

Water quality and ecological risks of water pollution and chemical mixtures

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Amendment of EQS in Annex I to Dir. 2008/105/EC

Extension of mixture toxicity assessment:

A limit of 0.5 μ g/L for the sum of all pesticides and relevant metabolites \rightarrow Based on use of the substances (a.i. in plant protection or biocidal products)

 \rightarrow Other use types not considered

Substances in Annex I can be grouped based on molecular similarity and mode of toxic action, e.g.:

Pyrethroid insecticides Triazine & phenylurea herbicides Neonicotinoid insecticides Estrogens (and BPA) Macrolide antibiotics PFAS (as sum)

Cypermethrin, Bifenthrin, Deltamethrin, Esfenvalerat, Permethrin
Atrazin, Terbutryn, Diuron, Isoproturon
Imidacloprid, Acetamiprid, Clothianidin, Thiachlorprid, Thiametoxam
17 alpha-ethinylestradiol, 17 beta-estradiol, Estrone; (and BPA)
Azithromycin, Clarithromycin, Erithromycin
24 substances







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1.1 PFAS: Challenges and concerns



panthermedia.net/romrodinka

- Large and complex group of chemicals
- Ubiquitously used
- Ubiquitously spread in environmental compartments
- Stability, «forever chemicals»
- Up-concentration in food chains (biomagnification)
- Effects on human immune system

1.2 PFAS: EQS for the sum of 24 substances

Overview of the quality standards for the Water Framework Directive¹



Mixture approach for EQS derivation

- concept of concentration additivity
- «relative potency» using PFOA as reference substance
 - Most data available
- Relative potency factor for other 23 substances based on liver toxicity

Critical QS

- QS for human fish consumption
- QS for drinking water

¹derivation according to EU Guidance Document No. 27

²https://circabc.europa.eu/ui/group/9ab5926d-bed4-4322-9aa7-9964bbe8312d/library/e6137ae7-3056-4d01-ae44-de003185ab1c/details,

1.3 PFAS: Fish filet concentrations vs. limit values



EQS/WFD



- At many sites at least once the EQS to protect birds and otters is exceeded
- Almost all fish samples exceeded the EQS for human consumption at least 10x

Food items EU 2022/2388

Many samples exceed the regulatory values for PFAS residues in fish for infants and small children (food basket approach)

Risks would not be revealed by single-substance based assessment

Data from Valsecchi et al. (2021) Environmental Toxicology and Chemistry 40(3) 658-676

2.1 Estrogens: Mixture effects and low effect thresholds

Important sources: agriculture and treated wastewater

EQS are based on single substances which has two important limitations:

Mixture effects

- The included substances and other compounds with estrogenic activity are agonists of the estrogen receptor (ER) and act in a mixture (concentration addition)
- Strong evidence that the monitoring of E1, E2 and EE2 alone is insufficient to assess the overall risk of estrogenic endocrine disruption in water (Annex III.1, EBM report)

Suggestion: group-based approach, see next example on neonicotinoids

Low effect thresholds (pg/L range) A number of Member States (MS) are not able to quantify at EQS levels due to insufficient LOQ

Suggestion: implementation of effectbased quantification (EBM) complementing chemical analytics to better appreciate risks

2.2 Estrogens: Partial mitigation by upgrade of WWTP

Progesterone-like activity

PC = primary clarifier, SC = secondary clarifier, OZ = ozonation

Kienle et al. (2022), Water Research 212, 118084, https://doi.org/10.1016/j.watres.2022.118084

3.1 Pesticide mixtures EQS: one size does not fit all

Example sample from monitoring in German small streams:

Adding the risk quotients for the 4 neonicotinoid insecticides¹ leads to double the exceedance than the sum of 0.5 μ g/L

 \rightarrow Using 0.5 µg/L as a mixture EQS for pesticides renders the mixture risks of the neonicotinoids negligible

 \rightarrow It is very much appreciated that the proposal intends to account for the mixture toxicity of pesticides

 \rightarrow BUT, the general sum EQS of 0.5 µg/L does not account for the actual risk of the pesticides

risk mitigation measures will be ill informed

→ implement mixture risk limits for substance groups with same mode of action

¹ acetamiprid (no. 48), imidacloprid (no. 62), thiacloprid (no. 67) and thiametoxam (no. 68)

3.2 Proposal for a better (pesticide) mixture risk limit

Concentration Addition

same concept as in

- Relative Potency
- PFOA (and dioxin) equivalent concentrations footnotes 28 (and 24)
- 2) Effect-based-trigger values (see estrogen monitoring)

Add mixture risk limit for substances with same mode of action

Pesticides:

- Neonicotinoids (numbers 48, 62, 67, 68)
- Pyrethroid insecticides (41, 50, 55, 58, 64)
- Triazine and phenylurea herbicides (3, 13, 19, 40, 45)

And other groups:

- Estrogenic hormones (no. 46, 47, 49)
- Macrolide antibiotics (no. 49, 53, 57)

By means of a footnote indicating that summed risk quotients may not exceed value of 1:

 (²⁹) For the group of neonicotinoids (no. 48, 62, 67, 68), the summed risk quotients defined as the ratio between the measured environmental concentration and the individual EQS may not exceed a value of 1; the same applies for the group of....

3.3 A decision tree is already available

Adopted by SCHER, SCENHIR, SCCS in 2012; Opinion on Toxicity and Assessment of Chemical Mixtures

Regular updates and considering mixture toxicity are essential

- It is essential that the list of new substances in the EQSD Annex is adopted to better meet the protection goals of the WFD
- Stringent consideration of mixture risks still needs to be implemented in the future
 - Based on mode of action and toxic effects
 - Consider decision tree (SCHER, SCENHIR, SCCS 2012) as basis
- Different sources of micropolutants need to be covered
- EQS to be updated more regularly to incorporate new scientific knowledge

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Thanks a lot !