Strategy for micro-pollutants
Integrated assessment of micro-pollutants and measures aimed at reducing inputs of urban and industrial wastewater

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1. Introduction

1. The 14th conference of Rhine Ministers on 18 October 2007 required the ICPR among others to develop a joint and comprehensive strategy for reducing and avoiding micro-pollutant inputs from urban wastewater and other (diffuse) sources into the Rhine and its tributaries by improving knowledge on emissions, eco-toxicological reactions in nature and to draft suitable treatment methods.

2. In its Plenary Assembly in July 2010 in Mainz, the ICPR presented the "Strategy for micro-pollutants - Strategy for urban and industrial wastewaters"[1] as first work result in this field. The strategy aims at presenting problems and lacks of knowledge, and to present recommendations to improve the situation. Its target is that

> "Substances in Rhine water may neither individually, nor in mutual interaction have detrimental impacts on the biocoenosis of flora, fauna and micro-organisms and water quality must be such that drinking water production is possible with simple, natural treatment methods.
> This means to avoid pollutions by reducing discharges, emissions and losses of micro-pollutants with detrimental effects in order to achieve concentrations near the background values for naturally occurring substances and to achieve concentrations near zero for synthetic substances."

3. Today, wastewater contains various substances, e.g. residues of household chemicals, personal care products and pharmaceuticals which are not sufficiently broken down or withheld in conventional mechanical-biological wastewater treatment plants. Modern analytics are able to determine a large number of substances as micro-pollutants in water bodies. An assessment of the environment toxicity is partly possible for individual substances but not for the sum of individual substances. Certain micro-pollutants may detrimentally affect the Rhine biocoenosis or drinking water production and drinking water quality.

4. Based on expert judgement, 10 groups of substances were chosen among the great variety of possible substances[2] for which, with the help of indicator substances, the quantities consumed and applied, input pathways into waters, monitoring data from surface waters, groundwater and drinking water as well as quality criteria and potential measures were analysed and summarized in evaluation reports[3]. Based on these data, possible measures aimed at reducing inputs into water bodies were chosen among the entire scope of measures and presented, beginning with those to take at the source (e.g. substance licensing, reduced use) and including technical measures in wastewater treatment plants of overriding interest.

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[1] ICPR 2010 – Strategy for urban and industrial wastewaters -

[2] Radio contrast agents, medicinal products for human use, animal health products, biocidal products and anti-corrosive agents, pesticides, industrial chemicals, complexing agents, oestrogents, cleaning and detergent agents, personal hygiene products, odiferous substances

[3] So far, the following evaluation reports have been published on the ICPR website
ICPR 2010 - Evaluation Report Medicinal Products for Human Use
ICPR 2010 - Evaluation Report Biocidal Products and Anti-Corrosive Agents
ICPR 2011 – Evaluation Report Oestrogens
ICPR 2011 – Evaluation Report Radio-Contrast Agents
ICPR 2011 – Evaluation Report Odiferous Substances
ICPR 2011 – Evaluation Report Complexing Agents
ICPR 2013 – Evaluation Report Industrial Chemiclas, ICPR report no. 202

5. This summary report looks into synergetic effects of the possible measures presented in the assessment reports, and thus into measures acting on several substance groups. Based on the results, recommendations will be made for measures aimed at avoiding and reducing the pollution of drinking water and the aquatic environment by different relevant substances.

6. In addition, a strategy on avoiding and reducing micro-pollutants of so-called diffuse origin comparable to the strategy for urban and industrial wastewater is to be drafted. It will equally concern substances partly discharged with the wastewater of urban wastewater treatment plants and partly input into waters by other pathways.

2. Substance relevance

7. The Rhine figures among Europe's most intensively used rivers. About 58 million people live in its catchment area with a mean population density of 290 inhabitants/km². With 680 inhabitants/km² the population density along the Lower Rhine is remarkable. About 96 % of all inhabitants in the Rhine catchment are connected to a wastewater treatment plant treating municipal wastewater. Thus, wastewater treatment plants considerably contribute to the runoff of the Rhine. During low water periods, its share of biologically treated wastewater can amount to 20% and more. The share of wastewater from wastewater treatment plants in the water body may be particularly high in densely settled regions along the Rhine tributaries. Due to climate change, the runoff of the Rhine will increase in winter and fall in summer[4] (which will increase the share of wastewater from municipal discharges) and thus the trend already emerging during the last century will continue.

8. A considerable share of the worldwide chemical industry is settled in the Rhine catchment and many of the industrial plants have their own on-site wastewater treatment plant. Further uses in the Rhine catchment include open-cast lignite mining areas, water abstraction for cooling water purposes, for hydro power production, for irrigation in agriculture and for drinking water production for some 30 million people. In addition, the Rhine is an important shipping lane.

9. The high pressures from uses have entailed a considerable pollution of the river. During the past decennia, international conventions, e.g. within the ICPR have clearly contributed to improve the chemical water quality as well as the biological state of the Rhine. Today, micro-pollutants range among the challenges to water protection. Many micro-pollutants are not or only partly treated in today's wastewater treatment plants and are thus discharged into the water bodies.

10. With respect to micro-pollutants, the following statements apply to water quality (present state)

a. In the Rhine and in tributaries with a high wastewater share, certain representatives of the following substance groups are often detected:
- Medicinal products for human use
- Biocidal products
- Anti-corrosive agents
- Iodine based radiological contrast agents
- Oestrogens
- Complexing agents
- Further industrial chemicals such as flame retardants and fluorosurfactants

[4] Study of Scenarios fort he Discharge of the Rhine

b. Furthermore, concentrations of refractory substances are comparably high in the lower parts of the Rhine (Delta Rhine). Examples are certain representatives of the following substance groups:

- o Medicinal products for human use
- o Anti-corrosive agents
- o Iodine based radiological contrast agents
- o Complexing agents except for DTPA (pentetic acid)
- o Further industrial chemicals such as flame retardants and fluorosurfactants.

11. The findings for the individual substance groups are:

a. Active pharmaceutical ingredients are largely detected in the Rhine catchment area. The highest concentrations are detected in the lower course of the Rhine and in tributaries with a high share of municipal wastewater. The highest individual monitoring values lie above the proposals for environmental quality standards[5]. Today there are no legally binding EQS. Active pharmaceutical ingredients are found in raw water of drinking water treatment plants and partly in drinking water, particularly if it is produced from bank filtrate.

b. The concentrations of biocidal products and anti-corrosive agents found in the Rhine catchment vary. Concentrations of biocidal products may be near the order of magnitude of eco-toxicologically relevant values. Legally binding WFD-EQS do not exist. For biocidal products and anti-corrosive agents the data are partly insufficient and complex patterns of discharge have been found.

c. For oestrogens, there are few monitoring data from the main stream of the Rhine. In the Rhine and in its big tributaries, monitoring values are all below the limit of detection of < 1 ng/l, in other tributaries they lie around some ng/l. However, the threshold value for endocrine disruptive effects is even lower[6]. Present proposals for EQN for oestrogens are below the possible limit of analytical detection.

d. Radio-contrast agents are developed as biologically inactive substances. Due to their polarity and stability they are partly detected in drinking water. There are no eco-toxicologically relevant data available from which EQS could be derived. In the lower course of the Rhine and in tributaries used for drinking water production concentrations of radio-contrast agents and of their transformation products are found in excess of IAWR[7] and GOW[8] values (in this case general preventive values for drinking water production; at the time being specific GOW values of radio-contrast agents do not exist.

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[5] European Commission 2012: Proposal for a „DIRECTIVE 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 (LINK)

[6] European Commission 2002: Study on the scientific evaluation of 12 substances in the context of endocrine disrupter priority list of actions; report: UC 6052. Johnson I and P Harvey (2002)

[7] Target value for xenobiotic organic substances oft he Internationale Arbeitsgemeinschaft der Wasserwerke im Rheineinzugsgebiet – IAWR (see LINK)

- Substances impacting biological systems: per substance 0.1 µg/l unless toxicological findings require a lower value
- Persistent substances without any known impact : per substance 1.0 µg/l
- Synthetic complexing agents, per substance 5.0 µg/l

Normally, surface waters corresponding to these target values are apt for drinking water production using simple treatment techniques.

[8] The GOW is considered to be a precautionary value for radio-contrast agents in drinking water and drinking water resources or in waters, from which raw water is taken for drinking water supply. It is a general precautionary value for verifiably non genotoxic substances for which data for toxicity by way of mouth, immunotoxicity and on the potential to harm reproductive cells do not lead to a value below 1 µg/l (GOW4) (see UBA 2003). As such, it is also applicable to components of sums of substances acting simultanously in a similar way.

e. From the point of view of drinking water supply, complexing agents are conspicuous, since they cannot be eliminated by traditional treatment processes. During the last 20 years, total EDTA emissions into the Rhine catchment have been considerably reduced. Concentrations of several µg/l have been measured in the Rhine and its tributaries during the past years, they increase in the longitudinal course of the Rhine and have several times been in excess of the IAWR value for complexing agents set to 5 µg/l. Concentrations in drinking water tolerable from an eco-toxicological point of view under lifelong exposition and the eco-toxicological effect threshold value are many times higher than the EDTA concentrations measured.

f. The synthetic odiferous substances HHCB (galaxolide) and AHTN (tonalide) are highly liposoluble, biologically persistent and bio-accumulate in organisms and are found in the Rhine, but their concentrations are below values at which detrimental effects are expected for aquatic organisms. The IAWR value set to 1µg/l is not exceeded. There is no EQS for these substances.

g. With respect to industrial chemicals, findings are as follows:

(i) In the main stream of the Rhine, diglyme are in excess of the relevant IAWR target value set to 1.0 µg/l, but there do exist peak burdens following isolated events in factories.

(ii) In the main stream of the Rhine, TECP and TCPP values in excess of the IAWR target value set to 0.1 µg/l are monitored. TCPP values in excess of the IAWR value are also detected in some Rhine tributaries. However, no contents in excess of the PNEC values have been detected. There does not yet exist any legally binding EQS for this group of substances.

(iii) In many cases, the concentrations of the fluorosurfactant PFOS measured along the Rhine are many times higher than the proposal of the EU Commission for an average annual EQS. In individual cases, the IAWR value set to 0.1 µg/l is topped.

(iv) The flame retardants (TCCP, TCEP and TBEP) and PFOS are detected in the bank filtrate of the main stream of the Rhine or its tributaries. As far as TCPP and TBEP are concerned, values measured in bank filtrate are above the IAWR target values.

12. Findings can be summarized as follows:

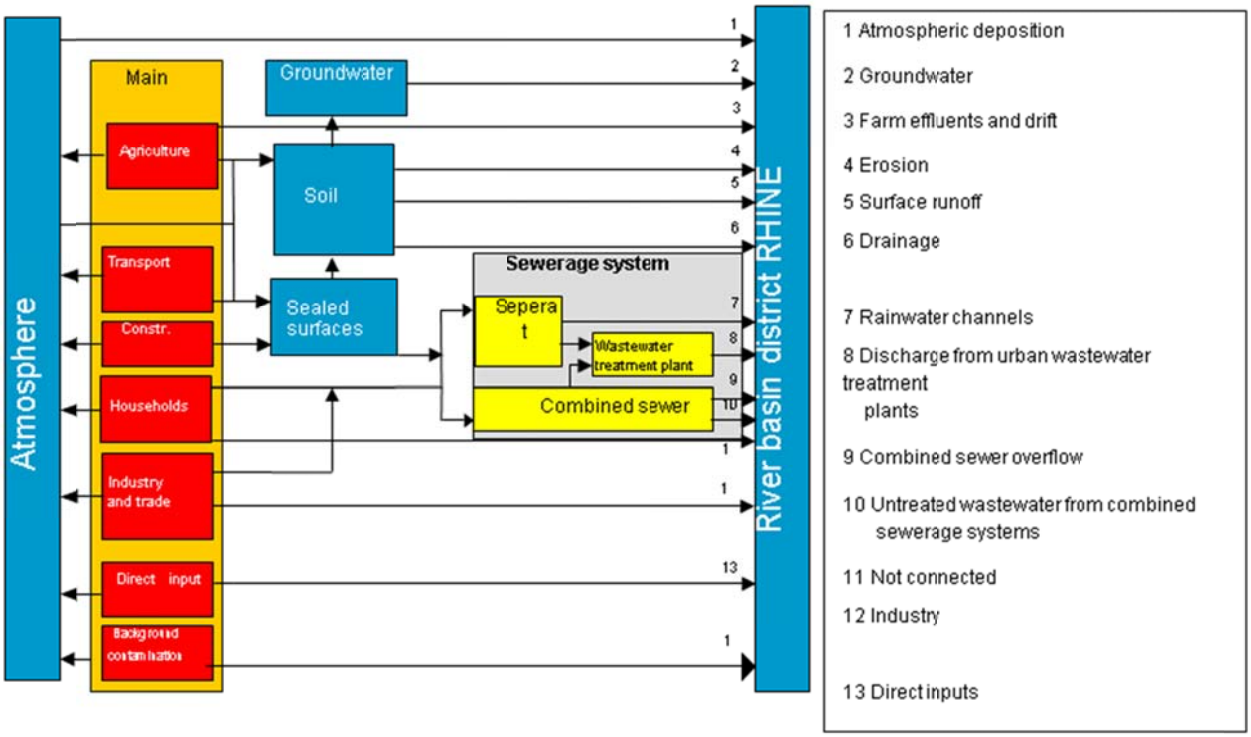
a. Monitoring data collected for the micro-pollutants considered in the Rhine catchment and considered in this report largely differ according to substance and region. For the classes of substances mentioned in this report, the highest individual monitored values detected in the Rhine and its great tributaries lie above the proposals for environmental quality standards or assessment criteria derived according to WFD rules.

b. For most of the substance groups dealt with or their indicator substances there do not exist any national or European environmental quality standards. At times, the precautionary values for drinking water production are topped in the lower course of the Rhine and in certain tributaries The highest individual values in surface water bodies were found in water bodies presenting a high wastewater share. In particular, as far as certain substances are concerned, negative ecological or eco-toxicological effects cannot be excluded for (smaller) tributaries with a high wastewater share.

c. Polar, persistent substances are in particular found in the raw water of drinking water works and are partly also detected in drinking water. On the Lower Rhine and in the Delta Rhine they increase expenses for drinking water production out of Rhine water.

3. Analysis of input pathways and sources

13. Based on concentrations detected in the Rhine catchment, the main sources of the substance groups is presented in an analysis of discharge pathways.



14. With respect to concentrations and loads this analysis shows that for many of the substances considered, treated municipal wastewater (emission pathway 8) is the relevant, decisive discharge pathway and that households, industry and trade are the most important sources. With respect to complexing agents, this pathway as well as direct discharges from industry (emission pathway 12) are of importance. As far as biocides (mecoprop) and some oestrogens are concerned, agriculture may be a relevant source.

4. Integrated assessment of all measures

15. A distinction can be made between the following types of measures described in the evaluation reports (details concerning the parts a. to c. - see annex):

a. **Measures at the source** (licensing, restriction of the use of substances, production processes, prescription for disposal);

b. **Decentralized measures** (treatment of wastewater split streams in plants);

c. **Centralized measures in municipal wastewater treatment plants** (implementation of up-to-date measures aimed at eliminating micro-pollutions from wastewater);

d. **Adaptation of monitoring and assessment programmes** (complementation of surveillance concepts and monitoring programmes, taking into account new substances when assessing the ecological state of waters, derive quality criteria);

e. **Information of the public** (about the substance impact on the environment and drinking water as well as about changes in use and disposal of substances).

16. Reduction measures were judged through an analysis of input pathways based on immissions and considering the types of measures.

Measures at the source

17. On the long run, a more detailed assessment of possible effects of the analysed substances on the environment and their consideration during licensing could contribute to reducing the micro-pollutant burden of waters.

18. Measures at the source are in particular useful in industrial production and the use of products in industry, trade and households but will, on the short term, only lead to a noticeable emission reduction of a limited number of substances.

Decentralized measures

19. Decentralized measures may make sense, if individual plants account for a considerable share of certain micro-pollutants in waters even in cases, where these substances pass by a wastewater treatment plant, where they are not or insufficiently eliminated.

Centralized measures

20. Fora broad scope of substances, centralized measures like applying further treatment procedures (e.g. ozonisation, active carbon treatment) when eliminating micro-pollutants can considerably improve the efficiency of wastewater treatment plants. The reduction of the micro-pollutant concentration in surface waters is greatest where the (biologically treated) effluent from wastewater treatment plants represents a considerable share of the receiving water.

Monitoring and assessment systems

21. For many micro-pollutants in the Rhine catchment a vast number of measurements is available within monitoring programmes of the ICPR, IAWR and the bordering states.

22. However, the extent of data collected highly varies according to the substance and region concerned. Therefore, a quantitative appraisal concerning the relevance of the different input pathways (see chapter 3) was only partly possible and in particular not possible for biocides and anti-corrosive agents.

Information of the public

23. With a view to avoiding or reducing eventual discharges of micro-pollutants into waters, the public must be informed about (i) the relevance of consumer products for the environment and drinking water, (ii) the use of the products according to good practice, (iii) the possibilities of environmentally friendly disposal or collection, (iv) environmentally friendly alternatives and (v) eco-labels.

24. With the same target in mind, the trade public must be informed about (i) recycling possibilities, (ii) environmentally friendly disposal of waste containing micro-pollutants and (iii) existing eco-lables.

5. Conclusions

25. Even though the amount of monitoring data collected for the micro-pollutants considered in this report considerably varies according to the substance and the region of the Rhine catchment concerned, the following conclusions can be drawn.

26. Substances of all substance groups considered occur in Rhine water and are detected in measurable concentrations in the main stream as well as in the tributaries. Comparatively high concentrations are detected in the lower course of the Rhine or in water bodies with a high share of treated wastewater. This is in particular true of the groups of medicinal products for human use, biocidal products and anti-corrosive agents as well as radio-contrast agents.

27. For most of the substance groups dealt with or their indicator substances there do not exist any national or European environmental quality standards for the Rhine catchment.

28. Polar, persistent substances are in particular found in the raw water of drinking water works and are partly also detected in drinking water.

29. Wastewater from secondary effluent is the most important discharge pathway for micro-pollutants into surface water bodies. Wastewater from households, plants and rain water from sealed surfaces in urban areas flows into wastewater treatment plants via the municipal sewer.

30. Taking into account the target of the strategy for micro-pollutants, their total emissions into water bodies should be reduced.

31. Discharges can be reduced by implementing the following measures:

a. Measures at the source may in particular prove to make sense in industrial production and in the use of products in plants and households. They might lead to a distinct emission reduction, but they are only applicable for a limited number of micro-pollutants.

b. Decentralized measures in plants may further reduce the discharges of problematic substances by optimizing process control and using appropriate procedures when treating wastewater split streams or wastewater to be discharged.

c. Centralized measures in municipal wastewater treatment plants, such as further treatment procedures (e.g. ozonisation, active carbon filtration) can eliminate a broad scope of micro-pollutants, taking into account that the effectiveness of elimination may differ from one substance or substance group to the next.

d. Targeted information of the public and trade public concerning e.g. the impact of consumer products on the environment or drinking water or concerning recycling possibilities may contribute to avoid and reduce possible discharges of micro-pollutants into water bodies.

32. Regular updating/checking of existing monitoring programmes is aimed at filling gaps of knowledge concerning the occurrence of the substances concerned in water bodies.

33. Knowledge on emission pathways will be enhanced by substance balances and model estimations.

34. The ICPR will elaborate recommendations for measures based on these conclusions.

Annex

Possible measures

The types of measures a. to c. mentioned in chapter 4 are presented more detailed below.

a. **Measures at the source** (licensing, restriction of the use of substances, production processes, prescription for disposal);

During substance licensing for marketing, a more detailed assessment of the environmental impact can be taken into consideration. Furthermore, development, test and use of biologically less persistent substitutes are relevant.

Specific measures at the source:

- Medicinal products for human use: Distribution of smaller packing units and improved collecting of pharmaceutical residues;

- Radio contrast agents: Collecting urine and arranging for centralized collection points for the further urine treatment;

- Odoriferous substances: More eco-labelled consumer products like detergents and cosmetics excluding the use of environmentally harmful odoriferous substances.

- Nonylphenol: Bans on import for products with problematic constituents (e.g. textiles containing NPOE), limiting their use or substitute them by more eco-friendly substances.

b. **Decentralized measures** in production and processing plants (optimization of production procedures, wastewater treatment in split streams or not):

A minimization of substance emissions is possible by:

- Optimizing the production process;
- Updating and applying the state of the art / the best available technology (BAT, BEP);

- Using more eco-friendly formulations;

- Replacing problematic substances by eco-friendly alternatives;

- Wastewater treatment, eventually in split streams;

- Improving suitable wastewater treatment procedures.

Specific decentralized measures:

- Radio-contrast agents in hospital wastewater are of particular interest, as these substances are almost only distributed by hospitals and institutes for radiology and are normally excreted by patients within 24 hours.

  Possible measures aimed at minimizing the inputs of radio-contrast agents are: separate urine collection followed by centralized further treatment, incineration or disposal along with waste. As a matter of principle, these measures may also apply to pharmaceuticals.

In individual cases the treatment of sanitary waters (as a whole or of split streams of individual departments) could represent an appropriate measure.

- Oestrogens: Treatment of wastewater split streams from plants with high oestrogen concentrations or during slurry treatment.

- Complexing agents: Implementation of (advanced) procedures to eliminate persistent complexing agents. Whether a target-aimed wastewater is possible and with what measures depends on the pH-value, temperature, concentration and other substances contained in the wastewater.

c. As a matter of principle, centralized - additional - measures in wastewater treatment plants are possible in order to reduce micro-pollutants in wastewater. Analysis and first experience in wastewater treatment plants show that a broad scope of micro-pollutants can be reduced by adsorption to active carbon or ozonisation of the secondary effluent. The degree of elimination thus achieved depends on the substance. For pharmaceuticals, biocides, oestrogens, odoriferous substances and flame retardants a considerable improvement of the elimination effect is achieved. A number of substances, such as radio-contrast agents or certain pharmaceuticals and complexing agents cannot be withheld by these treatment methods or are only withheld to a very limited extent.