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FEATURES OF THE INTRA-ANNUAL VARIABILITY OF THE HYDROCHEMICAL AND HYDROBIOLOGICAL STATE OF VARNA LAKES IN THE PERIOD 2022–2023

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Abstract

This study continues the presentation [1] of the results from long-term (June 2022–July 2023) observations in Varna lakes. The analysis focuses on data from in situ measurements taken with multiparameter sondes at two points, covering the following parameters: i) oxygen saturation, dissolved oxygen, fluorescence, turbidity, and blue-green algae; these are continuous time series recorded at a depth of 1.5 m below the lake surface by anchored autonomous buoys; ii) *OS* and *DO*, turbidity, pH, chlorophyll-*a*, and *BGA* – vertical profiles of the water column from the surface to the bottom received during 11 periodic control measurements. As a result, the peculiarities of intra-annual variability and the vertical distribution of the observed parameters have been identified, along with a number of cause-and-effect relationships. Oceanographic factors (temperature, salinity, and content of the two oxygen forms) play a key role in the analysis. Special attention is given to extreme situations. Cases of a strongly negative impact of the Provadiyska river on the ecological status have been identified. The unstable ecological condition is evidenced by recorded periods of high (up to 300%) *OS* or oxygen deficiency and hypoxia, high concentration of *Chl-a*, as well as turbidity (exceeding by two orders of magnitude the standard sensor calibration scale).

Key words: Varna Lake, Beloslav Lake, dissolved oxygen, oxygen saturation, pH, turbidity, chlorophyll-*a*, fluorescence, blue-green algae

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Introduction. This work continues the started in [1] presentation of the results from a complex research in the aquatory of Varna (*VL*) and Beloslav (*BL*) Lakes in the period 2022–2023. The goal set is within the framework of an independent problem of the European DOORS Project to update the knowledge of the state of the lakes' environment based on an objective analysis of experimental data. To achieve this goal, the task was set to maintain continuous direct measurements of basic oceanographic parameters for a longer period at two points in combination with periodical polygonal direct measurements according to the classical organization with oceanographic stations. Two autonomous oceanographic buoys were moored – one buoy in each lake, each one equipped with an YSI EXO 2 multi-parameter CTD sonde, installed at a depth of 1.5 m below water surface, with sensors for temperature T, salinity S, oxygen (dissolved DO and saturated OS), pH, turbidity (Tb), chlorophyll-a (Chl), and blue-green algae BGA. The measurement period with a discreteness of 20 min is from the beginning of June 2022 until the beginning of Aug. 2023. In order to get an idea on the spatial distribution of the next parameters: T, S, DO, OS, Tb, pH, and Chl-a, in the period May 2022–May 2024 seven polygon boat based surveys and other four control measurements for only the buoys were made. As a result, 103 profiles from the surface to the bottom for each parameter were collected; the basic instrument for measurement was again an YSI EXO2 sonde with water pressure meter.

Preliminary oceanographic notes. The analysis of the obtained results begins with a general assessment of the role of some oceanographic factors and their expected impacts on the observed hydrochemical and hydrobiological processes. The intensity of lake water renewal is directly related to the water and salt balance and to heat flows through the surface; their long-term change reflects climate change. The water dynamics and the hydrological background are essential factors for the redistribution of hydrochemical and hydrobiological characteristics and for the intensity of the processes taking place. The system of lake currents, which ensures mass exchange, has not yet been clarified. Due to the small depth and the presence of relatively long and not very wide channels between the individual basins (filtering the direct sea influence), the wind role is clearly decisive as a dynamic factor. The absence of changes for T in *VL* during pronounced upwelling processes in Varna Bay [1] indicates the specific nature of the water exchange between the separate basins. From the analysis of atmospheric data for the study period, it follows that winds below 6 m/s prevail and no winds above 13–15 m/s are observed [1]. It can be assumed that there is no stable, developed water circulation system in the lakes, the speed of the current is low, and its direction quickly adjusts to changes in the wind field. With global air and water temperatures rising, the influence of winter convection – one of the important mechanisms for the water ventilation at depth, is clearly weakened. In the warm half-year, the processes of intensive photosynthesis and consumption of biogenic elements often occur in conditions of quasi-homogenized vertical distribution of

T and S [1]. Enhanced photosynthesis leads to O_2 oversaturation in the surface layer, especially when the amount of allochthonous and anthropogenic sediments coming from the Provadiyska river, increases. Then, due to the positive inverse relationship between the water transparency and the height of the photic layer, the intensity of photosynthesis in the direction towards the bottom drops sharply and given the shallow depth of lakes the relative role of the processes in the immediate vicinity of the bottom increases. In the bottom layer, the consumption of O_2 during the decomposition of sediment organic matter leads to hypoxia and a release of biogenic elements[1]. In cases of a prolonged increase in their concentration, conditions are created for the penetration of biogens into the nearby upper layers, where, if sufficient O_2 is still available, the process of photosynthesis is reactivated. Conversely, when the hypoxic waters that have risen to the surface remain in an environment with a low O_2 content, conditions for extreme ecological situations arise. In the cases of sharp decrease of S in *BL* [1] it is natural the influence of river inflow to subside more slowly with distance from the mouth and to spread over a larger water area compared to the spread of a river plume from a seacoast. During increased river inflow the greater speed of the incoming water masses is an additional factor, expanding the area of their penetration; the bottom's area, in which the suspended matter sediments, also expands. The river material passes through the mixing zone without noticeable changes in its chemical composition until the marine characteristics of the water begin to prevail[2].

Peculiarities of the intra-annual variability. The observations from the buoys (Fig. 1) cover an annual cycle of variability between July 1, 2022, and Aug. 9, 2023. The chemical and biological data in these time series have a wide range of variability, caused primarily by the diurnal, synoptic and seasonal course of T and solar activity, and of the water and salinity balance. For the purposes of analysis, the monthly mean and extreme values of the study parameters are given in Table 1, which also facilitates comparison with historical data. The period of the measurements of **dissolved oxygen** and **oxygen saturation** is slightly shorter than that of the others – starting from Aug. 2022. The comparison of the graphs (Fig. 1a, b), together with the data from Table 1, shows a qualitatively similar character of the changes in *OS* and *DO* over time. The differences between the respective lakes are mainly quantitative and most clearly noted in the period March-May 2023. The values in *VL* of both *DO* and OS usually exceed those in *BL*. Under the influence of local conditions, the extrema of the O_2 and T regimes are not in a clearly pronounced antiphase. The amplitude of the *OS* changes

[1] Insufficient ventilation during vertical mixing processes together with eutrophication resulting from the decomposition of organisms after the phytoplankton bloom period are two natural sources for the formation of H_2S, already recorded in [2,3], when strong anthropogenic pressure was absent.

[2] It is considered that the sedimentation rate of the incoming suspended sediment into the plume would accelerate sharply upon reaching a saltier (and denser) water mass.

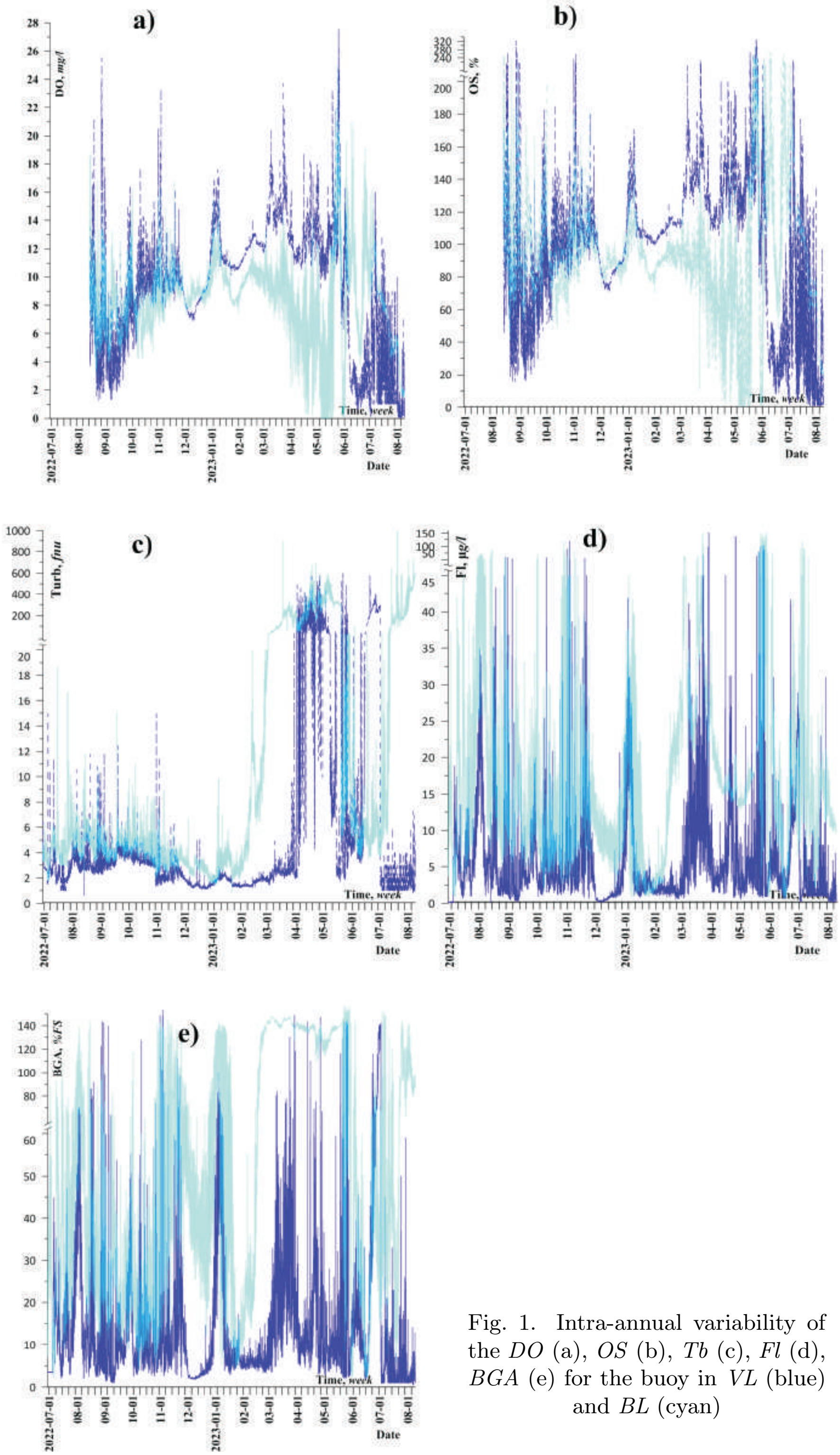

Fig. 1. Intra-annual variability of the *DO* (a), *OS* (b), *Tb* (c), *Fl* (d), *BGA* (e) for the buoy in *VL* (blue) and *BL* (cyan)

Table 1

Monthly mean and extremums of the surface *OS*, *DO*, *Tb*, *Fl*, and *BGA* for both buoys

Month	Varna					Beloslav				
	OS	DO	Tb	Fl	BGA	OS	DO	Tb	Fl	BGA
2022 Jul			**2.3**	**6.3**	**14.5**			**4.4**	**16.9**	**35.8**
			1.0	0.0	2.0			1.7	0.8	2.4
			15.0	26.7	52.7			18.7	62.8	117
Aug	**82.5**	**6.7**	**3.1**	**7.6**	**16.5**	**110**	**8.1**	**5.0**	**23.2**	**43.0**
	14.8	1.2	0.6	0.2	2.0	41.0	3.1	2.4	5.1	11.0
	322	25.5	63.6	61.0	148	254	18.7	11.8	88.0	144
Sep	**69.9**	**6.1**	**3.6**	**4.5**	**12.0**	**96.8**	**7.6**	**4.4**	**13.8**	**26.3**
	15.6	1.3	2.3	0.3	0.9	51.7	4.0	3.1	4.7	9.3
	186	16.6	12.5	53.9	140	183	14.9	15.0	52.0	92.5
Oct	**102**	**9.9**	**3.4**	**4.6**	**10.1**	**86.9**	**7.6**	**4.6**	**11.0**	**22.5**
	50.4	4.7	1.3	0.9	2.5	47.7	4.2	1.9	1.4	3.8
	236	20.7	15.0	89.3	149	99.6	16.2	11.0	115	142
Nov	**111**	**10.1**	**2.3**	**7.2**	**15.2**	**101**	**9.3**	**3.5**	**14.7**	**61.3**
	85.4	7.6	1.3	0.6	2.4	73.6	6.5	2.0	2.7	11.6
	260	23.3	11.6	120	154	185	16.7	8.9	93.1	146
Dec	**85.6**	**8.6**	**1.4**	**1.9**	**5.5**	**87.7**	**8.9**	**2.7**	**9.8**	**45.7**
	70.5	7.0	1.1	0.2	1.8	74.1	7.4	1.6	2.2	12.3
	135	14.0	5.0	23.2	55.0	118	12.2	6.7	29.0	134
2023 Jan	**115**	**12.0**	**1.7**	**6.7**	**17.4**	**96.3**	**10.0**	**2.8**	**12.6**	**63.2**
	8.7	10.0	1.2	0.8	2.9	70.7	7.4	0.8	0	4.3
	170	17.6	3.1	41.8	100	152	15.6	9.8	45.1	142
Feb	**110**	**12.1**	**1.6**	**1.8**	**5.6**	**93.1**	**10.1**	**8.8**	**13.4**	**72.0**
	101	10.7	1.2	0.5	3.3	78.3	8.3	2.4	1.5	11.2
	127	14.1	2.6	5.8	16.3	114	12.5	20.3	31.5	145
Mar	**142**	**14.6**	**2.6**	**10.0**	**23.1**	**93.1**	**9.5**	**140**	**33.7**	**143**
	15.1	2.3	1.4	0.6	3.5	10.1	3.6	18.3	18.7	128
	235	23.7	33.6	153	150	148	14.6	895	148	148
Apr	**135**	**12.9**	**143**	**6.8**	**15.8**	**68.8**	**6.6**	**285**	**16.4**	**133**
	105	10.5	1.9	0.8	2.8	2.4	0.2	45.8	13.0	109
	200	18.8	586	138	148	159	14.3	692	29.9	142
May	**148**	**13.0**	**34.7**	**6.7**	**13.8**	**85.5**	**7.3**	**239**	**25.3**	**111**
	75.6	6.3	1.7	0.6	2.0	0	0	4.9	1.0	2.1
	332	27.6	598	106	145	301	24.9	594	151	157
Jun	**52.9**	**4.2**	**111**	**7.1**	**31.9**	**128**	**9.9**	**5.6**	**14.0**	**33.0**
	5.9	0.5	3.1	0.6	1.9	1.1	0.1	3.5	0.6	2.0
	204	16.4	575	41.6	140	270	20.9	99.2	77.9	144
Aug	**57.7**	**3.9**	**12.8**	**2.6**	**9.5**	**107**	**8.1**	**130**	**16.7**	**61.6**
	1.0	0	0	0	0	54.6	4.0	3.7	2.0	5.6
	231	16.0	308	31.0	142	214	16.2	>1000	117	153

between the separate months is greater in the smaller *BL*. The most significant differences in the O_2 distribution in the two lakes begin at the end of winter and can be associated with the absolute February minimum of T. Convection processes lead to the renewal of the nutrient environment in the upper layer and subsequent accelerated development of phytoplankton and oxygen production, further supported by the typical spring increase in the river runoff and amount of biogens entering with it. Changes in the O_2 content directly affect biological processes, clearly reflected in the increase in *Fl*, *Tb*, and the content of *BGA* (Fig. 1). The period April-May 2023 is critical for the *BL* due to a hypoxia appearance in the surface layer, supported by the decay processes in bottom layer, as well as to the sharp change in living conditions after the decrease in S [1]. Another, less pronounced peak in the annual course of O_2 is observed in October-November. If in cold season the average monthly values of *DO* in *VL* fluctuate around 12–15 mg/l (the absolute maximum of 27.6 mg/l is in May), then the fall average level is ∼10 mg/l with a local maximum in November (Table 1). The content of both oxygen forms decreases sharply in May and November, at the end of each period. The maximal *OS* in the lakes was noted in Aug. 2022 and May 2023. The comparison of *DO* and *OS* with the range for their changes during two periods (1975–1979, 1980–1984) of maximum anthropogenic load on *BL* [4] show correspondence and even an increase in modern values. Regardless of the limitations inherent in comparing data from a one-time sampling (in all previous studies) and from long-term, uninterrupted measurements, and from the differences in the measurement methods used, this is a worrying result for the current ecological state of the lakes.

Turbidity as an integral measure of the degree of scattering and absorption of light depends on a number of factors with different dynamics and mutual feedback between the processes, for most of which in this case there is no objective information available. This is an important environmental characteristic, affecting the height of the photic layer, but tracking changes in *Tb* it is often difficult to separate the cause from the effect. In the period from July 2022 to Jan. 2023 (March for the *VL*), *Tb* changes relatively smoothly with average monthly values in the range of 3–5 fnu and 2–3 fnu for the *VL* and *BL*, respectively (Fig. 1c, Table 1). In the subsequent observing period the qualitative change between the two extreme (winter and summer) phases for plankton, is well pronounced, especially drastically for the shallower *BL*. Turbidity values increase by two orders of magnitude with a maximum in April; the course of monthly changes has an oscillation character, with sharper changes in the shallower basin. Since the sensor calibration scale is for commonly observed limits of change, i.e. up to ∼20 fnu, the high values (Fig. 1d, Table 1) are primarily qualitative in nature. The comparison with the annual course of *BGA* in the *BL* (Fig. 1e) shows a very similar development of the processes in the period Feb.–July 2023. It is clear that the rapid development of **blue-green algae** contributes to the high *Tb*, but the main reason remains unclear. Moreover, in the *VL*, the nature of the changes in *BGA* is different and has a well-pronounced oscillatory regime. The dredging/deposition activities in lakes had an undeniable influence; however, there is no available information about the specific quantities and their space-temporal distribution. The sensors used to determine *Chl* **fluorescence** are corrected based on phycoerythrin, as the characteristic salinity suggests a predominance of marine microorganisms. In the cases of a sharp decrease in *S*, an accumulation of species containing phycocyanin is also possible. The analysis of the primary measurement data showed a qualitative correspondence between the changes in *Chl* and phycoerythrin *Fl*. The latter predominates for both lakes, remaining high even when the *S* decreases. However, from a methodological point of view, the influence of the auxiliary sensor used requires further verification. Monthly mean changes have an oscillatory regime, with maximum in March for *VL* (10.0 µ/l) and *BL* (33.7 µg/l); the level of *Fl* in Varna Lake is lower. Well-pronounced fluctuations with a period of 2 months are also present in the *BGA* average monthly values in the cold half-year (Fig. 1d, Table 1), as for *OS* in both lakes and for *DO* – in the *VL*. The nature of such cyclicality is to be investigated in a more detailed analysis of the results obtained.

Peculiarities of the vertical distribution. By analogy with [1], the features of the vertical distribution of observed parameters are presented through the profiles for the Varna buoy. Its location (in the middle of the eastern half of the lake at a depth of 16.5 m), relative nearness to the canal connecting the *VL* to Varna Bay, and sufficient distance from the Provadiyska river, suggest greater representativeness of the vertical profiles shown and supplement the results from the previous paragraph. The analysis of the data for **oxygen** content and its time variability plays a key role in assessing the ongoing biochemical processes. The graphs (Fig. 2a, b) show that the similarity in the nature of the changes in *DO* and *OS*, established above for the surface layer, also manifests itself vertically. The registered profiles are of different types: quasi-uniform (Aug. 24 and Oct. 30, 2022; Jan. 21, 2023) and those with a more complex, layered structure. The maximal content of O_2 – between 7.5 and 13.5 µg/l, was concentrated in the oxy-homogeneous surface layer with thickness from 2 to 8 m. The oxidation processes occurring near the bottom cover the layer below 10–12 m, sometimes below 14–15 m. The decrease in oxygen content with the depth may also be a consequence of the biological consumption of O_2. The intensification of the oxidation of unstable organic matter near the bottom and in bottom sediments should lead to a decrease in pH, but this is not observed (Fig. 2e). The examples of oxygen deficiency are clearly outlined when *DO* falls below the upper limit of hypoxia 2 µg/l or is even absent. Typically, in almost all profiles a positive gradient is maintained throughout the whole water column. An interesting feature in evolution of the surface layer was manifested on Aug. 28, 2022, measuring the absolute maximum (16.0 µg/l) for *DO*: the layer was reduced into a 3-meter layer of the sharpest changes:

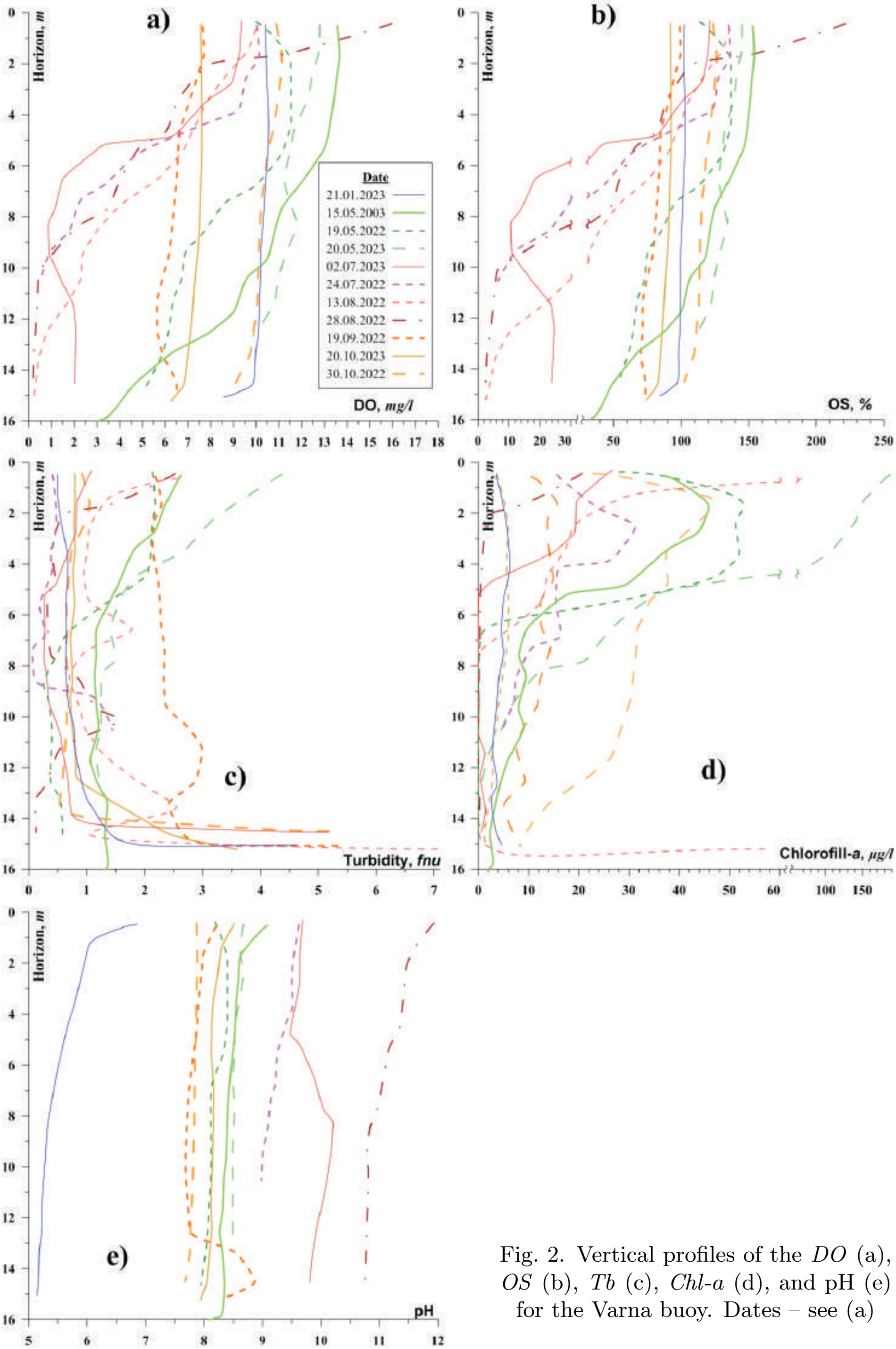

Fig. 2. Vertical profiles of the *DO* (a), *OS* (b), *Tb* (c), *Chl-a* (d), and pH (e) for the Varna buoy. Dates – see (a)

$DO = 6.6$ µg/l at a depth of 3.4 m. Below this depth, *Chl* practically disappears (Fig. 2c), changes in O_2 content are smoother and hypoxia occurres at a depth of 9 m. Another interesting distribution was recorded on July 02, 2022, when a well-defined intermediate layer with a high-gradient upper and lower boundary is located below 5 m. Its appearance is a consequence of hydrological changes below the upper homogeneous layer: between 5 and 8 m, T decreases by 2.5 °C, and S increases by ~2.1 psu [1]. The resulting vertical gradient in density limits the water exchange, as evidenced by the sharp changes in *Chl-a*, *Tb* and pH (Fig. 2c–e). Chlorophyll (the plankton that releases O_2) is absent between 5 and 10 m, but after an oxygen inversion reappears in minimal quantities below 11 m. The high levels of OS and the cases of hypoxia, present in Fig. 2b, are a criterion for the instability of the lake ecosystem and for the continuing anthropogenic impact. In conditions of stratified vertical distribution, when separate layers with different oxygen contents are mixed, the total level of O_2 decreases, which can also lead to a deficiency and conditions for the death of living organisms. If plankton bloom is a sign of a self-cleaning reaction of the environment, then the negative impact on the trophicity of bottom organisms and O_2 depletion are among the main threats to the ecosystem.

The **turbidity** values (Fig. 1c, Fig. 2c) demonstrate the strength of the anthropogenic pressure. The scale of changes for the two graphs is completely different, as the profiles were measured during periods of interruption of dredging activities. The layer at a depth below 14 m (in some cases 11–12 m) is often characterized by increased *Tb*, significantly exceeding the surface one. Slow and prolonged sedimentation of fine fractions (especially the clay component with a size below 2–4 µ) during dredging and dredging spoil disposal contributes to such levels of higher *Tb*. Effects of intensification of the bottom currents are also possible [5].

The chlorophyll-*a* profiles reflect the complicated vertical distribution of the biota (Fig. 2d). In some cases, the relationship with T, S and O_2 in the separate layers is clearly expressed, in others – it is not detected. In the May profiles, the upper 6–7 m layer has a high concentration of *Chl*. The absolute maximum (188 µg/l) was recorded on May 20, 2023, the high content of *Chl* (over 20 µg/l) persisting up to horizon 8–9 m. The satellite monitoring [6] shows a large-scale and prolonged coccolithophore bloom. Starting with an intense summer development, the plankton covered the entire Black Sea from the late 2022 to the winter blooming 2023. In some cases, the maximum *Chl* content is at a depth of 2–3 m, in others it is depleted in the upper 4–5 m. On Aug. 13, 2022, a sharp and strong increase in the bottom concentration (66.5 µg/l) was noted, exceeding the surface one. It can be assumed this was related to the specific stratification at a depth of 14 m after penetration of denser seawater: T decreases by 2 °C and S increases with 0.2 psu [1].

For most of the profiles in Fig. 2e, the **pH** values fall within the standard range of 7–8 with a quasi-uniform distribution. The lowest values in the interval 6.9–5.9 were measured in Jan. 2023 in the upper gradient layer with thickness ~ 2 m; below it, the pH gradually decreased up to 5.1 at a depth of 15 m. Another, opposite situation with unusually high alkalinity stands out for three profiles: the two from July and this from Oct. 20, 2023. The question naturally arises as to the reason for such values. It is known that *Chl* can affect alkalinity: its increased content is a criterion for intensive photosynthesis, CO_2 consumption, H^+ absorption, and OH^- release, i.e. an increase in pH. However, during the decomposition of dead phytoplankton and the oxidation by methane-producing bacteria in the bottom layer, reverse processes occur: CO_2 is released, $CaCO_3$ sediments, and the concentration of H^+ increases, i.e., the total alkalinity decreases. The manifestation of such opposite effects is local, and individually they can hardly cover the entire water column. Doubts about the correctness of the hypothesis are reinforced by a comparison with the other *Chl* and pH profiles (Fig. 2d, e), where no abnormal deviations from standard alkalinity have been recorded for similar layers with high *Chl* content. Another reason for the high pH could be found in unstable operation of the sensor, despite its careful preliminary preparation and calibration immediately before each cruise. Furthermore, the results of several measurements taken in the period after the first registration (July 24, 2022) of increased alkalinity, until the next anomalous ones, give no cause for doubt. The impact of the Provadiyska river (caused by wastewater from soda production) can be considered a third hypothesis. Values of pH above 9 for *BL* first appeared in the period 1955–1963, when the soda plant began operating, reaching 9.8 in 1967–1971. In subsequent periods, the maximal measured values were close to or exceeded 9 [4], even in the *VL*, an absolute value of 9.84 had been measured [7]. The highest value (12.22) is shown for the waters in the canal carrying the "purified" waters to the Provadiyska river [8]. Therefore, the currently measured high pH values should not be ignored. It is logical to assume that in the event of an extreme discharge of high alkalinity wastewater (after intense or prolonged rains) a local analogue of "*soda lake*" is created: high concentrations of sodium carbonate and related salt complexes. The climatic changes favour increased evaporation, the accumulation of dissolved salts and minerals. On the background of delayed water exchange and weak dynamics, spots with increased pH can migrate and exist continuously in the lakes' aquatory. Establishing the real cause of the measured high pH is subject to well-planned future studies.

Conclusions. The presented analysis does not claim to be exhaustive – it is only a preliminary summary of the results from one-year continuous direct in situ measurements. There is a high degree of temporal and spatial variability of the observed parameters, with traditional approaches based on sporadic observations at oceanographic stations, many of the distinctive features of the processes observed here would remain hidden. The operation under real-world conditions of the monitoring system demonstrates its effectiveness, its greatest advantage is the ability to monitor the environment changes as a process, rather than as a diagnosis of the momentary "frozen" state. Despite the general qualitative similarity between the chemical processes in the two lakes, the dynamics of biological ones in the *BL* is greater and leads to local differences. The lake ecosystem continues to experience significant anthropogenic pressure, expressed by the registered cases of hypoxia, oxygen super (up to 300%) saturation, the excessively high *Tb*, the high *Chl* concentration. Negative effects from the Provadiyska river impact can be observed not only in the immediate vicinity of its mouth. Due to a weak water dynamics and limited water exchange, an overall high biological activity, and a periodically spotty hydrological structure, anomalies of the studied characteristics can migrate throughout the entire aquatory before disappearing. The peculiarities in O_2 and pH distribution are directly related to the changes in the amounts, composition and dynamics of suspended and dissolved organic matter and the bottom sediments, to the phase of the hydrological regime of the river runoff and its chemical composition (due to the possibility to discharge of high alkalinity water from Devnya tailings). Overcoming the negative impact of the river outflow requires targeted detailed studies of its plume and spatial transformation.

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