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Environmental Impacts of Fracking Related to Exploration and Exploitation of Unconventional Natural Gas Deposits

Risk Assessment, Recommendations for Action and Evaluation of Relevant Existing Legal Provisions and Administrative Structures

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Environmental Impacts of Fracking Related to Exploration and Exploitation of Unconventional Natural Gas Deposits

Risk Assessment, Recommendations for Action and Evaluation of Relevant Existing Legal Provisions and Administrative Structures

by

Dr. H. Georg Meiners, Dr. Michael Denneborg, Frank Müller
ahu AG Wasser-Boden-Geomatik

Dr. Axel Bergmann, Dr. Frank-Andreas Weber, Prof. Dr. Elke Dopp, Dr. Carsten Hansen, Prof. Dr. Christoph Schüth
IWW Rheinisch-Westfälisches Institut für Wasser-, Beratungs- und Entwicklungsgesellschaft mbH

in cooperation with

Hartmut Gaßner, Dr. Georg Buchholz
Gaßner, Groth, Siederer & Coll.; Rechtsanwälte Partnerschaftsgesellschaft

Prof. Dr. Ingo Sass, Sebastian Homuth, Robert Priebs
TU Darmstadt, Institut für Angewandte Geowissenschaften

On behalf of the Federal Environment Agency (Germany)

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Study performed by: ahu AG Wasser – Boden - Geomatik
Kirberichshofer Weg 6
52066 Aachen

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Publisher: Federal Environment Agency (Umweltbundesamt)
Wörlitzer Platz 1
06844 Dessau-Roßlau
Germany
Phone: +49-340-2103-0
Fax: +49-340-2103 2285
Email: info@umweltbundesamt.de
Internet: http://www.umweltbundesamt.de
http://fuer-mensch-und-umwelt.de/

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Abstract

We examine the water-related environmental impacts and the risks for human health and the environment that could potentially be caused by hydraulic fracturing (fracking) during exploration and exploitation of unconventional natural gas reservoirs in Germany. This study covers both scientific-technical aspects and the existing mining and environmental regulations. Both were analyzed with respect to consistency, differences and current gaps of knowledge and lack of relevant information.

After a general introduction, this study is divided into four sections: We first focus on the description of geospatial conditions, technical aspects and the chemical additives employed by hydraulic fracturing (Part A) and the existing regulatory and administrative framework (Part B), before we conduct a risk and deficit analysis (Part C) and derive recommendations for further actions and proceedings (Part D).

The foundation of a sound risk analysis is a description of the current system, the relevant effect pathways and their interactions. We describe known and assumed unconventional natural gas reservoirs in Germany based on publicly available information. We present qualitatively the relevant system interactions for selected geosystems and assess potential technical and geological effect pathways.

With regard to the technical aspects, we describe the principles of rock mechanics and provide an overview of the technical fracturing process. In terms of groundwater protection, the key focus is on borehole completion, modelling of fracture propagation and the long-term stability of the borehole (incl. cementation).

The injected fracturing fluids contain proppants and several additional chemical additives. The evaluation of fracturing fluids used to date in Germany shows that even in newer fluids several additives were used which exhibit critical properties and/or for which an assessment of their behaviour and effects in the environment is not possible or limited due to lack of the underlying database. We propose an assessment method which allows for the estimation of the hazard potential of specific fracturing fluids, formation water and the flowback based on legal thresholds and guidance values as well as on human- and ecotoxicologically derived no-effect concentrations. The assessment of five previously used or prospectively planed fracturing fluids shows that these selected fluids exhibit a high or a medium to high hazard potential.

The flowback redrawn after the pressure release contains fracturing fluids, formation water, and possibly reaction products. Since the formation water can also exhibit serious hazard potentials, environmentally responsible techniques for the treatment and disposal of the flowback is of primary importance.

With respect to groundwater protection, regulatory requirements result from both the mining and the water law. The water law requires the examination, whether concerns can be excluded that hydraulic fracturing and the disposal of flowback may cause adverse groundwater effects. This requires a separate authorization according to the water law. Due to the primacy of the environmental impact assessment directive (EIA Directive, "UVP-Richtlinie") over the national EIA mining regulation ("UVP V-Bergbau") it has already to be assessed in a case-by-case examination, whether an environmental impact assessment is required. The previous administrative practices thus exhibit certain lack of enforcement.

Regulatory deficits exist concerning the application of the requirements of the EIA Directive and concerning some uncertainties in applying specific terms of the water law (groundwater, requirement of and conditions for authorization). We recommend constituting a mandatory environmental impact assessment for all fracking projects in federal law, with a derogation clause for the federal states. The public participation required in the EIA Directive should be extended by a project-accompanying component to improve public access to the assessment of knowledge that is generated after the initial authorization of the project. The examination of the legal requirements should be ensured by clarification and revision of an integrated authorization procedure under the auspices of an environmental authority subordinated to the Ministry of the Environment or by an integration of the mining authority in the environmental administration.

A risk analysis is always site-specific, but must also consider large-scale groundwater flow conditions, which generally requires numerical models. We provide considerations for application of a site-specific generic risk analysis, which integrate both the hazard potential of the fluids and the specific relevance of each effect pathways in the geosystem.

In summary we conclude that basic knowledge and data are currently missing preventing a profound assessment of the risks and their technical controllability (e.g., the properties of the deep geosystem, the behaviour and effects of the deployed chemical additives, etc.). In this setting we propose several recommendations for further action, which we specify for each of the aspects geosystem, technical guidelines and chemical additives.

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1 Introduction

The exploration and exploitation of unconventional gas deposits especially as it involves "hydraulic fracturing" – "fracking" – has been generating intensive public discussion. Such discussion has focused especially on relevant projects' potential impacts on the environment and on human health – in particular, on how the techniques and substances used in fracking can affect the environment and human health. The Federal Environment Agency (UBA) has published a statement/report on shale gas production in Germany[1]. A number of the aspects that that Federal Environment Agency statement/report simply touched on have now been detailed and scientifically analysed in the framework of the present study.

Approval authorities and operators must observe numerous mining and environmental laws in connection with approval and execution, respectively, of measures related to exploration and exploitation of unconventional natural gas deposits. And yet the applicable requirements, under substantive and procedural law, are not always clear in areas in which mining law and water law overlap.

The present study seeks to describe the potential environmental impacts of fracking, and the potential risks for human beings, and to describe the additional findings and knowledge that are needed in order to properly assess such impacts and risks. In addition, it describes the existing applicable provisions under mining law, environmental law and – especially – water law, and analyses those provisions with regard to areas in which they agree, areas in which they differ and areas they fail to address.

The present study does not include assessments and analyses of the following issues:

- Aspects of regional planning covering above-ground and underground areas, especially with regard to potentially excluded areas, potentially competing uses, etc..
- Potential hazards related to handling of (fracking) chemicals at ground level (transports to and from the site, storage, etc.),
- The (legal) significance of copyright law in connection with (required) publication of chemicals used in fracking,
- Issues related to the overall energy balance / climate impacts of projects,
- Direct environmental impacts in connection with the setting up and operation of drilling sites (land use, noise, etc.),

[1] http://www.umweltbundesamt.de/chemikalien/publikationen/stellungnahme_fracking.pdf

- Potential seismic impacts resulting from fracking and/or flowback injection (disposal),
- Concrete, site-specific issues (for example, with regard to geological impact pathways, etc.).

Objectives and procedures

The objectives of the overall project include:

1. Assessing the risks of exploitation of unconventional natural gas deposits, and especially of such exploitation via fracking, from scientific, technical and legal standpoints.
2. Describing the available technical alternatives.
3. Developing recommendations for action and procedures that lawmakers and enforcement authorities can implement as a basis for managing the risks entailed in exploitation of unconventional natural gas deposits. This also includes development of suitable criteria for public participation in the framework of environmental impact assessment (EIA).

The study focuses especially on the substances used in fracking, on those substances' toxicity for humans and for aquatic organisms, on the pertinent potential pathways involved and on the relevant legal framework.

A well-founded risk analysis will be based on a precise description of the existing relevant system (its sensitivity), of the impacts related to the project (intervention) and of the relevant cause-and-effect relationships. The existing system and its sensitivity must be assessed site-specifically. In the case of exploration and exploitation of unconventional natural gas deposits, such activities must consider the following:

- Underground gas deposits,
- The condition of the site in terms of geology, hydrogeology and water-resources management,
- Surface areas, and near-surface underground areas, along with their pertinent uses, ecosystem compartments, impact pathways and interactions with human beings.

Project-related impacts in connection with exploration and exploitation of unconventional natural gas deposits (intervention) depend primarily on the techniques and equipment used, which can vary from site to site. The key aspects in this regard include:

- Drilling techniques and well completion,
- Techniques for stimulation of the deposit (fracking), along with the substances used in the process,
- Disposal (flowback), gas extraction and water drainage.

The key characteristics of exploration and exploitation of unconventional natural gas deposits include use of the following two technologies (cf. Tab. 1):

- Horizontal drilling
- Hydraulic fracturing (fracking)

Tab. 0 1: Use of horizontal drilling and of hydraulic fracking in exploitation of unconventional natural gas deposits (source: EXXON 2011)

Types of unconventional natural gas	Use of horizontal drilling	Use of hydraulic fracking	Production in Germany (current)
Tight gas	Yes	Yes	Yes
Shale gas	Yes / no	Yes	No
Coal bed methane	Yes / no	Yes / no	No

The nature, extent (depth) and duration of a project's environmental impacts (intervention intensity) can vary in keeping with the possible combinations of types of reserves and the technologies used to exploit them. As a result, the two subsystems "environment" and "technology" have to be considered first; then, the two can be combined in useful ways for systematic, comprehensive analysis of the possible cause-and-effect relationships.

In each case, the risks related to use of unconventional natural gas are spatially connected with the natural gas deposits concerned. Such risks arise in exploration for natural gas, in stimulation of suitable deposits (with various techniques, including fracking) and in exploitation of economically exploitable reservoirs (= natural gas deposits). They also arise in the post-project phase. One must consider a range of aspects, including the pertinent individual case (a single borehole), the summed effects of many boreholes/fracks in a single exploitation area, the long-term integrity of wells and aspects of both normal operations and disruptions/incidents.

In keeping with its defined task, the present study focuses especially on the environmental impacts and risks related to fracking. Use of fracking in any specific project can begin in exploration of potential deposits. Normally, multiple fracking of a single borehole is used only to prepare the way for production, however.

Figure 1 shows the systemic relationship between risk studies and later safety management for a given project. A risk study consists of a system analysis (covering hydrogeology, cause-and-effect relationships, etc.) and a system assessment (current condition and condition following the intervention). It summarises all aspects of the relevant risk (especially with regard to fracking) for human beings, the environment and natural systems, taking account of the situation at the site, the techniques and substances to be used (introduction, final location, toxicity, changes, flowback) and the applicable legal regulations. In the process, it identifies, describes and assesses the key cause-and-effect relationships that could present hazards for human beings, the environment and natural systems.

Concepts for measures (such as catalogues for assessment and approval) relative to implementation (exploration and exploitation) are then prepared in light of the so-illuminated risks and cause-and-effect relationships. Safety management is then guided and controlled via specific and general monitoring (including monitoring during the project). The conditions on which project approval is based can then be adjusted in light of any emerging additional findings that are relevant with regard to system assessment and risk analysis.

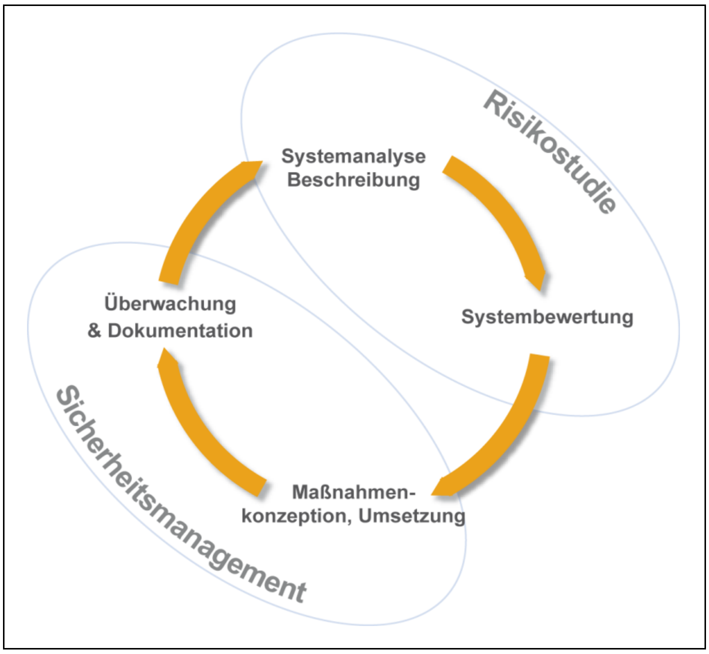

Fig. 0 1: Relationship between a risk study and (later) safety management [From top, clockwise: System analysis, description; Risk study; System assessment; Design and implementation of measures; Safety management; Monitoring and documentation]

A project's risks for humans and the environment are normally determined and assessed primarily by the competent mining and water authorities, on the basis of the substantial and procedural requirements of mining law and water law. Although relevant projects can entail significant environmental impacts, and although such projects are matters of considerable public concern, the applicable German EIA ordinance for the mining sector (UVP-V Bergbau) normally does not impose environmental impact assessment (EIA) obligations, along with obligations for pertinent public participation, either for overall projects for exploration and exploitation of unconventional natural gas deposits or for specific measures such as fracking; under that ordinance, EIA obligations are tied to gas-production quantities of at least 500,000 m^3/day (per project).

This is why calls for introduction of wider EIA obligations have been prominent in relevant public and political discussion. The EIA is primarily a procedural-law instrument, however. The standards for assessment of relevant projects, and for determining the level of investigative detail required for proper assessment, are defined by substantive mining law and water law. What is more, the instruments required for suitable risk management are defined not by EIA law, but by relevant specific legislation and by general laws on administrative procedures. In addition, authorities' organisational structures and defined responsibilities play an important role, in practice, in practical application of such standards.

Data availability

The study made use solely of openly accessible information and data; the pertinent sources are listed in the individual chapters' closing references sections.

The descriptions of the geological and hydrogeological conditions of potential exploration and exploitation areas provided in Part A are on a relatively general, overarching level. They thus cannot take the place of detailed studies and analyses relative to specific potential sites. The detailed considerations presented with regard to the geology and hydrogeology of the Münsterland draw on work and findings for/of a study carried out for North Rhine – Westphalia (commissioned by the Ministry for Climate Protection, Environment, Agriculture, Nature Conservation and Consumer Protection of the German State of North Rhine-Westphalia (MKULNV)). They are presented by way of example, to illustrate the structure and content of proper hydrogeological system analysis.

The data used for assessment of the fracking fluids and preparations used in Germany were obtained, in most cases, from openly accessible sources. In a few cases, the data were supplemented with non- openly accessible data that was obtained by special request. The available data were inadequate. For only 28 of the fracking fluids used in Germany between 1983 and 2011 was it possible to determine the additives used. That figure is equivalent to a database comprising about 25 % of the some 300 fracking measures carried out to date in Germany. As to the compositions of fracking fluids, all of the information available to the study authors was obtained via evaluation of the material safety data sheets for the additives used. Those material safety data sheets often lack information relative to the (unique) identities of the additives used, to the quantities in which they are (were) used, to the additives' physical, chemical and toxicological properties and to the additives' short-term and long-term behaviour in the aquatic environment. The decision on whether or not the biocidal agents used in fracking fluids in Germany, as slimicides, should be included in Annex I or IA of the Biocidal Products Directive is still pending, and thus no data from the ongoing review procedure are available. Furthermore, Germany does not at present require the sector's service contractors to publish pertinent substance information, nor does it require any central collection of such information in databases.[2]

The relevant specific chapters in Parts A and C of the present study discuss the problems related to assessment and analysis of researched data.

[2] Note: With regard to the assessment of the risks of biocidal agents and products, Regulation (EU) No 528/2012 of the European Parliament and of the Council of 22 May 2012 concerning the making available on the market and use of biocidal products does obligate applicants to provide the competent authorities with certain core sets of data relative to substances to be asssessed (including data on physical and chemical properties).

Structure of the report

The structure of the present report is shown schematically in Figure 2.

Part A describes the physiogeographic and technical parameters applying to fracking:

- Description and characterisation of unconventional natural gas deposits in Germany, and sample system analysis of selected geological and hydrogeological regions,
- Description of the best available technology for fracking,
- Description and assessment of the substances / substance mixtures used in fracking,
- Description and assessment of flowback and of the best available technology for flowback disposal.

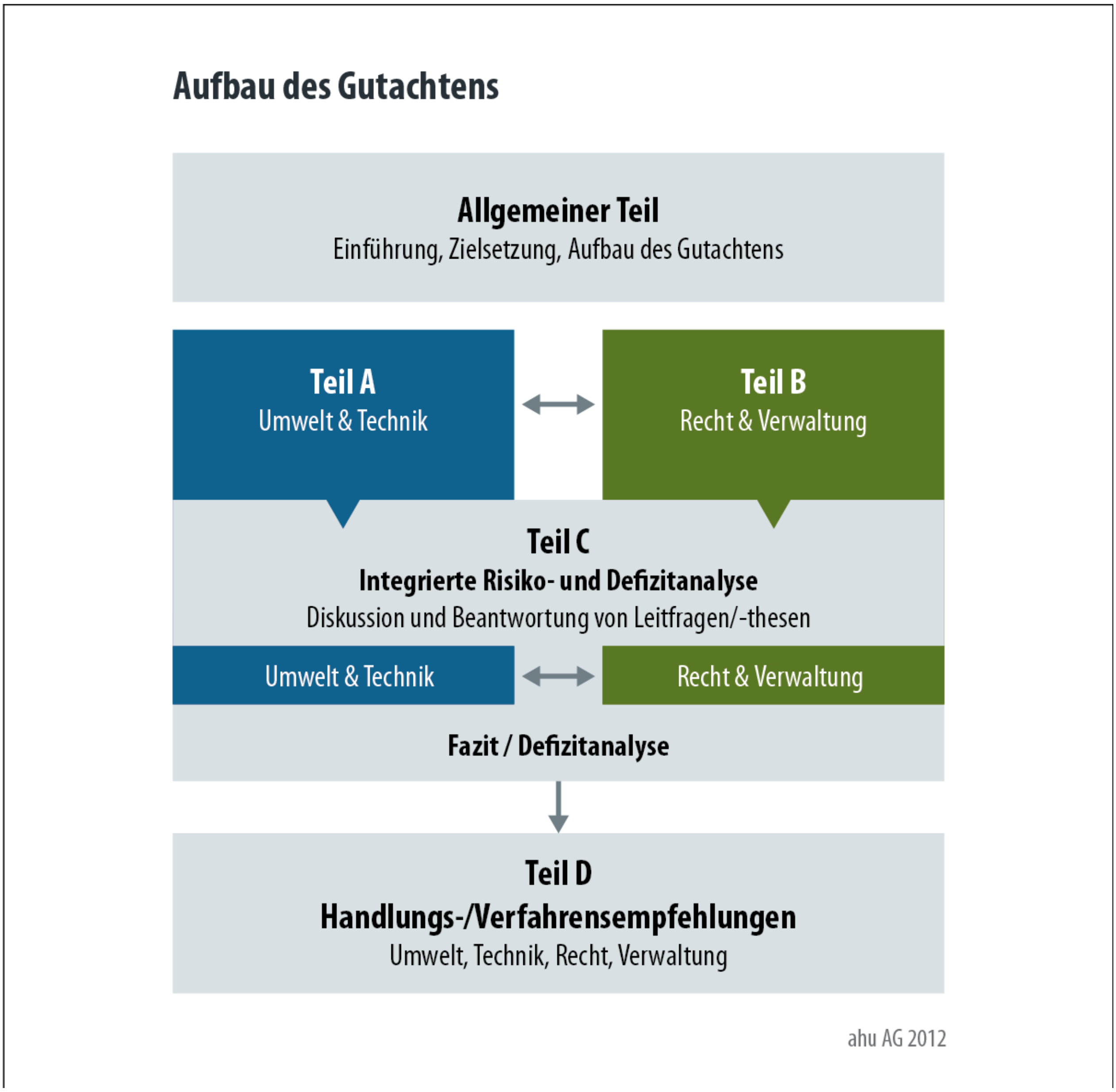

Fig. 0 2: Structure of the report [General part; introduction, objectives, structure of the study; Part A; environment and technology; Part B; legal and administrative aspects; Part C; Integrated risk and deficits analysis; discussion and answering of main questions / theses; environment and technology; legal and administrative aspects; Summary / deficits analysis; Part D; recommendations for action and procedures; environment, technology, legal aspects, administrative aspects]

Part B describes the applicable legal framework:

- The general requirements and assignment of responsibilities under mining law, environmental law and (especially) water law,
- Overview of the regulations pertaining to management of above-ground risks (requirements pertaining to transport, storage and handling of substances used),
- Detailed description of the substantive and procedural requirements, under mining law and water law, pertaining to the drilling and completion of boreholes and to execution of fracks,
- Requirements, under mining law and water law, pertaining to management of flowback,
- Any requirements pertaining to environmental impact assessment (EIA) and to preliminary review of EIA requirements.

Part C presents an analysis of the specific risks that are, or can be, related to fracking. This includes detailed consideration of the following aspects:

- Identification and assessment of the most important pathways for impacts on natural systems, via the water-related aspects of fracking studied,
- Control and monitoring of fracture formation during fracking,
- Assessment of selected fracking fluids, of formation water and of flowback,
- Assessment of aspects related to permanent deposition of fracking additives in underground formations,
- Assessment of methods for disposal / re-use of flowback.
- Methodological information relative to execution of site-specific risk analyses.

Basic aspects relative to the aforementioned points are analysed and assessed in light of facts presented in Parts A and B.

Part C concludes with a summary and a deficits analysis that identifies and details the most important scientific, technical and legal areas in which action is needed.

On the basis of the results of the summary and deficits analysis presented in Part C, **Part D** then derives specific recommendations for action and procedures with regard to further steps in general and to the specific aspects considered.

No translation has been included of the extensive **Annex** to which reference is made especially in Parts A and C. The Annex is thus available only in German.

PART A: DEPOSITS, TECHNOLOGIES AND SUBSTANCES

A1 Unconventional gas deposits in Germany

A1.1 Information and data on which the study is based

The following assessments relative to unconventional gas deposits are based on openly accessible literature and information; all references are duly noted in the text (cf. References, Chap. A6). On 29 February 2012, a coordination discussion was held in this context with the Federal Institute for Geosciences and Natural Resources (BGR), located in Hannover. The BGR is carrying out the project "NiKo: Erdöl und Erdgas aus Tonsteinen – Potenziale für Deutschland"[1] ("NiKo: Oil and gas from clay rock – the Potential for Germany"; running from February 2011 through June 2015). The primary aim of the project is to determine the potential for exploiting domestic natural gas deposits in clay rock formations and – in a second step – the potential for exploiting domestic oil deposits in such formations. A first interim report on the NiKo project was published in June 2012 (BGR 2012).

Openly accessible information was also used for description of the geological and hydrogeological conditions of the selected locality types. The assessments for the Münsterland region are based largely on evaluations carried out in the framework of the NRW report on exploitation of unconventional gas deposits (NRW-Gutachten zur Gewinnung von unkonventionellen Erdgas-Vorkommen; ahu AG / IWW / Brenk Systemplanung 2012).

A1.2 Introduction

Except in the case of tight gas, natural gas in "unconventional deposits" refers to gas that, instead of migrating into a deposit rock (such as porous sandstone), has been bound to the source rock (such as a bituminous clay formation) in which it was originally formed. In each case, the composition of such gas depends on the type of source rock involved and on the conditions under which the gas was formed (primarily pressure and temperature). As a rule, the composition of such gas does not differ from that of conventional natural gas. The deposit pressures prevailing in unconventional deposits tend to be considerably lower than those occurring in conventional deposits. For that reason, the gas does not flow

[1] http://www.bgr.bund.de/DE/Themen/Energie/Projekte/laufend/NIKO.html

freely, and pathways for its upward migration have to be created via suitable technical methods.

The present study of the relevant risks considers those unconventional gas deposits in Germany whose development and exploitation, depending on the prevailing deposit parameters, could necessitate hydraulic stimulation (hydraulic fracturing – fracking) to increase the permeability of the rock containing the deposits.

Unconventional natural gas deposits can be divided into the deposit categories coal bed methane (CBM), shale gas and tight gas deposits. Figure A 1 shows a possible means of differentiating between conventional and unconventional gas deposits on the basis of the permeabilities in the deposit rocks, pursuant to KING (2011). As the figure indicates, tight gas is an "intermediate form" that, depending on the author in question, is classified either with conventional gas deposits (since the gas migrated from a source-rock formation into a reservoir-rock formation) or with unconventional gas deposits (on the basis of the permeabilities involved). In the present study, tight gas is classified with unconventional gas deposits, since its exploitation can require hydraulic stimulation – as, for example, has long been the case in northern Germany.

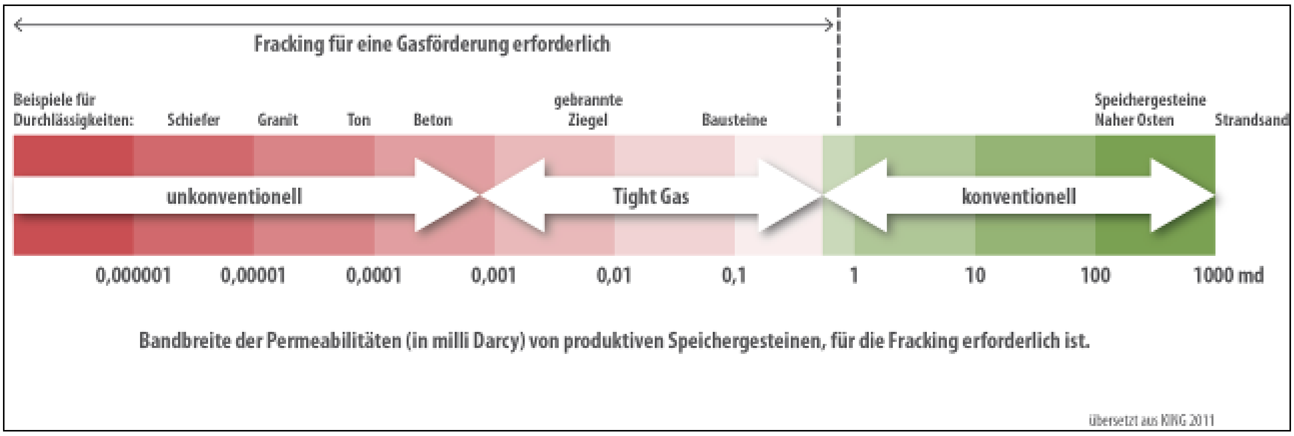

Fig. A 1: Bandwidth of permeabilities, and requirements for hydraulic stimulation in natural gas exploitation (pursuant to King 2011) [Top row: Fracking required for gas production; Next row, left to right: Examples of permeabilities: shale, granite, clay, concrete, fired bricks, construction blocks; Deposit rocks, Near East, beach sand; Middle row: unconventional; tight gas; conventional; Bottom row: Bandwidth of permeabilities (in milliDarcy) of productive deposit rocks for which fracking is required.]

The following types of unconventional gas reserves are differentiated:

- **Tight gas**

  Tight gas is gas that has moved from a source-rock formation into sand or limestone formations with very low permeabilities. In Germany, such formations normally occur at depths below 3,500 m. The productivity of a given tight gas reservoir depends on its permeability and porosity and on the way the gas is distributed throughout the rock.

- **Shale gas** (see also the box on page 3)

  Shale gas is thermogenic gas created via cracking of organic matter at high temperatures and pressures. Under such processes, the gas is adsorbed into the source rock in various ways. The exploration and exploitation techniques used with such gas involve breaking the relevant bonds and creating suitable pathways for gas migration. While some shale gas reserves in Germany are presumed to lie at relatively shallow depths, beginning at about 500 m (overlying alum shale in the Rhenish Massif), many of the deposits are known to be at considerably greater depths.

- **Coal bed methane(CBM):**

Coal bed methane is formed via coalification of organic matter in coal deposits. Such deposits are found at a number of different depths in Germany. The pressure of the formation water in such deposits binds the gas to the surface of the coal. Consequently, before gas can be extracted from them, such deposits first have to be drained of water, to relieve such pressure. It remains to be seen whether gas exploitation from such deposits always requires hydraulic stimulation (fracking). The economic exploitability of a given coal bed methane deposit will also depend on the quantity of water it contains and, thus, the amount of time required for drainage to relieve pressure[2].

The natural geological conditions in a shale gas formation at a depth of 3,000 m

Unconventional gas deposits are complex systems that differ widely, in many respects; it is thus difficult to make generalizations about them.

Origins and mineralogy

In general, shale gas deposits may be described as fine-grained clastic sediments with organic fractions (clayey shale). Such deposits tend to have similar depositional histories and similar depositional environments, factors which determine a number of properties of the resulting rock. Such properties include low permeability, due to the deposits' high clay fractions and organic carbon content. In addition, clay-mineral content and carbon concentrations can vary, by several orders of magnitude, both within a single shale gas formation and between different formations. The petrographic composition of such deposits, which can be predominantly argillaceous, silicate or carbonate, determines their mechanical and hydraulic properties. Along with thermal maturity, the organic carbon fraction is the key factor that de-

2 http://www.europaunkonventionelleserdgas.de

termines what type of gas forms, and in what quantities (thermogenic, biogenic or a mixture of the two).

The sediments that formed such deposits were deposited in seas with layered water columns, i.e. water columns that rarely experienced mixing via currents. The conditions prevailing on the floors of such seas tended to be anoxic and reducing. Due to such lack of oxygen, animal and plant matter that sank did not decompose, and putrid slime formed at the bottoms of such seas.

Constituent substances

In the putrid slime, hydrogen sulfide (H_2S) formed, which promoted precipitation, as sulfides, of the heavy metals and metals in the sea water (such as vanadium). Such precipitates also contained radioactive elements such as uranium and thorium; in the resulting rocks, those elements are present as accessory constituents (< 1 %) (Fesser 1968). The radioactive compounds occurring in the rock, and their decay products radium and radon, which are also radioactive, are referred to collectively with the term NORM (Natural Occurring Radioactive Material).

High pressure and high temperature

The pressures and temperatures within formations increased as the formations were covered by more and more layers of younger sediments and thus buried ever more deeply. Such processes took place over geological time periods, over millions of years (the typical depths of cover amount to 2 to 3 km). The pressures compacted the sludge that had once been loosely layered. In a slow chemical process, the increased temperatures resulting from the deep cover transformed the kerogens in the organic fractions. The temperature range in which gas forms, the "gas window", is 120 to 225 °C. The temperatures in the "oil window" range are lower, between 60 and 120 °C. Depending on the type of kerogen involved, and on the degree of transformation achieved – which, in turn, depended on the temperatures attained – the kerogens were transformed into petroleum, natural gas or both (Selley 1998).

Gas deposits

Shale gas deposits are special types of hydrocarbon systems that combine the source-rock, reservoir-rock and seal-formation functions that are differentiated with regard to conventional deposits. After gas is formed in such systems, over many millions of years some of it migrates upward, driven by buoyancy, through the rock. Natural structural discontinuities in the rock serve as the most important migration pathways for the gas. The gas that remains in the shale gas formation fills the pores within the rock, to various degrees, or is adsorbed by its organic constituents and clay minerals. The aim of hydraulic stimulation measures (fracking) is to mobilize such gas. As the pressure in a formation decreases, adsorbed gas within it is released. Gas extraction will reduce the pressure in a deposit.

The type and extent of stimulation measures are determined in accordance with the prevailing key geological parameters. Those parameters, in turn, can be determined via exploration. The most important such parameters include the formation's thickness, depth position, lateral distribution, petrography and stress pattern. In shale gas formations, the prevailing temperatures can range from ca. 60 to 160° C, while the prevailing pressures can exceed one hundred bar, depending on the formations' origins (Hartwig et al. 2010; Curtis 2002).

Formation water

Typically, formation water is highly mineralized at such pressure / temperature conditions (> 20 g/L total salinity). Hydrochemically speaking, such water must be termed "brine". In addition, formation water can contain a number of dissolved and trace substances, such as heavy metals, aromatic hydrocarbons, dissolved gases and naturally occurring radioactive material (NORM). In fracking, formation water is extracted along with natural gas, as "flowback", and has to be disposed of.

The following section describes the potential "unconventional" natural gas deposits in Germany, along with their associated geological formations. For selected potential deposits, more detailed descriptions of the pertinent geological and hydrogeological situations are provided, taking account of the applicable special regional characteristics.

In a final chapter, then, findings from the various system analyses are summarized, and their importance with regard to risk analysis is explained.

A1.3 Deposits and exploration fields in Germany

In Germany, unconventional natural gas deposits are thought to be present in a number of different types of geological formations. Such presumptions are based on available findings relative to the properties and origins of the relevant rock formations. At the same time, they need to be confirmed and detailed via exploration of the relevant deposits. Table A 1 presents an overview of potential target geological formations for exploration of unconventional gas deposits in Germany, broken down by the different types of unconventional gas deposits involved. It also lists the deposits that are currently thought to offer the greatest promise for exploitation. The majority of the potential deposits listed in Table A 1 can be assigned to the major hydrocarbon provinces in Germany[3]. Additional shale gas deposits are presumed to be present in the Rhenish Massif (overlying alum shale).

[3] http://www.aapg.org/europe/newsletters/index.cfm

Tab. A 1: Potential unconventional natural gas deposits in Germany

Type of deposit	Most promising deposits	Regions
Coal bed methane (source rocks)	Seam-bearing Upper Carboniferous	Northern Ruhr region / Münsterland Basin (NRW)
		Ibbenbühren (NRW)
		Saar Basin (Saarland)
Shale gas (source rocks)	Tertiary clay formations (e.g. Fischschiefer)	Molasse Basin (BW)
	Posidonia Shale (Black Jurassic)	Northwest German Basin (e.g. Lünne) (NI)
		Molasse Basin (BW)
		Upper Rhine Graben
	Wealden clay formations (Lower Cretaceous)	Weser Depression (NRW / NI)
	Permian clay formations (e.g. black shale ("Stinkschiefer"), copper shale)	Northeast German Basin (NI / SA)
	Carboniferous and Devonian clay formations e.g. alum shale (Lower Carboniferous)	Northern edge of the Rhenish Massif (NRW)
		Northwest German Basin
		Harz Mountains (NI / SA)
	Silurian slates	Northeast German Basin
	Cambro-Ordovician clay formations ("alum shale")	(not yet studied in detail)
Tight gas (deposit rocks)	Red sandstone	Northwest German Basin (NI / SA)
	Permian sandstones (Rotliegend) and carbonates (Zechstein)	Northeast German Basin (e.g. Leer) (NI)
	Permian sandstones (Rotliegend) and dolomite (Stassfurt series) sandstones (Triassic)	Thuringian Basin (TH)
	Upper Carboniferous sandstones	Northwest German Basin (e.g. Vechta) (NI)

green = relevant potential shale gas deposits pursuant to the Federal Institute for Geosciences and Raw Materials (BGR; 2012)

A recent assessment of the potential natural gas deposits in shale gas deposits was carried out, in the first phase of the project "NiKo: Erdöl und Erdgas aus Tonsteinen – Potenziale für Deutschland" ("NiKo: Oil and gas from clay rock – the Potential for Germany"; running from February 2011 through June 2015), by the Federal Institute for Geosciences and Natural Resources (BGR); in June 2012, that assessment was then published as an interim report[4] (BGR 2012). Table A 2 lists deposits of Gas in Place (GIP, a term for the possible quantity of natural gas present in a given formation) and the resulting quantities that are likely to be technically exploitable (based on the assumption that about 10 % of the total

[4] http://www.bgr.bund.de/DE/Themen/Energie/Projekte/laufend/NIKO.htm

quantity is technically exploitable). For the coal bed methane deposits in seam-bearing Upper Carboniferous layers in North-Rhine – Westphalia (NRW), the estimates point to quantities > 2,000 km^3 GIP (BGR 2012, GD NRW 2011). For the Saarland, the GIP is estimated to be about 1,000 km^3 (BGR 2012).

Tab. A 2: Gas in Place (GIP) and technically exploitable quantities of shale gas in Germany, under the assumption of a technical exploitation factor of 10 % (from BGR 2012) (figures in 1,000 km^3)

Formation	Gas in Place			Technically exploitable		
	Minimum	Median	Maximum	Minimum	Median	Maximum
Lower Cretaceous – Wealden	1.1	2.4	4.4	0.1	0.2	0.4
Lower Jurassic – Posidonia Shale	0.9	2.0	3.8	0.1	0.2	0.4
Lower Carboniferous	2.5	8.3	17.7	0.3	0.8	1.8
Total	6.8	13.0	22.6	0.7	1.3	2.3

Exploration fields

Most of the hydrocarbon provinces known in Germany already contain approved or applied-for exploration fields for exploration of conventional and unconventional oil and gas deposits. Figure A 2 shows the status of concessions for exploration of conventional **and** unconventional oil and gas deposits as of 8 March 2011. Figure A 3 shows the areas that contain (planned) activities for exploration of unconventional gas deposits in Germany (BGR 2012).

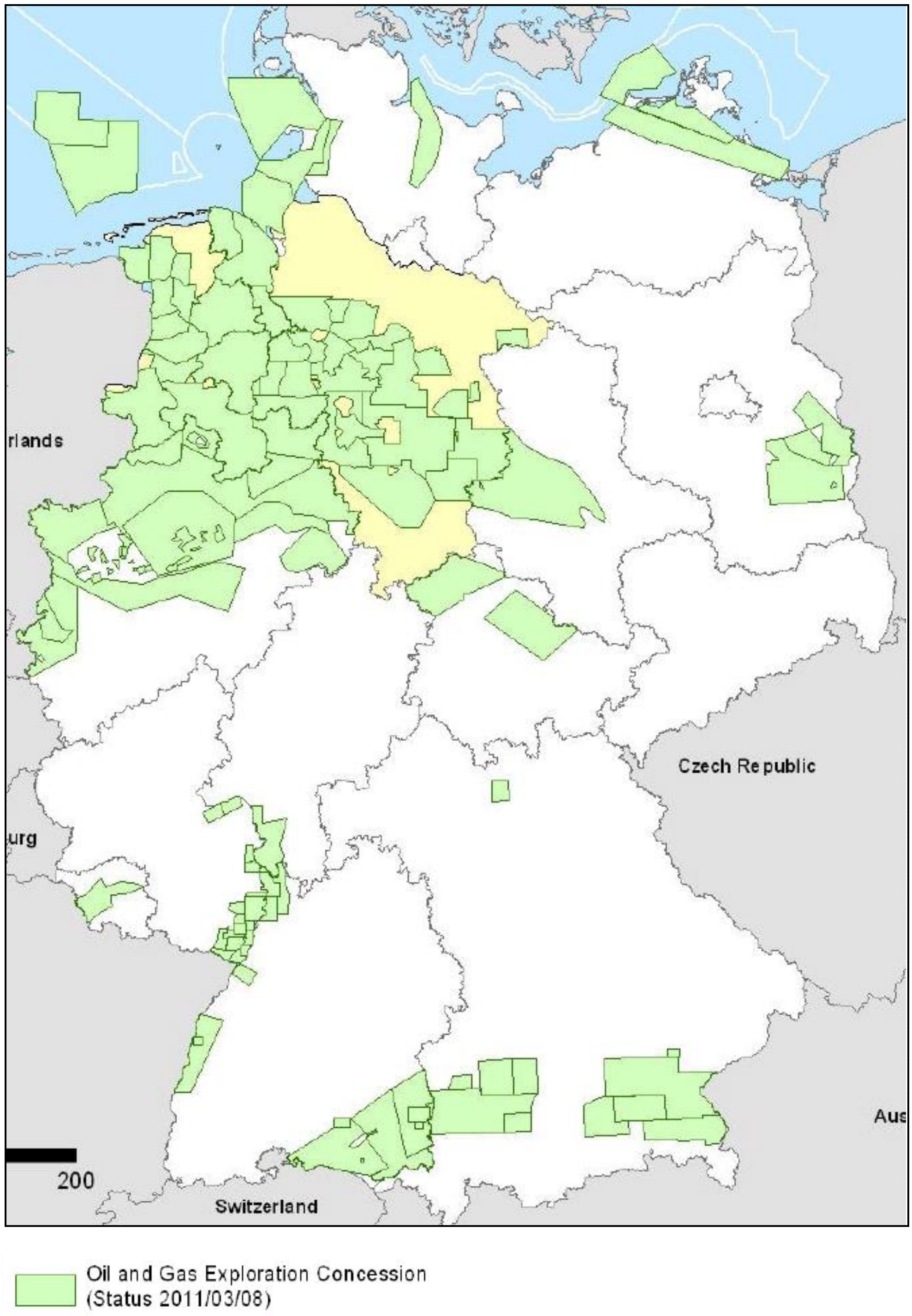

Fig. A 2: Approved exploration fields for exploration of conventional and unconventional oil and gas deposits (Source: Söntgerath 2011)

Fig. A 3: Mining authorisations in Germany (= yellow, last revision: 31 December 2011) for exploration of unconventional hydrocarbon deposits (background: ochre = regions with the basic geological conditions for formation of shale gas) (source: BGR 2012)

A1.4 Fracking in Germany

According to the information available to the study authors, at least 275 fracks have been carried out to date, in a total of more than 130 boreholes, in tight gas and conventional deposits in Lower Saxony. While that figure refers primarily to fracking in boreholes for natural gas, it may also include a few instances of fracking in boreholes for petroleum. The study authors are aware of no fracks in tight gas or conventional deposits in other Länder (German states) (Tab. A 3). To date, a total of three fracks have been carried out in shale gas deposits in Germany (exploratory drilling at the Damme 3 site, in the Vechta district in Lower Saxony, in November 2008). Thus far, fracking fluids have been used in only two fracks in coal bed methane deposits in Germany (Natarp 1 borehole, Warendorf district, North Rhine – Westphalia, 1995).

Tab. A 3: Numbers of fracking measures carried out to date in natural gas deposits in Germany, as shown by information available to the study authors

	Tight gas and conventional deposits	Shale gas deposits	Coal bed methane deposits
Lower Saxony	at least 275 fracks* (at least 130 boreholes)	3 fracks (Damme 3 – 2008)	0
NRW	0	0	2 fracks (Natarp – 1995)
Other Länder	None of which the study authors are aware	0	0

* Possibly, some fracks have also been carried out in petroleum deposits.

In Lower Saxony, following a detailed review of the relevant records by Lower Saxony's state office for mining, energy and geology (Niedersächsisches Landesamt für Bergbau, Energie und Geologie – LBEG), and the Wirtschaftsverband Erdöl- und Erdgasgewinnung (WEG) German oil and gas industry association, a database is now being prepared of the fracks carried out to date in natural gas deposits. The database includes data on the pertinent target formations and the quantities of fluids used. Because the database is still being established, the study authors were unable to review it before the study was completed. The firm of ExxonMobil Production Deutschland GmbH reports that it and its affiliated companies have carried out some 180 fracks in Germany to date (Dr. Kalkoffen, cited in the newspaper Neue Osnabrücker Zeitung 2012). In addition, ExxonMobil Production Deutschland GmbH estimates that about 300 fracks have been carried out in Germany over the past 50 years[5]. The majority of those fracks have been carried out since the mid-1990s (Fig. A 4).

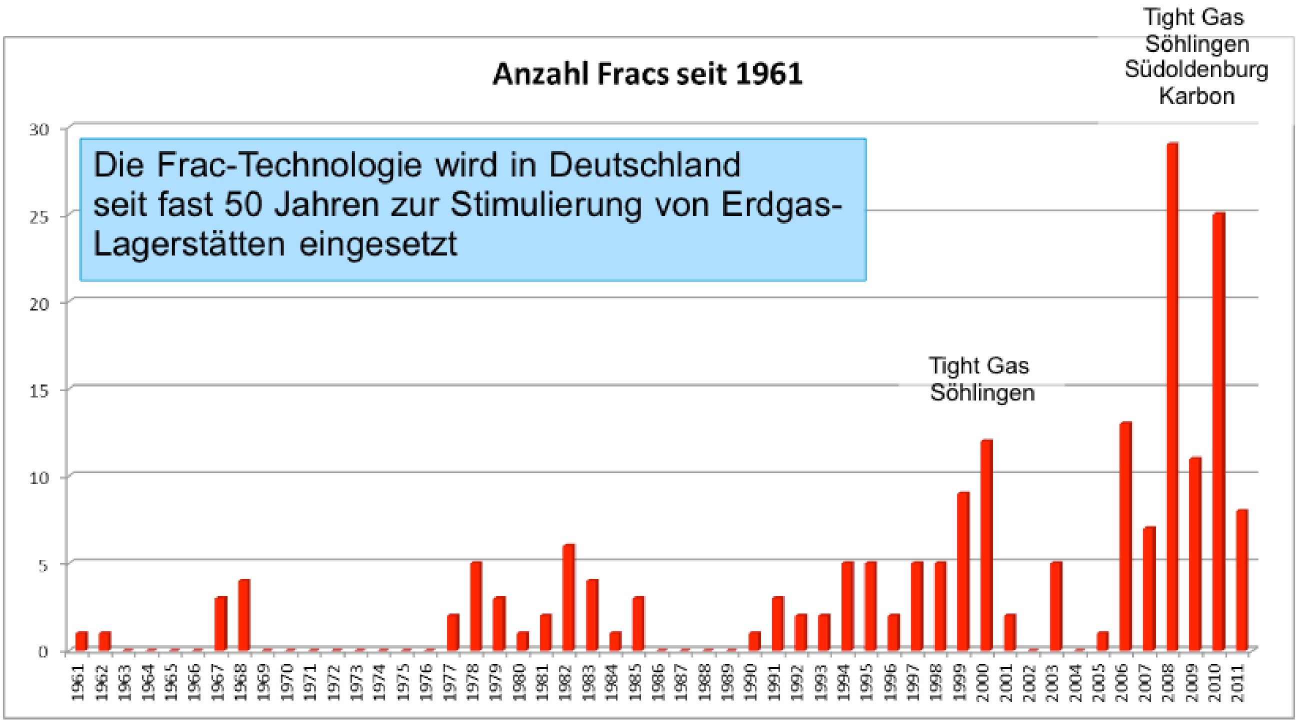

Fig. A 4: Numbers of fracks carried out annually in natural gas deposits in Germany since 1961 (Source: http://www.erdgassuche-in-deutschland.de/) [Text: Fracking technology has been used for nearly 50 years in Germany for stimulation of natural gas deposits]

5 http://www.erdgassuche-in-deutschland.de/hydraulic_fracturing/index.html

A2 System analysis and impact pathways

A2.1 System analysis

As the remarks made in Chapter A 1 indicate, unconventional natural gas deposits are presumed to occur in various different geological formations in Germany. A "geological system" within the meaning of the present study is a large-scale unit that forms a geological and hydrogeological complex (e.g. Molasse Basin, Thuringian Basin, etc.). In analysis of such a system, the key aspects to consider include the geological position of the potential gas-bearing formation – regardless of the type of unconventional gas deposits involved – within the relevant hydrogeological system. To understand local flow systems (which can vary widely) within such a geological system, in the context of a site-specific consideration, and to assess the pertinent risks, one must understand/analyse the large-scale system involved.

A "groundwater flow system" is a large-scale system of groundwater aquifers and aquicludes, with varying degrees of permeability, and in which flow processes can occur via hydraulically active pathways, such as hydraulic windows (for example, gaps in aquicludes) and hydraulic pathways at and above faults. In regional groundwater flow systems, such flow processes normally take place slowly. However, they can be accelerated, or triggered, by technical measures carried out in connection with exploitation of unconventional natural gas deposits, such as horizontal drilling and/or hydraulic stimulation.

The driving forces in a groundwater flow system – apart from any diffusion processes – are the potential differences between the various aquifers involved, differences that normally derive from the differences in elevation between the topographic positions of groundwater-replenishment and groundwater-infiltration areas.

To be able to determine and assess risks, from exploration and exploitation of unconventional natural gas deposits, for groundwater and related resources/assets at specific locations within geological systems, one must first describe and analyze the relevant hydrogeological system at the project site.

The results of hydrogeological system analysis include information about

- the spatial distributions of various parameters, such as thickness and permeability,
- the prevailing pressure potentials and hydrochemical conditions,
- the flow volumes (inflows and outflows) between the groundwater bearing layers and the rivers (inflow and outflow areas),

- the relevant impact pathways and the key characteristics of the system's dynamics (such as direction of flow), both before and after any interventions/changes.

The following section describes the systematic framework for assessing potential impact pathways in connection with exploration and exploitation of unconventional natural gas deposits. The analysis of geological systems / type localities that then follows focuses solely on those impact pathways that result from the relevant regionally specific geological and hydrogeological conditions and their special characteristics. An analysis of the importance of the various impact pathways, and of the related risks, is then provided in Chapter C1.

A2.2 Impact pathways

Potential water-related impact pathways resulting from exploration and exploitation of unconventional natural gas deposits, via fracking, are shown schematically in Figure 5 and are described in the following. For an impact pathway to be relevant, it must have both permeability and a potential difference (pressure differential), the two factors needed for a directed flow. Whether or not the two factors are present will depend a) on the relevant natural conditions and b) on the nature and scope of the intervention involved.

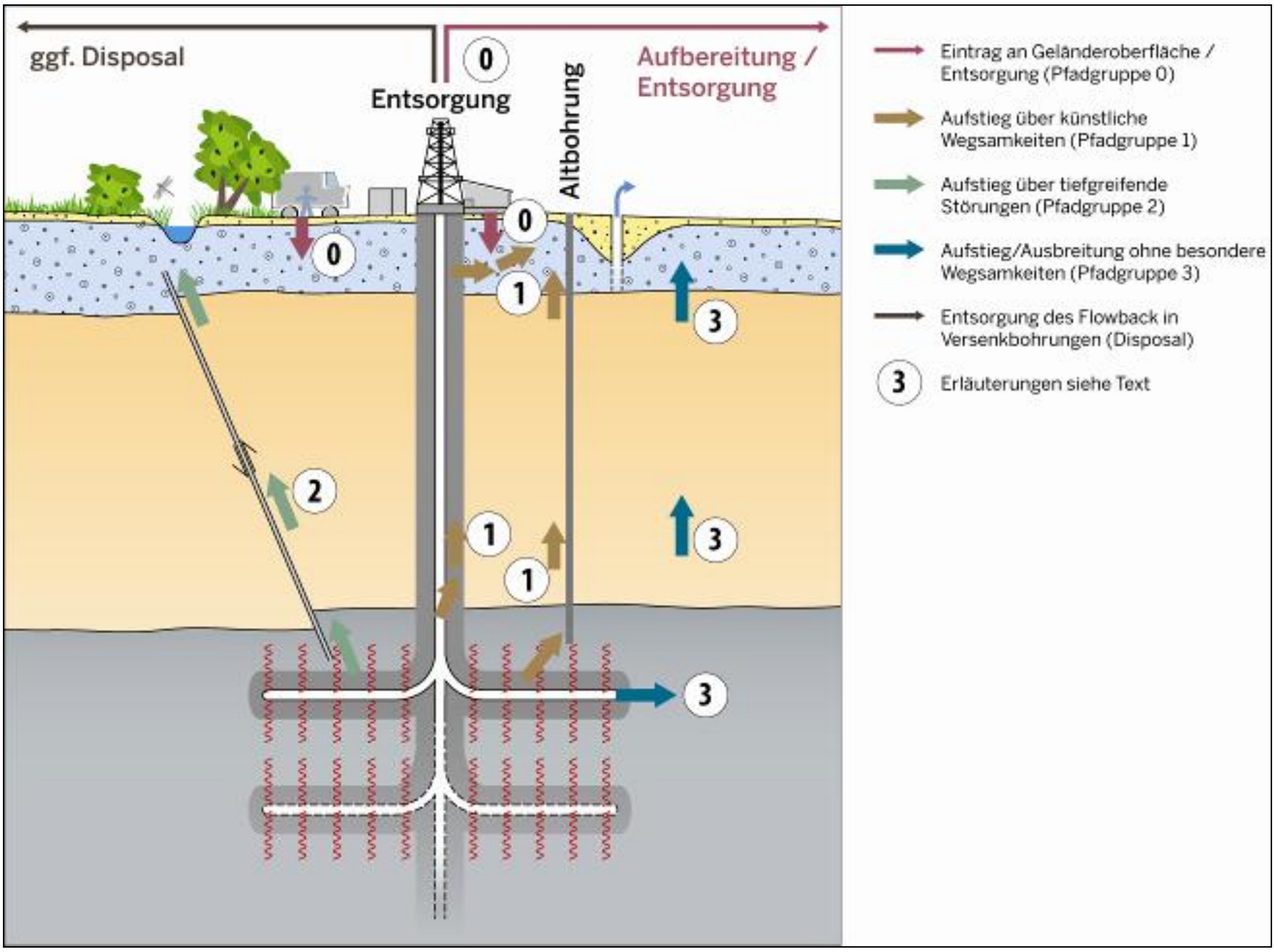

Fig. A 5: Schematic diagram of potential impact pathways [Entsorgung = Management; Treatment/disposal; Altbohrung = old borehole; Discharge onto site surface / disposal (pathway group 0); rise via artificial pathways (pathway group 1); rise via deep-reaching faults (pathway group 2); rise / spreading without use of special pathways (pathway group 3); flowback disposal in injection wells; for explanations see text]

Pathway group 0

Pathway group 0 refers to (pollutant) discharges that occur directly at the ground surface, and especially in handling of fracking fluids (transport, storage, etc.) and in management of flowback (not including disposal; see below). With regard to analysis of hazards for near-surface groundwater, the protective function of covering strata (vulnerability) is of especial importance, since (pollutant) discharges occur "from above". Often, such discharges will be preceded by a failure of the equipment being used.

For pathway group 0, and with regard to the risk of groundwater pollution, it is especially important to make a basic distinction between normal cases and disruptions. In addition, the range of technical and legal measures (accident-prevention regulations, well-pad design, etc.) available for minimizing risks of groundwater pollution must be taken into account (cf. Chapter C1).

Pathway group 1

Pathway group 1 refers to potential (pollutant) discharges and spreading along wells, i.e. to artificial underground pathways. The following must be differentiated:

- Rises into/at exploration or production boreholes, due to partial/complete failure of cementations, or to inadequate sealing off from the penetrated rock formation,
- Failures of casings (and of cementations) during fracking, leading to direct discharges, and
- Rises into/at old boreholes, because the boreholes' sealing structures (casing and cementation) are either inadequate or no longer intact.

The applicable hydrogeological and hydrochemical conditions play a key role with regard to the long-term integrity of boreholes. Borehole casings and cementations can be subject to corrosion as a result of the high temperatures, salt concentrations and carbon-dioxide concentrations, etc., prevailing in underground layers. In the long term, such corrosion can lead to casing/cementation failures. Depending on the prevailing potential differences, fluids and/or gases can then rise or descend.

Pathway group 2

Pathway group 2 includes all impact pathways along geological faults, which, at the earth's surface, appear – more or less – as linear stresses (they can also appear as points, if the rise that occurs lies in the intersection of two faults / fault systems). Significantly, the permeability along any given fault can vary, section-wise. With regard to hazard potential, the following must be differentiated:

- Deep-reaching faults / fault zones that extend continuously from the deposit zone into (near-surface) exploitable groundwater resources and have considerable permeability, and
- Faults / fault zones that extend only part of the way between the deposit and (near-surface) exploitable groundwater resources and have considerable permeability.

Whereas deep-reaching, continuous faults can often be monitored, since the near-surface locations of their outcrops are usually known, faults that affect only parts of the overburden are difficult to monitor. Where such faults are hydraulically active (with permeability and potential differences) they can serve – at least in some areas – as upward pathways for fluids and gases, which can then rise and spread in all directions.

Pathway group 3

Pathway group 3 comprises extensive rising, as well as lateral spreading, of gases and fluids through geological strata (for example, via an aquifer), **without** preferred pathways similar to those described for pathway groups 1 and 2. Impact pathways in pathway group 3 depend primarily on the prevailing geological and hydrogeological conditions. In pathway group 3, the following impact pathways are differentiated:

- Direct discharge of fracking fluids into underground regions, during fracks,
- (Diffuse) rising of gases and fracking fluids via covering layers, and
- (Diffuse) lateral spreading of gases and fracking fluids (in various areas of the hydrogeological system).

In pathway group 3, combinations of impact pathways are possible – to a much greater extent than in the other pathway groups. Here as well, suitable permeabilities and potential differences are the key to any "activation" of the aforementioned pathways.

Flowback disposal via disposal wells

Operators currently refer to injection options as an important parameter for (cost-effective) production of unconventional gas deposits. From the perspective of the consortium of study authors, flowback disposal via deep-underground injection entails a number of hazards, such as displacement of formation water (as occurred in Hesse, for example, when saline produced water was injected into platy dolomite and saline water rose into the Triassic sandstone (buntsandstein)). There may be some formations with gas-filled pores in which injection would not displace any fluids. No information on such formations is available to the study authors. In any case, any deep-underground injection calls for site-specific risk analysis and monitoring. In addition, systematic study of the experience gained in Lower Saxony could be of use in assessing the relevant hazards.

Summation and combination of different impact pathways and long-term impacts

With regard to their potential hazards for groundwater, as a result of fracking, potential impact pathways have to be considered both individually and in combination, i.e. in terms of their combined effects. Since many flow processes deep underground take place very slowly, the relevant long-term impacts have to be estimated – also in connection with effects that must be summed. Such assessments must be made in light of the geological system's entire hydrogeological system. Examples of conceivable scenarios for combined, large-scale effects include

- Connections to large-scale groundwater flow systems, leading to transport of fracking fluids into other systems,
  - for example, in the Molasse Basin, with its complex, multiply overlapping groundwater flow systems with areas of diffuse groundwater infiltration,
  - for example, in the Münsterland Basin.
- Fracking over extensive areas can considerably increase the permeability of target formations that previously had low permeability for groundwater. When fracking zones are connected, continuous zones with increased permeability can occur.
- Overlapping and interactions with other uses of deep underground regions,
  - for example, in the Molasse Basin, with its deep geothermal resources and depleted hydrocarbon deposits,
  - for example, in the southern part of the Münsterland Basin, in which deep drainage via hard-coal mining has occurred.

The impacts on a hydrogeological system overall can take the form of long-term changes that lead to significant effects only years/decades later (for example, when intensive fracking over large areas has created the basis for such effects, or when interactions with existing uses occur). For no geological systems are data currently available, along with corresponding numerical forecast models, that would suffice to support relevant assessments.

For this reason, no matter what area/region is being considered, one must understand the relevant hydrogeological system, if one wishes to identify, model and monitor the possible large-scale and combined impacts of exploration and exploitation of unconventional natural gas deposits.

A2.3 (Potentially) competing uses of underground areas

In the present study, "(potentially) competing uses" refers to uses whose target geological formations could be the same as those in which unconventional gas deposits are presumed, as well as to uses in higher or deeper strata. Examples of such uses include geothermal energy, natural gas storage (in caverns) and CO_2 storage (carbon capture and sequestration – CCS). For the present purposes, (production of) drinking water from exploitable groundwater resources is seen as a resource and not as a competing use.

Among (potentially) competing uses in the geological systems chosen for consideration, the present study focuses primarily on geothermal energy, since that is a use that is already taking place, and one that is taking place largely in the same regions in which unconventional gas deposits are presumed (cf. Fig. A 6). Competition with other potential uses of underground areas (such as CCS) is not considered further in the present study. The Federal Environment Agency has commissioned a separate research project on that subject, but its results were not available to the study authors as of the editorial deadline (June 2012).

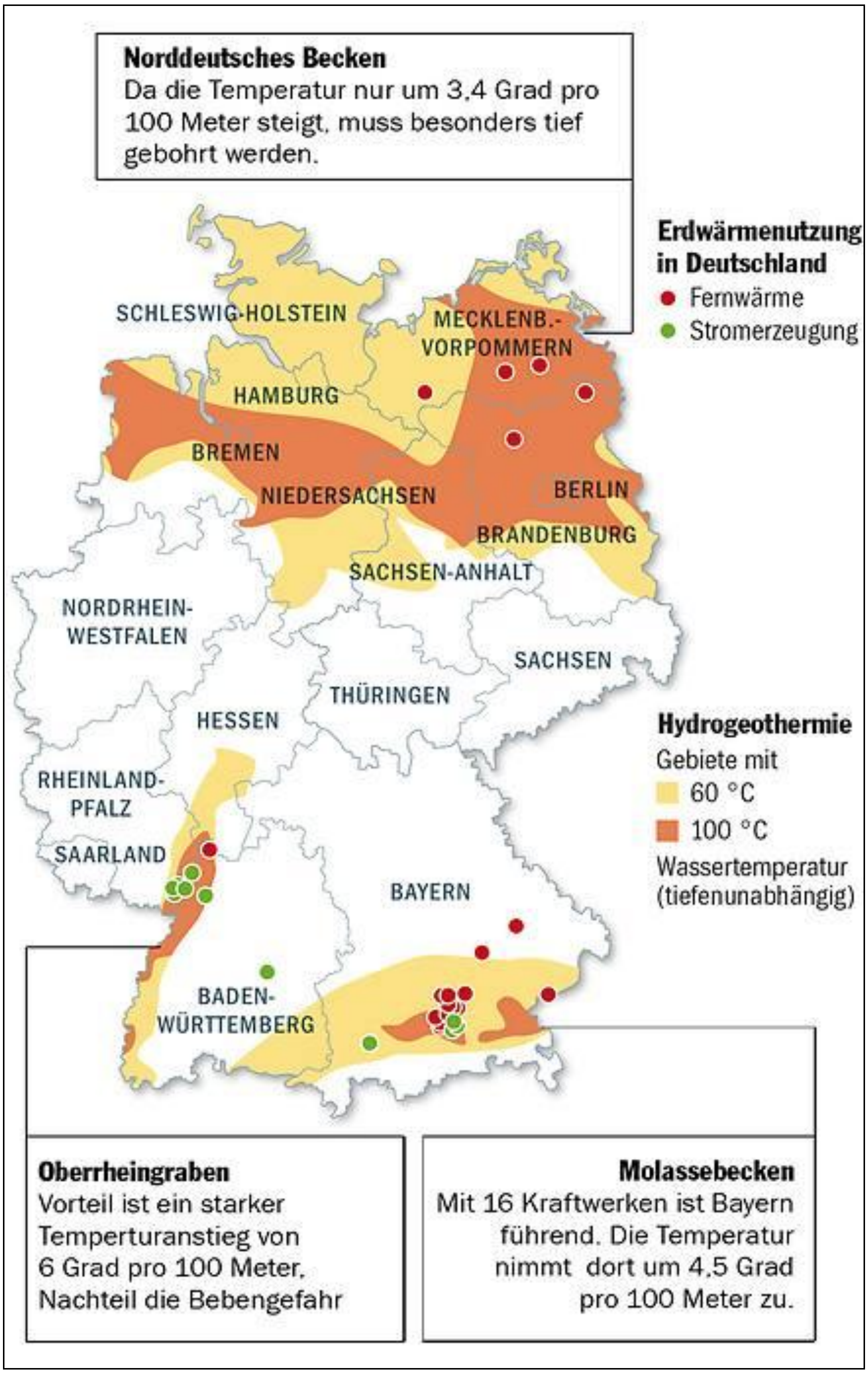

Fig. A 6: Uses for deep geothermal energy systems (Source: http://www.geothermie.de/wissenswelt/geothermie/einstieg-in-die-geothermie.html#c237) [Text (clockwise): **Northern German Basin**; Since the temperature increases by only 3.4 degrees per 100 meters, boreholes must be especially deep; **Use of geothermal energy in Germany**; District heat, Electricity generation; **Hydrogeothermal** areas with water temperatures of 60°C / 100° C (independent of depth); **Molasse Basin**; With 16 power stations, Bavaria is Germany's leading state in geothermal energy use; the temperature here increases by 4.5 degrees per 100 meters; **Upper Rhine Graben**; Its advantage is a rapid temperature rise of 6 degrees per 100 meters; its disadvantage is a danger of earthquakes]

A2.4 System analyses for selected geological systems / type localities

In the following sections, the geological and hydrogeological parameters for selected geological systems with possible unconventional natural gas deposits (cf. Tab. A 2) are described and analyzed on the basis of publicly available and accessible information. The aims of the descriptions are to illuminate the basic differences and similarities between the various geological systems and to highlight the importance of system analysis in identification and assessment of the relevant risks. This said, it must be remembered that such descriptions cannot, and should not, take the place of detailed system analysis that takes account of all available data, that generates and considers additional data as necessary, and that makes use of suitable numerical models.

The system descriptions provided are provided by way of example in each case, either for the large-scale system in question or for selected type localities. The remarks are organized as follows:

- Position and large-scale geological / hydrogeological situation,
- Potential unconventional natural gas deposits,
- Hydrogeological system analysis,
- Potentially competing uses of underground areas,
- Special characteristics of the impact pathways involved, and the pathways' importance, with regard to risk analysis.

A2.4.1 Tight gas deposits

The special characteristic of tight gas deposits is that while their gas is found in strata with low permeability, it has migrated out of its source rocks and collected within structures that trap it (geological barriers). As a result, depending on the classification system, tight gas deposits may be classified as either conventional or unconventional deposits (see the remarks in Chap. A 1). For the purposes of the present study, tight gas deposits are of special importance in that decades of experience have been gained with exploration and exploitation of natural gas in tight gas deposits (including use of fracking) in the Northern German Basin.

In the following, the Northwest German Basin and the Thuringian Basin are described, by way of example, as geological systems / type localities for tight gas deposits.

Northwest German Basin

Position and large-scale geological / hydrogeological situation

In northern Germany, hydrocarbon deposits occur throughout a basin structure that extends east-west for nearly 1,250 km, is divided into several tectonic sub-units and continues eastward into Poland. A key difference between the Northwest German Basin and the Northeast German Basin has to do with the specific types of (gas-) deposit rocks the two basins contain. In both basins, the most important source rock for natural gas is seam-bearing Upper Carboniferous rock. The same basic types of deposit rocks – aeolian sandstones of the Lower Permian (Rotliegend) – occur in both (sub-) basins. In the Northeast German Basin, carbonates (Hauptdolomit of the Stassfurt sequence) of the Upper Permian (Zechstein) also play an important role.

The following remarks focus primarily on the Northwest German Basin in the German state (Land) of Lower Saxony. As Figure A 2 shows, concessions for hydrocarbon exploration have been awarded for large sections of the Northwest German Basin. With regard to exploration and exploitation of unconventional natural gas deposits, in the northern area tight gas deposits tend to be of greater interest, while in the southern area (along the state's boundary with the state of North Rhine – Westphalia) shale gas and coal bed methane gas deposits play the more prominent role (cf. Fig A 3).

In the Northern German Basin, Paleozoic (Carboniferous) strata are covered by thick Mesozoic, Tertiary and Quaternary deposits. Since local geological conditions can vary widely in that area, in keeping with the prevailing deposition conditions and salt tectonics, we confine our system analysis to a type locality at a specific borehole. Figure A 7 shows a schematic geological profile in the area of the Leer gas field (Lower Saxony), as an example of a relevant tight gas deposit in the Northern German Basin.

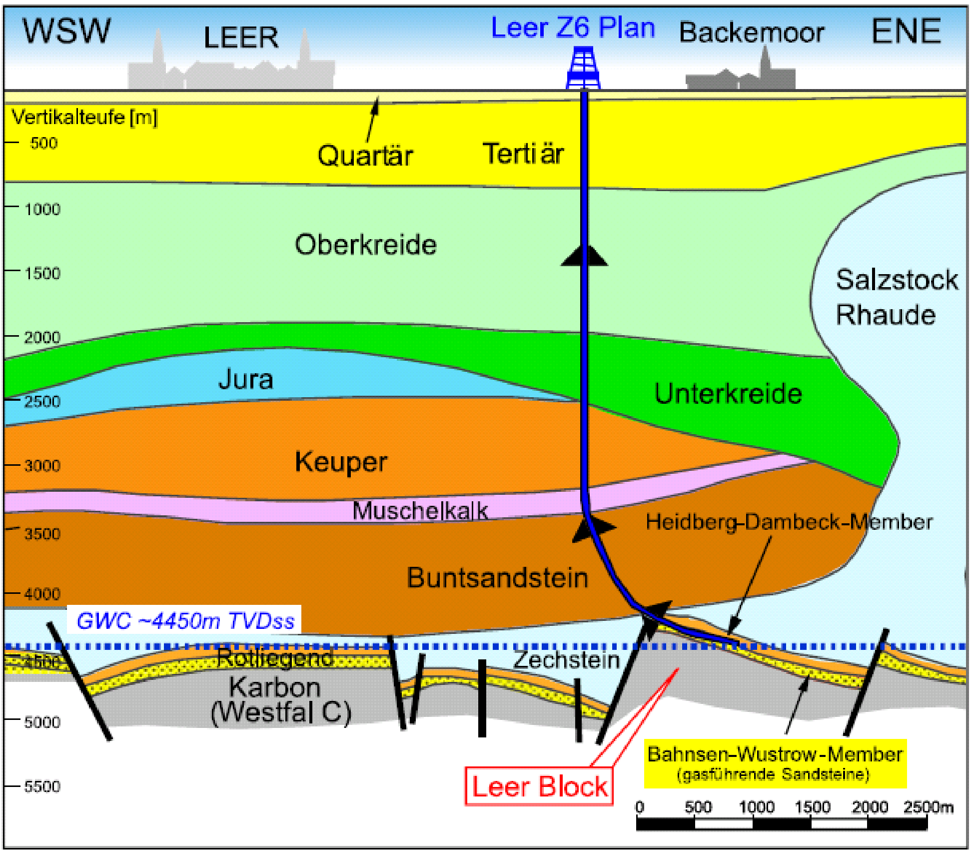

Fig. A 7: Schematic representation of the geological conditions in the Leer gas field (Source: http://www.gdfsuezep.de/cms/upload/PDF/FlyerLeerZ6.pdf)

Since the 1970s, the target horizon for exploration, by the former Gas de France (now Wintershall Holding GmbH) has consisted of the aforementioned sandstones of the Rotliegend (Permian). The covering layers, which may be groundwater-bearing layers, consist primarily of

- Buntsandstein sandstones,
- Sandstones and limestones of the Lower Cretaceous, and
- Quaternary glacial sediments with high permeability (outwash plains (sandurs), meltwater gullies, etc.).

The Rotliegend sediments in the Northwest German Basin consist of sand-stones and clay formations, and of evaporitic rocks (sulfates, rock salt) that can vary widely in thickness.

Potential unconventional natural gas deposits

The Northwest German Basin has more than 400 oil and gas fields, while the Northeast German Basin has about 60 such fields. The tight gas deposits, in particular, in these areas have been developed and exploited for decades. That said, it must be remembered that the transitions between conventional deposits and tight gas deposits can be seamless and continuous (see above).

The primary pertinent target horizons are aeolian sandstones of the Rotliegend (Permian), which cover the seam-bearing Upper Carboniferous, the most important source rock for natural gas.

A special aspect of nearly all of these gas deposits is that they are located at great depths (> 4,000 m) and are covered by Zechstein salts. The thicknesses of the Zechstein layers can range up to several hundred meters. Although much of the salt has shifted into large underground salt structures (salt domes, pillows, walls), horizontally deposited salt can still be found; such layers, in conjunction with other deposited layers of low permeability (such as salt clays), can function as barriers. For example, such Zechstein deposits have prevented natural gas from migrating toward the surface (i.e. they form trap structures) and, within their distributions, they also serve as barriers – and, often, are multiply divided – for overlying groundwater flow systems.

The salt concentrations in the area's aquifers are very high and can easily exceed 200 g/l at greater depths. The deep saline aquifers (Buntsandstein / Lower Cretaceous) are quasi-stationary systems. No information on groundwater flow movements is available to the study authors. Uses for drinking water are possible only in near-surface Quaternary aquifers and in underlying Tertiary aquifers (lignite sands), where the Northern German Basin's salt concentrations are lower. Such layers are part of local groundwater flow systems.

In the Northern German Basin as well, unconventional gas deposits are presumed in Posidonia Shale (Jurassic) and in Wealden layers (Lower Cretaceous) (see also BGR 2012). Such potential deposits would be found at lesser depths, **above** the barrier formed by the Zechstein salts. In recent years, explorations have been undertaken in south Lower Saxony with focuses that include shale gas and coal bed methane. The four shale gas wells (Lünne, Damme, Schlahe and Niedernwöhren) and two coal bed methane wells (Bad Laer, Osnabrück-Holte) drilled to date are shown in Figure A 8.

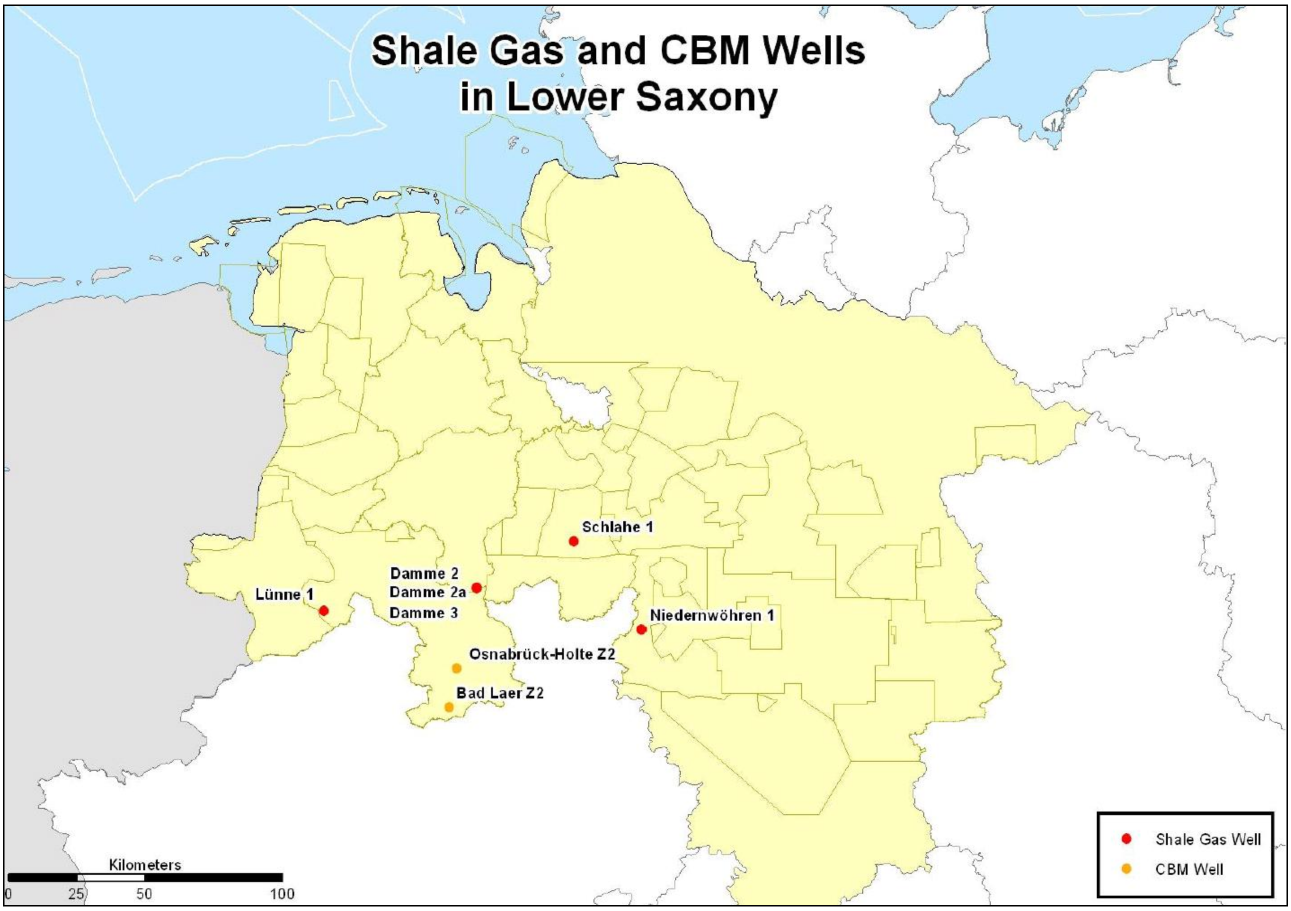

Fig. A 8: Shale gas and coal bed methane gas exploration in the Lower Saxony section of the Northwest German Basin (Source: Söntgerath 2011)

Hydrogeological system analysis

In the Northern German Basin, drinking water is extracted primarily from Quaternary and Tertiary aquifers. As shown in Figure A 7, Quaternary strata in the Northern German Basin are about 100 m thick. In certain structures, however – such as ancient river valleys – such strata can be up to several hundred meters thick. In Schleswig-Holstein, drinking water is extracted from Tertiary lignite sands at depths of up to about 150 m. Groundwater found at greater depths tends to be too saline for use as drinking water. In some cases, such salinity is also due to the groundwater's proximity to nearby salt deposits and the manner in which groundwater is extracted, since extraction frequently causes upward migration of brine. At depths of about 2,000 m, salt concentrations exceed 200 g/l.

The decisive factor to consider in hydrogeological system analysis, with regard to the potential impacts of exploration and exploitation of unconventional natural gas, is the positions and distribution of Zechstein deposits, since such deposits can function as hydraulic barriers under certain circumstances. Normally, in overlying Mesozoic sequences, aquifers alternate with aquicludes. No information was available to the study authors with regard to the relevant potential differences and large-scale groundwater flows. Where exploration and exploitation of shale gas takes place in Jurassic strata (Posidonia Shale), the Zechstein deposits are lacking that could function as hydraulic barriers.

Potentially competing uses of underground areas

Discussion has been intensifying regarding the possibility of exploiting deep geothermal energy in the Northern German Basin, and five relevant projects are already underway in the states of Mecklenburg – West Pomerania and Brandenburg. The geothermal-energy target horizons are found at various depths, depending on the relevant project aims (electricity and heat generation), as the following examples show:

- Brandenburg: Cenoman/Turon Kalke (1,000 to 1,200 m) (http://www.lbgr.brandenburg.de/sixcms/media.php/lbm1.a.3310.de/TiefenGeothermie.pdf)
- Neustadt Glewe, sandstones (2,335 m)
- Waren, Räth-Keuper sandstones (Contorta strata) (depth information not available to the study authors)
- Neuruppin: Aalen sandstone (1,700 m)
- Hamburg: Räth (Upper Triassic) (3,500 m)
- Groß Schönebeck: below the Zechstein (Rotliegend sandstones and volcanites at the Permian-Carboniferous boundary) (4,400 m)

The most important requirement for use of hydrothermal (geothermal) energy is that the target horizon must have sufficient porosity. Such porosity can be increased via borehole stimulation (for example, via fracking). In general, however, it is assumed that natural porosity is too low at depths of 2,000 to 2,500 m and greater. As a rule, the target horizons for hydrothermal (geothermal) energy are found above Zechstein deposits and above tight gas deposits (exception: Gross Schönebeck).

Where exploration and exploitation of shale gas takes place in Jurassic strata (Posidonia Shale), the Zechstein deposits are lacking that could function as hydraulic barriers, and competition with use of deep geothermal energy could result.

Special characteristics of the impact pathways involved, and the pathways' importance, with regard to risk analysis.

In consideration of potential impact pathways in the Northwest German Basin, a basic distinction can be made between unconventional natural gas deposits above Zechstein deposits and unconventional natural gas deposits below Zechstein deposits. For impact pathways to be relevant within the meaning of the definition used in the present study, they must involve permeability and a potential difference that promotes rising.

No large-scale flow movements within deep, saline aquifers are known.

For the unconventional gas deposits below the Zechstein deposits (tight gas), the gas deposits that are the current focus of exploration, impact pathways via continuous faults or directly through covering strata are probably not relevant. Wells and old boreholes could be relevant in some cases, however, even though open boreholes may gradually be sealed by plastic salts (so-called "salt flows").

At present, no exploration and exploitation of unconventional gas deposits above the Zechstein deposits (shale gas) are being discussed. In contrast to other shale gas deposits (such as Rhenish Massif, Weser Depression), these deposits are overlaid by thick, but highly saline, aquifers. To assess the risks presented via impact pathways, one would require concrete information about the pertinent target horizons.

A2.4.2 Coal bed methane deposits

It has not yet been determined whether, and to what extent, hydraulic stimulation of target formations would be required for any exploitation of natural gas from coal bed methane deposits in Germany. No relevant experience has yet been gathered in Germany. Pursuant to U.S. EPA (2004) data for 11 coal bed methane deposits studied in the U.S., fracking is consistently required in 8 of the deposits, while it is occasionally required in 3 of them. The water present in a given deposit plays an important role in determining whether the deposit can be economically exploited (see above).

By way of example, the following section describes the Münsterland Basin, since it is currently considered to be the most important coal bed methane deposit in Germany.

Münsterland Basin

Position and large-scale geological / hydrogeological situation

The Münsterland Basin coal bed methane deposit lies in the northern part of the state of North Rhine – Westphalia. To the south, the area under consideration is bounded by the Haarstrang ridge and the Paderborn Plateau, while its eastern boundary consists of the Egge range (Eggegebirge) and its northern boundary is formed by the Teutoburg Forest. Figure A 9 presents a schematic hydrogeological NE-SW cross-section of the Münsterland Basin, showing the basin's most important hydrogeological units.

In Quaternary strata, locally important groundwater resources (near-surface groundwater flow systems) occur that are used for drinking water production (especially the Münsterland Kiessandzug ridge, and terrace sediments of the Ems and Lippe rivers). Where the Emscher Mergel marl layer is near the surface and outcrops, only the so-called "loosening zone" contains usable groundwater resources. Such resources are used intensively for individual water supply systems (a total of some 40,000). Beginning at depths of 100 to 150 m, the groundwater is too saline to be used for the drinking water supply without being treated.

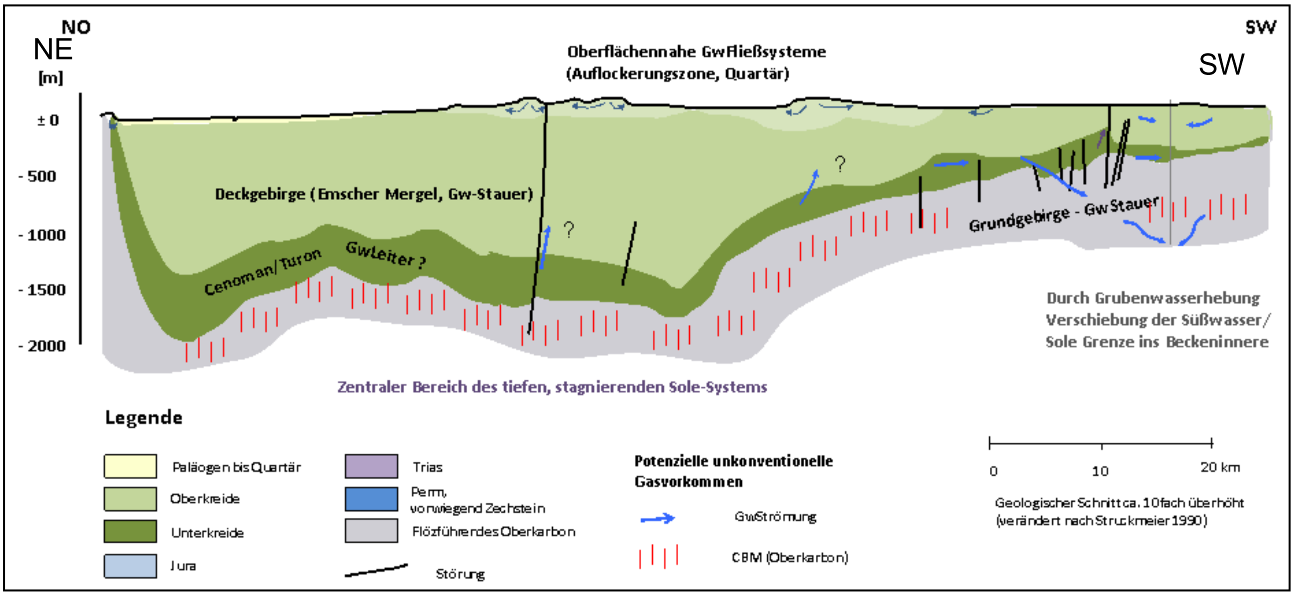

Fig. A 9: Hydrogeological NE-SW cross-section of the Münsterland Basin, with the central Münsterland and peripheral Münsterland geological systems (modified pursuant to Struckmeier 1990) [Text: Near-surface groundwater flow systems (loosening zone, Quaternary); Covering layer (Emscher Mergel marl, aquiclude for groundwater; Cenomanian-Turonian boundary, groundwater aquifer?; Covering layer – aquiclude for groundwater; Mine-water removal causes the freshwater-brine boundary to shift into the interior of the basin; Central region of the deep, stagnating brine system; **Legend**; Paleogenic to Quarternary; Upper Cretaceous; Lower Cretaceous; Jurassic, Triassic; Permian, primarily Zechstein; Seam-bearing Upper Carboniferous; Fault; **Potential unconventional gas deposits**; Groundwater flow; CBM (Upper Carboniferous; Relative height of geological cross-section increased 10-fold (modified pursuant to Struckmeier 1990)]

The Emscher Mergel marl layer is up to 1,000 m thick and consists of low-permeability argillaceous marl rock of the Upper Cretaceous. At the southern edge of the basin, sand intercalations up to 300 m occur (such as the Recklinghausen Sandmergel sandy marl formation, and the Halterner Sande sandy formation). Below the Halterner Sande sandy formation, the Emscher Mergel marl layer reappears. The formation is a supraregionally important aquifer for the drinking water supply. Below the Halterner Sande formation, active mining operations are still in progress, leading to the usual mining subsidence and mine drainage (cf. Fig. A 10 with regard to overlapping between the Halterner Sande formation and the mining zone).

The Emscher Mergel marl layer is underlain by a largely pure limestone layer (Cenomanian and Turonian) that is up to 500 m thick and that still provides the basis for the area's lime and cement industry. That layer's hard, weathering-resistant limestones also form the morphological border of the basin (Teutoburg Forest, Egge range (Eggegebirge), Haarstrang ridge). Near the terrain surface, the limestones are well stratified and jointed and, to some extent, highly karstified. Assessments vary regarding the degree of karstification in the interior of the basin. No clear hydrogeological indications have been found of any regional karst formation and, thus, of formation of a regional, deeper aquifer (such as that in the Molasse Basin).

The next underlying layer is the Lower Carboniferous, several thousand meters thick. In its upper 3,000 m, that layer consists of a regular stratigraphic sequence of coal seam, clay and silt rock; sandstones/conglomerates; silt rock; and clay rock; and the next seam, etc. (cyclothems). The vertical permeabilities of the layers are determined primarily by the clay formations, with their low permeability, while the horizontal permeabilities are determined by the sandstones, which are well stratified in some areas.

The tectonics of the overburden differ fundamentally from those of the basal complex. On the other hand, the presence of continuous faults, reaching from the basal complex up into the groundwater-bearing loosening zone, cannot be ruled out. To date, no indications have been found of any deep, permeable faults (such as geothermal water rises) in the central Münsterland Basin. A number of geothermal water rises and springs have been documented in peripheral Münsterland areas (see below).

Potential unconventional gas deposits

In the Münsterland Basin, the target horizon for exploration of coal bed methane deposits is the seam-bearing Upper Carboniferous layer. The seam-bearing Upper Carboniferous has a total thickness of about 3,000 m (Namur C to Westfal D). It contains about 200 seams. The thicknesses of the seams ranges from a few centimeters to 5-6 m. Overall, their coal fraction is estimated to be about 3 to 5 %. In general, it is assumed that the adjoining rock contains again as much carbon, finely distributed, carbon that could have contributed to gas formation.

Hydrogeological system analysis

For purposes of hydrogeological system analysis, the area to be considered is divided into three geological systems, taking account of the regional geology, the structure of the Münsterland Basin and the hard-coal mining in the southern section of the area. These geological systems have the following characteristics:

a. Central Münsterland geological system:
   Deep brine system under the Emscher Mergel marl layer

b. Mining zone geological system:
   Impacts on groundwater flow conditions, from draining sumping related to hard-coal mining

c. Peripheral Münsterland geological system, with two sub-areas, one south and one north:
   No impacts from deep hard-coal mining; geothermal water rises; spring areas in the southern, eastern and northern sections of the Münsterland Basin, reaching to the saltwater/freshwater boundary in the interior of the basin; relatively thin to nonexistent cover of Emscher Mergel marl.

The presence of any large-scale groundwater flow system in the deep Münsterland Basin (central Münsterland geological system) depends primarily on the regional permeability of the Cenomanian/Turonian limestones. Hydrogeological findings to date point instead to a deep, highly saline and quasi stationary system with Cenomanian/Turonian limestones of low permeability. No potential maps of groundwater in the Upper Carboniferous and in the Cenomanian/Turonian limestones, such as those prepared for the Molasse Basin, for example, have yet been prepared. Furthermore, the study authors cannot determine whether the available data would support such evaluations, since the data on the some 1,000 boreholes drilled for hard-coal exploration are not publicly accessible.

In peripheral areas, dynamic groundwater flow systems are found in karstified Cenomanian/Turonian limestones (peripheral Münsterland geological system). In keeping with the differences in geological and tectonic structures, two sub-areas are differentiated: a sub-area in the south (Paderborn Plateau / Haarstrang ridge), with very flatly dipping layers, and a sub-area in the north (Teutoburg Forest), where the bed succession dips very steeply toward the basin and is subject to greater tectonic stresses. The northern sub-area also includes the northwest area around Gronau and Ahaus, where the Cenomanian/Turonian limestones crop out within a narrow, multiply faulted strip.

In both sub-areas, the peripheral zone is of similar hydrogeological importance. Groundwater that forms on the high elevations of the Haarstrang ridge and in the Teutoburg Forest flows toward the central Münsterland area. The groundwater then emerges at the periphery of the Münsterland Basin, when it has reached the range of the overlapping, low-permeability Emscher Mergel marl layer and the heavy brine (salty water). In former times, many springs (and wells) in those areas were artesian. As one moves toward the interior of the basin, the groundwater becomes more and more highly mineralized. For this reason, it has often been used for balneological purposes, and wells have been drilled especially to tap it in its mineralized state.

In large-scale studies, it would be necessary to study whether, and to what extent, activities in the central Münsterland area may have impaired these groundwater flow systems, which play an important role in the drinking water supply. Any special local hydrogeological/tectonic characteristics would need to be taken into account in any more detailed system analyses.

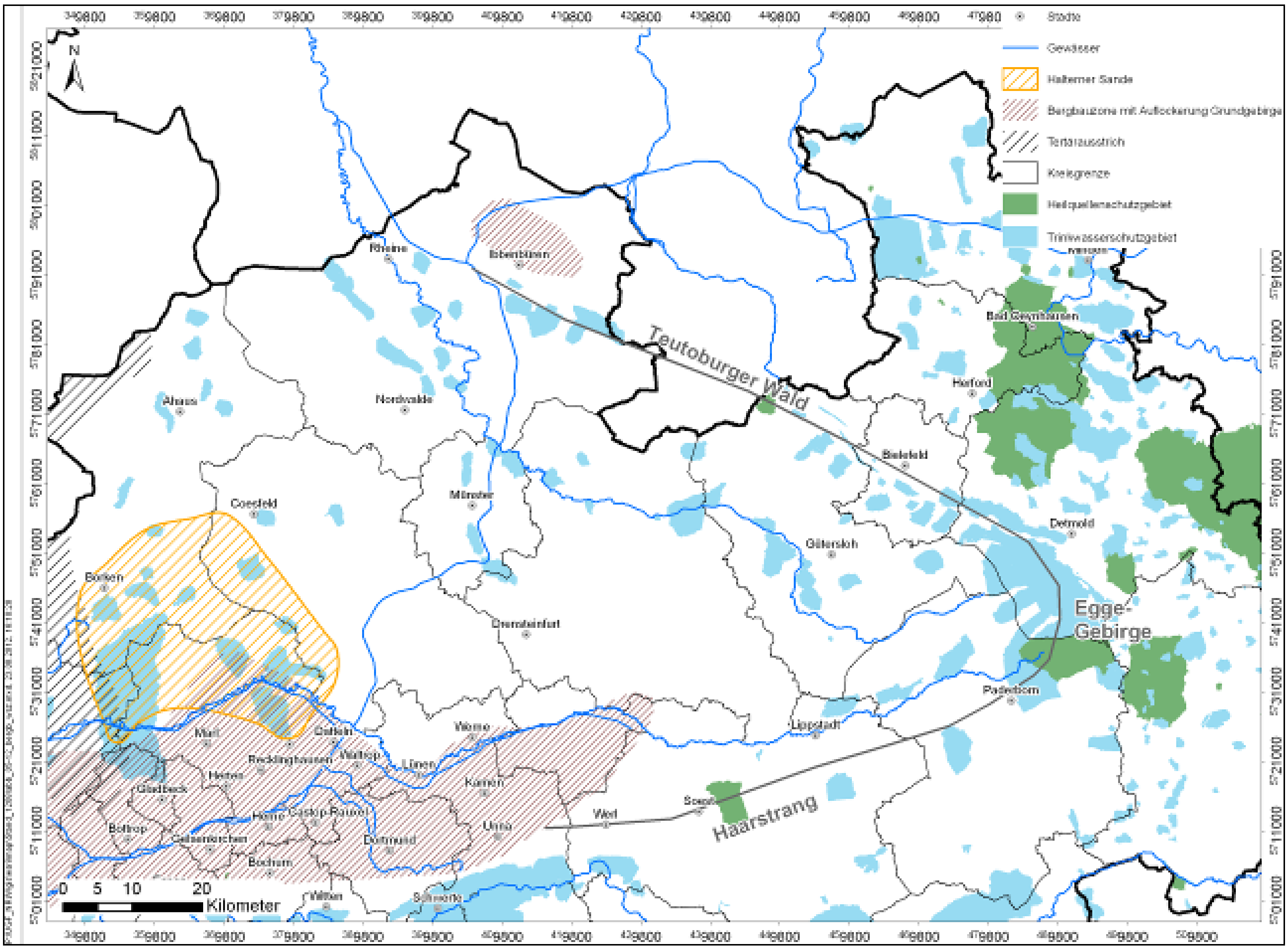

Fig. A 10: Mining zone, range of the Halterner Sande sandy formation, and location of drinking water protection zones (Database: LANUV and GD NRW)

Hard-coal mining (mining-zone geological system), which has been carried out for decades at the southern edge of the Münsterland Basin, has raised large quantities of groundwater (mine water) from depths of up to about 1,500 m. In the heyday of the mining era, the water quantities involved reached 160 million m^3/a. In 2010, they still amounted to 75 million m^3 (RAG 2011). While the majority of that water was (fresh) groundwater, a considerable portion was saline deep groundwater. As a result, many artesian seepage springs in the area of the line of springs fell dry, and in mining areas, the freshwater/saltwater boundary shifted some 1.5 to 2 km toward the interior of the basin.

Potentially competing uses of underground areas

While in individual cases other uses, such as use of deep geothermal energy, could compete directly in the Münsterland Basin, the study authors are not aware of any such actually competing uses. In the mining zone, plans call for water drainage from mines to maintain water levels at a level of about 700 m below the terrain surface, until at least 2027. As a result, there are still large catchment areas that could influence the groundwater flow conditions of neighbouring exploration fields for exploration of unconventional gas deposits.

Special characteristics of the impact pathways involved, and the pathways' importance, with regard to risk analysis.

One special aspect involves the frequent occurrence of methane in the Emscher Mergel marl layer and in individual water supply systems. Although rising of thermogenic methane from Upper Carboniferous strata cannot be ruled out, to date there are many indications that the methane is biogenic methane that formed in the Emscher Mergel (inter alia, Melchers 2008). No systematic gas monitoring has been carried out to date.

In addition, the some 1,000 old boreholes left from exploration for hard coal, some of which are now decades old, could potentially function as pathways if suitable connections were created via fracking. Especially in areas with high densities of such boreholes, as in the planned fields for northward movement of hard-coal mining, the condition of the boreholes must first be checked, and suitable distances to boreholes must be maintained.

Continuous faults present another potential impact pathway, one that in the central Münsterland geological system – as a result of that area's thick overlying Emscher Mergel layer – is less likely to become active than it is in the two other, peripherally located geological systems. The possible existence of such faults should be studied in the framework of exploration – for example, with the help of 3D seismic imaging – to ensure that suitable distances can be maintained, in keeping with the applicable permeabilities.

In the central Münsterland geological system, any substances and gas that migrate without having special pathways, i.e. that migrate directly through the Emscher Mergel marl layer, are not likely to pose hazards for near-surface groundwater resources. The reasons for this are the great thickness and the low permeability of the Emscher Mergel layer. Cenomanian/Turonian limestone could be an exception in this regard; its lateral permeability is not (yet) known. If further exploration should reveal a regional permeability, and a potential difference pointing toward the springs, then that limestone could possibly prove to be an important impact pathway.

A2.4.3 Shale gas deposits

Detailed descriptions of the origins and occurrence of shale gas in Germany are provided in BGR (2012). In the following, the south German Molasse Basin and the Harz / Harz Foreland regions are described, by way of example, in the context of type-locality analysis.

South German Molasse Basin

Position and large-scale geological / hydrogeological situation

Throughout an east-west orientation, and roughly parallel to the Alpine arc, the Molasse Basin extends for 900 km, from France to Vienna. Over a period of about 35 million years, it has absorbed the erosional sediments of the Alps. As the overburden pressure caused by the sediments increased, the area's existing layers (basal complex to Upper Jurassic) were pushed down and buried at ever-greater depths. Figure A 13 shows a SE-NW cross-section of the Molasse Basin east of Lake Constance. Further east, near Munich, and at the edge of the Alps, the Molasse Basin is up to 5,000 m thick (eastern Molasse Basin). For hydrogeological system analysis, it is important to know that the deposition took place under conditions that changed repeatedly (peripheral – interior of the basin; marine – transition zone – fluviatile), with the result that at any given location sediments with considerably varying permeabilities were deposited that are now interlocked, laterally and vertically, in complex ways.

The following remarks focus specifically, by way of example, on the western Molasse Basin in Baden-Württemberg, since that area already contains exploration fields for esploration of unconventional gas deposits (cf. Figs. A 2 and A 3).

In keeping with the insight that the changing depositional factors in the Molasse Basin must play a key role in any understanding of the area's regional geology and hydrogeological system, Figures A 11 and A 12 show the relevant depositional system and a stratigraphic profile diagram of the lower seawater and freshwater Molasse (UMM, USM). Comparable conditions prevailed in the upper marine and freshwater Molasse (OMM, OSM).

Initially, the Molasse sediments consisted of marine deposits in a fairly deep sea basin. Beginning in the Middle Oligocene period, the marine invasion took place from the east, with the result that the Lower Marine Molasse (UMM) is mainly found in Bavaria (eastern Molasse Basin). In the Lower Marine Molasse, bitumen-rich Fischschiefer shale (Fig. A 9), which also can hold shale gas deposits, was also deposited. Fine-grained sediments with low permeability predominated.

Beginning in the Upper Oligocene, and as a result of the increasing filling of the Molasse depression, a gradual process of alluviation and freshening of the Molasse took place, moving in from the west, and fluviatile sediments of the Lower Freshwater Molasse (USM) were deposited (Fig. A 11). By nature, such sediments are coarser (sand, gravel) in the river deltas at the edge of the Alps and on the Swabian-Franconian platform; toward the interior of the basin, they become more and more finely grained, and thus have less and less permeability. Repeatedly, in the shallow waters, reef limestone formed and marl was deposited.

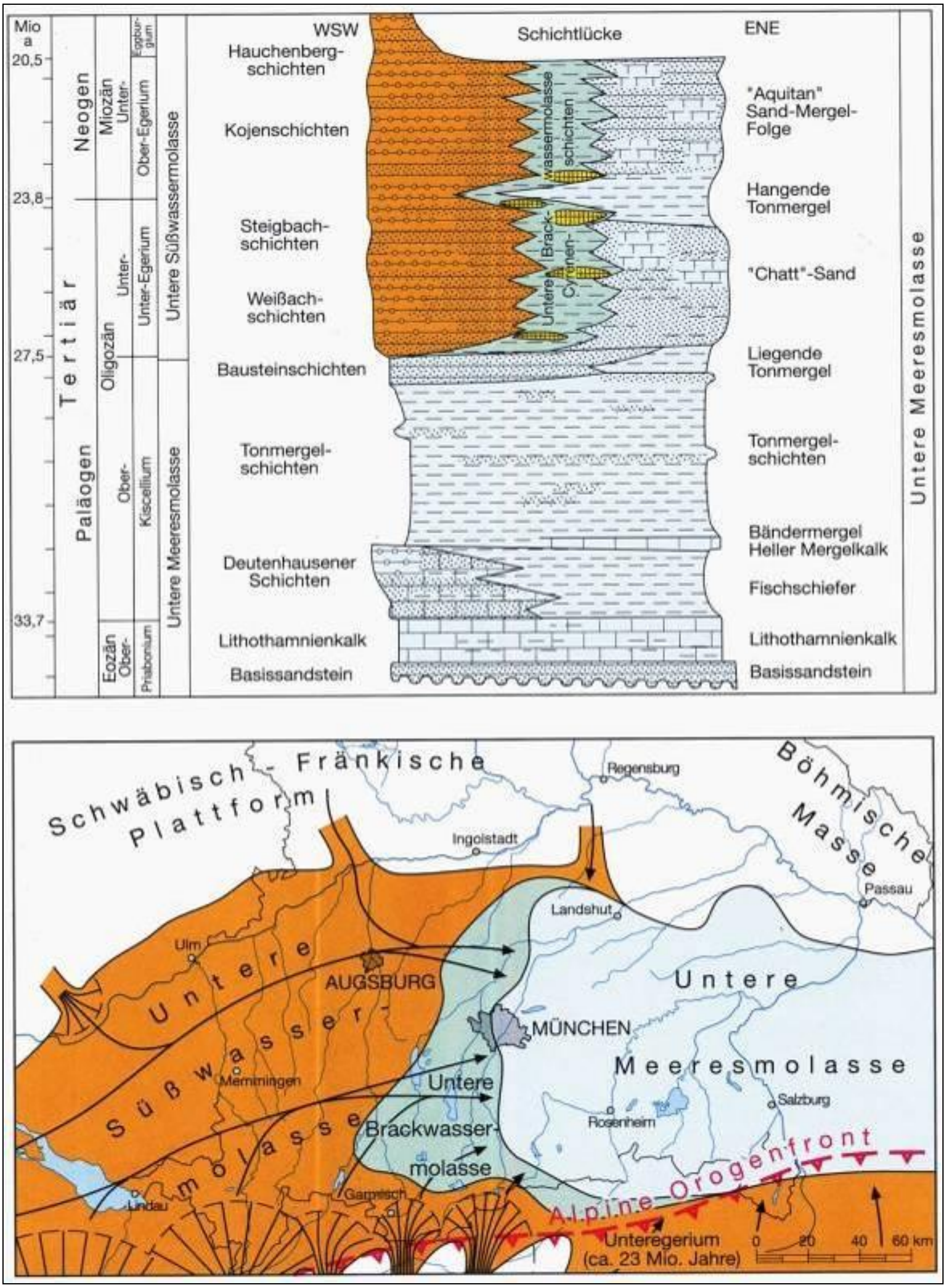

Fig. A 11: Depositional system of the lower marine and freshwater Molasse (Source: http://www.lfu.bayern.de/geologie/geologie_bayerns/ueberblick/doc/22_umm_usm.pdf from Glaser et al. 2004)

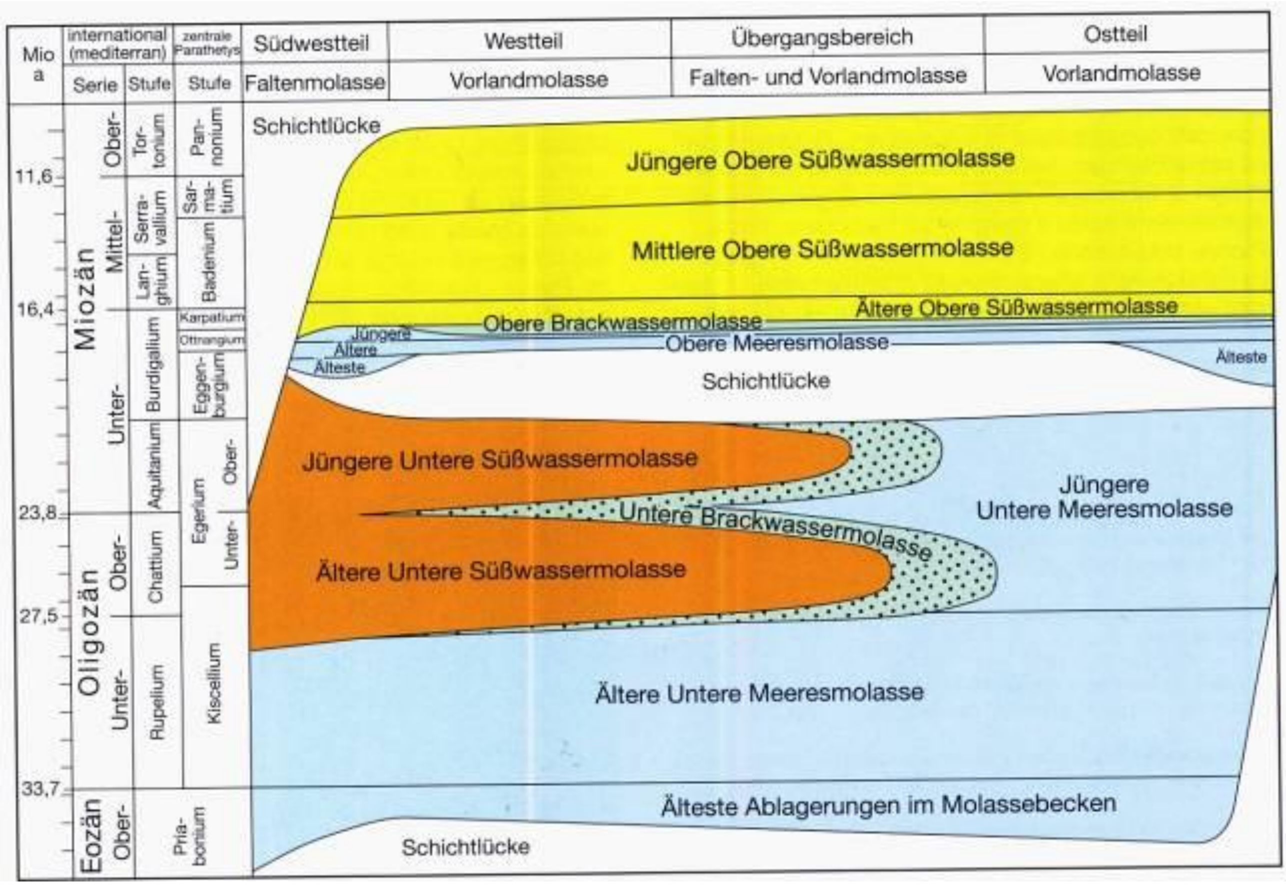

Fig. A 12: Profile diagram of the lower seawater and freshwater Molasse (Source: Glaser et al. 2004)

After the Lower Freshwater Molasse (USM), and in another period of sea encroachment, the Upper Marine Molasse (consisting extensively of fine sand, marl and clay) was deposited. Then, in a new period of freshening, the Upper Freshwater Molasse (consisting extensively of river gravel) was deposited.

As a result of the depositional histories involved, hardly any continuous aquifers occur in the Lower Marine Molasse (UMM). In the Lower Freshwater Molasse (USM), lateral interlocking of strata with different degrees of permeability (higher or lower) does occur. No continuous aquifers occur here either, however. In the Upper Marine Molasse (OMM), stratum segments with higher permeability often do occur (such as coarse-sand chains, Baltringen strata, Heidenlöcher beds, fine-sand series). In Baden-Württemberg, such segments have also made the formation of a unified groundwater surface possible. In the Upper Freshwater Molasse (OSM), highly permeable and planarly distributed river gravel from the Alpine region predominate (such as "Ortenburger Schotter" gravel in southern Bavaria).

Under the Molasse sediments, Upper Jurassic layers follow. The prominent features within the Upper Jurassic include Malmkalke limestone and dolomite layers, which are 350 to 550 m thick. In the Franconian Alb and Swabian Alb regions, where they outcrop at the surface, these layers are often heavily karstified. In the subsided area of the Molasse Basin, areas of high permeability and productivity have repeatedly been discovered in boreholes, areas that are indicative of some karstification at great depths. In keeping with the relevant facies and diagenesis, regional differences in the prevalence of such areas are seen. Basically, the Upper Jurassic can be divided into three facies areas:

- the Swabian Facies,
- the Franconian Facies and
- the Helvetian Facies,

In the area of the Swabian and Franconian Facies (Germanic facies), a distinction can be made between basin and reef facies. In general, the massive limestones of the reef facies may be classified as readily karstifiable. The strata in the Middle and Upper Kimmeridge (Middle Upper Jurassic) are especially permeable. This is due to early diagenetic dolomitization and cavity formation ("zuckerkörniger Lochfels" – "sugar-grained Lochfels rock"). As a result, the thickness of the actual aquifer is reduced to about 10 % of the total thickness of the "Malm" (Upper Jurassic).

As the spatial distribution of the total circulation losses in hydrocarbon and geothermal-water boreholes in the karst-water and crack-water aquifer of the Upper Jurassic indicates, karstification processes along major fault zones tend to be especially intensive, due to the greater fissuration found in such areas, which provides better pathways for water flowing through. A distinction must be made between a) the hydrogeologically ineffective karst formation at the Jurassic surface and b) karstification of pore, porous and crack structures within the aquifer, which structures determine the aquifer's permeability and productivity.

Toward the south, the Germanic facies gives way to the Helvetian Facies, which consists largely of stratified Quintner limestones. As far as is known, such limestones are of low permeability here, and thus the Helvetian Facies is considered to be hardly karstifiable at all. To a first approximation, the northern boundary of the Helvetian Facies may be seen as the southern edge of the Malm aquifer (Villinger 1988).

Unfavourable permeabilities for any deep geothermal energy use are found in the triangle formed roughly by Konstanz (Lake Constance) – Augsburg – Füssen.

Another layer that is of interest for use of deep geothermal energy, due to its permeability, is the Upper Muschelkalk limestone (porous to finely cavernous dolomites), which is also karstified and is separated from the Malm aquifer by aquicludes of the Keuper and the Lower and Middle Jurassic.

Potential unconventional natural gas deposits

A number of smaller hydrocarbon deposits in the Molasse Basin (primarily petroleum, and some gas), in various geological formations, have been exploited in the past (Felder Wald, Markdorf, Fronthofen, Hofkirch, Pfullendorf, Gaisbeuren, Wurzach, Oberschwarzbach, Hauerz, Ellwangen). These classical deposits are now all depleted, with the exception of the Saulgau field.

The study authors are not fully aware of which layer segments are potential unconventional gas deposits and are to be explored. According to the authors' current knowledge, the main segments under such consideration are the Fischschiefer shale areas in the Upper Marine Molasse (OMM). The BGR study (BGR 2012) states that the Fischschiefer shale lacks adequate thermal maturity and thus is not expected to have formed significant quantities of gas. The same study concludes that the Posidonia Shale in the Upper Jurassic of the Molasse Basin is only about 20 m thick and is thus at the limit of any technical recoverability. In addition, while bituminous layers can occur in Malmkalke limestones, such layers are relatively thin and, for facies-related reasons, are locally confined. Also, bitumen-rich limestones occur within Muschelkalk limestones, and are potential deposits, but the study authors also lack information about those layers.

Hydrogeological system analysis

Figure A 13 schematically depicts the most important aquifers, along with the distribution of the hydrocarbon-rich strata that are being focussed on with regard to exploration of unconventional gas deposits. The vertical arrows in Figure A 13 show the potential differences with respect to the underlying aquifers.

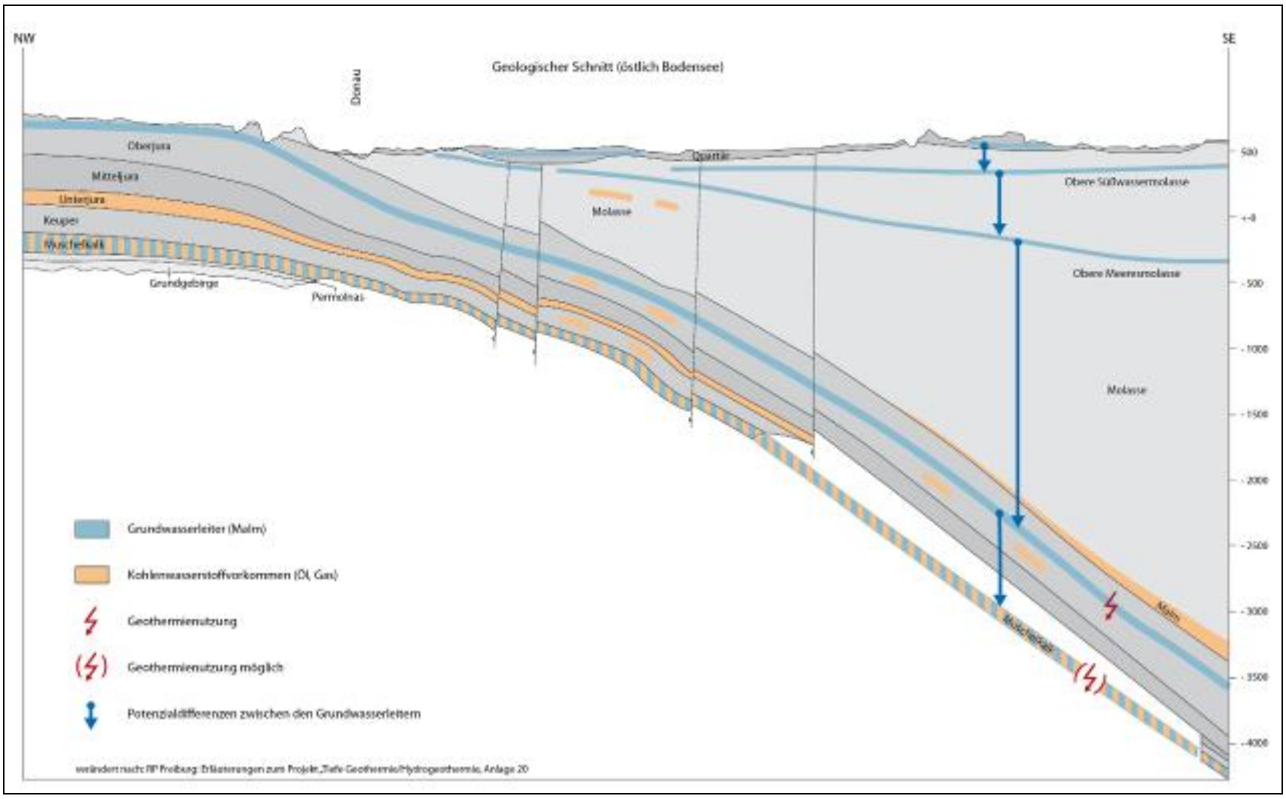

Fig. A 13: Hydrogeological NW – SE cross-section of the Molasse Basin, at the western – eastern Molasse Basin boundary, with potential hydrocarbon deposits and geothermal potentials (Source: ahu AG) [Legend: Groundwater aquifer (Malm); Hydrocarbon deposits (oil, gas); Geothermal energy use; Geothermal energy use possible; Potential differences between groundwater aquifers]

The following description of the large-scale groundwater flow systems in the Upper Marine Molasse (OMM) and in the Malm aquifer is based on publications of the Freiburg regional council (Regierungspräsidium) relative to deep geothermal energy in the Lake Constance - Upper Swabia area[6].

Upper Marine Molasse and Malm

In Baden-Württemberg (western Molasse Basin), the large-scale groundwater flow systems in the Upper Marine Molasse (OMM) and in the Malm are oriented, over a wide area, from the heights of the Swabian Alb (about 700 to 150 m above NHN) to Lake Constance (395 m above NHN). In the val-

[6] http://www.lgrb.uni-freiburg.de/lgrb/Fachbereiche/geothermie/projekte/gbo/pdf_pool/gbo_Erlaeuterungen.pdf

leys around Lake Constance, both aquifers are artesian. Although the two aquifers are located below Lake Constance (about 800 m – Upper Marine Molasse (OMM); and about 3,200), both of their potentials are adjusted to that lake's water level. As a result, Lake Constance seems to be the receiving water level for both aquifers. Only with the help of numerical models would it be possible to determine, quantitatively, whether a horizontal flow movement toward Lake Constance, through the two aquifers, actually occurs, and whether rising water movements occur.

Current opinions regarding the relatively large age of the two aquifers, and the lack of groundwater replenishment in them, point to quasi-stationary systems. And the presence of such systems, in turn, would point to very low permeabilities in the intermediate layers and to the lack of relevant hydraulically permeable faults.

<u>Muschelkalk</u>

In the western Molasse Basin, the groundwater levels in the muschelkalk limestone are about 200 to 250 m deeper than they are in the Malm – and, thus, are considerably lower than the level of Lake Constance. It is unclear where the receiving stream for the Muschelkalk aquifer is located, and it is unclear why the relevant large potential difference has not equalized over the geological time spans involved.

One reason for this could be that the potentials in the Muschelkalk are the "image" of a groundwater flow system whose receiving streams were considerably lower than those of the present-day system. That system, for example, could have been active prior to deposition of the Upper Freshwater Molasse (OSM) in the Middle Miocene. The strata that separate the Malm and the Muschelkalk, strata which have very low permeability, are the reasons why, to this day, the groundwater levels have not been replenished and the potentials have not equalized. Another explanation could be that there is an underflow, into even deeper layers, that is larger than the inflow from the Malmkalke limestones above. In either case, the situation would be a manifestation of the layers' very low permeabilities and of the faults between the aquifers.

The mineralization of deep water increases with depth. In the deep Malmkarst formation, NaCl concentrations increase to 20 g/l. In muschelkalk limestone, the salt concentrations are even higher; they can reach levels of up to 80 g/l (Bertleff et al. 1988).

Hydrochemical markers in the groundwater in the Malm indicate that some groundwater formation occurred in a glacial period (i.e. more than 12,000 years ago). In the southern peripheral areas, even older, highly mineralized Tertiary formation water occurs (connate water). Current replenishment of that water, via influent seepage from overlying layers or via groundwater replenishment, is known to occur only in the Molasse Basin's peripheral area, which falls into the range of moderate (geo-) thermal activity. By contrast, in the center of the basin, no groundwater replenishment – especially for the Upper Jurassic layers – can be substantiated. It is thus either very small or nonexistent. Consequently, the geothermal water resources there are also referred to as "deposits" (Bertleff & Watzel 2002).

Potentially competing uses of underground areas

In the Molasse Basin, deep underground layers are used in a number of different ways. In particular, the groundwater in the Malm is being used increasingly for energy production, via deep geothermal wells. Currently, a total of 12 geothermal facilities are in operation, 11 facilities are under construction and 24 facilities are being planned (source: Geothermische Vereinigung e.V. 2012). Geothermal energy uses raise groundwater, remove part of its heat and then inject it, at a cooler temperature, back into the same formation from which it was taken, at some distance from the withdrawal borehole. Such injection ensures that no triggering of mass deficits occurs (so-called "doublet" and "triplet" operation). For such operations, local groundwater-flow and heat-transport models are often available that serve as a basis for site selection and for estimation of the flow and heat quantities that can be recovered over the long term.

By way of example, Figure A 14 shows the geothermal energy uses in the eastern Molasse Basin in Bavaria. Those uses overlap to some degree with the exploration fields pursuant to Figure A 14. Further information on geothermal energy uses in the Molasse Basin is provided, inter alia, by the Bayrischer Geothermieatlas (Bavarian geothermal atlas)[7].

[7] http://www.stmwivt.bayern.de/energie-und-rohstoffe/erneuerbare-energien/energieatlas/#c1903

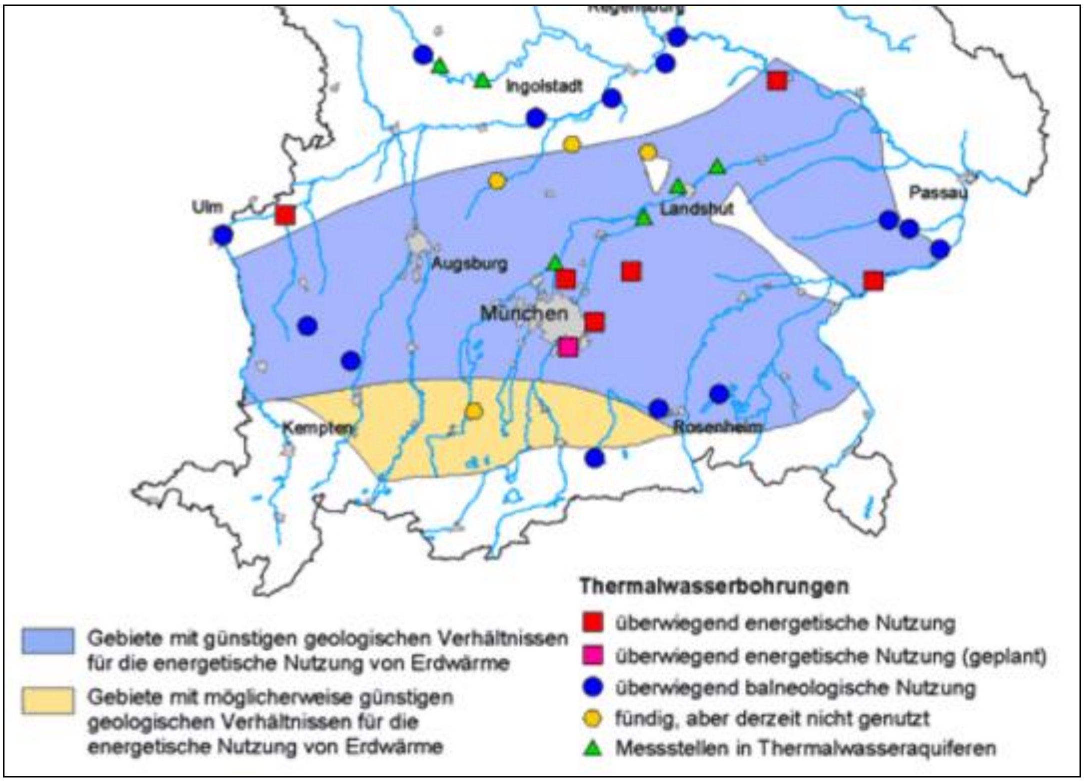

Fig. A 14: Geothermal energy uses in the eastern Molasse Basin (http://www.lfu.bayern.de/geologie/geothermie/geothermie_tief/index.htm) [Legend: Areas with favourable geological conditions for geothermal energy use; Areas with possibly favourable geological conditions for geothermal energy use; **Hydrothermal boreholes**; Primarily for energy purposes; Primarily for energy purposes (planned); Primarily for balneological purposes; Tapped, but not used at present; Measuring stations in hydrothermal aquifers]

Special characteristics of the impact pathways involved, and the pathways' importance, with regard to risk analysis

The Molasse Basin is characterized especially by its asymmetric structure and by the fact that the depth positions of potential target formations for exploration of unconventional gas deposits increase sharply in an eastward direction. In addition, the Molasse Basin's depositional history has produced a complex hydrogeological structure with alternating and interlocked strata of varying permeabilities.

The groundwater levels in the Malm, in the Upper Marine Molasse (OMM) and in the Muschelkalk (muschelkalk limestone layer) are confined, with the result that drilling into water-bearing layers causes groundwater levels to rise, by up to several thousand meters. In valley areas, the water levels are artesian. The upwardly pointing potential differences are thus present throughout the entire Molasse Basin, even in areas in which drinking water resources are used. This also applies, to some extent, to deep groundwater from the muschelkalk limestone layer.

Natural pathways (or potential impact pathways) are present in the Molasse Basin primarily in the form of faults. The Molasse Basin's many spas with mineral and brine springs provide numerous examples of rising of mineralized deep water.

When the necessary pathways are not present, vertical groundwater flows either do not occur or occur only in very small quantities and very slowly, as the great age (inter alia) of the relevant water indicates. On the other hand, significant horizontal groundwater flows do take place, as the analyses of the Freiburg regional council (Regierungspräsidium) on potential distribution reveal. In the eastern Molasse Basin, flow processes from the Malmkalk limestones into higher groundwater bearing layers also take place via hydraulic windows (Bayerisches Landesamt für Umwelt 2008).

In the past, many boreholes have been drilled in the Molasse Basin, into different depth ranges, especially for purposes of hydrocarbon exploration and exploitation. Such old boreholes are now potential impact pathways. The study authors are not aware whether any cadastre of such boreholes exists that would show the manner in which they have been backfilled and their current condition (monitoring).

In future, increasing use of deep underground layers for geothermal energy deep can be expected. Concern with regard to such uses focuses less on the boreholes themselves and more on the locally significant hydraulic interventions involved. Even in cases in which the applicable mass balances are in equilibrium, flow processes can be triggered in the long term – for example, via temperature changes.

With regard to large-scale hydraulic stimulation of target formations, in connection with exploitation of unconventional gas deposits, the following would also need to be considered, in addition to the aforementioned aspects: planar increases in permeabilities, and further interventions in hydraulic potentials, as a result of fracking (brief increases in potentials) and exploitation (longer-lasting reduction of potentials). It might be possible in some cases, for example, for several old and new uses to overlap via stacking (depleted hydrocarbon deposits, geothermal energy uses, and exploitation of unconventional natural gas).

Additional regional and local studies would have to be carried out, throughout the entire Molasse Basin, to determine the extent to which the aforementioned interventions could lead first to hydraulic interactions in deep underground layers (geothermal energy – fracking) and then, ultimately, to interactions – via faults and/or old boreholes – with large-scale groundwater flow systems.

In sum, complex interactions could occur via the many existing and planned uses and the basin's several overlapping groundwater flow systems and, while relatively much is known about the basin's deep underground – in comparison to what is known about other basin structures such as the Münsterland Basin – such potential interactions have not all been explored, and they can be comprehensively analysed only via individual-case and local/regional studies.

Harz Mountains

In the following, the geological and hydrogeological conditions in the Harz region are described, by way of example, with respect to potential shale gas deposits in Paleozoic bedrock, although at present is it unclear whether such strata contain economically exploitable shale gas deposits. BGR (2012) refers to the Harz as a region in which potentially gas-bearing rocks occur. Descriptions of other bedrock regions (such as the Rhenish Massif) are provided in the study carried out for the state of North Rhine – Westphalia (ahu et al. 2012).

Position and large-scale geological / hydrogeological situation

The Harz is the northernmost German upland area. Located within the area in which the borders of the three states Lower Saxony, Saxony-Anhalt and Thuringia meet, it extends about 100 km on a general northwest-southeasterly axis. The breadth of the low mountain chain is about 30 to 40 km. It is commonly divided into the Upper Harz in the northwest, with elevations of up to 800 m, and culminating in the 1,142 m Brocken Massif at its southeasterly edge, and the eastern Lower Harz, with elevations of up to 400 m.

Together with the Ardennes, the Rhenish Massif and the Flechtingen Hills (Flechtinger Höhenzug), the Harz belongs to the Rhenohercynian Zone of the central European Variscan belt (Walter et al. 1995). The Harz mountain chain forms a prominent half-horst along the border fault running northwest-southeast. Morphologically, the mountains slope relatively steeply toward the west and northeast and flatten gradually toward the south. They are transected by numerous deep valleys. On their southern side, the Harz mountains plunge shallowly under the Permian and Mesozoic covering strata of the Thuringian Basin, while their NE flanks are divided, by a steep upthrust fault, from the Permian and Mesozoic strata of the Subhercynian Basin, which are upturned nearly to the point of inversion (Schönenberg & Neugebauer 1997). The internal structure of the Harz range is characterized by elements running parallel to the strike defined by the Ore Mountains (SW-NE; Erzgebirge) (Fig. A 15).

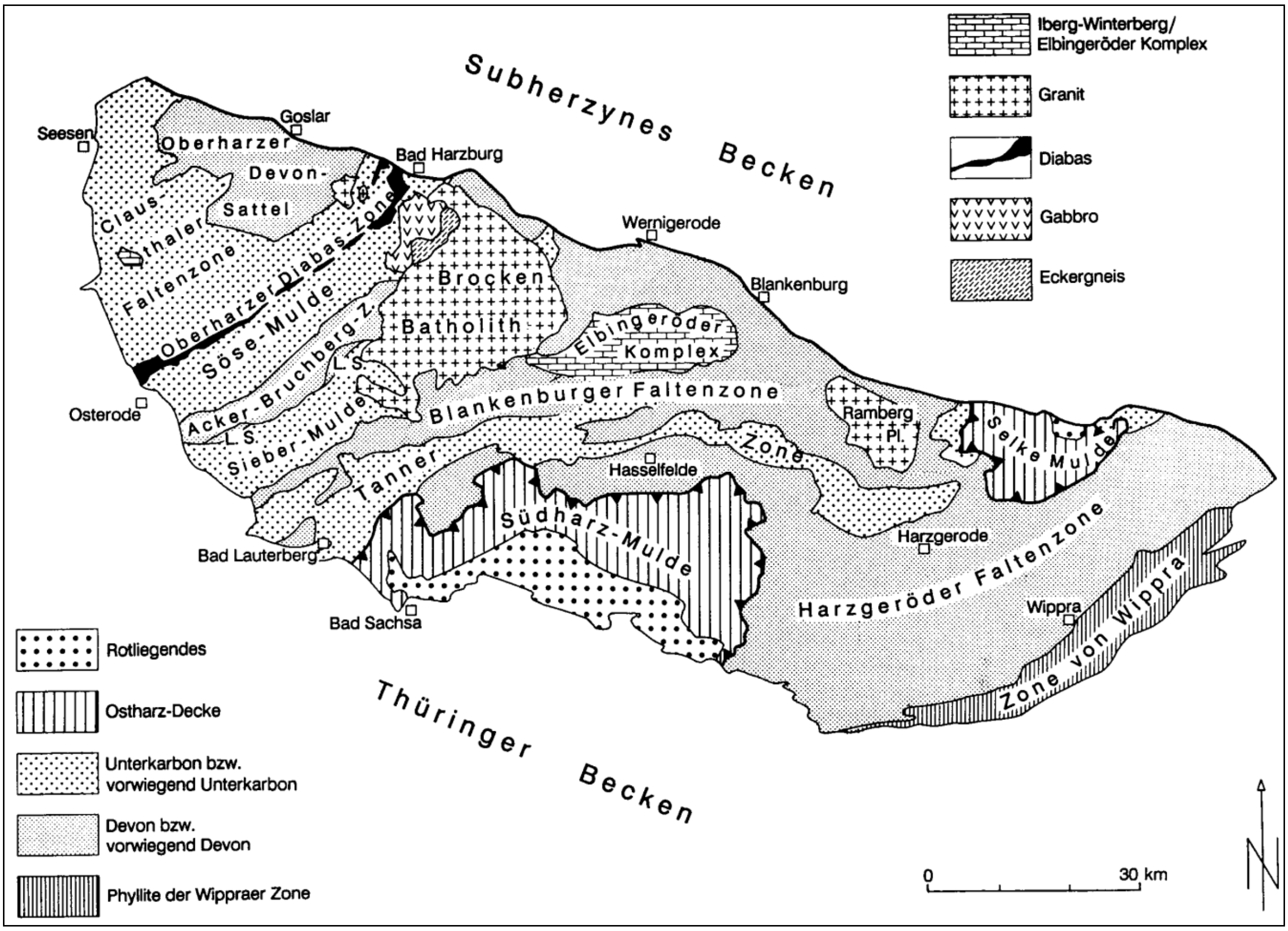

Fig. A 15: Geological overview map of the Harz region (Wachendorf 1986)

The geosynclinal development of the depositional environment took place between the Old Red continent in the north and the mid-German crystalline rise in the south. The sequence, Ordovician-Silurian through Lower Devonian, is represented by clay rock, siltstone, sandstones and carbonates of an offshore sedimentary environment. As of the Middle Devonian, however, Wissenbach Shale is the characteristic lithotype of the basin facies. In the Middle Devonian, initial basaltic magmatism began in all structural units of the Harz, following predominantly Variscan-oriented stretch faults. The Lower Carboniferous is present largely as the Kulm facies. Bituminous clay rock and cherty clay rock were deposited; locally, they are linked with volcanites. Filling with more coarsely clastic material began in the Lower Carboniferous and led to deposition of Kulm greywacke. The higher Lower Carboniferous is characterized by greywacke fills up to 2,000 m thick. Following the main folding of the Harz, and toward the end of the Upper Carboniferous, uplifting and intensive erosion began (Walter et al. 1995)

The Harz has a complex, diverse geological structure, and has experienced centuries of mining and smelting of ores. While stratiform ore bodies were extracted from the Rammelsberg, ore mining in the Harz mountains was pursued especially as vein mining, oriented to extraction of silver, lead, copper and zinc. To a smaller extent, iron ores, iron pyrite, and fluorspar and heavy spar were also mined. Mineshafts several hundred meters deep – and, in some cases, over 800 meters deep – were excavated along ore veins, which usually plunged vertically.

Pursued over the course of centuries, mining left its stamp on the appearance of the area's landscapes and on its above-ground and below-ground drainage systems. The "Upper Harz Water Shelf" (Oberharzer Wasserregal) was built, an artificial system of ditches and dammed ponds via which drainage sumping, and operation of drawing-off shafts via waterpower, were managed. Groundwater was removed underground via water-drainage galleries. In addition, numerous dams have been constructed in the Harz regions, for purposes of flood protection and of supplying water to nearby cities (including Hannover, Braunschweig and Bremen).

Potential unconventional natural gas deposits

In the Harz, potential unconventional natural gas deposits may well be bound to organically rich clay rocks and to shale of the Middle and Upper Devonian ("Wissenbach Shale") and of the Lower Carboniferous. The intensive folding and foliated structure of the Wissenbach Shale, which is more than 600 m thick, as well as that shale's high illite crystallinity and high vitrinite-reflectance values (> 5.5 Ro; Jordan & Koch 1979), are indicative of the depth to which it was buried, and of the tectonic stresses it underwent, in the course of Variscan mountain formation. The criteria listed by the BGR for the natural gas potential of clay rocks include thermal maturity to 3.5 Ro and thicknesses of over 20 m (BGR 2012). In light of its overly high thermal maturity, the Wissenbach Shale in the Harz region is likely to have a low potential for unconventional natural gas. The underlying alum shales in the Harz are only a few meters thick, while the overlying alum shales there are seldom present as black shales. The layers following immediately above are chert, cherty clayey shale, diabase and greywacke; then, overlying alum shale – of only slight thickness, and seldom present in the form of black shale – marks the boundary to the Upper Carboniferous. Due to the slight thicknesses of the shales involved, the diversity of their lithological forms and the increasing maturity of the rocks as one moves east, the alum shales are also likely to have only a small potential for unconventional natural gas.

To the knowledge of the study authors, no mining authorisations have been requested, or issued, for the Harz region for the purpose of exploring for unconventional hydrocarbons. Such authorisations have been issued for the northeastern and the southwestern foreland (Subhercynian Basin, Thuringian Basin) (BGR 2012).

Hydrogeological system analysis

In keeping with its heavy rainfall – between 1,000 and 1,600 mm in the Upper Harz, and 600 mm in the East Harz – the Harz region has many dams and water-retention basins. The dams' primary purpose is flood protection, but they also provide drinking water for the region and surrounding regions. Such surface water resources are replenished primarily via surface runoff, by interflow and, to a small extent, by near-surface, local aquifers.

Locally more-productive aquifers may be expected in valley gravel fills and in more heavily jointed and/or faulted areas of Paleozoic sediments and in crumbly sections of granites. Locally, such areas are indeed of importance for production of drinking water and mineral water. The water involved consists of local groundwater flow systems oriented near to the surface, with general underflows in the direction of the Harz valleys and to the Harz forelands. Except in areas with greater jointing and in fault zones, the shale series have little water flow, as well as low permeability. They thus may be classified as aquicludes.

Presumably, in most of the larger Harz valleys, near-surface groundwater flow systems in deep-reaching fault zones are connected to deeper groundwater systems of the forelands. Artesianally rising hot brine is used balneologically near Bad Harzburg, for example. The brine originates in the Mesozoic strata outcropping below the overthrusted Harz Paleozoic. Little is known about the deeper groundwater dynamics in the Harz, and about any connections to saline, deeper aquifers in the bordering forelands. Presumably, exchanges between these two systems take place, and such exchanges may well be related to the mining-related drainage that has taken place over centuries in the region. For example, ingresses from the peripherally bordering Zechstein saline formations have been suggested as the reasons for the brine that has emerged in the central Upper Harz mining district (Mohr 1992).

Potentially competing uses of underground areas

No information on competing uses is available to the study authors. In the Harz, drinking water production is confined to surface reservoirs, to local, shallow aquifers and to heavily jointed, near-surface areas within the shale/greywacke series that are actually aquicludes. In peripheral regions of the Harz, production of mineral and medicinal water could possibly be a competing use.

No information is available to the study authors regarding the existence and planned use of deep geothermal energy, and thus they are unable to assess the possibility of competing uses and interactions in that regard. It is considered unlikely that ore mining will be revived in the Harz mountain area. And, to the study authors' knowledge, while projects involving underground pumped-storage plants for energy production and for energy storage are being discussed, such ideas have not reached a concrete stage.

Special characteristics of the impact pathways involved, and the pathways' importance, with regard to risk analysis

In the Harz, natural pathways and potential impact pathways tend to be connected to deep-reaching fracture and fault zones, as well as to man-made structures connected to those zones: former ore mines, and their excavations, shafts and galleries, some of them left open, and some filled up. In these areas, man-made pathways (pathway group 1) and natural pathways (pathway group 2) overlap. The possibility that brine is ingressing from the Zechstein area into the central mine pits of the Upper Harz has been suggested, highlighting the possibility of hydraulic connections into the forelands. In addition, the springs and artesian wells via which saline water reaches the peripheral areas of the Harz clearly point to pathways and potential differences.

In light of what is currently known, harzards to surface water resources (dams and reservoirs) that are replenished via surface and near-surface water cycles seem unlikely – with the exception of hazards via pathway group 0 – due to the high elevations of the reservoirs in comparison to foreland areas and to the potential depths at which exploitation would take place. At the same time, the possibility of such hazards must be assessed site-specifically in each case. On the other hand, hazards to exploited and exploitable water resources (drinking water, mineral and medicinal water) in peripheral Harz areas cannot be ruled out. In light of the known relevant pathways, and of the brine rises seen, such hazards should be taken into account in any exploration and exploitation of unconventional gas deposits in the Subhercynian Basin or in the Thuringian Basin.

A2.5 Conclusion, and summary of specific site characteristics of relevance for risk analysis

The above remarks relative to selected geological systems and type localities illustrate how diverse the geological and hydrogeological conditions can be in areas in which unconventional natural gas deposits are presumed. At the same time, in keeping with the scale of focus chosen for the present study, the study's analyses remained at an overarching level and were unable to take account of site-specific circumstances. They thus cannot be considered exhaustive. The key specific uncertainties and knowledge deficits prevailing with regard to relevant hydrogeological systems can be identified only through intensive scientific evaluation of all available data (and of additional data that may need to be obtained) and information. Such knowledge gaps will be specific to the regions and sites involved in each case.

It is clear that, in each case, detailed analysis of the pertinent regional hydrogeological system, and of the specific conditions prevailing at the potential site, play an indispensable role in any assessment of the risks related to exploration and exploitation of unconventional natural gas, via hydraulic stimulation. And such analysis must include development of suitably adapted numerical site and region models. Furthermore, the potential relevance of the various possible impact pathways must be reviewed in each individual case. In the process, it can be useful to break down larger regions in terms of geological, hydrogeological and/or use-related criteria (as in the example of the Münsterland Basin).

For the regions studied, the following Table A 4 presents, by way of example, a (non-exhaustive) list of the various special aspects that would need to be considered and assessed more closely in analysis of potential impact pathways, in the context of risk analysis.

In all regions considered, uses that compete with, or would compete with, other underground uses, either exist or can be expected. In the runup to any specific planning, intensive studies, and suitable balancing and description of regional-planning considerations, would be required.

At an overarching level, knowledge deficits are seen especially with regard to the actual target horizons for exploration of unconventional natural gas deposits and with regard to such horizons' positions and functions within the applicable hydrogeological systems.

The key with regard to all systems is to understand the potential distributions for the relevant groundwater resources (such distributions determine the flow directions), the permeabilities of interbedded strata and the locations and functions of possible pathways (faults, old boreholes, etc.). Detailed exploration and cataloguing of continuous faults, and of old boreholes that are important by virtue of their depth, should be carried out as part of all exploratory measures related to unconventional gas deposits.

Tab. A 4: Special issues to be considered in risk analysis relative to selected geological systems

Type of deposit	Region	Subsystem	Special issues to be considered in risk analysis
Tight gas	Northern German Basin	Deposits overlying Zechstein	Geological barriers Existence of continuous faults Permeability of covering strata Distribution of regional groundwater flow systems

Type of deposit	Region	Subsystem	Special issues to be considered in risk analysis
		Deposits underlying Zech-stein	Barrier function / effect of Zechstein deposits Other geological barriers
Coal bed methane gas	Münsterland Basin	Central Münsterland	Permeability of Emscher Mergel marl (including naturally formed gas rises) Permeability and potential deposits of Cenoma-nian/Turonian limestones Existence and relevance of continuous faults Impacts of exploratory boreholes from hard-coal mining
		Mining zone	Scenarios for further use of water resources (development of mine-water drainage, etc.) and its impacts on the hy-draulic system Hydraulic connections to mine-water drainage areas
		Peripheral areas of Münsterland	Impairment of source lines Permeability and potentials of Cenomanian/Turonian limes-tones
Shale gas	Molasse Basin	Western area	Structure of regional groundwater flow systems Groundwater flows rising from deeper aquifers Existence of continuous faults Uses that compete with geothermal energy uses
	Harz Mountains		Position of target horizons Existence and permeability of continuous faults Rising of brine

A3 Exploration, stimulation and exploitation technologies

A3.1 Basic information, and procedures

This chapter explains the mechanical fundamentals of stimulation of deposits via fracking, and describes how fracking is carried out for exploitation of unconventional gas deposits. The primary emphasis of this section is on describing the techniques used for hydraulic stimulation. A general description of deep-drilling technology has not been included; instead, references have been provided, in the Annex, to technical literature that describes that technology.

A3.2 Description of general strategies for exploitation of unconventional gas deposits

The Federal Mining Act (BBergG) differentiates between exploration for mineral resources and exploitation of such resources. While exploration is an activity aimed, either directly or indirectly, at discovering mineral resources, or determining the extent of mineral resource deposits, exploitation is an activity aimed at extracting mineral resources, and it includes all related preparatory, supporting and follow-up activities (cf. Art. 4 (1) and (2) BBergG) (UBA 2011).

The key aspects of exploration and exploitation of conventional and unconventional natural gas deposits include use of horizontal drilling and hydraulic stimulation techniques, as well as the resulting additional risks and requirements (fracking). Horizontal drilling is also routinely used in development of conventional deposits. In the manner in which they are applied, the strategies for exploration and exploitation of unconventional natural gas deposits differ only slightly from those for exploration and exploitation of conventional deposits. In the case of unconventional deposits, special stimulation is required, because of such deposits' low permeability, and, in comparison to exploitation of conventional deposits, larger numbers of boreholes have to be drilled to develop a given deposit cubage.

The overall process of exploration and exploitation of unconventional deposits includes the following phases/aspects, of which only "stimulation" (and related insertion of casing) and "increased water consumption" are fracking-specific and are described in subsequent sections:

- Exploration,
- Site selection and preparation of the well pad,
- Drilling and completion of the well,
- Stimulation,

- Production,
- Restoration of the drilling site / renaturation.

In each case, an exploitation strategy is based on the results of ongoing exploration of the potential target formation, as carried out in the framework of the exploration permits awarded (BGR 2012) (Fig. A 3). Such results are used to select and determine the fracking procedures to be carried out.

Important aspects with regard to the resources/assets groundwater and surface water emerge especially in connection with underground hydraulic stimulation. In particular, such aspects include:

- Water supply and consumption,
- Storage of fracking fluids,
- Protection of surface water, and prevention of any above-ground pollutant discharges and seepage,
- Disposal of flowback and drilling debris, and
- Protection of groundwater.

Site selection for drilling sites forms part of the authorisation procedure, under mining law, for approving operational plans for exploration and exploitation of mineral resources. Existing provisions under the relevant authorization laws take account of residential areas, water protection areas, nature conservation areas, FFH areas, etc.. In comparison to exploitation of gas from conventional deposits, exploitation of unconventional deposits requires significantly larger numbers of boreholes (and, thus, of well pads) for complete-coverage deposit exploitation. As a rule, several boreholes are drilled from a single well pad. This is done by moving the drilling rig to different drilling points within the well pad, with the distances between drilling points amounting to only several meters (cluster drilling).

To protect surface water bodies, and groundwater, from any pollutant discharges above ground, the well pad – and especially those areas where substances hazardous to water are stored – has to be properly sealed. Rainwater has to be collected, cleaned and then managed in conformance with applicable laws (WEG 2006). Well-pad-preparation practices in Germany differ – markedly, in some areas – from those in the U.S., as a result of the official regulations to which operators in Germany are subject.

A3.3 Fracking – best available technology

The term "fracking" denotes a procedure in which fluids are injected, under high pressure, into open borehole sections (i.e. sections without any casing, and with perforated or slit liners). The process is designed to cause fractures to form in the rock, by exceeding the shear resistance of the rock. In deposits with low permeability, fracking thus generates secondary porosities that increase permeability for fluids (liquids and gases). In the most favourable cases, fracking produces a three-dimensional network of widened natural structural discontinuities and artifically produced fractures. Such a network increases the deposit formation's permeability in the vicinity of the borehole (throughout a range of several meters to several hundred meters, depending on the petrophysical properties of the formation). Without artificial stimulation to increase permeability, low-permeability formations cannot be exploited cost-effectively. The process was used for the first time in 1948, to increase the production rates of oil wells in deposits with low permeability (Atkinson 1987)

The hydromechanical components of fracking are also used in other areas, i.e. areas unrelated to development of unconventional deposits. Such areas include stimulation of deep drinking-water wells, creation of underground heat exchangers in use of geothermal energy in hot rocks (HDR – Hot Dry Rock) and in in-situ measurements of ground stresses.

The types of drilling rigs and drilling techniques used in development of unconventional natural gas deposits are largely the same as those that are used in development of conventional deposits. Furthermore, the boreholes tend to be of the same sizes in both cases (drilling depths, lengths). Hydraulic stimulation of a well is carried out after the borehole has been drilled and completed (cf. section A 3.3.2).

One drills a borehole into a natural gas deposit in order to tap the deposit; one wishes the gas in the deposit to flow into the borehole. The fluid mechanical laws governing this process can be quantified, approximately, in two and three dimensions. The basic law governing the process is Darcy's law. Darcy's law applies to the flow of fluids (liquids or gases) in porous media – for example, to the flow of gas in shale. In general, it is applied to all extraction (flow) of fluids from porous media. Equation 1 shows a possible form of the law:

$$q \approx \frac{kh}{\mu} \frac{\Delta p}{\Delta x} \left(\frac{A}{h}\right) \qquad (1)$$

q = Förderrate [m³/s]
k = Permeabilität [m²]
h = Mächtigkeit [m]
μ = Viskosität des Fluids [m²/s]
$\frac{\Delta p}{\Delta x}$ = Potenzialgefälle [-]
A = Fläche [m²]

[Förderrate = extraction rate; Permeabilität = permeability; Mächtigkeit = thickness; Viskosität des Fluids = viscosity of the fluid; Potenzial-gefälle = potential difference; Fläche = area]

The purpose of stimulation of a well via fracking is to increase the well's production rate, by increasing the permeability of the relevant formation.

The mechanical process that leads to fracture formation can be described, in a simplified way, by the Mohr-Coulomb failure criterion (cf. Equation 2). The failure line describes the linear relationship between normal stress and the resulting shear stress (shear resistance) in the shear plane, in the limit state (Fig. A 16).

$$\tau = c + \sigma \cdot \tan \varphi \qquad (2)$$

τ = Scherspannung [Pa]

c = Kohäsion [Pa]

σ = Spannung [Pa]

φ = Reibungswinkel [°]

[shear stress; cohesion; stress; friction angle]

In a Mohr stress diagram (Mohr's circle), such a limit state can be represented via a stress circle and the failure line. The normal stresses in the rock are plotted on the abscissa. The distance between them defines the diameter of the stress circle. The resulting shear stress is plotted on the ordinate. In fracking, fluids are pumped into rock formations, under high pressure. This increases the pore pressures in the rocks and, thus, the total ground stresses. The effective stresses decrease by an amount *p* (Equation 3). In Figure A 16, the reduction of the effective stresses is represented by a blue stress circle.

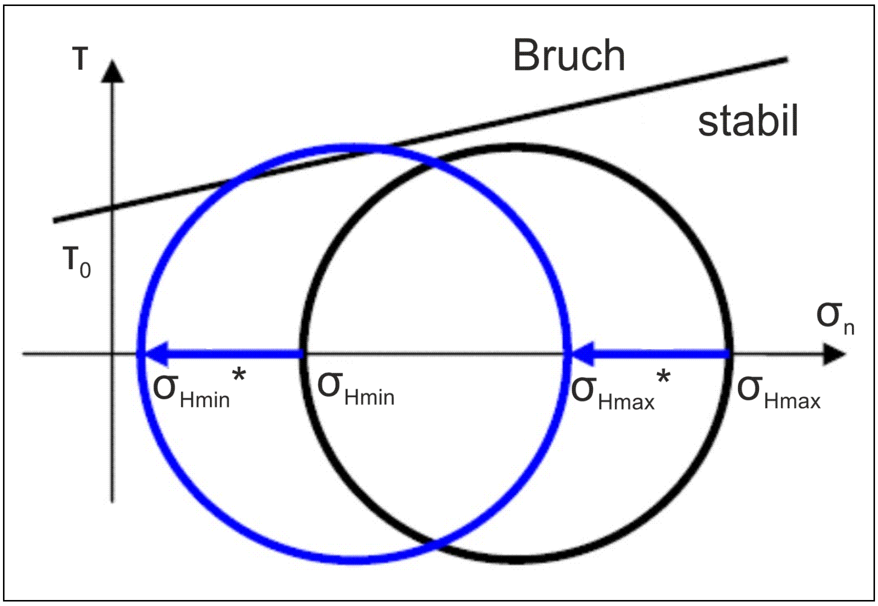

Fig. A 16: Hydraulic inducing of fractures: generation of stresses that exceed the shear resistance. Illustrated with the Mohr-Coulomb failure criterion. Generation of high pore water pressures, via injection of fluids, shifts the stress circle beyond the failure criterion (cf. Equations 2 and 3); τ: Shear stress [Pa], τ_0: Cohesion [Pa], σ_n: Normal stress [Pa], p: Pore water pressure [Pa] (pursuant to Homuth & Sass 2010) [Bruch = failure; stabil = stable]

In bedrock, such stress changes can cause the resistance to brittle fracture (fracture toughness) of joint systems, or of the rock matrix, to be exceeded, thereby creating fractures and/or movement along dividing surfaces (shear fracture) (Fig. A 17). Like the energy of a natural earthquake, the energy released in the process can be measured with seismometers (geophones). In relevant operations, monitoring equipment takes continual energy measurements and records them for later analysis.

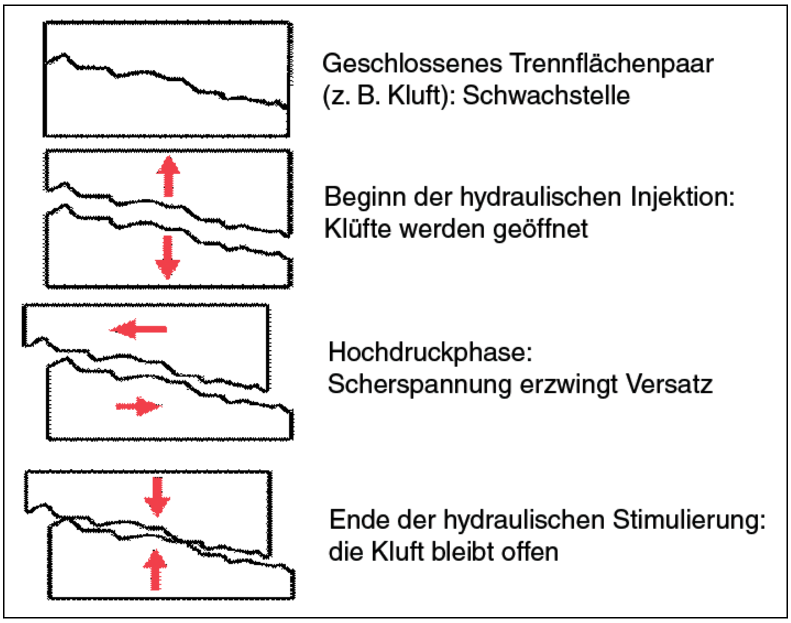

Fig. A 17: Widening of natural dividing-surface pairs via hydraulic stimulation of bedrock (highly simplified depiction) (Homuth & Sass 2010) [from top to bottom: Closed pair of dividing surfaces (such as fissure): weak point; Beginning of hydraulic injection: fissures are widened; High-pressure phase: shear stress causes shifting; End of hydraulic stimulation: the fissure remains open

Many different processes and systems are used in industrial hydraulic stimulation, and such processes and systems are continually being refined. Figure A 18 presents a schematic representation of the aboveground components of such systems. The great diversity of processes and systems is tied to the great diversity of conditions encountered in gas-bearing rock formations. The types of equipment and processes chosen depend on key rock properties, such as permeability and strength, and on the stresses prevailing throughout formations, and the magnitude of such properties and stresses can vary throughout several orders of magnitude. Fracking of horizontal drilling footage is a technique developed on the basis of techniques previously used routinely in vertical and deviated boreholes. While all such techniques rely on the mechanical fundamentals described below (Section A3.3.4), they differ in numerous ways. The different techniques' fracking fluids and proppants differ in basic ways, in terms of types and composition, and the techniques differ in the manner in which they pump fluids and proppants into created fractures, in order to achieve lasting effectiveness (Daneshy 2011, Economides & Nolte 2000).

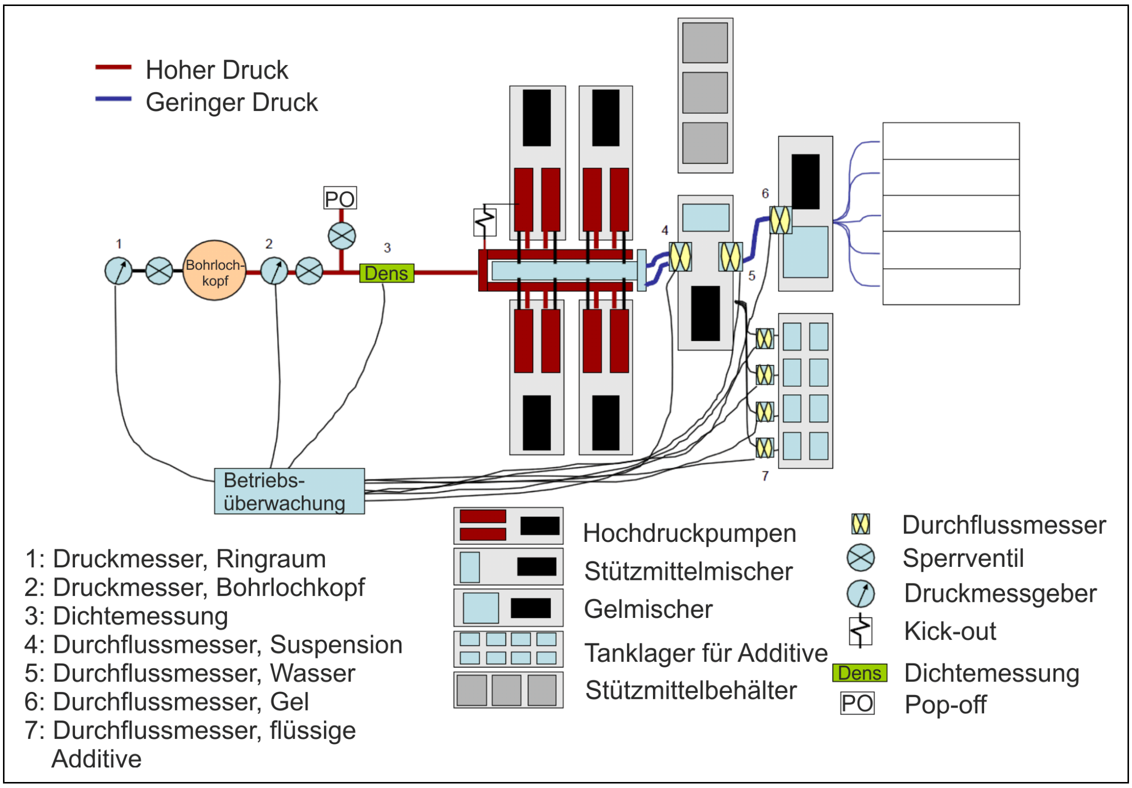

Fig. A 18: Schematic representation of a rig for hydraulic stimulation (kick-out: mechanical or electrical device that switches the rig's high-pressure pumps off at a pre-set pressure level; pop-off: mechanical device that is activated at a pre-set pressure level, in order to prevent damage to equipment, both above and below the ground) (EPA 2011) [by columns, from left to right: High pressure, Low pressure; Pressure meter, annulus; Pressure meter, well head; Density meter; Flow meter, suspension; Flow meter, water; Flow meter, gel; Flow meter, liquid additives; High-pressure pumps; Proppant mixer; Gel mixer; Storage tanks for additives; Proppant containers; Flow meter; Shutoff valve; Pressure meter; Kick-out; Density meter; Pop-off]

The drilling technique used most frequently in development of shale gas deposits is deviated drilling. The resulting boreholes are fracked section-by-section. Fracking in the horizontal section of a borehole begins at the deepest point of the borehole and is carried out in several successive stages of stimulation (Section A3.3.3). During fracking treatments, the sections are isolated from the rest of the borehole by means of packers. In each section, before a hydraulic gradient is applied, numerous perforations are created in the wellbore, leading into the rock formation (clusters). Depending on the rock properties involved, the section of the borehole may be cased, cased and cemented or non-cased. Various techniques also differ with regard to the manner in which perforations are created, as well as to the positions of perforations.

The duration of a single frack is usually no more than just a few hours. In multistage fracking, the total fracking duration is the sum of such stages of fracking. In deep drilling, the process of pulling the drill string out of the borehole – in order, for example, to replace the drill bit – and then reinserting it (a "round trip"), is particularly time-consuming. The unproductive time taken up in such round trips can be considerably reduced through the use of coiled tubing, in which the drill string consists not of sections that are screwed together but of a single length of tubing that can be coiled on a drum.

A3.3.1 Well completion

During drilling, fracking and production, a cemented steel casing is used to isolate groundwater-bearing formations from the fluids circulating within the borehole (drilling fluid, fracking fluids, hydrocarbons). The cementing, which fills the annulus, seals penetrated groundwater horizons off from each other and from hydrocarbon-bearing formations. The dimensions of the borehole casing are selected in keeping with the following factors, to ensure that all operational stresses, during all operational phases, are taken into account:

- Density of the drilling fluids,
- Formation pressure,
- Fracking pressure,
- Landing depths of casing strings,
- Casing diameter,
- Deviation of the drilling path,
- Casing cementation,
- Temperature profile,
- Composition of fracking fluids, the type of proppant used, and the maximum concentration of the proppant,
- The maximum expected fracking pressure,
- Composition and quantities of extracted gas and deposit water.

Casing

Figure A 19 presents a schematic representation of a vertical deep borehole. The casing diameter decreases, in telescoping sections, as the depth increases. Such casing techniques are also used in deviated boreholes with horizontal sections. The conductor pipe is the first wellbore tubular inserted, and it has the largest diameter (usually, 20 to 36") and wall thicknesses ranging from 10 to 20 mm. It prevents cave-ins of near-surface soil and weathering horizons, as well as washing under and undermining of drilling-rig supports. It is inserted, usually through ramming, to a depth at which it reaches sealing layers – usually, 15 to 50 m – and then cemented into the bottom of the cellar shaft (Buja 2011).

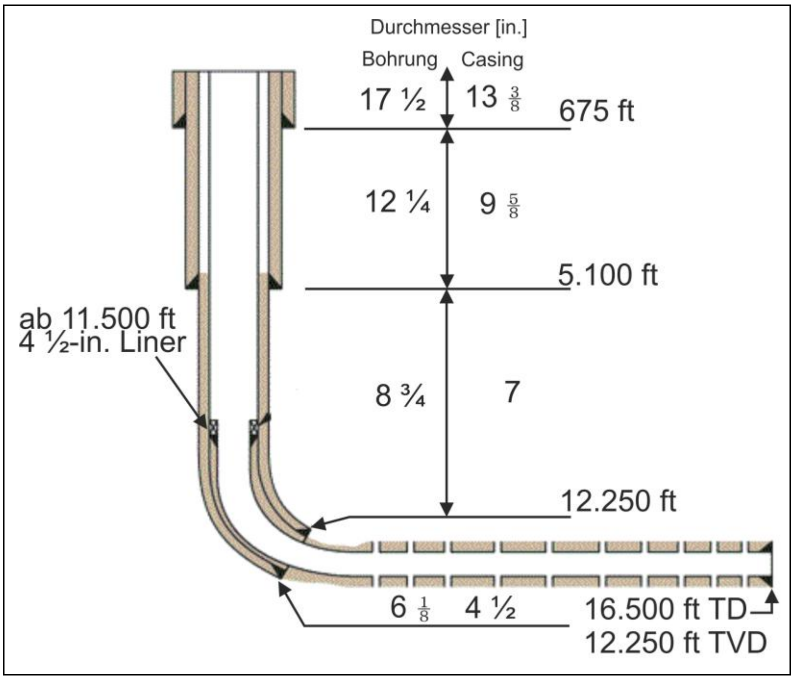

Fig. A 19: Schematic casing diagram of a horizontal borehole (not to scale). TD: Length of the borehole from the starting point (total depth); TVD: Vertical distance from the starting point to the deepest point of the well (true vertical depth); units conversions: 1 ft = 0.3048 m; 1 in. = 2.54 cm (pursuant to Rohwer et al. 2006) [Durchmesser = Diameter; Bohrung = Borehole]

The depth at which the surface casing, which follows next, is set can vary, depending on the geological conditions, between several hundred meters and up to a thousand meters. Its task is to bear the loads exerted by the following strings, as well as to divert reservoir pressures into the formation when the blowout preventer, which is attached to this string, is closed. The higher the expected pressures, the deeper the depth at which it is set, and the thicker its walls will be. The surface casing also serves the purpose of protecting penetrated drinking water aquifers and of preventing circulation losses. The diameters for surface casing normally range from about 13 3/8" to 18 5/8" (33.9 to 47.3 cm) (Buja 2011). The casing strings that are placed between the surface casing and the production casing are referred to as intermediate casing strings. They are used when the surface casing and the production casing are set at widely different depths. Sometimes they are also used because the geological conditions require their use. The sorts of formations that are tricky to drill through, and that thus are sealed off with intermediate casing strings, include salt and clay formations. The length and diameter of intermediate casing strings can vary greatly. Their diameters range from 9 5/8" to 18 5/8"’ (24.4 to 47.3 cm). Their wall thicknesses are chosen in keepnig with the expected pressures. When drilling has penetrated far enough into the deposit, the production tubing is inserted. It serves as the connection between the deposit and the ground surface (and above-ground equipment). Of all tubulars, the production tubing is subject to the greatest pressures and stresses, and when it reaches up to the surface, it is also the longest. Sometimes, a final casing string, that does not reach up to the wellhead, is simply hung from the preceding casing string. In that case (i.e. when the production casing does not extend to the surface), it is referred to as a "production liner". When a production liner is used, the preceding casing string must also have suitable dimensions as a production casing. A liner is hung, with the help of "liner hangers", from the inside of the preceding casing string, with an overlap; the length of such overlaps ranges from 30 to 150 m (Buja 2011).

Cementation

Cement is used in both drilling operations and insertion of well casings, for various purposes involving sealing and supporting/stabilizing of boreholes. Many different types of cementing processes are used. Similarly, many different methods are used to check cementing and determine that the annulus has been properly filled with cement as desired. Where checking of cementing reveals gaps and, thus, indications of possible leakages, such defects can be corrected via additional (and, often, involved and time-consuming) processes (Buja 2011).

Cementing of the casing in a well provides the key barrier against contamination of groundwater-bearing formations via migration/penetration of hydrocarbons, formation water and fracking fluids. In addition, the cement used for this purpose shields casing from corrosive formation water that could appear, and it considerably enhances the stability of the well. In the interest of ensuring that all cement seals function properly, standards have been established for cementing processes (API RP 10B-2 / ISO 10426-2), such as processes for ensuring that the annulus is completely and evenly filled with cement. The relevant API standards include stringent provisions for relevant preparatory work, such as steps to remove filter cakes, as well as provisions on the required quality grades for borehole cement. For specific applications, taking account of the casing string involved, the depth, and the temperature and corrosiveness of occurring formation water, the standards specify the additives that are to be used (such as setting accelerators or retarders) and the quantities of mixing water that are to be used. The important requirements pertaining to the quality of deep-well cements include constant volume during setting (or even volume expansion), since the shrinkage that normal occurs in setting of cement can promote the formation of microannular spaces (Buja 2011).

In most cases, acoustic equipment is used to confirm that the annulus has been completely and evenly filled. Such equipment comprises a transmitter and a receiver. The quality of the bond between the cement and the casing can be determined via the acoustic signal's attenuation and transit time, since the air gap formed by a microannular space tends to swallow some of the signal and thus reduce the quality of the return transmission. The commonly used proceduces include Cement Bond Log (CBL), Cement Evaluation Tool (CET) and the Variable Density Log (VDL) (Buja 2011).

It is not always necessary to fill the annulus with cement all the way to the surface. In every case, however, it is necessary to ensure that the annulus has been filled with cement up to the desired depth. This can be determined via measurement of the heat of hydration, which is given off as the cement hardens. Another method involves mixing a radioactive tracer into the cement and then determining its position, after the cement has set and the heat of hydration has been given off, with the help of gamma ray logging (Buja 2011).

There continues to be a lack of reliable data on the long-term stability of cementations, especially data relative to the thermal and hydrochemical conditions prevailing at the depths at which unconventional gas deposits in Germany are expected.

A3.3.2 Steps involved in fracking

Perforation

The important preparatory steps for hydraulic stimulation include perforating the production string. If the production string is cased and cemented, then perforation through it has to reach into the surrounding rock. Uncased production strings are also perforated prior to hydraulic stimulation as a means of controlling the direction of fracture propagation. Such perforations are commonly carried out with the help of shaped charge perforators (Figs. A 20 and A 21). Such perforators contain recesses filled with explosives and shaped charges. When the explosives are detonated, explosively formed projectiles penetrate the casing and the cement, at high speed, and continue on into the rock. The conical housings of the shaped charges concentrate the detonation energy in a predetermined direction, thereby shaping the charge and producing a projectile of liquid metal. Such projectiles move at a speed of about 30,000 km/h, under pressures of up to 1 million bar (Bellarby 2009). With this technique, multiple perforations per meter are produced simultaneously. To keep the perforations free of rock fragments and projectile remnants, perforation is usually carried out at flushing pressures (mud pressures) lower than the pore pressures prevailing in the formation.

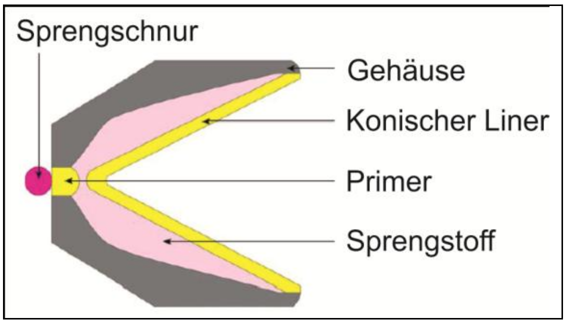

Fig. A 20: Schematic representation of a shaped charge perforator (jet perforator) (pursuant to Bellarby 2009) [Detonating cord; Housing; Conic liner; Primer; Explosive]

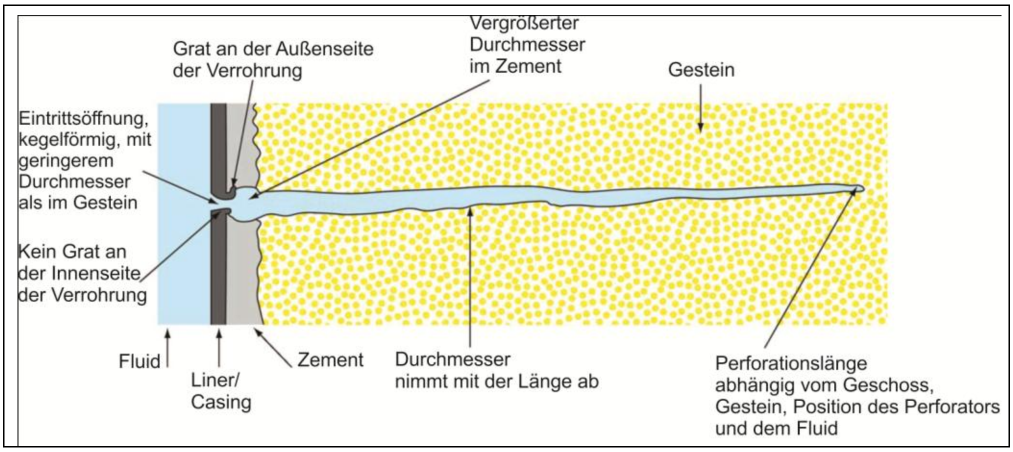

Fig. A 21: Scheme of a perforation produced with a shaped charge perforator (pursuant to Bellarby 2009) [from left to right, by the two "rows": Conically shaped entry opening, with smaller hole diameter than in the rock; Burr on the outside of the casing; Larger diameter in cement; Rock; No burr on the inside of the casing; Fluid; Liner/casing; Cement; Diameter decreases with length; Perforation length depends on the projectile, on the rock, on the position of the perforator and on the fluid]

Extreme Overbalance Perforating (EOP), another perforation technique (Fig. A 22), differs from the previously described technique in that it creates high overpressure, via compressed gas, when the shaped charges are fired. Packers are used to isolate the borehole section in which the shaped charge perforator, along with a fluid, is located. The compressed gas presses the fluid into the perforation with such force that the perforation continues into the rock in the form of a fracture. Rock fragments created via the perforation are pressed into the fracture, where they keep the fracture from closing as soon as the pressure drops. Due to the short duration of the action, and the small volume of material pressed into the fractures, the fractures are shorter and narrower than those produced via high-volume hydraulic fracturing (HVHF). Nonetheless, this process serves as a transition to hydraulic stimulation with use of fluid additives, although the stimulation involved is confined to the close proximity of the borehole (Bellarby 2009).

Erosion perforation is an alternative to shaped charge perforation. An erosion perforator consists of nozzles, at the end of the coiled drilling string, through which water carrying quartz sand is pumped at high pressure. The amounts of sand added range from about 30 to 50 kg/m³, while the exit velocity at the nozzles is about 200 m/s. In most cases, this procedure is used in open, uncased borehole sections (Neu & Gedzius 2009).

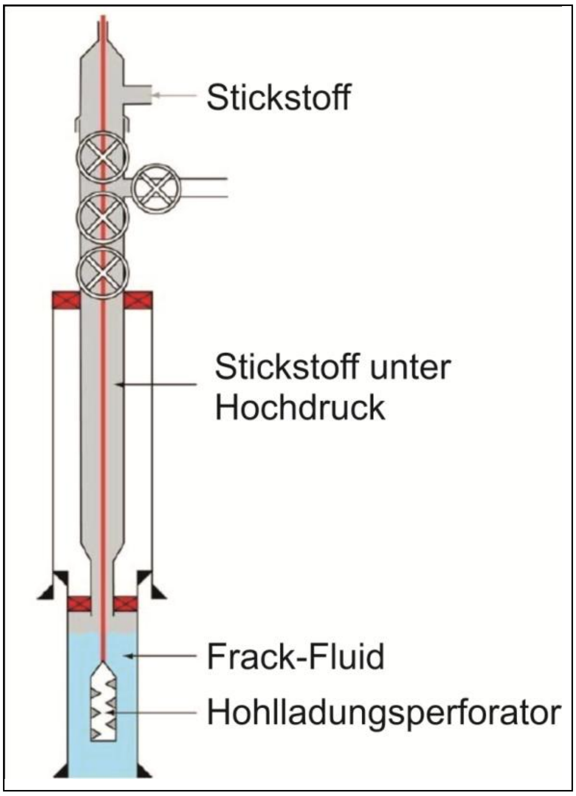

Fig. A 22: Scheme for extreme overbalance perforating (pursuant to Bellarby 2009) [From top: Nitrogen; Nitrogen under high pressure; Fracking fluid; Shaped charge perforator]

Fracking

Fracking generally involves pumping a fluid at a higher rate into the borehole than the fluid can exit the borehole via infiltration into the rock. As a result, the pressure on the rock increases to a point at which the rock begins to fracture. Centrifugal pumps are used to mix and transport fracking fluids, at low pressures, to the sites at which they are needed. High-pressure displacement pumps then transport the mixed fluids (suspensions) into the borehole.

A frack is divided into the following "stages" (phases) (Fig. A 23):

1. Acid stage: Diluted acid (HCl) is used to clean the borehole of cement residues in the area of the perforated casing, to dissolve carbonates and to break open and widen existing fissures (cleavages and crevices) in the area immediately around the borehole.
2. Pad stage: Fracking fluids, with friction reducers (Chap. A4), are injected, without proppants, at gradually increasing pressures and injection rates. This initiates fracture formation.
3. Prop stage: In this stage, after fracture formation has been initiated, gradually increasing concentrations of proppants, in suspension, are added to the fluids. As fluids infiltrate into the rock, the concentration of the suspension increases as it flows into the fractures, since the proppants cannot infiltrate and thus remain behind, in suspension. The aim in this stage is to fill fractures evenly with proppants. The suspension with the lowest proppant concentration, namely the suspension with which the prop stage is initiated, moves farthest into the fractures and thus loses the most fluid via infiltration into the rock. At the end of the prop stage, a highly concentrated suspension is injected.
4. Flush stage: This stage has the purpose of flushing any proppants remaining in the borehole into the fractures. Water is used for this purpose.

After these stages have been completed, fluid injection is terminated, and the borehole is closed (shut-in) for a time. As a result of continuing infiltration into the rock, the pressure gradually decreases, and fractures close to the extent permitted by the proppants. In each case, fracking fluids are mixed, and used, in accordance with the requirements for the specific deposit in question, and fluids are adjusted suitably as fracking progresses.

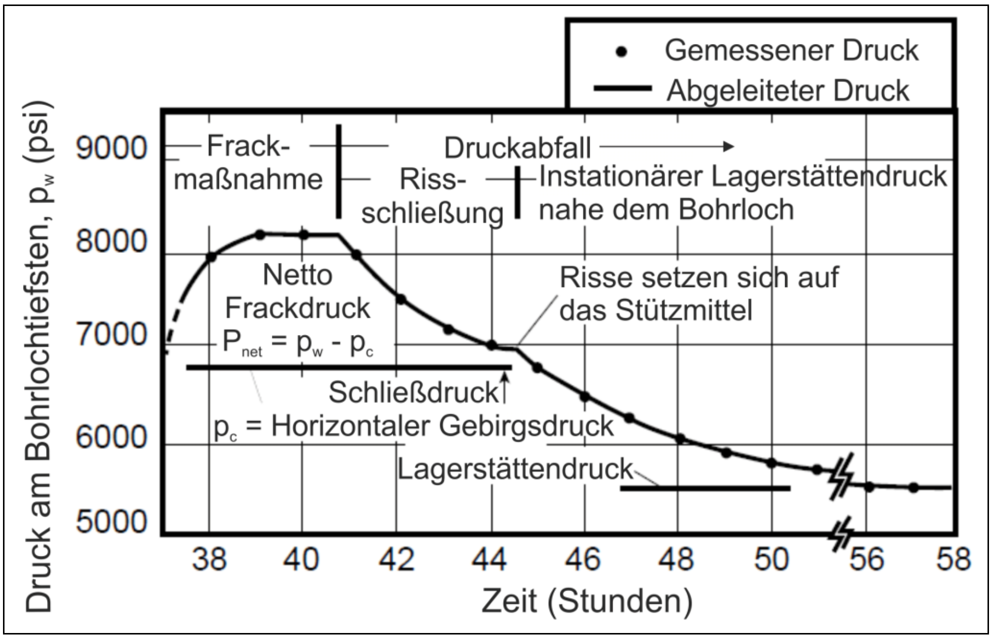

Fig. A 23: The different phases of a frack (pursuant to Economides & Nolte 2000) [y axis: Pressure at the deepest point of the borehole; x axis: Time (hours); Gemessener Druck = Measured pressure; Abgeleiteter Druck = Derived pressure; Frackmaßnahme = Frack; Netto-Frackdruck = Net fracking pressure; Rissschließung = Fracture closure; Druckabfall = Pressure drop; Instationärer Lagerstättendruck... = Transient pressure in the deposit, near the borehole; Risse setzen sich auf ... = Fractures collapse onto proppant; Schließdruck = Closure pressure; Horizontaler Gebirgsdruck = Horizontal overburden pressure; Lagerstättendruck = Formation pressure]

Dual-injection process

In this process, the fracking fluids are pumped into the borehole through two separate lines: one within the drill string (for example, a coiled drill string) situated within the cased borehole, and one in the annulus between the drill string and the borehole casing. The drill string may be of the conventional screwed variety (rather than being coiled tubing, which is more efficient). Fracking fluids flow in both lines (within the drill string and the above-described annulus), but the proppant suspension is pumped (for example) only through the inner line (within the drill string), while the fracking fluid in the annulus contains no proppants. By varying the pumping rates in the two lines, one can adjust the proppant concentration directly within the section being fracked, and virtually at a moment's notice (Daneshy 2011).

A3.3.3 Propagation of hydraulically induced fractures

The key factor that determines the directions in which fractures propagate is the stress field prevailing in the reservoir. That field can be described with three vectors: one vertical and two horizontal. Fractures tend to propagate perpendicularly to the direction of the lowest stress (Hubbert & Willis 1957) (Fig. A 24). The decisive parameters in each case are the directions and the contributions of the various stresses. In most cases, the direction of lowest stress will be in the horizontal plane, and that is conducive to vertical fracture propagation (Lyons & Plisga 2005). In each case, there is an optimal orientation, depending on the prevailing stresses, for the horizontal borehole at which the pressure required for fracture formation is minimized (Hossain et al. 2000).

Several different mechanical processes are involved in fracture formation. Overcoming the rock's shear resistance is the most important process for opening new fractures. The pressure required to open new fractures is equal to the sum of a) the smallest horizontal stress and b) the shear resistance of the rock. Lower pressures tend to suffice to widen existing, open fissures. For such purposes, only the ground stresses acting perpendicularly to the fissure surface have to be overcome, by the fracking pressure; this causes shearing off (Schulte et al. 2010; Pine & Batchelor 1984) (cf. Fig. A 17). The pressure of the injected fluid reduces the normal stress on the fissure surface, without significantly affecting the shear stress. The mechanism for fissure widening thus begins with a shearing-off component along natural fissure systems (Baria et al. 1999).

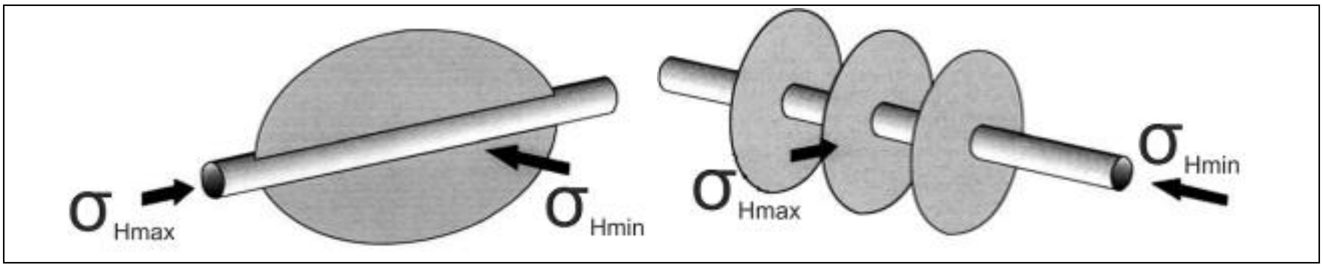

Fig. A 24: Fracture propagation as a function of the borehole's orientation with respect to the main directions of stress The following relationship holds: $\sigma_{vertical} > \sigma_{Hmax} > \sigma_{Hmin}$ (Crosby et al. 2002)

The stress state within the reservoir can be determined directly, via studies with test drilling, or indirectly, through approximation methods based on mechanical properties of rock (cf. Equation 4). Such approximations without any direct measurements are subject to high degrees of uncertainty, however. The horizontal stresses are governed by large-scale tectonic processes, while the vertical stress is caused largely by the load of the overburden and increases proportionally with depth. It can be calculated with Equation 4, although the actual stress may be higher, as a result of geological factors, than the results obtained with that equation would suggest.

$$\sigma_V = \int_0^H \rho\ g\ dH \qquad (4)$$

σ_V = Vertikale Spannung [Pa]
ρ = Dichte [kg/m³]
g = Erdbeschleunigung [N/kg]
H = Mächtigkeit [m]

[Vertikale Spannung = Vertical stress; Dichte = Density; Erdbeschleunigung = Earth's gravitational force; Mächtigkeit = Thickness]

Along with the in-situ stress field, the mechanical properties of the reservoir rock play a decisive role. In addition to shear resistance, the most important such properties include the modulus of elasticity E, the shear modulus G and the Poisson ratio v (transverse contraction). Such properties can be determined via laboratory tests with rock samples. From any two of them, one can calculate all other mechanical rock properties, via simple relationships. The values relate to each other as follows:

$$G = \frac{E}{2\ (1+v)} \qquad (5)$$

G = Schubmodul [Pa]

E = Elastizitätsmodul [Pa]

v = Poissonzahl [-]

Normally, the mechanical rock properties modulus of elasticity (E) and Poisson ratio (v) are estimated from dipole sonic log data. The in-situ stresses can be calculated from those data.

$$\sigma'_{Hmin} = \frac{\nu}{1-\nu} \sigma'_{v} \quad (6)$$

σ'_{Hmin} = Effektive minimale Horizontalspannung [Pa]

ν=Poissonzahl [-]

σ'_{v} =Effektive vertikale Spannung [Pa]

[Effective minimum horizontal stress; Poisson ratio; Effective vertical stress]

An upper limit for the pressure required for fracture formation can be calculated in accordance with the Terzaghi failure criterion (Lyons & Plisga 2005):

$$p_b = 3\,\sigma_{Hmin} - \sigma_{Hmax} + T_0 - p \quad (7)$$

p_b = Frackdruck [Pa]

T_0 = Zugfestigkeit des Gesteins [Pa]

p = Porendruck [Pa]

[Fracking pressure; Rock tensile strength; Pore pressure]

Before a frack is carried out, the fracture propagation is simulated with the help of mathematical models, and as a function of rock parameters, stress state and fracking pressure. In the following, two early models for calculation of fracture geometries are presented. Theoretical models for calculation of fracture propagation are generally based on the assumption that fractures will propagate symmetrically around the borehole axis, in patterns of mutually opposing directions. In such models, the geometry of a fracture is described in terms of a length x, a width w and a height h (Fig. A 25). The width is normally several orders of magnitude smaller than either the height or the length.

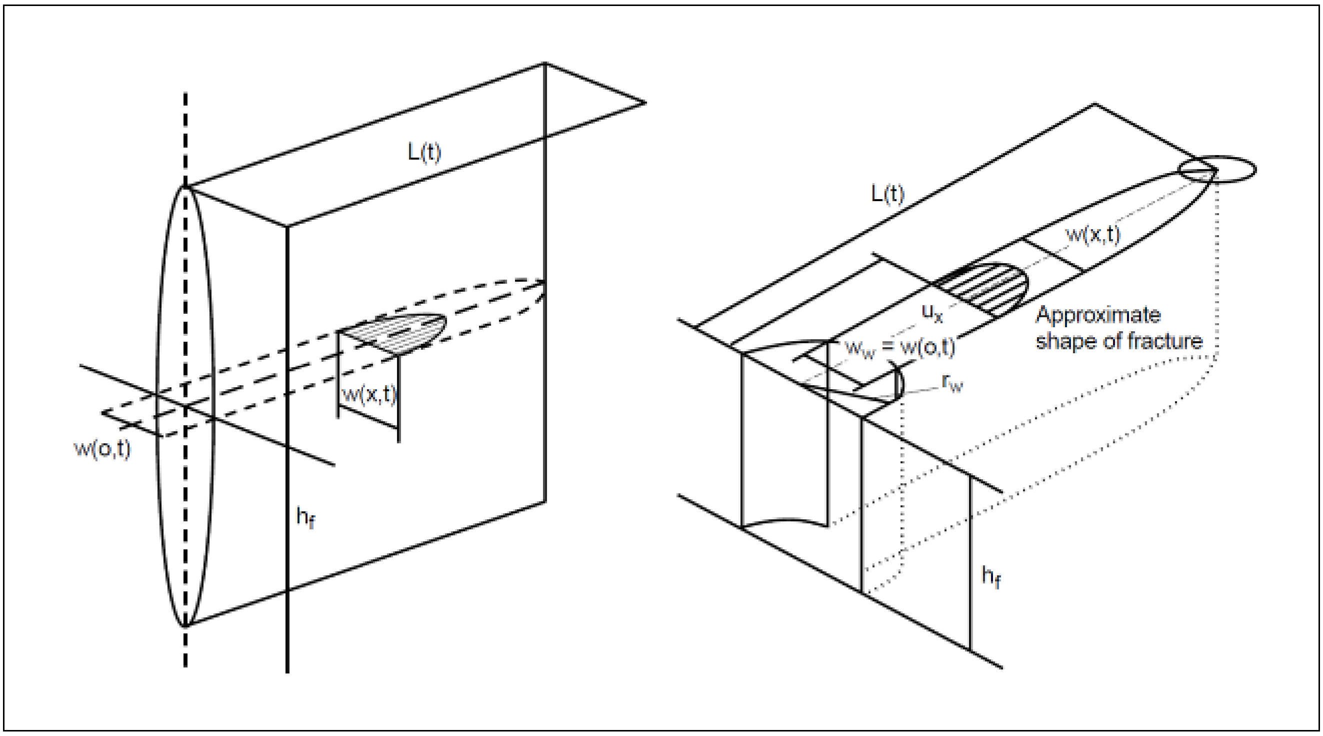

Fig. A 25: PKN (left) and KGD (right) (Economides & Nolte 2000)

Hydraulically formed fractures are modelled on the basis of principles formulated by Perkins & Kern (1961) and Khristianovich & Zheltov (1955). The resulting models calculate fracture geometries – especially their width, for a given length and flow-through rate – without assuming volumes in equilibrium. Geertsma & de Klerk (1969) and Nordgren (1972) expanded the models of Khristianovich & Zheltov (1955) and of Perkins & Kern (1961). Those models, the "PKN model" (Perkins & Kern 1961, Nordgren 1972) and the "KGD model" (Geertsma & de Klerk 1969), were the first to include both volume analysis and mechanical analysis of the solid bodies involved. The basic assumption for both models is that fracture propagation in a homogeneneous, isotropic and linearly elastic solid body, and assuming an even state of stress, is planar, and perpendicular to the smallest main stress. The fracking fluid is assumed to be Newtonian. The PKN model considers a fracture, of limited height, with an elliptical cross-section both perpendicular to the length and perpendicular to the height (Fig. A 25). The fracture width depends on the height and the length. In the KGD model, the fracture width depends solely on the length. As a result, the cross-section perpendicular to the length is rectangular, while the cross-section perpendicular to the height is elliptical (Geertsma & de Klerk 1969).

The two models are not compatible with each other. They differ in the assumptions they use in order to translate the three-dimensional problem into a form that lends itself to two-dimensional analysis. The PKN model is suitable, for example, for modelling fracture propagation in formations that are confined by overlying and underlying rocks that tend to limit fracture propagation. The KGD model can provide approximations for relatively unlimited growth of fracture height and for limited fracking measures.

The models are being continually improved, in order to take account of additional factors such as infiltration of fracking fluids into the rock (Valko & Economides 1995, Economides & Nolte 2000).

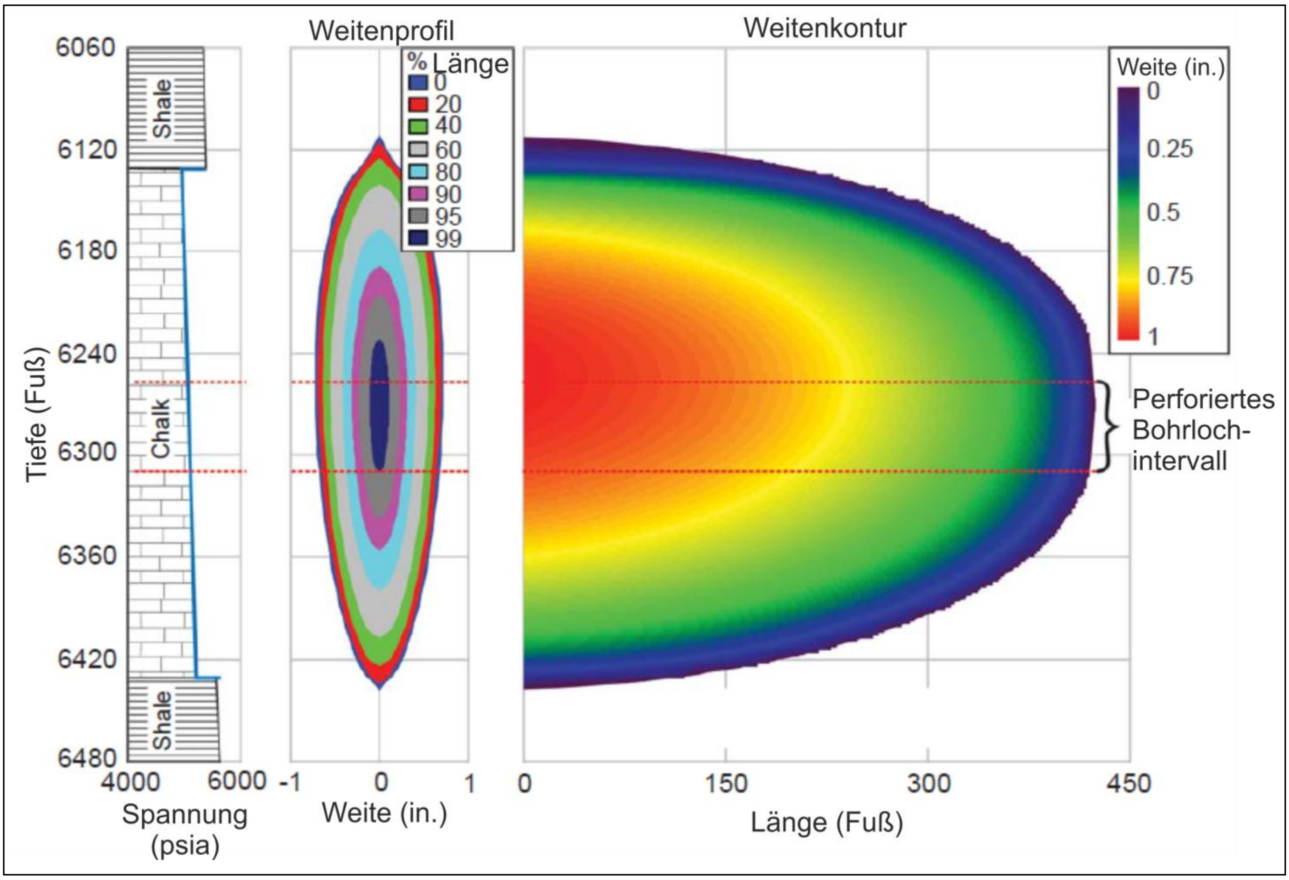

Fig. A 26: Sample result of a three-dimensional simulation of fracture propagation in chalk between shale layers: Depiction of fracture geometry at the end of a frack, before fractures collapse onto the proppant (pursuant to Bellarby 2009) [y axis: Depth (feet); x axis; Pressure (psia); Width (in.); Length (feet); top: Width profile; Length; Width contour; Width (in.); right: Perforated borehole interval]

A3.4 Uncertainties / knowledge deficits

Drilling techniques and well-pad layouts/design are subject to a range of standards and legal provisions. These include the Länder ordinances on deep-drilling (Tiefbohrverordnungen der Bundesländer – BVOT) and various technical guidelines and industry standards (WEG 2006). The issue of the extent to which such standards and regulations can be applied to the new requirements involved (such as cluster drilling, multilateral drilling, etc.), or may need to be supplemented, has to be reviewed.

No generally binding technical requirements exist relative to the techniques used to complete a well for exploration and exploitation of unconventional natural gas deposits via hydraulic stimulation – for example, requirements pertaining to cementing. The dimensions of casings and well cementation are determined on the basis of existing regulations, taking account of the stresses caused via the planned/applied fracking pressures (WEG 2006). In some cases, operators apply their own safety standards in this area. No consistent, binding (national) requirements and standards are yet in place.

In addition, no studies have been carried out to date of the long-term integrity of casings and cementation. The experience gained from 30 years of tight gas exploitation in Lower Saxony is of limited use, since, to our knowledge, no specific monitoring of the leakproofness of cementation in such wells has been carried out.

Models for forecasting fracture orientation and extent exist and are continually adapted in keeping with new findings. In fracking, fracture formation is now controlled primarily through the pressure applied via the fracking fluid, while monitoring of fracture extent is carried out geophysically, with the help of geophones. However, there are no binding requirements specifying the degree of accuracy with which the position and orientation of fractures is to be predicted and determined.

A4 Fracking fluids

The hydraulic medium used in hydraulic fracturing, i.e. the medium used to apply pressure to rock strata, to induce fracture formation, is referred to as "fracking fluid". Normally, proppants (quartz sand or ceramic particles) are introduced, with the fracking fluid, into the fractures formed in the rock. Their function is to keep the fractures open, against the overburden pressure, to ensure that the created pathways remain open during the production phase, so that natural gas will readily flow into the production well. Fracking fluids also contain other additives, with functions such as facilitating transport of proppants into fractures; preventing deposits, microbial growth, formation of hydrogen sulfide and swelling of clay minerals within the frack horizon; preventing corrosion; and minimising fluid friction at high pump power.

Normally, when fracking pressure on the gas-bearing formation is relieved, only some of the injected fracking fluid – along with formation water and the natural gas flowing into the borehole – is brought back to the surface, as part of "flowback".

Fracking fluids are divided into four groups, by carrier fluid (Fink 2012):

- Water-based systems, usually containing gelling agents to increase viscosity and enhance proppant transport; slickwater fluids are water-based fluids that are optimized, with added friction reducers, for high pumping rates at low fluid viscosities and, thus, relatively low proppant concentrations.
- Foam-based systems, consisting of water-gas emulsions; they are produced with foaming agents, with the help of inert gases such as nitrogen (N_2) or carbon dioxide (CO_2);
- Oil-based systems (usually built around diesel oil, whose viscosity can be increased via additives), which are sometimes used in water-sensitive formations with swellable clay minerals;
- Acid-based systems (usually built around hydrochloric acid) for stimulation of low-permeability, acid-soluble formations such as limestone or dolomite.

The fracking measures carried out to date in unconventional deposits in Germany have relied largely on water-based fluid systems and, to a lesser extent, on foam-based systems. According to selected operators, plans relative to potential fracking measures in shale gas and coal bed methane deposits generally call for use of water-based fracking fluids. As a result, only that type of fracking fluids is considered in the following.

The following sections first provide an overview of the fracking additives used in water-based and foam-based systems, including the purposes of the various additives. They also describe the criteria used to select additives for specific deposits. Then, the available information about the fracking fluids used in unconventional deposits in Germany is evaluated, and possible future trends / developments are presented.

No translation has been included of the extensive Annex, to which frequent reference is made in the following. The Annex is thus available only in German.

A4.1 Overview; product functions

Services related to selection of suitable recipes, to production of fracking fluids and to actual execution and monitoring of fracks are provided by specialised services companies that usually operate globally (service contractors). Service contractors offer a range of special products for production of fracking fluids. In each case, the fracking fluid is usually prepared directly at the well-pad, via mixing with water.

In the following, a distinction is made between prepared fracking products (products produced by fracking-services companies that are sold under brand names and that usually are mixtures of various different chemicals) and fracking fluids (the fluids that are injected into wells; they are usually prepared by combining several prepared fracking mixtures with water). "Fracking additives" refers to all substances that are mixed with a carrier medium and injected, as part of the fracking fluid, into the well.

Water-based fracking fluids are mixtures of water (80 - 95 %) and proppants and other additives. Proppants are added in fractions accounting for 5 % to more than 30 % by weight. Additives usually account for fractions between 0.2 and more than 10 % by weight. Additives are used for a wide variety of different purposes (Tab. A 5). Often, depending on the fluid system being used and the conditions in the deposit, only a selection of the additives / additive groups listed in Table A 5 will be needed.

In some cases, additives are used sequentially in the fracking process (US EPA 2011). In a first step, acid pre-treatment may be used to remove cement or remnants of drilling fluids from sections with perforated casing. Along with acids, corrosion inhibitors or iron control agents will be used, to prevent rusting and precipitation. When the fracking pressure is applied, fluids with friction reducers are used, to optimize pumping rates. As soon as proppants are added to the fracking fluid, other additives, such as gelling agents and crosslinkers, may be added as well, to enhance proppant transport. In the process, fine-grained proppants are usually added first, since they penetrate the farthest into fractures. Coarser-grained proppants are added afterwards. In a final step, encapsulated breakers may be added to reduce the viscosity of the fluid, to support proppant deposition within fractures and to enhance the return flow of the fracking fluid (US EPA 2011).

Tab. A 5: Functions of the different types of additives added to fracking fluids (pursuant to UBA 2011a, Tyndall Centre 2011, NYSDEC 2011, US DOE 2009).

Additive	Function
Proppants	Keeping rock fractures created through fracking open
Scale inhibitors	Preventing deposits of poorly soluble precipitations, such as carbonates and sulfates
Biocides	Preventing bacterial growth, biofilms and formation of hydrogen sulfide via sulfate-reducing bacteria
Iron control	Preventing iron-oxide precipitation
Gelling agents	Improving proppant transport
High-temperature stabilizers (temperature stabilizers)	Preventing early gel decomposition at high temperatures within the target horizon
Breakers	Reducing the viscosity of gel-containing fracking fluids for depositing proppants
Corrosion inhibitors	Protecting against corrosion of equipment
Solvents	Improving the solubility of additives
pH regulators and buffers (pH control)	Adjusting the pH levels of the fracking fluid
Crosslinkers	Increasing viscosity at higher temperatures, to improve proppant transport
Friction reducers	Reducing friction within fracking fluids
Acids	Pretreating perforation intervals of the borehole, and cleansing them of cement and drilling mud; dissolving acid-soluble minerals
Foams	Supporting proppant transport
H_2S scavengers	Removing toxic hydrogen sulfide, to guard against equipment corrosion
Surfactants	Reducing surface tension of fluids
Clay stabilizers	Reducing swelling and deposition of clay minerals

Proppants

Proppants serve the purpose of keeping the fractures open that are created during hydraulic fracturing, in order to provide the permeability needed for the production phase. Commonly used proppants include quartz sand, of various grain sizes. Ceramic products and sintered bauxite are also used. To improve proppant retention in fractures, in some cases proppants are used that have been coated with epoxy or phenolic resins or other, similar coatings (Fink 2012).

Scale inhibitors

Scale inhibitors are used to inhibit precipitation of poorly soluble salts such as carbonates and sulfates (barium sulfate, for example), which tend to reduce permeability. A range of different substances are used for this purpose, including ammonium chloride, ethylene glycol, polyacrylates and various phosphonates (Fink 2012).

Biocides

Biocides are added in order to inhibit the growth of bacteria that could reduce permeability (by forming biofilms) or form toxic or corrosive gases (expecially hydrogen sulfide, H_2S) (Tyndall Centre 2011, NYSDEC 2011). The biocides in use include a mixture of 5-chloro-2-methyl-2H-isothiazol-

3-one and 2-methyl-2H-isothiazolin-3-one (sold under the trade name Kathon®).

Iron control agents

These chemicals have the purpose of inhibiting precipitation of ferrous minerals in the formations to be fracked, especially in cases in which acid pre-treatment takes place. The substances that are frequently used for this purpose include citric acid and ethylenediaminetetraacetate, which are able to form iron complexes.

Gelling agents

Gels are used to increase viscosity in the fracking fluid, in order to enhance proppant transport into fractures. The commonly used gelling agents include polysaccharides such as guar derivatives (e.g. carboxymethyl guar, hydroxyethyl guar, hydroxypropyl guar) and other cellulose ethers such as methylcellulose, carboxymethyl cellulose and hydroxyethyl cellulose. In addition, synthetic polymers such as acrylamide copolymers and vinyl sulfonates are used.

High-temperature stabilizers

Stabilizers, such as sodium thiosulfate, are used to prevent premature decomposition of gels in the borehole.

Breakers

Breakers, which are designed to break down gel structures, are used to reduce the viscosity of fracking fluids in connection with use of gel systems, in order to improve proppant deposition in created fractures and to enhance fluid recovery. The group of breakers includes substances such as ammonium persulfate, sodium persulfate, sodium bromate and enzymes; selection of breaker in each case depends on what gelling agents have been used used.

Corrosion inhibitors

Corrosion inhibitors are used to protect equipment such as casing and tanks when acids are added. The corrosion inhibitors commonly used in fracking operations include methanol, isopropanol, porpargyl alcohol and ammonium salts (NYSDEC 2011).

Solvents

Solvents are used to improve the water solubility of added additives. The solvents used include 2-Butoxyethanol and isopropanol.

pH buffers and pH regulators

A range of substances are used to adjust and buffer acidity, such as aliphatic acids, sodium hydroxide and sodium bicarbonate.

Crosslinkers

Crosslinkers further increase fluid viscosity by linking the gelling agents used. Crosslinkers are chosen in keeping with the gelling agents used; the commonly used crosslinkers include borate salts, 2,2',2''-Nitrilotris[ethanol] and organozirconium compounds.

Friction reducers

Friction reducers reduce friction within fracking fluids, thereby reducing the energy required to apply the fracking pressure. The substances used for this purpose include polyacrylamides, glycol ether and petroleum distillates.

Acids

Sometimes, perforation intervals of cement and drilling muds have to be cleaned, prior to the actual fracking process, in order to improve access to the rock formation. Such cleaning (pre-treatment) is accomplished with the help of acid. In most cases, concentrated mineral acids such as hydrochloric acid are used for this purpose.

Foams

In foam-based fracking fluids, proppants are transported by foams produced from water and carbon dioxide or nitrogen. The foaming agents used for this purpose include tertiary alkylamineethoxylates, coco betain and alfa olefin sulfonates (Fink 2012).

H_2S scavengers

H_2S scavengers help to prevent equipment corrosion resulting from reactions with hydrogen sulfide, which occurs in concentrated form in the natural gas contained in "acid gas reservoirs". The substances used for this purpose include aromatic aldehydes.

Surfactants

Surfactants reduce surface tension in fluids, thereby enhancing the wettability of contact surfaces and facilitating formation of additive-water emulsions. The substances used for this purpose include alcohol ethoxylates and nonylphenol ethoxylates.

Clay stabilizers

Clay stabilizers are used to prevent swelling of clay minerals upon contact with aqueous fluids, and migration of such minerals, since such swelling and migration reduces permeability by tending to block pore spaces. For this purpose, potassium and ammonium salts, or quaternary ammonium compounds, are used; such cations prevent clay minerals from swelling by migrating into the minerals' intermediate layers.

A4.2 Criteria for selection of fracking additives

Composition of fracking fluids, and the types and numbers of additives used in them, vary in keeping with the expected conditions in the gas-bearing formation. Frequently, additives are selected specifically for individual wells. A number of technical issues, as well as criteria resulting from chemicals laws, have to be taken into account in selection of suitable additives.

A4.2.1 Technical requirements

Fracking additives are selected especially in accordance with the required fluid viscosities; the pressures and temperatures prevailing in the gas-bearing formation; the mineralogical, geochemical and petrophysical composition/characteristics of the target horizon; the hydrochemical composition of the formation water; and the risks of causing damage to the formation. Additive quantities are chosen in keeping with prevailing temperatures. Special additives become necessary in deep formations with higher in-situ temperatures (cf. US EPA 2004). As a rule, foam-based systems are used only in formations with lower pressures, at drilling depths of less than 1,500 m (cf. US EPA 2004).

The resources used to support site-specific design of fracking fluids, and selection of additive types and concentrations, in keeping with deposit characteristics and project requirements, include key data obtained through experience, decision matrices, flow charts and/or computer-based expert systems (US EPA 2004; Halliburton 2008; Fink 2012). In some cases, modelling programmes are used to simulate fracking processes, taking account of the deposit characteristics, in order to determine requirements pertaining to fluid composition and characteristics, to the required proppant quantities and to relevant operational parameters (pumping rates, pressure levels, etc.). In exploration of new deposits, sometimes laboratory tests are carried out with rock samples, and at the temperatures and pressures prevailing in the deposit, in order to identify suitable recipes (Rickman et al. 2008).

Halliburton (2008) compares different types of fracking fluids for coal bed methane deposits, in light of aspects such as costs, formation damage and proppant-placement effectiveness (Tab. A 6).

Tab. A 6: Assessment of different fluid systems for stimulation of coal bed methane deposits (Halliburton 2008)

	Cost	Formation Damage	Proppant Placement	Propped Length
Water w/o proppant	Good	Good	Poor	Poor
Water w/ proppant	Good	Good	Poor	Poor
Linear gel	Fair	Poor	Fair	Fair
Crosslinked gel	Fair	Poor	High	High
Nitrogen foam	High	Good	Good	Good

US EPA (2004) refers to the flow charts developed by Economides & Nolte (2000) for selection of fracking fluids and proppants. Those charts focus especially on the pressures and temperatures prevailoing in deposits (Fig. A 27 and Fig. A 28).

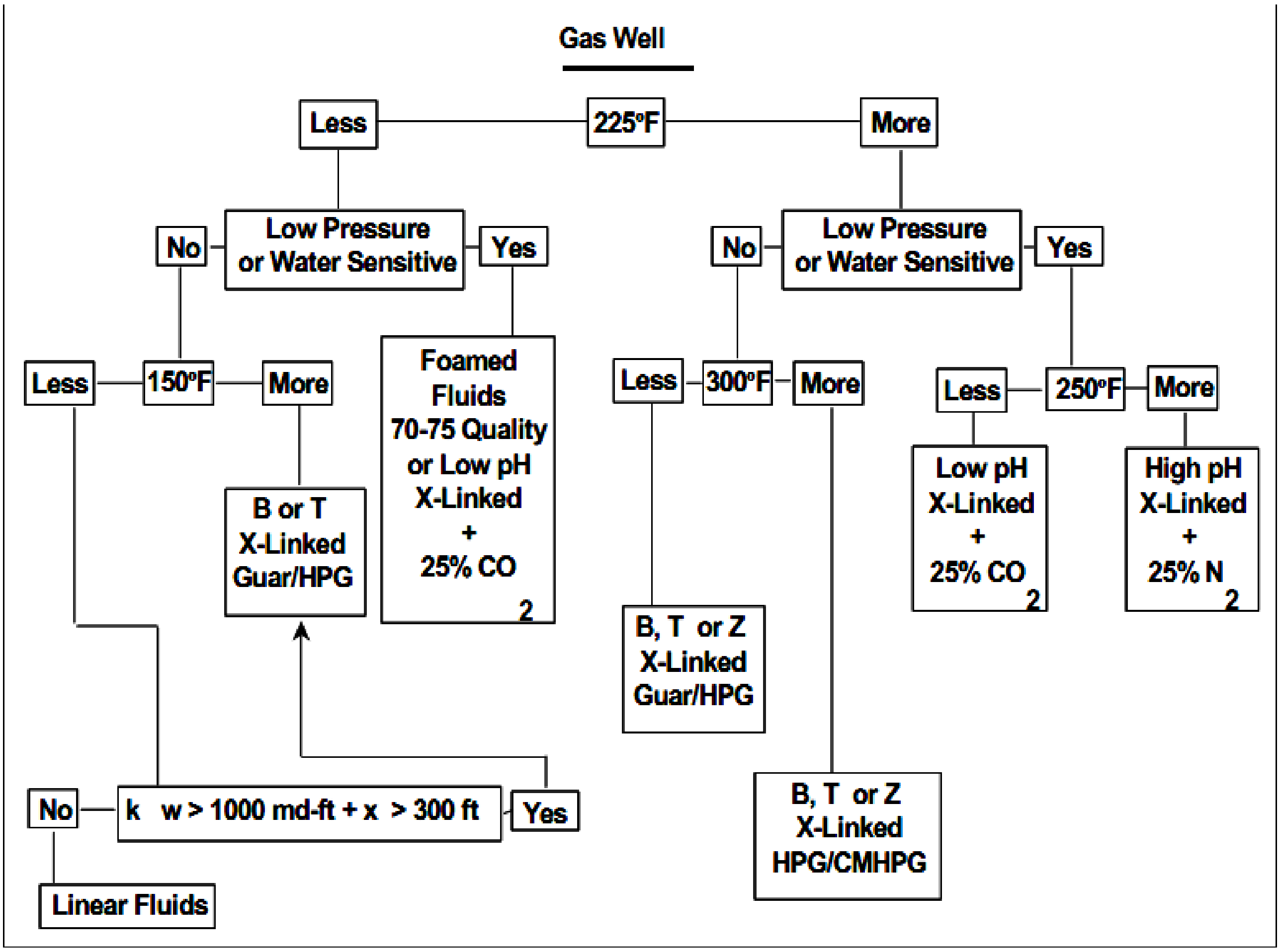

Fig. A 27: Flow chart for selection of fracking fluids
(Economides et al. 2000, cited in US EPA 2004). 225 °F is equivalent to 107 °C

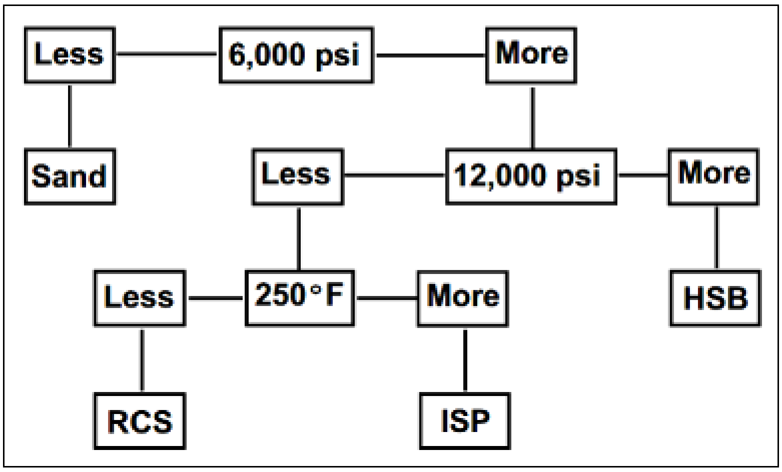

Fig. A 28: Flow chart for selection of proppants (RCS: resin-coated sand, ISP: intermediate strength proppant, HSB: high-strength bauxite; Economides et al. 2000, cited in US EPA 2004)
6,000 psi is equivalent to 414 bar. 250 °F is equivalent to 121 °C.

Rickman et al. (2008) use simple correlations between petrophysical parameters (especially brittleness and fracture behaviour) as a means for optimising selection of fracking fluids for various shale gas deposits (Fig. A 29).

Rock brittleness	Fluid system	Frack geometry	Fluid volume	Proppant quantity
70 %	Slickwater		High	Low
60 %	Slickwater			
50 %	Hybrid			
40 %	Linear gel			
30 %	Foam			
20 %	Cross-linked gel			
10 %	Cross-linked gel		Low	High

Fig. A 29: Selection of fracking fluid systems for shale gas deposits, as a function of rock brittleness (pursuant to Rickman et al. 2008)

A4.2.2 Requirements under chemicals law

Along with technical requirements, a wide range of requirements under chemicals law affect selection of suitable additives. These especially include prohibitions and restrictions on use of substances and mixtures, requirements pertaining to biocidal products, requirements under the REACH Regulation, requirements under mining laws and requirements under the Ordinance on Hazardous Substances (Gefahrstoffverordnung). The various requirements are described in Part B.

A4.3 Fracking fluids used in Germany

A4.3.1 Information and data on which the study is based

To obtain information about the fracking fluids and fracking products used in unconventional deposits in Germany, the report authors relied primarily on the sources listed below, most of which are publicly accessible. In a few individual cases, it proved possible to supplement those sources with information that is not publicly accessible; it was obtained via specific requests.

- Internet publications of the firm ExxonMobil Production Deutschland GmbH, regarding fracking fluids used in various boreholes (ExxonMobil 2012), supplemented by selected material safety data sheets (MSDS) and personal communications from Dr. Kassner, ExxonMobil Production Deutschland GmbH. According to ExxonMobil, the published data have been produced solely on the basis of evaluations of MSDS;

they do not include any additional information from fracking-services contractors or from the producers of the products used.

- Drucksache (publication) 16/3591 zur Unterrichtung des Präsidenten des Niedersächsischen Landtages (for the information of the President of the Parliament of the State of Lower Saxony) Niedersächsischer Landtag (2011).
- Studies carried out by an impartial group of experts in the framework of the ExxonMobil information and dialogue process (Ewen et al. 2012, Schmitt-Jansen et al. 2012; Ewers et al. 2012).
- Information provided by the Arnsberg district government regarding two fracks carried out in 1995 in the Natarp 1 borehole (BR Arnsberg 2011a; BR Arnsberg 2011b).
- Internet publication of the firm of RWE Dea, with information on the composition of a fracking fluid (RWE Dea 2012). In response to a request for information, the firm of Wintershall Holding GmbH indicated that it would provide no information on the fracking fluids used under commission to it, adding that the fluids had been used more than 10 years earlier and that it would no longer be possible to reconstruct the precise composition of the fluids for all relevant cases. The firm of BNK Deutschland GmbH reported that no boreholes had been drilled or stimulated in Germany, under commission to it (BNK Deutschland GmbH 2012).
- Safety data sheets of the firm of Halliburton that are available on the company's website, in various languages and formats.[8]
- To the study authors' knowledge, no material safety data sheets can be downloaded from Schlumberger's website. Schlumberger refused to cooperate with the study authors in any way, and it failed to respond to several requests for provision of specific material safety data sheets. The firm of ExxonMobil Production Deutschland GmbH made selected material safety data sheets available.

The information presented below on the composition of the fracking fluids used is based mainly on analyses of material safety data sheets for the mixtures used to prepare fracking fluids. In many cases, approval authorities also have to rely on the information provided in material safety data sheets – for example, as a basis for approvals of the fracking products listed in special operational plans. Pursuant to Art. 31 in conjunction with Annex II No 0.2.1 REACH Regulation, the information provided in material safety data sheets "*should enable users to take the necessary*

[8] http://www.halliburton.com/toolsresources/default.aspx?navid=1061&pageid=2

measures relating to protection of human health and safety at the workplace, and protection of the environment". Material safety data sheets are not required to list all substances used and their proportions by weight. Pursuant to Article 15 of Directive 1999/45/EC, where the person responsible for placing a preparation on the market can demonstrate that disclosure of the chemical identity of a substance will put at risk the confidential nature of his intellectual property, then he may, under certain conditions, refer to that substance either by means of a name that identifies the most important functional chemical groups or by means of an alternative name (cf. Art. 4 (2) and (6) Ordinance on Hazardous Substances (Gefahrstoffverordnung; GefStoffV), Art. 24 CLP Regulation 1272/2008). As the following chapters show, this constraint has the consequence that a number of additives used cannot be unambiguously identified, even though a range of pertinent information is available.

A4.3.2 Quantities used

Information on the quantities of fracking fluids used was available to the report authors for a total of 30 fracking fluids used in various unconventional deposits[9] in Germany between 1982 and 2011. Most of the deposits involved were tight gas deposits in the Söhlingen district (Lower Saxony) (Tab. A 7).

Evaluation of the available information reveals that in some cases large quantities of fracking fluids were injected in individual boreholes, especially in cases involving multi-frack stimulations. It must also be noted that the fluid quantities used varied considerably, in keeping with the fluid systems involved and the formation characteristics. The relevant quantities injected per borehole, in fracking fluid, included: from less than 100 m^3 to more than 12,000 m^3 of water, up to nearly 1,500 t of proppants and between 2.6 t and 275 t of additives (Tab. A 7). In cases involving hybrid systems, up to 513 t of liquid petroleum gas were also injected per borehole. From such information, it can be calculated that the applicable proportions by weight for proppants ranged from 5 % by weight (in a slickwater fluid) to more than 30 % by weight (in some gel fluids). The concentrations of dissolved additives in fracking fluids ranged from 0.2 % by weight in a slickwater fluid and up to 14 % by weight in a gel fluid (Tab. A 7).

The high additive concentrations (more than 10 % by weight) used in the 1980s and 1990s for some gel fluids were the result of use of large quantities (up to 240 t) of organic solvents (including methanol). Additive

[9] One fracking fluid (Buchhorst T12) was used in a conventional deposit.

concentrations are also high when the clay stabilizer potassium chloride is used, as can be seen in that potassium chloride is added as a diluted aqueous solution. Table A 8 lists the applicable quantity data provided by ExxonMobil (2012), adjusted, by analogy to Drucksache (publication) 16/3591 (Niedersächsischer Landtag 2011), to correct for the water fraction in the potassium chloride solution.

Tab. A 7: Information available to the study authors regarding the fracking fluids used in Germany in unconventional natural gas deposits[d] (T = tight gas, S = shale gas, C = coal bed methane, Nds = Lower Saxony, NRW = North Rhine – Westphalia).

Borehole	Administrative district	German Land (state)	Type of deposit	Frack Year	Number of fracks	Fracking-fluid system	Water quantity (m^3)[a]	Gas CO_2/N_2 (kg)	Proppants (kg)	Additives (kg)	Proppants (% by weight of total fluid)[b]	Dissolved additives (% by weight of water)[c]	Water per frack (m^3)	Additives per frack (kg)	Preparations known	Frack additives known
Buchhorst T12	Diepholz	Nds	Conv.	2011	1	Gel:	212	-	85,800	6,553	28%	3.0%	212	6,553	x	x
Cappeln Z3a	Cloppenburg	Nds	T	2011	7	CO_2 hybrid	3,214	512,529	810,000	45,928	18%	1.4%	459	6,561		x
Damme 3	Vechta	Nds	S	2008	3	Slickwater	12,119	-	588,000	19,873	5%	0.2%	4,040	6,624	x	x
Goldenstedt Z23	Vechta	Nds	T	2010	13	CO_2 hybrid	5,716	428,400	520,600	93,120	8%	1.6%	440	7,163	x	x
Natarp	Warendorf	NRW	C	1996	2	N_2 hybrid	121	81,750	41,700	1,230	17%	1.0%	61	615	x	x
Söhlingen Z2	Rotenburg	Nds	T	1996	1	Gel	446	-	47,100	6,284	9%	1.4%	446	6,284		x
Söhlingen Z3	Rotenburg	Nds	T	1982	1	Gel	1,693	-	N. e.	196,436	N. e.	10.4%	1,693	196,436	x	
Söhlingen Z4	Rotenburg	Nds	T	1982	1	Gel	2,336	-	N. e.	274,764	N. e.	10.5%	2,336	274,764	x	
Söhlingen Z5	Rotenburg	Nds	T	1985	1	Gel	1,382	-	450,000	15,308	24%	1.1%	1,382	15,308		x
Söhlingen Z6	Rotenburg	Nds	T	1996	1	Gel	377	-	71,600	5,724	16%	1.5%	377	5,724	x	x
Söhlingen Z7	Rotenburg	Nds	T	1997	1	Gel	383	-	61,900	4,343	14%	1.1%	383	4,343	x	x
				2010	1	Gel	353	-	125,000	5,421	26%	1.5%	353	5,421		x
				2006		CO_2 hybrid							37			x
Söhlingen Z9a	Rotenburg	Nds	T	2009	1	Gel	182	-	37,523	2,803	17%	1.5%	182	2,803		x
Söhlingen Z10	Rotenburg	Nds	T	1994	4	Gel	2,138	-	1,038,200	56,587	32%	2.6%	534	14,147	x	x
Söhlingen Z11	Rotenburg	Nds	T	1997	1	Gel	495	-	83,600	9,767	14%	1.9%	495	9,767	x	x
Söhlingen Z12	Rotenburg	Nds	T	1999	1	Gel	302	-	52,000	8,036	14%	2.6%	302	8,036	x	x
				2008	1	Gel	194	-	80,400	9,926	28%	4.9%	194	9,926	x	x
Söhlingen Z13	Heidekreis	Nds	T	1999	5	Gel	2,508	-	1,094,700	51,822	30%	2.0%	502	10,364	x	x
Söhlingen Z14	Rotenburg	Nds	T	2000	8	Gel	3,686	-	1,477,000	58,528	28%	1.6%	461	7,316	x	x

Borehole	Administrative district	German Land (state)	Type of deposit	Frack Year	Number of fracks	Fracking fluid System	Water quantity (m^3)[a]	Gas CO_2/N_2 (kg)	Proppants (kg)	Additives (kg)	Proppants (% by weight of total fluid)[b]	Dissolved additives (% by weight of water)[c]	Water per frack (m^3)	Additives per frack (kg)	Preparations known	Frack Additives known
Söhlingen Z15	Rotenburg	Nds	T	2003	5	Gel	1,805	-	740,000	90,291	28%	4.8%	361	18,058	x	x
Söhlingen Z16	Rotenburg	Nds	T	2008	9	Gel	824	-	170,100	38,079	17%	4.4%	92	4,231	x	x
Söhlingen Ost Z1	Heidekreis	Nds	T	1983	1	Gel	415	-	115,800	58,818	20%	12.4%	415	58,818	x	x
				2007	1	CO_2 hybrid	229	49,000	53,000	6,715	16%	2.9%	229	6,715	x	x
Söhlingen Ost Z3	Rotenburg	Nds	T	1990	1	Gel	760	-	202,000	8,878	21%	1.2%	760	8,878		x
Söhlingen Ost Z4	Heidekreis	Nds	T	1991	1	Gel	622	-	205,000	101,817	22%	14.1%	622	101,817	x	x
Söhlingen Ost Z5	Heidekreis	Nds	T	2009	1	Gel	285	-	108,787	4,463	27%	1.5%	285	4,463		x
Söhlingen Ost Z7	Rotenburg	Nds	T	1991	1	Gel	989	-	198,000	29,491	16%	2.9%	989	29,491		x
				2009	1	CO_2 hybrid	350	39,300	48,800	16,832	11%	4.6%	350	16,832	x	x
Söhlingen Ost Z8	Rotenburg	Nds	T	1992	1	Gel	538	-	165,300	80,203	21%	13.0%	538	80,203	x	x

a Conversion from mass to volume: Density of 998 kg/m^3 for water and density of 807 kg/m^3 for liquid nitrogen.
b Calculated by dividing the mass of proppants used by the total mass of water, gas, proppants and additives.
c Calculated by dividing the mass of additives used by the masses of water and additives.
d Including a fluid used in a conventional (conv.) deposit (Buchhorst T12).

Tab. A 8: Quantities of water, gas, proppants and additives injected per frack, for gel, hybrid and slickwater fluid systems, between 1982 and 2000, and between 2000 and 2011, in Germany (The figure given in each case is the average; the ranges are shown in parentheses.)

	Gel fluid		CO_2/N_2 hybrid fluid		Slickwater
	1982-2000	2000-2011	Natarp 1995	2000-2011	Damme 2008
Water (m^3/frack)	**785** (302-2,336)	**268** (92-461)	**61**	**303** (37-459)	**4,040**
Liquid petroleum gas (kg/frack)	-	-	**40,875**	**48,589** (32,684-73,218)	-
Proppants (kg/frack)	**163,907** (47,100-450,000)	**98,629** (18,900-184,625)	**20,850**	54,429 (14,583-115,714)	**196,000**
Additives (kg/frack)	**54,959** (4,343-274,764)	**7,346** (2,803-18,058)	**615**	7,709 (1,276-16,832)	**6,624**

Table A 8 presents an evaluation of injected quantities with respect to numbers of fracks. With the modern gel fluids used since 2000, an average of about 100 t of proppants and about 7.3 t of additives were used per frack. An average of about 7 to 8 t of additives were also used in connection with the newer hybrid and slickwater fluids. The higher average quantities of additives used (seven times again as high) prior to the year 2000 are partly the result of use of large quantities of organic solvents (such as methanol) in some older gel fluids (see above).

A4.3.3 Fracking products used

Information on the fracking products used to date in Germany was available only from the sources ExxonMobil (2012) and BR Arnsberg (2011b) (Annex 1). That information covers 21 fracking fluids (Tab. A 7) that were used in a total of 62 fracks between 1982 and 2011. It thus covers only about 21 % of the some 300 fracks carried out to date in Germany. Presumably, therefore, the compilation of fracking products used to date in Germany (Annex 1) is incomplete; additional preparations were also used.

The 88 products listed in Annex 1 (8 proppants and 80 other preparations) were either produced or imported by a total of three fracking-services contractors (Halliburton, Schlumberger and Baker Hughes). For 80 of the 88 preparations, the report authors were able to obtain producers' or importers' material safety data sheets (MSDS) that either are current or were valid at the time of the relevant fracks.

Evaluation of the available 80 material safety data sheets revealed that

- 6 preparations are classified as toxic,
- 6 are classified as dangerous to the environment,
- 25 are classified as harmful to human health,
- 14 are classified as irritant substances,

- 12 are classified as corrosive substances and
- 27 are classified as non-hazardous

pursuant to Directives 67/548/EEC and 1999/45/EC (Annex 1). A number of the preparations exhibit several of the hazard characteristics. According to the information in the material safety data sheets,

- 3 preparations are classified as severely hazardous for water (WGK 3 (water hazard class 3)),
- 12 preparations are classified as hazardous for water (WGK 2 (water hazard class 2)),
- 22 preparations are classified as low hazards to waters (WGK 1 (water hazard class 1)),
- 10 preparations are classified as not hazardous for water.

A total of 33 of the material safety data sheets available to the study authors provided no information on the water hazard class of the relevant preparation (Annex 1).

A4.3.4 Fracking additives used

The study authors had access to information on the fracking additives in **28 fracking fluids** that were used in 76 fracks, in 24 boreholes in Germany, between 1983 and 2011 (Tab. A 7). The evaluated data thus cover only about 25 % of the some 300 fracks carried out in Germany.

The data have been obtained largely from publications of the firm of ExxonMobil (2012). The composition data published by the firm of ExxonMobil Production Deutschland GmbH, for 27 fracking fluids, refer to fluids used in a total of 74 fracks in Lower Saxony (Tab. A 7). For two other fluids used in the Söhlingen Z3 and Z4 boreholes, only the preparations involved are known; no list of the substances that went into them was published. With regard to the some 180 fracks carried out in Germany by the firm of ExxonMobil Production Deutschland GmbH and its affiliations (Dr. Kalkoffen, cited in: the newspaper Neue Osnabrücker Zeitung, 2012), the compositions of the fracking fluids used were thus published for about 41 % of the fracks carried out. The composition of the fracking fluids used in the Söhlingen natural gas field in Lower Saxony was assessed for the purpose of answering an oral request of Ralf Borngräber (SPD), member of the Lower Saxony state parliament, and then published in Drucksache (publication) 16/3591 (Niedersächsischer Landtag 2011).

Along with the information in ExxonMobil (2012), the information available on a fracking fluid used in 1995, under commission to a consortium consisting of Conoco Mineralöl GmbH, Ruhrgas AG and Ruhrkohle AG, in a coal bed methane deposit (Natarp 1, Warendorf district, North-Rhine –

Westphalia (NRW)), was evaluated (BR Arnsberg 2011a; BR Arnsberg 2011b). For the consortium, gas yields from the test production were unsatisfactory, and the borehole was backfilled after that production (BR Arnsberg 2011a). The fracking fluid listed in the website of RWE Dea (RWE Dea 2012) was not assessed in detail, because it is unclear whether, and in which boreholes, that fluid was actual used. What is more, the composition of that fluid does not differ fundamentally from those of the evaluated fluids that were used by ExxonMobil Production Deutschland GmbH in tight gas deposits.

Evaluation of the published information on the 28 fracking fluids used revealed that a total of at least 112 substances / substance mixtures (13 proppants and 99 additives, with various applications) were used in Germany (Annex 2), not including the liquid CO_2 and N_2 gases that were used. For 76 of the 112 substances / substance mixtures, either unique CAS numbers were provided or it proved possible to correct or determine the CAS number on the basis of unique designations of the relevant substances / substance mixtures (marked "corr." in Annex 2). A total of 36 substances / substance mixtures could not be uniquely identified via a CAS number, either because their composition was unknown or because the pertinent material safety data sheets used designations that referred only to chemical groups (such as aromatic ketones, inorganic salts) (Annex 2). As a rule, material safety data sheets do not list substances that are not subject to specific labelling requirements. Where such substances were used, their identities are not known to the study authors.

A compilation of the additives in use was also prepared in the framework of the ExxonMobil information and dialogue process; it lists a basic total of 149 chemicals (Schmitt-Jansen et al. 2012). The reasons for the differences between that list and the list of 112 substances considered in the present study (Annex 2) are that a) the work of Schmitt-Jansen et al. (2012) included fracking fluids whose use was planned but had not (yet) taken place (Bötersen Z11, Mulmshorn Z6) (Schmitt-Jansen et al. 2012) and b) that list also included substances that are used in drilling fluids (Gordalla & Ewers 2011). No information was available to the study authors on the drilling fluids used. Presumably, those drilling fluids did not differ from those used in boreholes for exploitation of conventional natural gas deposits. Chapter C3 presents an assessment of the additives used with regard to their hazardousness characteristics.

A4.3.5 Current improved versions of fracking fluids

The firm of ExxonMobil Production Deutschland GmbH has announced that the numbers of additives used could be reduced to fewer than 10 substances for shale gas deposits and to 20 to 30 substances for tight gas deposits. In future, use of highly toxic substances, and of carcinogenic, mutagenic and reprotoxic substances (CMR substances) is to be completely discontinued (ExxonMobil 2012, ExxonMobil 2011, Ewers et al. 2012). Furthermore, the additive polyethyleneglycoloctylphenylether, which was still being used in 2008, is no longer to be used, as a result of fundamental concerns (ExxonMobil Production Deutschland GmbH, press information of 14 September 2011)[10].

With regard to the current status of considerations regarding recipes for possible future fracking fluids, the firm of ExxonMobil Production Deutschland GmbH informed the study authors about the compositions of two fluids (one slickwater fluid and one gel fluid) that could be used in future in fracking in shale gas deposits and (possibly) in coal bed methane deposits (Ewers et al. 2012). The compositions of the two fluids, and an assessment of their hazard potentials, are presented in Part C.

Part C also presents a discussion of conceivable options for stimulation techniques that use no chemicals whatsoever.

A4.4 Uncertainties / knowledge deficits

The report authors found a considerable lack of information on the additives used and their concentrations in injected fracking fluids; the material safety data sheets for mixtures are often the only available source of information relative to the identities of additives and the quantities in which additives are used. For approval authorities, this situation creates considerable uncertainties and knowledge gaps regarding the additives that are actually used and the pollutant loads involved.

In assessment of the available information, the study authors found that when the recipes for preparations are changed, different versions of the pertinent material safety data sheets can co-exist, thereby creating uncertainties regarding the additives actually used. In one concrete case, the firm of ExxonMobil Production Deutschland GmbH published data on seven fracking fluids in which the substance nonylphenol ethoxylate had been used as a component in the surfactant Halliburton SSO-21 (ExxonMobil 2012). In response to a relevant query, Halliburton, the producer / importer of the product SSO-21, stated that Halliburton, as of the mid-1980s, had prohibited use of nonylphenols within the company's operations in Europe and that the product in question, which had been produced in France and used in Germany until 2004, contained no nonylphenols (personal communication of Halliburton of 18 April 2012). The safety data sheet used by ExxonMobil Production Deutschland GmbH for the assessment, so Halliburton, referred to a product of the firm of Univar/MagnaBlend that

[10] http://www.erdgassuche-in-deutschland.de/kommunikation/ presseinformationen/index.html

had the same trade name but had never been used in Germany. The composition data published in the Internet on seven fracking fluids injected in the Söhlingen area between 1994 and 2000 still show that nonylphenol ethoxylate was used, however (ExxonMobil 2012), and thus it is currently unclear whether that substance was used in Lower Saxony or not. In the view of the study authors, such uncertainties regarding the additives actually used are unacceptable, especially since use of nonylphenol ethoxylates has been sharply restricted since 2003 in the EU as a result of the substances' estrogenic effects and the high bioaccumulation potential of nonylphenol, a degradation product of those substances (Directive 2003/53/EC[11]). Pursuant to Annex XVII Regulation (EC) No 1907/2006 [REACH Regulation], products that contain nonylphenol ethoxylate concentrations of 0.1 % or greater may not be placed on the market for a wide range of purposes (including industrial cleaning, as a co-formulant in plant pesticides and biocides) involving use outside of closed systems.

Part C describes and discusses additional knowledge deficits, and discusses current practice in disclosure of fluids used.

[11] Directive 2003/53/EC of the European Parliament and of the Council of 18 June 2003 amending for the 26th time Council Directive 76/769/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations (nonylphenol, nonylphenol ethoxylate and cement), 17 July 2003. The restriction has been adopted in Annex XVII of the REACH Regulation.

A5 Flowback

In fracking, after pressure has been applied to the gas-bearing formation, some of the injected fracking fluids are extracted along with the gas and formation water that flows into the well; the majority of the proppants used remains in the fractures opened up via the fracking process. The fluid that is so extracted, fluid that usually has to be extracted and managed (disposed of) throughout the entire gas-production phase, is known as "flowback".

Flowback consists of varying proportions of injected fracking fluids and co-extracted formation water. Initially, fracking fluids account for the larger share of flowback; later, formation water begins to predominate. As a result of various hydrogeochemical processes that can occur within the deposit horizon (Fig. A30), flowback can contain a number of other substances in addition to fracking additives and formation water (Energy Institute 2012, King 2011, NYSDEC 2011; UBA 2011a):

- Solutes mobilised from the deposit,
- Organic substances mobilised from the deposit (such as toluene and benzene),
- Transformation and degradation products of the additives used,
- Naturally occuring radioactive material (NORM),
- Clay, silt and sand particulates (proppants, or mobilised from the deposit),
- Bacteria, such as sulfate-reducing bacteria, and
- Gases (such as methane and hydrogen sulfide).

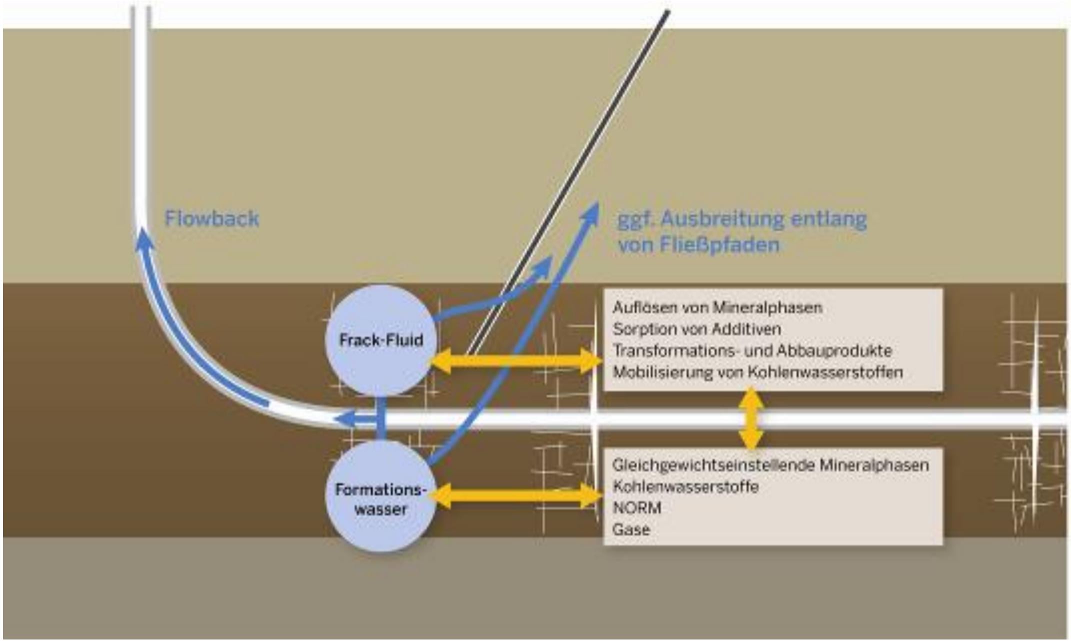

Fig. A 30: Schematic depiction of flowback formation via mixing of fracking fluids and formation water in connection with property-changing hydrogeochemical processes (IWW & ahu AG) [by "columns", from left to right: Flowback; Fracking fluid, Formation water; Possibly, spreading along flow pathways; Dissolution of mineral phases; Sorption of additives; Transformation and degradation products; Mobilisation of hydrocarbons; Equilibrium mineral phases; Hydrocarbons; NORM; Gases]

In keeping with the temperatures and pressures prevailing in the deposit, flowback initially appears in a liquid state. As extraction continues, the deposit pressures decrease, and some of the flowback appears in a gaseous form that includes volatile hydrocarbons (Rosenwinkel et al. 2012). Flowback in gaseous form tends to condense at the surface, in keeping with the pressures and temperatures it encounters there.

A5.1 Quantities

The literature data on flowback volumes and flow rates vary widely, depending on the natural gas deposits involved. For one shale gas deposit, a return-flow rate of about 0.5 to 1 m^3/min, in the initial hours following the pressure decrease, was determined (Tyndall Centre 2011). Within the first 24 hours, the return-flow rate dropped to about 0.1 m^3/min, and after an additional two to three weeks, it had dropped to just a few m^3/d. According to the Tyndall Centre (2011), about 60 % of the entire flowback volume return to the surface in the first four days after fracking has taken place. Because the flow rates diminish rapidly, the total quantity of recovered flowback depends especially on the duration of natural gas extraction from the borehole.

Many references compare recovered flowback volumes – in addition to absolute flowback quantities – to the pertinent volumes of injected fracking fluids. It must be remembered that because flowback contains co-extracted formation water, one cannot assume that fracking fluid was completely recovered from the deposit even if the flowback volume is equivalent to the volume of injected fracking fluids.

In the framework of the Exxon dialogue and information process, Rosenwinkel et al. (2012) assessed the cumulative flowback volume in the Damme 3, Buchhorst T12 and Cappeln Z3a boreholes (Fig. A 31). The recovered flowback volumes vary widely, ranging from < 100 m^3 to 3,058 m^3 in nearly 60 days. Taking account of the quantities of fluid injected (Tab. A 8), it is clear that, in the three boreholes, the recovered flowback volumes amounted to only 17 to 27 % of the corresponding injected volumes (Fig. A 31).

Chapter C4 describes methods for determining fractions of recovered fracking fluids in fracking fluid.

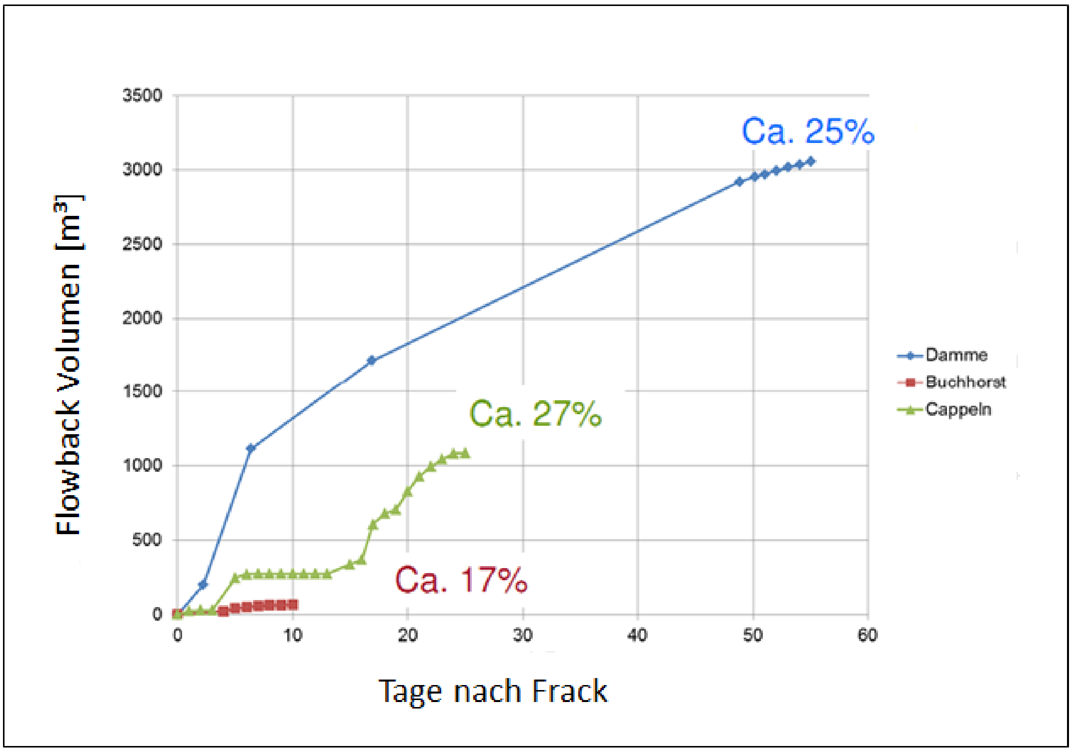

Fig. A 31: Volumes of flowback recovered after fracking (from: Rosenwinkel et al. 2012) [Flowback volume; Days after frack]

A5.2 Chemical characteristics

Because the characteristics of formation water are always deposit-specific, and because the proportions of extracted fracking additives vary, the characteristics of flowback have to be individually assessed for each site and pertinent time.

A5.2.1 Tight gas deposits

Analyses of flowback from various fracking projects in Lower Saxony were provided in the framework of the Exxon Mobil information and dialogue process (ExxonMobil 2012). Possible reaction and degradation products of fracking additives in flowback are described in Chapter C4.

Ewers et al. (2012) analysed the spectrum of data provided from analysis of organic and inorganic trace substances in buntsandstein and compared those data with relevant assessment values (Tab. A 9 and Tab. A 10). Their analyses indicate that flowback tends to consist of highly saline solutions that in some cases also have high concentrations of hydrocarbons, especially benzene (up to 13 mg/l) and polycyclic aromatic hydrocarbons (PAH; concentrations of up to about 10 mg/l). The total concentrations for BTEX hydrocarbons vary widely (from 0.07 to 19.4 mg/l). In some cases, very high concentrations of mercury, chromates and lead were also found. The concentrations of many parameters exceed relevant assessment values by factors of more than 1,000. In fact, benzene and mercury concentrations exceed relevant assessment values by a factor of 100,000, while total PAH concentrations exceed those values by a factor of 1,000,000 (Tab. A 10).

Tab. A 9: Analysed inorganic trace substances in flowback from various natural gas boreholes in buntsandstein (Söhlingen, Söhlingen Ost, Borchel, Mulsmhorn, Takken, Bötersen, Goldenstedt)
(Evaluation of 13 analyses carried out from 25 July to 6 September 2011; from: Ewers et al. 2012) [see translation immediately following]

Parameter	Typischer Werte-bereich (µg/l)	Extreme Einzel-werte (µg/l)	Beurteilungswert				Verdünnung zur Erreichung der Beurteilungs-werte
			GW – TrinkwV[1)] (µg/l)	SW[2)] (µg/l)	PW[3)] (µg/l)	JD-UQN[4)] (µg/l)	
Antimon	<5...120	265, **575**	**5**	**5**[a)]	**5**[c)]	-	**1 : 1.000**
Arsen	<0,5...18	**130, 175**	**10**	**10**[a) b)] **10**[c)]	**10** [c)]	-	**1 : 100**
Blei	<25...**135**	-	10	10[b)] **7**[a) c)]	**7** [c)]	7,2	**1 : 100**
Cadmium	<5...**<25**	-	3	0,5[a)] 0,25[c)]	0,25 [c)]	<**0,08**...0,25	**1 : 1.000**
Chrom, gesamt	<10...70	**115**	50	**7**[a)]	**7** [c)]	-	**1 : 100**
Chromat	<50...<100	-	1 [d)]	-		-	1 : 100
Kobalt	<10...**<50**	-	-	**8**[a)]	**8** [c)]	-	**1 : 10**
Kupfer	<10...**56**	-	2000	**14**[a)]	**14** [c)]	-	**1 : 10**
Molybdän	<10...**90**	-		**35**[a)]	**35** [c)]	-	**1 : 10**
Nickel	<5...**50**	-	20	**14**[a)]	20 [c)]	20	**1 : 10**
Quecksilber	6,0...49	**730**	1	0,2[a) b)] **0,05** [c)]	**0,05** [c)]	**0,05**	**1 : 100.000**
Selen	**<5**	-	10	7[a)]	7 [c)]	**3**	**1 : 10**
Zink	<25...930	**9700**	-	**58**[a)]	**58** [c)]	-	**1 : 100**
Zinn	<25...<125	-	-	-		-	**-**
Cyanide, gesamt	<5...**22**	-	-	5[a)] 50[a)]	5 [c)] 50 [c)]*	10	**1 : 10**

* wenn kein leicht freisetzbares Cyanid vorliegt

1) Parameterwert, Anlage 2 der Trinkwasserverordnung (TrinkwV 2001).
2) Schwellenwert für das Grundwasser.
3) Prüfwert für das Grundwasser.
4) Jahres-Durchschnitts-Umweltqualitätsnorm für die Wasserphase für oberirdische Gewässer ohne Übergangsgewässer nach Anlage 7 der Oberflächenwasserverordnung (OGewV 2011).

a) LAWA (2004)
b) GrwV 2010, Anlage 2
c) BMU (2011), vorgeschlagener Wert
d) Zur Zeit vom UBA in Erwägung gezogener Leitwert (LW) für das Trinkwasser (PD Dr. Hermann Dieter, persönliche Mitteilung Mai 2012).

Parameter	Typical value range (µg/l)	Extreme individual values (µg/l)	Assessment value				Dilution to achieve the assessment values
			GW –- TrinkwV[1)] (µg/l)	SW[2)] (µg/l)	SW[3)] (µg/l)	JD-UQN[4)] (µg/l)	
Antimony							
Arsenic							
Lead							
Cadmium							
Chromium, total							
Chromate							
Cobalt							
Copper							
Molybdenum							
Nickel							
Mercury							
Selenium							
Zinc							
Tin							
Cyanide, total							

* If no easily liberatable cyanide is present
1) Parameter value, Annex 2 of the Ordinance on Drinking Water (TrinkwV 2001)
2) Threshold value for groundwater.
3) Test value for groundwater.
4) Annual average environmental quality standard for the water phase, for above-ground waters without transitional waters pursuant to Annex 7 of the Ordinance on the Protection of Surface Waters (OGewV 2011).

a) LAWA (2004)
b) Groundwater Protection Ordinance (GrwV 2010), Annex 2
c) BMU (2011), proposed value
d) Guidance value for drinking water (GVDW) currently being considered by the Federal Environment Agency (UBA)(PD Dr. Hermann Dieter, personal communication of May 2012).

Tab. A 10: Analysed hydrocarbons in flowback from various natural gas boreholes in buntsandstein (Söhlingen, Söhlingen Ost, Borchel, Mulsmhorn, Takken, Bötersen, Goldenstedt)
(Evaluation of 13 analyses carried out from 25 July to 6 September 2011; from: Ewers et al. 2012) [see translation immediately following]

Parameter	Typischer Werte-bereich (µg/l)	Extreme Einzelwerte (µg/l)	Beurteilungswert				Verdünnung zur Erreichung der Beurteilungs-werte
			GW – TrinkwV[1)] (µg/l)	SW[2)] (µg/l)	PW[3)] (µg/l)	JD-UQN[4)] (µg/l)	
BTEX	4524…**19438**	70		**20[a)]**	**20[c)]**		**1 : 1.000**
Benzol	3370…**13300**	61	**1**	**1[a)]**	**1[c)]**	10	**1 : 100.000**
Toluol	840…**4280**	7	-	20[a)]*	20[c)]*	**10**	**1 : 1.000**
Ethylbenzol	24…**350**	<1	-	20[a)]*	20[c)]*	**10**	**1 : 100**
p-Xylol	115…**1650**	<1	-	20[a)]*	20[c)]*	**10**	**1 : 1.000**
m-Xylol	11…**510**	<1	-	20[a)]*	20[c)]*	**10**	**1 : 100**
o-Xylol	115…**1060**	2	-	20[a)]*	20[c)]*	**10**	**1 : 1 000**
Styrol	<1		-	20[a)]*	20[c)]*	-	-
Cumol	<1…25	105, **165**	-	20[a)]*	20[c)]*	**10**	**1 : 100**
PAK, gesamt	1,97...836	2253...**10444**	**0,1*******	0,2******	0,2******c)	-	**1 : 1.000.000**
Naphthalin	1,27...1750	**9300**	-	**1[a)]****	2[c)]**	2,4	**1 : 10.000**
Acenaphthylen	0,1...12,3	65	-	-	-	-	-
Acenaphthen	0,02...27	205	-	-	-	-	-
Fluoren	0,09...71	200...765	-	-	-	-	-
Phenanthren	0,45...570	**1340**	-	-	-	0,5	**1 : 10.000**
Anthracen	<0,02...6,5	**9,0**	-	**0,01[a)]**	0,1[c)]	0,1	**1 : 1000**
Fluoranthen	<0,02...9,8	**18,8**	-	**0,025[a)]**	0,1[c)]		**1 : 1000**
Pyren	0,04...14	39	-	-	-	-	-
Benz(a)-anthracen	<0,02...6,5	24	-	-	-	-	-
Chrysen	<0,02...0,6	12,5	-	-	-	-	-
Benzo(b)-fluoranthen	<0,02...0,5	**2,8**	-	**0,025[a)]**	0,03[c)]***	Σ = 0,03	**1 : 1000**
Benzo(k)-fluoranthen	<0,02...0,2	**0,4**	-	**0,025[a)]**	0,03[c)]***		**1 : 100**
Benzo(a)pyren	<0,02...**0,5**		**0,01**	**0,01[a)]**	**0,01[c)]**	0,05	**1 : 100**
Dibenz(a,h)-anthracen	<0,02...0,2	**0,4**		**0,01[a)]**	**0,01[c)]**	-	**1 :100**
Benzo(ghi)-perylen	<0,02...0,7	**1,2**		-	**0,002******	Σ = 0,002	**1 : 1.000**

* Summe BTEX
** gilt für die Summe mit Methylnaphthalinen
*** gilt für die Summe aus Benzo(b und k)fluoranthen
**** gilt für die Summe aus Benzo(ghi)perylen und Indeno(1,2,3-c,d)pyren
***** gilt für die Summe aus Benzo(b und k)fluoranthen, Benzo(ghi)perylen und Indeno(1,2,3-c,d)pyren
****** gilt für die Summe aus 15 Einzelsubstanzen ohne Naphthalin und Methylnaphthalin

1) Parameterwert, Anlage 2 der Trinkwasserverordnung (TrinkwV 2001).
2) Schwellenwert für das Grundwasser.
3) Prüfwert für das Grundwasser.
4) Jahres-Durchschnitts-Umweltqualitätsnorm für die Wasserphase für oberirdische Gewässer ohne Übergangsgewässer nach Anlage 7 der Oberflächenwasserverordnung (OGewV 2011).
a) LAWA (2004)
b) GrwV 2010, Anlage 2
c) BMU (2011), vorgeschlagener Wert

Parameter	Typical value range (µg/l)	Extreme individual values (µg/l)	Assessment value				Dilution to achieve the assessment values
			GW –- TrinkwV[1)] (µg/l)	SW[2)] (µg/l)	SW[3)] (µg/l)	JD-UQN[4)] (µg/l)	
BTEX							
Benzene							
Toluene							
Ethylbenzene							
p-Xylene							
m-Xylene							
o-Xylene							
Styrene							
Cumene							
PAH, total							
Naphthalene							
Acenaphthylene							
Acenaphthene							
Fluorene							
Phenanthrene							
Anthracene							
Fluoranthene							
Pyrene							
Benz(a)-anthracene							
Chrysene							
Benzo(b)-fluoranthene							
Benzo(k)-fluoranthene							
Benzo(a)-pyrene							
Dibenz(a,h)-anthracene							
Benzo(ghi)-perylene							

* Total BTEX
** Applies for total with Methylnaphthalenes
*** Applies for total of Benzo(b+k)fluoranthene

**** Applies for total of Benzo(ghi)perylene and Indeno(1,2,3-c,d)pyrene
***** Applies for total of Benzo(b+k)fluoranthene, Benzo(ghi)perylene and Indeno(1,2,3-c,d)pyrene
****** Applies for total of 15 individual substances, not including naphthalene and methylnaphthalene
1) Parameter value, Annex 2 of the Ordinance on Drinking Water (TrinkwV 2001)
2) Threshold value for groundwater.
3) Test value for groundwater.
4) Annual average environmental quality standard for the water phase, for above-ground waters without transitional waters pursuant to Annex 7 of the Ordinance on the Protection of Surface Waters (OGewV 2011).
a) LAWA (2004)
b) Groundwater Protection Ordinance (GrwV 2010), Annex 2
c) BMU (2011), proposed value

Under certain circumstances, flowback can also contain naturally occurring radioactive substances (NORM), such as radium-226, radium-228 and radon. In Germany, radioactive residues from the oil and gas industry, in the form of sludges and deposits, are subject to monitoring by authorities in keeping with the provisions of the Radiation Protection Ordinance (Strahlenschutzverordnung; StrlSchV). According to Rosenwinkel et al. (2012), the reason that analysis reports provided by ExxonMobil relative to concentrations of radioactive substances show no overly high concentrations is that such substances normally precipitate in connection with formation of barium sulfate incrustations and then either remain in pipelines or are brought back to the surface as solid particles.

A5.2.2 Shale gas deposits

To assess the characteristics of formation water and flowback in shale gas deposits, the analysis data provided in the framework of the ExxonMobil information and dialogue process, relative to flowback from the Damme 3 borehole, were evaluated. In that borehole, a total of three fracks in clay rocks of the Bückeberg formation (Wealden, Lower Cretaceous) were carried out (ExxonMobil 2012; Rosenwinkel et al. 2012). For assessment of the characteristics of formation water, data were used from analysis of flowback with an assumed formation-water fraction > 90 %.

The analysed flowback shows high salt concentrations and high concentrations of iron and manganese. The concentrations of all analysed trace components were lower than the specified limit of determination. For the parameters nickel, chromium, arsenic and lead, the limit of determination was considerably higher than the assessment values applied, and thus no assessment on the basis of the available data was possible. No data were provided for concentrations of dissolved hydrocarbons or for concentrations of dissolved naturally occurring radionuclides (Tab. A11).

Tab. A 11: Characteristics of formation water in the shale gas deposit "Damme 3", and comparison of the pertinent values with the assessment values described in section C3.2.2
(Values exceeding the most stringent value for at least one of the listed regulatory contexts are highlighted with boldface type.)

Parameter	Units	Wealden formation		Assessment values**						
		Med.	Max	WHO	Ordinance on Drinking Water (TrinkwV)	Mineral and table-water ordinance	Ground water Protection Ordinance (GrwV)	GFS	Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV)	Ordinance on the protection of surface waters (OGewV)
General parameters										
pH value		5.7	5.9		*6.5-9.5*					
Electrical conductivity	µS/cm	**138,000**	**161,000**		*2,790*					
Main components										
Sodium	mg/l	**33,740**	**36,390**		*200*					
Potassium	mg/l	110	157							
Calcium	mg/l	15,760	16,550							
Magnesium	mg/l	2,030	2,130							
Strontium	mg/l	1,600	1,720							
Barium	mg/l	**490**	**593**	*0.7*		*1.0*		*0.34*		
Chloride	mg/l	**87,100**	**88,440**		*250*		*250*	*250*		
Sulfate	mg/l	7	15		*250*		*240*	*240*		
H'carbonate	mg/l	200	230							
Secondary components										
Boron	mg/l	**2.5**	**3.3**	*2.4*	*1.0*	*4.9*		*0.74*		
Bromium	mg/l	480	540							
Iodine	mg/l	4	4							
Ammonium	mg/l	N. e.	N. e.		*0.5*		*0.5*			
Nitrate	mg/l	N. e.	N. e.	*50*	*50*	*50*	*50*			*50*
Lithium	mg/l	6.4	6.4							
Iron	mg/l	**115**	**160**		*0.2*					
Manganese	mg/l	**2**	**3.7**	*0.4*	*0.05*	*0.5*				
Zinc	mg/l	0.4	0.5					*0.058*	*0.5*	
Trace components										
Aluminium	mg/l	N. e.	N. e.		*0.2*					
Copper	mg/l	< 0.2	< 0.2	*2.0*	*2.0*	*1.0*		*0.014*	*0.05*	
Nickel	mg/l	< 1	< 1	*0.07*	*0.02*	*0.02*		*0.014*	*0.05*	*0.02*
Chromium	mg/l	< 0.25	< 0.25	*0.05*	*0.05*	*0.05*		*0.007*	*0.05*	
Arsenic	mg/l	< 0.25	< 0.25	*0.01*	*0.01*	*0.01*	*0.01*	*0.01*	*0.01*	
Selenium	mg/l	N. e.	N. e.	*0.04*	*0.01*	*0.01*		*0.007*	*0.01*	
Lead	mg/l	< 1	< 1	*0.01*	*0.01*	*0.01*	*0.01*	*0.007*	*0.025*	*0.0072*
Cadmium	mg/l	N. e.	N. e.	*0.003*	*0.003*	*0.003*	*0.0005*	*0.0005*	*0.005*	
Mercury	mg/l	N. e.	N. e.	*0.006*	*0.001*	*0.001*	*0.0002*	*0.0002*	*0.001*	*0.00005*
Molybdenum	mg/l	N. e.	N. e.					*0.035*	*0.05*	
Vanadium	mg/l	N. e.	N. e.					*0.004*		
Radionuclides										
^{226}Ra	bq/l	N. e.	N. e.	*1.0*		*0.125**				
^{228}Ra	bq/l	N. e.	N. e.	*0.1*		*0.020**				

Parameter	Units	Wealden formation		Assessment values**						
		Med.	Max	WHO	Ordinance on Drinking Water (TrinkwV)	Mineral and table-water ordinance	Ground water Protection Ordinance (GrwV)	GFS	Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV)	Ordinance on the protection of surface waters (OGewV)
Organic substances in the water										
BTEX	mg/l	N. e.	N. e.						*0.02*	
Benzene	mg/l	N. e.	N. e.		*0.001*			*0.001*	*0.001*	*0.001*
Σ PAH	mg/l	N. e.	N. e.		*0.0001*			*0.0002*	*0.0002*	
Naphthalene	mg/l	N. e.	N. e.					*0.001*	*0.002*	*0.0024*

*: Commercially sold table waters labelled as "suitable for infants" must conform to activity concentrations of less than 125 mBq/l for ^{226}Ra and of less than 20 mBq/l for ^{228}Ra. Their total activity concentrations may not exceed 100 mBq/l.

**: For explanations of abbreviations, see Part C, section C3.2.2

A5.2.3 Coal bed methane deposits

In the framework of the NRW study (NRW Gutachten; ahu / IWW / Brenk Systemplanung 2012), the expected characteristics of formation water in coal bed methane deposits in North Rhine – Westphalia were determined on the basis of mine-water analyses – focusing primarily on the Aachen, Erkelenz, Ruhr and Ibbenbüren coalfields – and compared with relevant assessment values (Tab. A 12).

The formation water in seam-bearing strata tends to have high salt concentrations. This is true especially in the northern and northwestern parts of North Rhine – Westphalia. In these areas, salt concentrations higher than that of seawater must be expected; they result from subrosion of rock-salt deposits. In southwestern areas, brines' salinities do not exceed that of seawater. As to secondary components, values higher than relevant assessment values can be expected for the parameters boron, ammonium and nitrate, iron, manganese and zinc. Data on trace-component concentrations are not available for all mine-water districts. Nonetheless, it is clear that values for the trace components / parameters aluminium, nickel, chromium, lead, cadmium and molybdenum exceed the listed assessment values.

The natural radioactivity of mine water in Upper Carboniferous strata is tied especially to radium concentrations, and it increases as salt concentrations increase. With regard to the highly mineralized mine water in Ruhr carboniferous strata, the reported radionuclide activity values include 60 Bq/l for ^{226}Ra and 30 Bq/l for ^{228}Ra (Wiegand & Feige 2002, Leopold et al. 2002). No significant radionuclide concentrations or activities are known from decay chains above that of radium (such as uranium or thorium). The activities mentioned considerably exceed the respective WHO guideline values of 1.0 and 0.1 Bq/l.

On the basis of an adult person's average water consumption of 2 liters per day, the listed maximum concentrations of the dominant radionuclides would correspond to a dose of about 5.8 mSv/a from the isotope ^{226}Ra and of 7.25 mSv/a from the isotope ^{228}Ra. Both of those individual doses, and the resulting total dose, considerably exceed the total guideline dose specified by the Ordinance on Drinking Water (TrinkwV), 0.1 mSv/a. In addition, the maximum activity concentrations permitted under the Mineral and Table Water Ordinance, for suitability for consumption by infants, are exceeded by more than two orders of magnitude.

The study authors are not aware of any data on concentrations of dissolved hydrocarbons in mine water of the coal-mining regions mentioned or in formation water of the potential target horizons involved. Oil and asphalt impregnations in the rock series above the seam-bearing Upper Carboniferous have long been known, however (Wegner 1924: 631 f), and thus contamination of formation water with (inter alia) polycyclic aromatic hydrocarbons (PAH) or BTEX (benzene, toluene, ethylbenzene, xylene) cannot be ruled out.

Tab. A 12: Characteristics of formation water in seam-bearing Upper Carboniferous strata in North Rhine – Westphalia, and comparison of the pertinent values with the assessment values described in section C3.2.2
(Values exceeding the most stringent value for at least one of the listed regulatory contexts are highlighted with boldface type.)

Parameter	Units	Southern NRW (southern Lower Rhine Bight)		Northern NRW (northern Lower Rhine Bight, Münsterland)		Assessment values**						
		Med.	Max	Med.	Max	WHO	Ordinance on Drinking Water (TrinkwV)	Mineral and table-water ordinance	Ground-water Protection Ordinance (GrwV)	GFS	Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV)	Ordinance on the protection of surface waters (OGewV)
General parameters												
pH value		8.43	9.29	N. e.	N. e.		*6.5-9.5*					
Electrical conductivity	µS/cm	N. e.	N. e.	N. e.	N. e.		*2,790*					
Main components												
Sodium	mg/l	**1,735**	**7,570**	**30,000**	**73,000**		*200*					
Potassium	mg/l	32.5	115	300	1,180							
Calcium	mg/l	34.5	474	2,200	11,300							
Magnesium	mg/l	28.5	290	800	2,740							
Strontium	mg/l	0.9	14	190	1,530							
Barium	mg/l	0.6	**104**	**50**	**2,550**	*0.7*		*1.0*		*0.34*		
Chloride	mg/l	**1,730**	**13,200**	**55,000**	**128,000**		*250*		*250*	*250*		
Sulfate	mg/l	13.5	**241**	120	**4,820**		*250*		*240*	*240*		
H'carbonate	mg/l	863	3,250	150	1,570							
Secondary components												
Boron	mg/l	N. e.	N. e.	3	**13**	*2.4*	*1.0*	*4.9*		*0.74*		
Bromium	mg/l	3.5	16	70	256							
Iodine	mg/l	0.16	1.1	4	50							
Ammonium	mg/l	N. e.	N. e.	**4**	**111**		*0.5*		*0.5*			
Nitrate	mg/l	N. e.	N. e.	15	**174**	*50*	*50*	*50*	*50*			*50*
Lithium	mg/l	0.75	8.9	8	62							
Iron	mg/l	**0.5**	**17**	**8**	**160**		*0.2*					
Manganese	mg/l	0.07	**1.24**	**3**	**91**	*0.4*	*0.05*	*0.5*				
Zinc	mg/l	<0.05	<0.05	**1**	**32**					*0.058*	*0.5*	
Trace components												
Aluminium	mg/l	< 0.5	< 0.5	**0.65**	**1.0**		*0.2*					
Copper	mg/l	<0.05	<0.05	**0.12**	**0.3**	*2.0*	*2.0*	*1.0*		*0.014*	*0.05*	
Nickel	mg/l	N. e.	N. e.	**0.11**	**0.62**	*0.07*	*0.02*	*0.02*		*0.014*	*0.05*	*0.02*
Chromium	mg/l	N. e.	N. e.	**0.06**	**0.26**	*0.05*	*0.05*	*0.05*		*0.007*	*0.05*	
Arsenic	mg/l	N. e.	N. e.	0.004	0.007	*0.01*	*0.01*	*0.01*	*0.01*	*0.01*	*0.01*	
Selenium	mg/l	N. e.	N. e.	0.006	0.01	*0.04*	*0.01*	*0.01*		*0.007*	*0.01*	
Lead	mg/l	<0.05	<0.05	**0.04**	**0.6**	*0.01*	*0.01*	*0.01*	*0.01*	*0.007*	*0.025*	*0.0072*
Cadmium	mg/l	N. e.	N. e.	**0.005**	**0.02**	*0.003*	*0.003*	*0.003*	*0.0005*	*0.0005*	*0.005*	
Mercury	mg/l	N. e.	N. e.	<0.001	<0.001	*0.006*	*0.001*	*0.001*	*0.0002*	*0.0002*	*0.001*	*0.00005*
Molybdenum	mg/l	N. e.	N. e.	**0.43**	**0.48**					*0.035*	*0.05*	
Vanadium	mg/l	N. e.	N. e.	<0.01	<0.01					*0.004*		
Radionuclides												
^{226}Ra	bq/l	N. e.	N. e.	N. e.	**60**	*1.0*		0.125*				
^{228}Ra	bq/l	N. e.	N. e.	N. e.	**30**	*0.1*		0.020*				
Organic substances in the water												
BTEX	mg/l	N. e.	N. e.	N. e.	N. e.						*0.02*	
Benzene	mg/l	N. e.	N. e.	N. e.	N. e.		*0.001*			*0.001*	*0.001*	*0.001*

Parameter	Units	Southern NRW (southern Lower Rhine Bight)		Northern NRW (northern Lower Rhine Bight, Münsterland)		Assessment values**						
		Med.	Max	Med.	Max	WHO	Ordinance on Drinking Water (TrinkwV)	Mineral and table-water ordinance	Ground-water Protection Ordinance (GrwV)	GFS	Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV)	Ordinance on the protection of surface waters (OGewV)
PAK	mg/l	N. e.	N. e.	N. e.	N. e.		*0.0001*			*0.0002*	*0.0002*	
Naphthalene	mg/l	N. e.	N. e.	N. e.	N. e.					*0.001*	*0.002*	*0.0024*

* Commercially sold table waters labelled as "suitable for infants" must conform to activity concentrations of less than 125 mBq/l for ^{226}Ra and and of less than 20 mBq/l for ^{228}Ra. Their total activity concentrations may not exceed 100 mBq/l.

For explanations of abbreviations, see Part C, section C3.2.2

A5.3 Disposal pathways

At present, the formation water and flowback resulting from natural gas exploitation in Germany – from both conventional and unconventional deposits – is disposed of primarily via disposal wells. According to the firm of ExxonMobil Production Deutschland GmbH, the drill / production sites it operates generate a total of about 0.5 million m³ of formation water and flowback per year. The injection wells used in such cases are usually wells sunk into depleted oil or gas deposits, or into other rock horizons with the necessary properties and capacities. ExxonMobil Production Deutschland GmbH reports that previously fracked horizons are not used for flowback disposal. Flowback is transported to injection wells via pipelines or tanker trucks. According to a survey conducted by Lower Saxony's state office for mining, energy and geology (LBEG) in 2010, and later supplemented to include the disposal wells approved through May 2012, a total of 46 disposal wells are known in Lower Saxony[12]. The relevant figures show that in 2010, for example, 27,439 m³of formation water were injected into the Soltau Z6 borehole, 37,859 m³ were injected into Sottrum Z1 and 53,442 m³ were injected into Gilkenheide Z1[13].

12 http://www.mw.niedersachsen.de/portal/live.php?navigation_id=5459&article_id=106793&_psmand=18

13 http://www.erdgassuche-in-deutschland.de/sicherheit_und_umwelt/lagerstaettenwasser/index.html

Prior to being injected, Flowback is processed: after the natural gas in it has been separated out, the remaining hydrocarbons and solids are separated out, to the extent possible, via density separation (Fig. A 32, from: Rosenwinkel et al. 2012).

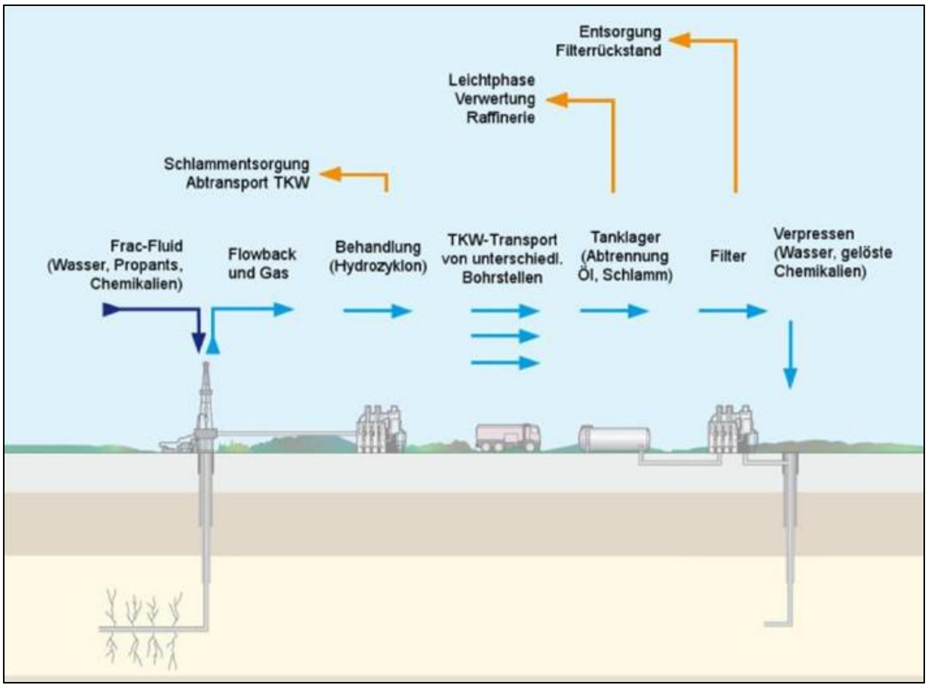

Fig. A 32: General scheme showing how flowback is currently managed (Rosenwinkel et al. 2012) [from left to right: Fracking fluid (water, proppants, chemicals); Sludge disposal, removal via tanker truck; Flowback and gas; Treatment (hydrocyclone); Light phase refined in refinery; Transport by tanker truck, from various boreholes; Disposal of filter residues; Tank storage (separation of oil, sludge); Filter; Injection (water, dissolved chemicals)]

In some cases, mercury and hydrogen sulfide are also separated out. The hydrocarbons that are separated out are processed in refineries, and the solids are disposed of by special companies.

Treating flowback in industrial wastewater-treatment facilities is seen by operators as an option that, while technically feasible, is not economically feasible. They thus tend to prefer disposal via injection and disposal wells. Possible technical processes for treating flowback are described in Rosenwinkel et al. (2012). However, Rosenwinkel et al. (2012) conclude that none of those flowback-treatment processes, at present, qualifies as "best available technology" within the meaning of the Federal Water Resources Act (Wasserhaushaltsgesetz).

A further discussion of the current legal situation with regard to flowback disposal is presented in Part B.

A5.4 Uncertainties / knowledge deficits

Litle information is available about the characteristics of formation water in tight-gas, shale-gas and coal-bed-methane deposits in Germany, such as information about about primary, secondary and trace components, dissolved gases, organic substances and NORM, and absolutely no breakdowns of such information by region or depth are available.

As noted, flowback is a mixture of fracking fluids, formation water and possible reaction products. At present, there is a complete lack of the reliable analyses and mass-balancing data that would make it possible to quantify the varying mixture fractions of fracking fluids and formation water, as well as the fractions of extracted fracking fluids and possible reaction products. To date, no systematic measurements have been carried out for the purpose of identifying transformation and decomposition products in flowback.

In the view of the report authors, flowback disposal via injection into underground layers can pose risks that can be analysed and assessed solely in the framework of site-specific risk analyses. To our knowledge, the binding requirements that would be needed to assure and guide such analysis and assessment are lacking.

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TOC

PART B: EVALUATION OF LEGAL REGULATIONS AND ADMINSTRATIVE STRUCTURES

B1 Legal regulations and administrative structures

The legal section of the study considers issues of water protection and water-pollution control related to procurement, handling, use and disposal of injected and extracted fluids. The key regulations applying to such activities include provisions of mining and water law, along with regulations relative to environmental impact assessment. The study focuses especially on use of substances during actual fracking and on handling and disposal of flowback. In addition, it considers legal requirements pertaining to procurement, storage and transport of fracking fluids.

The present short version of the study includes a summary of the deficits seen, from a legal standpoint, with regard to applicable regulations and administrative structures, also in light of the prevailing scientific and technical parameters and of relevant risk assessment.

B1.1 Mining law

Mining law establishes central requirements for fracking projects, including prerequisites for approvals of operational plans, and the Länder ordinances on deep-drilling (Tiefbohrverordnungen der Bundesländer – BVOT). Such requirements mandate that precautions must be taken to guard against risks, in conformance with generally accepted rules for safety technology and with special requirements, in ordinances on deep-drilling, designed to prevent damage.

At the same time, mining law does not have a "concentration effect" (blanket effect with regard to approvals). Neither does it take precedence over water law. In fact, requirements under water law have to be reviewed either as part of review of whether harmful impacts (for the public sphere) must be expected (Art. 55 (1) No. 9 Federal Mining Act (BBergG)) or as part of review of whether approval of the relevant operational plan would conflict with predominating public interests (Art. 48 (2) Sentence 2 BBergG).

Where an approval procedure under water law is required, water-law aspects must be given priority in review within the procedure. This results from general jurisdiction on delineation of parallel authorization procedures. On the other hand, for deep-drilling, mining authorities have not, to date, routinely carried out approval procedures under water law.

B1.2 Water law

Applicable water law requires the execution of an approval procedure under water law for drilling of boreholes for which fracking is planned (for some future date), for fracking itself and for injection of flowback.

Discharging of substances directly into groundwater, in connection with fracking or with flowback injection, is deemed to constitute a "real use" ("echte Benutzung") that is subject to permit requirements. Discharging of substances into geological formations in which groundwater is not directly encountered is deemed to constitute an "artificial use" ("unechte Benutzung") that is also subject to permit requirements. On the one hand, applicability of permit requirements can result in that an indirect adverse effect on groundwater in the immediate or wider surroundings of the deepest point of the well cannot be ruled out with a sufficient degree of certainty. On the other hand, the Water Framework Directive requires such applicability, since that directive allows the introduction of substances into geological formations only when the relevant conditions have been found to be suitable for such introduction (Art. 11 (3) Letter j WFD). Under German water law, the suitability of the prevailing conditions must be determined as part of the relevant approval procedure under water law.

In the case of wells drilled for later fracking, the applicability of permit requirements results in that all drilling introduces substances into groundwater (drill bits, drilling fluid, casing, cement), as well as in that the planned fracking poses a risk of substance discharges into groundwater via failure of the sealing function of the casing and cementation. To ensure that groundwater is properly protected, the applicable requirements for casing and cementation have to be reviewed, and defined, in a water-law procedure carried out prior to the insertion of the casing.

A permit under water law may be issued only if no adverse impacts on groundwater must be expected (principle of prophylactic water protection, Art. 48 Federal Water Resources Management Act (WHG)). The principle of prophylactic water protection applies to both "real" and "artificial" uses.

No adverse impact on groundwater is deemed to be present if the de minimis thresholds derived from applicable maximum permitted levels, and via toxicological and eco toxicological standards, are not exceeded in exploitable groundwater integrated within natural cycles.

Groundwater is subterranean water in the saturation zone that is in direct contact with the ground or with underground regions. It includes deep groundwater containing salt or pollutants. With regard to deep groundwater containing pollutants, the "suitability for protection", i.e.

any presence of an adverse effect, must be determined on an individual-case basis. For such groundwater, exceeding of the de minimis thresholds developed for exploitable groundwater integrated within natural cycles does not directly constitute an adverse impact on groundwater.

The principle of prophylactic water protection accepts not even the smallest possibility of water contamination; i.e. it requires that such contamination be completely improbable in light of human experience. The law is extremely stringent in this area. In any individual case, all circumstances must be considered. This extends to the possibility of disruptions / incidents, improbable developments and extensive and long-term impacts.

And even when all permit requirements are fulfilled, the decision on whether a permit under water law is actually granted is subject to management discretion. Under such management discretion, residual risks for the safety of the drinking water supply, and for the quality of groundwater, may be considered apart from specific precautions with regard to adverse impacts on groundwater and weighed against the economic benefits of gas exploration and exploitation.

To be sure, these stringent requirements under water law have been upheld by jurisdiction. And yet, water law, like mining law, contains many hazy legal concepts that leave room for interpretation, latitude that can be exploited – and is exploited – by the competent authorities, in various ways. It can be argued that, in practice, such interpretive latitude can lead to a considerable neglect of various aspects of water law. For this reason, the aforementioned situation should be clarified, in the interest of consistent interpretation of water law and of assuring the necessary groundwater protection. This should be accomplished in connection with mining-sector projects, at a suitable level – i.e. either via amendment of federal or Länder law or simply via internal administrative regulations or directives of authorities.

B1.3 Handling of fracking fluids and flowback

With regard to above-ground handling of substances, a distinction has to be made between a) procurement and handling of water and additives, and of the fracking fluids formed by mixing them, and b) handling of flowback.

Procurement of water is subject to the normal requirements, under water law, applying to removal of groundwater and surface water, except in cases in which the water is obtained by other means. Procurement and handling of additives are subject to requirements under laws on chemicals and substances (REACH Regulation, laws on biocides), mining law (ordinances on deep-drilling), water law (facilities for handling substances hazardous to water) and occupational health and safety legislation (mining ordinances, Ordinance on Hazardous Substances (Gefahrstoffverordnung)). Pursuant to requirements under laws on chemicals and substances, for each substance and each mixture involved, it must be determined whether a general or special prohibition on use, a constrainment on approval, a registration obligation or an obligation to prepare a safety data sheet or a use-based safety study applies. For many substances, provisions on transitional periods and on exemptions apply (for example, below certain concentration levels).

Handling of flowback is subject to requirements under legislation on mining waste and on wastewater. Where they are radioactive residues, sludge and deposits fall under legislation on radiation protection, except where compliance with legally defined monitoring limits is assured. Flowback is both liquid mining waste and wastewater, since flowback – recovered water – contains both (unaffected) formation water and injected water that has been affected via human use – addition of additives, injection, mixing with formation water and extraction.

B1.4 Coordination and integration of authorization procedures under mining law and water law

To date, mining law and water law contain no provisions on coordination of parallel procedures. All authorization procedures for mining projects should be completely coordinated – as has been accomplished for legislation on authorization of industrial plants – in order to ensure that before any project commences all relevant conditions for authorization have been met and all required authorizations have been issued. In addition, minimum requirements pertaining to submitted application documents should be established.

The procedure for approval of operational plans should be redesigned, via a federal-level legislative amendment, as an integrated project-approval procedure under environmental law. This would ensure that comprehensive review, under water law, is always carried out, without creating the need for an additional approval procedure to achieve that aim. Compliance with requirements under water law should be ensured either a) by making the mining authority, which serves as the environmental and water-quality authority, subject to the specialized supervision of the highest-level water authority, or b) ensuring that approvals may be issued only with the consent of the water authority.

B1.5 Development of general standards

The key deficits applying to execution of authorization procedures under mining law and water law, for fracking projects, include a lack of specific material standards – especially with regard to requirements under water law – and discrepancies in the stringency of co-existing requirements under mining law and water law.

The applicable requirements level under mining law is the level of generally accepted rules and principles of sound engineering practice. By contrast, under water law, discharges of substances into groundwater are subject to the principle of prophylactic water protection, without any weakening via clauses pertaining to equipment/technology/engineering. Under wastewater law, the higher requirements level of the "best available technology" applies.

The differences between the requirements levels of mining law and of water law have practical implications in that requirements under mining law are detailed via pertinent technical regulations, while either no specifications, or only very general specifications, exist with regard to the principle of prophylactic water protection, relative to groundwater protection, and to "best available technology" requirements for wastewater-treatment equipment used in connection with mining projects. This complicates the task, for mining and water authorities, of reliably assessing requirements under water law. Requirements under mining law (which tend to be less stringent) are easier to apply.

To eliminate this deficit, use of "best available technology" should be made a standard condition for approval under mining law, as it already is under legislation on authorization of industrial plants.

B1.6 Water protection areas

At present, ordinances on protected areas usually contain constraints on approvals for drilling and for certain uses of substances hazardous to water. They also contain prohibitions on discharges of substances hazardous to water, and of wastewater, into underground regions. Normally, such regulations should already mean that drilling and operation of boreholes for fracking and for injection are prohibited, in general, in water protection areas and may be approved only via special exemptions.

Legislative deficits apply to fracking projects within water protection areas in that actual drilling is subject only to certain constraints on approval, while fracking is only prohibited insofar as it is carried out using substances hazardous to water. Currently, it cannot be concluded, with sufficient certainty, that the risks posed by fracking using no substances hazardous to water would be significantly lower than those posed by fracking with substances hazardous to water. For this reason, all fracking – even fracking that uses no substances hazardous to water – should generally be prohibited in water protection areas.

B1.7 Environmental impact assessment (EIA) and public participation

Under German national law, EIA obligations currently apply solely to projects, subject to obligations to prepare operational plans, oriented to gas exploitation at daily production levels greater than 500,000 m^3. That scope violates the provisions of the EIA Directive, however. That directive mandates that EIAs be carried out for deep-drilling, and for above-ground facilities for gas production, even for projects below that threshold, taking account of certain selection criteria. Pursuant to the jurisdiction of the European Court of Justice (ECJ), such projects may not be completely exempted from EIA obligations. What is more, so the ECJ, the applicable selection criteria must be applied either directly via the thresholds or via (supplementary) individual-case review. Since the German EIA ordinance for the mining sector (UVP-V Bergbau) does not fulfil those requirements, the EIA Directive already applies directly, because it takes precedence. For each individual case, it requires that preliminary review be carried out to determine if the specific project involved, at the site in question, is subject to EIA requirements.

Apart from that requirement, the EIA Directive has to be transposed via directive-conformal redefinition of EIA obligations for fracking projects. According to current findings, it cannot be denied that such projects could have extensive, lasting and irreversible adverse impacts on the drinking water supply and on the natural environment. In light of the precautionary and preventive-action principle, this indicates that the threshold for EIA obligations should be set very low for the time being, i.e. that general EIA obligations should be introduced for fracking projects. To ensure they are able to take pertinent new findings into account, the Länder could be given the option, for certain projects carried out under certain geological conditions, of imposing EIA obligations only following preliminary review in individual cases.

In general, EIA obligations should be oriented to drilling and operation of boreholes in which fracking takes place or flowback is injected. And EIA obligations should apply even to set-up and operation of drilling sites with a single borehole (for example, an exploration borehole). Furthermore, the obligations should apply to all drilling and auxiliary facilities taking place / used at a drilling site.

Another central deficit in current legislation is that thus far it has been possible for fracking projects to be carried out without any public participation. Introduction of EIA obligations would immediately eliminate this deficit, because public participation forms part of any procedure involving environmental impact assessment.

Mining projects differ from many other types of environmentally relevant projects in that their environmental impacts are very difficult to predict before the projects actually commence. The potential environmental impacts of such projects will become easier to assess in advance as knowledge and findings in this area advance. On the other hand, such orientation to advancing knowledge is somewhat at odds with the objective of any EIA, namely to ensure that the relevant impacts on the environment are taken into account, in keeping with the EIA results, and as early as possible, in the relevant authorization procedure.

We recommend that advancement of knowledge relative to fracking projects be taken into account by providing new possibilities for public participation in such projects. In addition, it should be ensured that renewed authorization and EIA obligations, following preliminary review in individual cases, arise not solely through project changes that can have significant environmental impacts, but also through adverse changes in key parameters (such as new findings) significant to assessment of a project's environmental impacts.

Site-related environmental impact assessment is inadequate to the task of reviewing plans for exploration and exploitation of unconventional gas over large areas, via numerous boreholes, i.e. plans for systematic, complete-coverage drilling. Due to their above-ground implications, and the need they create for coordination with other area-related planning, such plans should ideally be subject, and may even need to be subject, to regulations at the regional-planning level. The state-wide zoning plans and regional plans of the Länder are suitable instruments for achieving such regulation.

B1.8 Responsibilities

In various ways, as defined by the relevant Länder laws in each case, mining authorities are responsible not only for permits under mining law, but also for central monitoring tasks under water law and other environmental legislation. In general, this is to be welcomed; it is in keeping with modern practice in environmental protection legislation, which seeks to have a single authority function as a "fence authority" ("Zaunbehörde"), i.e. be responsible for all tasks of relevance for environmental protection. This approach prevents fragmentation of responsibilities.

On the other hand, mining authorities tend to be organized as part of ministries for industry and economics, and this is problematic. The core tasks of such authorities include promoting business interests. Only in some areas – in keeping with applicable Länder law, within the framework of tasks entrusted to them under environmental law and, especially, water law – are mining authorities subject to the detailed supervision of the supreme environmental authorities (ministries of the environment). In light of the significant environmental relevance of mining projects, and of environment ministries' responsibility for enforcing environmental legislation, it should at least be ensured that all environmentally relevant decisions, i.e. all decisions relative to approvals under water law, and to environmental impact assessments, and execution of supervisory measures under environmental law, be completely subject to the detailed oversight of environment ministries. Only environment ministries have the necessary competence relative to environmental protection, and environmental protection law, for such oversight.

In addition, we recommend that overall approval and monitoring of mining projects, with regard to environmental and safety legislation, be assigned to the portfolios of environment ministries. Such assignment would be in keeping with the way such tasks are assigned with regard to industrial facilities. Decades ago, responsibilities for monitoring such facilities, with regard to environmental legislation, were transferred from economics ministries to environment ministries, in connection with removal of emission-protection law from the sphere of commercial/industrial law. This was done in order to assure proper enforcement of environmental law.

Careful, impartial review and monitoring of environmental impacts, by the competent authorities, plays an especially important role in connection with publicly controversial projects – such as fracking projects. Without public confidence and trust in such review and monitoring, even detailed study of pilot projects' environmental impacts will hardly be likely to meet with sufficient public acceptance.

PART C: RISK ASSESSMENT AND DEFICIT ANALYSIS

The following assessment of the risks that can be related to exploration and exploitation of unconventional natural gas deposits, and the following analysis of the deficits of knowledge and information that are still relevant, builds on the results of Parts A and B of the present study. In addition, it is limited to the following aspects that, in the perspective of the Federal Environment Agency and of the study authors, may be considered of central importance for risk assessment:

- Identification and assessment of the most important pathways for impacts on natural systems, via the water-related aspects of fracking studied.
- Control and monitoring of fracture formation during fracking.
- Assessment of fracking additives and of the flowback returning to the surface.
- Assessment of aspects related to permanent deposition of fracking additives in underground formations.
- Assessment of methods for disposal / re-use of flowback.
- Methodological information relative to execution of site-specific risk analyses.

The following remarks are limited in scope to the water-related risks that can arise via use of fracking technologies in exploration and exploitation of unconventional natural gas deposits. Other environmental impacts (noise, light, dust, seismic impacts, etc.) were not considered.

No translation has been included of the extensive Annex to which frequent reference is made in the following. The Annex is thus available only in German.

C1 Water-related impact pathways

Chapter A2.2 (Part A) describes, in detail, the potential water-related impact pathways that must be considered in relation to fracking. In sum, they can be characterised as follows:

- Pathway group 0: (Pollutant) substance discharges directly at the ground surface ("from above").
- Pathway group 1: (Pollutant) substance rises and spreading along boreholes.

- Pathway group 2: (Pollutant) substance rises and spreading along geological faults.
- Pathway group 3: Direct discharges of fracking fluids into underground regions, and (pollutant) substance rises and spreading without the presence of preferred pathways (diffuse).
- Flowback disposal via disposal wells.
- Summation and combination of different impact pathways and long-term impacts.

For an impact pathway to function effectively, it must have adequate permeabilities and potential differences. For this reason, for each site being considered, one must understand the relevant hydrogeological system, if one wishes, in advance of any exploration and exploitation, to identify, model and monitor the possible large-scale and combined impacts of such exploration and exploitation. Such understanding must, in particular, include an understanding of the applicable large-scale interrelationships (the geological system).

"Hydraulic head or piezometric head is a specific measurement of liquid pressure above a geodetic datum" (http://en.wikipedia.org/wiki/Hydraulic_head (18.12.2012)). In the case of groundwater, the hydraulic potential ("head") for an open groundwater surface may also be expressed as the groundwater level. But since in many cases the groundwater surface is usually not open (this is the case, for example, in deep groundwater flow systems), the term "potential" ("head") is used. Water always flows from a higher potential to a lower potential. The decisive factor is the potential difference. In the case of upwardly pointing potential differences, the groundwater rises against gravity (for example, in artesian systems), while downwardly pointing potential differences have the opposite effect (for example, in the case of infiltration of rain water).

Pathway group 0 represents an exception in that geological and hydrogeological factors play no more than a subordinate role in it (protective function of covering strata). Discharges via this pathway group are direct discharges "from above".

C1.1 Water-related risks of fracking, via impact pathways

Under suitable geological and hydrogeological conditions, the following can rise and spread via the impact pathways described in Section A2.2:

- Fracking fluids,

- Formation water,
- Solution, reaction and transformation products formed from combinations of fracking fluids and formation water, and
- Gases,

and can rise and spread into near-surface (exploitable) groundwater. When such rising and spreading occurs, pollutants and gases can enter near-surface water cycles and qualitatively impair existing uses and systems (drinking water production, surface waters, groundwater-dependent ecosystems, etc.). Furthermore, project-related changes in natural permeabilities and hydraulic potentials can lead to changes in large-scale hydrogeological flow systems (for example, when fracking in a target horizon increases permeabilities throughout nearly all of a large area).

The potential water-related risks via the identified impact pathways thus include:

- Discharges of fracking fluids into near-surface (exploitable) groundwater (surface / underground),
- Discharges of fracking fluids into deep (in part heavily mineralized) groundwater (underground),
- Discharges of fracking fluids into near-surface (exploitable) groundwater (surface),
- Rising of deep water (with / without fracking fluids) into near-surface (exploitable) groundwater (underground),
- Hydrogeological impacts on the system as a whole (changes in permeabilities and potentials; interactions between different groundwater flow systems; and interactions between such systems and near-surface systems, underground),
- Supraregional impacts on water resources (water requirements / disposal),
- Rising of gases (including methane) (underground).

C1.2 Importance of water-related impact pathways, and legal requirements

With the exception of pathway group 0, the importance of the impact pathways depends, in each case, on the prevailing geological and hydrogeological conditions (permeabilities and potentials). In each case, such importance must thus be assessed site-specifically, on the basis of suitable preliminary work. The sample remarks in Part A (Sections A2.4 and A2.5) relative to selected geological systems illustrate how each such system must be expected to have specific issues of its own (cf. Tab.

A 4) that must be addressed before the importance of the applicable impact pathways can be assessed. With regard to geological systems with potential unconventional natural gas deposits in Germany, no generally valid assessment of the importance of the various impact pathways is possible in the framework of the present study.

On the other hand, it is possible to assess, qualitatively, the importance of the impact pathways with regard to the various operational phases in exploration and exploitation of unconventional natural gas deposits via fracking. Each operational phase involves (different) interventions of its own that can have environmental impacts via (different) impact pathways. The present study differentiates between the following phases:

- Fracking for exploration/exploitation
- Production (operation)
- Post-operational phase (long-term safety)

The various phases differ in terms of the scopes of their phase-specific interventions (the scale considered), and thus the areas to be considered, in assessment of potential environmental impacts, differ for the different phases. Exploration via drilling without fracking was not considered, since the present study focuses on the risks related to fracking.

Interventions in the operational phase of a "fracking for exploration" project are tied to the individual case involved. They mainly involve local impacts on the site in question (although they also include surrounding areas in the case of deviated drilling).

With regard to the phases "fracking for exploitation" and "production", the focus is both on local impacts and on the wider framework of the summed effects of large-scale, multiple hydraulic stimulation and exploitation of deposits.

The "post-operational phase" comprises the follow-on care phase after production has terminated. In that phase as well, the focus is primarily on summed and long-term impacts, as well as on local impacts.

In the following, the importance of the impact pathways in the various operational phases is assessed. This assessment should be understood as an indication of the focus and effort that one must invest, in analysis of impact pathways in advance of a project's operational phase, if one is to be able to assess the water-related risks sufficiently precisely. The various required prevention, reduction and monitoring measures are derived from such analysis.

Pathway group 0: (Pollutant) substance discharges directly at the ground surface

Pathway group 0 is relevant especially during the fracking phase, when handling of fracking fluids and of flowback – including transport, storage and disposal – is most intensive. Pollutant discharges at the ground surface can occur via accidents, disruptions or improper handling.

During production, production water removed from the borehole has to be transported away and disposed of. Such transport and disposal also entails potential risks for near-surface water cycles.

The pertinent legal provisions are discussed in detail in Part B.

Pathway group 1: Spreading of pollutants along boreholes

With regard to impact pathways in pathway group 1, a distinction must be made between production boreholes and existing old boreholes, such as boreholes remaining from other types of exploration and uses (geothermal energy, hydrocarbon exploration).

During fracking, leakages can occur along a production borehole, leading to an unintentional release of fracking fluids into the annulus or into the surrounding rock. In a worst-case scenario, fracking fluids can be released directly into an aquifer. A number of factors determine whether a casing failure, and a resulting release of fracking fluids into the annulus, will be detected during the fracking process itself (in the form of a rapid loss of pressure). Such factors include the size of the leak and the permeability of the annular-space seal. The risk of direct discharges into near-surface groundwater aquifers, via leakages in the annulus, can be reduced via suitable technical measures in connection with insertion of the casing (cf. section A3.3.1)

Remarks regarding the relevant technical standards are provided in Chapter A3. The mining-law provisions that apply during drilling operations are discussed in Part B.

Options for controlling and monitoring crack formation in fracking also play an important role with regard to old boreholes (cf. section 3.3.3) and Chapter C2), since fractures can open up direct hydraulic connections to old wells.

During production, and depending on the hydrogeological conditions and the techniques being used, a local, temporary potential drop can occur in the area affected by the production well. This would tend to reduce the likelihood of any unregulated rising of gases and fluids along the borehole. In any individual case, such possibilities have to be analysed with the help of numerical groundwater-flow modelling.

In the post-operational phase, issues of long-term integrity – and especially of the integrity of cementations and casing – are especially important, with regard to both production wells and old boreholes. Normally, the original potential conditions tend to restore themselves when production is terminated. In the case of upwardly pointing potentials, in connection with suitable permeabilities, rising of gases, fracking fluids and formation water can then occur along boreholes.

Pathway group 2: Spreading of pollutants along faults

In pathway group 2 – assuming the relevant permeability – continuous faults / fault systems leading from the area of the target horizon (in which fracking is taking place) to the ground surface must generally be considered more significant, with regard to hazards for near-surface groundwater resources, than faults that penetrate only partial areas of the basement and covering layers. On the other hand, given the right pressure and permeability conditions in the rock, the latter faults can function as shorter pathways through which gases and fluids can rise. In the present context, the importance of such pathways as pathways for rising is seen less in connection with the relatively short period over which fracking actually takes place (normally, periods of just a few hours) and more in a long-term perspective, after the conclusion of production.

Options for controlling and monitoring fracture formation in fracking play an important role also with regard to pathway group 2 (cf. Chapter C2), since fractures can open up direct hydraulic connections to faults and fault systems.

Pathway group 3: Pollutant spreading apart from preferred pathways

Like spreading through the impact pathways of pathway group 2, (diffuse) rises through the overburden, and lateral spreading of fluids and gases, depend primarily on the relevant permeabilities and potential conditions. With regard to fracking, the phases actually involving fracking itself – at the depths > 1,000 m that are currently being discussed – are considered to be too short to be able to directly impair near-surface groundwater resources via this pathway. During production, uncontrolled rising of gases via these impact pathways would be the primary relevant factor. These impact pathways are also considered significant for post-operational phases, when pertinent permeabilities and potentials are present or reappear.

Pathway group 3 also includes direct – intended – injection of fracking fluids, during the actual fracking process, into underground regions and, thus, possibly also into groundwater. The hydrochemical properties of underground groundwater can be impaired both by such direct discharges and by reaction processes that can occur between fracking fluids, formation water and rocks.

The legal aspects of injection of fracking fluids into underground regions are discussed in Part B.

Summation and combination of different impact pathways and long-term impacts

Summation and combination of the aforementioned impact pathways play a role in all operational phases considered, and they must be appropriately taken into account. Such assessment is possible only on the basis of an extensive understanding of the geological and hydrogeological conditions prevailing in deep underground layers. Numerical groundwater models are useful tools for making predictions in this regard.

Since many flow processes deep underground take place very slowly, the relevant long-term impacts have to be estimated – also in connection with effects that must be summed. In such estimation, the geological and hydrogeological properties of the relevant geological system must be taken into account. In the main, impacts on a hydrogeological system are long-term changes that would be likely to appear as significant impacts only after periods of years / decades (such as impacts of intensive fracking over large areas).

Disposal

Disposal of flowback and production water, by injection into underground regions via disposal wells, plays a significant role with regard to substance discharges, both during the actual fracking process (or during withdrawal of fluids) and during the production phase (flowback disposal). With regard to long-term borehole integrity, one must also consider, however, the extent to which substances injected into underground regions represent hazards for the aquatic environment. Additional remarks on this issue are provided in Chapter C5. The pertinent legal aspects are discussed in Chapter B4.

C2 Control and monitoring of fracture formation during fracking

The theoretical foundations of the fracture-formation process during fracking are described in detail in Part A (cf. section A3.3.3).

The main risk presented by "uncontrolled" fracture formation is that it can form an (unintended) connection to a hydraulically active element (old well, fault, permeable rock layer) (cf. the remarks in section C1). The possible impacts include:

- Creation of a connection to a hydraulically active old borehole or fault, leading to – unintended – rising of gases and fluids into near-surface groundwater,
- Formation of fractures into areas with increased hydraulic permeability (and, possibly, with groundwater flows), leading to diffuse rises of gases and fluids into near-surface groundwater.

Prior to actual fracking, fracture formation can be modelled with the help of coupled hydraulic-mechanical models (cf. also section A3.3.3 and BGR 2012). For such modelling, one requires a detailed knowledge of the geomechanical properties of the target formation and of the stresses prevailing underground.

While simulations of fracture formation can be carried out prior to fracking, such simulations are subject to certain uncertainties, in keeping with the parameters selected; it is not possible to predict fracture propagation precisely (cf. also US EPA 2011).

The following options are available for monitoring fracture formation during fracking:

- Monitoring of pressure during the fracking process: The possibility of detecting a connection to a hydraulically active underground element (along with a related release of fracking fluids) during the fracking process, via pressure monitoring (for example, via detection of a rapid loss of pressure), depends on a number of factors, including the size of the pertinent connection (i.e. the magnitude of the loss of fracking fluids), the pressure conditions prevailing in it, the permeability of the element involved and the nature and intensity of the monitoring (slow losses are difficult to detect).
- Fracture formation can be monitored seismically with the help of geophones. The key factors for minimizing uncertainty in interpretation of relevant measurements include geophone placement, the horizontal and vertical distances between geophones and the area in which stimulation is taking place. It often proves useful to array measuring instruments in one or more neighbouring boreholes, at various depths,and at the smallest possible distances to the area

being stimulated (< 1 km) (Warpinski 2009). So arrayed, instruments are able to detect micro-seismic events, such as those that occur in fracture formation. Via analysis of the resulting measurements, relevant events can be localized, and interpreted with regard to their underlying processes.

Overall, the authors of the report see a need for improvement in modelling, control and monitoring of fracture propagation, since the position and size of created fractures can be key factors in determining the relevance of the impact pathways of pathway groups 1 through 3, and in derivation of pertinent "safety distances" (cf. also US EPA 2011, p. 37 f).

C3 Potential hazards of fracking fluids

C3.1 Use of fracking additives

The study authors are aware of a total of 112 substances that have been used in the past in fracking fluids in Germany (cf. Chapter A4 and Annex 2). Unambiguous identification was possible for only 76 of those substances – either on the basis of a CAS number or via determination of the proper, unique names of the substances / substance mixtures involved (this involved research and produced a number of corrections; these have been marked "korr." in Annex 2). In the following, these 76 substances (of which 9 are proppants and 67 are additives for a range of different applications) are used as a referential database. It was not possible to assess the remaining 36 substances / substance mixtures that could not be uniquely identified via a CAS number, nor was it possible to assess substances not listed in pertinent Material Safety Data Sheets or not subject to specific labelling requirements.

For the 76 substances / substance mixtures involved, the status of pertinent REACH registration, the applicable water hazard classification pursuant to VwVwS[1] and the pertinent classification and designation pursuant to the CLP Regulation[2] were determined via research (Annex 2). The status of REACH registration was determined by querying the ECHA databases *"registered substances"* and *"preregistered substances"*, using the pertinent CAS numbers (ECHA 2012). The water hazard classifications were determined via evaluation of the Federal Environment Agency's Rigoletto database (UBA 2009). Classification pursuant to the CLP Regulation was determined via evaluation of the Classification and Labelling (C&L) Inventory of ECHA (ECHA 2012). Where, for substances with non-harmonised classification, different classifications had been reported to ECHA, the most extensive classification was chosen from among the three most frequently reported classifications.[3]

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[1] Administrative regulation on the classification of substances hazardous to water (Verwaltungsvorschrift wassergefährdende Stoffe) of 17 May 1999, last amended on 27 July 2005.

[2] Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006.

[3] The frequency of such reporting can be influenced by multiple notifications by corporate groups with multiple legal units. Furthermore, substances with no classification are not listed in the C&L Inventory.

REACH registration

Of the 76 substances uniquely identified via a CAS number, 49 have been fully registered within the REACH system (Annex 2), and thus have been described in published dossiers (ECHA 2012). One of the substances (zirconium oxychloride, CAS No. 7699-43-6) has been registered only as an intermediate product. An additional 24 substances have been preregistered under REACH. Two substances used in the past in fracking in Germany (formaldehyde, polymer with 4-nonylphenol and phenol, which is likely to be used as a proppant coating, CAS No. 40404-63-5; and the substance mixture "alcohols, C11-14-iso-,C13-rich, ethoxylated propoxylated", CAS No. 78330-23-1) have neither been registered nor been preregistered under REACH. It should be noted that polymers are not subject to registration under the REACH system (Article 2 (9) REACH Regulation).

Classification in water hazard classes

The Federal Environment Agency's Rigoletto database contains a water hazardousness classification for a total of 65 of the 76 substances with unique CAS numbers (Annex 2):

- Only one of the compounds among the 76 additives has been classified as a severe hazard to waters (WGK (water hazard class) 3): a biocide that is a mixture of 5-chloro-2-methyl-2H-isothiazol-3-one and 2-methyl-2H-isothiazol-3-one (and is sold under the trade name (inter alia) Kathon®). This biocide is the biocide most frequently used in the fracking fluids assessed; it was used in a total of 11 fluids after the year 2000 (Annex 2).
- 17 other substances have been classified as hazards to waters (WGK 2). After the year 2000, a total of 11 additives with water hazard class (WGK) 2 were used. Of these, the additive most frequently used was tetraethylenepentamine, the sodium salt of chlorous acid and 2-bromo-2-nitro-1,3-propanediol.
- A total of 40 other substances have been classified as low hazards to waters (WGK 1). Of those, 31 continued to be used in fracking fluids after the year 2000.
- 6 substances, predominantly proppants, have been classified as not hazardous to waters (nwg).
- For another proppant, ceramic materials (bauxites) with CAS No. 66402-68-4, the classification varies (water hazard class (WGK) 1-3), depending on the specific substance composition in each case.

Classification and labelling pursuant to the CLP Regulation

Classification and labelling specifications pursuant to CLP Regulation (EC) No 1272/2008 have been reported to ECHA for 69 of the 76 substances.

Classification and labelling have been harmonised, pursuant to Annex VI of the Regulation, for 34 of the substances (Annex 2).

- 31 substances have been classified in the hazard class acute toxicity (acute oral, dermal and or inhalation toxicity). Six of the substances have been classified in the hazard categories acute toxicity categories 2 and 3, while the other 25 substances have been classified in acute toxicity category 4. A total of 22 of the 31 substances classified as acutely toxic are still found in newer fracking fluids in use since 2000 (Annex 2).
- 9 substances have been classified in the hazard class carcinogenicity. Three of these substances (Stoddard solvents with CAS No. 8052-41-3, aromatic solvents with CAS No. 64742-95-6, and the ceramic materials (bauxites) with CAS No. 66402-68-4 that are used as proppants) have been classified as carcinogenic category 1B, meaning they are likely to be carcinogenic in humans. An additional 6 substances have been classified as carcinogenic category 2, meaning they are suspected of triggering carcinogenic effects in humans (Annex 2). A total of 7 of the 9 substances that have been classified as probably or possibly carcinogenic are still found in newer fracking fluids in use since 2000.
- 2 substances, the Stoddard solvent and the aromatic solvent, have also been classified in the hazard class germ cell mutagenic (mutagenic category 1B). The Stoddard solvent has also been used in newer fracking fluids in use after 2000.
- 4 substances (boric acid, disodium octaborate tetrahydrate, sodium tetraborate and potassium iodide) have been classified as probably toxic for reproduction (Repr. category 1B). All 4 substances have been used in newer fracking fluids in use since the year 2000 (Annex 2).
- 13 substances have been classified as acutely or chronically hazardous to the aquatic environment. Four of these substances (the biocide 2-bromo-2-nitro-1,3-propandiol, the sodium salt of chlorous acid, citrus terpene and the biocide consisting of 5-chloro-2-methyl-2H-isothiazol-3-one and 2-methyl-2H-isothiazol-3-on) have been classified as acutely hazardous to the aquatic environment (category 1 - Aquatic Acute 1), and the last two have also both been classified as chronically hazardous to the aquatic environment, category 1 (Aquatic Chron. 1). 11 of the 13 substances classified as hazardous to the aquatic environment have been used in newer fracking fluids in use since 2000 (Annex 2).

The applicable classifications in other health-relevant hazard classes are listed in Annex 2; due to limitations of space, they are not discussed further here.

C3.2 Assessment of the hazard potential of selected fracking fluids

The potential hazards of a release of fracking fluids, formation water and/or flowback, for water systems – and especially groundwater – are assessed primarily in light of human use of such water resources for drinking water and in light of the organisms living in the aquatic environment. In the following section, an assessment method is first presented and then applied for assessment of five selected fracking fluids.

The classifications of the preparations and fracking fluids used, with respect to requirements for above-ground facilities (classification in water hazard classes) and to occupational health and safety (classification and labelling in accordance with laws pertaining to hazardous substances), are discussed separately (cf. sections C3.2.5 and C3.2.6).

C3.2.1 Assessment method

Under water law, the key requirement to be applied in assessing releases of substances into the environment is that releases must not adversely affect the water quality of groundwater (Art. 48 (1) Federal Water Resources Management Act (WHG)). An adverse effect on the quality of near-surface groundwater – i.e. of the exploitable groundwater that is integrated within natural cycles – has occurred, if water quality has worsened more than slightly. In general, mineralized deep groundwater is also subject to the WHG's scope of application. In determination of whether, and as of which threshold, an adverse effect on such groundwater has occurred, one must consider the possibly affected groundwater's need for protection in light of potential human uses and of the water's importance with regard to the natural environment.

An adverse effect on the water quality of groundwater must be assumed if relevant legal and sublegal limit values, guide values and maximum values, and especially the de minimis thresholds[4] ("Geringfügigkeitsschwellenwerte" - GFS) of the Federal/Länder Working Group on Water (LAWA 2004), are exceeded in exploitable groundwater. Those de minimis thresholds are based primarily on the maximum permitted concentrations specified by the Ordinance on Drinking Water (TrinkwV), and on human-

[4] The de minimis threshold (Geringfügigkeitsschwelle – GFS) for a substance is the maximum concentration of the substance at which, in spite of an increase in groundwater with respect to regional background values, no relevant ecotoxicological effects can occur, and conformance with the requirements of the TrinkwV, or with pertinent derived values, is still assured (LAWA 2004).

toxicologically and ecotoxicologically established effect thresholds, in order to ensure that groundwater remains available as drinking water for human consumption, and remains intact as a habitat and as part of the natural environment.

For a majority of the substances used as fracking additives, no de minimis thresholds, or other values for assessment under water law, are available. For such substances, therefore, health-related guidance values[5], or health orientation values[6] and ecotoxicologically established PNEC values[7], were researched, or derived using published methods, following the relevant concept of LAWA (2004) (cf. sections C3.2.3 and C3.2.4). The database so produced, on selected additives, is presented in Annex 3 (hygienic guidance values and orientational values in Tables 1 and 2, ecotoxicologically effective concentrations and PNEC values derived from them, in Tables 3 and 4), and physical and chemical properties in Table 5).

The pertinent potential hazards of fracking fluids are assessed on the basis of the individual substances involved. This is achieved by calculating substance-specific risk quotients of substance concentrations and assessment values (de minimis threshold (GFS), GVDW, HOV or PNEC):

$$\textit{Risk quotient} = \frac{\text{Substance concentration in the fluid}}{\text{Assessment value}}$$

When a substance has a risk quotient < 1, no hazard potential is expected, while a risk quotient ≥ 1 represents a human-toxicological or ecotoxicological hazard potential. In the present report, a risk quotient > 1,000 is assumed to represent a high hazard potential. That value, which is used by way of example, and has not been scientifically established, would need to be site-specifically reviewed on the basis of exposure scenarios – for example, scenarios based on numerical models. The aim of such efforts is to identify and assess, on the basis of the

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5 The health-related guidance value for drinking water (GVDW) is the maximum concentration of a substance in drinking water that can be tolerated for a lifetime without suffering adverse effects on health.

6 The health orientation value (HOV) is a precautionary value for substances that cannot be (or can only partially be) toxicologically assessed (UBA 2003).

7 The PNEC value (Predicted No Effect Concentration) is the maximum concentration of a substance at which no effects on organisms of an aquatic ecosystem are expected (EC TGD 2003).

individual substances involved, the human-toxicologically and ecotoxicologically relevant substances with high hazard potentials.

The present study makes no attempt to estimate the total toxicity of fracking fluids by aggregating the risk quotients of the relevant individual substances, because the common methods for such estimation (such as assuming that the total, combined effects of relevant individusl substances can be determined by summing the substances' concentrations) cannot take account of possible synergistic or antagonistic effects in complex fluids.

C3.2.2 The substance concentrations to be considered

In the case of substance discharges at the surface (pathway group 0 in Fig. C1), the substance concentration must be considered at the groundwater surface (seepage water). On the other hand, and by analogy, in the case of a possible release from the fracking horizon (and related rising via pathway groups 1 through 3), the base of the exploitable aquifer is to be used as the focus site for assessment (cf. Fig. C1).

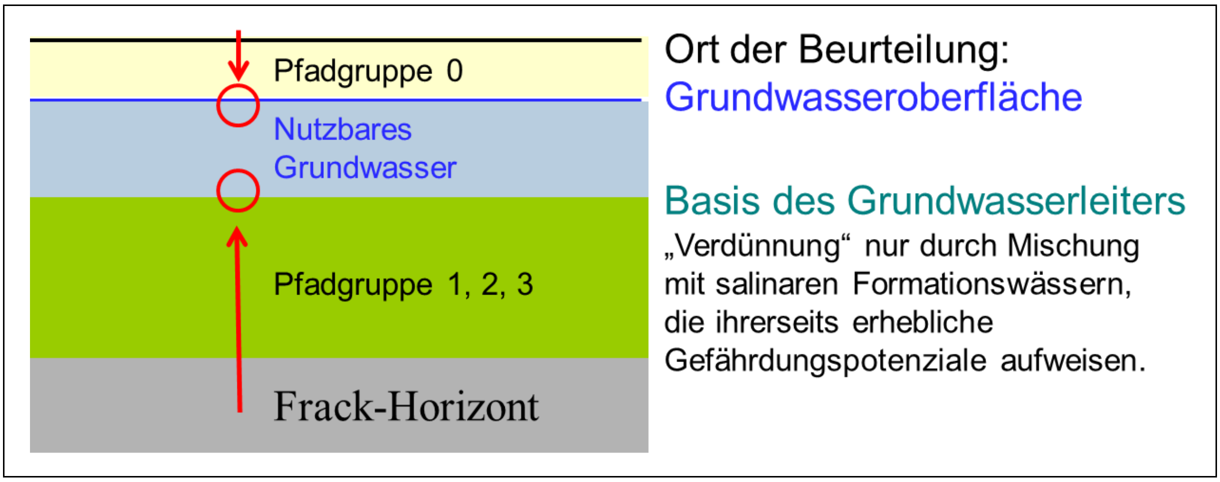

Figure C1: Focus sites for assessment (red circles) in connection with substance discharges into a near-surface, exploitable aquifer (blue) via input pathways from the surface (pathway group 0) and from the fracking horizon (pathway groups 1-3) (source: IWW) [right side, from top to bottom: Assessment site: Groundwater surface; Base of the aquifer; "Dilution" solely via mixing with saline formation water, which itself has significant hazard potential.]

The relevant substance concentrations can properly be assessed only site-specifically, for possible discharge and exposure scenarios, using suitable models that take account of all relevant hydraulic and geochemical transport, mixing, decomposition and reaction processes along the underground flow pathways. No such models are available at present that have the necessary resolution.

As long as suitable models are lacking, hazard potentials are assessed on the basis of substance concentrations in (undiluted) fracking fluids and formation water. This approach is intentionally designed to ignore any possible substance-dilution effects in connection with discharges into the environment. The reasons for this are as follows:

- In pathway group 0, only slight dilution effects can be expected.
- In pathway groups 1 through 3, mixing and reactions with saline deep groundwater can occur via the overburden, and such groundwater can itself present high potential hazards. Dilution can be expected to reduce the hazard potentials substantially only when freshwater resources are reached. On the other hand, such dilution entails contamination of exploitable water resources.

The hazard potential of possible fluids discharged into an exploitable aquifer via pathway groups 1 through 3 is thus estimated by assessing the two end elements of the mixture sequence (fracking fluids and deposit-specific formation water). Due to acute knowledge deficits, it is not possible at present, in making such assessments, to take account of possible transformation and degradation reactions, or of sorption and dissolution processes, along flow pathways. On the other hand, in assessment of individual substances we do call attention to the substances' physical and chemical properties, degradability and degradation products.

In the view of the study authors, dilution calculations, unaccompanied by quantitative, model-based approaches, are of little use in assessing fracking fluids. The assessment method presented here thus differs from work carried out in the framework of the ExxonMobil information and dialogue process, in which the hazard potentials of fracking fluids were assessed in light of assumed degrees of dilution (with selected factors ranging from 1,000 to 100,000) (Ewers et al. 2012).

C3.2.3 Assessment values with regard to water law

Under water law, the key requirement to be applied in assessing discharges or releases of substances into groundwater is that such discharges or releases must not adversely affect the water quality of groundwater (Art. 48 (1) Federal Water Resources Management Act (WHG)). An adverse effect on the quality of near-surface groundwater – i.e. of the exploitable groundwater that is integrated within natural cycles – has occurred, in any case, if the maximum permitted concentrations pursuant to the Ordinance on Drinking Water (TrinkwV) are exceeded. It has not occurred if water quality has changed only slightly. Consequently, the de minimis thresholds ("Geringfügigkeitsschwellen" – GFS) developed by LAWA, taking account of the test values specified by the Federal Soil Protection Ordinance (BBodSchV), may be used as a basis in such assessment.

In general, mineralized deep groundwater is also subject to the WHG's scope of application. In determination of whether, and as of which threshold, an adverse effect on such groundwater has occurred, one must consider the possibly affected groundwater's need for protection in light of potential human uses and of the water's importance with regard to the natural environment.

Hazards to resources/assets can occur via rising of formation water – rising either triggered or intensified by a frack – into near-surface groundwater or via accidents in recovery, processing or storage of flowback. The values for assessing such hazards were obtained from the regulations listed in the following, on the basis of relevant resources/assets-based or use-based maximum permitted values, guideline values, threshold values and test values, and environmental quality standards. In each regulatory context, the most stringent value specified was chosen for assessment purposes.

- GFS: De minimis thresholds (Geringfügigkeitsschwellenwerte; LAWA 2004)
- TrinkwV: Ordinance on Drinking Water (Trinkwasserverordnung; version as of May 2011
- WHO: Guidelines for drinking water quality 4th ed. - World Health Organisation 2011
- MTVO: Mineral and Table Water Ordinance (Mineral- und Tafelwasserverordnung) of 1 August 1984, version of December 2006; the maximum concentrations permitted as of 1 January 2008 are used as the basis for assessment
- GrwV: Groundwater Protection Ordinance (Verordnung zum Schutz des Grundwassers), version of 9 November 2010
- OGewV: Ordinance on the Protection of Surface Waters (Verordnung zum Schutz der Oberflächengewässer – Oberflächengewässerverordnung), version of 20 July 2011; the values used are the environmental quality standards (Umweltqualitätsnormen – UQN) for aboveground water bodies (not including transitional waters)
- BBodSchV: Federal Soil Protection and Contaminated Sites Ordinance (Bundes-Bodenschutz und Altlastenverordnung) of 12 July 1999 (Federal Law Gazette I, p. 1554), last amended by Article 5 (31) of the Act of 24 February 2012 (Federal Law Gazette I, p. 212).

The suitability and admissability of water, as drinking water or mineral water, are assessed on the basis of the TrinkwV, WHO and MTVO. When groundwater loses its exploitability as drinking water, as a result of pollutant discharges, an adverse impact on groundwater has occurred.

The chemical condition of groundwater and surface waters is assessed on the basis of the threshold values pursuant to the Groundwater Protection Ordinance (GrwV), and of the environmental quality standards for surface water pursuant to the Ordinance on the Protection of Surface Waters (OGewV). An adverse change is also deemed to have occurred when the condition of groundwater or surface waters is no longer good, as the result of a pollutant discharge.

Every instance of groundwater pollution in which the pollution level is greater than "slight" is an instance of an adverse impact on groundwater. The de minimis thresholds ("Geringfügigkeitsschwellen" – GFS) for assessment of locally confined groundwater pollution have been specified by the Federal/Länder Working Group on Water, taking account of the maximum permitted concentrations set forth by the Ordinance on Drinking Water (TrinkwV) and of human-toxicologically and ecotoxicologically established effect thresholds (LAWA 2004). The GFS are closely related to the assessment principles of the Federal Soil Protection Act (Bundesbodenschutzgesetz) and of the Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV). Pursuant to those principles, the presence of a harmful soil change, or of a contaminated site, need no longer be suspected if the test values in Annex 2 BBodSchV for the impact pathway "soil – groundwater" are not exceeded at the assessment site (transition between the unsaturated and saturated zones).

C3.2.4 Derivation of human-toxicological assessment values

In an approach similar to that of the European Commission's "Technical Guidance Document on Risk Assessment" (EC TGD 2003), fracking fluids were assessed on the basis of available human-toxicological data. The relevant toxicological data were obtained via the substance names or CAS numbers of the fracking additives concerned, and the available NOAEL and TDI values (No Observed Adverse Effect Level and Tolerable Daily Intake, respectively) were compiled via evaluation of technical databases and publications of the following organisations:

- Hazardous Substances Data Bank (HDSB):
  http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB
- Toxicological Data Network (Toxnet):
  http://toxnet.nlm.nih.gov/
- Integrated Risk Information System (IRIS):
  http://www.epa.gov/iris/
- Health Environmental Research Online Database (HERO):
  http://www.epa.gov/hero/

- United States Environmental Protection Agency (U.S. EPA): http://www.popstoolkit.com/tools/HHRA/TDI_USEPA.aspx
- Health Canada: http://www.popstoolkit.com/tools/HHRA/TDI_HealthCanada.aspx
- World Health Organization (WHO): http://www.who.int/en/
- PAN Pesticide Database: http://pesticideinfo.org/
- European Chemicals Agency (ECHA): http://echa.europa.eu/

Determination of the health-related guidance value for drinking water (GVDW)

With regard to a hypothetical case of contamination of drinking water with fracking fluids, the availability of data on the individual substances involved, with regard to the substances' adverse impacts on human health, was reviewed. For substances for which adequate data are available, the pertinent health-related guidance value for drinking water (GVDW) was determined. Where drinking water that contains a potentially toxic substance conforms to the GVDW, the relevant database is considered adequate, and thus humans may drink the water for a lifetime without having to expect adverse impacts on their health, in light of that database. The GVDW is calculated as the product of the tolerable daily intake (TDI), the average body weight involved (this works out to 70 kg) and the TDI percentage ingested with drinking water (10 - 80 %), divided by the volume of drinking water consumed per day (this works out to an average of 2 l).

The TDI value itself is calculated from the No Observed Adverse Effect Level (NOAEL) or Lowest Observed Adverse Effect Level (LOAEL), divided by an extrapolation factor that consists of up to four parts (EF_{1-4} = 1 - 1000, maximum of 10 per EF_x), and that is used for extrapolation of animal-experiment data to humans, and, possibly, also divided by an assessment factor (Sicherheitsfaktor (SF) = 1 - 10). The total factor TF (Gesamtfaktor – GF) is the product of all factors EF and SF via which the NOAEL or LOAEL values are divided. For substances without a defined TDI value, the NOAEL value reported in the literature (where the data were considered adequate – no further EFs and no further SF required) was thus divided by 1,000.

Calculation of the GVDW was based on the conservative assumption that, for lifelong ingestion of 2 L of drinking water per day, no more than 10

% of the tolerable daily intake of a substance harmful to human health would be ingested with the drinking water[8].

The NOAEL and TDI values reported in the literature for selected fracking additives, and the health-related guidance values for drinking water calculated from those values, are listed in Annex 3.

Use of the health orientation value (HOV)

For those substances for which no sufficiently reliable, human-toxicologically evaluatable data were available, the Federal Environment Agency's precautionary concept for "substances carried in drinking water which cannot be assessed, or which can be assessed only partially" (HOV concept) was applied (UBA 2003). The lowest HOV (0.01 µg/L) applies for potently genotoxic substances, while the second-lowest (0.1 µg/L) applies for substances that either a) have been proven to be not genotoxic or b) have not been genotoxically tested (and for which no other toxicologically evaluatable data are available). Substances proven to be not genotoxic, and for which data on neurotoxicity (*in vivo* and *in vitro*) and on other specific toxicity endpoints are available, receive an HOV of 0.3 µg/L, if no lower value can be justified with the same data. Where data on subchronic oral toxicity are also available for a substance, the substance may be given an HOV of 1.0 µg/L if no lower value can be derived from such subchronic data. Similarly, substances for which a chronic oral toxicity study has also been carried out receive an HOV of 3 µg/L if the pertinent chronic data do not justify a lower value.

C3.2.5 Derivation of ecotoxicological assessment values

Method for deriving PNEC values

The PNEC value (Predicted No Effect Concentration) is is the maximum concentration of a substance at which no effects on organisms of an aquatic ecosystem are expected. The PNEC concentrations have been derived by analogy to the technical guidelines of the *Institute for Health and Consumer Protection* within the *European Commission Joint Research Centre* (EC TGD 2003) and to the ECHA guidelines *Guidance on information requirements and chemical safety assessment* (ECHA 2008). In the relevant procedure, the PNEC concentration is derived from effect data obtained via standardized laboratory tests with test organisms of various trophic levels. In the process, it is assumed that the ecosystem's function as a whole remains intact if the pollutant concentration remains below the

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[8] http://www.who.int/water_sanitation_health/dwq/gdwq3_8.pdf; http://www.bfr.bund.de/cm/343/risikobewertung_genotoxischer_und_kanzerogener_stoffe_soll_in_der_eu_harmonisiert_werden.pdf

maximum concentration at which the most sensitive organism in the aquatic environment shows no (adverse) effects. Since not every organism can be tested, it is assumed that laboratory tests with test organisms from different levels of the food chain ("trophic levels", including primary producers (algae), invertebrates (daphnia) and vertebrates (fish)) will be very likely to include the most sensitive organism. An *assessment factor* is used in the effects analysis, to take account of uncertainties, or gaps in relevant knowledge; this is in keeping with the meaning of a conservative assessment oriented to reliability (EC TGD 2003):

- Variability of effect data in execution of tests with various organisms and with various species (biological variability), and in various laboratories (test variability).
- Uncertainties in extrapolation from short-term studies to long-term studies.
- Uncertainties in extrapolation from controlled laboratory studies, with selected reference species, to entire ecosystems with complex plant/animal communities.

The size of the assessment factor is based on the available data (EC TGD 2003). If chronic NOEC values (No Observed Effect Concentration), from long-term tests with organisms from 3 different trophic levels, are available, an assessment factor of 10 is considered adequate. If, on the other hand, NOEC values are available for only two trophic levels, or for only one trophic level, the assessment factor increases to 50 or 100, respectively. If no chronic effect data are available, acute toxicity data from short-term tests have to be used. Such data are then subjected to a conservative assessment factor of 1,000. Table C1 provides an overview of the assessment factors to be used pursuant to EC TGD (2003).

Tab. C 1: Assessment factors used for derivation of PNEC concentrations (assessment factor of 10 - 1,000, from EC TGD 2003; the high assessment factors (5,000 and 25,000) found in Hanisch et al. 2002 should be seen as an indication that the database for derivation of PNEC values is inadequate.)

Available data	Assessment factor
Chronic studies (NOEC) with at least three species, representing different trophic levels (algae/bacteria, invertebrates, vertebrates)	10
Two chronic studies (NOEC) with species from different trophic levels (algae/bacteria and/or invertebrates and/or vertebrates)	50
One chronic study (NOEC), with invertebrates or vertebrates	100
One short-term study (EC_{50}/LC_{50}) for each of the following, as representatives of different trophic levels: algae/bacteria, invertebrates and vertebrates	1,000
Two short-term studies (EC_{50}/LC_{50}) with species from different trophic levels (algae/bacteria and/or invertebrates and/or vertebrates)	5,000
One short-term study (EC_{50}/LC_{50}) with species from a specific trophic levels (algae/bacteria or invertebrates or vertebrates)	25,000

For many of the fracking additives used, neither long-term toxicity data nor adequate effective-concentration data from short-term tests are available. In keeping with this fact, and by analogy to the procedure introduced by Hanisch et al. (2002), higher assessment factors of 5,000 (only 2 short-term tests) and 25,000 (only 1 short-term test) were introduced. These high assessment factors should be seen as an indication that, for such additives, the database for estimating PNEC values is inadequate and needs to be expanded before any well-founded ecotoxicological assessment can be carried out.

To calculate the PNEC value for a given additive, one first determines the lowest effective concentration (NOEC for chronic tests, EC_{50}/LC_{50} for acute tests) published in the literature for the most sensitive test organism on each trophic level. Then, one selects the lowest effect value, from among all the trophic levels, and divides it by the assessment factor that corresponds to the applicable data availability:

$$\mathrm{PNEC} = \frac{\text{lowest known effective concentration}}{\text{Assessment factor}}$$

On the first trophic level, ecotoxicological effect data for microorganisms (bacteria and protozoa) are also taken into account (if available) and combined with data for algae, the primary producers, i.e. are combined on one trophic level. This takes account of microorganisms' importance for aquatic ecosystems in groundwater systems. To compensate for gaps in the relevant data, the following procedures are followed for the second and third trophic levels: On the second trophic level, effective concentrations (as reported in the literature) are compiled both for daphnia, the standard organism, and for other invertebrates; on the third trophic level, such effective concentrations are compiled both for fish and for other vertebrates; then, the PNEC values are calculated using the most sensitive test organism in each case.

The effective concentrations of fracking additives used were derived from the literature via the following strategy:

First, the available literature was reviewed to determine whether PNEC values for the additives in question had already been derived in other studies. Where PNEC values were already available for relevant substances, those data were critically reviewed and then were adopted, following any necessary supplementation with data from additional database searches. Where different PNEC values were given, in different publications, the lowest values were chosen, in keeping with the aim of carrying out conservative, safety-oriented assessments.

The literature to date provides no PNEC values for the majority of the fracking additives to be assessed. For such substances, the available experimental effect data were obtained via research in the following relevant databases and publications:

- Ecotoxicological data in the Material Safety Data Sheets for the preparations used for production of the pertinent fracking fluids,
- ETOX database of the Federal Environment Agency (UBA 2012),
- ECOTOX database of the U.S. Environmental Protection Agency (US EPA 2012),
- ECHA CHEM database of the European Chemicals Agency (ECHA 2012),
- IUCLID (International Uniform ChemicaL Information Database), publications in the framework of the *European Chemical Substances Information System* (IUCLID 2000),
- GESTIS (Gefahrstoffinformationssystem – hazardous-substance information system) of Deutsche Gesetzliche Unfallversicherung (German Statutory Accident Insurance system) (GESTIS 2012).
- GSBLpublic (Gemeinsamer Stoffdatenpool Bund / Länder – joint Federal/Länder substance-data pool) – openly accessible database (GSBL 2012)

In cases of gaps in the data, pertinent scientific publications were found, with the help of the Thompson ISI Web of Science[9], and reviewed.

C3.2.6 Classification pursuant to legislation on plants/installations

In the interest of protection of water bodies, plants/installations that handle substances hazardous to water have to be constructed and operated in ways that give no cause for concern with regard to pollution or adverse changes of water bodies (cf. Part B). To that end, the substances used in such plants/installations are studied and classified with regard to their hazardous properties for waters. In keeping with the Administrative regulation on substances hazardous to water (Verwaltungsvorschrift wassergefährdender Stoffe – VwVwS) of 17 May 1999, last amended 27 July 2005), substances are classified in three water hazard classes (WGK):

- WGK 1: low hazard to waters
- WGK 2: hazard to waters
- WGK 3: severe hazard to waters

The classifications for substances classified pursuant to Annexes 1, 2 and 3 of the VwVwS, or classified via resolution of the "Commission for

[9] http://wokinfo.com/products_tools/multidisciplinary/webofscience/

the Evaluation of substances hazardous to water" ("Kommission Bewertung wassergefährdender Stoffe" – KBwS), calling for inclusion in Annexes 1 or 2 as part of the next amendment of the VwVwS, are available online in the Rigoletto database operated by the Federal Environment Agency (UBA 2009).

A substance's classification in a water hazard class imposes requirements relative to the manner in which the substance is to be stored and handled. In the water laws of the Länder, such requirements, which for any substance are both tied to the substance's water hazard class and graduated in accordance with the quantities of the substance involved, are implemented by ordinances on installations dealing with substances hazardous to water (Verordnungen über Anlagen zum Umgang mit wassergefährdenden Stoffen – VAwS). A federal regulation that is to supplant such Länder ordinances is currently being prepared (BMU 2009).

The "water hazard class" is enshrined in water law as a key standard for the safety and protection of industrial installations. It serves as a basis for defining requirements levels applying to the design of installations, for the purpose of preventing any substance discharges into the soil or into water bodies. On the other hand, it was not designed to serve as a basis for assessing the potential risks of intentional underground injection of substances, and thus it is poorly suited, at best, for that purpose (cf. UBA 2011a). In particular, assessment solely on the basis of water hazard classes fails to take account of the specific exposure conditions prevailing in a given case. Classifications in accordance with water hazard classes should thus not be used as the sole basis for assessing the hazard potential of fracking fluids in use – i.e. such classifications should not be used outside of their intended scope of application (cf., regarding relevant concerns, UBA 2011a).

C3.2.7 Classification pursuant to laws pertaining to hazardous substances

The purpose of the Ordinance on Hazardous Substances (Gefahrstoffverordnung), which has its basis in occupational health and safety legislation and in chemicals laws[10], is to protect humans and the environment from substance-related damage, via

- Regulations pertaining to the classification, labelling and packaging of hazardous substances and preparations,
- Measures for the protection of employees and other persons engaged in activities involving hazardous substances, and

[10] Ordinance on Hazardous Substances (Gefahrstoffverordnung) of 26 November 2010 (Federal Law Gazette I p. 1643, 1644), amended by Article 2 of the Act of 28 July 2011 (Federal Law Gazette I p. 1622).

- Restrictions on the production and use of certain hazardous substances, preparations and products.

The classification and labelling of substances and mixtures are regulated by Regulation (EC) No 1272/2008 (CLP Regulation)[11]. The new version of the Regulation entered into force on 20 January 2009 and has been applicable since then. Until 1 December 2010, classification and labelling of substances pursuant to Directive 67/548/EEC was permitted. For classification of mixtures and preparations, transition periods until 1 June 2015 have been provided during which classification and labelling may still be carried out in accordance with Directive 1999/45/EC[12].

In the majority of the existing Material Safety Data Sheets, fracking products (preparations) are classified pursuant to Directive 1999/45/EC; newer Material Safety Data Sheets with classifications pursutant to Regulation (EC) No 1272/2008 (CLP Regulation) are available for only some preparations. For this reason, the classifications and labelling requirements for fracking products (preparations) that, to the knowledge of the study authors, have been used in the past, have all been listed in Annex 1 in accordance with Directive 1999/45/EC. For the additives used, classifications and labelling requirements have been given pursuant to the CLP Regulation (Annex 2).

C3.2.8 Selection of fracking fluids for sample assessment

Since recipes for fracking fluids are normally tailored to specific deposits, the hazard potentials of such fluids can be assessed only by way of illustration, for selected fluids. In the framework of the present study, the following were selected for detailed assessment: a fluid used recently in one of the largest tight gas deposits in Lower Saxony (Söhlingen Z16); two fluids used in shale gas and coal bed methane deposits (Damme 3 and Natarp); and two fracking fluids that one operator has improved and found to be potentially suitable for shale gas and coal bed methane deposits in Germany (improved versions of a slickwater fluid and a gel-based fluid) (Tab. C 2).

[11] Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006.

[12] http://www.reach-clp-helpdesk.de/de/CLP/CLP.html

Tab. C 2: Fracking fluids that have been used in, or would be suitable for, unconventional deposits, and that were selected for assessment of their hazard potential

Tight gas			
Söhlingen Z16 Rotenburg district (Wümme), Lower Saxony	9 fracks in 2008 Final depth: 6,872 m Dethlinger sandstone (late rotliegend)	Gel: Water requirements: Proppants: Additives:	 824 m^3 170,100 kg 38,079 kg
Shale gas			
Damme 3 Vechta district, Lower Saxony	3 fracks in 2008 Wealden clay formation 1,045-1,530 m	Slickwater Water requirements: Proppants: Additives:	 12,119 m^3 588,000 kg 19,873 kg
Coal bed methane			
Natarp Warendorf district, North Rhine – Westphalia	2 fracks in 1995 Seam-bearing Carboniferous 1,800-1,947 m	Gel: Water requirements: Nitrogen: Proppants: Additives:	 121 m^3 81,750 kg. 41,700 kg. 1,230 kg.
Future improvements			
Slickwater Figures of Exxon Mobil (Last revised 04 Feb. 2012)	Planning	Slickwater Water requirements: Proppants: Additives:	 1,600 m^3 unknown 5,600 kg.
Gel: **Figures of Exxon Mobil** (Last revised 04 Feb. 2012)	Planning	Gel: Water requirements: Proppants: Additives:	 1,600 m^3 unknown 6,530-7,080 kg

The fracking fluid used in Söhlingen Z16 was selected for assessment, instead of newer fracking fluids used in tight gas deposits (Goldenstedt Z23 borehole: 13 fracks in 2010; Cappeln Z3a borehole: 7 fracks in 2011), since information on the composition of the fracking fluids, and on the preparations used, was available to the study authors for Söhlingen Z16, but not for Z23 and Cappeln Z3a.

C3.2.9 Hazard potential of the fracking fluid in "Söhlingen Z16" (tight gas)

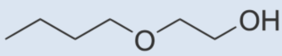
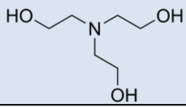
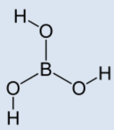
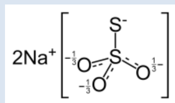
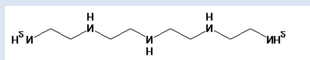
The Söhlingen Z16 borehole (Rotenburg (Wümme) administrative district, Lower Saxony) was drilled in 2007 by Exxon Mobil Production Deutschland GmbH (EMPG), under commission to a consortium consisting of BEB Erdgas und Erdöl GmbH, Mobil Erdgas-Erdöl GmbH, RWE-DEA AG and Wintershall AG.

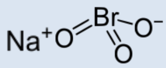
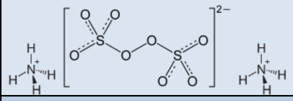
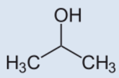
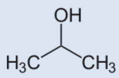
It was drilled to a total depth of 6,872 m. In a horizontal borehole about 1,500 m long, the borehole taps deposits in the Dethlinger sandstone (late-rotliegend). In 2008, nine fracks were carried out in the formation.

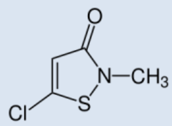
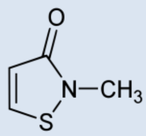
The fracking fluid used was produced from a total of 13 preparations (Tab. C 3) and was injected into the borehole along with water and proppants (ExxonMobil 2012). The mean concentrations of the additives dissolved in the water, in the injected fracking fluid, were calculated on the basis of the pertinent quantities used, and in light of the ingredients listed in the pertinent Material Safety Data Sheets, and their proportions by weight (Tab. C 4). It is important to note that in some cases the additives were injected successively into the borehole, with the result that in some stimulation phases the concentrations of some additives were higher than the relevant mean concentrations given.

Information on the preparations and additives used, including, in particular, their classification pursuant to the Administrative regulation on substances hazardous to water (Verwaltungsvorschrift wassergefährdender Stoffe – VwVwS) and to laws pertaining to hazardous substances, is provided in Annexes 1 and 2. Selected additives are described in detail, with regard to their use, their physical and chemical properties and degradability and their human-toxicological and ecotoxicological properties, in Annex 3.

Tab. C 3: Composition of the fracking fluid "Söhlingen Z16" that was used in 2008 in a tight-gas deposit in Lower Saxony [N.e. = No entry, i.e. no information provided]

Substances used	Quantity used	Concentration within the fracking fluid (dissolved in water)	Structural formula[a] or sum formula
Water	**824 m³**		
Proppant (trade name unknown)	**170,100 kg**		
• **Ceramic materials (bauxites)**		*Solid not dissolved*	
Gelling agent (Schlumberger Environmental Slurry J584)	**23,846 kg**		
• **2-Butoxyethanol** (CAS 111-76-2)	9,538-16,692 kg (40-70 % by weight)	**11,576-20,258 mg/L**	
• **Guar flour (not listed in MSDS)** (CAS unknown)	7,154-14,308 kg (30-60 % by weight)	**8,682-17,364 mg/L**	UVCB [c]
Cross-linker (Schlumberger ThermaFRAC High Temperature Crosslinker J596)	**1,871 kg.**		
• **2,2',2''-Nitrilotris[ethanol]** (CAS 102-71-6)	281-748 kg (15-40 % by weight)	**341-908 mg/L**	
• **Boric acid, orthoboric acid (inorganic borates)** (CAS, researched, 10043-35-3)	56-131 kg (3-7 % by weight)	**68-159 mg/L**	 $Na_2[B_4O_5(OH)_4]$ x $8H_2O$
• **Inorganic salts** (CAS unknown)	56-131 kg (3-7 % by weight)	**68-159 mg/L**	?
• **Substances not subject to specific labelling requirements**	861-1,478 kg (46-79 % by weight)	**N. e.**	?
High-temperature gel stabilizer (Schlumberger High-Temperature Gel Stabilizer J353)	**622 kg**		
• **Sodium thiosulfate pentahydrate** (CAS 10102-17-7)	622 kg (60-100 % by weight)	**481 mg/L b**	
Stabilizer (Schlumberger ThermaFRAC Stabilizer J599)	**7,200 kg**		
• **Tetraethylenepentamine** (CAS 112-57-2)	7,200 kg (60-100 % by weight)	**8,738 mg/L**	

Substances used	Quantity used	Concentration within the fracking fluid (dissolved in water)	Structural formula[a] or sum formula
Encapsulated breaker (Schlumberger EB-Clean J490 HT Encapsulated Breaker)	**37 kg**		
• **Sodium bromate** (7789-38-0)	37 kg (60-100 % by weight)	**45 mg/L**	
Encapsulated breaker (Schlumberger EB-Clean J569 MT Breaker)	**37 kg**		
• **Ammonium persulfate** (CAS 7727-54-0)	37 kg (60-100 % by weight)	**45 mg/L**	
Clay stabilizer (trade name unknown)			
• **Potassium chloride** (CAS 7447-40-7)	**518 kg**	**629 mg/L**	KCl
Wetting agent (Schlumberger Microemulsion Cleanup Additive B203)	**648 kg**		
• **Citrus terpene** (CAS 94266-47-4)	65-194 kg (10-30 % by weight)	**79-236 mg/L**	UVCB [c]
• **Isopropanol** (CAS 67-63-0)	65-194 kg (10-30 % by weight)	**79-236 mg/L**	
• **Linear alcohol ethoxylates** (CAS unknown)	65-194 kg (10-30 % by weight)	**79-236 mg/L**	?
• **Glycol ether** (CAS unknown)	65-194 kg (10-30 % by weight)	**79-236 mg/L**	?
Wetting agent (Schlumberger Methanol Surfactant Foamer F107)	**1,010 kg**		
Amphoteric alkyl amines (CAS unknown)	152-404 kg (15-40 % by weight)	**184-490 mg/L**	?
• **Isopropanol** (CAS 67-63-0)	101-303 kg (10-30 % by weight)	**123-368 mg/L**	
• **Not subject to specific labelling requirements**	303-756 kg (30-75 % by weight)	**N. e.**	?
Solvent (Schlumberger Mutual Solvent U66)	**27 kg**		

Substances used	Quantity used	Concentration within the fracking fluid (dissolved in water)	Structural formula[a] or sum formula
• **2-Butoxyethanol** (CAS 111-76-2)	27 kg (60-100 % by weight)	**33 mg/L**	
pH buffer (Schlumberger Acid Buffer J488)	**972 kg**		
• **salts of aliphatic acids** (CAS unknown)	292-583 kg (30-60 % by weight)	**354-708 mg/L**	?
• **Not subject to specific labelling requirements**	389-826 kg (40-70 % by weight)	**N. e.**	?
pH regulator (Schlumberger Caustic Soda M2)	**1,115 kg**		
• **Sodium hydroxide** (CAS 1310-73-2)	1,115 kg 60-100 % by weight	**1,353 mg/L**	$NaOH$
Biocide (Baker Hughes M275)	**45 kg**		
Mixture (3:1) of • **5-chloro-2-methyl-2H-isothiazol-3-one (CMIT)** (CAS 26172-55-4) • **2-methyl-2H-isothiazolin-3-one (MIT)** (CAS 2682-20-4)	2.25-4.5 kg (5-10 % by weight)	**2.73-5.46 mg/L**	 
• **Magnesium nitrate** (CAS 10377-60-3)	2.25-4.5 kg (5-10 % by weight)	**2.73-5.46 mg/L**	$Mg(NO_3)_2$
• **Magnesium chloride** (CAS 7786-30-3)	0.45-2.25 kg (1-5 % by weight)	**0.55-2.73 mg/L**	$MgCl_2$
• **Not subject to specific labelling requirements**	33.8-40.1 kg (75-89 % by weight)	**N. e.**	?

a Structural formulae from Wikipedia and www. merckmillipore.com.
b Calculated as sodium thiosulfate non-aqueous
c UVCB substance (Substances of Unknown or Variable composition, Complex reaction products or Biological materials)

In Table C 4, the concentrations of the additives used in the fluids are compared to the relevant de minimis thresholds ("Geringfügigkeitsschwellenwerte"), derived health-related guidance values for drinking water and orientation values and PNEC values.

- No information is available on the ceramic materials (bauxites) that are used as proppants. According to current knowledge, the proppants, which are largely insoluble and are largely immobile underground, present no hazards for aquatic environments.

- The guar flour was used as a gelling agent, in high concentrations up to 17.4 g/L. No values for assessing this substance are available. In light of its use as a food additive, and of its ready degradability, this substance is presumed not to have a high hazard potential.
- For the solvent 2-Butoxyethanol, a health-related guidance value of 0.35 mg/L, and a PNEC value of 0.0894 mg/L, were derived (Annex 3). The high 2-Butoxyethanol concentrations used in the fracking fluid (up to 20.3 g/L) exceed the aforementioned assessment values by a factors of 58,000 and 227,000 (Tab. C 5). At present, it is not possible to assess the degradability of 2-Butoxyethanol, especially in saline formation water at higher temperatures. In light of the high concentrations used, therefore, the 2-Butoxyethanol used must be assumed to present a high human-toxicological and ecotoxicological hazard potential.
- The concentration used for the solvent isopropanol, on the other hand, is higher, by a factor of < 100, than the derived guidance value of 8.4 mg/L and the PNEC value of 98 mg/L. A low to medium human-toxicological and ecotoxicological hazard potential may thus be assumed for the isopropanol used.
- The concentrations used for the alcohol ethoxylates exceed both the derived guidance value and the PNEC value by a factor of about 1,400, with the result that, in spite of the substances' good degradability, a high hazard potential must be assumed.
- The biocide agents CMIT and MIT were used in the fracking fluid in a total concentration of 5.46 mg/L. That concentration is higher, by four orders of magnitude (a factor of 10,920), than the de minimis threshold for the sum of the biocidal products, 0.0005 mg/L; and it is higher, by five orders of magnitude (factor of 105,000) than the derived PNEC value of 0.000052 mg/L (Tab. C 5). Similar risk quotients result for the individual substances CMIT and MIT (13,650 through 194,800). It is not possible, at present, to assess the degradability of the biocidal agents, especially their degradability in saline formation water at higher temperatures.

  The biocidal-agent mixture of CMIT and MIT has been identified as an old biocidal agent, and it has been added to the list of agents to be examined in the review programme in the second phase of the ten-year work programme (Annex II of Regulation (EC) No 1451/2007

[13]). Testing of these biocidal agents is to cover a range of different product types (PT), including PT12 "Slimicides" and PT11 "Preservatives for liquid-cooling and processing systems", which could be of relevance for assessment of biocides in fracking products. The decision on whether or not to include these product types in annexes I or IA of Directive 98/8/EC (Biocidal Products Directive) had not yet been made as of 22 February 2012[14]. Therefore, neither the EU Commission's assessment report, nor the data in the review documents to be submitted by producers or notifiers in the review procedure, are currently available. In the framework of the applicable transition provisions, the agent mixture will remain marketable for the duration of the test procedure – but no later than 14 May 2014, however. In light of the concentrations used in the fracking fluid, and the current poor data availability, therefore, these biocidal agents must be assumed to present a high hazard potential.

- For the substances nitrilotris[ethanol], tetraethylenepentamine and citrus terpene, no de minimis thresholds or maximum permitted concentrations under the Ordinance on Drinking Water (TrinkwV) have been established. In the framework of the present study, it was not possible to carry out a comprehensive study of literature data for health-related guidance values for drinking water and for PNEC values. It is thus unclear whether it is justifiable, for these substances, to use the HOV concept applied by Ewers et al. (2012) (assessment value for tetraethylenepentamine and for citrus terpene of 0.3 µg/L in each case). In the time framework available for preparation of the present study, it was not possible to carry out a scientifically sound, conclusive assessment in this regard.
- For the substances glycol ether, amphoteric alkyl amines, salts of aliphatic acids and inorganic salts, no assessment is possible, since the non-specific information available for these substances precluded any positive substance identification. In addition, up to 3,100 kg of substances not subject to labelling requirements were used in the fracking fluid, and the identities of those substances are not given in the Material Safety Data Sheets for the pertinent preparations. The study authors have no information available on these substances; no assessment is possible.

[13] Commission Regulation (EC) No 1451/2007 of 4 December 2007 on the second phase of the 10-year work programme referred to in Article 16(2) of Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market, OJ EU L 325 of 11 December 2007, pp. 3 ff.

[14] http://ec.europa.eu/environment/biocides/pdf/List_dates_product_2.pdf

- Potassium chloride was used as a clay stabilizer, at a concentration of 629 mg/L. The resulting potassium concentration is higher, by a factor of 28, than the former maximum permitted concentration of 12 mg/L set forth by the Ordinance on Drinking Water (TrinkwV) of 1990. Presumably, the ecotoxicological effects of this substance result mainly from its high ionic strength and the high osmotic pressure it thus induces, a pressure to which freshwater organisms in particular react sensitively (Schmitt-Jansen et al. 2012). The underground mobility of potassium is limited via sorption on clay minerals. The potassium concentrations used may thus be presumed to present a low hazard potential.
- Dissolution of the salts contained in the fracking products produces magnesium, sodium, chloride, nitrate and ammonium concentrations in the fracking fluid that are lower than, or only slightly higher than, the assessment values. Such ions thus have no hazard potential or low hazard potential; this is all the more so the case in that the concentrations are sometimes lower than the relevant concentrations expected in formation water.
- Sodium thiosulfate, which is used as a high-temperature gel stabilizer, is a substance that is also used in drinking-water treatment (according to the list (of substances used for such treatment) pursuant to Art. 11 Ordinance on Drinking Water (TrinkwV) 2001, version of Nov. 2011)[15]. Following the example of Ewers et al. (2012), the thiosulfate concentrations in the fracking fluid are assessed on the basis of the maximum concentration permitted at the end of the treatment process (3 mg/L thiosulfate). The sodium thiosulfate concentrations used in the fracking fluid exceed those assessment values by a factor of 114, with the result that a low to medium hazard potential may be assumed for this substance.
- Borate salts (presumably, sodium borate, i.e. disodium tetraborate, borax) and boric acid have been used as chain extenders and cross-linkers. The de minimis threshold (GFS value) derived for borates is 0.74 mg Bor/L; the maximum permitted concentration allowed by the Ordinance on Drinking Water (TrinkwV) 2001 is 1.0 mg/L. The concentrations of borate salts and boric acid used exceed the de minimis threshold (GFS value) by a factor of 38, with the result that a medium hazard potential may be assumed. As a result of recent studies of reproductive toxicity, in June 2010 disodium tetra-

[15] List of treatment substances and disinfection processes pursuant to Art. 11 Ordinance on Drinking Water (TrinkwV) 2001. 16th amendment Last revision: November 2011 http://www.umweltbundesamt.de/wasser/themen/trinkwasser/trinkwasseraufbereitung-stoffliste.htm

borate (CAS nos. 1303-96-4, 1330-43-4, 12179-04-3) and boric acid (CAS nos. 10043-35-3 and 11113-50-1) were added to the candidate list of substances of very high concern (SVHC) of the European Chemicals Agency (ECHA)[16]. Upon the entry into force of Regulation (EC) No 1272/2008 on the classification, labelling and packaging of substances and mixtures (CLP Regulation, introducing the Globally Harmonised System (GHS) in the EU), and of Commission Regulation (EC) No 790/2009 of 10 August 2009 amending, for the purposes of its adaptation to technical and scientific progress, Regulation (EC) No 1272/2008 of the European Parliament and of the Council on classification, labelling and packaging of substances and mixtures (REACH-amendment regulation), disodium tetraborate and boric acid are labelled as toxic for reproduction (Repr. 1B) (Annex 2). In the time framework available for preparation of the present study, it was not possible to carry out a scientifically sound, conclusive assessment of the use of borate salts and boric acid in fracking products.

- The strong oxidizing agents sodium bromate and ammonium persulfate were used as breakers.

  No de minimis threshold (GFS value) has been derived for bromates (LAWA 2004). The maximum permitted concentration set forth by the Ordinance on Drinking Water (TrinkwV) 2001, 0.010 mg/L, was defined primarily with reference to formation of bromates, which can occur in oxidation of bromide-containing water with ozone, in drinking-water treatment. The bromate concentration used exceeds the maximum permitted concentration set forth by the Ordinance on Drinking Water (TrinkwV) by a factor of 3,800, with the result that a high hazard potential must be assumed. In use of sodium bromate as a breaker, toxicologically harmless bromide ions are formed when the bromate reacts with the gel fluid. While the reaction thus helps to reduce the relevant hazard potential, the extent of such reduction cannot be quantified at present.

  Ammonium persulfate, a strong oxidizing agent, has also been used as a breaker. The sodium and potassium salts of persulfate are also used as active agents in drinking-water treatment[3]. The persulfate concentrations occurring in fracking fluid are calculated on the basis of the maximum concentrations permitted at the end of the treatment process (0.56 mg/L persulfate, calculated from 0.1 mg/L H_2O_2). The concentrations used exceed these assessment values by a factor of 68. Since the sulfate concentration resulting from the reaction of persulfate is also considerably lower than the de mini-

[16] http://echa.europa.eu/web/guest/candidate-list-table

mis threshold of 240 mg/L, a low to medium hazard potential may be assumed for this substance.

In light of the individual-substance assessment carried out – and especially in light of the concentrations chosen for biocides and one solvent in the fluid – it must be concluded that the Söhlingen Z16 fracking fluid used in 2008 in Lower Saxony has a high human-toxicological and ecotoxicological hazard potential. Additional information about the hazard potential of the mixture is needed, and a suitable means of obtaining such information would be to test the complete fluid toxicologically, with a range of different test methods.

Tab. C 4: Assessment of the additive concentrations used in the Söhlingen Z16 fracking fluid, on the basis of de minimis thresholds ("Geringfügigkeitsschwellenwerte"), of health-related guidance values and orientation values and of ecotoxicological effect thresholds. The properties of selected additives are described in Annex 3.

Substances used	Quantity used	Dissolved concentration in fracking fluid (maximum value)	De minimis thresholds (GFS)	Health-related guidance value (GVDW)	Health orientation value (HOV)	Assessment on the basis of GFS or GVDW or HOV (risk quotient)	Predicted No Effect Concentration (PNEC)	Assessment on the basis of PNEC (risk quotient)
Proppants	170,100 kg	*Solid not dissolved*	-	N. e.	N. e.	No assessment possible	N. e.	No assessment possible
Guar flour (CAS unknown)	7,154-14,308 kg	**17,364 mg/L**	-	N. e.	N. e.	No assessment possible	N. e.	No assessment possible
2-Butoxyethanol (CAS 111-76-2)	9,565-16,719 kg	**20,290 mg/L**	-	0.35 mg/L	-	58,000	0.0894 mg/L	227,000
Isopropanol (CAS 67-63-0)	166-497 kg	**604 mg/L**	-	8.4 mg/L	-	72	98 mg/L	6
Linear alcohol ethoxylates (CAS unknown)	65-194 kg	**236 mg/L**	-	0.175 mg/L	-	1,350	0.17 mg/L	1,390
Mixture of CMIT:MIT (CAS 26172-55-4 and 2682-20-4) • Active-agent mixture CMIT:MIT • Active agent CMIT • Active agent MIT	2.25-4.5 kg	 **5.46 mg/L** **4.09 mg/L** **1.37 mg/L**	 0.00050 mg/L 0.00010 mg/L 0.00010 mg/L	 - - -	 - - -	 10,920 40,900 13,700	 0.000052 mg/L 0.000021 mg/L 0.000050 mg/L	 105,000 194,800 27,400
2,2',2''-Nitrilo-tris[ethanol] (CAS 102-71-6)	281-748 kg	**908 mg/L**	-	N. e.	N. e.	Substance not assessed	N. e.	Substance not assessed

Substances used	Quantity used	Dissolved concentration in fracking fluid (maximum value)	De minimis thresholds (GFS)	Health-related guidance value (GVDW)	Health orientation value (HOV)	Assessment on the basis of GFS or GVDW or HOV (risk quotient)	Predicted No Effect Concentration (PNEC)	Assessment on the basis of PNEC (risk quotient)
Tetraethylenepentamine (CAS 112-57-2)	7,200 kg	8,738 mg/L	-	N. e.	N. e.	Substance not assessed	N. e.	Substance not assessed
Citrus terpene (CAS 94266-47-4)	65-194 kg	236 mg/L	-	N. e.	N. e.	Substance not assessed	N. e.	Substance not assessed
Glycol ether (CAS unknown)	65-194 kg	236 mg/L	-	N. e.	N. e.	No assessment possible	N. e.	No assessment possible
Amphoteric alkyl amines (CAS unknown)	152-404 kg	490 mg/L	-	N. e.	N. e.	No assessment possible	N. e.	No assessment possible
Substances not subject to specific labelling requirements (CAS unknown)	1,587-3,100 kg	*Substances unknown*	N. e.	N. e.	N. e.	No assessment possible	N. e.	No assessment possible
Dissociated salts								
Potassium (K+)	from KCl	330 mg/L	(12 mg/L) b	-	-	(28)	-	-
Magnesium (Mg^{2+})	from Mg salts	2 mg/L	(50 mg/L) c	-	-	no concern (< 1)	-	-
Sodium (Na^{+})	from Na salts	924 mg/L	(200 mg/L) d	-	-	(5)	-	-
Chloride (Cl^{-})	from KCl and $MgCl_2$	301 mg/L	250 mg/L	-	-	1.2	-	-
Nitrate (NO_3-)	from $MgNO_3$	5 mg/L	(50 mg/L) d	-	-	no concern (< 1)	-	-
Borate (BO_3^{3-})	from boric acid and borate salts	28 mg-B/L [a]	0.74 mg-B/L	-	-	38	-	-

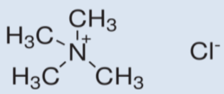
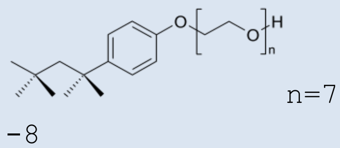
Substances used	Quantity used	Dissolved concentration in fracking fluid (maximum value)	De minimis thresholds (GFS)	Health-related guidance value (GVDW)	Health orientation value (HOV)	Assessment on the basis of GFS or GVDW or HOV (risk quotient)	Predicted No Effect Concentration (PNEC)	Assessment on the basis of PNEC (risk quotient)
Thiosulfate ($S_2O_3^{2-}$)	from sodium thiosulfate	**341 mg/L**	(3 mg/L) e	-	-	(114)	-	-
Bromate (BrO_3^-)	from $NaBrO_3$	**38 mg/L**	(0.010 mg/L) d	-	-	**(3,800)**	-	-
Ammonium (NH_4^+)	from ammonium persulfate	**7 mg/L**	(0.5 mg/L) d	-	-	(14)	-	-
Persulfate ($S_2O_8^{2-}$)	from ammonium persulfate	**38 mg/L**	(0.56 mg/L) e	-	-	(68)	-	-
salts of aliphatic acids (CAS unknown)	292-583 kg	**708 mg/L**	N. e.	N. e.	N. e.	**No assessment possible**	N. e.	**No assessment possible**
Inorganic salts (CAS unknown)	56-131 kg	**159 mg/L**	N. e.	N. e.	N. e.	**No assessment possible**	N. e.	**No assessment possible**

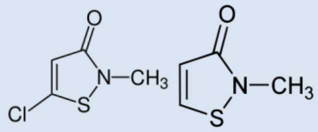
a calculated as H_3BO_3
b No de minimis threshold derived. The Ordinance on Drinking Water (TrinkwV) of 1990 imposed a maximum permitted concentration of 12 mg/L, although it permitted geogenically related higher values.
c No de minimis threshold derived. The Ordinance on Drinking Water (TrinkwV) of 1990 imposed a maximum permitted concentration of 50 mg/L, although it permitted geogenically related higher values.
d No de minimis threshold derived. The maximum permitted concentration set forth by the Ordinance on Drinking Water (TrinkwV) of 2001 has been used.
e No de minimis threshold derived. List of treatment substances and disinfection processes pursuant to Art. 11 Ordinance on Drinking Water (TrinkwV) 2001. Last revision: Nov. 2011

C3.2.10 Hazard potential of the "Damme 3" fracking fluid (shale gas)

In Germany, experience with use of fracking fluids in shale gas deposits is limited to one fluid that was used in 2008, under commission to the firm of ExxonMobil Production Deutschland GmbH, in three fracks in the Damme 3 borehole (Vechta district, Lower Saxony) in Wealden clay rock, at depths ranging from 1,045 to 1,530 m below the ground surface. In those fracks, injection of the fracking fluids produced underground pressures ranging from 110 to 150 bar (Ewers et al. 2012). The temperature within the fracking horizon was about 80 °C. The water required, amounting to a total of 12,119 m^3, was provided by the Holdorf waterworks.

Tab. C 5: Mean concentrations of fracking additives in the Damme 3 fracking fluid.

Substance	Quantity used	Mean conc. in the fracking fluid	Structural formula[a] or sum formula
Water	**12,119 m^3**		
Proppant (trade name unknown)	**588,000 kg**		
Quartz sand and/or bauxites			
Clay stabilizer (Schlumberger L064)	**10,612 kg**		
Tetramethyl ammonium chloride(CAS 75-57-0)	6,367 kg (60 % by weight)	**520 mg/L**	
Substances not subject to specific labelling requirements	4,245 kg (40 % by weight)	**347 mg/L**	**?**
Friction reducer (Schlumberger J313)	**8,801 kg**		
Petroleum distillate, hydrogenated, light (CAS 64742-47-8)	2,640 kg (30 % by weight)	**220 mg/L**	**UVCB**
Polyethyleneglycoloctylphenylether (CAS 9036-19-5)	440 kg (5 % by weight)	**36 mg/L**	
Substances not subject to specific labelling requirements	5,721 kg (65 % by weight)	**467 mg/L**	**?**
Biocide (Baker Hughes M275)	**460 kg**		

Mixture (3:1) of			
5-chloro-2-methyl-2H-isothiazol-3-one (CMIT) (CAS 26172-55-4) **2-methyl-2H-isothiazolin-3-one (MIT)** (CAS 2682-20-4)	46 kg (10 % by weight)	**3.76 mg/L**	
• **Magnesium nitrate** (CAS 10377-60-3)	46 kg (10 % by weight)	**3.76 mg/L**	$Mg(NO_3)_2$
• **Magnesium chloride** (CAS 7786-30-3)	23 kg (5 % by weight)	**1.88 mg/L**	$MgCl_2$
• **Substances not subject to specific labelling requirements**	345 kg (75%)	**28.18 mg/L**	?

[a] Structural formulae from Wikipedia.

The fracking fluid, as injected into the Damme 3 borehole, was produced by mixing three preparations with water and proppants. According to the pertinent Material Safety Data Sheets, all three of the preparations used have been classified as dangerous preparations pursuant to Directive 1999/45/EC (Annex 1). The available Material Safety Data Sheets provide no information regarding classifications pursuant to the Administrative regulation on substances hazardous to water (Verwaltungsvorschrift wassergefährdender Stoffe – VwVwS). On the basis of the additive compositions published by the firm of ExxonMobil Production Deutschland GmbH (ExxonMobil 2012), and of the information provided to the study authors in the framework of the ExxonMobil information and dialogue process (Ewers et al. 2012), the mean concentrations of the dissolved additives in the injected fracking fluid were calculated from pertinent quantities used, in keeping with the constituent substances as listed in the Material Safety Data Sheets and with their proportions by weight in the water quantities used (Tab. C 5).

The available information on the additives used, particularly with regard to their classifications in water hazard classes, and to their classification and labelling pursuant to the CLP Regulation, and including information about the substances' uses, their physical and chemical properties and their human-toxicological and ecotoxicological properties, is provided in detail in Annex 3.

In Table C 6, the concentrations of the additives used in the fluids are compared to the relevant de minimis thresholds ("Geringfügigkeitsschwellenwerte"), derived health-related guidance values for drinking water and orientation values and PNEC values.

- The solids used as proppants cannot be assessed with the available assessment procedure. According to current knowledge, the proppants, which are largely insoluble and are largely immobile underground, present no hazards for aquatic environments.

- At 520 mg/L, the concentration of the substance tetramethyl ammonium chloride, which is used as a clay stabilizer, is the highest of any individual-substance concentration within the fluid. Although tetramethyl ammonium chloride has been used in large quantities in Germany in at least 6 other fluids, the pertinent available data must be considered inadequate for any proper assessment of tetramethyl ammonium chloride (Annex 3). Relevant health-oriented guidance values are lacking. The concentration used is larger, by six orders of magnitude (factor of 1,733,000), than the health-based orientation value. In addition, the concentration exceeds ecotoxicologically established effect thresholds by more than six orders of magnitude (risk quotient > 2,600,000) (Tab. C 8). Although log K_{ow} is low, at -4, the substance can be expected to have high specific sorption on clay minerals, which retard the substance's underground mobility. Since no information (apart from the high risk quotients) about the degradability of tetramethyl ammonium chloride is available, this substance must be expected to have a <u>high hazard potential</u>.
- The concentrations of the petroleum distillates used in the fracking fluid exceed the de minimis threshold (GFS value) for hydrocarbons by a factor of 2,200. For polyethyleneglycoloctylphenylether, no de minimis thresholds or GVDWs are available; the substance can be assessed only on the basis of its HOV (risk quotient of 120,000). The concentrations used for both substances exceed relevant ecotoxicological effect thresholds by more than four orders of magnitude (risk quotients ranging from 20,000 to 55,000). The data available for this assessment of PNEC concentrations may be considered adequate. For both substances, the concentrations used are likely to present a <u>high hazard potential</u>, especially since the substances are not considered to be rapidly degradable, and since octylphenol, a hormonally active substance, occurs as a metabolite during degradation of polyethyleneglycoloctylphenylether. That substance is classified as a priority substance in the Water Framework Directive, and it has been included in the European candidate list of substances of very high concern (UBA 2011b).
- The biocide agents CMIT and MIT were used in the fracking fluid in a total concentration of 3.76 mg/L. That concentration is higher, by a factor of 7,520, than the de minimis threshold for the sum of the biocidal products, 0.0005 mg/L; and it is higher, by a factor of 72,000, than the derived PNEC value of 0.000052 mg/L for the biocide mixture. The data available for this assessment of PNEC concentrations may be considered ade-

quate. It is not possible, at present, to assess the degradability of the biocidal agents, especially their degradability in saline formation water at higher temperatures. In the concentrations used, the biocidal agents must thus be assumed to present a high hazard potential.

- Dissolution of the salts contained in the fracking products produces magnesium, nitrate and chloride concentrations in the fracking fluid. For nitrate and chloride, those concentrations are lower than the de minimis thresholds and the (GFS values) and the maximum permitted concentrations set forth by the Ordinance on Drinking Water (TrinkwV) 2001 (in the 2011 version). In addition, the concentrations are considerably lower than those expected in formation water. The magnesium salts may thus be considered harmless.

In light of the individual-substance assessment carried out (Annex 3), it must be concluded that the sole fracking fluid used to date in shale gas deposits in Germany has a high human-toxicological and ecotoxicological hazard potential. Due to the inadequacy of the available data, and to the possibility that the individual substances could have combined effects, no conclusive assessment of the hazard potentials of the complete fluid is possible. Additional information about the hazard potential of the mixture is needed, and a suitable means of obtaining such information would be to test the complete fluid toxicologically, with a range of different test methods.

Comparison to classifications pursuant to laws pertaining to installations and to hazardous substances

Pursuant to the Federal Environment Agency (UBA 2008), the fracking fluid should be classified as a low hazard to waters (water hazard class – WGK 1), since substances in water hazard class 3 (WGK 3) (mixture of CMIT and MIT) were added to it, in quantities leading to concentrations < 0.2 % by weight in the fluid (Annex 2).

In the fracking fluid, the mean concentrations of the constituent substances are ≤ 0.052 % by weight for each individual substance (Annex 2). As a result, none of the constituent substances must be classified as a significant component within the meaning of the CLP Regulation (Ewers et al. 2012). The fluid is not a dangerous mixture within the meaning of the CLP Regulation.

In assessment of the Damme 3 fracking fluid, the results obtained with different assessment approaches differ fundamentally. Under the Administrative regulation on substances hazardous to water (Verwaltungsvorschrift wassergefährdender Stoffe – VwVwS), the fracking fluid only has to be classified as a low hazard to waters. Pursuant to the CLP Regulation, it does not have to be classified as a "dangerous mixture". By contrast, when assessed on the basis of the de minimis thresholds of LAWA (2004), and of human-toxicologically and ecotoxicologically established effect thresholds, the fluid must be assumed to have a high hazard potential. This comparison makes it clear that classifications in water hazard classes, and pursuant to the CLP Regulation, should serve as no more than guidelines for describing and assessing the hazard potentials of fracking fluids, following a discharge into the environment, with regard to drinking water protection and to protection of aquatic ecosystems.

Comparison with other assessment approaches described in the literature

The Damme 3 fracking fluid was also assessed in the framework of the ExxonMobil information and dialogue process (Schmitt-Jansen et al. 2012; Ewers et al. 2012). The procedure used by Schmitt-Jansen et al. (2012) for ecotoxicological assessment of the fluid is largely similar to the procedure chosen in the present study. The two procedures differ in their details, however. On the one hand, differences occur in that Schmitt-Jansen et al. (2012) are stricter in their selection of effect data; they relied on the U.S. EPA's ECOTOX database solely for data for the organism groups algae, daphnia and fish. Of the data so obtained, they considered only mortality data, and thus did not take account of other effect data (such as data on effects due to hormonally active substances). What is more, they did not consider effect data for bacteria. In yet another key difference, they did not apply assessment factors, in spite of the gaps in the data they considered.

In spite of such differences in methods, the work of Schmitt-Jansen et al. (2012) also concludes that the petroleum distillate, the polyethyleneglycoloctylphenylether and the tetramethyl ammonium chloride, in the concentrations used, present a hazard potential from an ecotoxicological perspective. The hazard potential of the biocide was not assessed, because their self-imposed restriction to mortality data for algae, daphnia and fish precluded any determination of effective concentrations. The data researched in the present study, however, indicate that for both the individual substances CMIT and MIT and the substance mixture, extensive effect data are available, for species on different trophic levels, that also make it possible to assess the hazard potential of these biocidal agents.

The human-toxicological assessment of the Damme 3 fluid carried out by Ewers et al. (2012) used largely the same assessment values (de minimis thresholds (GFS values) and maximum permitted concentrations under the TrinkwV; health-oriented guideline and orientational values) that were used in the present study. With these assessment values, Ewers et al. (2012) also conclude that the additive concentrations used exceed the assessment values by a factor of more than 10,000 and, in some cases, even exceed those values by a factor of 100,000. Their overall assessment of the fluid differs fundamentally from the assessment presented here, however, since Ewers et al. (2012) assume that dilution of the fluid would be expected to reduce its hazard potential to a completely harmless level. In a worst-case scenario, the entire fluid quantity used, about 4,000 m^3 per frack, would be released. In such a case, an extremely large volume of water, 400,000,000 m^3 (equivalent to 0.4 km^3), would be required to achieve the necessary dilution. In the present study, we note, by contrast, that the fracking-fluid dilution that would occur in connection with rising via the overburden would primarily involve saline deep groundwater, water that itself can present a high hazard potential. A considerable reduction of the hazard potential could not be expected until the fluids reached freshwater resources. In such a case, however, that would mean that exploitable water resources had already been contaminated.

Tab. C 6: Assessment of the additive concentrations used in the Damme 3 fracking fluid, on the basis of de minimis thresholds ("Geringfügigkeitsschwellenwerte") and health-related guidance values and orientational values, and on the basis of ecotoxicological effect thresholds (The data used as a basis are described in Annex 3.)

Substances used	Quantity used	Mean dissolved concentration in the fracking fluid	De minimis thresholds (GFS)	Health-related guidance value (GVDW)	Health orientation value (HOV)	Assessment on the basis of GFS or GVDW or HOV (risk quotient)	Predicted No Effect Concentration (PNEC)	Assessment on the basis of PNEC (risk quotient)
Proppants	588,000 kg	***Solid not dissolved***	-	N. e.	N. e.	**No assessment possible**	N. e.	**No assessment possible**
Tetramethyl ammonium chloride(CAS 75-57-0)	6,367 kg	**520 mg/L**	-	N. e.	0.0003 mg/L	**1,733,000**	Inadequate data (<0.0002 mg/L)	**Inadequate data (>2,600,000)**
Petroleum distillate, hydrogenated, light (CAS 64742-47-8)	2,640 kg	**220 mg/L**	0.1 mg/L [a]	-	-	**2,200**	0.004 mg/L	**55,000**
Polyethyleneglycoloctylphenylether (CAS 9036-19-5)	440 kg	**36 mg/L**	-	N. e.	0.0003 mg/L	**120,000**	0.0018 mg/L	**20,000**
Mixture of CMIT:MIT (CAS 26172-55-4 and 2682-20-4) • **Active-agent mixture CMIT:MIT** • **Active agent CMIT** • **Active agent MIT**	 46.0 kg 34.5 kg 11.5 kg	 **3.76 mg/L** **2.82 mg/L** **0.94 mg/L**	 0.0005 mg/L 0.0001 mg/L 0.0001 mg/L	 - - -	 - - -	 **7,520** **28,200** **9,400**	 0.000052mg/L 0.000021 mg/L 0.000050 mg/L	 **72,000** **134,000** **19,000**
Magnesium (Mg^{2+}) from Mg salts		**1.1 mg/L**	(50 mg/L) [b]	-	-	**no concern (< 1)**	-	-
Nitrate (NO^{3-}) from $Mg(NO_3)_2$		**3.1 mg/L**	(50 mg/L) [c]	-	-	**no concern (< 1)**	-	-
Chloride (Cl^-) from $MgCl^2$ and **tetramethyl ammonium chloride**		**169.6 mg/L**	250 mg/L	-	-	**no concern (< 1)**	-	-
Substances not subject to specific labelling requirements	6,349 kg	***Substances unknown***	-	N. e.	N. e.	**No assessment possible**	N. e.	**No assessment possible**

a De minimis threshold (GFS) for hydrocarbons. The de minimis thresholds for benzene (0.001 mg/L), and for the sum of alkylated benzenes (0.020 mg/L), may have to be considered in light of the aromatics concentration in the petroleum distillate; no data on aromatics concentrations were available to the study authors, however.

b No de minimis threshold derived. The Ordinance on Drinking Water (TrinkwV) of 1990 imposed a maximum permitted concentration of 50 mg/L, although it permitted geogenically related higher values.

c No de minimis threshold derived. The maximum permitted concentration pursuant to the Ordinance on Drinking Water (TrinkwV) 2001 was used.

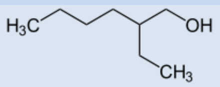
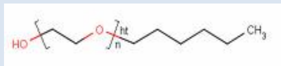
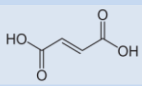
C3.2.11 Hazard potential of the "Natarp" fracking fluid (coal bed methane)

To date, use of fracking fluids in coal bed methane deposits in Germany has been limited to two fracks that were carried out in 1995, under commission to a consortium consisting of the firms Conoco Mineralöl GmbH, Ruhrgas AG and Ruhrkohle AG, in the Natarp 1 borehole (Warendorf district, North Rhine – Westphalia), at depths ranging between 1,800 and 1,947 m below the ground surface and at pressures up to 350 bar (BR Arnsberg 2011a). For the consortium, gas yields from the test production were unsatisfactory, and the borehole was backfilled after that production (BR Arnsberg 2011a).

The fracking fluid, as injected into the borehole, was produced by mixing the six preparations described below with water and sand. The information provided in Table C 8 on the composition of the fracking fluid is based on assessments of the Arnsberg district government (BR Arnsberg), carried out by reviewing the application documents for the project and notifications of pertinent changes (BR Arnsberg 2011a; BR Arnsberg 2011b). While the application requested approval for use of 475 m^3 of fracking fluid, the consortium's final report indicates that only 121.2 m^3 were actually used (BR Arnsberg 2011a). The study authors calculated the preparation quantities used on the basis of the concentration data for the main frack (BR Arnsberg 2011b) and of the quantity of water used.

The information on classification of the fracking products used is based – except for that for the preparation SSO-21M – on information provided in the current relevant material safety data sheets (Halliburton 2010/2011). Through consultation with the producer and the importer, it was learned that the recipe for the preparation SSO-21M had been changed in the past. The current material safety data sheet for the preparation Halliburton SSO-21M (last revision: 04 January 2011) shows that Poly(oxy-1,2-ethandiyl), a-(nonylphenyl)-w-hydoxy- is used (no CAS no. provided; synonym: nonylphenolethoxylates) instead of the alcohol ethoxylates and 1-hexanol ethoxylated listed in the older material safety data sheet (in each case, with CAS no. 31726-34-8) (Halliburton SSO-21M Winterized 1995). Table C 7 shows the information provided in the material safety data sheet submitted for the 1995 authorisation procedure. The classification under the old material safety data sheets and that under the new material safety data sheets are compared in BR Arnsberg (2011b).

Tab. C 7: Concentrations of fracking additives in the Natarp fracking fluid.

Substance	Quantity used	Mean conc. in fracking fluid (dissolved in water)	Structural formula and/or sum formula [a]
Water	121.2 m^3		
Nitrogen	81,750 kg		
Proppants: Quartz sand 20/40	41,700 kg		
Gelling agent (Halliburton WG-11)	436 kg		
Hydroxypropyl guar gum (CAS unknown)	60-100 % by weight	2,160 - 3,600 mg/L	UVCB
Clay stabilizer (Halliburton potassium chloride)	671 kg		
Potassium chloride (CAS 7447-40-7)	60-100 % by weight	3,324 - 5,540 mg/L	KCl
Wetting agent (Halliburton SSO-21M)b	44 kg		
2-Ethylhexanol (CAS 104-76-7)	5-10 % by weight	18 - 36 mg/L	
Alcohol ethoxylates (1-Hexanol, ethoxylated) (CAS 31726-34-8)	30-60 % by weight	108 - 216 mg/L	
Ethylene glycol monobutyl ether (2-Butoxyethanol) (CAS 111-76-2)	10-30 % by weight	36-108 mg/L	
Methanol (CAS 67-56-1)	10-30 % by weight	36-108 mg/L	CH_3OH
Gel breaker (Halliburton GBW-3/30)c	7 kg		
Carbohydrate (CAS unknown)	85-95 % by weight	51 - 57 mg/L	?
Cellulase, hemicellulase (enzyme) (CAS 9012-54-8)	5-15 % by weight	3 - 9 mg/L	UVCB
Auxiliary agent (Halliburton HYG-3)	36 kg		
Fumaric acid (CAS 110-17-8)	60-100 % by weight	180 - 300 mg/L	
pH buffer (Halliburton K-34)	36 kg		
Sodium bicarbonate (CAS 144-55-8)	60-100 % by weight	180 - 300 mg/L	$NaHCO_3$

a Structural formulae from Wikipedia and hgspace.com
b Data for Halliburton SSO-21M Winterized from safety data sheet, versions of 27 September 1995 and 30 October 1995
c Data for Halliburton GBW-30 breaker from safety data sheet, version of 28 March 2011

In Table C 8, the concentrations of the additives used in the fluids are compared to the relevant de minimis thresholds ("Geringfügigkeitsschwellenwerte"), derived health-related guidance values for drinking water and orientation values and PNEC values.

- The hydroxypropyl guar gum was used as a gelling agent, in high concentrations up to 3,600 mg/L. No values for assessing this substance are available. In light of its use as a food additive, and of its ready degradability, this substance is presumed to have no hazard potential.
- At 5,540 mg/L, the concentration of the substance potassium chloride, which is used as a clay stabilizer, is the highest of any individual-substance concentration within the fluid. The resulting chloride concentration exceeds the maximum permitted concentration of the Ordinance on Drinking Water (TrinkwV) 2001 (in the version of 2011) by a factor of 11, while the resulting potassium concentration exceeds the former maximum concentration permitted by the TrinkwV of 1990, 12 mg/L, by a factor of 240. Presumably, the ecotoxicological effects of this substance result mainly from its high ionic strength and the high osmotic pressure it thus induces, a pressure to which freshwater organisms in particular react sensitively (Schmitt-Jansen et al. 2012). The underground mobility of potassium is limited via sorption on clay minerals. Therefore, only a low to medium hazard potential must be assumed for it.
- Health-oriented guidance values (GVDW) are available for the substances used in the preparation SSO-21M. The concentrations used exceed the GVDW by factors of 62 to 1,230. The calculated ecotoxicological risk quotients lie between 570 and 21,200, and the risk quotient of 2-Ethylhexanol is an order of magnitude larger than the others. The substance concentrations used in the preparation SSO-21M must be assumed to present a medium-to-high hazard potential.
- The hemicellulase concentration used exceeded the listed PNEC by a factor of 90. No human-toxicologically established assessment values are available. In light of its use as a food additive, and of its ready degradability, this substance is presumed to have no hazard potential.
- The fumaric acid concentration used exceeds the derived GVDW by a factor of 21. The listed PNEC is exceeded by a factor of 1,400. In light of the substance's ready degradability, a low to medium hazard potential is assumed.
- The sodium and bicarbonate concentrations resulting from use of sodium bicarbonate as a pH buffer (82 and 218 mg/L) are considered safe, by comparison to the relevant maximum permitted concentrations of the Ordinance on Drinking Water (TrinkwV) and to the concentrations found in mineral water.

- According to current knowledge, the quartz sands, which are used as proppants, present no danger whatsoever, since they are largely insoluble and inert and largely immobile underground.

In light of the individual-substance assessment carried out, it must be concluded that the sole fracking fluid used to date in coal bed methane deposits in Germany has a medium-to-high hazard potential, primarily as a result of the substances used in the preparation SSO-21M. Due to the inadequacy of the available data, and to the possibility that the individual substances could have combined effects, no conclusive assessment of the hazard potentials of the complete fluid is possible.

Tab. C 8: Assessment of the additive concentrations used in the Natarp fracking fluid, on the basis of de minimis thresholds ("Geringfügigkeitsschwellenwerte") and health-related guidance values and orientational values, and on the basis of ecotoxicological effect thresholds (The data used as a basis are described in Annex 3.)

Substance	Quantity used (maximum quantity)	Dissolved concentration (maximum value)	De minimis thresholds (GFS)	Health-related guidance value (GVDW)	Health orientation value (HOV)	Assessment on the basis of GFS or GVDW or HOV (risk quotient)	Predicted No Effect Concentration (PNEC)	Assessment on the basis of PNEC (risk quotient)
Hydroxypropyl guar gum (CAS, researched: 39421-75-5)	436 kg	**3,600 mg/L**	_	N. e.	-	**No assessment possible**	N. e.	**No assessment possible**
Potassium chloride (CAS 7447-40-7)	671 kg	**5,540 mg/L**	_	> 3.0 mg/L	-	**< 1,850**	N. e.	**N. e.**
• Potassium (K^+)		**2,905 mg/L**	(12 mg/L)[a]	-	-	**240**	N. e.	**N. e.**
• Chloride (Cl^-)		**2,635 mg/L**	250 mg/L	-	-	**11**	250 mg/L b	**11**
2-Ethylhexanol (CAS 104-76-7)	4 kg	**36 mg/L**	-	0.175 mg/L	-	**206**	0.0017 mg/L	**21,200**
1-Hexanol, ethoxylated (CAS 31726-34-8)	26 kg	**216 mg/L**	-	0.175 mg/	-	**1,230**	0.17 mg/L	**1,270**
Ethylene glycol monobutyl ether (2-Butoxyethanol) (CAS 111-76-2)	13 kg	**108 mg/L**	-	0.35 mg/L	-	**309**	0.0894 mg/L	**1,210**
Methanol (CAS 67-56-1)	13 kg	**108 mg/L**	-	1.75 mg/L	-	**62**	0.19 mg/L	**570**

Carbohydrate (CAS unknown)	7 kg	**57 mg/L**	N. e.	N. e.	N. e.	**No assessment possible**	N. e.	**No assessment possible**
Hemicellulase (enzyme) (CAS 9012-54-8)	1 kg	**9 mg/L**	-	N. e.	-	**No assessment possible**	0.1 mg/L	**90**
Fumaric acid (CAS 110-17-8)	36 kg	**300 mg/L**	-	14 mg/L	-	**21**	0.01 mg/L	**1,400**
Sodium bicarbonate (CAS 144-55-8)	36 kg	**300 mg/L**	-	-	-	**no concern (< 1)**	-	**-**
• Sodium (Na^+)		82 mg/L	(200 mg/L) [b]	-	-	**no concern (< 1)**	-	**-**
• Bicarbonate (HCO_3^-)		218 mg/L	_	-	-	**no concern (< 1)**	-	**-**

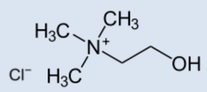
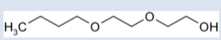
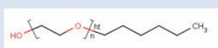
a The Ordinance on Drinking Water (TrinkwV) 2001 lists no maximum permitted concentration for potassium. The Ordinance on Drinking Water (TrinkwV) of 1990 imposed a maximum permitted concentration of 12 mg/L, although it permitted geogenically related higher values.
b No GFS derived. The maximum permitted concentration set forth by the Ordinance on Drinking Water (TrinkwV) of 2001 has been used.

C3.2.12 Hazard potential of the fracking fluids "improved Slickwater" and "improved gel"

In this section, the hazard potentials are assessed for two similar fracking fluids (a slickwater fluid and a gel fluid) that the firm of ExxonMobil Production Deutschland GmbH indicated (to the study authors) have compositions that could make them suitable for future use in shale gas deposits and, possibly, coal bed methane deposits, in Germany. The planned additive concentrations are listed in Table C 9 and Table C 10.

According to the firm of Firma BNK Deutschland GmbH, the recipe involved (which does not indicate that a biocide was used) has already been used in the Saponis Lebork S-1 borehole in Poland (BNK Deutschland 2012).

Tab. C 9: Additive concentrations in the fracking fluid "improved slickwater" ("Weiterentwicklung Slickwater").

Substance	Planned quantity	Mean concentration in the fracking fluid	Structural formula[a]
Water	**1,600 m³**		
Proppants	unknown		
Clay stabilizer (Schlumberger L071)	**1,600 kg**		
Choline chloride (CAS 67-48-1)	1,120 - 1,200 kg (70-75 % by weight)	**700 - 750 mg/L**	
Substances not subject to specific labelling require-ments	400-480 kg (25-30 % by weight)		?
Gelling agent (Schlumberger J568)	**800 kg**		
Butyldiglycol (CAS 112-34-5)	320 - 560 kg (40-70 % by weight)	**200 - 350 mg/L**	
Substances not subject to specific labelling requirements	240 - 480 kg (30-60 % by weight)		?
Wetting agent (Schlumberger F112)	**1,600 kg**		
Ethylene glycol monohexyl ether (= 1-Hexanol ethoxylated) (CAS 31726-34-8)	112 - 208 kg (7-13 % by weight)	**70 - 130 mg/L**	
Substances not subject to specific labelling require-ments	1,392 - 1,488 kg (87-93 % by weight)		?
Biocide (M-I SWACO MB-5111)	**1,600 kg**		

Ethylene glycol bis(hydroxymethyl ether) (CAS 3586-55-8)	960 - 1,600 kg (60-100 % by weight)	600 - 1,000 mg/L	
Substances not subject to specific labelling requirements	0 - 640 kg (0-40 % by weight)		?

[a] Structural formulae from Wikipedia and hgspace.com.

Tab. C 10: Additive concentrations in the fracking fluid "improved gel" ("Weiterentwicklung Gel")

Substance	Planned quantity	Mean concentration in the fracking fluid	Structural formula[a]
Water	**1,600 m3**		
Proppants	unknown		
Clay stabilizer (Schlumberger L071)	**1,600 kg**		
Choline chloride (CAS 67-48-1)	1,120 - 1,200 kg (70-75 % by weight)	**700 - 750 mg/L**	
Substances not subject to specific labelling requirements	400-480 kg (25-30 % by weight)		?
Gelling agent (product name unknown)			
Carbohydrate polymer derivative (CAS unknown)	1,730-2,280 kg	**1,080 - 1,800 mg/L**	?
Wetting agent (Schlumberger F112)	**1,600 kg**		
Ethylene glycol monohexyl ether (= 1-Hexanol ethoxylated) (CAS 31726-34-8)	112 - 208 kg (7-13 % by weight)	**70 - 130 mg/L**	
Substances not subject to specific labelling requirements	1,392 - 1,488 kg (87-93 % by weight)		?
Biocide (M-I SWACO MB-5111)	**1,600 kg**		
Ethylene glycol bis(hydroxymethyl ether) (EGHM) (CAS 3586-55-8)	960 - 1,600 kg (60-100 % by weight)	**600 - 1,000 mg/L**	
Substances not subject to specific labelling requirements	0 - 640 kg (0-40 % by weight)		?

[a] Structural formulae from Wikipedia and hgspace.com.

In Table C 12, the planned concentrations in the fluid are compared to the relevant de minimis thresholds ("Geringfügigkeitsschwellenwerte"), derived health-related guidance values for drinking water and orientation values and PNEC values.

- The use of choline chloride as a clay stabilizer, instead of the tetramethyl ammonium chloride used in the "Damme 3" fracking fluid, must be seen as a positive move, due to choline chloride's considerably lower human toxicity and ecotoxicity. Due to the high concentrations used, the derived PNEC value is exceeded by a factor of 300 - 330, however (Tab. C 12). In light of the substance's ready degradability, a low hazard potential may be assumed.
- The use of butyldiglycol as a friction reducer in the slickwater fluid, instead of the petroleum distillates used in the Damme 3 fluid, must also be seen as positive, from a human-toxicological perspective, since it reduces the factor by which the health-related guidance values is exceeded to < 50. The resulting reduction of the ecotoxicological risk quotient is less pronounced; the planned concentration exceeded the PNEC value by a factor of 3,770 - 6,600. In light of the substance's ready degradability, a medium hazard potential may nonetheless be assumed.
- For ethylene glycol monohexyl ether, both the derived GVDW and the PNEC are exceeded by a factor of 400-760, and thus a medium hazard potential may be assumed.
- The biocide ethylene glycol bis(hydroxymethyl ether) (EGHM), which splits off formaldehyde, has been classified as a low hazard to waters. Substitution of that substance for the biocide CMIT and MIT, which is classified as severely hazardous to waters (water hazard class 3 – WGK 3), has reduced the relevant water hazard class. As a result of the high planned concentrations for the biocide EGHM (600 - 1,000 mg/L instead of 3.76 mg/L CMIT and MIT), the de minimis threshold (GFS value) for biocidal products is exceeded by a factor of 6 to 10 million (Tab. C 11). The pertinent PNEC value, which has been estimated due to the inadequacy of the available data, is exceeded by a factor of more than 83,000. No data on the degradability of the biocide are available. In light of the inadequate (publicly accessible) data, and of the possibly significant, but not estimatable concentrations of free formaldehyde in the fracking fluid, this substitution must be seen critically from a toxicological perspective, however. A high hazard potential must be assumed for this substance.
- EGHM (synonym:(ethylene dioxy)dimethanol) has been identified as an old biocidal agent pursuant to Directive 98/8/EC (Biocidal Products Directive) (Art. 3 (1) in conjunction with Annex I of Regulation (EC) No 1451/2007), and it has been added to the list of substances

to be examined in the review programme in the second phase of the ten-year programme of work (Art. 3 (2) subpara. 1 in conjunction with Annex II of Regulation (EC) No 1451/2007). The rapporteur Member State for the review is Poland (Art. 3 (2) subpara. 3 in conjunction with Annex II of Regulation (EC) No 1451/2007). Testing of these biocidal agents is to cover a range of different product types (PT), including PT12 "Slimicides" and PT11 "Preservatives for liquid-cooling and processing systems", which could be of relevance for assessment of biocides in fracking products. The decision on whether or not to include these product types in annexes I or IA of Directive 98/8/EC (Biocidal Products Directive) had not yet been made as of 22 February 2012. Therefore, neither the EU Commission's assessment report, nor the data in the review documents to be submitted by producers or notifiers in the review procedure, are currently available. In the framework of the applicable transition provisions, the agent mixture will remain marketable for the duration of the review procedure – but no later than 14 May 2014, however. Pursuant to Commission Decision 2008/681/EC, covering, inter alia, PT11 and 12, formaldehyde (CAS no. 50-00-0) has not been included in Annex I or IA. This does not rule out the possibility of inclusion of the EGHM, which splits off formaldehyde,in PT11 and PT12, however (cf. Guidance document agreed between the Commission services and the competent authorities of Member States regarding the in-situ generation of active substances and related notifications)[17].

- No information is available to the study authors regarding the proppants to be used, the substances used that are not subject to specific labelling requirements and the carbohydrate polymer derivative used in the gel fluid. It is not possible to assess these substances.

In sum, it is clear that in the improved version of the slickwater and gel fluid, as compared to the "Damme 3" fracking fluid, a number of additives have been replaced with substances with lower hazard potentials. The possible combined effects of the individual substances involved cannot be assessed without toxicological testing of the complete fluid.

The fundamental changes made in the slickwater recipes (with substitution of all additives used), in the space of only 3 1/2 years since the fluid was used in the Damme 3 borehole, in November 2008, attest to the rapid pace of development of, and of the search for, suitable fracking additives. On the other hand, it also shows that additives have been used, even in the recent past, that within just a few years had to be considered in need of improvement or obsolete.

[17] http://ec.europa.eu/environment/biocides/pdf/insitugeneration.pdf

The remaining hazard potential of the aforementioned improvements is determined primarily by the hazard potential of the biocide used. In light of the high concentrations planned for the biocide EGHM, which splits off formaldehyde, and in light of the inadequacy of the pertinent data at present, a high human-toxicological and ecotoxicological hazard potential must also be assumed for the improved slickwater and gel fluids. What is more, it is questionable whether the use of biocides that split off formaldehyde can be reconciled with ExxonMobil's declared aim of discontinuing use of formaldehyde as an additive in fracking fluids (Westdeutsche Allgemeine Zeitung of 11 October 2011).

Tab. C 11 Assessment of the planned additive concentrations in the "improved Slickwater and gel" fracking fluids, on the basis of de minimis thresholds ("Geringfügigkeitsschwellenwerte") and health-related guidance values and orientational values, and on the basis of ecotoxicological effect thresholds
(The data used as a basis are described in Annex 3.)

Substance	Planned quantity	Planned concentration in the fracking fluid	De minimis thresholds (GFS)	Health-oriented guidance value (GVDW)	Health orientation value (HOV)	Assessment on the basis of GFS or GVDW or HOV (risk quotient)	Predicted No Effect Concentration (PNEC)	Assessment on the basis of PNEC (risk quotient)
Choline chloride (CAS 67-48-1)	1,120 – 1,200 kg	**700 - 750 mg/L**	-	≥17.5 mg/L	-	**< 43**	3.49 mg/L	**200-210**
Butyldiglycol (CAS 112-34-5)	320 – 560 kg	**200 - 350 mg/L**	-	8.75 mg/L	-	**23-40**	0.053 mg/L	**3,770-6,600**
Carbohydrate polymer derivative (CAS unknown)	1,730 – 2,280 kg	**1,080 - 1,800 mg/L**	N. e.	N. e.	N. e.	**No assessment possible**	N. e.	**No assessment possible**
Ethylene glycol monohexyl ether (CAS 31726-34-8)	112 – 208 kg	**70 - 130 mg/L**	-	0.175 mg/L	-	**400-743**	0.17 mg/L	**410-760**
Ethylene glycol bis(hydroxymethyl ether) (CAS 3586-55-8)	960 – 1,600 kg	**600 - 1,000 mg/L**	0.0001 mg/L	-	-	**6,000,000-10,000,000**	Inadequate data (0.0072 mg/L)	**Inadequate data (83,000-139,000)**
Formaldehyde (CAS 50-0-0)	Use of biocide that splits off formaldehyde	**Unknown (< 490 mg/L)**	-	N. e.	0.010 mg/L	**No assessment possible**	0.00026 mg/L	**No assessment possible**
Substances not subject to specific labelling requirements	1,792-3,088 kg	Substances unknown	N. e.	N. e.	N. e.	**No assessment possible**	N. e.	**No assessment possible**

C3.2.13 Summary assessment, and knowledge deficits

The assessment of 28 fracking fluids has revealed that a widely diverse range of additives, comprising at least 112 different additives, has been used in the past in unconventional natural gas deposits in Germany. A total of 88 preparations, most of them originating with two producers, have gone into the fracking fluids used. In light of the hazard characteristics of the substances used, it is clear that even the newer fluids injected into boreholes since the year 2000 have made use of preparations, and additives, with properties of very high concern (including substances that are highly toxic, carcinogenic, mutagenic and/or toxic for reproduction).

The quantities used have varied considerably, depending on what fluid systems were used and on the characteristics of the deposits involved; the quantities of fracking fluids used per frack have ranged from less than 100 m^3 to more than 4,000 m^3. With the modern gel fluids used since 2000, an average of about 100 t of proppants and about 7.3 t of additives (of which usually less than 30 kg were biocidal products) were used per frack. The quantities used can be quite large especially with multi-frack stimulations and/or use of slickwater fluids: For example, a total of about 12,000 m^3 of water, 588 t of proppants and 20 t of additives (of which 460 kg were biocides) were injected into the Damme 3 in connection with three fracks.

The assessments of selected fracking fluids used in Germany conclude that the fluids have high, or medium-to-high, human-toxicological and ecotoxicological hazard potentials. Comparison of these assessments with the classifications of the fluids pursuant to the Administrative regulation on substances hazardous to water (Verwaltungsvorschrift wassergefährdender Stoffe – VwVwS), and to the CLP Regulation, clearly indicates that classifications pursuant to legislation on plants and industrial facilities, and to laws pertaining to hazardous substances, should serve as no more than guidelines for describing and assessing the hazard potentials of fracking fluids, following a discharge into the environment, with regard to drinking water protection and to protection of aquatic ecosystems.

The possible compositions of two improved fracking fluids that potentially could be used in Germany highlight the efforts of the involved companies to replace some of the additives used in the past with substances with lower hazard potentials. Such improvements notwithstanding, in light of the high concentrations planned for a biocide that splits off formaldehyde, and of the gaps in the data available for assessing that biocide, such improved fluids must also be assumed to have a high hazard potential.

The possible replacement of three hazardous additives that were still being used in 2008 with substances with lower hazard potentials must be critically evaluated, since it highlights the fact that additives used in the recent past were found to be improvable, or obsolete, within just a few years. Since the underlying database for assessing those additives has been available for years now, it is necessary to review whether, in the past, service companies, operators and/or authorities have adequately considered the possibilities for finding substitutes for hazardous additives.

Current relevant development work aimed at reducing the number of additives used, at finding substitutes for substances that are highly toxic, carcinogenic, mutagenic or reprotoxic (cmr substances), and at reducing use of or replacing biocidal agents, points to potential progress in development of environmentally compatible fracking fluids. The assessment method described can serve as a starting point for efforts to develop additives with lower hazard potentials.

C4 Assessment of aspects related to permanent deposition of fracking additives in underground formations

C4.1 Fracking-additive quantities as percentages of flowback

Various different methods can be conceived of for determing quantities of recovered fracking fluids as percentages of total flowback volume (Rosenwinkel et al. 2012):

- Measurement of changes in salt concentrations,
- Determination of concentrations of 1,5-Naphtalenedisulfonate,
- Determination of concentrations of oxidation and degradation products of the gels and ethers used,
- Determination of selected isotope ratios,
- Halogen chemistry methods (such as use of the Br/Cl ratio as a "fingerprint") (Siegel & Kight 2011, cited pursuant to Energy Institute 2012).

On the basis of the development of chloride concentration, Rosenwinkel et al. (2012) determined the quantity of recovered fracking fluids, as a percentage share of flowback, at the Damme 3 borehole (Fig. C 2).

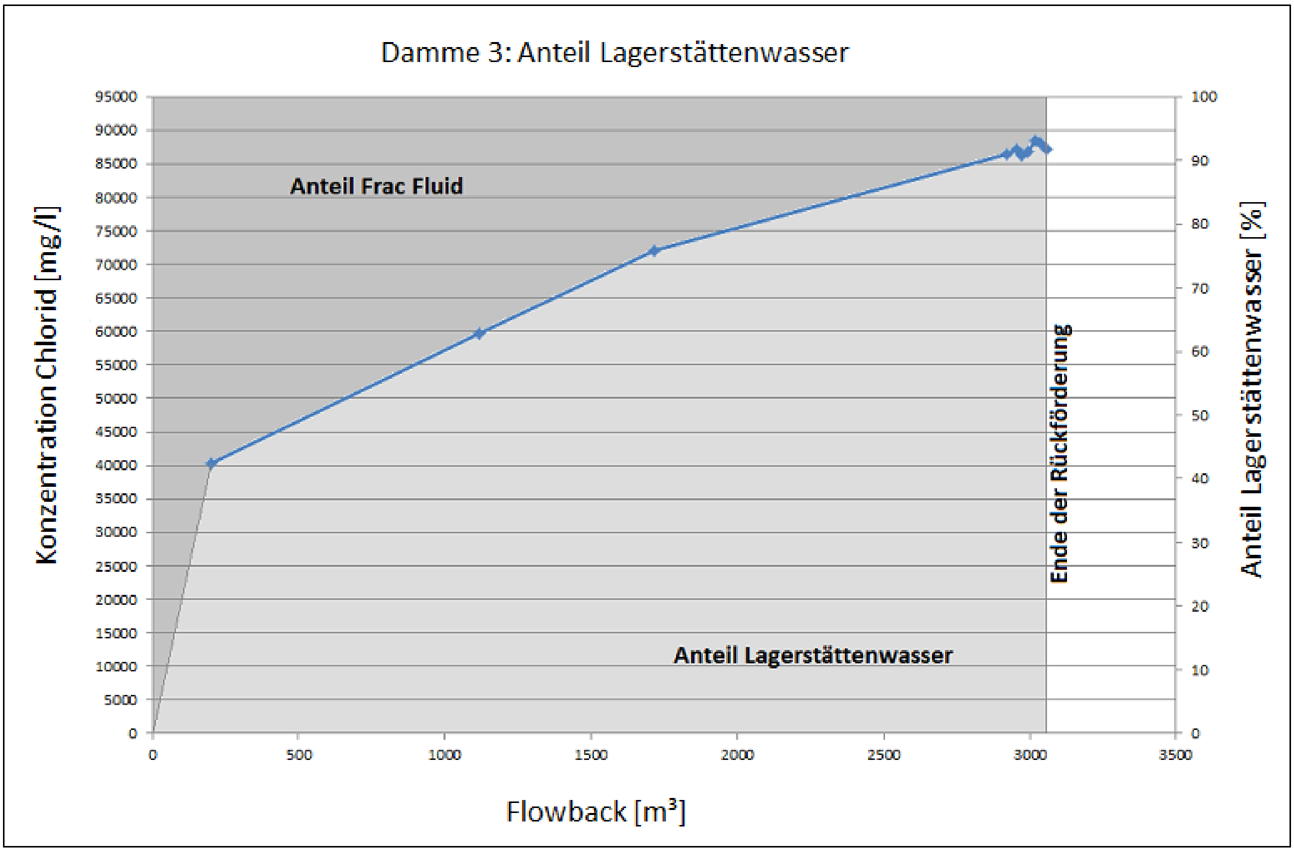


Fig. C 2: Determination of fracking-fluid fractions in flowback in the Damme 3 borehole, on the basis of measured chloride concentrations (Rosenwinkel et al. 2012) [y axis: Chloride concentration; Top: Damme 3: Formation water fractions in flowback; y axis, right: End of flowback recovery; Fracking fluid fraction; Formation water fraction]

The chloride concentration is seen to converge toward a constant value of about 95,000 mg/L, which is assumed to be the same as the chloride concentration in the original formation water. For a total flowback volume of 3,058 m^3, for the period from 20 November 2008 to 12 January 2009, Rosenwinkel et al. (2012) calculated average percentages (i.e. percentages of flowback) of 31 % for the fracking fluid and of 69 % for the formation water. The assessment concluded that only 8 % of the total quantity of injected fracking fluids was recovered along with flowback (Rosenwinkel et al. 2012). Even though that percentage can be expected to increase as production continues, it seems certain that a substantial proportion of the fracking additives involved remain underground.

The figure for the recovered fraction of fracking fluid, as determined via chloride concentration, is valid only for those additives that are not sorbed within the deposit horizon. Additives with strong sorption properties (such as clay stabilizers) will largely have actually remained underground even when complete recovery of such fluids has been calculated, on the basis of the chloride balance. In a rigorous approach, therefore, mass-balancing of recovered additives, and of additives remaining underground (and possibly undergoing transformation and degradation there) actually needs to be carried out substance-specifically, i.e. individually for each additive.

C4.2 Hydrochemical and hydraulic changes caused by fracking additives remaining underground

At the high pressures and temperatures prevailing in the target horizon, it must be assumed that injected fracking additives will undergo chemical transformation and degradation reactions in the presence of saline formation water. Microbiological degradation reactions can occur as soon as the effects of injected biocides diminish. It cannot be ruled out, in such reactions, that stable metabolites will form that can present human-toxicological and ecotoxicological hazard potentials that can even exceed the risks posed by the outset substances that were injected.

No information is available to the study authors regarding the extent to which significant transformation and degradation reactions can take place within the fracking horizon. To our knowledge at present, no systematic measurements have been carried out to date, by operators or services companies, for the purpose of identifying reaction and degradation products in flowback (Ewers et al. 2012).

Along with pressure, temperature and pH, the key factor influencing formation of transformation products is the redox conditions in the deposit. The conditions in deposit horizons are usually anaerobic and reducing, as is indicated by the high iron concentrations in their formation water. Often, large quantities of oxidizing agents are introduced along with fracking fluids (for example, sodium persulfate and sodium bromate are often used as breakers). When that happens, oxidizing conditions must be expected within fracking horizons – at least for certain periods. Under such conditions, the organic compounds in the deposit are subjected to oxidation reactions, reactions which can produce toxic reaction products.

Working on the basis of experience gained with oxidation technologies for water treatment, Ewers et al. (2012) have identified possible reaction and degradation products for a number of additives. Caution must be applied, however, in applying such results directly to reactions and degradation occurring in the presence of saline formation water, at the high pressures and temperatures prevailing in fracking horizons. In light of existing knowledge deficits regarding such significant transformation and degradation products, we propose that research be carried out to study such products, and their toxicological properties and possible persistence and bioaccumulation. Such research should include simulation of the conditions prevailing in deposits.

Within the solid matrix prevailing in a deposit, substances can be expected to be sorbed in ways, depending on the surrounding rock's substance-specific sorption properties (such as K_{ow} value) and sorption capacity, that will influence the underground transport behavior of fracking additives.

The relevant fluid dynamics depend on the potential differences and pathways in the surrounding rock (cf. Chapter C1). When high-pressure injection is discontinued, the fractures that have been widened, and filled with proppants, in the process close somewhat and permeability decreases in comparison to its level at maximum injection pressure. Then, flows reverse, as flowback recovery begins, and move toward the perforated drill string. Flowback moves considerably more slowly than injection flows. As fractures close, section by section, fluids that have penetrated far into the rock can be encapsulated. Some of the fracking fluids are injected into the rock matrix, where they move very slowly, because such matrices (usually) have very low matrix permeability, along the resulting gradient. During production, that gradient points toward the perforated drill string. After production, when the partially drained pores and fissures in the surrounding rock have filled again, natural groundwater flows restore themselves. When deep water rises – along faults, for example – fluids can rise as well and reach groundwater aquifers above.

Fracking additives that remain underground then pose a risk for near-surface (exploitable) groundwater, if there is a possibility (probability of occurrence) that they could reach the region of near-surface (exploitable) groundwater, in significant concentrations, via one or more of the impact pathways mentioned in Chapter C 1. The question of whether, and to what extent, substance transport in the direction of exploited groundwater resources occurs thus depends on the relevant, site-specific, geological and hydrogeological conditions, as well as on the sorption properties of fracking additives and the surrounding rock.

C5 Assessment of methods for disposal / re-use of flowback

C5.1 Assessment of the hydrochemical properties of flowback, with regard to disposal

Because the composition of flowback, as a mixture of fracking fluid and formation water, varies (Chaper C 3), the hazard potential of flowback is estimated by assessing those two end elements of the mixture sequence. That approach takes account of the variance in fluid composition and reflects the current level of relevant knowledge. Because much remains to be learned about sorption and dissolution processes in rock formations, and about the related possible reaction products, such processes cannot be taken into account at present in the assessment. In the assessment, attention is called to the physical and chemical properties of the substances involved, and to the substances' degradability and degradation products, wherever such aspects are known (Annex 3).

In light of the hazard potentials of fracking fluids and formation water, flowback must be considered to have considerable hazard potential. Even if it should prove possible to produce fracking fluids with reduced hazard potentials, the hazard potential of flowback will likely remain significant, in light of the probable properties of formation water. Environmentally compatible flowback disposal is thus one of the high-priority tasks to be carried out in connection with fracking.

C5.2 Options — basic or already in practice — for flowback disposal and re-use, and environmental assessment of such options

Possible technical processes for treating flowback are described in Rosenwinkel et al. (2012). However, Rosenwinkel et al. (2012) conclude that none of those flowback-treatment processes, at present, qualifies as "best available technology" within the meaning of the Federal Water Resources Act (Wasserhaushaltsgesetz).

In general, the following options are available for disposing of / managing / recycling flowback:

- Injection via disposal wells,
- Treatment, for discharge into surface water,
- Treatment, for discharge into the sewer system,
- Re-use in additional fracks,
- (Atomisation / evaporation / agricultural irrigation).

The listed options for flowback disposal / re-use must be assessed as follows with regard to environmental compatibility:

Injection via disposal wells

This type of disposal is commonly used in those areas in which conventional and unconventional gas deposits are already being exploited. Nonetheless, the possible related hazards to water resources have not been adequately studied. In the view of the study authors, such risks cannot be ruled out. The hydrodynamics of deep groundwater, and the environmental impacts of such disposal injection, need to be studied site-specifically in each case.

Injection into the unconventional gas deposits being fracked is neither feasible nor useful, since it would run counter to the aim of draining water from target rock formations in order to permit production of unconventional gas resources.

Discharge into surface water

Because of its high pollutant concentrations (salts, organic compounds, fracking additives and transformation products, NORM, heavy metals, etc.) flowback has to be treated before it can be discharged into surface water.

The question of whether existing industrial wastewater-treatment facilities can be used for that purpose, and of whether certain treatment processes would have to be used, must be answered in light of the quantity and chemical composition of the specific flowback involved.

Discharge into the sewage network

Because of its high pollutant concentrations (salts, organic compounds, fracking additives and transformation products, NORM, heavy metals, etc.) flowback has to be pre-treated before it can be discharged into the sewage network.

The question of whether existing municipal wastewater-treatment plants can be used for that purpose, and of whether certain treatment processes would have to be used, must be answered in light of the quantity and chemical composition of the specific flowback involved.

Re-use in additional fracks

As noted, flowback composition is always deposit-specific, because fracking additives are mixed site-specifically and because the characteristics of formation water are always site-specific. The question of whether, and to what extent, it would be technically feasible to reuse/recycle flowback can be answered only via analysis of the characteristics and concentrations of extracted additives.

Atomisation/evaporation

Under the climatic conditions that prevail in Germany, large-scale evaporation of fracking fluids, possibly with the support of atomisation systems, is not feasible.

Agricultural irrigation

Because flowback would be expected to have high salt loads, as well as high concentrations of organic and inorganic pollutants, use for agricultural irrigation – for example, via infiltration – would presumably not be permitted.

C6 Identification and assessment of possible fracking processes that use no chemical additives

C6.1 Fracking processes that use no chemical additives

Along with efforts to find substitutes for various individual additives, efforts are being made to develop fracking fluids that are completely free of certain additive groups. The following section presents information about current developments in this area. The authors wish to emphasise that they are not in a position to assess such projects in terms of their feasibility.

The firm of Halliburton is testing possibilities for using UV light to inhibit growth of microorganisms, in order to reduce use of biocides. The relevant process uses a mobile unit that mixes fracking fluids efficiently[18]. In May 2011, in Texas (U.S.), the "CleanStim Fluid", with UV disinfection, was used for the first time in an actual frack. Irradiation of about 18,000 m^3 water with UV light saves about 9 m^3 of biocides (per borehole)[19].

OMV, an oil and gas company, working in cooperation with the University of Leoben (Montanuniversität Leoben), is developing a process that uses no chemicals, relying instead solely on water, bauxite and corn starch[20]. Plans call for process's technical feasibility to be tested through early 2015 and its cost-effectiveness to be tested through 2018/19. Test drills, to depths down to 6,000 m, along with suitable test fracks, are to be carried out as of summer 2013. Plans also call for UV disinfection of the water injected to fracture the rock. Recovered water and extracted gas are to be transported via pipelines, in closed circuits. Process water is to be treated. Fresh water is to be required only for the first two boreholes; the third borehole is to be fracked using recycled fluids[20].

In exploitation of deep geothermal energy, hydraulic fracturing (fracking) is used to create artificial pathways in which water

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18 http://www.halliburton.com/ps/Default.aspx?navid=93&pageid=4184&prodid=PRN%3a%3aKWTBF215&TOPIC=HydraulicFracturing].

19 http://www.halliburton.com/public/news/pubsdata/press_release/2011/corpnws_050211_1.html?SRC=ElPasoandHalliburton

20 http://www.wirtschaftsblatt.at/home/boerse/bwien/omv-will-mega-gasvorrat-im-weinviertel-ab-2020-foerdern--504947/index.do?_vl_pos=r.1.NT

circulating as a heat-exchange medium can flow. In the two GeneSys projects[21] of the Federal Institute for Geosciences and Natural Resources (BGR) being carried out in Hannover and Horstberg, water, free of chemical additives, has been tested as a stand-alone fracking fluid[22]. Development of the water-stimulation concept draws on research work carried out at Soultz-sous-Forêts (Alsatia / Upper Rhine Graben; France) that demonstrated the feasibility of creating highly permeable fissures, in crystalline rock, that could support circulation between deep boreholes. In such efforts, hydraulic stimulation with water causes dividing surfaces to shift with respect to each other. Due to their surface roughness, dividing surfaces that fit over each other no longer fit when the injection pressure is removed – the surfaces are "self-propping". With this effect, the process is thus able to create new spaces and to create lasting permeabilities without the help of proppants. Fracking without chemical additives, using the "self-propping effect", is suitable for formations with rigid rock mechanics, and with anisotropic stress fields (cf. section A3.3).

The process is probably not suitable for plastically reacting clay formations, such as those typically encountered in shale gas exploitation. It might be suitable for coal bed methane deposits with accompanying sandstone horizons.

Extreme overbalance perforating

In the extreme overbalance perforating method, short fractures are created with the help of compressed nitrogen, in a work step combined with the perforation of the casing string. The stimulation effects are limited to the close proximity of the borehole, however (tens of meters). The method may be an option for reducing quantities of fracking fluid and fracking additives.

Cavitation hydrovibration (Fig. C 3)

This stimulation technique was developed at the Institute for Technical Mechanics of the University of Dnipropetrovsk (Ukraine). In it, stimulation functions via the pressure resulting from a bubble implosion in the drill string, following artificially induced cavitation. The fluid used is pure water, without any added chemicals or proppants. The process has been tested in exploitation of sulphur deposits, via the Frasch process, in Ukraine's Lviv region (Novojarovskoje deposit). The process has also

[21] www.genesys-hannover.de

[22] http://www.geothermie.de/fileadmin/useruploads/Service/Publikationen/Hintergrundpapier_Stimulation_GtV-BV.pdf

been used successfully in regeneration of drinking water wells in Russia's Moscow and Pskov regions and in Kazakhstan. The cavitation hydrovibrator is mounted above the drill head, within the drill string. Operated via the pressure of the drilling fluid, it has no moving parts and is subject to virtually no wear and tear. The longitudinal accelerations it produces, pulsing at frequencies of 100 to 7,300 Hz, are transmitted directly to the drill head. The pulsating downhole mud pressure breaks up the rock in front of the drill head, thereby accelerating drilling progress and reducing wear on the drill head (Palypenko et al. 2005).

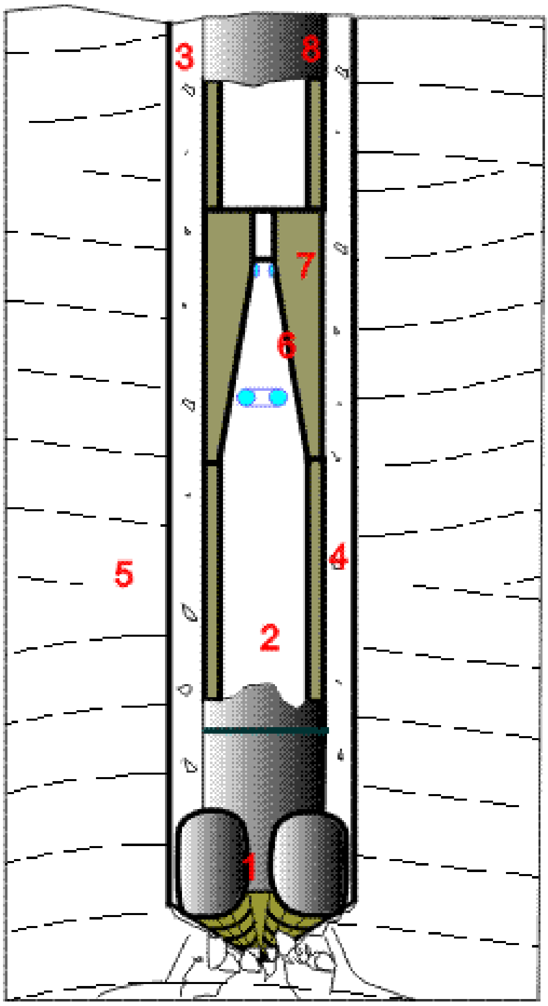

Fig. C 3: Principle behind the cavitation hydrovibration process (2009)
(Animation at: http://smarteconomy.typepad.com/smart_economy/2009/12/a-green-alternative-to-chemicalbased-hydraulic-fracturing-or-fracking-for-shale-gas-drillingcavitati.html)

The process ultimately leads to a controlled "blowout"[23] in the target formation, creating a large hollow space (up to 4 m in diameter) and suddenly flushing large quantities of material and fluids to the surface. The drilling equipment must thus meet certain special requirements, and special safety precautions must be taken, to ensure that no uncontrolled releases of material occur. In the view of the study authors, it seems unlikely that this technique could be used in Germany.

LPG fracking

LPG fracking, a process patented by the Canadian firm GasFrac, uses gelled liquid petroleum gas (LPG) as the fracking fluid. LPG, which consists primarily of propane (C_3H_8), dissolves in the natural gas present in natural reservoirs (Gasfrac Energy Services Inc.). The liquid petroleum gas, with suspended proppants, is injected into the target rock, where it undergoes a liquid-to-gas phase transition. The resulting gaseous fracking fluid is then recovered nearly completely, together with the natural gas contained in the rock formation. The process is particularly useful in very dense clay strata, since it precludes any closure of pores and fractures via remaining fracking fluid. In comparison to the water-based fracking techniques currently used, this increases the effective permeability of stimulated reservoirs. What is more, the LPG does not cause clay minerals to swell when it comes into contact with them. In addition,LPG does not promote the bacterial growth that, in water-based fracking, biocides are used to prevent. The factors hindering the broader acceptance of this process include higher costs and the limited availability of pertinent services – such services are offered only by a single provider, the holder of the rights to the process (Goodman 2012). In addition, stringent safety standards have to be applied, since the process makes use of large quantities of a volatile, flammable gas.

Since 2008, the process has been used a total of about 1,000 times, including 900 times in the Canadian provinces Alberta, British Columbia and New Brunswick. It has also been used in the U.S. states Colorado, New Mexico, Oklahoma, Pennsylvania and Texas (Goodman 2012).

Chemical stimulation

Chemical stimulation of reservoirs is not used in shale gas exploitation. As a rule, in such operations, hydrochloric acid is used to clean the borehole, and its immediate vicinity within the production horizon, of drilling-mud residues. Acid treatments have been tested in petrothermal

[23] Uncontrolled release of fluids and/or gases.

and geothermal reservoirs (Schulte et al. 2010), and acids are also used in hydrothermal systems to clean the borehole and its immediate vicinity of residues upon completion of drilling. Following successful hydraulic stimulation, the productivity of production wells in Soultz-sous-Forets has been further increased, by up to 50 %, through use of hydrochloric acid, hydrofluoric acid, tetrafluoroboric acid and citric acid (Nami et al. 2008). Drill core analyses had revealed that carbonates and other soluble minerals were filling joints within the reservoir. The injection pressures used in such acid treatments are lower than those used in hydraulic stimulation. In conventional oil and gas production, this process is commonly used in carbonate deposits, and it is used to clean boreholes of cement residues (Economides et al. 2000).

Thermal stimulation

Thermal reservoir stimulation is used to increase productivity in high-enthalpy geothermal deposits – usually volcanic or metamorphic rock formations. In the process, water with a temperature that is considerably lower than that prevailing in the reservoir is injected at relatively low pressure (10 – 60 bar at the drill head) (Schulte et al. 2010). Via several different thermally induced geomechanical mechanisms, this improves the borehole's connections to the reservoir. The relative importance of the different mechanisms involved is being studied in current research (Siratovich et al. 2011). In the first place, injection of cold water into reservoirs with temperatures of over 300°C, immediately following the completion of the borehole, cleans the borehole and its immediate vicinity of drilling residues. In addition, the resulting thermo-elastic stresses thereby created in the rock tend to widen existing fractures and create new ones.

C6.2 Assessment of the alternatives

Fracking without chemical additives would eliminate the hazard potential tied to such substances. However, it would not reduce the hazard potential tied to creation of (exit) pathways for formation water and to extraction of flowback, which would then consist solely of formation water (cf. Chapter C3). The risks presented by formation water, along possible impact pathways, are always site-specific and depend primarily on the water's chemical composition and mineralisation. As a result of such dependence, to assess the risks one would have to study and assess the formation water in each individual case.

As such examples indicate, while various pertinent procedures are currently being developed and tested, much more research will be required before fracking processes become available that do completely without chemical additives.

C7 Methodological information relative to execution of site-specific risk analyses

As the above remarks have shown, projects for exploration and exploitation of unconventional natural gas deposits need to be preceded by specific risk analysis that takes account of the relevant site-specific circumstances (geology/hydrogeology, uses, etc.), as well as of the technical measures planned in accordance with those circumstances (including selection and use of fracking additives). In this regard, Chapter C7 presents relevant methodological information, some of which is also included in the foregoing assessments of the individual components involved (such as the assessment of the hazard potential of fracking fluids presented in Chapter C3).

C7.1 Risk analysis structure/method

Exploration and exploitation of unconventional natural gas deposits entail a number of environmental impacts, including noise, land use, substance emissions, etc. Such impacts, which vary in magnitude depending on the operational phase involved, can be specifically determined. Given suitable requirements, they can be assessed on the basis of applicable legal provisions – for example, via environmental impact assessment (EIA) – and then regulated via authorisations and imposed requirements.

Along with direct environmental impacts, unconventional gas exploration and production (like operations of many technical installations) present a range of other, delayed and spatially separated risks for people and the environment (cf. Figure C4). Such risks include, for example, upward migration of gas and groundwater contamination via rising fluids.

A commonly used approach for determining and estimating risks is to link a relevant event's probability of occurrence with the resulting damages. Different methods are available, depending on the available data, for doing this:

- If a great deal of relevant experience and measurements have been gathered, the probability of occurrence can be expressed numerically, in the context of probabilistic risk analysis (for example, numbers of accidents on roads, for a given amount of truck mileage).
- Where few reliable data are available, the risks can be described in terms of selected risk scenarios (deterministically). Usually, the risks tied to "worst-case scenarios", and their consequences, are described and then used as a basis for deriving the possible

costs of remediation and assessing the possible costs of prevention.

- In certain cases, if no, or too few, experiential data are available for determination of mathmatical probabilities of occurrence, the risks can be estimated with the help of ecological risk analysis (cf. SCHOLLES, 2001). In such cases, assessment is normally expressed qualitatively, using three- or five-level scales (i.e. high – medium – low).
- Finally, combinations of these different methods can be used.

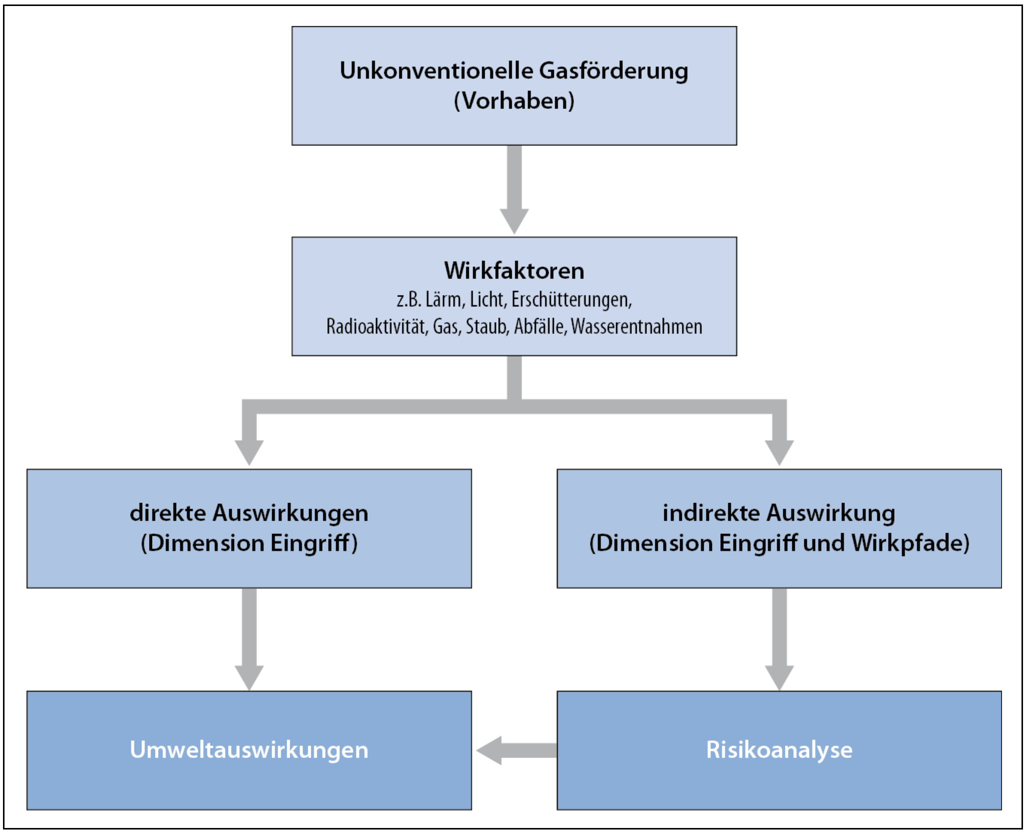

Fig. C 4: Assessment of environmental impacts via effective factors (source: ahu AG et al. 2012) [Unconventional gas exploitation (projects); Effective factors – such as noise, light, vibrations; radioactivity, gas, dust, waste, water removals; Direct impacts (intervention dimension); Indirect impacts (intervention and impact pathways dimension); Environmental impacts; Risk analysis]

In the present case, involving unconventional gas production, it is difficult to determine the relevant risks – primarily as a result of the paucity of available data. On the one hand, certain basic information – especially key geological and hydrogeological information – is lacking. On the other, while experience has been gained in Germany with exploitation of tight gas deposits, no concrete experience has been gained in this country with exploitation of shale gas and coal bed methane deposits.

We thus propose that the required (site-specific) risk analyses for projects for exploration and exploitation of unconventional natural gas deposits be carried out using a combination of the different available risk-analysis methods. Such a combination is shown schematically in Figure C 5, and it is described in the following section.

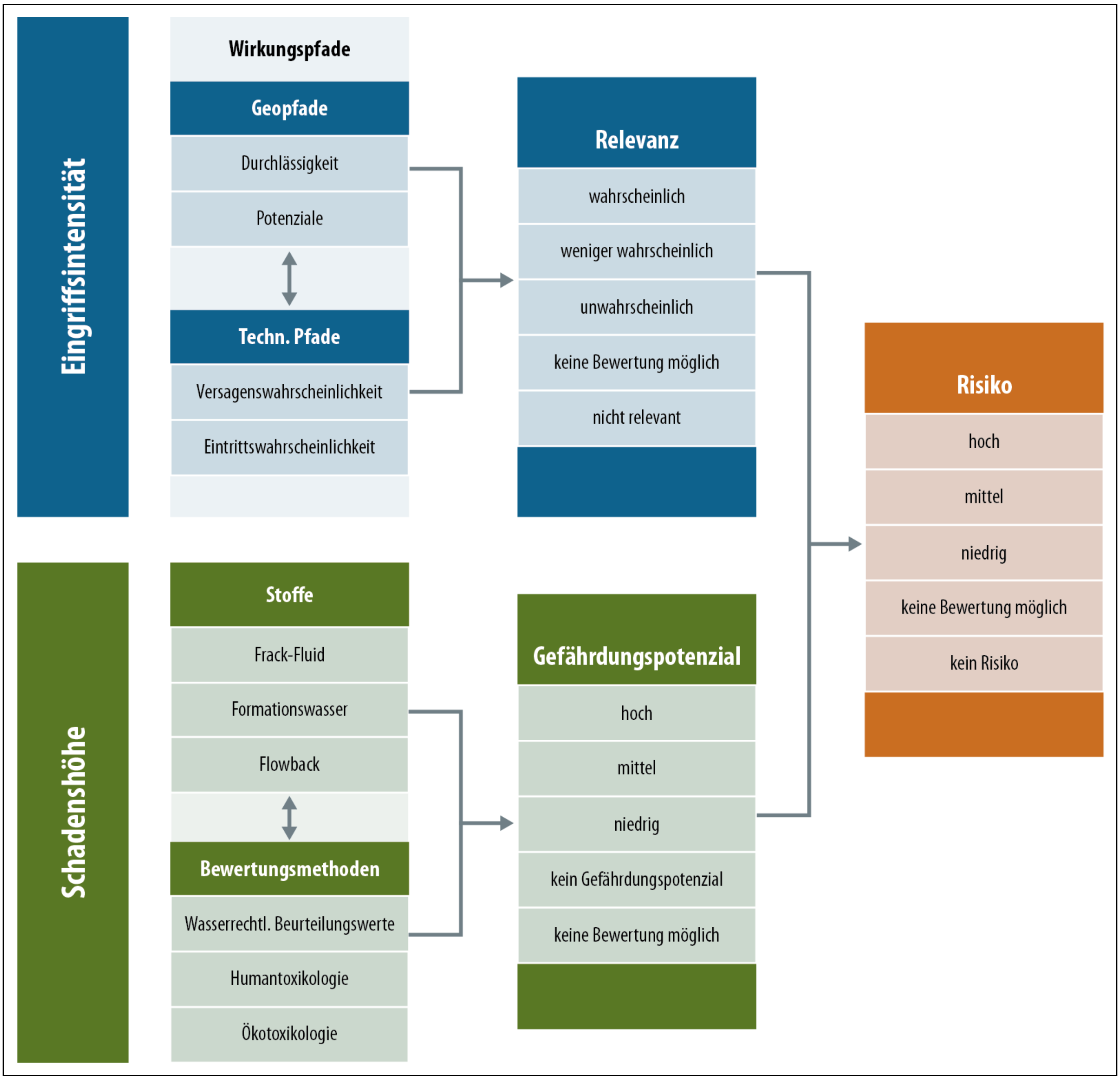

Fig. C 5: Structure of risk analysis for assessment of exploitation of unconventional natural gas deposits [by columns, left to right, top to bottom: Intervention intensity (blue); Extent of damages (green); Impact pathways; Geopaths; Permeability; Potentials; Technical pathways; Probability of failure; Probability of occurrence; Substances; Fracking fluids; Formation water; Flowback; Assessment methods; Values for assessment under water law; Human-toxicology; Ecotoxicology; Relevance; Probable; Less probable; Improbable; No assessment possible; Not relevant; Hazard potential; High; Medium; Low; No hazard potential; No assessment possible; Risk; High; Medium; Low; No assessment possible; No risk]

C7.2 Impact pathways (intervention intensity)

In consideration of the risks that exploitation of unconventional natural gas deposits can pose for exploitable groundwater resources, consideration of impact pathways takes the place of consideration of intervention intensity. The reason for this is that a risk can lead to actual damage only if the pertinent impact pathway is relevant.

Both technical impact pathways (such as failures of borehole casings) and geological impact pathways (such as faults) have to be considered. Very often, combinations of the two impact pathways will be involved. For technical impact pathways, substantiated probabilities of occurrence or failure can be determined if adequate data are available. Geological impact pathways depend on the geological systems involved. They are defined primarily via the two parameters permeability and hydraulic potential (referred to below as "potential"). The directions in which gases and fluids flow depend on potential differences. The potential differences prevailing between the site(s) of pertinent hazard potentials and the site(s) of resources/assets thus play a central role in assessment of relevant risks.

Without suitable numerical quantification, the relevance of any impact pathways cannot be assessed. An impact pathway is relevant, when it presents a probability for transport of gas and/or fluids that could result in an environmentally harmful impact. One way of qualitatively assessing the relevance of impact pathways is to apply the classifications pursuant to the safety requirements of the Federal Ministry for the Environment, Nature Conservation and Nuclear Safety (BMU) for final storage of heat-generating radioactive waste[24]. At present, the data and information that one would require in order to draw reliable conclusions regarding the relevance of impact pathways are lacking, for all pertinent geological systems.

The various different pathway groups, and their importance, were discussed in Chapter C1. It cannot be ruled out that incidents during delivery and storage of fracking products, and during production and use of fracking fluids, would cause part of the preparations and/or fracking fluids being used to reach exploitable groundwater, via pathway group 0. Incidents could also lead to discharges of recovered flowback into near-surface groundwater, and via pathway group 0. Given suitable pathways and potential differences, fluids could also be released, via pathway groups 1, 2 or 3, that would consist of fracking fluid and formation water, in varying mixing ratios, and that could contain additional solution, reaction and degradation products.

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[24] http://www.bmu.de/atomenergie_ver_und_entsorgung/downloads/doc/42047.php

C7.3 Hazard potential

Suitable methods for assessing the hazard potential of fracking fluids, of formation water, of flowback and, if relevant, of applicable mixtures, are described in Chapter C3. In the component-based methods used, assessment is based on the human-toxicologically and ecotoxicologically effective concentrations of the individual substances involved.

Although the recipes for fracking fluids, and the characteristics of formation water and flowback, need to be assessed site-specifically, the following risk assessment considers such recipes and characteristics generically, i.e. from an overarching, site-independent perspective. In general, fracking fluids and formation water can be classified into the categories "no hazard potential", "low hazard potential", "medium hazard potential" and "high hazard potential". Placement of a substance in the category "no hazard potential" is defined as meaning that the concentrations of all individual substances involved lie below the applicable assessment values under water law and under the applicable human-toxicological and ecotoxicological effect thresholds (risk quotients < 1). The overall assessment for a fluid may have to take account of possible synergistic or antagonistic effects of the fluid's constituent substances.

To differentiate between low, medium and high levels of hazard potential, in any scientifically sound way, one must use exposure scenarios for specific resources/assets, such as scenarios developed with the help of numerical models.

Hazard potential of fracking fluid / Hazard potential of formation water	High	Medium	Low	No hazard potential
High	High	High	High	High
Medium	High	Medium	Medium	Medium
Low	High	Medium	Low	Low
No hazard potential	High	Medium	Low	No hazard

Fig. C 6: Possible assessment of the hazard potentials of flowback, and of the fluids that could be released via the pathway groups 1, 2 or 3, i.e. mixtures of fracking fluid and formation water
(According to current knowledge, the case "formation water with no hazard potential" (cross-hatched area) is only hypothetical.) (Sample explanation of high: The fracking fluid / formation water mixture has a high hazard potential if the hazard potential of the fracking fluid is low and the hazard potential of the formation water is high.)

Flowback, and the fluids that can be released via pathway groups 1, 2 and 3, consist of variable mixtures of fracking fluids and formation water. Since the fractions in such mixtures vary by site and over time, in the following it is assumed that the hazard potential of such fluids is determined by the higher of the hazard potentials of the initial components of such mixtures, namely fracking fluids and formation water. In light of current knowledge, it is not possible, in the present assessment, to take account of possible solution, reaction and degradation products in the fluids.

The fracking fluids assessed in Chapter C3 have either high hazard potentials or medium-to-high hazard potentials. According to current knowledge, it must be expected that formation water will also contain such high concentrations of certain substances that it cannot fail to have hazard potentials.

As Figure C 6 shows, a high or medium hazard potential must be expected for flowback and for the fluids that could be released via the pathway groups 1, 2 and 3. Where non-critical fracking fluids are used in deposits with formation water with low hazard potential, the resulting fluids could possibly have a low hazard potential.

C7.4 Risk matrix

Consideration of the hazard potential of fluid-water mixtures focuses on near-surface groundwater resources (cf. Fig. C 1). The sensitivity of near-surface groundwater resources is very high throughout. Mixing with formation water (for example, following rising of such water from deeper layers) is not considered to be dilution that would lower the hazard potential, since formation water also can have negative impacts on near-surface groundwater resources (see above). Fluid discharges into deep (saline) groundwater resources are an inherent risk and have to be assessed separately (and also from a legal standpoint, inter alia).

The hazard potential is determined by combining the pathway-based consideration (intervention intensity) and the hazard potential of the fluids involved (fracking fluids and formation water). Figure C 7 shows an example of a risk matrix.

Hazard potential of fluids / Relevance of impact pathways	High	Medium	Low	No hazard potential
Probable	High	hoch	Medium	No hazard
Low probability	High	Medium	Low	No hazard
Unlikely	Medium	Low	niedrig	No hazard

Fig. C 7: Example of a risk matrix for assessment of exploitation of unconventional natural gas deposits (Sample explanation for high: In combination with a probable impact pathway, a fluid with a medium hazard potential presents a high hazard)

C8 Summary and deficit analysis from a scientific and technical standpoint

In Part A of the present study describes the scientific and technical aspects of exploration and exploitation of unconventional natural gas deposits, via fracking, while Part B discusses the relevant legal framework. On the basis of those two parts, Part C then assesses the key factors that must be considered in analysis of the potential hazards. Each part also calls attention to the deficits in our knowledge and understanding of these areas.

The following section summarises the results of parts A and C and analyses the deficits in our knowledge from scientific and technical perspectives. A deficits analysis from a legal perspective is included in Part B. The results of the deficits analyses form the basis for the derived recommendations for action presented in Part D.

Exploration and exploitation of unconventional natural gas deposits, via fracking, are like virtually any technical projects in that they involve concrete environmental impacts such as noise, land use, etc.. The intensities of such impacts vary, depending on the operational phases concerned. Such environmental impacts can be described; assessed in light of applicable legal provisions, in preliminary procedures (such as environmental impact assessment (EIA)); and regulated and controlled via authorisations and imposed requirements.

In addition to the "direct" environmental impacts expected, exploration and exploitation of unconventional natural gas deposits, via fracking, also involve environmental risks that can lead to additional environmental impacts. In the present case, such additional impacts include such effects as groundwater contamination and rising of gases. Detailed risk assessments can be carried out only on a site-specific basis. Furthermore, a range of key basic information, such as information about the geology and hydrogeology of the systems involved (geological systems), is lacking especially for shale gas and coal bed methane deposits.

To analyse the risks involved in exploration and exploitation of unconventional natural gas deposits, via fracking, in each case one links the intervention intensity of the planned project with the magnitude of the potential damages (cf. Chapter C7). The intervention intensity is described in terms of impact pathways and their relevance in the relevant system. The magnitude of the potential damages in exploitable groundwater, a valuable resource, depends directly on the hazard potential of the additives used, on the formation water encountered and on the composition of flowback.

Impact-pathway analysis identified five generally possible impact pathways via which fracking projects could influence valuable groundwater resources. In this regard, one must distinguish between technical impact pathways (such as failures of borehole casings) and geological impact pathways (such as faults). Where suitable data are available, technical impact pathways can be assessed via statistically determined probabilities of occurrence or failure. The information required for such assessment is largely present in the industrial sector (such as the DNV/Scandpower data on analysis of blowout probabilities). In specific cases, it may have to be purchased, however, and its transferability to other cases must be carefully reviewed. Geological impact pathways depend on the geological systems involved. They are defined primarily via the two parameters permeability and hydraulic potential. To date, relatively little reliable information has been obtained about these parameters, especially with regard to the deep geological systems of relevance in the present context.

A selection of fracking fluids from different deposit types was considered and assessed in terms of hazard potentials. The assessments revealed that a widely diverse range of additives has been used in the past in unconventional natural gas deposits in Germany. A hazard potential in connection with release into the aquatic environment must be seen for a number of such fluids, due to the fluids' classifications pursuant to the Administrative regulation on substances hazardous to water (Verwaltungsvorschrift wassergefährdender Stoffe – VwVwS) and to laws pertaining to hazardous substances. When suitable impact pathways are present, upper groundwater-bearing layers can be influenced, both at specific points and over wide areas. The assessments also indicate that even if new fracking fluids with low or no hazard potential are developed, via additional research, there will still be cause for concern that rising formation water, or formation water extracted as part of flowback, could impair near-surface groundwater resources.

Needless to say, the present assessments had to rely extensively on information and experience gained in the past (in some cases, the relatively distant past) and gained in other countries (especially the U.S.). Where use is made of such information and experience, this is noted at the relevant junctures in the text. New information and studies became available, on an ongoing basis, as the present study was being prepared. Such information and studies indicated that all aspects of fracking projects are evolving rapidly. Additional studies have been announced or are already in progress (such as US EPA 2011). With regard to such studies, special attention has to be given to the manner in which existing practice, and trends in development of relevant substances, is assessed. In addition, the relevant research activities at German and international universities, and the experience now being gained in other European countries (such as Poland), also have to be followed carefully.

Wherever possible, the current trends and developments are taken into account, especially with regard to recommendations for future actions. On the other hand, the extent to which findings of the research and industry sectors, both in Germany and abroad, are of relevance to the concrete projects at issue, and can be applied to such projects, must be reviewed in detail in each individual case.

In the following, deficits in our knowledge and understanding are described from scientific and technical perspectives, broken down according to the aspects "geological systems", "technology", "substances" and "flowback". The recommendations for action derived from this basis are then presented in Part D of the present study.

C8.1 Deficits with regard to geological systems

As expected, description of the different geological systems involved (Part A) revealed large regional differences in terms of structures, characteristics and groundwater dynamics. In most cases, much is known about the near-surface groundwater flow systems involved. The structures of such systems, and the manner in which they react to interventions, etc. are routinely understood. All projects that represent interventions (such as the construction of a well for the public drinking water supply) are intensively studied in advance (for example, through monitoring wells), monitored, and supported by the relevant authorities.

By contrast, little reliable, detailed knowledge is available, apart from just a few exceptions, about the deep, large-scale groundwater flow systems of interest in connection with exploration and exploitation of unconventional natural gas deposits. This also applies to information of fundamental importance for assessment of fracking-related interventions, such as the nature, structure and permeability of faults, the potentials and permeabilities of deep groundwater aquifers, etc.. Conceptual models can provide an idea of the structure and characteristics of such geological systems.

With regard to geological systems, the impact pathways 1 (boreholes / old boreholes), 2 (faults) and 3 (discharges/rises/spreading underground) must be considered, partly in connection with the relevant technical aspects. While long-term risks of boreholes / old boreholes with regard to seepages of gas and/or fluids in groundwater horizons or at the surface are known, they have been difficult to pinpoint statistically to date. In particular, failures of cementations and casing, after periods of decades, are seen as potential mechanisms for creation of pathways via which gases and fluids can be transported to the surface.

To assess all such impact pathways, one must carry out hydrogeological system analysis with a view to obtaining a detailed knowledge and understanding of the applicable permeabilities and pressure differences, and to interpreting them properly. To that end, one must prepare suitable conceptual models, as well as numerical models in some cases.

In each case, since such hydrogeological system analysis must consider both the large-scale groundwater flow system and the local geological and hydrogeological conditions, relevant studies must be carried out on different levels (local, regional, supra-regional). Along with regional studies, site-specific studies also play an important role.

In the present study, we find, for the great majority of relevant geological systems, a lack of the key basic data, especially data for deeper regions, that would be needed for assessment of the identified impact pathways. In summary, these include:

- Basic data with regard to geological and hydrogeological characterisation of deep underground regions (permeabilities, thicknesses and potential differences), providing a basis for development of conceptual models for gaining a basic understanding of the systems involved (including aspects such as flow pathways, flow speeds, etc.). Such information is indispensable to the tasks of assessing the impact pathways and of identifying areas with relevant permeabilities and upwardly pointing potential differences (artesian / confined groundwater aquifers).
- Numerical groundwater models (based on the conceptual models, and used in accordance with their usefulness) may be needed for quantification of the risks via certain impact pathways, and for analysis of scenarios and impacts in advance of a specific planned project.
- Knowledge of the positions, depths, nature and condition of old boreholes:
  Such information must often be gathered from a range of different stakeholders (water authorities, mining authorities, water utilities, entrepreneurs, etc.). In some cases, additional studies (such as inventories, etc.) may have to be carried out. Aspects of long-term integrity and safety are especially important in this area.
- Knowledge of the positions, depths and permeabilities of faults and fault zones:
  In addition to evaluating existing documents, one may have to carry out field studies (for example, 3D seismic studies) to obtain such information.
- Technical aspects play a central role in determination of whether hazards to exploitable groundwater resources could arise via impact pathways 1 through 3. The important aspects in this regard espe-

cially include the cementations and casing of production wells (including their long-term integrity) and factors relative to the propagation of fracture formation and to the control and monitoring of fractures. Incomplete knowledge, and uncertainties, with regard to the extent of fractures formed during fracking are important insofar as they must be taken into account in derivation of minimum distances to hydraulically active old boreholes and faults (cf. Chapter C 2).

To date, specific requirements pertaining to monitoring with regard to fracking are still lacking. This also applies to requirements pertaining to the baseline measurements (for example, with regard to the initial methane concentrations in near-surface groundwater) that would provide the basis for later evidence.

C8.2 Deficits in the area of technology

Extensive experience has been gained in the area of drilling technology, and stringent standards apply to such technology and equipment. Such standards include the Länder ordinances on deep-drilling (Tiefbohrverordnungen der Bundesländer – BVOT) and various technical guidelines and industry standards (WEG 2006). The BVOT govern procedures for setting up and operating drilling sites, including such aspects as requirements pertaining to casing dimensions and to certification of staff involved in a deep-drilling operation.

The following section lists a number of deficits in the area of technology and equipment:

- With regard, in particular, to boreholes for exploitation of unconventional natural gas deposits via hydraulic stimulation, there are no generally applicable technical standards for well casings and completion (such as end-to-end cementation, etc.). Casing dimensions and specifications for borehole cementation are determined on the basis of existing regulations, taking account of the stresses resulting from the planned / applied fracking pressures (WEG 2006). In some cases, operators apply their own safety standards in this area. No consistent, binding (national) requirements and standards are yet in place.
- There is a lack of studies of the long-term integrity of casing and cementations. The experience gained in over 30 years of tight gas extraction in Lower Saxony is of little help in this area, since no monitoring has been carried out specifically with regard to the leakproofness of cementations.

- In fracking, fracture formation is now controlled primarily through the pressure applied via the fracking fluid. Major "leaks" are detected via rapid losses of pressure, and this makes it possible to respond accordingly in the fracking process. "Creeping" losses are very difficult to detect via pressure monitoring, however.
- The extent of fractures is monitored primarily geophysically, via geophones. In the case of deep boreholes, such monitoring procedures tend to be imprecise. There are no binding requirements specifying the degree of accuracy with which the position and orientation of created fractures is to be predicted and determined.

C8.3 Deficits with regard to substances

At present, it is not possible to state, conclusively, the precise compositions of the fracking fluids that will be used in future. What is more, it is likely that fracking fluids will be modified in keeping with new findings relative to relevant deposit characteristics and with new lines of products that producers will place on the market. The assessment methods described in the present study can serve as a starting point for efforts to develop additives with lower hazard potentials.

The study authors see considerable deficits in two areas in particular:

- Disclosure of the identities of the additives used and of additive concentrations in injected fracking fluid, and
- Knowledge relative to the physical and chemical properties of fracking fluids and of their short-term and long-term behaviour in the environment.

Disclosure practice relative to additives used in Germany

In many cases, material safety data sheets for preparations are often the only source of information relative to the identities of the additives used and to the quantities in which they are used. For approval authorities and operators, this situation creates considerable uncertainties and knowledge gaps regarding the additives that are actually used and the pollutant loads involved. By way of example, we refer to the disagreement that resulted, between the service contractor and the operator involved, regarding the question of whether nonylphenol ethoxylates (NPEs, which are listed in the Chemicals Prohibition Ordinance (ChemVerbotsV)) were used in various fracks in Lower Saxony or not (cf. Part A, section A4.4). While the operator, after reviewing German-language material safety data sheets for the preparations used, concluded that NPEs were used, the service contractor indicated that it had not used nonylphenols in Europe since the 1980s and that the safety data sheet in question referred to a product with the same name that was produced by a different company and that was not used in Germany. In the view of the study authors, such uncertainties / knowledge gaps are unacceptable.

The fundamental issue in question involves a conflict between the aim of achieving disclosure, for the purpose of assessing environmental impacts, and the aim of providing justified protection for operational secrets. Consequently, a distinction must be made between disclosure of substance identities to authorities and such disclosure to the general public.

Authorities are required to protect operational secrets (Art 30 Administrative Procedures Act (VwVfG)). For this reason, entrepreneurs must disclose to authorities all information of relevance to assessment of whether the conditions for authorisation are fulfilled. Where they are unable to make such disclosure – for example, because they use products of other companies whose composition is not known to them – they must at least present complete pertinent material safety data sheets or, as in the case of biocides, show that the substances have been approved. Where such information does not suffice for the necessary assessment, it can be necessary to find ways whereby the producer of the product in question, or the state agency responsible for authorisation or registration of the product, can transmit the necessary decision-relevant information directly to the competent authority for the project, without disclosing it to the company carrying out the project (such as the services contractor). Where the necessary information cannot be provided, it may be necessary to conclude that an adverse impact on groundwater cannot be ruled out and, thus, to deny authorisation for the project.

In general, producers' interests in maintaining confidentiality with regard to other companies and to the public are to be recognised as being worthy of protection. This applies, for example, to the complete details of the composition of a preparation (cf. Art. 118 (2) EU REACH Regulation). At the same time, such interests in maintaining confidentiality must be weighed against applicable interests in achieving disclosure (cf. for example Art. 29 Administrative Procedures Act (VwVfG), Art 9 (1) Environmental Information Act (UIG) and Art. 118 (2) Sentence 2 EU REACH Regulation). And such weighing must be carried out in accordance with applicable legal standards. For example, access to environmental information relative to emissions may not be denied on the grounds of operational and business secrets (Art. 9 (1) Sentence 2 Environmental Information Act (UIG)). Furthermore, certain types of information about substances, such as information about substances' physical and chemical properties and evaluations of relevant toxicological and ecotoxicological tests, may not be considered operational or business secrets (Art. 22 (3) Chemicals Act (ChemG)).

Discussion in the U.S. regarding disclosure

Disclosure practice regarding the constituent substances in fracking fluids used has been intensively discussed in the U.S. (Soraghan 2010 in New York Times). Requirements pertaining to disclosure of fracking fluids used are currently defined at the level of U.S. states, with the result that some considerable differences apply with regard to basic requirements, the scope of the information to be provided and procedures relative to operational secrets (Murrill & Vann 2012). A total of eleven U.S. states in which natural gas is produced require some form of disclosure. Those states' requirements range from requiring publication on the publicly accessible website FracFocus (www.fracfocus.org; applies to Colorado, Pennsylvania and Texas) to requiring disclosure to state agencies (with or without subsequent publication) and to permitting voluntary provision of information by operators or service contractors. The required scope of published information varies from individual specification of each constituent substance used, with CAS number and with the maximum concentration used in fracking fluids, for each relevant borehole (applies to Colorado), to listing of additives used, with no quantity information. Some U.S. states also require submission or publication of the material safety data sheets for preparations used. Furthermore, U.S. states differ in the way they treat constituent substances that are protected as intellectual property or as operational secrets, and thus the quality of published information can differ from state to state, even in cases in which the basic disclosure requirements are similar. Differences also apply in provisions relative to disclosure in cases of incidents and medical emergencies. A detailed compilation of the current legal situation in various U.S. states is presented in Murrill & Vann (2012).

Currently, a number of relevant pieces of legislation are being moved forward in the U.S. at the federal level. In March 2011, the "Fracturing Responsibility and Awareness of Chemical Act (FRAC Act)" was introduced in the Senate and the House of Representatives. It would amend the *Safe Drinking Water Act* to repeal exemptions on certain restrictions granted to hydraulic fracturing operations and to require oil and gas companies to disclose the chemicals used in hydraulic fracturing operations (Murrill & Vann 2012). In his 2012 State of the Union Address, U.S. President Barack Obama announced that all firms that drill for natural gas on public lands would be required to publish the names of the chemicals they use in such drilling operations (cited in in Murrill & Vann 2012). In addition, the Bureau of Land Management (BLM) has drafted relevant regulations that are now in the public-comment phase.

Adoption of all such legislation in the U.S. could also improve data availability in Germany, with regard to the constituent substances of preparations used in fracking, since at least part of the preparations involved are sold worldwide.

Physical, chemical and toxicological substance data

Many of the material safety data sheets available to the study authors contain incomplete information about relevant physical, chemical and toxicological parameters. This indicates that mining authorities, in previous authorization procedures, have not required such information to be submitted and reviewed. For some additives, information is available, in specialised databases and in scientific publications, that is not included in the relevant material safety data sheets. For other additives, no data on relevant physical, chemical and toxicological parameters were found in publicly accessible databases. It is clear that a number of additives have been used in the past for which it was not possible, or possible only to a limited degree, to reliably assess behaviour and environmental impacts.

Knowledge gaps are seen with regard both to the human-toxicological and ecotoxicological properties of substances used and to substances' degradability, formation of transformation products and reactivity. In addition to the gaps in knowledge seen with regard to individual substances, critical knowledge gaps are seen with regard to assessment of preparations and fracking fluids as entire systems and in terms of their reactivity with formation water under the conditions prevailing in deposits.

C8.4 Deficits in management of flowback

As noted, flowback is a mixture of fracking fluids, formation water and possible reaction products. At present, there is a complete lack of the mass-balancing data and analyses that would make it possible to quantify the varying mixture fractions of fracking fluids and formation water, as well as the fractions of recovered fracking fluids and possible reaction products.

Little information is available about the characteristics of formation water in unconventional deposits, such as information about primary, secondary and trace components, dissolved gases, organic substances and naturally occurring radioactive materials (NORM), and virtually no breakdowns of such information by region or depth are available.

The procedures for managing flowback have not been properly defined. The environmental risks related to flowback disposal via disposal wells have not yet been considered in adequate detail. In particular, it needs to be asked (and answered) whether Germany will theoretically even have enough capacities in disposal wells, once all of its shale gas and coal bed methane fields are exploited.

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Part D: RECOMMENDATIONS FOR ACTION AND PROCEDURES

D1 Preliminary remark

The following recommendations for action and procedures are based on the results of our studies, which are described in the previous sections. In this connection, we again call attention to the most important resulting points:

According to current estimates (BGR 2012), the technologically recoverable gas reserves (assumption: 10 % of the gas in place (GIP) are technologically recoverable) present in shale gas deposits in Germany amount to about 700 to 2,300 km^3. For coal bed methane deposits, the GIP is estimated to be > 3,000 km^3 (BGR 2012, GD NRW 2011). No analysis of the technical recoverability of coal bed methane deposits in Germany has been carried out to date. Most of the hydrocarbon provinces known in Germany already contain approved or applied-for exploration fields for exploration of conventional and unconventional oil and gas deposits. To our information, no permits have yet been issued for production of natural gas from unconventional shale gas and coal bed methane reserves. Furthermore, we have not yet seen any specific planning detailing such production.

To assess the risks related to fracking, we had to rely on the extensive range of relevant literature available internationally (such as US EPA 2004, US EPA 2011, Tyndall Centre 2011) and on information provided by this country's national authorities and operating companies. Extensive experience has been gained in Germany with fracking in tight gas deposits (primarily in Lower Saxony). Nonetheless, according to the information available to us, no systematic study has been conducted of the substances used in such operations – covering such aspects as substance types, quantities, behaviour and final locations – nor has any focused, systematic monitoring of the relevant environmental impacts been carried out.

Unconventional gas deposits are parts of larger geological systems, and such systems differ in terms of their geology and hydrogeology. As a result, exploration methods and production strategies have to be locally specific. And such methods and strategies have to be assessed specifically, using suitably differentiated perspectives, in terms of their environmental impacts and risks. The differences, as described in Part A, between the various geological and hydrogeological parameters of the unconventional natural gas deposits known or presumed to be present in Germany could make it necessary to use a differentiated approach in authorisation and execution of projects for development of tight-gas, shale-gas and coal-bed-methane deposits.

With regard to techniques used, the key fracking-specific aspects to consider include specifications for site layout and design (single well or clusters of wells); the manner in which fracture propagation is modelled, controlled and monitored; and the long-term integrity of wells (cementation and casing).

A broad range of different chemical additives have been used to date in fracking fluids, some of them with properties that present concerns from human-toxicological and ecotoxicological perspectives. An assessment of three fluids that have been used in Germany, in various types of deposits, found that the fluids had high, or medium-to-high, hazard potentials. In addition, two improved fracking fluids that operators brought to our attention must also be expected to have high hazard potential, primarily because of their high concentrations of a biocide and the spottiness of the available data for assessing that biocide. Current relevant development work aimed, inter alia, at reducing the number of additives used, at finding substitutes for highly toxic, carcinogenic, mutagenic or reprotoxic substances and at reducing or replacing biocidal agents, points to potential progress in development of environmentally compatible fracking fluids. The report authors cannot evaluate the feasibility or progress of such efforts at present, however. In our view, the observation that the hazard potentials of fracking fluids could possibly be reduced via dilution with saline groundwater, along underground flow pathways, does little to reduce such concerns, since formation water can have significant hazard potential of its own.

The flowback recovered following the fracking process consists of fracking fluid and formation water and can include reaction products. Flowback can present significant risks. In our view, the common practice – common also in Germany – of disposing of flowback by injecting it into "suitable permeable layers" underground can also present hazards for groundwater and the environment.

In combination with relevant technical and geological impact pathways, the hazard potentials of the substances involved can create environmental risks. We have found that geological systems, of which there are various types, can contain several such impact pathways. No reliable data are currently available that would provide a basis for reliably ruling out risks to near-surface water resources. What is more, because of the sketchiness of the available data, the relevant tools and methods available at present (such as numerical groundwater models) can yield only rough estimates.

In our view, a great many pieces of basic information are lacking that would be needed for any well-founded assessment of the pertinent risks and the degree to which they can be controlled by technical means. Examples of such information include information regarding the structures and properties of deep geological systems (permeabilities, potential differences), the identities of the fracking additives used and the chemical and toxicological properties of such additives. There are several reasons for this lack of information and data: (a) the information and data are not (openly) accessible, (b) the information and data have not yet been evaluated, and/or (c) there are gaps in our knowledge that can be closed only through additional studies and research.

Mining law and water law establish legal requirements that apply to fracking projects, with regard to groundwater protection. Under water law, fracking projects and flowback injection have to be reviewed with a view to determining whether any risks of adverse impacts on groundwater can be ruled out. Such review must be carried out in the form of an approval procedure under water law. Because the EIA Directive takes precedence over the German EIA ordinance for the mining sector (UVP-V Bergbau), all fracking projects are already subject to the requirement that preliminary review must be carried out, in each individual case, to determine if an EIA is required. Enforcement to date in this area exhibits shortcomings. Regulatory deficits are found in implementation of requirements under the EIA Directive, and in the uncertainties seen in application of water law (definition of "groundwater", applicability of permit requirements, fulfilment of permit requirements).

We expressly note that stimulation in connection with development of deep geothermal reservoirs was not considered in the present context, and that thus our recommendations cannot be directly applied to techniques for geothermal stimulation.

D2 Overarching recommendations

In light of the current situation as described, and on the basis of our assessments, we have developed the following overarching recommendations:

(2.1) The risks of projects for exploration and exploitation of unconventional gas deposits can be reliably analysed only insofar as reliable information on the relevant geological systems (and potential impact pathways) is available, along with information about the characteristics of the formations in which the pertinent gas deposits are found. We thus recommend that exploration of gas deposits be combined with exploration of the relevant geological systems, in order to place the resulting site-specific information in a larger, regional context. In our view, mining authorities and gas companies should routinely consult with each other regarding the issue of what information is required. The information should be largely publicly accessible, in order to enhance public acceptance. In our view, in each case the authorities and gas companies should communicate clear information regarding the geological systems involved, the gas deposits involved and the planned exploration strategies (including their potential impacts).

(2.2) We recommend that the many relevant data that are available and that have not yet been evaluated (cadastre of old boreholes, cadastre of disposal wells, etc.) be evaluated and that the results be published. Pertinent experience should also be so evaluated and published. At the same time, we maintain that without new data it will not be possible to answer the questions of whether, and where, economically exploitable unconventional gas deposits are present in Germany and of what technology (with or without fracking) could be used to develop them. We thus can support the idea of carrying out further exploration, including exploration involving deep drilling (but without fracking), and carrying out targeted research in the above-described framework, for the purpose of answering those questions.

(2.3) We recommend that further actions be taken step-by-step: Clear criteria should be established for deciding whether or not fracking should be allowed, at a later time, in wells. Such criteria should cover both the risk potential of fracking additives and the availability of reliable information about the geological and technical impact pathways involved. As a matter of course, both exploration and any later production should be subject to clear criteria for approval. A catalogue of criteria for approval should be developed step-by-step. In this area as well, we recommend that transparent approaches be applied, possibly approaches involving the interested public.

(2.4) In light of the sketchiness of the currently available data, and of the fact that environmental risks cannot be ruled out, the report authors recommend, from the standpoint of water-resources management, that above-ground and below-ground activities for unconventional gas production not be approved, for exploration and production companies that use fracking, in water protection areas (classes I through III), in water-extraction areas for the public drinking water supply (even if not set aside as water-protection areas), in mineral spa protection zones and near mineral water deposits, and that the aforementioned areas be made off-limits for such activities. As better data become available, this recommendation on denial of approval should be reviewed. In areas known to have unfavourable – with regard to potential environmental impacts – geological and hydrogeological conditions (groundwater potentials and pathways), no unconventional gas exploration and production (via deep-drilling and fracking) should be carried out.

(2.5) We recommend that research and development be intensified in areas such as enhancement of the long-term integrity of wells; improvement of techniques for forecasting the widths and lengths of fractures caused by fracking; and development of fracking fluids with lower hazard potential. Practical application of the relevant research findings should be monitored scientifically.

(2.6) Site-specific risk analyses should be carried out with regard to any future drilling with fracking, and to drilling and use of disposal wells for injection of flowback. Such analyses should take account of all relevant substances, whether introduced or encountered (fracking additives, formation water and its reaction products, and flowback), and of the relevant geological (and technical) impact pathways. In addition, risk analysis involving both overarching and site-specific approaches should be carried out. We recommend that use of human-toxicologically and ecotoxicologically unsafe fluids, and flowback disposal in disposal wells – and even such use and disposal in tight gas deposits in Germany that have already exploited for many years – be reassessed.

(2.7) With regard to EIA obligations, we recommend that fracking projects be subject to general federal EIA obligations, and that such obligations include an "opening clause" to allow Länder participation. The public participation required under EIA legislation should be expanded to include a project-monitoring component, since many findings regarding projects' potential environmental impacts cannot be obtained until the projects are actually underway. Careful review of requirements under water law should be assured, via clarification of pertinent requirements, and via a) introduction of an integrated project-approval procedure to be directed by an environmental authority subordinate to the Ministry for the Environment, or b) integration of mining authorities within the environmental administration.

(2.8) In our view, the following two aspects are of central importance with regard to any continuation of exploration and exploitation of unconventional gas deposits in Germany, regardless of the procedures applied: all work processes and results should be fully transparent, and all stakeholders should exercise trust in their dealings with each other. Efforts to further these aims should include the establishment of a publicly accessible cadastre listing all fracking measures carried out, along with the quantities of fluids used and the compositions of the fluids used. To our knowledge, such a database is currently being prepared, in Lower Saxony, with the participation of Lower Saxony's state office for mining, energy and geology (Niedersächsisches Landesamt für Bergbau, Energie und Geologie – LBEG) and of the Wirtschaftsverband Erdöl- und Erdgasgewinnung (WEG) German oil and gas industry association. The report authors were unable to view that database by the time the present report was completed, however.

(2.9) In our view, it would be useful to carry out a comparative analysis of the studies/reports carried out / prepared to date in Germany, with regard to the risks of exploration and exploitation of unconventional gas deposits, in order to identify the areas in which the studies/reports agree, and the areas in which they differ, with a view to finding strategies for resolving the latter. In addition to the present study, such comparative analysis should especially cover the studies undertaken as part of the information and dialogue process initiated by ExxonMobil and the study prepared under commission to the state (Land) of North Rhine – Westphalia (ahu AG et al. 2012). Furthermore, the comparative analysis should also cover, if possible, any available (interim) results of the study announced by the U.S. EPA (US EPA 2011).

Special recommendations

In the following sections, we have developed special recommendations with regard to further steps relative to the issue of unconventional gas production in Germany. The focus of the recommendations is on the next phase of sample exploration, especially exploration in geological systems for which no information, or very little information, is yet available about the unconventional gas deposits they may contain. The objectives of our recommendations include:

- Closing gaps in knowledge (Chapters D2 through D5),
- Identifying hydrogeologically problematic areas, and possible impact pathways, at an early stage, and proposing measures for ongoing monitoring (Chapter D2),
- Making pertinent drilling and handling techniques safer (Chapter D3),
- Reducing the hazard potential of the substances used, or making it possible to assess such hazard potential (Chapter D4), and
- Suitably shaping and structuring legal and organisational procedures in this area (Chapter D5).

D3 Special recommendations with regard to the area environment / geological systems

The cause-and-effect relationships between deep-reaching and near-surface groundwater flow systems are of particular importance with regard to the water-related environmental impacts of unconventional gas production projects (impacts on people, flora and fauna). To properly assess such water-related risks, and even to quantify them, one must have a detailed understanding of the hydrogeological systems involved.

The remarks made in Part A regarding various selected deposits illustrate the degree to which geological and hydrogeological parameters can vary from site to site. In many cases, the information required for such analyses can be obtained only through consultation of many different sources. The information has to be compiled and studied, and then assessed from an overarching perspective. Such efforts should include the following main steps:

(3.1) Conceptual hydrogeological models should be prepared that support reliable risk analysis for all potential impact pathways. The scope of such conceptual models should be large enough to support assessment of the impacts of exploration and exploitation of unconventional gas deposits – via fracking – both for the specific sites involved and with regard to the large geological systems involved.

(3.2) For areas in which water-related environmental impacts cannot be ruled out (as shown by risk analysis), numerical groundwater-flow models should be prepared/refined with which the pertinent risks can be quantified. As a rule, this will entail preparing a regional-level model that can then serve as a basis for local models within and around the actual gas-production area.

(3.3) Normally, the work mentioned under (3.1) and (3.2) will necessitate additional evaluations and terrain studies (system-oriented exploration).

(3.4) The aforementioned models have to be continually verified and calibrated on the basis of data and information obtained through monitoring (both preliminary and during the project).

The models resulting from the aforementioned work steps provide an important basis for competent authorities' decisions regarding the general authorisability of submitted projects and design and structuring of ancillary provisions (under water law) for specific projects.

(3.5) The necessary regional and local models must be prepared by the relevant mining companies, in the framework of authorisation procedures under mining law and water law, and in keeping with the requirements imposed by the competent mining and water authorities. In the current early phase of use of fracking technology, however, the competent mining and water authorities should first develop the requirements applying to such models. And such development should be carried out step-by-step. In our view, a fracking project may be approved only when enough pertinent knowledge has been gained, and adequate precautions have been taken, to make it possible to rule out the possibility of an adverse impact on groundwater.

Requirements pertaining to conceptual hydrogeological models

In preparation for, or along with, exploration in a particular area, a large-scale conceptual hydrogeological model of the area should be prepared.

Information on the procedures to be used in preparing a conceptual hydrogeological model (hydrogeological system description) can be found in the relevant technical literature (inter alia). The main steps in preparing a conceptual model include:

- Collection of all available information about the relevant regional (i.e. extending beyond the bounds of specific area in question) geological and hydrogeological conditions (depositional sequences, lithology, faults, permeabilities, groundwater flow systems, hydrochemical characteristics, etc.);
- Analysis of the structure-forming geological and hydrogeological processes involved;
- Analysis of the significant anthropogenic influences and their impacts on the hydrogeological system, including forecasting of the expected further development (drainage, groundwater removal, old mines, use of deep geothermal energy, other planned or existing deep underground uses, etc.);
- Any further studies needed for the preparation of a conceptual model (for example, in the framework of exploration carried out by the company behind the project).

The resulting data have to be compiled, evaluated and interpreted. Such a conceptual model is based on working hypotheses that must continually be reviewed, and improved as possible, in light of available data, conclusions/findings by analogy, etc.. And this process must always make use of available local expertise and know-how (geological services, water associations, water utilities, mining companies, etc.).

Requirements pertaining to numerical regional and local groundwater-flow models

Regional models

For the present purpose, regional models must represent groundwater flow three-dimensionally and dynamically (i.e. in its time dependence). In such a regional model, the gaseous phase can be represented, with sufficient accuracy, via a calculation of partially saturated groundwater flow. The impacts of substance discharges, substance releases and transport processes, and their large-scale relevance, can be determined via local modelling of fluid dynamics resulting from exploration and exploitation of unconventional gas deposits. This must also include modelling of the hydrogeochemical interactions involved. The requirements include:

- Basic representation of the large-scale groundwater flow systems involved, including groundwater-replenishment and groundwater-infiltration areas (such as Münsterland Basin, Molasse Basin),
- Description of the basic interactions between groundwater aquifers,
- Estimation of the relevant flow speeds and groundwater-flow quantities,
- Determination of parameters for local site models.

Local models

Local models can be developed on the basis of the regional model. In the preparatory phase prior to exploitation measures, models of typical sites and typical drilling-site layouts can provide basic information relative to the local impacts of exploratory measures (including exploration for gas). It may be necessary to prepare a special site model for each exploration site. In such cases, the site model supports the entire project. It is continually updated with data gained in the exploration phase. The requirements include:

- Systematic analysis of a project's impacts on water resources, throughout all operational phases: Potential distributions and flow quantities, sizes of underground catchment areas, summed effects of neighbouring fracks and well pads;
- Representation of rock formations' barrier functions;
- Representation and assessment of pathways leading from the system into the biosphere;
- Determination of the impacts of singular permeabilities (old boreholes and faults);
- Representation of sensitive material parameters and systemic influences;
- Development of key information relative to further system exploration and monitoring.

Requirements pertaining to system exploration and monitoring

The following phases must be differentiated, taking account of the above remarks:

- Required system exploration: Collection of data and information in the framework of system-oriented exploration, and for the development of conceptual and numerical models
- Monitoring: Monitoring of the impacts of activities in connection with exploration and exploitation of unconventional natural gas deposits (during preparations for the project, and during the project itself).

Required system exploration

The aims result from the requirements pertaining to hydrogeological system analysis and to development of conceptual and numerical models. In contrast to monitoring per se, system exploration takes place prior to any decision on use of fracking for exploration and exploitation of unconventional natural gas deposits. The key elements of such system-oriented exploration include a comprehensive inventory of the current situation (for example, with respect to the gas and substance concentrations in near-surface groundwater).

Routine monitoring

As it is understood by the study authors, routine monitoring has the primary purpose of guiding activities relative to previously defined objectives (such as ensuring that fracking does not impair drinking water resources).

In general, monitoring includes the following elements:

- Objectives, achievement of objectives, and information requirements
  → The information requirements, which are determined on the basis of the objectives, guide the monitoring process. Monitoring must always be designed in accordance with such information requirements (strategy, monitoring network, parameters, indicators, evaluation methods, etc.).
- Monitoring strategy and indicators
  Overarching strategy, covering all environmental media and based on an understanding of the relevant system, for detecting system-relevant parameters and changes, in light of meaningful indicators.
  → Clear detection and assessment of the processes involved.
- Assessment system
  → Logical, fast and clear communication of relevant developments and assessments (such as a "traffic-light" system).
- Options for action, and control
  → Proven, defined actions for controlling undesired developments.

For monitoring to be effective, it must be based on an adequate understanding of the system involved (see above). At the same time, the understanding of the system involved (conceptual or numerical model) can be improved with the help of data obtained via monitoring.

Monitoring-based project control requires meaningful indicators (derived directly from measurements and/or calculations) for which an evaluation system is available. Ultimately, options must be available for stopping, limiting or reversing any undesired developments, to ensure that no damage occurs and that risks do not increase.

Once the above-mentioned core elements have been defined, the remaining elements of the monitoring system can be developed. Such elements especially include the monitoring network(s), the scope of data collection and the methods used to derive indicators and structures for communication and decision-making.

D4 Special recommendations with regard to the area of equipment / techniques

The current key regulations applying, in Germany, to drilling equipment and techniques for developing conventional gas resources, and for developing unconventional gas deposits, result from the provisions of the Federal Mining Act (BBergG) and its secondary legislation – such as the ordinance on deep-drilling (Mining ordinance on deep-drilling, underground storage areas and on resources extraction via wells (Bergverordnung für Tiefbohrungen, Untergrundspeicher und für die Gewinnung von Bodenschätzen durch Bohrungen – BVOT); the ordinance can differ slightly from Land (state) to Land) – and from other relevant environmental provisions found in the permits for such operations.

This legal framework also contains numerous different implementation provisions that may be applied by gas-production companies.

Companies choose exploration and production strategies on an individual-case basis, in keeping with the equipment and techniques to be used, with the specific geological and hydrogeological characteristics of the site's deposits and, not least, with their own experience in developing the deposits in question (companies' internal standards).

(4.1) Approval authorities should apply implementation provisions consistently and logically (and, in each individual case, in keeping with the prevailing geological and technical parameters).

(4.2) The international drilling standards established in the gas-production sector (API standards, guidelines of the Wirtschaftsverband Erdöl- und Erdgasgewinnung (WEG) German oil and gas industry association, etc.) are technically adequate in terms of the current state of the art in drilling technology. Nonetheless, efforts should be made to reconcile operators' own internal safety standards, which in some cases are quite stringent, and to mandate a binding overall safety level. Inter-Länder coordination of such efforts should be sought.

(4.3) In order to enhance safety, particular attention should be given to ensuring compliance with applicable guidelines for boreholes and casings, and to ensuring that casings are fully cemented. In addition, – and this is also in keeping with standard practice – we recommend that completed wells be inspected and checked for pressure-tightness in light of the fracking pressures expected in them.

(4.4) The existing requirements applying to the leaktightness of cementations should be reviewed, and further detailed if necessary, in light of the specific requirements applying to fracking. Such review should also include suitable studies and monitoring procedures for ensuring the long-term integrity of wells (casing and cementations).

(4.5) For cases involving hydraulic stimulation, we recommend that fracture propagation be monitored via suitable procedures (cf. Chapter C2). Here as well, suitable standards and minimum requirements need to be agreed on by all Länder.

(4.6) Recommendations for action in the area of flowback treatment and disposal are described in Chapter D5.

D5 Special recommendations with regard to the area of substances

Assessment of selected fracking fluids used in unconventional deposits in Germany, along with the available information on the characteristics of flowback, have revealed that injected fluids, and fluids requiring disposal, can pose considerable risks. In light of the gaps in knowledge, uncertainties and data deficits identified via the research and assessment for the study, the following recommendations for action are seen as important:

(5.1) Complete disclosure of all substances used, with regard to substance identities and quantities.

(5.2) Assessment of the human-toxicological and ecotoxicological hazard potentials of substances used, and provision, by the applicant, of all physical, chemical and toxicological substance data required for that purpose. If relevant substance data are lacking, the gaps in the data must be eliminated – if necessary, via suitable laboratory tests or model calculations. In the process, the effects of relevant substance mixtures must be taken into account.

(5.3) Substitution of unsafe substances (especially substances that are highly toxic, carcinogenic, mutagenic or reprotoxic [CMR substances]), reduction or substitution of biocides, reduction of the numbers of additives used, lowering of concentrations used.

(5.4) Determination and assessment of the characteristics of site-specific formation water, with regard to ingredients of relevance to drinking-water quality (salts, heavy metals, Naturally Occurring Radioactive Material – NORM, hydrocarbons).

(5.5) Determination and assessment of the characteristics of site-specific flowback, with regard to ingredients of relevance to drinking-water quality (salts, heavy metals, NORM, hydrocarbons), and with regard to additives used (primary substances) and their transformation products (secondary substances); determination and assessment of the proportion of fracking fluids extracted with flowback.

(5.6) Determination of the behaviour and final locations of substances in underground regions at the site, via mass-balancing of the additives used.

- Quantities of primary substances used
- Substances, and concentrations (after mixing with water) of primary and secondary substances in the fracking fluid
- Discharges and behaviour of primary and secondary substances following underground injection

- Substances, and concentrations (after mixing with formation water) of primary and secondary substances underground
- Quantification of sorption, transformation and degradation processes underground
- Quantification of permanent deposition of fracking additives in underground formations.
- Long-term behaviour and transport of substances in local and regional groundwater systems
- Substances, and concentrations of primary and secondary substances, in flowback
- If applicable, substances and loads disposed of via underground injection
- If applicable, substances and loads following technical treatment

(5.7) Modelling of substance transport, for assessment of possible risks to groundwater, within any exploitable aquifer, from any rising formation water and fracking fluids.

- Compliance with de minimis thresholds, or with human-toxicological and ecotoxicological effect thresholds, at the assessment site – for example, at the base of the exploitable groundwater aquifer

(5.8) Technical treatment and "environmentally compatible" flowback disposal

- Description of the technically feasible treatment processes
- Description of the possibilities for re-using substances
- In cases involving injection into underground regions, site-specific risk analysis, and description of the impacts on water resources that accumulate spatially and over time.

(5.9) Monitoring (cf. also Chapter D2)

- Installation of near-surface groundwater monitoring stations to determine the reference condition with regard to additives and methane
- If appropriate, installation of deep groundwater monitoring stations to determine the characteristics of formation water and the relevant hydraulic potentials

D6 Special recommendations with regard to the area of legislation / administration

In Part B of the present study, the applicable legal framework was analyzed in detail with regard to deficits. That analysis is based on the working hypothesis that existing basic concerns about adverse impacts on groundwater could be eliminated in the framework of required authorisation procedures – at least for a significant number of sites and projects, and, if necessary, after issue of specifications relative to technical implementation and to monitoring of environmental impacts. In sum, the following specific recommendations for action have resulted:

(6.1) Already under currently applicable laws, preliminary, individual-case review of fracking projects must be carried out to determine whether an environmental impact assessment is required. This results from the direct applicability of the EU EIA Directive. The German EIA ordinance for the mining sector (UVP-V Bergbau), and mining authorities' existing practice, based on that ordinance, of not requiring a preliminary review of EIA requirements, do not conform to requirements pertaining to implementation of that directive as specified by the European Court of Justice.

(6.2) The EIA Directive must be properly transposed. To that end, EIA obligations should be introduced from which only minor cases would be exempted. At the same time, the Länder should be empowered to determine, for all or parts of their territories, that EIAs for certain types of projects (to be determined), are required only if so indicated by the results of a general or site-specific preliminary review of EIA requirements, or may be waived if such results lie below certain thresholds (to be determined). In the short term, EIA obligations should be established via amendment of the German EIA ordinance for the mining sector (UVP-V Bergbau). In the medium term, they should be established via amendment of the Environmental Impact Assessment Act (UVPG), with integration of provisions on EIA obligations for mining projects in the list in Annex 1 of the Environmental Impact Assessment Act.

(6.3) The decision on whether an EIA is required, in a given case, should be made by the mining authority, in keeping with the pertinent assessment by environmental authorities, if the mining authority is not also the environmental authority and is subject to the detailed supervision of the highest environmental authority. This assignment of responsibilities should be defined at the federal level.

(6.4) Both a) establishment and operation of drilling sites intended to be used later for fracking, and b) establishment and operation of self-contained drilling sites with injection wells for flowback, should automatically be deemed projects subject to EIA obligations. And EIA obligations should apply even to set-up and operation of drilling sites with a single well. And they should apply to all wells drilled and operated from a single drilling site. Furthermore, as necessary in keeping with the relevant company's project concept, they should also apply to set-up and operation of drilling sites linked as part of a single project. Injection wells intended solely as ancillary facilities for a unified fracking project should also be subject, as parts of the project, to EIA obligations.

(6.5) Where EIA obligations apply, EIA requirements dictate that public participation is required. For fracking projects, public participation should be expanded to include ongoing participation during the project, to ensure that the public is informed about whether, and to what extent, the assumptions are confirmed, in the course of further site exploration, that were made in the EIA carried out prior to the setting-up of the drilling site (for example, assumptions regarding the lack of any faults), and to enable the public to ensure that the competent authority addresses new risks properly as they emerge. To that end, the possibility should be provided of establishing monitoring groups modelled after the "Asse-II Monitoring Group" (Asse-II-Begleitgruppe; focussing on radioactive waste stored in the Asse II former salt mine), such groups would include representatives of municipalities and municipal organisations, of environmental groups and of citizens' initiatives, and would engage in ongoing dialogue with the relevant mining company and mining authority in each case. In addition, it should be ensured that renewed authorisation and EIA obligations, following preliminary review in individual cases, arise both through project changes that can have significant environmental impacts and through adverse changes in key parameters (such as new findings) significant to assessment of a project's environmental impacts.

(6.6) With regard to the definition of "groundwater", which determines the scope of application of water law, it should be clarified that water in deep geological formations is groundwater within the meaning of the Federal Water Resources Management Act (WHG), regardless of the depth at which it occurs, regardless of any hydraulic connections to near-surface groundwater and regardless of its quality. Such clarification is required especially with regard to the issue of salt content, because mining authorities sometimes deem water law to be inapplicable when water salt-content levels justify classification as brine.

(6.7) At the same time, it should be clarified that an adverse effect on deep groundwater may be deemed present only for water that qualifies for human uses or that is part of the biosphere's natural systems. "Water that qualifies for human uses" should refer not only to uses that are cost-effective at present, but also to possible uses under changed framework conditions. The de minimis thresholds used to evaluate whether an adverse impact on near-surface groundwater has occurred thus cannot be used, in the same way, for assessment of changes in deep groundwater.

(6.8) In any case, for fracking boreholes and wells for flowback injection, review, under water law, should be carried out with regard to casing and cementation, as well as with regard to discharges of substances in connection with fracking and with injection.

(6.9) Preferably, such review under water law should be carried out in the framework of an integrated project-approval procedure, and should have a concentration effect relative to water law. In addition, it should be carried out under the direction of an environmental authority subordinate to the Ministry of the Environment. For introduction of such procedures, the Federal Mining Act would have to be amended. As long as applicable laws have not yet been suitably amended, it should be clarified that review with regard to water law must be carried out within an approval procedure under water law, in agreement with the water authority.

(6.10.) The conditions for a permit under water law should be defined via general standards for required preliminary exploration, for the design of technical components, for knowledge of the systems involved and for monitoring of impacts on groundwater. Where such standards cannot be derived at an abstract regulatory level, due to a lack of relevant knowledge, they should be developed, via a coordinated process, in the framework of pending individual authorisation procedures.

(6.11) An integrated project-approval procedure should also be required by law for facilities for treatment of flowback, and for pipelines for transport of flowback, where the project-approval procedure for the relevant drilling site does not automatically extend to such facilities. As long as such a project-approval procedure is not required by law, it should be ensured that conformance with requirements under wastewater law is reviewed within the relevant procedure under mining law, if no separate approval procedure under wastewater law is carried out.

(6.12) In general, drilling and operation of fracking and injection wells should be prohibited within water-protection zones and mineral spa protection zones. At the same time, it should be possible, in individual cases, and in connection with overriding reasons of the public interest, to issue an exemption if a procedure with environmental impact assessment and public participation has been carried out. If it becomes clear that fracking technology is to be used on a large scale, as a precautionary measure, all fracking projects and projects for flowback injection within a certain radius (to be defined) of a protected area should be made subject to a constraint on approval, in keeping with all available findings at that time, via amendment of the relevant protected-area ordinances or via individual-case decisions.

(6.13) In accordance with a step-by-step procedure, water-law permits for pending fracking projects should be issued first for relatively low-impact projects, in areas of relatively low sensitivity, and such permits should be tied to comparatively stringent requirements relative to preliminary study, technical design and ongoing monitoring, as long as concerns regarding adverse impacts on groundwater cannot be eliminated for other projects or in other areas. While requirements applied to approved projects should primarily have the purpose of eliminating concerns regarding projects' adverse impacts on groundwater, they should also be evaluated as a basis for assessing comparable future projects.

(6.14) In accordance with a step-by-step procedure, water-law permits for specific fracking projects should be structured, via suitable provisions and ancillary provisions, so as to ensure that measures about which concerns regarding adverse impacts on groundwater cannot immediately be eliminated are approved only if assessment of the execution and monitoring of authorisable, safe measures (such as measures with lower pressures, of shorter durations, or with lower pollutant concentrations or quantities) has shown that measures with potentially greater impacts also give no cause for concern.

(6.15) In the framework of management discretion under water law, the (provisional) denial of a permit under water law may be justified if relevant concerns falling into the "boundary area" between concerns that would automatically lead to denial of a permit and the remaining residual risks cannot be eliminated, in light of the most recent relevant findings. In this "boundary area", management discretion allows weighing of the economic interest in development of unconventional gas deposits against the economic interest in assuring the drinking water supply. In this framework, it may also be taken into account whether, and to what extent, the gas supply is assured via imports. That criterion may only be considered, however, if in a relevant concrete case a residual risk for the drinking water supply indeed cannot be ruled out. In this framework, if findings from ongoing (pilot) projects could, in the foreseeable future, provide a better basis for assessment, the potential relevance of such findings may also be taken into account, and a decision made on whether the permit decision should thus be postponed until then. Where approval for exploration and production projects is to be denied for reasons other than considerations related to water-resources management, or if such approval is initially to be limited to just a few test or demonstration projects, the possibility of amending the Federal Mining Act should be considered (for example, for introduction of management discretion under mining law).

(6.16) As long as no integrated project-approval procedure has been defined by law, the authorisation procedure under water law, and the operational-plan procedure under mining law, could be completely coordinated, in the manner used for parallel authorisation procedures for industrial facilities. Operational-plan approvals for relevant measures subject to permit requirements under water law – specifically, drilling wells and furnishing them with casings; fracking; and flowback injection – should not be issued until it is clear, from the status of the relevant procedures under water law, that there is no cause for concern regarding adverse impacts on groundwater and thus a permit under water law may be issued.

(6.17) For purposes of review under water law, a project's required application documents must include a detailed description of the project (specific technical design, full disclosure of the substances to be used, description of the relevant operational procedures and of the boundaries of the operations to be authorised). The permit issued for a project must specifically define the content of the approved measure. For that purpose, it does not suffice simply to refer to general legal requirements or to general provisions of technical regulations, without including a precise description of the specifically approved measures.

(6.18) While legal provisions, or secondary legislation, are not absolutely necessary for implementation of most of these recommendations for action, such provisions and legislation are useful. They can be implemented, without regulatory overhead, in the framework of applicable laws, via suitable implementation by the competent mining and water authorities. We recommend at least that these matters be regulated via directives of the highest water authorities (Länder environment ministries), ideally in cooperation with the highest mining authorities (usually the ministries of economics of the Länder – in Baden-Württemberg and Hesse, they are also the environment ministries). In the medium term, requirements pertaining to fracking projects should be defined via an integrated procedure under mining law and water law. This should be achieved via supplementation of the mining ordinances on deep-drilling, underground storage areas and on resources extraction via wells (Bergverordnungen für Tiefbohrungen, Untergrundspeicher und für die Gewinnung von Bodenschätzen durch Bohrungen – BVOT), to provide for relevant water-law regulations at the Länder level, or via introduction of an integrated BVOT at the federal level.

(6.19) For the legislation level, we recommend that safety requirements under mining law be integrated within environmental law, in an approach similar to that used in the 1970s in integrating legislation on authorisation of industrial plants within environmental protection legislation, in order to assure effective, efficient environmental protection.

(6.20) With regard to responsibilities, we recommend that, overall, approval and monitoring of mining projects, under environmental and safety legislation, be sited in keeping with the approach used in integration of trade oversight within environmental administration – i.e. be assigned to the portfolio of environment ministries, in order to assure effective, efficient environmental protection and to functionally and organisationally separate business-promoting tasks of economic ministries from efforts to foster trust in authorities' oversight, which trust is an indispensable basis for public acceptance of fracking projects. As long as responsibilities have not been so assigned, mining authorities should take all important environmentally relevant decisions in keeping with decisions of the primarily responsible environmental authorities, except in cases – as in North Rhine – Westphalia – in which they are themselves environmental authorities and as such are subject to the instructional authority of the environment ministry.

D7 References

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