



## The influence of climate changes on the quality of water and sediments in the Sulina branch of the Danube River



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**Abstract:** The researchers of the REXDAN Research Infrastructure have carried out a series of studies on the state of the aquatic ecosystems in the area of the Sulina branch of the Danube river. In the last 2 years, several sampling campaigns were carried out from the critical points of the study area located on one of the most navigable channels of the Danube. The following physico-chemical parameters were determined for the water samples: pH, temperature, oxygen regime (DO, BOD5 and COD), nutrient regime (N-NH<sub>4</sub><sup>+</sup>, N-NO<sub>3</sub><sup>-</sup>, N-NO<sub>2</sub><sup>-</sup>, N-total, P-total), salinity (SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>) and heavy metals (Fe-total, Zn<sup>2+</sup>, Cr-total; Cd<sup>2+</sup>, Ni<sup>2+</sup>). Sediment samples were analysed to assess the concentration of heavy metals, such as Fe-total, Zn<sup>2+</sup>, Cr-total; Cd<sup>2+</sup>, Ni<sup>2+</sup>. Spectrophotometric method, ion exchange chromatography, electrochemical method and inductively coupled plasma mass spectrometry were used to determine the value of water and sediment parameters. (WFD). With these results, as well as historical data, a number of machine learning prediction algorithms were trained and validated. In this way, an analytical framework based on virtual sensors was developed, the purpose of obtaining them is to increase the sustainability of monitoring activities. In this way, an effective monitoring of the quality of aquatic ecosystems can be carried out, any changes that occur as a result of climate change (especially during periods of extreme drought or flooding) can be noticed and alarm signals can be given to the authorities that manage water resources.

### MATERIALS and METHODS

The studies included in this paper were carried out within the Horizon DALIA project and aimed at research on: water, sediments, biodiversity; developing of prediction models; forecasting models based on water quality and sediments; developing of a deep-learning.

Water and sediment sampling campaigns were carried out in the period 2023-2024 in summer, autumn, and winter seasons from different stations located on the Sulina Branch.

The determination of the physico-chemical parameters was carried out in the laboratories of the REXDAN Research Infrastructure, on the research vessel laboratories and fixed center laboratories, using state-of-the-art equipment: High-resolution LC-MS / MS, Vanquish Flex UHPLC Systems coupled to Orbitrap Exploris 120



Mass Spectrometer -Thermo Fisher Scientific, Ion chromatograph IC Dionex ICS-6000 Thermo Fisher Scientific, ICP-MS with speciation Nexion 2000C, PerkinElmer.

During the campaigns, studies were also carried out on the granulometry and the speed of the water flow: Acoustic Doppler current profile (ADCP) AQUASCAT1000S.

Historical data and those obtained from analyzing water and sediment samples were processed by applying various methods from the machine learning algorithm (MLA): *XGBoost ML, Decision Random Forest MLA etc.*

Fig. 1. REXDAN Research vessel

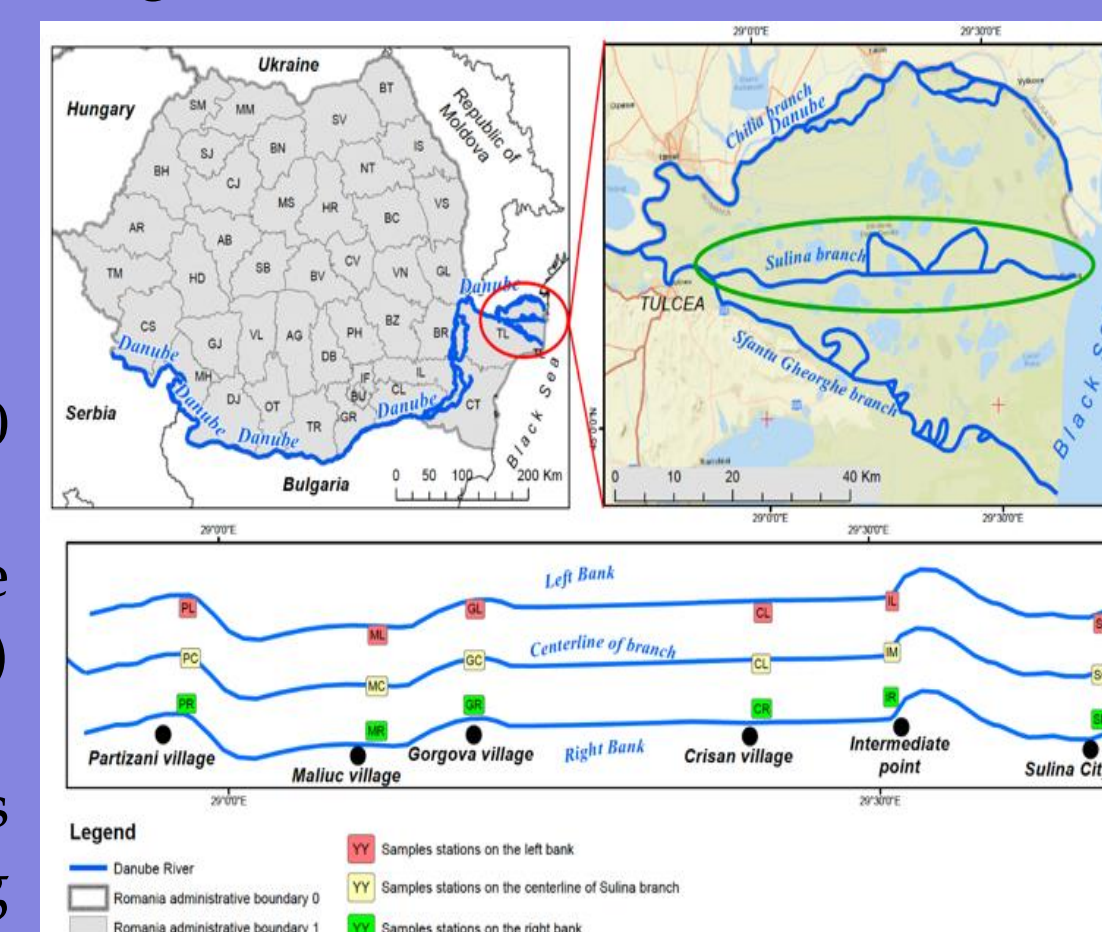


Fig. 2. Water and sediments sample points from the studied area

### RESULTS and DISCUSSIONS

The results obtained from the analysis of the samples were evaluated following the regulations of the Water Framework Directive (WFD).

In the summer and autumn seasons, dissolved oxygen (DO) recorded values corresponding to quality classes II-III, while in the winter season values specific to class I were reported. Regarding the results for BOD<sub>5</sub> and COD, specific values to quality classes I, respectively I-II were observed. Nutrients recorded concentrations corresponding to quality classes I (N-NH<sub>4</sub><sup>+</sup>, N-NO<sub>3</sub><sup>-</sup>, P-total) and II (N-total and N-NO<sub>2</sub><sup>-</sup>). The salinity level corresponds to class I.

Regarding the monitoring of heavy metals (Fe-total, Zn<sup>2+</sup>, Cr-total; Cd<sup>2+</sup>, Ni<sup>2+</sup>), it was found that the permissible limits according to the legislation in force were not exceeded. However, in August 2023 and August 2024, increases in the concentrations of all parameters were noted as a result of the decrease in flows due to the prolonged drought period.

During the 4 campaigns, studies were also carried out on the granulometry and the speed of the water flow. The graph on fig. 3 represents discharge measurements and water velocity mapping for all monitoring section. with ADCP we can view an integrated image of the quantity and characteristics of the particulate matter (sediment, aquatic life, etc.) in the water column. Thus, complex analysis of data (Fig. 4) offers detailed information regarding the grain size of each particle (grain radius - with clasification of particles in grainsize clases) and the concentration of suspended sediment particles.

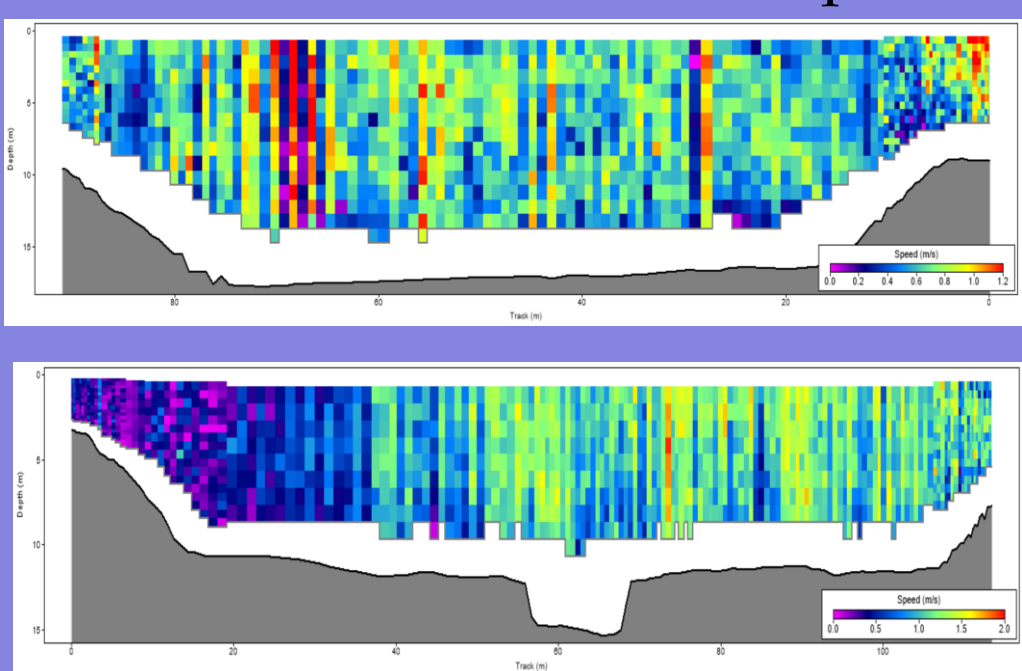


Fig. 3. Acoustic Doppler current profile (ADCP) transect measurements

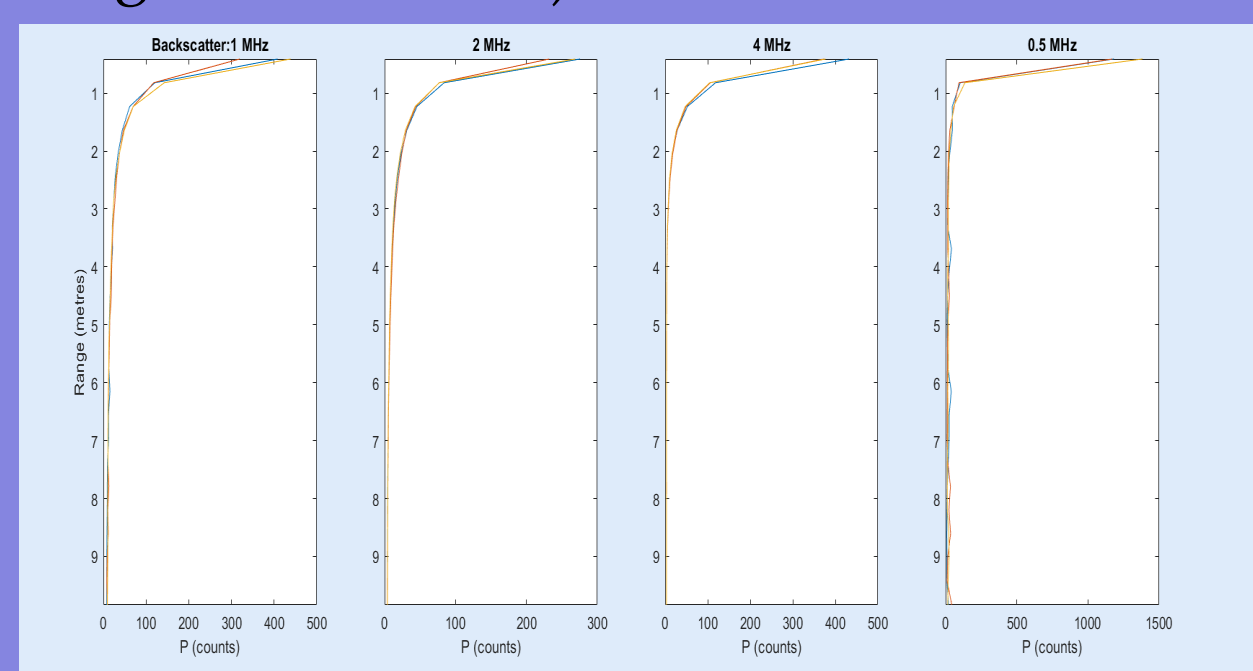


Fig. 4. Sediments concentration (g·L<sup>-1</sup>) and grain radius (µm) per water column.

If considering the resulting sediment prediction models, based on fewer predictors compared to water quality ML models, it can be concluded that Ni concentration in sediments can be predicted mostly based on Zn concentration in sediments (fig. 7), while the prediction of Cr concentration in sediments involves, mostly, the Fe, as a main predictor, and Zn, as a secondary predictor (fig. 8).

An important part of the studies conducted consists of using artificial intelligence to generate so-called virtual sensors. The results obtained so far by applying machine learning are promising for some of the heavy metals monitored. The best results were obtained for Fe concentration in water (fig. 5 and. 6).

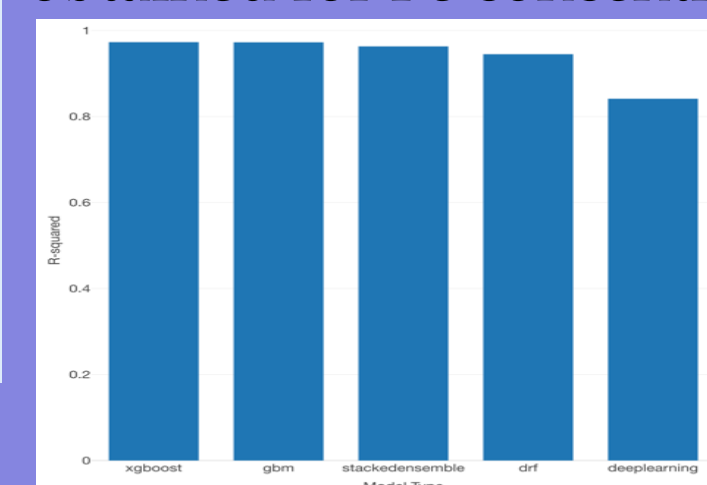


Fig. 5. The accuracy of the main ML algorithms tested for the prediction of Fe concentration in water

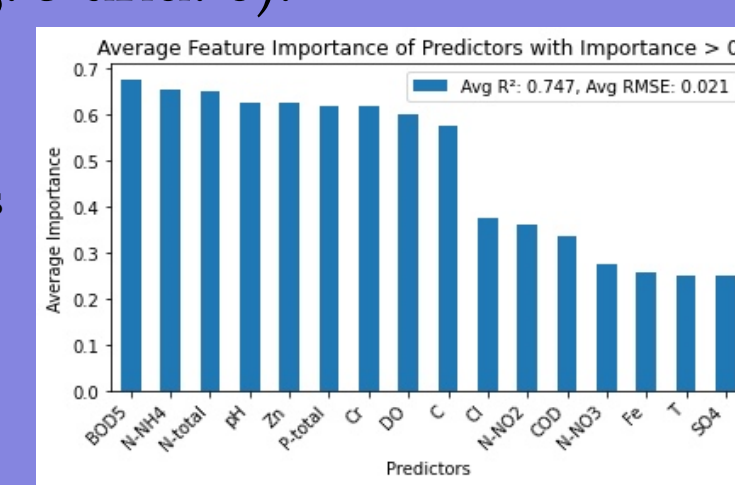


Fig. 6. The average feature importance of each analytical framework predictor, in determining the Fe concentration in water

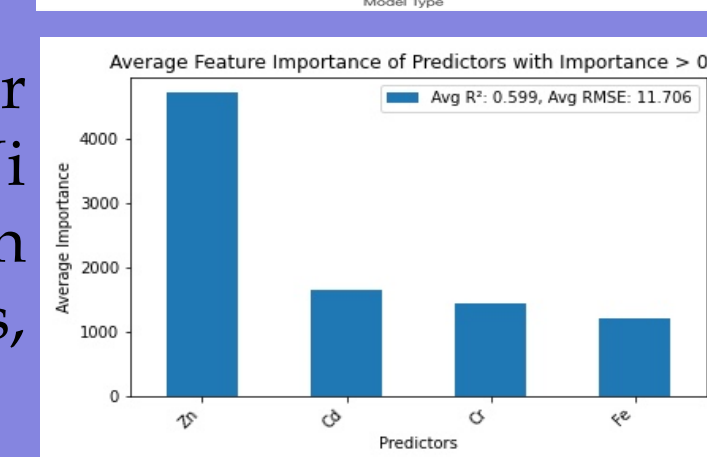


Fig. 7. The average feature importance of each analytical framework predictor, in determining the Ni concentration in sediments

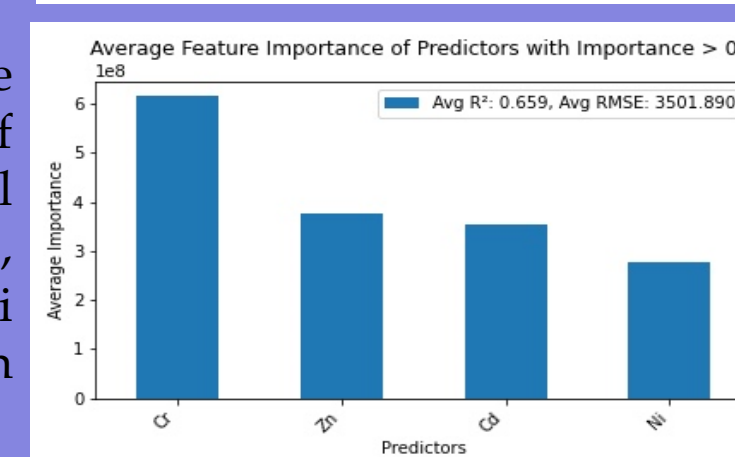


Fig. 8. The average feature importance of each analytical framework predictor, in determining the Fe concentration in sediments

### CONCLUSIONS

The studies carried out between September 2023 and August 2024 showed that in the area of the Sulina arm the physicochemical parameters measured for both water and sediments, fall within the limits established by national legislation and the Water Framework Directive, being able to classify the area in quality class II. The comparison of the values obtained during the study period with the historical ones does not indicate remarkable changes except for the dry period, climate changes not having an important impact in this area.

The results obtained by applying the MA algorithms are encouraging and will be continued to obtain virtual sensors for determining the concentrations of heavy metals whose experimental determination is laborious and involves high costs.

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