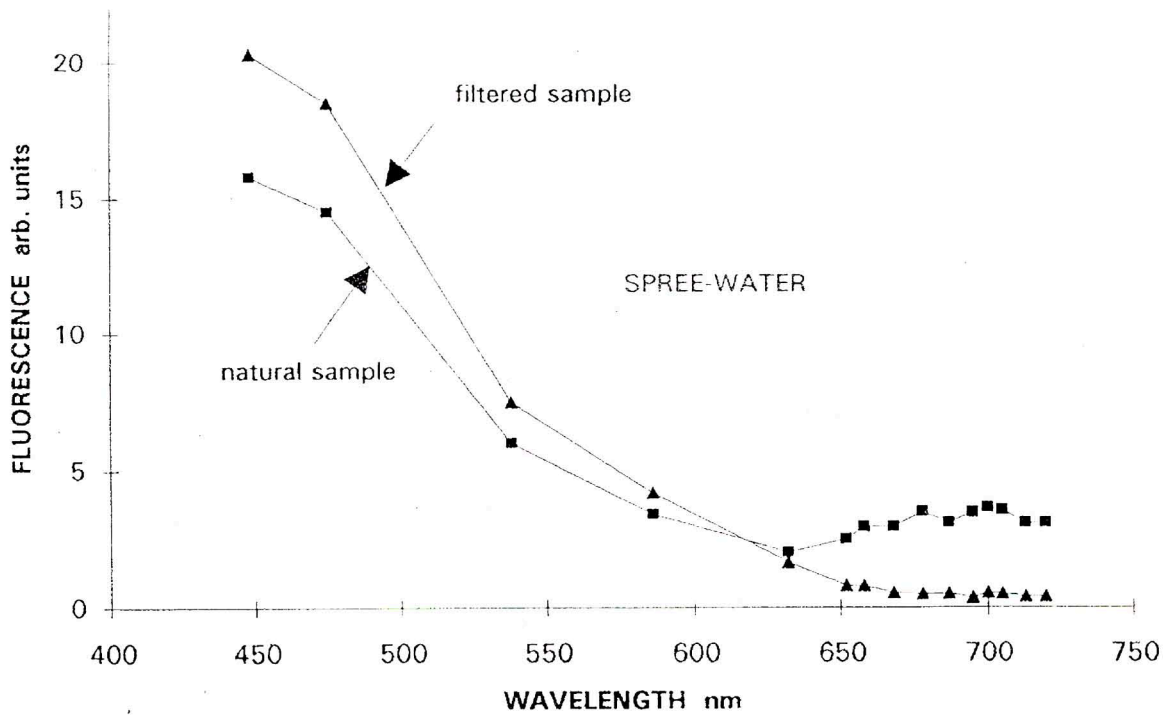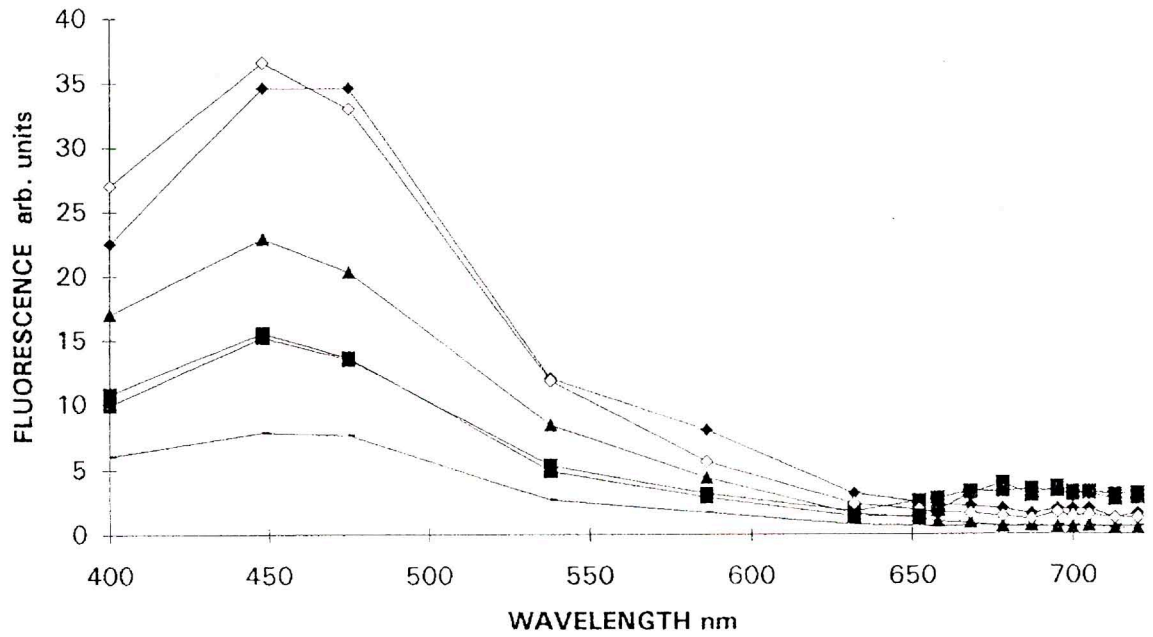
TYPICAL SPECTRA

Fig. 3 - Above: Some spectral fluorescence of the six investigated waters. Below: Spectral fluorescence of natural sample and the filtered one.
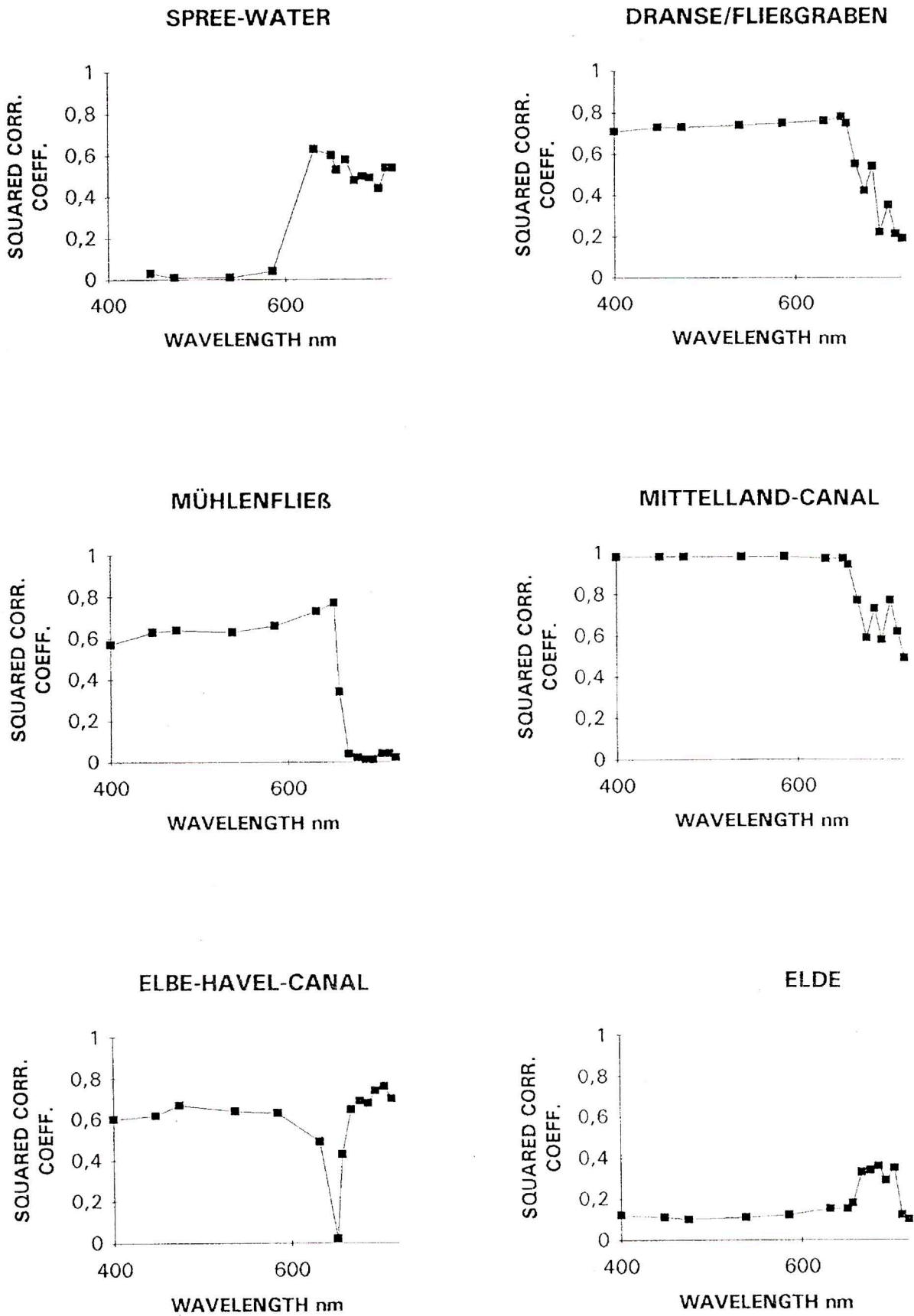
Fig. 4 - Squared correlation coefficient as a function of the wavelength for the investigated waters on the basis of a quadratic fit concerning COD.

A reason for this could be, that COD-substances, which are covariant to the algae fluorescence are of lower influence. Thus, we think, that the COD is dominated by YS, which are not covariant to algae. This is in contrast to class 1-waters. An influence of algae to the blue-green fluorescence, as it could be seen for class 1-waters, cannot be observed. According to this class-2-waters are called "YS-controlled waters".

Class 3 is characterized by two different maxima in the blue-green range and in the red range, which can be seen for the Elbe-Havel-Canal. It is interesting to note that the fluorescence in the blue-green range decreases if the COD increases. We can not yet give an explanation for this phenomenon. The correlation between COD and red fluorescence can be caused by substances such as algae-borne YS, carbon hydrates, amino- and fatty acids. In such a case it could be comparable with class 1-waters.

Class 4 is characterized by low r^2-values in the full spectral range. A reasonable interpretation is not possible at the moment.

Now we want to discuss the r^2-functions with respect to COD, DOC, and UV$_{254}$. Fig.5 shows them for Mittelland-Canal (MLC), Elde (E), and Elbe-Havel-Canal (EHC).

MLC: r^2(λ)-functions show similar behaviour for COD, DOC, and UV$_{254}$. This means, that there are high correlations between these parameters. The substances which cause the sum parameters and the fluorescence in the blue-green-orange range seem to be the same. COD, DOC, and UV$_{254}$ represent the fluorescent matter in a good quality. According to the above discussion the dominant substance is YS. COD, DOC, and UV$_{254}$ as well as the fluorescence will be essentially influenced by YS.

E: The UV$_{254}$ seems to be the best parameter to represent the fluorescence in the blue-green-orange range. The absorption of E should be controlled by fluorescent matter. COD is not able to represent the fluorescence.

EHC: In contrast to E and MLC, DOC is the best parameter. Because of the inverse function of DOC=f(I$_F$) in the blue-green-orange range we cannot discuss the EHC in detail at present.
UV$_{254}$ is not able to represent the fluorescence.

4.2.2 Model-based fit

The calculations on the basis of the quadratic fit yield only

medium or small r^2-values for Spree-waters. To analyze this further we developed a fluorescence model for these waters.

We assume, that YS in Spree-waters are dominated by dissolved humic compounds DHC. We consider a sample with phytoplankton and DHC, which should be optically dominant. For the purpose of DHC detection we use only the fluorescence in the blue-green part of the spectrum, where DHC exhibit a fluorescence maximum. Phyto plankton does not show any fluorescence in this region.
After calculation and simplification we get (MITTENZWEY et al.):

$$C_{DHC} \sim COD_{Cr} = A * I_F \, (blue - green)^B * e^{C I_F \, (red)} \qquad (1)$$

where A, B, and C are constants; I$_F$ is the fluorescence intensity. The COD is used as a measure for DHC.
The exponential term stands for the correction of the disturbing influence of phytoplankton on the blue-green fluorescence (see Fig. 3 below). Principally, the blue-green fluorescence of DHC decreases if the phytoplankton content increases. This should be caused by a "shadowing" of DHC by phytoplankton at the excitation wavelength as well as by inner absorption of the DHC-fluorescence by phytoplankton. For phytoplankton concentrations of 0 (red algae fluorescence = 0) the blue-green fluorescence is a direct measure for C$_{DHC}$.
A weak nonlinear behaviour of the DHC fluorescence due to self-absorption effects is expressed by the constant B. According to the theory B is not much greater than 1 in the case of Spree-waters.
Using I$_F$(blue-green)=F*I$_F$(538nm) and I$_F$(red)=I$_F$(658nm)/I$_F$(632) the regression analysis yields the best correlation. r^2 increases from around 0.6 up to around 0.85.
By using the ratio I$_F$(658)/I$_F$(632) a possible disturbing influence of DHC fluorescence in the red can be reduced.
The factor F is the ratio of τ_{max}:τ. τ and τ_{max} are the measured and maximal decay time of the green fluorescence. In our experiments τ ranges from 2.4 to 5.2ns. An explanation with respect to F can be given as follows: The measured decay time is proportional to fluorescence quantum efficiency Q$_F$ (τ=τ_n*Q$_F$ with τ_n = natural decay of fluorescence). The faster the fluorescence decay or the shorter the decay time τ, the lower the quantum efficiency. It seems to be possible that DHC molecules interact with their environment, e.g. with metal- and H$^+$-ions, which can lead to energy transfer processes causing a change of fluorescence (e.g. quenching). Thus, the fluorescence intensity can vary, although the concentration remains constant. We think, that the parameter F seems to be able to take this phenomenon into account.
It should be noted, however, we did not consider possible

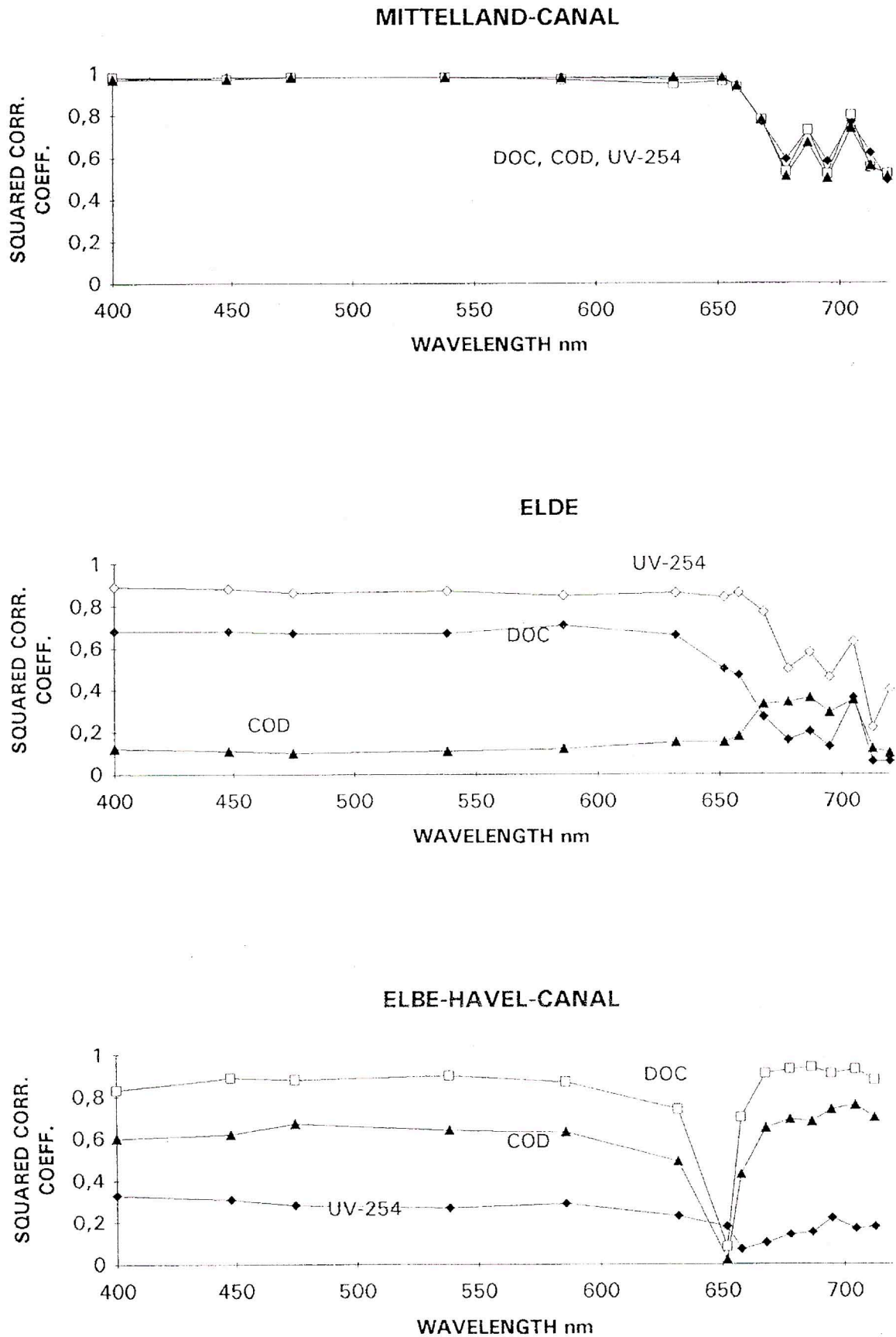## MITTELLAND-CANAL

ELDE

ELBE-HAVEL-CANAL

Fig. 5 - Squared correlation coefficient as a function of the wavelength for some investigated waters on the basis of a quadratic fit concerning COD, DOC, and UV$_{254}$.

algae-borne substances, e.g. fatty acids and carbon hydrates as mentioned in 4.2.1 (class 1). Such substances can influence the COD, but not the fluorescence. If there is really such an influence, then the exponential term stands not only for a disturbing effect of algae, but possibly also for algae-borne substances.

CONCLUSION

On the basis of the results of r^2(λ) with respect to COD (quadratic fit) it seems that surface waters can cause different spectral r^2 values. It is possible to classify "algae-controlled waters" (class 1) and "YS-controlled waters" (class 2).

For such waters an estimation of YS could be possible by fluorescence measurements: e.g. blue-green fluorescence for class 2-waters, and modelbased fluorescence (green and red) according to Equ.1 for class 1-waters.

On the basis of the results of r^2(λ) with respect to COD, DOC, and UV$_{254}$ (quadratic fit) different waters can cause different relations between sum parameters and fluorescence. The best sum parameters for representing the fluorescence are:

Mittelland-Canal: COD, DOC, and UV$_{254}$.

Elde: UV$_{254}$.

Elbe-Havel-Canal: DOC.

Because the sum parameters are based on various methods (COD: chemical oxidation, DOC: burning, UV$_{254}$: absorption) we conclude that the waters could be of different nature. This means, for example, the fluorescent matter of Elde is mainly "UV-controlled"; in contrast to this, the fluorescent matter of Mittelland-Canal is "COD*DOC*UV-controlled".

Knowing the relations between different sum parameters and fluorescence allows the choise of an appropriate sum parameter for calibrating the fluorimetric YS estimation.

The effort of calibrations can be decreased if the relations discussed above show a certain longtime stability.

Principally, for the purpose of remote sensing of YS it seems useful to know the behaviour of r^2(λ) at different sum parameters. According to this, appropriate fluorescence and sum parameter for calibration purposes could be chosen. In our opinion the r^2-function should be a part of ground-truth-measurements or for the calibration of remote sensing methods.

A number of problems have to be solved, e.g.:
– What are the reasons for an inverse function DOC(I$_F$) in the blue-green-orange range for Elbe-Havel-Canal?
– Why are there relatively small r^2-values in the full spectral range concerning the COD for the river Elde?
– Does a change of the fluorescence quantum yield disturb the fluorimetric detection and how can it be taken into account?
– Principally, further experiments are necessary, because there are only first results for verification purposes.

ACKNOWLEDGEMENTS

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