

## SPECTRAL CHARACTERIZATION OF TERRESTRIAL AND COASTAL WATERS IN ESTONIA

S. BABICHENKO, A. LEEBEN  
L. PORYVKINA, E. RULL  
S. LAPIMAA

Tallinn University of Educational Sciences,  
Institute of Ecology  
2 Kevade St., Tallinn  
10137 Estonia

*The Spectral Fluorescent Signatures (SFS) technology has been applied to investigate the seasonal and annual variability of dissolved organic matter (DOM), dissolved organic carbon (DOC), phytoplankton and organic pollution in Estonian rivers and coastal zone. Statistical analysis of data collected in 1996–1998 allowed to perform the classification of natural waters by using DOM/DOC ratio as a characteristic parameter.*

### Introduction

The quality of natural waters in Estonia varies in the coastal zone as well as in different land areas. Anthropogeneous load to the water environment causes an increased amount of technogeneous organics in the sea and river waters. It is known that contamination of waters by phenolic compounds is typical for some rivers in the Estonian North-East; oil pollution is probable to be detected in coastal zone, especially in harbor areas [1, 2]. Chemical pollution can cause the exceptional growth of phytoplankton as well as the changes of taxonomic composition of phytoplankton community. The living phytoplankton is well known as an indicator of the ecological status of water environment [3]. Among the common indices determining the quality of natural waters, the content and composition of dissolved organic matter (DOM) are the important characteristics [4–6]. DOM is considered the most inert part of organic matter and therefore reflects the inherent properties of natural waters. It is originated in a result of a long-term biochemical activity of aquatic ecosystem and is influenced also by the organic materials coming from the surrounding land areas. The technogeneous organic substances in water environment arise from the industrial and agriculture activity and are

superimposed on the background of natural organic matter forming the complex conglomerate of organic materials. The knowledge of this background and its possible variations helps much in the analysis of water quality changes.

The method of Spectral Fluorescent Signatures (SFS) has been developed to carry out the proximate diagnostics of organic compounds in water environment [7]. In general case the SFS is the sum total of the emission spectra of an object at different excitations. It is recorded as a matrix of fluorescent intensity in co-ordinates of excitation and emission wavelengths. The size of spectral window is defined according to diagnostic task. UV emission/excitation matrix allows one to analyze DOM and most of technogenic organic compounds. The spectral characteristics of DOM are defined by its highly fluorescent humic substance (HS) portion [8]. Due to various combinations of HS in different water areas the spectral shapes of excitation and emission spectra can vary causing the variability in SFS patterns. It provides the possibility to use SFS in DOM analysis and, therefore, in characterization of natural waters. Such characterization has been performed earlier for sea waters [9]. The results of numerous field studies demonstrated that DOM composition is subjected to seasonal variability and influenced by external factors like temperature and solar radiation [10, 11]. Extension of SFS spectral window to visible range makes it possible to include the phytoplankton into analysis. As its fluorescence properties are connected primarily with the composition of photosynthetic pigments in cells, SFS method is sensitive to the variability of pigment composition [12, 13]. The information on suspended matter (SM) can be also derived from measured SFS, as the emission spectra always contain the scattering of excitation light, and part of it is due to suspended solids in water.

The main concept of the SFS method assumes that the water status can be generally characterized by the normal state and deviation from it. In these definitions the normal state is characterized by specific spectral shape and intensity of SFS, statistically stable, peculiar to the certain water area, and varying in definite margins. The deviation is treated as any observable variations in spectral patterns of SFS higher than ones for the normal state are. This approach was effectively applied in various applications to detect and identify organic compounds contaminating industrial and wastewater [14–16]. In such application the normal state of water and possible deviations from the normal state are defined mainly by technological processes or purification efficiency. The definition of the normal state is more complicated in the analysis of natural waters due to complex processes in water ecosystem and number of environmental factors influencing it [17]. The goal of the present work was to study the characterization of Estonian terrestrial and coastal waters basing on seasonal and annual variability of DOM content, phytoplankton and chemical pollution and phytoplankton by using SFS approach.

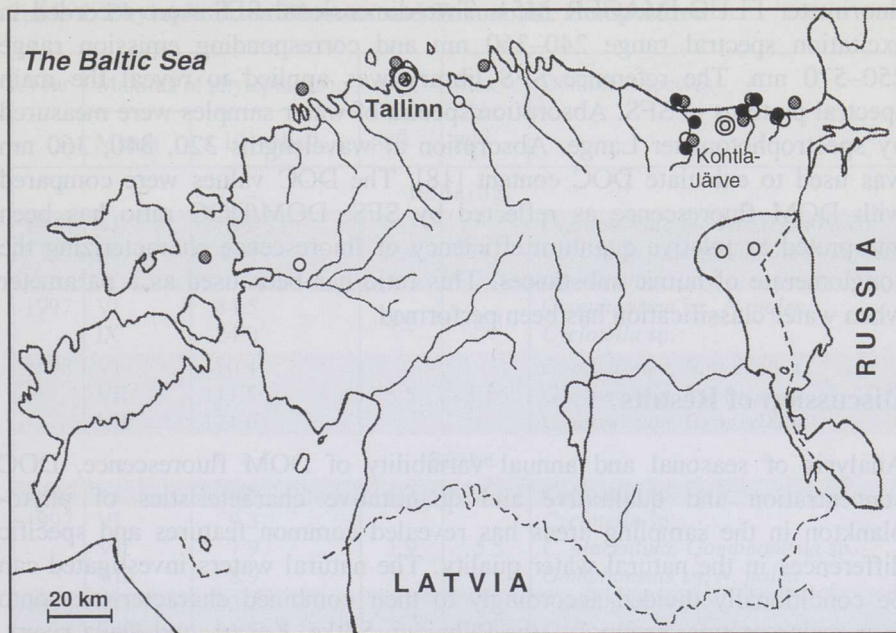


Fig. 1. Location of sampling points. Legend: white circles – 1996, gray circles – 1997, black circles – 1998

## Materials and Methods

The water samples were collected in 1996–1998 in small rivers of North-East (Kohtla, Purtse, Pühajõgi, Sõtke) and West (Kasari, Keila) land areas and in the sea coastal zone (Tallinn Central Bay, Pirita, Toila). In 1997, the sea water samples were collected also at Sillamäe, Kolga, Paldiski and Väinameri. Location of sampling points is shown in Fig. 1. Every year sampling was made in a period from May to September with averaged time interval of ten days. Water samples were measured in parallel by different techniques to analyse the content of DOM, organic pollution (OP), SM, DOC, phytoplankton taxonomic composition and pigment (chlorophyll *a*, *b*, *c*, phaeopigments) concentrations.

Phytoplankton abundance was investigated by recording excitation spectra of fluorescence with FLUO-IMAGER M32B. The spectra were measured in excitation range 400–640 nm at the emission wavelength 680 nm. Use of spectral library of accessory pigments [13] derived the fluorescence intensities corresponding to different pigments of phytoplankton. Standard extraction procedure with following absorption measurements was performed for each sample to get the concentrations of Chl *a*, *b*, *c* and phaeopigments. The taxonomic composition of phytoplankton and biomass were analyzed by microscope.

The values of DOM, OP, and SM were analyzed by the SFS method. The water samples without pre-treatment were measured by using spectro-

fluorimeter FLUO-IMAGER M51. Two-dimensional SFS were recorded in excitation spectral range 240–360 nm and corresponding emission range 250–570 nm. The reference SFS library was applied to reveal the main spectral patterns in SFS. Absorption spectra of water samples were measured by spectrophotometer Lange. Absorption at wavelengths 320, 340, 360 nm was used to calculate DOC content [18]. The DOC values were compared with DOM fluorescence as reflected by SFS. DOM/DOC ratio has been interpreted as relative quantum efficiency of fluorescence characterizing the conglomerate of humic substances. This ratio has been used as a parameter when water classification has been performed.

## Discussion of Results

Analysis of seasonal and annual variability of DOM fluorescence, DOC concentration and qualitative and quantitative characteristics of phytoplankton in the sampling areas has revealed common features and specific differences in the natural water quality. The natural waters investigated can be conditionally divided accordingly to their combined characteristics onto four major groups: group 1 – the Pühajõgi, Sõtke, Kasari, and Keila rivers, group 2 – the Purtse River and its mouth, group 3 – the Kohtla River, group 4 – sea waters in the coastal zone.

The weather conditions obviously influenced the characteristics of natural waters. Indeed, the summer of 1998 was the rainiest one in the period of observations, and the increase in DOC and DOM was observed in July in all rivers. It was probably due to intensive inflow of organic materials from river floodplain marginal areas, occurred as a result of decomposition of terrestrial and higher aquatic plants. Summer phytoplankton development was more intensive this year than in two others (Table). Figure 2 shows selected data of DOC, DOM and phytoplankton dynamics in 1996–1998. Basing on fluorescent features of different waters, the SFS reflecting the normal state in every group were defined by single SFS averaging over the period of investigation. Averaged spectral fluorescent signatures and their seasonal variations are shown in Fig. 3. DOM is characterized by wide spectral structure with excitation/emission maximums at 350/450 nm.

Additional spectral structures in SFS are mainly due to technogeneous organic materials. High- and low-molecular fractions of DOM are revealed in changes of the SFS shape. It is known that HS molecules with higher molecular weight cause red shift in excitation and emission spectra and typically lower quantum yield of fluorescence at the same concentration of DOC [19]. Low-molecular fractions of HS have fluorescence at shorter wavelengths. Basing on this feature one can see that waters of groups 1 and 2 (Fig. 3,I and II) contain HS with higher molecular fractions than coastal waters (group 4, Fig. 3,IV). Spectral fluorescent signatures for group 3 contain additional structures typical for spectral patterns of oil and phenol pollution.

Table 1. Phytoplankton Biomass and Taxonomic Composition

Year	Maxima of phytoplankton		Avg Chl <i>a</i> , µg/l	Max Chl <i>a</i> , µg/l	Dominant species
	Month	× 10 <sup>3</sup> cells/l			
Pühajõgi					
1996	VI	173.2	7.4	14.7	<i>Diatoma vulgare</i> , <i>Nitzschia palea</i> <i>Cocconeis placentula</i> , <i>Gomphonema olivaceum</i>
	IX	40.4			
1997	VI	84.5	4.2	8.3	<i>Gomphonema</i> sp., <i>N. palea</i> <i>Cyclotella</i> sp.
	IX	24.0			
1998	VI	110.4	5.5	12.5	<i>G. olivaceum</i> , <i>N. paleacea</i> <i>G. olivaceum</i> , <i>N. paleacea</i> <i>G. olivaceum</i> , <i>G. parvulum</i>
	VII	117.5			
	VII	121.0			
Sõtke					
1996	VI	36.5	4.7	14.0	<i>Cyclotella</i> sp.
1997	VI	9.3	1.9	5.5	<i>Cyclotella</i> sp. <i>C. placentula</i> , <i>Gomphonema</i> sp. <i>Gomphonema</i> sp., <i>N. palea</i>
	VII	7.9			
	VIII	8.9			
1998	VI	43.2	1.9	3.8	<i>Achnanthes</i> sp. <i>Cyclotella</i> sp., <i>C. placentula</i>
	VII	31.5			
Kasari					
1996	VIII	14.3	3.9	8.0	<i>Cyclotella</i> sp. <i>Cyclotella</i> sp.
	IX	14.1			
Keila					
1996	V	23.0	3.9	11.4	<i>Cyclotella</i> sp.
Purtse					
1996	VI	29.2	3.4	12.0	<i>Tabellaria fenestrata</i> , <i>Synedra ulna</i>
1997	VI	8.8	1.6	2.8	<i>N. palea</i> , <i>Nitzschia acicularis</i>
	VI	63.3			
1998	VI	51.0	2.0	4.2	<i>Achnanthes</i> sp., <i>N. paleacea</i> <i>Achnanthes</i> sp.
	VII	51.0			
Purtse mouth					
1997	VI	195.0	4.8	8.9	<i>N. palea</i> , <i>N. acicularis</i> , <i>D. vulgare</i> <i>N. palea</i> , <i>Gomphonema constrictum</i>
	VII	148.0			
1998	VI	521.1	13.7	55.4	<i>N. palea</i> , <i>Diatoma elongatum</i> <i>Microcystis</i> sp.
	IX	612.8			
Kohtla					
1998	VII	62.7	3.9	11.1	<i>Cyclotella</i> sp. <i>Phormidium</i> sp., <i>Achnanthes</i> sp.
	VIII	79.9			
Toila					
1997	VI	369.5	11.4	30.5	<i>Gomphonema</i> sp. <i>Gomphonema</i> sp.
	VII	279.0			
1998	VIII	979.9	16.5	27.7	<i>Microcystis</i> sp.
Pirita					
1997	V	435.0	4.5	11.1	<i>Synura</i> sp. <i>Gomphonema</i> sp., <i>Anabaena</i> sp.
	VII	117.3			

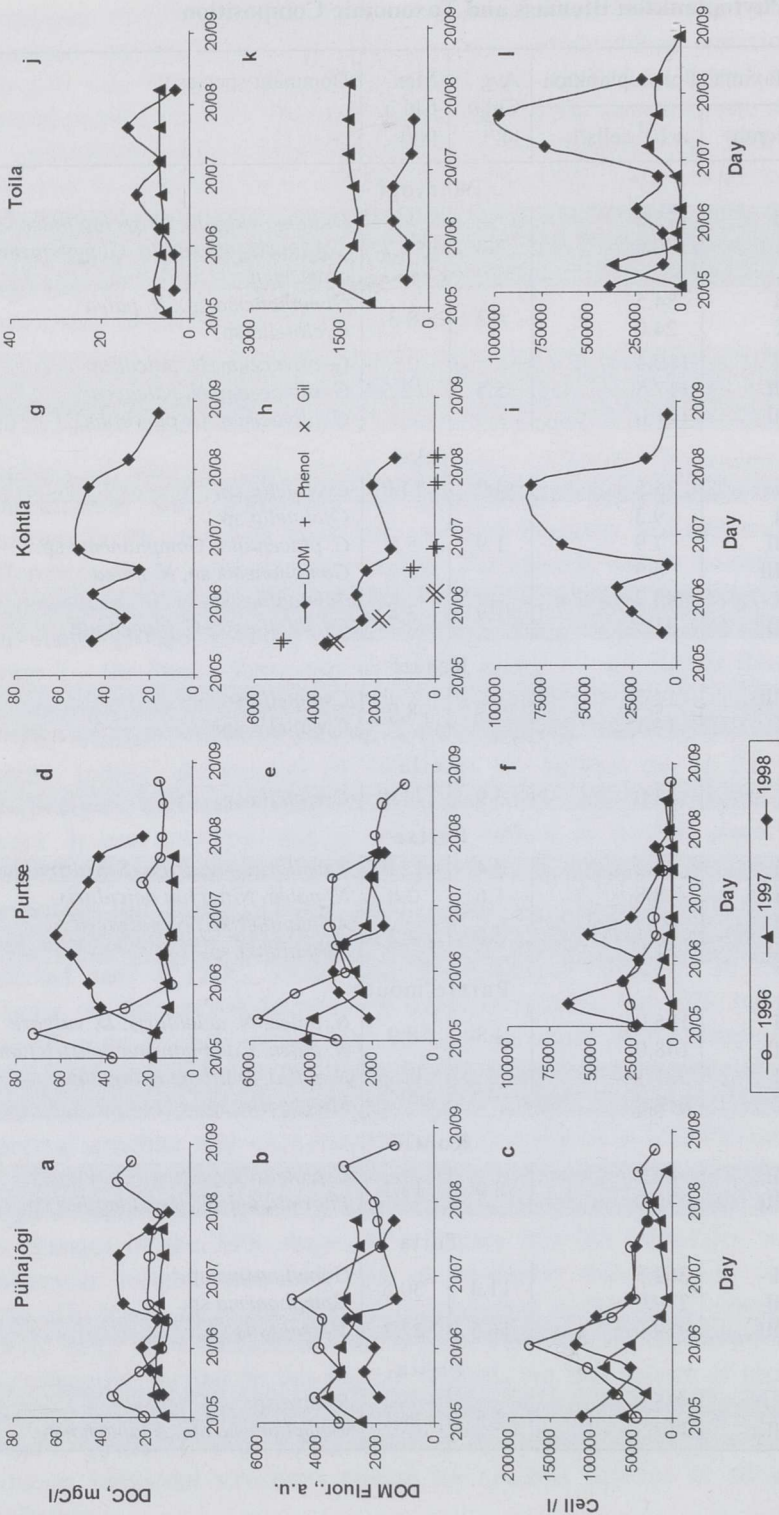


Fig. 2. Dynamics of DOC, DOM and phytoplankton in 1996–1998 for four groups of natural waters

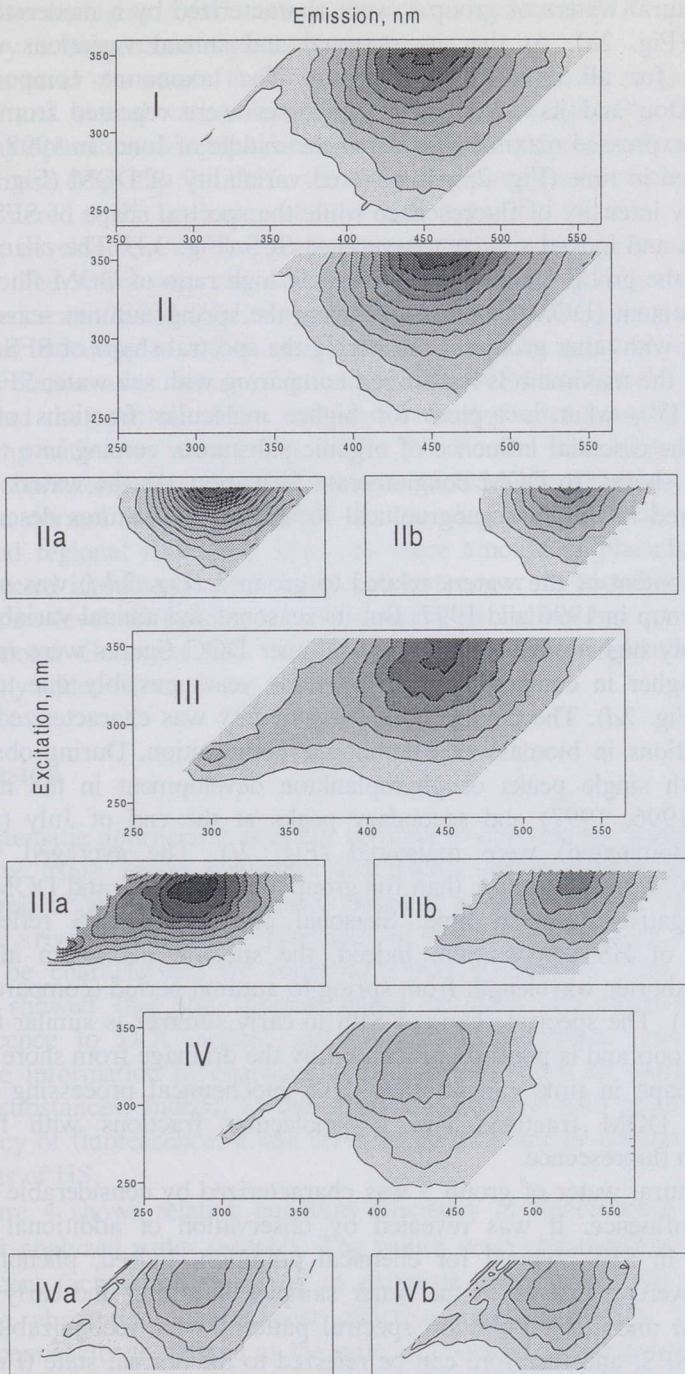


Fig. 3. Spectral Fluorescent Signatures (SFS) reflecting the normal state of water: I – group 1, II – group 2 (IIa – May 1998, IIb – September 1998), III – group 3 (IIIa – May 1998, IIIb – September 1998), IV – group 4

The natural waters of group 1 were characterized by a moderate content of DOC (Fig. 2a). At that its seasonal and annual variations were not systematic for all rivers in this group. The taxonomic composition of phytoplankton and its development processes were repeated from year to year with expressed maximal growth in the middle of June. In 1998 the peak was delayed in time (Fig. 2c). Registered variability of DOM (Fig. 2b) was revealed by intensity of fluorescence while the spectral shape of SFS did not vary much and looked similar to averaged SFS (Fig. 3,I). The characteristic feature of the group 1 waters is a relatively high ratio of DOM fluorescence to DOC content (DOM/DOC ratio) during the spring–autumn season, when comparing with other groups. Considering the spectral shape of SFS, one can notice that the maximum is red-shifted comparing with sea water SFS (group 4, Fig. 3,IV), what is typical for higher molecular fractions of HS. It indicates the essential influence of organic substance, coming into the water from river shores, to DOM conglomerate formation. As the waters in group 1 are related to different geographical locations, the features described are not regional.

DOC content of the waters related to group 2 (Fig. 2d-f) was similar to the first group in 1996 and 1997. But its seasonal and annual variability was considerably higher. In 1998 the mid-summer DOC figures were more than 5 times higher in comparison with previous years possibly due to raining weather (Fig. 2d). The phytoplankton community was characterized also by high variations in biomass and taxonomic composition. During observation period both single peaks of phytoplankton development in the middle of June (in 1996, 1997) and secondary peaks at the end of July (in 1998, Diatoms dominated) were registered (Fig. 2f). The averaged value of DOM/DOC ratio was lower than for group 1. Both DOC and DOM figures had a negative trend in time. Seasonal changes of SFS reflected the variations of HS composition. Indeed, the spectral maximum in SFS is shifted to shorter wavelength from spring to autumn period (compare IIa and IIb, Fig. 3). The spectral shape of SFS in early summer is similar to one in the first group and is possibly influenced by the drainage from shore. Change of SFS shape in time can be caused by biochemical processing of high-molecular DOM fractions into low-molecular fractions with following decrease in fluorescence.

The natural water of group 3 was characterized by considerable antropogeneous influence. It was revealed by observation of additional spectral structures in SFS, typical for chemical pollution. Indeed, phenol and oil pollution were registered in the water samples in spring and early summer (Fig. 3,IIIa and IIIb). Pollution spectral patterns were recognizable also in averaged SFS, and therefore can be referred to the normal state (Fig. 3,III). The time dynamics of DOM and DOC was similar to the second group (negative trend in time), while intensive peaks of phytoplankton development (Diatoms dominated) were recorded mainly in the autumn period (Fig. 2g-i). The DOM/DOC ratio was even lower than for groups 1



and 2 due to higher DOC content in water. Increased DOC amount was caused by technogeneous organic materials.

The natural sea waters in the coastal zone were referred to group 4. The seasonal and annual variability of HS was not revealed (Fig. 2j and 2k), while phytoplankton development varied from year to year both in taxonomy and biomass (Fig. 2l). In 1997, the early summer bloom of phytoplankton was registered at the beginning of June with dominated Diatoms. In 1998, an intensive development of blue-green phytoplankton was registered in August (Table). The water was characterized by the lowest DOC content, DOM fluorescence and DOM/DOC ratio. This is caused by the prevalence of low-molecular fractions in DOM conglomerate and is in good correspondence with the conservative nature of low-molecular DOM fractions. The SFSs of DOM had the spectral shape extended toward shorter wavelengths, when comparing with river waters (Fig. 3,IV). The normal state of coastal waters can be characterized by spectral patterns of HS only. Observed deviations from the normal state were mainly due to chemical pollution and had an expressed regional character. Thus the trace amount of phenol derivatives was detected in summer 1997 in the sea water near the mouth of the Purtse River. Low-level oil pollutions were detected in Tallinn bay in all years of observations. Collected data of SM and phytoplankton pigments did not reveal any added values to the results described above.

## Conclusion

In a systematic approach it is rather difficult to describe the status of natural water by using single indicators like DOC, phytoplankton biomass and taxonomy, or suspended materials. Since it is influenced by many factors (weather, river environment, processes in water ecosystem etc.), the status should be characterized by some combined parameters. The analysis of results showed that the spectral shape of SFS and relation of DOM fluorescence to DOC values, determined by absorption, can add some valuable information to characterize the natural water by conglomerate of humic substances. Indeed, as this ratio is connected with relative quantum efficiency of fluorescence, it can serve as an indicator of different molecular fractions of HS.

Figure 4 shows relative quantum efficiency of fluorescence  $Q$  ( $\lambda_a$ ,  $\lambda_{ex}$ ,  $\lambda_{em}$ ) for analyzed water samples. The values were calculated as the ratio of fluorescent factor, corresponding to maximal intensity in SFS matrix ( $\lambda_{ex}$ ,  $\lambda_{em}$ ), to absorption at the most effective wavelength ( $\lambda_a$ ). In turn, the fluorescent factor is defined as the ratio of maximal fluorescence intensity in SFS to the intensity of Raman scattering at the same excitation wavelength. The average  $Q$  value characterizes the group of water its minimal and maximal magnitudes define the margins of variability inside the group.

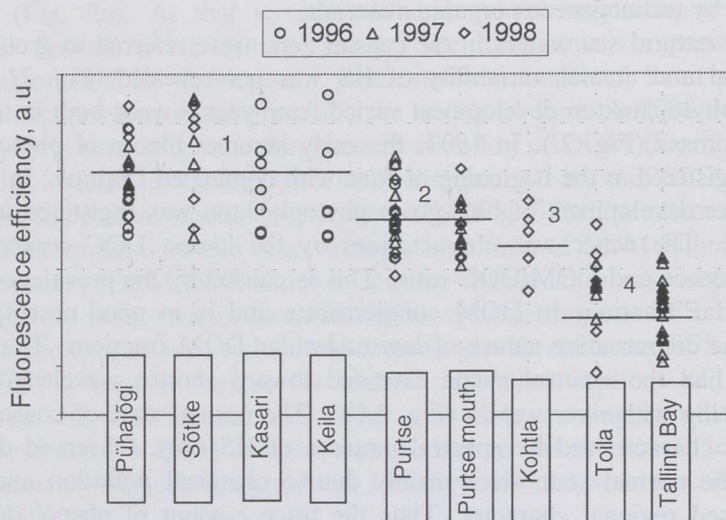


Fig. 4. Average relative efficiency of fluorescence and its variation for different water groups

By using this approach the four groups of investigated natural waters were defined. Generally the deviations from the normal stage in river waters were described by seasonal changes in HS composition. In the areas of antropogeneous loading (North-East region of Estonia) the normal stage of river water included phenolic pollution, and the deviations from the normal stage were caused by changes of antropogeneous influence due to the processes of oil shale mining. Although the coastal waters were described by similar normal state, the deviations had regional character and depended on discharge of river waters and mixing of different water types. In North-East region the deviations were due to phenolic compounds coming from river waters. In the areas of intensive navigation (Tallinn bay) the deviations of water quality were mainly due to oil pollution. Performed studies showed that the combination of SFS technique with spectral absorption allows one to characterize the water status both qualitatively (spectral shape of SFS) and quantitatively ( $Q$  value).

## Acknowledgement

This work was supported by Estonian Science Foundation (Grant No. 2401).

## REFERENCES

1. *Veldre I., Sergejev B., Trapido M.* Polycyclic arenes in the rivers of the oil shale region of Estonia // Proc. "Problems of Contemporary Ecology". Tartu, Estonia, 1991. P. 187–188 [in Estonian].
2. *Trapido M., Munter R., Kallas J.* Oil shale ash dump waste as a polycyclic aromatic hydrocarbons and phenols pollution source // Proc. "Problems of Contemporary Ecology". Tartu, Estonia, 1994. P. 203–205 [in Estonian].
3. *Paerl H. W.* Nuisance phytoplankton blooms in coastal, estuarine, and inland waters // *Limnol. Oceanogr.* 1988. Vol. 2, No. 4. P. 823–847.
4. *Malcolm R. L.* The uniqueness of humic substances in each of soil, stream and marine environments // *Anal. Chem. Acta.* 1990. Vol. 232. P. 195–199.
5. *Moran M. A., Pomeroy L. R., Sheppard E. S., Atkinson L. P., Hodson R. E.* Distribution of terrestrially derived organic matter on the southeastern U.S. continental shelf // *Limnol. Oceanogr.* 1991. Vol. 36, No. 6. P. 1134–1149.
6. *McCarthy M. D., Hedges J. I., Benner R.* The chemical composition of dissolved organic matter in sea water // *Chem. Geol.* 1993. Vol. 107. P. 503–507.
7. *Babichenko S., Poryvkina L., Orlov Y., Persiatsev I., Rebrik S.* Fluorescent signatures in environmental analysis // *The Encyclopedia of Environmental Analysis and Remediation / John Wiley & Sons Inc.* New-York, 1998. P. 1787–1791.
8. *Kalle K.* The problem of the gelbstoff in the sea // *Oceanography and Marine Biology Annual Review.* 1966. Vol. 4. P. 91–104.
9. *Poryvkina L. V., Babichenko S. M., Lapimaa J.* Spectral variability of humus substance in marine ecosystems // *AMBIO.* 1992. Vol. 21, No. 7. P. 465–467.
10. *Pennanen V.* Humic Fractions in Dimictic Lakes in Finland / Department of Limnology, University of Helsinki, SF-00710 : Thesis. – Helsinki, Finland, 1988.
11. *Wetzel R. G., Hatcher P. G., Bianchi T. S.* Natural photolysis by ultraviolet irradiance of recalcitrant dissolved organic matter to simple substrates for rapid bacterial metabolism // *Limnol. Oceanogr.* 1995. Vol. 40, No. 8. P. 1369–1380.
12. *Hilton J., Rigg E., and Jaworski G.* Algal identification using *in vivo* fluorescence spectra // *J. Plankton Res.* 1989. Vol. 11. P. 65–74.
13. *Poryvkina L., Babichenko S., Kaitala S., and Kuosa H., Shalapjonok, A.* Spectral fluorescence signatures in characterization of phytoplankton community composition // *J. Plankton Res.* 1994. Vol. 16, No. 10. P. 1315–1327.
14. *Babichenko S., Poryvkina L., Varlamov V.* ON-LINE fluorescent techniques for diagnostics of water environment // Proc. Int. Symp. Optics for Environment and Public Safety, EUROOPTO, June 1995, Munich, Germany. 1995. Vol. 2503. P. 157–161.
15. *Babichenko S., Orlov Y., Persiantsev I., Poryvkina L., Rebrik S.* Diagnostics of organic substances in water by spectral fluorescent signatures (SFS) // *American Environmental Laboratory.* 1996. Vol. 8. P. 6–8.
16. *Poryvkina L., Leeben A.* Diagnostics of organic compounds in water quality monitoring // Proc. 4th Intern. Conf. on Remote Sensing for Marine and

- Coastal Environments, March 1997, Orlando, Florida. 1997. Vol. 2. P. 469–475.
17. Poryvkina L., Babichenko S., Davydova O. SFS characterization of oil pollution in natural water // Proc. 5th Intern. Conf. on Remote Sensing for Marine and Coastal Environments, 5–7 October 1998, San Diego, California. 1998. Vol. 2. P. 520–524.
  18. Arnvidarson B. Studies of Fluorescence in Relation to Oceanographic Problems. – Copenhagen University, 1986.
  19. Belin C., Quellec C., Lamotte M., Ewald M. Characterization by fluorescence of the dissolved organic matter in natural water. Application to fractions obtained by tangential ultrafiltration and XAD resin isolation // Environ. Technol. 1993. Vol. 14 P. 1131–1144.

Presented by J.-M. Punning

Received December 22, 1999