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ditor in Chief:		Table of Contents:	
Ramona Pîrvu, University of Craiova, Romania		Waste Utilization Potential of Oil Palm Industry in North Kalimantan Province,	
Co-Editor: Cristina Mihaela Barbu , Spiru Haret University, Romania	1	Indonesia Mohamad Nur UTOMO, Ahmad MUBARAK, Sulistya Rini PRATIWI, Najmudin NAJMUDIN Legal Regulation of Civil Liability for Environmental Damage: How Appropriate are	2159
ditorial Advisory Board: Omran Abdelnaser, University Sains Malaysia, Malaysia	2	Civil Liability Provisions with the Privacy of Environmental Damage? Lana AL-KHALAILEH, Tareq AL-BILLEH, Majd MANASRA, Abdullah ALKHSEILAT, Noor ALZYOUD, Noor AL-KHAWAJAH	2174
Huong Ha, Singapore University of Social Sciences, Singapore	3	Study the Nexus between Indicators of Surface Water Quality on the Small River for Better Basin Management	2187
Harjeet Kaur, HELP University College, Malaysia		Attracting Investment for Rural Development: Introduction of Organic Agriculture and	
Janusz Grabara, Czestochowa University of Technology, Poland	4	ESG Principles in Kazakhstan Marzhan KUANDYKOVA, Aidos AKPANOV, Santay TLEUBAYEVA, Anuar BELGIBAYEV, Askar MAKHMIDOV, Aigul ATCHABAROVA	2196
Vicky Katsoni, Technological Educational Institute of Athens, Greece	5	Forty-Seven Years of Environmental Management Accounting Research: A	2207
Sebastian Kot, Czestochowa University of Technology, The Institute of Logistics and	5	Chetanraj DB, Senthil Kumar JP Accumulation of Heavy Metals in the Needles of Scots Pine of the Seminalatinsk Pre-	2201
Andreea Marin-Pantelescu, Academy of Economic Studies Bucharest, Romania	6	Irtysh Region and Burabay National Park Botakoz YELKENOVA, Raikhan BEISENOVA, Rumiya TAZITDINOVA,	2242
Piotr Misztal , The Jan Kochanowski University in Kielce, Faculty of Management and Administration, Poland	7	Zhanar RAKHYMZHAN, Nurziya KARIPBAEVA Identifying Karst Aquifer Recharge Area Using Environmental Stable Isotopes and Hydrochemical Data: A Case Study in Nusa Penida Island	2253
Agnieszka Mrozik, Faculty of Biology and Environmental Protection, University of Silesia, Katowice, Poland		I Wayan Sandi ADNYANA, Lambok HUTASOIT, Irwan ISKANDAR, MUSTIATIN, Putu Doddy Heka ARDANA	v
Chuen-Chee Pek , Nottingham University Business School, Malaysia		Regulatory and Legal Support for the Development of Digital Infrastructure in Rural areas as a Factor in Improving the Level of Sustainable Development and Quality of Life of the Rural Population Serikbai YDYRYS, Nazgul IBRAYEVA, Fariza ABUGALIYEVA, Mira ZHASKAIRAT,	
Roberta De Santis, LUISS University, Italy	ŏ		
Foggia, Italy Dan Selişteanu, University of Craiova, Romania	9	Alman OVALIYEVA Do Environmentally Responsible Practices in Accommodation Establishments Matter? Lulama NDZUNGU, Carina KLEYNHANS, Antoinette ROELOFFZE	2281
Lesia Kucher, Lviv Polytechnic National University, Ukraine	D 10 A	Development of a Model of Strategic Priorities for Sustainable Development of Rural Areas in Kazakhstan until 2030. Example of the East Kazakhstan Region	2290
Lóránt Dénes Dávid, Eötvös Loránd University, Hungary		Kalamkas NURALINA, Raisa BAIZHOLOVA, Yergali ABENOV, Dinara MUKHIYAYEVA, Yerkezhan MOLDAKENOVA	
Laura Ungureanu , Spiru Haret University, Romania	11	Investing in Human Capital for Green and Sustainable Development Ansagan BEISEMBINA, Alla GIZZATOVA, Yerlan KUNYAZOV, Takhir ERNAZAROV,	2300
Sergey Evgenievich Barykin , Peter the Great St. Petersburg Polytechnic University, Russian Federation	12	Nurlan MASHRAPOV, Sergey DONTSOV Top Management Support, Green Intellectual Capital and Green HRM: A Proposed Framework for Sustainability	2308
Omar Abedalla Alananzeh, Faculty of Tourism and Hotel Management, Yarmouk	1	Abdur Rachman ALKAF, Mohd Yusoff YUSLIZA, Amauche Justina EHIDO, Jumadil SAPUTRA, Zikri MUHAMMAD	2000
Marco Martins, Polytechnic Institute of Tomar, Portugal	13	Human Capital Management Based on the Principles of Green Economy and the Creation of Green Jobs for Sustainable Territorial Development Gulmira RAKHIMZHANOVA, Aigul MAIDYROVA, Ainura KOCHERBAEVA	2319
Konstantinos Antoniadis, University of Macedonia Thessaloniki, Greece			

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Fall 2023 Volume XIV Issue 5(69)

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ona Pîrvu , rsity of Craiova, Romania	14	Integrated Urban Solid Waste Management: Knowledge, Practices, and Implementation Riza Stephanie A. ALFARAS	2328
itor: ina Mihaela Barbu , Haret University, Romania	15	Issues Concerning the Improving Organizational and Legal Support of Victimological Prevention for Environmental Crimes DaurenMALIKOV, Natalya SIDOROVA, Saltanat ATAKHANOVA, Manshuk RAKHIMGUI OVA, Sholpan MALIKOVA, Larissa KUSSAINOVA	2336
al Advisory Board: n Abdelnaser, University Sains sia, Malaysia	16	Management of Bioculture Potential with Environmental Perspective Based on Local Wisdom Trio Beni PUTRA, Thamrin THAMRIN, Zulfan SAAM, Sofvan HUSEIN	2345
g Ha , Singapore University of Social ces, Singapore	47	Analysis of the Environment Impact on the Inclusion of Children with Special Educational Needs	0054
et Kaur, HELP University College, sia	17	Marzhan TURLUBEKOVA, Valeriy BIRYUKOV, Zulfiya MAGRUPOVA, Galiya KISHIBEKOVA, Roza BUGUBAYEVA	2354
sz Grabara , Czestochowa University of nology, Poland		Perception and Awareness of Marine Plastic Pollution in Selected Tourism Beaches of Barobo, Surigao del Sur, Philippines	
Katsoni, Technological Educational te of Athens, Greece	18	Sherley Ann T. INOCENTE, Carlo S. GUTIERREZ, Maria Pia M. SISON, John Roderick V. MADARCOS, Judea Christine M. REQUIRON, Christing Joy M. PACILAN, Shiela Mag M. CAPOX, Joyanna Laigh M. SECOVIA	2367
stian Kot, Czestochowa University of ology, The Institute of Logistics and		Hernando P. BACOSA Role of State Institutions in Protecting the Environment Improving Management	
eea Marin-Pantelescu, Academy of pomic Studies Bucharest, Romania	19	System of the Public Services Yuliya KIM, Serik DARIBEKOV, Laura KUNDAKOVA, Dinar SIKHIMBAYEVA,	2379
Misztal , The Jan Kochanowski rsity in Kielce, Faculty of Management dministration, Poland	20	Gulnara SRAILOVA Interactive Planning as Part of a Territorial Strategy to Develop Tourism Sites Edwin RAMIREZ-ASIS, Abu Bakar Bin Abdul HAMID, Nor Hazila Binti Mohd ZAIN,	2390
eszka Mrozik, Faculty of Biology and onmental Protection, University of a, Katowice, Poland	21	Travels and Sustainable Tourism in Italy. Selected Dilemmas	2398
n-Chee Pek , Nottingham University ess School, Malaysia	22	Safety Management Model of Tourism City Municipalities in Eastern Economic	2406
rta De Santis, LUISS University, Italy Gaetano Santeramo, University of	~~~	Chayapoj LEE-ANANT	2400
a, Italy Selişteanu, University of Craiova, nia Kucher, Lviv Polytechnic National	23	Impact of War on the Natural Preserve Fund: Challenges for the Development of Ecological Tourism and Environmental Protection Anatolii KUCHER, Anna HONCHAROVA, Lesia KUCHER, Mariia BIELOBORODOVA, Liudmyla BONDARENKO	2414
rsity, Okraine it Dénes Dávid , Eötvös Loránd rsity, Hungary	24	Sustainable Development and Environmental Tourism. The Case of Lake Karla – Thessaly, Greece Georgia TRAKALA Aristotelis MARTINIS Georgios KARRIS Charicleia MINOTOLI	2426
i Ungureanu , Spiru Haret University, nia		Achilleas TSIROUKIS	
y Evgenievich Barykin , Peter the St. Petersburg Polytechnic University, an Federation	25	Post-COVID-19 Community-Based Tourism Sustainable Development in China. Study Case of Hebian Village Mingjing QU, Wong Ming WONG	2440
Abedalla Alananzeh, Faculty of om and Hotel Management, Yarmouk rsity, Jordan	26	Predicting the Intention to Implement Green Practices by Small and Medium Sized Hotels in South Africa	2455
Martins , Polytechnic Institute of		FIOCEEU LEIALO MASEDE, OIAWAIE FATORI	

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Konstantinos Antoniadis, University of Macedonia Thessaloniki, Greece

Call for Papers

Winter Issues 2023

Journal of Environmental Management and Tourism

Journal of Environmental Management and Tourism is an open access, peer-reviewed interdisciplinary research journal, aimed to publish articles and original research papers that contribute to the development of both experimental and theoretical nature in the field of Environmental Management and Tourism Sciences. The Journal publishes original research and seeks to cover a wide range of topics regarding environmental management and engineering, environmental management and health, environmental chemistry, environmental protection technologies (water, air, soil), pollution reduction at source and waste minimization, energy and environmental education and optimization for environmental protection; environmental biotechnology, environmental education and sustainable development, environmental strategies and policies.

Authors are encouraged to submit high quality, original works that discuss the latest developments in environmental management research and application with the certain scope to share experiences and research findings and to stimulate more ideas and useful insights regarding current best-practices and future directions in Environmental Management.

Also, this journal is committed to a broad range of topics regarding Tourism and Travel Management, leisure and recreation studies and the emerging field of event management. It contains both theoretical and applied research papers and encourages obtaining results through collaboration between researchers and those working in the tourism industry.

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Study the Nexus between Indicators of Surface Water Quality on the Small River for Better Basin Management

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Abstract: Purpose is determination of interdependencies between hydrochemical indicators of surface water quality in the example of a small river as a limiting factor of formation of aquatic ecosystem of territories. Correlation analyses of the studied indicators of water quality was conducted on an average value of each indicator (pH, phosphates, nitrates, BOD, COD, soluble oxygen). Found a significant increase in phosphates with time, with a coefficient of correlation R=0.71, indicating contamination of the water facility. This can be explained by the arrival of various surface-active substances and, to a lesser extent, the lack of quality sewage treatment facilities. Positive changes are founded in water object that is related to a decrease in the value of BOD. This is due to a decrease in the use of oxygen on oxidation of inorganic and organic substances. In general, the use of river runoff of the river above normal, and the overall environmental state of river basin is defined as "extremely poor".

Keywords: pollution; quality water indicators; small river; correlation analysis.

JEL Classification: Q53; R11.

Introduction

The problem of natural water pollution is especially important in terms of monitoring studies and studying the interdependencies between water quality indicators. It is especially true in regions with developed infrastructure and agriculture, where there is a significant source of pollutants in water systems. On the other hand, aquatic ecosystems consist of various elements, some of which are small rivers. Small rivers form the water resources of medium and large rivers, hydrochemical water quality and creating lands large areas. Environmental monitoring is one of the country's priorities for achieving the goals of sustainable development. The one is the goal of the

roadmap for the implementation of environmental policy in Ukraine, as a country that has set a course for European integration in terms of implementing programmes aimed at national security and sustainable development of society. Environmental issues outlined in the legislation and regulations of the European Union, namely: Millennium Development Goals (Millennium Development Goals, 2015); Objectives of 2050 of the Seventh Environment Action Programme (7th Environment Action Programme, 2013; Ishchenko *et al.* 2019), Water Framework Directive 2000/60/EC (Directive 2000/60/EC of the European Parliament and of the Council, 2000; Charis and Galanakis 2010); Industrial Pollution Directive 2010/75/EU (Directive 2010/75/EU of the European Parliament and of the Council, 2010); Water Code of Ukraine (Water Code of Ukraine, 1995).

1. Research Background

The scientific works of scientists have acquired significant scientific significance in the study of environmental problems related to water resources management and anthropogenic impact on the state of water bodies. Staddon C. *et al.* study the socio-economic issues of water resources management, the structure of water consumption in different countries (Staddon 2016).

Meyer A.M., Klein C., Fünfrocken E., Kautenburger R., Beck H.P. *et al.* study the correlations between chemical components, as well as the patterns of distribution of pollutants in the aquatic environment, study the problems of pollution of small rivers (Meyer *et al.* 2019; Mitryasova and Pohrebennyk 2017; Mitryasova *et al.* 2020).

Obolewski K., Glinska-Lewczuk K., Szymanska M., Astel A., Lew S. study the issues of green chemistry of water bodies, search for patterns between the content of chemical components of the aquatic environment and its biological component (Obolewski *et al.* 2018).

Issues of assessing the impact of industrial enterprises on the water resources state present in the works Kapelewska J. *et al.* (2019). Schickele A. *et al.* (2020) investigate the influence of temperature on the morphological composition of water bodies.

The works of Snizhko S. *et al.* became especially important issue - multifactorial impact on surface water quality (Snizhko 2004); Grebin V. *et al.* - regional landscape-hydrological analysis of the modern water regime of the rivers of Ukraine (Grebin and Khilchevskyi 2016). Thus, the study of Grebin V. and Khilchevsky V., following the requirements of the Water Framework Directive developed a method of hydrographic zoning of rivers of Ukraine, assessment of aquatic ecosystems.

Vasenko O. *et al.* develop methods of comprehensive assessment of water bodies taking into account the factors of degradation processes, carry out scientific research to improve the methodology for establishing environmental standards of surface water quality, taking into account landscape and geographical features of aquatic ecosystems, ranking of observation points (Vasenko *et al.* 2016; Bezsonov *et al.* 2017; Pohrebennyk *et al.* 2019; Mitryasova and Pohrebennyk, 2020a).

However, a comprehensive analysis of water resources from the standpoint of assessing the state of small rivers for effective integrated management for sustainable development of the region and achieving proper environmental status of water bodies, under Ukrainian legislation and the Water Framework Directive, processes of adaptation to EU environmental policy.

Small rivers are an important component of the natural environment. Small rivers form the hydrochemical conditions of water resources and water quality of medium-sized and large rivers, creating landscapes large areas. An important feature of small rivers in the fact that they are the starting point of the river network, and any changes that occur in their mode, marked on the hydrological chain (Tanriverdi *et al.* 2010; Pohrebennyk *et al.* 2016; Zeinalzadeh and Rezaei, 2017; Zhang *et al.* 2018; Alifujiang *et al.* 2021; Thuy *et al.* 2021; Mitryasova *et al.* 2021b; McBean *et al.* 2022; Tha *et al.* 2022; Ward 2021). Water resources of small rivers are part of the shared water resources and are often the main and sometimes the only one source of local water. Small rivers have some features that need to be considered when developing environmental management measures (Petrov *et al.* 2020). The first is the dependence of water content, hydrological regime and water quality of small rivers on the state of the catchment. The second is climatic and weather factors (Mazlum *et al.* 1999; Mitryasova *et al.* 2021a; Arndt *et al.* 2022).

The object of the research is a small river Mertvovod in Mykolaiv region (Ukraine).

The length of the river is 114 km, the area of the drainage basin is 1820 km². The river valley is predominantly trapezoidal, width up to 3 km, depth up to 40-50 m. The floodplain is 200-300 m wide, up to 1-1,5 km below the ground. The generator is twisted; its average width in the lower reaches is up to 20 m. The slope of the river is 1,8 m/km (Southen Bug River Basin Management in Mykolaiv Region, 2021).

Monitoring studies are conducted by Southern Buh River Basin Management in Mykolaiv region at the point of monitoring near Voznesensk (Mykolaiv region, Ukraine) (fig. 1).



Figure 1. The sampling point location on the Mertvovod River

2. Methodology

The study methods used: observation; comparisons and analogies; analysis; synthesis; generalization. Also, we have used research: Google Maps, Microsoft Excel, Origin software. Calculations are made using the correlation formulas 1 and 2 (Buda and Jarynowski 2010; Kupalova 2008; Mitryasova *et al.* 2021):

$$r = \frac{\sum(x - \bar{x})(y - \bar{y})}{\sqrt{\sum(x - \bar{x})^2 \sum(y - \bar{y})^2}}$$

r = -1; +1

2.1

where x, y are the numeric values of the variables, which set the correlation connection; where \overline{x} , \overline{y} are average arithmetic values.

$$R = \sqrt{1 - (1 - r_{yx1}^2)(1 - r_{yx2/x1}^2)}$$

r = 0; +1 2.2

where ryx1 - doubles correlation coefficient;

 $r_{yx2/x1}$ – partial correlation coefficient.

To describe the magnitude of the correlation coefficient are the following, which are presented in table 1.

Value	The correlation coefficient interpretation
≤ 0,2	very weak
≤ 0,5	weak
≤ 0,7	average
≤ 0,9	high
≥ 0,9	very high

Correlation analysis was used to find quantitative relationships between natural water quality indicators (pH, phosphates, nitrates, COD, soluble oxygen). Trend analysis using the Shapiro-Wilk test in the Origin program allowed determining changes in the water body.

3. Case Studies

To study the relationship between the indicators of surface water quality on the small river example, three integrated indicators were selected, namely soluble oxygen, pH, COD, BOD as well as hydrochemical parameters that fall into the risk zone are: nitrates, phosphates and ammonium for the period from 2007 to 2021.

The value of pH characterizes the active acidity, its value is influenced by the following factors:

- the content of carbon dioxide and oxygen in the water;
- content of humic acids;

3.3

- the presence of heavy metal ions;
- temperature regime of the reservoir.

The content of hydrogen ions of natural reservoirs is determined by the quantitative ratio of carboxylic acid and its ions by chemical equation 3.1:

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-}$$
3.1

The formation of bicarbonates occurs due to the dissociation processes of equations 3.2 and 3.3:

$$Ca(HCO_3)_2 \leftrightarrow Ca^{2+} + 2HCO_3^{-}$$
 3.2

$$Mg(HCO_3)_2 \leftrightarrow Mg^{2+} + 2HCO_3^{-}$$

Due to the hydrolysis of bicarbonates, the pH increases according to the chemical equation 3.4:

$$\mathsf{HCO}_3^- + \mathsf{H}_2\mathsf{O} \leftrightarrow \mathsf{CO}_2 + \mathsf{OH}^-$$

Surface waters with low carbon dioxide content have a slightly alkaline reaction medium; $pH \le 7$ with large amounts of CO₂. pH values are closely related to the processes of photosynthesis due to the consumption of carbon dioxide by aquatic vegetation. The source of hydrogen ions is also humic acids, which are contained in soils.

During the hydrolysis of heavy metal salts, strongly acidic waters with pH≤3 are formed (chemical equation 3.5):

$$FeSO_4 + 2H_2O \leftrightarrow Fe(OH)_2 + 2H^+ + SO_4^{2-}$$
3.5

Such waters are formed when significant amounts of iron, aluminum, copper and many other heavy metals ions enter the water. A similar process of oxidation of heavy metal sulfides occurs during the discharge of mine water by chemical equations 3.6 and 3.7:

$$4FeSO_4 + 2H_2SO_4 + O_2 \rightarrow Fe_2(SO_4)_3 + H_2O \qquad 3.7$$

The sources of hydrogen ions are humic acids. Acidic, weakly acidic waters (pH = 3-6.5) are formed during the decomposition of organic compounds, as well as the influx of carbon dioxide and sulfonic acids. Therefore, the pH value of natural waters depends on the content of carbon dioxide, humic and other organic acids, as well as the content of cations of weak bases (ammonium ions, aluminum, iron, organic bases). In these cases, the pH is not below 4.5.

High values of COD and BOD in natural waters are due to some indicators, namely the high content of inorganic and organic pollutants, humic substances, hydrogen sulfide, sulfites, sulfides, nitrites, ammonium nitrogen.

The correlation nexus between COD, phosphates, and nitrates. Phosphates and nitrates, as the main forms of the most important nutrients of Phosphorus and Nitrogen, often limit the development of water productivity. Therefore, the inflow of excess phosphorus and nitrogen compounds from the catchment (in the form of mineral fertilizers with surface runoff from fields (for example, from a hectare of irrigated land is taken out 0 4-0.6 kg of phosphorus), with runoff from farms (0.01-0.05 kg/day per animal), with untreated or untreated domestic wastewater (0.003-0.006 kg/day per capita), as well as with some industrial waste leads to a sharp uncontrolled increase in plant biomass of the water body (This is especially true for stagnant and low-flowing reservoirs.) There is a so-called change in the trophic status of the reservoir, accompanied by the restructuring of the entire water community and most importantly to the predominance of putrefactive processes.

The presence of nitrates in natural waters is associated with: internal processes in the reservoir - nitrification of ammonium ions with the participation of oxygen under the action of nitrifying bacteria; atmospheric precipitation, which absorbs oxides of nitrogen formed during atmospheric electric discharges (the concentration of nitrates in precipitation reaches 0.9-1 mg; industrial and domestic wastewater, especially after biological treatment, when the concentration reaches 50 mg/dm³; runoff from agricultural lands and runoff from irrigated fields where nitrogen fertilizers are applied.

The main processes aimed at reducing the concentration of nitrates are their consumption by denitrifying bacteria and phytoplankton, which in the absence of oxygen use nitrate oxygen to oxidize organic matter.

In surface waters, nitrates are in dissolved form. The concentration of nitrates in surface waters is subject to seasonal fluctuations: minimal in the growing season, it increases in autumn and reaches a maximum in winter,

Journal of Environmental Management and Tourism

when the minimum consumption of nitrogen is the decomposition of organic matter and the transition of nitrogen from organic to mineral forms. The amplitude of seasonal fluctuations can be one of the indicators of eutrophication of a water body.

The value of COD in all investigated samples exceeded the maximum permissible concentration, minimum value of $-15.24 \text{ mgO}_2/\text{dm}^3$ and maximum $-68.6 \text{ mgO}_2/\text{dm}^3$ (MPC < 15 mgO₂/dm³).

Exceeding the maximum permissible concentrations by phosphates and nitrates were observed. Exceeding the maximum permissible concentration of COD is associated with oxidation of organic substances which fall into natural water from surface runoff and dumping sewage. There was a weak correlation between indicators (fig. 2).



Figure 2. The nexus between COD and phosphates, and nitrates

This confirms the fact that high COD values may be due to oxygen-free compounds of nitrogen and phosphorus, such as ammonium phosphide forms. So, with the increase of phosphates COD vice versa decreases, which is typical. The increase of phosphates is caused by deterioration of the river water quality due to the discharge of domestic sewage.

The correlation nexus between soluble oxygen, nitrates, and pH. The values of soluble oxygen in the water were in the norms and were > $4.00 \text{ mgO}_2/\text{dm}^3$. The values of nitrates were in the norms and not exceeded MPC. The value of pH was in the rules in not all the samples and was up 8.74 (MPC of pH = 6.5-8.5).

The smallest dependence observed between O_2 , nitrates and pH (fig. 3.) Correlation coefficient equals about 0.36, that is, there is a weak dependence between parameters. In the period the soluble oxygen (O_2) decreases, and nitrates on the contrary increase that is typical of data indicators and associated with the maximum increase of COD in the given period that makes up 52.47 mgO₂/dm³ (MPC < 15 mgO₂/dm³).

Such excess allows the claim about water pollution by organic and inorganic substances. Oxidation-reduction process of conversion of nitrogen-containing compounds into nitrates occurs.



Figure 3. The nexus between by soluble oxygen, nitrates and pH

The correlation nexus between BOD, phosphates, and nitrates. In the studied period there was observed exceeding of MPC by BOD, the maximum value of which was 20.4 mgO₂/dm³ (MPC < $3 \text{ mgO}_2/\text{dm}^3$). The correlation changes in most cases from 0.6 to 1.0 which indicates a close functional connection.

Excess value of BOD confirms receipt of the organic substances of plant and animal origin. With a high content of organic matter in the water, aerobic bacteria multiply rapidly, which require oxygen to function. This can lead to a decrease in the content of dissolved oxygen, create hypoxic conditions and the death of certain species of organisms that live permanently in the aquatic environment. The smallest correlation is observed between BOD, phosphates and nitrates (r = 0.31) that is a weak link between indicators. Also, this confirms the fact that high BOD values may be due to oxygen-free compounds of nitrogen and phosphorus, such as ammonium phosphide forms. So, with the increase of phosphates BOD vice versa decreases, which is typical also.

A sharp increase of nitrates is observed, which is 25.6 mg/dm³ (with MPC=45 mg/dm³) (fig. 4). The concentration of nitrates is subject to seasonal variations: the minimum is in the growing season, the maximum is in autumn, when the organic substances decay and nitrogen compounds transition from organic forms in the mineral. Nitrates come mainly from surface runoff, which contains residues of used nitrogen fertilizers.



Figure 4. The nexus between BOD, phosphates and nitrates.

Another source of no-waste is groundwater, which can have fairly high concentrations (up to 100 mg/dm³) and increase the content of nitrates in the areas of discharge into surface waters. Groundwater is the main source of nitrates in the limited period when the supply of surface water is mainly due to groundwater runoff. There are also a significant many other sources of nitrates in surface waters: surface runoff from landfills, urban areas, wastewater from animal complexes, urban wastewater. In the research period, the maximum concentration of nitrates was observed in autumn. The amplitude of seasonal fluctuations of the nitrates is an indicator of the eutrophication of the water object.

The correlation nexus between pH, ammonium, and soluble oxygen. There is excess of MPC on pH that is 8.74 (MPC = 6.5-8.5), exceeding by ammonium, which is 0.84 mg/dm³ (MPC = 0.39 mg/dm³), the value of dissolved oxygen is normal and is $4.00 > mgO_2/dm^3$. The smallest dependence between parameters observed in the sample №15 and the coefficient of multiple correlation is weak 0.223 (fig. 5).



Figure 5. The nexus between pH, ammonium and soluble oxygen.

At the all-test period the highest concentration of ammonium is 0.84 mg/dm³ (MPC = 0.39 mg/dm³) and meets the sample №17. A sharp increase of ammonium is associated with agricultural ranges, growing downpours the day before sampling.

Conclusion

The status of the small river is an indicator of the water security of natural surface water. Correlation analysis of dependences between COD, phosphates, and nitrates; and also, soluble oxygen, nitrates and pH; BOD, phosphates and nitrates; pH, ammonium and dissolved oxygen show stable links between chemical components that are caused by chemical interconversions, the influence of external factors (weather conditions, the hydrological regime of the river, the anthropogenic factor).

As a result of the environmental analysis of the river Mertvovod identified periods of excess MPC by hydrochemical indicators of water quality. The sources of pollutants in the water are discovered and analyzed.

Using correlation analysis gave a clear idea about weak correlations between BOC, COD and nitrates, phosphates. These confirm the fact of increasing BOC and COD due to non-oxine-containing forms of phosphorus and nitrogen compounds. A significant increase in phosphates is detected, which is associated with the collection of cleansers with domestic waters and more with the lack of quality sewer facilities. A significant reduction of COD over the years is detected.

A further perspective is to study ways to reduce the supply of phosphates to the water body. It is also relevant to further study the dependencies between water quality indicators, as well as their interpretation.

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Credit Authorship Contribution Statement

Olena Mitryasova: Conceptualization, Methodology. Andrii Mats: Software, Writing –review and editing. Ivan Salamon: Validation, Supervision. Viktor Smyrnov: Formal analysis. Vadym Chvyr: Data curation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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