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Redox state assessment for the Danube water in the Sulina channel using a mobile water quality monitoring station

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Abstract:
The monitoring of the Danube River water quality was performed by using a complex device including dissolved oxygen (DO), pH, redox potential (ORP) and temperature measurements, installed on a passenger cruise ship travelling between Tulcea and Sulina. This ship equipped with the water monitoring station served as a mobile device during the daytime cruise along the Sulina channel and as a fixed one when the ship was docking in Tulcea or Sulina ports, including the nighttime. The values of the Eh and rH revealed that apart from the assumed dissolved oxygen, other species of peroxide types are supposed to form in the natural water by complex biologic mechanisms.

Keywords: water pollution, flowing surface water, ORP, DO, pH, Eh, rH

1. INTRODUCTION

The use of a mobile station for the water quality monitoring instead of a classic stationary facility station allows detecting more precisely the time and place of the pollutants entry into the surface water body. Thus, additional benefits could be foreseen concerning the better control of water quality indicators [1], pointing out the changes in real time of the eutrophication and water pollution status [2,3]. The redox potential (ORP) of the water plays a key role for the estimation of the Eh and rH of the natural water [4], also called eco-chemical indicators, which are useful to provide assumptions about the occurrence of temporary toxicity situations in the water body ("redox toxicity") [5]; in the presence of thereof, the death of hydrobionts could occur, despite the normal values of all other water quality indicators.

The aim of this work was to assess the redox state of the Danube River water in September 2022, based on data collected by using a mobile water quality monitoring station installed on a passenger ship cruising along the Sulina channel, between the settlements of Sulina and Tulcea.

2. EXPERIMENTAL

The human communities are located in about 10 settlements situated along the Sulina channel, which are shown on the map from Figure 1; for easier corresponding references, numbers thereof have been allocated, starting from Sulina to Tulcea (Table 1).

The passenger cruise ship hosting the water monitoring system sailed from Sulina to Tulcea on the September 4th and 6th 2022, in about 3h 32 min (departure time: 07:00 AM) and in the opposite sense on September 5th and 7th 2022, respectively (departure time 13:30, journey time 3h 22 min, a little shorter than the other sense trip, when moving in the same sense with the flow of the water); the journey intervals are distinctively marked on Figure 2. The average ship speed was about 25 km/h and the standing time in the main stop points was between 3-5 minutes. Apart from these cruises, the ship was docking in Sulina harbour, respectively in Tulcea port, being able to act as a fixed monitoring point for the water monitoring system.

Figure 1. Map of the monitored area and the inhabited communities

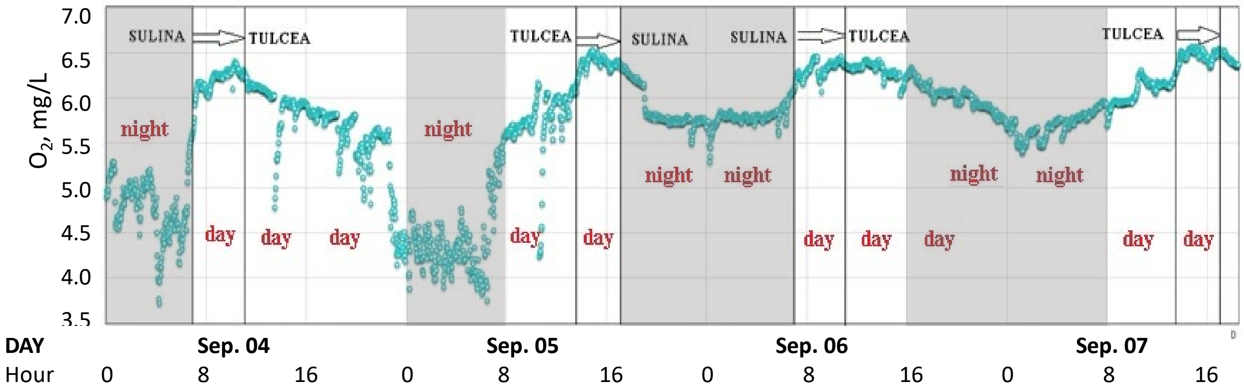

Figure 2. Dissolved oxygen concentration correlated with the ship cruising/stationing time diagram.

Particularly, the diagram in Figure 2 highlights the day/night cycle related to the photosynthesis of the aquatic algae (changing in O_2/CO_2 concentrations values) [2,3].

The water monitoring system makes the object of a filed patent [6], therefore it cannot be presented in detail in this paper. The PHEHT sensor of PONSEL type (MESURE-Groupe AQUALABO, France) is a part of the monitoring system, dedicated to pH/ORP measurements, being able to simultaneously perform potentiometric measurements for both the above mentioned parameters, by combining two pairs of electrodes: a glass bulb sensitive to H^+ ions for pH measurement plus a reference electrode (***Eref***) of Ag/AgCl and a platinum disk for Redox (ORP) measurement plus the same ***Eref*** (Ag/AgCl). A NTC thermistor was incorporated in this sensor body, for temperature measuring and for performing the automatically temperature compensation during the pH and ORP measurements.

The characterization of the Danube water quality was performed with a sampling frequency of 3 min at a depth of about 1 m, consisting in measurements of the following water indicators needed for the proposed objective: the temperature, the dissolved oxygen concentration, the redox potential and the pH.

3. RESULTS AND DISCUSSION

Based on the measured experimental data (temperature, ORP, pH), the values for Eh/rH, were calculated using the equation (1) and the described methodology [7], and the results were centralized in Table 1.

$$rH = E(V)/0.0295 + 2\,pH = (ORP + Eref)\,(mV)/29.5 + 2\,pH \qquad (1)$$

Table 1. Eh and rH calculated values for the Danube water at 1 meter depth (September 2022) near several points between Sulina and Tulcea during daylight period

No.	Settlements	***ORP, mV****	***Eh, mV*****	***rH*****
1	Sulina	283 + 6	503 ± 6	33.2 ± 0.3
2	Crisan	285 + 1	505 ± 1	33.27 ± 0.04
3	Mila 23 (proximity)	284 + 12	503 ± 13	33.2 ± 0.6
4	Gorgova	285 + 2	505 ± 2	33.30 ± 0.09
5	Maliuc	284 + 2	504 ± 2	33.3 ± 0.1
6	Vulturu	285 + 1	504 ± 1	33.30 ± 0.07
7	Partizani	284 + 1	504 ± 2	33.27 ± 0.08
8	Ilganii de Sus	286 + 7	506 ± 8	33.4 ± 0.4
9	Tudor Vladimirescu	284 + 2	504 ± 2	33.2 ± 0.1
10	Tulcea	285 + 1	505 ± 2	33.29 ± 0.08

*Average measured value during the cruise; **Average calculated value

Based on the results displayed in Table 1, the Eh average value is 504±4mV and the rH average value is 33.3±0.2, respectively, being considered valid for the whole channel. The close values for all the measurement points indicate that the changes thereof during daylight hours are insignificant. The oxidizing compounds in natural water prevail over the compounds with reduction character, as indicated by the value of rH over 28.

Preliminarily, it can be assumed that the main oxidizing agent from water is the dissolved oxygen. However, a difference of 1.2 mg O_2/L was noticed during the docking in the nighttime: a decrease from 5 mg O_2/L during the cruise to 3.8 mg O_2/L in the stationing period. This suggests the decrease of the photosynthetic activity of the algae and of the working functions of the aquatic microorganisms, especially on the benthic ones. Combining this observation with the almost constant values of Eh and Rh suggests the occurrence of other oxidizing species than oxygen, such as peroxide radicals resulting from biological processes, especially due to the hydrobionts metabolism.

When comparing the actual study results with another monitoring case study concerning the Dniester River [4, 8-10] performed at a less deep level (about 0.2 m), in which the redox potentials have been also measured, we could also consider the following main reaction mentioned for the Dniester river [5], as possible for the Danube river as well:

$$O_2 + 4e + 2H_2O \Leftrightarrow 4OH^- \qquad (2)$$

However, this hypothesis would be valid only if the experimental values of Eh were close to the ones calculated using the formula [4]:

$$Eh_{O_2\_pH} = Eh^0{}_{O_2} - KpH + \frac{K}{4}\lg P_{O_2} \qquad \text{where: } K = \frac{2.3RT}{F} \qquad (3)$$

It should be mentioned that for the monitoring of the water from the Danube River, the calculated values of the Eh based on the measured ORP values were significantly higher than the ones calculated using the above equation, indicating that the reaction (2) is not supported by the experimental data collected at 1 m depth in the water from the Sulina channel and can not be thus considered at a the depth of around 1 m. This aspect suggests that other species of peroxide types are supposed to form in the natural water by means of complex biologic mechanisms.

4. CONCLUSIONS

The monitoring values of the dissolved oxygen concentration, redox potential (ORP) and pH measured in stationary and dynamic conditions at around 1 m underwater depth, corrected against the temperature, allowed the calculation of Eh and rH. The calculations allow to establish the eco-toxicity status of the Sulina channel, showing a clean water with the predominant presence of oxidation agents, including the oxygen and other oxidation species that are naturally produced in the flowing river water, most likely hydrogen peroxide of biological origin. The confirmation of this supposition is possible when combining the ongoing hydro-monitoring with additional chemical and biological studies.

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