Evaluation report

on biocidal products

and anti-corrosive agents

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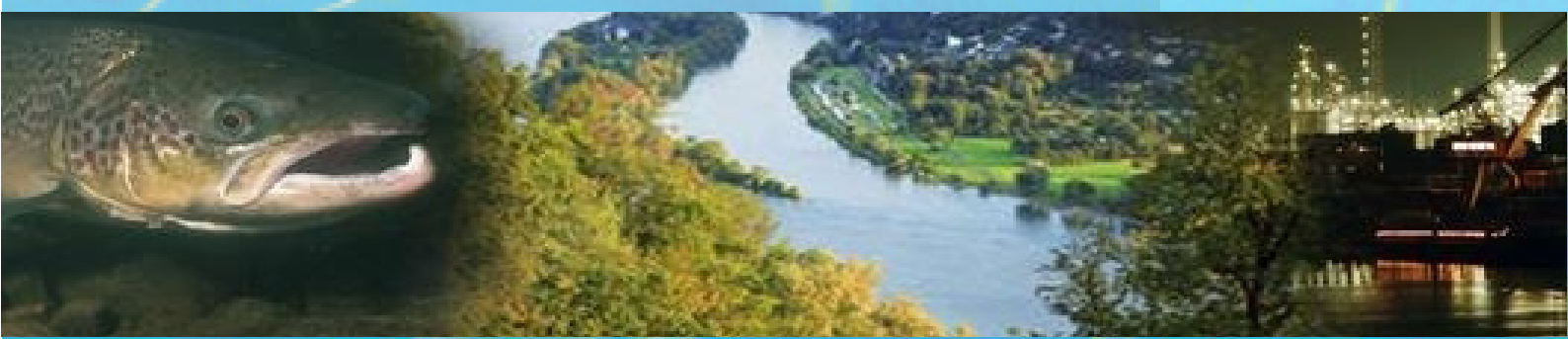

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1. Introduction

Biocidal products and anti-corrosive agents comprise a wide range of substances widely used in many applications in private households, health care, industry and trade as well as in other fields.

According to the European Biocidal Products Directive, biocides (or biocidal products) are "active substances and preparations, containing one or more active substances put up in the form in which they get are supplied to the user, intended to destroy, deter, render harmless, prevent the action of, or otherwise exert a controlling effect on any harmful organism by chemical or biological means." Protective agents for coatings or cooling systems, disinfectants, conservation agents or wood preservatives belong to the wide spread biocidal products. At present, about 18,000 biocidal products are available on the German market. In Switzerland, annually some 7,400 tons of biocidal products are estimated to be used (1 kg per inhabitant and year, taking into account that 40 % of these substances are not rapidly degraded in water). This amount is about five times higher than the amount of pesticides used in Switzerland. For the substance group of biocides, three particularly wide spread and often detected substances have been chosen among the great amount of substances applied to serve as indicator substances:

- Carbendazime
- Mecoprop
- Diethyl-meta-toluamide (DEET)

The indicator substances mecoprop and carbendazime – both biocidal agents – are used as plant protection agents in agriculture and are used in non agricultural applications in comparable amounts. For carbendazime, the non agricultural uses as fungus inhibiting agent in silicon sealants are of greater importance for inputs into waters. Mecoprop is used as chemical construction substance for sealants for flat roofs.

The indicator substance diethyl-meta-toluamide (DEET) is a biocidal agent, which is, among others, much used for fighting insects in private households.

Anti-corrosive agents protect materials against corrosion attacks and the resulting loss of the material's characteristics.

Benzotriazole and butylated hydroxytoluene (BHT) are proposed as indicator substances for the goup of anti-corrosive agents. Benzotriazole is used in cooling liquids, antifreeze agents and deicing agents or as silver protection agent in dishwashing detergents. Additionally, this substance may be used in further specific applications in industry and trade. It may e.g. be used as cooling lubricant in metal processing or in photo developing agents to reduce the formation of haze on films. BHT is used in many consumer products such as cosmetics or packing material. Under the denomination *E 321* it is equally licensed as food additive. However, the substance data sheet indicates that no applicable data are available for BHT. Therefore, BHT is not used as indicator substance.

Numerous applications of biocidal and anti-corrosive products lead to relevant emissions into the aquatic system. Due to the high consumption and the stability of these substances it is not surprising that they may be detected in the surface waters, in bank filtrate (e.g. benzotriazole) and partly also in drinking water. Therefore, these substances must be taken into account when assessing water quality. Also, due to their use, biocidal products are biologically active substances and may thus be a potential danger for man and the environment. There are distinct differences between the areas of application and inputs into waters of the proposed indicator substances.

The following statements are based on information derived from the substance data sheet.

2. Problem analysis

The indicator substances for the biocide substance group (carbendazime, diethyl-meta-toluamide (DEET), mecoprop) and that of anti-corrosive agents (benzotriazole) are regularly detected in surface waters in concentrations of few nanogrammes per litre (ng/l) to some microgrammes per litre (µg/l). All depending on the substance and group of substances, concentrations vary considerably and depend on different factors, such as the amounts consumed, use, pathways of input, elimination due to percolation or in wastewater treatment plants, degradation and dilution in surface waters, mobility in the aquatic phase.

The following statements apply to water quality:

- The highest biocide concentrations detected in waters in the Rhine catchment may be in the order of magnitude of ecotoxicologically relevant values (e.g. carbendazime). Concentrations measured in municipal wastewater are distinctly in excess of these values.
- In particular for the indicator substance benzotriazole, concentrations in surface waters may reach 1 µg/l and up to 10 µg/l in the outlets of wastewater treatment plants and in waters with a high share of wastewater. 1 µg/l corresponds to the IAWR value for persistent individual substances. In addition, benzotriazole is detected in the raw water of drinking water plants. There are no binding environmental quality standards (EQS) for this substance.
- Compared to other groups of substances, much less monitoring data are available which might permit a broad analysis of the situation.

The indicator substances considered are largely detected in the Rhine catchment area. In Rhine tributaries with a high share of (biologically) treated municipal wastewater concentrations may occur which detrimentally impact water organisms. Persistent substances such as benzotriazole complicate the drinking water production from Rhine water in the downstream section of the Rhine. This observation underlines the need for improved surveillance of water pollution with these substances.

3. Analysis of pathways

As far as emissions are concerned, in particular those applications are crucial which lead to relevant substance transfer into the wastewater or runoff rainwater. This is e.g. the case when weld backing agents are eroded from flat roofs, when anti-corrosive agents are used in dishwashing detergents or when insect fighting agents leach or are washed out or when cosmetics are washed off and in wastewater from indirectly discharging plants. All indicator substances are largely detected in municipal wastewater.

Due to its application, the indicator substance benzotriazole is mainly discharged into waters via wastewater treatment. Concentrations in municipal wastewater amount to some microgrammes per litre and are thus distinctly higher than the concentrations observed in water bodies. In this respect and concerning inputs in waters, the anti-corrosive agents taken into account are comparable to agents in medicinal products for human use.

The indicator substance DEET is also applied in private households (or used by private persons) and is thus primarily discharged into waters by municipal wastewater treatment plants. Eventual direct inputs (e.g. due to leisure activities) represent a possible pathway of input which is however difficult to quantify.

The indicator substance carbendazime is also applied in agriculture. However, for the Swiss part of the Rhine catchment, inputs from this source seem to be negligible. There are no data available for the entire Rhine catchment. But uses in settlements lead to a

continuous input via municipal wastewater treatment plants. There is uncertainty with respect to inputs passing by rainwater channels of two-pipe systems. Such inputs have been observed but are difficult to quantify and to generalize as the precise areas of application of this agent are only roughly known.

As far as the agent mecoprop is concerned, inputs as agent from agriculture are comparable to inputs form settlement wastewater. Inputs passing by wastewater treatment plants occur intermittently following the wash-out of these substances during precipitation events. Also, inputs from agricultural surfaces and storm sewers of two-pipe systems (e.g. wash-out from material protection in outside areas) have their own complex dynamics. This and the fact that this agent has inputs from different applications underline the complex character of substance inputs of different biocidal agents.

Due to the complex patterns of input determined for several substances and the partly insufficient amount of data, an in depth analysis of the situation must be carried out with respect to biocidal products and anti-corrosive agents. In particular, this comprises a systematic inventory of application areas and quantities consumed.

4. Possible measures

There are options for action in the following areas:

- Measures at the source;
- Information of the public
- Treatment of split wastewater streams;
- Centralized measures in wastewater treatment plants;
- Adaptation of monitoring programmes.
- Inventory of areas of application and quantities used.

In the following, the potential measures are developed more in detail.

Measures at the source

- Reduction of the pollution of water bodies by:
    - Information on appropriate disposal;
    - Use of more environmentally friendly formulations (kind of protective agent, concentration, composition)
    - Replacement by more environmentally compatible agents.

Measures at the source are particularly required for substances which do not reach the waters by means of centralized wastewater treatment plants (e.g. by storm sewers from two pipe systems).

Information of the public

The public as well as experts must be informed about the appropriate application and disposal as well as environmental relevance and impact of certain biocides and anti-corrosive agents on drinking water production.

Decentralized measures – treatment of split wastewater streams

The production of agents in industry and trade and the use of such agents in different applications in industry and trade may equally lead to high substance load inputs. The following measures may be taken into account in order to minimize these inputs:

- Optimization of processes relevant for wastewater in industry and trade

- Use of further procedures to eliminate micro-pollutions
- Sufficient size of combined sewer overflows
- Investigation programmes and sector specific inventories of relevant indirect inputs into the municipal network.

Centralized measures in urban wastewater treatment plants

The use of further treatment procedures to remove micro-pollutions (ozonisation, activated carbon) will increase the elimination performance of wastewater treatment plants. The estimated 3.200 wastewater treatment plants in the Rhine catchment dispose of a total volume of at least 98 million population equivalents. 191 of these wastewater treatment plants (that is 6 % of all wastewater treatment plants) dispose of a total volume of more than 100.000 population equivalents). But these wastewater treatment plants dispose of more than half of the entire treatment capacity (54 %) in the Rhine catchment. If these 191 wastewater treatment plants were extended by the afore mentioned further treatment procedures, the inputs of biocides and anti-corrosive agents (and of many other organic micro-pollutants from municipal wastewater treatment) into the Rhine could be reduced by at least 30 %.

The extension of the largest plants could be controlled by formulating minimum emission requirements or by the States in the Rhine catchment creating incentive systems.

This would distinctly reduce the contamination of the downstream section of the Rhine and grant improved protection of drinking water protection along the main stream of the Rhine. The extension of the greatest plants could be controlled if the Rhine bordering states formulated minimum emission requirements.

In individual cases, an extension of small to average wastewater treatment plants (10.000 to 100.000 population equivalents) could be considered which would regionally improve the ecological/chemical status of the Rhine tributaries. Furthermore, due to the large number of plants, the improvement of the treatment performance of small/average treatment plants has a positive impact on the protection of drinking water resources in the Rhine catchment.

Adaptation of monitoring programmes and systems of assessment

- Based on an assessment of the environmental relevance resulting from substance balances, risk assessments, simple model estimations, eventual indications resulting from licensing procedures and comparable methods.
- Based on the results of new analytical research methods
- Development of cumulative risk assessment (for repeated inputs of agents from different applications) and the possibility to take into account the effect of mixtures in licensing procedures and substance balances
- Taking into account relevant biocides and anti-corrosive agents and their relevant metabolites when the ecological and chemical status of waters is assessed by EU Member States within the framework of the Water Framework Directive and within the framework of the Swiss legislation on water protection.
- With a view to assessing the ecological/chemical status and to protecting drinking water resources, binding quality criteria must be derived on an appropriate institutional level.

Systematic inventory of application areas and quantities

- Systematic inventory of application areas and quantities to carry through risk assessments and substance balances

- Clarification of the legal basis with respect to taking into account data on the production and formulation derived from the licensing procedure

5. Conclusion

Summary of the most efficient measures to be further elaborated and examined.

- **Measures at the source** aimed at reducing water pollution by information on adequate disposal; use of more environmentally compatible formulations; replacement by environmentally compatible agents
- **Information of the public** and of experts on the appropriate use and disposal as well as on environmental relevance and the impact on drinking water production in the Rhine catchment.
- **Decentralized measures:** Minimization of substance inputs due to organizational measures; optimization of procedures relevant for wastewater and eventual use of further procedures aimed at removing micro-pollutions
- **Centralized measures:**
  The experience made in wastewater treatment plants, in which further treatment procedures are used to remove micro-pollutions (e.g. ozonisation, activated carbon) must be collected and interpreted in order to be exploitable for future decisions. Centralized measures taken in a very limited number of municipal wastewater treatment plants may e.g. lead to a 30 % reduction of inputs of biocides and anti-corrosive agents. These measures might also contribute to reducing a broad range of other micro-pollutions from municipal wastewater in the Rhine catchment.
- **Adapt monitoring programmes** based on simple substance balances, risk assessments, eventual indications from licensing procedures or based on the results of new analytical research methods
- **Adapt assessment systems:** Development of a cumulative risk assessment for licensing and taking into account anti-corrosive agents and biocides when assessing the ecological and chemical state of waters in the Rhine catchment
- **Systematic inventory of application areas and quantities**