

# Proposal for applying a component-based mixture approach for ecotoxicological assessment of fracturing fluids

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**Abstract** Hydraulic fracturing is increasingly being used to produce gas from unconventional resource sites for energy supply. Therefore, concerns about risks of this technology related to human health and the environment have to be addressed. Among the major issues is the potential contamination of surrounding water systems by chemical additives used in fracturing fluids. In this study, the ecotoxicological hazards of fracturing fluids, both, their individual components (chemicals) as well as their mixtures (product) were assessed using a component-based mixture approach. For five exemplary fracturing fluids, 40–90 wt% of the contained substances could unambiguously be defined in their chemical identity. The concentrations used in the applied fluid mixture were considered as (maximum) exposure concentrations. For components with mass fractions between 10 and 74 wt%, the effect concentrations for acute and chronic toxicity of fish, daphnia and algae were retrieved from experimental databases and through predictive modeling. The hazard indices calculated from the ratio of exposure to effect concentration were  $>1$  for all fracturing fluids, using different scenarios. This indicated a hazard from the undiluted fracturing fluids. The assessment framework presented in this study allows for dealing with data gaps and uncertainties in a tiered fashion and in particular accommodates for combined effects resulting from chemical mixtures. It

might be employed for ecotoxicological risk assessment of products containing chemical mixtures and optimization of their environmental performance.

**Keywords** Mixture toxicity · Fracking/fraccing · Hazard assessment · Hazard quotient · Hazard index · Eco-/toxicological product assessment

## Introduction

The growing demand of energy in conjunction with limited natural resources makes unconventional primary energy sources such as shale gas economically attractive. Shale gas utilization requires special techniques for exploitation, as hydraulic fracturing, whereby cracks and fissions are produced in the deep underground to get access to gas. For the fracturing process, chemicals are required in large quantities. These chemicals might contaminate sources of drinking water or harm aquatic ecosystems when reaching ground or surface water (The Tyndall Centre 2011; UBA 2011; US EPA 2011a). Although the issue of potential implications on the water quality was raised (The Tyndall Centre 2011; UBA 2011; US EPA 2011a; Gordalla et al. 2013), first attempts to describe the eco-/toxicity of chemicals used in hydraulic fracturing were restricted due to a lack of detailed information on the chemical composition applied (The Tyndall Centre 2011; UBA 2011). Hence, disclosure of the identity and concentration of chemicals used in fracturing processes is a matter of legal debate (The Tyndall Centre 2011; US EPA 2011a; Thompson 2012). However, to assess ecotoxicological hazards, information on the chemicals and their effects is required.

There is no generally accepted legal frame for assessing the ecotoxicological hazard and risk of fracturing fluids yet.

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In general, environmental risk assessment of chemicals is performed for specific processes and uses of these chemicals and the legal requirements may vary accordingly. For industrial chemicals requirements are determined by the REACH regulation (EC/1907/2006 2006). Here, the assessment scale and thus amount of information depends on the production volume of the chemicals in use. The most comprehensive predictive assessment is required for pesticides (EC/1107/2009 2009). This is commonly justified because these chemicals are designed to harm at least target organisms and are applied directly in the environment. Fracturing fluids are applied for different purposes, among others explosion and biocidal activity. Therefore, they might be related to different regulations with different requests on the risk assessment procedure. A specific regulation, and thus a legal frame, for assessing the ecotoxicological hazard and risk of the chemicals contained in fracturing fluids is not available at present. Tiered assessments generally start with information easily obtainable and suitable for a generic estimate and if indicated go on with more detailed study requests that is considered to lead to a higher degree of realism in assessments. Thus, an approach is sought suitable for an initial ecotoxicological assessment of fracturing fluids starting with hazard identification and quantification by evaluating effect and exposure data without considering yet unavailable exposure information and probabilities.

The fluids used for hydraulic fracturing consist of water, sand and a mixture of organic and inorganic chemicals (US EPA 2011a). The chemicals are added to the water–sand-suspension for different purposes, covering a broad range of use classes such as biocides, surfactants, corrosive protectors, or scale inhibitors (UBA 2011). Consequently, they belong to different chemical classes. Organic chemicals comprise alcohols, ethoxylates, aromatics or polymers; inorganic substances used consist of acids, salts or metal oxides (Schmitt-Jansen et al. 2012). These chemicals differ in their physicochemical properties as well as their ecotoxicological potential (The Tyndall Centre 2011; Schmitt-Jansen et al. 2012). Currently, about 600 chemicals are listed by the US EPA as fracturing fluid additives (UBA 2011). In Germany, a list of about 150 chemicals (potentially) used in fracturing fluids was generated upon information provided by ExxonMobil Production Deutschland GmbH during a process of information and dialogue (Schmitt-Jansen et al. 2012; Ewen et al. 2012). The first attempts to evaluate the hazard of chemicals in fracturing fluids were based on a substance-by-substance evaluation (UBA 2011) or by summarizing the hazard classifications according to CLP (EC/1272/2008 2008; The Tyndall Centre 2011). Substance-by-substance evaluation might provide detailed information on individual components of mixtures and become relevant for substances of higher

concern, such as biocides. This, however, lacks a comprehensive picture of the mixture and does not allow for quantification and comparison. Hazard classifications are mainly based on substance intrinsic toxicities and/or physicochemical properties. This can give a first insight into substances of high concern but neglects the exposure situation. For hazard considerations, as understood in the present study, both effect and exposure need to be taken into account, considering especially that several tons of chemicals are used during a single fracturing process (US EPA 2011a).

Fracturing fluids commonly contain up to 25 chemicals. The number and concentration of these chemicals in a fracturing fluid may vary depending on the geological characteristics of the deep underground and the intended effect of the fracturing process (UBA 2011). Thus, mixture effects of the fracturing fluid might become relevant and need to be addressed in the hazard assessment. In principle, the hazard of chemical mixtures can be addressed as a whole, after fractionation or based on the individual components of the mixture (SCHER/SCCS/SCENIHR 2012). Measuring the ecotoxicological effect of a fracturing fluid in an experimental set up would give realistic information on the overall mixture effect of all chemicals contained in the fracturing fluid, but would lack perspective for inference when, e.g., extrapolation to a change in the composition is needed. Component-based prognostic models allow for the estimation of combined effects from single effects of the mixture components (SCHER/SCCS/SCENIHR 2012) with potential for more flexible application. One such approach is the hazard index (HI) that is based on the concept of concentration addition (SCHER/SCCS/SCENIHR 2012). The HI estimates mixture effects from the so-called hazard quotients (HQs), the ratios of exposure versus effect concentration of the individual mixture components (SCHER/SCCS/SCENIHR 2012; for further details see conceptual section).

The HQ-approach for single substances is frequently applied in human health as well as in ecological risk assessment for evaluating risks from non-carcinogenic contaminants (US EPA 1997; Health Canada 2004). It usually serves as a screening tool in a first tier. For instance, the HQ is used in prospective risk assessment related to pesticide application in agriculture (Campbell et al. 2000; Raybould et al. 2011). Also retrospectively, the ecotoxicological impact of environmentally occurring industrial chemicals (Lemly 1996), pharmaceuticals (Sanderson 2003; Han et al. 2006; Lienert et al. 2007) or ingredients of personal care products such as parabens (Yamamoto et al. 2011) in streams or effluents were evaluated using HQ-type approaches. As measurable quantity, the HQ allows for prioritization of substances of concern and may support decision-making as shown by

Lienert et al. (2007). In that perspective, the HQ was already proposed for evaluation of chemical use and possible discharge in off-shore oil production (Scholten et al. 2000; Sheahan et al. 2007). The HQ was implemented as a ranking tool in the CHARM (Chemical Hazard and Risk Management) model, which is the basis for regulating the use and reduction of offshore chemicals in the North-East-Atlantic (OSPAR Convention 2000; Thatcher et al. 2005). All of these applications investigated the hazards of single substances, while only a few studies also considered mixtures. Yamamoto et al. (2011), for example, calculated the additive effect of seven parabens, Lienert et al. (2007) considered the mixture effects of a pharmaceutical with its metabolites and Thatcher et al. (2005) evaluated preparations used offshore by selecting the chemical component with the highest HQ as mixture representative. However, the potential of the concentration additive approach using the HI to estimate the hazard of a product as a complex mixture seems not to be explored yet.

The objective of this study was to assess the ecotoxicological hazard of real case fracturing fluids using data available at present and to develop a framework generally applicable for mixtures composed of several components. For this purpose, a component-based mixture approach was applied to five fracturing fluids provided by ExxonMobil Production Deutschland GmbH. First, the components of the fracturing fluids needed to be chemically unambiguously identified. Second, ecotoxicological data were retrieved from a database research. Third, hazard quotients (HQs) were calculated and compared for individual chemicals, following which the hazard index (HI) was estimated for fluid mixtures. Furthermore, a decision scheme was developed for evaluating the ecotoxicological impact of mixtures where specific scenarios might provide a frame for risk assessment as well as provide options for product optimization.

## Conceptual framework

### Scope of the study

This study was focused on the evaluation of the ecotoxicological impact of chemicals used in the fracturing process. Other potential toxic effects concerning human health as well as drinking water contamination were addressed elsewhere (Gordalla et al. 2013; The Tyndall Centre 2011). Further, the study explicitly aimed to investigate the ecotoxicological implications of fracturing fluids as chemical mixtures. Implications due to the transport of chemicals to the drilling place or the flowback composed of fracturing fluid and deposit water were partially addressed by Olsson et al. (2013) and must be further investigated. In this

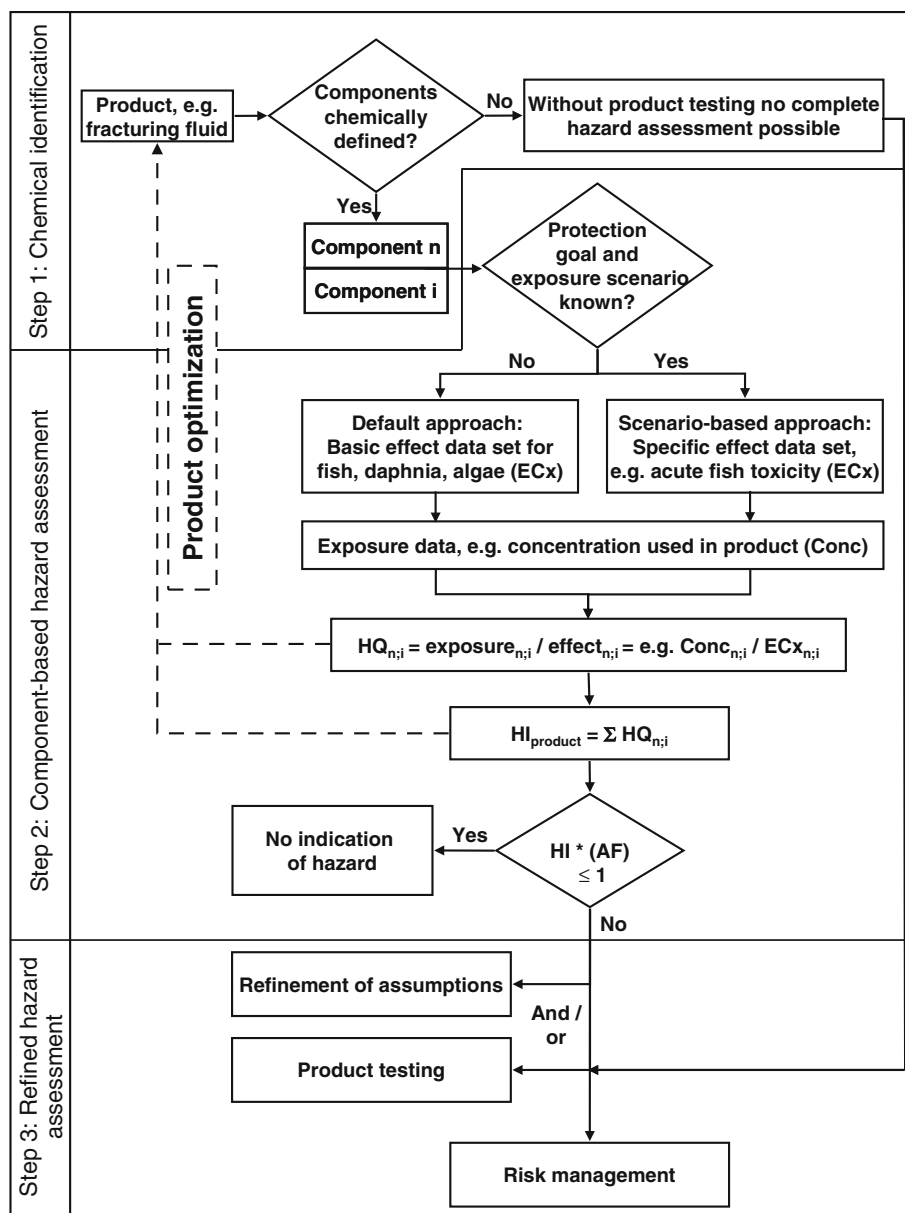
literature-based study, the hazard of fracturing fluids was assessed by considering exposure and effect of the mixture components. For this purpose, the fracturing fluid was assumed to be a product with a defined chemical composition and concentration, namely in the undiluted solution. These concentrations and the retrievable aquatic toxicity data were used for the hazard estimate carried out here. Changes of the product composition, e.g. due to sorption, biodegradation or metabolization in the environment might then be considered in a next step. As environmental fate of the components in the real case would typically lead to dilution and thus reduced exposure and therewith resulting effects, the assessment performed in this study may be considered worst case. Further, while often additional factors accounting for uncertainty in the data are applied within risk assessment, in this work no assessment factors are included in the calculations as this could be based on arbitrary choices only at the present stage. All of this might be taken up by the relevant stakeholders to develop and perform refined hazard and risk assessments.

### Assessment framework

Fracturing fluids are designed for the application in the deep underground, but up to now, there is no European legal regulation that covers environmental risk assessment for this specific use and thus would provide instruments for the chemical assessment (Ewen et al. 2012). By evaluating fracturing fluids using the component-based hazard index (HI), suggestions were put into practice that are currently debated in the EU to implement concepts for environmental risk assessment of chemical mixtures (Backhaus and Faust 2012; SCHER/SCCS/SCENIHR 2012). Backhaus and Faust (2012) suggested that summing up the ratio of PEC-to-PNEC (predicted environmental concentration-to-predicted no effect concentration; EC/1907/2006 2006) is appropriate to extrapolate mixture effects in a first-tier assessment. This might be transferred to the HI-approach, which is derived on a similar basis with the main difference that the hazard quotients (HQs; exposure concentration-to-effect concentration) in contrast to PNECs do typically not include uncertainty factors (US EPA 1997).

The HQ of an individual chemical is defined as the ratio of its exposure concentration to its effect concentration. If the HQ is larger than one, the concentration the organism is exposed to exceed the concentration causing detectable (e.g. EC50), low (e.g. LOEC, lowest observed effect concentration), or just not yet detectable effects (e.g. NOEC, no observed effect concentration) in the organism. Thus, a  $HQ > 1$  would indicate a hazard of this chemical for the environment. By contrast, if the HQ is smaller than one, only low or no effects are expected for the observed organisms at the defined exposure concentration and thus

**Fig. 1** A framework for the ecotoxicological evaluation of products based on the calculation of hazard indices comprising chemical identification, component-based hazard assessment and refined hazard assessment. In this study, step one and two were applied for fracturing fluids to provide initial hazard estimates for further consideration in risk assessment and regulation of fracturing fluids through the different stakeholders. *ECx* effect concentration, e.g. EC50, NOEC. *Conc* exposure concentration, *HQ* hazard quotient, *HI* hazard index, *AF* assessment factor, also uncertainty factor



no hazard is assumed. The HI of a mixture is derived by summing up the HQs of all chemicals of this mixture. This component-based HI calculation is an adaptation of the concentration addition model, one of the basic concepts for predicting mixture toxicity (Altenburger and Greco 2009). It has been shown that concentration addition typically provides conservative estimates of expectable mixture effects for different types of chemicals (Backhaus and Faust 2012). Based on the assumption of concentration addition for all substances in the fracturing fluid, the HI should, therefore, give a conservative estimate of the mixture effects of fracturing fluids. Comparable to the HQ, a mixture with a  $HI > 1$  may be regarded as hazardous to environmental organisms, whereas no hazard is assumed if the HI is smaller than one.

The assessment framework is proposed for mixtures composed of several chemicals making up the product. Prospective ecotoxicological assessment of products is relevant, e.g. in the context of authorization or optimization. Therefore, the developed decision scheme suggests a standardized approach and also allows for flexible assessment of varying product compositions and exposure situations. The three steps with regard to the example of fracturing fluids are illustrated in Fig. 1 and described below. The first step requires the unambiguous identification of the chemicals in the product: What is considered as fracturing fluid? Which chemicals are contained in it? The second step deals with hazard identification and quantification comprising questions on the protection goal, exposure and effect: What is the protection goal of

concern, e.g. the water quality of a sensitive ecosystem or a fish pond, the productivity of agricultural land or the biodegradability in a waste water treatment plant? Which specific exposure scenarios might occur? Which ecotoxicological effects should be considered? Which exposure concentration might be assumed? Using this information, a HQ-type procedure for individual substances and the HI for the chemical mixtures of the product are proposed as a method for quantification. If indicated, the results might then be used for directed product optimization starting again with the first step or might serve as starting point for the refined assessment in the next step. The third step comprises probabilistic considerations as options for refinement of the assumptions made in the first steps: Is the HI representative of the real case contamination? Which extrapolations have to be considered? Is there more detailed information available to refine the assumptions? At this level, uncertainty may be accommodated by inclusion of additional assessment factors. Also, product testing might be considered in the process to refine the risk estimates for the fracturing fluids before finally deciding on risk management measures. Finally, in this study, step one and two of the proposed scheme were applied for fracturing fluids and might provide initial hazard estimates for further consideration in risk assessment and regulation of fracturing fluids.

## Materials and methods

### Fracturing fluids

A fracturing fluid is a heterogeneous complex mixture with a volume of up to thousand cubic meters. It is a technical product prepared at the drilling place prior to its application. One fracturing fluid is applied for one drilling event. In this study, five fracturing fluids were investigated in detail. These fracturing fluids contain chemicals in a water-bauxite-suspension which are considered as components of a mixture here. They were designed by ExxonMobil Production Deutschland GmbH for application in northwest Germany. The fracturing fluids are called Buchhorst T12, Cappeln Z3a, Damme 3, Böttersen Z11-Biocide and Böttersen Z11-UV. For simplification, only the names, not the numbers are used throughout the manuscript. Their composition was provided by the applicant as far as available, comprising chemical names and CAS registry numbers (CAS RN) of the fluid components as well as their concentrations applied in the fluid. This information is summarized in Annex I available as supplementary material.

### Identity of chemical components

Altogether, 84 components (partly identical) were named, but chemical identity was not unambiguous for all of them. In this study, chemical identity was assumed to be unambiguous when the chemical structure was mirrored by the chemical name and the CAS RN. This was the case for 62 of the components. In four cases neither the chemical name nor the CAS RN was mentioned in the chemical data sheet of the producer; thus these components were not included. 12 components provided without CAS RN and ambiguous chemical names or group names such as polysaccharide derivative or ampholytic alkyl amine were excluded from further consideration as well. For six other components without CAS RN, a representative structure was deducible by the chemical name and thus included in the evaluation. For example, different ethoxylated linear alcohols were defined as ethoxylated C9-C11 alcohols with the CAS RN 68439-46-3 in this study. In another case, the amount of a preliminary binary product was not correctly assigned, and thus the concentration was attributed to the more toxic substance and handled as one component. Finally, 68 out of 84 components were considered in the toxicity evaluation of the five investigated fracturing fluids.

### Ecotoxicological effect data

Experimental ecotoxicological effect data were retrieved from the ECOTOX database (US EPA 2007) and supplemented by IUCLID information from the ESIS platform (European Union 1995–2012). Additionally, available measured data from the ECOSAR software (US EPA 2011b) was considered in some cases. Substances were identified in the databases by their CAS RN. A basic data set was collected comprising effect concentrations for three aquatic organisms, namely fish, daphnia and algae as well as for both, acute and chronic toxicity for each organism (Annex II, supplementary material). In this work, for fish and daphnia acute toxicity means short-term exposure (up to 4 days for fish and 1–3 days for daphnia, respectively) and chronic toxicity stands for long-term exposure. In contrast, for algae acute toxicity is defined as the effect concentration, which inhibits 50 % of the population growth (EC50), while chronic toxicity refers to the concentration without a significant (NOEC) or with a low effect (LOEC, EC10). Search criteria were set to retrieve data from assays performed in accordance with the OECD guidelines 201–204 and 211 considering (1) species group and/or organism, (2) effect level, (3) endpoint, (4) exposure duration and (5) the unit of concentration. These search criteria were organized in flowcharts (Annex III,

supplementary material). They were used to filter the entries of the public databases to derive a basic data set as consistent and comprehensive as possible. The lowest value meeting the defined criteria for each of the six effect parameters was taken as entry in the basic data set. Data, not fulfilling these criteria, were not included in the basic data set. More details are presented in Schmitt-Jansen et al. (2012).

Quantitative structure–activity relationships (QSAR) were used with the aim of filling data gaps for those substances, for which no experimental ecotoxicity data were available. For organic fluid components with the logarithmic octanol–water partition coefficient between one and six, baseline toxicity was estimated using QSARs implemented in the ECOSAR software (US EPA 2011b). Hence, in addition to experimental values for three substances effect values were predicted. Predictions may comprise fish, daphnia and algae toxicity in short-term exposure (96, 48, 96 h, respectively) as well as for chronic values and are included in the basic data set (Annex II, supplementary material). Baseline toxicity may underestimate the ecotoxicological effects for these substances due to potential non-narcotic mode of actions indicated by their toxic ratios.

#### Hazard quotient and hazard index

The hazard quotient (HQ) of a single substance was calculated from its exposure concentration divided by its effect concentration (Fig. 1). In this study, the hazard assessment was based on the undiluted fracturing fluid, so the concentration of the chemical in the technical product was taken as exposure concentration for calculating the HQ. On the effect side, the basic data set retrieved for each mixture component comprises as a best case of experimental and predicted data for each, the acute and chronic toxicity to fish, daphnia and algae. The lowest effect concentration of this data set was used to determine the component-specific HQ (Annex I, supplementary material). The hazard index (HI) of each fracturing fluid was then derived by summing up the HQs of all chemicals present in this mixture (Fig. 1). These HIs provide a worst-case hazard estimate to initially identify whether the application of fracturing fluids may harm ecosystems.

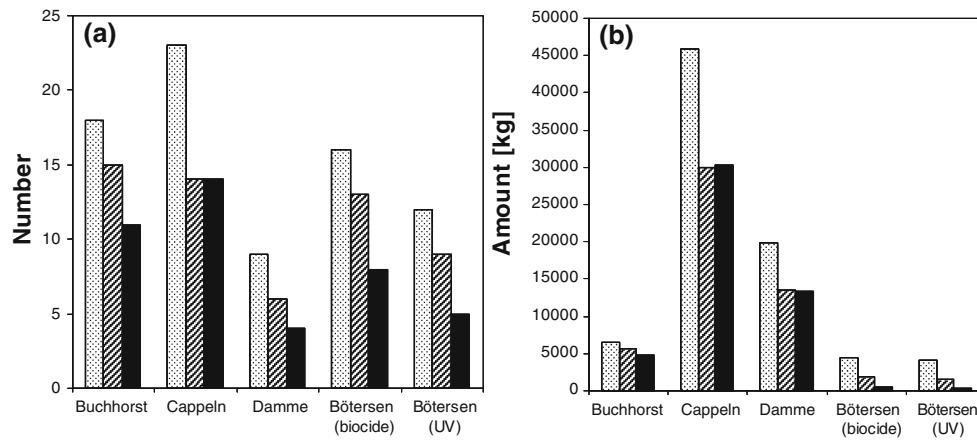
#### Default and scenario-based approaches

The HI derived as described above based on the complete effect data sets of the fracturing fluid components represents the default approach without assumptions for a specific scenario. In addition, exposure scenarios have been considered in this study to illustrate more specific hazard estimates. These scenarios were used to refine the hazard

assessment based on available ecotoxicological effect data; they were not applied for an exposure assessment as site-specific information for fracturing fluids, agreed settings for exposure estimates and a frame which would define these are still lacking. For the hazard refinement, exposure situations specified for different ecological receptors were assumed and reflected by selecting specific effect data sets. In the scenario-based approach two options were investigated exemplarily: First, a spill of fracturing fluid into a fish pond was assumed and reflected by considering short-term (acute) exposure and toxicity of fish for the assessment only. Second, a long-term (chronic) exposure of agricultural plants caused by a leakage reaching arable land was assessed using chronic algae data. The HQ calculation in the scenario-based approach was then based on the lowest effect value, either the experimental or the predicted value, of these specific effect data sets (Annex I, supplementary material) and, as for the default approach, on the concentration of the chemicals in the undiluted fracturing fluids. Thus, in the default and in the scenario-based approach the same exposure concentration has been applied for the hazard estimate. Hence, for the more specific hazard estimates in this study, the scenarios were specified by selecting the affected target organisms (fishes, plants) in combination with the exposure situations investigated in the bioassays (acute, chronic). Comparable to the default approach, the exposure concentration was still assumed to be worst case as no real case specifications were available at present.

#### Results

In this study, the proposed assessment framework (Fig. 1) was applied to five fracturing fluids. These fracturing fluids consist of water (70–95 %), bauxite (5–28 %), carbon dioxide (18 % only in one fracturing fluid) and chemical additives (0.2–2 %). Although the mass fraction of chemical additives is small, between four and 46 tons of chemicals were used in these five fracturing fluids. An overview about the available data used to assess these five fracturing fluids is provided in Annex I (supplementary material). The chemical components in these fracturing fluids are heterogeneous in terms of number, amount and thus ratio of the substances in the mixture (Fig. 2). For example, between nine and 23 substances have been used in the five fluids, with their applied amounts varying over one order of magnitude. The chemical identity of only 40–90 % of the substances, on a weight basis, could be unambiguously characterized by their CAS RNs and the concentrations applied in the fracturing fluids (Fig. 2). Moreover, basic toxicity data are lacking for 26–90 % of the substances in the fracturing fluids, referring to their



**Fig. 2** Number (a) and amount (b) of chemical components totally contained (dotted bars), chemically identified (striped bars) and characterized by ecotoxicological effect and hazard quotient (black bars) used in selected fracturing fluids

total weight in the product. Therefore, for the different fluids, the hazard quotients (HQs) could be calculated for only 10–74 % of the contained substances. This equals a substance amount of 2–16 tons that could not be included in the hazard assessment.

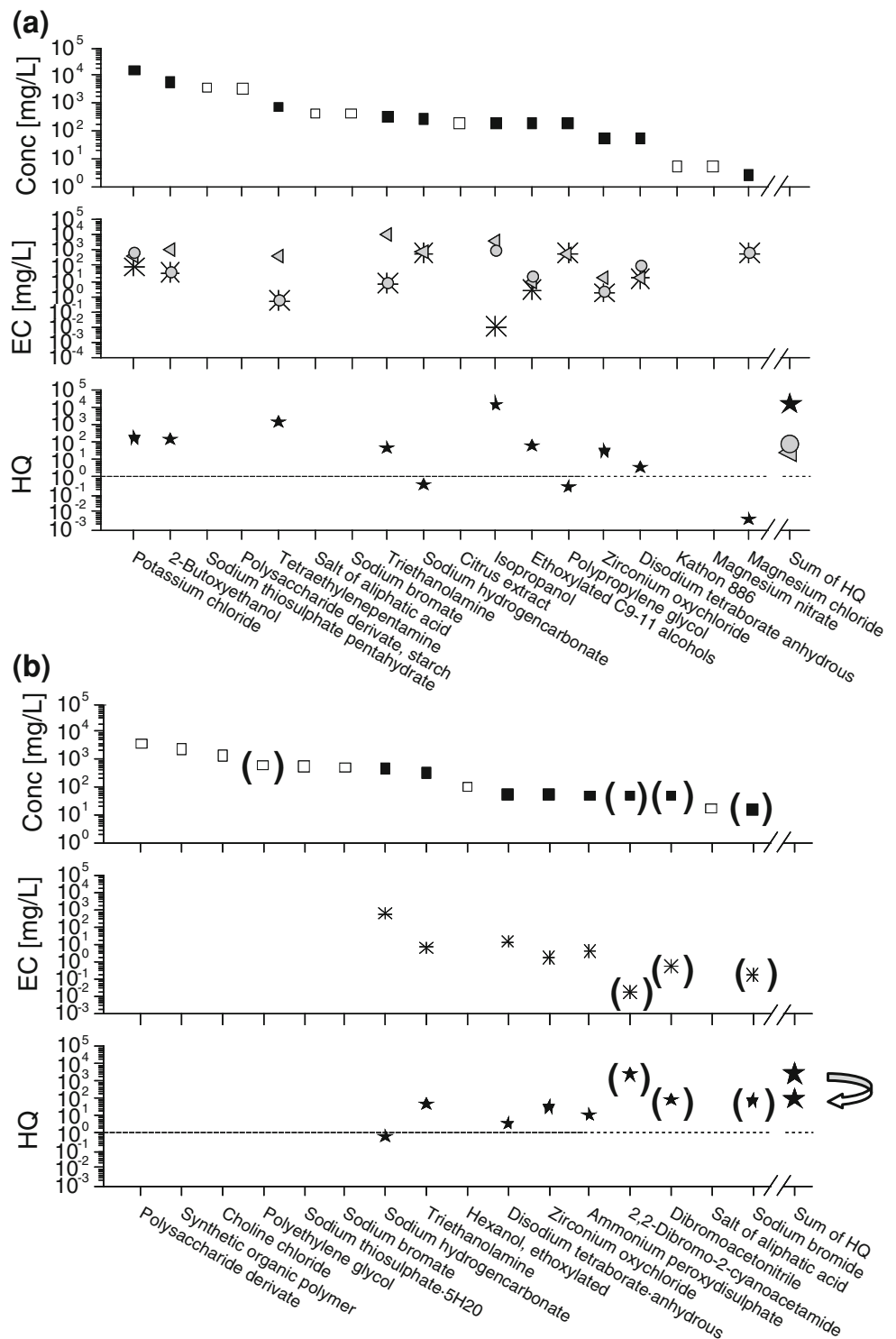
The ecotoxicological evaluation of fracturing fluids in this study was based on calculated HQs illustrated in detail for two examples (Fig. 3). Substances are sorted by the concentration used in the fracturing fluid. Further, the lowest effect value of the basic data set is depicted for each substance. This lowest value is used as default when the exposure scenario for a product is not further specified. In addition, effect values are depicted for acute fish toxicity and chronic algae toxicity representing two effect data sets, which are relevant for the two specific scenarios. Substance-specific effect values of the basic data set showed great variation in some cases (Annex II, supplementary material). This is although the data were retrieved using standardized search criteria conforming to OECD protocols (Annex III, supplementary material). They varied, e.g., by about three orders of magnitude for tetraethylenepentamine or by four orders of magnitude for triethanolamine. In other cases they were in the same range, e.g., within a factor of ten as for disodium tetraborate or sodium hydrogencarbonate. Thus, the effect data set depending on the exposure scenario information might lead to distinctly different HQs for the individual substances and this might then be propagated into the sum of all HQs of a fracturing fluid (Fig. 3a).

The HQ indicates if a hazard of a single substance in a product exists. Summing up the HQ for all substances in a product gives an estimation of the product’s hazard based on its mixture components. For the five fracturing fluids considered, all calculated hazard indices (HI >1) of the default as well as of the scenario-based approaches indicate a hazard for the ecosystem (Fig. 4). This means that the

exposure concentrations, which were as a worst case assumed to be equal to the concentrations of the chemicals in the undiluted product, are larger than the effect concentrations for the organisms or populations. Moreover, while individual components contribute distinctly to the estimated overall hazard, none of the mixtures could be made smaller than unity by eliminating just one or two of the major drivers. The HIs were based on the lowest effect concentration of the basic data set in the default approach and vary for more than two orders of magnitude for the five fracturing fluids (HI = 100–54,000). In turn, a decrease by factors between 100 and 54,000 for the respective frags would reduce the hazard indices for the fracturing fluids below one (HI <1). Thus, these hazard estimates might provide an orientation to deduce potentially hazardous exposure situations. However, the hazard indication for the five fracturing fluids was found despite only about half of the substances (42–61 %) contained in the mixture were included in the calculation of these HIs (Fig. 2). For example, for eight substances of the frac Böttersen a HQ could be determined, but eight other substances, and among them, just those dominant in concentration, were not ecotoxicologically characterized (Fig. 3b). Thus, it can be assumed that the calculated HIs would increase if data gaps were filled.

As subsidiary tool for extrapolating missing effect values of mixture components, one may assume that the components with unknown effects are as toxic as the component with the lowest effect concentration in the mixture. Applying this exemplarily for the frac Böttersen, hazard quotients for eight (50 %, Biocide-frac) and seven components (58 %, UV-frac) per mixture have to be extrapolated and concentrations of 9.3 g/L (90 %) for the first and 8.6 g/L (90 %) for the latter need to be related to the most toxic mixture component for which data are available. Based on 2,2-dibromo-2-cyanoacetamide and zirconium dichloride

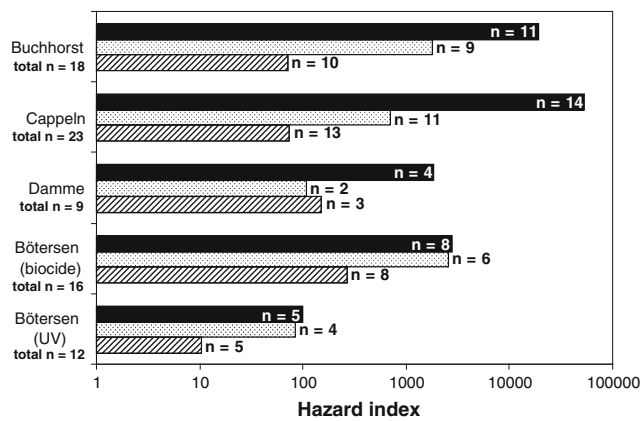
**Fig. 3** Concentration (Conc), effect concentration (EC: LC50/EC50 for fish, daphnia and acute algae data; NOEC/LOEC/EC10 for chronic algae data) and hazard quotient (HQ) of each chemical in the fracturing fluid of **a** Buchhorst and **b** Böttersen. *Square* Conc in mg/L, *open/closed* not considered/considered in HQ calculation. *Cross* lowest EC in mg/L of the basic data set in the default approach (experimental or predicted, acute or chronic fish, daphnia or algae data). *Triangle*, *grey* EC in mg/L for acute fish data in the scenario-based approach. *Circle*, *grey* EC in mg/L for chronic algae data in the scenario-based approach. *Star*, *small* HQ. *Star*, *big* sum of all HQs (=hazard index, HI). *Dashed line* indicates a HQ level of 1. *Brackets* chemicals removed for product optimization leading to a reduced HI, as indicated by the *arrow*



oxide, respectively, extrapolated HQs of 460,000 for the Biocide-frac and 5,100 for the UV-frac were retrieved. Hence, the resulting HIs of the default approach would increase by a factor of 170 and 50, respectively. For the frac Buchhorst with missing effect values for seven components

(39 %) and an amount of 26 %, the extrapolation would lead to an HI increased by a factor of 40. For the frac Cappeln, it is a factor of ten for nine components and an amount of 34 % and for the frac Damme a factor of two with five missing values and an amount of 32 %.





**Fig. 4** Hazard indices (HIs) of selected fracturing fluids. *Black bars* default approach based on the lowest effect concentration of either acute or chronic fish, daphnia or algae data. *Dotted bars* scenario-based approach assuming chronic exposure of agricultural land using chronic algae toxicity. *Striped bars* acute exposure scenario for a fish pond using acute fish toxicity. The concentration of the components in the undiluted product served as worst case exposure concentration for all HI calculations. The number (*n*) of chemical components considered for calculating the HI compared to all chemical components (*total n*) in the fracturing fluid

In Fig. 4, the HIs are also depicted for two specific data sets, chronic algae data and acute fish data, respectively. Both were lower for the same fracturing fluid compared with the default approach. At the same time, the number of substances that could be considered for the HI calculation was lower for the specific than for the basic data set. Comparing the two specific data sets it seems that a higher hazard from a fracturing fluid was indicated for the long-term scenario based on chronic algae data than for the short-term scenario represented by acute fish data. This was observed although a higher number of substances were included in the calculations of the short-term scenario compared with the long-term scenario. However, comparing HIs for different fracturing fluids or scenarios should be handled with care if not all components of the mixture can be considered for the HI determination as the overall quantities may rely on the data available at present.

For the Böttersen frags, distinct HIs were obtained (Fig. 4). Both fracturing fluids were comparable in their chemical composition except for four substances (Fig. 3b). These four substances were used in the fracturing fluid (Böttersen-biocide) for biocidal purposes. Three of them show the highest HQ values and thus the highest contribution to the HI of this fracturing fluid (Fig. 3b). Removing the biocide and substituting by other techniques, e.g., UV radiation (Böttersen-UV) leads to a reduction of the HI from about 3,000 to 100 for the Böttersen frac (Fig. 3b).

## Discussion

In this study, a framework for ecotoxicological hazard assessment of chemical products was presented and applied to chemical composite fracturing fluids. As a strategy, a component-based hazard quotient (HQ) approach and estimation of expected mixture effects (hazard index, HI) were applied for assessing the potential ecotoxicological impact of fracturing fluids. For each fracturing fluid investigated in this study, clearly the assumed exposure concentrations of most substances in the mixture were higher than the concentrations provoking an effect for the organisms considered. In terms of risk assessment, the HI level might be regarded as a first-tier screening approach and the assessment might be refined in higher tiers by providing additional and more detailed information like, e.g. on the exposure concentration. The proposed framework was shown to be suitable for fracturing fluids and might be transferred to other products such as personal care or industrial products as well. Moreover, it may be useful for product optimization as it allows predictive assessment without product testing. Here, we discuss the potential and limitations of the component-based approach as a basis for an ecotoxicological assessment of mixtures.

### Mixture assessment

The component-based HI may serve as first estimate for mixture toxicity of products. For fracturing fluids, a quantification of the mixture effects could be achieved based on the HQs for the chemical components of the mixture. Chemical toxicity assessment has long been conducted mainly for single substances. Mixtures have rarely been addressed and then often subsidiary tools have been applied such as assessing the most hazardous component as mixture representative (Thatcher et al. 2005). However, this neglects combined effects of the mixture (Altenburger et al. 2004). Two basic concepts for combined effect determination, concentration addition for similar acting components and effect addition of independent action, are scientifically established (Altenburger and Greco 2009). Further, mixture assessment within chemical regulation is currently debated in the EU to achieve a generally accepted approach for risk assessment of mixture chemicals (SCHER/SCCS/SCENIHR 2012). Here, component-based approaches, using the concept of concentration addition, such as the HI, are explicitly suggested. However, if effect data basis is heterogeneous regarding bioassay parameters such as organism, duration or endpoint as is often the case for data available in chemical assessment, their appropriateness is disputed (SCHER/SCCS/SCENIHR 2012). The concepts, concentration addition and

effect addition, do both require homogeneity of the data with respect to endpoint and level of effect (Backhaus and Faust 2012). Therefore, the HI-based mixture toxicity estimate violates this requirement. However, Backhaus and Faust (2012) suggested that PEC-to-PNEC as an exposure-to-effect ratio based on effect data for different trophic levels might be an adequate approximation for concentration addition. It has been observed that concentration addition tends to give a more conservative mixture estimate compared with effect addition. The HI calculation using any lowest effect value from the data set would then be expected to be even more conservative in most cases. Only if several substances of the mixture act specifically or interact in one species, and these values would be missing values, then, an underestimation of the mixture effect level could be expected. Therefore, the chosen HI approach seems a reasonable tool for a first-tier mixture assessment.

Common practice in mixture considerations is still to only consider those mixture components that contribute to a certain percentage to the mixtures weight. For example, when labeling products according to the CLP regulation only substances contained for more than 1 wt% (or 0.1 wt%) are considered (EC/1272/2008 2008). For assessing the security of industrial plants with respect to water quality in the German legislation, 0.2 wt% (or 0.1 wt%) is applied as cut-off criterion (VwVwS 2005). Applying these rules for determining hazard classifications of mixtures may lead to considerable underestimation of the mixture effects in some cases. This is exemplarily illustrated for the fracturing fluid Buchhorst, which was designed for one application in the northwest of Germany. This fluid comprises of 19 substances with a total amount of 92 tons including 86 tons of bauxite and 6.5 tons of chemical additives. Only three substances out of 19 contribute to the mixture for more than 1 wt% and would thus be considered in the mixture effect estimation. Even if the large part of bauxite is excluded from the overall amount, only eight substances out of 18 contribute to the mixture weight for more than 1 wt%. Together, these eight substances make up 6,300 kg (96 wt%) of the chemical additives in the fluid and give a HI of 1,900 ( $n = 4$ ). However, the ten substances below 1 wt% are added up to another 250 kg and a HI of 17,400 ( $n = 7$ ). Following the 1 wt% rule suggested in the CLP regulation (EC/1272/2008 2008), these substantial effects would not be included in the mixture calculations. Further, even with the lower limit of 0.1 wt% three components of the Buchhorst fluid would be left out from consideration, among them the biocide Kathon which is designed to be harmful at least for bacteria. Thus, the weight percentage seems not an adequate measure for selecting the mixture compounds of concern to be considered for a toxicology-oriented evaluation.

Another common practice for capturing the hazard of chemical mixtures is focusing on components with a large intrinsic toxicity. This alternative approach might also lead to underestimation of the mixture effect. The applied concentration of the substance matters as well, as seen for the compound 2-butoxyethanol in the fracturing fluid Buchhorst. This component is labeled as irritant and also classified to exhibit low acute toxicity (Cat. 4, EC/1272/2008 2008). However, 1,200 kg of this substance are added to the fracturing fluid Buchhorst resulting in a concentration of 5.6 g/L. This concentration exceeds the lowest observed effect concentration for algae by a factor of 160 and also the other available experimental effect values indicating that this large concentration might affect aquatic organisms and algae populations in the ecosystem. Taking both, exposure concentration and effect concentration, into account is fundamental for an adequate hazard assessment, and as a consequence should be put into practice for chemical mixture effect estimation. Further, hazard evaluation of chemical mixtures should comprise all components of the mixture regardless of their proportion or intrinsic toxicities. Thus, a reasonable screening of the mixture toxicity might be based on the exposure-to-effect ratio and the subsequent HI calculation should include the hazard values of all substances in the product (SCHER/SCCS/SCENIHR 2012).

#### Product optimization

A component-based approach enables prioritization of substances of concern and product optimization. At the screening level, hazard comparison between products might be based on testing the product itself or on component-based calculations as shown in this study. Using the component-based HI approach, substances of high concern might be identified in a product by their HQ and eventually substituted by a component with a lower HQ to improve the environmental performance of this product. As exemplarily shown, the HI of one fracturing fluid was reduced by replacing the biocidal effect of a four-component mixture with UV treatment. Further, substances of high concern might be replaced by substances with low concern as asked for by the REACH regulation (EC/1907/2006 2006). With the same purpose, a HQ ranking was discerned valuable as a primary tool for selecting chemicals used and possibly discharged by the offshore oil and gas production industry (OSPAR convention 2000). Although at the beginning a definite and comprehensive set of information is necessary to evaluate the hazard of each chemical in the mixture and thus the mixture itself (Scholten et al. 2000; Sheahan et al. 2007), this approach offers advantages if optimization is an option or if comparison of very similar products is the goal. An optimization of the environmental performance is strived in green chemistry, green pharmacy, green

engineering and hence all kinds of products. In addition to parameters such as resource and energy consumption or emissions of the production processes, the eco-/toxicological potential of chemical components is increasingly considered for product design (McDonough et al. 2003; Braungart et al. 2007). Also, comparison of products is now a legal request, e.g. in plant protection product authorization where products of concern may become substituted. For this, hazard quantification with the HI is a useful tool not only for comparison of products but also for risk communication. Further, the component-based structure of the approach is valuable for selection of least hazardous substances. Thus, the product optimization potential was shown for fracturing fluids and the presented approach can be regarded as widely applicable.

#### Scenario-specific hazard assessment

A component-based approach is suitable for a protection goal- and exposure scenario-specific ecotoxicological evaluation of a product. For appropriate environmental risk assessment, protection goals have to be defined prior to the assessment (van Leeuwen and Vermeire 2007). The protection of an aquatic ecosystem as such is a quite general and abstract goal often addressed in first instance in chemical regulation (EC/1907/2006 2006; EC/1272/2008 2008). In regulatory risk assessment, this is usually further specified and subsequently reflected in the use of specific ecotoxicological data. Which data are actually available and included in the final assessment might depend, e.g. on the production volume of the substance as in the REACH regulation (EC/1907/2006 2006), on the stringency of the relevant regulation (e.g. plant protection products), or follows the precautionary principle (EC/1272/2008 2008; VwVwS 2005). In this study, as a conservative approach, the lowest effect value for each substance, available in public databases and fulfilling the search criteria, was used to calculate a default worst case HI. However, compared substance-wise effect data across species for acute and chronic exposure were similar for some substances and deviated over several orders of magnitude for other substances. These deviations may comprise systematic variations due to species sensitivity (Sanderson 2003) or test design (Länge et al. 1998). Thus, this information might be used productively for scenario-specific evaluation.

For fracturing fluids, different exposure scenarios could be envisaged (Thompson 2012; Lange et al. 2013; Kissinger et al. 2013) and several resources at risk such as ground- and surface-water, have been discussed (Ewen et al. 2012). However, legislation has not yet defined specific protection goals for the case of chemical usage in the deep underground that could be used for fracturing fluids (Ewen et al. 2012; Rossnagel et al. 2013). In the present study, two

specific scenarios have been developed. One aimed to reflect the protection of the functionality of crop production, the other of fish production. Based on acute fish data and chronic algae data, distinct HIs have been derived for both scenarios. Fish seems less susceptible after short-term exposure towards the selected fracturing fluids compared with algae after chronic exposure. The susceptibility of algae was on average higher than of daphnia or fish, revealed by a systematic evaluation of pharmaceuticals in the environment using ECOSAR predictions (Sanderson 2003). Evaluating specific scenarios by selecting suitable data sets might increase precision of hazard prediction for fracturing fluids and other products as well. Exposure scenarios might be invented for all kinds of products, but need to be defined for each product group as some are intentionally applied in the environment (e.g. pesticides, biocides), and others are likely and known to reach the environment (e.g. pharmaceuticals, rinse-off cosmetic products) or might reach the environment only in minor fractions of their original use (e.g. solvents for chemical synthesis). Thus, refining the protection goal might lead to a more specific and realistic hazard assessment while a smaller but more complete data set is necessary.

#### Data availability and data gaps

The developed scheme reveals that different levels of information are necessary for evaluating the ecotoxicological impact of a product depending on the specific aim of the assessment. Hereby, data availability for the composition of a defined product and for the properties of its components might be determining for a hazard screening based on the literature data. In addition to the data available, data gaps may in particular lead to an underestimation of the HI and thus hinder appropriate comparisons on a quantitative level. When applying the component-based HI approach for fracturing fluids, a hazard was indicated for all mixtures although only part of the mixture components could be taken into account.

Choosing the component-based approach is imperative to know the chemical identity of all compounds in the mixture/product. Thus, for comprehensive evaluation of a product its composition needs to be disclosed despite these might be proprietary data. The chemical legislation of the EU addresses this issue and data should become available at least for authorities (EC/1907/2006 2006). For fracturing fluids this is still under debate (The Tyndall Centre 2011; US EPA 2011a; Thompson 2012). Although the lack of information about chemicals in use might be filled by the REACH legislation, relating a clear chemical identity still remains challenging in some cases (ECHA 2012).

Ecotoxicological effect data for all components of a mixture/product are crucial as well for a final hazard

assessment. However, to allow an initial hazard estimate in the first instance appropriate data available should be used prior to considerations on missing data. In this study, effect concentrations were limited to the data available in public databases and could only be marginally supplemented with modeling data. The assessment based on specific exposure scenarios requires only less but consistent effect data. However, in our study, data availability across species was better than that for single species. Therefore, the default approach provided a more robust hazard estimate for the investigated fracturing fluids simply through consideration of a higher amount of data points. Modeling missing ecotoxicological data via lipophilicity estimates using quantitative structure–activity relationships has been successfully used with the HQ approach for pharmaceuticals (Sanderson 2003; Lienert et al. 2007), but the mixture components of fracturing fluids only rarely profited due to the limitations of current prediction models (Thatcher et al. 2005; Sheahan et al. 2007). Thus, efforts to improve access to reliable data through comprehensive public databases and extended applicability of toxicity prediction models might strengthen hazard estimates at a screening level. This might also be beneficial when additional experimental testing is avoided due to expenses and ethical demands for less animal testing (EC/1907/2006 2006).

Data gaps lead to an uncertainty of the hazard estimates. These uncertainties might be addressed at several levels. Extrapolation of potential effects for missing data using the most toxic substance of the mixture might be one approach, which would still be related to, but also dependent on the data available. This was shown for the two approaches of the frac Böttersen. A comparable amount of components was missing with only one distinct substance between the approaches, but the extrapolation was related to substances differing in their effect concentrations by two orders of magnitude. This was leading to tremendously varying hazard estimates between both approaches mainly influenced by the extrapolated HQs for missing values rather than the observed HQs for the data available. Other options might be multiplying mixture effect estimates with safety factors or evaluating components on a monographic basis through access of expert knowledge. Dealing with data gaps and uncertainties might be especially relevant for decision-making in regulatory risk assessment and to guarantee the precautionary principle as long as data situation based on rational instruments is incomplete.

## Conclusion

The scheme developed in this study could be shown to be a useful measure for evaluating the potential ecotoxicological impact of fracturing fluids. The component-based

mixture approach is flexible, extendable and generally applicable. The HI as used in this study was demonstrated to be valuable to quantify and compare the expectable mixture toxicity of different products. In the presented work, hazards from the chemicals in fracturing fluids for the environment were indicated. This information should be included in the usage and management considerations by the different stakeholders. Fracturing fluids might be optimized in their composition regarding their ecotoxicological hazards by substituting or reducing chemical components of concern. The assessment carried out here might be considered as providing initial hazard estimate based on easily available data. An advanced environmental risk assessment could include specified and refined exposure assessments. For instance, environmental fate of the mixture components could be considered in addition to their ecotoxicological effects. Further, hazard estimates of fracturing fluids might be elaborated by separating toxicity based on chemical-target interaction from, e.g. osmotic stress due to salts. Finally, the general framework proposed may be transferred to other products such as personal care or industrial products to facilitate the design of products with improved environmental performance and support predictive environmental risk assessment.

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