A water quality index for the removal requirement and purification treatment effort of micropollutants

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ABSTRACT

The European Water Framework Directive (WFD) states that measures should be taken to improve the quality of water bodies to prevent further required extension of current (drinking) water treatment. Hence, for water managers it is of key importance to evaluate and report on the quality of water and the level of purification treatment that is required. For this purpose a novel framework of indices is defined, and their definition allows the inclusion of new, emerging substances. The indices can be calculated based on micropollutant characteristics alone and do not require any knowledge of specific purification treatment installations. Applying this framework of indices to water bodies provides an objective and reproducible way of evaluating the required purification treatment level. The indices were calculated for water quality data for up to 600 micropollutants from five sampling locations along the river Rhine in the Netherlands. This revealed differences between the sampling sites (index values ranged from 145 to 273) and showed that for the river Rhine the required purification treatment level, as well as the underlying removal requirement and purification treatment effort, have not improved over the years, despite the introduction of the WFD in 2000.

Key words | micropollutants, purification treatment, Water Framework Directive, water quality index

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HIGHLIGHTS

- The framework of water quality indices can serve as water management tool for the European Water Framework Directive.
- Water quality can be assessed integrally as well as separately on removal and purification requirements based on characteristics of micropollutants (MP).
- Novel and upcoming MP are also included.
- The framework indicates no improvement in water quality since 2000 in the river Rhine.

GRAPHICAL ABSTRACT
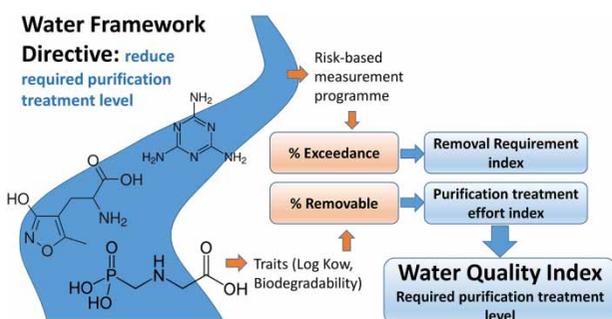
INTRODUCTION

Water utilities and water managers strive for, and have to meet, strict requirements regarding the quality of (sources for) drinking water. In addition to extensive monitoring and early warning systems, water utilities invest in combinations of basic and advanced treatment technologies, including membrane processes (e.g. Tul Muntha *et al.* 2017), advanced oxidation processes (e.g. Miklos *et al.* 2018), and biological treatment technologies (Abu Hasan *et al.* 2020). The required level of purification treatment is lower with an improved quality of the source water.

In Europe, the Water Framework Directive (2000/60/EC) (WFD) has been the most comprehensive instrument of European Union water policy since its introduction in 2000. The main objective of the WFD is to protect and improve the quality of freshwater bodies, with the aim of achieving good ecological and chemical status of European waters. In the WFD, preamble 24 states 'Good water quality contributes to securing the drinking water supply of the population.' Furthermore, Article 7 contains statements related to water used for drinking water:

- WFD Article 7.1 requires member states to designate water bodies for the production of drinking water
- WFD Article 7.2 states that water quality objectives must be achieved in these water bodies
- WFD Article 7.3 states '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.'

Looking back over the years since the introduction of the WFD, the question arises to what extent deterioration of water quality has been prevented since the WFD was established. Article 7.3 does not mention a quantitative measure that aids water utility managers. Therefore, the main goal of this study is to develop a quantitative measure to assess water quality in light of the level of required purification treatment using available monitoring data of chemical parameters. The challenge is how the impact and effort of treatment on water quality can be quantitatively defined such that the definition will give insight into this required level.

Water quality relates to many aspects, so there is a need to aggregate quality indicators into one water quality index (WQI). In the WFD, the ecological status of water bodies is classified based on observations of different biological quality elements, i.e. for phytoplankton, aquatic flora, benthic invertebrates and fish (e.g. Birk *et al.* 2012). In this paper, the specific focus is on chemical status and its relation to the purification treatment of drinking water in particular.

Indices relating to chemical parameters have long been used to communicate water quality in a single aggregated score that is representative of quality impairments (Horton 1965; Hurley *et al.* 2012; Borges Garcia *et al.* 2018). In general, any index is obtained by applying the following procedure. Firstly, parameters are selected that represent water quality. Secondly, for each parameter, a sub-index is established, in which these parameters are weighted. Finally, the sub-indices are aggregated into one index according to some function (Tyagi *et al.* 2013; Borges Garcia *et al.* 2018).

Horton (1965) was one of the first who introduced a WQI. This consisted of a weighted sum of a maximum of 10 sub-indices, divided by the sum of the weights. This number was then multiplied by two coefficients related to the temperature and pollution of a water source. Since then, some of the more well-known variations on this are the WQI-NSF (Brown *et al.* 1970) and its variations, in which nine (or 10) specific parameters are weighted and aggregated. Bascaron (1979) defined a WQI that balances the influence of each of the parameters by normalisation. Other parameters can be added to this index. The O-WQI (Cude 2001) is a variant where weights are omitted. The WQI-CCME was introduced by the Canadian Council of Ministers of the Environment in 2001 (CCME 2001). Three elements determine the score: the number of parameters that do not meet the quality standard at least once, the percentage of samples that do not meet this standard, and the deviation from the quality standard.

For decision makers at water utilities and water boards it is of key importance to evaluate and report the quality of water in relation to the effort that is required for purification treatment. More recently, efforts are being directed at developing WQIs specifically for assessing the treatability of water for the production of drinking water. Hurley *et al.* (2012) described a variation on the Canadian WQI-CCME that relates to the purification treatment effort (PTE). A fixed core set of eight parameters (temperature, total organic carbon, turbidity, pH, *Escherichia coli*, nitrate, total coliforms and iron) reflect the most common water concerns. Drinking water quality standards are established, based on the expected treatment efficiency of two treatment techniques: chlorination alone and chlorination after slow sand filtration. Deviations from this standard (from 0 to a maximum of 100) were taken as the quality impairment.

Dutra De Oliveira *et al.* (2019) used the WQI-NSF as a basis for the RW-WQIF for raw water quality for purification by conventional treatment processes, using a set of parameters selected to represent chemistry (e.g. manganese), biology (e.g. *E. coli*), and the physical state (e.g. apparent color), deriving values by a specific algorithm. This way, they could relate the index value to a required coagulant dose. In their preprint, Van den Doel *et al.* (2019) published their method for adjusting the WQI-CCME for assessing removal efforts relating to micropollutants by using a very broad selection of chemical parameters, taking values from the Dutch Drinking Water Decree (Drinkwaterbesluit; DWB) (2018) as their standard and adding a score for each element's removability based on Gibbs free energy. Van den Doel *et al.* (2019) use the same concept as in our approach, estimating removal effort based on parameter characteristics. However, their calculation differs by being a more indirect and complex calculation of the contribution of parameters to the index based on frequency and number of parameters that pass the quality threshold (see the description of the WQI-CCME above) and it uses a fixed number of parameters.

In current times it is important to have a measure that includes new and emerging contaminants because these are a potential threat to water quality (van Wezel *et al.* 2017). This is also feasible, or will be in the near future, as water boards and utilities at present turn to risk-based monitoring to flexibly monitor significant emerging substances (Brunner *et al.* 2020). In this paper, we define and describe a novel framework of indices that relate to micropollutant quantities and the removal effort that is required to meet water quality regulations. In this defined framework these two aspects can be assessed separately as well as being integrated. In this way, two questions can be answered: does the source water have micropollutants that are, on average, difficult to remove, and how extensive is the pollution. The required purification treatment level is calculated based on the characteristics of the micropollutants and is expressed in percentages, which naturally relate to purification efficiency. If for any source water the treatment effort is low, and/or removal requirement (RR) is low, or it is declining through time, it can be argued that less advanced techniques or less capacity is needed, resulting in lower investment and operational costs for drinking water purification treatment. The index can serve as a relatively simple instrument to evaluate the need to reduce required purification treatment level, as specifically mentioned in the EU WFD. This will enable water managers or drinking water companies to establish if these goals are met, or if additional measures need to be taken.

As a case study, we apply the water quality indices to evaluate the water quality of the Rhine at several drinking water intakes. Based on these indices we assess how the

quality of the Rhine and the required purification treatment have developed since the introduction of the WFD in 2000.

METHODOLOGY

The WQI for required purification treatment level is composed of two elements: the WQI RR and the WQI PTE.

Calculation of the WQI RR

The DWB (2018) contains quality standards for both organic and inorganic substances and chemical organoleptic/aesthetic or signalling indicators. For good quality drinking water, all of these quality standards have to be met by drinking water companies. Table S1 in the Supplementary Information lists the water quality standards mentioned in the DWB (2018).

To calculate the removal requirement to meet these standards, the ratio of the maximum measured concentration in a given period and the corresponding DWB standard (see Table S1, Supplementary Information) is calculated for each reported micropollutant. For each micropollutant that exceeds its corresponding quality standard, the percentage exceedances are added up for all those micropollutants. This means that the WQI RR value increases with each measured peak concentration of a micropollutant that exceeds its corresponding DWB standard. There is no upper boundary. A high index value thus indicates that there is a high removal requirement for different micropollutants. Equation (1) shows the calculation for the removal requirement for a single micropollutant. Equation (2) shows the calculation for the total WQI RR for the water.

$$RR_i = 100 * \left(1 - \frac{C_{DWB,i}}{C_{MAX,i}}\right) \quad \text{if } C_{MAX,i} > C_{DWB,i} \quad\quad (1)$$

$$WQI\_RR = \sum_{1}^{n} RR_i \quad\quad (2)$$

where C_{DWB} is the DWB standard for a micropollutant, C_{MAX} is the maximum measured concentration of a micropollutant in a period, i is a micropollutant and n is the total number of micropollutants. Every micropollutant that exceeds its standard will at most add between 0 and 100% to the index. The WQI RR indicates source water quality in terms of the removal requirement and this is independent of the type of treatment.

Calculation of the WQI PTE

For this index we assign a weighting factor to each substance that has to be removed; its value depends on the estimated removal effort.

The estimated removal effort is based on two substance properties: the octanol-water partition coefficient K_{ow} and a biodegradation constant (for more information see Text S4, Supplementary Information). Log K_{ow} is a measure of hydrophobicity. In general, the more hydrophobic a substance is (high log K_{ow}), the easier it is to remove from water because of a tendency to adsorb to matter. The higher the biodegradability of a substance, the easier the removal by biological processes. We choose to use log K_{ow} and biodegradation rate constants for calculating the removal effort because both adsorption and biodegradation processes occur during conventional, 'simple' drinking water treatment. We do not explicitly define purification steps in any particular treatment, as this will differ per treatment installation (Stackelberg *et al.* 2007; Fischer *et al.* 2019).

The values per micropollutant are predicted by the model suite in EPIsuite (US EPA 2019), a Windows®-based suite of physical/chemical property and environmental fate estimation programs. From EPIsuite we use the model Kowwin (Meylan & Howard 2005) for log K_{ow}. Whenever there was an experimentally obtained value available for log K_{ow}, this was preferred over the calculated value. For biodegradation we use Biowin3 (Boethling *et al.* 2004), which predicts a biodegradation rate. A value of >4.75–5 means hours, >4.25–4.75 means hours to days, >3.75–4.25 means days, >3.25–3.75 means days to weeks, >2.75–3.25 means weeks, >2.25–2.75 means weeks to months, >1.75–2.25 means months, <1.75 means persistent (Boethling *et al.* 2004).

All possible values of the two properties log K_{ow} and biodegradation are stored in four bins with a weighting factor (*w1* and *w2*) per property; see Table 1. This approach is adopted from the work of Fischer *et al.* (2011). Biodegradation weights are set at only half of that of log K_{ow}.

Table 1 | The categories of values for mircropollutant traits determining removal efficiency, and their resulting normalised bins (0–1)

	Normalised bins	Value 1	Value 2	Value 3	Value 4
Log K_{ow}	Normalised bin *w1*	0	0.33	0.66	1
EPIsuite model Kowwin	Log K_{ow} (*t1*)	$t_1 > 6$	$3 < t_1 \leq 6$	$0 < t_1 \leq 3$	$t_1 < 0$
Biodegredation	Normalised bin *w2*	0.5	0.67	0.83	1
EPIsuite model Biowin3	Biodegradation (*t2*)	$t_2 > 4.75$	$3.25 < t_2 \leq 4.75$	$3.25 < t_2 \leq 2.25$	$t_2 < 2.25$

The values for log K_{ow} and biodegradation (t1 and t2) are binned to indicate the ease of removal of substances (see Fischer *et al.* (2011) for a similar approach) with weightings (w1 and w2). A weighting of 1 indicates no removal. A weighting of 0 indicates full removal.

Biodegradation is an important process, especially in wastewater treatment plants (WWTPs). However, WWTP processes differ from drinking water treatment processes. The water quality (presence of nutrients) is different, and typically, the residence time of water in a WWTP is significantly longer (1–3 days) than the contact time in a (rapid) sand or activated carbon filter (typically 20–40 min). Therefore, if not downscaled, the application of biodegradability constants as indicators may overestimate the contribution of biodegradation in drinking water treatment plants.

These scaled weighting factors *w1* and *w2* are used to obtain an estimate of the effort to remove the substance in question. As drinking water treatment consists of several sequential processes, in which each process results in a certain removal, multiplication is considered more realistic than a simple averaging of the removal properties. This is the PTE (see Equation (3)).

$$PTE_i = w1_i \cdot w2_i \cdot 100 \qquad (3)$$

where PTE is the removal estimate for micropollutant *i*, *w1* and *w2* are weights, as in Table 1. As an example, a PTE value of 0 means that it is expected that the substance will be fully removed. In contrast, a PTE value of 100 means that the removal of the substance is expected to be negligible. The actual estimated removal in percentages can be calculated for a substance as 100-PTE. Table S2 (Supplementary Information) shows these predicted removal percentages by our method, with a validation based on expert judgement of how accurate these are predicted by the PTE calculation in Equation (3). In 66% of substances, the established PTE (Table 1, Equation (3)) has a realistic removal in the validation by expert judgement for a 'conventional' treatment setup where sorption and biodegradation processes constitute the main removal mechanisms (see Table S2,

Supplementary Information). In the calculation of the WQI PTE summed micropollutants are omitted, because removal can differ between members of a group that are summed.

The WQI PTE is calculated as the average of the removal indication PTE (see Equation (3)) for all substances *i* that exceed their standard in the DWB (2018) (see Equation (4)).

$$WQI\_PTE = \frac{\sum_1^n PTE_i}{n} \qquad (4)$$

where WQI PTE is calculated for all substances *n* that exceed the standard in the DWB (2018). The WQI PTE yields a value between 0 and 100, representing full removal and no removal respectively.

Note that EPIsuite is not able to calculate the property constants *t1* and *t2* (see Table 1) for inorganic substances, since these constants fall outside its modeling domain. For inorganic micropollutants, the PTE was set at a low value to ensure that the removal effort index value corresponds to an easy to remove indicator value (17) as for most of these compounds this will generally be the case in practice. Exceptions to this assumption are compounds such as chloride, fluoride, sulfate, nitrite, ammonium, and nitrate, as these are known to be difficult to remove. These micropollutants are given a high PTE (90) to indicate this, based on expert judgement.

Combining the WQI RR and WQI PTE for a residual removal indication

WQI RR combined with WQI PTE indicate to what extent the micropollutants that exceed their standard in the DWB (2018) are removable by purification treatment. If the removal efficiency is insuficient to cover the removal requirement for a micropollutant *i*, there will remain a

percentage that can be considered to be a residual removal requirement (RR_PTE). Equation (5) shows how this combination can be made for each micropollutant *i*. If a micropollutant *i* has a removal efficiency indication (100-PTE) that *exceeds* the removal requirement, which is the case when (100-PTE) > RR, the residual removal requirement is set to 0.

$$RR\_PTE_i = \frac{RR_i - (100 - PTE_i)}{PTE_i} \quad \text{if} \quad 100 - PTE_i < RR_i \qquad (5)$$

$$WQI\_RR\_PTE = \sum_1^n RR\_PTE_i \qquad (6)$$

If the WQI RR_PTE is high, this means the combination of removal requirement and PTE is high for the combination of different micropollutants reported.

Figure 1 provides an overview of the inputs, equations, and water quality indices in this methodology section.

Data processing

To test our indices in a real-world setting, we use measurement data from the RIWA base (RIWA 2012). This database contains measurements from existing monitoring programs, including micropollutants listed in the DWB (2018) from 1972 onwards. For our evaluation we consider the period 2000–2018, which is the implementation of the WFD in the European Union. The number and type of parameters measured in the monitoring programs are optimized continuously and differ per location. We consider five locations along the river Rhine; one at the German–Dutch border at Lobith and four drinking water intake locations: Nieuwegein (river Lekkanaal), Nieuwersluis (Amsterdam–Rhine canal), Andijk (lake IJsselmeer) and Stellendam (river Haringvliet), as depicted in Figure 2.

Quality standards in the DWB (2018) can be micropollutant specific, micropollutant group specific, or contain 'sum' micropollutants. For instance, a specific standard for the pesticide aldrin exists, which is 0.03 µg/L. For pesticides without a specific standard, the quality group standard is 0.1 µg/L. However, the standard for the sum of all pesticides is 0.5 µg/L. All types of quality standards are listed in Table S1 (Supplementary Information). The reported data from RIWA were recalculated for every (sum) micropollutant to a peak concentration value per year. More detailed information on data processing can be found in Text S2 (Supplementary Information).

All data processing and visualisations were done in the coding language R. This script, with the accompanying data sources, can be accessed at https://doi.org/10.5281/zenodo.4165486.

RESULTS

Data characterization

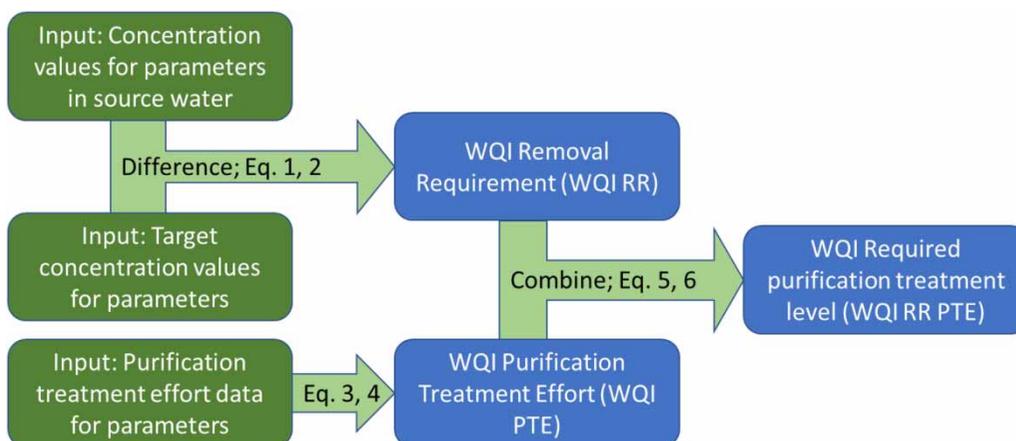To gain insight into the extent of the measuring program at different Rhine locations and how many of these measured

Figure 1 │ Scheme of relationships between input, equations, and WQIs that lead to the WQI RR_PTE. The abbreviation 'Eq.' stands for Equation.

Figure 2 │ The Netherlands and the river Rhine. Lobith, Nieuwegein, Nieuwersluis, Haringvliet and Andijk are the locations of the measurement programs for water quality that were used to evaluate the required purification treatment level.

micropollutants exceed their DWB (2018) value, we illustrate them in Figures 3 and 4. Figure 3 shows the number of measured and reported micropollutants with a DWB standard at the five locations. In Figure 3 it can be seen that the number of micropollutants measured increases over the years by a factor of two to 16, depending on the location. This is because parameters are added continuously to measurement programs, based on new insights into possible pollutants. Parameters are less often discarded. Figure 4 shows the number of micropollutants per location that exceed their DWB quality standard. Micropollutants with exceeding concentrations show only a slight increase (a factor of one to four, depending on location) (Figure 4).

From Figures 3 and 4 it can be observed that the difference in size of the monitoring program between locations apparently does not necessarily lead to more micropollutants exceeding their quality threshold. In other words, if the random addition of parameters causes the finding that more compounds exceed their standard, the locations with the larger measurement programs would have more exceeding parameters. As an additional check, we compared different locations with different sizes of monitoring program within the same year. We extended data with three locations in the river Meuse that have similar extensive
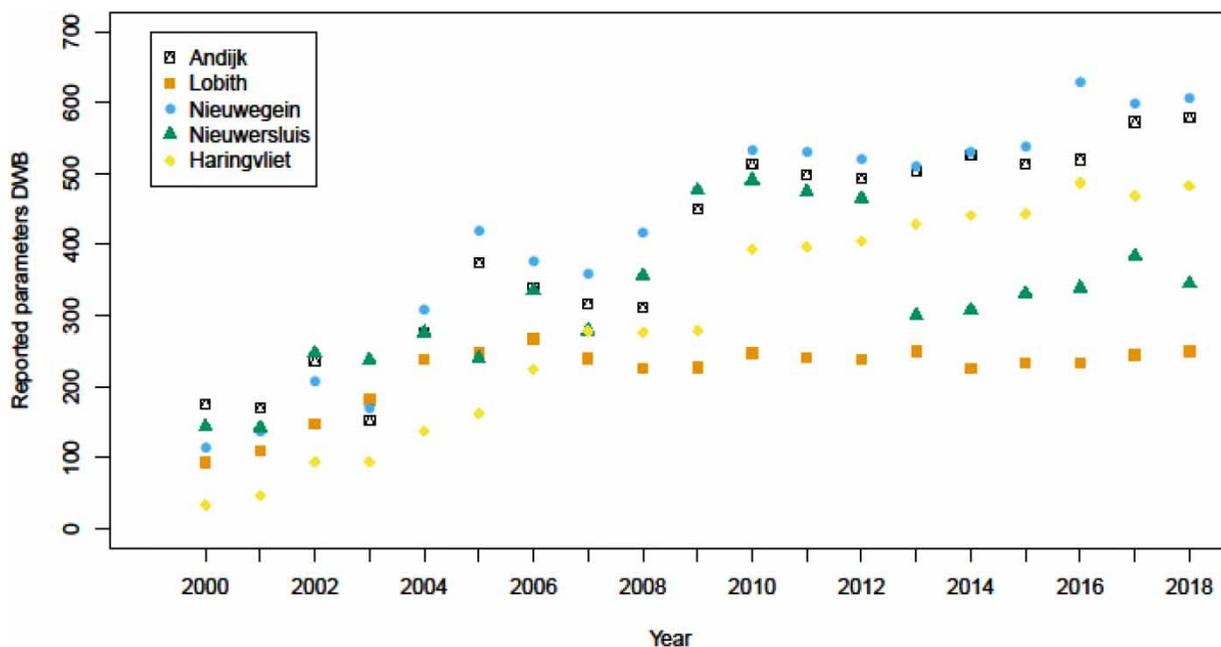

Figure 3 │ The number of reported micropollutants per year per location with a DWB standard (see Table S1, Supplementary Information).
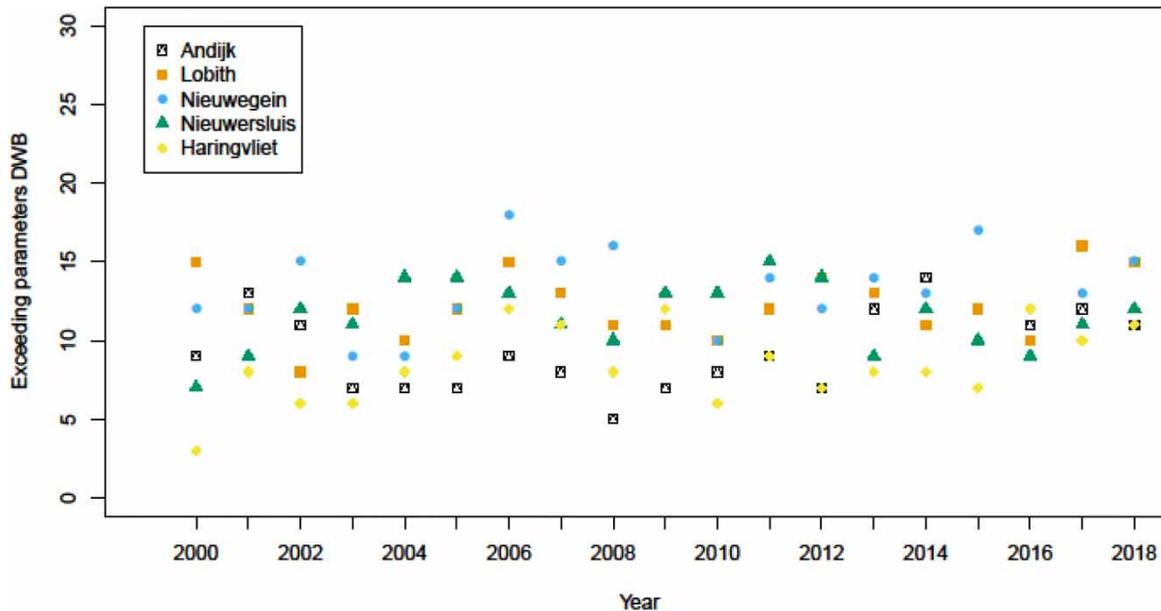
Figure 4 | The number of micropollutants per year per location that exceed their DWB standard (see Table S1, Supplementary Information).

monitoring programs, to be able to provide this conclusion with a more robust base. The relationship between the number of reported micropollutants and the number of micropollutants exceeding their standard at the locations is positive in some years and negative in others. None of the relationships is statistically significant, following a linear regression model. This means there is no statistically significant increase or decrease in exceeding micropollutants with a larger measuring program, for this set of locations. The results of the analysis can be viewed in Figure S1 (Supplementary Information).

Notwithstanding that, Figures 3 and 4 still raise the question of whether more micropollutants are found to be exceeding because in time more micropollutants are measured in these monitoring programs, or if these newly exceeding micropollutants were added because they were suspected to be new or emerging. We think the latter is more likely. Nevertheless, we will be careful in interpreting a deterioration, and will be more confident in an improvement. This issue is discussed in more detail in the discussion.

Values and trends in the WQI RR

We calculated the WQI RR values for source waters for drinking water production at the five locations along the river Rhine in the period 2000 to 2018 and determined if these show a (significantly) improving trend, according to a linear regression model. In Table 2 the significance value (*p*-value) of these calculated trends in WQI RR is shown. The WQI RR does not seem to improve in any of the locations.

In Table 2 it can be seen that historically, Haringvliet has the best water quality on average. Andijk has the lowest WQI RR in 2018, and therefore has the best recent water quality with regard to the index for removal requirement.

Contribution of substance categories to the WQI RR

To get an idea of the kind of substances that contribute to the trend in WQI RR in Table 2, we looked at the exceedance of standards per year per location per group of micropollutants, for four categories:

1. General parameters and nutrients
2. Plant protection products, biocides and their metabolites
3. Industrial pollutants and consumer products
4. Pharmaceuticals and endocrine disrupting chemicals (EDCs)

These categories are derived from the labels used in the RIWA (2012) database. Because some micropollutants have

Table 2 | Trend and average values in WQI RR between 2000 and 2018

	Andijk	Lobith	Nieuwegein	Nieuwersluis	Haringvliet
WQI RR average 2000–2018	468	696	723	641	382
WQI RR in 2018	587	816	648	670	608
p-value trend WQI RR 2000–2018	0.10 (+)	0.22 (+)	0.31 (+)	0.66	0.13 (+)

A '+' indicates the WQI RR is increasing, which implies there is no improvement. No '+' or '−' is given for trends with significance level $p > 0.5$.

more than one label, some micropollutants are counted in more than one parameter category.

Table 3 shows the significance values (*p*-values) of the trends according to a linear regression in removal requirement in the parameter categories over the years 2000–2018, per location. Table 3 also shows that the total WQI RR is comprised of parameter categories with sometimes opposite trends per location. Only the WQI RR of the parameter category Pharmaceuticals and EDCs is increases at all locations. These increases are significant at Lobith, Nieuwegein and Haringvliet and almost significant at the other locations. The WQI RR for the other parameter categories increase or decrease, depending on the location. The WQI RR for Industrial pollutants and consumer products shows no significant trend at any of the locations, because the index for this parameter category is very variable from year to year at all the locations.

Lobith is of strategic importance because this is the where the Rhine enters the Netherlands. As an example, for this location, we plot the individual removal requirement for micropollutants per parameter category (Table 3) over the years in Figure 5. Every micropollutant can be seen as a colored ribbon.

Figure 5 shows that at Lobith, micropollutants in 'General parameters and nutrients' often structurally exceed the DWB standard. This includes iron, NO_2, aluminum, and manganese. Pharmaceuticals and EDCs exceeded from

2007 onwards, including jomeprol, di (2-ethylhexyl) phthalate (DEHP), guanylureum, and metformin. The Industrial contaminants and consumer products alternate, emerge and disappear again. Only the sum parameter polycyclic aromatic hydrocarbons (PAHs) exceeds its standard during a longer period of time. Plant protection products, biocides and their metabolites generally exceed for longer periods, occasionally remaining below their standard in, for example, isoproturon, glyphosate, trichloroacetic acid (TCA). Aminomethylphosphonic acid (AMPA) and the pesticide group structurally exceed quality standards (around 80% and 60–70% respectively).

The purification treatment effort index WQI PTE

The effort of meeting the removal requirement, as explained in the Methodology section, can differ depending on the difficulty of removing micropollutants. We address this aspect by calculating WQI PTE (see Equation (4)) for all locations. A high value indicates that the substances in the WQI RR are hard to remove in drinking water treatment.
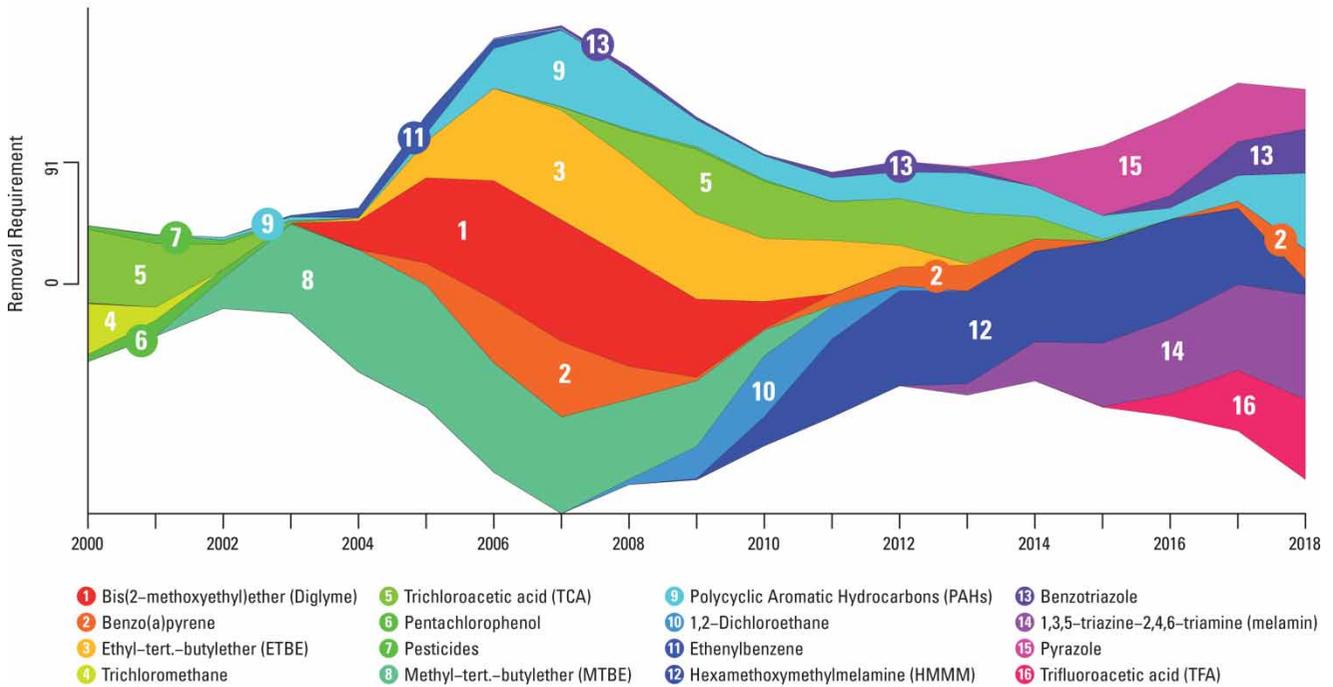
Table 4 shows the significance (*p*-values) of the trends observed according to a linear regression model for the last 20 years for the river Rhine locations. The WQI PTE shows no signs of improvement. This indicates that in recent years, substances that have exceeded their DWB

Table 3 | Trends of removal requirement per parameter category of 2000–2018

	Andijk	Lobith	Nieuwegein	Nieuwersluis	Haringvliet
Ppp/Bioc/Metab	<0.01 (+) *	0.03 (−) *	0.45 (−)	0.41 (−)	0.03 (+) *
Ind/Cons	0.48 (−)	0.10 (+)	0.902	0.95	0.10 (+)
Pharm/EDC	0.08 (+)	<0.01 (+) *	<0.01 (+) *	0.09 (+)	<0.01 (+) *
GPar/Nutr	0.91	0.05 (−) *	0.01 (+) *	0.06 (+)	0.41 (−)

Numbers indicate the significance value (*p*-value) of the trend. The symbol '−' indicates an improvement, '+' indicates no improvement. No indication is given for trends with $p > 0.5$. Significant trends ($p < 0.05$) are indicated with an asterisk. Ppp/Bioc/Metab = plant protection products, biocides and their metabolites. Ind/Cons = industrial pollutants and consumer products. Pharm/EDC = pharmaceuticals and EDCs. GPar/Nutr = general parameters and nutrients.

(a)   Industrial pollutants and consumer products Lobith

① Bis(2–methoxyethyl)ether (Diglyme)   ⑤ Trichloroacetic acid (TCA)   ⑨ Polycyclic Aromatic Hydrocarbons (PAHs)   ⑬ Benzotriazole
② Benzo(a)pyrene   ⑥ Pentachlorophenol   ⑩ 1,2–Dichloroethane   ⑭ 1,3,5–triazine–2,4,6–triamine (melamin)
③ Ethyl–tert.–butylether (ETBE)   ⑦ Pesticides   ⑪ Ethenylbenzene   ⑮ Pyrazole
④ Trichloromethane   ⑧ Methyl–tert.–butylether (MTBE)   ⑫ Hexamethoxymethylmelamine (HMMM)   ⑯ Trifluoroacetic acid (TFA)

(b)   Plant protection products, biocides and their metabolites Lobith

① Aminomethylphosphonic acid (AMPA)   ⑤ Parathion–methyl   ⑨ Pesticides   ⑬ Monolinuron
② Glyphosate   ⑥ Isoproturon   ⑩ chloridazon–methyl–desphenyl
③ Chlortoluron   ⑦ Trichloroacetic acid (TCA)   ⑪ Metolachlor
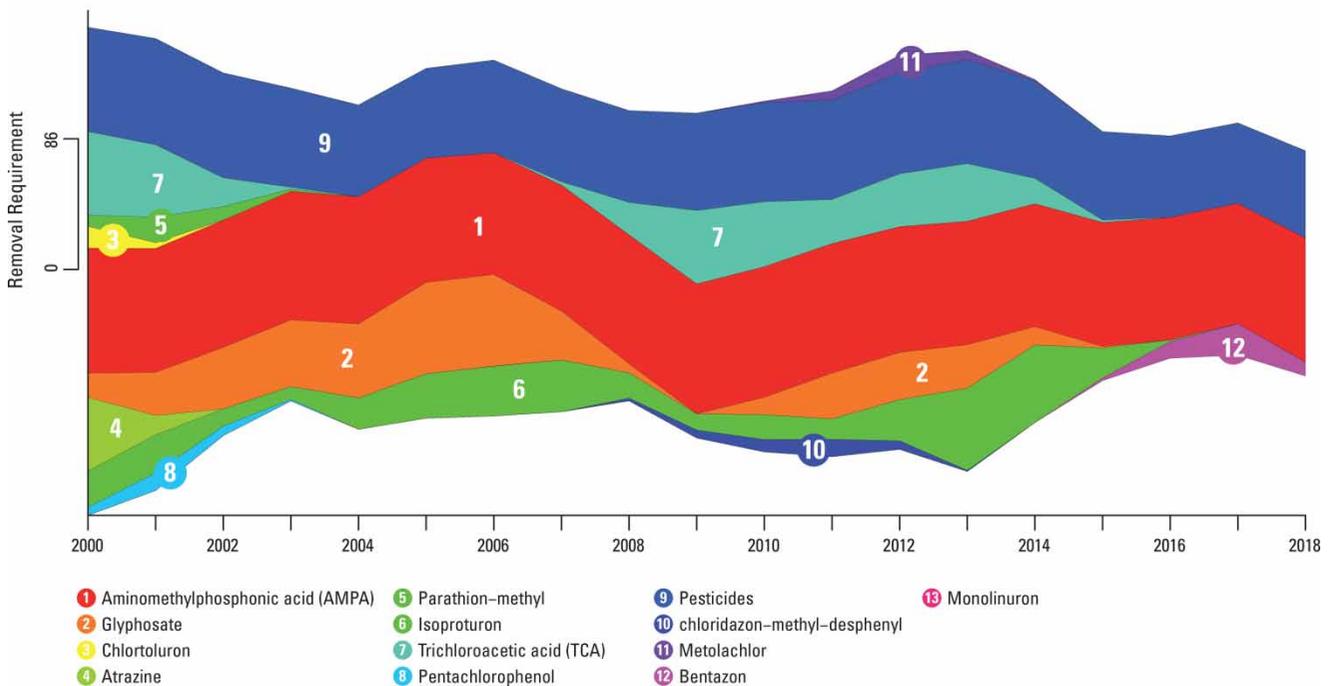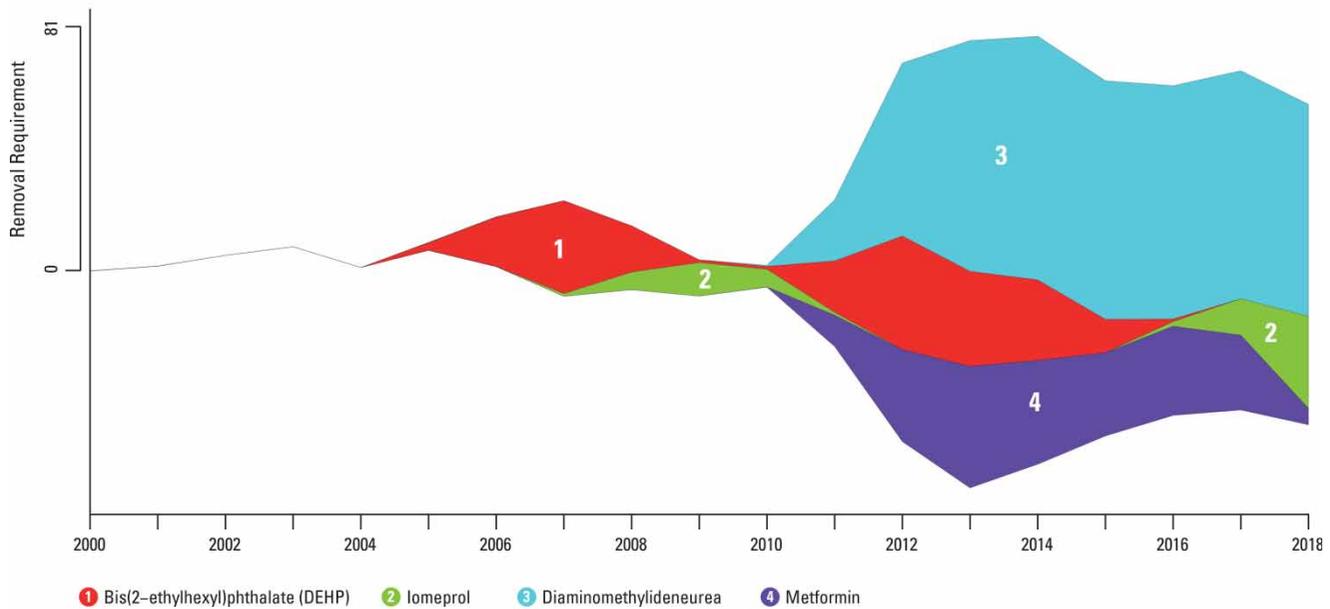④ Atrazine   ⑧ Pentachlorophenol   ⑫ Bentazon

Figure 5 │ The WQI RR shown as removal requirement for individual micropollutants. Individual micropollutants are shown as colored 'ribbons' per parameter category (in the individual plots) for Lobith. The peaks per micropollutant are slightly spread out over adjacent years because of the use of a smoothing factor when drawing these figures. Every individual micropollutant has a theoretical maximum removal requirement of 100%. Please refer to the online version of this paper to see this figure in color: http://dx.doi.org/10.2166/ws. 2020.289. *(Continued.)*

(c) Pharmaceuticals and endocrine disrupting chemicals (EDCs) Lobith

① Bis(2–ethylhexyl)phthalate (DEHP) ② Iomeprol ③ Diaminomethylideneurea ④ Metformin

(d) General parameters and nutrients Lobith

① Nitrite (NO2) ③ Aluminium ⑤ Lead ⑦ Chloride
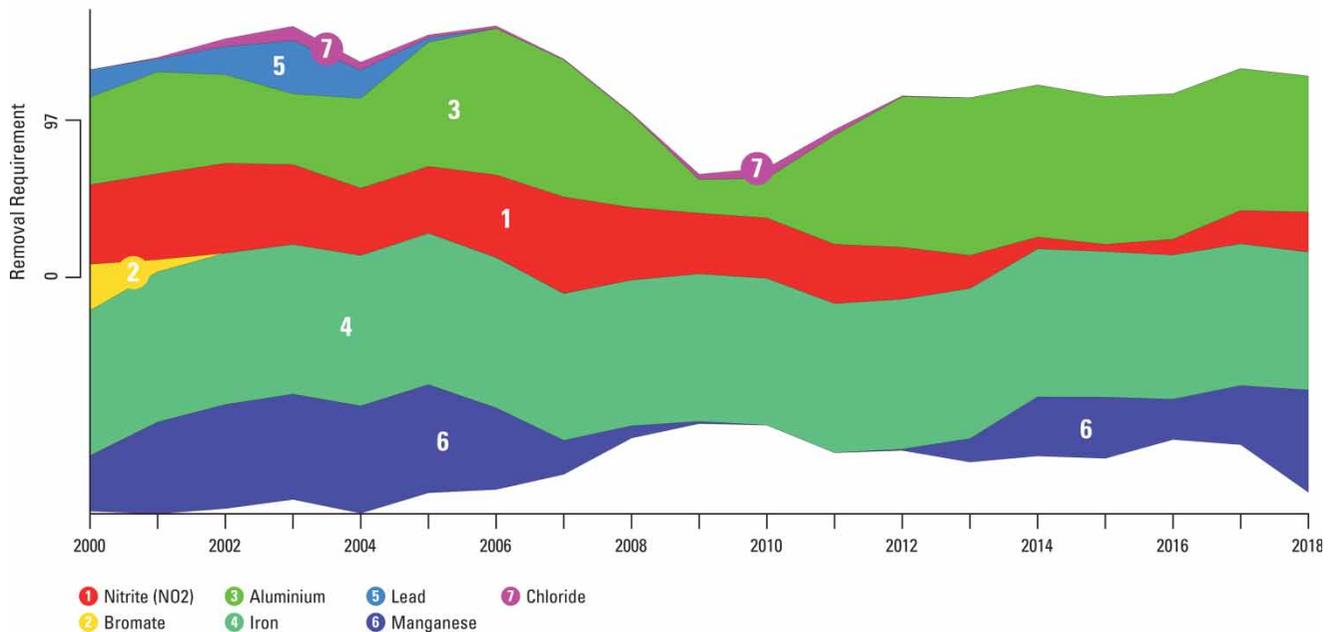② Bromate ④ Iron ⑥ Manganese

Figure 5 │ Continued.

standards on average have not become easier to remove. Part of the increasing trends in purification treatment effort at Andijk and Lobith are due to novel reported substances with difficult removal (e.g. see Figure 7), for instance pharmaceuticals.

Nieuwegein and Nieuwersluis have the lowest WQI PTE in 2018, and therefore have the best water quality with regard to this purification treatement effort index in 2018. Haringvliet has the worst water quality. Andijk has on average the best water quality with regard to purification treatment effort.

Table 4 │ Trend in WQI PTE between 2000 and 2018

	Andijk	Lobith	Nieuwegein	Nieuwersluis	Haringvliet
WQI PTE average 2000–2018	46	54	47	50	53
WQI PTE in 2018	53	52	48	48	56
p-value trend WQI PTE 2000–2018	0.28 (+)	0.06 (+)	0.99	0.83	0.98

A '+' indicates the WQI PTE is increasing, which implies there is no improvement. No '+' or '−' is given for trends with significance level $p > 0.5$.

The lowest WQI PTE was calculated in Andijk in 2008 and was 26. The highest WQI PTE calculated was 69, which occurred in Haringvliet 2002 and 2017 and in 2009 in Lobith. The order of the locations in terms of quality according to the WQI PTE is quite different from the WQI RR.

The required purification treatment level index WQI RR_PTE

The two indices WQI RR and WQI PTE aggregated into the WQI RR_PTE (see Equations (5) and (6)) can evaluate the required purification treatment level for water. Figure 6 shows the development of the WQI RR_PTE for the five locations along the Rhine for the period 2000–2018. The size of the circles indicates the WQI RR value, and the color indicates the WQI PTE value. The height of the circles is the WQI RR_PTE value, multiplied by 100 to align it to the WQI RR value. For the five locations, including Nieuwegein, which seems to have a negative slope, there is no (significantly) declining trend in the WQI RR_PTE (see Table 5), which implies the water quality in terms of required purification treatment level is not improving.

The WQI RR_PTE is more sensitive to the removal requirement than to the purification treatment effort, and this inequality increases with more exceeding micropollutants. This is because the first is a summation, which increases with every new micropollutant with a removal requirement, and the latter is an average that will not change dramatically with an extra value.

In 2018, the order of locations based on their WQI RR_PTE from low (better), to high (worse) was:

Andijk (140) < Nieuwegein (173) < Nieuwersluis (215) < Haringvliet (224) < Lobith (273).

Andijk has the lowest WQI RR_PTE in 2018, which means that it has the best water quality with regard to this index. When comparing the order of the locations according to the WQI RR_PTE to those according to the WQI RR, Haringvliet has changed places with Nieuwegein and Nieuwersluis, due to the relatively high WQI PTE for Haringvliet.

Table 5 shows the significance (*p*-values) of the trends in WQI RR_PTE per location according to a linear regresssion model. In none of the locations is there a decreasing trend in the WQI RR_PTE. This means that at these locations, over time, more micropollutants have indications for difficult removal by the size of their exceedance of the DWB (2018) value and/or difficult removal.

As an example how the WQI RR_PTE results from individual micropollutants, we show the micropollutants that contribute to the calculated WQI RR_PTE for Lobith in Figure 7. On the left bar are the intrinsic PTEs modeled for the micropollutants from low (yellow/light, easy removal) to high (red/dark, difficult removal). On the right is their contribution to the WQI RR_PTE (Equation (5)), the darker, the higher.

Logically, substances with high intrinsic PTE (red/dark, in the left bar) have a tendency to require more extensive purification treatment. Most of the substances in Figure 7 have a high intrinsic PTE. In contrast, most substances with a low intrinsic PTE (easy removal) do not contribute to the WQI RR_PTE (not shown). These are substances such as bis(2-ethylhexyl)phthalate (DEHP) and benzo(a) pyrene. Some substances with medium PTE also do not contribute to the WQI RR_PTE (not shown). This is because these micropollutants exceeded their DWB standard in this location with a low percentage (RR) and the PTE was enough to cover this. These are substances such as bentazon and monolinuron. Iron and aluminum also have a low PTE (left bar in Figure 7, yellow/light). However, these micropollutants exceeded the DWB standard to such a high extent in this location (represented in their RR) that their PTE was insufficient for complete removal. This is why they still
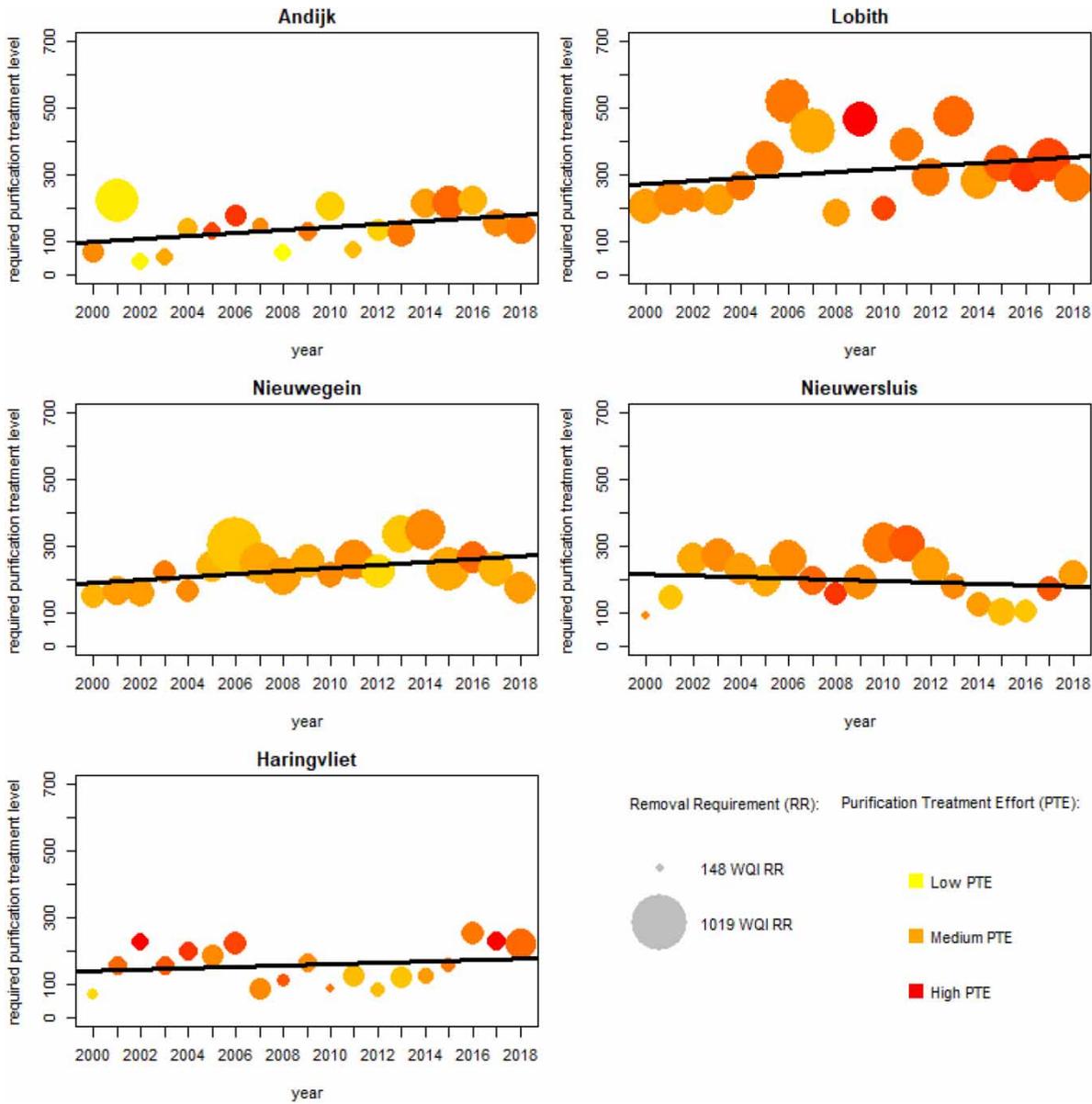
Figure 6 | The WQI RR_PTE for five locations along the Rhine for the years 2000–2018 (x-axis). The height of the circles is the WQI RR_PTE value (y-axis). The size of the circles indicates the WQI RR, and the color indicates the WQI PTE. The black line is a fitted linear regresssion model. Please refer to the online version of this paper to see this figure in color: http://dx.doi.org/10.2166/ws.2020.289.

Table 5 | Trend in WQI RR_PTE between 2000 and 2018

	Andijk	Lobith	Nieuwegein	Nieuwersluis	Haringvliet
p-value trend WQI RR_PTE 2000–2018	0.07 (+)	0.31 (+)	**0.05** (+) *	0.52	0.41 (+)

Numbers indicate the significance value (p-value) of the trend. The symbol '−' indicates an improvement, '+' indicates no improvement. No indication is given for trends with $p > 0.5$. Significant trends ($p < 0.05$) are indicated with an asterisk.

contribute to the WQI RR_PTE, shown in Figure 7. Substances that have improved over the years (these have a dark color mostly in earlier years) are glyphosate, NO_2, atrazine, ammonium (see Figure 7). Substances that contribute
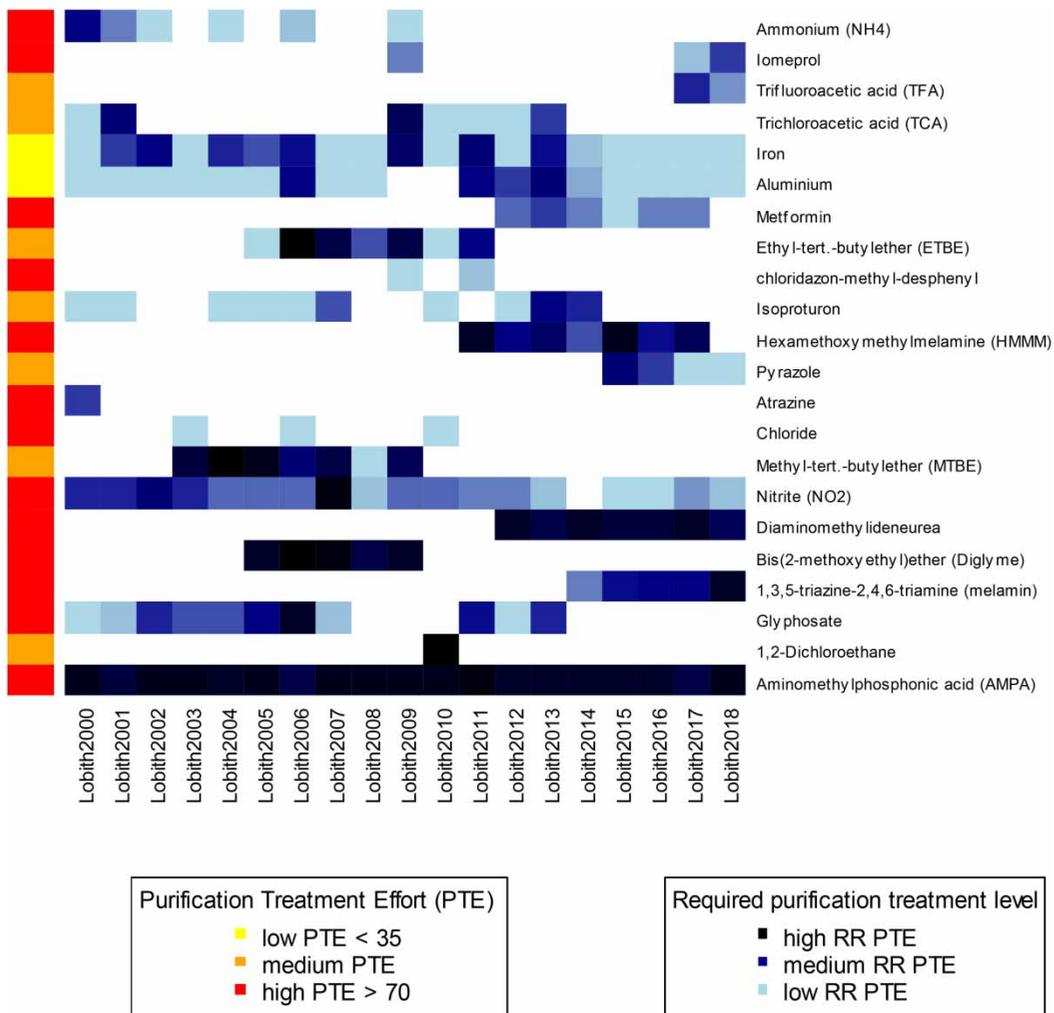
Figure 7 │ The calculated RR_PTE per micropollutant for Lobith. On the left, in yellow/light to red/dark, the intrinsic purification treatment effort per micropollutant (PTE). On the right is the RR_PTE per micropollutant from blue/light to black. White spots are micropollutants that did not have a removal requirement for that year, or micropollutants for which the PTE was enough to cover the removal requirement for the micropollutant (see Equation (5)). Micropollutants with zero RR_PTE in all years were omitted. Please refer to the online version of this paper to see this figure in color: http://dx.doi.org/10.2166/ws.2020.289.

to the deterioration of the WQI RR_PTE at Lobith (these have a dark color in later years) are melamin, pyrazole, HMMM, isoproturon, metformin, TFA, and iomeprol.

DISCUSSION

Data and trends

We developed a framework containing three indices for an evaluation of source water quality in relation to level of purification treatment required. The indices are

based on substance characteristics and are therefore not dependent on the specifications of any specific purification treatment plant. The WQI RR_PTE can be assessed separately based on the extent of micropollution (WQI RR) and the difficulty of removal of the micropollutants (WQI PTE). The locations and also separate years affected the relative height of the WQI RR_PTE by the combined influence of the WQI RR or WQI PTE. Both WQI RR and WQI PTE and their combination, the WQI RR_PTE, show no improvement in locations along the river Rhine since the introduction of the WFD in the year 2000. The height of the indices was

caused partly by some substances that are persistent or recurring, and partly by new substances.

It is important to have a measure that also includes new and emerging contaminants because these are a potential threat to water quality. An increasing number of these chemicals find their way into the freshwater system (van Wezel *et al.* 2017). Note that the number of substances on the European market is increasing, with no less than 22,468 chemical substances registered in the European Union in 2019 (ECHA 2019). As a result, an increase in substances that exceed their quality standard is plausible. Also, due to (amongst others) new legislation, the application of certain substances are restricted and alternative substances come in use. Hence, pollution is a dynamic problem. The monitoring program for the drinking water intake along the Rhine and other rivers is constantly adjusted accordingly (e.g. RIWA 2017, Table 1.2) based on the latest insights obtained from scientific literature, reports, or monitoring with improved analytical techniques such as non-target screening (e.g. Brunner *et al.* 2020). In our framework, we were able to include the dynamic nature of monitoring programs in an index value of required purification treatment level.

Contribution of substance categories to the WQI RR

Zooming in on the specific micropollutants that cause the changes in WQI RR at location Lobith, we see dynamic behavior. Plant protection products, biocides and their metabolites and General parameters and nutrients in particular form a large part of the WQI RR over the years. Plant protection products, biocides and their metabolites are increasing in some of the locations. Industrial contaminants and consumer products are unpredictable and vary in time, per year. Pharmaceuticals and EDCs form a small group, but they are increasing at every location without exception and are therefore of increasing concern. An increase in pharmaceuticals matches expectations based on a growing and ageing population (van der Aa & Kommer 2010). For the index on purification treatment effort, the non-declining or even increasing trend in two of the locations (one almost significant) of WQI PTE is in accordance with the findings by, for instance, Schoep & Schriks (2010) that a relationship exists between Registration, Evaluation, Authorisation and Restriction of

Chemicals (REACH) regulation and the tendency to have recalcitrant substances in the environment, represented by a low log K_{ow}.

Improvement of WQI PTE

Being part of a framework, the WQI PTE can be improved in the future. The WQI PTE is currently based on two properties, the biodegradability and log K_{ow} (Fischer *et al.* 2011). More properties affect purification treatment efficiency, such as sorption processes based on electrostatic interaction, volatility, chemical reactivity and molecular size (van Leeuwen & Vermeire 2007; van Wezel *et al.* 2017; de Munk 2018). In general, the compounds that are hydrophilic, small, have low volatility, high solubility, low biodegradability and reactivity and adsorption will be hard to remove. Adding more properties may improve the removal efficiency correlation (Vries *et al.* 2013). Also, the PTE value calculation may be improved by using more direct parameters like molecular weight, aromaticity, and the number of halogens present, rather than indirect parameters such as K_{ow} and biodegradability. In a different approach, the current calculated indications of ease of removal in the WQI PTE can even be replaced by actual removal efficiencies of micropollutants in specific drinking water purification treatment processes. However, these data are often not widely or centrally available. A general estimation for a full scale treatment is unrealistic because the exact treatment processes applied per installation largely determine the treatment efficiency for different micro-pollutants (Stackelberg *et al.* 2007; Fischer *et al.* 2019). Treatment efficiencies are mostly studied per treatment step (e.g. activated carbon, advanced oxidation, membrane filtration techniques) and the treatment efficiency of compounds varies with each of these steps. Even within treatment steps between different installations this efficiency may differ (de Munk 2018) depending on water matrix composition, the exact doses of purification aids used, physical design of the applied treatment or fouling degree (age) of membranes. The current WQI PTE and the validation of outcomes by expert judgement should therefore be seen as a rough estimate. The PTE may also be improved by adding a removal indication for group micropollutants. These can be based, for instance for pesticides, on the average of the individual PTEs of pesticides that

require removal in a specific location. The removal of micro-biological parameters currently is not implemented, and a different trait set should be established to estimate their purification treatment effort.

The WQI RR_PTE and monitoring programs

As already mentioned, the WQI RR and WQI PTE are not limited to a pre-defined set of substances, i.e. 'all' micropollutants that have a removal requirement contribute, including the upcoming and newly measured micropollutants. This is important because recently reported substances also contribute to potential risks and therefore to the need to remove them. The advantage of using 'all' micropollutants for the WQI RR and WQI PTE is the independence between timeframes or locations because there is no need for a fixed list of micropollutants. Including 'all' micropollutants does mean that the approach is suitable for locations where the measurement program has the means and the goal of measuring 'all' known or suspected micropollutants. For locations where this is not the case, the comparison of the WQI RR between locations will be hampered by gaps in the reported micropollutants. The framework described here can still be used, but in those cases it is recommended to keep to a fixed set of micropollutants in calculating the indices.

One uncertainty introduced by also including 'all' newly reported substances is that we cannot exclude the possibility that some of the micropollutants have already been exceeding their standard before they were or could be measured. In these cases, the indices are underestimated in the early years and will seem to have a tendency to increase, but the appropriateness of the measurement program affects how large this effect is. An estimation of the likelihood of emission routes existing for these micropollutants could indicate the potential of underestimation, but this is beyond the scope of this paper. In the future, the likelihood that newly measured parameters are added because there was some indication for their potential novel threat to water quality will increase with the introduction of risk-based monitoring. For now, it enough to point out that the indexes were at least not improving for the locations under investigation and that there were differences in water quality between the locations.

In addition to a complete measurement program, the measurement frequency in the monitoring program is important. The fewer times a micropollutant is measured within a period, the higher the chance that some peak concentrations will be missed, therefore underestimating the value of the indices. The current indices are not suitable for indicating adverse effects on the environment or people, as the exposure period to the pollution is not incorporated, which is important for risk assessment. In addition, we did not use water quality standards directly linked to human health. The index presented may rather be seen as an index for the relative complexity of treatment processes required to produce safe, good quality drinking water according to the Dutch DWB, to a point at which water utilities do not have to interrupt water intake because micropollutants exceed their quality standard.

CONCLUSION

Despite all assumptions and potential drawbacks of our indices and calculations, applying such a calculation framework reveals differences between locations and in time in an objective and reproducible manner, which allows us to study trends in very complex data. We conclude that it is possible and useful to base the indices on data from evolving monitoring programs, to also capture new and upcoming threats. The approach and indices applied to drinking water can also be applied to the influent and effluent of WWTPs, and to (industrial) reuse of water that has to meet quality standards.

Based on the calculations of these three indices, we conclude that the objectives of the WFD have not led to improvement of the water quality in the river Rhine.

Clearly, extra effort is needed in the field of emission reduction, with a focus on new and emerging substances and their removal, in order to reduce the purification treatment level required for the preparation of drinking water. Measurement programs must remain aligned to this, for instance with the help of risk-based monitoring for early signals of new and possibly problematic substances. In addition, measures should be taken to limit emissions of these substances before they become a real problem.

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DATA AVAILABILITY STATEMENT

Processed monitoring data and the script to reproduce WQI figures are available in the data package at https://doi.org/10.5281/zenodo.4165486. Raw data can be requested at RIWA-Rijn. Other relevant data are included in the paper or its Supplementary Information.

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