Overall Assessment of Water Quality on Lower Danube River Using Multi-parametric Quality Index

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This study aims to assess the water quality of the Lower Danube River (km 375 - km 175), in sections where hydro-technical works took place for the improvement of navigation conditions. The samples were collected for 36 months from 2011 – 2014 and the quality indicators according to M.O. 161 of 2006: thermal conditions and acidification, oxygen regime, nutrients, salinity, specific toxic pollutants of natural origin, other relevant chemical indicators and 4 hydrological indicators velocity, flow rate, level and turbidity were analyzed. Quality indexes are mathematical tools that are designed to assess overall water quality. The final ICPM value for month 34 is 86 % depicting an increased ecosystem pressure compared to the other evaluated months showing ICPM values between 46 and 58 %.

Keywords: water quality, multi-parametric quality Index, Danube River

Rivers are important water resources, which are used directly for domestic consumption, agriculture, transport, power generation, recreation, etc. [1, 2].

One of the major factors of ecosystem degradation is environmental pollution with chemicals [3] resulting mainly from industrial wastewater discharge, and in a short time the water quality can be influenced by anthropogenic impact [4, 5].

Pollutants are distributed differently between biotic and abiotic compartments or between solid and liquid phases at abiotic level. At the same time, the physical and chemical structure of the pollutant which leads directly or indirectly to environmental effects is important [6, 7].

In Romania, the role of the Danube as local and European waste water collector makes it an important source of pollution in the Black Sea [8].

Numerous hydrological studies had highlighted the major ecological importance of surface waters for the world, so that research on sustainable water management was intensified [9-11].

The overall problem of water quality monitoring programs is derived from providing in relatively short time periods of extensive physicochemical databases that bring challenges regarding results interpretation and in drawing relevant conclusions, the development of mathematical mechanisms that can reduce the amount of evaluated data becoming necessary.

One of the available evaluation mechanisms of monitoring data is the quality indices. These indices are usually developed using reference data regarding the pollutants and a specific ecosystem associated with a water body, the quality of the reached conclusions depending mainly of the similarity between the reference and the evaluated water bodies.

Water quality index is a mathematical tool that integrates complex data into a numerical score to describe an overview of the general water quality [12, 13]. Application of a quality index is of great importance, and this is evident by the development of a significant number of different types of quality indexes in different countries around the world, applied from general to specific purposes [14-16].

This study aims to assess the water quality of the Lower Danube River, in sections where hydro-technical works took place for the improvement of navigation conditions, using information obtained from the analysis of 41 water quality indicators (37 quality indicators from the M.O. 161/ 2006 and 4 hydrological indicators: velocity, flow rate, level, and turbidity) [17].

The hydro-technical works include activities such as dredging, embankments, and sills that may have a potential impact on water quality and biodiversity [18, 19].

An earlier version of this multi-parametric quality index (ICPM) was already in the publishing stages. The previous model used data for just 32 months, only pH was considered a median optimum quality indicator and the anthropic pressure weight was calculated after a different approach relating only to the historical values [20].

The ICPM algorithm involves corroboration of information from related branches of science such as chemistry, biology, ecology, ecotoxicology, hydrology, meteorology, geography, statistics and many other fields of knowledge which are deeply intertwined in an effort to describe the environment.

Developing an ICPM index involves detailed knowledge of ecosystems and the contribution of experts from related fields that allow an optimum adjustment of its mathematical model.

The general mathematical algorithm used for the ICPM computations is presented in figure 1. The evaluated data are the results from the latest months of the monitoring program (4 sets of 41 quality indicators from 30 sampling points – 10 locations) and the calibration data covers the historical results of the monitoring program for 32 months (32 sets of 41 quality indicators from 30 sampling points and 7 sets of 41 quality indicators from another 30 sampling points – another 10 locations).

The calibration sets are filtered to avoid erroneous results influenced by extreme values caused by anomalies at

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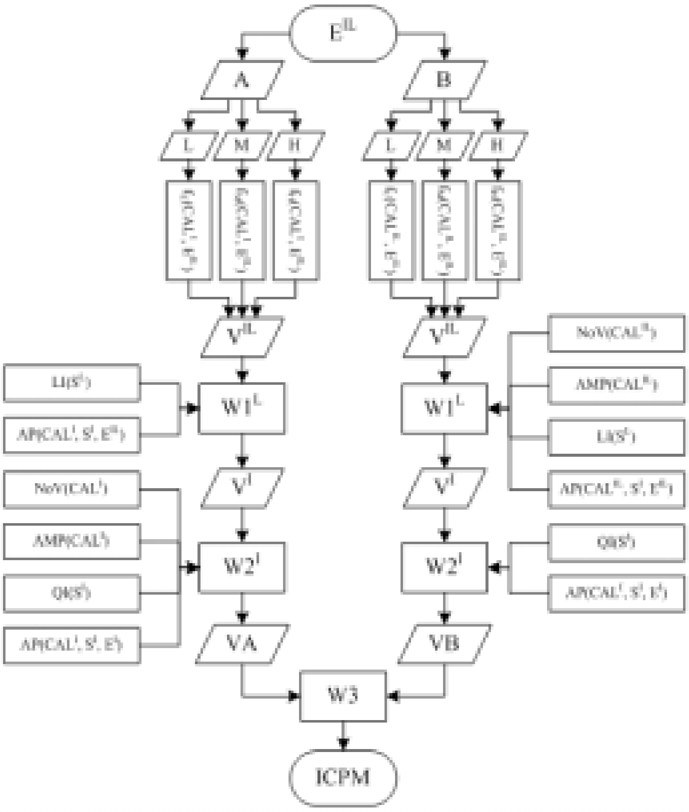

^{I} – at quality indicator levels
^{L} – at location levels
E – evaluated data
A – quality indicators with location independent values
B – quality indicators with location dependent values
L – quality indicators with low optimum values
M – quality indicators with median optimum values
H – quality indicators with high optimum values
f – interpolation/extrapolation functions
CAL – calibration data sets
S – information sources other than CAL
V – sets of intermediary values
W – weighted average
NoV – weight derived from the number of values used in CAL
AMP – weight derived from the amplitude of variations in CAL
LI – weight derived from the location importance
AP – weight derived from the anthropic pressure
QI – weight derived from the quality indicator importance
ICPM – the final ICPM value for the evaluated data

Fig. 1. ICPM algorithm flowchart.

Table 1
INTERPOLATION AND EXTRAPOLATION FUNCTIONS BASED ON THE EVALUATED DATA VALUES VERSUS THE CALIBRATION SETS FOR TYPE A AND B QUALITY INDICATORS WITH LOW, MEDIAN OR HIGH OPTIMUM VALUES (*PERCENTRANK* – MS EXCEL FUNCTION)

Type	Class	$E^{IL} < \min(CAL)$	$\min(CAL) \le E^{IL} \le \max(CAL)$	$E^{IL} > \max(CAL)$
A	L	$\frac{E^{IL} - \min(CAL^{I})}{\min(CAL^{I})}$	$\mathrm{PercentRank}(CAL^{I}; E^{IL})$	$1 + \frac{E^{IL} - \max(CAL^{I})}{\max(CAL^{I})}$
	M	$1 + \frac{\min(CAL^{I}) - E^{IL}}{\min(CAL^{I})}$	$2 \cdot \lvert \mathrm{PercentRank}(CAL^{I}; E^{IL}) - 0.5 \rvert$	$1 + \frac{E^{IL} - \max(CAL^{I})}{\max(CAL^{I})}$
	H	$1 + \frac{\min(CAL^{I}) - E^{IL}}{\min(CAL^{I})}$	$1 - \mathrm{PercentRank}(CAL^{I}; E^{IL})$	$\frac{\max(CAL^{I}) - E^{IL}}{\max(CAL^{I})}$
B	L	$\frac{E^{IL} - \min(CAL^{IL})}{\min(CAL^{IL})}$	$\mathrm{PercentRank}(CAL^{IL}; E^{IL})$	$1 + \frac{E^{IL} - \max(CAL^{IL})}{\max(CAL^{IL})}$
	M	$1 + \frac{\min(CAL^{IL}) - E^{IL}}{\min(CAL^{IL})}$	$2 \cdot \lvert \mathrm{PercentRank}(CAL^{IL}; E^{IL}) - 0.5 \rvert$	$1 + \frac{E^{IL} - \max(CAL^{IL})}{\max(CAL^{IL})}$
	H	$1 + \frac{\min(CAL^{IL}) - E^{IL}}{\min(CAL^{IL})}$	$1 - \mathrm{PercentRank}(CAL^{IL}; E^{IL})$	$\frac{\max(CAL^{IL}) - E^{IL}}{\max(CAL^{IL})}$

sampling or laboratory levels. From a calibration set consisting of approximately 1000 values, up to 6-10 maximum or minimum values may be eliminated.

Firstly, the 41 quality indicators are classified in two categories based on the degree in which the different sampling locations influence the indicator's value.

For the monitored ecosystem, most of the quality indicators fall in the "type A" category, with values that are not significantly influenced by the specific sampling point. The values for the indicators in the "type B" category (water level, velocity, flow rate, Chlorophyll 'a' and turbidity) are influenced by the specific sampling point.

In the next step, type A and B quality indicators are classified based on their desirable environmental values. Pollutants and other microelements are included in the low optimum value (L) indicators class. Indicators such as *p*H, water level, velocity, flow rate and temperature are included in the median optimum value (M) indicators class. The dissolved oxygen and oxygen saturation are included in the high optimum value (H) indicators class.

Each quality indicator calibration and evaluation data sets are arranged in tables with locations in rows and sampling month in columns. The interpolation/extrapolation functions for each type of indicators are presented in table 1.

The values obtained from the interpolation/extrapolation functions undergo 3 stages of weighted averages which will lead to the final ICPM value. The first weighted average (W1) is designed to merge the locations for each quality indicator, focusing on the values in locations that are deemed more important for various reasons. The second weighted average (W2) is designed to merge the quality indicators from each type (A and B), focusing on the values for indicators that are deemed more important for various reasons. The third weighted average (W3) combines the type A and B intermediary values based on the number of quality indicators in each group, leading to the final ICPM value.

The weighting process (W1 and W2) is different for type A and B quality indicators and uses weights derived from the location importance (LI), the anthropic pressures (AP), the number of values (NoV) in the calibration sets, the amplitude of variations (AMP) in the calibration sets and the quality indicator importance (QI). The location importance and quality indicator importance weights are derived from other sources of information (S) such as local protected areas or toxicology reasons which allows the expert to focus more importance on specific locations or groups of indicators. The number of values and the amplitude of variations are derived from the calibration sets and focus more importance for values obtained from larger calibration sets with lower variations. For W2 type A weighting, the AMP has the form:

$$AMP = \frac{\overline{CAL^I}}{0.5 \cdot \overline{CAL^I} + \max\left(CAL^I\right) - \min\left(CAL^I\right)} \qquad (1)$$

and for W1 type B weighting, CAL^I parameter becomes CAL^{IL}.

The anthropic pressures weight is derived from the maximum closeness of the calibration sets minimum and maximum values and the evaluated value to environmental low (LL) and/or high (UL) thresholds imposed by toxicological reasons. For type A indicators in W1, the AP has the form:

$$AP = \max\begin{pmatrix} \dfrac{2}{1+\alpha^{100\left(\frac{UL-\max\left(CAL^I\right)}{UL}\right)}}; \\ 2-\dfrac{2}{1+\alpha^{100\left(\frac{LL-\min\left(CAL^I\right)}{LL}\right)}}; \\ \dfrac{2}{1+\alpha^{100\left(\frac{UL-E^{IL}}{UL}\right)}}; \\ 2-\dfrac{2}{1+\alpha^{100\left(\frac{LL-E^{IL}}{LL}\right)}} \end{pmatrix} \qquad (2)$$

the functions allowing an adequate S – shaped behavior surrounding either LL or UL, varying towards 0 for values far below the threshold, towards 1 for values equal to the limits and towards 2 for values that exceed the limits. The $\alpha = 1.03$ parameter controls the slope of the transition between 0 and 2. For type B quality indicators, the CAL^I parameter becomes CAL^{IL} and for W2 type A and B, the E^{IL} value becomes $\max^L(E^{IL}) = E^I$.

The numerical values for the scores involved in each weighting process are normalized by category to sum = 1 and summed by location in W1 or quality indicator in W2.

Experimental part

Sampling Area

The study area is represented by the Lower Danube River between km 375 - km 175.

The samples were collected for 36 months from September 2011 – August 2014, water samples being collected monthly in 30 locations (10 cross sections with center, left and right banks) and quarterly in 30 additional locations (another 10 cross sections) from the Lower Danube (fig. 2).

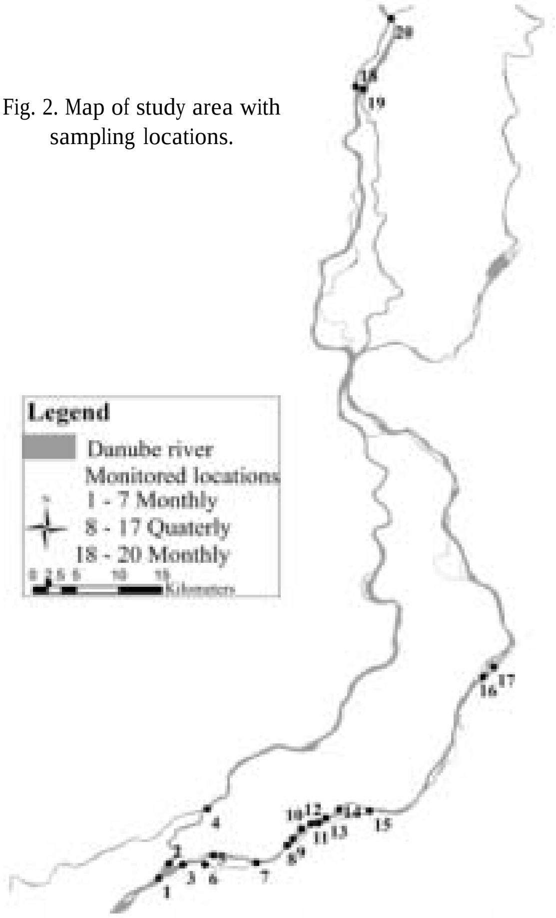

Fig. 2. Map of study area with sampling locations.

Data and Methods

The quality indicators according to M.O. 161 of 2006: thermal conditions and acidification, oxygen regime, nutrients, salinity, specific toxic pollutants of natural origin, other relevant chemical indicators and 4 hydrological indicators velocity, flow rate, level and turbidity, were analyzed in accordance with the current standard methods of analysis.

Results and discussions

This study aims to present the behavior of the ICPM algorithm applied for 4 evaluated data sets covering the monthly sampled locations from month 33 to month 36 and using as calibration the previous 32 months of the Lower Danube monitoring program.

Due to available space limitations, the following examples will be focused on the type A, low optimum quality indicator Total Iron.

The first step was to assemble and filter the calibration tables. From the Fe calibration table consisting of 1170 values, 4 high values and 1 low values were filtered. The fragments of the Fe calibration and evaluation tables presented in table 2 depict 2 high values and 1 low value removed from the calibration set and 1 extreme value (*1689 L3 RB Month 33*) present in the evaluation table.

The next step used the interpolation/extrapolation functions to obtain the intermediary values for each month, quality indicator and location.

As it can be seen from table 3, the obtained intermediary values are dimensionless and relate to the historical evolution of the quality indicator.

The extreme Fe evaluated value has a corresponding intermediary value almost double versus de filtered calibration table (197%).

Table 2
FRAGMENTS FROM THE TOTAL IRON (mg/L) CALIBRATION AND EVALUATION TABLES

No.	Location	Sampling Point	Calibration Values (CAL^{Fe})									Evaluated Values (E^{Fe})			
			...	Month 18	Month 19	Month 20	...	Month 24	Month 25	Month 26	...	Month 33	Month 34	Month 35	Month 36
...												...			
1687	L3	LB	...	0.39	1.00	0.34	...	0.08	0.07	0.17	...	0.64	0.52	0.15	0.28
1688		CN		0.38	0.87	0.63		0.06	0.08	0.13		0.60	0.55	0.16	0.27
1689		RB		0.31	0.81	0.44		0.07	0.07	0.14		**1.97**	0.75	0.16	0.40
1690	L4	LB		0.44	(~~1.05~~)	0.67		0.09	0.16	0.16		0.88	0.63	0.13	0.58
1691		CN		0.42	0.87	0.52		0.10	0.14	0.15		0.93	0.56	0.13	0.36
1692		RB		0.41	(~~1.05~~)	0.70		0.05	0.11	0.17		0.84	0.56	0.15	0.74
1693	L5	LB		0.34	0.82	0.60		0.03	0.09	0.14		0.69	0.58	0.17	0.37
1694		CN		0.38	0.70	0.63		0.07	0.09	0.10		0.89	0.54	0.13	1.12
1695		RB		0.38	0.66	0.48		0.08	0.04	0.07		0.57	0.71	0.14	0.45
1696	L6	LB		0.31	0.83	0.50		0.02	0.02	0.13		0.70	0.53	0.32	0.50
1697		CN		0.43	0.85	0.58		0.02	0.03	0.14		0.65	0.59	0.14	0.32
1698		RB		0.17	0.85	0.55		0.05	(~~0.00~~)	0.11		0.62	0.56	0.17	0.32
...												...			

Table 3
FRAGMENT FROM THE INTERMEDIARY VALUES FOR TOTAL IRON AFTER INTERPOLATION/EXTRAPOLATION

No.	Location	Sampling Point	Intermediary Values (V^{Fe})			
			Month 33	Month 34	Month 35	Month 36
...			...			
1687	L3	LB	89.8%	86.5%	20.0%	56.4%
1688		CN	88.8%	87.4%	22.4%	54.2%
1689		RB	**197%**	93.8%	22.4%	81.6%
1690	L4	LB	98.6%	89.4%	16.1%	88.5%
1691		CN	99.4%	87.8%	16.1%	74.2%
1692		RB	97.7%	87.8%	20.0%	93.8%
1693	L5	LB	92.2%	88.5%	24.6%	76.0%
1694		CN	98.7%	87.2%	16.1%	112%
1695		RB	88.2%	93.1%	17.7%	84.7%
1696	L6	LB	92.8%	86.8%	64.0%	85.9%
1697		CN	90.2%	88.7%	17.7%	64.0%
1698		RB	89.3%	87.8%	24.6%	64.0%
...			...			

Table 4
FRAGMENT FROM THE W1 WEIGHTS FOR TOTAL IRON

No.	Location	Sampling Point	LI W.	AP Weights			
				Month 33	Month 34	Month 35	Month 36
...			...	...			
1687	L3	LB	0.019	0.032	0.033	0.033	0.033
1688		CN	0.031	0.032	0.033	0.033	0.033
1689		RB	0.019	**0.083**	0.033	0.033	0.033
1690	L4	LB	0.019	0.032	0.033	0.033	0.033
1691		CN	0.031	0.032	0.033	0.033	0.033
1692		RB	0.019	0.032	0.033	0.033	0.033
1693	L5	LB	0.019	0.032	0.033	0.033	0.033
1694		CN	0.031	0.032	0.033	0.033	0.038
1695		RB	0.019	0.032	0.033	0.033	0.033
1696	L6	LB	0.019	0.032	0.033	0.033	0.033
1697		CN	0.031	0.032	0.033	0.033	0.033
1698		RB	0.019	0.032	0.033	0.033	0.033
...			...	...			
Monthly Sum			1.000	1.000	1.000	1.000	1.000

Table 5
INTERMEDIARY VALUES FOR THE EVALUATED TYPE A AND *B* QUALITY INDICATORS AFTER LOCATION WEIGHTED AVERAGING

Quality Indicator	Intermediary Values (V^{i})			
	Month 33	Month 34	Month 35	Month 36
BOD^5	24.3%	28.0%	7.4%	-4.6%
COD^{Mn}	51.0%	79.6%	14.2%	4.6%
COD^{Cr}	37.4%	99.1%	31.3%	31.5%
DO	77.4%	73.6%	80.3%	78.2%
OS	49.0%	13.1%	6.7%	28.6%
$N\text{-}NH_4^+$	20.6%	14.7%	32.5%	20.1%
$N\text{-}NO_2^-$	56.5%	-0.3%	57.6%	22.5%
$N\text{-}NO_3^-$	49.5%	64.5%	33.8%	48.7%
TN	79.8%	86.9%	45.8%	53.5%
$P\text{-}PO_4^{3-}$	88.3%	112.8%	67.0%	94.4%
TP	95.9%	134.9%	43.0%	89.0%
Chlorophyll "a"	80.2%	78.3%	93.8%	71.2%
Conductivity	12.5%	46.2%	53.4%	17.4%
TDS	11.7%	41.1%	61.1%	31.8%
Cl^-	25.8%	11.4%	6.3%	-2.3%
SO_4^{2-}	41.0%	63.3%	26.5%	26.6%
Ca^{2+}	19.5%	53.4%	33.6%	45.4%
Mg^{2+}	-0.1%	9.5%	48.7%	25.9%
Na	1.2%	21.9%	25.7%	30.3%
Cr	94.8%	174.6%	53.9%	82.9%
Cu	64.9%	272.7%	78.6%	86.4%
Zn	88.4%	165.5%	38.7%	65.1%
As	17.1%	68.1%	7.4%	40.9%
Ba	31.5%	37.1%	6.8%	37.8%
Se	70.7%	94.0%	47.7%	98.2%
Co	75.2%	131.7%	32.6%	71.1%
Pb	96.4%	344.2%	49.1%	67.7%
Cd	19.6%	115.6%	60.0%	27.2%
Fe	**95.7%**	90.0%	44.9%	76.8%
Hg	0.0%	0.0%	0.0%	0.0%
Mn	68.1%	126.6%	40.2%	58.7%
Ni	73.3%	262.4%	68.4%	81.2%
MBAS	7.1%	11.8%	11.1%	8.4%
Phenol Index	29.8%	51.6%	21.2%	42.5%
AOX	25.4%	28.7%	10.2%	16.2%
Temperature	24.9%	79.2%	87.5%	69.3%
pH	20.8%	46.6%	76.9%	68.0%
Turbidity	80.1%	82.2%	99.3%	99.4%
Flow Rate	87.1%	81.0%	23.5%	50.9%
Velocity	40.4%	62.8%	98.9%	98.9%
Level	92.1%	81.0%	22.4%	53.0%

Since Fe is a type A quality indicator, in the first weighting stage only LI and AP weights were calculated. For type B quality indicators all 4 weights were calculated. As it can be observed in Table 4, the LI weight focus center sampled versus river banks values and the AP focuses the extreme values versus the calibration behavior and toxicological limits.

After the first weighting process the intermediary values at indicator levels are obtained (table 5).

Although the extreme iron value of 197% had an AP weight of 2.6 times larger than its surrounding values, the cumulated weight (LI+AP) where only 1.6 times larger than the average for the other locations. This is due to the fact that the extreme value was recorded near the Right Bank and the LI focus the Center sampling points. A further improvement to the algorithm would be to introduce the possibility to differentiate the weight type importance towards AP.

The larger intermediary values obtained for month 34, mostly for the total metals content indicators, are due to an increase in the solid suspended matter content in samples, suggesting the re-suspension of sediments under hydro-meteorological pressures in the Danube Catchment Area.

Table 6
INTERMEDIARY AND FINAL ICPM VALUES

	Month 33	Month 34	Month 35	Month 36
VA	46%	88%	41%	47%
VB	61%	71%	83%	85%
ICPM	59%	86%	46%	52%

The next steps of the ICPM algorithm consists in calculating the indicator level weights and the second weighted average by indicator type. The intermediary type A and type B values (VA and VB) are then weighted averaged with the number of type A and B quality indicators yielding the final ICPM value (table 6).

The final ICPM value for month 34 is 86% depicting an increased ecosystem pressure compared to the other evaluated months showing ICPM values between 46 and 58%.

Based on interpolation/extrapolation functions, the final ICPM value can range from negative values to zero if the vast majority of quality indicators are lower than historical minimum values, between 0 and 100% if the majority quality indicators have values that were found in the range of the historical data and values over the unit (> 100%) when the vast majority of quality indicators have values exceeding the maximum historical values.

Considering the ICPM algorithm development so far, further improvements could be made regarding a subroutine to favor some types of weights in contrast to the others. Also, further work is needed to adequately correlate the final ICPM values and factual effects at ecosystem level.

Conclusions

Based on the interpolation and extrapolation functions, the final ICPM value varies from negative numbers to zero if most of the evaluated quality parameters have lower values than the historical volume, from zero to one hundred if most of the evaluated values are in the range of the historical volume and numbers greater than one hundred if most of the evaluated values are higher than the historical volume.

The ecosystem quality assessment through ICPM evaluation is a versatile way to account for various changes in environmental parameters and the final results are accessible to all interested parties.

Multi-parametric quality index (ICPM) is a dimensionless number used to evaluate the overall quality of the water, being a useful tool in quality management, for policy makers and the public.

The presented ICPM algorithm is still at the development stages, further studies being necessary to achieve its full potential as an ecosystem level index.

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