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Analytical, Organic, Microbiological, and Hydro-Biological Methods Used in Surface Water Quality Evaluation in Slovakia

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Abstract. This article concerns the information about the monitoring of surface water of Slovakia which is performed every month at 157 places of four river basins. Analytical, organic, microbiological and hydro-biological determinations are performed in Geoanalytical Laboratories of Geological Survey of Slovak Republic, Spišská Nová Ves. All the methods which are used for determinations are validated, accredited and they are checked by the participation in the interlaboratory comparision. The results are provided for Slovak Hydro – Meteorological Institute in Bratislava which is by the Ministery of Environment in charge of setting – up the monitoring of surface water and of the evaluation of results.

Key words: surface water, river basin district, surface water quality, organic factors, bacteria, control of analytical date

Introduction

Monitoring of Ecological and Chemical State of Surface Water

The surface water quality of Slovakia has been monitored systematically since 1963.

In 1982 the Slovak Hydro-Meteorological Institute in Bratislava took the role of monitoring the quality of surface water in Slovakia. They set up a monitoring network that provides a complete and organized survey of ecological and chemical state of every River Basin District, and they divide water formations into five quality classes. Monitoring sites are selected where a sample of water is representative for an entire basin.

The main goals of this network are to determine the current state of surface water quality in Slovakia, to identify and to quantify the main sources of pollution, to evaluate the trends of surface water quality development in Slovakia, to provide information for The Ministry of Environment of Slovakia and water-economic offices for their decision process, and to use the analyses for expert research and reports.

Monitoring Network

The total length of rivers with basins over 5 sq kilometers is 24.777 km. The monitoring of surface water quality is done in four basins – the Vah, the Hron, the Danube, and the Bodrog and the Hornad. There are 157 testing locations in all. Since 2001, surface water analysis has been provided by Geonalytical Laboratories, accredited testing Laboratories of Geological Survey of Slovakia.

The basic method of evaluating surface water quality is to classify the surface water according to STN (Slovak Technical Norm) 75 7221, which establishes five classes of water quality:

1. very clean water, 2. clean water, 3. polluted water, 4. strongly polluted water, 5. very strongly polluted water. Monitoring parameters of surface water can be divided into two groups, tab. 1:

Basic factors – which are determined in all testing locations twelve times a year.

Additional factors – which are determined only in specially selected river basin sources, and less frequently.

Table 1. Monitoring parameters of surface water

Basic factors	Additional factors
dissolved oxygen, % dissolved oxygen	total nitrogen
BOD, COD	PO_4^{3+}, HCO_3^-, CO_3^{2-}
total dissolved solids, suspended solids(dried, ignition)	phenol Index- FNI, anionic surfactants, total cyanide
Chloride,sulfate, total alkalinity	chlorophyl "a"
NH_4^+, NO_3^-, NO_2^-, total phosphor	Ca^{2+}, Mg^{2+}, Na^+, K^+
Saprobic index	Fe, Mn, Cr, Cu, Zn, Cd, Pb, Ni
Coliformn organism	Hg, As, Al,
	total volumetric activity alpha and beta, Sr, Ba
	Organochloride Pesticide
	Volatile Halocarbons
	Polynuclear Aromatic Hydrocarbons
	Polychlorinated Biphenyls
	Triazine Herbicides
	Cyclohexanol, Cyclohexanone
	Formaldehyde

Analytical Methods Used in Evaluation of Surface Water Quality in Slovakia

Basic Physical-Chemical Factors

Proper sampling and storage of water is essential for accurate results. All water samples are evaluated according to STN norms. Sample parameters (elements and properties) which could change during transportation have to be determined in situ (pH, water temperature, dissolved oxygen). Sample parameters which change have to be also preserved by adding special chemical reagents upon extraction. Cyanids and fenol volatized with water steam are preserved with NaOH to pH 11, to avoid their loss. Ca, Mg, Na, K, Fe, Mn, Cu, Cr, Zn, Ni, Pb, Cd, Hg, As, AL, Ba are fixed after filtration by 5ml/l of HNO_3 to avoid their precipitation. P_{total} is preserved by adding 2 ml/l chlorophorm and has to be kept at temperature from 3 to 4 ^{0}C till the expertise. On the day of sampling it is necessary to measure ammonium and nitrites to avoid their oxidation or reduction.

Biochemical oxygen demand must be determinated within 24 hours because the biggest reduction of oxygen occurs in the first 24 hours and the results measured after this time will not be accurate. Within 24 hours of sampling it is also necessary to measure electrical conductivity, phosphates, nitrates, total dissolved solids. If chemical oxygen demand cannot be determinated within 24 hours, the sample water has to be conserved with 2 ml/l of H_2SO_4, and kept at 3-4 ^{0}C. Within 48 hours after extraction, it is possible to determinate chloride and sulfate but the samples have to be kept at 3-4 ^{0}C.

Analytical methods of measurement can be divided into the following groups:

1. spectrophotometric methods – determination of NH_4^+, NO_2^-, PO_4^{3-}, $P_{tota.}$, $N_{total.}$, FNI, CN, COD, anionic surfactans,
2. volumetric method – the determination of total alkalinity,
3. ion chromatography – the determination of Cl^-, NO_3^-, SO_4^{2-},
4. gravimetric method – the determination of solids (dried and ignited),
5. oximetry – the determination of BOD,
6. ICP-AES – inductively coupled plasma atomic emission spectrometry – the determination of Ca, Mg, Na, K, Fe, Mn, Cr, Cu, Zn, Cd, Pb, Ni, Al, Ba, Sr,
7. HG - AAS – hydride generation atomic absorption spectrometry - the determination of As,
8. AAS – atomic absorption spectrometry – the determination of Hg
9. Counting – the determination of HCO_3^-, CO_3^{2-}

Monitoring of Organic Compounds

The amount of organic compounds in the hydrosphere is growing and so has their harm to the environment. The main cause of artificial organic pollution is chemical waste, due to human activity. Organic pollutants are harmful for surface water quality, have the ability to remain in the environment for long periods of time, to disperse widely, and to accumulate in tissues hurting the environment and its inhabitants, even in small concentrations.

Organochloride pesticide (OCP) – chemical substances or their mixtures used mostly in agriculture against organisms that harm cultural plants or are harmful to humans.

Volatile Organic Halocarbons (VOC) – chlorinated organic materials are used such as additives to colours or plastics, adhesives, for producing of plastic materials, for desinfection materials, bleach and solvents.

Polynuclear Aromatic Hydrocarbons (PAH) – a group of materials with two or more bensen nucleus. Basic Polynuclear Aromatic Hydrocarbons are the following sixteen compounds: naftalene, acenaftylene, acenaftene, fluorene, pyrene, fenantrene, antracene, fluorantene, chryzene, benzo (a)antracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenzo(a,h) antracene and benzo(g,h,i)perylene.

Polychlorinated biphenyls (PCB) – the complexity of PCB mixture and their thermal breakdown products are toxic for environment and people. PCB were added into paints, transformer and condenser oils, plastic matters and caoutchouc.

Triazine herbicides – chemical materials used mostly in agriculture as OCP.

Sampling

The samples of water are taken into glass bottles and kept at 4 ^{0}C.

They are not conserved.

Determination of organic compounds

Extraction methods, methods of analyses and detection limits of monitored organic groups are shown in the following table 2.

Table 2. Analytical methods, extraction methods and detection limits of monitored organic groups.

Substance	Type of extraction	Method	Detection limit ($ug.l^{-1}$)
OCP	Solid phase extraction	GC/ECD	0,003-0,03
VOC	Purge&Trap	GC/FID	0,01-0,03
PAH	Solid phase extraction	GC/MSD	0,003-0,03
PCB	Liquid liquid extraction	GC/ECD	0,003
Herbicides	Solid phase extraction	GC/MSD	0,02

Microbiological and Hydro-Biological Evaluation of Surface Water

Microbiological analysis of surface water consists of Quality Classification, which means the identification of harmful bacteria and Quantity Classification, which means the exact amount of bacteria.

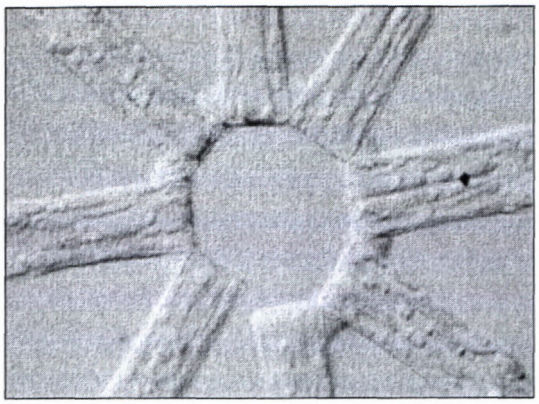

Figure 1: Tabellaria flocculosa – bacillariophyceae, microscopic, one-celled organism living in clean water.

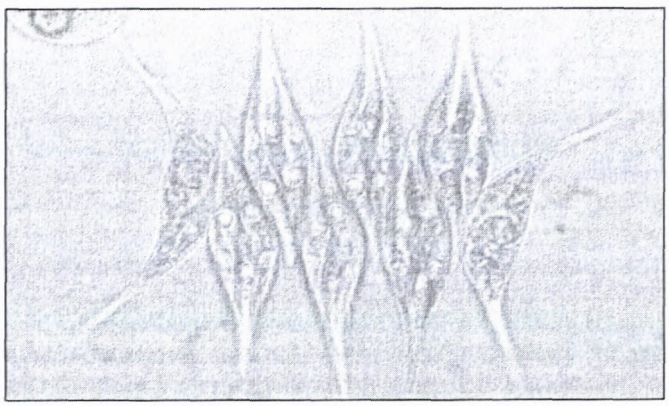

Figure 2: Scenedesmus acuminatus – green, cenoby river weed with cells in two rows that lives in plankton and in river bank of moderately clean water.

In surface water were determined these groups of organisms:

- Detection and enumeration of coliform organisms, thermotolerant coliform organisms.
- Detection and enumeration of faecal streptococci.
- Microbiological analysis of surface water. Total plate count at 37°C and at 20°C.

Microbiological analyses identify the groups of bacteria that indicate the presence of faecal from both private homes and industrial complexes. The presence and concentration of these contaminants measure the degree of water pollution and their hygienic level.

Hydro-Biological analysis consists of:

- Determination of saprobic index.
- Spectrometric determination of the chlorophyl-a concentration.

The content of organic saprogenic compounds, which are the nutritive source for other microscopic one-or-more-celled organisms, is determined by hydro-biological analysis of surface water. Microscopic identification and measurement of these agents is a basic step in the determination of water quality.

The presence and concentration of particular groups of microorganisms can indicate the current stage of water pollution. By hydro-biological parameters we monitor the ecosystem – all the organisms in our environment and how they interrelate. The results of microbiological analyses determine the cleanliness of surface rivers. By their regular monitoring we also monitor the environment in which we live.

Quality Control of Surface Water

The goal of every analytical laboratory is to produce reliable experimental results which guarantee high qualitative level and which are comparable with other laboratories. Providing such a level depends on all laboratory activities, starting with sample preparation, its analysis and finally making of a protocol. Each step could be a possible source of errors. Quality assurance and quality control must be elaborated to control each step of analytical procedure and therefore minimalize producing of random and systemetic errors.

Quality control of analytic data is assured on two levels: Internal an External control.

Used analytical techniques are regularly verificated by meteorological characteristics such as precision and accuracy of measuring, stability of signal, amount of noise e. g. Long term stability of analytical signal is monitored and evaluated by a regulation diagram.

1. Internal control of quality (IK) is provided by analysis of reference materials, multiplying analysis of sample from the same location, analysis of sample that was sampled twice from the same place and analyzed simultaneously.

2. External control of quality is provided by the national and international interlaboratory comparisons tab. 3.

Table 3. External control

Matrix	Measurements	Organizer
water drinking surface waste	– basic physical and chemical analysis – trace elements – special organic analysis – ecotoxicological tests – microbiological tests – hydrobiological tests	
water drinking	– trace elements	PIG Varšava, Poľsko
water drinking	– trace elements – basic physical and chemical analysis	VKI Hornsholm, Dánsko

Tests are performed for basic physical-chemical analysis, the determination of metal and organic parameters in surface water, and for the evaluation of hydro-biological and microbiological analysis of surface water.

The evaluation of results of IK control samples is performed by statistical analysis of comparing files of duplicate analysis, for each parameter separately. The result of evaluation is provided in graphical form. An example of graph of comparing values of test and control samples for nitrate is showed in Figure 3.

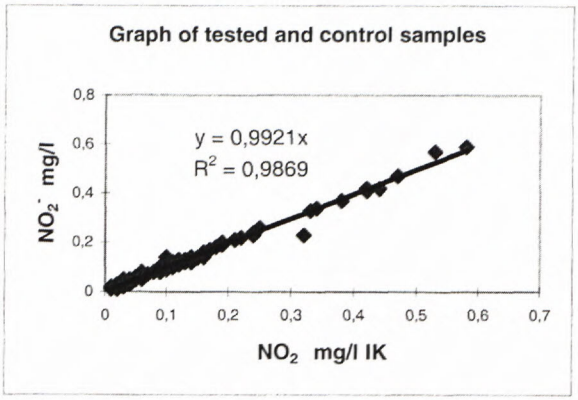

Figure 3. Graph of comparing values of test and control samples for nitrite

Conclusion

Nowadays Slovakia is trying to become a member of European structures and that is why it will be necessary to harmonize all used analytical methods applied in monitoring of surface and underground water to obtain comparable results. To achieve this goal the system of quality and further education of employees are needed to be improved.

References

STN 75 7221 Water Quality. Classification of Surface Water Quality, (1999).