



# **Report on watch list of substances monitoring in the Slovak Republic**



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**Ministry of Environment of the Slovak Republic  
Water Research Institute  
Slovak Hydrometeorological Institute**

## INTRODUCTION

A watch list of substances for which Union-wide monitoring data are to be gathered for the purpose of supporting future prioritization efforts is established according to Directive 2013/39/EU of the European Parliament and of the Council amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy.

According to the then effective (beginning of 2020) Commission implementing Decision (EU) 2018/840 from June 2018 establishing watch list of substances for Union-wide monitoring in the field of water policy, the watch list substances in 2020 are 17-alpha-ethinylestradiol (EE2), 17-beta-estradiol (E2), estrone (E1), macrolide antibiotics (erythromycin, clarithromycin, azithromycin), methiocarb, neonicotinoids (acetamiprid, imidacloprid, thiacloprid, clothianidin, thiamethoxam), metaflumizone, amoxicillin and ciprofloxacin. Each substance should be monitored at the required concentration level.

By 2021 a new watch list established by the Commission implementing Decision (EU) 2020/1161 (notified under document number C(2020) 5205) is in force.

## MONITORING

The Slovak Water Monitoring Framework Programme was developed in 2015 for the period from 2016 to 2021. It was approved in January 2016 by the Minister of Environment of the Slovak Republic.

The Water Monitoring Framework Programme for the period 2016-2021 contains as a part of investigative monitoring of surface waters also a section dedicated to watch list. Information about sampling sites, water bodies and sub-basins is listed in Table 1.

In 2020 Slovak Republic monitored nine required substances or groups of substances from the second watch list (second updated Union-wide watch list) on four selected monitoring sites as described in the following chapter (Table 2).

In selecting the representative monitoring stations, the monitoring frequency and sampling period for each substance, usage patterns and possible occurrence of the substance have to be taken into account. The monitoring frequency must be at least one sampling per year.

## METHODS

Monitoring was carried out in 2020 according to the second watch list of substances under review (Commission Implementing Decision EU 2018/840), which included nine substances or groups of substances. These are hormonal contraceptives, antibiotics and active substances of plant protection products. Their list with description, occurrence and recommended monitoring periods is given in Table 2.

The following table (Table 1) lists the sampling sites that were selected to monitor watch list substances. These monitoring sites were chosen so that the rivers collected water from the largest sub-basins of Slovakia (Váh, Hron, Hornád, Figures 2, 3, 4), i.e. these are the watersheds' pour points. For Danube, Bratislava sampling site was chosen (Figure 1) in order to incorporate also Morava River sub-basin. These sites are part of the national and international monitoring network, ensuring possibility of comparing results with other monitoring programs (e.g. bilateral monitoring programs - Danube, Váh, Hron, Hornád, monitoring within ICPDR –Trans National Monitoring Network - Danube, Váh, Hron).



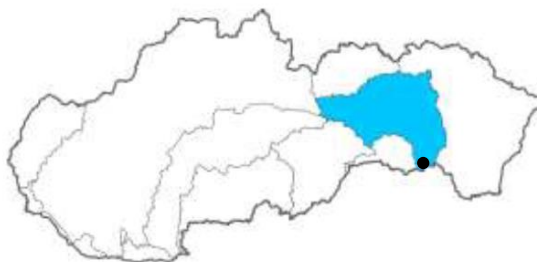
*Figure 1. Map of Danube sub-basin with indication of sampling point.*



*Figure 2. Map of Váh sub-basin with indication of sampling point.*



*Figure 3. Map of Hron sub-basin with indication of sampling point.*



*Figure 4. Map of Hornád sub-basin with indication of sampling point.*

The watch list substances are expected to occur at selected sampling sites. The sampling sites are accessible in every season. Basic information on sampling points is given in Table 1.

Table 1. Characteristics concerning sampling sites, water bodies and sub-basins.

River	DANUBE	VÁH	Hron	HORNÁD
Water body	SKD0019/SKD0016	SKV0027	SKR0005	SKH0004
WB type	D1(P1V)	V3(P1V)	R2(P1V)	H2(K2V)
Character	HMWB/NAT	HMWB	NAT	NAT
Catchment area (km <sup>2</sup> ) above water body	118,63 (Slovak territory only)	18 969,89	5 462,63	4 427,03
Sampling site	Bratislava	Komárno	Kamenica nad Hronom	Hidasnémeti
r, km	1 869,0	1,50	1,70	0,00
SK code (NEC)	D002051D	V787501D	R365010D	H385000D
EÚ/EEA code	SKIDK022	SKIDK052	SKIDK127	SKIDK202
Type of monitoring site	KHV/TNMN/ EEA/SM/OM/IM	KHV/TNMN/ EEA/SM/OM/IM	KHV/TNMN/ EEA/SM/OM/IM	KHV/TNMN/ EEA/SM/OM/IM
Catchment area of the whole sub-basin	1 158 km <sup>2</sup> (GIS 1 096 km <sup>2</sup> )	18 769 km <sup>2</sup> (GIS 18 794 km <sup>2</sup> )	5 465 km <sup>2</sup> (GIS 5 463 km <sup>2</sup> )	4 414 km <sup>2</sup> (GIS 4 420 km <sup>2</sup> )
Total river length	2 888 km, (in Slovakia: 172 km)	367,2 km	279,0 km	178,8 km (transboundary stretch: 0,00 – 11,7 km)
Long-time annual discharge	2264 m <sup>3</sup> .s <sup>-1</sup> (Štúrovo)	195,8 m <sup>3</sup> . s <sup>-1</sup> (confluence)	55,2 m <sup>3</sup> .s <sup>-1</sup> (confluence)	28,9 m <sup>3</sup> .s <sup>-1</sup> (end of border)
Counties	Trnava, Bratislava, Nitra	Žilina, Trenčín, Nitra, Trnava, Bratislava, Prešov, Banská Bystrica	Nitra, Banská Bystrica Trenčín	Košice, Prešov, Banská Bystrica
Population in sub-basin	333 413 (in 2006)	2462300 (in 2006)	481424 (in 2006)	697 589 (in 2006)
Cities above 50 000 citizens	Bratislava	Žilina, Martin, Trenčín, Trnava, Prievidza, Nitra, Bratislava	Banská Bystrica	Košice, Prešov

**Note:**

Catchment area of sub-basin in GIS – calculated according to ArcView and therefore different from maps.

Sampling took place on the following dates (for the respective substances):

10.2.2020	Danube – Bratislava, Váh – Komárno, Hron – Kamenica nad Hronom, Hornád – Hidasnémeti (hormones and antibiotics)
4.3.2020	Hornád – Hidasnémeti (methiocarb and metaflumizone)
9.3.2020	Danube – Bratislava, Váh – Komárno, Hron – Kamenica nad Hronom (methiocarb and metaflumizone)
5.8.2020	Hornád – Hidasnémeti (neonicotinoids)
10.8.2020	Danube – Bratislava, Váh – Komárno, Hron – Kamenica nad Hronom (neonicotinoids)

Sampling and analyses were performed in the National Water Reference Laboratory in Slovakia at the Water Research Institute in Bratislava, which is a laboratory accredited according to STN EN ISO / IEC 17025. The analyses were performed using the methods given in the Table 3. The required criteria of analytical methods were met except for the hormone EE2.

Table 2. Watch list substances according to the Commission Implementing Decision (EU) 2018/840.

Watch list substance	Description	Occurrence	Recommended period for sampling
17- $\alpha$ -ethinylestradiol (EE2)	<i>hormonal contraceptives</i>	<i>irregular/ non-seasonal occurrence</i>	<i>January/ February</i>
17- $\beta$ -estradiol (E2)	<i>hormonal contraceptives, veterinary drug</i>	<i>non-seasonal occurrence, the highest concentration is expected in winter due to degradation</i>	<i>January/ February</i>
Estrone (E1)	<i>Oxidation product of the 17-<math>\beta</math>-estradiol</i>	<i>non-seasonal occurrence, the highest concentration is expected in winter due to degradation</i>	<i>January/ February</i>
Erythromycin, Clarithromycin, Azithromycin	<i>Macrolide antibiotics</i>	<i>winter</i>	<i>January/ February</i>
Methiocarb	<i>insecticide, repellent, application to plant seeds</i>	<i>early spring</i>	<i>March</i>
Neonicotinoids (Imidacloprid, Thiacloprid, Thiamethoxam, Clothianidin, Acetamiprid)	<i>insecticides</i>	<i>summer, autumn</i>	<i>July/ August</i>
Metaflumizone	<i>plant protection product, insecticide</i>	<i>early spring</i>	<i>March</i>
Amoxicillin	<i>antibiotic</i>	<i>winter</i>	<i>January/ February</i>
Ciprofloxacin	<i>antibiotic</i>	<i>winter</i>	<i>January/ February</i>

Table 3. Watch list substances, CAS number, analytical methods, required maximum acceptable method detection limits according to the Commission Implementing Decision (EU) 2018/840 (LOD) and limits of quantification (LOQ) of analytical methods.

Watch list substance	CAS	Analytical method used	Required LOD <sub>max</sub> ( $\mu\text{g/l}$ )	LOD method used ( $\mu\text{g/l}$ )	LOQ method used ( $\mu\text{g/l}$ )
17- $\alpha$ -ethinylestradiol (EE2)	57-63-6	SPE (der.)-LC-MS-MS	0,000035	<b>0,0001</b>	<b>0,0003</b>
17- $\beta$ -estradiol (E2)	50-28-2	SPE (der.)-LC-MS-MS	0,0004	0,0001	0,0003
Estrone (E1)	53-16-7	SPE (der.)-LC-MS-MS	0,0004	0,0001	0,0003
<b>Macrolide antibiotics:</b> Erythromycin, Clarithromycin Azithromycin	114-07-8 81103-11-9 83905-01-5	SPE -LC-MS-MS	0,019	0,003	0,010
Methiocarb	2032-65-7	SPE-LC-MS-MS	0,002	0,0006	0,002
<b>Neonicotinoids:</b> Imidacloprid	105827-78-9/138261-41-3	SPE-LC-MS-MS	0,0083	0,0006	0,002
Thiacloprid	111988-49-9				
Thiamethoxam	153719-23-4				
Clothianidin	210880-92-5				
Acetamiprid	135410-20-7/ 160430-64-8				
Metaflumizone	139968-49-3	LC-MS-MS	0,065	0,02	0,06
Amoxicillin	26787-78-0	LC-MS-MS	0,078	0,012	0,04
Ciprofloxacin	85721-33-1	LC-MS-MS	0,089	0,015	0,05

**Notes:** SPE – solid phase extraction, LC – liquid chromatography, MS – mass spectrometry, der. – derivatization, LOD<sub>max</sub> – maximum acceptable method detection limit, LOQ – limit of quantification of analytical method; based on 2018/840 EU

Commission set out requirements of analytical methods as „maximum acceptable method detection limits“, however results of analysis refer to the LOQ. Their relationship is  $LOD = 0.3 \times LOQ$

## RESULTS

Results of watch list substances monitoring in Slovakia in 2020 are listed in the Table 4.

Table 4. Results of watch list substances analyses in 2020.

Substance (µg/l)	Sampling date											
	10.2.2020	10.2.2020	10.2.2020	10.2.2020	9.3.2020	9.3.2020	9.3.2020	4.3.2020	10.8.2020	10.8.2020	10.8.2020	5.8.2020
	River											
	Danube	Váh	Hron	Hornád	Danube	Váh	Hron	Hornád	Danube	Váh	Hron	Hornád
Acetamiprid									<0,002	<0,002	<0,002	<0,002
Amoxicillin	< 0,04	< 0,04	< 0,04	< 0,04								
Azithromycin	<b>0,016</b>	<b>0,038</b>	<b>0,041</b>	<b>0,028</b>								
Ciprofloxacin	< 0,05	< 0,05	< 0,05	<0,05								
Estrone E1	<0,0003	<b>0,0003</b>	<0,0003	<0,0003								
17-beta-estradiol E2	<0,0003	<0,0003	<0,0003	<0,0003								
17-alpha-ethinylestradiol EE2	<0,0003	<0,0003	<0,0003	<0,0003								
Erythromycin	<0,010	<0,010	<0,010	<0,010								
Imidacloprid									<0,002	<0,002	<0,002	<0,002
Clarithromycin	<b>0,013</b>	<b>0,011</b>	<b>0,011</b>	<b>0,066</b>								
Clothianidin									<0,002	<0,002	<0,002	<0,002
Methiocarb					<0,002	<0,002	<0,002	<0,002				
Metaflumizone					< 0,06	< 0,06	< 0,06	< 0,06				
Thiacloprid									<0,002	<0,002	<0,002	<0,002
Thiamethoxam									<0,002	<0,002	<0,002	<0,002

Except for macrolide antibiotics azithromycin and clarithromycin and in case of Váh for estrone E1 hormone, the results measured were below the quantification limit of analytical methods used for all sampling sites.

## MODEL CONCENTRATIONS OF ESTROGENS IN SURFACE WATERS

### Methods

Except for one value at LOQ level (for E1 at river Váh), concentration of estrogens in surface waters did not exceed LOQ of used analytical method. The same situation, with a few exceptions, repeats during watch list monitoring in case of estrogens every year. For EE2, the used analytical method ( $LOD = 0,0001 \mu\text{g/l}$ ) does not meet the maximum acceptable method detection limit

established by Decision EU 2018/840 ( $LOD_{max} = 0,000035 \mu\text{g/l}$ ). This may cause a situation in which the limit concentration is exceeded in the monitored water bodies but not detected. In an effort to obtain relevant quantitative data we used results of point-sampling from selected municipal waste water treatment plants (WWTP). Based on information about flow rates at the WWTP's effluent and in the recipient, we used simple dilution factor to model possible concentrations of measured analytes in the recipient.

All measurable results from WWTPs were in units or in case of estrone in maximum tens of nanograms per litre (ng/l).

## Results

According to data from WWTP Košice and from hydrological station at river Hornád, concentrations for estrone and 17-alpha-ethinylestradiol could range from hundredths to tenths of ng/l, i.e. below LOQ of the method ( $LOQ = 0,3 \text{ ng/l}$ ) but above  $LOD_{max}$  according to the Commission Implementing Decision EU 2018/840 for 17-alpha-ethinylestradiol. Similar results for estrone were modelled also in Váh River near Strečno and in Nitra River.

Model estrone concentration below 1 ng/l can be expected in Krivánsky potok in town Lučenec, according to the sample from WWTP Lučenec. In case of 17-alpha-ethinylestradiol the value is in order of hundredths of ng/l.

The highest measured concentration for estrone was at WWTP Trnava-Zeleneč (14 ng/l) with the rest of the results at level of 1 ng/l. The nearest hydrological station was station Dolný Dudváh-Čierny Brod. On the sampling date, considered calculated concentration for estrone could be several ng/l and for the other estrogens around the value of 0,3 ng/l.

All three analytes were measured also at WWTP Banská Bystrica at river Hron. Here the assumed concentrations did not exceed tenths of ng/l (or 0,3 ng/l) either.

We would like to emphasize that this is a simplified model. The calculated values are prone to quite a large uncertainty because the suitable hydrological station was not always available and there is also an effect of flow-mixing and unknown concentrations of monitored analytes in the tributaries of the affected water bodies. However, the obtained results show a future potential in focusing more on municipal waste water monitoring for estrogens where more measurable results could be obtained with available analytical technique. With detailed information about flow rates and discharges in the relevant time and space, the measured values could be used for estrogens concentration modelling in surface waters.

## **CONCLUSION**

According to watch list established by Commission Implementing Decision (EU) 2018/840 nine substances or groups of substances were monitored in Slovakia in 2020: 17-alpha-ethinylestradiol (EE2), 17-beta-estradiol (E2), estrone (E1), macrolide antibiotics (erythromycin, clarithromycin, azithromycin), methiocarb, neonicotinoids (acetamiprid, imidacloprid, thiacloprid, clothianidin, thiamethoxam), metaflumizone, amoxicillin and ciprofloxacin.

Sampling season was selected by taking into account character and possible occurrence of monitored analytes. At the same time, the sampling sites were chosen so that the rivers collected water from the largest areas of Slovakia. These sites are also part of the national and international monitoring network.

The analyses were performed using the recommended methods. The required criteria of analytical methods were met with the exception of estrogen EE2.

Except for macrolide antibiotics azithromycin and clarithromycin and in case of Váh for estrone E1 hormone, the results measured were below the quantification limit of used analytical methods. The required maximum acceptable method detection limit was exceeded only for azithromycin in the rivers Váh, Hron and Hornád and for clarithromycin in the Hornád River. Similar assumption cannot be made for 17-alpha-ethinylestradiol as the available analytical method does not meet the required detection limit.

Based on the calculated results from concentrations measured in samples from municipal WWTPs and water discharge/flow rates information, it can be said that in most model cases the surface water concentrations of estrogens did not exceed 2018/840 EU maximum acceptable LOD of analytical method. The exception would be 17-alfa-etinylestradiol (EE2). Because of that, there is a certain probability that in some water bodies in Slovakia the concentrations of estrogens are at a toxic level for aquatic organisms but the used analytical technique is not able to detect this condition.

As more measurable results for estrogens can be obtained in municipal waste water effluents, sampling should be focused on this sample type in future. Measured data can be used for concentration modelling in the recipient, i.e. in the surface water bodies of concern.

## REFERENCES

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- Information about water discharges/flow rates from WWTPs and hydrological stations, source: relevant waste water treatment plants and Slovak Hydrometeorological Institute