Evaluation report
Complexing agents

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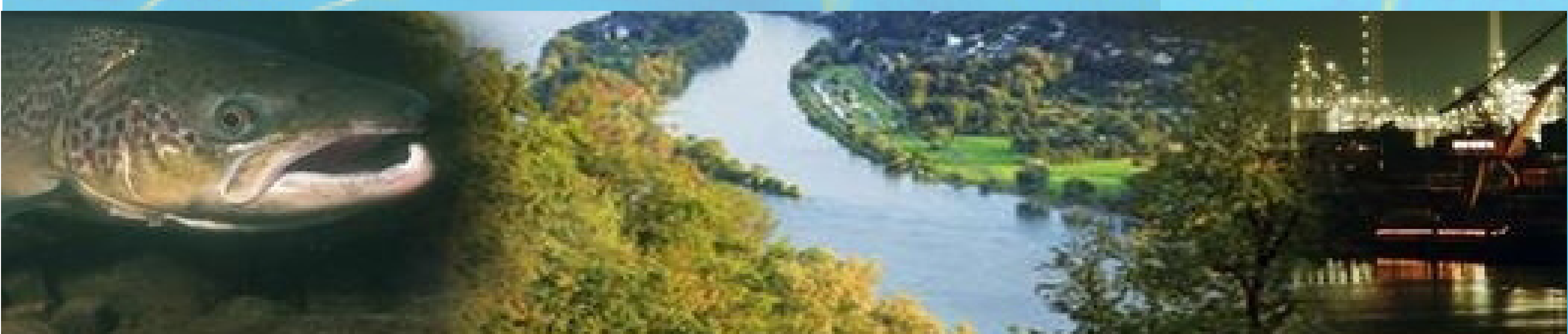

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Within the strategy aimed at reducing micro-pollutant inputs originating from urban and industrial waste water, evaluation reports are being drafted for 10 groups of substances targeted at summarizing scientific and technical facts and at pointing out gaps of knowledge. Also, the evaluation reports present a variety of possible measures at the source (e.g. registration of substances, limitation of uses) and technical measures in crucial wastewater treatment plants (e.g. introducing a further treatment stage). The “Conclusions” of the evaluation reports list the most efficient measures to be further investigated into within a holistic ICPR strategy. However, these measures are no recommendations the ICPR addresses to its member states. Measures listed in this chapter will be integrated into a survey report of all measures in order to be able to take into account eventual synergetic effects of measures (effects of measures on different groups of substances) when proceeding with the final evaluation. Based on the final evaluation of all measures the ICPR will determine recommendations for the Member States.

1. Introduction

Complexing agents are wide spread industrial chemicals used in numerous fields. In surface waters, complexing agents are regularly determined in concentrations varying between one-digit and double digit micrograms per litre (µg/l). The indicator substances taken into account (EDTA, DTPA) because of their distribution and their poor biological degradability are synthetically produced and belong to the group of substances of amino polycarboxylic acids. In the main stream of the Rhine and its tributaries, these indicator substances are detected in comparatively high concentrations. These are comparatively strong complexing agents agglutinating in particular heavy metal ions. In applications, they inhibit unwanted reactions (e.g. formation of poorly soluble deposits of hard-water minerals or heavy metal salts) and provide for the stability of heavy metal containing solutions. To this end they must behave inert in contact with elements of the formulation, which means that in contact with acids, alkalis, oxidizing and reducing substances and thermal influence they must be as stable as possible. [1, 2]

On average, between 2005 and 2009, in Germany 3,700 tons of EDTA were annually deposited; for DTPA, 1,600 t were annually deposited [3]. In the other Rhine bordering countries, the relative consumption rates are in the same order of magnitude. It is assumed that the largest amounts are used in trade and industry. Furthermore, products containing complexing agents are also used in households. There are no precise data on the distribution of the quantities used. In 2009, the use of EDTA was estimated for the following areas of use for the German share of the Rhine basin [3]: 10-15 % in the photo industry, 1-2 % in the textile industry and the by far greatest share (80-85 %) by the category “Others”, also comprising the use in wood processing/paper industry, metal processing and galvano technique [4], cleaning agents, cosmetics, pharmaceuticals [4], food additives [4], water supply and wastewater treatment as well as micronutrients.

Between 1991 and 2002 and within the "Declaration on the Reduction of Water Pollution by EDTA" it has been possible to achieve an EDTA emission reduction of 44 % for the German Rhine basin [5]. Increasingly, EDTA is being substituted by other complexing agents (e.g. DTPA, NTA phosphonates, etc.). Since 2004 it has been possible to reduce the EDTA emissions of a large chemical concern by further 50 % by putting into work a UV oxidation plant [6].

Several studies on the environmental impact are available. The toxicological and ecotoxicological properties of EDTA have, among others, been largely assessed by the authorities of the European Communities [7]. Further documents on this issue are the report of the Dutch Institute for Health and Environment [8] and the background document of the WHO (World **H**ealth **O**rganization) [4] which also derives guidance values for EDTA in drinking water [4], [9].

According to the German Umweltbundesamt (UBA) [2], the mechanisms of the many possible interactions involving complexing agents are only partly clarified or known. Partly, assessments largely vary. According to the UBA the quantification of effects and thus a risk assessment is highly uncertain.

2. Problem analysis

From the point of view of drinking water supply, complexing agents are conspicuous, since they cannot be eliminated by traditional treatment processes.

Monitoring data of the drinking water works along the German R. Ruhr indeed reveal that concentrations of some µg/l of EDTA and DTPA are regularly detected in drinking water. However, due to the low level of direct toxicity, these concentrations in drinking water are distinctly lower than the toxicologically admitted concentrations for lifelong exposition (compare the WHO guidance value for EDTA: 600 µg/l). With respect to drinking water production, the IAWR/AWWR (Internationale Arbeitsgemeinschaft der Wasserwerke im Rheineinzugsgebiet / Arbeitsgemeinschaft der Wasserwerke an der Ruhr) and the DVGW (Deutscher Verein des Gas- und Wasserfaches) target 5 µg/l for each single synthetic substance value, e.g. complexing agents. This target value is often exceeded both in the Rhine and its tributaries.

On the other hand, ecotoxicological effect threshold values are several times higher than the concentrations to be detected in the water bodies. Within EU risk assessment, a PNEC (Predicted No-Effect Concentration) of 2,200µg/l was derived for EDTA.

Except for DTPA, concentrations of complexing agents increase along the course of the Rhine, the highest concentrations being measured in the Lower Rhine, the Delta Rhine and in several Rhine tributaries.

During 2007-2008, mean EDTA values between 3.6 and 5.4 µg/l were measured in the Rhine downstream Karlsruhe. The maximum values measured in the German part of the Rhine within this lapse of time vary between 7 and 10 µg/l, in the Netherlands they achieved upto 17 µg/l (Kampen). In 2007 and 2008, the mean EDTA concentrations and the maximum values in the tributaries, in particular in the rivers Neckar, Main, Nahe, Mosel, Ruhr and Emscher were above those in the main stream.

DTPA is also detected in the Rhine and its tributaries. During 2007 and 2008, about 50 % of the values measured were below the limit of detection. During the monitoring period 2001-2008, the maximum value measured in the Rhine at the German-Dutch border (Lobith) amounted to 18 µg/l. In the R. Main at Bischofsheim, DTPA was measured in all samples, the maximum value during 2007 to 2008 amounted to 13 µg/l, in the R. Ruhr the maximum concentration amounted to 21.6 µg/l. Contrary to EDTA, no increase in concentration is measured downstream the Rhine.

Nevertheless, eventual detrimental environmental effects of EDTA and complexing agents generally have little to do with this substance specific toxicity, but rather with the complexing properties of complexing agents which interact with other substances (in particular with heavy metals, hardness components and micronutrients). If heavy metals form complexes with EDTA in wastewater, they will not be eliminated by precipitation and adsorption to sewage sludge but will to a large extent reach surface waters. The metal complexes which may exist depend on local conditions.

The following statements apply to substance properties and water quality:

According to OECD methods (Organisation for Economic Co-operation and Development) EDTA is not easily biodegradable [7]. If pH values are in excess of 8, degradation is possible. Given the European law on chemicals, EDTA may thus be classified as “enhanced biodegradable” [10, 11]. Since pH values in municipal wastewater treatment plants are generally below 8.5, EDTA is only slightly eliminated and gets into water bodies. During ground passage, EDTA and DTPA microbiologically degrade slowly. A high degree of elimination may be achieved in the wastewater treatment plant of individual enterprises, e.g. in dairy farms. This is extremely important to take into account when conceiving eventual emission reduction measures.

Apart from eventual negative effects on the natural balance of waters in the middle and lower part of the Rhine (and some tributaries), the production of drinking water may become more complicated.

3. Analysis of pathways

The major share of inputs of complexing agents is due to industry and trade. From the amounts used it may also be concluded that households equally emit an important share. The relevant industrial branches apart from the chemical industry are the paper and photo industry, beverages filling and production, textile industry, diary industry and galvanic industry. Due to avoiding and substituting measures and decentralized treatment, a considerable reduction of complexing agents input has been registered since the mid 1990ies. Also, the digital technique in photography has contributed to reducing the use of complexing agents (in particular of EDTA).

However, a systematic inventory is required, in order to get a better overview over areas of application and amounts applied to be able to carry out a risk assessment and substance balances.

In North Rhine-Westphalia (NRW) the analysis of inputs with respect to complexing agents for the period 2007 to 2010 has shown that, as far as EDTA in concerned, the ratio for loads from municipal wastewater plants to industrial direct inputs during 2007 to 2010 was 40 to 60. DTPA almost completely originates from industrial inputs. In the Ruhrgütebericht 2009 (quality report for the River Ruhr), a specific EDTA load (mean value) of 4.7 mg/inhabitant/day (mg/E*d) was determined for the municipal wastewater treatment plant of the Ruhrverband [14].

The population-specific EDTA load of a wastewater treatment plant in the Ruhr basin together with discharges of the paper industry amounted to 550 mg/(E*d, inhabitant equivalent per day) and was thus by a factor 100 higher than the median value of all wastewater treatment plants [14]. In a study from February 2005 through May 2007, the daily loads emitted by this individual discharging plant were a multiple of the emissions of the municipal wastewater plant (EDTA), for the sum of the complexing agents (EDTA, DTPA) investigated into, they were even more than a tenfold higher [15]. The example shows that individual dischargers from industry and trade may be extremely relevant and that the discharge into wastewater treatment plants may considerably vary from one region to another – or even locally.

4. Possible measures

To minimize the input of complexing agents, emission reduction measures can be taken at different levels:

- Measures at the source;
- Information of the public and the trade public;
- Treatment of wastewater split flows;
- Measures in wastewater treatment plants;
- Measures in urban wastewater treatment plants;
- Adaptation of monitoring programmes.

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

Measures at the source

- Reduction of the pollution of water bodies by:

- o Developing, testing and using biodegradable substitutes easier to eliminate in wastewater treatment plants;
- o Enhanced environmental impact assessment during licensing of complexing agents;
- o Optimization of production processes or continuing already optimized processes; in particular the optimization of procedures in plants to reduce amounts used (optimised dosage);
- o Renouncing to cleaning agents and cosmetics containing complexing agents which are hard to degrade or ecotoxic (from sides of the users of products, consumers, trade);
- o Information about the choice of products and adequate disposal.

Information of the public

The public and the trade public (trade and users of products, e.g. beverage filling and producing industry, cleaning and wastewater treatment plants, households, agriculture) must be informed about the relevance of substances for water and drinking water and about eventual alternatives. The corresponding BAT (**B**est **A**vailable **T**echnology) reference documents of the textile and paper industry, of the beverage and dairy industry and of surface treatment already comprise parts on complexing agents and their reduction, their biological and chemical degradability and their elimination from drinking water (reverse osmosis, precipitation) [16, 17, 18, 19]. The contents of these technical documents and further information will be spread more widely using appropriate instruments. Alternatives might be an economical use, to renounce to the product or use more environmentally friendly alternative products or environmentally friendly cleaning/bleaching or (e.g. physical or biological) treatment procedures. A particular product labelling is imaginable for products belonging to the paper, photo and textile industry.

Decentralized measures (treatment of split wastewater streams)

Individual industrial or trade enterprises may considerably contribute to the load of complexing agents reaching the surface waters via wastewater treatment plants. The following measures can be taken into account in order to minimize these loads:

- Optimization of the in-house procedures to avoid or reduce wastewater (e.g. closed loop circulation);
- Further treatment procedures aimed at eliminating persistent complexing agents (such as EDTA and DTPA) and eventually further substances contained in wastewater and relevant for the environment. Eventually, multiple effects may thus be achievable. Whether an effective wastewater treatment is possible as well as the choice of procedure [17] will depend on pH value, temperature, concentration of complexing agents, other wastewater substances and the BAT.

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. If 191 selected wastewater treatment plants in the Rhine basin were expanded by the afore-mentioned further treatment procedures, the inputs of certain micro-pollutants (e.g. pharmaceuticals) into the Rhine could be reduced by at least 30 %.

However, for EDTA, the thus achievable effect for the Rhine is estimated to a maximum of 10 %, for a combination of activated carbon and ozonisation the best achievable effect might be slightly above. For DTPA the effect would equally be low, as only a small share of this substance is discharged by municipal wastewater. Thus, the elimination of complexing agents by further treatment procedures is considerably less than for many other micro-pollutants.

Against this background, a central elimination of EDTA/DTPA does not make sense.

Adaptation of monitoring programmes and systems of assessment

- With a view to assessing the effects on water ecosystems (taking into account eventual interaction with other substances and a shift of species) and with a view to the protection of drinking water resources, binding quality criteria should be deducted on a convenient institutional level;
- Limit discharges of relevant direct and indirect dischargers: Determine orientation values or limit values for complexing agents in wastewater;
- As far as substances relevant for drinking water in the catchment of drinking water works are concerned: Consider the requirements of drinking water use within the surveillance of water bodies and wastewater as well as in the wastewater assessment;

5. Conclusion

Summary of possible measures for the further elaboration and efficiency testing:

- **Measures at the source** aimed at reducing water pollution by information on adequate use and 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 processes relevant for wastewater and implementation of further treatment procedures concerning wastewater split streams and wastewater discharges of individual industrial plants. As a matter of principle, these measures should be preferred, as a large share of the load is discharged by a limited number of industrial plants and trade.
- **Centralized measures:**
  With a view to efficiently reducing the pollution of water bodies and drinking water by complexing agents, centralized measures in municipal wastewater treatment plants prove to be of little efficiency, as their effects are more than limited.

  Therefore, measures at the source and decentralized measures are to be preferred.

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