

European freshwater silver monitoring data do not suggest a potential European-wide risk

Katrien Arijis^{1,2}, Karel Viaene², Patrick Van Sprang², Jelle Mertens¹

INTRODUCTION

- ‘**Priority substances**’ under the Water Framework Directive 2000/60/EC (‘WFD’) are identified as substances posing a significant risk to or via the aquatic environment. To properly assess the potential **risk** of a substance, high-quality representative monitoring data should be compared to a safe threshold concentration.
- For **silver (Ag)**, a freshwater quality threshold of 0.116 µg dissolved Ag/L has recently been derived that protects 95% of the organisms. Using a conservative assessment factor of 3, this results in a Predicted No Effect Concentration (PNEC) of 0.039 µg Ag/L.
- In this work, several publicly available **monitoring data sets for silver** in the freshwater environment are assessed and checked for a potential European-wide risk using the above PNEC and according to the methodology used by the European Commission.

MATERIALS AND METHODS

DATA SETS

- **Waterbase**: public database from European Environment Agency; part of the monitoring data used by the European Commission for its prioritisation exercise under the WFD.
- **Member state (MS) specific monitoring data**: publicly available datasets from France (FR), Germany (DE), The Netherlands (NL).

RISK ASSESSMENT

- Main summary statistic: 95th percentile (P95) of the processed monitoring data (also used by the European Commission in its assessments under e.g. the WFD).

Country	Total samples	Non-detects (< LOQ)	LOQ range (µg/L)	Total samples after data processing (% of original data set)	95th percentile of processed data (µg/L)
Waterbase (2010 - 2019)					
5 countries	13 528	96%	0.00001 - 5	2 824 (21)	0.044
FOREGS (1997 - 2001)					
26 countries	807	NR	0.002	807 (100)	0.011
Member state specific data					
France (2010-2021)	72 754	95%	0.0005 - 50	57 889 (80)	0.025
Germany (2010-2020)	1 882	86%	0.003 - 0.1	1 441 (77)	0.021
The Netherlands (2010-2020)	9 136	82%	0.004 - 1	6 588 (72)	0.026

Table 1: Summary of considered silver monitoring data sets. LOQ = limit of quantification. NR = not reported.

Country	Total samples	Non-detects (< LOQ)	LOQ range (µg/L)	Total samples after data processing (% of original data set)	95th percentile of processed data (µg/L)
Waterbase					
Norway (2015 - 2019)*	937	42%	0.002 - 0.05	937 (100)	0.00761
Poland (2013 - 2014)	1 697	96%	0.0002 - 1	1 693 (100)	0.001
The Netherlands (2014 - 2015)	1 032	80%	0.005 - 5	830 (80)	0.037
Member state specific data					
France (2021)	1 737	97%	0.01	1 737 (100)	0.005
The Netherlands (2019-2020)	1 717	78%	0.004	1 691 (98)	0.0069

Table 2: Summary of subsets of the silver monitoring data sets for countries and years where low LOQs were achieved.

*Total Ag measurements so worst case (whereas all other measurements in Table 1 and 2 are dissolved Ag measurements).

RESULTS

- The **Waterbase** data set is dominated by measurements < LOQ and for which LOQ >> PNEC, so provides very little info about the actual Ag concentrations in the EU and about the potential EU-wide risk posed by Ag. The data set is highly censored after data processing (only 21% of original data set remains), due to the wide range and often high LOQs (Figure 1).
- Several **substitution approaches** were compared (Figure 2), showing that summary statistics of the Waterbase data set are defined by LOQ values: P95 moves from 0 µg Ag/L (all non-detects substituted by zero) to 2 µg Ag/L (all non-detects substituted by LOQ) → considerable differences between the approaches highlight uncertainties associated with the data set.
- A **country-specific assessment** from the Waterbase was also performed → for those countries where Ag could be reliably measured (Table 2), Ag does not pose a risk to freshwater environment.
- MS specific data from FR, DE and NL also contain many non-detects (>80%) but were mostly measured with sufficiently sensitive techniques (=low LOQ) to allow comparison with the PNEC, so >70% of the data set remains after data processing. The P95 are all < PNEC (Table 1). For FR and NL, detection techniques have improved over time: when focusing on the most recent data, with LOQ < PNEC, the P95 for both countries is 6 to 8 times < PNEC (Table 2).

CONCLUSION

- High-quality silver monitoring data for all European countries are currently lacking.
- Most of the available silver monitoring data sets contain a **large proportion of undetected samples** (concentration < LOQ), leading to considerable uncertainty in the data set. For silver, this LOQ is often ≥ the safe threshold concentration and **the way undetected samples are treated during data processing considerably impacts the assessment**.
- For **large data sets** like the Waterbase covering many EU countries (and often a wide range of LOQs), the uncertainty in the data set does not allow to make any general conclusion about EU-wide risk.

DATA PROCESSING

- Measurements > 100 000 x PNEC omitted as outliers.
- ‘**Detects**’: measurements ≥ limit of quantification (LOQ).
- ‘**Non-detects**’: measurements < LOQ → methodology European Commission:
 - ½ LOQ ≤ PNEC: non-detects substituted by ½ LOQ
 - ½ LOQ > PNEC: values removed from data set prior to analysis.

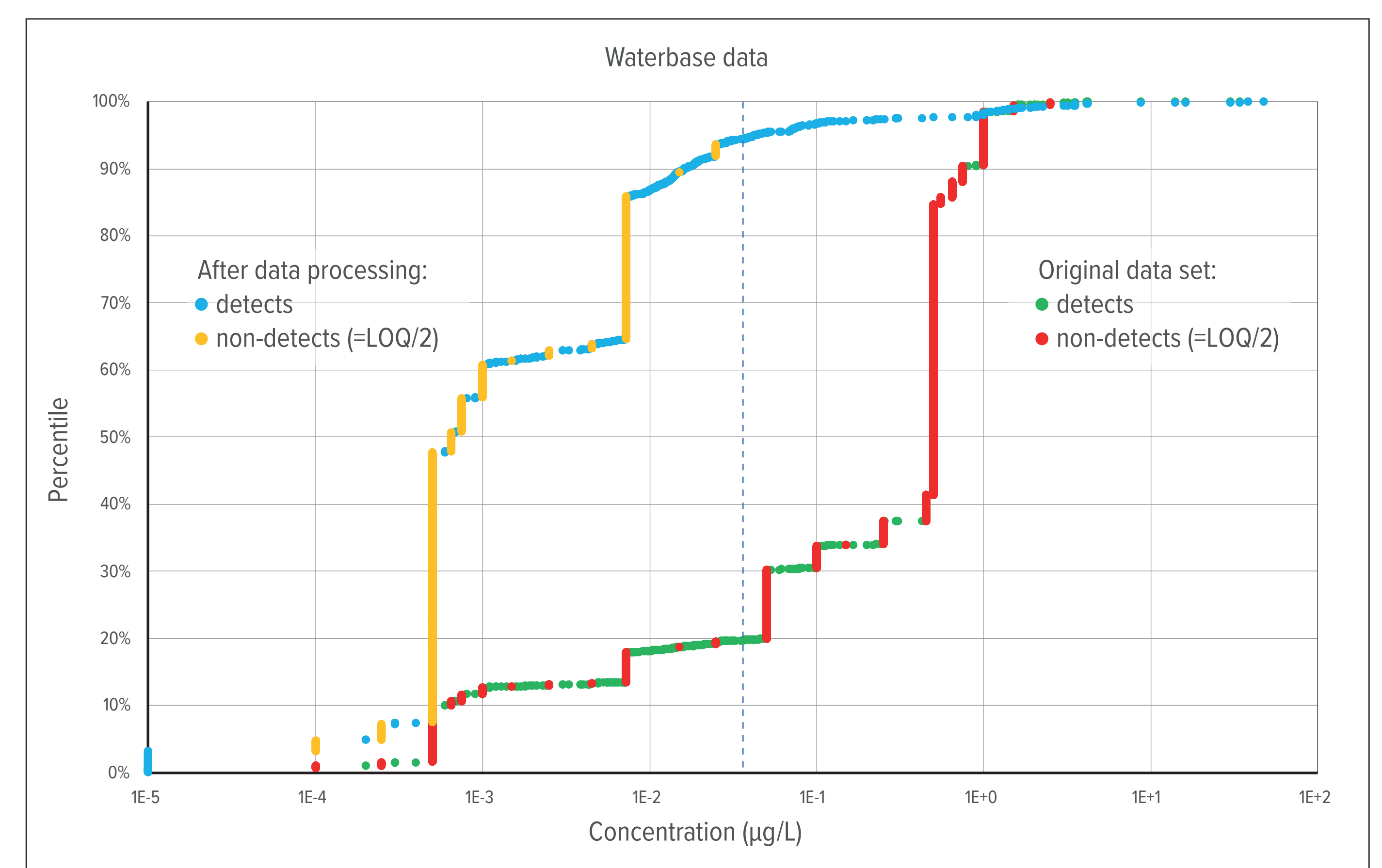


Figure 1: Cumulative frequency distribution of the Waterbase silver data set before and after data processing. The vertical dotted line is the PNEC value of 0.039 µg/L.

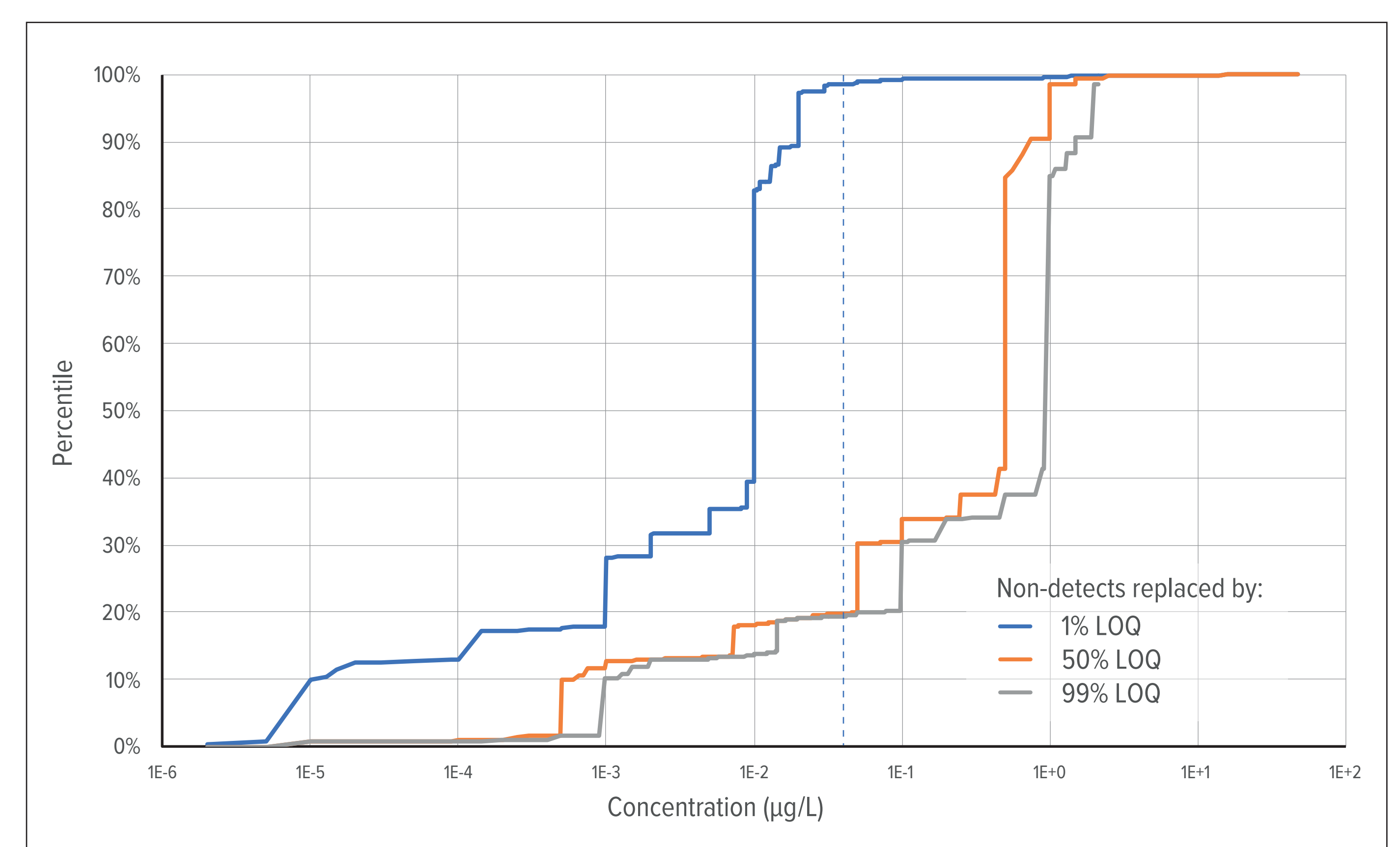


Figure 2: Comparison of cumulative frequency distribution of the original Waterbase silver data set with different substitution approaches for the non-detects. The vertical dotted line is the PNEC value of 0.039 µg/L.

