# Workshop on "Biocidal Products"

Committee on the Environment, Public Health and Food Safety (ENVI)
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## Environmental aspects of biocides – Occurrence and behaviour in the aquatic environment, approaches to prevent future impacts

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1.Biocides by definition

Biocidal active substances are substances that are used for controlling harmful organisms. The term "biocides" derives from the Greek word "bios" for "life" and the Latin word "caedere", which means "to kill".

In the Directive 98/8/EC of the European Parliament and the Council "biocides" are defined as "Active substances and preparations containing one or more active substances, put up in the form in which they 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" [1]. The proposal for a regulation concerning the placing on the market and the use of biocidal products (2009/0076 COD) takes over this definition correspondingly [2].

2. Biocides – background information

The range of applications for biocides that have been previously referred to as "non-agricultural pesticides" is very wide. In Germany for example, approximately 8,000 different biocidal products are on the market containing one or more of the 900 active substances approved in Europe. The biggest markets for biocides are Western Europe (20% of the market), the USA and Japan. It is assumed that the use of biocidal products will increase in the emerging economies of China and India in the next years.

Biocides are components in many everyday products, e.g. in cosmetics and hygiene products such as soaps, shampoos, skin creams or hair gels, as well as in liquid detergents and household cleaners. Furthermore, biocides are used as an antifouling agent in paints and water based glues, in wood preservatives or in cooling lubricants. In addition, disinfectants in the manufacturing and processing of various products, such as in food, textiles, wood and paper are essential. Biocides are also used as a preservative for cooling liquids (prevention of microbial growth in cooling systems) and as a preservative of materials, such as leather, fibres and rubber. In any case biocides are used to prevent growth of microorganisms and microbial degradation of key ingredients. The increasing use of biodegradable ingredients in many products at the same time demands for a more intensively use of biocides as the degradation should not occur before or during the use of such products.

The Biocides Directive defines certain types of biocidal products. The main groups cover

1. disinfectants and general biocidal products that are used for human hygiene and health care (e.g. skin disinfection, disinfection in swimming pools),
2. preservatives for materials and processing systems (industry),
3. pest control and
4. other biocidal products such as antifouling agents.

A large number of biocidal active substances are used in both pesticides and biocides [3]. Examples of substances used for both purposes are mecoprop, which is used as a herbicide in agriculture and as a biocide on flat roofs, or dichlofluanid, which is used as a fungicide in agriculture but also as a wood preservative.

Important biocidal active substances are nitrogen-containing aliphatic compounds (e.g. 2-bromo-2-nitropropane-1,3-diol or 5-bromo-5-nitro-1,3-dioxane), isothiazolinones (e.g. 5-chloro-2-methyl-4-isothiazolin-3-one, 2-methyl-4-isothiazolin-3-one or 1,2-benzisothiazolin-3-one), quaternary ammonium compounds (e.g. benzalkonium chloride) and compounds from the group of parabens (e.g. butyl or ethyl-4-hydroxybenzoate). In addition, various individual substances (e.g. triclosan), but also some substances primarily known as pesticides (such as mecoprop and dichlofluanid) are important.

A variety of biocidal products and their consumption have been investigated in a study by the Danish Environmental Protection Agency for the years 1998/1999 [4]. Up to 1150 t/a of biocides were used in the private and public sectors in Denmark. Wood preservatives, antifouling agents in paints and disinfectants in the food sector also showed a very high consumption from 250 to 620 t/a.

## 3. Direct pathways of biocides in the environment

Applications of biocides can have multiple impacts on the environment through direct and indirect pathways. A direct entry of biocides in the environment is proven for example for anti-fouling products or preservatives for liquid-cooling systems. Various studies have dealt with the occurrence and spread of anti-fouling agents, such as irgarol, chlorothalonil or dichlofluanid in surface waters. As these biocides are used in boat paints a strong correlation was found between their occurrence in surface waters (more than 0.1 µg/L [5]) and the navigational use of these waters. Studies on the effect of irgarol were carried out in inland waters showing adverse effects in mesocosms [6].

Rainwater discharges (separate sewer system) or rainwater overflows are another direct pathway for the immission of biocides into the environment. This is the case when rainwater overflows are discharged into combined sewer systems and surface waters without any treatment. Rainwater can contain heavy metals as well as biocidal active substances that are used externally on surfaces (facades, roofs, fences, etc.). It is estimated that copper from roofs, gutters and facade materials cause a load of 32.1 t/a in storm sewers in Germany [6]. Field measurements of newly painted facades in Switzerland showed terbutryn concentrations in the range of several hundred µg/L [7]. Despite being prohibited as a pesticide in Germany since 1997, terbutryn is still be found in concentrations of up to 48 ng/L in German surface waters and of up to 140 ng/L in large rivers [6] which can be contributed to its use as biocide.

## 4.Indirect pathways of biocides in the environment

Biocides also end up in the environment on indirect pathways. Particularly disinfectants, with hospitals as a major emission source, are introduced to surface waters by passing waste water treatment plants [8]. Also preservatives e.g. for fibres and leather can be discharged into municipal and industrial wastewater after cleaning of the treated materials (e.g. textiles).

Triclosan, a disinfectant and preservative for fibres, and its metabolite methyl-triclosan have been detected in wastewater (110-650 ng/L) and surface water (up to 70 ng/L; [9]), whereas methyl-triclosan is more stable and stronger bioaccumulated in fish as triclosan.

Another study revealed triclosan concentration in influents to wastewater treatment plants of up to 9.07 µg/L and in wastewater effluents of up to 1.12 µg/L [12]. The relevance of triclosan in sewage sludge has also been clearly demonstrated [12]. The removal rate for triclosan in wastewater treatment plants varies between 30% and 93% depending on the treatment technique in place [13, 14, 15]. The fungicides tebuconazole and propiconazole, both preservatives of various product types of biocides, were found in numerous wastewater treatment plants (propiconazole 5-40 ng/L, tebuconazole 1-10 ng/L, [10]) and in some lakes (< 1-2 ng/L; [10]) in Switzerland.

Biocides deposited on soils can reach waters by surface runoff events, or by leaching into deeper soil layers and into groundwater. In addition, direct pollution of soils is possible when biocides leach from plasterings, paintings, etc.

## 5. Behaviour and impacts of biocides in the environment

The knowledge of the presence of biocides and their behaviour in the aquatic environment is still very limited due to a lack of analytical methods for aqueous samples.

In waters biocides might be subject to abiotic and biotic degradation processes or to sorption to sediments or suspended matter. Examples of sorptive biocides are permethrin (a wood preservatives, etc.) and chlorocresol (a disinfectant), which have been found in dry marine sediment samples in concentrations of up to 20 ug/kg [11]. The degradation of biocides will be accompanied in most cases with the formation of persistent metabolites, which may be toxicologically relevant. Methyl-triclosan, a metabolite of triclosan, and dimethylsulfamide, a metabolite of tolylfluanid (preservatives and antifouling agent), are prominent examples here.

Regarding the impacts of biocides on aquatic ecosystems, the availability of biocide specific data is limited. In some waters, the toxicity levels of sensitive organisms for irgarol were exceeded. Furthermore bioaccumulation and secondary poisoning in food chains can increase the negative effects of biocides. For difenacoum and difethialone (two rodenticides) a large potential to bioaccumulate was determined. Furthermore, substances with endocrine disrupting properties are considered more intensively in the last years.

An adequate risk assessment for aquatic environments has to take into account that individual biocides are often used in several areas of application (as an industrial chemical, for pest control, in cosmetics, etc.). Therefore, the analysis of the particular applications and emission sources is crucial to take measures to avoid negative environmental impacts of biocides. The concurrent presence of various biocides and metabolites in waters is another important issue, since this usually generates stronger effects, which are more difficult to handle than the presence of a single substance.

## 6. Outlook and need for action

Biocides contain active substances and are used against harmful organisms in order to protect human and animal health. Due to their intrinsic properties and uses, biocides themselves can be harmful to the environment. Therefore with the new regulation on biocides the chance should be taken to increase the level of protection for the environment. In this context active substances with poor hazard profiles have to be phased out and a sound set of exclusion criteria have to be determined to prevent the authorisation of substances which are persistent, bioaccumulative, toxic (PBT) as well as those causing endocrine disrupting effects.

Since groundwater and surface water are also important resources for drinking water production the occurrence of biocides and their metabolites can pose risks on drinking water quality which has to be wholesome and clean. Therefore water suppliers are interested to rely on water resources of good quality, esp. without any xenobiotics. A good raw water quality allows them to produce drinking water with only natural treatment methods like sedimentation or flocculation. To protect the environment and esp. drinking water resources is essential to provide a high water supply safety.

The need for actions is obvious and responsibilities have to be taken by regulators, producers, researchers and users to place biocides on the market which protect human and animal health as well as the environment.

Action is required on several issues:

<u>1. Regulatory aspects:</u>

- Establishing a data exchange between biocide authorisation and environmental monitoring
- Implementing measures in water resources protection in compliance with the objectives of the Water Framework Directive
- Development of environmental quality standards (EQS) for biocides in surface waters
- Establishing a new Eco-labelling scheme for biocides
- Implementing a link between CE-marking of biocidal products and information about environmental and human health risks
- Developing a strategy and guidance for the sustainable use of biocides

<u>2. Research and development aspects:</u>

- Improving the data base of emissions and immissions of biocides
- Research on the formation of metabolites
- Development of risk assessment methods regarding the cumulative and combined effects of biocides and their metabolites
- Developing methods for the analysis of biocides and their metabolites in water

Literature


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