

Added value of concentration-duration-frequency curves of wastewater treatment plant effluent and river water quality

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Abstract: Effluents of wastewater treatment plants are a major source of contaminants in river catchments. Several pollutant modelling and simulation complexities can be used to predict the pollutant concentration in rivers. In contrast to classic deterministic simulations, uncertainty and variability are explicitly accounted for in probabilistic modelling, e.g. by means of Monte Carlo simulations. In this paper, an even more detailed modelling framework is presented, i.e. the dynamics of the processes are explicitly included in the model. One possibility to achieve this is to calculate pollutant time-series. To interpret these detailed time-series, the possibility of concentration-duration-frequency curves (CDF-curves) is explored and compared with the less detailed probabilistic methods. The use of CDF-curves is demonstrated to be more realistic. In addition, it is illustrated how this method can be used as a decision-support tool in risk assessment practice.

Keywords: *Probabilistic environmental risk assessment; Ammonia; Dynamic models*

1. INTRODUCTION

Yearly, many existing and new chemicals are released in the environment. Regulation puts constraints on these chemical emissions and these are based on environmental risk assessment. The goal of risk assessment is to estimate the likelihood and the extent of adverse effects occurring to humans and ecological systems due to exposure(s) to substances. Environmental risk assessment is based on the comparison of a predicted or measured exposure of environmental concentration (EC) (determined in an exposure assessment) with a 'no effect concentration' based on a set of (acute or chronic) ecotoxicity test results (i.e. testing species sensitivity (SS) in an effects assessment).

Environmental risk assessment is typically prone to uncertainty and variability. Variability represents inherent heterogeneity or diversity in a well-characterised population. Fundamentally a property of nature, variability is usually not reducible through further measurement or study. The two main sources of variability in the exposure assessment are temporal and spatial variations of chemical concentrations in e.g. the environment such as rivers. In the effects assessment, different species have different

sensitivities towards the same chemical. This inter-species sensitivity is therefore an important source of variability. But, spatial and temporal variability of species sensitivity are also important. For example, the toxicity of a chemical towards a species depends on the duration and frequency of the exposure. Uncertainty represents partial ignorance or lack of perfect information about poorly characterised phenomena or models (e.g. sampling or measurement error), and can partly be reduced through further research (Cullen and Frey 1999).

Different levels of complexity can be distinguished to deal with uncertainty and several types of variability in the exposure and effects assessment. Figure 1 shows an overview of several tiers of different level of detail. In the top panel, the deterministic environmental risk assessment is visualised. A (random) variable (be it the exposure concentration or the species sensitivity) is considered as a crisp value. Uncertainty is partly ignored, partly considered in assessment or safety factors. The well-known environmental quality standard would fit in this tier. The second panel represents the probabilistic environmental risk assessment. It is an extension of the deterministic approach since both the inherent variability and uncertainty (shown as a

grey band) is explicitly quantified and assessed (Verdonck et al. 2002). However, all types of variability are considered in one distribution. This can lead to large variances (wide distributions) and thus result into conservative assessments having a higher probability of a large risk. Time-referencing would further increase the level of detail and realism as time-specific information would be accounted for. This is represented in the lower panel of Figure 1. Time related information can be formatted in two ways in an attempt to capture the temporal variability. First, time-series can be used as such or second, time-series can be translated into Concentration-Duration-Frequency curves (CDF curves). CDF curves are three-dimensional plots with on the three axes the concentration, the duration of an exceedance above a particular concentration and the frequency of an exceedance above a particular concentration with a particular duration. Geo-referencing could also further increase realism. An example is given in Verdonck et al. (2002), but not dealt with here.

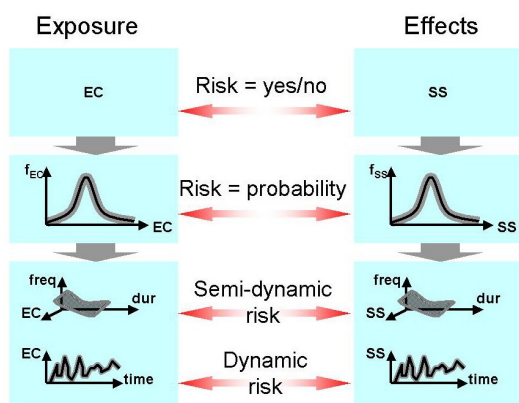


Figure 1. Several tiers of environmental risk assessment of chemicals: top: deterministic risk assessment, below top: probabilistic risk assessment, bottom: (semi-)dynamic risk assessment (EC: Exposure Concentration, SS: Species Sensitivity, grey band: 90% uncertainty band)

The goals of this paper are to explore the possibility and usefulness of CDF curves and to compare them with the less detailed probabilistic methods. In addition, it will be illustrated how this CDF method can be used as a decision-support tool in risk assessment practice. The comparison between the two will be done by means of a case study.

2. CASE STUDY

2.1. Problem formulation

One of the challenges Aquafin NV, the company responsible for WasteWater Treatment Plant (WWTP) infrastructure in Flanders (Belgium), is now facing is to upgrade the patrimony of old municipal WWTPs. These plants need to be retrofitted towards strict phosphorus and nitrogen removal consents. With this aim, a risk assessment procedure was developed based on a dynamic WWTP model with an uncertainty analysis module (Rousseau et al. 2001). The two main outputs of the procedure are a probabilistic exposure concentration distribution and an exposure Concentration-Duration-Frequency curve (CDF_{exposure}). Both are accompanied with an uncertainty or confidence band.

A simplified case study is worked out here. The effect of total ammonia in the effluent of the WWTP in Hove (Belgium) (Bixio et al. 2002) on the aquatic salmonid community in the receiving river “Bautersembeek” is studied (see Figure 2). Only the direct, acute toxic effects on salmonid fish populations are more specifically studied. Indirect effects as eutrophication and chronic effects are not dealt with here. Note that there are no combined sewer overflows considered.

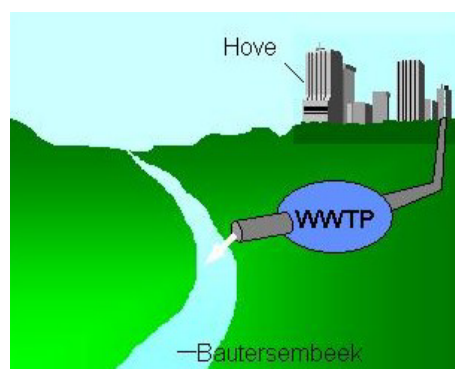
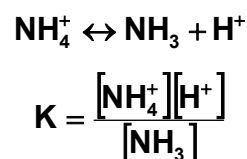


Figure 2. Situation sketch (WWTP: WasteWater Treatment Plant)

A key factor is the chemical speciation of ammonia. In aqueous solution, ammonia primarily exists in two forms, un-ionised ammonia (NH_3) and ammonium ion (NH_4^+), which are in equilibrium with each other according to:



The individual fractions of NH_3 and NH_4^+ vary markedly with temperature and pH. The

mechanisms of these effects are poorly understood, but the pH dependence strongly suggests that joint toxicity of NH_3 and NH_4^+ is an important component (EPA 1999). NH_3 is much more toxic than the NH_4^+ . Because of the importance of NH_3 , it became a convention in the scientific literature to express ammonia toxicity in terms of NH_3 , and water quality criteria and standards followed this convention. However, there are reasons to believe that NH_4^+ can contribute significantly to ammonia toxicity under some conditions (especially pH) (EPA 1999). Therefore, all concentrations will here be expressed as Total Ammoniacal Nitrogen (TAN).

2.2. Dynamic model + uncertainty analysis

The total ammonia probability distributions and CDF curves in the river are both based on the daily effluent time-series of the WWTP Hove. These effluent time-series are predicted by means of a dynamic WWTP simulation model. More details on the model and its calibration and verification can be found elsewhere (Bixio et al. 2002; Peterson et al. 2003). No dilution is assumed to convert the total ammonia probability distribution and CDF curve of the WWTP effluent to the river. This assumption was made because the river flow is mainly determined by the effluent discharge flow of the WWTP and for conservative reasons. Obviously, a more realistic approach would be to account for the upstream river flow and TAN concentration time-series, and as a result to obtain time-series of dilution factors. Nevertheless, the main goal of this paper is to show the possibilities and potential of both proposed applications. This assumption is therefore acceptable in this perspective.

The Monte Carlo simulation takes into account both parameter and input uncertainty, in this way dealing with the difficulties to estimate model parameters and taking into account the inherent uncertainty in specific processes. As a consequence, the two resulting model outputs, namely the effluent probability distributions and CDF curves, will be accompanied by an uncertainty or confidence band expressing the prediction uncertainty due to the uncertainty of the input variables. More information on this can be found in Rousseau et al. (2001) and Rousseau et al. (2000).

3. PROBABILISTIC RISK ASSESSMENT

3.1. Exposure assessment

In probabilistic environmental risk assessment, the two most important sources of variability for the exposure concentration are spatial and

temporal variability. Spatial and temporal variations of chemical concentrations in a river or WWTP effluent can be captured in a variability distribution, called Exposure Concentration Distribution (ECD). In the left part of Figure 3, the total ammonia exposure concentration distribution in the river (predicted by the simulation model) is shown as a cumulative distribution function by the black line. The 90% uncertainty band (resulting from the Monte Carlo analysis) is shown in Figure 3 as a grey band around the exposure concentration distribution. Point A in Figure 3 (indicated by arrow) on this distribution can be interpreted as follows: 60% of the TAN concentrations are lower than 10 mg of total ammonia nitrogen TAN/l. A 90% confidence or uncertainty interval on that is 8-13.2 mg TAN/l.

3.2. Effects assessment

Acute ecotoxicity data were collected from EPA (1999). The assessment endpoints are $\text{LC}_{50\text{S}}$ which are lethal concentrations at which 50% of the organisms will die. Only data on salmonid species were considered. The $\text{LC}_{50\text{S}}$ were expressed as TAN at pH 8 (equivalent to EPA (1999)).

Various species have different sensitivities towards a chemical (i.e. there exists inter-species sensitivity/variability). These differences can also be captured in a variability distribution called a Species Sensitivity Distribution (SSD). In the right part of Figure 3, the (salmonid) SSD is shown as a cumulative distribution function (black line). The sampling uncertainty is shown as a 90% confidence band and was determined by a parametric bootstrap method (Verdonck et al. 2001). Point B in Figure 3 (indicated by arrow) can be interpreted as follows: there is 95% certainty that 80% of the fish species will not be affected (50% lethality) at TAN concentration lower than 12.6 mg TAN/l.

3.3. Risk assessment

Characterisation of the risk of toxicants towards species, when both exposure and effects are variable and uncertain, is the central issue in probabilistic environmental risk assessment. The resulting risk is a probability and can be calculated mathematically (Verdonck et al. submitted). In addition, the risk probability can be accompanied with a confidence or uncertainty interval (e.g. mean risk of 23% and its 90% confidence or uncertainty interval is 15-30%).

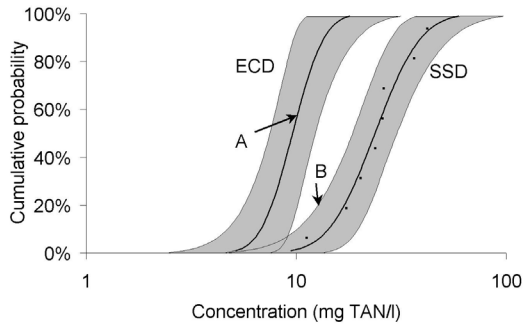


Figure 3. The Exposure Concentration Distribution (ECD) and the salmonid Species Sensitivity Distribution (SSD) of Total Ammonia Nitrogen (TAN) downstream of the wastewater treatment plant of Hove

A probabilistic environmental risk assessment was conducted for this case study based on the ECD obtained from dynamic model predictions and an SSD of salmonid species (with LC_{50} endpoints). The resulting risk is 8.4%, which may not be acceptable for a water manager. This is especially true when its accompanying 90% uncertainty interval, based on parameter uncertainty in the WWTP model and sampling uncertainty of the ecotoxicity tests, is also considered. Risk is expected to range between 0.3-28%. This means that a water manager is 95% certain that the risk is smaller than 28%. This may not be accepted especially because the LC_{50} endpoints are not suitable for sustainable salmonid fishery.

There are two possibilities to refine this risk assessment. First, the uncertainty could be reduced by either performing more toxicity tests that will result in a smaller uncertainty band on the SSD. Or, the uncertainty on the input parameters of the WWTP model could be reduced by collecting more samples or knowledge. This could be a reasonable option if the median risk of 8.4% is around an acceptable level. Indeed, reducing uncertainty does not make the risk decrease. Second, one could make the risk assessment more realistic by explicitly considering duration and frequency of an exposure exceedance into the analysis. This is discussed in the next section.

4. SEMI-DYNAMIC RISK ASSESSMENT (BASED ON CDF CURVES)

In this method, temporal variations of the exposure concentration (in the exposure assessment) and the ecotoxicity data (in the effects assessment) are not summarized into a probability distribution. Instead, the temporal variations are summarized in a bit more detail:

Concentration-Duration-Frequency curves (CDF curves). A CDF curve is based on a time-series analysis and can be determined for both exposure and effects (FWR 1998).

4.1. Exposure assessment

CDF curves are basically histograms of the durations of exceedance of a set of (predefined) concentrations. This results in three-dimensional plots with on the three axes the concentration, the duration of an exceedance above a particular concentration and the frequency of an exceedance above a particular concentration with a particular duration. However in practice, two-dimensional plots are more frequently used. Here, Duration-Frequency curves are used because current legislation is still mainly based on standards, i.e. effects are considered as a crisp value instead of a (random) variable. The considered critical concentration was set at 4 mg TAN/l. For ease of use, we shall continue to use the term CDF curve.

The dynamic model and successive time-series analysis resulted in a $CDF_{exposure}$ as shown in Figure 4. The small uncertainty band indicates that input uncertainty had a small effect on the CDF output. Point A in Figure 4 can be interpreted as follows: there is 95% certainty that there are 7.2% exceedances of a TAN concentration of 4 mg TAN/l lasting for 2 hours or longer.

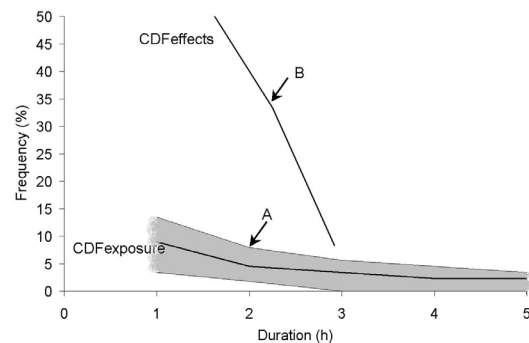


Figure 4. Concentration-Duration-Frequency (CDF) exposure and effect curves ($CDF_{exposure}$ also has an 90%-uncertainty band)

4.2. Effects assessment

Similarly as in the exposure assessment, CDF curves can be constructed for an effects assessment based on ecotoxicity tests. Such CDF curve will be named as $CDF_{effects}$.

CDF_{effect} curves for sustainable salmonid fishery were given in the Urban Pollution Management Manual (FWR 1998). The data can also be found in Table 1.

Table 1: CDF-curve for un-ionised ammonia (mg TAN/l) for an ecosystem suitable for sustainable salmonid fishery (FWR 1998)

Return period	Frequency by month (%)	Duration (h)		
		1	6	24
1 month	100	3.25	1.25	0.90
3 months	33.333	4.75	1.75	1.25
1 year	8.333	5.25	2.00	1.50

The return period, the duration (expressed in hours) and the concentration (expressed as mg NH₃-N/l) are shown. A three dimensional representation is shown in Figure 5. Since the effect is assessed in terms of total ammonia, NH₃ concentrations need to be transformed into total ammoniacal nitrogen (TAN) values using the ammonia equilibrium equation. However, the equilibrium constant is dependent on the temperature. The temperature was set at 11°C. This is the average river water temperature in the Bauterseembeck.

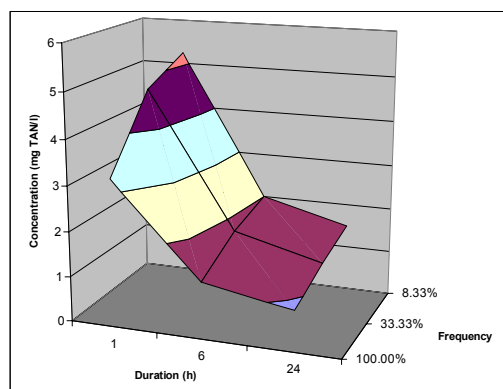


Figure 5. CDF_{effect} curve for sustainable salmonid fishery (FWR 1998)

Equivalent to the exposure assessment, two-dimensional Duration-Frequency curves were derived from this three-dimensional CDF_{effect} surface. The concentration was, as in the CDF_{exposure} determination, set at 4 mg TAN/l (= 0.08 mg NH₃-N/l). This curve can be determined through linear interpolation (see Figure 5). The resulting curve is shown in Figure 4. Note that no 90%-uncertainty band could be determined because of insufficient number of data points. Point B can be interpreted as follows: there are no adverse effects for salmonid species if the TAN concentration of 4 mg TAN/l is exceeded with a frequency of less than 33.3% and with a duration of 2.25 hours or longer.

4.3. Risk assessment

Finally, the CDF_{exposure} and CDF_{effects} are overlaid on the same graph (Figure 4). There is no risk if the CDF_{effects} is situated above the CDF_{exposure}. There is potential risk if the CDF_{effects} curve is situated below the CDF_{exposure}. We are not aware of any quantitative risk measures that integrate the CDF_{exposure} and CDF_{effects} curves.

This analysis shows that there is no risk as long as the duration of an exceedance does not last longer than 3 hours. Moreover, the salmonid species can even stand more frequent exceedances (again for durations shorter than 3 hours). This conclusion is very useful for the operation of the WWTP. It reassures the WWTP operator that more frequently he or she can exceed the standard (but only for a couple of hours). Unfortunately, no assessment can be made for durations longer than 3 hours because no ecotoxicity data were available. Such situations could occur in cases of equipment failure that take relatively long to repair.

This semi-dynamic method is expected to be more realistic and refined compared to the probabilistic method. However, due to lack of more CDF_{effect} data and simulations, the case study could insufficiently confirm this.

5. CONCLUSIONS & FURTHER RESEARCH

The risk of a chemical was determined using two methods: a probabilistic method in which exposure and effects are considered as probability distributions and a semi-dynamic method in which the duration and frequency of exceeding a standard of exposure and effects are considered. The probabilistic method resulted in a risk of 8.4% (0.3-28% is a 90% confidence interval). No quantitative risk measure could be calculated for the semi-dynamic method. Both methods can be used as a decision-support tool in risk assessment practice.

The comparison of both methods by means of a case study mainly indicated that further research should be undertaken to collect more data to build a more extensive three-dimensional effects and exposure concentration-duration-frequency curve (CDF-curve). In this way, the magnitude of an exceedance would also be considered and a distinction would be made between exceedances of e.g. 4 and 8 mg/l.

6. ACKNOWLEDGEMENTS

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