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Occurrence and Concentration of Dissolved Silver in Rivers in England and Wales

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Abstract There is a paucity of monitoring data for silver in freshwater environments in Europe. There are several reasons for this, including the relatively low levels of silver in the aquatic environment and the requirement for commensurately low levels of detection (<100 ng l^{-1}), which are generally not routinely achieved in analytical laboratories. In this study 425 separate analytical determinations for dissolved (<0.45 μm) silver from 84 Environment Agency monitoring stations were carried out. Sampling was carried out on a monthly basis over a period of 6 months. Of the 425 samples, 346 were reported as having dissolved silver concentrations below the limit of quantification (6.6 ng l^{-1}) and, of these, 280 samples were reported as below the reporting limit of detection (3 ng l^{-1}). The mean of the maximum dissolved silver concentrations reported at each station was calculated as 6.1 ng l^{-1} using a statistical extrapolation technique to allow for the high level of censorship in the dataset. The maximum mean dissolved silver concentration recorded at a station was 19.8 ng l^{-1}. A freshwater Predicted No Effect Concentration (PNEC) of 40 ng l^{-1} was used in this study.

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There is a paucity of monitoring data for silver in freshwater environments in Europe. There are several reasons for this, including the relatively low levels of silver in the aquatic environment and the requirement for commensurately low levels of detection (<100 ng l^{-1}), which are generally not routinely achieved in analytical laboratories. Uses of silver and silver-containing compounds in England and Wales include their use as laboratory reagents, in alloys and in the photographic industry. Silver is also employed in biomedical, dentistry and therapy applications.

To assess potential aquatic risks of silver there is a requirement for both effects and exposure data. A draft freshwater long-term predicted no effect concentration (PNEC) for dissolved silver of 40 ng l^{-1} has been derived by the Environment Agency of England and Wales (Paul Whitehouse personal communication). The objective of this paper is to describe the collection of the silver exposure data from England and Wales surface waters that provides context to this PNEC and to interpret these monitoring data in accordance with European regulatory drivers such as REACH and the Water Framework Directive (WFD).

Materials and Methods

Site selection and sampling were undertaken in collaboration with the Environment Agency of England and Wales, one of the principal environmental regulators in the UK. The monitoring programme was based on 86 sampling stations selected from the Environment Agency's network of river monitoring sites. The selected sites were from

across all the Environment Agency's eight geographic regions and the variation in water chemistry across the subset is broadly representative of the variation in surface water chemistry that occurs across Great Britain and the wider EU (Table 1).

Dissolved silver and dissolved organic carbon (DOC) analyses were conducted on the routine water samples collected from each site on a monthly basis by Environment Agency sampling staff on up to six occasions at monthly intervals from January 2010 to June 2010. Samples for dissolved silver were filtered in the field (0.45 μm filter) according to standard Environment Agency sampling protocols, which require that filters are flushed through thoroughly before samples are collected and stored in 125 ml HDPE bottles. Samples for DOC analysis were not filtered and were stored in 500 ml PET bottles. Samples were chilled and transported to the Environment Agency's National Laboratory Service (NLS) Starcross Laboratory for analysis.

The concentration of dissolved silver was determined by inductively coupled plasma mass spectrometry (ICP MS). An updated method for low level dissolved silver was developed specifically for this monitoring programme. The achieved limit of detection (LOD) was 2.2 ng l^{-1} (although a minimum reporting limit of 3 ng l^{-1} was used by the laboratory). The LOD was calculated from an analysis of the within-batch standard deviation of blank samples. The LOD of 2.2 ng l^{-1} is equivalent to a limit of quantification (LOQ) of 6.6 ng l^{-1} (calculated as three times the LOD). This method is 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 (i.e. 30% of 40 ng l^{-1} dissolved silver). Details of the analytical performance criteria for the low-level silver method are summarised in Table 2. DOC concentrations were analysed using an automated Skalar system. The limit of detection for DOC analyses is 0.2 mg l^{-1} and the normal range of application is up to 10 mg l^{-1}, although samples with higher DOC were analysed by dilution of the sample.

Where the concentration of dissolved silver in a sample was reported as below the limit of quantification (LOQ = 6.6 ng l^{-1}), a value of half the LOQ was substituted for the purposes of calculating arithmetic mean concentrations for each monitoring site. Where all silver results for a site were reported as below the limit of quantification, the mean value for the site was reported as "below the limit of quantification" (<LOQ). This treatment of censored data is consistent with the technical specification for chemical analysis and monitoring of water status set out by the European Commission (2009) and Chapter R.16 (Environmental Exposure Estimation) of the European Chemicals Agency (ECHA) Guidance on Information Requirements and Chemical Safety Assessment (ECHA 2008).

Monitoring data were subject to a compliance assessment against the PNEC of 40 ng l^{-1} dissolved silver. The compliance assessment comprised both "face-value" comparisons of the PNEC with measured mean concentrations of dissolved silver at the sites, and an assessment of the statistical "confidence of failure" (according to ISO 5667-20:2008). Confidence of failure calculations take into account the mean, standard deviation and number of samples available at each monitoring site. In practice, sites that exceed a PNEC with a "confidence of failure" of greater than or equal to 95% are considered by the Environment Agency to have exceeded the PNEC with statistical certainty.

Results and Discussion

The results of replicate dissolved silver and DOC measurements at each of the regional monitoring sites are

Table 1 Percentile distributions for key physicochemical parameters of freshwaters in Great Britain (n = 916; Environment Agency 2009), the subset of the Environment Agency network used for silver monitoring (n = 86) and EU SWAD database

Percentile	DOC (mg l^{-1})			Calcium (mg l^{-1})			pH		
	GB	EA	SWAD[a]	GB	EA	SWAD[a]	GB	EA	SWAD[a]
5th	1.27	1.55	–	1.68	3.86	–	6.41	7.2	–
10th	1.76	1.78	2.6	2.49	8.52	3.0[b]	6.64	7.3	6.6
50th	4.59	4.02	6.4	30.62	53.59	40.0	7.66	7.8	7.5
90th	9.40	7.16	12.4	120.23	123.4	119.0	8.12	8.1	8.1
95th	11.77	9.18	–	133.12	135.6	–	8.23	8.2	–

GB Great Britain, *EA* Environment Agency

[a] *SWAD* Surface waters database. A compilation of EU monitoring data used as part of the voluntary EU risk assessment of copper (ECI 2007)

[b] Estimated by graphical interpolation

Table 2 Analytical performance criteria for the analysis of dissolved silver in surface water, sewage, and trade effluent samples

Method parameter			
System blanks	0.6 ng l^{-1}	Mean blank determined from 11 independent batches of analyses	
	Mean	Recovery range	90% confidence interval of mean recovery
Recovery from:			
Ultra pure water	100%	99.1–101%	0.313
River water	99.3%	99.1–99.5%	0.232
Precision (% RSD)	2.01%	Data from 46 reference samples (250 ng l^{-1}) analysed randomly within batches of routine samples	
Bias (%)	−1.38%		

summarised as arithmetic means (with standard deviation) and maxima in Table 3. Of the 86 sampling stations, selected samples were available for 84 of these. A total of 425 separate analytical determinations for dissolved silver were carried out as part of the surface water monitoring programme. A total of 346 individual samples (~80% of all samples) were reported as having silver concentrations below the limit of quantification (6.6 ng l^{-1}). Of these, 280 samples (~65% of all samples) had measured concentrations below the reporting limit of 3 ng l^{-1}. The best estimate of the overall median value from the whole dataset is therefore,<3 ng l^{-1}, but it is reported as <6.6 ng l^{-1} owing to the requirement to report "less than" analytical data on the basis of the limit of quantification rather than the limit of detection (as per EC (2009) and ECHA (2008)). As a result of this, many sites at which the measured silver concentrations were <3 ng l^{-1} on every sampling occasion are reported as having a dissolved silver concentration of <6.6 ng l^{-1}. None of the sites had mean concentrations of silver that exceed the PNEC of 40 ng l^{-1} dissolved silver, either on a face-value or confidence of failure basis (Fig. 1).

Table 3 Summary of the results of the regional silver monitoring programme

	Average dissolved silver (ng l^{-1})	Median DOC (mg l^{-1} C)
No. of sites	84	84
Minimum	<LOQ[a]	0.61
5th percentile	<LOQ[a]	0.87
10th percentile	<LOQ[a]	1.20
25th percentile	<LOQ[a]	1.88
50th percentile	<LOQ[a]	2.88
75th percentile	5.3	4.85
90th percentile	11.2	5.81
95th percentile	16.4	6.94
Maximum	19.8	15.3

[a] *LOQ* limit of quantification (6.6 ng l^{-1})

To assess whether any of the monitoring sites may be affected by local emission sources of silver an approach previously applied to distinguish between background and contaminated samples in soils was applied to the data (Davies 1983; Environment Agency 2008). This approach seeks to identify a breakpoint in a plot of concentration against rank scores for the samples to distinguish between samples from different populations. Sites with mean concentrations which are expressed as 0.5 times the LOQ are not included in the analysis of the breakpoint. Sites that are identified as belonging to a different distribution may be subject to local emissions, and are therefore not suitable for inclusion in the set of sites from which the measured regional background concentration is calculated.

Following this approach, a breakpoint was identified at a dissolved silver concentration of 16.2 ng l^{-1}, with a 95% confidence interval between 15.1 and 17.3 ng l^{-1}. Five sites were identified as having mean dissolved silver concentrations above the identified breakpoint, although only three of these sites had mean dissolved silver concentrations above the 95% upper confidence limit of the breakpoint. These three sites were therefore excluded from the dataset used for the calculation of the measured regional background concentration, as it is possible that they are affected by local emission sources of silver. These sites were on the River Severn, the River Douglas, and the River Alt. The maximum mean dissolved silver concentration measured at these sites was 19.8 ng l^{-1} (standard deviation = 32.5 ng l^{-1}, number of samples = 5) on the river Alt. The maximum dissolved silver concentration in an individual sample (68.1 ng l^{-1}) was reported at the River Severn.

The remaining 81 sites were included in the derivation of the regional background concentration for dissolved silver. The highest mean dissolved silver concentration measured at these sites was 16.8 ng l^{-1} in the Arrow River.

Fig. 1 Results of the regional silver monitoring in England and Wales, mean values from 6 months sampling

Of these 81 sites, 54 (67%) had maximum silver concentrations which were below the limit of quantification. Amongst these sites, silver was not found above the limit of detection on any of the sampling occasions at 37 of the sites (46%). The remaining 24 sites had maximum dissolved silver concentrations of between 6.6 and 34.2 ng l^{-1}.

Because a high proportion of the data were censored (comprising sites reporting silver concentrations below the analytical limit of quantification)), the regional background concentration was calculated (after ECHA 2008) as the mean of the maximum values measured at each site using four alternative approaches to deal with censored data. The data treatments and mean values derived using them are shown below:

1. Substituting 0.5 × LOQ for sites where the maximum concentration was below the LOQ: 7.0 ng l^{-1}.
2. Substituting the LOD for sites where the maximum concentration was <LOD and 0.5 × LOQ for sites where the maximum concentration was below the LOQ: 6.9 ng l^{-1}.
3. Estimation of censored values (<LOQ) using a maximum likelihood estimation (MLE) approach (Cohen 1959): 6.9 ng l^{-1}.
4. Estimation of censored values (<LOQ) using the non-parametric Kaplan–Meier (KM) approach (Helsel 2005): 6.1 ng l^{-1}.

Substitution with 0.5 × LOQ is recommended in the ECHA technical guidance (ECHA 2008). However, such treatment is known to introduce a biased estimate of any subsequently calculated mean (Singh and Nocerino 2002) and represents a significant loss of information (Helsel and Cohn 1988). In general, substitution is only useful where the overall level of censorship in the dataset is small, e.g. <15%. In addition to substitution, the technical guidance provided by ECHA (ECHA 2008) also recommends the use of statistical extrapolation approaches which do not require a single arbitrary value to be substituted for values below the LOQ. The MLE and KM approaches are examples of such statistical approaches. However, these approaches can also be sensitive to the level of censorship in the dataset, although less sensitive than substitution. All of the methods used result in reasonably similar background concentrations, which provides reassurance that none is performing particularly badly given the overall level of censorship in the dataset. The mean value of 6.1 ng l^{-1} derived using the Kaplan–Meier method is selected as the most robust value for a regional background concentration of dissolved silver in freshwaters because the approach does not rely on substitution of censored data and does not assume the underlying distribution of the data (which MLE requires, e.g. log-normal). It is also considered to be more robust (less biased) at high levels of censorship than either substitution or MLE methods.

Mean concentrations of silver in surface waters are significantly ($p = 0.0001$) and positively correlated with the median DOC concentration measured at the same site ($r = 0.38$), although there is considerable variability in the observed relationship. The free silver ion is not expected to be the predominant species of silver in the freshwater environment and it is likely that the majority of dissolved silver (<0.45 μm) is associated with ligands such as DOC and metastable sulphide.

Silver is an extremely particle-reactive metal with distribution coefficients (Kd) between filtrate and particulate silver concentrations reported between $10^{4.5}$ and 10^{6} (Kramer et al. 2002). This is exceeded only by lead (Pb) among the most commonly considered metals. Dissolved silver measurements report the fraction which passes through a 0.45 μm filter and not free soluble silver. Silver also has a high affinity for colloids (Kramer et al. 2002). It is therefore likely that much of the silver reported as "dissolved" is actually associated with colloidal matter.

None of the surface water sites in the regional monitoring programme exceeded the PNEC for dissolved silver of 40 ng l^{-1}.

The measured regional background concentration includes all possible sources of silver. A measured regional background concentration therefore represents a worst case estimate of the possible regional background concentration of silver from any of the individual silver substances being registered under REACH. It will also include a contribution of silver from consumer uses of nanosilver-containing products and articles.

A potential complication with the regional surface water monitoring dataset is that it is likely to include sites which have an unidentified or unknown local emission source of silver, and therefore the dataset may not necessarily be restricted to sites which do not have a local emission source. A statistical approach was taken to identify sampling sites which are considered likely to receive unidentified local emissions of silver, and three of the sampling locations from the monitoring programme were removed for this reason.

The data obtained from this monitoring exercise indicate that if the silver PNEC of 40 ng l^{-1} were adopted as an EQS the potential compliance failure rate across England and Wales would be likely to be low. However, silver discharges were not specifically sampled in this study, although some of the sampling locations were considered to be impacted by silver discharges. There is, therefore, the potential for localised EQS failure in water bodies which receive emissions from silver producers and downstream users.

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