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Projected impact of climate change and chemical emissions on the water quality of the European rivers Rhine and Meuse: A drinking water perspective

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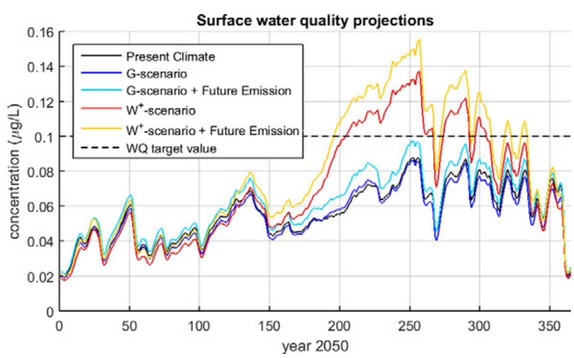
HIGHLIGHTS

- During prolonged dry periods the dilution of point sources is reduced.
- This study projects future water quality in Rhine and Meuse rivers for the year 2050.
- The projections include field data, climate change scenarios and future emissions.
- Peak concentrations in river water increase up to a factor two to four.
- These substances will be increasingly found in drinking water.

GRAPHICAL ABSTRACT



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ABSTRACT

Low river discharges of the rivers Rhine and Meuse are expected to occur more often and more prolonged in a changing climate. During these dry periods the dilution of point sources such as sewage effluents is reduced leading to a decline in chemical water quality. This study projects chemical water quality of the rivers Rhine and Meuse in the year 2050, based on projections of chemical emissions and two climate scenarios: moderate and fast climate change. It focuses on specific compounds known to be relevant to drinking water production, i.e. four pharmaceuticals, a herbicide and its metabolite and an artificial sweetener. Hydrological variability, climate change, and increased emission show a significant influence on the water quality in the Rhine and Meuse. The combined effect of changing future emissions of these compounds and reduced dilution due to climate change has leaded to increasing (peak) concentrations in the river water by a factor of two to four. Current water treatment efficiencies in the Netherlands are not sufficient to reduce these projected concentrations in drinking water produced from surface water below precautionary water target values. If future emissions are not sufficiently reduced or treatment efficiencies are not improved, these compounds will increasingly be found in drinking water, albeit at levels which pose no threat to human health.

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1. Introduction

Climate change can deteriorate water quality by the frequent and prolonged occurrence of low flows (Mosley, 2015; Murdoch et al., 2000; van Vliet and Zwolsman, 2008; Whitehead et al., 2009; Zwolsman and van Bokhoven, 2007). Due to climate change, droughts and floods are increasing in frequency and severity in many regions of the world (Dai, 2013; IPCC, 2014; Trenberth et al., 2014). In Europe, several rivers including the Rhine are projected to have increases in drought frequency and intensity in the 21th century relative to the historic records over the 20th century despite increases in annual precipitation (Hirabayashi et al., 2008).

During droughts emissions from point sources are less diluted and thus concentrations of compounds will increase. While most studies on the impact of water scarcity on drinking water supply focussed on basic physico-chemical parameters, such as chloride, nutrients and inorganic micropollutants (Baurès et al., 2013; Delpla et al., 2011; Delpla et al., 2009; van Vliet and Zwolsman, 2008; Wright et al., 2014; Zwolsman and van Bokhoven, 2007), research on organic micropollutants is scarce (Coppens et al., 2015; Masiá et al., 2013; Osorio et al., 2012). Both Masiá et al. (2013) and Osorio et al. (2012) observed high compound concentrations, for respectively pesticides and pharmaceuticals, in surface water during low river flows compared to high flows. In the modelling study of Coppens et al. (2015) the dilution of sewage treatment plant (STP) effluents in surface water bodies was modelled to vary within a factor of 10 between seasons. With an increase of droughts during summer as a consequence of climate change, this variation could become larger.

Research on the impact of climate change on the concentration of organic micropollutants in surface water and the consequences for the drinking water production is limited and mostly concentrated on regions with expected high water scarcity (Arenas-Sánchez et al., 2016; Navarro-Ortega et al., 2012; Navarro-Ortega et al., 2015; Ricart et al., 2010). However, in the Netherlands a modelling study with a more theoretical approach was conducted on the effects of climate change on water quality at drinking water abstraction points in surface water (Wuijts et al., 2012).

Climate models are used to predict the extent of climate change impacts on water scarcity; and translate greenhouse gas emission scenarios into climate change scenarios. The primary tools for providing future climate projections are coupled General Circulation Models (GCMs), which simulate climate changes under a range of possible future scenarios of greenhouse gas emissions. Currently, GCMs have a spatial resolution of 100–250 km, so these models cannot fulfil the requirements of high spatial detail required. Therefore, these models are generally supplemented with statistical or dynamical downscaling to produce future climate projections at regional scales (Dai, 2013; Gampe et al., 2016; Prinsen et al., 2015). In the Netherlands regional climate models were used to obtain four KNMI'06 climate scenarios by the Royal Netherlands Meteorological Institute (KNMI, 2006; van den Hurk et al., 2006; van den Hurk et al., 2007).

Organic pollutants in surface water are directly linked to human activities of urban, industrial or agricultural origin (van Wezel et al., 2017). Chemicals are used for various beneficial purposes, such as crop protection, flame retardation, and food conservation. Over 347,000 compounds are registered and regulated via national and international authorities (CHEMLIST), and increases in synthetic chemical production and diversification outpace other divers of global change (Bernhardt et al., 2017). Demographical changes could lead to changing pharmaceuticals consumption (van der Aa et al., 2011). Both the parent compounds and their transformation products enter the aqueous environment. Consumers express their concerns regarding chemical contamination of drinking water (Kher et al., 2013), although risk assessment points out that adverse human health effects are not to be expected based on occurring concentrations of individual compounds (de Jongh et al., 2012; Houtman et al., 2014; Schriks et al., 2010).

In the Netherlands, surface water from the rivers Meuse and Rhine accounts for 40% of the drinking water production. For these rivers, located in a temperate oceanic climate zone, water scarcity is less extreme than in Mediterranean regions (Ludwig et al., 2011). Yet, wetter winters and drier summers are expected under climate change, mainly for the Meuse River (de Wit et al., 2007). Their current water quality does not meet the surface water quality standards as set by the Water Framework Directive and the target values for the use of drinking water production, according to the Association of River Water Companies (RIWA-Meuse, 2016) and the European Environment Agency (EEA, 2012). In the Meuse, concentrations of pharmaceuticals, diagnostic contrast media and endocrine disruptors exceed target values as set in the European River Memorandum (ERM) by the Internationale Arbeitsgemeinschaft der Wasserwerke im Rheineinzugsgebiet (IAWR, 2013) in >10% of the measurements (RIWA-Meuse, 2016). Although the risks to human health are considered negligible, exceedance of target values is undesirable from an ecotoxicological and drinking water perspective (European Commision, 2000).

In the current study, we project the concentrations of a selection of drinking water relevant compounds in the rivers Rhine and Meuse in the year 2050. The water quality projections are based on current water quantity and quality field data, which are extrapolated to future hydrological regimes and future changes in chemical emissions based on demographic projections assuming a constant water treatment efficiency. The discharge projections were modelled by Klijn et al. (2012) based on widely accepted KNMI climate scenario's for the Netherlands (van den Hurk et al., 2006; van den Hurk et al., 2007). The projections provide insight into the effects of climate change and changing chemical emissions on the water quality of two large European rivers important for drinking water production. The results can assist governments, water agencies and drinking water companies in selecting and evaluating long term investments in efficient measures to ensure good surface water quality and safe drinking water in the future.

2. Materials and methods

2.1. Selection of drinking water relevant compounds and chemical analyses

Seven compounds were selected as representative drinking water relevant compounds. The selection is based on their current concentrations in the Rhine and Meuse rivers (Table 1), their classification as a substance of attention (Association of River Water companies), and the fact that they represent relevant classes of compounds, such as pharmaceuticals, diagnostic contrast media, pesticides and consumer products. Glyphosate and its metabolite aminomethylphosphonic acid (AMPA) frequently exceed the surface water quality standard set by the Water Framework Directive (0.1 resp. 1.0 μg/L), especially in the Meuse. Carbamazepine, metoprolol, and diatrizoic acid exceed the target value from the IAWR (2013) for surface water used for drinking water production (0.1 μg/L), as does acesulfame K (1 μg/L).

Chemical and discharge data were derived from the database of the RIWA (2015). Samples were taken every four weeks from January 2010 till December 2011 from water at the three monitoring stations, i.e. Eijsden/Leige and Keizerveer at the Meuse and Lobith at the Rhine, see Fig. 1. Grab samples (1 L) were taken in pre-rinsed bottles and immediately transported in a refrigerated van to the laboratory and kept at 4 °C until processing. Glyphosate and AMPA were derivatised and analysed by high-performance liquid chromatography (HPLC) combined with fluorescence detection (Houtman et al., 2013).

2.2. Relating concentrations to river discharge

The dilution rate of anthropogenic compounds was described by the discharge-concentration relation (Eq. (1)). It is applicable to non-reactive compounds with stable point source emissions, and has been applied to chemical loads of conservative major elements in rivers

Table 1
Selected organic micropollutants and their current concentrations (μg/L) in the Rhine and Meuse rivers within the Netherlands: average concentration [minimum-maximum] over 2010–2011. More details found in Supporting information I.

Compound	Type	Rhine (Lobith)	Meuse upstream (Eijsden)	Meuse downstream (Keizersveer)
Glyphosate	Herbicide	0.04 [0.02–0.22]	0.13 [0.01–0.66]	0.07 [0.02–0.18]
AMPA	Metabolite glyphosate	0.32 [0.1–0.78]	0.69 [0.05–2.5]	1.1 [0.1–3]
Carbamazepine	Pharma, anti-epileptica	0.07 [0.02–0.17]	0.04 [0.01–0.08]	0.08 [0.02–0.13]
Metoprolol	Pharma, β-blocker	0.07 [0.03–0.14]	Not detected	0.15 [0.04–0.29]
Sulfamethoxazole	Pharma, antibiotic	0.04 [0.02–0.07][a]	0.02 [0.01–0.03]	0.04 [0.01–0.07]
Diatrizoic acid	Diagnostic contrast medium	0.21 [0.08–0.62]	0.1 [0.02–0.24]	0.13 [0.02–0.38]
Acesulfame K	Artificial sweetener	2 [0.62–3]	No data	No data

[a] Sulfamethoxazole was measured during 2013–2014, not during 2010–2011.

(Davis and Zobrist, 1979; van Bokhoven and Zwolsman, 2007; van der Weijden and Middelburg, 1989; van Vliet and Zwolsman, 2008). For reactive compounds and compounds with discontinuous (seasonal or stochastic) emissions, besides dilution, emission dynamics, transformation and sorption processes affect the surface water concentration. Depending on the magnitude of these processes, the Q-C relation may therefore deviate considerably from Eq. (1), which only takes account of dilution of the chemical loading.

$$c = \frac{a}{Q} + b \tag{1}$$

c = concentration (μg/L), a = chemical load (mg/s), Q = discharge (m^3/s), b = background concentration (μg/L).

The chemical specific Q-C relation was based on actual field data over 2010–2011 of discharge (Q) and chemical concentration (c) at the three

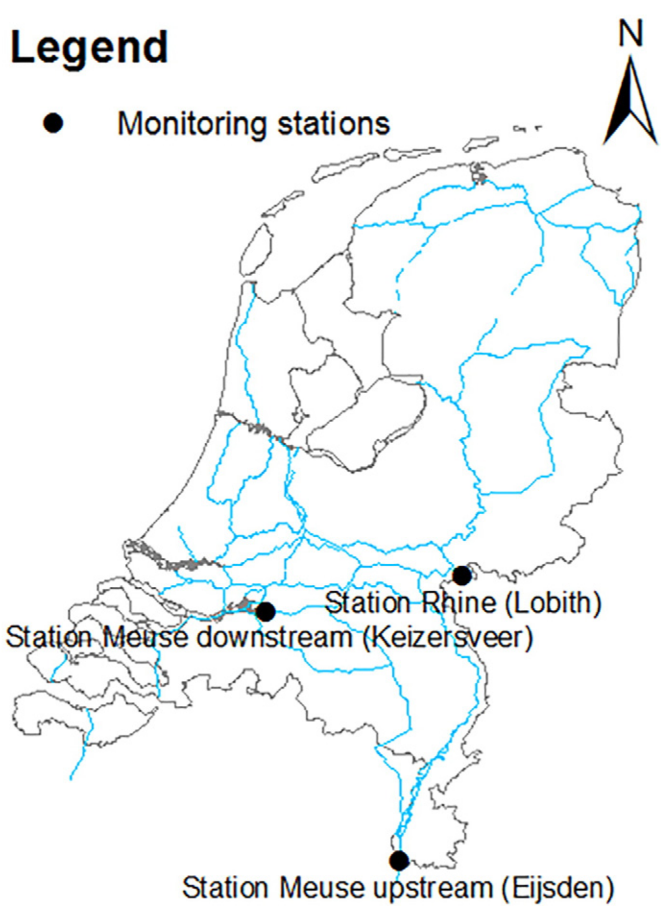

Fig. 1. Location of the three monitoring stations.

monitoring stations in the Rhine and Meuse rivers. For each chemical at each location, the load (a) and the background concentration (b) were fitted as constant in time based on Eq. (1). We selected data for the year 2011, characterized by a prolonged low flow period, with the year 2010 as the reference period (Table 2). Measurements below the detection limit were set to concentrations half the detection limit (Haas and Scheff, 1990). We assumed a background concentration for the anthropogenic compounds to be present during high flows, due to the exchange of compounds between the sediment and the water phase. Compounds could attach to sediment (Williams et al., 2009; Yamamoto et al., 2009); the adsorbed compounds can move into solution (desorption) when the concentration of chemicals in the water phase drops.

All data processing was performed off-line using the commercial software MATLAB R2015a (The MathWorks Inc., 2015). The function polyfit was used to fit the variables of Eq. (1). With the corrcoef function the Pearson correlation coefficient (r) and the p-value were obtained. The squared correlation coefficient (R^2) describes the goodness of fit of the linear regression model and implies which part of the variability in concentrations can be explained by variations in discharge. The significance, expressed by the p-value, describe whether the discharge and the concentrations are significantly correlated. The p-value is the probability of getting a correlation as large as the observed value by random chance, when the true correlation is zero. A p-value below 0.05 indicates a significant correlation between discharge and concentration.

2.3. Projections of river discharge

The water quality projections made use of discharge projections from the modelling study by Klijn et al. (2012). The discharge projections were based on the KNMI'06 climate scenarios, created within the framework of the Dutch Delta Programme (Bruggeman et al., 2011; Kielen et al., 2011; Klijn et al., 2012; Prinsen et al., 2015).

The KNMI'06 climate scenarios, presented in the year 2006 (KNMI, 2006), is a set of four scenarios considered representative for the full set of (down-scaled) IPCC SRES AR4 scenarios of greenhouse gas emissions from the Intergovernmental Panel on Climate Change (van den Hurk et al., 2006; van den Hurk et al., 2007). The four KNMI'06 scenarios are based on two selected extremes for temperature increase and two selected extremes for atmospheric circulation response, since the Dutch climate is tightly linked to direction of atmospheric flow. Within the four KNMI'06 scenarios climate models construct temperature, precipitation and potential evaporation for the year 2050 in the Netherlands. Therefore, sophisticated global climate models (General Circulation Model, GCM), were combined with an ensemble of Regional Climate Model (RCM) simulations, and empirical/statistical downscaling using local observations in the Netherlands (van den Hurk et al., 2007). The representative RCM model runs project a large (W) and moderate (G) temperature increase, with or without a change (+) in atmospheric circulation according to the four KNMI'06 climate scenarios. Historical observed meteorological time-series were modified by the RCM runs. The climate scenario G projects moderate climate change for 2050: 1 °C temperature increase and 15 cm sea level rise relative

Table 2
River discharge characteristics in the two selected years 2010–2011 of the Rhine and Meuse rivers.

Discharge (m^3/s)	Rhine (Lobith)		Meuse upstream (Eijsden)		Meuse downstream (Keizersveer)	
	2010	2011	2010	2011	2010	2011
Minimum	1260	788	17	6	30	30
5th percentile	1317	875	23	14	45	42
10th percentile	1386	948	27	18	59	47
50th percentile	2002	1375	123	47	183	84
90th percentile	3192	2801	462	471	558	597
95th percentile	4062	3951	680	772	785	934
Maximum	5692	8199	1638	2272	1452	2069
Average	2184	1759	210	175	274	234

to 1990. The W^+ scenario a quicker and more extreme climate change is projected for 2050: 4 °C temperature increase and 35 cm sea level rise (van den Hurk et al., 2007).

The upstream boundary conditions for the Rhine and Meuse for the current and future climate have been derived from these meteorological time-series, including precipitation and temperature, using the HBV models (Bergström, 1976) for the Rhine and Meuse catchments (de Wit et al., 2007; te Linde et al., 2010). The Delta Model is a consistent set of models within the Delta Programme for analysing the decisions related to the long-term fresh water supply (Prinsen et al., 2015). The surface water distribution is modelled by the national SOBEK-1D hydrodynamic surface water model (LSM), part of the Delta model (Prinsen et al., 2015). This model resulted in time series of average daily discharge in 2050 at different locations in the Netherlands. The model has a good fit with the observed data, although there are course locations where the model can be improved (Prinsen et al., 2015).

Time series discharge projections consist of nine scenarios adopted from Klijn et al. (2012). The time series include the discharge time series of three representative hydrological years under current climate and transformed to future climate in the year 2050, according to a moderate climate change scenario (G-2050) and a fast climate change scenario (W^+-2050). The three representative hydrological years illustrate hydrological variability of the Rhine and Meuse rivers an average year (1967), a dry year (1989) and an extremely dry year (1976) (Kielen et al., 2011; Klijn et al., 2012). The change for the reference years 1967, 1989 and 1976 to occur is respectively 0.5, 0.1 and 0.01; equal to an occurrence time of once in two years, once in 10 years and once in 100 years. The year 1976 was characterized by a prolonged dry period ranging from April to November with discharges below 100 m^3/s; in 1989 this period ranged from mid-June to October (Fig. 2). The variation in time series of river discharge between hydrological years is of a greater extent than the variation of climate change effects (Fig. 2, Supporting information II). The hydrological years were transformed using evaporation and precipitation projections within the G and W^+ climate scenarios.

2.4. Emission projections

In general, the number of different pesticides, pharmaceuticals, and other synthetic compounds, as well as their production volumes have been increasing at a rate that outpaced well-recognized drivers of global change since the 1960s (Bernhardt et al., 2017). Projections for use and application of individual compounds and in turn their emissions and environmental concentrations are complex as they depend on multiple factors such as regulation, production, marketing, media attention, and consumption behaviour. Calculating future emissions from historical trends and demographics thus comes with a high uncertainty for these compounds.

In the water quality projections we used both the 'stand still scenario' (current chemical load) and the 'future scenario' (projected chemical load). The current chemical load was obtained from monitoring data from 2010 to 2011 by Eq. (1); the projected chemical load for 2050 is the current load times the predicted emission factor. The projected emissions were based on previous assessments for pharmaceuticals (van der Aa et al., 2011), or on expert judgment (Table 3).

Based on demographical changes, the pharmaceuticals carbamazepine, metoprolol, sulfamethoxazole are projected to increase with respectively 13%, 36% and 19% in the year 2050 compared to present day (van der Aa et al., 2011). For the herbicide glyphosate, its metabolite AMPA, the diagnostic contrast medium diatrizoic acid and the artificial sweetener acesulfaam K we decided to use generic numbers for the emission factor. In the following paragraphs these generic estimates of the emission increase and decrease factors are supported with available information.

The authorization of the herbicide glyphosate is currently under review (European Comission, 2016). It is expected that the use of glyphosate in the Netherlands will decrease as the use of herbicides (including glyphosate) on paved surfaces has been prohibited in the Netherlands since March 2016. This ban will be extended to unpaved surfaces such as recreational areas in 2017 (Dutch Ministry of Infrastructure and Environment, 2013; Dutch Ministry of Infrastructure and Environment, 2016). As glyphosate and AMPA emissions could thus not be accurately predicted, we project it to decrease by 50% in the year 2050 compared to present-day.

Diatrizoic acid is a diagnostic contrast medium. The use of diagnostic contrast media is projected to increase by a combination of demographical changes and the increase of medical diagnostic equipment. The number of procedures increased with 5–7% per year from 1985 to 1997 (Morris, 1993) and is still likely to increase globally (Frenzel et al., 2015). The type and amount of diagnostic contrast media used in medical imaging vary per region and change in time. We can assume increasing diatrizoic acid emissions in western Europe, however not accurately. Therefore we project diatrizoic emissions to rise by a conceptual 50% in the year 2050 compared to present-day.

Acesulfame K is an artificial sweetener used widely in food products. Since 1990 the use of artificial sweeteners has steadily been increasing (van Rooij-van den Bos et al., 2004) according to a report by the Global Industry Analysts (2007), the global market for artificial sweeteners is growing at a rate of 5.5% (Supporting information III). At this rate, within 30 years the market would increase by >200%. The consumption volumes of individual artificial sweeteners vary per region and change in time. We can thus not predict acesulfame K consumption and in turn emission in western Europe accurately. However, we can assume increasing acesulfame K emissions, which we project to rise by a conceptual 50% in the year 2050 compared to present-day.

2.5. Water quality projections

We projected the concentrations of the selected seven compounds at three locations in the Rhine and Meuse rivers in the year 2050. In order to do so, we applied the Q-C relation to the nine river discharge projections to project water quality. The climate change scenarios (G and W^+) are combined with current and projected chemical load. In total the water quality projections include fifteen scenarios per chemical per location.

2.6. Uncertainty analysis

Uncertainties arise within the taken assumptions and projections of 1) the current load, 2) the projected discharge and 3) the projected emissions.

The load and the background concentration were estimated as a constant value over time, based on the dilution rate (the Q-C relation in Eq. (1)). The reliability of the Q-C relation was expressed by the

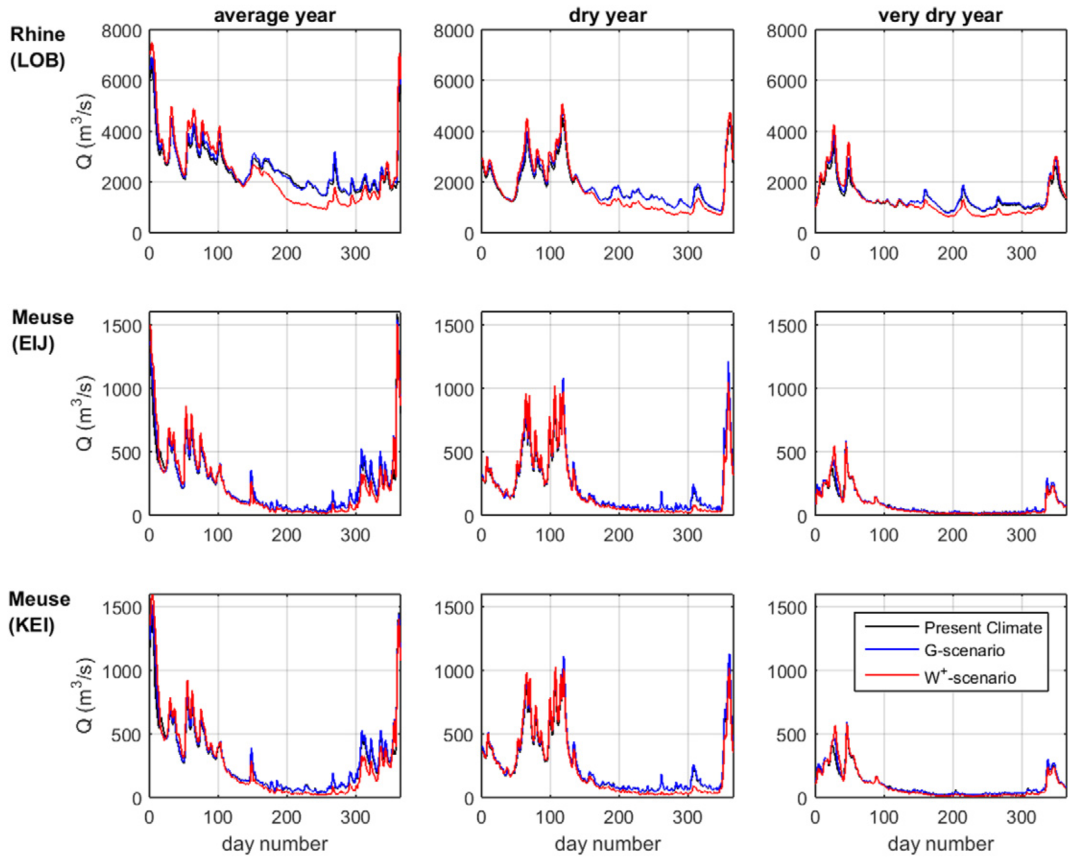

Fig. 2. Projected discharge for three hydrological years, i.e. an average year (1967), a dry year (1989) and an extremely dry year (1976), under current climate and transformed according to the climate scenarios G_{2050} (moderate climate change) and $W^{+}{}_{2050}$ (fast climate change).

standard deviation of the Q-C relation and the actual concentrations over the selected years. This standard deviation describes the variation of surface water concentration independent of dilution effects and the effect of varying emissions. In the water quality projections this statistical uncertainty was included as the 95% confidence interval, expressed as two times the standard deviation of the Q-C relation.

The accuracy of the hydrological models were subjected by the model performance and boundary conditions, addressed by de Wit et al. (2007) and Prinsen et al. (2015). The model performance was not accounted for in the water quality projections, since the simulation performance error of the quantity model was negliable in respect to the other components.

The projections of chemical use and emissions are complex and can be influenced by hard-to-predict factors. Therefore, as stated in the paragraph 'projection of future emission', the water quality projections include two boundary conditions for future emissions: the 'stand still scenario' and the 'future scenario'.

Table 3
Selected organic micropollutants and their predicted emission factor, the increased emission in the year 2050 compared to present year.

Compound	Type	Emission factor[a]
Glyphosate	Herbicide	0.5
AMPA	Metabolite of glyphosate	0.5
Carbamazepine	Anti-elepticum	1.13
Metoprolol	β-Blocker	1.36
Sulfamethoxazole	Antibiotic	1.19
Diatrizoic acid	Diagnostic contrast medium	1.5
Acesulfame K	Artificial sweetener	1.5

[a] Emission factor of the pharmaceuticals based on van der Aa et al. (2011).

2.7. Assessment of water quality projections

Glyphosate and AMPA have mandatory water quality standards set by the Water Framework Directive, 0.1 μg/L and 1 μg/L respectively. In contrast, the pharmaceuticals carbamazepine, sulfamethoxazole, diatrizoic acid and the artificial sweetener acesulfame K have no mandatory water quality standards; however, these compounds were evaluated using the target values set by the European River water Memorandum (ERM) intended to protect sources of drinking water (IAWR, 2013). Pesticides, biocides, pharmaceuticals, diagnostic contrast media and endocrine disruptors have an ERM target value of 0.1 μg/L (IAWR, 2013). Compounds classified by IAWR (2013) as 'Evaluated substances without biological activity and poorly degradable substances' such as acesulfame K have an ERM target value of 1.0 μg/L. The generic target values have been set according to a precautionary principle and have no legal consequences. Exceedance of the ERM target values implies a potential threat to drinking water production based on simple water treatment technology.

2.8. Impact for drinking water production

The water quality projections of the intake water are used to predict drinking water quality, based on the current treatment efficiency for these compounds at the three water treatment plants (Table 4). At each location, treatment efficiencies were calculated based on average concentrations of the untreated and treated water measured over

Table 4
Treatment efficiencies of the three specific drinking water treatment plants for the seven studied compounds. Treatment efficiencies indicated by (>) are minimum values, as the concentration in drinking water was measured below detection limit.

Compound	Type	Drinking water produced from the Rhine[a]	Drinking water produced from the Meuse (upstream)[b]	Drinking water produced from the Meuse (downstream)[c]
Glyphosate	Herbicide	97%	>83%	>70%
AMPA	Metabolite glyphosate	99%	>90%	96%
Carbamazepine	Anti-elepticum	100%	90%	>75%
Metoprolol	β-Blocker	100%	–	80%
Sulfamethoxazole	Antibiotic	98%	–	>50%
Diatrizoic acid	Diagnostic contrast medium	66%	>70%	17%
Acesulfame K	Artificial sweetener	46%	–	–

[a] Advanced water treatment, including soil passage.
[b] Relatively simple water treatment, including soil passage.
[c] Advanced water treatment, but no soil passage.

2010–2014 by the drinking water companies (Table 4). The treatment efficiencies were not differentiated for river flow (Delpla et al., 2011).

3. Results and discussion

3.1. Discharge-concentration relation

The discharge-concentration relation (Q-C relation) describes the dilution rate for a specific chemical. The relation applies to conservative compounds such as chloride, but is also applicable to compounds which are slowly degradable, depending on the residence time within the river system.

All of the selected anthropogenic compounds showed a significant correlation with river discharge ($p < 0.01$) at one or more monitoring stations (Table 5). The determination coefficient (R^2) of the established significant Q-C relations of the studied compounds varied between 0.14 for diatrizoic acid and 0.78 for carbamazepine. In comparison, in the case of the conservative compound chloride, dilution could explain up to 70% of the variability (see Supporting information IV). The Q-C relations including the standard deviation, based on paired measurements of river discharge and the concentration of all selected compounds,

Table 5
Results of the Q-C relation (Eq. (1)) in the Rhine and Meuse rivers based on field data (2010–2011). Non-significant relations in red.

Compounds	R^2	p–Value	Number of measure–ments	a = chemical load (mg/s)	b = background concentration (μg/L)	Standard deviation Q–C relation
Rhine (Lobith)						
Glyphosate	0.01	0.71	26	13.3	0.03	0.02
AMPA	0.38	<0.01	26	454.3	0.11	0.11
Carbamazepine	0.69	<0.01	26	124.3	0	0.01
Metoprolol	0.01	0.69	26	9.5	0.07	0.02
Sulfamethoxazole	0.42	<0.01	19[2]	53.1	0.01	0.01
Diatrizoic acid	0.16	0.04	26	232.1	0.12	0.09
Acesulfame K	0.69	<0.01	25	2244.1	0.73	0.25
Meuse upstream (Eijsden)						
Glyphosate	0.38	<0.01	25	28.7	0.26	0.08
AMPA	0.73	<0.01	26	4.7	0.05	0.31
Carbamazepine	0.78	<0.01	31	0.9	0.013	0.01
Metoprolol	–	–	<dl[1]	–	–	–
Sulfamethoxazole	0.59	<0.01	26	0.3	0.004	0.002
Diatrizoic acid	0.57	<0.01	26	2	0.06	0.03
Acesulfame K	–	–	No data	–	–	–
Meuse downstream (Keizersveer)						
Glyphosate	0.26	<0.01	63	3.2	0.04	0.03
AMPA	0.53	<0.01	63	75.4	0.39	0.34
Carbamazepine	0.56	<0.01	50	4.4	0.03	0.02
Metoprolol	0.57	<0.01	26	7.3	0.08	0.03
Sulfamethoxazole	0.52	<0.01	26	1.8	0.02	0.01
Diatrizoic acid	0.14	0.06	26	5.2	0.13	0.07
Acesulfame K	–	–	No data	–	–	–

[1]Metoprolol is not detected at monitoring station Eijsden, as this pharmaceutical is mainly used in The Netherlands and hardly in Belgium.
[2]Data of sulfamethoxazole in the Rhine available over 2013-2014.

are shown in Fig. 3. Non-significant Q-C relations in Table 5 (in red) were not used for water quality projections.

3.2. Water quality projections

In Fig. 4 the projections for carbamazepine are highlighted; the projections for all studied compounds are shown in Supporting information V. Per compound and location, the future concentration was calculated according to combinations of climate and emission projections, as applied to three hydrological years.

Hydrological variability, climate change especially the W^+ scenario, and expectations with regard to future changes in emission had a significant influence on the water quality of the rivers Rhine and Meuse. The impact of current hydrological variation was substantial; between the hydrological years the 90th percentile peak concentration varied within a factor of 1.5 in the Rhine and 2.5 in the Meuse. Interannual hydrological variation in the very dry year (1976) was projected to effect carbamazepine concentrations in the Meuse within a factor of 10 (90th and 10th percentiles compared, Fig. 4), comparableto the modelled variation in concentration between seasons by Coppens et al. (2015). Climate change, according to the W^+ scenario, increased the interannual variation of the projected carbazepine concentrations in the Meuse up to a factor of 20.

Irrespective of the hydrological year, the 90th percentile peak concentrations increased up to a factor 1.7 in the Meuse and 1.4 in the Rhine in the W^+-scenario compared to current climate scenario. In total, concentrations in the Meuse River increase up to a factor 4 in a very dry year combined with a fast climate change scenario (W^+)

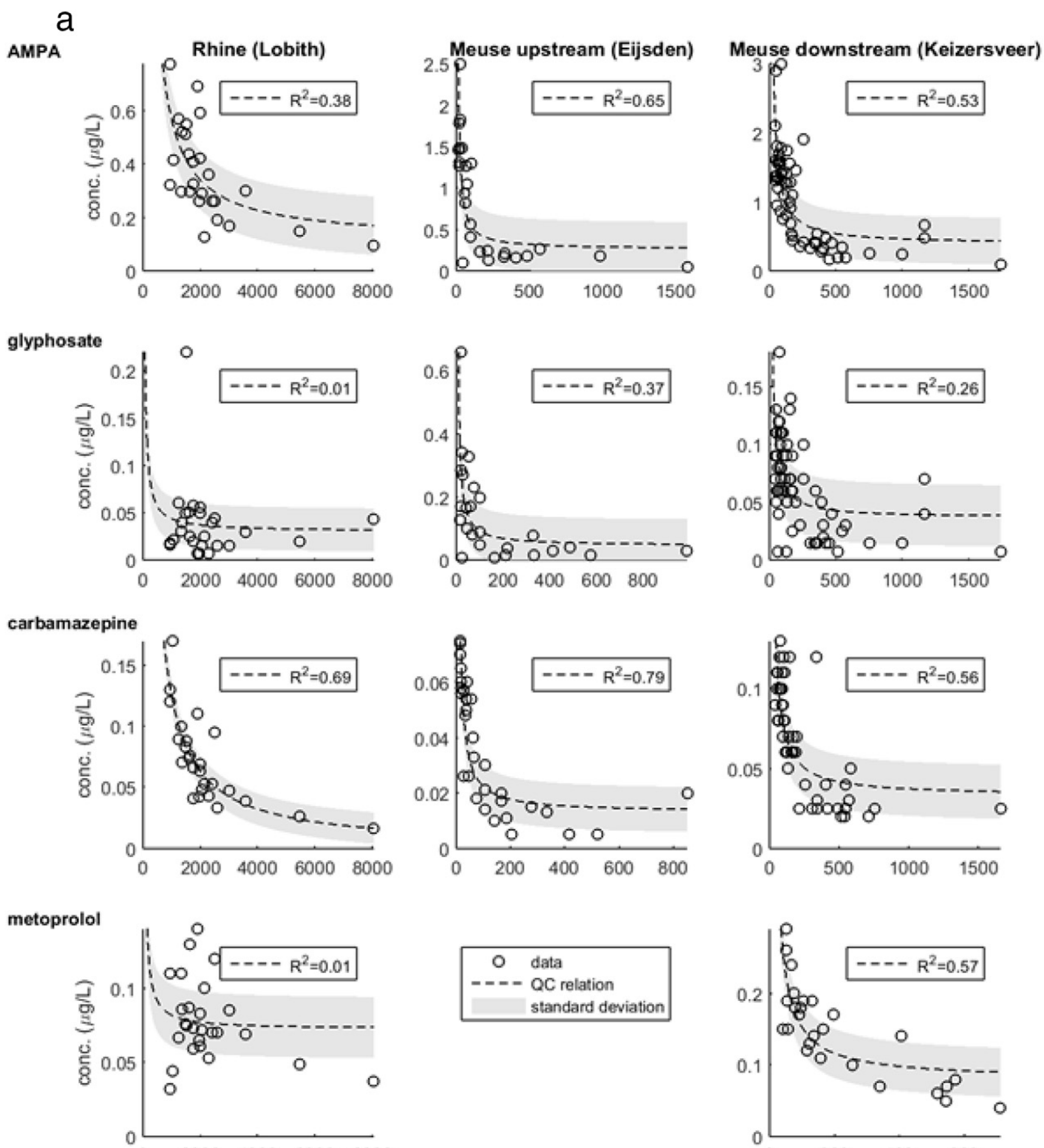

Fig. 3. Q-C relations including the standard deviation for the selected compounds based on monitoring data (2010 − 2011) of the Rhine and Meuse rivers. Metoprolol was not detected at the upstream Meuse station (Eijsden). Note the different scaling on the X-axis and Y-axis for the different stations.

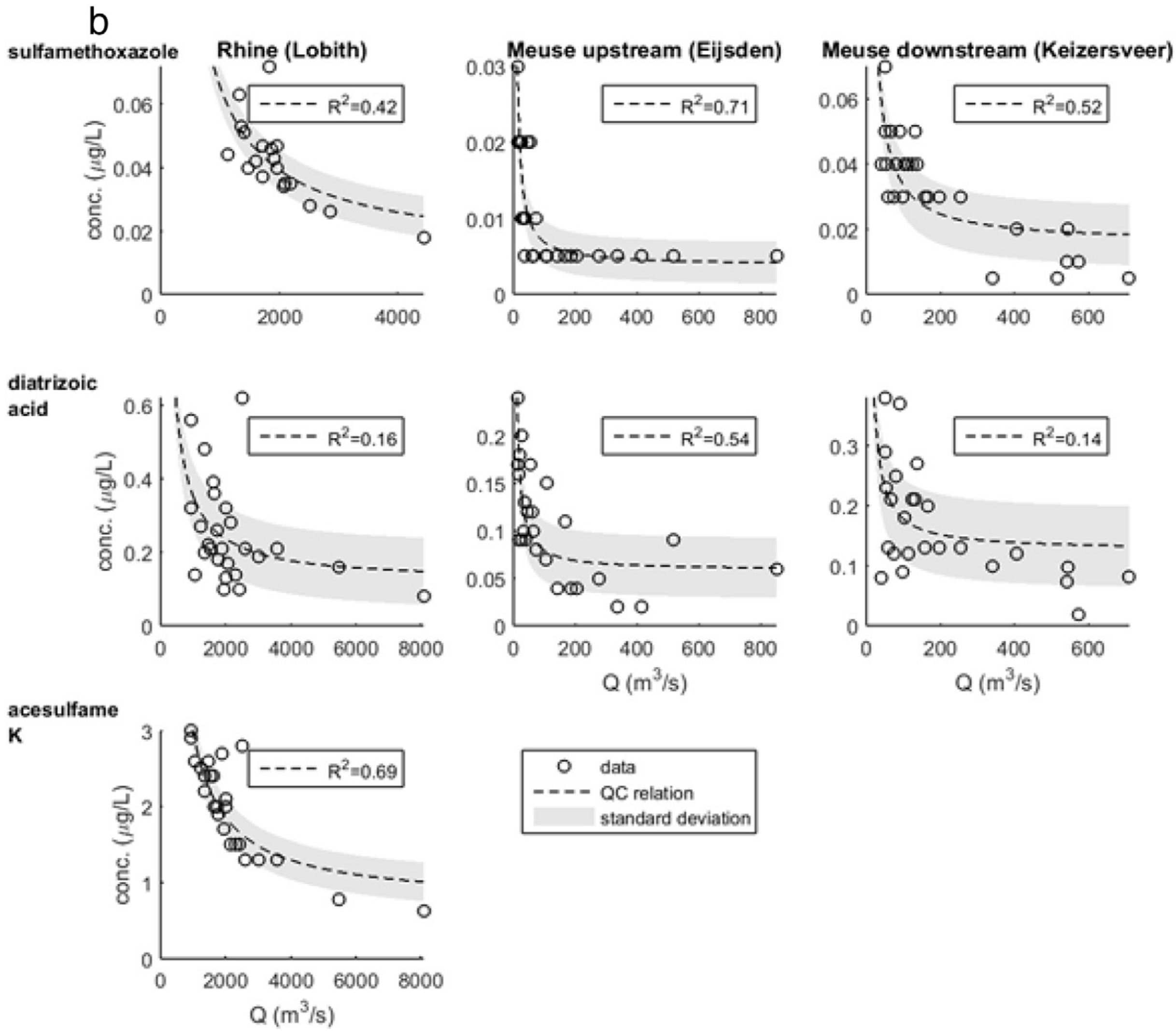

Fig. 3 (*continued*).

compared to a normal hydrological year under current climate. In the Rhine concentrations increase up to a factor of 2. The effect of both the hydrological variability and climate change on surface water quality (factor 2–4) was projected to be smaller in this study compared to the Dutch modelling study of Wuijts et al. (2012).

The response of the Meuse River to hydrological variability and climate change is more extreme because the Meuse is a typical rain-fed river and its response to rainfall in the catchment area is fast. By contrast, the Rhine River has a large catchment area and two major sources of water (rainwater and snowmelt), which leads to a more buffered hydrological system. As long as the Rhine is fed with melt water from the Alps during dry spells (Swaiger, 2007) the discharge drops less than the Meuse.

3.3. Forward progression of uncertainties

The water quality projections were subject of uncertainties related to the Q-C relation, the projected river discharge and the emission projections.

The reliability of the Q-C relation is described by statistical parameters as the determination coefficient (R^2) and the p-value. As indicated by the R^2 of the Q-C relation, the variation in river discharge could describe the variation in compound concentrations for 14% to 78% with Eq. (1) (Table 5). In addition, the variation in chemical concentration is described by the standard deviation of the Q-C relation and the field data. The uncertainty regarding the Q-C relation is presented as the confidence interval in Fig. 5 and Supporting information VI, based on current emissions only. The confidence interval of diatrizoic acid in the Meuse upstream at station Eijsden was narrow because the concentrations could largely be explained from (variation in) discharge ($R^2 = 0.54$). The discharge in the Meuse downstream at Keizersveer ($R^2 = 0.14$) and the Rhine at Lobith ($R^2 = 0.16$) could explain a small part of the variation in concentrations, so the confidence interval at these locations is much wider.

The uncertainty of the Q-C relation could be due to several factors, including the variation in amount and location of the emissions, such as seasonal variations in emissions, e.g. for pesticides or pharmaceuticals (Roberts et al., 2016). Another factor is short-lived hydrological events, e.g. a rapid increase in discharge after peak showers (first flush). In combined sewer systems peak showers occurring over the year may lead to sewer overflows and reduce the treatment efficiency of waste water treatment plants (Fortier and Mailhot, 2015; Mailhot et al., 2015). In addition, the transformation rate of compounds in surface water or treatment plants will vary with temperature, light and travel time (Azzouz and Ballesteros, 2013; Roberts et al., 2016).

The surface water discharge in the rivers Rhine and Meuse in 2050 under different scenarios were projected by well-supported and accepted hydrological models (Prinsen et al., 2015) and climate scenarios (van

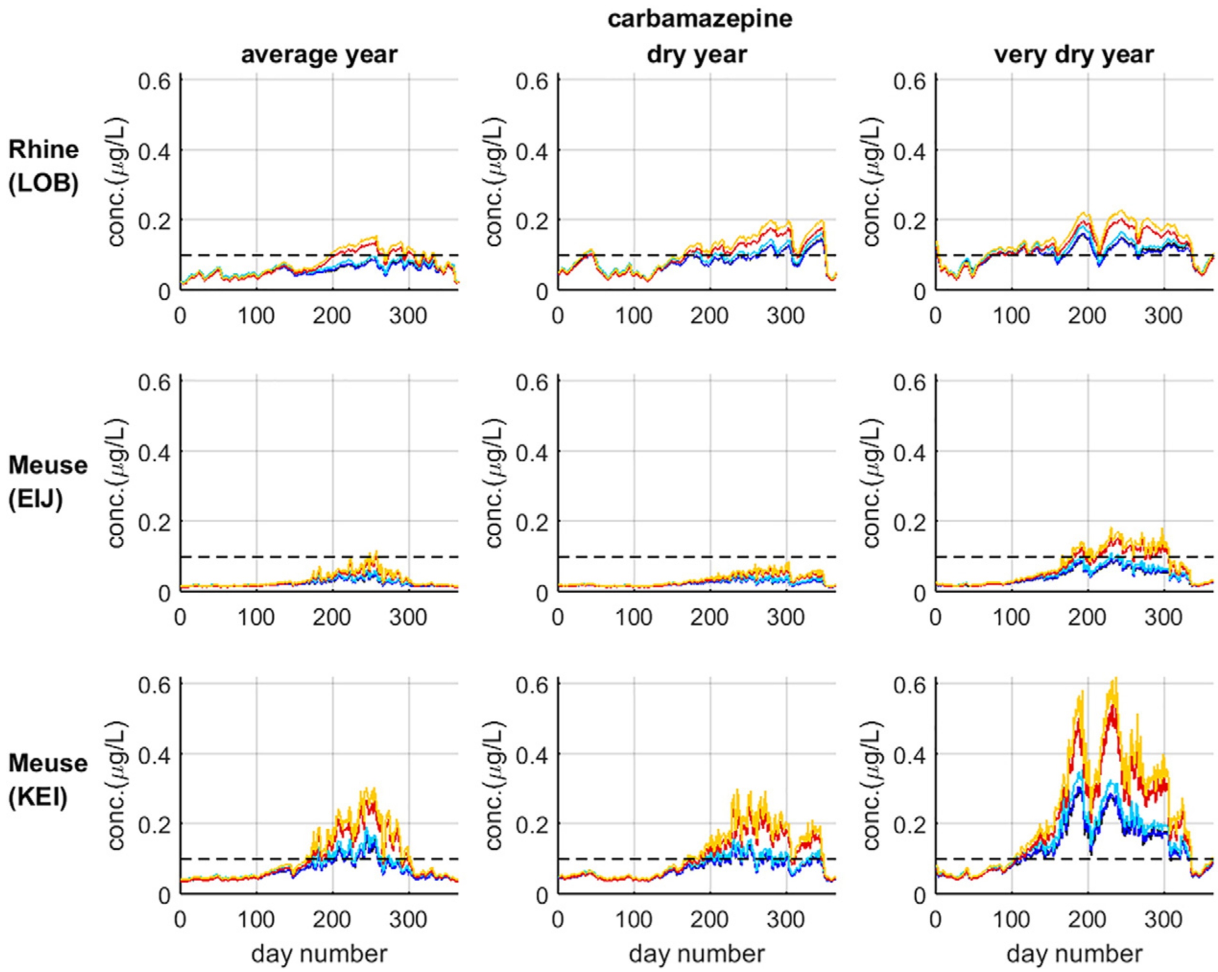

Fig. 4. Water quality projections as compared to the water quality (target) values for carbamazepine in the Rhine River at Lobith (LOB) and the Meuse River at Eijsden (EIJ) and Keizersveer (KEI), for three hydrological years, under current climate and transformed according to the climate scenarios G_{2050} (moderate climate change) and $W^{+}{}_{2050}$ (fast climate change), with or without a future emission (FE) factor applied.

den Hurk et al., 2007). However, the hydrological models were subjected by boundary conditions and model performance. The HBV model had a total discharge error of just 1%. Monthly average discharges were well simulated for the months with the lowest (August) discharge. However, the monthly average discharges were generally overestimated during spring and underestimated during autumn (de Wit et al., 2007). More information on the uncertainties of the HBV model are found in Hegnauer et al. (2014). The LCM model performs satisfactory and had a good match with observed data. Differences between model results and observations were typically caused by operational aspects (Prinsen et al., 2015).

Projections of chemical use and emissions are complex because the change is determined by several factors: regulation, supply and demand, chemical developments and substitutes and changed consumer behaviour. The water quality projections include two scenarios: 'stand still scenario' as a 'future scenario'. The emission projections in the year 2050 vary between scientifically supported projections for pharmaceuticals to conceptual increase factors for the other compounds (glyphosate, AMPA, diatrizoic acid and acesulfame K). The projected emissions of the pharmaceuticals are well-established from demographic changes by van der Aa et al. (2011). In reality however, consumption of pharmaceuticals can be subject to other influences such as hard-to-predict factors as epidemiological changes and developments in the provision of health care and medicinal technology (van der Aa et al., 2011). Furthermore, changes in treatment, water consumption and recycling of waste water lead to changing emission volumes and—routes, these are not included in the projections.

3.4. Impact of future water quality for drinking water production of Rhine and Meuse water

The projected concentrations of the studied compounds in surface and drinking water were evaluated using the chemical target values set by the ERM for surface water used for drinking water production (see materials and methods). The extent of target value exceedance in all scenarios had been summarized in Fig. 6, showing that target values for the drinking water function of the Rhine and the Meuse were widely exceeded, already under current climate. The impact of hydrological variability could be assessed by comparing the results for an average, dry or a very dry year. The impact of climate change on water quality was shown by comparing water quality under current climate (first column) to that of water quality in the year 2050, for the moderate climate scenario G (second column) and the fast climate change scenario W^{+} (third column). The impact of changing chemical emissions could be seen by comparing the second and fourth column (for scenario G), or the third and fifth column (for scenario W^{+}). The largest extent of water quality deterioration occurred in the fast climate change W^{+}-scenario (third and fifth column) in combination with a very dry year (third row).

In particular, carbamazepine and diatrizoic acid exceeded the target value extensively in the projections, in both the Rhine and the Meuse, ranging from 0 to 76% of the year 2050. Sulfamethoxazole exceeded the target value to a lesser extent, ranging from 0 to 42% of the year 2050 dependent on the scenario. Acesulfame K exceeded the target value all year round in the Rhine in all scenarios; in the Meuse this

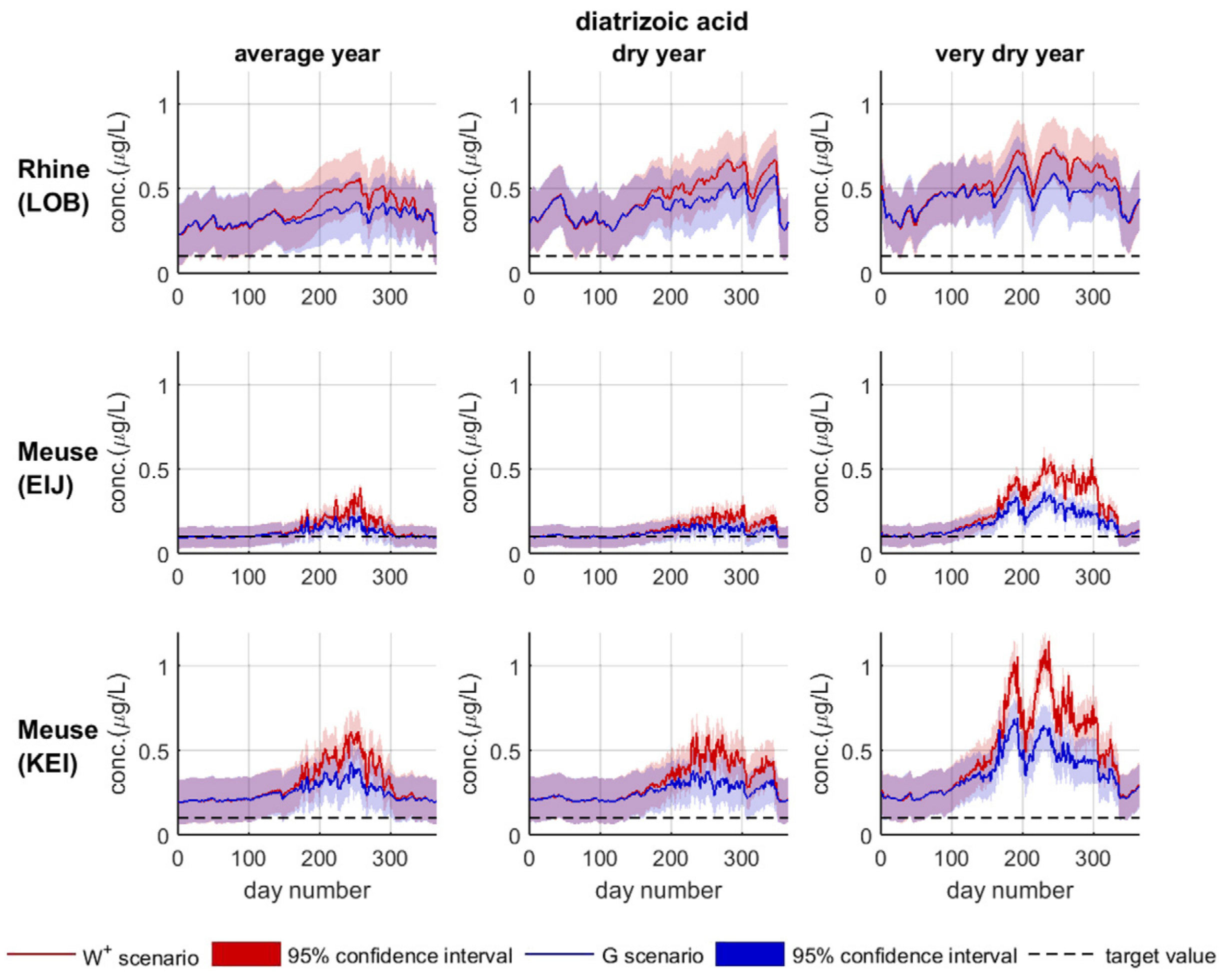

Fig. 5. Water quality projections for diatrizoic acid in 2050 including the 95% confidence interval in the Rhine River at Lobith (LOB) and the Meuse River at Eijsden (EIJ) and Keizersveer (KEI), for three hydrological years transformed according to the climate scenarios G_{2050} (moderate climate change) and $W^{+}{}_{2050}$ (fast climate change).

was also to be expected, but field measurements were lacking. Metoprolol exceeded the target value almost all year round (67–100% of the year 2050, dependent on the scenario) in the downstream Meuse; projections for the Rhine were not made. Glyphosate and AMPA are problematic compounds in the Meuse with regard to drinking water production. Despite the 50% reduction of glyphosate projected in the year 2050, the compound and its metabolite AMPA keep exceeding the target value in the Meuse River, now and in the future.

During periods of highly contaminated surface water, drinking water companies could decide to stop the intake of surface water for drinking water production (Baken et al., 2016). Drinking water companies could be faced with increased concentrations during low flow periods; which lead to more frequent and prolonged stops of surface water intake.

3.5. Implications for drinking water quality

In the projections, the studied compounds were not all effectively removed with existing water treatment, i.e. below the level of 0.1 μg/L or 1.0 μg/L in drinking water (Fig. 6). In drinking water produced from Rhine water, the projected concentrations of acesulfame K and diatrizoic acid exceeded the target value by the largest extent. In drinking water produced from Meuse water, projected concentrations of diatrizoic acid exceeded the target value in all scenarios, glyphosate and carbamazepine, metoprolol and sulfamethoxazole in very dry year scenarios.

Current concentrations of glyphosate are within the range of 0–0.2 μg/L in Rhine and Meuse water and for AMPA between 1.0 and 3.0 μg/L in Meuse and 0–0.8 μg/L in Rhine water. Despite the expected emission reduction, concentrations will presumably increase with a factor 2–4 due to climate change. Climate change may increase AMPA concentrations in the Meuse up to 10 μg/L (Fig. 5). However, AMPA and glyphosate are not expected to exceed the drinking water quality standard because of the high treatment efficiency (>90% for AMPA and >70% for glyphosate), except for the Meuse River under extremely low river flows (W^{+}-scenario combined with very dry year; see Fig. 6).

Current concentrations of carbamazepine and sulfamethoxazole in the Rhine and Meuse are within the range 0.01–0.20 μg/L. In the projections concentrations increased by a factor of 2–4 due to the influence of climate change and the estimated increased emissions. The future concentrations of carbamazepine and sulfamethoxazole in drinking water may not be reduced below the target value of 0.1 μg/L during a very dry year (Fig. 6). The removal of these pharmaceuticals varied among drinking water production locations, depending on the water treatment technology installed (Table 4). Projected concentrations of carbamazepine and sulfamethoxazole in drinking water were below derived provisional guideline values (Schriks et al., 2010).

Diatrizoic acid is currently present in concentrations above the ERM target value in Rhine water (0–0.6 μg/L) and Meuse water (0–0.4 μg/L). These concentrations could increase 2–4 fold in the year 2050 due to climate change and the estimated increased emission. The removal efficiencies for diatrizoic acid were limited, especially by the drinking

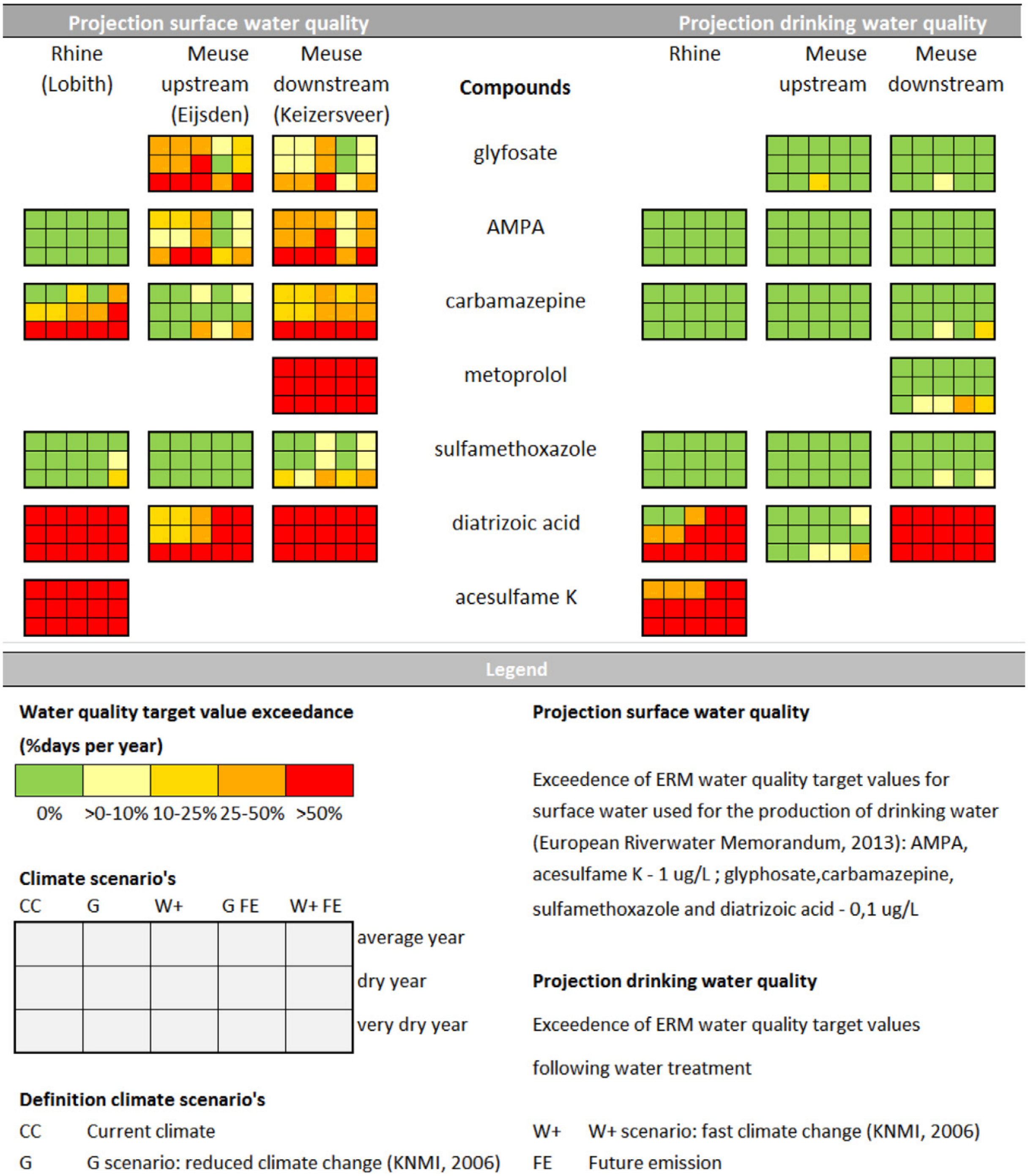

Fig. 6. The extent of target value exceedance in surface water for drinking water production (left panel) and the conversion to drinking water quality based on current location specific treatment efficiency (right panel).

water production station that do not incorporate soil passage in their treatment steps (Table 4). Although the increase of diatrizoic acid is undesirable, concentrations in this order of magnitude are unlikely to pose risks to human health (Moermond, 2014; Schriks et al., 2010).

Acesulfame K is currently present in concentrations above the ERM target value in the Rhine River (0.6–3 μg/L). Climate change could double these concentrations by the year 2050. As acesulfame K is currently reduced by 65% in drinking water treatment of Rhine water (Table 4), it is likely to exceed the target value of 1 μg/L in drinking water up to 2 to 4 times. However, it is not likely that this poses a human health risk, because concentrations in drinking water are five orders of magnitude lower than the acceptable daily intake (9 mg/kg bodyweight (SCF, 2000)).

4. Conclusions

The water quality of the Rhine and Meuse is influenced by hydrological variability, changing emissions and climate change effects. The increasing occurrence of prolonged dry periods deteriorates water quality, due to limited dilution of point source contaminations. In general, the lower the river flow, the higher the impact on water quality, and the more often drinking water standards or ERM target values are exceeded. In the projections, the effect of a dry year and climate change had a greater impact on the quality of the Meuse River compared to the Rhine River, because of the fundamentally different hydrology of these rivers. Peak concentrations of the studied compounds in the Meuse may increase up to a factor 3–4 during prolonged low flow periods while the peak concentrations in the Rhine increase up to a factor 2. The drinking water function of the Rhine and especially that of the Meuse is under pressure in the current climate. This pressure will increase in a future climate, due to the increasing severity and frequency of low river flows. If future emissions are not sufficiently reduced, or treatment efficiencies are not improved, these compounds will be increasingly found in drinking water. Although generic thresholds for drinking water quality are exceeded in some cases, the projected concentrations remain below indicative health-based guideline values, hence for the studied compounds, human health is not in jeopardy.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2017.05.250.

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