Challenges in reducing hazardous substances

International for the Protection of the Danube River

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1. Introduction

The purpose of the background document is to prepare the participants of the ICPDR Workshop on Joint Program of Measures (4 - 5 April 2013, Vienna) for the discussion by illustrating the challenges, problems and recommendations for the hazardous substances pollution.

The Joint Program of Measure currently under the implementation in the Danube countries includes the improvement of knowledge on the emissions, losses and discharges of priority substances, through the preparation of the first Danube inventories of emissions, losses and discharges of priority substances, as the most important actions to reduce hazardous substances pollution in the DRB by 2015 and also beyond.

Participants at the workshop – experts and decision makers, all acting proactively on water management and financing of measures have the opportunity to gain knowledge on the emissions, losses and discharges of priority substances, status of the measures implementation and to seize the opportunities through discussions and be the best prepared to deal with remaining challenges to achieve the Water Framework Directive 2000/60/EC (WFD) objectives.

2. What we know

WFD environmental objectives, visions and managements objectives for the DRB

Hazardous substances pollution can seriously damage riverine ecology and consequently impact upon water status and affect the health of the human population. Types of hazardous substances include: man-made chemicals, naturally occurring metals, PAH, phenols, endocrine disruptors and pesticides.

Article 16 of the WFD has put in place a mechanism through which a list of 33 *priority pollutants* has been created and 8 other pollutants¹. Their inclusion on the list was based on the risk to or via aquatic environment and ranked based on a combined approach (intrinsic hazard of substances, exposure based on monitoring information and production volumes and use patterns). The chemical status was assessed based on the environmental quality standards

¹ According to WFD Article 2(30), priority substances mean substances identified in accordance with Article 16(2) and listed in Annex X. Among these substances there are *priority hazardous substances*, which are defined as substances identified in accordance with Article 16(3) and (6) for which measures have to be taken in accordance with Article 16(1) and (8).

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set for these substances². From this list of 33 priority substances, a group of 14 *priority hazardous substances* has been identified as being toxic, persistent and bioacculative substances or giving and equivalent level of concern. These types of substances are to be subject to cessation or phasing out of discharges, emissions and losses within 20 years of appropriate EU regulatory measures being introduces.

Member State must aim to reach good chemical and ecological status/potential of surface and ground waters by 2015 subject to certain limited exceptions. It is designed to:

- enhance the status and prevent further deterioration of aquatic ecosystems and associated wetlands which depend on the aquatic ecosystems;
- promote the sustainable use of water;
- reduce pollution of water, especially by priority and priority hazardous substances;
- ensure progressive reduction of groundwater pollution.

In order to address the pollution caused by hazardous substances, the Danube countries have agreed in the DRBM Plan on the basin-wide vision for hazardous substances pollution aiming that "no risk or threat to human health and the aquatic ecosystem of the waters in the Danube River Basin District and Black Sea waters impacted by the Danube River discharge".

Reducing hazardous substances emissions is a complex task that requires tailor made strategies as the relevance of different input pathways is highly substance-specific and generally shows a high temporal and spatial variability.

The Danube countries are making much progress in supplementing the insufficient information of the 2009 DRBM Plan, improving the understanding on the magnitude and implications of problems associated with hazardous substances at a basin-wide level, and taken actions in implementing relevant EU Directives, such as the UWWTD and the IPPC Directive, to ensure the reduction and elimination of discharges of the hazardous substances. This is particularly the case because hazardous substances can remain in the environment for a very long time, can bioaccumulate and can harm ecosystems and human health, even in very low concentrations.

The sources of hazardous substances are variable. They include: direct and indirect discharge from industrial point sources (including air pollutants); municipal wastewater from households and through urban runoff; direct application of pesticides and other hazardous substances and accidental pollution. Therefore, measures to reduce or eliminate hazardous substances need to be based on a variety of approaches addressed to the individual pressures and sectors.

² Annex I in the Directive 2008/105/EC of the European Parliament and of the Council on environmental quality standards in the field of water policy (EQS Directive)

Existing knowledge gaps in the Danube Basin Analysis (2004) and Danube River Basin Management Plan (2010)

For the Danube Basin Analysis (DBA 2004), the ICPDR Emission Inventory and results from the JDS 1 provided the basis for the pressure analysis regarding hazardous substances.

A list of substances/parameters of relevance in the DRB was prepared by the ICPDR³ consisting of two separate annexes:

- Annex A: 33 priority substances, in accordance with the Annex X of the EU WFD;
- Annex B: 8 additional substances (of which four are hazardous), divided into two groups:
 - B1: General Parameters (COD, NH₄-N-ammonia, Total N, Total P);
 - B2: Danube Specific Substances (arsenic, copper, zinc, chromium).

In the DBA 2004, out of the 33 priority substances identified, only 7 were included in the parameters assessed in the Transnational Monitoring Network (TNMN). Very limited basin-wide information was available for the other 26 substances.

In the DRBM Plan, the respective lack of data on hazardous substances continued, although new reporting schemes, improved analytical capabilities and results from the JDS 2 (that took place in 2007) improved the knowledge gap. The DRBM Plan recommended that the significant uncertainty in our current knowledge of pressures due to hazardous substances, as well as their impact on water status needs to be improved in the future.

To this extent, the inventory of emissions, discharges and losses required under the EU Daughter Directive on Priority Substances, adopted by the Environment Council in October 2008, should be used. The Danube countries should perform this inventory in a comparable and coordinated way. The ICPDR and its expert groups should ensure coordination and reporting.

3. Results of testing in the Danube river basin

As mentioned above one of the main environmental objectives of the WFD is to cease or phase out the emissions, discharges and losses of priority hazardous substances and to reduce the pollution from priority substances. As a matter of fact, Member States of the EU shall establish the necessary measures at each river basin district and assess the compliance with these obligations, in particular as regards the consideration of significant emission, discharges and losses. In order to meet these needs as well as the requirements of Article 5 of EQS Directive, Member States of the EU have the obligation to establish an inventory of emissions, discharges and losses for each river basin district or part of a river basin district in its territory.

³ ICPDR document: List of Priority Substances 2001/2002 (see www.icpdr.org).

The European Commission had launched in 2010 a new activity to develop guidance for the establishment of an inventory on discharges, emissions and losses of priority substances, in accordance with article 5 of EQS Directive. An EC Drafting Group has been established to prepare the technical guidelines with the involvement of the Secretariat and PM EG, under the coordination of the P&M EG Chairperson. The Guidance Document No. 28 Technical Guidance on the Preparation of an Inventory of Emissions, Discharges and Losses of Priority and Priority Hazardous Substances has been published in 2012. The P&M Expert Group was selected as a platform to deliver the case study, based on a concept and a road map prepared for this purpose. Consequently, based on the EU Drafting Group on Priority Substances recommendations, a Danube case study was developed.

The aim of the case study was to make use of the guidelines in preparing national inventories on discharges, emissions and losses in accordance with article 5 of EQS Directive in the DRB, and to test in a two-step approach the guidelines for specific substances of Danube basin wide relevance. The first step consisted in the assessment of the relevance of the substances at the river basin level and the second one in a more in-depth analysis using riverine load approach.

For the purpose of *establishment of relevant* WFD Annex X substances (33 priority substances + 8 other pollutants, called generically further below "priority substances") all available data for the Danube River and its tributaries, from the period 2008 - 2009 as follows:

- MA EG Excel file on chemstatus non-complinace;
- data provided by for the purpose of the initial testing of the CIS Guidance; 7 countries (DE, HR, HU, MD, RO, SI and SK) delivered the data for the water bodies failing to achieve the chemical status (non-compliance with the environmental quality standards (EQS) laid down in the Directive 2008/105/CE). In addition, HU delivered data on non-priority substance such us cooper and zinc and SK delivered information on more than 2 water bodies showing average concentration in the range of 0.5 and 1 EQS.
- TNMN data extracted from the Danube River Basin quality database for the period 2008-2009. 11 countries (AT, BG, DE, HR, HU, RO, RS, SK, SI, BA, MD) have provided data for the 32 out of 33 group of priority substances and 7out 8 other pollutants. Annual average values have been calculated for each of those substances as well as maximum allowable concentrations.

However, before starting analysis of relevance, it was check whether the minimum technical requirements laid down in Article 4 and 5 of the QA/QC Directive 2009/90/CE are fulfilled. The information on limit of quantification (LoQ) was not available and thus it was calculated based on limit of detection. A closer look at the available data showed that big part of these data cannot match the LoQ less than 30% of the annual average value laid down in Part A of Annex I of the Directive 2008/105/CE. Taking into account the small number of data made available by the countries, it was decided to skip this step and to go straightforward to the relevance one.

The criteria used for the assessment of relevant priority substances are the same as those described in the CIS Guidance no 28:

- The annual average value found in the aquatic environment is grater than the annual average value laid down in Part A of Annex I of the Directive 2008/105/CE;
- The maximum allowable concentration found in the aquatic environment is grater than the maximum allowable concentration laid down in Part A of Annex I of the Directive 2008/105/CE;
- The annual average value found in the aquatic environment is grater than half of the annual average value laid down in Part A of Annex I of the Directive 2008/105/CE;
- The maximum allowable concentration found in the aquatic environment is grater than half of the maximum allowable concentration laid down in Part A of Annex I of the Directive 2008/105/CE;
- Monitoring results show an increasing trend of concentration.

All the information coming from the sources mentioned above have been combined in order established a list of relevant substances at the DRB. The final decision for the selection was based on an arbitrary criterion of minim 3 Danube countries (at least 3 countries have fulfilled one of the relevance criteria mentioned above). The priority substances that have passed the relevance test for the DBR are presented in the Table 1.

Table 1

No	CAS number ⁽¹⁾	EU number ⁽²⁾	Name of priority substances or groups of substances
(1)	120-12-7	204-371-1	Anthracene
(2)	1912-24-9	217-617-8	Atrazine
(3)	7440-43-9	231-152-8	Cadmium and its compounds
(4)	not applicable		para-para DDT
(5)	7439-92-1	231-100-4	Lead and its compounds
(6)	7439-97-6	231-106-7	Mercury and its compounds
(7)	7440-02-0	231-111-4	Nickel and its compounds
(8)	50-32-8	200-028-5	(Benzo(a)pyrene)
(9)	191-24-2	205-883-8	(Benzo(g.h.i)perylene)
(10)	207-08-9	205-916-6	(Benzo(k)fluoranthene)
(11)	122-34-9	204-535-2	Simazine
(12)	67-66-3	200-663-8	Trichloromethane (Chloroform)

List of Priority Substances relevant for the the Danube River Basin District

⁽¹⁾CAS: Chemical Abstract Services

⁽²⁾ EU-number: European Inventory of Existing Commercial Chemical Substances (EINECS) or European List of Notified Chemical Substances (ELINCS)

The list contains only the relevant priority substances for rives (e.g. Danube and its tributaries) and not for lakes, transitional and coastal waters for which information provided by the countries of concern it is very scarce.

The second step of the testing was the *riverine loads approach*. In practical terms, the riverine loads considered as the mass of a contaminant transported per unit of time and expressed as tone/year were calculated.

The load calculation has been applied taking as pilot the Danube River itself (without tributaries) for the twelve priority substances selected as been relevant at the DRB level (Table 1). For this purpose the available monitoring data have been extracted from the TNMN database for the years 2008 and 2009 considering the riverine concentration of the relevant priority substances.

According to the methodology established at the EU level. The total annual riverine load of a certain transported relevant priority substance could be calculated with the following formula:

$$L_{y} = Q_{y} \cdot \frac{\sum C_{i} \cdot Q_{i} \cdot U_{f}}{\sum Q_{i}} \cdot 0.31536$$

where:

 $L_v = total annual riverine load (t/y)$

 Q_y = annual average of all daily flow data (m³/s)

 Q_i = flow value when the sample i is sampled (m³/s)

 C_i = concentration measured in the sample i (microg/l)

 $U_{\rm f}$ = correction factor applied when the location of flow monitoring station is different from the one for the water quality monitoring

Due to the fact that there was no information on whether the location of the gauging station coincides or not with the water quality station, the U_f factor was neglected and the following simplified formula had been applied:

$$L_y = Q_y \cdot \frac{\sum C_i \cdot Q_i}{\sum Q_i} \cdot 0.31536$$

It should be stressed that the diffuse load could not be estimated based on existing data submitted by the Danube countries.

A statistical overview of the results of the second testing based on load calculation for the Danube River, period 2008 - 2009 is showed in Table 2.

Table 2

Load range for the Danube River for the relevant priority substances

Name of the substance	No of countries		Number of stations		Load range (t/y)	
	2008	2009	2008	2009	2008	2009
Anthracene	1 (SK)	1 (SK)	3	3	0	0
Atrazine	7 (DE, AT, SK, HU, RS, RO, BG)	5 (DE, SK, HU, RS, BG)	27	24	0 - 93.18	0 - 0.323
Cadmium	7 (DE, AT, SK, HU, HR, RS, RO)	7 (DE, AT, SK, HU, HR, RS, RO)	32	31	0 – 166.01	0 - 83.02
para-para DDT	6 (SK, HU, HR, RS, RO, BG)	5 (SK, HU, HR, RS, BG)	29	23	0 – 9.32	0
Lead	7 (DE, AT, SK, HU, HR, RS, RO)	7 (DE, AT, SK, HU, HR, RS, RO)	32	31	0 - 232.36	0 - 671.35
Mercury	7 (DE, AT, SK, HU, HR, RS, RO)	7 (DE, AT, SK, HU, HR, RS, RO)	32	30	0 – 10.40	0 – 12.83
Nickel	7 (DE, AT, SK, HU, HR, RS, RO)	7 (DE, AT, SK, HU, HR, RS, RO)	31	30	0 - 335.41	0 – 741.56
Benzo(a)pyrene	2 (SK, RS)	1 (SK)	5	3	0	0
Benzo(g.h.i)perylene	2 (SK, RS)	1 (SK)	5	3	0	0
Benzo(k)fluoranthene	2 (SK, RS)	1 (SK)	5	3	0	0
Simazine	2 (SK, RS)	2 (SK, RS)	12	13	0	0
Trichloromethane	3 (DE, SK, RO)	3 (DE, SK, HU)	14	10	0 - 139.92	0 - 235.52

If certain countries do not appear in the Table is due to the fact that no monitoring data (i.e. concentration values) has been found in the TNMN database. Also, it is important to mention that the zero load does not mean that the substances do not exist in the aquatic environment. This is the result of zero concentration that was provided by many countries. In these cases, it is assumed that this value was given only to fulfil a mandatory cell and not because this was the concentration found in the environment. Moreover, no information was found on limit of quantification and very scarce on the limit of detection. Also, sometimes the load could not be

calculated either due to the lack of flow value when the sample was sampled or the lack of daily flow data.

4. Introducing the new ICPDR priority list of substances

Apart for priority substances for which the results of the relevance test were presented in section 3, the non priority substances (i.e. general parameters and specific pollutants) have been investigated as well. Due to the lack of time, only the data for the Danube River, from the same period (2008 - 2009) have been taken into consideration to establish the relevance of types pf substances. Having in view that for the general parameters and the specific pollutants the quality standards are not harmonised at the EU level, the criteria used for the priority substances have been adjusted accordingly as follows:

- The annual average value found in the aquatic environment is greater than the mean value of annual averages of the reported data;
- The maximum allowable concentration found in the aquatic environment is greater than the mean value of maximum allowable concentration of the reported data;
- Monitoring results show an increasing trend of concentration.

A non priority substance passed the relevance test when at least one of the criteria mentioned above was met from more than 50% of the stations.

Table 2 shows the general parameters and specific pollutants that are relevant at the Danube River level.

More likely the list will be extended once more data will be made available by the Danube countries and the investigation period will cover a lager period of time. Furthermore, if the same approach will be applied for the tributaries of the Danube River, additional information collected may offer a different picture than the one from Table 3.

Table 3

No	CAS number	Name of substances or groups of substances		
General parameters				
(1)	Not applicable	Total Organic Carbon		
(2)	Not applicable	Chemical Oxygen Demand		

List of general parameters and specific pollutants relevant at Danube River level

(3)	Not applicable	BOD5		
(4)	Not applicable	Ammonical Nitrogen (N-NH ₄)		
(5)	Not applicable	Total Nitrogen		
(6)	Not applicable	Total Phosphorous		
Specific pollutants				
(7)	7440-38-2	Arsenic and its compounds		
(8)	7440-50-8	Cooper and its compounds		
(9)	7440-47-3	Chromium and its compounds		
(10)	Not applicable	Adsorbable organic halogens (AOX)		

The results obtained above were correlated with the available information found the E-PRTR and the UWWTD databases. Different criteria were used for the two databases (E-PRTR, UWWTD) in order establish the relevance of substances. The Danube River (without tributaries) was chosen as case study for the analysis of interface between the E-PRTR, UWWTD and TNMN databases. As regards the substances taken into consideration for the purpose of this analysis, a list was compiled based on the list of priority substances and other pollutants (Annex I of the EQS Directive), the list of relevant substances that are monitored under the UWWTD and the list of substances required under the E-PRTR.

The relevance criteria used are described here below for each case.

The data available for 2008 – 2009 have been extracted from the E-PRTR official website http://prtr.ec.europa.eu/PollutantReleases.aspx. The reported releases include introduction of any of the listed pollutants into the environment as a result of any human activity, whether deliberate, accidental, routine or non-routine, at the site of the facility. E-PRTR does not contain information on releases from diffuse sources into water for the period chosen (2008 – 2009). The E-PRTR covers the 27 EU Member States as well as Iceland, Liechtenstein, Norway, Serbia and Switzerland and contains the annual data for industrial facilities from the following industrial sectors: energy, production and processing of metals, mineral industry, chemical industry, waste and waste water management, paper and wood production and processing, intensive livestock production and aquaculture, animal and vegetable products from the food and beverage sector and other activities.

The criteria of releases to water that exceed the specific threshold (laid down in Annex II of the E-PRTR) have been applied and thus exceedances have been registered for at least one country and one of the two years for the following substances: Anthracene, Benzene, Brominated diphenylether, Cadmium, Carbon tetrachloride, C10-13-chloroalkanes, Chlorpyrifos, Isodrin, 1,2-dichloroethane, Dichloromethane, DEHP, Diuron, Endosulfan, Dexachlorocyclohexane, Isoproturon, Lead, Mercury, Nickel, Nonylphenol, Octylphenol, Pentachlorophenol, Benzo(g,h,i)perylene, Tetrachloroethylene, Trichloroethylene, Tributyltin, Trichlorobenzenes, Trichloromethane, TOC, Total nitrogen, Total phosphorus,

Arsenic, Cooper, Zinc, Chromium, AOX, Phenols, PCBs, Vinyl Chloride, Toxaphene, Triphenyltin, Dioxines and Furans.

As regards the UWWTD, the metadata reported by the Danube countries either for 2007 or for 2008 according to the EMIS Inventory template have been used. It is acknowledge that all 8 parameters required to be reported under EMIS Inventory template (BOD5, COD, Ntot, Ptot, cadmium, lead, mercury, N-NH4) are relevant substance. It should be underlined that data has been provided by AT, DE, RO, SI, SK and UA for at least one these substances.

In conclusion, based on the information extracted from the E-PRTR, UWWTD and TNMN databases and considering the combined approach (emissions and riverine concentrations) the following substances have been set as being relevant at the Danube River level:

Priority substances: Cadmium and its compounds, Lead and its compounds, Mercury and its compounds, Nickel and its compounds, Benzo(g,h,i)perylene, Trichloromethane (Chloroform)

General parameters: Total organic carbon (TOC), COD, BOD5, ammonical nitrogen, total nitrogen, total phosphorus

Other pollutants (specific pollutants): Arsenic and its compounds, Copper and its compounds, Chromium and its compounds, Adsorbable organic halogens (AOX).

5. EQS Directive implementation recommendations

Co-ordinated compilation of the national inventories by the ICPDR

The significant uncertainty in the current knowledge of pressures exercised by priority substances, including priority hazardous substances and of their impact on the chemical status of waters should be improved. One of the most important way is the development of the inventories on emissions, discharges and losses. Moreover, according to Article 5(4) of the EQS Directive, EU Member States should include these inventories as part of the WFD Report that has to be carried out by the end of 2013.

The co-ordinated compilation of the national inventories for each part of the DRB by the ICPDR will ensure a comparable and harmonised development of the first inventory of emissions, discharges and losses at the entire DRB level.

Perform checking requirements of the national analytical methods

Before starting the preparation of the inventory on emissions, discharges and losses, the Danube countries should investigate whether their analytical methods fulfil the minimum criteria laid down in the Directive 2009/90/EC (called QA/QC Directive) and in particular the requirement stated in Article 4 of this Directive.

Ensure reliable and comparable data input into the inventories

For the purpose of this inventory, it is suggested providing the monitoring data for which there are adequate analytical methods. In this way only reliable data will fit the inventory that needs to be developed, ensuring so a better comparability of data and a more accurate picture at the Danube River Basin District level. If this is done, the inventory will fit for one of its main purposes: measures will be established only for real situation and their effective implementation of measures will be properly looked at. However, basin wide information should be available to establish a common programme of measures for priority substances at the DRB level.

Make use of the TNMN and JDS

Thus the TNMN as well the JDS shall continue to be done being not only an important source of data that will fill in the information gaps, but also allowing Danube countries harmonising their existing monitoring methodology and testing of new methods.

Also, the inventories of urban and industrial pollution sources done by PM EG shall be periodically updated, considering the E-PRTR, UWWTD reporting templates, for both for EU and non-EU member states, having in view the correlation between discharges/emissions and riverine loads, setting the proper measures, evaluation of the efficiency of implemented measures.

Anticipate further needs for meeting the ICPDR vision and WFD objectives

Based on the conclusions of the assessment of the first RBMP of the DRBD, it seems that the environmental objectives of the WFD will not be achieved by 2015 regarding the hazardous substances. Moreover, more monitoring data concerning these types of substances should be collected in order to increase the confidence of chemical status evaluation. Also, a robust and exhausting documentation on sources and relevant pathways is required to support an appropriate control of water pollution of the sources (combined approach principle) and stricter emissions controls where needed.

Facilitate appropriate assessment tools

For diffuse emissions (of the relevant priority substances and specific pollutants), the development of models shall be done. The mathematical models should be developed in order assess the pollution sources emissions, background inputs (for naturally occurring substances), the pollution pathways, the possible measures and the scenarios development in order to achieve the management objectives at the DRBD level as well as the good chemical status of all water bodies. In this respect, the inventory of emissions, discharges and losses of priority substances will be done according the EU guidelines.

Guarantee proper policy coherence and synergies

There is also essential to better coordinate the measures applied at the national level to tackle pollution problems through the EQS Directive, Dangerous Substances Directive 2006/11/EC,

IPPC Directive (new Industrial Emission Directive 2010/75/EU), UWWTPs Directive, New Regulation on Plant Protection Products Directive 1107/2009/EC (amending the Directive 91/414/EEC) and Biocide Directive 98/8/EC in order to reduce the load of priority and priority hazardous substances.