LONG-TERM (30 YEARS) STUDY OF DISSOLVED ORGANIC MATTER IN THE NORTHERN ADRIATIC SEA; AN INDICATION OF GLOBAL CHANGES **AND THE BIOS VARIATIONS**



<u>Ciglenečki^{*a},</u> I. Vilibić^a, J. Dautović^a, <u>N. Simonović^a</u>, V. Vojvodić^a, B. Ćosović^a, P. Zemunik^b, N. Dunić^b, H. Mihanović^b

^aRuđer Bošković Institute, Division for Marine and Environmental Research, Bijenička cesta 54, 10000 Zagreb ^bInstitute of Oceanography and Fisheries, Setalište I. Meštrovića 63, 21000 Split, Croatia

Long-term data sets from freshwater, estuarine and marine ecosystems provide a unique information on complex dynamics within the ecosystems themselves, especially when they respond to anthropogenic pressure and climate change. Today, they become even more important since they play a key role in comprehensive discussions and conclusions concerning the climatic and anthropogenic pressure. The importance of long-term research in the aquatic environment is crucial for many reasons, such as: the interpretation of main processes within ecosystems, detecting the occurrence of complex conditions which might be indiscernible in short-time scale, documenting physical, chemical and biological phenomena and discovering the complexity of interactions as well as dynamics and the population ecology. Therefore, long-term research is an ideal basis for the evaluation and creation of legislation focused on environmental quality and pollution control, and monitoring and prediction of climate change.

In this paper an unique time series of dissolved organic carbon (DOC) and its surface active fraction (SAS) that were collected between 1989 and 2020 with monthly or bimonthly temporal resolution along the transect Po River delta - Rovinj in the northern Adriatic (NA) (Fig.1) will be presented.

Results

•NA is very dynamic system with periods of high and low organic carbon content; decreasing DOC and SAS increasing trend since 1989, Fig.2,3 (1-2).

•Maximum AVG DOC value in the summer of 1990 (high SAS) is followed by significant accumulation and frequent appearance of "mucilages" (2000-2004) that reflected on high DOC Lowest AVG DOC value in 2006 (extremely low Po flux) is followed by an increasing trend in the period 2006-2011- antyciclonic BiOS circulation (1-3)

2012-2016 – relatively low OM content with different SAS properties – more hydrophobic



Fig. 1. Study area, transect Po River delta - Rovinj in the northern Adriatic (NA) as the most investigated and the most productive (occasionally eutrophic) part of generally oligotrophic Mediterranean.



ŝ

S

9

material (Fig.4)

•2017- 2020 increase of SAS/DOC; BiOS circulation is changing to antyciclonic (1-3); appearance of gelatinous zooplankton blooms (*M.Leidyi*) (4,5) (Fig.4); hydrophobic material





0



Fig. 5. Mean DOC, SAST and SASdiss values over the NA transect. The values are computed on the series with annual and semiannual cycles removed; increasing trend from west to east of the transect, and from bottom to surface.

Methodology

0,06 0,04

0,02

0,00

High-temperature catalytic oxidation with Pt/Si as a catalyst and non-disperzive infrared detection is used to analyse dissolved organic carbon, DOC (TOC-V_{CPH}, Shimadzu, Japan). The method is highly sensitive (<1%RSD), enabling detection of temporal and spatial variability of DOC content in the sea. SAS measurements were performed by a.c.voltammetry (Ćosović, Vojvodić, Electroanalysis 1998)

REFERENCES

[1] J. Dautović, V. Vojvodić, N. Tepić, B. Ćosović, I. Ciglenečki, Sci. Tot. Environ. 2017, 587/588, 185-195.

[2] I. Ciglenečki, I. Vilibić, J. Dautović, V. Vojvodić, B. Ćosović, P. Zemunik, N. Dunić, H. Mihanović, Sci. Tot. Environ. 2020, 730, 139104, doi:10.1016/j.scitotenv.2020.13910. [3] H. Mihanović, I. Vilibić, N. Dunić, J. Šepić, J. Geoph. Res. Oceans, 2015, 120, 5615-5630 [4] I. Ciglenečki, B. Ćosović, V. Vojvodić, M. Plavšić, K. Furić, A. Minacci, F. Baldi, Mar. Chem. **2000**, *71*, 233–249.

[5] I. Ciglenečki, P. Paliaga, A. Budiša, M. Čanković, J. Dautović, T Djakovac, M. Dutour-Sikirić



CONCLUSION

Significant changes in DOC, SAS can be recognized as a possible indicator of biogeochemical and climate induced variabilities influenced by local and global (climate) processes – changes

•Factors influencing the distribution and properties of OM in the NA:

 hydrographic conditions (mainly river Po) and water masses circulation driven by
BiOS, i.e. inflow of different water masses from the Ionian sea

***** BiOS is responsible for advection of either highly saline ultraoligotrophic Levantine Intermediate Water from the Eastern Mediterranean (cyclonic circulation) or nutrient richer less saline Western Mediterranean waters (anticyclonic circulation), that reflects on OM amounts (DOC, SAS) and properties at different phase lags of -1 to -4 years

* changes in OM conc. and properties are direct consequence of biological, mainly phytoplankton activities, and changes in its abundance and community compositions

* enrichment of dinoflagellates, with intensive blooms of Noctiluca scintillans, i.e. red tides in the nortwestern NA (2007-2016) contribute to higher DOC and SAS values



Financial support of Croatian Science Foundation projects SPHERE-1205,

MARRES-1717, ADIOS-1995, and EcoRENA-4764 is highly acknowledged.

* other unusual phenomena such as mucilaginous algal blooms, and gelatinous

zooplankton blooms (M.Leidyi) [4,5], contribute to eutrophication characterized by

anomalous accumulation of organic carbon in the sea.