

Biochemical responses of oligotrophic Adriatic Sea surface layers to atmospheric deposition inputs

S. Frka¹, A. Miliković¹, A. Penezić¹, S. Bakija Alempijević¹, B. Gašparović¹,
S. Skejić², D. Šantić², S. Brzaj³, V. Džaja Grgičin³, S. Vidič³, I. Šimić⁴, I.
Bešlić⁴, S. Žužul⁴, R. Godec⁴, G. Pehnc⁴

Email: frka@irb.hr

¹Division for marine and environmental research, Ruđer Bošković Institute, Zagreb, Croatia

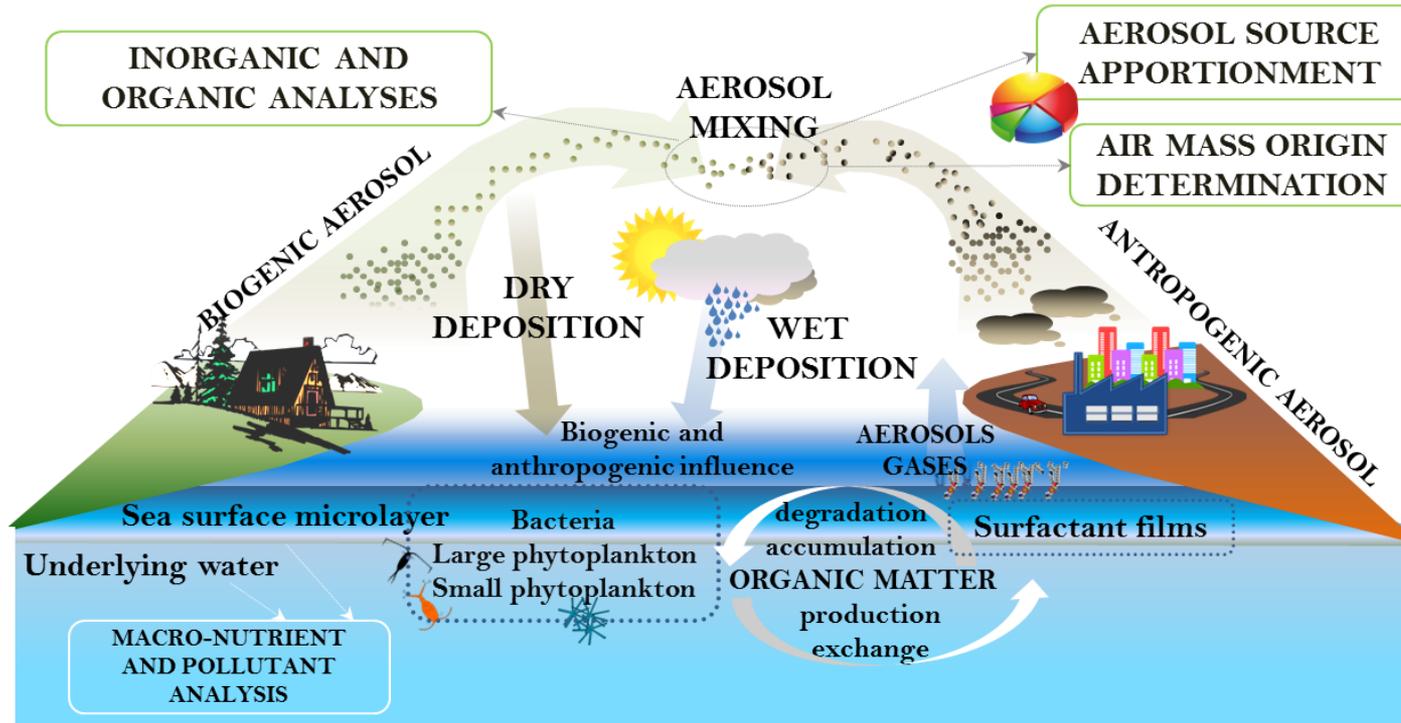
²Institute of Oceanography and Fisheries, Split, Croatia

³Croatian Meteorological and Hydrological Service, Zagreb, Croatia

⁴Institute for Medical Research and Occupational Health, Zagreb, Croatia

CSF project (2018-2022): Biochemical responses of oligotrophic Adriatic surface ecosystems to atmospheric deposition inputs (BiREADI)





Atmospheric deposition (AD) - dominant pathway by which material is transported from continents to coastal and open seas

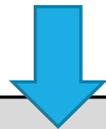
- an external source of macro (N and P) and micro (Fe) nutrients, organic and inorganic pollutants
- impact on quality and quantity of organic matter (OM) produced by the phytoplankton
- change of CO₂ uptake

Atmosphere-ocean interface - sea surface microlayer (SML)

- top 1 mm of the sea surface
- surface films - air-sea gas exchange, photochemical production of VOCs - formation of organic aerosols

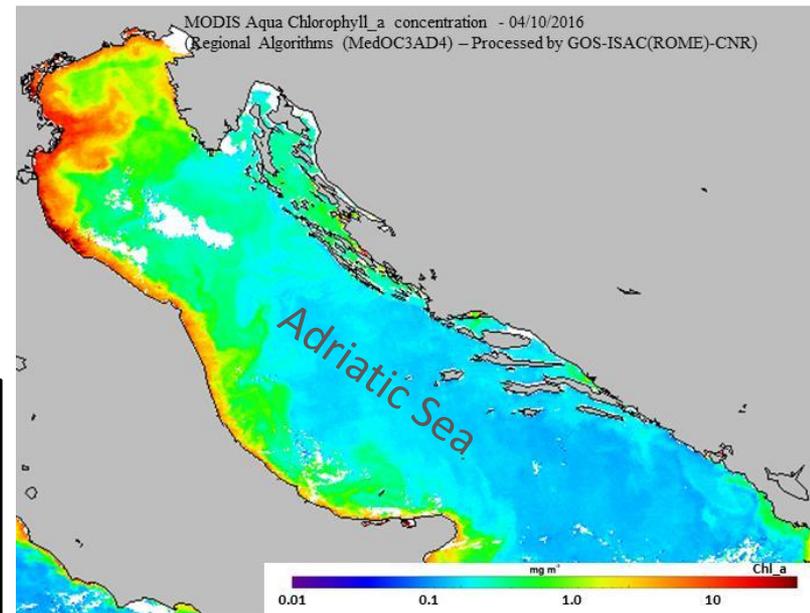
The input of **atmospheric deposition** - important for **oligotrophic environments** representing 60% of the global ocean

- **Mediterranean Sea**
 - biodiversity hotspot
 - low nutrient, low chlorophyll region
 - impacts of mineral dust, industrial and domestic emissions, wildfire emissions
- **Adriatic Sea**
 - combined influence of local, regional and long-distance natural and pollution sources
 - Middle and Southern oligotrophic regions
 - impact of AD generally unknown



BiREADI project aim:

- to evaluate the impacts of AD on biochemical responses of oligotrophic Adriatic Sea regions, considering the effects on phytoplankton, and the consequent altering of the surface water chemistry, including the SML at the air-water interface.



Map of the Adriatic Sea presenting satellite obtained Chlorophyll a distribution

Middle Adriatic campaign (February 2019 – July 2019) - Analyses

➤ Marine samples

sea surface microlayer (SML) underlayer water samples (ULW)

Dissolved (fraction $<0.7 \mu\text{m}$)
Particulate (fraction $>0.7 \mu\text{m}$)

Particulate and dissolved organic carbon, lipid classes, monosaccharides and total carbohydrates surfactants, nutrients, trace metals, Chlorophyll a

Abundance of microphytoplankton, nanophytoplankton, nanoflagellate, cyanobacteria, pico-eukaryotes, heterotrophic bacteria, bacteria with high nucleic acid contents, bacterial production

➤ Atmospheric samples

Black carbon

Aethalometer (AE33) - 1 min resolution

Aerosol samples (PM_{10})

PM_{10} mass, organic carbon (OC), elemental carbon (EC), water soluble organic carbon (WSOC), surfactants, anions, cations, levoglucosan, trace metals, polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB)

Bulk deposition samples

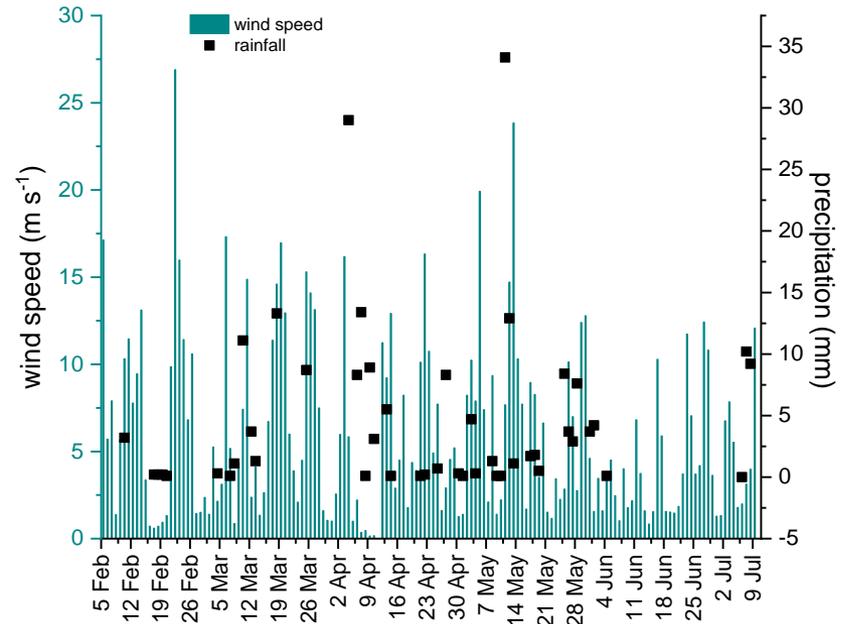
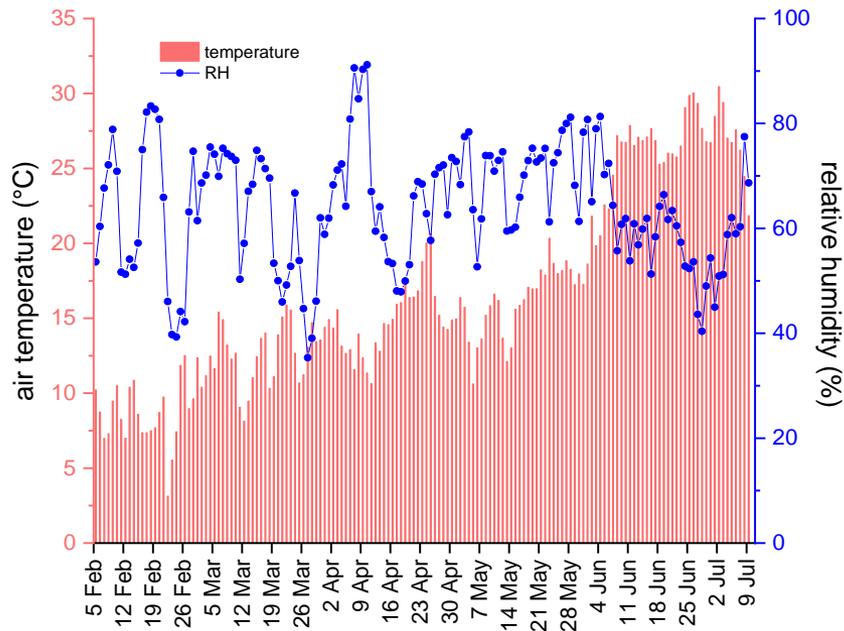
total deposition mass, OC, EC, WSOC, surfactants, trace metals, anions and cations, PAH, PCB

Wet deposition samples

OC, WSOC, surfactants, anions, cations, trace metals, PAH, PCB

Middle Adriatic campaign (February 2019 – July 2019)

Meteorological conditions



Temporal variability of average meteorological parameters at the coastal Middle Adriatic site.

Ambient concentrations and chemical characteristics of PM₁₀, bulk and wet deposition:

- affected by contrasting air-mass inputs, meteorological conditions, Saharan dust inputs as well as regional and/or local biomass burning and traffic emissions



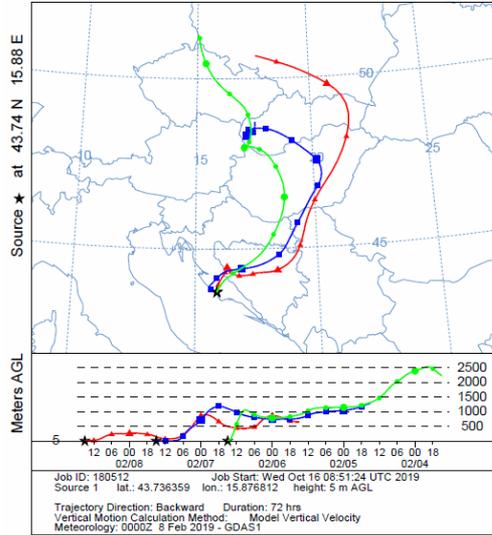
Negative correlation between wind speed and PM₁₀ mass concentration ($r=0.226$, $p<0.05$, $N=77$) - PM₁₀ dispersal with the increasing wind speed

Intensive rain events in April, May and July - scavenging of PM₁₀ particles

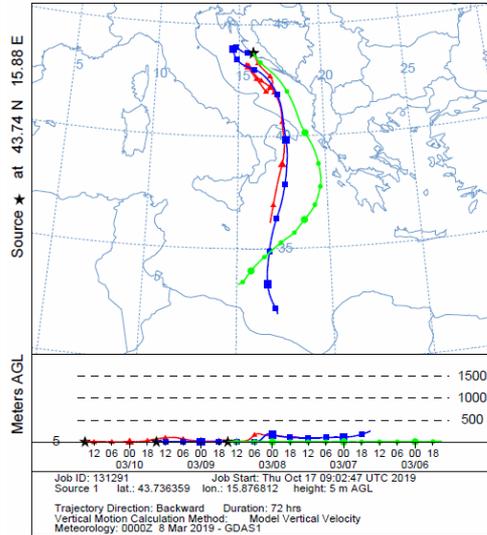
Middle Adriatic campaign (February 2019 – July 2019)

Contrasting air-mass inflows

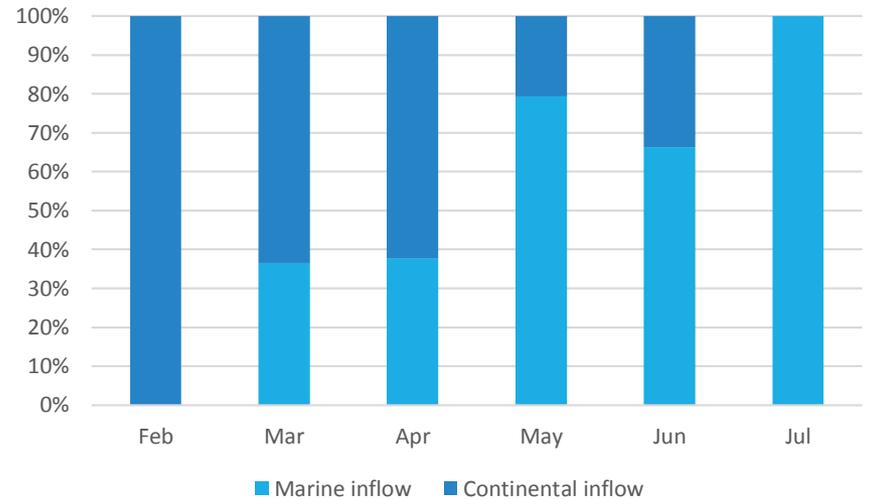
NOAA HYSPLIT MODEL
Backward trajectories ending at 1500 UTC 08 Feb 19
GDAS Meteorological Data



NOAA HYSPLIT MODEL
Backward trajectories ending at 1500 UTC 10 Mar 19
GDAS Meteorological Data



Example of NOAA HYSPLIT air-mass backward trajectories ending at a measuring station determined as a) continental and b) marine.



Monthly change of the continental (N/NE) and marine (S) air-mass contributions at the eastern Middle Adriatic coastal site.

More polluted continental N/NE air-mass inflow affected the area, especially during winter. Marine sector dominantly affected the area during spring and summer period.

Middle Adriatic campaign (February 2019 – July 2019)

Special events

Open-fire emissions

- defined according to Šibenik county fire department archive data* and air-mass backward trajectory analysis
- within the radius of ~ 30 km from the sampling site

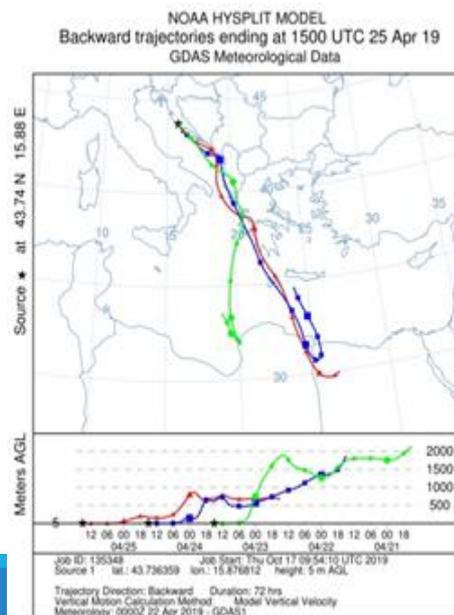
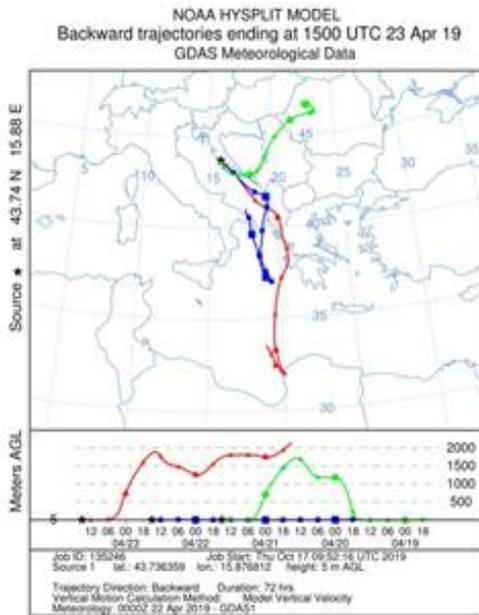
16.02.-21.02.2019 - agricultural waste and pine forests

31.03.-03.04.2019 - agricultural waste

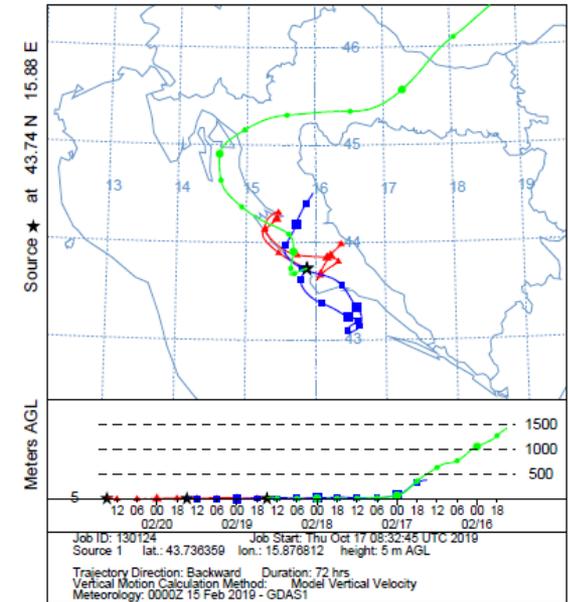
06.06.-14.05.2019 - low plants, pine and olive tree forests

*URL <http://www.vatrogastvo-sibenik-knin.hr/>

Saharan dust inputs



NOAA HYSPLIT MODEL
Backward trajectories ending at 1500 UTC 20 Feb 19
GDAS Meteorological Data



Example of NOAA HYSPLIT air-mass backward trajectories ending at a measuring station during regional/local biomass burning events.

21.04.-25.04. 2019

NOAA HYSPLIT air-mass backward trajectories ending at a measuring station in the period from 21.4-25.4.2019.

Middle Adriatic campaign (February 2019 – July 2019)

Source apportionment

- Aethalometer model & levoglucosan data
 - Estimation of the site specific α_{ff} and α_{bb}
 - Contribution of biomass burning and fossil fuel sources
- LOTOS-EUROS chemical transport model - source apportionment module
- Inter-relationship between the main ions and trace metals
- Specific PAH diagnostic tools

Main contributing sectors at the eastern Middle Adriatic coastal area:

- public power sector outside Croatia
 - energy production
 - traffic
 - residential combustion
 - shipping
- Open-fire emissions
Saharan dust

Middle Adriatic campaign (February 2019 – July 2019)

Nutrient and trace metal enrichment (EF) in the SML

- atmospheric deposition impacts
 - intensive events as open-fire and Saharan dust inputs
 - intensive precipitation
 - solubility of trace metals
- wind speed - > negative correlation

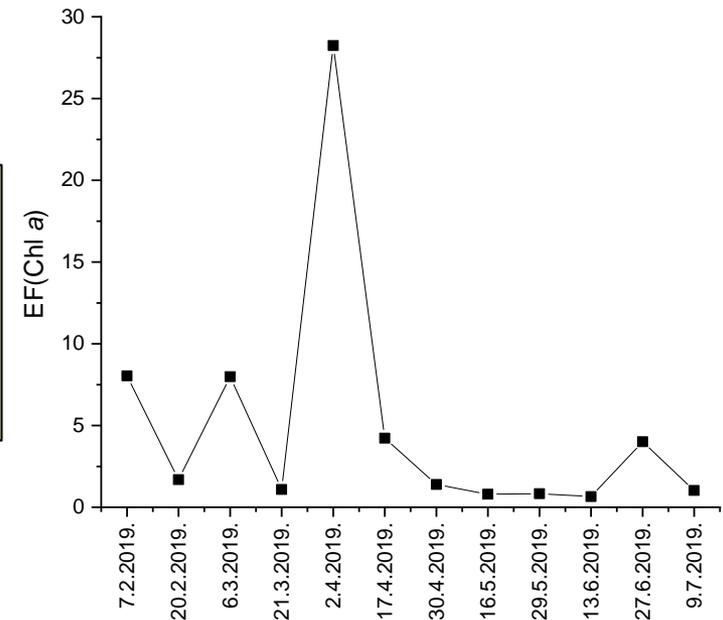
Biological parameters within sea surface layers

- SML: nutrient supply related to atmospheric deposition
 - intensive events as open-fire and Saharan dust inputs
 - intensive precipitation
- ULW: nutrient supply within the water column

Organic matter enrichments in the SML

- atmospheric deposition impacts
 - intensive events as open-fire and Saharan dust inputs
 - intensive precipitation
- wind speed
- biological responses

$$EF(x) = \frac{(x)SML}{(x)ULW}$$



Temporal variability of Chlorophyll *a* (Chl *a*) enrichment (EF) in the SML at the coastal Middle Adriatic site during BiREADI campaign.

Acknowledgements

BiREADI project team

Asta Gregorič

Aerosol, Ljubljana, Slovenia

Anne Kasper-Giebl

Vienna University of Technology, Austria



This work has been supported by Croatian Science Foundation under the project IP-2018-01-3105



COST STSM CA16109 COLOSSAL