NEPTUNE

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1 Introduction

The list of priority substances chosen for the evaluation of the chemical status of water bodies as described in the water framework directive (WFD) will be revised in certain intervals (e.g. 4 years). The criteria of the revision procedure are under discussion. In the past a variety of different selection criteria were applied, in order to find those pollutants which are most hazardous to aquatic organisms on the European level. Hereto pollutants occurrence data have to be available for rivers and streams in at least three European countries. **Based on this criterion it is obvious that pollutants are ignored which have been only recently identified in research project and thus are not included in national monitoring programs.**

Furthermore, the available data about ecotoxicological hazards should clearly indicate that these pollutants possess a high potential to be harmful to the environment. In addition to ecotoxicological effects the human health risks have to be considered due to an accumulation in organisms foreseen for human diet as well as due to a contamination of groundwater and drinking water. However, to our knowledge the human toxicology was inadequately considered as well as the (bio)transformation of pollutants. A “non detection” in surface waters DOES NOT mean that the compound was mineralized. There are several examples that pollutants were only transformed into persistent transformation products (TPs) by minor changes in the molecular structure. Hence, it can be expected that the TPs posses comparable (eco)toxicological effects already known for the target compounds.

It has to be noted that it is not the objective of the Neptune project to establish a list for new potential priority substances. Neptune is focused on the development and the assessment of technological solutions to diminish the overall toxicity of treated wastewater as well as to remove toxic emerging pollutants. For the later objective it is crucial to understand the fate (sorption, biodegradation) of the pollutants in processes of the wastewater treatment as well as in rivers and streams. An overall approach for an ecotoxicological assessment was applied including biological in-vitro and in-vivo test systems. Furthermore, approaches were developed to elucidate (bio)transformation pathways and to determine the removal efficiency by sorption. Based on the conclusions of these Neptune results potential consequences for the revision of the WFD priority substances is discussed in the current deliverable.

According to the WFD the environmental quality standards (EQS) of the selected priority substances are the main criteria for assessing the chemical status of European water bodies. In this chapter potential selection criteria for priority substances are discussed considering the outcome of Neptune: i) removal/fate in municipal WWTPs, ii) appropriate ecotoxicological test designs, iii) consideration of human toxicology, iv) the likelihood to contaminate water resources for drinking water and v) compounds being discharged directly to water bodies.

2 Prediction of environmental risks: WFD procedure in comparison to regulations for pharmaceuticals

In the Water Framework Directive (WFD) Environmental Quality Standards (EQS) are determined at a European Union (EU)-wide level for Priority Substances and Priority Hazardous Substances (EC 2000). EQS establish a threshold concentration below which the chemical status of a water body may be determined as being at least “good“, i.e. human activity may not fundamentally change the ecological functions and the community structure of the water body. The process of deriving EQS is mainly built on the internationally accepted

effect assessment procedures for neutral (i.e. non-ionic) industrial chemicals which lead to the derivation of the environmental compartment specific Predicted No Effect Concentration (PNEC; Lepper 2005). The PNEC is the concentration of a substance below which adverse effects in the environmental compartment of concern are not expected to occur (ECHA 2008). Consequently, it can be stated that the PNEC established for marketing authorization of a compound (prospective evaluation) and the EQS established to assess the causes of adverse effects that have already occurred (retrospective evaluation; Calow and Forbes 2003) follow the same objective; i.e., to define a concentration below which effects on ecosystems do not occur.

In contrast to neutral industrial chemicals, pharmaceuticals exhibit special characteristics, since drugs are designed to have a specific pharmacological action in mammals or a biocidal activity. For example, approximately 60% of all active substances in pharmaceuticals are charged and many are relatively hydrophilic or polar compounds (Comer and Tam 2000). Nevertheless, the basic testing and risk assessment procedures applied to neutral industrial chemicals can also be applied to biologically active substances as demonstrated for pesticides and biocides (DG SANCO 2002; ECHA 2008). Hence, the European guidelines for the Environmental Risk Assessment (ERA) of human pharmaceuticals (EMEA/CHMP 2006) follow the approaches established for compound groups like industrial chemicals, biocides and pesticides by characterising the environmental risk through the comparison of compartment specific Predicted Environmental Concentrations (PEC values), which is the outcome of the exposure assessment, with compartment specific Predicted No Effect Concentrations (PNEC values), which is the outcome of the effects assessment.

In the following section the focus will be on the comparison between PNEC (industry chemicals) and EQS (WFD) values determined for pharmaceuticals in the aquatic and benthic compartment.

PNEC vs. EQS

In general, the PNEC is derived by applying assessment factors (i.e. a numerical safety factor) to the endpoint of an ecotoxicological test, which compensate for the uncertainties when extrapolating measured effects data from the laboratory to the real environment and from individual organisms to populations. For pharmaceuticals the PNEC is determined for the pelagic compartment if the PEC value calculated according to a crude exposure model is equal or higher then 10 ng/L or if there are indications that the pharmaceutical may affect the reproduction of organisms at low concentrations. Three long-term toxicity tests with algae, *Daphnia*, and fish are performed which represent three trophic levels; the lowest of the three toxicity values is divided by 10 (assessment factor) to obtain the PNEC.

Similar to the derivation of the PNEC for pharmaceuticals in the pelagic compartment the determination of the Annual Average Environmental Quality Standard (AA-EQS) according to the WFD prefers toxicity data from three long-term toxicity tests to which also a safety factor of 10 is applied. However, if sufficient long-term toxicity data are not available, the WFD allows determining the AA-EQS according to the EU Technical Guidance Document (TGD; EC 2003) which accepts short-term toxicity tests in combination with a safety factor of up to 1000. In a recently published overview on effects data for pharmaceuticals by Schmitt et al. (2009) it is shown that for 3 out of 11 substances the assessment factor of 1000 applied to short-term toxicity data would not be protective; i.e. the long-term toxicity data are lower by more than a factor of 1000 than the short-term toxicity values.

For pharmaceuticals the water-sediment study according to the OECD Guideline 307 prescribes effect assessments in the benthic (sediment) compartment if the transfer of the substance to sediment is ≥ 10% within 14 days, whereas according to the WFD an $EQS_{sediment}$ for the benthic community has to be determined when either the log K_{OC} or the log K_{OW} are equal or larger than 3. Since a large number of pharmaceuticals are ionic or polar (Comer and Tam 2000) the selection of methods to determine K_{OC} or K_{OW} may be relevant in

this context (i.e. influence whether follow-up studies are required; ECHA 2008, Tarazona et al. 2009). Another source of uncertainty for the initiation of the toxicity assessment in sediment is the use of not standardized water and sediment matrices when performing the OECD 307 water-sediment study. Furthermore differences for the effect assessment of the sediment compartment become obvious when comparing the requirement of toxicity data for sediment dwelling organisms. According to WFD (retrospective assessment) 3 tests with organisms showing different feeding strategies are required (Lepper 2005), while for the prospective assessment with pharmaceuticals according to EMEA/CHMP (2006) one study with a sediment dwelling organism is sufficient.

These and other differences in the prospective and retrospective assessment strategies may lead to inconsistencies in the environmental risk assessment of pharmaceuticals as shown by Knacker et al. (2008).

Conclusion: When considering pharmaceuticals, the EQS for the pelagic compartment should be based exclusively on long-term effect studies. Furthermore and as proposed by the 'Strategy for a Future Chemicals Policy' (White Paper, EC 2001) efforts should be made to harmonise the prospective and retrospective environmental risk assessment schemes for pharmaceuticals.

3 Fate/removal of emerging contaminants in municipal WWTPs

For pollutants which are mainly applied in households and hence entering the municipal wastewater, the removal in WWTPs is an important factor to avoid a contamination of rivers and streams. Therefore, at least the sorption and biotransformation of emerging compounds should be known for common WWTP processes such as nitrification, denitrification and phosphate removal.

The removal by sorption can be easily predicted by the results of batch experiments or by models using K_{OW} to Kd (K_f) relationships (eq. 1 and 2). Whether emerging pollutants can be eliminated in a WWTP depends essentially on the level of development of the biological treatment stage. In Europe over the last 40 years, biological wastewater treatment has been adapted step by step in response to the tightening of discharge quality conditions. However, the applied processes were neither optimized nor designed for the removal of polar emerging pollutants.

The most important elimination processes in common European WWTPs are:

a) Sorption to *suspended solids* in the wastewater and subsequent removal by sedimentation as primary and secondary sludge;

b) Biological transformation or mineralization of substances by bacteria in activated sludge treatment;

c) Stripping by aeration: for most PPCPs under consideration, this process is negligible due to their low volatility (less than 10% is stripped even for rather volatile musk fragrances).

Additionally in Neptune more advanced technologies were tested such as the sorption on powdered activated carbon (PAC) and the oxidation by ozone and ferrate (Fe^{+VI}). Those techniques might become common WWTP processes in future. However, since they are not yet state-of-the-art, they will not be discussed in the current deliverable regarding the selection of WFD priority substances. The most important processes for advanced wastewater treatment are:

d) Sorption to *powdered activated carbon* used as polishing process

e) Transformation by ozonation and Fe(VI) used as polishing process.

Sorption to suspended solids

The quantity of a substance sorbed per liter of wastewater (C_{sorbed}) can be expressed by a Freundlich Isotherm (eq. 1) or if m = 1 by the simplified linear equation (eq. 2). It is dependent on the sorption constant K_d (partitioning coefficient of a compound between the suspended solids and wastewater), and either the suspended solids concentration (SS; spiking or batch experiment) or the sludge production per m^3 of treated waste water treated to which the substance can sorb (SP; continuous operation), as well as on the dissolved concentration of the substance (C_w).

$$C_{sorbed} = K_F \cdot SS \cdot C_w^{\,m} \qquad (1)$$

if m = 1 then:

$$C_{sorbed} = K_d \cdot SS \cdot C_w \qquad (2)$$

For municipal activated sludge a significant removal (> 5%) can only be expected for K_d > 0.5 L/gSS which can be calculated according to equation 3.

For compounds not being degraded to a significant extent as well as not being stripped, the compound removal efficiency via withdrawal of excess sludge (η_{sorp}) corresponds to:

$$\eta_{sorp} = \frac{SP \cdot K_d}{1 + SP \cdot K_d} \qquad (2)$$

with SP = 0.1-0.4 gSS/L for average municipal wastewater

For most polar emerging contaminants the η_{sorb} is negligible or contributes only to a minor extend to the overall removal. An exception is the antibiotic norfloxacin and ciprofloxacin (administered in the US for anthrax attacks as a reserve antibiotic and excreted as a metabolite of enrofloxacin) which sorbs onto suspended solids of the sewage sludge to a high degree, despite being an extremely polar compound. The sorption might be based on electrostatic interactions between the positively charged amino group (at a neutral pH) and the negatively charged surfaces of the microorganisms or by an uptake (absorption) into microbial cells. Elevated sorption portions can also be found for musk fragrances such as AHTN (tonalide) and HHCB (galaxolide). Many acidic pollutants such as the anti-inflammatories ibuprofen and diclofenac are negatively charged at neutral pH due to the de-protonation of their carboxylic moieties and hence sorption onto sludge was found to be negligible.

Conclusion: For most polar contaminants (K_{OW} < 3) removal by sorption can be neglected for WWTPs. For a removal of > 50%, K_d values of > 3-5 L/gSS are required. The tendency to sorb may represent a way to prioritize tests for risk assessment, since sorbing compounds will be found primarily in sediments.

Biological transformation

The transformation or decomposition of a pollutant is influenced by its affinity to the bacterial enzymes present in the activated sludge. The variety of compounds which are biologically decomposed increases with the age of the sludge. It is expected that this might be due to the following mechanisms. The bacterial population may become more diversified with increasing sludge age (residence time of microorganisms), possibly because slow-growing bacteria also reach relevant numbers in the sludge. Alternatively, the lower sludge loading (i.e. lower substrate availability) may result in increased diversification of microbial activity: only the expressed enzyme spectrum and not necessarily the microbial community are then broadened. One examples is the contraceptive 17α-ethinylestradiol. For both compounds, significant removal was only observed when the aerobic sludge age was ≥ eight days. However, many WWTPs in the EU do not satisfy these requirements in terms of solids retention time.

The redox conditions are also important for the transformation ability of the bacteria. Transformation can take place under aerobic (molecular oxygen available), denitrifying (no molecular oxygen available, nitrate available) or anaerobic (neither molecular oxygen nor nitrate available) conditions. For example, the natural estrogens 17β-estradiol and estrone are transformed in the aerobic and anoxic tanks of the activated sludge system, while the synthetic contraceptive 17α-ethinylestradiol is removed only under aerobic conditions. Due to the low concentrations of trace-organic pollutants, the degradation occurs primarily as a first-order reaction ($r_{degradation} = k_{degradation} \cdot SS \cdot C_{trace\ substance}$), where $k_{degradation}$ is the rate constant, SS the suspended-solid concentration and $C_{trace\ pollutant}$ the dissolved concentration of the pollutant.

However, it has to be noted that a primary transformation does not necessarily lead to mineralisation or smaller molecules which could be incorporated into biochemical pathways of the microorganisms. Based on the Neptune results the transformation products (TP) formed in the biological WWTP processes are often stable compounds with similar chemical structure and have therefore to be considered in addition to the target compound. For instance, the TPs of codeine and the X ray contrast medium Iopromide identified in WWTPs clearly indicate that both compounds are not degraded, but only transformed into stable and polar TPs. In the case of codeine it can be assumed that the TPs are still biological active. Similar results for these two compounds were found in water/sediment-systems. The primary transformation of contaminants is insufficient to evaluate the successful removal of a biological active process.

Conclusion: The main biological TPs of priority substances should additionally be selected and monitored. A "non-detection" of the target compound does not mean that the toxicity is removed, since stable compounds with comparable biological effect may be formed.

4 Ecotoxicity (in-vivo versus in-vitro)

The WFD (2000/60/EC) aims to establish a legal framework for the protection of water quality in European countries and recognizes that specific measures have to be adopted at a European level against water pollution by individual pollutants, or groups of pollutants, presenting a significant risk to the aquatic environment. These measures aim to progressively reduce the level of pollution for priority substances, which have the potential to threaten ecosystems. The goal is to decrease naturally occurring pollutants to the background value and man-made synthetic pollutants to values close to zero. The complete removal of emissions from all potential sources is obviously impossible for substances produced through natural processes, but the legal framework should prevent all emissions and discharges of those priority substances which derive from human activities. The latest list of 33 priority substances has been established as annex X of the WFD and includes 11 priority hazardous substances. These are substances which are toxic, persistent and likely to bioaccumulate and other substances which give rise to equal concern (Art 2.29 of the WFD). However, the WFD and its supporting directives do not lay down the thresholds for persistency, liability to bioaccumulate and toxicity.

Organizations such as EU, OSPAR and the US EPA have undertaken prioritization exercises to identify substances which fulfill the PBT requirements (**p**ersistence, **b**ioaccumulation potential and **t**oxicity). Since the majority of these characteristics can be indicated by chemical properties, several organizations have agreed threshold criteria by which PBT substances are defined. As well as P, B and T, it is accepted that very persistent and bioaccumulative substances also present serious concerns even though there may not be evidence of toxicity. These substances have the potential to build up in organisms present in the environment and subtle long-term effects (such as reduced fertility) could become apparent only in the future. Hence, "vPvB" criteria have also been developed. The standard EU criteria are defined in the Technical Guidance Document (TGD) for risk assessment. The criteria are summarized in table 1.

Table 1: PBT and vPvB criteria as defined by the TGD for risk assessment. Entries in italics refer to "screening" criteria, which can be used for a preliminary assessment in case of missing measured data. CMR: carcinogenic, mutagenic or reprotoxic; BCF: bioaccumulation factor; LC: lethal concentration; EC: Effect concentration, NOEC: no observable effect concentration.

Criterion	PBT criteria	vPvB-criteria
P	Half-life > 60 d in marine water or > 40 d in freshwater or Half-life > 180 d in marine sediment or > 120 d in freshwater sediment or *Not readily or inherently biodegradable or* *Predicted biodegradability in a time frame of weeks to months*	Half-life > 60 d in marine- or freshwater or >180 d in marine or freshwater sediment or *Not readily or inherently biodegradable or* *Predicted biodegradability in a time frame of weeks-months*
B	BCF > 2,000 or *log K_{OW} > 4.5*	BCF > 5,000 or *log K_{OW} > 5*
T	Chronic NOEC or EC_{10} < 10 µg/L or CMR or endocrine disrupting effects or *Acute L(E)C_{50} < 0.1 mg/L*	-

For priority substances, environmental quality standards (EQS) have been derived. The character and purpose of EQS is imposed by the WFD, and more detailed guidance on the methodology for determining EQS from toxicological and ecotoxicologial data, and data on persistence and bioaccumulation, is given in section 1.2.6 of annex V to the WFD (see also sections 2 and table 1 of this document) The WFD provides that EQS can be established for water, for sediments and/or for biota. Moreover, the WFD refers to the TGD for the risk assessments developed and agreed in the context of the Existing Substances Regulation (EEC) No 793/93. The TGD provides an agreed methodological basis and data requirements for sound risk assessment.

The criteria summarized in table 1 are internationally accepted for the classification of P, B and vPvB, however the toxicity criterion does not reflect the current state of scientific knowledge:

- The consideration of acute toxicity data (LC_{50} or EC_{50}) for a preliminary assessment in case of missing chronic data is suitable for chemicals which are not characterized by a specific mode of action (MoA) but is inadequate for pharmaceuticals (as has been convincingly demonstrated in section 2). Due to their short duration of up to 96 h, acute toxicity tests generally provide results for the baseline toxicity of test compounds which mainly reflect their hydrophobicity and the resulting partition into the lipid fraction of an organism, including the biological membrane. The baseline toxicity correlates very well with the lipophilicity of the test compounds in the log K_{OW} range between 2 and 5.5. Short-termed or acute tests are generically not suited to cover specific MoA such as interactions with membrane and cytosolic receptors, inhibition or induction of enzymes, transporter proteins or interferences with nucleic acids. Therefore, it is indispensable to use exclusively data from chronic toxicity studies (NOEC or EC_{10}) for the identification of T compounds.
- The proposed NOEC or EC_{10} threshold of 10 µg/L or the classification as a CMR compound (**c**arcinogen, **m**utagen or **r**eproductive toxicant) or as an endocrine disruption chemical (EDC) is a pragmatic and widely accepted decision although

hampered by the fact that internationally standardized guidelines for the ecotoxicological identification of EDCs *in vivo* are not yet available. A range of *in vitro* tests has been developed which allow to assess the mutagenic and receptor-mediated endocrine disrupting potential of test compounds. However, *in vitro* assays are limited in their explanatory power for predicting effects in intact organisms or on the population level which is the ultimate protection target in ecotoxicology. On the other hand, these *in vitro* assays have their value (e.g. for screening) and an important relevance in the identification of potential MoAs of test compounds and may thus open the possibility of a targeted testing strategy. Depending on the outcome of an *in vitro* screening, a specific *in vivo* test battery which is responsive to the previously identified MoA can be used. This approach has been characterized as "intelligent testing" within the flexible testing approach of REACH.

- So far, sediments have only been considered for the P and B but not for the T criterion. This is an obvious gap because it has been shown that sediments can act as an important sink for contaminants in aquatic ecosystems. In this compartment, chemicals may pose a specific risk for sediment-dwelling organisms and for higher trophic levels by secondary poisoning due to potential uptake in the food chain (e.g. fish). In compliance with the WFD and the TGD chronic sediment tests should be performed when either the log K_{OC} or the log K_{OW} are equal or larger than 3.
- For future ecotoxicity testing it is necessary to consider not only the mother compound but also major transformation products irrespective of the selected exposure route (via water or sediment).

Conclusion: For the identification of toxic compounds according to the PBT criteria, chronic *in vivo* ecotoxicity data should be used exclusively. *In vitro* assays are important tools for the identification of potential MoAs of test compounds and open the possibility of a subsequent targeted testing strategy with selected *in vivo* test batteries which are responsive to the identified MoA. For chemicals with either a log K_{OC} or a log K_{OW} of equal or larger than 3 ecotoxicity should also be determined in chronic sediment tests. Irrespective of the selected exposure route, major transformation products of the analysed test chemicals should be considered in ecotoxicity testing.

5 Human toxicity

Mainly two characteristics of chemicals are relevant for the classification as priority substances within the WFD based on their potential to pose a risk for human health:

1. Biomagnification along the food chain with a consequent contamination of organisms which serve as human food sources.
2. Contamination of groundwater and other drinking water resources by compounds or their transformation products which are not completely or only insufficiently retained by current treatment techniques for raw drinking water. Of special concern are toxic substances and their transformation products which comply with the CMR criteria or considered as endocrine disrupters.

A biomagnification risk has generally to be assumed for persistent substances that bioaccumulate. Therefore, the respective PBT criteria provided in table 1 should be considered to identify such compounds, i.e. an experimentally determined BCF of at least 2,000 or alternatively, if BCF values are not available, a log K_{OW} of more than 4.5 combined with half-lives of more than 40 d in freshwater or more than 120 d in limnic sediments. In addition to these physico-chemical properties, the identification of new priority substances which pose a potential risk for human health should be driven by the results of residue

monitoring programmes for human food sources, for example in fish and shellfish. Such programmes are implemented in the majority of EU member states.

The second of the above mentioned characteristics is addressed in detail in the following section. For the characterisation of the potential CMR and endocrine disrupting properties of candidate substances, *in vivo* data from tests with human-relevant laboratory animals such as rodents should be used whenever possible.

The effects of exposure to substances in humans are generally classified in the following broad categories: organ-specific, neurological/behavioural, reproductive/developmental, immunological, carcinogenic and mutagenic. These effects are manifested at the biochemical, cellular, histopathological and morphological levels. Such effects vary depending upon the dosage, route of exposure (mainly ingestion in case of drinking water while inhalation or dermal absorption are of lower-ranking importance), frequency and/or duration of exposure, species (and strain in the case of laboratory animals), physiological state, sex and age of the exposed population. The nature, number, severity, incidence and/or prevalence of specific toxicological effects in populations (of either humans or animal species) exposed to chemical substances generally increase with increasing dose or level of exposure. Consequently, a chronic or even life-long exposure at comparatively low doses may nevertheless give rise to adverse effects in a cohort.

For most existing substances, data on the toxicological effects resulting from exposure are restricted to information obtained from studies involving laboratory animals. Occasionally, information derived from studies of human populations (principally epidemiological investigations) is available; however, in most cases, such data are limited or inadequate.

Often, there are case reports on the health of exposed individuals included in the literature. But normally these reports are not weighted heavily in assessments for priority substances, owing to the nature of and general lack of quantitation of exposure (generally short-term exposure to concentrations much greater than those in the general environment) and lack of statistical reliability.

An alternative in cases where *in vivo* data are not available – this is the default situation for transformation products occurring in drinking water resources – is the use of data from *in vitro* assays which are predictive for specific MoA in humans. Potential CMR and endocrine disrupting compounds can be identified on the basis of *in vitro* test batteries.

Conclusion: Priority substances posing a probable risk for human health should mainly be selected based on the potential for biomagnification along the food chain with a consequent contamination of organisms which serve as human food sources and on the potential to contaminate groundwater and other drinking water resources.

6 Likelihood of drinking water contamination

Even though the relevance of micropollutants for drinking water is discussed in the WFD, these aspects are typically not considered in the selection of the priority substances and in the calculation of the EQS. Within the WFD, there are some rules with regard to derivation of EQS for drinking water abstraction from surface water in contradiction with other legislations (Lepper 2005):

1. A “A1 value” is fixed in directive 75/440/EEC (directive for drinking water abstraction from surface water) and this value is lower than the EQS for other objectives of protection:
   ⇒ EQS ought to be harmonized with the “A1 value” of the council directive (CD) 75/440/EEC

2. No “A1 value” is fixed in CD 75/440/EEC but a drinking water standard (DWS) is available in CD 98/83/EC (drinking water directive) and this value is lower than the EQS:
   ⇒ Assessment (experts): identification of substance-specific removal efficiency in drinking water treatment
   ⇒ for the not removable fraction EQS ≤ DWS
3. Priority compounds for which no “A1 value” or drinking water standard exists:
   a) calculation of a provisional drinking water standard
   b) assessment based on expert knowledge with regard to:
      1. Removal efficiency of substances during drinking water treatment
      2. toxicological evaluation of the drinking water standard

   ⇒ EQS ≤ provisional drinking water standard for priority compounds not removed

Even though these rules cover a certain range of compounds, in general, drinking water aspects are not considered adequately in the WFD. (i) A large fraction of the drinking water is extracted from groundwater, which is often not treated at all, or with a simple one-step disinfection (UV or chemical, such as chlorine or chlorine dioxide). In these waters, the micropollutants present in the water resources often get into the drinking water with no or only limited removal. (ii) Certain groundwater extraction wells are mainly fed by riverbank filtration as the main barrier between the surface water and the groundwater. In these systems, the biological transformation of micropollutants in the infiltration zone is the main barrier. This transformation depends heavily on the redox milieu in this zone. Even though most compounds are better biodegradable under oxic conditions, some compounds are preferably degraded under reducing conditions. (iii) For the fraction of drinking water derived from surface water, often a multi-barrier treatment including adsorption and oxidation steps is applied with removal efficiencies which depend on the physical chemical properties of the target compounds.

Based on these considerations, the following criteria can be defined to avoid contamination of drinking waters by micropollutants:

1. Groundwater
   Since the treatment of most groundwater is minimal, all compounds which are not retained in the soil passage by adsorption and biological degradation will get into the drinking water without attenuation.
   ⇒ additional tests should be done to investigate the adsorption and biodegradation of micropollutants in the unsaturated zone of soils
2. Riverbank filtration
   Since the extraction wells are often close to the rivers, compounds which are not retained in the infiltration zone, will get into the drinking water.
   ⇒ additional tests should be done to investigate the biodegradation of micropollutants under oxic and anoxic conditions in the saturated infiltration zone (small-scale columns).
3. Surface waters
   These waters are mostly treated by multi-barrier systems. The main treatment options for removal of micropollutants are adsorption processes (granular activated carbon, powdered activated carbon) and oxidation (ozone, chlorine, chlorine dioxide and advanced oxidation processes, etc.). To assess the efficiency of these processes, the following additional tests should be done:
   ⇒ Adsorption: Continuous small-scale column tests for the removal efficiency for various water qualities (varying type and concentration of dissolved organic matter (DOM)). A first assessment of the expected removal efficiency can already be made based on the physical-chemical properties of the target compounds (e.g. log K_{ow}).
   ⇒Oxidation: Batch type oxidation experiments to test the removal efficiency as a function of the oxidant dose for varying water qualities (type and concentration of DOM). A first assessment about the expected efficiency can already be made based on the reaction kinetics which is either published or can be estimated from the

structure of the chemical compound. In the context of chemical oxidation, the formation of (potentially) toxic transformation products (e.g. nitrosamines) has to be considered as well.

Conclusion: Even though drinking water aspects are one aspect for priority substances in the WFD, in practice, drinking water relevant parameters are not considered sufficiently. Depending on the type of drinking water, the removal efficiency for micropollutants should be tested in the unsaturated zone of groundwater systems, in the infiltration zone during riverbank filtration and for adsorption and chemical oxidation processes during multi-barrier treatment in water supplies.

7 Compounds discharged directly to water bodies

Polar and toxic compounds not entering the sewer may deserve special attention for selection in the priority list since these are not conveyed to a centralized treatment, where state-of-the-art as well as advanced treatment can be applied for targeted removal. Further monitoring concentrations is very difficult for these compounds mostly emitted from non-point-sources at concentration varying strongly (e.g. due to rain events or human activity).

For example biocides leaching from facades are designed to be toxic for algae and fungi, and are released during rain events at very dynamic concentrations. Similarly for compounds used in agriculture.

Conclusion: Polar compounds not entering the sewer system during disposal may deserve special attention, since for these the option of centralized treatment is not given.

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