Journal of Sustainable Development of Energy, Water and Environment Systems

http://www.sdewes.org/jsdewes

Year 2025, Volume 13, Issue 2, 1130552

Original Research Article

Changes in the Physicochemical Parameters of Surface Water Over a Period of 35 Years

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Cite as: Gotal Dmitrovic, L., Čerepinko, D., Changes in the physicochemical parameters of surface water over a period of 35 years, J.sustain. dev. energy water environ. syst., 13(2), 1130552, 2025, DOI: https://doi.org/10.13044/j.sdewes.d13.0552

ABSTRACT

The research was based on the change in physical and chemical parameters of surface water over 35 years. Surface water (river) flows in a sensitive area according to the Nitrate Directive. Statistical analysis was used to examine the connection between changes in the quality of surface water and the construction of municipal waste water drainage systems, changes in agricultural production and demographic changes. The research highlights significant positive changes in surface water quality, primarily attributed to the implementation of sewage systems, municipal wastewater treatment, and reduced agricultural pollution. Regulatory modifications in agriculture, demographic transformations, and the influence of the Nitrates Directive on agricultural output have contributed to the decline in pollution levels in the river.

KEYWORDS

Plitvica river, Sewerage, Agriculture, Varaždin County, Pearson correlation coefficient.

INTRODUCTION

One of the primary global environmental concerns is the quality and availability of freshwater resources. Intensive agriculture, industrialization, and population growth are increasing demands on water resources, which remain as limited today as they were two millennia ago [1]. Furthermore, all water users contribute to pollution, posing significant health risks that are now more apparent than in the past. Freshwater constitutes only 3% of the Earth's total water supply and is unevenly distributed across regions, exacerbating shortages in certain areas. Water scarcity can be classified into two levels based on assessments of a nation's renewable water resources and per capita water needs [2]. According to Population Action International [3], by 2025, 54 countries facing water stress or scarcity could be home to over 2.8 billion people, a figure projected to exceed 4 billion by 2050. It is anticipated that many future conflicts will arise from the pressures associated with the limited availability of clean freshwater. Currently, between five to twelve million people die annually from waterborne diseases, scarcity, and unsanitary living conditions, making contaminated water the leading cause of environmental mortality worldwide. In addition to undermining economic and developmental initiatives, water pollution severely hampers the health and well-being of millions [4].

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Two major river basins delineate the Croatian territory: the Adriatic Sea Basin, which encompasses the coastal region, and the Danube River Basin, which includes the continental portion of the country. The hydrological, geographical, and geological characteristics of these two basins, along with their vegetation cover, are distinctly different. Consequently, pressures on water quality vary based on these geographic differences.

In the continental region, the primary threats to water quality are attributed to widespread pollution from agricultural practices. The majority of the Adriatic coast is characterized by karst topography, rendering it particularly susceptible to pollution. Beyond these fundamental physical features, the impacts on water quality are significantly influenced by human activities and the extent of catchment areas. Additionally, smaller rivers are generally more vulnerable to various forms of contamination compared to larger rivers [5].

Human activities significantly impact aquatic ecosystems and can pose substantial threats to freshwater resources, affecting both water quantity and quality. Water pollution is defined as any alteration in water quality resulting from the introduction, release, or disposal of nutrients and other substances into water bodies, as well as the influence of energy and other factors that modify the properties of water.

Water pollution encompasses the degradation of water quality due to physical, chemical, biological, or radiological contaminants. The sources of water pollution can be categorized into several distinct types, including [6]:

- Natural - volcanic eruptions, sandstorms, forest fires…
- Artificial - exploitation of raw materials, transport, agriculture, waste dumps, energy.
- Physical – change in the basic characteristics of water
- Microbiological – caused by the presence of pathogenic microorganisms that are not indigenous to water systems, and have arrived as waste materials.

Pollution in natural surface water is frequently attributed to inadequate wastewater treatment. Domestic wastewater typically exhibits elevated concentrations of phosphorus, nitrogen, carbon compounds, pathogens, endocrine disruptors, heavy metals, and pharmaceuticals [7]. Additionally, various agricultural practices significantly contribute to water pollution through the excessive application of pesticides and chemical fertilizers. These substances can leach into groundwater and subsequently enter surface water bodies, leading to alterations in the physicochemical properties of water that adversely affect aquatic ecosystems. Nutrients originating from agricultural runoff contribute to eutrophication, resulting in decreased dissolved oxygen levels and posing serious challenges for aquatic organisms [8].

Agriculture is primarily categorized as a diffuse source of soil and water pollution. According to data from the United Nations Economic Commission for Europe (UN/ECE, 1993), the predominant cause of water pollution in agricultural production arises from the excessive and inefficient application of nitrogen and phosphorus fertilizers, followed by the use of pesticides and heavy metals [9]. Agriculture is a significant contributor to water pollution, introducing contaminants such as nutrients, plant protection products (pesticides), microorganisms, and genetically modified organisms into aquatic systems. Notably, agriculture is the leading source of nitrogen pollution, contributing to more than half of the total nitrogen load on water resources in Europe. When considering only anthropogenic sources of nitrogen, agriculture’s contribution to nitrogen pressure on water resources increases to approximately 63%. Nitrogen compounds, including nitrites, nitrates, and ammonium, are highly mobile in the soil solution and readily leach into water bodies. These nutrients enter surface waters through various pathways, including surface runoff, drainage water, soil erosion, and direct input methods, such as the application of mineral fertilizers along the edges of watercourses [10].

The Nitrates Directive (Council Directive 91/676/EEC), enacted in 1991, is a European Union regulation aimed at protecting water resources from nitrate pollution originating from agricultural activities. This directive mandates that EU member states identify areas vulnerable to nitrate contamination and develop and implement operational programs designed to prevent such pollution [11]. The Nitrates Directive mandates that EU member states implement its provisions through a five-step process, which includes:

1. determination of polluted, i.e. waters threatened by nitrate pollution,
2. determination of areas (zones) vulnerable to nitrates where the use of nitrogen fertilizers should be limited,
3. development of principles of good agricultural practice, the application of which is mandatory in areas vulnerable to nitrates, and recommended in other areas,
4. creation of an action plan within areas vulnerable to nitrates, and
5. creation of a national monitoring program for nitrate concentration and water eutrophication, as well as evaluation of the effect of applied measures and reporting on the success of their implementation.

The directive delineates the conditions for the application of animal manure, specifying the methods and duration of its storage, as well as the timing and techniques for its application. It also imposes limitations on the use of nitrogenous mineral fertilizers. Agricultural producers whose farms are located in areas designated as vulnerable to nitrates must comply with the requirements established by the Nitrates Directive [12].

Croatia has complied with the Nitrate Directive (91/676/EEC) whose aim is to reduce water pollution by nitrates originating from agriculture and to prevent further pollution. According to research conducted from 2002 to 2007 [13], in the areas with a relatively high degree of agricultural activity, there is no statistically significant difference over the years or seasons within the year, but the interaction between locations and years was significant.

Also, floods can cause significant economic and social damage, as well as serious environmental consequences by transporting pollutants from inundated areas into water bodies. Flooding can also lead to habitat destruction, resulting in reduced biodiversity [14]. Moreover, floods often facilitate the discharge of untreated wastewater, leading to an increase in pathogenic microorganisms [15] and raising the risk of outbreaks of acute gastrointestinal diseases [16]. Additionally, flooding contributes to elevated turbidity [17] and increased concentrations of dissolved organic matter (DOM) [18] and suspended solids [19]further compromising water quality and aquatic ecosystems.

To assess how the aforementioned changes have influenced the variation of the specified parameters, data from the Plitvica River were employed. [20]

MATERIALS AND METHODS

A total of three samples were taken at each location during each sampling event. The following physicochemical parameters of the surface water (river) were subsequently analyzed to establish a comprehensive baseline assessment:

a - pH-value
b - dissolved oxygen
c - saturation
d - biochemical oxygen demand in 5 days (BOD_5)
e - chemical oxygen demand (COD)
f - total dry matter (TDM)
g - total suspend solids (TSS)
h - combustible dry matter
i – ammonia (NH_3)
j – nitrites (NO_2)

Sampling and testing were performed by an accredited laboratory at the Institute of Public Health of Varaždin County, the Health Ecology Service. The procedures followed the accredited methods outlined in Table 2.

The laboratory is authorized by: the Ministry of Health of the Republic of Croatia (Class: UP/I-541-02/17-03/04; Registration No.: 534-07-2-1-2/3-17-03, dated October 16, 2017), the Ministry of Environmental Protection and Energy of the Republic of Croatia (Class: UP/I-325-07/19-02/04; Registration No.: 517-07-1-2-1-19-3, dated April 17, 2019), and the Ministry of Agriculture of the Republic of Croatia (Class: UP/I-322-01/15-01/73; Registration No.: 525-10/1308-16-8, dated April 11, 2016).

Table 1 Analytical methods

The name of the parameter	Method
Sampling	HRN ISO 5667-6:2016 (ISO 5667-6:2016)
Temperature	method P-7.2.1-40, ed. 1, 2020-06-08; Standard methods, 20th edition, 2550 A., 2550 B.
pH value	HRN EN ISO 10523:2012 pH value at 25°C
Dissolved oxygen	Method according to Winkler * mg/O_2L Standard methods, 20th edition
Biochemical oxygen demand (BOD)	incubation for 5 days at 20°; Standard methods, 20th edition
Chemical oxygen demand (COD)	method P-7.2.1-45, ed. 1, 2020-06-08
Ammonium	method P-7.2.1-80, ed. 1, 2020-09-03
Nitrates	HRN EN ISO 10304-1:20098
Nitrites	HRN EN ISO 10304-1:20099
Oxygen saturation	Calculation
Total dry residue	gravimetry
Filtered dry residue	gravimetry
Combustible dry residue	gravimetry

Additionally, demographic data were sourced from the population register for the Community of Varaždin Municipalities (excluding the Municipality of Čakovec) for the year 1980 and from Varaždin County for 2021. This data was stratified by sampling location and included the following parameters:

- The number of farmers
- The number of residents living in households or apartments with sanitary wastewater drainage

Specifically, data regarding the population in each settlement traversed by the Plitvica River was compiled for the years 1980 and 2021.

Using the collected data, the study aims to investigate potential correlations between the concentration of pollutants in the Plitvica River, the assessed physicochemical parameters, and the increase in the number of households with municipal wastewater drainage, as well as the usage of fertilizers and changes in population density. Statistical methods applied for data analysis include descriptive statistics and regression techniques (including correlation analyses), which are further elaborated upon in the subsequent sections.

Means - measures of central tendency are determined by describing a set of variable data with a single number, a constant. Mean values obtained using all data are called complete. Complete mean values, used in this work, include the arithmetic mean. If the mean value is determined by the position of the data in the series, then it is called the positional mean. Positional mean values, used in this work, are the median and the mode [21].

The **mode** is the form of a qualitative or quantitative characteristic that occurs most often, and is the form of the characteristic (value) with the highest frequency. It is disadvantageous that the mode cannot always be determined, e.g. when there are no two identical values in the data set (e.g.

Table 5, Table 6, Table 7, Table 8, Table 9, Table 10 and Table 11). If the mode is the smallest or largest value in the data set, then the mode is not a suitable mean value [21].

The **median** is the value of a feature and represents the value that divides a ranked data set into two equal parts. Therefore, in order to determine the median of ungrouped numerical data, they should be sorted by size. If the data number is even, the median is equal to half the sum of the values of the middle two members of the ordered series. The median is the positional mean that is not affected by very small or very large values in the series. This property is desirable because it provides a mean value that represents the series well [21].

The **arithmetic mean** is the most important mean value and is the most commonly used. It belongs to the complete means because it is calculated based on the data values of the entire population [21]. The arithmetic mean is the ratio of the sum of the values of a numerical series to the number of its members (1):

$$\bar{x} = \frac{1}{N}\sum_{i=1}^{N} x_i \tag{1}$$

where:
$\sum_{i=1}^{N} x_i$ - the sum of the values of the numerical series and
N - the number of members.

The arithmetic mean is calculated only for numerical values, and its value does not have to coincide with any value in the data set. Since it belongs to the complete means, it is affected by all the values in the data set. If there is a very small or very large value in a data set that stands out from the others, the arithmetic mean will be influenced by them and may therefore poorly represent the data set. Mean values are usually not sufficient to describe a data set since different sets may have the same mean values, so measures of dispersion are used in addition to mean values to describe a data set. The most commonly used measures of dispersion are: the range of variation, which is based on a portion of the data, and the variance, standard deviation, and coefficient of variation, which are based on all data [22].

The most important measure of dispersion in statistics is the variance, the standard deviation derived from it, and the coefficient of variation. **Variance** (3) is the mean square of the deviation of the value from the arithmetic mean [21]:

$$\sigma^2 = \frac{1}{N}\sum_{i=1}^{N} (x_i - \bar{x})^2 \tag{2}$$

The positive square root of the variance is the **standard deviation** (4) [21]:

$$\sigma = \sqrt{\frac{1}{N}\sum_{i=1}^{N} (x_i - \bar{x})^2} \tag{3}$$

The ratio of the standard deviation to the arithmetic mean multiplied by 100 is the **coefficient of variation** (5) [21]:

$$V = \frac{\sigma}{\bar{x}} \cdot 100 \tag{4}$$

The State Statistical Office collects and publishes data on the population, as well as other data on the population of the Republic of Croatia, every 10 years. The data collected depend on the year of collection, only the population is collected every 10 years.

The population of the observed area for the years relevant to this research, according to the above source, is shown in Table 3.

Table 2 Number of inhabitants (population) [23]

Year	Number
1971	183 711
1981	186 899
1991	187 343
2001	184 769
2011	175 951
2021	159 487

Since this is a functional (non-stochastic) relationship between phenomena (population - year), using a scatter diagram, a "cloud of points" is obtained. Based on the position, direction and width of the "cloud of points", conclusions are drawn about the existence of relationships, or their: direction, strength and shape. If points appear on the scatter diagram that deviate significantly from other pairs of points, they should be ignored, or excluded from the analysis [24]. In this case, it is a curvilinear nonlinear form, or nonlinear regression is applied.

Since it is a curvilinear shape, the "cloud of points" is divided into two parts in order to achieve a more accurate analysis. In this way, the assessment of the relationship between the variables changes as follows:

a) In the first part, up to the maximum value, for 1991, there is a curvilinear positive relationship between the variables

b) In the second part there is a negative curvilinear relationship. [25]

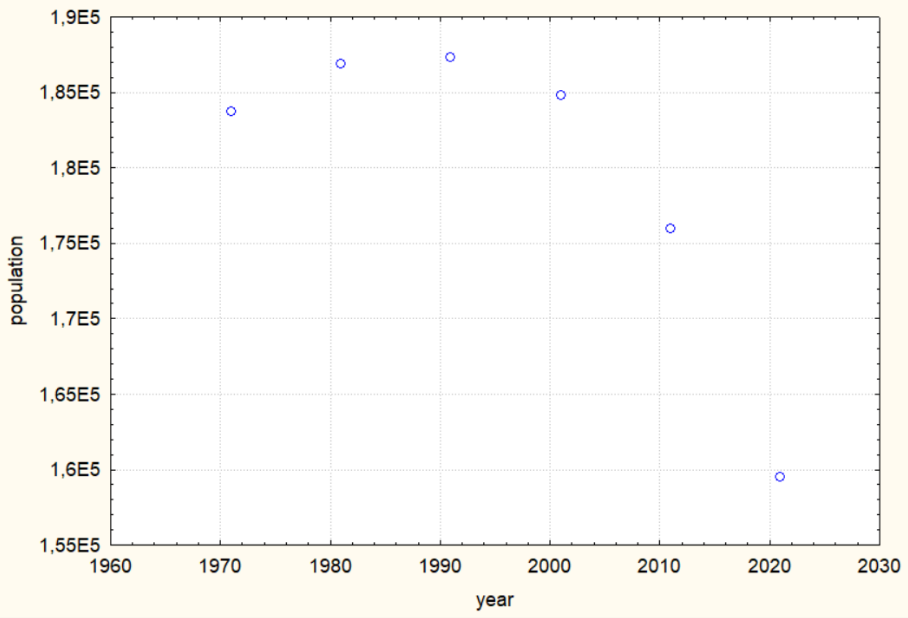

Figure 1 Graph of the function - dependence of the population on the year

For the year 1988, the population is calculated according to the line equation (6). By inserting the value (7), the population for the year 1988 is obtained.

$$f(x) = -1.7377 \cdot 10^5 + 181.6\, x \tag{5}$$

$$f(x) = -1.7377 \cdot 10^5 + 181.6\ \cdot 1\,988 = \ 187\,250.8 \tag{6}$$

For the year 2023, the population is calculated according to the line equation (8). By inserting the value (9), the population for the year 2023 is obtained.

$$f(x) = 2.7155 \cdot 10^6 - 1\,264.1\, x \tag{7}$$

$$f(x) = 2.7155 \cdot 10^6 - 1\,264.1 \cdot 2\,023 = \ 158\,225.7 \tag{8}$$

The approximation for Figure 14, Figure 15 and Figure 16 was made in the same way.

The relationship between physicochemical parameters of surface water (BOD_5, COD, total dry residue, filtered dry residue, combustible dry residue, NH_3 and NO_2) and coverage by the sewage network, i.e. agriculture, is expressed by Pearson's correlation coefficient. According to the definition [25], the Pearson correlation coefficient (r) is a measure of the direction and degree of statistical association, and is calculated according to (9):

$$r = \frac{\sum x_i y_i - n\bar{x}\bar{y}}{\sqrt{\sum x_i^2 - n\bar{x}^2} \cdot \sqrt{\sum y_i^2 - n\bar{y}^2}} \tag{9}$$

When the correlation coefficient is greater than 0.5, it can be determined that there is a medium-strong correlation, and from 0.8 it is strong.

RESULTS AND DISCUSSION

Plitvica river has been subjected to long-term monitoring for various parameters related to water pollution. The collected data were compared with information on demographic trends and economic activity derived from decennial population censuses. The Plitvica River is a right tributary of the Drava River, characterized by its meandering course, which lies entirely within the boundaries of Varaždin County (Figure 1). The Plitvica basin encompasses the area south of the Drava River, extending to the Varaždinsko-Topličko Gorje (Varaždinsko-Topličko Mountains) to the south, which delineate the watershed with the Bednja River, and to Vinica-Breg in the west, where the source of the Plitvica River is situated. This basin extends eastward to the confluence with the Drava River.

The Plitvica springs from the northeastern hills of the Maceljsko Gorje, at the foot of the Viničko Gorje at an elevation of approximately 300 meters above sea level. It flows into the Drava River near Veliki Bukovac, slightly upstream from the confluence of the Bednja and Drava rivers. The valley of the Plitvica River is predominantly composed of Drava alluvium (gravel and sand) overlaying a relatively thin layer of humus. The course of the Plitvica River and its valley represent some of the most prominent landscape features in Varaždin County. The total length of the Plitvica River, from its source to its mouth, is 62.9 kilometers.

The area of the Plitvica River basin is approximately 283 km², of which around 40% is classified as mountainous. The main tributaries of the river include Crna Mlaka, Tužna, Piškornica, and Zbel. All right tributaries are lowland streams, exhibiting only minor elevations along their courses, while the left tributaries are predominantly lowland streams with minimal gradients in certain sections.

The basin is characterized by an elongated shape throughout its entirety, with slight elevation changes in the lower and middle reaches. This topography contributes to the meandering nature of the river and results in a very slow discharge of water from its banks. Mosaic habitats are the most prevalent ecological communities along the Plitvica River.

Surrounding the river, defined as a low-velocity watercourse, a riparian vegetation belt has developed, prominently featuring species such as willows, black alders, field ashes, holm oaks, and field elms. In some areas, this riparian belt extends to include groves of willow, alder, and poplar, as well as mesophytic meadows. There are no extensive forest complexes in this region. In addition to the groves and meadows, cultivated agricultural areas predominantly reach the riparian vegetation belt [26].

The Plitvica River exhibits both seasonal and torrential characteristics, resulting in elevated water levels and flow rates during the spring and autumn, followed by significantly reduced levels during the summer months. Human activities, such as the construction of hydrotechnical infrastructure, unauthorized water extraction for irrigation, unregulated gravel excavation, and improper waste disposal, contribute to the occurrence of "deadlocks" or slowdowns at specific locations, thereby disrupting the natural flow regime of the river. Additionally, the challenges posed by drought conditions and excessive precipitation, exacerbated by climate change, further complicate the hydrological dynamics of the Plitvica River [27].

Figure 2 Research location with sampling points

For years, the water quality in the Plitvica River has indicated significant pollution primarily originating from agricultural land, particularly in the form of nitrogen compounds. Settlements that discharge municipal wastewater into the Plitvica River must address wastewater treatment, as the river's limited flow capacity prevents effective self-purification. Consequently, connections to the Plitvica River should be prohibited for drainage systems that lack an accompanying wastewater treatment facility [28].

The assessment of agricultural soil sensitivity to pollutant leakage encompasses 26,594 hectares of agricultural land within the Plitvica-Drava region alluvial plain of Varaždin County. Since the 1960s, most of these areas have engaged in conventionally intensive agricultural practices that often utilize ecologically questionable plant protection agents and mineral nitrogen fertilizers. Additionally, monoculture corn cultivation and reduced crop rotation practices, lacking nitrogen-fixing legumes, are prevalent.

The analysis reveals that 5,193.8 hectares of agricultural soils are classified as highly sensitive to pollutant leakage, while 6,955.8 hectares are categorized as low-sensitive, 5,618.2 hectares as moderately sensitive, and 8,826.6 hectares as weakly sensitive. Agricultural soils along the banks and in the upper and middle reaches of the Plitvica River exhibit very low sensitivity to pollutant leakage (Class I). Weakly sensitive soils (Class II) and moderately sensitive soils (Class III) predominantly occur in the eastern area of the Plitvica-Drava alluvial plain. In the northwestern lowlands, agricultural soils with moderate (Class III) and strong (Class IV) sensitivity to pollutant leakage are primarily present.

Based on these findings, it can be concluded that the first aquifer in the Plitvica-Drava plain is of an open type and is potentially very vulnerable to mineral nitrogen pollution, particularly from nitrates [29]. The study area is located in a Nitrate Vulnerable Zones (NVZs) according to the Nitrates Directive (Figure 2).

Figure 3 Nitrate vulnerable zones (NVZs) [30]

Since the Plitvica River was originally studied back in 1988, the physicochemical parameters of surface water that were assessed were typical for the time period in evaluating pollution of surface water. State Statistical Office of the Republic of Croatia's 1993 Statistical Yearbook of Croatian Counties [31], shows that the population of the Union of Municipalities of Varaždin (excluding the Municipality of Čakovec) was 183,711 in 1971, 186,899 in 1981, and 187,343 in 1991 [25]. Data from the lists of the Municipalities of Varaždin, Ivanec, Novi Marof, and Ludbreg are used for this paper. Varaždin County is home to 159,487 people, according to the State Bureau of Statistics' 2021 Census [23].

Due to the economic stagnation experienced at the end of the 1970's and into the 1980's, attributable to the global oil crisis and escalating interest rates in international financial markets, a significant portion of the population shifted towards more intensive agricultural practices [32]. [28] After an extended economic crisis, the homeland war, and the transition from socialism to capitalism in the early 1990's, Croatia's economy experienced significant growth [29]. Regrettably, waste management and environmental preservation were subordinate to economic development in terms of priority.

By the end of the 20th century, sites designated for the legal and sanitary disposal of waste with waterproof foundations were scarce. Similarly, the municipal water filtration and drainage infrastructure within settlements faced comparable challenges, leading to frequent pollution of small surface watercourses [20].

The objective of this paper is to assess changes in fundamental physicochemical parameters over a 35-year period and to investigate how the construction of sewage systems, modifications in agricultural practices (including the reduction of agricultural land along the Plitvica River prior to the enforcement of the Nitrates Directive), and population decline have impacted these physicochemical parameters.

Water sampling of the Plitvica River in 1988 and in 2023 was done along its entire course at 14 locations (Table 1 and Figure 1).

Table 3. Locations

Number	Locations
1	Plitvica Peščenica Vinička
2	Plitvica Vočanska
3	Plitvica Ladanje Donje
4	Plitvica Korenjak
5	Plitvica Druškovec
6	Plitvica Greda
7	Plitvica Cerje Tužno
8	Plitvica Vidovec
9	Plitvica Jalkovec
10	Plitvica Varaždin
11	Plitvica Kneginec Donji
12	Plitvica Kelemen
13	Plitvica Jalžabet
14	Plitvica Zamlaka

The comparison of the values of the analysis results from 1988 and 2023 is shown graphically by sampling location for each parameter in Figure 4 – Figure 13 and Table 5 – Table 14.

In the analysis of pH values (Figure 4, Table 5), there are no large deviations between the measurement values from 1988 and 2023.

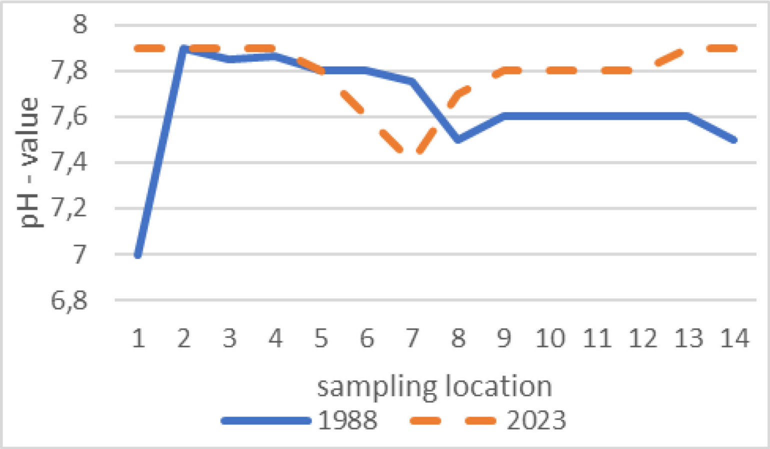

Figure 4 Comparison between 1988 and 2023 for pH-value

Table 4 Descriptive statistics for pH-value

Parameter	1988	2023
Average	7.64	7.79
Median	7.6	7.8
Mode	7.6	7.9
St. deviation	0.23	0.14
Variance	0.05	0.02
Coef.var. (%)	2.99	1.85

The results regarding the concentration of dissolved oxygen (Figure 5, Table 6), indicate a noticeable decrease in 2023 compared to 1988. This reduction can be attributed to the partial regulation of the flow of the Plitvica River.

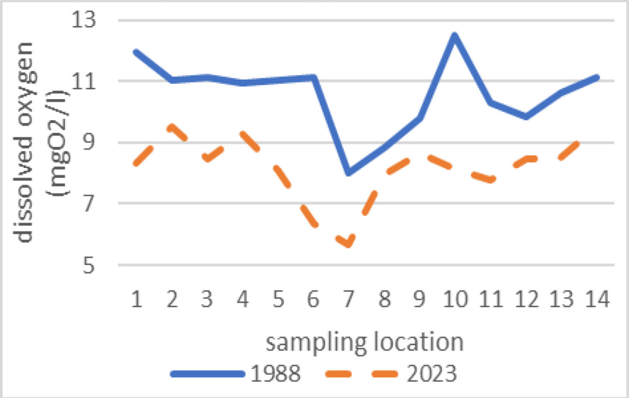

Figure 5 Comparison between 1988 and 2023 for dissolved oxygen

Table 5 Descriptive statistics for dissolved oxygen

Parameter	1988	2023
Average	10.59	8.19
Median	10.99	8.39
Mode	-	9.51
st. deviation	1.39	1.16
Variance	1.39	1.16
coef.var. (%)	11.13	13.13

The observed decrease in oxygen saturation (Figure 6, Table 7), alongside the reduction in dissolved oxygen concentration in 2023 compared to 1988, can also be attributed to the partial regulation of the Plitvica River, which has led to a reduction in flow velocity.

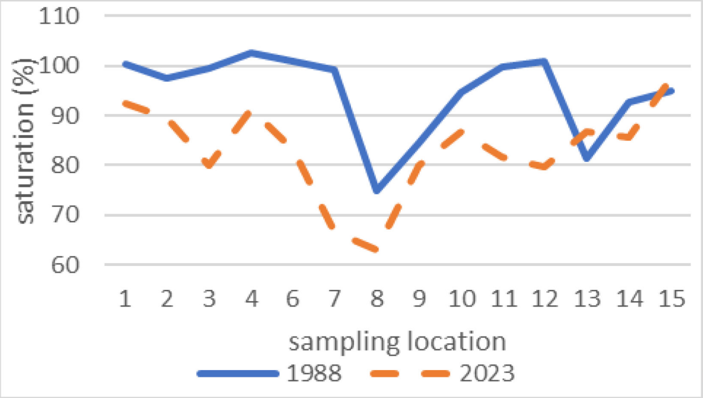

Figure 6 Comparison between 1988 and 2023 for saturation

Table 6 Descriptive statistics for saturation

Parameter	1988	2023
Average	94.58	83.2
Median	98.37	84.35
Mode	-	-
st. deviation	8.44	9.37
Variance	71.23	87.88
coef.var. (%)	8.92	11.27

Biochemical oxygen demand over five days (BOD_5) is a standardized metric used to quantify the oxygen consumed by microorganisms in one liter of water at 20°C in the dark over a five-day period. The BOD_5 values recorded in 1988 exhibit significantly higher peaks, with an extreme value noted at measurement location 10 (Figure 7, Table 8). In contrast, the BOD_5 measurements obtained in 2023 demonstrate more consistent values.

BOD is instrumental in assessing the oxidation of natural organic matter and organic waste present in water. Unlike BOD_5, which measures the reduction in dissolved oxygen attributable to aerobic organisms, the chemical oxygen demand (COD) test involves incubating a water sample with a strong oxidizing agent, in combination with boiling sulfuric acid, for a specified duration and temperature.

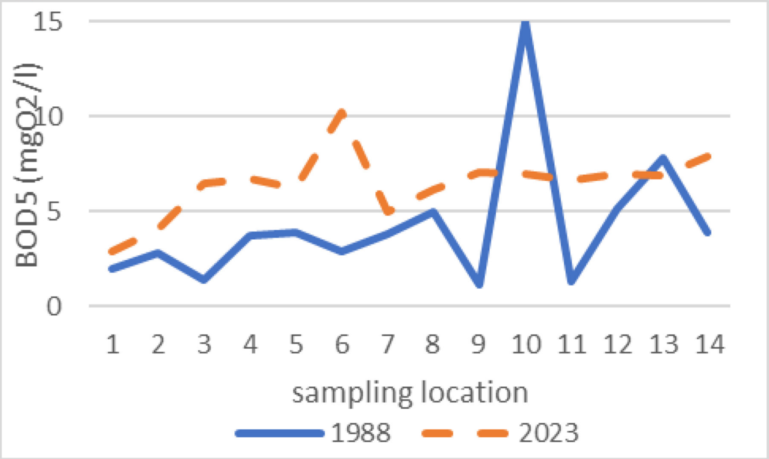

Figure 7 Comparison between 1988 and 2023 for BOD_5

Table 7 Descriptive statistics for BOD_5

Parameter	1988	2023
Average	4.26	6.44
Median	3.78	6.68
Mode	-	-
st. deviation	3.57	1.70
Variance	12.74	2.90
coef.var. (%)	83.71	26.45

Chemical oxygen demand (COD) refers to the quantity of oxygen required for the chemical oxidation of both organic and inorganic compounds present in wastewater, utilizing strong oxidizing agents such as potassium dichromate and potassium permanganate. This method is particularly relevant for determining the organic content in highly toxic heavy sewage.

The COD values, along with BOD_5 measurements from 1988 at sampling location 10, reveal extreme levels (Figure 8, Table 9). Location 10 is the location of the only town on the Plitvica River (the city of Varaždin). In contrast, the measurements obtained in 2023 exhibit lower and more uniform values, particularly in the lower reaches of the river.

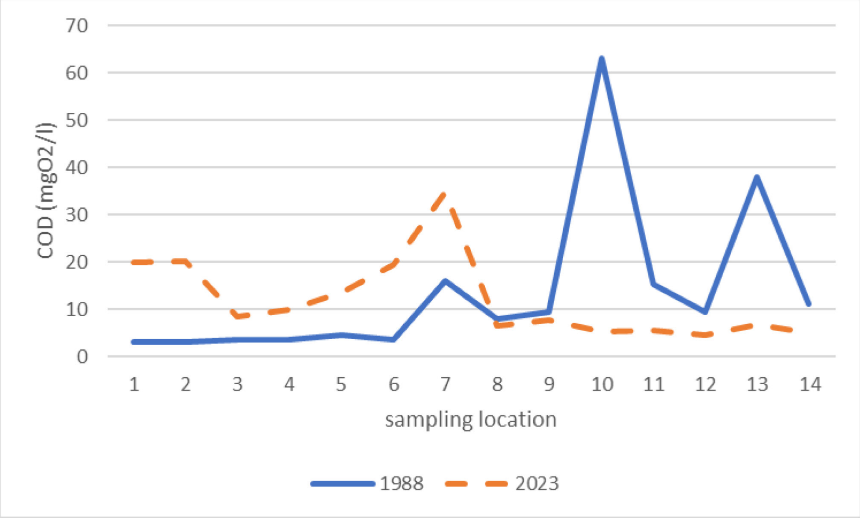

Figure 8 Comparison between 1988 and 2023 for COD

Table 8 Descriptive statistics for COD

Parameter	1988	2023
Average	13.70	11.98
Median	8.69	8.13
Mode	3.48	-
st. deviation	16.97	8.71
Variance	288.00	75.82
coef.var. (%)	123.90	72.72

Total solids content, or dry matter (TDM), comprises both suspended solids and dissolved salts. Consistent with the trends observed in other tested parameters, the total dry matter in 2023 displays less variability from the mean values, particularly in the lower reaches of the river. In contrast, the data from 1988 revealed a significant spike in total solids content in this area (Figure 9, Table 10).

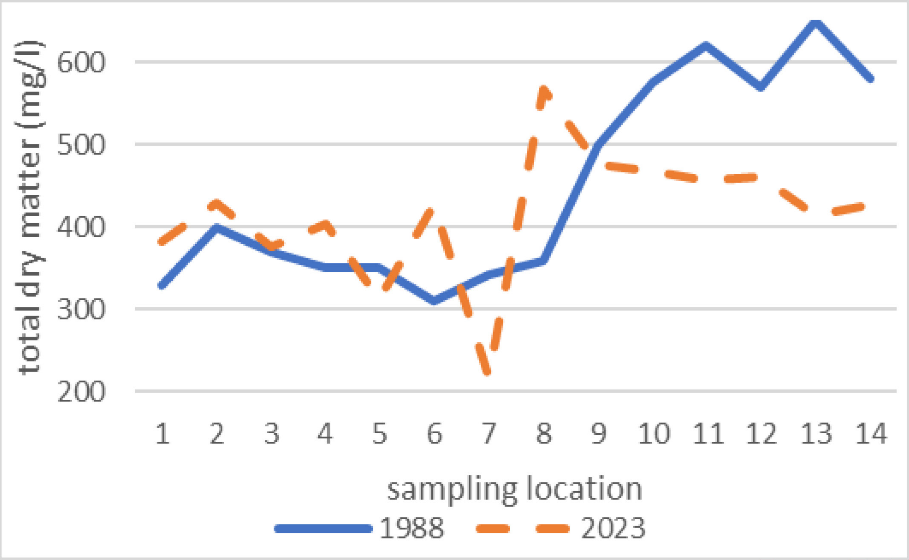

Figure 9 Comparison between 1988 and 2023 for total dry matter

Table 9 Descriptive statistics for total dry matter

Parameter	1988	2023
Average	450.5	426.7
Median	385	426.5
Mode	350	-
st. deviation	124.34	80.92
Variance	15 460.4	6 547.6
coef.var. (%)	27.60	19.46

Total suspended solids (TSS) is the dry weight of suspended particles in a water sample that can be caught by a filter and evaluated using a filtering device called a sintered glass crucible. These particles are not dissolved. TSS is a water quality metric that can be used to evaluate a sample of any kind of water or body of water. Plumbing systems, capital equipment, and filtration systems' performance can all be impacted by high suspended solids (TSS) levels.

Elevated levels of suspended solids (TSS) in rivers, lakes, streams, and reservoirs can be detrimental to the ecosystem. TDM in water can come from a variety of sources, including natural sources, urban runoff, industrial and municipal waste, chemicals used in water treatment, and the plumbing system itself. TDM is a measure of water quality even if it is not regarded as a principal pollutant.

Total suspended solids (TSS) in the Plitvica River were elevated from sampling locations 10 to 13 in 1988 (Table 11, Figure 10). In contrast, TSS values recorded in 2023 are lower, with no significant fluctuations observed at any point during the sampling period.

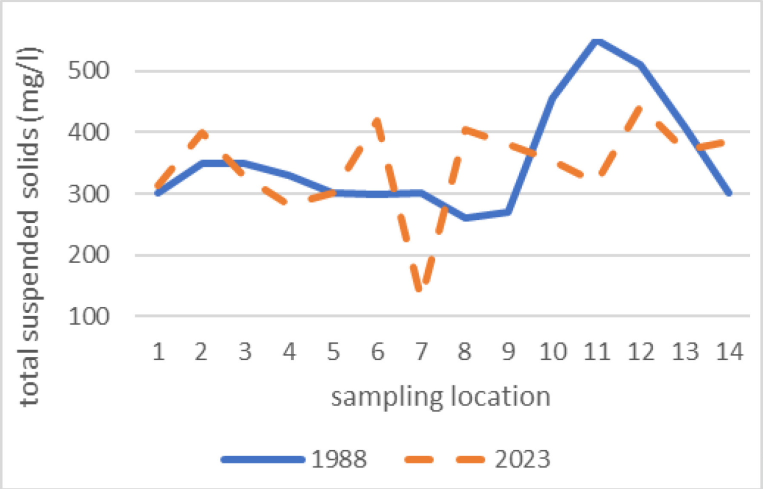

Figure 10 Comparison between 1988 and 2023 for total suspend solids (TSS)

Table 10 Descriptive statistics for total suspend solids (TSS)

Parameter	1988	2023
Average	355.9	344.6
Median	315	363.5
Mode	300	-
st. deviation	90.87	78.22
Variance	8 256.7	6 117.6
coef.var. (%)	25.53	22.69

Combustible dry matter refers to the non-combustible (inorganic) dry matter present in water, primarily consisting of minerals (salts). Similar to the trends observed in total dry matter (TDM), and total suspended solids (TSS), combustible dry matter exhibited a decline in measurements recorded in 2023 compared to those from 1988, particularly in the lower reaches of the river (Figure 11, Table 12).

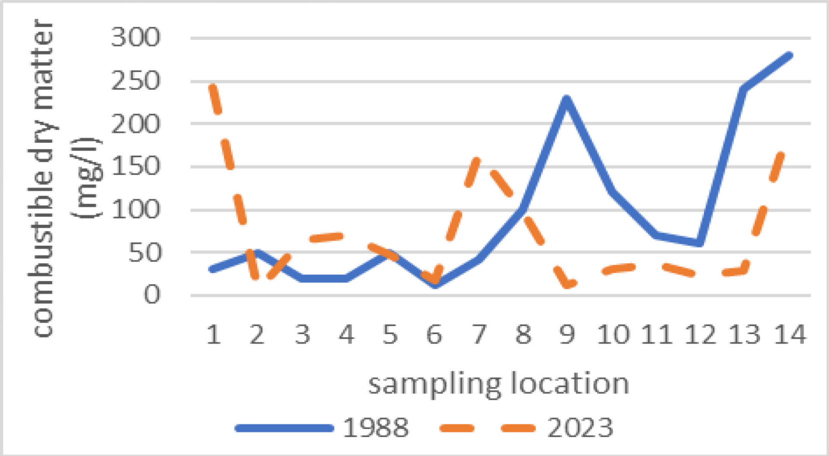

Figure 11 Comparison between 1988 and 2023 for combustible dry matter

Table 11 Descriptive statistics for combustible dry matter

Parameter	1988	2023
Average	94.6	74
Median	55	42
Mode	50	-
st. deviation	90.0	74.4

Variance	8 092.0	5 539.0
coef.var. (%)	95.12	100.57

All surface waters contain trace levels of ammonia, which is produced during the decomposition of plant and animal matter, typically in concentrations below the limit of detection. The presence of ammonia and its salts serves as an indicator of the degradation of nitrogen-containing organic materials. Elevated ammonia concentrations suggest contamination from fertilizers or fresh sanitary wastewater, as ammonia has not yet undergone oxidation to nitrites and subsequently to nitrates.

A comparison of the ammonia concentrations in the Plitvica River between 2023 and 1988 reveals a significant decrease overall, with the exception of sampling location 13 (Table 13, Figure 12).

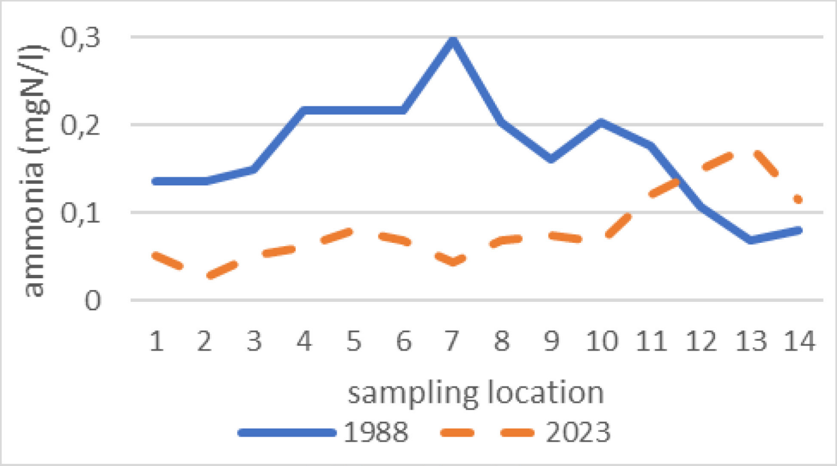

Figure 12 Comparison between 1988 and 2023 for ammonia

Table 12 Descriptive statistics for ammonia

Parameter	1988	2023
Average	0.169	0.082
Median	0.169	0.069
Mode	0.217	0.051
st. deviation	0.062	0.042
Variance	0.004	0.002
coef.var. (%)	36.69	51.89

Nitrites are intermediate products in the biochemical process of ammonia oxidation to nitrates. Their presence in water indicates that pollution is not recent, suggesting that some time has passed since the initial contamination. Consistent with trends observed in other parameters, nitrite concentrations in the 2023 samples are lower than those recorded in the 1988 samples (Figure 13, Table 14).

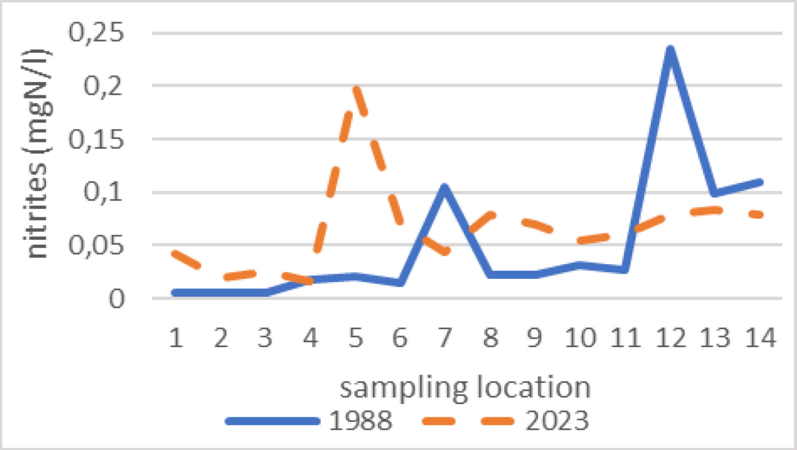

Figure 13 Comparison between 1988 and 2023 for nitrites

Table 13 Descriptive statistics for nitrites

Parameter	1988	2023
Average	0.051	0.066
Median	0.022	0.065
Mode	0.005	0.079
st. deviation	0.065	0.045
variance	0.004	0.002
coef.var. (%)	127.04	68.54

The comparison of the population size and the percentage of the population that has wastewater drainage in their household from 1988 and 2023 is shown graphically by sampling location in Figure 14 and Figure 15. Figure 16 shows the percentage of farmers within the population for 1988 and 2023.

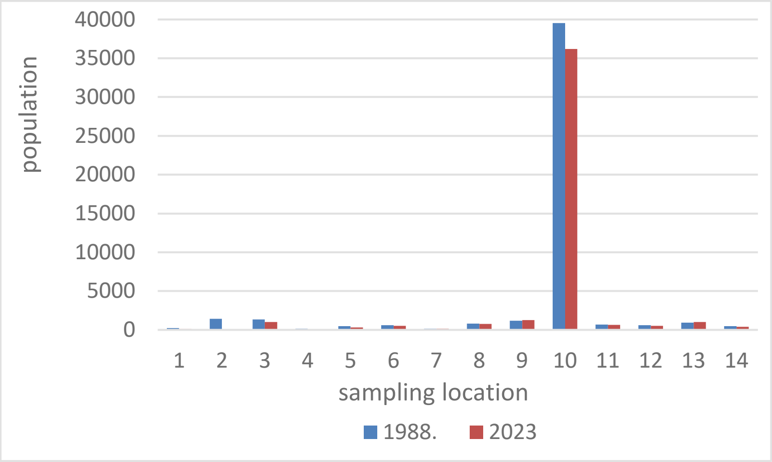

Figure 14 The comparison of the population size

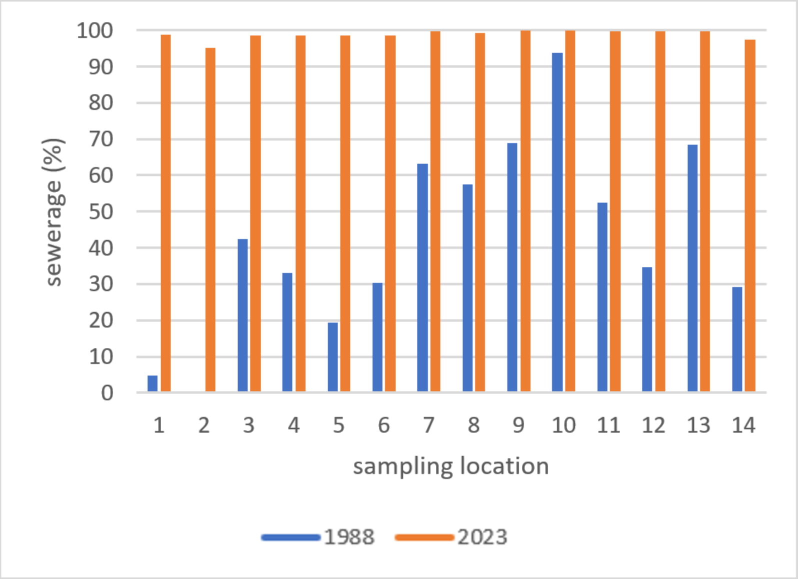

Figure 15 The comparison of the population that has wastewater drainage in their household

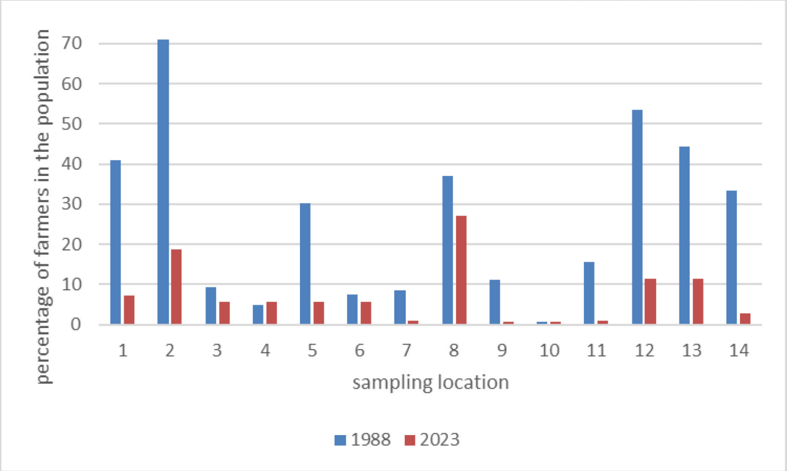

Figure 16 The comparison of the percentage of farmers in the population

The Pearson correlation coefficient was employed to identify the factors influencing the concentration of each physicochemical parameter assessed in the Plitvica River. The results of this analysis are presented in Table 15.

Table 14 Pearson correlation coefficient (|r|)

	1988			2023		
	sewerage	agriculture	both	sewerage	agriculture	both
BOD_5	**0.59**	0.13	0.43	0.23	0.25	0.27
COD	**0.77**	0.24	**0.60**	0.10	0.25	0.06
total dry residue	**0.50**	0.15	0.25	0.08	**0.50**	0.46
filtered dry residue	0.08	0.27	0.12	0.20	0.47	0.48
combustible dry residue	0.41	0.14	0.19	0.04	0.10	0.09
NH_3	0.24	**0.61**	0.45	0.41	0.05	0.09
NO_2	0.14	0.35	0.09	0.19	0.02	0.04

The findings presented in Table 15 indicate that municipal wastewater significantly impacts the majority of the evaluated parameters. In 1988, there was virtually no sewage network in the upper reaches of the Plitvica River, where it received several small tributaries from the surrounding hills. Instead, municipal wastewater was discharged into septic tanks, which were periodically emptied and often used to fertilize nearby fields.

The implementation of a sewer system markedly improved the water quality of the Plitvica River. The most pronounced effects of untreated municipal wastewater are observed in the BOD_5, COD, and dry matter (TDM) parameters. This is anticipated, as BOD_5 measures organic matter pollution and the amount of organic waste in the river, while COD assesses both organic and inorganic oxidizable compounds. The total solids content, or dry matter (TDM), indicates the quantity of suspended solids present.

In 2023, agricultural activities more significantly contributed to the pollution of the Plitvica River, primarily because the influence of municipal wastewater pollution had been largely mitigated. In 1988, ammonia and nitrite concentrations were the only indicators more impacted by agricultural practices than by the absence of a sewage network. Fertilizers, manure, and synthetic fertilizers are commonly applied in agricultural areas, although the negative effects of these practices can be reduced by minimizing fertilizer use.

The winding course of the river, coupled with slow water discharge from the banks, is a result of the basin's extended length and minimal gradient in the lower and middle reaches. Consequently, the Plitvica has been regulated from its source to the drainage channel, significantly increasing the longitudinal drop and transverse profile. Large waterways' outflow was enhanced as a result. A divider and connection to the Plitvica-Drava relief canal was constructed at the 26th kilometer of the Plitvica.

Controlling the middle course of the Plitvica reduces the risk of flooding during high water levels and stabilizes the saturation and concentration of dissolved oxygen. By mitigating flood risks, the potential for river pollution from surrounding land after flooding is also diminished.

CONCLUSION

The analysis of water quality data from the Plitvica River over the years reveals significant trends that reinforce theoretical assumptions about the impacts of agricultural and wastewater management practices on freshwater resources.

In comparing physicochemical parameters between 1988 and 2023, notable changes emerged. For instance, the average dissolved oxygen concentration decreased from 10.59 mg/L in 1988 to 8.19 mg/L in 2023, a decline attributed to the river's partial regulation and reduced flow velocity. Similarly, oxygen saturation dropped from an average of 94.58% to 83.2%, indicating potential ecological stress. Although the regulation of river flow mitigates flood risks and diminishes the likelihood of agricultural runoff contaminating the river post-flooding, thereby stabilizing the saturation and concentration of dissolved oxygen, further interventions are required to improve oxygen levels in the river.

The biochemical oxygen demand (BOD_5) increased from an average of 4.26 mg/L in 1988 to 6.44 mg/L in 2023, while the chemical oxygen demand (COD) showed a slight decrease from 13.70 mg/L to 11.98 mg/L. The BOD_5 rise indicates a higher level of organic matter pollution, likely exacerbated by intensified agricultural activities over the past decades, which align with theoretical assumptions regarding the detrimental effects of such practices on water quality.

Ammonia concentrations saw a significant decline from 0.169 mg/L in 1988 to 0.082 mg/L in 2023, suggesting improvements in wastewater management as the population transitioned to a more structured sewerage system. However, nitrite levels rose from 0.051 mg/L in 1988 to 0.066 mg/L in 2023, reflecting ongoing pollution issues.

The Pearson correlation coefficients revealed that municipal wastewater had a more pronounced impact on water quality parameters in 1988, while by 2023, agricultural runoff became a significant contributor, particularly influencing BOD_5 and ammonia levels. The correlation with agricultural practices intensified, highlighting the need for targeted management strategies to mitigate these impacts as agricultural activity continues to grow.

Overall, these findings underscore the critical need for improved agricultural management and pollution control measures to safeguard freshwater resources. The evidence indicates that while some progress has been made in managing wastewater, agricultural runoff remains a pressing challenge that threatens the ecological integrity of the Plitvica River. This aligns with broader theoretical frameworks predicting that human activities, especially in agriculture, significantly alter water quality, thus necessitating urgent action to mitigate these impacts for the future health of the river ecosystem.

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