EPMF comments on the JRC report ‘Second Review of the Priority Substances list under the Water Framework Directive: Monitoring-based Exercise’

Executive summary

- We support a strong evidence-based, transparent prioritisation process for the selection of chemicals for which to potentially derive an EQS under the Water Framework Directive. However, it appears that the prioritisation process for silver is not transparent nor evidence-based.
- There is comprehensive scientific evidence that identifies that the driver for ecotoxicity of all silver forms (incl. nano silver) is caused by dissolution of silver ions. Measuring the dissolved silver fraction instead of the ‘whole water’ concentration is thus the correct way to monitor / assess silver. Furthermore, silver speciation and bioavailability is strongly influenced by prevailing water chemistry.
- Comparing ‘whole water’ monitoring data with a PNEC derived for compliance assessment in dissolved silver concentrations and also based on “added risk”, which have not been taken into account here, is scientifically incorrect.
- We consider the UK EQS for silver and the REACH freshwater PNEC more reliable than the EQS used in the JRC monitoring report as it is more robust.
- There is a need for sensitive analytical techniques to adequately measure silver. It remains open as to whether the data used here followed such a methodology.
- Available silver monitoring data are significantly lower than the values reported in the JRC monitoring report. Indeed, the mean total silver concentration was 221 ng/L (Sc2-PNECQC), compared to a mean maximum dissolved concentration from 425 samples from 84 sites in the UK of just 19.8 ng/L (Peters et al. 2011). The maximum concentration recorded from the JRC data set was 1900 ng/L. However, the worst case predicted concentration of high effluent discharge and low flow scenario by Johnson et al. (2014) is only 135 ng/L.

1. Need for transparent, evidence-based prioritisation

a. Silver is the only metal listed as substance which could be short listed as potential Priority Substance or should deserve more investigation by e.g. inclusion in the watch list. However, as can be seen in Table 21 of the JRC report, **silver is not the metal with the greatest STE score**, but is only the 4th metal and only the 16th substance on the list of all chemicals processed. We would therefore request that a scientific narrative is provided to outline the process that has been followed to specifically identify silver as a priority based on the evidence available, as it appears currently it is neither transparent nor evidence-based.

b. In the rationale for the selection of silver (page 70), reference is made to the inclusion of silver in the CoRAP and the ongoing **substance evaluation**. We would like to clarify that the concern / scope of the substance evaluation is limited to the nanoform of silver, and that only about 3 t/a of the total aggregated tonnage of > 100.000 t/a registered under REACH relates to nanosilver. Therefore, using the inclusion of silver in the CoRAP as justification for selection of silver is in our view disproportionate. Moreover, the evaluation is still ongoing, and conclusions can only be made when the outcome would become available.

2. Scientific inconsistencies in using whole water data for STE scoring of silver

In the rationale for the selection of silver (page 70) it is further mentioned: *'The complexity of silver (metallic, nano and ionic forms) and the different forms found in the aquatic environment should justify the* ***measurement in whole water*** *since measuring only the dissolved fraction would be limited to ionic silver and not detect the dynamic state of the different forms of silver.'* We would like to provide the following input on this assertion:

a. In the regulatory documents, such as the UK EQS and the REACH dossiers for silver and silver compounds, the **driver for ecotoxicity of all silver forms (including nanosilver) is the silver ion**. This hypothesis is based on an overwhelming weight-of-evidence, taking into account all reliable and relevant studies dealing with the environmental effects of ionic silver and nanosilver. While it is recognised that there are individual studies that may be debatable in this regard, or that suggest that the effects of the tested nanosilver are comparable to those of ionic silver, the overwhelming body of scientific evidence shows that the primary mechanism of toxicity for nanosilver is related to dissolved fraction of nanosilver particles into silver ions. Notter et al. (2014) presents a meta-analysis of published EC50 values for ionic silver and nanosilver, and demonstrates that almost 94% of (acute) toxicity values assessed show that the nanoform of silver is less toxic than the ionic form when normalised for a similar nominal Ag concentration. Therefore, taking the full body of scientific evidence into account, the read-across of ecotoxicity threshold values from ionic silver to other silver forms (including nanosilver) as a 'worst case' approach is scientifically justified and conservative. Consequently, **measuring the dissolved silver fraction (instead of the 'whole water' concentration) is the correct way to monitor / assess silver.**

b. Silver is known to be **rapidly removed and complexed in the water column** (e.g. Adams and Kramer 1999; Kramer et al. 2002). The influence of water chemistry upon the behaviour, fate and subsequent ecotoxicity of silver has long been recognised[1] (e.g. Gorsuch and Klaine 1998, and papers therein; Grosell et al. 2000). There is scientific evidence that metastable sulphide complexes and dissolved organic carbon mitigate silver ecotoxicity and reduce dissolved silver concentrations (e.g. Bianchini and Bowles, 2002; Reader et al. 2005). The development of a silver biotic ligand model (BLM) has been ongoing for many years. In validating the acute BLM for silver Bielmyer et al. (2007) gave data for acute silver toxicity to *Pimephales promelas* in waters of different chemistry. The table below shows the LC50s (µg/L dissolved silver), 95% confidence intervals (CI), and water effect ratios (WER) for a range of waters. The key message is the observation that the LC50s vary by a factor of over 20 simply due to the water chemistry. **Not accounting for bioavailability or even dissolved silver and simply using a whole silver measure, is therefore not environmentally relevant.**

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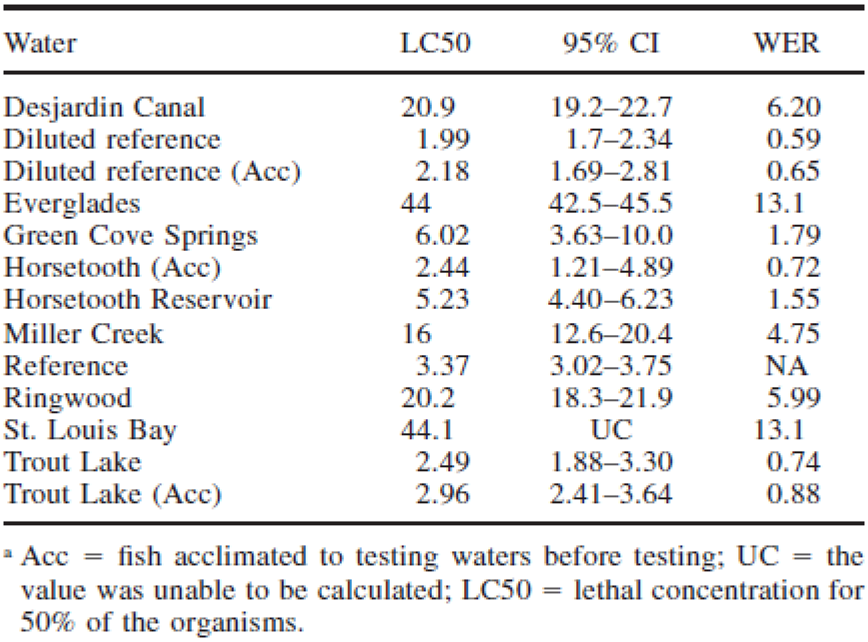
[1] See also report produced by Hydroqual "An evaluation of the potential for adverse effects due to exposure to silver in waters of the European Union" available upon request.



Water	LC50	95% CI	WER
Desjardin Canal	20.9	19.2–22.7	6.20
Diluted reference	1.99	1.7–2.34	0.59
Diluted reference (Acc)	2.18	1.69–2.81	0.65
Everglades	44	42.5–45.5	13.1
Green Cove Springs	6.02	3.63–10.0	1.79
Horsetooth (Acc)	2.44	1.21–4.89	0.72
Horsetooth Reservoir	5.23	4.40–6.23	1.55
Miller Creek	16	12.6–20.4	4.75
Reference	3.37	3.02–3.75	NA
Ringwood	20.2	18.3–21.9	5.99
St. Louis Bay	44.1	UC	13.1
Trout Lake	2.49	1.88–3.30	0.74
Trout Lake (Acc)	2.96	2.41–3.64	0.88

[a] Acc = fish acclimated to testing waters before testing; UC = the value was unable to be calculated; LC50 = lethal concentration for 50% of the organisms.

c. The referred statement contradicts what is mentioned on page 19 of the JRC report: *'For metals, however, a strict separation between "whole water" and "dissolved phase" was performed because in the case of metals the EQS refers to the dissolved concentration, i.e. the dissolved phase of a water sample obtained by filtration through a 0,45 µm filter or any equivalent pre-treatment (Directive 2008/105/EC). **STE for metals was run only in the dissolved phase**.'* This statement is supported by PMC, as it is valid for many metals including silver. Regrettably this methodology is not applied to silver: **only 'whole water' concentrations are considered for the silver STE scoring** while the EQS used is for dissolved silver (and added risk)**.** In this respect, we would also like to support the statement on page 71 of the JRC report, which also applies to silver: '*However, the obtained high STE scores for the metals measured only in whole water fraction (for example uranium, thallium) should be considered carefully before taking a decision for their possible listing as potential PS.'* Silver should have been included here as well next to uranium and thallium.

d. **Using whole water monitoring data and comparing them with a PNEC derived from and for dissolved silver concentrations is not scientifically justifiable**, leads to an overestimation of risk levels and a high STE score for silver. Exposure concentrations and effect levels need to be expressed (and thus also compared) in the same form (in this case the EQS expressed as dissolved silver vs monitoring data measured as dissolved silver) to allow a correct interpretation of potential risks. One of the challenges in reviewing the JRC document for silver is that, in light of the need for sensitive analytical techniques to adequately measure silver (see also point 4 below), the provision of limited summary statistics for whole waters does not support a transparent, evidence-based process. There is a need to share these data and we would be willing to adhere to the restrictions of any confidentially agreement that would facilitate this process.

3. REACH freshwater PNEC and UK EQS as reliable reference

The JRC report correctly states that the **PNEC value is a very important parameter in the prioritisation process** (page 39). The REACH freshwater PNEC and UK EQS for silver is 40 ng/l, while JRC uses the DEPA EQS for silver of 17 ng/l, which is more than 2 times lower and gives rise to a higher STE score for silver. We consider the **REACH freshwater PNEC / UK EQS more robust** for the following reasons:

a. The EQS selected by JRC is from Denmark and is derived using a probabilistic approach, with an assessment factor of 4 on the HC5, which we consider overly conservative. The EQS is an EQS_{add} derived to be compared with measured ambient dissolved silver concentrations corrected for **ambient silver background concentration**. Yet, in the JRC report the Denmark EQS has been compared to total silver measures, without accounting for background. The probabilistic approach uses 14 species from 8 taxonomic groups.

b. The **REACH freshwater PNEC** has been derived in accordance with Chapter R.10 of the European Chemicals Agency's guidance on information requirements and chemical safety assessment under REACH (ECHA, 2008) by using a probabilistic approach, with an assessment factor of 3 on the HC5. In addition, this PNEC is also the **UK EQS** for silver derived according to the EQS TGD. All relevant ecotoxicity studies were assessed for reliability and relevance using the criteria developed by Klimisch et al. (1997) and only high quality studies (assessed as "reliable without restriction", or "reliable with restrictions") were used. The underlying database for SSD modelling used the lowest available threshold values for 16 different aquatic species representing in total 8 taxonomic groups, and estimates the threshold concentration for silver using the identified effects on multiple species.

c. Importantly, silver was prioritised by the UK in 2008 as a potential specific pollutant (Annex VIII)[2]. However, the UK EQS was not implemented as it was demonstrated that **measured silver exposures in freshwaters were not sufficiently high to suggest a potential risk, or not sufficiently widespread in the UK to be of potential concern** (Peters et al. 2011; Johnson et al. 2014).

It is also important to repeat that the REACH PNEC / UK EQS for silver (as well as the above referred EQS of 17 ng/l) is derived using **measured dissolved silver concentrations**. Again, comparing total silver concentrations (reported as the 'whole water' monitoring data in the JRC report) with a PNEC/EQS derived for dissolved silver concentrations is scientifically incorrect and has resulted in an overestimated STE score for silver.

4. Need for sensitive analytical techniques to adequately measure silver

a. As currently reported, in the JRC report, it seems that the majority of the reported **silver monitoring data do not have a sufficiently low detection limit to allow a proper comparison**

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[2] Paul Whitehouse personal communication.

with the proposed PNEC (i.e. LoD < 10 ng/L). Unfortunately, we do not have access to the underlying database used by JRC and thus not to the actual LoD/LoQ in this monitoring-based exercise. Nevertheless, from the summarised silver data and by comparing the number of samples in Sc2 and Sc2-PNECQC in Table II-2, it appears to us that for only 11% of all the samples, the LoD/LoQ is < 34 ng/L (2 x EQS) and that the LoD/LoQ for the remaining 11% is between 25 ng/L (2 x min. concentration) and 34 ng/L, which is above the EQS used in the monitoring-based exercise (17 ng/L). This would suggest that methods of analytical determination are not compliant with the technical specification for chemical analysis set out by the European Commission for water quality monitoring (EC 2009), which requires a method to have an LOQ of equal to or below a value of 30% of the relevant environmental quality standard. Furthermore, this strongly suggests that the analytical techniques used to determine the silver concentrations for the underlying monitoring data of the JRC report are not sufficiently sensitive to make conclusive statements about silver exposures or potential aquatic silver risks.

b. **Dissolved silver data have successfully been generated in the past using more sensitive analytical techniques**. As an example: in 2010, PMC undertook a 6-month monitoring programme in rivers and effluents from 84 sites across England and Wales in collaboration with the UK Environment Agency. This project covered a wide range of aquatic systems with potential exposures to silver, and included aquatic systems downstream from silver users (Peters et al., 2011). For this study, ICP-MS was used, and an updated protocol was developed to allow a low level detection of dissolved Ag concentrations (LoD of 2.2 ng/L and LoQ of 6.6 ng/L). This shows that it is possible to measure low dissolved Ag levels but specific analytical techniques are needed. This study concluded that the concentrations of dissolved silver are low: about 80% of all samples from the 84 sites had dissolved silver concentrations below 6 ng/l and none of the sites had mean dissolved Ag concentrations that exceeded the REACH PNEC of 40 ng/l. The mean of the maximum dissolved silver concentrations reported at each site (reflected as the **regional background concentration** and calculated according to REACH guidance) was calculated as **6 ng/l (dissolved silver)**. This is about 40 times lower than the mean values for silver (expressed as ‘whole water’ silver) listed in the JRC report (221 ng/l).
Given the analytical challenges in measuring silver, measured datasets are generally highly censored. We expect that the datasets used by JRC are similarly censored. There are numerous methods of dealing with these types of data to deliver robust summaries of monitoring samples (e.g. Kaplan–Meier approach, e.g. Helsel 2005) and we would strongly recommend one of these specific methods is used for silver. If not, the data are likely to be highly skewed and therefore not robust for the purpose intended.
Considering the data mentioned above it is not straightforward to reconcile those summarised in the JRC report. Additional evidence of silver concentrations in the aquatic compartment, measured at appropriate LoDs can be found in the open literature (e.g. Wen et al. 2002; Johnson et al. 2014). In this respect, and as further supporting evidence on typical background ranges of Ag in aquatic systems, we would like to refer to Reimann and Birke (2010), who reported a median and 75th percentile of dissolved silver concentration in bottled waters below the LOD of 2 ng/l, and to Salminen et al. (2005), who report a 95th percentile for dissolved silver concentration in European surface waters of about 10 ng/l.

c. An earlier JRC report specifically mentions the need for sensitive analytical techniques to determine silver concentrations in water ("Feasibility of a Monitoring Mechanism Supporting a Watch List under the Water Framework Directive", see https://ec.europa.eu/jrc/en/publication/eur-scientific-and-technical-research-reports/feasibility-monitoring-mechanism-supporting-watch-list-under-water-framework-directive?search). On page 61 of this report it is mentioned: *'The tentative analyses of silver was introduced into the feasibility study in order to investigate the mechanism's applicability to non-organic compounds. All measurements were done with a routine method using ICP-MS operated by the Flemish VMM laboratories.* ***Unfortunately, the method's performance characteristics (LoD = 150 ng/L, LoQ = 390 ng/L) did not allow the detection of Ag ions in the samples taken. Consequently, no conclusive statement can be made.****'*

5. Appropriateness of screening score for silver

In addition to the STE score, a screening score has also been derived for the 'top-ranked' substances (including silver), including an **exposure score**. However, the quantification of exposure is merely based on tonnages (Table 19) and a "use index" is not appropriate, especially not for those substances for which monitoring data are available. There is an extremely high uncertainty associated with this method, whereas the actual measured concentration provide a realistic picture of exposure.

Furthermore, in the **hazard score**, the persistence (P), Bioaccumulation (B), Toxicity (T), Carcinogenicity (C), Mutagenicity (M), Reproduction toxicity (R), and Endocrine Disruptor activity (ED) have been evaluated. However, for insoluble or sparingly soluble substances such as metals and metal compounds, persistence and bioaccumulation are neither appropriate nor useful[3].

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[3] http://www.eurometaux.org/MetalsToday/MetalsFAQs/PBTforrankingthehazardsofinorganicmetals.aspx

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