Evaluation and characterization of selected pollutants in condition of surface water sources

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Hodnotenie a charakterizácia vybraných škodlivín v prípade zdrojov povrchovej vody

High quantities of organic matter can reduce the chemical and biological quality of river water. The key indicator of the oxygenation status of water bodies is the biological oxygen demand (BOD) and ammonium. These are main indicators for the water quality classification. Although countries have different river classification schemes they give a general indication of river quality, respective of whether there has been an improvement or not.

The paper illustrates the current situation regarding the biological oxygen demand and the concentrations of ammonium in river classification schemes.

Key words: *water quality classification, organic matter, surface water*

Introduction

Organic matter (microbes and decaying organic waste) can affect the quality of rivers. Sources of organic matter are discharges from wastewater treatment plants, industrial effluents and agricultural run-off. High quantities of organic matter can lead to a reduced chemical and biological quality of river water, impaired biodiversity of aquatic communities, and a microbiological contamination that can affect the quality of drinking and bathing water.

The key indicator of the oxygenation status of water bodies is the Biological Oxygen Demand (BOD). BOD is the demand for oxygen resulting from organisms in water and sediment acting on the oxidisable organic matter. The organic pollution also normally results in increased concentrations of ammonium. This exerts a demand on oxygen in water as it is transformed to oxidised forms of nitrogen. In addition, ammonium is toxic to the aquatic life at certain concentrations, depending on the water temperature, salinity and pH [1]. BOD and ammonium belong amougsmain indicators for the water quality classification.

River classification schemes are often designed to give an indication of the extent of pollution. There are many different types of schemes. Some are based solely on chemical and general physico-chemical parameters (for example, pH, dissolved oxygen, ammonium and biochemical oxygen demand), some on biological indices (usually based on macro-invertebrates) and some on a combination. Although countries have different schemes, they give a general indication of river quality, particularly whether (according to a country's scheme) there has been an improvement or not [2].

The paper illustrates the current situation regarding the Biological Oxygen Demand (BOD) and concentrations of ammonium (NH_4) in river classification schemes.

Achieved knowledge

The indicators of oxygen consuming substances in rivers are not related directly to a specific policy target. The environmental quality of surface waters with respect to the organic pollution is, however, an objective of several directives including the Surface Water for Drinking Directive (75/440/EEC) which sets standards for the BOD and the ammonium content in drinking water, the Nitrates Directive (91/676/EEC) aimed at reducing the nitrate and organic matter pollution from the agricultural land, the Urban Waste Water Treatment Directive (91/271/EEC) aimed at reducing the pollution from sewage treatment works and certain industries, the Integrated Pollution Prevention and Control Directive (96/61/EEC) aimed at controlling and preventing the pollution of water by the industry, and the Water Framework Directive (WFD) which requires the achievement of good ecological status or good ecological potential of rivers across the EU by 2015. It is an expression of the quality of the structure and functioning of aquatic ecosystems associated with surface waters. The ecological quality reflects the effects of all chemical and physical pressures on the biological system [4]. The directive 2000/60/EC establishes a framework for the Community action in the field of water policy. WFD requires that all impacts on water will have to be analysed and actions will have to be taken within river basin management plans [3].

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None of the classification schemes meet the requirements of the water framework directive and hence there is at present no information enabling a direct assessment of the situation in relation to the objectives of the directive [5].

Different types of schemes (biological, physico-chemical, combined) cannot be quantitatively compared. Some countries have more than one national classification scheme and so results for each scheme have to be shown separately. This separation into types of scheme also illustrates that whilst one scheme may show an improvement in the quality, another may show a deterioration; for example, the UK (Northern Ireland) chemical scheme showed an improvement whilst the biological scheme showed a deterioration. This was because the biological scheme reflects degradation in habitat the quality as well as changes in the water quality. The majority of river classification schemes show an improvement in the quality reflecting the effects of a reduced pollution by human activities on the aquatic environment [5].

There are large differences between countries such as the Czech Republic, Latvia and Poland. However, there is a wide variation in the length of national rivers included in classification schemes. The average length of rivers classified was only about 30 % of the total length of rivers in the country. This means that the real picture can be very different from that presented here.

Material and Methods

The data for the water quality classification (WQC) are collected through the water management processes and assembled for the purpose of providing comparable indicators. The river stations selected for WQC are representative stations or stations that are deemed to be representative. The determinants selected for the indicator of organic pollution are BOD_5 and total ammonium. Annually aggregated data are used.

In 1974 a river quality classification scheme in Scotland was developed to monitor the quality of all rivers [5]. Since the formation of SEPA in 1996 the scheme has been enhanced to incorporate developments in the technology and science. The scheme is based on a five point scale (Table 1) and includes all rivers with a catchment area of 10 km^2 or more and specific smaller rivers where pollution problems exist. The quality or "class" is calculated from the monitoring point results. The water chemistry in parameters BOD and $N\text{-}NH_4$ and limit concentrations for every class is show in Tab. 1.

Tab. 1. River water quality classification categories [5]

Class	**Description**	**BOD** [mg/l]	**$N\text{-}NH_4$** [mg/l]
A1	Excellent	≤ 2.5	≤ 0.25
A2	Good	≤ 4	≤ 0.6
B	Fair	≤ 6	≤ 1.3
C	Poor	≤ 15	≤ 9.0
D	Seriously Polluted	> 15	> 9.0

The methodology of classification is following:

a) Based upon 3 years data, at least 12 samples, unless there has been a significant change in conditions (e.g. a discharge eliminated or an identified major pollution incident in the previous year), which justifies an assessment based upon a lesser data set collected after a step change. In such conditions a minimum monitoring period of 12 months must have elapsed since the change and where there are fewer than 12 samples the significance of the step change should be confirmed by a statistical test. The estimating of percentiles is by a parametric method, assuming BOD and ammoniacal nitrogen are log normal distributed. Annual mean concentration volumes are used in the time series and present concentrations in rivers.

b) Based on the data for year, preferably 3 samples (spring, summer and autumn), at least 2 (spring and autumn).

c) Based on the first year's monitoring data, preferably 3 samples, at least 2. The overall class is determined from the mean field score and means ASPT (Average Score per Taxon) of the individual samples.

According to STN 75 7221/1999, the characteristic value of water quality (the statistical value that represents and replaces measured values of indicators) is evaluated as following:

a) If there are 24 samples or more in a year, the characteristic value is the 90 % probability of overload. This value is counted according to the Annex 1 in the mentioned standard (STN 75 7221/1999) with the 90 % probability of overload.

b) If there are usually 12 samples in a year it is necessary to evaluate 2 years. The classification of water quality is related to the 2 years period. It is a most common process.

c) If there are 11 to 24 samples in a year, the characteristic value is an the arithmetical mean of three most unfavorable values.

d) If there are less than less 11 samples in a year, the characteristic value is a maximum value in this year.

The water quality classification according to STN 75 7221 (five classes) and limit concentrations for parameters BOD_5 and $N\text{-}NH_4$ are shown in Tab. 2.

Tab. 2. River water quality classification categories [6]

Class	Description	BOD_5 [mg/l]	$N\text{-}NH_4$ [mg/l]
I.	Very Clean Water	< 3	< 0.3
II.	Clean Water	< 5	< 0.5
III.	Polluted Water	< 10	< 1.5
IV.	Bad Polluted Water	< 15	< 5.0
V.	Very Bad Polluted Water	> 15	> 5.0

For the water quality classification, various statistical methods are used. In the following it is a presented suggested methodology for the characteristic value of the WQC determination. This methodology has been worked out on counting statistical values such as the mean, median, modus, histogram etc., presented in [7, 8].

This value is counted according to [7, 8]; it is the value of upper quartile in an ascending sequence and is expressed by the equation:

$$Q_3 = \frac{3 \cdot (n+1)}{4} \tag{1}$$

where n is the number of samples.

So, the value Q_3 is in the ¾ position in the ascending sequence of measured samples. It is a value between the characteristic value (counted according to STN) and statistical values like the arithmetical mean (counted according SEPA) or median, modus.

A great advantage of using this methodology, apart from the standard STN, is that the upper quartile is not-affected by accidents in surface water. Because the STN characteristic value considers mostly values have could be influenced by an accident in the water stream.

Results

In this paper is presented the water quality classification in the station Petrovce Laborec river. The Slovak Water Management Enterprise provided data for indicators BOD_5 and total ammonium. These data were statistically evaluated in the period 1981-2003. For each year, there were 12 samples. The classification was provided for the 2 years period.

Tab. 3. Values for WQC according to different methodologies

Year	**BOD** [mg/l]			$N\text{-}NH_4$ [mg/l]		
	Characteristic Value (STN 757221)	**Median (Suggested methodology)**	**Mean (SEPA)**	**Characteristic Value (STN 757221)**	**Median (Suggested methodology)**	**Mean (SEPA)**
1981-1982	11,033	8,100	6,504	4,007	2,950	1,703
1982-1983	11,033	6,700	5,870	4,160	1,710	1,321
1983-1984	8,267	6,500	5,170	2,433	1,100	0,793
1984-1985	8,267	5,600	4,766	1,063	0,620	0,455
1985-1986	6,367	4,900	4,208	1,603	0,850	0,602
1986-1987	7,200	5,600	4,583	1,917	1,090	0,777
1987-1988	7,200	5,600	4,491	1,890	0,780	0,682
1988-1989	6,000	4,400	3,500	1,603	0,780	0,649
1989-1990	5,733	3,000	2,891	1,993	0,850	0,729
1990-1991	4,600	2,800	2,800	1,617	0,700	0,605
1991-1992	3,267	3,000	2,750	0,960	0,660	0,533
1992-1993	3,333	3,000	2,683	0,883	0,630	0,485
1993-1994	3,267	3,200	2,816	1,310	0,680	0,575
1994-1995	3,800	3,400	3,158	1,310	0,960	0,805
1995-1996	4,400	3,600	3,383	0,983	0,910	0,682
1996-1997	4,400	4,000	3,483	0,855	0,569	0,394
1997-1998	4,067	3,600	3,195	0,530	0,382	0,216
1998-1999	3,333	3,000	2,670	0,483	0,273	0,217
1999-2000	3,300	2,900	2,658	0,810	0,760	0,755
2000-2001	4,150	3,100	2,883	0,631	0,530	0,630
2001-2002	4,010	3,500	2,983	0,605	0,360	0,344
2002-2003	3,515	3,100	2,695	0,530	0,380	0,296
2003-2004	3,200	2,500	2,170	0,483	0,250	0,207

The evaluation according to SEPA (Scotland Environmental Protection Agency), STN 75 7221 (Standard for Classification of Surface Water Quality in Slovak Republic) and according to the suggested methodology for the water quality classification is presented in Table 3.

The mentioned results present a comparison of characteristic values for WQC and classification into five qualitative classes. Results in Tab. 3 show that evaluation of surface water quality is the strictest according STN 75 7221. An improvement in these qualitative classes for the parameter BOD_5 was in 7 cases (evaluation according to the suggested methodology – limit concentrations were considered according to Tab. 2); in 4 cases (evaluation according to SEPA – limit concentrations were considered according to Tab. 1). Qualitative classes differ from 1 to 5 (A1 to D) according to Tab. 1. and Tab. 2. for limit concentrations and there are appropriate colored differences. An improvement in the qualitative classes for the parameter $N\text{-}NH_4$ was in 12 cases (evaluation according to the suggested methodology); and in 17 cases (evaluation according to SEPA).

Conclusion

A control of the point-source pollution from urban areas and industry has led to significant improvements in the quality of many water bodies across Europe. Notable is a reduction of organic matter in rivers lakes resulting from an improved treatment of urban wastewaters as well as a reduction in the use of fertilizers in agriculture.

A water quality classification was worked out according to STN 75 7221 (characteristic value), a suggested methodology (Q_3 – median), methodology SEPA (arithmetical value) in the monitoring point – station Petrovce, during the period 1981 – 2003. Classification classes for the water quality vary from excellent (very clean water) to poor (badly polluted water). A value for the water quality classification at the monitoring point for each parameter has to be representative and objective from all measured samples. A recommended evaluation is the suggested methodology because these representative values are between the STN evaluation and the SEPA evaluation.

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