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Analysis of chemical constituents and additives in hydraulic fracturing waters

1. Technical review and proposal for a non-target approach

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1. Cover, B. Gawlik, UHC Gas pumping station in Pennsylvania, 2014, Source: private collection
2. Page 4, M. Wilkins, Overview Hydraulic fracturing process, 2016, Source: Ohio State University

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Abstract

This technical report is addressing the issue of chemical constituents and additives used in hydraulic fracturing and their occurrence in wastewaters resulting from hydraulic fracturing operation in the exploration and exploitation of unconventional hydrocarbons. Specific focus is on the types of chemical constituents disclosed as used in hydraulic fracturing fluids by well operators and found in flowback, produced waters and potentially exposed ground and surface water.

It gives an overview on typical approaches followed for baseline and or operational monitoring of water quality. With regard to organic constituents it addresses the typically examined compounds and investigates to which extent non-targeted approaches for water monitoring with accurate mass spectrometry can be used to fill existing knowledge gaps.

The concept of a feasibility study for a improved baseline/operational assessment of water quality prior to the start or during and after hydraulic fracturing operations is proposed too.

1 Introduction

1.1 The Principle of the Hydraulic Fracturing Process

Hydraulic fracturing is a gas and oil well stimulation technique introduced on commercial basis on the 1950s with the scope to access alternative sources for hydrocarbons. It is also commonly and informally known as "hydrofracking, fracking, fracing, or hydrofracturing".

The process causes the fracturing of rocks by use of a pressurized liquid, the so-called fracking fluid (Figure 1). This fluid is composed primarily of water and sand or other proppants as well as thickening agents. The pressurised injection into the wellbore creates cracks in the rock formations containing the oil or gas of interest. Through these cracks and after removal of the hydraulic pressure stimulation natural gas or petroleum are released. The proppants used ensure that the fractures remain open. The technique is of particular interest to exploit amongst others shale gas, tight gas or coal bed methane.

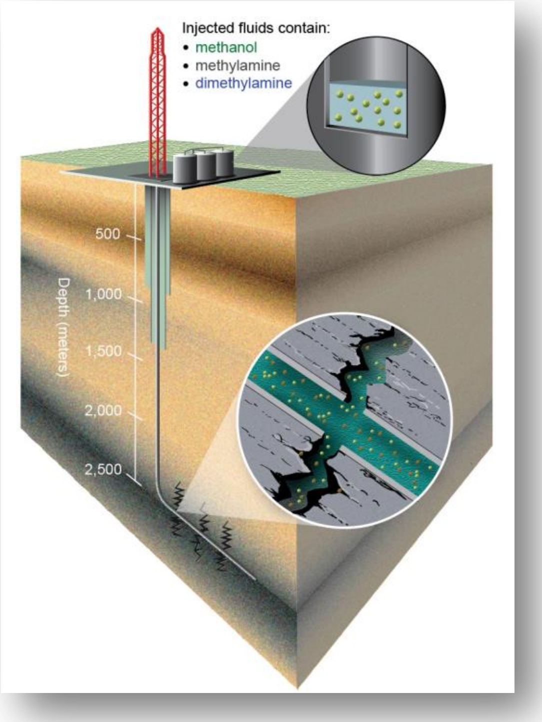

Figure 1 – Cross-section of the hydraulic fracturing process.
Credit: Michael Wilkins, courtesy of The Ohio State University.

1.2 The water dimension

Many of the environmental concerns in the discussion on the use of hydraulic fracturing are related to water, both in terms of quantity and quality and knowledge gaps exist in particular with regard to the European specificity. Water quality is affected by natural processes and anthropogenic activities within a watershed, and oil and gas development and production operations at the surface and below ground can affect water quality. Other risks include below-ground activities, such as drilling prior to casing installation, leaks during or following hydraulic fracturing, failed casing seals, pipeline breaks, abandoned wells, etc.

This needs to be monitored in order to assess the potential threats to ground and surface water supplies pertinent to the fracturing sites, but also to define the necessary baseline as a reference for a proper environmental assessment.

Indeed, as stated in the *Commission Recommendation of 22 January 2014*[1] *on minimum principles for the exploration and production of hydrocarbons (such as shale gas) using high-volume hydraulic fracturing (2014/70/EU)*, Member States are invited to ensure the determination of environmental status (baseline) of the installation site and its surroundings surface and underground area potentially affected by fracking activities.

Baseline determination should define, *inter alia*, "quality and flow characteristics of surface and ground waters".

In addition, oil and gas formations themselves often contain significant amounts of water that come up with the petroleum or gas: this is referred to as produced water. Such produced waters contain dissolved trace minerals from their formations of origin and maybe hence also be a source of naturally occurring radioactive materials.

1.3 The chemical dimension

1.3.1 Europe

Although used only in smaller amount compared to water, chemicals serve several functions in hydraulic fracturing: from limiting the growth of bacteria to preventing corrosion of the well casing. The fracking fluid itself generally contains 99% water, 0.5 of a proppant (sand or silica) and 0.5% of chemical additives (Barcelo & Bennet, 2016) although this varies from site to site. These additives are typically corrosion inhibitors, biocides, breaker, clay and shale stabilization reagent, friction reducer and surfactants.

The number of chemical additives used in a typical fracture treatment depends on the conditions of the specific well being fractured, but is also the result of intense R&D.

A typical fracture treatment will use very low concentrations of between 3 and 12 additive chemicals, depending on the characteristics of the water and the shale formation being fractured.

Each component serves a specific, engineered purpose and different concentration of the same component may exert different functions.

For example, the predominant fluids currently being used for fracture treatments in the gas shale plays are water-based fracturing fluids mixed with friction reducing additives (called slickwater). The addition of friction reducers allows fracturing fluids and sand, or other solid materials called proppants, to be pumped to the target zone at a higher rate and reduced pressure than if water alone was used.

In addition to friction reducers, other additives include: biocides to prevent microorganism growth and to reduce biofouling of the fractures; oxygen scavengers and other stabilizers to prevent corrosion of metal pipes; and acids that are used to remove drilling mud damage within the near wellbore area.

Fluids are used to create the fractures in the formation and to carry a propping agent (typically silica sand) which is deposited in the induced fractures to keep them from closing up[2].

Based on the available literature on chemical composition of fluid in hydraulic fracturing operations, the most prominent knowledge gap is the missing full disclosure of all chemicals and their used amounts. Tracing the fate of individual chemicals and chemical

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[1] Commission Recommendation of 22 January 20141 on minimum principles for the exploration and production of hydrocarbons (such as shale gas) using high-volume hydraulic fracturing (2014/70/EU): http://ec.europa.eu/environment/integration/energy/unconventional_en.htm

[2] Source: www.fracfocus.org (last visited: 14/03/2017)

mixtures used in hydraulic fracturing operations is necessary from injection to production and water treatment.

The full disclosure of the applied chemicals also is prerequisite for a knowledge-based decision about the necessary water treatment and possible ways of disposal for the amounts of flowback and produced waters.

Moreover, if spills, leakages or other accidents happen where fracturing fluids or flowback and produced waters are released to the environment (e.g. soil, surface and groundwater) also information on the chemical composition is necessary for proper treatment and remediation. With full disclosure of chemicals it will be possible to elucidate suitable chemical tracers of the applied fracturing fluids in order to address possible contamination issues. Full disclosure of the chemicals should not be limited to CAS numbers but should also provide the IUPAC name, which is essential for further research (Elsner et al., 2015). (Andrea Vieth-Hillebrand, 2015)

Several initiatives encouraged the disclosure of the composition of the hydraulic fracturing fluids used.

In Europe, the International Association of Oil and Gas Producers (OGP) supported the on-line voluntary disclosure of chemical additives used in hydraulic fracturing of shale gas exploration wells from 2011 onwards. It has developed a website[3] where companies operating in EU can disclose the chemicals used in their shale gas exploration wells..

In Poland, where, according to the data of Ministry of the Environment, by April 2016, a total of 72 exploratory wells were drilled, the Polish Exploration and Production Industry Organisation (i.e.: OPPPW) encouraged the disclosure of the composition of hydraulic fracturing fluids through a website dedicated section fed on voluntary basis. However, OPPW decided to stop its activities; their website is therefore no longer updated.

The chemicals used in hydraulic fracturing fluids of 13 different shale gas exploration wells have been published on the NGS website and summarised in the following table

Table 1 Most frequently used chemicals in hydraulic fracturing operations of shale gas exploration wells in Poland (n=13)

(data from ngsfacts.org, last visited 10/05/2017).

Chemical compound	Number of disclosures
Ethyleneglycol	13
Hydrochlorid acid	13
Methanol	12
Silicate material (quartz)	11
Prop-2-yn-1-ol	8
Aliphatic alcohols (ethoxylated)	8
5-chlor-2-methyl-2H-isothiazol-3-one and 2-methyl-2H-isothiazol-3-one	6
Propan-2-ol	6
Boric acid	5
Formic acid	5
Guar gum	5
Heavy aromatic naphtha	5

Beside this, BNK petroleum reported the additives used during hydraulic fracturing of the Saponis Lebork S-1 Ordovician stimulation to be butyl diclycol (foaming agent, 0.02 %),

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[3] www.ngsfacts.org

cholinium chloride (clay control, 0.07%) and polyethylene glycol monohexyl ether (emulsifier, 0.007%) (bnk petroleum, 2015).

The most frequently used natural polymer is guar and its derivates (50% of chemical additives), other used additives are crosslinkers (boron, titanium and zirconium compounds), buffers (hydrofluoric acid, ammonium bisulfate), biocides, stabilizers (sodium chloride, ethylene glycol, calcium chloride, isopropanol, methanol), surfactants (amines, glycol ethers, (nonyl-)phenol ethoxylates), viscosity breakers (lithium hypochlorite, ammonium persulfate, calcium peroxide), clay control (acids, phosphonates, polyglycol) and gelling agents (cellulose, guar) (OPPPW 2015).

In the United Kingdom only one shale gas well has been hydraulically fractured until now, i.e.: Preese Hall 1 well in the Bowland shale. According to information from the company Cuadrilla, fracturing fluid consisted of fresh water (about 8400 m^3), sand (463 m^3), polyacrylamide emulsion in hydrocarbon oil (3.7 m^3) as friction reducer and sodium salt as chemical tracer. No addition of biocide was necessary as the water was treated by the supplier before (Cuadrilla 2015).

In Germany, hydraulic fracturing is in operation for the exploitation of tight gas reservoirs in the deep sandstone of Lower Saxony since the 1980s (Gordalla et al., 2013). The chemical additives used by ExxonMobil in different HF operations in Germany have been published online (ExxonMobil 2015a). About 150 substances with different chemicals could be identified, 119 of them were specified by CAS numbers (Gordalla et al., 2013). The only HF in shale was performed in well Damme3 in 2008, the composition of the fracturing fluid is presented in table 2.

Table 2 Constituents of fracturing fluid at well Damme3 in Germany

(data from Gordalla et al., 2013).

Function	Chemical Compound	CAS-No	Employed mass (kg)
Base fluid	water	7732-18-5	12095000
proppant	proppant	66402-68-4	588000
biocide	“Kathon”® 5-chlor-2-methyl-2H-isothiazol-3-one; 2-methyl-2H-isothiazol-3-one (3:1)	55965-84-9	46
Stabilizing component of biocide	Magnesium chloride	7786-30-3	23
Stabilizing component of biocide	Magnesium nitrate	10377-60-3	46
Component of biocide	n.a.	n.a.	345
Clay stabiliser	Tetramethylammonium chloride	75-57-0	6367
Component of clay stabiliser	n.a.	n.a.	4245
Friction reducer	Polyethylene glycol-octylphenyl ether	9036-19-5	440
Friction reducer	Hydrotreated light petroleum	64742-47-8	2640

Function	Chemical Compound	CAS-No	Employed mass (kg)
	distillates		
Component of friction reducer	n.a.	n.a.	1760
Component of crosslinker	Inorganic salts, n.a.	n.a.	103

Here, it is surprising to see that there is no chemical disclosure for 4 out of 10 additives and these 4 not-disclosed additives represent 40% by mass of all chemical additives. With respect to possible future HF operations, the application of chemicals may be limited to biocide (ethylenedioxy-dimethanol), clay stabilizer (choline chloride), surfactant (polyethylene glycol monohexyl ether), friction reducer (2-butoxy-ethoxy-ethanol), or thickener (carbohydrate polymer derivative) (Gordalla et al., 2013). ExxonMobil provided a public statement that future fracturing fluids will only consist of water, proppant and only 2 chemical additives (clay stabilizer choline chloride and friction reducer butoxyethoxyethanol) (ExxonMobil 2015b).

1.3.2 USA

In the US, EPA published in 2015 a report based on the analyses of data from more than 39,000 FracFocus disclosures provided to the U.S. Environmental Agency (EPA) by the GWPC in March 2013. FracFocus is a publicly accessible website (www.fracfocus.org) where oil and gas production well operators can disclose information about the ingredients used in hydraulic fracturing fluids at individual wells in the US. The report identified ca. 700 different chemicals being used.

However, as in Europe, this assessment does not consider impurities of industrial-grade chemicals. In addition, there was no systematic assessment of the chemical baseline in groundwater and surface water prior to hydraulic fracturing activities in the US.

The composition of initial fracturing fluids is also reflected in flowback and produced waters, being these latter the results of possible interactions between the fracturing fluid itself and the shale system over time and at the in situ conditions. To date, most publications on composition of flowback and produced water deal with samples from the Marcellus shale gas exploitation and only few publications exist from other shale gas sites in the US, Canada or Europe.

2 Geo-chemical baseline assessment

In the current section, references to on-going Horizon 2020 projects facing the issue of geo-chemical baseline assessment are reported. Furthermore, a selection of peer-reviewed scientific papers is reported.

The rapid development of natural gas from the Marcellus shale has raised considerable concern in the scientific community and the public regarding possible accidental contamination of surface and groundwater resulting from such activities. In this context, the establishment of a local baseline prior to the start of drilling operations is key to a sound scientific assessment. While in Europe, this is facilitated by the implementation of the provisions under the Water Framework Directive 2000/60/EC and the Groundwater Directive 2006/118/EC and Recommendation 2014/70/EU, a common methodology on how to assess such a baseline still needs to be developed.

This geo-chemical assessment looks mainly at variations of the inorganic profile of groundwater samples and tries to connect this to particular patterns in flowback/produced waters in areas during UHC exploitation. The challenges here are in particular regarding the identification of naturally occurring variations due to the spatial heterogeneity, the understanding of naturally occurring temporal variations and the induced changes due to UHC activities.

2.1 On-going Horizon 2020 projects

Several Horizon 2020 Projects are on-going at European level with the main aim to develop science-based best practice recommendations for minimising the environmental footprint of the shale gas exploration and exploitation in Europe.

Hereafter, references to the activities regarding the geochemical assessment are summarised for M4SHALEGAS Project, the Sheer Project and for FrackRisk Project.

In the framework of the M4SHALEGAS Project (Measuring Monitoring, Mitigating, Managing the Environmetal Impact of Shale Gas) a review on the geochemical species to monitor well leakage during shale exploitation has been recently published (Bruno Garcia, 2017). The review considers that geochemical species are present and must be identified:

- in the shale formation itself,
- in aquifers around this shale formation, and also
- in the fracturing fluid injected for the process.

The review concludes that:

- concerning the deep aquifers, the main geochemical species to monitor are the hydrocarbon's species from C1 in case of gas phase to C30 corresponding to relative soluble hydrocarbon's species.
- H_2S is one of non-hydrocarbon specie which is important to monitor too at this location, to be sure that there is no risk of H_2S contamination.
- Finally, organic compounds used in base fluid have to be monitor too in deep aquifers, to put in evidence if the fracturing process is efficient avoiding deep aquifers contamination.
- Concerning the sub-surface aquifers, the same geochemical species have to be monitored too.

The Sheer (Shale gas Exploration and Exploitation induced Risks) project (http://www.sheerproject.eu, Last visited 05/05/2017) aims, inter alia, to monitor and analyse water quality before, during and after hydraulic fracturing operations at a test site on Wysin site in Pomerania, Poland. Water samples are collected in dedicated sampling containers and are stored in chilled conditions during transportation to the lab for analyses. Duplicate samples and blanks are collected on a regular basis for quality assurance purpose.
To date, inorganic analysis showed low levels of the following chemical species:

- Arsenic
- Barium
- Chromium
- Fluoride
- Manganese
- Nickel

With the exception of manganese, these are all present in minor quantities and do not cause any concern for drinking water quality. Manganese levels resulted to be variably 2-3 times higher than the statutory EU drinking water standard of 50 µg/l.

The FrackRisk project (http://www.fracrisk.eu) aims to correlate contaminants with sources either in the shale mineralogy or within the chemical additives used in the fracturing process, through the creation of an unique batch reaction cells capable to imitate the reservoir conditions during hydraulic fracturing, with the aim of replicating the geochemistry flowback and produced waters generated by these operations.

2.2 Peer reviewed scientific literature

In 2014, Brantley *et al.* published the at that time situation with regard to water resource impacts during UHC developments in Pennsylvania. The authors reviewed information on ca. 1000 complaints received by the state authorities in the period of 2008-2012. While no cases of sub-surface transport of fracking or flowbacks fluids was identified in this paper, most problems related to brine salt components and natural gas. The authors complain about lack of access to transparent and accessible data to better assess impacts. The study identified the following main reasons for this situation:

- Lack of information about location and timing of recorded incidents
- Non-release of incident specific water quality data due to liability and confidentiality agreements
- Sparseness of sample and sensor data for analytes of concern
- Pre-existence of water impairments
- Malfunctioning of sensors

Rhodes and Horton (2015) describe in their paper the outcome of a 2.5 year long study of 35 private drinking water well in Susquehanna County, in the Marcellus Shale gas region. 150 samples were collected from these sites and analysed for their inorganic geochemical profile. The aim of the study was to separate influences such as road run off from the natural geochemical background prior to UHC exploitation. The study concluded that overall groundwater chemistry varies more spatially in the study site than temporally at single sites. Heterogeneity of minerals in the bedrock aquifer and varying inputs to road salt run off from paved roads were identified as main reasons. The study identified some elements being more characteristic for grasping contamination by flowback fluid chemistry, i.e. Ba, Br, Ca, Cl, Mg, Na and Sr. These indicators featured generally also a much less variability at local sites.

Hildenbrand *et al.* (2016) performed a similar, yet less conclusive study in the Permian Basin of Texas over a period of 13 months and using 42 private water wells. LeDoux *et al.* (2016) reported results on 59 groundwater samples in the Central Appalachian Basin.

Pancras *et al.* (2015) described a similar approach using ICP-OES for the assessment of surface water samples in Western Pensylvania. Upon evaluation of 53 emission lines from 30 elements, the elements B, Ca, K, Li, Mg, Na and Sr were identified as potential tracers for the sources impacting public drinking water supply systems. The authors recommended using conductivity of samples to be inferior to 10 mS/cm, which can be achieved by gravimetric dilution prior to ICP-OES measurements.

Farag and Harper (2014) reviewed in particular the influence of the salt content in the large volumes of flowback and produced waters on aquatic wildlife. While much attention has been paid on the regulation of chloride contents, the knowledge of impact of hardness and accompanying factors is still limited. The authors postulate inter alia to better investigate the ionoregulatory upset with associated enzyme level changes in target species.

Wilke and co-workers (2015) reported findings of leaching tests and tests on induced mobility from black shales in Germany.

Another inorganic parameter of high concern are the elevated concentration of bromide in brines generated from oil and natural gas production, which may reach levels of up to 1 g/L (Sun *et al.*, 2013).

Shrestha *et al.* (2017) reviewed the water resource impacts of hydraulic fracturing in the Bakken Shale due to deterministic, i.e. freshwater withdrawal and produced water management, as well as due to probalistitic, i.e. spills due to leaking pipelines and truck accidents, events. The authors conclude on the importance of the need of a detailed investigation of hydrology and hydrogeology as well as water chemistry using the recently developed geochemical and isotopic tracers (e.g. $^{87}Sr/^{86}Sr$) to confirm or refute the evidence of water resource contamination due to UHC in North Dakota. The same table provides also an overview on major chemistry, isotopic rations and trace metal contents of produced water and flowback water in Bakken and compares it to information regarding nearby groundwater.

Zhang *et al.* (2016) investigated the water chemistry of 119 samples of collected of 4 years from 47 coal-bed methane exploitation sites in Southern China. They concluded on a similarity between coproduced water chemical signature compared to other coal seam waters around the world. The same inorganic parameters were studied than in other comparable studies namely Ca^{2+}, Mg^{2+}, K^{+}+Na^{+}, Cl^{-}, SO_4^{2-}, HCO_3^{-}, CO_3^{2-}. The samples were characterised by sodium-chloride-bicarbonate waters depleted in calcium and magnesium ions and exhibiting reduced sulphate concentrations.

Olsson *et al.* (2013) addressed the impact of this high salinity as regards necessary treatment options prior to flowback treatment and disposal in a German perspective. The study investigated the situation in three test sites in Lower Saxony in Germany and identified an increase of chloride concentrations up to the saturation limit.

With the aim to enable a conceptual feasibility study concerning treatment strategies suitable for use in Germany, the study examined available different methods and measures for flow-back from hydraulic fracturing treatment and disposal, concluding that no single technology revealed to be adequate to meet suitable effluent characteristics.

The authors argued further that there is a need for further research and investigations as regards the degree of success and economic efficiency of the respective wastewater treatment. The flowback evaluation was based on 17 inorganic quality parameters. Esmaeilirad *et al.* (2015), too, investigated impact on different treatment processes on produced water.

Appropriate treatment technology would also enable to use alternative water resources such as brackish water thus reducing the freshwater consumption (Esmaeilirad *et al.*, 2016).

Generally, the interest of reuse of flowback and produced water is high, but requires a thorough understanding of the water including its temporal variability (Kim *et al.*, 2016). Closing the water cycle loop in this industry depends critically on the wastewater treatment prior to reuse. Rosenblum *et al.* (2016) illustrated the potential of metal salts such as ferric chloride to remove turbidity and total petroleum hydrocarbons. Lester (2015) proposed a suite of analytical tools to anlyze both the inorganic and organic chemical composition of an oil/gas well flowback water from the Denver-Julesberg basin in Colorado. Subsequently, they translated the data to respective necessary treatment solutions aiming at reuse of the treated water. Ziemkiewicz and He (2015) published data on water chemistry of a case study in West Virginia. Special attention was paid to make-up water, flowbacks and HF fluid composition.

Nelson and co-workers (2015) identified another challenge to be addressed with the rapid rate of expansion of UHC exploitation in some areas of the US, i.e. the monitoring of naturally occurring radioactive materials (NORM) and the alteration of concentrations in a pre- and post fracture settings. Although their pilot-study in vicinity of 131 gas wells did not reveal statistically significant difference in the monitored radionuclide concentrations of uranium, lead-210 and polonium-210, they called for more systematic monitoring with special emphasis of private drinking wells.

Due to the known issue of elevated NORM-concentrations in North Sea oil and gas production, Garner *et al.* (2015) investigated NORM profiles in the East Midlands', UK. They confirmed the presence of radium-containing scales and sludges from two conventional oil-producing sites in the East Midlands, with samples exceeding national exemption levels of NORM. The team concluded that should unconventional exploitation of shale gas reserves from the same formations take place, the use of aggressive reagents at elevated temperatures and pressures may present an even more acute NORM management issue.

He *et al.* (2016) proposes the use of abandoned mine drainage (AMD) to be used in a co-treatment process to control NORM content in flowback water in the Marcellus Shale. The study describes that 99% of radium present in flowback water can be incorporated in form of barite and the resulting product can be used as weighting agent in drilling fluids.

3 Occurrence of organic constituents in hydraulic fracturing waters

In the next sections, a collection of literature citations on analytical studies addressing the issue of chemical ingredients in hydraulic fracturing fluids, in flowback and produced water as well as in pertinent surface and groundwaters is reported with the aim to summarising the present knowledge and define the background scenario in which the proposed JRC sampling campaign would fit.

3.1 Hydraulic fracturing fluids and flowback waters

Lester *et al.* (2015) summarised information on volatile and semi-volatile organic compounds identified in flowback water samples prior to its treatment for reuse. Ziemkiewicz and He (2015) compared make-up water concentrations, with HF fluid composition and the flowback water in a case study in the Marcellus Shale.

In their review Ferrer and Thurman (2015a) listed the broad mix of chemical constituents presentin fracking fluids and/or in both flowback and produced waters associated with the process of hydraulic fracturing. They also described a range of different analytical techniques used to analytically characterise such mixtures. The authors in particular underlined the unexploited potential of liquid chromatography-mass spectrometry for such purposes.
Both continue (Ferrer & Thurman, 2015b) to illustrate how liquid chromatography coupled with quadrupole time-of-flight mass spectrometry can be used for the elemental composition identification of individual compounds whereas triple quadrupole methods using tandem mass spectrometry can be used to accurately follow and monitor these compounds in associated waters form hydraulic fracturing operations.

3.2 Produced waters

Orem *et al.* (2014) were among the first addressing the issue of unknown constituents in produced and formation water from UHC exploitation using a combination of target and non-target analytical approach. They identified the known organic compound classes such as polycyclic aromatic hydrocarbons, various heterocyclic compounds, alkyl phenols, aromatic amines, alkyl aromatics, long-chain fatty acids and obviously aliphatic hydrocarbons with concentration ranging from <1 µg/L to 100 µg/L. In addition, the authors reported extremely high levels of TOC (5500 mg/L) and a range of chemicals including solvents, biocides, scale inhibitors and other organic chemicals to levels of 1000s of µg/L. The authors concluded that although the environmental impacts of the organics in produced wastewater is not sufficiently defined, their results raised concern about the environmental toxicity of the substances. They also underlined the necessity to improve databases and libraries needed for the proper identification of numerous unidentified substances stemming from the non-target approach.

Akob *et el.* (2015) published some data on produced water from 13 wells in Pennsylvania reporting VOCs in only 4 of the 13 samples in a range from 1 to 11.7 µg/L. . The team of Khan *et al.* (2016) identified 1400 compounds using high-resolution solid phase micro extraction gas chromatography time-of-flight mass spectrometry. The paper presented also 3D van Krevelen and DBE diagrams used to evaluate molecular variability. Schymanski and co-worker (2015) addressed the use of non-target screening with high-resolution mass spectrometry in a collaborative trial demonstrating the principle feasibility to compare such data from different origins. Although the test was conducted on surface water, a substantial degree of data homogeneity could be demonstrated, thus rendering the technique interesting for the baseline assessment in this context.

3.3 Pertinent surface and groundwaters

Gordolla and co-workers published in 2013 a paper discussing the toxicological dimension of hydraulic fracturing for groundwater and drinking water resources in Germany.
The study deals with the human-toxicological assessment of the substances used and mobilised in the process, especially with regard to a possible influence on groundwater quality. Contamination of groundwater by ingredients of fracking fluids may occur from under-ground or may results from above ground accidents associated with the transport, storage and handling of hazardous substances used as additives for fracking fluids.
Considering that the degree of groundwater contamination cannot be predicted in a general sense, the authors considered the concentration of ingredients, classified as hazardous, in fracking fluids by regarding the dilutions necessary to meet limit values for drinking water.
For doing this, three selected fracking fluids were considered. The authors concluded that the concentration of various ingredients in the selected fluids would be below the limit values of the European Drinking Water Directive, the WHO Guideline Value for Drinking water-Quality and other health-based guide values if a dilution factor 1:10,000 up to 1:100,000 time would be applied.

In order to better understand the composition of dissolved organic compounds as well as the main controls on their mobilisation from natural organic matter, Zhu *et al.* (2015) extracted black shales and coals from five different locations using deionized water. The results, however, are less useful to understand the possible risks of transfer to groundwater or eventually impacts on surface water quality by flowback.

Manz and co-workers (2016) published first findings on adsorption of two hydraulic fracturing fluid ingredients, i.e. 2-butoxyethanol (2-BE, a surfactant) and furfural (used as biocide) onto shale rock material, with the aim of understanding the potential for chemical constituents to migrate to shale formation from hydraulic fracturing operation and of evaluating their potential to cause groundwater contamination.

The authors evaluated if considered chemicals could be adsorbed onto Granular Activated Carbon (i.e.: GAC, a method for removing organics and toxic metal compounds, widely used by hydraulic fracturing companies) and how they may compete for adsorption sites to better understand the interaction between these chemicals and the shale. From experimental evidences the authors concluded that:

- GAC may be used to adsorb 2-BE and furfural;
- the chemicals compete for adsorption sites, differently;
- neither 2-BE nor furfural adsorb to the shale rock, implying that these chemicals may be able to migrate through shale formations and into water resources.

Quast *et al.* (2016) investigated the occurrences and levels of tertiary-butyl alcohol (TBA) to elucidate whether UHC exploitation was source of TBA occurrences in shallow water wells. Reported TBA data were significantly below s conservative risk-based drinking water screening levels of 8000 µg/L.

The non-target approach seems from this clearly being an emerging path to generate the missing data as described e.g. by Yost *et al.* (2017) or similar studies on impact on water resources, e.g. as outlined by Vandecasteele and co-workers (2015).

4 The challenge of baseline assessments

Considering the existing knowledge gap and lack of information regarding the identification, occurrence and concentrations of many compounds used in hydraulic fracturing operations, a new approach for tackling the analytical challenge in baseline assessment is needed. The digitalisation of what can be called a "chemical fingerprinting" using a non-targeted approach employing accurate mass spectrometry either linked gas or liquid chromatography seems to be the most promising way forward.

Non-target screening methods with accurate mass determination consider all components detected in a sample, where no prior information is available. The reason accurate mass seems to be favoured in the field of hydraulic fracturing water characterisation is the fact that unknown chemical components can be identified, even without authentic standards when using MS-MS analysis. This is highly important given the difficulty of obtaining standards of chemical addittives use din hydraulic fracturing fluids.

To this end, JRC intends to perform a pilot exploratory analytical campaign aimed at feasibility demonstration of monitoring surveys in order to identify a chemical finger-printing of waters resulting from hydraulic fracturing operations.

The chemical finger-printing will be useful for the control of quality/identification of possible contamination of the ground and surface waters, but also for flowback and produced water characterisation in the EU. Both, non-target screening and contaminant-specific screening approaches will be used for the feasibility study. This is necessary to intercalibrate the non-targeted analytical approach.

The activity will support the identification and detection of native constituents and help to better distinguish them from chemical additives and impurities thereof.

4.1 Execution of pilot campaign

To perform the sampling operations, an in-house developed device for water sampling – the so-called MARIANI-Box, which has been used already successfully in other monitoring exercises, will be used. The device will be used at participating sampling stations with the aim of collecting of:

- flowback water samples: considering the differences in composition between flowback waters and original hydraulic fluids used in the fracking operation, changes in fingerprinting compared to well operator's disclosure will be carefully taken into consideration, being possibly due to both on-going interactions with the formation and/or to other sources of contamination. Collected data will serve as basic information for the further evaluation.
- produced water samples: their analysis will account for the contamination by chemical ingredients used in hydraulic fluids and the contamination due to the interaction of hydraulic fluid and shale formation.
- pertinent surface and groundwater samples.

The JRC sampling device is a cheap, portable and versatile tool which allows the on-site solid phase extraction of water samples using a polymeric phase disk for easier transport and storage.

An ad-hoc training and troubleshooting session will be provided to participating stations' personnel in order to guarantee the correct sample collection and reliability of analytical data. JRC internal pick-up service will be activated in order to collect samples at JRC facilities for future analysis.

4.2 Analytical determinations

Samples will be analysed for the following multiple objectives:

- identification of chemical ingredients used in the hydraulic fracturing fluids in collected pertinent waters, by using advanced mass spectrometric techniques able to perform scan analysis for compounds identification (i.e.: GC-MS-Ion Trap, LC-MS/MS). The results of these analyses will be compared to well operator's disclosure, if available, in order to verify their consistency as well as to highlight the possible presence of other chemicals.
- characterisation of collected water samples (i.e.: their nature will be subject to the state of the operation at the enrolled site) and evaluation of any possible relation in the propagation of chemical contamination;
- selection of chemical pollutants to be used as tracers of possible contamination;
- development of a contaminant-specific screening approach (multi-residual GC and LC-MS methods) for the accurate quantification of chemicals previously selected as tracers of possible contamination and its application in the pertinent matrix.
- analysis and characterisation of pertinent environmental surface and/or groundwaters, according to the state of hydraulic fracturing operations and evaluation of the possible impact of hydraulic fracking operations on water quality

According to participants' availability and to the status of operations in the selected fracking site, the aforementioned samples will be asked and collected using the JRC in-house sampling device.

The ideal case for the pilot study execution should be the following:

- surface and groundwater monitoring before the start of fracking activities;
- analysis of frac fluid, produced water and flowback water, upon kind provision by well operator, and following comparison to operator's disclosure on fluid chemical composition;
- identification of trigger chemicals that can be used as tracers of possible contamination;
- analysis of relevant surface and groundwater samples to identify any possible contamination issue.

4.3 Chemical constituents

A tentative list of chemicals has been compiled considering the relevant literature matched by searching the following key-words:

- Unconventional hydrocarbon;
- Hydraulic fracturing;
- Chemicals;
- Waters.

The list appears as follows:

<u>Additives of fracking fluids</u>

- Biocides used to prevent bacteria growth in water: glutaraldehyde, 2-2-dibromo,3-nitropropionamide (DBNPA), quaternary ammonium compounds (dodecyl dimethyl ammonium chloride, alkyl dimethyl benzyl ammonium chloride, etc.)
- Surfactants used to increase the viscosity of the fracking fluid: lauryl sulfate, etc.
- Corrosion inhibitors use to prevent corrosion of the pipe: amines, amides and amino-amides.
- Scale inhibitors used to prevent the formation of scale (mineral) in the pipe: carboxylic acid and acrylic acid polymers.

Native constituents from the geologic formation

Hydrocarbons migrated into the formation waters during the fracking process:

- Polycyclic aromatic hydrocarbons (PAH)
- heterocyclic compounds
- phenols
- long chain fatty acid
- alkyl benzenes
- aliphatic hydrocarbons.

4.4 Next steps and perspectives

Based on the aforementioned data gaps and considering the layout described a first pilot exercise is envisaged on at least one test site, during 2017, which can be a shale gas, tight gas or coal bed methane exploration or extraction site in the EU, . This pilot aims at assessing the feasibility of a non-target approach of monitoring water quality, addressing different types of waters resulting from hydraulic fracturing, with special focus on flowback, produced water and eventually exposed surface and groundwaters.

The participating operator will be contacted by JRC for his formal enrolment in the pilot study and a confidentiality agreement will be signed for the disclosure and dissemination of results obtained.

According to the state of activities in the selected site, an ad-hoc sampling program will be discussed and proposed in order to enable the collection of water samples suitable for the application of both non-target and contaminant-specific analytical methods.

The participating operator will be provided with the JRC in-house developed sampling device for sample collection and personnel involved in sampling activity will be opportunely trained for its use.

In case of special needs, JRC personnel will be available on-site for technical support.

The duration of sampling activity and type of samples to be collected will be defined once the enrolment phase will be concluded.

The main output of the entire activity will be the evaluation of the suitability of the proposed non-target approach for the characterisation of water samples resulting in the fracturing process. Furthermore, it will also give the chance to identify target markers of possible contamination for which a contaminant specific screening method will also be developed.

Pertinent surface and groundwater samples will be collected as well, if possible; they will serve for the application of the developed contaminant-specific screening method and for comparison with applicable standards and rules.

The developed sampling and analytical procedures together with the analytical results will be reported in a final technical document.

The report will include the final dataset and the technical evaluation of both the proposed sampling campaign design and the technology used.

Conclusive operative suggestions on suitable methodological approaches for monitoring water quality near unconventional oil and gas exploration and production sites will be included as well for their possible future implementation and use at EU level.

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List of abbreviations and definitions

3D	three dimensional
AMD	abandoned mine drainage
cm	centimetre
DBE	double bond equivalence (plots)
DBNPA	2-2-dibromo,3-nitropropionamide
EC	European Commission
EPA	Environment Protection Agency
et al.	et alii (lat: and others)
EU	European Union
GC	gas chromatography
GWPC	Groundwater Protection Council
HR	high resolution
ICP	inductively coupled plasma
IUPAC	International Union of Pure and Applied Chemistry
JRC	Joint Research Centre
LC	liquid chromatography
mS	milliSiemens
MS	mass spectrometry
NORM	naturally occurring radioactive material
OES	optical emission spectrometry
PAH	poly aromatic hydrocarbon
R&D	research and development
TBA	tertiary butyl alcohol
TOC	total organic carbon
UHC	unconventional hydrocarbons
US	United States of America

Throughout this report chemical nomenclature rules of IUPAC are applied.

Flowback water: commonly defined as the water that is released within the initial two weeks following the completion of the HF process (Abualfaraj et al., 2014).

Produced water, however, is the naturally occurring water within the shale formation (Stringfellow et al., 2014).

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