Journal of Environmental Protection and Ecology 14, No 3, 864–874 (2013)

Water pollution

SPATIAL AND TEMPORAL VARIATION OF CHLOROPHYLL '*a*' ALONG THE DANUBE RIVER

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Abstract. The spatial and temporal variation affects the processes and patterns of the environment, particularly in structured systems such as river networks. Chlorophyll is bound within the living cells of algae and other phytoplankton found in surface water. The aim of the study was to describe the seasonal and spatial distribution of surface chlorophyll *a* (Chl *a*) in relation to some environmental variability factors, based on data collected in 2012 from 16 sampling sections along the Danube river. The concentration of Chl *a* was measured from the surface layer using a spectrometric method and the values ranged from 2.3 μg/l in November to 68 μg/l in July. Chl *a* showed temporal variability related to the anthropogenic pressures and meteorological conditions. After significant lower concentrations in late spring and early summer, Chl *a* exhibited its strongest maximum in summer: July and August. The high concentration of Chl *a* indicated high productivity, also noted in numerical abundance and biomass of phytoplankton. The understanding of Chl *a*, phytoplankton population and its distribution enables researches to draw conclusions about a water body health, composition and ecological status.

Keywords: chlorophyll *a*, the Danube river, phytoplankton.

AIMS AND BACKGROUND

As the assurance of waters quality intended for human consumption is the main objective for high-life quality, the more responsible humans to protect freshwaters resources should be. The national and European legislation by Integrated Romanian Monitoring System and Water Framework Directive (WFD) (Ref. 1) require waters quality monitoring based on biological, physicochemical and hydro-morphological parameters. Chlorophyll is bound within the living cells of algae and is a commonly used parameter for the estimation of phytoplankton biomass and primary production. Chlorophyll '*a*' (Chl *a*) was included in the list of indicators of eutrophication within WFD. The Chl *a* content explains how energy flows through an aquatic ecosystem and how nutrients are cycled in the environment.

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The aim of the study was to describe the spatial and temporal distribution of Chl *a* in relation to environmental variability factors, based on the data collected in 2012 from 16 sampling sections along the Danube river.

Monitoring of aquatic biota throughout Romania was seasonally conducted in the frame of the National Water Monitoring System started from 1978. Additionally, Chl *a* concentration was analysed to evaluate the trophic state of aquatic ecosystems[2–4]. Many studies concerning spatial, temporal, seasonal and annual variation of Chl *a* and primary production have been carried out along the Danube river[5–15] using various analytical methods[16–23]. Rivers are dynamic systems, where the pollution, acidification, toxicity, eutrophication problems decrease the water quality standard.

It is already known that the main problems which affect water quality of the Danube river are high load of nutrients (N, P) leading to eutrophication, contamination with hazardous substances and O_2 depletion due to anthropogenic activities associated with urbanisation, industrialisation and agriculture[24,25].

In this study Chl *a* was used to estimate the quantity of algae and the quality of water body with respect to its fertilisation.

EXPERIMENTAL

The Danube river basin is the second largest river basin of Europe covering territories of 18 states including EU-Member States, Accession Countries and other states. The Danube flows predominantly to the south-east and reaches the Black Sea after 2780 km where it divides into 3 main branches, the Chilia, the Sulina, and the Sf. Gheorghe Branch. At its mouth the Danube has an average discharge of about 6.500 m^3/s (Ref. 26). Figure 1 shows the geographical coverage of sampling stations along the Danube river – Romanian sector and St. Gheorghe branch.

A total of 105 surface samples were collected during March–November 2012, with a monthly frequency along St. Gheorghe branch and seasonal frequency (in July and November) along the Danube river in the Romanian sector. The Chl *a* content was measured in relation to environmental variables such as: water temperature, dissolved oxygen, hydrogen ion concentration, nutrients, phytoplankton biomass and numerical density. The concentrations of dissolved oxygen, temperature, and pH were measured *in situ* using mobile devices from Environmental monitoring autolaboratory. Nutrients samples were kept at 2°C until their subsequent analysis in laboratory. NH_4–N, NO_3–N, NO_2–N, PO_4–P, were determined according to standard methods (ISO 7150-1:2001; ISO 7890-3:2000; EN 26777:2002/C91:2006, EN ISO 6878:2005).

This integrative approach, which included *in situ* determinations and laboratory analysis, indicated strong correlations between abiotic and biotic components.

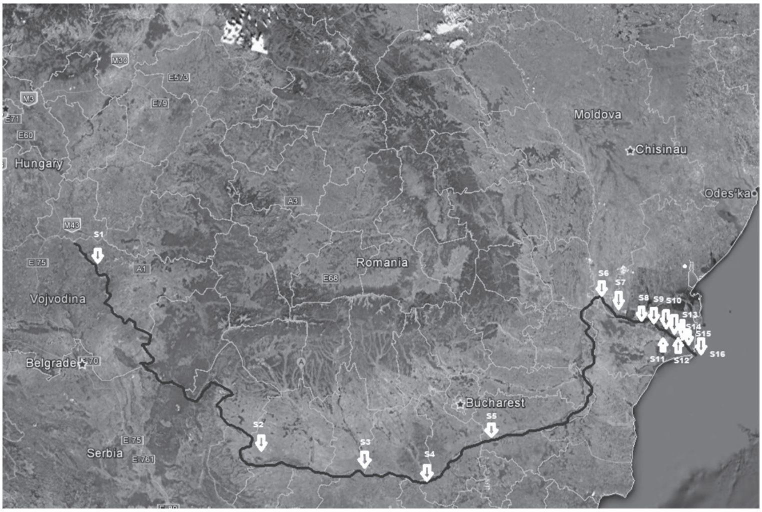

Fig. 1. Location of sampling sections along the Danube river **(**S1 – Bazias; S2 – Calafat; S3 – Bechet; S4 – Turnu Magurele; S5 – Giurgiu; S6 – Isaccea; S7 – Tulcea upstream; S8 – Tulcea downstream; S9 – Nufaru; S10 – Baltenii de Sus; S11 – Mahmudia; S12 – Murighiol; S13 – Uzlina; S14 – Ivancea; S15 – St.Gheorghe port; S16 – the Black Sea confluence)

For Chl *a* measurements, the samples were filtered after collection as chlorophyll pigments react with light and oxygen. A known volume of sample water (usually 0.5 l) was vacuum filtered through 47 mm GF/F Whatman filters. The Chl *a* was extracted with 90% ethanol and measured spectrophotometrically (Specord BU 205). The absorbance of the extract was measured before and after acidification at 665 and 750 nm (ISO 10260:1996).

The samples for phytoplankton determination were preserved with 4% formaldehyde solution. Qualitative and quantitative phytoplankton determinations were made according to standard methods (EN 15204:2007).

RESULTS AND DISCUSSION

Spatial and temporal variation of surface Chl *a* along the Danube river and St. Gheorghe branch was examined in relation to water temperature, hydrogen ion concentration, dissolved oxygen, nutrients and phytoplankton production potential.

In terms of spatial distribution, Chl *a* ranged between 2.3 μg/l at S2 (Calafat), S5 (Giurgiu), S6 (Isaccea) to 68 μg/l at S12 (Murighiol) (Fig. 2). The seasonal pattern of surface Chl *a* distribution showed low variability.

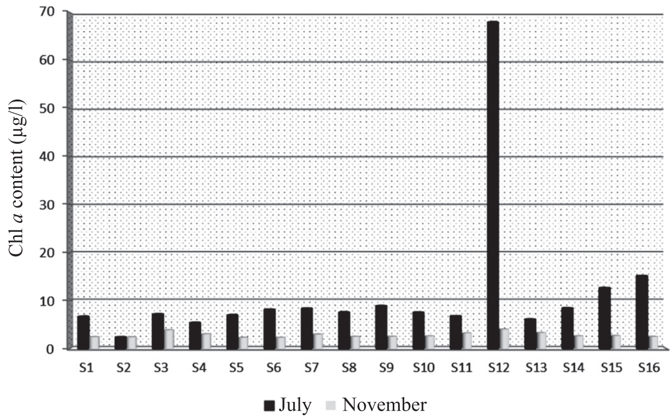

Fig. 2. Chl *a* (µg/l) variation along the Danube river and St. Gheorghe branch in July and November 2012

In spring (March–May 2012), Chl *a* distribution was quite homogeneous, varying between 4.39 and 13.41 µg/l. The highest values were recorded on S16 (Black Sea confluence), 13.41 µg/l in March and 10.5 µg/l in May, where the maximum phytoplankton biomass was also found (0.047 and, respectively, 0.11 mg/l) (Fig. 3). However, Chl *a* exhibited its strongest maximum in summer: July and August. The high concentration of Chl *a* indicated high productivity, also noted in numerical abundance and biomass of phytoplankton.

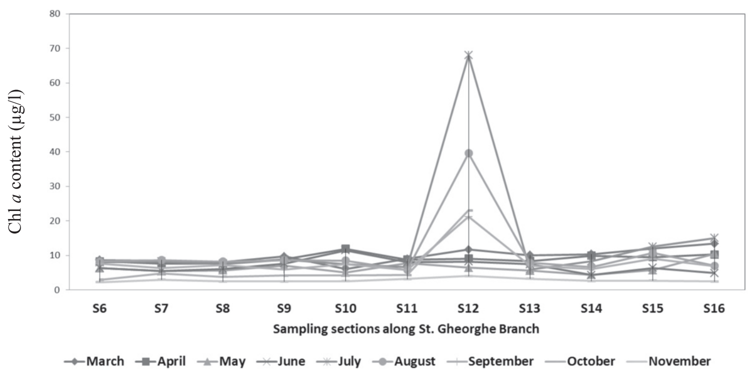

Fig. 3. Chl *a* (µg/l) variation along St. Gheorghe branch in March–November 2012

The maximum concentrations of Chl *a* were measured in the Danube delta – St. Gheorghe branch, especially at S12 (Murighiol) in all sampling campaigns. In July 2012 Chl *a* concentration was 68 µg/l which exhibited the IInd quality class according to WFD and national legislation (Law of water No 107/1996). Total phytoplankton biomass in the surface layer varied between 0.006 in March at S7 (the Tulcea upstream) and 0.25 mg/l in July at S12 (Murighiol). Moreover, between Chl *a* and total phytoplankton (Phpk) biomass was registered a strong linear relationship during the whole monitoring period, showing similar seasonal dynamics (Fig. 4).

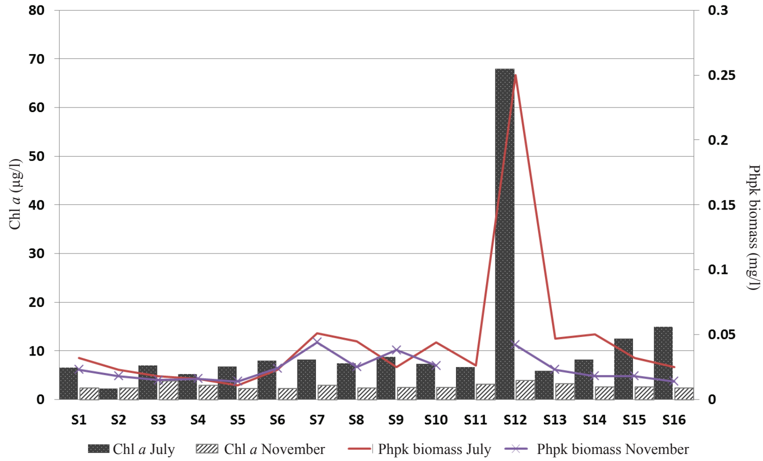

Fig. 4. Seasonal and spatial variation of Chl *a* and phytoplankton biomass along the Danube river and St. Gheorghe branch

The level of water pH in March–November 2012 period ranged between 7.32–8.8 without significant changes; the highest pH value 8.8 was recorded in April at S4 (Nufaru). The water temperature ranged from 4.9 to 25.6°C and dissolved oxygen (DO) – 0.17 to 9.66 mgO_2/l, due to drought and high temperature, recorded in July and August. The highest values of dissolved oxygen varied in spring (April) and late autumn (November) (Figs 5 and 6). Chl *a* showed temporal variability related to the anthropogenic pressures and meteorological conditions.

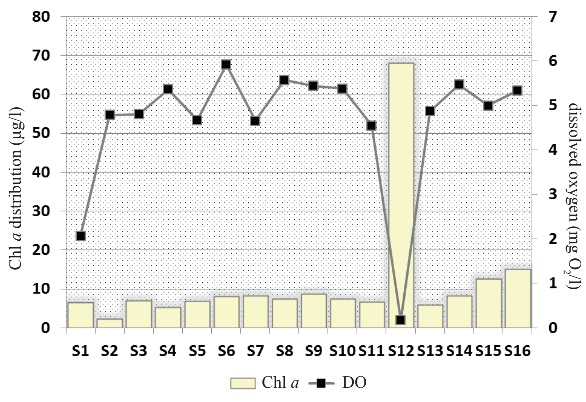

Fig. 5. Spatial distribution of Chl *a* and DO along the Danube river and St. Gheorghe branch in July 2012

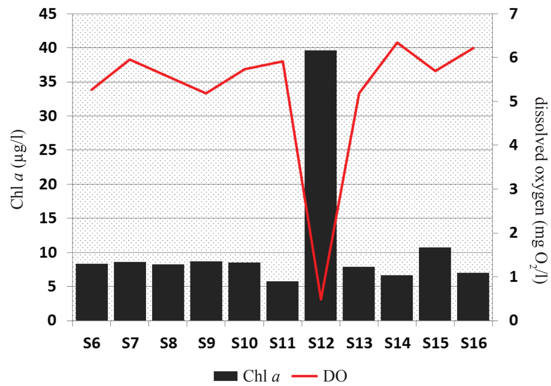

Fig. 6. Spatial distribution of Chl *a* and DO along St. Gheorghe branch in August 2012

During spring period when the Danube discharges exhibited highest values, surface Chl *a* regime was significantly related to freshwater and nutrients inputs. Also, Chl *a* showed a large spatial variability along St. Gheorghe branch sections than the Danube river sections.

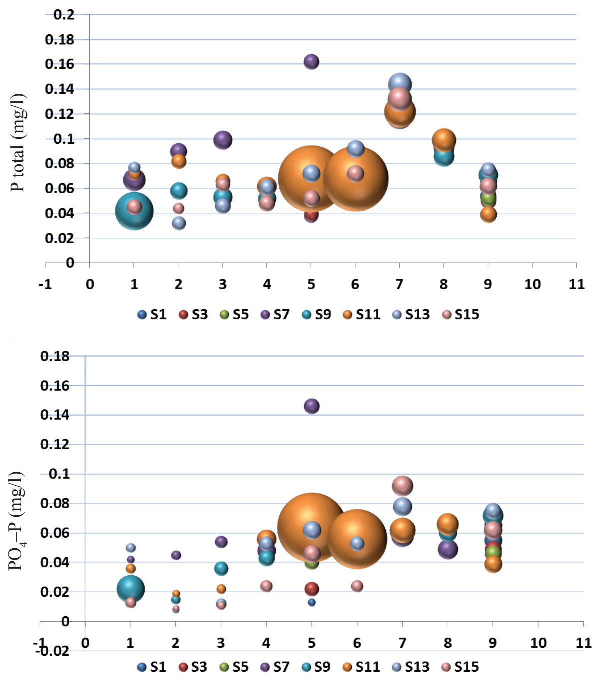

Fig. 7. Spatial and temporal distribution of total phosphorus (P) (mg/l) and PO_4–P (mg/l) along the Danube river and St. Gheorghe branch from March to November 2012

The seasonal variation of phosphate in the surface layer highlighted the lowest value in April (0.008 mg/l) and the highest one in July (0.94 mg/l). Also, the total phosphorus concentrations ranged between 0.03 mg/l in March and 0.98 mg/l in July maintaining the almost the same seasonal variation trend as phosphate (Fig. 7).

Chl *a* was related to seasonal variation of the Danube flow over the whole study period. There was found a correlation between Chl *a* and the total inorganic nitrogen and no significant correlation between chlorophyll and phosphate, probably as a result of P consumption in the growth of diatoms, which prevail over the populations in the Danube phytoplankton community.

The seasonal variation of NH_4–N showed lower concentrations in spring and early summer (0.28–0.35 mg/l), increasing in late summer (August – 0.98 mg/l) and autumn (October – 1.12 mg/l). The NH_4–N in the whole monitoring period ranged between allowable limit values 0.4 and 1.12 mg/l (Fig. 8). The highest surface NH_4–N was measured in October 2012 at S12 (Murighiol).

NO_3–N concentrations were higher in sampling stations situated along the St. Gheorghe branch than those from the Danube river – Romanian sector. The summer period, when the temperature was high, drought and lowest dissolved oxygen values, the nitrate concentrations decreased around 0.81–1.06 mg/l in June, 0.92–1.12 mg/l in July and 2.14–2.92 mg/l in August. Higher values were registered in November 2012 along all sampling stations due to higher dissolved oxygen concentrations (Figs 9 and 10). The nitrite concentrations had also seasonal and spatial variation. The highest nitrite values was recorded in warm period at S12 (Murighiol), S13 (Uzlina) and S14 (Ivancea) (Fig. 11).

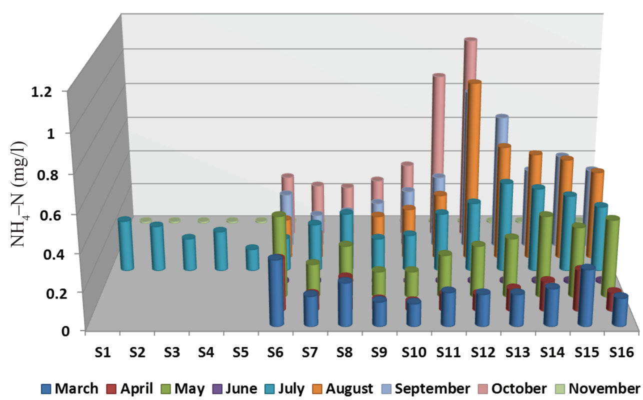

Fig. 8. NH_4–N (mg/l) variation along the Danube river and St. Gheorghe branch from March to November 2012

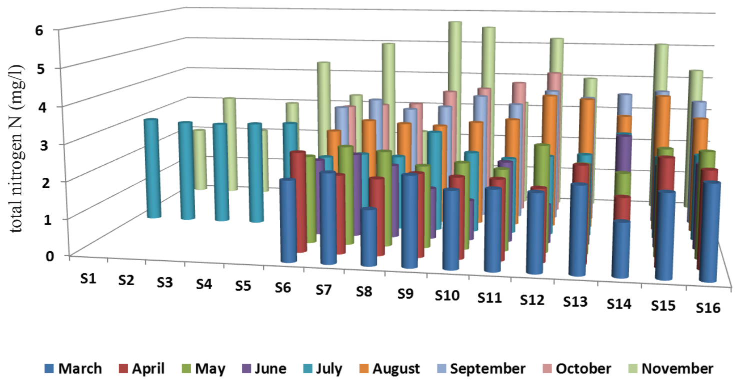

Fig. 9. Total nitrogen (mg/l) variation along the Danube river and St. Gheorghe branch from March to November 2012

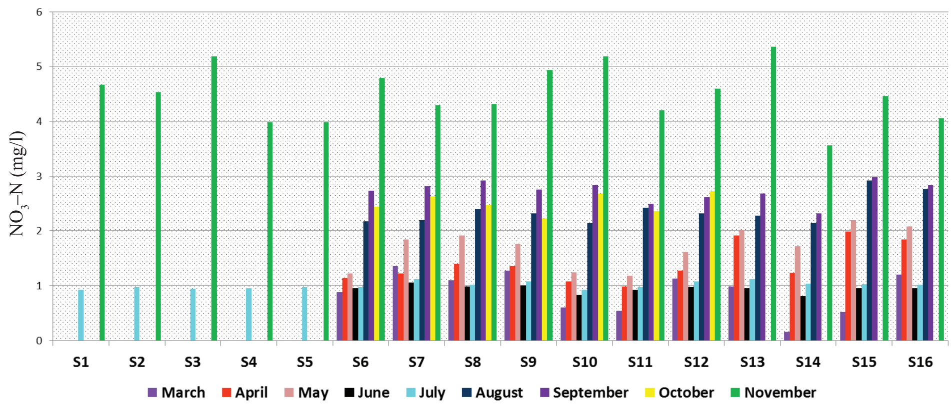

Fig. 10. NO_3–N (mg/l) variation along the Danube river and St. Gheorghe branch from March to November 2012

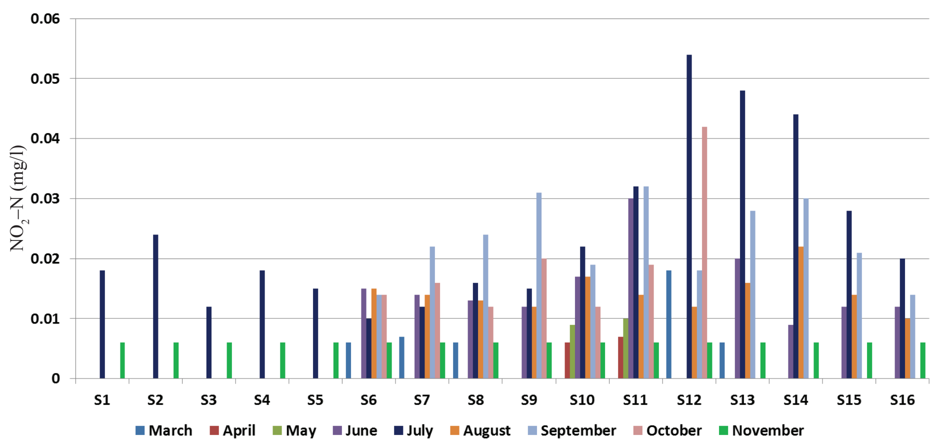

Fig. 11. NO_2–N (mg/l) variation along the Danube river and St. Gheorghe branch from March to November 2012

The point sources nutrients discharges seem to be the main factor controlling the seasonal and spatial surface Chl *a* distribution in the Danube water, as well as morphological alterations and flow regime[11]. The relationships between Chl *a,* nitrates and phosphates indicate that surface layer is a favourable environment for intense phytoplankton growth, suggested by the high proportion of diatoms biomass and numerical abundance (95 and 98% of total biomass and numerical abundance, respectively).

Considering the above-mentioned, it may be concluded that the biological and physicochemical processes played an increased role in the quantitative structure of phytoplankton community.

CONCLUSIONS

The study described the seasonal and spatial distribution of surface Chl *a* in relation to some environmental variability factors, based on the data collected in 2012 from 16 sampling sections along the Danube river. The concentration of Chl *a* was measured from the surface layer using a spectrometric method. Chl *a* showed temporal variability related to the anthropogenic pressures and meteorological conditions. Spatial and temporal variation of surface Chl *a* along the Danube river and St. Gheorghe branch was examined in relation to water temperature, hydrogen ion concentration, dissolved oxygen, nutrients and phytoplankton production potential.

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Received 27 June 2013
Revised 22 July 2013