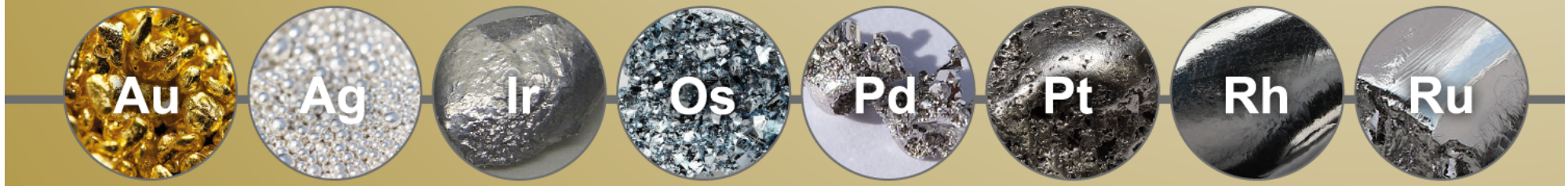
European Precious Metals Federation

Monitoring-based Exercise: 2nd Review of the PS List under the WFD SILVER MONITORING DATA



Dissolved silver versus total silver (1)

- Extracts JRC Report:
  1) *For metals, however, a **strict separation between "whole water" and "dissolved phase"** was performed by JRC 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).*
  2) *For those metals lacking monitoring data for the dissolved phase the STE was run for "whole water" instead.*
  3) *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.*

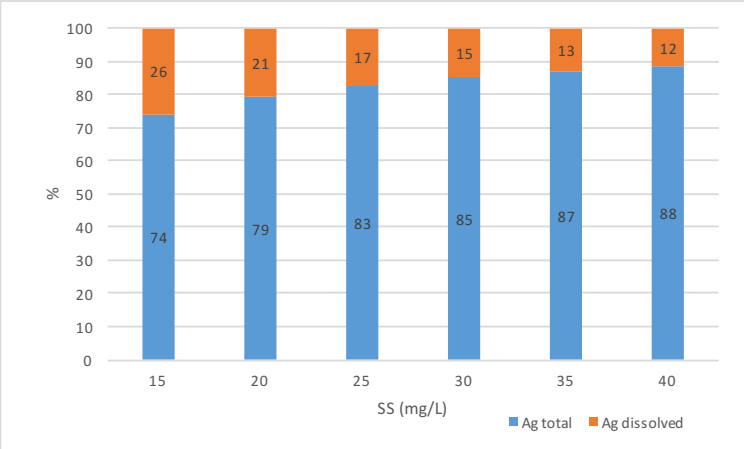
- For silver: initially **"whole water" monitoring data were compared with a PNEC/EQS derived for dissolved silver**
  - Not scientifically justifiable
  - Leads to **overestimation of risk / STE score!**

Dissolved silver versus total silver (2)

- Ag fractions (measured) in STP (CEH, 2011):
  - "total":
    - Particulate fraction: > 0,45 µm (93%) – not bioavailable!
    - Colloidal fraction (incl. nanosilver): 0,002-0,45 µm (7%)
    - 'Truly' dissolved fraction: < 0,002 µm

  Measured in 0,45 µm = "dissolved"

- Ag fractions in surface water (modelling using SS & Kd)



Ag particulate >> Ag dissolved in aquatic environment (10-20% as dissolved Ag)

- Ag fractions (modelled) in surface water (CEH, 2011):
  - 0-5 ng/L as colloidal fraction
  - 0-50 ng/L as particulate fraction

Particulate:colloidal:dissolved – approximately 100:10:1

Important to compare like with like!

Analytical techniques to monitor silver

- High LOD/Qs in comparison to the used PNEC (17 ng/L)
  - LOD/Qs for total Ag: ≥ 25 ng/L for 30% of samples / not available for 70% of samples
  - LOD/Qs for dissolved Ag: ≥ 50 ng/L

- Methods of analytical determination should be 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**

- **Analytical techniques used to determine the silver concentrations for the dataset are not sufficiently sensitive** -> brings substantial uncertainty in dataset and thus STE score

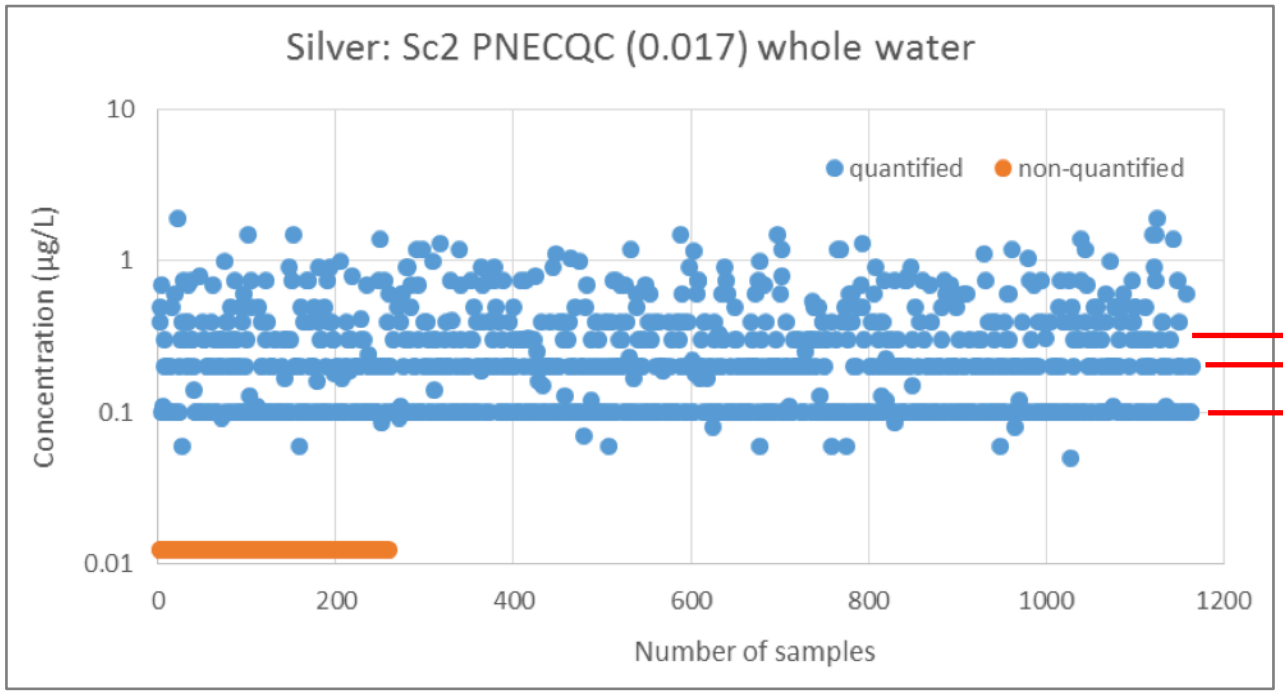
Total monitoring data silver (1)

	Samples	% in Sc2	% in Sc2-PNECQC
Non quantified records with LOD/Q not available	?	Excluded	Excluded
Non-quantified records with LOD/Q > 0.034 µg/L	11772	89.2%	Excluded
Non-quantified records with LOD/Q = 0.025 µg/L	259	2.0%	18.2%
Quantified records with LOD/Q not available	988	7.5%	69.4%
Quantified records with LOD/Q = 0.1 µg/L	175	1.3%	12.3%
Quantified records with LOD/Q = 0.8 µg/L	2	0.0%	0.1%
Total	**13196**		

- **Sc2**: non-quantified records set to ½ LOD/Q
  - ➡ overestimation of STE score because 89% potentially artificial PNEC exceedances
- **Sc2-PNECQC**: non-quantified records for which ½ LOD/Q > PNEC excluded
  - ➡ 89% of non-quantified records (which are likely < PNEC) excluded
  - ➡ **overestimation of STE score for total silver because dataset highly skewed towards quantified record (= highest concentrations)**

+ Overestimation of STE score because total concentrations compared with dissolved PNEC!

Total monitoring data silver (2)



Numerous 'quantified' values are exactly same value: **are they really quantified or are they LOD/Qs?**

min	mean	SD	median	P25	P75	P90	P95	P99	max
0.0125	0.221	0.251	0.1	0.1	0.3	0.5	0.75	1.2	1.9

≥ 25% of the quantified concentrations are exactly 0.1 µg/L

JRC remark: "*some of the reported 0.1 µg/L concentrations might be **"false positive"** non-quantified measurements"*

➡ **Dataset not sufficiently reliable**

Dissolved monitoring data silver (1)

countries	sites	samples	samples < LOD	samples < LOQ	% non-quantified
2	22	476		316	66.4

- Dissolved data only available for 2 MS + only quantified data for 1 MS

  ➡ **Representativeness criteria not fulfilled**

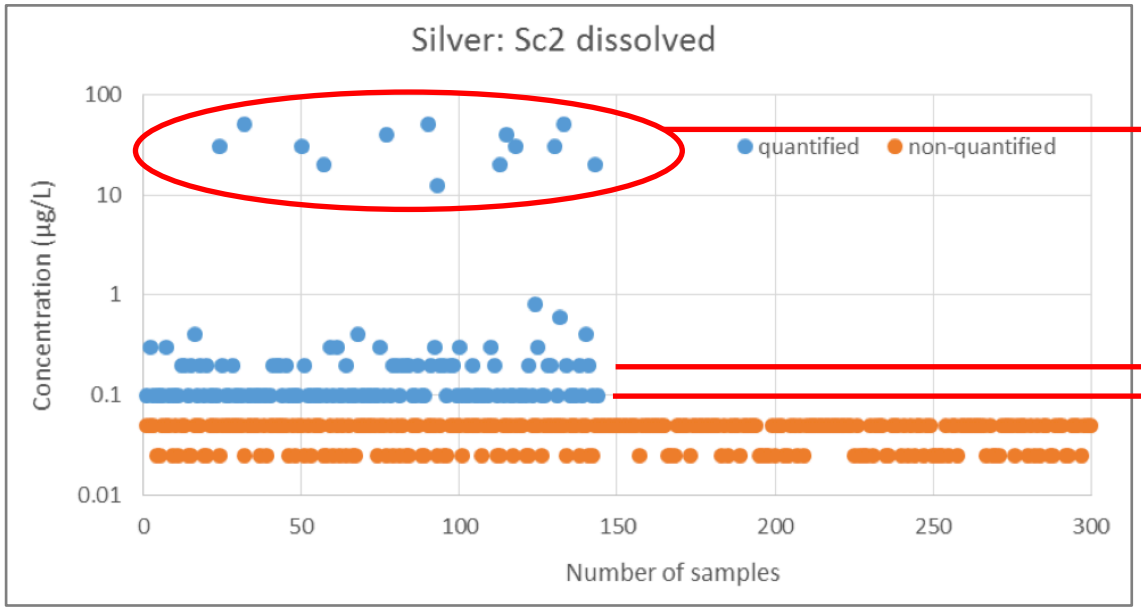
- **Sc2** used to derive STE score for the dissolved fraction:
  - non-quantified records (= 66.4% of the dataset) set to ½ LOD/Q
  - LOD/Q ≥ 50 ng/L (based on min reported in the factsheet)

  ➡ **Overestimation of STE score for dissolved silver because of high number of potentially artificial PNEC exceedances**

min	mean	SD	median	P25	P75	P90	P95	P99	max
0.025	5.935	21.00	0.05	0.05	0.1	0.4	60	85	210

- Dataset highly skewed because of 'outliers'
- **Range of dissolved concentrations (25 – 210.000 ng/L) could not be confirmed by any publicly available data (cf. next slides) – how to explain extremely high concentrations?**

Dissolved monitoring data silver (2)



Highest values factor 100 higher than others: **to be explained**

Numerous 'quantified' values reported as 0,1 and 0,5 µg/L: **are they really quantified or are they LOD/Qs?**

Country 6		2010	2011	2012	2013
50th %	Total	0,125	0,125	0,125	0,125
	Dissolved	0,1	0,025	0,025	0,1
95th %	Total	0,4	0,28	2,5	2,5
	Dissolved	0,68	0,295	0,29	30

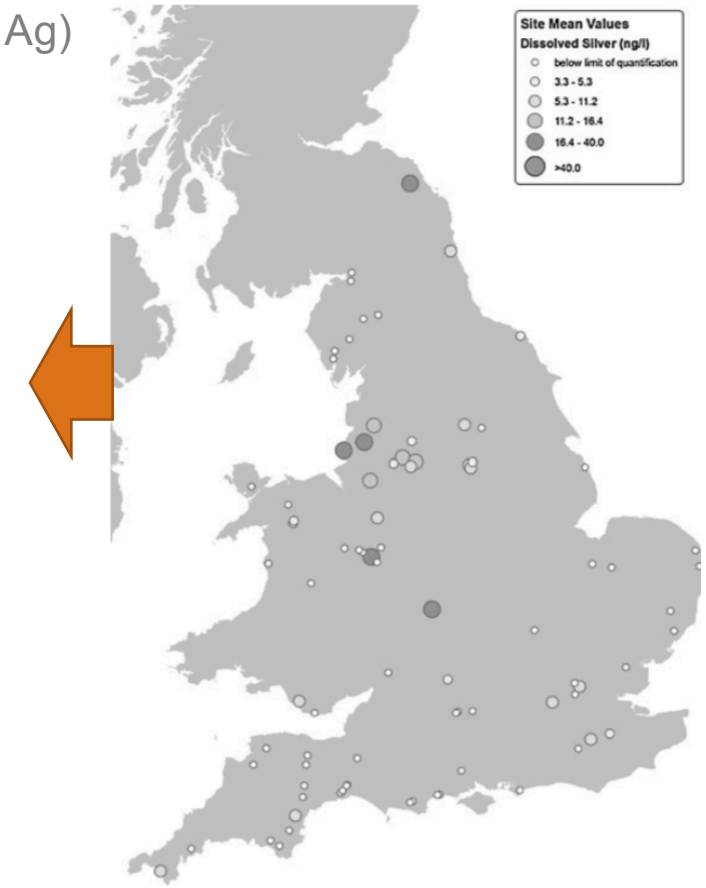
- Dissolved concentrations as 95th % >> total concentrations as 95th %?
- Dissolved Ag concentrations as 95th % increased by a factor of 100 between 2012 and 2013?
- Very high dissolved concentrations not confirmed by other datasets (cf. next slides)

Uncertainty too high to make any scientific conclusion !

Dissolved monitoring data: publicly available info (1)

- Data from literature (**United Kingdom**) – Peters et al., 2011
  - Data from 2010 (dissolved Ag)
  - 425 samples; 84 stations
  - LOQ: 6,6 ng/L

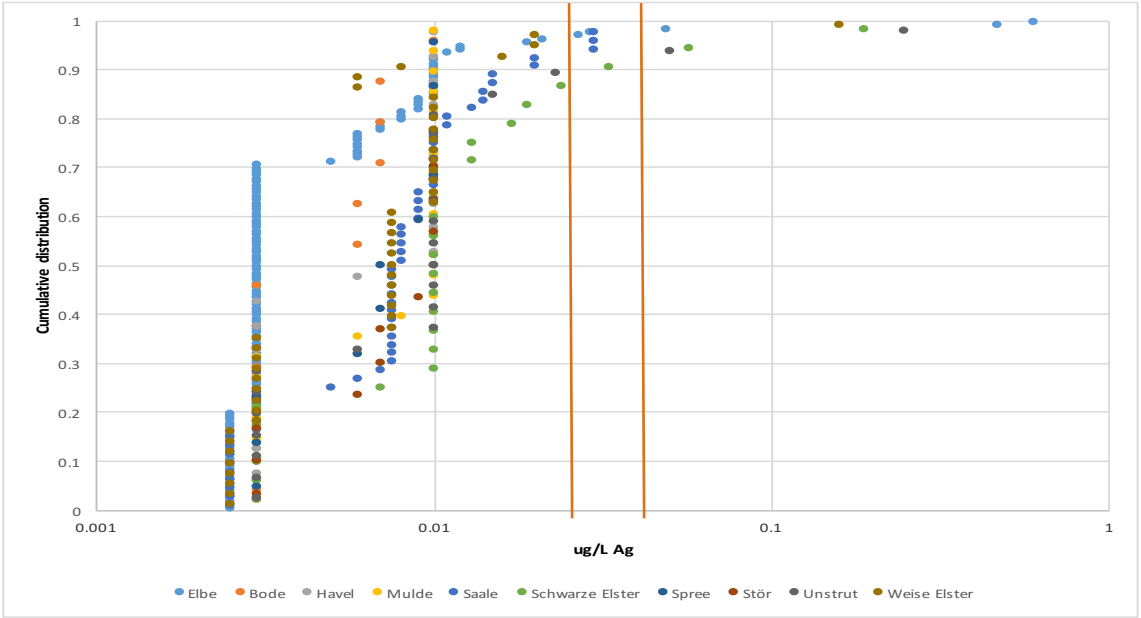
5th %	< 6,6 ng/L
50th %	< 6,6 ng/L
95th %	16,4 ng/L
Max	19,8 ng/L



Dissolved monitoring data: publicly available info (2)

- Data from literature (**Germany**) – www.elbe-datenportal.de

  - Data from 2013-2015 (Dissolved Ag)
  - 545 samples; 10 rivers
  - LOQ: 6 - 20 ng/L



µg/L	Bode	Elbe	Havel	Mulde	Saale	Schwartze Elster	Spree	Stör	Unstrut	Weise
5th %	0,003	0,0025	0,003	0,003	0,0025	0,003	0,003	0,0025	0,003	0,0025
95th %	0,0084	0,0123	0,01	0,01	0,03	0,051	0,001	0,0048	0,0214	0,0188

➡ 95th %: 1 - 51 ng/L

Dissolved monitoring data: publicly available info (3)

- Data from literature (**Belgium**) – www.vmm.be
  - Data from 2015 (dissolved Ag)
  - 6189 samples; representative for all rivers in Flanders
  - LOQ: 120 - 240 ng/L
  - All but one dissolved Ag concentrations < LOQ
  - One measured Ag dissolved conc. of 0,83 µg/L

- Data from literature (**The Netherlands**) – http://live.waterbase.nl/
  - Data from 2010 (dissolved Ag)
  - 744 samples; 53 monitoring sites

Almelo/ Amsterdam/Belfeld/Bocht van Watum/Boomkensdiep/Bovensluis/Brienenoord/Buitenhaven/Dantziggat/Doove Balg West/Dreischor/Eefde/Eemmeerdijk/Eijsden/Enschede/Genemuiden/Goeree/Gouda/Hagestein/Hansweert/Haringvlietsluis/Hasselt/Huibergat/Ijmuiden/Kampen/Keizersveer/Ketelmeer/Lobith/Maassluis/Markermeer/Nederweert/Nieuwegein/Nieuwersluis/Noordwijk/Oesterdam/Pampus/Puttershoek/Rottumerplaat/Sas van Gent/Schaar van Ouden Doel/Schouwen/Soelekerkepolder/Steenbergen/Stevensweert/Terneuzen/Teschelling/vlissingen/Vrouwezand/Vuren/Walcheren/Westzaan/Wiene/Wissenkerke/De Zwaan

- All but one dissolved Ag concentrations < 0,1 or < 1,0 µg/L
- One measured Ag dissolved conc. of 0,13 µg/L (Amsterdam)

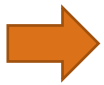
Total monitoring data: publicly available info (1)

- Data from literature (**The Netherlands**)– www.watergegevens.rws.nl
  - Data from 2013 (total Ag)
  - 35 samples; 4 monitoring sites

µg/L	Maassluis	Eysden	Sas van Gent	Schar
Ag dissolved	/	/	/	/
Ag total	0,0068 – 0,13	< 0,1	0,0074-0,016	0,005– 0,331

Total monitoring data: publicly available info (2)

- Data from literature (**Sweden**) - http://miljodata.slu.se/mvm/Default.aspx
  - Data from 2013 (total Ag)
  - 86 stations waterbodies
  - LOQ: 10,0 ng/L

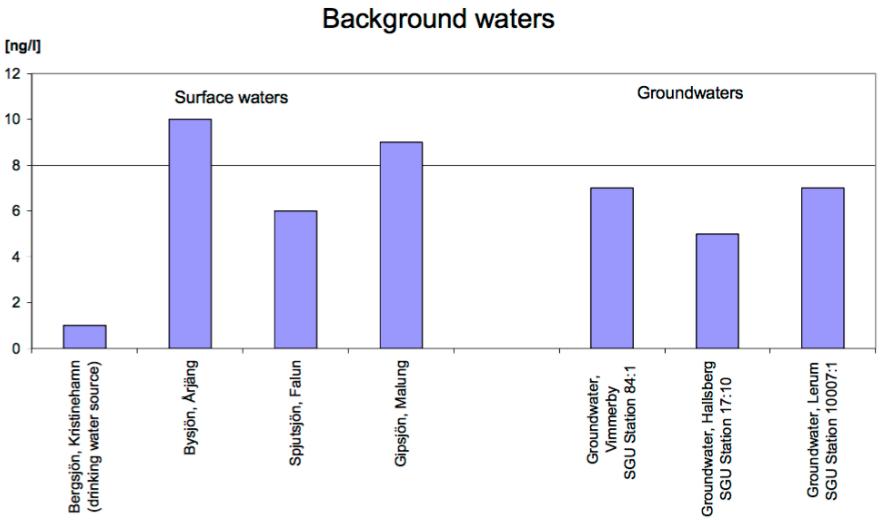


- All but one total Ag concentrations < 0,01 µg/L
- One measured conc. of 0,01 µg/L (station: Liffedarve)

Total monitoring data: publicly available info (3)

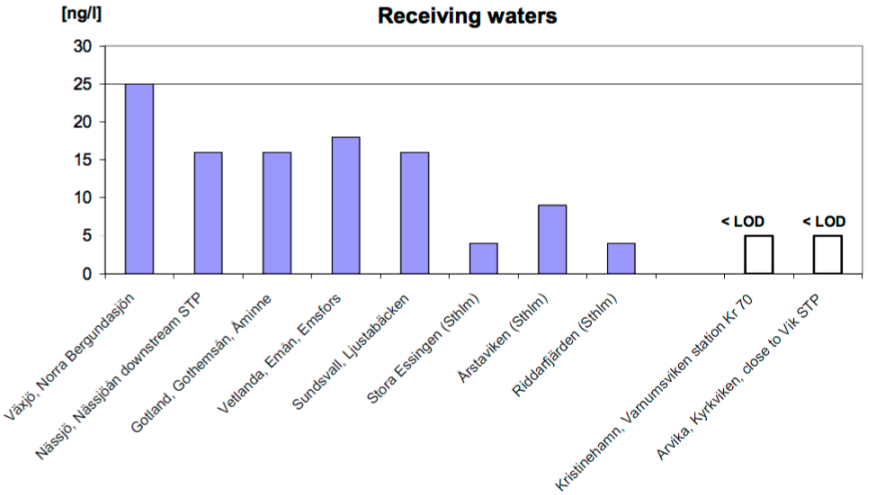
- Data from literature (**Sweden**) -
  http://www.lansstyrelsen.se/gavleborg/SiteCollectionDocuments/sv/miljo-och-klimat/tillstandet-i-miljon/miljogifter/Screening2007_silver.pdf
  - Data from 2007 (total Ag)
  - 9 waterbodies
  - LOQ: 5,0 ng/L

Without anthropogenic sources



Between 6,0 – 9,0 ng/L (Ag_{total})

With anthropogenic sources



Between < 5,0 – 25,0 ng/L (Ag_{total})

Total/dissolved monitoring data: publicly available info

- Data from EEA website (**Europe**) - http://cdr.eionet.europa.eu
  - Data from 2011-2013 (total/dissolved Ag)
  - Austria, Belgium, Bulgaria, Croatia, Cyprus, Denmark, Finland, France, Iceland, Norway, Portugal, Slovakia, Sweden, Switzerland: not reported/measured
  - Spain: no access to data

Country	Type of system	Year	Nr of stations	Nr of samples	LOQ (µg/L)	Ag concentration (µg/L)
Germany	Rivers	2012	/	757	0,005-0,5	725 samples < LOQ; 32 measured values: aggregated data with max values of 0,96; 0,019; 0,012; 0,013; 1,6; 0,04; 0,29; 0,021; 0,074; 0,026; 0,018; 0,03; 0,03 µg/L (dissolved Ag)
Ireland	Rivers	2012	/	56	0,5	54 samples < LOQ; 2 measured values: 0,6; 0,9 µg/L (total Ag)
England	Rivers	2012	/	4	1	All samples < LOQ (total Ag)
Italy	Rivers	2011	14	160	0,5	Median values of all stations < LOQ; 3 measured values: 0,25 µg/L
The Netherlands	Rivers	2012	/	228	0,1	All values < LOQ
	Lakes	2012	/	238	0,05-0,1	235 datapoints < LOQ; 3 measured values: 0,0599; 0,0862; 0,0916 µg/L
Poland	Rivers	2012	/	80	1,5	79 datapoints < LOQ; 1 measured value: 1,97 µg/L
Romania	Rivers	2012	14	97	0,1	90 values < LOQ; maximum measured values: 0,14; 0,1, 0,49, 0,64; 0,65 µg/L; median values all below LOQ

Influence PNEC on STE score

- PNEC changes assessed on the STE score for Sc2 rather than Sc2-PNECQC
- Non-quantified records set to ½ LOD/Q, and LOD/Qs high compared to PNEC (even if PNEC of 0.04 µg/L is used) -> 89% of potentially artificial PNEC exceedances introduced in Sc2
- **STE scores based on Sc2 will be artificially high, regardless of the PNEC used!**

JRC Conclusion

(1)

*"The **STE score of Sc2-PNEC QC is high** (2.108 with PNEC=0.017 µg/L). Silver with a proposed PNEC of 0.01, 0.02 and 0.04 µg/L has been analysed in 9 MS. In Sc2-PNEC QC samples were available in seven countries, with **only 18% of them not quantified**. These monitoring data are from "whole water"; however, the **STE score is high (2.354; for Sc2) even when the highest PNEC of 0.04 µg/L is used**. Available monitoring data from **dissolved fraction (from 2 MS)** were analysed by STE with two PNECs (0.01 and 0.04 µg/L), and the **STE score still shows high value** (2.016)."*

(2) (3) (4)

EPMF comments on JRC conclusion

(1) Total Ag concentrations compared with dissolved PNEC; Dataset highly skewed towards highest values + not reliable, high uncertainty

(2) 89% of non quantified values already removed from Sc2-PNEC QC

(3) PNEC influence assessed on basis of Sc2 and thus a lot of artificial PNEC exceedances are included

(4) Dissolved data only available for 2 MS with only quantified values in 1 MS + assessed on the basis of Sc2 with a lot of artificial PNEC exceedances included; Dissolved concentrations >> data publicly available; Dissolved concentrations >> total concentrations

- **Substantial uncertainty in the STE score derived for silver**
- **Currently available evidence too weak to put silver forward as PS**
- **Need for reliable monitoring data using more sensitive analytical techniques**