Evaluation report
Estrogens

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Within the strategy aimed at reducing inputs of micro-pollutants originating from urban and industrial waste water, evaluation reports are being drafted for 10 groups of substances and are aimed 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) to 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 of measures for the Member States.

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1. Introduction

The term "Endocrine effects" is a generic term for different effects of numerous different substances which have in common that they change the normal functions of the endocrine system. These effects may change the functioning of (aquatic) organisms in different ways: Change in behaviour, congenital abnormalities, sex change and infertility. In the past, the endocrine effects known so far were mostly discovered by chance. Near the outlets of wastewater treatment plants a feminization of male fish seemed to appear in regional waters. This estrogenic endocrine effect in fish is among others due to natural and synthetic hormones. Further substances may generate endocrine effects in aquatic organisms[1]. The contribution of these substances is relatively much less than the endocrine effect of the natural human and animal hormones 17β-estradiol and estron and of the synthetic hormone 17α-ethinylestradiol originating from contraceptive pills.

Therefore, this evaluation report only concentrates on two natural hormones, 17β-estradiol and estron as well as the synthetic hormone 17α-ethinylestradiol.

The most important input pathway of these three estrogen hormones are human excretion products getting into surface waters via municipal sewerage and wastewater treatment plants. A further input pathway for natural hormones is natural application of semi-liquid manure to agricultural surfaces. Furthermore, these hormones get into water bodies via fermentation plants for semi-liquid manure. In the Netherlands, the gross emissions of these natural hormones from semi-liquid manure are estimated to 17,000 kg/year[2]. This exceeds the total amount of hormones originating from the Dutch population by more than a factor 10.

Based on available monitoring data[3] it is being assumed that, due to the continuous discharges of wastewater treatment plants into surface waters their wastewater plays a more important part in the endocrine effects on the aquatic environment than indirect and discontinued leaching of semi-liquid manure from agricultural surfaces.

The following exposition is based on information derived from the substance data sheet.

2. Problem analysis

Due to the considerable population density in urban areas and (intensive) livestock keeping in agriculture along the Rhine, comparatively high concentrations of estrogen hormones are to be expected in the Rhine catchment. Concerning the three estrogen homones estron, 17β-estradiol and 17α-ethinylestradiol comparatively few monitoring data are available for the main stream of the Rhine, but we dispose of more data from individual regional tributaries[4] [5]. In the large water bodies concentrations of estrogen hormones are always below the limit of detection of less than 1 ng/l. In the tributaries, they are being detected with up to several ng/l, and, in general, contents rise

[1] Vethaak AD, GBJ Rijs, SM Schrap, H Ruiter, A Gerritsen and J Lahr (2002). Estrogens and xeno-estrogens in the aquatic environment of the Netherlands. Occurrence, potency and biological effects. RIZA/RIKZ-report 2002.001.

[2] Blok *et al. (2000)* Blok J and MAD Wösten (2000). Origin of natural estrogens in the environment. RIWA.

[3] Montforts *et al.* (2007). Montforts MHMM, GBJ Rijs, JA Staeb and H Schmitt (2007). Animal health products and natural hormones in surface waters of regions with intensive livestock breeding. RIVM report 601500004/2007.

[4] Adler *et al. (2001)* Adler, P., T. Steger-Hartmann, W. Kalbfuss (2001): Occurrence of natural and synthetic estrogen steroids in waters of southern and central Germany. Acta hydrochem. hydrobiol. 29 (4), 227-241.

[5] Micropoll DB Bafu (2009). Micropoll data bank BAFU (2009). Data bank of the Federal Agency for Environment (Switzerland) with monitoring data from entire Switzerland.

proportionally to the share of (biologically treated) municipal wastewater in the receiving body of water. The natural hormone estron is the one occurring with the highest frequency and in highest concentrations in the Rhine tributaries.

This statement for the Rhine catchment also applies to the rest of Europe. Therefore, the following assessment will use comparable considerations for the three estrogen hormones found in the EU evaluation report of 2002[6]. Also, more recent data[7] used by the EU to prepare evaluations whether the hormones 17β-estradiol and 17α-ethinylestradiol should be included in the list of priority substances of the EU Water Framework Directive are being used. From these data it may be concluded that the concentrations of some ng/l detected in surface waters do not have any acute toxic effects, but concentrations are nevertheless near the threshold values for possible specific (endocrine) effects. The threshold value for acute toxicity of the synthetic hormone 17α-ethinylestradiol is about 1 mg/l, while the threshold value for endocrine effects is about a factor of one million less (0.5 ng/l). As far as known, there are no accepted environment quality standards for these three hormones in the Rhine bordering countries. At the time being, such standards are being developed on EU basis for the hormones 17β-estradiol and 17α-ethinylestradiol. The EU evaluation report (2002) concludes that on the basis of the exposition concentration and NOEC threshold values (No Observed Effect Concentration) which do not detect any endocrine effects, a potential risk for fish due to the occurrence of the hormones 17β-estradiol, estron and 17α-ethinylestradiol in European waters may not be excluded in advance.

Thus, endocrine effects on fish and other aquatic organisms in the tributaries of the Rhine may not be discarded in advance. Above all, this applies to waters in the Rhine catchment considerably impaired by discharges of wastewater treatment plants.

3. Analysis of pathways

So far, effluents from wastewater treatment plants are considered to be the most important source spreading estrogen hormones into the aquatic environment. Locally, concentrations in the receiving body of water may be so high that estrogen effects are detectable in fish. The share of the effluent of a wastewater treatment plant in the receiving body of water seems to be decisive for this effect.

Estrogen hormones get into the wastewater of households, plants and ships via human excretions (diffuse). Wastewater from households not connected to the municipal sewer (about 1-2 %) is directly flowing into the surface waters without any or after some preliminary form for treatment. Often, wastewater from the toilets on board of ships is still being directly discharged into the water body without any preliminary treatment. After collection in municipal sewers and treatment in a wastewater treatment plant more than 95 % of the wastewaters from households and plants in the Rhine catchment are discharged into surface waters. Only a small percentage (about 1 – 3 %) of this municipal wastewater passes by storm-overflows and flows directly into surface waters. The degree of elimination depends on the conditions of the wastewater treatment plant and specific substance characteristics. For 17β-estradiol, the elimination performance of a wastewater treatment plant amounts to 90 %, for estron and 17α-ethinylestradiol it amounts to 60 % each. The biological degradation of these hormones in the receiving body of water is comparable, however, 17α-ethinylestradiol is most persistent and 17β-estradiol is rapidly transformed into estron and then mineralised.
So far, little attention has been paid to the input pathway into the aquatic environment of the natural hormones estron and 17β-estradiol originating from livestock keeping. It remains to be further quantified. In the Netherlands, the gross excretion originating from

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

[7] EU (2010). Drafting Group on review of priority substances Ethinylestradiol EQS draft dossier dd 20/09/2010 and Beta-estradiol dd 09/04/2010.

livestock is considerably higher (by a factor 10) than that of human origin. A (small) part of the semi-liquid manure is directly leaching from agricultural areas into the waters. In areas with intensive livestock keeping this might lead to high concentrations of natural hormones and possibly to detrimental consequences for fish living in these waters. Little is known about this aspect and the few investigations carried through so far have not detected any negative impact on the aquatic environment. A possible explanation could be the different input pattern. Contrary to a continuous, selective discharge from wastewater treatment plants the input of natural hormones from livestock keeping into surface waters is diffuse and discontinued.

This argument is not valid for sites processing semi-liquid manure for energy production purposes where wastewater is being discharged.

4. Possible measures

In order to reduce the pollution of surface waters with the hormones estron, 17β-estradiol and 17α-ethinylestradiol, emission reduction measures may be taken at different levels, but only partly for the natural hormones:

- Measures at the source;
- Information of the public
- Treatment of wastewater (split) flows;
- Centralized measures in wastewater treatment plants;
- Adapt monitoring programmes.

In the following, the potential measures are explained in greater detail.

Measures at the source

- Return unused contraceptive pills: By returning unused contraceptive pills to pharmacies or by disposing of them as 'minor chemical waste' it is avoided that the synthetic hormone 17α-ethinylestradiol gets into municipal wastewater.
- Product innovation concerning contraceptives: By applying less persistent active agents or optimizing the kind/dosage of the agent the pollution of the aquatic environment by the hormone 17α-ethinylestradiol may be limited.
- Manure-free agricultural surfaces: By respecting river bank strips along the shoulders of fields to which no slurry is applied it is being avoided that natural hormones leach into waters.
- Optimize the production process: A further improvement of the (production) processes in pharmaceutical companies, the health care sector, slurry processing works may contribute to avoid polluting wastewater.

Information of the public

In general, when informing about the application of contraceptive pills, their relevance for the environment must be taken into account; this particularly applies to an environmentally compatible disposal of unused contraceptive pills.

Treatment of wastewater (split) flows

Untreated inputs of domestic wastewater and semi-liquid manure may relevantly contribute to the load of estrogen hormones in local surface water bodies. This concerns wastewater originating from scattered settlements not connected to wastewater treatment plants, sewerage overflow and defective connections of buildings to storm water sewerage, but also untreated discharges of human excretions originating from ships. With respect to animal excretions, the wastewater arising from fermenting manure

and that arising from liquid manure processing plants is concerned. As for the synthetic hormone 17α-ethinylestradiol, wastewater arising from pharmaceutical works is also relevant. In all these cases the treatment of the final discharge from the wastewater treatment plant or of wastewater split flows with high concentrations of estrogen hormones is possible, in order to reduce the pollution of regional surface waters with these substances. The way in which this wastewater (split) flow is treated depends on specific (local) conditions.

The following emission reduction measures may be considered:

- Cleaning up of untreated discharges of excretions by:
  - Connecting settlements or scattered settlement unities to the municipal sewerage and wastewater treatment plant;
  - Reducing the frequency and amount of sewerage overflow;
  - Largely reducing defective connections of settlements to storm water sewerage and the washing-off of dog excretions;
  - Treating toilet water from ships or delivering it to on-shore structures.
- Substantial treatment of the wastewater arising from the fermentation of manure or its use as nutrient source in agriculture.
- Wastewater split flow treatment containing high concentrations of estrogen hormones.

Centralized measures in wastewater treatment plants

Wastewater from wastewater treatment plants is considered to belong to the most important emission sources when spreading estrogen hormones in the aquatic environment. Near discharges from wastewater treatment plants and in waters with a high share of wastewater originating from wastewater treatment plants located upstream the concentrations of estrogen hormones may be so high that detrimental impacts on fish and other aquatic organisms are possible. This is above all true of the Rhine tributaries. In the main stream of the Rhine this is not expected or only expected to a very limited extent. Extending wastewater treatment plants by an additional treatment stage in order to eliminate micro-pollutions (ozonisation, use of active carbon) is an efficient method of reducing the pollution of tributaries with estrogen hormones (complete elimination achieved by these further measures). This would result in a qualitative improvement of the receiving body of water near the point of discharge of wastewater treatment plants as well as downstream, and in the tributaries. This additional treatment stage will also have positive preventive effects on drinking water production from surface waters. This is not only true of the three estrogen hormones considered, but of a large scale of organic micro-pollutions originating from municipal wastewater.

Adapting Monitoring Programmes and Assessment Systems

The analysis of available information results in the following indications concerning the design of monitoring programmes and the further development of assessment systems:

1. the number of monitoring data available for the estrogen hormones estron, 17β-estradiol und 17α-ethinylestradiol in the main stream of the Rhine is insufficient for an adequate description of the state.
2. The relative share of gross excretions of the natural hormones estron and 17β-estradiol originating from livestock and from the population in the Rhine bordering countries in the total pollution of the aquatic environment is unknown. Therefore, further investigations into the pathways of emission of these hormones would be welcome.

3. Even though the limits of detection of the analysis methods for the estrogen hormones are low (< 0.1-0.5 ng/l), they are near, as far as 17α-ethinylestradiol is concerned even above concentrations, for which effects on fish have been detected. A further lowering of the detection limits would be welcome in order to dispose of more security with respect to the existence of estrogen hormones and their eventual, detrimental ecological impact on the Rhine.
4. Apart from chemical analysis methods in order to monitor certain substances, (inter-)nationally certified biological test methods are required in order to be able to detect detrimental effects of substances/mixtures of substances - in this case hormones - on the aquatic environment.
5. There are no binding quality criteria aimed at assessing the ecological/chemical state and at protecting drinking water resources. If necessary, these should be derived at a suitable institutional level.

5. Conclusion

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

- **Measures at the source** in households, plants and livestock breeding in order to largely avoid estrogen hormones getting into the aquatic environment;
- **Decentralized measures:** Cleaning-up of untreated inputs of excrements and urine from settlement unities, sewerage overflow, toilets in navigation, etc. and treatment of wastewater split flows with high hormone concentrations from plants or arising from manure processing;
- **Centralized measures in wastewater treatment plants:** Future application of further going treatment techniques (ozonisation, use of active carbon) in order to reduce the pollution with estrogen hormones from wastewater treatment plants into surface waters of the Rhine catchment presenting a considerable share of wastewater from wastewater treatment plants. These measures could at the same time contribute to achieving a reduction of the concentrations of a broad range of further micro-pollutions from settlement drainage. Experience with (pilot) plants with such further wastewater treatment plants must be gathered and assessed for further use for future decisions.
- **Improving Monitoring Programmes and Assessment Systems:** With respect to gaining further knowledge about emission pathways of natural hormones originating from semi-liquid manure from livestock breeding in agriculture in the Rhine catchment and reliable monitoring of low concentrations of estrogen hormones.