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WATER FRAMEWORK DIRECTIVE AND SPECIFIC POLLUTANTS IN SURFACE WATERS IN SLOVENIA

VODNA DIREKTIVA IN POSEBNA ONESNAŽEVALA ZA POVRŠINSKE VODE V SLOVENIJI

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Abstract

According to the European Water Framework Directive (Directive 2000/60/EC, 2000), the EU member states are required to prepare a list of specific pollutants and their environmental quality standards in the aquatic environment for the purpose of evaluating the ecological status of water. In addition, for the purpose of evaluating the chemical status, defined by the Directive 2013/39/EU (2013), a country must select biotic species that are relevant to surface water and determine the list of substances for monitoring in biota and/or sediment. In the period 2005-2010 we have successfully developed all the above mentioned standards and lists for Slovenia. In this article we present a list of river basin specific pollutants for surface water in Slovenia and their environmental quality standards compared to the values derived in The Netherlands, France and Germany. Values were derived for 29 specific pollutants and among them 6 are higher than in other countries. The review of background information on the derivation of environmental quality standards highlighted that a revision is needed for epichlorhydrin, hexachloroethane, terbutylazin and selenium. The presented approach serves as exemplary for similar evaluations to be carried out by various countries inside and outside Europe.

Keywords: Water Framework Directive, environmental quality standard, specific pollutant, surface water, ecological status, chemical status.

Izveček

V skladu z Vodno direktivo (Direktiva 2000/60/ES, 2000) morajo države članice EU za oceno ekološkega stanja površinskih voda med drugim pripraviti seznam posebnih onesnaževal in njihovih okoljskih standardov kakovosti. Razen tega mora država članica za ocenjevanje kemijskega stanja, ki je opredeljeno z direktivo 2013/39/ES (2013), izbrati biotske vrste, ki so relevantne za površinske vode in določiti seznam snovi za spremljanje v živih organizmih in/ali sedimentu. V obdobju 2005-2010 smo uspešno razvili vse zgoraj omenjene standarde in sezname za Slovenijo. V članku predstavljamo posebna onesnaževala za

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površinske vode v Sloveniji in njihove okoljske standarde kakovosti ter jih primerjamo z vrednostmi, pridobljenimi na Nizozemskem, v Franciji in Nemčiji. Vrednosti so bile izračunane za 29 posebnih onesnaževal, med njimi so za 6 snovi okoljski standardi kakovosti višji kot v omenjenih državah. Pregled podatkov o določitvi okoljskih standardov kakovosti je pokazal, da je v primeru epikloridrina, heksaklorešana, terbutilazina in selena potrebna revizija vrednosti za okoljske standarde kakovosti. Predstavljen pristop lahko služi kot zgled za podobne evalvacije v državah Evropske unije in zunaj nje.

Ključne besede: Vodna direktiva, okoljski standardi kakovosti, posebna onesnaževala, površinska voda, ekološko stanje, kemijsko stanje.

1. Introduction

The EU Water Framework Directive (Directive 2000/60/EC, 2000), which came into force in December 2000, represents a new framework governing the water policies of the European Union. The Water Framework Directive (WFD) promotes a new approach to water management through river basin planning. River basin districts have to be designated, not according to administrative or political boundaries, but rather according to the river basin as a natural geographical and hydrological unit. Such an approach ensures that neighbouring member states assume joint responsibility for managing the rivers and other bodies of water they share. The WFD commits EU member states to achieving good qualitative and quantitative status of all water bodies by the year 2015.

For the first time, the WFD has introduced the terms ecological and chemical status of surface waters into the European legislation. Ecological status is defined as a qualitative concept for the structure and functioning of a water ecosystem, while chemical status is defined with concentrations of selected chemical substances in relation to environmental quality standards (EQS). In the Republic of Slovenia, the ecological and chemical status of surface waters are under the regulation of the Decree on surface water status (2009; Official Gazette of the Republic of Slovenia, no. 14/09, 98/10 and 96/13). The ecological status is based on biological elements of an ecosystem (phytoplankton, macrophytes and phytobenthos, benthic invertebrate fauna, and fish fauna); general hydromorphological elements and physico-chemical elements (temperature, nutrients, dissolved oxygen concentration), including also a

number of specific synthetic and non-synthetic pollutants. The WFD requires the Member States to identify the relevant river basin specific pollutants and associated environmental quality standards. For this purpose, a list of river basin specific pollutants in Slovenia and their environmental quality standards has been established on the basis of ecotoxicological data (Kolar and Kos Durjava, 2006). The work presented in this paper has been performed in compliance with three guidelines: the guidelines used for the preparation of a draft list of priority substances on the EU level: A combined monitoring-based and modelling-based priority setting - COMMPS procedure (Klein et al., 1999) and the Fraunhofer's Institute Manual on the derivation of environmental quality standards (Lepper, 2005) and Technical Guidance for Deriving EQSs (European Commission, 2011).

The chemical status is determined by the concentrations of 45 priority (hazardous) substances and groups of substances in relation to associated EQS. The risk limit values are presented as EQS unified for all EU Member States and regulated under Directive 2013/39/EU (2013). The list of priority substances is not complete, as new substances and substance groups are being added continuously. In order to successfully transpose the Directive 2013/39/EU (2013) into Slovenian national law a list of biota for chemical monitoring of surface waters and a list of substances for sediment and/or biota monitoring were proposed in Kos Durjava and Kolar (2010).

The methodology for the derivation of EQS is generic and thus the values derived in other countries are expected to be similar. The objectives of this study were (1) to illustrate the derivation of

EQS, using arsenic as an example, (2) to compare the Slovenian environmental quality standards with the values derived in The Netherlands, France and Germany and (3) to clarify why for 6 substances the annual average – environmental quality standards (AA-EQS) seem to be less protective in Slovenia than in other selected EU countries.

2. List of River Basin Specific Pollutants in Slovenia

In composing the list of river basin specific pollutants, we followed the guidelines used for the preparation of a draft list of priority substances on the EU level in accordance with a classification procedure for substances relevant for the aquatic environment – COMMPS procedure (Klein et al., 1999), as approved by the European Commission. The substances were put on the list of specific pollutants on the basis of a simplified, tier 1 risk assessment. For chemical substances, exposure and effect comparisons were carried out. The details on the selection of the Slovenian specific pollutants can be found in Kolar and Kos Durjava (2006). In the following paragraphs, the selection process is described briefly.

The criteria for exposure of the aquatic environment were data on important production processes or application volumes of substances that might entail exposure of surface water in Slovenia, monitoring data of surface waters and sediment in Slovene rivers and the results of EUSES 2.0 computer program models (RIVM, 2012) for substances that have not been included in the monitoring so far.

The criterion for the selection of substances on the basis of toxic effects on the aquatic environment was the classification and labelling with risk phrases (R) according to the Directive on classification, packaging and labelling of dangerous substances (Directive 67/548/EEC, 1967). Substances were classified according to their acute toxic and long-term characteristics.

On the basis of the selected criteria, the substances were assessed in three steps. In the first step, an extended list of substances which complied with the exposure and effect criteria described above

was assembled. In the second step, the list was assessed through the information on fate and behaviour of substances in the environment. The assessment criteria were among others degradability of substances, biodegradability (for substances that do not degrade to relevant metabolites), bioconcentration factor and selected physicochemical properties (solubility, partition coefficients water/octanol, water/air and water/suspended particles). In the third step, a simple tier 1 risk assessment was carried out for the selected substances on the basis of measured environmental concentrations or predicted concentrations and the effect data. The resulting selected river basin specific pollutants presented in Table 1 are also listed in Annex 8 of the Slovenian Decree on surface water status (2009; Official Gazette of the Republic of Slovenia, no. 14/09, 98/10 and 96/13).

3. Environmental Quality Standards for Surface Water in Slovenia

The EQSs for substances from the list of river basin specific pollutants in Slovenia were established on the basis of ecotoxicological data (Kolar and Kos Durjava, 2006) in compliance with the technical guidance document of the Fraunhofer Institute (Lepper, 2005) and later also Technical Guidance for Deriving EQSs (European Commission, 2011). The Fraunhofer guidance (Lepper, 2005) covers many of the key technical issues involved in deriving EQSs. The updated Technical Guidance for Deriving EQSs (European Commission, 2011) includes also guidance on the derivation of biota and sediment EQSs and further guidance on setting EQSs for metals.

An EQS is defined as a concentration based on toxicity data of substances in the aquatic environment and its protection target. If the environmental concentration exceeds the surface water EQS, a risk for aquatic organisms can be assumed.

The Annual Average – Environmental Quality Standard (AA-EQS)

Chronic quality standards, AA-EQS, are recommended for water quality monitoring.

They can be used for assessing pollution over an extended time period. For continuous input of micropollutants from treated effluents, the chronic quality standard is particularly relevant and helps to protect the organisms against the consequences of long-term pollution. It is determined on the basis of chronic effects on aquatic organisms.

The Maximum Acceptable Concentration – Environmental Quality Standard (MAC-EQS)

A comparison of the environmental concentration and the acute quality standard MAC-EQS may be helpful for assessing the likelihood of possible damage to the organisms from peak or intermediate substance emissions within the next 24 to 96 hours. It is determined on the basis of acute effects on aquatic organisms.

The objective of determining the EQS is to establish a realistic toxicological limit value. Derivation of the EQS requires some form of extrapolation from the available data to estimate a threshold that takes into account uncertainties such

as inter- and intra-species variation and laboratory to field extrapolation. Two main approaches are possible: the deterministic and the probabilistic method. Essentially, the deterministic approach takes the lowest credible toxicity value, which is divided by an assessment factor (AF) (which may be as low as 1 or as high as 10000) to extrapolate to an EQS, the AF allowing for correction of the uncertainties in the available data. Probabilistic methods adopt the species sensitivity distribution (SSD) modelling in which all reliable toxicity data (usually chronic toxicity data NOEC – No Observed Effect Concentration) are ranked and a model is fitted. This statistical extrapolation technique is often used to calculate the concentration at which a specified proportion of species (typically 5%) are expected to suffer direct toxic effects, referred to as the Hazardous Concentration to 5% of the species (HC₅). A further AF is applied to the HC₅ arising from model extrapolation to account for residual uncertainties that are not accounted for by the SSD model. An AF of 5 is used by default but may be lower where evidence reduces residual uncertainty.

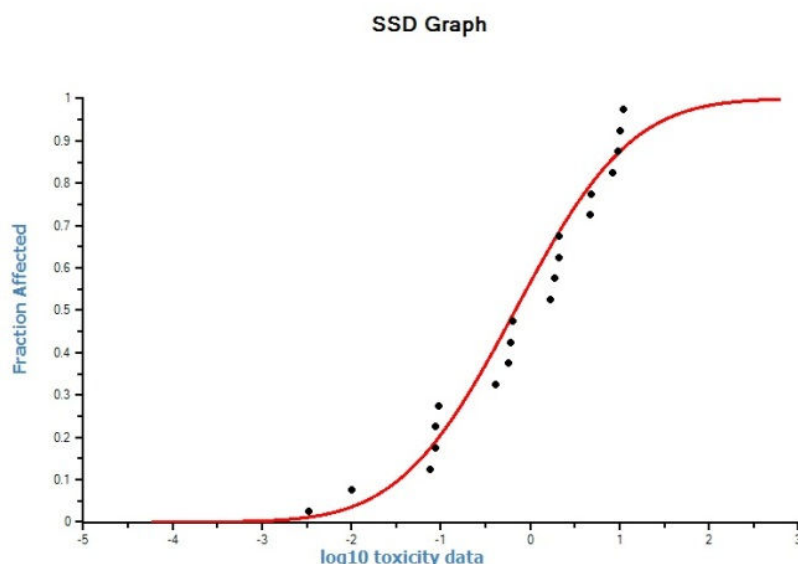


Figure 1: Species sensitivity distribution graph for arsenic chronic toxicity data using the ETX software (van Vlaardingen et al., 2004).

Slika 1: Porazdelitev občutljivosti vrst (SSD) za kronično strupenost za arzen, graf pripravljen z uporabo programa ETX (van Vlaardingen et al., 2004).

Table 1: River basin specific pollutants in Slovenia with derived annual average-environmental quality standards (AA-EQS) for inland surface waters compared to publicly available data for AA-EQS from INERIS, ETOX and RIVM and PNEC (predicted no effect concentration) values from EU Risk Assessment Reports.

Preglednica 1: Posebna onesnaževala za površinske vode v Sloveniji s pripadajočimi vrednostmi za letno povprečje-okoljski standard kakovosti (LP-OSK) za celinske površinske vode in primerjava z javno dostopnimi podatki o LP-OSK iz INERIS-a, ETOX-a in RIVM-a in PNEC vrednostmi iz evropskih ocen tveganja.

Specific pollutant	Unit	CAS RN	AA-EQS Slovenia	AA-EQS INERIS France ¹	AA-EQS ETOX UBA Germany ²	AA-EQS RIVM The Netherlands ³	PNEC EU RAR ⁴
1,2,4-trimethylbenzene	µg/L	95-63-6	2.0	n.a.	n.a.	n.a.	n.a.
1,3,5- trimethylbenzene	µg/L	108-67-8	2.0	n.a.	n.a.	n.a.	n.a.
Bisphenol-A	µg/L	80-05-7	1.6	1.6	0.1	64 ^{3b}	1.6
Chlorotoluron + Desmethyl chlorotoluron	µg/L	15545-48-9	0.8	0.1	0.4	0.4	n.a.
Cyanide - free	µg/L	57-12-5	1.2	0.6	10	0.23 ^{3b}	n.a.
Dibutyl phthalate	µg/L	84-74-2	10	10	10	10	10
Dibutyltin cation	µg/L	14488-53-0	0.02	n.a.	0.01	0.09	n.a.
Epichlorohydrin	µg/L	106-89-8	12	1.3	10	0.65	n.a.
Fluoride	µg/L	16984-48-8	680	n.a.	1000	1500 ^{3b}	n.a.
Formaldehyde	µg/L	50-00-0	130	10.2	n.a.	180 ^{3b}	n.a.
Glyphosate	µg/L	1071-83-6	20	28	28	77 ^{3b}	n.a.
Hexachloroethane	µg/L	67-72-1	24	0.98	10	0.67	n.a.
Linear alkylbenzenesulfonates LAS	µg/L	42615-29-2	250	n.a.	n.a.	250 ^{3a}	n.a.
n-Hexane	µg/L	110-54-3	0.2	n.a.	n.a.	n.a.	n.a.
Pendimethalin	µg/L	40487-42-1	0.3	0.07	0.27	0.3 ^{3b}	n.a.
Phenol	µg/L	108-95-2	7.7	7.7	n.a.	100 ^{3b}	7.7
S-metolachlor	µg/L	87392-12-9	0.3	n.a.	n.a.	n.a.	n.a.
Terbutylazine	µg/L	5915-41-3	0.5	0.06	0.1-0.5	0.19 ^{3b}	n.a.
Toluene	µg/L	108-88-3	74	74	10	74	74
Xylenes	µg/L	1330-20-7	185	1.3	n.a.	n.a.	n.a.
Arsenic and its compounds	µg/L	7440-38-2	7	4.4	n.a.	25 ^{3b}	n.a.
Antimony and its compounds	µg/L	7440-36-0	3.2	n.a.	20	6.5 ^{3b}	n.a.
Boron and its compounds	µg/L	7440-42-8	180	n.a.	100	240 ^{3b}	180
Chromium and its compounds (as total chromium)	µg/L	7440-47-3	12	n.a.	10	3.4	n.a.
Cobalt and its compounds	µg/L	7440-48-4	0.3	0.3	0.9	0.089	n.a.
Copper and its compounds	µg/L	7440-50-8	8.2	1.6	4	1.5 ^{3b}	7.8
Molybdenium and its compounds	µg/L	7439-98-7	24	n.a.	7	136	n.a.
Selenium	µg/L	7782-49-2	6	n.a.	2.5	0.052	n.a.
Zinc and its compounds	µg/L	7440-66-6	7.8 ⁵	7.8 ⁵	14	7.8 ⁵	7.8 ⁵

Table Footer: n.a. – not available ¹ Chemical Substance Portal (INERIS <http://www.ineris.fr/substances/fr>); ² Information System Ecotoxicology and Environmental Quality Targets – ETOX (UBA <http://webetox.uba.de/webETOX>); ³ Risico's van Stoffen (RIVM <http://www.rivm.nl/rvvs/>); ^{3a} (Feijtel and van de Plassche, 1995) ^{3b} RIVM data on Maximum Permissible Concentration (MPC). MPC is the scientifically-based standard indicating the concentration in an environmental compartment at which no effect to be rated as negative is to be expected for ecosystems. For the derivation of the MPC for water, the methodology used is in accordance with the Water Framework Directive; ⁴ The Predicted No Effect Concentrations (PNEC) from the EU Risk Assessment Reports (EU-RAR). According to the guidelines (Lepper, 2005) (European Commission, 2011) PNEC can be adopted as AA-EQS. ⁵ The EQS values vary depending on the hardness of the water, the lowest EQS is presented.

Where there were sufficient data, with results of toxicity tests from at least eight taxonomic groups available, both deterministic and probabilistic approaches to extrapolation were performed. This means that the resulting EQSs, whether they were derived using the deterministic method or the probabilistic method were all considered reliable. The final EQSs were preferably based on the results from the probabilistic method, since these entail a more robust approach towards assessing ecosystem effects. The selection of the final EQS remains subject to expert judgement.

In this study, the probabilistic approach was used by employing the SSD modelling with the use of ETX 2.0 software (van Vlaardingen et al., 2004). Figure 1 shows the SSD graph for arsenic for chronic toxicity data using the ETX software. After aggregation of the available data for arsenic the data set contained ecotoxicity data for 20 species for 8 major taxonomic groups from 3 trophic levels, which are available for the calculation of the HC₅ with the ETX 2.0 software. To account for uncertainty we used an AF of 2 on the calculated HC₅ for the final calculation of AA-EQS that amounts to 7 µg/L. The AF was chosen taking into account the overall quality of the database and the endpoints, as well as the diversity and representation of the taxonomic groups covered by the database.

When we used deterministic method to calculate AA-EQS for arsenic, the calculated value is 0.33 µg/L. The toxicity dataset for arsenic is large and AA-EQS calculated with deterministic method can be overprotective. Following the guideline (European Commission, 2011) we decided that the final AA-EQS for arsenic should be based on the probabilistic method (7 µg/L).

The setting of environmental quality standards was based on the toxicity data from databases of various institutes, also accessible online (e.g. EPA Ecotox, <http://cfpub.epa.gov/ecotox/>). As recommended in the guidelines (Lepper, 2005; European Commission, 2011) we used the Predicted No Effect Concentrations (PNECs) derived from this process and adopted as AA-EQSs. In reference to plant protection products, we followed the guidelines (Lepper, 2005; European Commission, 2011) and used the list of endpoints produced for the review process and published on the internet by the Commission from the risk assessment under Directive 91/414/EEC (1991). In the third column of Table 1 the derived AA-EQSs are presented. The environmental quality standards (AA-EQS and MAC-EQS) for Slovenian specific pollutants can be found in the Slovenian legislation (Official Gazette of the Republic of Slovenia, no. 14/09, 98/10 and 96/13).

4. Slovenian EQSs Compared to the Values Derived in Other Countries

To compare EQS values derived in Slovenia with the values derived in other EU countries, we chose to compare AA-EQS values, since the availability of these data was better than for MAC-EQS. We used the background information about the derivation method and the dataset used in France (INERIS, 2013), Germany (UBA - ETOX, 2013) and The Netherlands (RIVM, 2013). From 29 values, only 6 Slovenian AA-EQSs are less protective and differ by more than one order of magnitude from the values in selected EU countries.

- For epichlorohydrin the difference in derived AA-EQSs is around one order of magnitude (Slovenia 12 µg/L; INERIS 1 µg/L; RIVM

0.65 µg/L), while ETOX data are in the same range (10 µg/L). We used the same approach as INERIS, ETOX and RIVM for the derivation of AA-EQS value (deterministic approach with AF). The Dutch RIZA MPC value of 12 µg/L was derived as ad hoc-MPC in Beek (2000), we used practically the same dataset (the lowest value LC₅₀ (Lethal Concentration of a substance in environmental media expected to cause death in 50% of test animals) for fish 11.8 mg/L). RIVM and INERIS have used a more complete dataset with the lowest LC₅₀ value for fish 0.65 mg/L. A revision of Slovenian EQS values is needed for epichlorhydrin since there are new ecotoxicity data available that can be used for the refinement of EQS value.

- For formaldehyde the difference in the AA-EQSs is around one order of magnitude (Slovenia 130 µg/L; INERIS 10 µg/L). INERIS has used the deterministic approach with AF and this resulted in an AA-EQS that is one order of magnitude lower than the AA-EQS from RIVM. Our AA-EQS is in the same range as RIVM's AA-EQS (180 µg/L), as we both used the probabilistic approach with the statistical method for the calculation of AA-EQS, due to the availability of a large ecotoxicity database. In our opinion the dataset for formaldehyde contains sufficient data to justify the use of the probabilistic method and the derived AA-EQS is protective of the aquatic environment.
- For hexachloroethane the difference in AA-EQSs is more than one order of magnitude (Slovenia 24 µg/L; INERIS 1 µg/L; RIVM 0.67 µg/L). The same approach was used for the derivation of the AA-EQS values (deterministic approach with AF), while the dataset of INERIS contains more data. Revision of our EQS values for hexachloroethane is needed since there are new ecotoxicity data available that can be used for the refinement of EQS value.
- For terbutylazine the difference in derived AA-EQSs is around one order of magnitude

(Slovenia 0.5 µg/L; INERIS 0.06 µg/L; RIVM 0.19 µg/L). The three AA-EQS values were all derived using the deterministic approach with AF. The RIVM AA-EQS is in the same range, the INERIS value is almost 10 times lower than our value. The explanation is that the INERIS dataset was larger than the other sets. Our EQS values for terbutylazine need to be refined using the new ecotoxicity data.

- For xylenes the difference in AA-EQSs is around two orders of magnitude (Slovenia 185 µg/L; INERIS 1 µg/L). For the derivation different approaches were used. While INERIS used the deterministic approach with AF, we applied the probabilistic approach with the statistical method due to the availability of a large set of ecotoxicity data. The database for xylenes contains sufficient data to justify the use of the probabilistic method and the derived AA-EQS is protective of the aquatic environment.
- For selenium the difference in AA-EQSs is around two orders of magnitude (Slovenia 6 µg/L; RIVM 0.052 µg/L), while ETOX data are in the same range (3 µg/L). Both RIVM and we used the probabilistic approach with the statistical method, as there are a lot of ecotoxicity data available. The reason for the difference is the application of a different AF at the end of derivation. For selenium the new ecotoxicity data and the chosen assessment factors need to be evaluated to refine our EQS value.

5. Concluding Remarks

This contribution introduces the process of composing the list of specific pollutants and their environmental quality standards in Slovenia as required by the WFD. The classification of substances on the list of specific pollutants for surface waters followed the guidelines already used in the draft list of priority substances on the EU level. We collected the data on fate and behaviour of each substance from the list and assessed their ecotoxicological characteristics and derived AA-EQS and MAC-EQS.

Slovenian AA-EQS values derived by the National Laboratory of Health, Environment and Food are in general in the same range as the data from INERIS, ETOX and RIVM. Values were derived for 29 specific pollutants and among them 6 are higher than in other countries. After analysis of background information we conclude that a revision of EQS values is needed for epichlorhydrin, hexachloroethane, terbutylazin and selenium since there are new ecotoxicity data available that can be used for the refinement of EQS values. For xylenes and formaldehyde the refinement is not necessary since the reason for higher values in these cases is the use of the probabilistic method which is the preferred method in case a larger dataset is available.

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