



Project Acronym and Title:
**M4ShaleGas - Measuring, monitoring, mitigating and managing the
environmental impact of shale gas**

HANDLING FRACKING FLUIDS AND FLOWBACK FOR SHALE GAS

Authors and affiliation:
Ole Stig Jacobsen, Peter Gravesen
Geological Survey of Denmark and Greenland

E-mail of lead author:
osj@geus.dk

D8.2
Status: definitive

Disclaimer

This report is part of a project that has received funding by the *European Union's Horizon 2020 research and innovation programme* under grant agreement number 640715.

The content of this report reflects only the authors' view. The *Innovation and Networks Executive Agency (INEA)* is not responsible for any use that may be made of the information it contains.



Public introduction

M4ShaleGas stands for *Measuring, monitoring, mitigating and managing the environmental impact of shale gas* and is funded by the *European Union's Horizon 2020 Research and Innovation Programme*. The main goal of the M4ShaleGas project is to study and evaluate potential risks and impacts of shale gas exploration and exploitation. The focus lies on four main areas of potential impact: the subsurface, the surface, the atmosphere, and social impacts.

The European Commission's Energy Roadmap 2050 identifies gas as a critical fuel for the transformation of the energy system in the direction of lower CO₂ emissions and more renewable energy. Shale gas may contribute to this transformation.

Shale gas is – by definition – a natural gas found trapped in shale, a fine grained sedimentary rock composed of mud. There are several concerns related to shale gas exploration and production, many of them being associated with hydraulic fracturing operations that are performed to stimulate gas flow in the shales. Potential risks and concerns include for example the fate of chemical compounds in the used hydraulic fracturing and drilling fluids and their potential impact on shallow ground water. The fracturing process may also induce small magnitude earthquakes. There is also an ongoing debate on greenhouse gas emissions of shale gas (CO₂ and methane) and its energy efficiency compared to other energy sources. There is a strong need for a better European knowledge base on shale gas operations and their environmental impacts particularly, if shale gas shall play a role in Europe's energy mix in the coming decennia. M4ShaleGas' main goal is to build such a knowledge base, including an inventory of best practices that minimise risks and impacts of shale gas exploration and production in Europe, as well as best practices for public engagement.

The M4ShaleGas project is carried out by 18 European research institutions and is coordinated by TNO-Netherlands Organization for Applied Scientific Research.

Executive Report Summary

This report provides a summary of the knowledge that is in the North American shale gas area concerning environmental effects of handling chemicals, drill cuttings, drilling mud, flowback on the wellpad and transport to and from. Furthermore, a review of the different ways to dispose of, treatment or recycle flowback water. This whole technical area is under constant revision and development. Hence, there will be a need for a continuous updating of the knowledge and practice used in shale gas wells. Some of the methods that have been used in North America will probably not be able to be transformed to the EU area due to a more restrictive legislation.



TABLE OF CONTENTS

	Page
1 INTRODUCTION	3
1.1 Context of M4ShaleGas	3
1.2 Study objectives for this report.....	4
1.3 Aims of this report.....	4
2 OVERVIEW.....	5
3 TRANSPORT TO AND HANDLING AT THE DRILL SITE	7
3.1 Drilling mud	7
3.1.1 Chemicals in drilling mud	7
3.2 Fracking fluid	8
3.2.1 Chemicals in fracking fluids.....	8
3.3 Substances used in fracturing fluid products in the US and EU.....	9
4 FRACKING.....	11
4.1 Water use	11
4.2 Pipeline leaks.....	11
4.3 Well blowouts.....	12
4.4 Wastes from the drilling process	12
4.5 Leaks from Pits and Impoundments	13
5 FLOWBACK.....	14
5.1 Flowback water	14
5.2 Temporal changes in flowback water composition	14
5.3 The total dissolved solids (TDS)	15
5.4 Inorganic components.....	16
5.5 Organic components	16
5.6 Radioactive components.....	17
6 WASTEWATER MANAGEMENT	18
6.1 Treatment of wastewater	19
6.2 Overall wastewater treatment	19
6.3 Treatment in existing wastewater treatment plants	19
6.4 Industrial wastewater plants	20
7 WATER REUSE	22
7.1 Wastewater treatment	23
8 MANAGEMENT OF LIQUID RESIDUALS	24
9 OTHER DISCHARGE.....	25
10 UNDERGROUND INJECTION.....	26
11 ONSITE TREATMENT - NEW APPLICATIONS.....	28
12 SOLID WASTE AND RESIDUALS.....	29
13 POTENTIAL EFFECTS OF CONTAMINATED SOILS	31
14 FINAL REMARKS	32



15	CONCLUSIONS	34
16	REFERENCES	36



1 INTRODUCTION

1.1 Context of M4ShaleGas

Shale gas source rocks are widely distributed around the world and many countries have now started to investigate their shale gas potential. Some argue that shale gas has already proved to be a game changer in the U.S. energy market (EIA 2015¹). The European Commission's Energy Roadmap 2050 identifies gas as a critical energy source for the transformation of the energy system to a system with lower CO₂ emissions that combines gas with increasing contributions of renewable energy and increasing energy efficiency. It may be argued that in Europe, natural gas replacing coal and oil will contribute to emissions reduction on the short and medium terms.

There are, however, several concerns related to shale gas exploration and production, many of them being associated with the process of hydraulic fracturing. There is also a debate on the greenhouse gas emissions of shale gas (CO₂ and methane) and its energy return on investment compared to other energy sources. Questions are raised about the specific environmental footprint of shale gas in Europe as a whole as well as in individual Member States. Shale gas basins are unevenly distributed among the European Member States and are not restricted within national borders, which make close cooperation between the involved Member States essential. There is relatively little knowledge on the footprint in regions with a variety of geological and geopolitical settings as are present in Europe. Concerns and risks are clustered in the following four areas: subsurface, surface, atmosphere and society. As the European continent is densely populated, it is most certainly of vital importance to understand public perceptions of shale gas and for European publics to be fully engaged in the debate about its potential development.

Accordingly, Europe has a strong need for a comprehensive knowledge base on potential environmental, societal and economic consequences of shale gas exploration and exploitation. Knowledge needs to be science-based, needs to be developed by research institutes with a strong track record in shale gas studies, and needs to cover the different attitudes and approaches to shale gas exploration and exploitation in Europe. The M4ShaleGas project is seeking to provide such a scientific knowledge base, integrating the scientific outcome of 18 research institutes across Europe. It addresses the issues raised in the Horizon 2020 call LCE 16 – 2014 on *Understanding, preventing and mitigating the potential environmental risks and impacts of shale gas exploration and exploitation*.

¹ EIA (2015). Annual Energy Outlook 2015 with projections to 2040. U.S. Energy Information Administration (www.eia.gov).



1.2 Study objectives for this report

Report with knowledge and knowledge gaps that exist specifically for handling fracking fluids and flowback at the drill site and in storage pools, and rating of organic and inorganic substances, and content of radioactive components.

1.3 Aims of this report

Public dissemination of identified knowledge gaps regarding risk assessment studies for water quality around drill sites. The inventory of knowledge gaps is used as a basis for different risk assessment studies focusing on the impact of shale gas operations on water quality around drill sites.



2 OVERVIEW

The present drilling technologies (horizontal drilling) and well stimulation (hydraulic fracturing) have resulted in large increase of vast sources of unconventional gas across a wide range districts and geological settings in North America. They are unconventional as they are bound up in low-permeability reservoirs such as shales, mudstones, tight sands, limestone, and coal beds. To extract these resources high pressure hydraulic fracturing is practiced. This has resulted in a rising concern over potential impacts on human health and the environment, especially with regard to potential effects on drinking water sources. Environmental concerns include the potential for contamination of shallow groundwater by stray gases (methane), formation waters (brines), and fracturing chemicals associated with unconventional gas development.

Hydraulic fracturing is the process used also to stimulate gas production from conventional oil and gas reservoirs. For each fracturing stage between 1000 and 2000 m³ is used, which may amount in total to 10 – 20×10³ m³ of fluid per well. The fracturing fluid consists of at about 98% water and sand or ceramics and about 2% of chemicals having a specific function. More than hundred chemicals could be used as additives, but typically no more than 10 -15 chemicals are used in the fracking process. After stimulation, about 20% to 60% of the fluid flows back to the surface and disposed by any one of a number of options. Before final disposal the fluid normally will be stored in open air pits or tanks.

The four most common disposal options are:

- 1) recycling for additional fracking,
- 2) treatment and discharge to surface waters,
- 3) underground injection
- 4) used as road deicing or for agricultural purposes.

However, the large amounts of water used in hydraulic fracturing may limit gas production in the shale plays as scarcity of water may induce restrictions. A study surveyed the amounts of freshwater and recycled produced water used to fracture wells from 2008 to 2014 in Arkansas, California, Colorado, Kansas, Louisiana, Montana, North Dakota, New Mexico, Ohio, Oklahoma, Pennsylvania, Texas, West Virginia, and Wyoming (Chen and Carter, 2016). Results showed that the annual average water volumes used per well in most of these states ranged between 1000 m³ and 30,000 m³. The percentage of water used for hydraulic fracturing in each state was relatively low compared to water usages for other industries. About 10 % of wells produced by hydraulic fracturing were treated with recycled produced water. The percentage of wells where recycled wastewater was used was lower, except in Ohio and Arkansas, where more than half of the wells were fractured using recycled produced water.

EPA began to research the potential impacts of hydraulic fracturing on drinking water resources, if any, and to identify the driving factors that could affect the severity and frequency of any such impacts. The focus was primarily on hydraulic fracturing of shale formations, with some study of other oil-and gas-producing formations, including coal beds, (US-EPA, 2012).

Five topics were associated with a primary research concerns:



- Water acquisition
- Chemical mixing and fracturing fluid surface spills on or near well pads.
- Well injection impacts on drinking water resources.
- Flowback and produced water potential impacts on or near well pads on drinking water resources.
- Wastewater treatment and waste disposal.

This present report provides a brief review of the risks that can occur on or near a wellpad in connection with the construction of wells and the subsequent fracking. A large part of the collection of data and knowledge from North America have been carried out in connection with the preparation of a Danish national report on the possible consequences of extraction of shale gas in Denmark.

A comprehensive collection of data and compilation of results from US is found on the US-EPA homepage: <https://cfpub.epa.gov/ncea/hfstudy/recordisplay.cfm?deid=244651>.



3 TRANSPORT TO AND HANDLING AT THE DRILL SITE

Possible sources of contamination of freshwater from shale gas extraction may include 1) accident with chemical spills when handling the fracturing fluid and flowback fluid, 2) leakage of fluid through fractures in pipelines during flowback, 3) erosion and leaching from cuttings, drill mud etc. with sorbed chemicals and nutrients from the drilling area, 4) leakage of flowback fluid from the well, after sealing.

Chemicals used in hydraulic fracturing and drilling chemicals transported to the drilling site in tankers are stored and mixed on site. Although the chemicals do not exceeding 2% of the fracturing fluid, the total amount of chemicals used in a single hole may amount to several thousand cubic meters. Accidents are a possible loss during travel to and on the wellpad and creating chemical spills.

There will be a risk for the transportation of chemicals from the flowback fluid through fractures in the shale layer or broken pipes and the upper strata of groundwater and surface water (Brittingham et al., 2014; Michalski & Ficek, 2015). Well blowout may also cause spills.

Particle transport through surface runoff from the drill site has been documented in several studies (Williams et al. 2008; McBroom et al. 2012), and total suspended solids and turbidity in streams in areas with hydraulic fracturing has been demonstrated elevated (Burton et al. 2014).

3.1 Drilling mud

Drilling mud is a collective term for the suspension (slurry) incorporated during drilling in hard rock to drill. During the drilling, is pumped and circulated drilling mud down to the drill bit where it partly cools and lubricates the drill hole and partly compensates for the pressure which arises in connection with the well to prevent blowouts and partly brings cuttings to the surface (Hosterman and Patterson, 1992; King 2012; US EPA 2015d). In sedimentary sand and clay deposits, the drilling work typically takes place simply by adding tap water. Drilling mud is generally divided into different types: 1) water-based; 2) non-water-based, i.e., oil-based and 3) gas (pneumatic) (Schlumberger 2015; King 2012). Near the surface is used only water-based drilling mud, whereas the oil-based mud may be used in deeper layers, when water based muds are not enough to check the stability of a water sensitive formation, for example due to swelling clay (King 2012). Gas or compressed air operated drilling mud can be an advantage in consolidated formations which do not produce much fluid. In an air-raising drilling will be used water-based and oil-based muds, but the boring is under balanced, which means that the pressure inside the well is less than in the body of the formation.

3.1.1 Chemicals in drilling mud

There are a number of factors that influence the choice and the composition of drilling muds as the well design, the expected pressure level in the formation and chemical composition of the formation (Bloy et al. 1994). The drilling mud contains water, and a whole series of chemical substances. For most of these it applies that they are not only used in the drilling mud, but also in other parts of the shale gas extraction process. The exception to this rule is bentonite and barium sulfate, which is almost exclusively used



in the drilling mud (Bishop 2011). Bentonite is intended to provide viscosity and create a filter cake on the borehole wall to control loss of drilling fluid, while the barium sulfate is used to give weight to the drilling mud and the formation of offset pressure (Bloy et al. 1994). Bentonite is used in the upper part of the well together with water (92.6%) and carboxymethyl cellulose (CMC) (0.02%) as a viscosity agent that may be added to control where the drilling mud is flowing. Barium sulphate (7.2%) is used in the larger well depths, for example. Ultracap, UltraHib NS (2.7%) and DUOTECH NS (0.2%). Ultracap DUOTECH and NS are respectively stated to be a cationic acrylamide copolymer, and a viscosity agent, whereas UltraHib NS (2.7%) consists of a mixture of polyetheramine (10-40%) and polyetheraminacetat (30-80%).

3.2 Fracking fluid

Fracturing is usually performed with fracking fluids under high pressure and contains a proppant (sand or ceramic balls) together with auxiliary chemicals. The handling of the fracking fluid, which volumetric can be quite large, may result in losses to the surrounding environment. By the fracking procedure fracking fluid will open fractures in the formation and deposit the proppant to keep the fractures open to enhance the flow capacity of the hydrocarbons from the formation and to the well.

3.2.1 Chemicals in fracking fluids

Fracturing fluid is pumped down the well in order to optimize the formation's ability to transport gas to the well. The main substance of fracturing fluid is water and silicate / sand. The sand in the fracturing fluid incorporated into the formed fractures, as permeability of the formation is increased. Sand and water represents about 98-99% of the mass, while chemicals are the last one to two percent (typically 0.025% friction reducer; 0.005-0.05% biocides; 0.005-0.2% surfactants; 0.2-0.5% corrosion inhibitors). The substances included in the fracturing fluid have various functions such as the acid that reacts with and dissolves the crude; biocides which eliminate bacteria, in particular may give rise to corrosion products and the formation of biofilms, which undesirably increases the friction, which can block the extraction of the gas; detergents which are used to increase the viscosity, etc.

The composition of the fracturing fluid varies considerably as a consequence of the geology, and the drilling process. This means that the substances used from the drilling to drilling - and even in the same well - will vary over time. Therefore, the oil-gas industry use a number of ingredients so the list of possible fracturing fluid chemicals spanning several hundred substances, (see report D8.1).

The industrial organic chemicals are expected to be biodegradable. Either they are generally degradable due to pressure or high temperature or they can be degraded in a wastewater treatment plant with adapted biomass.



3.3 Substances used in fracturing fluid products in the US and EU

The first comprehensive report on substances used in fracturing fluid products, was published in April 2011 by US EPA (US EPA, 2011). The report is based on today's reports for the period 2005-2009 from the 14 largest oil and gas companies in the United States. The report shows that the use of more than 2,500 fracturing fluid products containing 750 different chemicals. Overall, a total of about 2.95 billion liters of chemicals (ex. Water / sand) was used in period. Methanol, which is found in 342 of fracturing fluid products, was the most commonly used additive, followed by isopropyl alcohol and ethylene glycol. It was also noted that the 650 different fracturing fluid products contained one or more of a total of 29 compounds, which are known or possible human carcinogens. The companies had overall used about 38,000 m³ of chemicals that are known or possible carcinogens in the period. In June 2015 came the (US-EPA, 2015a) with the draft report: 'Assessment of the Potential Impacts of Hydraulic Fracturing of Oil and Gas on Drinking Water Resources' and the associated databases. The report (and databases) provides the most complete description of the chemicals used in fracturing fluids. It describes 1,173 different substances (counted as substances with CAS numbers) which can either be or is being used in fracturing fluids based on analyzes of FracFocus database and own databases.

The European Commission by the Joint Research Centre, published a report on the use of fracturing fluid products in Europe in the context of REACH, the EU chemicals legislation from 2007, see JRC Scientific and Policy Reports. Assessment of the use of substances in hydraulic fracturing of shale gas reservoirs under REACH. September, 2013, (EU, 2013). In this report, 16 chemical substances were identified as related to shale gas exploitation in Europe, and there was also a REACH registration of the additive.

It is expected that the use of between 75 and 300 m³ chemicals per well in Europe. Biocides which are not licensed or is not under review for a specific application should not be used in Europe. The same applies to substances which are not registered in REACH and marketed by over 100 tons per year. Substances placed on the market in quantities of 1 to 100 tons per year, must first be registered for REACH in 2018, and they can until then legally be marketed. To date there are also no EU-wide register of fracturing fluid chemicals and the European Commission in July 2015 sent a call out on a project that among other things, help the European Chemicals Agency (ECHA) to create a database of these substances for Europe.

In 2014 the German environmental authorities (UBA) published as an article which summarizes the German experience with fracturing fluid and the approximately 300 frackings has been carried out in Germany. Out of these, only one location shale layers were fracked (Damme 3) at a depth of 1045-1530 m. The other frackings were in other strata (coal bed methane rock) where the liquid used, is different in shale layer. UBA found that there are at least 88 different fracturing fluid products on the market in Germany. It is used at least 112 different chemicals in the fracturing fluid products. The study concluded that there is a likelihood of potentially unacceptable environmental risk and that at the moments are many gaps in knowledge and data to conduct a thorough risk assessment in Germany. The German environmental authorities recommend based on the study that all substances used in fracturing fluid to be published. Data for their



environmental toxicity should be made available, the most toxic substances to be substituted, and each hole will have its own site-specific risk assessment (Bergman et al. 2014).

The shale gas well in Damme 3 is designed as a test drilling that used hydraulic fracturing (see Shal gas information platform: http://www.shale-gas-information-platform.org/nc/categories/water-protection/the-basics/fracturing-fluids.html?sword_list%5B0%5D=damme) as the only one of its kind in Germany so far. In the well 3 Damme contained the hydraulic fracturing fluid of tetra methyl ammonium chloride product which is a clay stabilizer; light petroleum distillates as friction reducer; the surfactant is ethoxylated octyl-phenol; and the isothiazoline biocide derivative or the mixture of 5-chloro-2-methyl-2H-isothiazol-3-one and 2-methyl-2H-isothiazol-3-one. Exxon Mobil is the only company in Germany, which has published the composition of their fracturing fluid consisting of 99.8% water and sand, and 0.2% consisting of two chemicals: choline chloride and 2-butoxyethanol (see EXXON Mobile homepage: http://www.erdgassuche-in-deutschland.de/hydraulic_fracturing/).

In England, the Department of Energy and Climate Change published a short report which states that only the company Cuadrilla has described what chemicals their hydraulic fracturing fluid contains, see report Department of Energy & Climate Change. Fracking UK shale (UK, 2014). The liquid, which they have applied for six wells in England, contained 0.075% polyacrylamide (friction reducer); 0.125% hydrochloric acid (acid) and 0.005% glutaraldehyde (biocide) (<http://www.cuadrillaresources.com/what-we-do/hydraulic-fracturing/fracturing-fluid/>).

All fracturing fluids contain biocides to prevent microbial interference.

Most commonly used is glutaraldehyde or MCI / MI. Glutaraldehyde has just been approved for the period October 2016-October 2026 on the basis of a report prepared by Finland. This report says that glutaraldehyde can be approved for use in drilling muds under the condition that the product be labeled. Finally it should be mentioned that, in four of the 13 wells also Polish used petroleum distillates.

The composition of hydraulic fracturing fluids will vary depending on the conditions and processes. They can therefore, in principle, contain one or more of the substances identified among the 1076 listed by the US EPA. However, it is more likely that they will contain one of the 16 substances EU Commission has identified and / or some of the substances used in England, Germany and especially in Poland. It can be expected that the liquid will contain max. 1-2% chemicals in the same distribution as mentioned above, and the rest will be water and gravel / quartz or other friction products. The percentage usage of the three most commonly used drugs in the United States and Poland are: methanol (72% in the US and 100% in Poland); hydrochloric acid (72% in the US and 92% in Poland); ethylene glycol (32% in the US and 83% in Poland), see information from Poland here:

http://www.oppw.pl/en/sklad_plynu_szczelinujacego/23.



4 FRACKING

4.1 Water use

Water consumption for unconventional gas production may increase pressure on freshwater resources, especially in areas where water abstraction is already intense. Within a shale gas production, it is therefore important to analyze the extent to which production will affect water resources. As shale gas production has been widely used, primarily in North America, several estimates of water consumption has been published calculated per well. From Canada reported a very large span of 2000 to 77,000 m³ / well, with an estimated average of 19,000 m³ / well (Council of Canadian Academies, 2014). An inventory of water consumption for seven shale formations in the United States ranged between 8,000 and 100,000 m³ / well with an average of 15,000 m³ / well (Vengosh et al., 2014). The latest (September 2015), and most comprehensive, inventory is based on 45,000 wells in seven formations and shows an average consumption of 16,000 m³ / well (Kondash and Vengosh, 2015). Average water consumption varies from 13,000 to 24,000 m³ / well. Hence it can be concluded that reported water consumption shows a considerable variation from 2000 to 100,000 m³ / well.

The total water consumption can also be estimated from water consumption per. m³ produced gas. For British shale gas production is estimated a consumption of 1.3-1.7 million m³ / year for a gas production of 9 billion m³ / year (Broderick et al., 2011), providing 0.14 to 0.18 L of water per. produced m³ gas. Kondash and Vengosh (2015) reports figures for total gas production from the six US gas provinces, of which water consumption per. m³ produced gas can be calculated. Here is a consumption of between 0.16 and 0.46 L of water / m³ of gas with an average of 0.28 L water / m³ gas. This average estimate is statistically better founded than the UK estimate.

4.2 Pipeline leaks

In some locations, pipelines are used to transport produced water. In Pennsylvania a leak from a broken 90-degree bend in an overland pipe carrying a mixture of flowback and freshwater between two impoundments impacted a stream. The release was estimated at 40,000 L. In response to the incident, the pipeline was shut off, a dam was constructed for recovering the water, water was vacuumed from the stream, and the stream was flushed with fresh water (PA DEP, 2009). In January 2015 11,000 m³ of produced water containing petroleum hydrocarbons (North Dakota Department of Health, 2015) were leaked from a broken pipeline that crosses a creek. The electrical conductivity and chloride concentration in water along the creek were found to be elevated above background levels. Other incidents from North Dakota are documented at the North Dakota Department of Health (NDDOH) Environmental Health web site (<http://www.ndhealth.gov/EHS/Spills/>). For the period from November, 2012 to November 2013, NDDOH reported 552 leaks of produced water which were retained within the boundaries of the production or exploration facility and 104 which were not, (see North Dakota Department of Health reports from 2015: <http://www.ndhealth.gov/ehs/foia/spills/>).



4.3 Well blowouts

Analyses of water from two monitoring wells in Killdeer, ND, were used to determine that brine contamination in the two wells resulted from a well blowout during a hydraulic fracturing operation. Another example of a well blowout associated with a hydraulic fracturing operation occurred in Clearfield County, PA. The well blew out, resulting in an uncontrolled flow of approximately 132 m³ of brine and fracturing fluid, along with an unquantified amount of gas; some of the fluids reportedly reached a nearby stream (Barnes, 2010). The blowout occurred while the company was drilling out the plugs used to isolate one fracture stage from another. In North Dakota, a blowout preventer failed, causing a release of between 7,900 L/day and 11,000 L/day of flowback water (Reuters, 2014).

4.4 Wastes from the drilling process

As shales lies in between 1.7 and 7 km depth substantial amounts of drill cuttings will be produced during the deep drilling. The drilling will pass through different geological materials depending on the geology. The drill cuttings can be very different in composition but will always include shale material. The expected volume of drill cuttings can be estimated from knowledge of drill diameter and depth of the well. The total amount of drill cuttings for the approximately 4000 m long well are given to 1900 tons at a rate of 1.3 tons / ongoing drilling meter in the top for some 100 kg / meters at the bottom. Cuttings are transported to the surface by the drilling mud during the drilling process and are separated and settled in a basin. Cuttings are removed from the basin and transported to the landfill. A portion of the added substances in drilling mud will be contained in the pore water in the wet cuttings or bound to the sediments by sorption or ion exchange processes. The generated waste will thus - besides the actual cuttings - contain additives from the drilling mud is why a pre-treatment may be necessary before final disposal.

However, special focus is required on drill cuttings from the Alum shale or Marcellus shales, as the shale has relatively high content of inorganic trace elements, many of them bound to reduced sulfur compounds (e.g. pyrite). It has been shown that shale may contain substances which give rise to increased reactivity. A comparative study of shale from the United States show elevated metal content in the Alum Shale from Sweden compared to shale from the United States - particularly for uranium (U), Vanadium (V), molybdenum (Mo) and nickel (Ni) (Leventhal, 1991). Studies have shown that the inorganic trace elements may be leached from the shales and the measurements showed a leaching of cadmium (Cd) (190 µg / kg shale) and molybdenum (Mo) (16 mg / kg shale), which is a rather high amount, (Lavergren et al. 2009). The content of especially Mo is high and close to the leaching limit for leaching of hazardous waste in coastal landfills. There is thus a need to have performed a general characterization of wastes containing drill cuttings from Alum shale before that can be appointed an environmentally sound waste management. It has been shown that the high content of reduced sulfur compounds (such as pyrite) can be oxidized by contact with atmospheric oxygen. The oxidation may lead to increased mobility of inorganic trace elements due to the oxidation formation of acidity with a consequent drop in pH (Falk et al. 2006,



Lavergren et al., 2009). The resulting pH drop (and thus the increased mobility) can be avoided by using the interference of the buffer material, such as lime (Jeng et al., 1992). It may therefore be necessary to relate to a time-dependent increase in leaching from landfilled shale waste in the general waste characterization.

Shale may contain radioactive materials that could mean the waste will not be received on ordinary landfills, but will be characterized as low-radioactive materials requiring special management. Similar challenges are reported in the United States with drill cuttings from the Marcellus shale, as reported examples of emissions of airborne radon arising from deposited shale drill cuttings in landfills (Walter et al., 2012).

4.5 Leaks from Pits and Impoundments

The wastewaters are managed in a variety of ways including treatment and reuse for new well completions, disposal through publicly owned or commercial wastewater treatment plants, or disposal in Class II underground injection control wells. However, before the management the wastewater is normally stored in pits, impoundments or tanks. Impacts on environmental health from accidental or intentional releases during handling, disposal, treatment, or reuse are poorly documented, with few reports in the literature, (Adams, 2011). Potential pathways for wastewater to enter surface water or groundwater include leaks from pipelines or tanker trucks transporting fluids, leakage from wastewater storage ponds through compromised liners and overflows from the ponds. More knowledge is needed to examine the potential impacts of wastewater releases on environmental health, which are likely to accelerate with the increased exploitation of shale gas.

Reports on leaks of flowback and produced water from on-site pits and impoundments have shown releases of more than 200 m³, which had caused surface and groundwater contamination (Vaidyanathan, 2013). In New Mexico VOCs have been detected in groundwater near the downgradient of an unlined produced water pit (Sumi, 2004; Eiceman, 1986).

In Pennsylvania two case studies found potential impacts from produced water impoundments with elevated chloride concentrations (U.S. EPA, 2015b) However, the two incidents were verified. Similar to this a case study in Texas, impacts to two water wells were attributed to brine, but the data were not sufficient to distinguish among four possible sources, one of which was leaks from reserve pits and/or impoundments. (Richer and Kreidler, 1993) reviewed sources of salinity to groundwater resources by evaluating reviewing major sources, as natural saline groundwater, halite dissolution, sea-water intrusion, oil-field brine, agriculture, saline seeps and road salt, which could be used as a general guide to potential sources of salt at a specific area of interest.



5 FLOWBACK

5.1 Flowback water

As the hydraulic fracturing is done under high pressure, a part of the injected fracking fluid will return to the surface mixed with the connate formation water. After end of the fracturing the fluid is pumped back to the surface to clean up the well. Usually the flowback water during the first 2 weeks amounts to 20- 50% of the total pumped volume. The flowback water might be stored in open pits or in closed tanks. Since fracking takes place in great depth (up to 5 km) the temperature will be correspondingly high (typically 60 - 130° C) and at the same time under a high pressure that overcome the lithostatic pressure. This means that substances such as released metals or dissolved salts from the formation may be brought up with the flowback water. This also applies trapped gases. Flowback water often contains high concentrations of total dissolved solids (TDS), heavy metals, suspended solids, sand and dissolved radioactive substances released from the formation (Zhang, 2015).

If the shales or the mud stones have an elevated content of uranium or thorium, the flowback and produced water normally will contain dissolved radium and radon, sometimes small amounts of the normally immobile uranium if there are applied oxidizing chemicals. Studies have shown that the content of radium may be close to 0, but in some cases it may be considerably larger (Kargbo et al. 2010). For example, Haluszczak et al. (2013) demonstrated values up to 176 Bq / m³, while Rowan et al. (2011) have measured concentrations of 148 Bq / m³. Radon, which follows the terrain with flowback water, is likely to disappear into the atmosphere and has a half-life time less than 4 days.

Significant volumes of flowback water with dissolved dry matter and suspended solids shall be handled at the drill site. In some cases the flowback water that contains heavy metals and radioactive substances which have been leached from the formation. In addition to this radioactive gases (radon) may be dissolved in the flowback water. From the fracturing fluid will also occur clay, sand or small ceramic particles or spheres.

5.2 Temporal changes in flowback water composition

Salts will naturally occur in all formation water in the sediments. Brines are commonly found in rock units in the subsurface in the region underlain by Marcellus Shale (Poth, 1962; Rose and Dresel, 1990; Dresel and Rose, 2010; Haluszczak et al., 2011; Warner et al., 2012). In the Marcellus Shale very little water is present in the formation (Engelder et al., 2014). In general, less than 3 % of the shale volume contains water and most is capillary bound. This means that only small volumes contain formation water in the shale before hydraulic fracturing (Engelder, 2012; Engelder et al., 2014). Data from several hundred wells shows that the Marcellus is only 23 ± 10% water saturated (Engelder, 2012). Diffusion of Na, Ca, Mg, and Cl from free or capillary-bound water in the matrix to fractures can explain observed temporal changes in flowback chemistry. After fracking an initial dissolution of salts and other constituents within the formation will give rise to mobilization in the brines constitute the major subsurface processes levels in flowback and produced water (Dresel and Rose, 2010; Blauch et al., 2009). At the same time a leaching of organic compounds from the shales / mudstones or coal



partly due to the injected chemicals and dissolved in flowback water (Orem et al., 2014). In addition, other ions, metals, naturally occurring radioactive compounds (NORM), and organics increase in concentration as water production continues (Barbot et al., 2013; Murali Mohan et al., 2013; Rowan et al., 2011). Several research studies described the possible processes leading to severe changes in the flowback water composition (Barbot et al., 2013; Haluszczak et al., 2013; Chapman et al., 2012; Davis et al., 2012; Gregory et al., 2011). Further, measurements have shown that the flowback increases in salinity during the time after hydraulic fracturing. Balashov et al (2015) has presented a model which simulate the increase in salinity. The model is consistent with diffusion of salt from brine into mobile hydraulic fracturing water. This brine is present in core samples from depth but, as expected, is not present in exhumed outcrop shale samples that have higher porosity because of exhumation, except perhaps in very small quantities that can only be detected by Sr isotope measurements. The model argues for a time lag of approximately 12 months after opening of the well before salt concentrations reach 90 % – 95 % of the steady-state values.

As the flowback water has even very high salt concentration due to formation water concentration (about 5 M of NaCl) it will be one of the most significant impacts of surface water and soil and the salt impact is therefore likely to affect the soil uses if an accidental spill or leaching may happened. In general, the addition of large amounts of salt to the soil is harmful for soil quality and salinization is a known threat to soil quality as stated in the reports from EU-JRC (see: <http://esdac.jrc.ec.europa.eu/content/esdac-themes>). Salinization occurs mostly as a result of irrigation and evaporation as well as in coastal areas, while in the Nordic countries also have experience for salting caused by road salting in the winter. In reports from Environment Canada (2001), Norwegian Public Roads Administration, Norway (2005) and Pedersen and Ingerslev (2007) are detailed descriptions of the effects of road salting on soil, plants and animals

5.3 The total dissolved solids (TDS)

The total dissolved solids (TDS) in wastewaters from shale and mudstone formations has generally high concentrations of sodium and chloride and may also elevated concentrations of bromide, bicarbonate, sulfate, calcium, magnesium, barium, strontium, radium, organic matter, and heavy metals (Sirivedhin and Dallbauman, 2004, Orem et al., 2007, Chapman et al., 2012, Rowan et al., 2011, Blauch et al., 2009). Flowback and produced water are generally high in TDS from shale and tight sandstone formations, with values ranging from less than 1,000 mg/L to more than 100,000 mg/L. However, between each play a rather high spatial variation is seen, which indicate that different management strategies such as reuse or treatment must be considered. In some plays the concentration ranging between 250 mg/L to 40,000 mg/L giving fewer treatment challenges and a wider array of management options. (Benko and Drewes, 2008, Van Voast, 2003).- For TDS levels of <500 mg/L the wastewater has been used in Pennsylvania for some industrial wastewater discharges.

Many compounds commonly found in TDS from hydraulic fracturing wastewaters may have potential impacts on health or may create undesirable conditions on downstream drinking water treatment plants if discharged at high concentrations to drinking water



resources. Bromide and iodine may contribute to the increased formation of disinfection by-products during drinking water treatment (Hammer and Van Briesen, 2012). The concentrations of metals (e.g., barium, cadmium, chromium, lead, copper, manganese, nickel, thallium, and zinc) in TDS are toxic to humans and aquatic life at certain concentrations. To ensure safe drinking water, the EPA has established primary MCLs for a number of these constituents (thallium, cadmium, chromium, copper a.m.). For other constituents as chloride, sulfate, barium, and boron regulations exists under the National Primary Drinking Water Regulations (U.S. EPA, 2015b, Hammer and VanBriesen, 2012, Shafer, 2011, Webb et al., 2009).

5.4 Inorganic components

There is no normal salt, which is found in up to 7 fold higher concentration than seawater. There are also high concentrations of divalent cations, which form the carbonate minerals in contact with the atmosphere and therefore results in large quantities of precipitated material. Furthermore, there are a number of metal ions, which can be toxic to the aquatic environment.

The trace elements in the flowback water (see report D8.1) are reported in g / L and the assumption about 1-30% water content in the soil will result in concentrations immediately is far lower than the soil quality requirements for those substances where limits are listed (soil quality is not specified for cobalt, vanadium and beryllium). Several of the trace elements have the option to precipitate in the ground as sparingly soluble salts, or they can ion exchange with salts in the soil, and this may result in an accumulation of concentrations above limit values. There may also be precipitation and release from the soil structure, so mobility of trace elements is increased, and thus leached from the soil, which can be increased to the high salinity of flowback water (Pedersen & Ingerslev 2007). Several of the substances are heavy metals (eg. Hg, Pb, Cd), which are all known for their harmful effects. At release to land there should be monitoring of compliance with limits. Exceeding the limits will result in reduced applications of soil or demands for removal and cleaning.

5.5 Organic components

The organic content in flowback can vary based on the chemical additives in the fracking fluids used and the formation but generally consists of polymers, oil and grease, volatile organic compounds, and semi-volatile organic compounds (Walsh, 2013; Hayes, 2009). Dissolution of organic matter from the shales might also contribute to the flowback organics. However, little information is at present available about organic constituents in hydraulic fracturing wastewaters, but several studies that include some analyses of organic constituents has been published. Other constituents detected include alcohols, naphthalene, PAH's, acetone, and carbon disulfide. Wastewater may have high concentrations of aromatic and halogenated organic contaminants that may require special treatment (Pashin et al., 2014, Sirivedhin and Dallbauman, 2004). Several organic compounds are critical in drinking water as they can cause damage to the human health (U.S. EPA, 2006). Some organics in chemical additives are known carcinogens, including 2-butoxyethanol, naphthalene, benzene, and polyacrylamide



(Hammer and VanBriesen, 2012). Many organics are regulated for drinking water under the National Primary Drinking Water Regulations. However, biocides (formaldehyde, glutaraldehyde and MCI / MI) may be considered as the most problematic in the fracking fluid (Arnaud 2015) and has an immediate effect on soil microorganisms. Therefore, the presence of biocides tends to reduce microbial decomposition of organic contaminants. However, glutaraldehyde and formaldehyde are unstable in sunlight and air, and have the potential to evaporate or be decomposed under aerobic conditions. The oil content of formation water is expected to be low in most cases depending on maturity of the source, and does not give rise to environmental impacts.

5.6 Radioactive components

Radionuclides are of concern in some hydraulic fracturing wastewaters and produced water, mainly with data obtained for the Marcellus Shale in Pennsylvania. Radioactive brine is naturally occurring in shales and contaminates wastewater during hydraulic fracturing. Analyses of radium levels in samples collected at the well pad discharged from Josephine Brine Treatment Facility into Blacklick Creek, which runs into a water source for western Pennsylvania, were 200 times greater than samples taken upstream. Such elevated levels of radioactivity are above regulated levels and would normally be seen at licensed radioactive disposal facilities. Results from a USGS report (Rowan et al., 2011) indicate that radium-226 and radium-228 were the predominant radionuclides in Marcellus Shale wastewater. As mentioned limited data are on radionuclides in wastewater from plays in US other than the Marcellus Shale, but information on the naturally occurring radioactive material in the shales, e.g. uranium and thorium, indicates a potential for high levels of radionuclides in produced water, especially at high TDS concentrations. The primary radioactive contaminants found in hydraulic fracturing wastewaters (radium, alpha radiation, and beta radiation) can increase the risk of cancer if consumed at elevated levels over time. Concentration of Ra-226 and Ra-228 in Marcellus Shale from three wells in Pennsylvania showed increased from several hundred pCi/L in the early stage of flowback period (< 10 days) to several thousand pCi/L after the well has been producing gas for more than two year in the produced water. Ra-228 - Ra-226 ratio is low mainly due to the lower Th content in Marcellus Shale, Barbot et al. 2013. However, it also increased from less than 400 pCi / L at the early stage to more than 1,000 pCi / L after two years of gas production. Total radium in Marcellus Shale produced water ranges from about 100 to more than 10,000 pCi / L with a median of 5,400 pCi / L, and is closely related to increases in salinity, Rowan et al 2011. However, in order to investigate the origin of radionuclides in Marcellus Shale produced water, it is important to determine whether the Ra existed in connate water, which has reached dynamic equilibrium with shale core, or is leached from the shale core into produced water as a consequence of frack fluid injection. Consequently, US-EPA has established drinking water MCLs for combined radium (radium-226 plus radium-228), gross alpha, and gross beta of 5 pCi / L, 15 pCi / L, and 0.04 mSv / year, respectively.



6 WASTEWATER MANAGEMENT

Wastewater from the production of shale gas consists of flowback water from wells and small amounts of fracking fluid collected from waste around the drill rig and residues in the tanks. In general, wastewater from the working space (toilets, etc.) is not different from what occurs at temporary work sites are not considered further.

There is at present no data that can be used to predict water production from a European shale gas well. However as a basic estimate of wastewater production for US shale gas wells can be expected that a well typically produces 13,300 m³ during gas production and half will be the first year where the waste consists of mixed fracturing fluid with frackings chemicals and formation water. The other half of the water is evenly over the well's remaining lifespan of 6-10 years and contains high concentration of salts and minor organic compounds. Thus, the need for treatment per well roughly estimated at 10 m³ / d in the first year and 3 m³ / d in the following years. The water produced in the first year, is probably also unevenly distributed throughout the year, so it is unrealistic to have a matching treatment technology that can purify the water as fast as it comes up in the first part of a well production period.

Shale gas operators may have several strategies for management of wastewaters, with the most common choice being disposal via Class IID wells (Clark et al., 2013; Hammer and VanBriesen, 2012). If possible reuse in a subsequent hydraulic fracturing operation could be an option after adequate treatment. Also treatment at a centralized waste treatment facility (CWT) are practiced or in other cases various other wastewater management strategies as treatment of unconventional wastewaters at publicly owned treatment works (POTWs), which was a common practice for wastewater in the Marcellus region (Lutz et al., 2013). However, this practice has been cancelled following a request from PA DEP that, by May 19, 2011, oil and gas operators stop sending Marcellus Shale wastewater to 15 POTWs and CWTs that discharged to surface waters (U.S. EPA, 2015d).

The regulations prohibit the discharge of waste pollutants into navigable waters from any source (other than produced water) associated with production, field exploration, drilling, well completion, or well treatment (i.e., drilling muds, drill cuttings, produced sands).

Unpermitted discharges of wastes related to hydraulic fracturing have been described in a number of instances. In Pennsylvania, discharges of brine into a storm drain that discharges to a tributary of the Mahoning River in Ohio. Analyses of the brine and drill cuttings that were discharged indicated the presence of contaminants, including benzene and toluene (U.S. Department of Justice, 2014). In California, an oil production company periodically discharged hydraulic fracturing wastewaters to an unlined sump for 12 days. It was concluded by the prosecution that the discharge posed a threat to groundwater quality (Bacher, 2013). These unauthorized discharges represent both documented and potential impacts on drinking water resources. However, data do not exist to evaluate whether such episodes are uncommon or whether they happen on a more frequent basis and remain largely undetected.



6.1 Treatment of wastewater

Sewage can be treated with different methods in dedicated facilities or to common wastewater treatment plant, as described in the next section. General will endeavor to recycle as much water as possible, so the need for treatment and discharge is reduced. Injection of the wastewater from the shale gas in a bore in the United States is the preferred method for disposal of wastewater by the bulk of the ongoing shale gas. It happens in dedicated wells for disposal (98% in the US, according to US EPA, 2015b). In EU this is not expected to be approved, so all wastewater must be handled and treated before discharge to the environment.

By recycling waste, technical chemicals presumably do not require treatment, but rather to help reduce chemical consumption. There will be need for removing particles of respect to equipment damage and risk of blockages in the well. Internationally, it is disclosed that it is often necessary to reduce the amount of dissolved salts. It may be done by precipitation, which will produce a limited amount of solid waste, or by using membrane filtration, which will produce a concentrated salt fraction to be disposed (US EPA, 2015b).

6.2 Overall wastewater treatment

In general, the treatment for the purpose of discharge could be divided into two ways, depending on the intended recipient's tolerance for the supply of salt. If the recipient cannot tolerate salt stress, water treatment, consist of a membrane filtration, which produces clean water that can be discharged without toxic effects. The membrane filtration produces a very saline concentrate, containing all the residues of organic chemicals from the fracturing fluid. This concentrate will be taken away for treatment at a wastewater treatment plant discharging water to a recipient that can withstand salt stress. An existing treatment plant will often have a large dilution capacity by mixing with other wastewater streams, which may dilute the salt concentration, so as not to affect the biological treatment process of the organic chemicals.

If a recipient who can tolerate salt load in the area where gas production takes place, would avoid transport by treating wastewater at a dedicated facility in connection with the gas installation. A plant will typically have first aeration and pH stabilization, followed by a biological cleaning step which must be compact and salt-tolerant, indicating that it would be a form of biofilm reactor. The system may also require a sorption filter or a form of precipitation to remove metals, radioactive components, or any non-degradable organic chemicals for the sake of that the discharge has not eco-toxic effects in the recipient.

6.3 Treatment in existing wastewater treatment plants

The treatment of wastewater or membrane concentrate will in some cases be treated in the existing wastewater treatment plant after consideration of the fate of all the constituents in the wastewater treatment plant and the expected concentrations in sludge and the end of all chemical ingredients. Municipal wastewater treatment plants will be advantageous because there will typically be a short transport distance wastewater. It must be ensured that the salt concentration is not too high in the wastewater treatment



plant. In addition, it considered whether the organic chemicals from the fracturing require adaption of the biomass before degradation becomes effective. There is several treatment plant of industrial wastewater, which will be more useful for treating shale gas wastewater. Municipal wastewater treatment facilities are not designed to handle hydraulic fracturing wastewater containing high concentrations of salts or radioactivity two or three orders of magnitude in excess of federal drinking water standards. As a result, high salinity and dissolved solids in Appalachian rivers have been associated with the disposal of Marcellus Shale hydraulic fracturing wastewater after standard wastewater treatment.

Generally, it is expected that the waste from shale gas installations containing organic drilling- and fracking chemicals before treatment and discharge, and will always be cleaned biologically to a level of acceptable low residues of organics. However, the degradability of the wastewater in a treatment plant is expected to be an important parameter for the choice of chemicals to the composition of fracturing fluids. Water volumes used in or produced by hydraulic fracturing vary from site to site and with the geology. In the Marcellus Shale the requirement is between 7-15 10^6 liters for each well, (Veil, 2010).

At the end of December 2011 4908 unconventional wells had been drilled in Pennsylvania, while at mid-June 2015 the numbers were 9240 (PA-DEP 2010). A significant fraction, about 10–40% of fracking water used returns to the wellhead as flowback within 14 – 30 days after fracturing. Later, gas production is accompanied by formation water or produced water, which emerges at a much lower flow rate for the rest of the well life. The effectiveness of regional wastewater treatment processes in removing flowback and produced water constituents is limited, with dissolved solids of particular concern. Unconventional gas wells will increase the total generation of oil-and-gas-related wastewater, (Lutz et al. 2013). Surface water quality impacts from incomplete wastewater treatment have been demonstrated for chloride, bromide, and radionuclides, (Olmsted et al. 2013; Wilson et al. 2012; Warner et al 2013). The impact from road-spreading of shale gas wastewater was associated with accumulation of radionuclides in surface sediment, (Skalak et al. 2014). Partially treated shale gas waste in surface water may increase risks to produced drinking water from disinfection byproducts, (Haarkness et al.2015, Parker et al. 2014).

6.4 Industrial wastewater plants

CWT facility is generally defined as a facility that accepts industrial materials, as hazardous, non- hazardous, solid, or liquids generated at another facility (off-site) for treatment and/or recovery (EPA, 2000). As a group, CWTs that accept oil and gas wastewater offer a wide variety of treatment capabilities and configurations. The fate of treated effluent at CWTs also varies, and can include the following: reuse in fracturing operations, direct discharge to a recipient water under a National Pollution Discharge Elimination System permit, indirect discharge to a public treatment plant, or a combination of these. Potential impacts on drinking water resources associated with treatment in CWTs will depend upon whether the CWT treats adequately for constituents of concern prior to discharge to surface water or to a public treatment plant, and whether treatment residuals are managed appropriately.



Clean Water Act regulations only apply to facilities that discharge treated wastewater to surface waters or POTWs. For zero-discharge facilities, Pennsylvania and Texas have adopted regulations to control permitting. PA DEP issues permits that allow zero-discharge CWTs to treat and release water back to oil and gas industries for reuse. The Texas Railroad Commission regulates and categorizes wastewater recycling facilities into different categories: mobile commercial recycling facilities which are capable of being moved from one location to another and stationary commercial recycling facilities. The Texas regulations also promote oil and gas wastewater treatment for reuse and water sharing. The transport of wastewater from the wellpad can be carried out by truck or by pipeline to and from a CWT plant, which as mentioned earlier may present vulnerability for spills or leaks (Easton, 2014). However, there are CWTs serving hydraulic fracturing in Texas and Wyoming. Because of low usable injection wells in Pennsylvania necessitates other forms of management, the CWT ty have served Marcellus Shale operations (Boschee, 2014). An US-EPA study has registered 73 CWT plants that have either accepted or plan to accept hydraulic fracturing wastewater and of these, 39 are located in Pennsylvania, (U.S. EPA, 2015c). They do not discharge to surface waters or POTWs, and they often do not include TDS removal. In other regions, a few newer facilities have raised in the last years, some of these with TDS removal capabilities. Few states maintain a full list of CWT facilities and the count provided by the EPA includes facilities that plan to accept unconventional oil and gas wastewaters, the registered facilities do not precisely reflect the number of facilities available at present (U.S. EPA, 2015c). New company announcements indicate that new wastewater treatment facilities are being planned (Greenhunter, 2014; Geiver, 2013; Purestream, 2013; Alanco, 2012; Sionix, 2011). Moreover, information available from PA DEP shows that although total amounts of wastewater have increased, the percentage managed through CWTs has decreased.



7 WATER REUSE

In the process of unconventional gas exploration, the fracking is one of the main measures to increase production of gas wells. Whether it is sand fracturing stimulation using conventional store, or large-scale shale gas extraction technology in recent years in the country requires the preparation of a large number of construction of liquid. Therefore, not only large-scale hydraulic fracking causes a pressure on the shortage of freshwater resources, but do generate a large volume of flowback waste which may threaten the environment. However to reuse the process water by technological treatment of flowback water might reduce the environmental water resources and pollution. Shale gas drilling in the United States shows that about 70 percent of the water from the hydraulic fracturing is reused. During the last the decade water reuse by hydraulic fracking has increased and flowback waters after treatment has been used to formulate hydraulic fracturing fluids for subsequent frackings (Boschee, 2014, 2012; Gregory et al., 2011; Rassenfoss, 2011). However, flowback water might be reused after different form of treatment depending on the requirements.

The reuse may a most cases be an economical benefit as it reduces the cost to with other forms of wastewater management. However, the reuse of wastewater will result in an increased accumulation of dissolved solids and concentrated liquid waste, as salts, metals and TENORMs. The produced water contains suspended solids, organics, and bacteria, whereas freshwater may have a typical river water composition, (Minnich, 2011). In a Marcellus survey indicates the presence of elevated hardness, as well as barium (Ba) and radium-226 (226Ra), (Silva et al. 2011). Finally, wastewaters with components that has been reused more than once, will need to be advanced treated, or injection. Liquid residuals from treatment will require careful management to avoid elevated impacts on the water resources (Kappel et al., 2013). The feasibility of produced water reuse hinges on the ability to create a blend of produced and fresh or brackish water that enables effective and economical well completion. Therefore, the composition of the produced water, the fresh/brackish water, and the target blend must be known. Produced and freshwater has to be treated before reuse with to remove iron, suspended solids, hardness, and bacteria., to avoid precipitation and to ensure that the blend composition has proper hydraulic fracturing chemistry, Minnich, 2011. Various methods are used to treat produced water for reuse. For example, one water treatment service provider removes iron, suspended solids, strontium, and barium, then returns the treated water to the customer for reuse. Another uses gravity settling with optional filtration to remove suspended solids before blending the produced and fresh water. Because water chemistry varies significantly among sources, treatment for reuse must be specified on a case-by-case basis.

Increasing recycled wastewater volume and decreasing freshwater demand would alleviate the effect of water scarcity on shale energy development. There were 6233 wells that reported use of recycled wastewater or produced water in the hydraulic fracturing fluids. Of these wells 6221 were fractured between 2008 and 2014. The annual number of wells fractured using recycled wastewater was less than 1,000, with the greatest number of wells located in Arkansas in 2011. The number of wells fractured with recycled wastewater was zero in Kansas, Montana, and North Dakota and in New Mexico. The greatest amount of recycled wastewater was 5.52 Mm³ in Colorado in



2012, while the maximum of recycled wastewater volume per well was 65,925 m³ in Louisiana in 2014. The median volume of recycled wastewater per well was 7127 m³, which was more than half of the 11,259m³ or the median volume of water used per well. This indicates that over half of the water used to fracture these wells came from recycled wastewater.

7.1 Wastewater treatment

Before reuse most wastewater has to be treated to obtain a standard for reuse.

Wastewater can be treated with different methods in dedicated facilities or to common wastewater treatment plant. General will endeavor to recycle as much water as possible, so the need for treatment and discharge is reduced. By recycling wastewater, technical chemicals presumably do not require treatment, but rather to help reduce chemical consumption. There will be need for removing particles of respect to equipment damage and risk of blockages in the well. Internationally, it is disclosed that it is often necessary to reduce the amount of dissolved salts. It may be done by precipitation, which will produce a limited amount of solid waste, or by using membrane filtration, which will produce a concentrated salt fraction to be disposed (US EPA, 2015b).

In general, the treatment for the purpose of discharge could be divided into two ways, depending on the intended recipient's tolerance for the supply of salt. If the recipient cannot tolerate salt stress, water treatment, consist of a membrane filtration, which produces clean water that can be discharged without toxic effects. The membrane filtration produces a very saline concentrate, containing all the residues of organic chemicals from the fracturing fluid. This concentrate will be taken away for treatment at a wastewater treatment plant discharging water to a recipient that can withstand salt stress. An existing treatment plant will often have a large dilution capacity by mixing with other waste water streams, which may dilute the salt concentration, so as not to affect the biological treatment process of the organic chemicals.

If a recipient who can tolerate salt load in the area where gas production takes place, would avoid transport by treating wastewater at a dedicated facility in connection with the gas installation. A plant will typically have first aeration and pH stabilization, followed by a biological cleaning step which must be compact and salt-tolerant, indicating that it would be a form of biofilm reactor. The system may also require a sorption filter or a form of precipitation to remove metals, radioactive components, or any non-degradable organic chemicals for the sake of that the discharge has no ecotoxicological effects to the recipient.



8 MANAGEMENT OF LIQUID RESIDUALS

As the increase in wastewater exceeded the available disposal methods during 2004 to 2009 with consequences for surface water quality there was a need for new methods in waste management. At the same time regulations were put into place to address waste disposal, shifting treatment methods from surface discharges to reuse, injection wells, and advanced waste treatment.

Reuse has already proven very flexible at diminishing large quantities waste, with an enormous increase between 2009 and 2011. However, reuse does not permanently omit waste and has limitations regarding the quality and timing of wastewater recovery. Advanced waste treatment options are producing increasing volumes of concentrated liquid as well as solid waste. Therefore, the regulatory authorities need to consider how to increase safe, viable alternatives to surface discharges by supporting reuse and advanced waste treatment to manage ever increasing wastewater volumes.

When the supply of wastewater exceeds the demand, the excess requires disposal. In Pennsylvania some of this wastewater was sent to publicly owned treatment works (POTWs) from 2007 through mid-2011. However, the practices for management of liquid residuals are similar as for untreated hydraulic fracturing wastewaters, although the reduced volumes tend to lower costs (Hammer and VanBriesen, 2012).

On the other hand, are the concentrations of contaminants higher. The concentrated liquids are mixed with other wastes and have been disposed of in landfills if the liquid concentration is low enough. If the liquid residual is not re-injected into a disposal well, an advanced treatment to remove salts would be required before surface water discharge to meet NPDES permit requirements and protect the water quality for downstream users and drinking water utilities. Due to some compounds of concentrated waste can by-pass or impact municipal wastewater treatment plants (Linarić et al., 2013; Hammer and VanBriesen, 2012), special care should be obtained. High salt concentrations and some metals, in particular, will reduce or inhibit microbiological treatment at municipal wastewater systems such as activated sludge treatment (Linarić et al., 2013).

Since 2011 waste water disposal in Pennsylvania has been solely by injection into Class II salt water disposal wells instead of POTWs (Rassenfoss 2011).

The disposal of wastewaters may be regulated through federal standards. NPDES effluent standards under the Clean Water Act do apply when such wastewater is discharged to a surface water body, (see

<https://www.netl.doe.gov/research/coal/crosscutting/pwmis/fed-state-regulations/epa>)

There is a zero discharge standard for direct discharge of oil and gas wastewater under the Clean Water Act, meaning that it may not be discharged to surface water without first being treated. Generally this treatment is performed at an industrial treatment facility.



9 OTHER DISCHARGE

The environmental impact and water pollution caused by deicing salt. Salt the most commonly used deicing chemical in the United States; it is spread at a rate of approximately 20 million tons per year. The U.S. Environmental Protection Agency does not regulate road salt but acknowledges that best management practices are used to protect drinking water interests close to treated highways and salt storage sites from contamination with road salt runoff. Almost all of the produced brine used for de-icing in the U.S. comes from conventional oil and gas wells or from naturally occurring deposits. Hydraulic fracking that includes part of New York, Ohio, and Pennsylvania produces high volumes of wastewater that can pose risks to humans and the environment if not treated, recycled, or safely disposed. One alternative method for disposing of the wastewater is to spread it on roads for dust and ice control, due to waste waters high salt content. However, Environmental Protection Agency (EPA) and the Natural Resources Defense Council (NRDC) advise against spreading wastewater on roads because of potentially exposes drinking water to natural contaminants, radioactive constituents, and drilling chemicals. New York, Ohio, and Pennsylvania permit the use of production brine from fracking operations to be applied to roads as a deicer based on its chemical composition, application rate, and other criteria. Some local governments in New York have also prohibited the practice by passing ordinances banning fracking and waste disposal. Massachusetts and Vermont have banned or are attempting to ban fracking and wastewater disposal. Ohio allows spreading brine from fracking wells on roads for dust and ice control.

A study analyzed roadside sediment where produced brine from wells had been spread as a deicer and found elevated levels of radium, strontium, calcium and sodium, Skalak et al. 2014. The results from the study showed that the use of road spreading of brines from conventional wells for deicing resulted in accumulation of Ra-226 and strontium, calcium and sodium in soil and sediment adjacent to roads.



10 UNDERGROUND INJECTION

In many states of the US, as Texas, North Dakota and Montana, deep-well underground injection is a normal method for the disposal of fracking fluids and other substances from shale gas extraction operations. However, in Pennsylvania the use of deep-well injection was outlawed some time ago. Consequently, fracking companies operating in Pennsylvania, which prefer deep-well inject of their wastewater, must have it trucked to Ohio for deposition. This rise a potential risk issue relating to transporting large volumes of wastewater and the municipalities are concerned about the safety of high numbers of trucks traveling on rural roads and through small towns and also problems with heavy trucks traveling on these roads.

The wells classified as Class II wells are used only to inject wastewater deriving from oil and gas production. Class II wastewater are primarily brines that are brought to the surface while producing oil and gas. Brines are separated from hydrocarbons at the surface and reinjected into the same or similar underground formations for disposal. Wastewater from hydraulic fracturing activities can also be injected into Class II wells. It is estimated that more than 8 mill m³ of wastewater are injected in the United States every day. Most these injection wells are situated in Texas, California, Oklahoma, and Kansas. Class II disposal wells make up about 20 percent of the total number of Class II wells. Approximately 180,000 Class II wells are in operation in the United States. A reliable national estimate of the amount of hydraulic fracturing wastewater injected into Class II wells has been difficult to calculate due to lack of available on data injection volumes specific to hydraulic fracturing operations that are compiled and able to be compared among states. Also, wastewater management methods are not well registered in all states. The decision to inject wastewater into Class IID wells depends on legislation, cost and on the proximity of the production well to the disposal well. For gas producers, underground injection is usually the least expensive management strategy unless significant trucking is needed to transport the wastewater to a disposal well (U.S. GAO, 2012).

Where injection is available at the other shale gas plays, the injection wells can be either onsite wells operated by the gas producer or offsite third-party commercial disposal wells. As necessary, the flowback and produced water are injected into a deep formation that has sufficient porosity and transmissivity to accept the water. Texas has about suitable 7,900 Class IID wells, with an estimated daily disposal volume of approximately 1.5 mill m³/day. This large disposal capacity is consistent with suitable geology and the demand for wastewater disposal associated with a mature and active oil and gas industry. Opposite situation is found in Pennsylvania, where less than 10% of the wastewater management in is via Class IID wells (PA DEP, 2015a) as the state has only nine injection wells. Wastewater is generally transported out of state when being managed through injection into Class IID wells.

Wastewater may be disposed into Class II injection wells regulated under the Underground Injection Control Program under the Safe Drinking Water Act, Clark and Veil, 2009. More than 98% of this volume was managed via some form of underground injection, with 40% injected into Class II wells. The local availability of Class IID wells and the capacity to accept large volumes of wastewater may begin to be affected by



recent state actions concerning seismic activity associated with injection (U.S. EPA, 2014).

Should the managing of hydraulic fracturing wastewater via underground injection be limited in some way or become less economically feasible, operators might adjust their wastewater management programs in to more local practices such as treatment and discharge or reuse. Any new wastewater management decisions would then have to be evaluated in terms of potential impacts on drinking water resources.



11 ONSITE TREATMENT - NEW APPLICATIONS

Massachusetts Institute of Technology researchers believe electro-dialysis shows promise in accomplishing the same goal. The process isn't new, developed over 50 years ago to desalinate brackish water or seawater, or for food processing and other uses. But it has not been used with waters of such high salinity, according to the researchers. The team found electro-dialysis actually works better with higher salt concentrations because water conducts electricity better at higher concentrations. By desalination the water in stages and to levels that fall short of potable standards but enough to be reused for fracking, they believe electro-dialysis has the potential to reduce costs and minimize disposal of contaminated water. Engineers still must determine the most effective level of salinity for fracking, say the researchers. Although initial capital costs are higher and there are increased risks for explosion, the company says drilling chemicals remain below ground and operators can recover up to 25% more products.



12 SOLID WASTE AND RESIDUALS

Just after the fracking of the shale, large quantities of water that are produced contain residues of the drilling mud, clay and sand, which are used for fracturing and possibly cuttings of shale. These inorganic components will settle upon storage and afterwards be treated as solid waste. Flowback and produced water from the well will increasingly consist of formation water from the fractured shale layers. Formation water is supersaturated with calcium, magnesium and strontium, which is likely precipitate as carbonates at equilibrium with the atmosphere. For instance concentrations of the ions in the formation water, it can be expected that the water being produced from a mature well has a total concentration of dissolved salts of, typically, 240 (170-350) kg / m³ and that will precipitate 60 (20-130) kg carbonate minerals per m³. It will therefore be produced near the wellpad, whether the creation of wastewater treatment plants in the wells, or the water is run off to external purification. Controlled precipitations of carbonate minerals can be carried out by aerate the wastewater during storage, in order to avoid precipitations in the equipment afterwards. As part of the treatment, chemicals may be added to the fracking wastewater to precipitate salts and metals and just like the wastewater from the plant, plant operators must have a place to send the precipitates to. However, the solid waste might be a potential risk to the quality of drinking water resources if contaminants leach to groundwater or surface water. Depending of the origin of the shales solid wastes might contain TENORMs and hence be problematic due to the possibility of radon emissions from the landfill (Walter et al., 2012). In Pennsylvania requires alarms to be set at all municipal landfills, with a trigger set at 10 µR / h above background radiation. Texas has set a radioactivity limit by waste disposed by burial to less than 30 pCi/g radium or 150 pCi / g of other radionuclides. In Pennsylvania a study showed that radium was detected in leachate from 34 of 51 landfills, with radium-226 concentrations ranging from 54 to 416 pCi / L, and radium-228 ranging from 2.5 to 1100 pCi/L (PA DEP, 2015). Radioactive material (TENORM) in wastewaters may cause residual wastes to have elevated gamma radiation emissions (Kappel et al., 2013, Zhang et al., 2014). Silva et al. (2012) estimated a radium-226 concentration of 58 pCi / g in sludge from lime softening processes, a level that would necessitate disposal of low level radioactive waste. A study calculated that typical solids produced by precipitation processes designed to remove barium and strontium from Marcellus Shale wastewater would contain between 2,571 and 18,087 pCi/g of radium in the barium sulfate precipitate (Zhang et al., 2014).

The accumulation of heavy metals from the formation of water in the organic sludge would be limited, since the organics that form the organic sludge, are mainly present in the wastewater in the initial phase of production. Since most of the water comes from the injection liquid, there will be a slight contamination with potentially toxic metals and radioactive materials from the formation water. A study in Pennsylvania on the potential leaching of barium, calcium, sodium, and strontium from sludge generated at a CWT receiving hydraulic fracturing wastewaters, Countess et al. (2014). The results showed that the extent of leaching varied by constituent and by fluid type, but illustrate the possibility of leaching of these constituents from landfills to surface water and groundwater. The solid residuals have to be treated for example with thickening,



stabilization, anaerobic digestion and dewatering prior to disposal. The solid residuals are then typically sent to a landfill, land applied, or incinerated (Morillon et al., 2002). Activities relating to the establishment and operation of a facility for the exploitation of shale gas can lead to the generation of waste requiring further handling. Ordinary waste such as municipal waste, combustible waste, construction waste etc., obtained by the establishment and operation of drill site, can be disposed of through municipal waste systems, and will not be treated further.



13 POTENTIAL EFFECTS OF CONTAMINATED SOILS

The most problematic substances in fracturing fluid and flowback water has a negative impact on the topsoil quality. Effect of land is not specifically mentioned in the EU Commission's guidance (EC 2014), which can be interpreted to emissions of fracking fluid and flowback water to land is only likely to occur with spills and accidents. Consciously release to the soil will be against the Environmental Protection Act intention that emissions must not be at risk of harming the environment. This is mainly due to the content of salts, organic pollutants and metal ions, which is expected to be high, as well as a possible content of radioactive substances. Consciously release to or spread on the ground is unlikely. Most substances that negatively affect ground and surface water will also have a negative effect on soil environment. The focus should therefore be on the waste associated with handling, transport and storage in lined sedimentation. The entire drilling is expected to take place in a closed system, so waste to land will only be done by accident; either corrosion, burst pipes, faulty handling of the drill site or by accident. The drilling site is expected to be a paved area with controlled drainage, then release to land will occur outside the sealed area and the road network or leak in the sealed area. Spills on the ground can consist of fracturing fluid supplied to the well, or drilling mud, drill cuttings and flowback water which is discharged from the well. Generally, both the drill cuttings, drilling fluids, fracturing fluids and flowback water contain substances which will pollute the soil; including salts, inorganic trace elements and hazardous organic compounds and radioactive substances, Maguire -Boyle and Barron 2014.



14 FINAL REMARKS

There are a number of preventive measures that can be taken to avoid waste and negative environmental impacts. EU Commission in a Recommendation to Member States (EU Commission, 2014) examined the minimum principles for the production of gas from shale formations.

Supervisors should ensure that operators, i.e. the companies which carry out exploration and possible production, conduct the characterization and risk assessment for the potential exploration and production as well as for the surrounding area above and below ground. The risk assessment should be based on adequate data makes it possible to characterize the potential exploration and production area and to identify all potential exposure pathways.

Regulators should also ensure that operators:

- Project-specific water management plans
- Ensure an adequate treatment plan for wastewater of different composition
- ensure wellpad, well design and construction are environmental safe by accidents or leaks
- That the use of chemical substances by hydraulic fracturing is minimized.

An important part of the EU Commission's recommendation is baseline studies. If you want to investigate whether an environmental parameter has changed as a result of shale gas exploration or production, one must necessarily know how things were before you started. Therefore, the operator should determine the environmental status (baseline) for the site and the surrounding area above and below ground, which could potentially be affected by the activities. Baseline studies should be reported to supervisors before activity begins. The results from the baseline survey should be used as reference in the subsequent monitoring, and at each plant development. In addition to the environmental parameters identified in the baseline survey, operators should monitor the following operational parameters: a) the exact composition of fracturing fluid for each well, b) the amount of water used for the fracturing of each well, c) the pressure used during fracturing, d) the liquids that come to the surface after hydraulic fracturing: backflow, quantities, properties, amounts recycled and / or treated volumes for each well, e) atmospheric emissions of methane, volatile organic compounds and other gases which may be harmful to the environment.

The Authority should also ensure that baseline studies and monitoring must results are reported and published, as well as to the operators to publish information on the chemicals and the amounts of water intended to be used and the quantities that ultimately was used for hydraulic fracturing for each well.

As can be seen, there is a risk of pollution associated with the water flowback. Flowback water can contain many trace elements released from the pierced formation and deep formation water with high salt content. In the vicinity of the drill site there should be a contingency plan in the form of powerful pumps and large containers so that the effects of waste on the surface can be reduced by rapid inflation of the spill. The liquid is often heavy compared to the upper groundwater and it may be necessary to



make a proper remedial pumping, which pumped groundwater to prevent contamination spreading in groundwater. Spread of pollutants from leaky wells for groundwater or via groundwater to surface water can also be prevented by remedial pumping.

The high consumption of groundwater in the fracturing fluid can cause a local reduction in the groundwater. The extent of draw down will depend on the hydrogeological conditions. Draw down can cause that parts of the aquifer containing reduced substances may be oxygenated. In the case of organic layer, revenue from the organic matter with invasive oxygen could result in sentences. In the case of pyritic ferrous iron layer may cause oxidation of the pyrite high sulfate concentrations and release of trace elements such as Ni, Co and As from the pyrite. If in connection with the monitoring observed signs of oxidation of the reducing substances in the groundwater should draw down reduced. The lowering of groundwater will reduce the inflow of groundwater into streams and lakes. This can cause problems for the ecosystems found in streams and lakes. Especially in the summer where a very large part of the flow in some rivers consists of groundwater should be aware of this. The problems can be somewhat dispelled by the prior hydrogeological modeling and derived sizing and alignment in space and time.

Flowback water has the potential to affect the quality of drinking water resources if it enters into a surface or groundwater body used as a drinking water resource. This can occur through spills at wellpads, or during transport of flowback. Specific impacts depend upon the spill itself, the environmental conditions surrounding the spill, water body and watershed characteristics, and the composition of the spilled fluid. Flowback and produced water may contain toxic constituents and can potentially render water unpalatable or unsafe to drink. Conclusive determination of impacts to water resources depends on commitment of resources to the implementation of sampling, analysis and evaluation strategies

The extent of the accidental spill is difficult to quantify but likely large spills immediately should be purified, while less continuous oozing spills can be more difficult to detect. This may cause a need for monitoring of soil and groundwater in relation to wellpads. The current situation in the ground and play its chemical composition and scope will therefore be crucial for the environmental impact. This should be specifically examined by every boring site in preparation for action in case of spills.

In addition to the negative impact of the soil will waste from fracturing fluid and flowback water on soil be a risk and have effects on groundwater infiltration of salts, inorganic and organic substances.

Wastewater and drill cuttings could potentially contain radioactive substances as radium and radon in a catchall that will require special handling and disposal. In addition to the radiation risks for people the radioactivity will also cause a radiation hazard to soil, the environment and a land. The spilled on the ground will therefore be implemented measures depending on the use of land, so the radiation hazard to humans and agricultural minimized.



15 CONCLUSIONS

Landscape impact consists primarily of land take to wellpads and the development of abstraction landscape. This means the cumulative impacts of the spatial distribution of the number of drilling sites and the distance between them are essential. Information about specific effects on the landscape, which is useful in an EU perspective, is sparse. The area of wellpad is shown in the literature to be between 1- 5 ha. To minimize the impact on the landscape and risk for spills an evaluation can and should be made in the advance by analysis of the drilling site and infrastructure located in the countryside. In connection with the drilling process a substantial amounts of cuttings will be produced during the creation of the deep well. Cuttings are expected to contain methane and additives from the drilling mud and high content of organic carbons. This means that the most hydrophobic organic additives in drilling mud can be tied to shale material and released over a longer time horizon by leaching from a waste treatment facility or by the subsequent deposition. In addition to organic compounds, the cuttings have a relatively high content of inorganic trace elements that are bound in the reduced sulfur compounds (pyrite), which in turn can lead to a decrease in pH which ultimately leads to increased mobility of inorganic trace elements.

Chemicals used in hydraulic fracturing and drilling chemicals are usually transported to the drilling site in tankers, stored and mixed on site. Although these chemicals seldom exceeding 2% of the fracturing fluid, the total amount of chemicals may be significant. Accidents are a possible loss of travel to the surface and groundwater if the traffic accident creates chemical spills.

Shale gas extraction causes also carrying material for the commencement of drilling, as well as personnel, equipment and raw materials in connection with each fracturing. The brines or pore water from deep formations contain large amounts of salt and salt in the wastewater is expected to pose a significant problem. A possible influence on groundwater, soil and freshwater has to clarified how high salinity will have implications for the choice of treatment technology. Ordinary biological / chemical treatment plants are sensitive to elevated salt concentrations, and as ultrafiltration or evaporation will lead to greater amounts of salt and concentrated salt solution that is subsequently to be handled.

There is little data that can be used to predict the wastewater production from European shale plant. If we estimate a wastewater production as of US shale gas wells, one can expect that a well produces on average about 13,000 m³ and that half will come in the first year. The handling of the large quantities of wastewater requires extensive transportation and storage facilities as well as several links in handling procedures. The risk of injection and the deposit of flowback water in the subsurface will bring a significant risk of groundwater and surface water contamination. Although this seems unlikely to be the practice in EU, as in those cases where the excess fracturing fluid deposited in sealed wells on the drilling site, a risk of leakage through fractures and macropores in the soil to nearby aquifers and surface water could occur.

Flowback water generated during drilling contains suspended solids in concentrations typically 500-1,000 mg / L but generally the contribution of suspended solids to be relatively modest in relation to the waste generated by the drilling process. At present, it requires further investigation of the leaching characteristics of waste types to assess



whether the waste types can be received on ordinary Danish landfills for inert mineral, mixed or hazardous wastes without additional pre-merchant activities.

Wastewater from shale gas production is always expected to be purified biologically before discharge so that there are only acceptable low residues of organic chemicals in the water. Based on the overview of fracturing chemicals used in Europe, it is considered possible to find chemicals that are biodegradable in wastewater treatment plants, and this is expected to be an important parameter for the choice of chemicals to the composition of fracturing fluids in the EU.

In general, the treatment for the purpose of discharge could be divided into two ways, depending on the receiving area of water tolerance for the supply of salt. If the water body cannot tolerate salt stress, water treatment, consist of a membrane filtration, which produces clean water that can be discharged without toxic effects. The membrane filtration produces a very saline concentrate, containing all the residues of organic chemicals from the fracturing fluid. This concentrate will be taken away for treatment at an industrial wastewater treatment plant. An existing wastewater treatment plants will often have a large dilution capacity because you can mix flow back water with other wastewater streams, which can dilute the salt concentration so as not to affect the biological treatment process for organic chemicals. The presence of municipal wastewater treatment plants will be advantageous because there will typically be a relatively shorter transport of wastewater. However, it is necessary to consider whether the salt concentration is and may become too high in a possible municipal wastewater treatment plants. There are several systems to treat industrial wastewater, which will be more useful for treating wastewater from shale.

In relation to waste management, one can expect that it is necessary to pretreat the waste before final disposal. It may therefore be necessary to relate to a time-dependent increase in leaching from landfilled shale waste in the general waste characterization. At release to soil / land surface, it should be kept under continuous monitoring of compliance with limits. Exceeding the limits will result in reduced applications of soil or demands for removal and cleaning. With regard to the impacts of soil at any spills, there is a need for monitoring of current conditions in the subsurface, at each drilling sites, in preparation for action in plan of spills. If the spill affects the quality of soil purification can take place, for example by chemical or biological purification, but often will extend over a longer period. An alternative is the removal of the contaminated soil. The extent to which the US experience with loads of local infrastructure will be the same in the EU requires the assessment of individual locations. Mitigation measures include locating wells associated with the major road network, well away from the city and with the minimum requirements for running through urban areas for material transport to / from the whole.



16 REFERENCES

- Adams, M. B. 2011. Land application of hydrofracturing fluids damages a deciduous forest stand in West Virginia. *J. Environ. Qual.* 40 (4), 1340–1344.
- Alanco. 2012. New subsidiary Alanco Energy Services, Inc. to provide produced water disposal services to natural gas industry. Alanco.
http://www.alanco.com/news_040912.asp
- Arnaud, C.H. 2015. Figuring out fracking wastewater. *Chemical Engineering News* March 16: 8-12.
- Bacher, D. 2013. Oil company fined \$60,000 for illegally discharging fracking fluid. Available online at
https://www.indybay.org/newsitems/2013/11/17/18746493.php?show_comments=1 (accessed March 6, 2015).
- Barbot, E. Vidic, N. S. Gregory, K. B. Vidic, R. D. 2013. Spatial and temporal correlation of water quality parameters of produced waters from Devonian-age shale following hydraulic fracturing. *Environ. Sci. Technol.* 47(6) 2562-2569.
- Barnes, T. 2010. 2 drillers fined for Pennsylvania gas well blowout. Available online at
<http://www.post-gazette.com/news/environment/2010/07/14/2-drillers-fined-for-pennsylvania-gas-well-blowout/stories/201007140241>.
- Benko, K.L, Drewes, J.E. 2008. Produced water in the Western United States: Geographical distribution, occurrence, and composition. *Environ. Eng. Sci.* 25: 239-246.
- Bergman, A., Weber F.A., Meiners, G.H., Müller, F. 2014. Potential water-related environmental risks of hydraulic fracturing employed in exploration and exploitation of unconventional natural gas reservoirs in Germany. *Environmental Sciences Europe* 26:10.
- Bishop, R.E. 2011. *Chemical and Biological Risk Assessment for Natural Gas Extraction in New York*.
http://www.hydrorelief.org/frackdata/economics/Risk_Assessment_Natural_Gas_Extraction.pdf
- Blauch, ME; Myers, RR; Moore, TR; Lipinski, BA. 2009. Marcellus shale post-frac flowback waters - where is all the salt coming from and what are the implications? In *Proceedings of the SPE Eastern Regional Meeting*. Richardson, TX: Society of Petroleum Engineers.
- Bloys, B., Davis, N., Smoken, B., Bailey, L., Houwen, O, Reid, P., Sherwood, J., Fraser, L., Hodder, M. 1994. *Designing and Managing Drilling Fluid*. *Oilfield Review*. April 1994, 33-43.
- Boschee, P. 2014. Produced and flowback water recycling and reuse: Economics, limitations, and technology. *Oil and Gas Facilities* 3: 16-22.
- Brittingham, M.C., Maloney, K.O., Farag, A.M., Harper, D.D., Bowen, Z.H. 2014. Ecological risks of shale oil and gas development to wildlife, aquatic resources and their habitats. *Environ. Sci. Technol.* 48: 11034-11047.
- Broderick, J., Anderson, K., Wood, R., Gilbert, P., Sharmina, M., Footitt, A., Glynn, S., Nicholls, F. 2011. *Shale gas: an updated assessment of environmental and climate change impacts*. A report commissioned by The Co-operative and undertaken by researchers at the Tyndall Centre. University of Manchester.



- Burton, G.A., Basu, N., Ellis, B.R., Kapo, K.E., Entekin, S., Nadelhoffer, K. 2014. Hydraulic “Fracking”: Are surface water impacts an ecological concern? *Environmental Toxicology and Chemistry* 33: 1679-1689.
- Chapman, EC; Capo, RC; Stewart, BW; Kirby, CS; Hammack, RW; Schroeder, KT; Edenborn, HM. 2012. Geochemical and strontium isotope characterization of produced waters from Marcellus Shale natural gas extraction. *Environ. Sci. Technol.* 46: 3545-3553.
- Chen, H, Carter, K E. 2016. Water usage for natural gas production through hydraulic fracturing in the United States from 2008 to 2014. *J. Environmental Management* 170: 152-159
- Clark, CE; Horner, RM; Harto, CB. 2013. Life Cycle Water Consumption for Shale Gas and Conventional Natural Gas. *Environ. Sci. Technol.* 47: 11829-11836. <http://dx.doi.org/10.1021/es4013855>
- Council of Canadian Academies. 2014. Environmental Impacts of Shale Gas Extraction in Canada. Ottawa (ON): The Expert Panel on Harnessing Science and Technology to Understand the Environmental Impacts of Shale Gas Extraction. Council of Canadian Academies.
- Countess, S; Boardman, G; Hammack, R; Hakala, A; Sharma, S; Parks, J. 2014. Evaluating leachability of residual solids from hydraulic fracturing in the Marcellus shale. In *Shale energy engineering 2014: Technical challenges, environmental issues, and public policy*. Reston, VA: American Society of Civil Engineers. <http://dx.doi.org/10.1061/9780784413654.012>
- Davies, RJ; Mathias, SA; Moss, J; Hustoft, S; Newport, L. 2012. Hydraulic fractures: How far can they go? *Marine and Petroleum Geology* 37: 1-6.
- Dresel, P. E., and A. W. Rose, 2010, Chemistry and origin of oil and gas well brines in western Pennsylvania: Pennsylvania Geological Survey, 48 p.
- Easton, J. 2014. Optimizing fracking wastewater management. *Pollution Engineering* January 13.
- Eiceman, GA. 1986. Hazardous organic wastes from natural gas production, processing and distribution: Environmental fates. (WRRRI report, no. 227). New Mexico: Water Resources Research Institute. <http://wrrri.nmsu.edu/publish/techrpt/abstracts/abs227.html>
- Engelder, T., 2012, Capillary tension and imbibition sequester frack fluid in Marcellus gas shale: *Proceedings of the National Academy of Sciences*, v. 109, p. E3625.
- Engelder, T., L. M. Cathles, and L. T. Bryndzia, 2014, The fate of residual treatment water in gas shale: *The Journal of Unconventional Oil and Gas Resources*, v. 7, p. 33–48
- Environment Canada. 2004. Threats to Water Availability in Canada. <http://www.ec.gc.ca/inre-nwri/default.asp?lang=En&n=0CD66675-1>
- EU, 2013. JRC Scientific and Policy Reports. Assessment of the use of substances in hydraulic fracturing of shale gas reservoirs under REACH. September, 2013. https://ec.europa.eu/jrc/sites/default/files/req_jrc83512_assessment_use_substances_hydraulic_fracturing_shale_gas_reach.pdf.
- European Commission. 2014. European Commission DG Environment. Technical support for assessing the need for a risk management framework for unconventional gas extraction. Doc Reg No: 32834rr014i7



- Fakhru'l-Razi, A; Pendashteh, A; Abdullah, LC; Biak, DR; Madaeni, SS; Abidin, ZZ. 2009. Review of technologies for oil and gas produced water treatment [Review]. *J Hazard Mater* 170: 530-551.
- Falk, H, Lavergren, H, Bergbäck, B. 2006. Metal mobility in alum shale from Öland, Sweden. *Journal of Geochemical Exploration* 90: 157–165
- Geiver, L. 2013. Frac water treatment yields positive results for Houston Co. Retrieved from <http://www.thebakken.com/articles/20/frac-water-treatment-yields-positive-results-for-houston-co>
- Greenhunter (Greenhunter Resources). 2014. Oilfield water management solutions. Available online at <http://www.greenhunterenergy.com/operations/owms.htm>
- Gregory, KB; Vidic, RD; Dzombak, DA. 2011. Water management challenges associated with the production of shale gas by hydraulic fracturing. *Elements* 7: 181-186.
- Haluszczak, L., 2011. Geochemical Analysis of Flow Back and Production Waters from Oil and Gas Wells in Pennsylvania. Senior thesis, Department of Geosciences, Penn State Univ.
- Haluszczak, L.O., Rose A.W. & Kump, L.R. 2013: Geochemical evaluation of flowback brine from Marcellus gas wells in Pennsylvania, USA. *Applied Geochemistry* 28, 55-61.
- Hammer, R; VanBriesen, J. 2012. In frackings wake: New rules are needed to protect our health and environment from contaminated wastewater. New York, NY: Natural Resources Defense Council. <http://www.nrdc.org/energy/files/fracking-wastewater-fullreport.pdf>
- Harkness, J. S.; Dwyer, G. S.; Warner, N. R.; Parker, K. M.; Mitch, W. A.; Vengosh, 2015. A. Iodide, bromide, and ammonium in hydraulic fracturing and oil and gas wastewaters: environmental implications. *Environ. Sci. Technol.* 49: 1955–1963.
- Hayes, T. 2009. Sampling and analysis of water streams associated with the development of Marcellus shale gas. Des Plaines, IL: Marcellus Shale Coalition. <http://eidmarcellus.org/wp-content/uploads/2012/11/MSCCommission-Report.pdf>
- Hosterman, J.W., Patterson, S.H. 1992. Bentonite and Fuller's Earth Resources of the United States. U.S. Geological Survey Professional Paper 1522. Washington, D.C.: United States Government Printing Office.
- Jeng, A.S., 1992. Weathering of some Norwegian alum shales: II. Laboratory simulations to study the influence of aging, acidification and liming on heavy metal release. *Acta Agriculturae Scandinavica. Section B, Soil and Plant Science* 42, 76–87
- Kappel, WM; Williams, JH; Szabo, Z. 2013. Water resources and shale gas/oil production in the Appalachian basin critical issues and evolving developments. (Open-File Report 20131137). Troy, NY: U.S. Geological Survey. <http://pubs.usgs.gov/of/2013/1137/pdf/ofr2013-1137.pdf>
- Kargbo, D.K., Wilhelm, R.G. & Campell, D.J. 2010: Natural Gas Plays in the Marcellus Shale: Challenges and Potential Opportunities. *Environ. Sci. Technol.* 44: 5679-5684.
- King, G.E. 2012. Hydraulic Fracturing 101: What Every Representative, Environmentalist, Regulator, Reporter, Investor, University Researcher, Neighbor and Engineer Should Know About Estimating Frac Risk and Improving Frac



- Performance in Unconventional Gas and Oil Wells. SPE 152596. Society of Petroleum Engineers.
- Kondash A, Vengosh A. 2015. Water Footprint of Hydraulic Fracturing. Environ. Sci. Technol. Lett. In press, DOI: 10.1021/acs.estlett.5b00211
- Lavergren, U, Åström, M E, Bergbäck, B, Holmström, H. 2009 Mobility of trace elements in black shale assessed by leaching tests and sequential chemical extraction. *Geochemistry: Exploration, Environment Analysis*, V. 9: 71–79
- Leventhal, J S: 1991. Comparison of organic geochemistry and metal enrichment in two black shales: Cambrian Alum Shale of Sweden and Devonian Chattanooga Shale of United States. *Mineral. Deposita* 26: 104–112
- Linarić, M; Markić, M; Sipos, L. 2013. High salinity wastewater treatment. *Water Sci. Technol.* 68: 1400–1405
- Lutz, B. D.; Lewis, A. N.; Doyle, M. W. 2013. Generation, transport, and disposal of wastewater associated with Marcellus Shale gas development. *Water Resour. Res.* 49: 647–656.
- Maguire-Boyle S J., Barron AR. 2014. Organic compounds in produced waters from shale gas wells. *Environ Sci. Processes Impacts* 16. 2237–2248.
- McBroom M, Thomas T, Zhang Y. 2012. Soil erosion and surface water quality impacts of natural gas development in east Texas, USA. *Water* 4: 944–958.
- Michalski R, Ficek A. 2015. Environmental pollution by chemical substances used in the shale gas extraction – a review. *Desalination and water treatment*. Doi: 10.1080/19443994.2015.1017331.
- Minnich, K. 2011. A water chemistry perspective on flowback reuse with several case studies. Minnich, K.
http://www2.epa.gov/sites/production/files/documents/10_Minnich_-_Chemistry_508.pdf
- Morillon, A., J. F. Vidalie, U. S. Hamzah, S. Suripno, and E. K. Hadinoto, 2002, "Drilling and Waste Management", SPE 73931, presented at the SPE International Conference on Health, Safety, and the Environment in Oil and Gas Exploration and Production, March 20–22, 2002.
- Murali Mohan, A; Hartsock, A; Hammack, RW; Vidic, RD; Gregory, KB. 2013. Microbial communities in flowback water impoundments from hydraulic fracturing for recovery of shale gas. *FEMS Microbiol. Ecol.*
<http://dx.doi.org/10.1111/1574-6941.12183>
- North Dakota Department of Health. 2015. Oil field environmental incident summary, incident 20150107160242. Available online at
http://www.ndhealth.gov/EHS/FOIA/Spills/Summary_Reports/20150107160242_Summary_Report.pdf
- Norwegian Public Roads Administration 2005. Recycled materials in road and airfield pavements – overcoming barriers. Conference proceedings from workshop on Recycled Materials in Road and Airfield Pavements, 2005/6/25, Oslo, Norway. Norwegian Public Roads Administration, Oslo, Norway
- Olmstead, S. M.; Muehlenbachs, L. A.; Shih, J.-S.; Chu, Z.; Krupnick, 2013. A. Shale gas development impacts on surface water quality in Pennsylvania. *Proc. Natl. Acad. Sci. U. S. A.* 110 (13), 4962–4967.



- Orem WH, Tatu CA, Lerch HE, Rice CA, Bartos TT, Bates AL, Tewalt S, Corum MD. 2007 Organic compounds in produced waters from coalbed natural gas wells in the Powder River Basin, Wyoming, USA. *Appl. Geochem* 22:2240–2256.
- Orem, W; Tatu, C; Varonka, M; Lerch, H; Bates, A; Engle, M; Crosby, L; McIntosh, J. 2014. Organic substances in produced and formation water from unconventional natural gas extraction in coal and shale. *Int J Coal Geol* 126: 20-31.
- PA DEP, 2009. (Pennsylvania Department of Environmental Protection). Inspection Report, inspection record #1835041, enforcement record #251134. Harrisburg, PA: Commonwealth of Pennsylvania Department of Environmental Protection, Oil and Gas Management Program.
- PA DEP, 2010. (Pennsylvania Department of Environmental Protection). DEP Fines Atlas Resources for drilling wastewater spill in Washington County. Available online at <http://www.portal.state.pa.us/portal/server.pt/community/newsroom/14287?id=13595&typeid=1> (accessed February 13, 2014).
- Parker, K. M.; Zeng, T.; Harkness, J.; Vengosh, A.; Mitch, W. A. 2014. Enhanced formation of disinfection byproducts in shale gas wastewater-impacted drinking water supplies. *Environ. Sci. Technol.* 48, 11161–11169.
- Pashin, JC; McIntyre-Redden, MR; Mann, SD; Kopaska-Merkel, DC; Varonka, M; Orem, W. 2014. Relationships between water and gas chemistry in mature coalbed methane reservoirs of the Black Warrior Basin. *Int J Coal Geol* 126: 92-105.
- Pedersen, L.B., Ingerslev, M. 2007 Alternativer til vejsalt som tømiddel i glatførebekæmpelse. Arbejdsrapport nr. 36, Skov & Landskab, Hørsholm, 2007. 49 s. (in Danish).
- Poth, C. W., 1962, The occurrence of brine in western Pennsylvania: Pennsylvania Geological Survey Bulletin, v. M47, p. 1–53.
- Purestream (Purestream Services). 2013. Purestream services will begin commercial operations to treat Eagle Ford Shale produced and frac flow-back water in Gonzalez County, Texas. Retrieved from <http://purestreamtechnology.com/index.php/component/content/article/72-press-releases/206-purestream-services-will-begin-commercial-operations-to-treat-eagle-ford-shale-produced-and-frac-flow-back-water-in-gonzalez-county-texas>
- Rassenfoss, S. 2011. From flowback to fracturing: Water recycling grows in the Marcellus shale. *J Pet Tech* 63: 48-51.
- Reuters. 2014. UPDATE 2-oil well in North Dakota out of control, leaking. Available online at <http://www.reuters.com/article/2014/02/14/energy-crude-blowout-idUSL2N0LJ15820140214> (accessed March 2, 2015).
- Richter, BC; Kreitler, CW. 1993. Geochemical techniques for identifying sources of ground-water salinization. Boca Raton, FL: CRC Press. <http://www.crcpress.com/product/isbn/9781566700009>
- Rose, A. W., and P. E. Dresel, 1990, Deep brines in Pennsylvania, in S. K. Majumdar, E. W. Miller, and R. R. Parizek, eds., *Water Resources in Pennsylvania: Availability, Quality and Management, Volume 12: Phillipsburg, New Jersey*, The Pennsylvania Academy of Science Publications, p. 420–431.



- Rowan, E.; Engle, M.; Kirby, C.; Kraemer, T. 2011. Radium content of oil-and gas-field produced waters in the Northern Appalachian basin (USA)—Summary and discussion of data. U.S. Geological Survey Scientific Investigations Report 2011-5135, U.S. Geological Survey.
- Schlumberger 2015. Drilling mud Schlumberger Oilfield Glossary.
http://www.glossary.oilfield.slb.com/en/Terms/d/drilling_mud.aspx
- Shafer, L. 2011. Water recycling and purification in the Pinedale anticline field: results from the anticline disposal project. In 2011 SPE Americas E&P health, safety, security & environmental conference. Richardson, TX: Society of Petroleum Engineers. <http://dx.doi.org/10.2118/141448-MS>
- Silva, JM; Matis, H; Kostedt, WL; Watkins, V. 2012. Produced water pretreatment for water recovery and salt production. (08122-36). Niskayuna, NY: Research Partnership to Secure Energy for America.
http://www.rpsea.org/media/files/project/18621900/08122-36-FR-Pretreatment_Water_Mgt_Frac_Water_Reuse_Salt-01-26-12.pdf
- Sionix (Sionix Corporation). 2011. Sionix to build Bakken water treatment plant. Retrieved from http://www.rigzone.com/news/article_pf.asp?a_id=110613
- Sirivedhin, T; Dallbauman, L. 2004. Organic matrix in produced water from the Osage-Skiatook petroleum environmental research site, Osage county, Oklahoma. *Chemosphere* 57: 463-469.
- Skalak, K. J.; Engle, M. A.; Rowan, E. L.; Jolly, G. D.; Conko, K.M.; Benthem, A. J.; Draemer, T. F. 2014. Surface disposal of produced waters in western and southwestern Pennsylvania: Potential for accumulation of alkali-earth elements in sediments. *Int. J. Coal Geol.* 126, 162–170.
- Sumi, L. (2004). Pit pollution: Backgrounder on the issues, with a New Mexico case study. Washington, DC: Earthworks: Oil and Gas Accountability Project.
<http://www.earthworkSACTION.org/files/publications/PitReport.pdf>
- U.S. Department of Justice. 2014. Company owner sentenced to more than two years in prison for dumping fracking waste in Mahoning River tributary. Available online at <http://www.justice.gov/usao/ohn/news/2014/05auglupo.html> (accessed March 4, 2015).
- U.S. EPA, 2000. Development document for effluent limitations guidelines and standards for the centralized waste treatment industry. (821R00020). Washington, DC: U.S. Environmental Protection Agency.
- U.S. EPA, 2006. National Primary Drinking Water Regulations: Stage 2 Disinfectants and Disinfection Byproducts Rule.
<http://water.epa.gov/lawsregs/rulesregs/sdwa/stage2/>
- U.S. EPA, 2011. Chemicals used in hydraulic fracturing. United States House of Representatives committee on Energy and Commerce, April 2011.
<http://democrats.energycommerce.house.gov/sites/default/files/documents/Hydraulic-Fracturing-Chemicals-2011-4-18.pdf>.
- U.S. EPA, 2012. Oil and Natural Gas Sector: Standards of Performance for Crude Oil and Natural Gas Production, Transmission and Distribution: Background Supplemental Technical Support Document for the Final New Source Performance Standards (April 2012).



- U.S. EPA, 2014. Minimizing and managing potential impacts of injection-induced seismicity from class II disposal wells: Practical approaches [EPA Report]. Washington, D.C. <http://www.epa.gov/r5water/uic/ntwg/pdfs/induced-seismicity-201502.pdf>
- U.S. EPA, 2015a. Assessment of the Potential Impacts of Hydraulic Fracturing for Oil and Gas on Drinking Water Resources (EPA/600/R-15/047a Jun 15 2015) http://www2.epa.gov/sites/production/files/2015-06/documents/hf_es_erd_jun2015.pdf
- U.S. EPA, 2015b. Effluent data from Pennsylvania wastewater treatment plants per Region 3 Information Request. Data provided by request. Washington, D.C.: Region 3, U.S. Environmental Protection Agency.
- U.S. EPA, 2015c. National primary drinking water regulations public notification rule and consumer confidence report rule health effects language. (parts 141.201, and 141.151), (U.S. Government Publishing Office 2015i). <http://www.ecfr.gov/cgi-bin/text-idx?SID=4d25ec04bc44e54b1efdf307855f3185&node=pt40.23.141&rgn=div5>
- U.S. EPA, 2015d. Technical development document for proposed effluent limitation guidelines and standards for oil and gas extraction. (EPA-821-R-15-003). Washington, D.C. <http://water.epa.gov/scitech/wastetech/guide/oilandgas/unconv.cfm>
- U.S. GAO 2012. (U.S. Government Accountability Office). Energy-water nexus: Information on the quantity, quality, and management of water produced during oil and gas production. (GAO-12-156). Washington, D.C. <http://www.gao.gov/products/GAO-12-156>
- UK, 2014. Department of Energy & Climate Change. Fracking UK shale: Water, Feb 2014. "Fracking UK shale: Water"
- Vaidyanathan, G. 2013b. XTO comes out swinging against 'unwarranted' criminal charges in Pa. E&E News 0.
- Van Voast, WA. 2003. Geochemical signature of formation waters associated with coalbed methane. AAPG Bulletin 87: 667-676.
- Vengosh A, Jackson RB, Warner N, Darrah TH, Kondash A. 2014. A critical review of risks to water resources from unconventional shale gas development and hydraulic fracturing in the United States. Environmental science and technology. 48, 8334-8348.
- Walsh, J M. 2013. Water management for hydraulic fracturing in unconventional resources Part 1. Oil and Gas Facilities 2.
- Walter, G R, Benke, R R, Pickett, D A. 2012. Effect of biogas generation on radon emissions from landfills receiving radium-bearing waste from shale gas development. J Air Waste Manag. Assoc. 62(9):1040-9
- Warner, N. R., R. B. Jackson, T. H. Darrah, S. G. Osborn, A. Down, K. Zhao, A. White, and A. Vengosh, 2012, Geochemical evidence for possible natural migration of Marcellus Formation brine to shallow aquifers in Pennsylvania: Proceedings of the National Academy of Sciences, v. 109, p. 11,961–11,966.
- Warner, N. R.; Christie, C. A.; Jackson, R. B.; Vengosh, A. 2013. Impacts of shale gas wastewater disposal on water quality in Western Pennsylvania. Environ. Sci. Technol. 47: 11849–11857.
- Webb, CH; Nagghappan, L; Smart, G; Hoblitzell, J; Franks, R. 2009. Desalination of oilfield-produced water at the San Ardo water reclamation facility, Ca. In SPE



- Western regional meeting 2009. Richardson, TX: Society of Petroleum Engineers.
<http://dx.doi.org/10.2118/121520-MS>
- Williams HFL, Havens DL, Banks KE, Wachal DJ. 2008. Field based monitoring of sediment runoff from natural gas well sites in Denton County, Texas, USA. *Environmental Geology* 55: 1463-1471.
- Wilson, J. M.; VanBriesen, J. M. 2012. Oil and gas produced water management and surface drinking water sources in Pennsylvania. *Environ. Pract.*, 14 (4), 288–300.
- Zhang, T. 2015: Origin and Fate of Radium in Flowback and Produced Water from Marcellus Shale Gas Exploration. Doctoral Dissertation, University of Pittsburgh, 154 sider.
- Zhang, T.; Gregory, K.; Hammack, R. W.; Vidic, R. D. 2014. Coprecipitation of radium with barium and strontium sulfate and its impact on the fate of radium during treatment of produced water from unconventional gas extraction. *Environ. Sci. Technol.* 48: 4596–4603.