Calculating Required Purification Effort to Turn Source Water into Drinking Water Using an Adapted CCME Water Quality Index

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Key Points:

- We have introduced a water quality index for the quality of water as a source for drinking water production
- Unlike previous water quality indices it compares measured contaminant concentrations in source water to drinking water guidelines
- We have performed an extensive sensitivity analysis on simulated data to validate our index

Abstract

The 2000 European Union Water Framework Directive (WFD) states that 'Member States shall ensure the necessary protection for the bodies of water identified with the aim of avoiding deterioration in their quality in order to reduce the level of purification treatment required in the production of drinking water'. However, it does not specify how to evaluate or quantify this level of purification treatment. The scientific literature contains several different Water Quality Indices (WQIs), but none are suited for this purpose. Therefore, we propose a novel WQI that we specifically designed to quantify the level of purification required to prepare drinking water from source water. It is based on the WQI of the Canadian Council of Ministers of the Environment (CCME WQI), which was chosen because it is widely accepted, can be used with any number of input parameters, does not require expert judgement and has been applied to assess source water quality before. We compare measured contaminant concentrations in source water to drinking water guidelines and additionally incorporate the resilience of contaminants to treatment processes in the index (which is not possible in the CCME WQI). Furthermore, we accommodate for varying sampling frequencies that are characteristic of the ongoing monitoring programme. These changes make our index more robust and sensitive to relevant changes in source water quality. We calculated index scores for source water from the Rhine and the Meuse rivers to monitor the effect of implementation of the WFD on the effort required to produce of drinking water.

1 Introduction

Water is a vital natural resource and plays an important role in everyday life. Amongst many things we use water for agriculture, industry, cleaning and drinking. In the Netherlands, like in many developed countries, drinking water has to meet strict requirements to ensure suitability for human consumption. Over a third of all Dutch drinking water comes from the rivers Rhine and Meuse, either directly or after infiltration (Pleijsier, 2001). The water quality of these rivers is therefore essential to protect drinking water supply. The Directorate-general for Public Works and Water Management (Dutch: *Rijkswaterstaat*) is responsible for monitoring the water quality of the main Dutch water system to ensure an adequate supply of clean water. It operates two monitoring stations which continuously check water quality by measuring chemical composition, toxicity, radioactivity and general parameters such as temperature and pH.

Water quality is not restricted by geographical boundaries; the Rhine flows through seven countries, so international cooperation is paramount to keep it ecologically healthy and suitable as a source for drinking water. In 2000 the European Committee issued the Water Framework Directive (WFD), which commits EU member states to ensuring their water is sufficiently clean and ecologically healthy by 2027 (European Parliament, 2000). To reach the goals stated in the WFD, EU member states have to take measures to improve water quality (Hering et al., 2010). Article 7 section 3 of the WFD states that "Member states shall ensure the necessary protection for bodies of water identified with the aim of avoiding deterioration in their quality in order to reduce the level of purification treatment required in the production of drinking water" (European Parliament, 2000).

The WFD does not specify how the level of purification treatment required should be assessed or quantified. We define the level of purification treatment required as the effort to prepare drinking water from source water, removing contaminants during the production process to levels specified by legislation, in this case the Dutch Drinking Water Decree (Dutch: *Drinkwaterbesluit*). We designate the ensuing index based on this metric as the 'purification effort index' (PEI). This is a water quality index (WQI) that takes the purification process into account as well.

The concept of water quality indices was first developed in the 1960s by Horton (1965). A water quality index can be defined as "a single dimensionless number expressing the water quality in a simple form by aggregating the measurements of selected parameters" (Sutadian et al., 2016). In general, the development of a water quality index consists of the following steps (Abbasi & Abbasi, 2012):

1. Parameter selection
2. Obtaining sub-index values (determination of a quality function for each parameter)
3. Establishing parameter weights
4. Aggregation of sub-indices (often through an arithmetic or geometric mean)

Not all WQIs follow all four steps, but Sutadian et al. (2016) provide an extensive discussion of the choices that can be made at each step. However, all methods have their limitations and there is no perfect WQI (Lumb et al., 2011; Sutadian et al., 2016). There is always subjectivity involved in the creation of a WQI (especially in the first three steps), which is why it is recommended to consult with local experts and do uncertainty and sensitivity analysis (Sutadian et al., 2016).

WQIs are often designed for a specific purpose and application. Several WQIs have been proposed to determine the suitability of water for human consumption or as a source for drinking water production. There is a difference between the two uses; source water is purified before consumption and this should be reflected in parameter selection, weights and sub-index values (e.g. putting more emphasis on contaminants that are difficult to remove). Boyacioglu (2010) and Hurley et al. (2012) have proposed WQIs for the suitability of source water, in which they compare measured water quality parameters to intake guidelines. We, on the other hand, compare concentrations of contaminants in the river directly to drinking water requirements. These differences are weighted by a factor that reflects removal efficiency in the purification process. That way we take the purification process into account directly, rather than indirectly through intake guidelines.

Contrary to existing WQIs, the PEI that we propose in this paper is uniquely suitable for quantifying the required purification treatment levels, as stated in the WFD. We have applied the PEI to a large historical database of concentration measurements in the Rhine and Meuse. The resulting scores summarize the water quality regarding drinking water production and provide an effective tool to evaluate the effect of implementation of the WFD. Furthermore, we compare our PEI with the water quality index of the Canadian Council of Ministers of the Environment (CCME WQI) (Saffran et al., 2001) on which it is based, and perform a thorough sensitivity analysis to show that our method has more desirable properties.

2 Materials and Methods

2.1 CCME WQI

One of the most widely used water quality indices is that of Canadian Council of Ministers of the Environment (Lumb et al., 2011; Saffran et al., 2001; Sutadian et al., 2016). It was introduced in 2001 and has since been used for many purposes, including in the context of drinking water (Boyacioglu, 2010; Hurley et al., 2012; Lumb et al., 2011; Rickwood, 2007; Sutadian et al., 2016). It relies on three factors that are relevant for water quality: *scope*, *frequency* and *amplitude*. The scope (F1) is the percentage of parameters whose objectives are exceeded at least once (failed parameters), the frequency (F2) is the percentage of all measurements whose objectives are exceeded (failed measurements) and the amplitude (F3) is a measure for the magnitude of the exceedance. Any number of parameters can be used as input, but it is recommended to use at least 4 parameters, measured at least 4 times (Saffran et al., 2001).

$$F_1 = \left(\frac{\text{Number of failed parameters}}{\text{Total number of parameters}}\right) \times 100 \#1$$

$$F_2 = \left(\frac{\text{Number of failed measurements}}{\text{Total number of measurements}}\right) \times 100 \#2$$

$$F_3 = \left(\frac{\text{nse}}{\text{nse} + 1}\right) \times 100 \#3$$

The *normalised sum of excursions* (nse) is given by

$$\text{nse} = \left(\frac{\sum_{i=1}^{n} \text{excursion}_i}{\text{Total number of measurements}}\right) \#4$$

where

$$\text{excursion}_i = \left(\frac{\text{Failed measurement value}_i}{\text{Objective}_i}\right) - 1 \#5$$

and *n* is the total number of measurements. The excursion is the ratio by which the objective is exceeded. The nse is the average excursion of all measurements. Equation 3 ensures that the amplitude has the same possible range (0 – 100) as the scope and frequency. The three factors are aggregated to a single number that indicates the water quality

$$\text{CCME WQI} = 100 - \left(\frac{\sqrt{F_1^2 + F_2^2 + F_3^2}}{1.732}\right) \#6$$

The value 1.732 (square root of 3), is used to normalize the index to a value between 0 and 100. The higher the index score, the better the water quality.

2.2 Adaptation of the CCME WQI

We want to develop a WQI that provides an estimate of the purification effort which is required to turn source water into drinking water. The CCME WQI provides an appropriate basis for this index because its input parameters, objective values and time interval can be specified by the user (as opposed to many other indices for which these are fixed (Sutadian et al., 2016)). That makes is possible to use available historical measurements and local objective values (e.g. from Dutch legislation). However, the CCME WQI is not equipped to incorporate the behaviour of compounds in the treatment process because it only compares measured concentrations to objective values. Furthermore, it lacks robustness to differences in measurement frequency between parameters.

The index is made invariant to differences in measurement frequency between parameters by averaging the frequency (F_2) and the nse per parameter This is implemented in accordance with Hurley et al. (2012):

$$F_2 = \frac{1}{P}\sum_{p=1}^{P}\left(\frac{\text{Number of failed measurements}_\text{p}}{\text{Total number of measurements}_\text{p}}\right) \times 100 \#7$$

$$\text{nse} = \frac{1}{P}\sum_{p=1}^{P}\frac{\sum_{i=1}^{n_p}\text{excursion}_{p,i}}{\text{Total number of measurements}_p}\#8$$

where P is the number of parameters and n_p is the number of measurements of parameter p. When the measurement frequency of all parameters is equal, the result is identical to that of the original CCME WQI. Otherwise, this modification ensures that all parameters have the same impact, regardless of measurement frequency.

The behaviour of compounds in the treatment process is incorporated by parameter weights, which give greater impact to contaminants which are difficult to remove. Assignment of weights is one of the four steps that is common in most water quality indices, but is not part of the original CCME WQI (Abbasi & Abbasi, 2012; Sutadian et al., 2016). We have implemented weights in the calculation of the excursion, because it relates directly to how much removal is required

$$\text{excursion}_{p,i} = w_p\left(\frac{\text{Failed measurement value}_i}{\text{Objective}_i} - 1\right)\#9$$

were w_p is the weight assigned to parameter p.

The amplitude in the CCME WQI is calculated from the normalized sum of excursions according to equation 3. In general, any equation of the form

$$F_3 = \left(\frac{\text{nse}}{\text{nse} + a}\right) \times 100\#10$$

in which a is a finite positive number will ensure that the amplitude is bound between 0 and 100. The size of a determines the rate at which the amplitude will approach 100. The smaller the value of a, the faster the Amplitude will approach 100, which makes it more sensitive towards small nse values. The larger the value of a, the slower the Amplitude will approach 100, which makes it more sensitive towards large nse values. The value of $a = 1$ in equation 3 is elegant and works well in many cases (Al-Saboonchi et al., 2011; Boyacioglu, 2010; Hurley et al., 2012; Khan et al., 2004), but for our data it makes the amplitude small (often negligible) compared to the scope and frequency, even though amplitude is arguably the most important factor in determining the required purification level. Therefore, we have optimized the value of a to ensure that the amplitude has the same average value as the scope and frequency. For our data set that results in a $a = 0.1$.

In the CCME WQI a higher index value indicates a better water quality, which is intuitive. But when reporting purification levels, it is confusing that a higher index score indicates a lower required purification level. To simplify communication, we report the aggregated sum of the factors without subtracting it from 100

$$PEI = \frac{\sqrt{F_1^2 + F_2^2 + F_3^2}}{1.732} \#11$$

This index is still bound between 0 and 100, but now a higher score indicates that more purification is required. A score of 0 would indicate that all measured parameters already meet drinking water standards and no purification is required at all.

2.3 Selection of parameters and objective values

There is no fixed set of parameters for the CCME WQI. Users are free to choose their own input parameters, depending on the goal and availability. That is also true for our PEI. Depending on the pollutions risk and existing monitoring programmes a user can choose parameters which are most relevant for a particular body of water. In our study, we calculate the PEI based on the concentrations of 49 compounds that are that explicitly mentioned in the Dutch drinking water decree. These compounds have a clearly defined maximum concentration in drinking water and when the measured concentration in the source water exceeds this threshold, the excess must be removed through purification. Therefore, the guideline values from the Dutch drinking water decree are used as objectives. A list of parameters and their objective values is included in Appendix A.

2.3 Parameter weights

The effort required to remove unwanted compounds from source water depends on their physical properties and the processes involved. Available purification processes vary between drinking water production facilities, but can include steps such as infiltration, flocculation, filtration, ozonation ultraviolet irradiation, activated carbon and membrane filtration—each with their own compound selectivity. Furthermore, purification efficiencies are often not readily available for all relevant compounds. Therefore, readily available approximate weights are preferred.

Assuming that the biological breakdown of compounds is a major component of drinking water production, we have chosen the Gibbs free energy as weight (divided by the molar mass). A high Gibbs free energy indicates that a molecule is resistant to decomposition through metabolic processes (Finley et al., 2009) or advanced oxidation processes (Ji et al., 2009; Zhang et al., 2017). An example of this principle would be (per)fluorinated compounds, which have a high Gibbs free energy and are generally poorly removed in drinking water production (Exner & Färber, 2006).

When available, the experimental Gibbs free energy was used (Dean, 1999; Finley et al., 2009; Holmes et al., 1993; Jolkkonen, 2000; Kotz et al., 2012), otherwise it was estimated with the Joback Group Contribution method (Joback & Reid, 1987). See appendix A for details. The Gibbs free energy can be estimated for a wide range of compounds, as long as group contributions for all functional groups in the molecule are known. Estimation of Gibbs free energy can be fully automated based on e.g. compound name or cas-number (Forsythe Jr et al., 1997; Jankowski et al., 2008), making this approach easily feasible for a large number of compounds.

2.4 Parameter influence

The influence of a parameter on the PEI is calculated by taking the difference in index score between a model including the parameter and a model excluding the parameter, similar to Hurley et al. (2012). The larger the difference, the bigger the effect of the parameter on the index. When the parameter never exceeds its objective, it is possible to have a negative difference (knowing that a parameter never exceeds its objective indicates cleaner water).

3 Data

3.1 Experimental data

The data consists of contaminant concentrations in the Rhine and Meuse between 2000 and 2016. They were measured by waterworks and regulatory bodies such as Rijkswaterstaat. A list of the 49 contaminants that we used as input parameters for our index is provided in Table A.1.To give an idea of the monitoring programme since the implementation of the Water Framework Directive, an overview of measurement characteristics of these parameters is provided in Appendix A. There are great differences in measurement frequency between parameters, which is why it is important to average per parameter (equations 7 and 8).

3.2 Simulated data

Simulated data sets were created based on the measured data in order to investigate the sensitivity of the PEI to changes in the monitoring programme or water quality. The procedures to generate these simulated data sets are described below; numerical examples of these procedures are given in appendix B.

3.2.1 Change in the number of parameters

Two scenarios were investigated in which the number of parameters is doubled: (a) one where the additional parameters are identically distributed to the original parameters and (b) one where the additional parameters exceed their objective values less frequently.

To create the data set with identically distributed additional parameters the real data was extended with exact copies of all original parameters (only changing their names). To create the data set with additional parameters that exceed their objective less frequently, half of the additional measurements that originally exceeded their objective (randomly selected within each parameter) were changed to a value below the objective.

3.2.2 Change of measurement frequency

Two scenarios were investigated: (a) one where the measurement frequency is doubled for the 5 parameters which exceed their objective most often and (b) one where the measurement frequency is doubled for the 5 parameters which exceed their objective least often. The measurement frequency of a parameter was doubled by duplicating each of its measurements.

3.2.3 Addition of artificial spikes

Four scenarios were investigated: (a) one where 10% of aldrin measurements (low weight; easy to remove) were increased to 50 times the objective value, (b) one where 25% of aldrin measurements were increased to 20 times the objective value, (c) one where 10% diglyme measurements (high weight; difficult to remove) were increased to 50 times the objective value and (d) one where 25% of diglyme measurements were increased to 20 times the objective value.

4 Results

The Rhine and Meuse are the major sources of surface water for the production of drinking water in the Netherlands (RIWA). In order to assess the impact of the WFD, the PEI score was calculated for source water from both rivers.

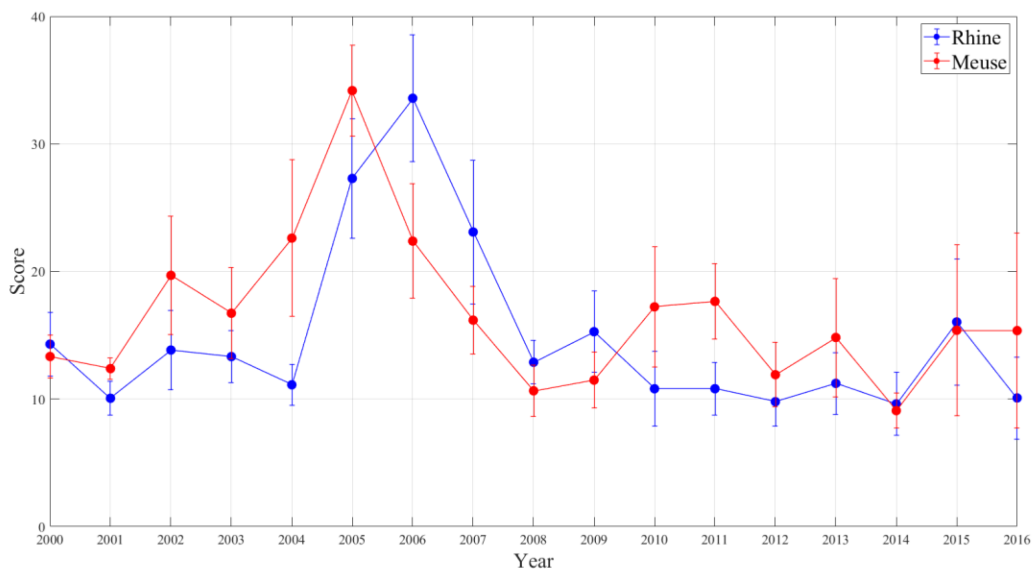
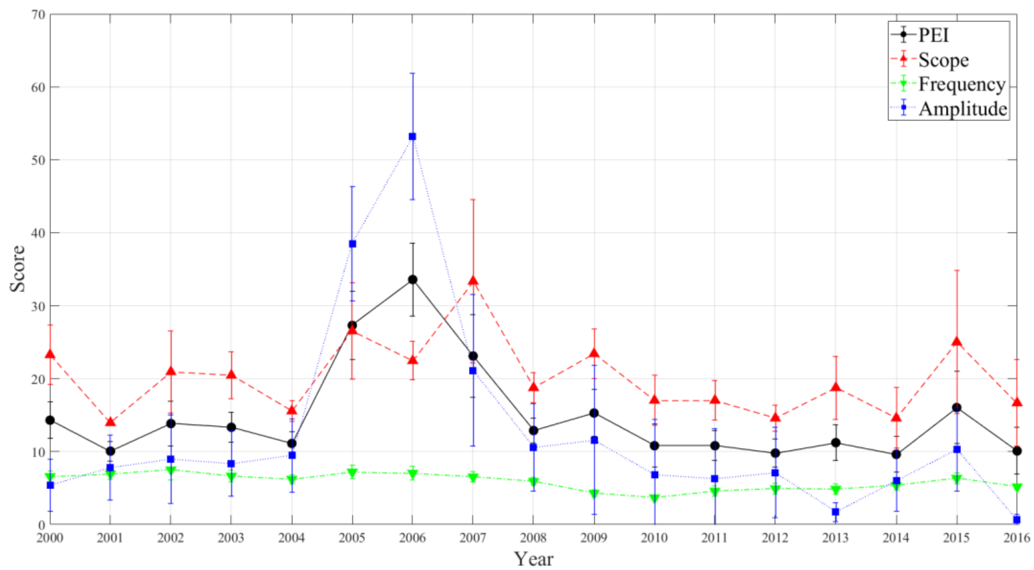


Figure 1. PEI score of the Rhine and Meuse. The error bars indicate 95% confidence intervals (determined by nonparametric bootstrapping).

4.1 Purification effort index for Rhine and Meuse

The PEI score was calculated for water from the Rhine and Meuse from 2000 until 2016. Figure 1 shows that there is no overall trend, but the index peaks around 2005 and 2006, indicating higher required purification levels in those years. To further interpret the index, it is possible to investigate the contributions of frequency, scope and amplitude and the influence of individual parameters on the score (see section 2.4). Figure 2 shows that the higher index scores around

2005 and 2006 compared to those of earlier years are mostly due to the amplitude. The frequency is not higher than usual. The scope is slightly increased in the Rhine only. The scope varies between 14% and 33%, indicating the number of individual contaminants that have to be removed from source water to meet the drinking water requirements. Some contaminants may be problematic only once a year due to an accident or rare pollution event, while others regularly exceed their norm. Therefore, the frequency, indicating the number of individual measurements that exceed their objective, is also important. It is logically lower than the scope and changes more gradually over time. It varies between 4% and 8%. A two sample t-test shows that there is a slight but significant decrease in frequency in the Meuse after 2007.



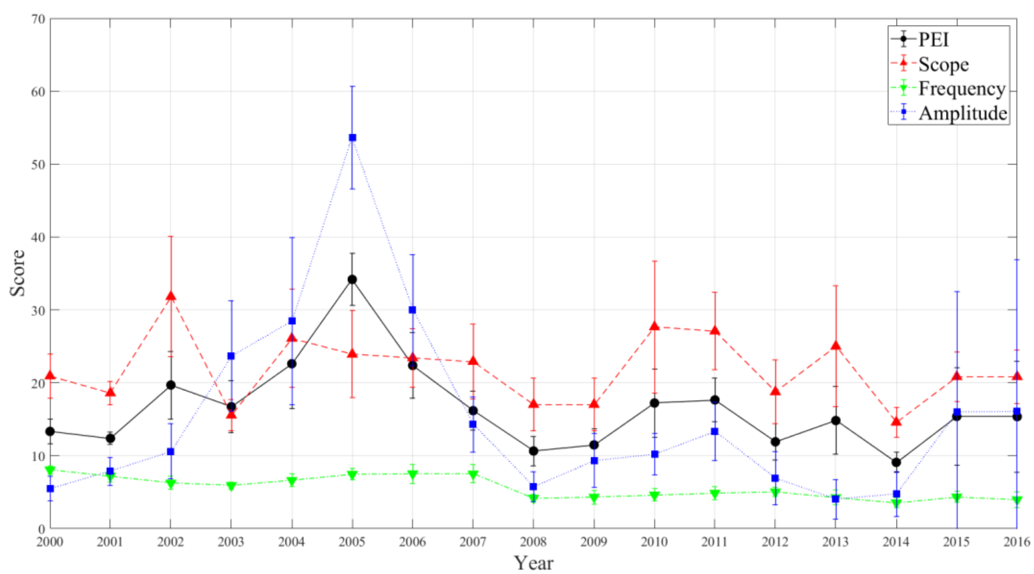
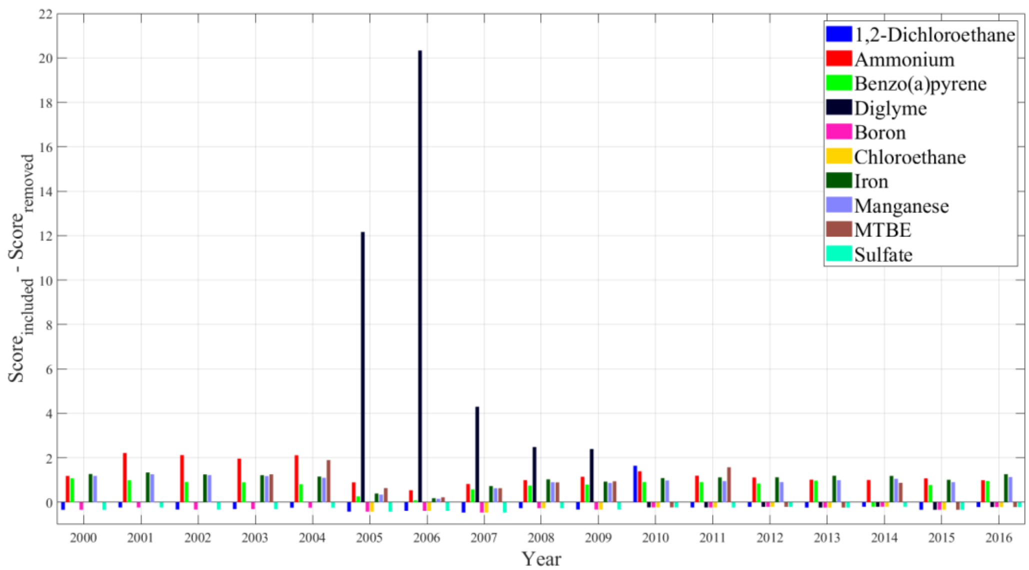


Figure 2. Factors contributing to the PEI score of the Rhine (top) and Meuse (bottom). The error bars indicate 95% confidence intervals (determined by nonparametric bootstrapping).

Figure 3 shows the effects of the ten parameters with the largest influence on the index scores. Some parameters, such as iron, manganese, nitrite, aluminium, and benzo(a)pyrene are prominent in both rivers, while others, such as chloroethane, diglyme, and sulfate, are much more temporarily prominent in either the Rhine or the Meuse.

An increase in the concentration of diglyme compared to earlier time points was first noticed in the Rhine in 2005, with levels about ten times higher than before. Diglyme is widely used in industry (including paintings, coatings, cosmetics, polymer industry). Although it poses little ecotoxicological threat, it is a specific threat to the compliance of drinking water. The source of the pollution was a factory located near Wiesbaden (Germany) and after the waste water treatment process at the source was improved, concentrations decreased at the end of 2006. MTBE (methyl *tert*-butyl ether) is a gasoline additive (anti-knocking agent), which can give drinking water an unpleasant taste. It is a common contaminant in surface water, but concentrations of MTBE in the Meuse were exceptionally high in 2005 and 2006 due to a leaking pipeline at Geleen.



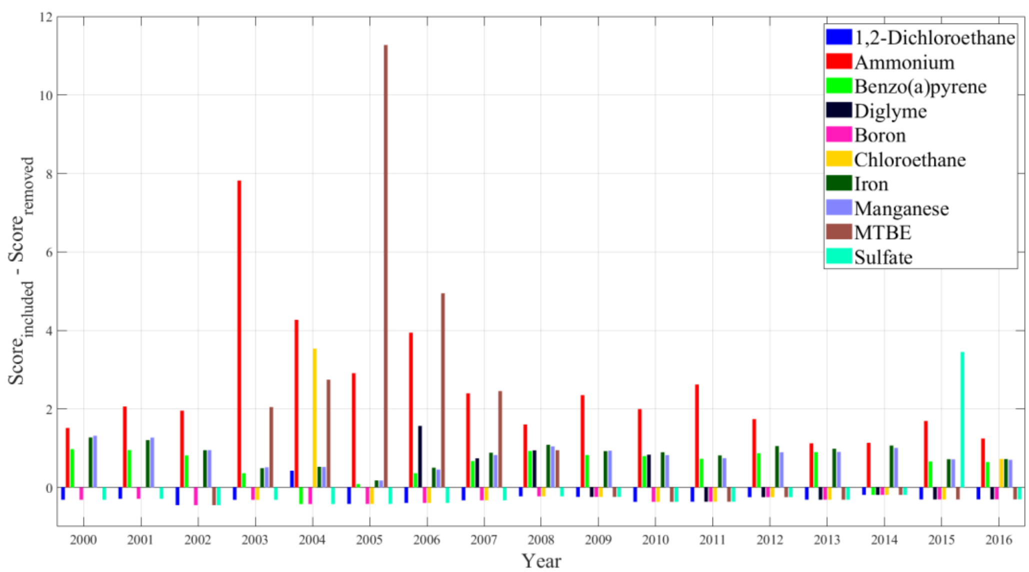
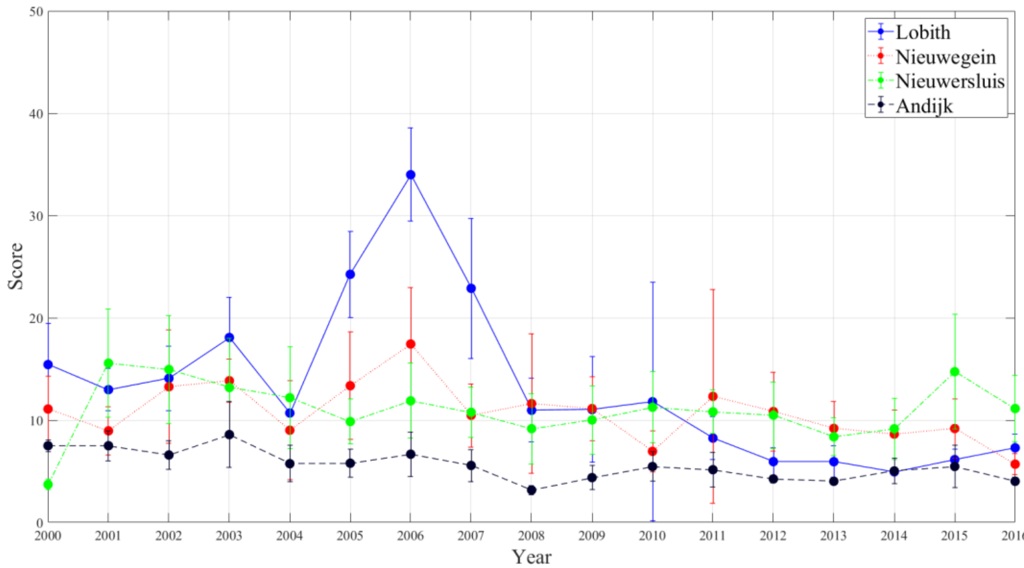


Figure 3. Effect of individual parameters on the PEI score of the Rhine (top) and the Meuse (bottom)

4.2 Purification effort index for Rhine and Meuse at individual sites

So far, we have calculated the PEI based on all measurements along the river. That provides a useful overview, but water quality varies from place to place; a source of pollution can be introduced at any point and diffusion and breakdown reduce concentrations of contaminants downstream. It is therefore also insightful to investigate individual sites separately. The results are shown in Figure 4, which includes all water intake locations along these rivers and the border measurement stations at Lobith and Eijsden. The required purification levels generally decrease downstream; the lowest PEI is found at Andijk, which is located at the edge of the IJsselmeer. Water from the Rhine flows via the IJssel river into the IJsselmeer where it can take months to reach Andijk. During that time, many contaminants are dispersed or degraded.

Further investigation of parameter contributions for each site (Supporting Information) shows that the effect of diglyme in the Rhine on the PEI is most prominent at Lobith, where the Rhine enters the Netherlands; at sites further downstream its effect is limited. Similarly, the effect of MTBE in the Meuse on the index score is most prominent in Heel, which is the first water intake location downstream from the leaking pipeline in Geleen.



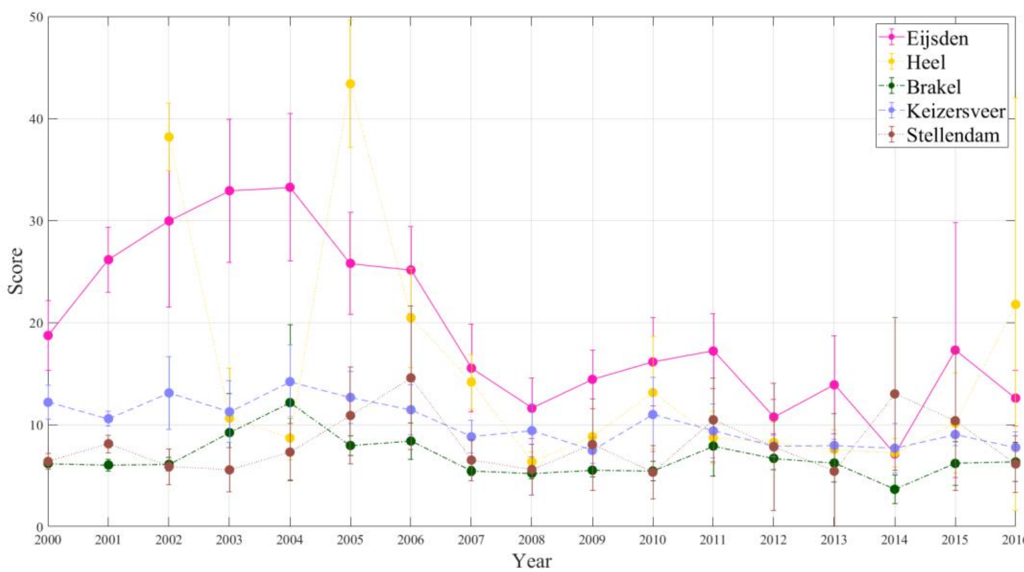
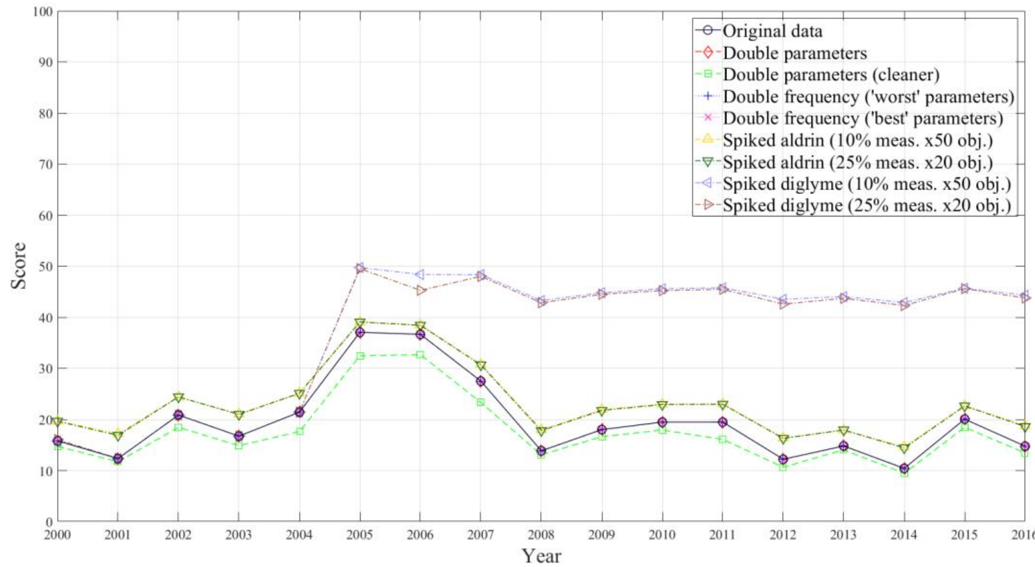


Figure 4. PEI score for water from several sites along the Rhine (top) and Meuse (bottom). The error bars indicate 95% confidence intervals (determined by nonparametric bootstrapping).

4.3 Sensitivity analysis and comparison with the original CCME WQI

The PEI is compared to the original CCME WQI on both historical and simulated data. Figure 5 shows the index scores for several simulated data sets, which contain either additional parameters, increased measurement frequency of some parameters, or spikes to individual measurement values.



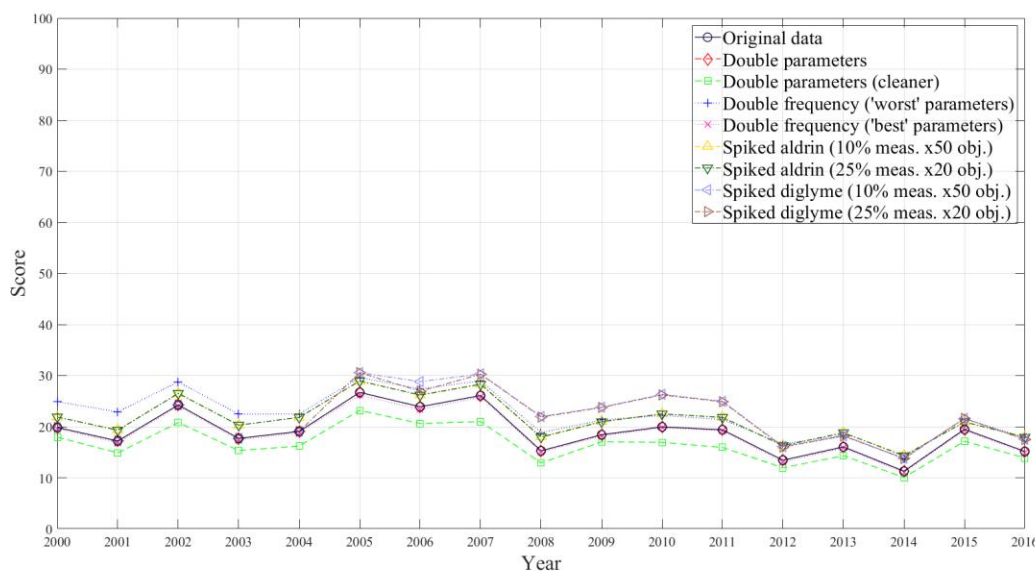


Figure 5. Effets of simulated changes to the data on the PEI score (top) and CCME WQI score (bottom). For easy comparison the CCME WQI is inverted by omitting the '100 -' term in equation 6 (similar to the PEI). A lower score now indicates a better water quality for both WQIs. Diglyme was first measured in 2005, so it is only included in the index from that year onwards.

Additional parameters affect the CCME WQI and the PEI similarly. When they are identically distributed to the original variables they do not affect the index, because both indices are normalized to the number of parameters. However, when the additional parameters exceed their objective values less often than the average parameters that were already in the index, the scores are lower because the water quality has increased and less purification is required. Changing the measurement frequency of some parameters affects the CCME WQI, but it does not affect the PEI because its factors are normalized per parameter. In this respect the PEI is preferable over the CCME WQI, because the number of measurements of a parameter should not affect the index score if the measurement values come from the same distribution (which is true for this simulation).

Spiking some measurements shows the advantage of using parameter weights. In the PEI spiking a high-weight parameter (diglyme) has a larger impact on the score than spiking a low-weight parameter (aldrin). This is desirable because high-weight parameters are more problematic in the purification process. The CCME WQI does not use parameter weights and therefore the effect of spiking is the same for all parameters (the small difference between spiking diglyme and aldrin is caused by a confounding difference in measurement frequency, which the original CCME WQI does not correct for either).

5 Discussion

We have developed a water quality index that can be used to characterize the required purification level for source water for drinking water production. This PEI was calculated for a large database of concentration measurements of Dutch surface water in the Rhine and Meuse. No evidence was found that the required purification level has decreased since 2000, when the Water Framework Directive was implemented. Index scores indicate a peak in required purification levels around 2005 and 2006 due to incidents, but no general trend. Investigating water intake locations separately reveals slight downward trends at Eijsden, Andijk and Keizersveer. The differences between locations are lost when measurements from multiple locations are combined to a single index for the whole river, but that is the essence of a water quality index: to exchange detail for simplicity. Depending on the goal it is possible to choose an appropriate level of detail.

The PEI is based on the widely used CCME WQI, but modifications have made it more robust to changes in measurement frequency and made it sensitive to the behaviour of contaminants in the treatment process. A comparison on simulated data has shown that the PEI is preferable over the original CCME WQI for the purpose of assessing the required purification level, because compounds that are more difficult to remove have a bigger influence on the index. Furthermore, the PEI is invariant to changes in measurement frequency, similar to the adaptation by Hurley et al. (2012), and the number of parameters measured, as long as they are identically distributed (i.e. the additional parameters are not better or worse than the existing ones).

Parameter selection is an important part of any water quality index. We have used available historical measurements, but the set of parameters that was measured varies substantially over time and between locations. We have considered 49 parameters (Table A.1), but only 6 of these were always available. That is too few to get an accurate estimate of the required purification levels. Instead, at every interval we have used all available parameters (out of the 49). That raises comparability issues because the index is not always based on the same parameters, but at every interval the index provides the most accurate approximation of the physical property of interest, i.e. the required purification level (because all available information is taken into account).

The PEI summarizes chemical measurements of water quality into a score that reflects the required purification level. It is not a linear model and the score is not simply the sum of the contribution of all parameters. The effect of a parameter on the index depends on the measurements of the other parameters in the same year. For example, the levels of benzo(a)pyrene in the Rhine are relatively constant, but around 2006 it had a smaller effect on the score than usual, because it was masked by the presence of high levels of diglyme (bis-(2-methoxyethyl)-ether). Although this invalidates direct comparison of the effects of a single parameter over time, the index thereby takes into account the relative decrease in urgency of the presence of benzo(a)pyrene together with such high levels of diglyme, which already require sophisticated purification methods.

The choice of parameter weights has a big effect on the index. Hurley et al. (2012) argue that individual parameter importance is already taken into account by its objective value, but that is not true when evaluating the quality of source water for drinking water production. In this case the objective value represents an acceptable concentration in drinking water, while the weight represents how problematic it is in the purification process. These are two separate factors that must both be taken into account.

The removal efficiency of a contaminant depends on the purification method that is used. We have used Gibbs free energy as weights, assuming enzymatic breakdown or advanced oxidation steps, but it would be interesting to investigate other weights and to model a complex scenario of multiple purification steps. Other physical properties could be used as well to reflect compound behaviour in different purification processes. For example, considering that highly volatile substances are easily removed through aeration, Henry's laws volatility constants could be used. Similarly, substances with a high log KOW tend to adhere to suspended matter and are removed without much difficulty through commonly applied filtration steps.

Water monitoring programmes and drinking water requirements can vary between countries. We have studied source water in the Netherlands, but the same methodology can also be applied in other countries, using a different set of parameters and objective values. This makes the index well suited for evaluating water quality in a broader European context.

6 Conclusions

We have provided a water quality index to assess the level of purification treatment required to produce drinking water from surface water. It aggregates a large number of measurements into an easily interpretable index. Unlike existing water quality indices, it compares measured contaminant concentrations to drinking water guidelines while taking into account the resilience of contaminants to the treatment process. Using process information makes the index more sensitive to relevant changes in source water composition. Our index is based on the CCME WQI, but an extensive comparison on simulated data shows that our PEI is better suited for evaluating required purification levels.

We have calculated our novel index for a large database of contaminant concentrations in Dutch surface water which was used as a source for drinking water production, but found no general decrease in required purification levels since the introduction of the WFD.

Acknowledgments, Samples, and Data

The data used in this study is collected by drinking water companies and the Dutch government (Rijkswaterstaat) and is stored in a database that is managed and maintained by RIWA-Rijn. RIWA-Rijn publishes annual reports on water quality and has a policy of sharing all water quality data upon request. Requests can be made through their website https://www.riwa-rijn.org.

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References

Abbasi, T., & Abbasi, S. A. (2012). *Water quality indices*: Elsevier.

Al-Saboonchi, A., Mohamed, A.-R. M., Alobaidy, A. H. M. J., Abid, H. S., & Maulood, B. K. (2011). On the current and restoration conditions of the southern Iraqi marshes: Application of the CCME WQI on East Hammar marsh. *Journal of Environmental Protection, 2*(3), 316.

Boyacioglu, H. (2010). Utilization of the water quality index method as a classification tool. *Environmental monitoring and assessment, 167*(1-4), 115-124.

Dean, J. A. (1999). *Lange's handbook of chemistry*: New york; London: McGraw-Hill, Inc.

Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy, (2000).

Exner, M., & Färber, H. (2006). Perfluorinated surfactants in surface and drinking waters (9 pp). *Environmental Science and Pollution Research, 13*(5), 299-307.

Finley, S. D., Broadbelt, L. J., & Hatzimanikatis, V. (2009). Thermodynamic analysis of biodegradation pathways. *Biotechnology and bioengineering, 103*(3), 532-541.

Forsythe Jr, R. G., Karp, P. D., & Mavrovouniotis, M. L. (1997). Estimation of equilibrium constants using automated group contribution methods. *Bioinformatics, 13*(5), 537-543.

Hering, D., Borja, A., Carstensen, J., Carvalho, L., Elliott, M., Feld, C. K., et al. (2010). The European Water Framework Directive at the age of 10: a critical review of the achievements with recommendations for the future. *Science of the total Environment, 408*(19), 4007-4019.

Holmes, D. A., Harrison, B. K., & Dolfing, J. (1993). Estimation of Gibbs free energies of formation for polychlorinated biphenyls. *Environmental science & technology, 27*(4), 725-731.

Horton, R. K. (1965). An index number system for rating water quality. *Journal of Water Pollution Control Federation, 37*(3), 300-306.

Hurley, T., Sadiq, R., & Mazumder, A. (2012). Adaptation and evaluation of the Canadian Council of Ministers of the Environment Water Quality Index (CCME WQI) for use as an effective tool to characterize drinking source water quality. *Water Research, 46*(11), 3544-3552.

Jankowski, M. D., Henry, C. S., Broadbelt, L. J., & Hatzimanikatis, V. (2008). Group contribution method for thermodynamic analysis of complex metabolic networks. *Biophysical journal, 95*(3), 1487-1499.

Ji, Y., Yang, Z., Ji, X., Huang, W., Feng, X., Liu, C., et al. (2009). Thermodynamic study on the reactivity of trace organic contaminant with the hydroxyl radicals in waters by advanced oxidation processes. *Fluid Phase Equilibria*, *277*(1), 15-19.

Joback, K. G., & Reid, R. C. (1987). Estimation of pure-component properties from group-contributions. *Chemical Engineering Communications, 57*(1-6), 233-243.

Jolkkonen, M. (2000). Retrieved from http://www.update.uu.se/~jolkkonen/pdf/CRC_TD.pdf

Khan, A. A., Paterson, R., & Khan, H. (2004). Modification and application of the Canadian Council of Ministers of the Environment Water Quality Index (CCME WQI) for the communication of drinking water quality data in Newfoundland and Labrador. *Water Quality Research Journal*, *39*(3), 285-293.

Kotz, J. C., Treichel, P. M., & Townsend, J. (2012). *Chemistry and chemical reactivity*: Cengage Learning.

Lumb, A., Sharma, T., & Bibeault, J.-F. (2011). A review of genesis and evolution of water quality index (WQI) and some future directions. *Water Quality, Exposure and Health*, *3*(1), 11-24.

Pleijsier, L. (2001). *Grondwater levert bijna 60% van leidingwater*. Retrieved from https://www.cbs.nl/nl-nl/nieuws/2001/17/grondwater-levert-bijna-60-van-leidingwater

Rickwood, C. G. M. C. (2007). Water Quality Index Development and Sensitivity Analysis Report. *United Nations Environment Program Global Environment Monitoring System/Water Program*.

RIWA. riwa.org. Retrieved from https://riwa.org/

Saffran, K., Cash, K., & Hallard, K. (2001). Canadian water quality guidelines for the protection of aquatic life, CCME water quality Index 1, 0, Users manual. *Excerpt from Publication*(1299).

Sutadian, A. D., Muttil, N., Yilmaz, A. G., & Perera, B. (2016). Development of river water quality indices—a review. *Environmental monitoring and assessment*, *188*(1), 58.

Zhang, S., Yu, G., Chen, J., Zhao, Q., Zhang, X., Wang, B., et al. (2017). Elucidating ozonation mechanisms of organic micropollutants based on DFT calculations: Taking sulfamethoxazole as a case. *Environmental pollution, 220*, 971-980.

Appendix A

This appendix contains a complete list of all contaminants we used as parameters for calculating the PEI (Table A1). The monitoring programme changed significantly over time and was not the same for all sites. Therefore, an overview of the number parameters and frequency per location is provided in Table A2.

Table A1. *List of parameters and their drinking water guideline and Gibbs free energy*

Contaminant	Drinking water guideline (µg/l)	Gibbs free energy (kJ/mol)	Contaminant	Drinking water guideline (µg/l)	Gibbs free energy (kJ/mol)
1,2-Dichloroethane	3	-72.969[a]	Chromium	50	0
PCB 138	0,1	158.0[b]	Chrysene	0,1	513.78[c]
PCB 153	0,1	151.8[b]	Heptachlor epoxide	0,03	-233.33[c]
PCB 101	0,1	167.5[b]	Dieldrin	0,03	-87.04[c]
PCB 52	0,1	186.4[b]	ETBE	1	-102.52[c]
PCB 118	0,1	173.6[b]	Phenanthrene	0,1	213.756[a]
PCB 180	0,1	137.1[b]	Fluoranthene	0,1	491.18[c]
PCB 28	0,1	210.6[b]	Fluoride	1000	62.3[e]
Aldrin	0,03	-48.2[c]	Iron	200	0
Aluminium	200	0	Copper	2000	0
Ammonium	200	-26.57[d]	Mercury	1	0
Antimony	5	0	Lead	10	0
Anthracene	0,1	213.756[a]	Manganese	50	0
Arsenic	10	0	MTBE	1	-125.348[a]
Benzene	1	124.516[a]	Sodium	150000	0
Benzo(a)anthracene	0,1	513.78[c]	Nickel	20	0
Benzo(a)pyrene	0,01	621.88[c]	Nitrate	50000	-111.25[f]
Benzo(b)fluoranthene	0,1	621.88[c]	Nitrite	100	51.3[e]
Benzo(ghi)perylene	0,1	729.98[c]	NDMA	0,012	-121.71[c]
Benzo(k)fluoranthene	0,1	621.88[c]	Pyrene	0,1	327.4[g]
Diglyme	1	-315.36[c]	Selene	10	0
Boron	500	0	Sulfate	150000	-744.53[f]
Bromate	1	-675.04[c]	Cyanide	50	124.7[d]
Cadmium	5	0	Zinc	3000	0
Chloroethane	0,1	-57.350[a]			

[a](Finley et al., 2009), [b](Holmes et al., 1993), [c]Calculated with Joback method (Joback & Reid, 1987), [d](Dean, 1999), [e](Jolkkonen, 2000), [f](Kotz et al., 2012).

Table A2. *Overview of monitoring programme in 2000 and 2016*

Location	Number of Parameters[a]		Lowest number of measurements per parameter		Highest number of measurements per parameter		Total number of measurements		Percentage of measurements exceeding objective	
	2000	2016	2000	2016	2000	2016	2000	2016	2000	2016
Andijk	42	47	6	4	66	17	728	592	9	3
Brakel	42	46	9	7	52	23	750	577	14	3
Eijsden	34	44	11	13	52	52	887	1247	12	9
Heel[b]	8	48	14	4	29	151	131	1373	38	6
Keizersveer	43	48	9	12	51	52	1535	854	10	6
Lobith	34	44	7	13	26	26	540	791	7	8
Nieuwegein	40	48	5	5	42	26	396	641	16	5
Nieuwersluis	18	46	7	12	13	13	176	592	4	8
Stellendam	30	48	4	6	52	50	521	730	7	1

[a]Out of the 49 that we consider for our index. [b]Measurements in Heel started in 2002, so this was taken as the first reference year instead.

Appendix B

This appendix contains a toy numerical example of the procedure used to generate simulated data sets (Figure B1). In this example there are two parameters, the objective value is 1 and measurements exceeding the objective are indicated in red. The examples in Figure B1 correspond with the scenarios described in section 3.2.1 (1a, 1b), 3.2.2 (2a, 2b) and 3.2.3 (3a, 3b)

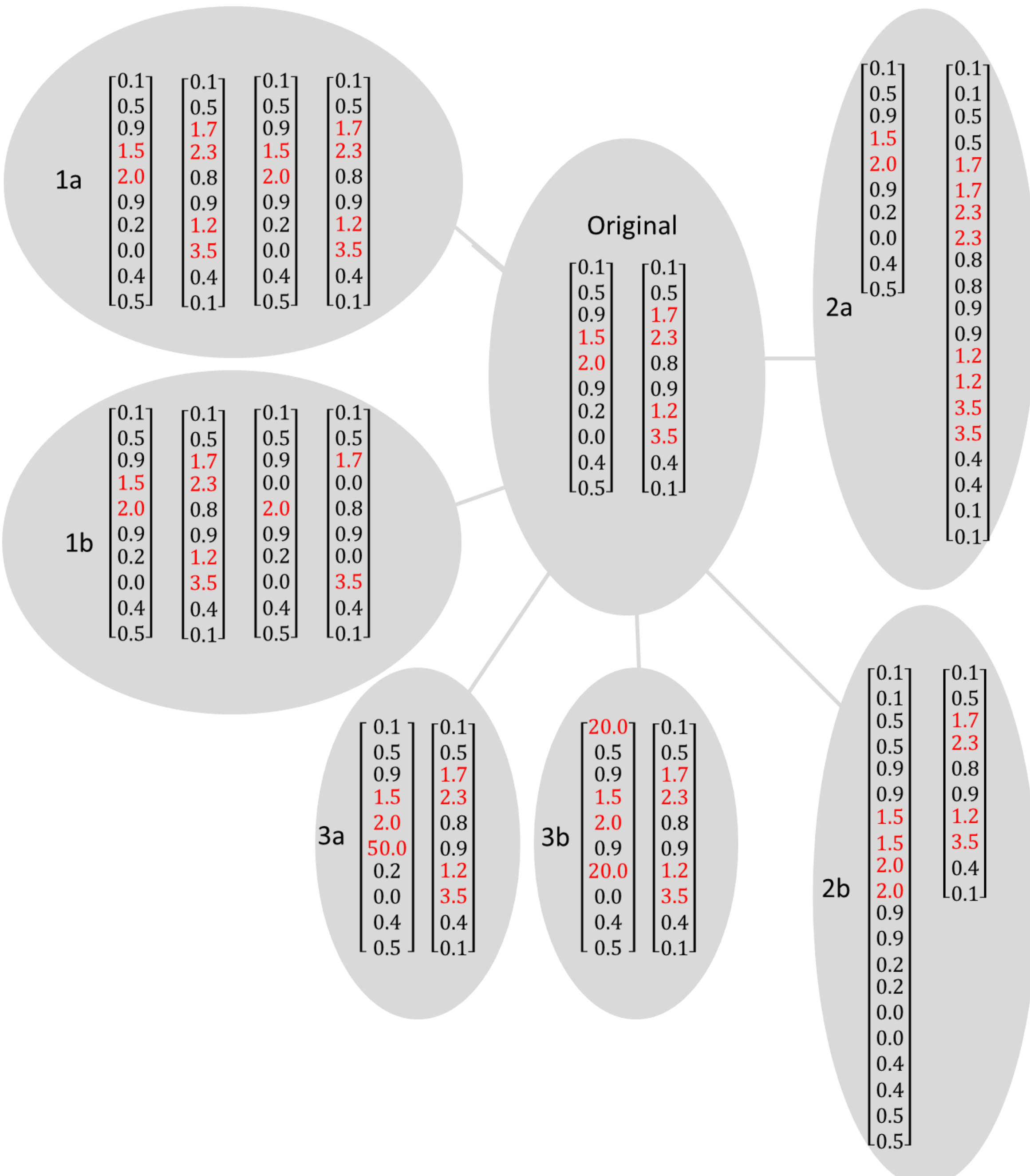

Figure B1. Numerical example of the procedure to generate simulated data sets.