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Hazard/Risk Assessment

PROBABILISTIC ENVIRONMENTAL RISK ASSESSMENT OF ZINC IN DUTCH SURFACE WATERS

PATRICK A. VAN SPRANG,*† FREDERIK A.M. VERDONCK,†‡ PETER A. VANROLLEGHEM,‡
MARNIX L. VANGHELUWE,† and COLIN R. JANSSEN§
†EURAS, Rijvisschestraat 118/3, B-9052 Ghent, Belgium
‡Department of Applied Mathematics, Biometrics and Process Control, Ghent University, Coupure links 653, B-9000 Ghent, Belgium
§Laboratory for Environmental Toxicology, Ghent University, J. Plateaustraat 22, B-9000 Ghent, Belgium

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Abstract—In the framework of the European Union (EU) New and Existing Chemicals Policy, a regional risk assessment for Zn according to the current technical guidance documents and a probabilistic approach, by mathematically integrating both best-fitting exposure concentrations and species-sensitivity distributions into a probabilistic risk quotient distribution using Monte Carlo analysis, was explored for The Netherlands. Zinc is an essential element, and the current probability distributions may not adequately deal with this property. The threshold Pareto distribution provided the best fit to the chronic Zn toxicity data, resulting in a predicted-no-effect concentration ($PNEC_{add}$) for dissolved Zn of 34.2 μg/L, whereas use of the conventional normal distribution resulted in a $PNEC_{add}$ for dissolved Zn of 14.6 μg/L. The extracted exposure data resulted in a regional predicted environmental concentration (PEC) for dissolved Zn in the Dutch surface waters of 20.1 μg/L and in PEC_{add} values for dissolved Zn of between 15.5 and 17.3 μg/L, depending on the background correction used. The conventional deterministic risk characterization identified a regional risk for Zn in the Dutch surface waters. The more comprehensive probabilistic approach used in the present study, however, identified only very limited potential risks for the Dutch region. A probabilistic median risk, that the environmental concentration is greater than the no-observed-effect concentration of a species in Dutch surface waters (0.5–0.6%), depending on the inclusion of background correction, was obtained from the best-fitting distributions. Because probabilistic approaches provide a quantifiable and improved assessment of risk and quantification of the uncertainty associated with that assessment, these techniques may be considered as a way to improve the EU risk assessment procedures for data-rich substances.

Keywords—Zinc Probabilistic risk assessment Species-sensitivity distribution

INTRODUCTION

In the framework of the European Union (EU) New and Existing Chemicals Policy, an overall generic risk assessment for Zn is currently being prepared. Traditionally, risk assessments in this framework are performed at different geographical scales (i.e., local, regional, and continental) according to the methodologies laid down in the technical guidance document (TGD) ([1]; http://ecb.jrc.it/php-bin/reframer.php?). The potential environmental risks typically are estimated in a deterministic way using point estimates for both exposure and effect input parameters. In reality, the outcome of such risk assessments is subject to both unquantified uncertainty and variability. An improved approach might be to replace point estimates by realistic probability distributions representing the quantified uncertainty and/or variability in the exposure and effect input parameters. Variability represents the inherent heterogeneity or diversity in a well-characterized population. A fundamental property of nature, variability usually is not reducible through further measurement or study [2]. Temporal and spatial variations of chemical concentrations can be captured in a variability distribution called an exposure-concentration distribution (ECD). The different sensitivities of various species to a chemical can be described in a variability distribution called a species-sensitivity distribution (SSD). Usually, such distributions use continuous, bell-shaped functions, such as the normal [3] or the logistic [4] distribution. Although the possibility of introducing distribution functions with a finite threshold has recently been investigated by Brix et al. [5] and van Straalen [6], to our knowledge they have not been implemented in any regulatory exercises. The application of such threshold models seems to be more appropriate when considering essential elements, such as Zn. Indeed, for these elements, a certain concentration range is required for normal metabolic functioning of the organism. Below a certain concentration, the organisms become deficient, and the principle of toxicological sensitivity loses its meaning [6–8]. Such a deficiency threshold for Zn has been established for *Daphnia magna* by Muyssen and Janssen [8,9]. In this context, special attention was given to the introduction of fitting parametric threshold distributions to the chronic Zn toxicity data.

Uncertainty represents partial ignorance or lack of perfect information about poorly characterized phenomena or models (e.g., sampling or measurement error) and can be partly reduced through further research [10]. Expressing the results of an exposure or effect characterization as a probability distribution rather than as a single point estimate allows one to use all relevant exposure monitoring data or single-species toxicity data. This approach has the additional advantage that quantitative expressions of risks to communities of organisms can be established, thereby providing information regarding the magnitude of risks to an ecological community [5]. The use of probabilistic approaches for characterizing effects and exposure has been suggested by numerous authors as a way to account for the range of species sensitivities and exposure scenarios frequently encountered in the risk assessment of data-rich substances [11–16].

* To whom correspondence may be addressed (patrick.vansprang@euras.be).

Table 1. Chronic toxicity dataset[a]

Species groups	Species name	Life stage	Test system	Test duration (d)	Test water	pH	Hardness (mg/L as $CaCO_3$)	Endpoint	$NOEC_{add}$ (μg/L)	Species mean $NOEC_{add}$ (μg/L)	Reference
Algae	*Chroococcus paris*	NR	Static	10	Artificial	7.8	54	Growth	200	200	Les and Walker [26]
	Raphidocelis subcapitata	NR	Static	3	Artificial	7.4	24	Growth	50	35	Van Woensel [27]
	Raphidocelis subcapitata	NR	Static	3	Artificial	7.5	24	Growth	24		Van Ginneken [28]
	Synechoccus sp.	NR	Static	14	Artificial	7.8	54	Growth	390	390	Mohanty [29]
	Cladophora glomerata	NR	Static	3	Artificial	8.4	>35	Growth	60	60	Whitton [30]
Poriferans	*Ephydatia fluviatilis*	Cells	Static	7	Artificial	8.0	250	Development	43	43	Van de Vyver [31]
	Ephydatia muelleri	Cells	Static	7	Artificial	8.0	250	Development	43	43	Van de Vyver [31]
	Spongilla lacustris	Cells	Static	7	Artificial	8.0	250	Development	65	65	Van de Vyver [31]
	Eunapsis fragilis	Cells	Static	7	Artificial	8.0	250	Development	43	43	Van de Vyver [31]
Molluscs	*Dreissenia polymorpha*	Juveniles	Renewal	70	Lake	7.9	270	Survival	400	400	Kraak et al. [32]
	Potamopyrgus jenkinsi	Juveniles	Renewal	112	Lake	8.0	160	Growth	75	75	Dorgelo et al. [33]
Crustaceans	*Ceriodaphnia dubia*	Neonates	Renewal	7	River	6.0	81	Reproduction	25	33	Belanger and Cherry [34]
				7	River	8.0	81		25		
				7	River	9.0	81		25		
				7	River	6.0	118		25		
				7	River	8.0	118		50		
				7	River	9.0	118		25		
				7	River	6.0	168		17		
				7	River	8.0	168		50		
				7	River	9.0	168		33		
	Ceriodaphnia dubia	Neonates	Renewal	4	River	8.0	169	Reproduction	50		Masters et al. [35]
				4	River	8.0	169		14		
				7	River	8.0	169		50		
				7	River	8.0	169		100		
	Daphnia magna	Neonates	Renewal	21	Well	7.5	52	Reproduction	97	78	Chapman et al. [36]
				21	Well	7.7	104		43		
				21	Well	8.4	211		42		
	Daphnia magna	Neonates	Renewal	49	Pond	8.3	50	Reproduction	25		Paulauskis and Winner [37]
				49	Pond	8.3	100		75		
				49	Pond	8.3	200		150		
	Daphnia magna	Neonates	Renewal	21	Lake	7.7	45	Reproduction	35		Biesinger and Christensen [38]
	Daphnia magna	Neonates	Renewal	21	Lake	7.7	45	Reproduction	74		Biesinger et al. [39]
	Daphnia magna	Neonates	Renewal	21	Lake	8.1	225	Reproduction	310		Enserink et al. [40]
		Cohort of various ages		17	Lake	8.1	225		460		
	Daphnia magna	Neonates	Renewal	21	Lake	7.7	65	Reproduction	100		Münzinger and Monicelli [41]
				21	Lake	7.7	65		100		
				21	Lake	7.7	65		25		
	Hyalella azteca	Larvae	Renewal	70	Tap	8.3	130	Reproduction	42	42	Borgmann et al. [42]
Insects	*Ephoron virgo*	Larvae	Static	10	River	7.8	200	Survival	718	1,100	Van der Geest [43]
				10	Artificial	8.0	250		1,724		
	Chironomus tentans	Larvae	Static	56	Lake	7.7	45	Survival	137	137	Sibley et al. [44]

Table 1. (Continued)[a]

Species groups	Species name	Life stage	Test system	Test duration (d)	Test water	pH	Hardness (mg/L as $CaCO_3$)	Endpoint	$NOEC_{add}$ (μg/L)	Species mean $NOEC_{add}$ (μg/L)	Reference
Fish	*Brachydanio rerio*	Eggs	Renewal	14	Artificial	7.5	100	Hatching	2,900	660	Dave et al. [45]
				14	Artificial	7.5	100		180		
				14	Artificial	7.5	100		720		
				14	Artificial	7.5	100		180		
				14	Artificial	7.5	100		180		
				14	Artificial	7.5	100		180		
				14	Artificial	7.5	100		2,900		
				14	Artificial	7.5	100		2,900		
				14	Artificial	7.5	100		1,400		
	Jordanella floridae	Larvae	Flow through	98	Lake	7.5	44	Growth	26	44	Spehar [46]
				98	Lake	7.5	44		75		
	Phoxinus phoxinus	Yearlings	Flow through	150	Tap	7.5	70	Survival, growth	50	50	Bengtsson [47]
	Pimephales promelas	Eggs	Flow through	240	Lake	7.5	46	Reproduction	78	78	Benoit and Holcombe [48]
	Salmo gairdneri	Eyed eggs	Flow through	730	Tap	6.8	26	Survival	130	113	Sinley et al. [49]
				25	Tap	6.8	26		25		
	Salmo gairdneri	Eggs	Flow through	72	Well	7.0	27	Survival	440		Cairns and Garton [50]
	Salvelinus fontanilis	Yearlings	Flow through	1,095	Lake	7.4	45	Hatching	530	530	Holcombe et al. [51]

[a] Individual and species mean no-observed-effect concentration ($NOEC_{mold}$) values (most sensitive endpoint) were used for deriving species-sensitivity distribution and hazardous concentration at which 5% of all species are assumed to be affected. NR = not relevant.

The main objective of the present study is to explore the variability and uncertainty associated with Zn regional exposure and effects and to conduct a refined, probabilistic EU risk assessment for Zn in the Dutch surface waters and, as such, contribute to the Zn risk assessment exercise presently being conducted in the EU. An extensive comparison between several possible distribution models is made, including an exploration of applying models with a finite lower threshold in the effects assessment. Finally, a full probabilistic risk assessment is performed, which is aimed at capturing both the Zn toxicity and monitoring data in a probabilistic way, thus providing a quantified and improved risk assessment.

MATERIALS AND METHODS

Effects assessment

Data collection and aggregation. Long-term ecotoxicity data regarding Zn for aquatic organisms belonging to different trophic levels were taken from the literature. The aquatic toxicity data that might be useful for the effects assessment were evaluated on the basis of both reliability and relevance criteria. Reliability criteria cover the inherent quality of a test relating to the test methodology and the way that the performance and results of a test are described (e.g., a proper description of the test methodology and the observation of a clear concentration–effect relationship); relevance criteria cover the extent to which a test is appropriate for a particular risk assessment. In relation to the latter, only toxicological endpoints, which may reflect effects at the population level, were taken into account (i.e., survival, growth, reproduction, hatching, and development). In addition, the test media used in the toxicity tests should be representative of the environmental compartment being studied. In that respect, the following values for pH, hardness, and background Zn concentrations were used for data selection, primarily departing from the current Organisation for Economic Cooperation and Development (Paris, France) guidelines: pH between 6 and 9, hardness between 24 and 250 mg/L as $CaCO_3$, and the background Zn concentration in the test media having a minimum value for soluble Zn of 1 μg/L.

The selected dataset is similar to the one used in the ongoing Zn risk assessment exercise conducted under the Commission Directive 93/67/European Economic Community and Commission Regulation 1488/94. According to the TGD [1], preference is given to the extraction of real no-observed-effect concentration (NOEC) values. However, the concentration that is estimated to be lethal or to cause an effect in 10% of the test organisms (L(E)C10) values could also be used if no NOEC values are available. If multiple chronic NOEC and/or L(E)C10 values for the same species and endpoint were available, geometric means were used as the input for the SSD. Such aggregation avoids overrepresentation of specific species within the SSD, and this approach is in agreement with that proposed in the TGD [1]. If for one species several mean chronic values were available, the lowest was selected. The selected data with additional background information are summarized in Table 1. In the present analysis, the results of the aquatic toxicity studies are reported as added Zn concentrations, which are the nominal or measured concentrations corrected for background Zn concentrations in the ecotoxicity tests. Note that the same NOEC is observed for three species of the poriferans tested in a single laboratory where the same test concentrations were used. The TGD suggests that this may cause a lack of fit in the determination of the SSD [1]. From the calculated species mean NOEC and/or L(E)C10 values,

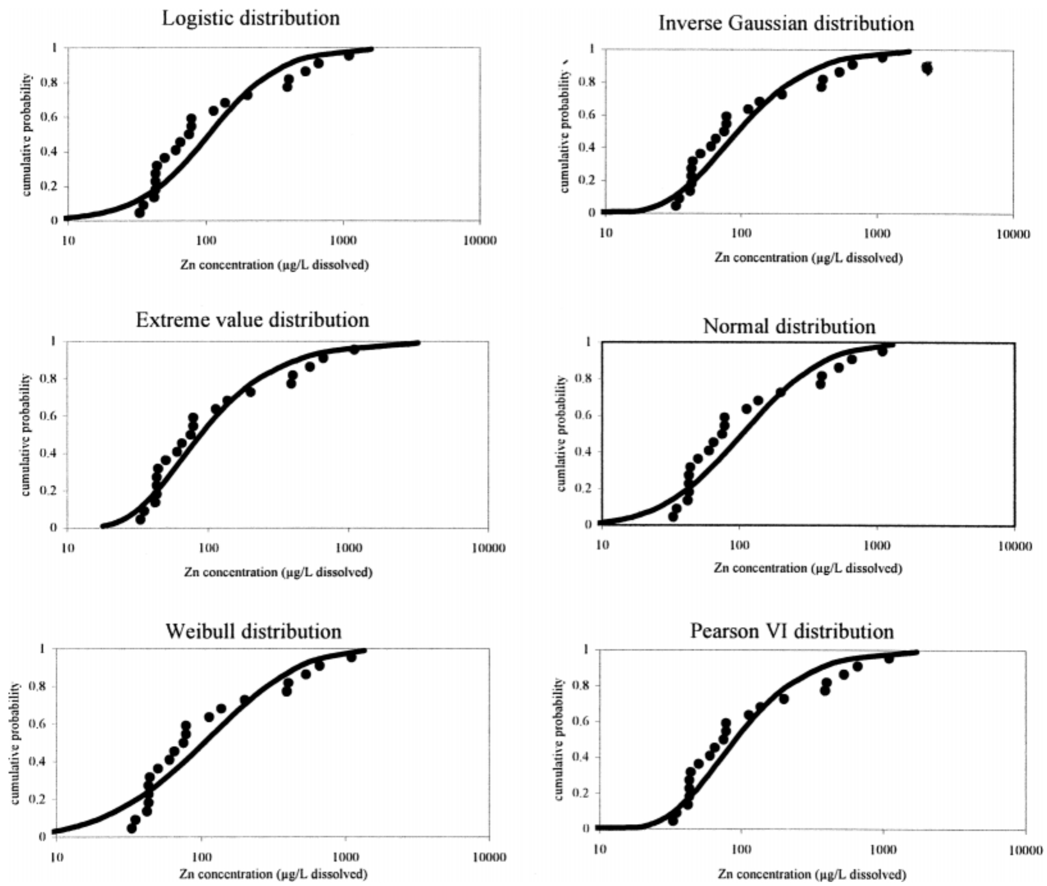

Fig. 1. Nonthreshold parametric distribution models fitted to the chronic no-observed-effect concentration.

different SSDs were generated, and the associated 95% protection level or a hazardous concentration at which 5% of all species (HC5) are assumed to be affected was estimated.

Determination of SSD, HC5, and uncertainty. Several parametric and nonparametric techniques were used to derive SSDs and their percentiles. Nonparametric techniques as described by Cullen and Frey [10] were used for computing the percentiles of a given dataset. These methods are referred to as plotting positions, which are estimates of the cumulative probability of a data point. The cumulative probability of a data point X_i is calculated according to the method described by Hazen [17], using the formula $F(X_i) = (i - 0.5)/n$. In this formula, i stands for the rank order of the sorted Zn toxicity data, and n stands for the total number of data points. After the observed data were plotted, the percentiles were calculated by taking the inverse empirical distribution function.

In addition, several parametric distributions (normal, logistic, beta, extreme value, inverse gaussian, Pearson VI, gamma, Weibull, Pareto, and triangular) were fitted to the log-transformed toxicity dataset using the Bestfit software package (Palisade, Newfield, NY, USA). From these fitted SSDs, the HC5 was derived [18].

To assess the fit of a specific distribution, both goodness-of-fit tests plots of cumulative distribution functions were used [19,20]. Preference is given to the Andersen–Darling goodness-of-fit test, because it places more emphasis on the tail of the distribution [19], which is the region of interest in risk assessments. The calculated goodness-of-fit statistic measures how good the fit is, and it is used in a relative sense by comparing that of a specific distribution to the goodness-of-fit statistics of other distributions. In addition, critical values are calculated and used to determine whether a fitted distribution should be accepted or rejected at the confidence level of 0.05. A value of the calculated Andersen–Darling statistic above the 95th percentile of the test statistic distribution leads to rejection of the null hypothesis; in other words, the distribution is not a good fit [10]. Another means for interpreting the results of fitting a distribution is by graphically assessing how well a distribution agrees with the input data.

The added HC5 was calculated as the median estimate (or 50% confidence level). To assess the sampling uncertainty of the SSD and its derived quantiles, bootstrap simulations [21] were performed. From the Zn toxicity dataset (of species means), random sampling with replacement of the freshwater NOEC data was conducted. In this approach, a nonparametric or parametric distribution was assumed, and 2,000 replications of the original dataset were performed by random sampling with replacement n values ($n = 21 =$ size of the Zn toxicity dataset). For these 2,000 replicates, HC5 values were calculated, and from these 2,000 HC5 values, the median and 90% confidence interval for HC5 was calculated. Note that all reported HC5 values in the present study are medians (as requested by the TGD). Finally, the predicted-no-effect concentration (PNEC) is calculated as [1]:

$$\text{PNEC} = \text{HC5}/AF \quad (1)$$

where AF represents an assessment factor of between one and five, depending on the uncertainties related to the derivation of the HC5. According to the TGD [1], the following points should be considered when determining the size of the as-

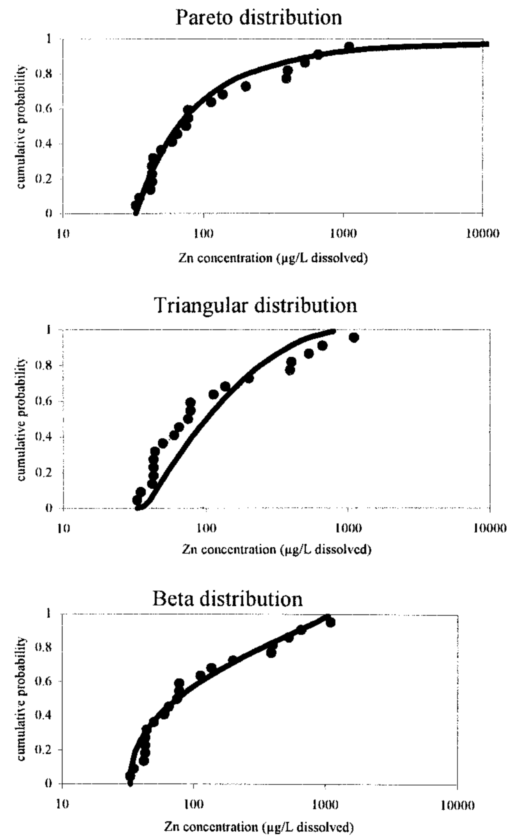

Fig. 2. Threshold parametric distribution models fitted to the chronic no-observed-effect concentration data.

sessment factor: The overall quality of the database and the endpoints covered, the diversity and representativeness of the taxonomic groups covered by the database, the mode of action of the chemical, the statistical uncertainties around the fifth percentile estimate, and the comparison between field/mesocosm studies and the fifth percentile. However, because no scientifically robust approach currently exists for the quantification of these uncertainties and, therefore, for the estimation the size of *AF*, this value has been set to one.

Exposure assessment

Data collection. The monitoring data for the Dutch surface waters were provided by the Institute for Inland Water Management and Waste Water Treatment. This database contained measured Zn concentrations in both small bodies of water (smaller streams, lakes, canals, and ditches) and large bodies of water (e.g., Meuse, Rhine, and Scheldt) in The Netherlands, and it was considered to be representative for the whole Dutch region. The database for small bodies of water contained 89,798 different individual measurements from 1990 to 1998, and the database for large bodies of water contained 23,637 individual data points from 1990 to 2000. Sampling frequency in the different databases varied, depending on the sampling year and site, from one sampling every two months up to two samplings per month. From the 2,183 individual Zn measurements in 1998 that were obtained from the Dutch surface-water database, total Zn concentrations ranged from 1 to 650 μg/L. No values less than the detection limit were reported in the database.

Determination of ECD, 90th percentile, and uncertainty.

Table 2. Goodness-of-statistics with ranking and null hypothesis testing at 95% confidence

Distribution	Goodness-of-fit statistic (Andersen–Darling)	Ranking	Critical values at 0.05 level
Pareto	0.67	2	2.49
Beta	0.66	1	2.49
Extreme value	0.70	3	0.76
Inverse gaussian	0.94	4	2.49
Pearson VI	0.96	5	2.49
Gamma	1.02	6	2.49
Weibull	1.13	7	0.76[a]
Normal	1.17	8	0.79[a]
Triangular	3.47	9	2.49[a]
Logistic	1.34	10	2.49

[a] Null hypothesis rejected (5% level).

Similar to the approach used in the effects assessment, the variability of environmental Zn concentrations was characterized using realistic ECDs based on the collected monitoring data and using parametric and nonparametric techniques. From these ECDs, a predicted environmental concentration (PEC) was computed as the 90th percentile of the measured Zn concentrations in the sampled surface waters. This approach is in agreement with the realistic worst-case philosophy as described in the TGD [1]. In addition, outliers were identified and removed from the dataset using the following quantitative statistical criterion [1]:

$$\log_{10}(X_i) > \log_{10}(p_{75}) + K(\log_{10}(p_{75}) - \log_{10}(p_{25})) \qquad (2)$$

where X_i is the *i*-th concentration (above which a measured value may be considered to be an outlier), p_i is the value of the *i*-th percentile of the statistic (calculated here based on the mean and standard deviation of the log-transformed data), and K is the scaling factor (default = 1.5).

When performing a risk assessment of a metal, it is of utmost importance that both the exposure and effect assessments are based on similar levels of bioavailability [1]. The monitoring data reported as total Zn concentrations were translated to dissolved Zn concentrations using the equilibrium partitioning methodology (K_d) with the following formula:

$$[\mathrm{Zn}]_{\mathrm{dissolved}} = [\mathrm{Zn}]_{\mathrm{total}}/(1 + K_d \cdot C_s \cdot 10^{-6}) \qquad (3)$$

where K_d is for the equilibrium partitioning coefficient (110,000 L/kg for Dutch rivers according to Stortelder et al. [22]), C_s is the suspended matter concentration (18.6 mg/L

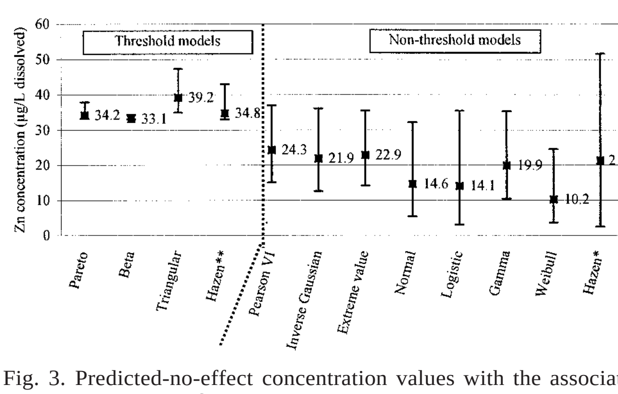

Fig. 3. Predicted-no-effect concentration values with the associated 90% uncertainty confidence limits. *Bounded by zero, **bounded by the lowest no-observed-effect concentration.

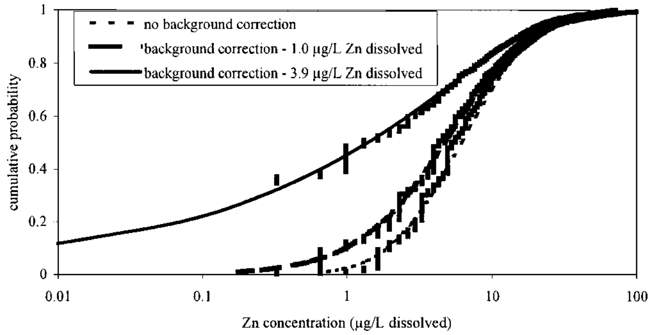

Fig. 4. Environmental concentration distribution for dissolved Zn with and without background correction in the Dutch region.

Table 3. Summary table of calculated deterministic risk quotients and probabilistic risks[a]

SSD[b]	ECD[b]	No backround (log-normal, PEC_{90} = 20.1 μg/L)	12 μg/L background (gamma, PEC_{90} = 15.5 μg/L)
Normal	PNEC = 14.6 μg/L	RCR = 1.4 2.2%	RCR = 1.1 Not calculated
Pareto	PNEC = 34.2 μg/L	RCR = 0.6 0.5%	RCR = 0.5 0.6%

[a] ECD = exposure-concentration distribution; PEC = predicted environmental concentration; PNEC = predicted-no-effect concentration; RCR = risk characterization ratio; SSD = species-sensitivity distribution.

[b] All distribution models fit on the log-transformed data.

calculated as the mean concentration in the Dutch surface waters), $[Zn]_{dissolved}$ is the dissolved Zn concentration (μg/L), and $[Zn]_{total}$ is the total Zn concentration (μg/L).

By subtracting the natural background from the measured ambient concentrations, the PEC anthropogenic (PEC_{add}) was also estimated. Zuurdeeg et al. [23] considered the geometric mean value of the ambient background concentrations (12 μg/L) as the best-guess estimate for the natural background concentration of total Zn in Dutch surface waters. According to those same authors, the lower limit of the natural background concentration of total Zn in these waters can be set at 3 μg/L. Hence, in the present study, these two different scenarios are used (both the lower limit of 3 μg/L and the mean value of 12 μg/L) for correcting the available monitoring data in the risk characterization.

Techniques similar to those used in the effects assessment were applied: The best-fitting distributions were selected using probability plots and goodness-of-fit tests, and bootstrap simulations were used to account for uncertainty. Random sampling of the exposure concentrations was conducted with replacement (2,000 replications) of the original dataset by random sampling with replacement n values (n = size of the original monitoring dataset = 21).

Risk characterization

The potential risks of Zn in Dutch surface waters were estimated using the conventional approach based on the quotient of single values representing exposure and effects (i.e., PEC/PNEC or risk characterization ratio) and using the probabilistic approach. A risk characterization ratio exceeding one suggests that Zn is present at levels that may pose a risk to the ecological receptors. In the probabilistic framework, the risk characterization results in probabilistic risk quotient distributions, which are based on the combination of both exposure and effect probability distributions. This approach is analogous to the joint probability curve method developed by Solomon et al. [24,25]. The potential risk is defined as the probability that some randomly selected environmental concentration (EC) exceeds some randomly selected species sensitivity (SS) for Zn. The probability of EC exceeding SS is equal to the probability that the risk quotient EC/SS becomes larger than one, and it can be regarded as a measure of adverse effects [16]. To calculate the probabilistic risk and its uncertainty interval two-dimensional (2D) Monte Carlo analysis was conducted (Splus; Insightful, Seattle, WA, USA). The 2D Monte Carlo simply consists of two Monte Carlo loops nested one inside the other [10]. The inner loop deals with the variability (i.e., ECD and SSD), and the outer loop deals with the uncertainty of the parameters specifying the ECD and SSD (1,000 × 100 shots, respectively, were simulated). This approach results in risk distributions surrounded by two confidence limits corresponding to the 5th and 95th percentiles of the uncertainty distribution.

RESULTS AND DISCUSSION

Effects assessment

Graphical assessment using cumulative distribution functions was used for an initial visual evaluation of the fit of a specific distribution. The plot indicates that the data deviate from the conventional normal distribution at the lower tail (Fig.

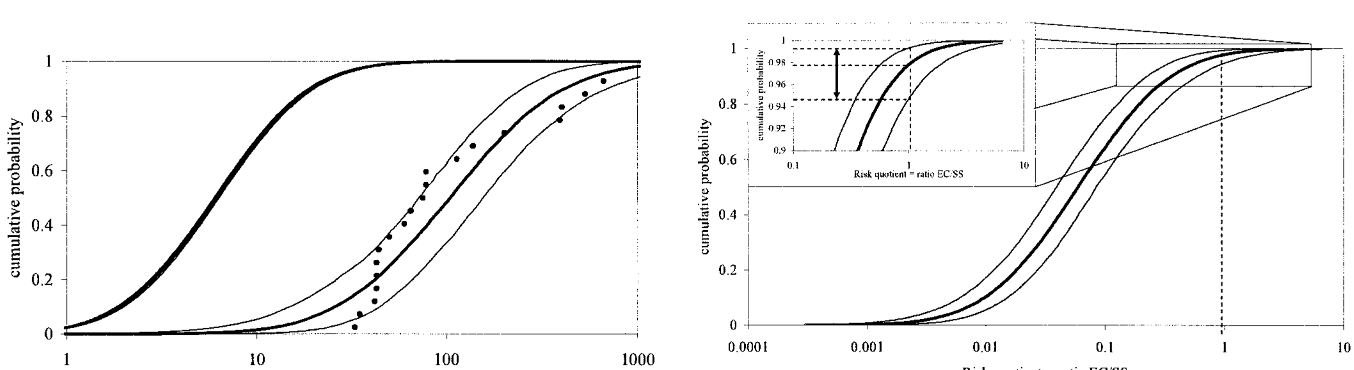

Fig. 5. Probabilistic risk quotient distribution and its uncertainty for the Dutch region based on log-normal exposure concentration (EC) distribution (no background concentration used) and normal species-sensitivity (SS) distribution.

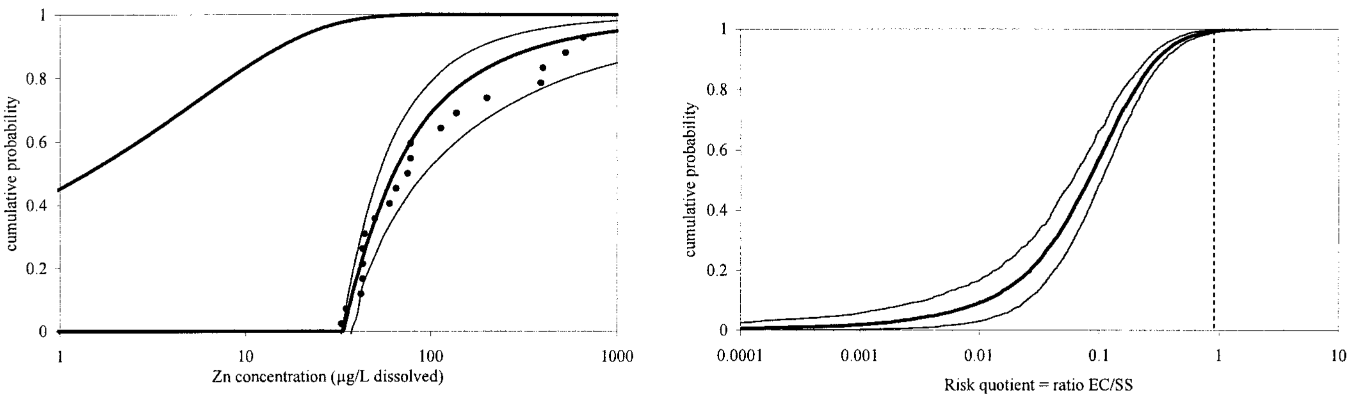

Fig. 6. Probabilistic risk quotient distribution and its uncertainty for the Dutch region based on log-normal exposure concentration (EC) distribution (background concentration of 12 μg/L used) and Pareto species-sensitivity (SS) distribution (both best-fit models).

1). Similar conclusions can be formulated for the other investigated parametric nonthreshold models. These models all tend to overestimate toxicity in the lower tail, which is the critical region for the PNEC derivation. The results of fitting different nonthreshold distribution models (logistic, inverse gaussian, extreme value, Weibull, gamma, Pearson VI, and normal distributions) to the chronic Zn toxicity data are summarized in Figure 1.

The data were also fitted to parametric distributions with a finite lower threshold, such as Pareto, beta, and triangular (Fig. 2). These distributions all produced threshold estimates corresponding to the lowest $NOEC_{add}$ of 33 μg/L of Zn in the Zn toxicity database. Except for the triangular distribution, which tended to underestimate the data in the lower concentration range, these threshold models produced a better fit than the nonthreshold models for the chronic Zn $NOEC_{add}$ data, especially in the region of interest (i.e., the lower tail).

Van Straalen [6] also explored the use of models that allow estimation of the finite threshold of a SSD. Van Straalen suggested that such models are more appropriate for use in the risk assessment of essential metals, such as Zn and Cu. His analysis suggested that among the various models explored, the threshold triangular model provided the best fit to the chronic aquatic toxicity data for Zn. Similarly, Brix et al. [5] recommended the use of alternative models to describe chronic SSDs for copper. With the exception of those for cladoceran data, logistic regressions tended to provide extremely poor fits of the toxicity data around the lower tail of the estimated chronic SSDs. Hence, those authors selected the threshold Pareto model to describe the chronic SSDs, and they suggested the existence of a chronic threshold for Cu reflecting the ability of an organism to regulate its internal concentration.

In addition to the graphical assessment, the performance of the distribution fitting to the data was assessed using goodness-of-fit statistics. The smaller the discrepancy between the hypothesized and the observed distributions, the better the fit. Goodness-of-fit statistics with ranking and null hypothesis testing at 95% confidence are summarized in Table 2. The threshold models Pareto and beta seemed to produce the best fits, whereas the conventional normal and logistic parametric models resulted in the poorest fits.

The goodness-of-fit statistic calculated according to the Andersen–Darling method was, for most distributions, less than the 5% critical value (i.e., 95% confidence), meaning that we had no reason to reject these fitted distributions (Table 2). However, the Weibull, normal, and triangular distributions produced a goodness-of-fit statistic larger than the critical value at 95% confidence. Therefore, the null hypothesis was not accepted, and the fitted distributions were rejected.

From both the cumulative probability plots and the Andersen–Darling statistics, the best fit of the Zn toxicity data was achieved with the Pareto distribution and, therefore, was selected for the final effects assessment. The estimation of the uncertainty around the HC5 values ($PNEC_{add}$ values with their 90% confidence interval) is presented in Figure 3. The analysis of such uncertainty for the conventional normal and logistic SSDs revealed very similar $PNEC_{add}$ values of, respectively, 14.6 and 14.1 μg/L of dissolved Zn. The $PNEC_{add}$ values es-

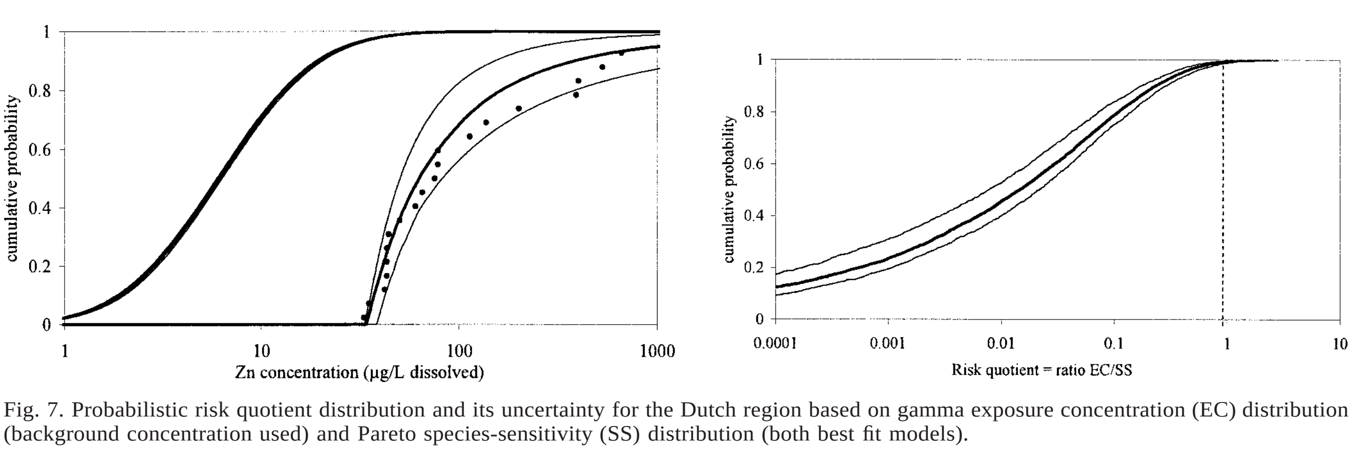

Fig. 7. Probabilistic risk quotient distribution and its uncertainty for the Dutch region based on gamma exposure concentration (EC) distribution (background concentration used) and Pareto species-sensitivity (SS) distribution (both best fit models).

timated with the nonthreshold models ranged between 10.2 and 24.3 μg/L of dissolved Zn and were consistently lower than those obtained with the better-fitting threshold models. Application of these latter models resulted in $PNEC_{add}$ estimates ranging between 33.1 and 39.2 μg/L of dissolved Zn.

Exposure assessment

The data treatment of these monitoring data revealed that the parametric method, assuming a log-normal distribution, provided a good fit of the monitoring data for the Dutch region. It also revealed that the PEC value was similar to that obtained with the nonparametric (Hazen plotting) approach (i.e., 90th variability percentiles of, respectively, 20.1 and 19.7 μg/L of dissolved Zn).

Subtracting a regional background concentration for The Netherlands of 3 or 12 μg/L of total Zn from each individual monitoring data point resulted in a poor fit of the data based on the conventional log-normal distribution. The effect of background correction was pronounced at the lower percentiles but negligible at the highest percentiles. The best fit for the background-corrected monitoring data using a parametric function was achieved using the gamma distribution for the background scenario of 12 μg/L of total Zn, whereas the Pearson VI distribution resulted in the best fit for the background scenario of 3 μg/L of total Zn (Fig. 4). Subtracting a regional background concentration of 12 μg/L of total Zn (or 3.9 μg/L of dissolved Zn) or of 3 μg/L of total Zn (or 1.0 μg/L of dissolved Zn) to all individual Zn measurements lowered the PEC value for The Netherlands, resulting in PEC_{add} values of, respectively, 15.5 and 17.3 μg/L of dissolved Zn (for each background concentration based on best fit). Removal of outliers from the monitoring database did not alter the PEC_{add} value for The Netherlands (data not shown).

The uncertainty analysis on the environmental concentration distributions revealed very narrow confidence limits because of the large sample size of monitoring data, resulting in a 5% confidence limit that can hardly be distinguished from the 95% confidence limit.

Risk characterization

According to the conventional deterministic risk characterization approach, a potential regional risk associated with Zn in the Dutch surface waters was identified. Indeed, the comparison of the regional PEC_{add} for The Netherlands—that is, 15.5 μg/L (using a background correction of 12 μg/L of total Zn) and 17.3 μg/L of dissolved Zn (using a background correction of 3 μg/L of total Zn)—with the $PNEC_{add}$ of 14.6 μg/L of dissolved Zn (using the conventional normal distribution) resulted in risk characterization ratios of 1.1 and 1.2, respectively. An overview of all calculated deterministic and probabilistic risks is provided in Table 3.

The application of the probabilistic risk assessment techniques revealed, conversely, very limited potential regional risks associated with Zn in the Dutch surface waters. The uncertainty (because of sampling error) is visualized as a confidence band around the ECD and SSD. When the SSD based on the conventional normal distribution was combined with the log-normal ECD, a low estimated regional risk of 2.2% of the PEC exceeding the NOEC of a species at 50% probability was calculated (Fig. 5). In other words, a 50% certainty existed that the potential risk in the Dutch surface waters because of the presence of Zn was less than or equal to 2.2%. At the 95% certainty level, the risk is less than or equal to 5.3%. These figures, however, represent a worst-case risk scenario, because no background correction was incorporated in the exposure assessment and the conventional normal SSD, which overestimates toxicity, was used in the effects assessment.

A first refinement of the probabilistic risk characterization was performed by replacing the conventional normal SSD with the (best-fitting) Pareto SSD. The results of this analysis are presented in Figure 6. The risk characterization shows a negligible median estimated risk of 0.5% at 50% certainty or of 0.9% at 95% certainty. The incorporation of a background correction of 12 μg/L of total Zn in the ECD combined with the best-fitting Pareto SSD, which can be considered as the most realistic scenario, had no further effect on the probabilistic risk estimates (Fig. 7). Indeed, very similar risk estimates were extracted from the probabilistic analysis (i.e., a risk of 0.6% at 50% certainty and a risk of 1.0% or less at 95% certainty). Similar to the exposure assessment, the effect of background correction was pronounced at lower percentiles but negligible at the highest percentiles, which is the region of interest in this specific probabilistic risk quotient distribution. The small differences in probabilistic risk estimates between both scenarios (i.e., inclusion of background correction or not) probably are caused by numerical–analytical differences.

CONCLUSION

The outcome of the risk characterization analysis depends considerably on the type and relevancy of the approach used to account for data variability and/or uncertainty. First, it should be emphasized that use of the conventional normal or logistic distributions are pragmatic choices, and goodness-of-fit statistics and graphical inspection should therefore be used to select the most appropriate distribution for the collected exposure and toxicity data, as shown here with threshold distributions for Zn. Second, the probabilistic assessment considers the quantitative information for the full range of possible Zn exposures in the aquatic environment and species sensitivity to Zn. This approach may therefore be considered as being more realistic compared to the conventional deterministic framework, which uses (conservative) point estimates of both exposure (PEC) and effect (PNEC), even if based on probabilistic methods. Probabilistic risk assessment estimates the probability that an environmental concentration exceeds the species sensitivity. In the present study, a probabilistic median risk of between 0.5 and 0.6%, depending on the inclusion of background correction, was obtained from the best-fitting distributions. It is therefore suggested to use this approach for the assessment of potential environmental risks from data-rich substances, such as Zn.

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