Project Acronym and Title:

M4ShaleGas - Measuring, monitoring, mitigating and managing the environmental impact of shale gas

CONCENTRATION BASELINES AND RAW SHALE GAS COMPOSITIONS

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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 CO_2 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 (CO_2 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

It has been argued that shale gas has already proved to be a game changer in the U.S. energy market. The European Commission in its Energy Roadmap 2050 identified gas as a critical energy source for the transformation of the energy system to a system with lower CO_2 emissions but environmental impact, namely the GHG emissions, associated with large scale shale gas development is of major concern to the public, policy makers and other stakeholders.
Besides identification of emissions to air associated with the Shale gas exploration and exploitation, issues that were addressed in previous reports, the aim for this report is to discuss the relevance of atmospheric concentration baselines. Furthermore the raw shale gas composition is investigated as part of the shale gas components may be used to identify gas leakages.
Concentration baselines of methane and other components in shale gas, can provide a standard of the pre-shale gas development state of the environment. The important objective of baselines is that upon implementation of shale gas activities there is clear and transparent information about the atmospheric composition before and after the activities started.
There is evidence that shale gas extraction has proceeded, in most cases, without adequate environmental baseline data being collected. This makes it difficult to properly identify, quantify and characterize environmental impacts that may be associated with shale gas development. Minimising these impacts on the atmosphere requires the monitoring of ambient air quality prior to and during operations, and the prevention and minimization of greenhouse gases and toxic chemicals emissions. Also a main concern already addressed in M4ShaleGas, when considering the global climate impact of a potential European Shale gas industry, is the leakage of methane. For establishing pre-fracturing baseline data as well as providing an integrated assessment of emissions from shale gas operation sites, needs to be developed and a low-cost sampling strategy needs to be settled. The shale gas industry is new in Europe and the UK is presented as a case study regarding the implementation of baselines.

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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 2015[1]). 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 CO_2 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 (CO_2 and methane (CH4)) 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

The M4ShaleGas program focuses on reviewing and improving existing best practices and innovative technologies for measuring, monitoring, mitigating and managing the environmental impact of shale gas exploration and exploitation in Europe. In previous reports (D14.1, D15.1 and D16.1) of the project the baseline concentration and the raw gas composition were identified as major knowledge gaps (Costa et al. 2015, Denier van der Gon et al. 2015, Costa et al. 2016).

To assess the impact of shale gas exploration on the atmosphere it is imperative to monitoring to ambient air quality prior to and during operations. The development of a low-cost sampling strategy, suitable for establishing pre-operations baseline data as well as an integrated monitoring program to assess the emissions from shale gas operation sites is needed.

The sub program 3 of M4ShaleGas project addresses the global climate impact of a potential European Shale gas industry. The main concern in this topic is the leakage of methane. The identification of methane leakage from Shale gas activities is complex due to the existence of several other CH_4 sources (e.g. cattle, landfills, wetlands. However, a unique feature of natural gas and shale gas is the presence of other hydrocarbons in the raw gas that are not emitted by other potential CH_4 sources. If measured at the same time as CH_4 concentrations, the information on the accompanying hydrocarbons can potentially be used as a tracer to distinguish the fossil fuel gas sources from the other CH_4 sources. The construction of a raw (shale) gas composition database will be a instrumental to identify leakage during the shale gas operations.In this particular activity of the M4Shalegas project it is investigate how atmospheric monitoring could be used to detect and identify any significant leakages from a potential future shale gas industry. The approach contains the following subtasks:

1. Identification of suitable tracers in (shale) gas
2. Construction of a (raw) gas composition database
3. Base line concentrations of selected tracer(s) over Europe
4. The location of a potential European shale gas industry and associated estimated potential loss rates.
5. Modelling the release and dispersion of the tracer(s) under various leakage scenarios
6. Compiling detection limits of suitable monitoring instruments and location of instruments in such a way that exceedance of acceptable loss rates would be picked up by the system.

In this deliverable especially steps 1-3 are addressed. A short introduction to step 4 is present but will be further executed in the final year of M4ShaleGas together with step 5-6.

1.3 Aims of this report

The aim for this report, in the frame of the Monitoring and mitigating emissions to atmosphere is to set the scenario of the concentration baselines and raw shale gas compositions and thereby to help to quantify atmospheric emissions resulting from shale gas operations. It will focus on the importance of monitoring baselines prior shale gas development and in the raw gas composition in order to promote the construction of a data base for Europe.

1.4 Structure of the report

This report is divided in six chapters. The first one is an introductory chapter where the objectives of the M4ShaleGas and of this report are presented. The importance of a baseline monitoring program to assess with accuracy the impact of shale gas exploration on the atmosphere is address in Chapter 2. Chapter 3 reports the issues related with raw gas composition. In this chapter the raw natural gas composition and shale gas composition are presented and the importance of a construction of a (raw) gas composition database is addressed. Chapter 4 presents monitoring strategies for emissions related to shale gas operations. In Chapter 5 some conclusion remarks are presented. References are listed in Chapter 6.

2 CONCENTRATION BASELINES

2.1 Introduction

Baseline observations can provide a standard of the pre-shale gas development state of the environment. In previous reports this issue was identified as an important knowledge gap. In fact baseline monitoring of air quality are missing in several regions, where there is a strong possibility of future shale gas exploration. Evidence shows that shale gas extraction has proceeded, in most cases, without sufficient environmental baseline data being collected. This makes it difficult to properly identify, quantify and characterize environmental impacts that may be associated with shale gas development.

Minimising the impact of shale gas exploration on the atmosphere requires the monitoring of ambient air quality prior to and during operations, and the prevention and minimization of greenhouse gases and toxic chemicals emissions. A low-cost sampling strategy, suitable for establishing pre-fracturing baseline data as well as providing an integrated assessment of emissions from shale gas operation sites, needs to be developed.

A baseline can be considered as the level or quantity of emissions in a specific scenario where there is a projection of possible activities to be implemented in future. Thus the baseline and the baseline scenario are hypothetical in nature and depend on a number of factors, such as demand for services, availability of various resources to implement the activity, environmental and other policies relevant to the activity to be implemented (Shrestha et al. 2005). There was not found relevant data on the literature about baseline measurements established before the shale gas exploration starts. Although the baseline monitoring of water, air and soil should be established at the moment that a potential site is identified (https://www.taskforceonshalegas.uk/shalegasissues).The implementation of a baseline air monitoring program is imperative to be able to assess the total emissions related with shale gas operations. In fact, any monitoring programme should be designed to provide indicative information on background levels.

A baseline air monitoring program should identify and characterize targeted air pollutants, most frequently described from monitoring and emission measurements, as well as those expected from Hydraulic fracturing activities, and establish ambient air conditions prior to start-up of potential emission sources from shale gas operations. The baseline monitoring should take place before and during well development, production and gas treatment. This allows a "before-during-after" comparison essential to characterize air quality impacts. This program has to be planned for at least one year accounting for ambient variations and the baseline sites have to be located at a spatial scale defined as "urban" or "regional" (NCDENR 2013).

The objectives of a Baseline study are (NCDENR 2013):

1. Measure target pollutant concentrations at least for one-year.
2. Collect enough data for the annual average concentrations estimation.

3. Implement monitoring program in line with existing monitoring systems to enable data comparability.
4. Apply standard monitoring protocols ensuring consistent high quality data.
5. Use conventional data reduction, data summary and analysis techniques to characterize the data.

In the literature, in addition to GHG emissions of CH_4, CO_2 and nitrogen oxides (NO_x), fugitive emissions from shale gas production can release volatile organic compounds (VOCs), aldehydes (formaldehyde, acetaldehyde) and hazardous air pollutants (HAPs). The VOCs include among other substances benzene, toluene, ethyl benzene, xylenes, hexanes, 2,2,4-trimethylpentane, styrene. The concentrations of six air pollutants, whose regional ambient air levels are regulated by the Environmental Protection Agency (EPA), are often discussed. These pollutants are: ozone, particulate matter (PM), carbon monoxide (CO), nitrogen oxides (NO_x), sulphur oxides (SO_x), and lead.

The National Emissions Inventory (NEI) implemented in the USA is a comprehensive and detailed estimate of air emissions of criteria pollutants, criteria precursors, and hazardous air pollutants from air emissions sources. The NEI is published every three years using data from the Emissions Inventory System (EIS) obtained by State, Local, and Tribal air agencies blend with data from other sources (EPA).

In Europe there is an air pollutant emission inventory guidebook which may be used to prepare emission inventories of the substances which, are emitted into the atmosphere as the result of human and natural activity. Pollutant emissions are divided into sectors which include: energy; industrial processes and product use; agriculture; waste; other. The Guidebook is structured to provide the user with general information on the basic principles of constructing an emissions inventory and the specific estimation methods and emission factors to compile one (EMEP/EEA 2016). European countries report their calculated emissions to the EU and to EMEP. The official reported emissions are available at the EMEP centre for emission inventories and projections (www.ceip.at/).

2.1.1 Establishing Baselines - The Key Elements

Different sources may influence air quality such as, cars, trucks, aircraft, biomass boilers and incinerators. Total emissions from the different sources and the distance to the receptor influences air pollution concentrations and air quality impacts.

The monitoring should not only provide a snapshot of the emissions and concentrations but should consider the changes over time (Jacobs 2014).

Methane is one of the main concerns regarding GHG emissions.

The understanding of background levels and the setting of baselines with the aim of minimizing the potential methane emissions requires the adoption of good practices for environmental management supported by strong regulation and high quality data (Skea

2015).The methodology to set the baseline scenario has to be in compliance with national or local regulations.

An integrated monitoring study of methane emissions may be a suitable mean of distinguishing the contribution of different sources of methane to ambient levels. This subject is linked with the potential presence of other methane sources (e.g. landfill, agricultural activity or gas pipeline/compressor station) and may also be important in the case of high levels of methane that are of potential concern in the local area. All data analysis needs to be carefully interpreted taking, also, into account the meteorological conditions of the site. This may require the implementation of a more intensive monitoring programme (Broomfield et al. 2014).

In the context of shale gas operations a monitoring programme is required to establish a baseline of methane levels and assess variations in methane concentrations during the different stages of Shale gas operations to verify the findings of preliminary calculations. Such report shall cover a timescale permitting both approval and implementation of the baseline monitoring module of the programme prior to the start of drilling operations (Broomfield et al. 2014).

The unconventional gas activities are still linked with major uncertainties considering the potential methane emissions. So, it is highly recommended that a strategic baseline monitoring should be implemented at representative shale gas exploration sites in Europe.

For new shale gas exploration the baseline measurements of methane needs to be required via permitting process. However if adequate methane baseline have already been carried out no further action is needed. The existence of this data would be useful for all stakeholders because it provides the baseline that sets the context for assessing any future measured data (Broomfield et al. 2014).

2.1.2 Monitoring technical guidance notes – key aspects

The UK Environment Agency provides a series of indications of the possible sources of uncertainty in the Technical Guidance Notes[2]: M2 (Environment Agency 2015), M3 (Environment Agency 2011), M8 (Environment Agency 2011a), M16 (Environment Agency 2012):

- The leakage in the sample handling line and losses to the walls of the sampling system must be quantified.
- The typical sources of uncertainty for instrumental methods include lack of linearity, zero drift, span drift, sensitivity to sample volume flow, to atmospheric pressure, to ambient temperature, to electrical voltage. Also, interferences from

[2] http://webarchive.nationalarchives.gov.uk/20140328084622/http:/www.environment-agency.gov.uk/business/regulation/31831.aspx

other gaseous components present in the flue gas, repeatability standard deviation in laboratory at span level, and calibration gas should be considered (Broomfield et al. 2014).

- The temperature and pressure measurements of sample gas volume at the gas meter have associated uncertainty. So, the uncertainty of the water vapour and oxygen concentrations must be included before reporting the result obtained at reference conditions.

- The portable emission monitoring systems can be used to make measurements in a wide variety of applications, such as fugitive emissions. For stack emission monitoring they may be used for indicative purposes. These systems have to comply with the Monitoring Certification Scheme for instruments, monitoring and analytical services.

- The continuous monitoring of emissions to air is desirable where the levels of emissions are environmentally significant and provides improved process control and public assurance. Relevant EC Directives (2000/76/EC, 2001/80/EC) require continuous monitoring, manual sampling and analysis methods.

- Monitoring standards should follow, in order of priority, as given in the IPPC Reference Document on the General Principles of Monitoring, (European Commission 2003):

    - Comité Européen de Normalisation (CEN)
    - International Organization for Standardization (ISO)
    - National standards

- Long term sampling programs should be implemented once short term sampling programmes are unlikely to give data representative of general conditions, e.g. meteorological conditions and source variations, which have significant effects on pollutant concentrations that are significantly affected by temporal variability.

- Open-path monitoring methods are the most suitable for fugitive emissions because they are usually emitted relatively close to the ground level, and are often monitored adjacent to the site boundary. However, in some occasions monitoring appreciably above ground level should be performed, e.g. when there is the need to remove the dominance of ground-level emissions in order to assess the impact of elevated releases.

- Methane is classified as a GHG and is also a VOC but not included in the definition of NMVOCs (Non-Methane Volatile Organic Compounds) as used in air quality reporting. There are two published CEN standards for measuring methane:

- manual method - EN ISO 25139:2011 – based on samples collection in an inert bag or canister, followed by analysis using gas chromatography in a laboratory.

- automated method - EN ISO 25140:2010 – uses an FID (Flame Ionization Detector) fitted with a catalytic converter which removes all organic compounds in the sample gas, except methane.

- Portable FIDs are also available for applications in fugitive emissions monitoring. However these simpler, unheated and portable FIDs have not the same accuracy and precision as the more complex and heated FIDs.

2.2 Case Studies

2.2.1 USA

A study regarding the issues of oil and gas exploration in the State and the use of horizontal drilling and hydraulic fracturing was requested to the Department of Environment and Natural Resources (DENR), in conjunction with other agencies in USA. This study made as one of the concluded remarks the need to collect baseline air quality information (NCDENR 2013). Following this study rules related to collection of baseline data in areas where oil and gas exploration were required (Session Law 2012). This responsibility is assigned to the Division of Air Quality (DAQ) which has the authority and expertise to accomplish baseline air monitoring objectives. This study also contains an assessment of the ambient monitoring network and a work plan to better characterize air quality in the areas identified for shale gas exploration and exploitation.

2.2.2 UK

The shale gas industry is new in Europe. The rational for monitoring emissions is linked to the potential effects emissions may have, either separately or collectively, for climate change, air quality and public and occupational health.

According to the British Geological Survey for areas where there is significant potential for shale gas exploitation the following actions should be undertaken by the government (http://www.bgs.ac.uk/research/groundwater/shaleGas/):

- inform communities and operators on baseline conditions;

- help regulators to improve their procedures for managing the UK shale gas industry;

- provide the stakeholders with information on the effects of shale gas extraction;

- improve the understanding of the sub surface and near-surface environment in the UK context of unconventional hydrocarbons;

- support development of new techniques for environmental monitoring;
- support industries with good practices in the development of unconventional hydrocarbons.

Here it is highlighted the integrated monitoring programme in the UK for the Lancashire proposed shale-gas well sites.
(source: http://www.bgs.ac.uk/research/groundwater/shaleGas/).

The study carried out in Lancashire site is the first independent, integrated monitoring programme with the aim of characterising the environmental baseline in an area with potential for the development of a UK shale-gas industry. Since December 2014, concentrations of background methane and carbon dioxide have been measured continuously as well as meteorological data.
A set-up for additional monitoring equipment includes air-quality parameters such as Particulate Matter (PM), NO_2, NMVOCs. The same monitoring design is foreseen for the Vale of Pickering (Yorkshire) site.

The British Geological Survey will conduct gas monitoring studies in soil and near surface. Background concentrations of CO_2, CH_4, O_2, hydrogen sulphide (H_2S) and radon (Rn) have been measured in the soil. Also, the CO_2 flux has also been measured. These data collected prior to shale gas operations in the area will provide baseline information.

It is interesting to know that the near–surface atmospheric gases (CO_2 and CH_4) were measured using laser gas analysers mounted on a quad bike or similar all–terrain vehicle. This methodology can provide continuous measurements as the vehicle is driven across the fields.

Vale of Pickering - site in Kirby Misperton
(http://www.bgs.ac.uk/research/groundwater/shaleGas/)

The activities of the monitoring programme are taking place between September 2015 and March 2017. In January 2016 the concentrations measurements of ozone (O_3), particulate matter (PM_1, $PM_{2.5}$, PM_4, and PM_{10}), nitrogen oxides (NO, NO_2 and NO_x), CH_4, non-methane hydrocarbons (NHMCs), H_2S and CO_2 as well as capturing meteorological information has been started.

3 RAW GAS COMPOSITION

3.1 Introduction

Shale gas is natural gas imprisoned within tiny pore spaces in shale formations. Shale is a compressed fine-grained laminated sedimentary rocks that were formed from mud silt, clay minerals, quartz, and small amounts of organic matter, fossils, carbonates and other minerals. Gas shale formations are usually black or dark due to the high organic content.

Shales are formed by the weathering of rocks and the transportation and deposit in lakes, river deltas and sea floor. Due to the action of anaerobic bacteria, dead plankton and animals and aquatic plants incorporated into the deposits are transformed into kerogen. This fossilized mixture of organic material when heated and subjected to high pressure is transformed into petroleum. When shale formation is buried even deeper, it reaches higher temperature and petroleum is converted into natural gas. Earth movement and rock compacting due to further burial may cause the migration of oil and gas from shale formations. However, same oil and gas will be kept within the shale, forming a potential shale oil or shale gas reservoirs.

The natural gas present in shale reservoirs has a similar composition to that of natural gas, they are both rich in methane that is the main component. The main difference between natural gas and shale gas is not the composition, but the geological and physical properties of the reservoirs. Shale reservoirs may contain oil and natural gas generated in the shale that usually has low permeability, around 0.001 mD (milidarcy). High conductivity channels in the form of fractures are created in shale reservoirs to allow the recovery of the gas.

Conventional natural gas is found in higher permeability reservoirs, usually higher than 0.1 mD in geological structural traps, which may include faults and anticlines and stratigraphic changes of rock types. Due to the presence of many and large pores inter connected, fluids can flow easily (Skea 2015).

3.2 Raw Natural Gas composition database

An extensive database of raw (well head) natural gas composition data was compiled from publically available data and from existing (partly confidential) databases by TNO. The focus was primarily on conventional on-shore natural gas production but for the UK and the Netherlands off-shore gas production was included as well. A large amount of data has been collected resulting in 2370 records of measured raw gas composition records. The best represented countries are the Netherlands, Germany and Poland, followed by Denmark and UK for which there is still considerable coverage and then finally some data for France, Italy and Romania. In spite of being one of Europe's major (associated) natural gas producers Norway is currently not included in the database due to legal complications between TNO and the holder of the Norwegian data, Gassco [note this had to do with liability of data use and whether the confidentiality agreement was valid under Norwegian law or under Dutch or Belgium law].

The observed frequency distribution of the ethane and propane molar fractions, as well as the molar fraction of total hydrocarbons higher than C1 relative to methane is shown in Figure 1. Ethane (blue bars) seems to be somewhat evenly distributed over the concentration range of 1 to 7%, but with still many incidences of a higher concentration, while propane (red bars) seems to occur in lower concentrations (primarily between 0 – 1% and to a lesser extent 1 – 2%). Hydrocarbons higher than C1 seem to be dominated by ethane that occurs in amounts between two and three times the amount of propane and making up about half of the total amount of higher hydrocarbons.

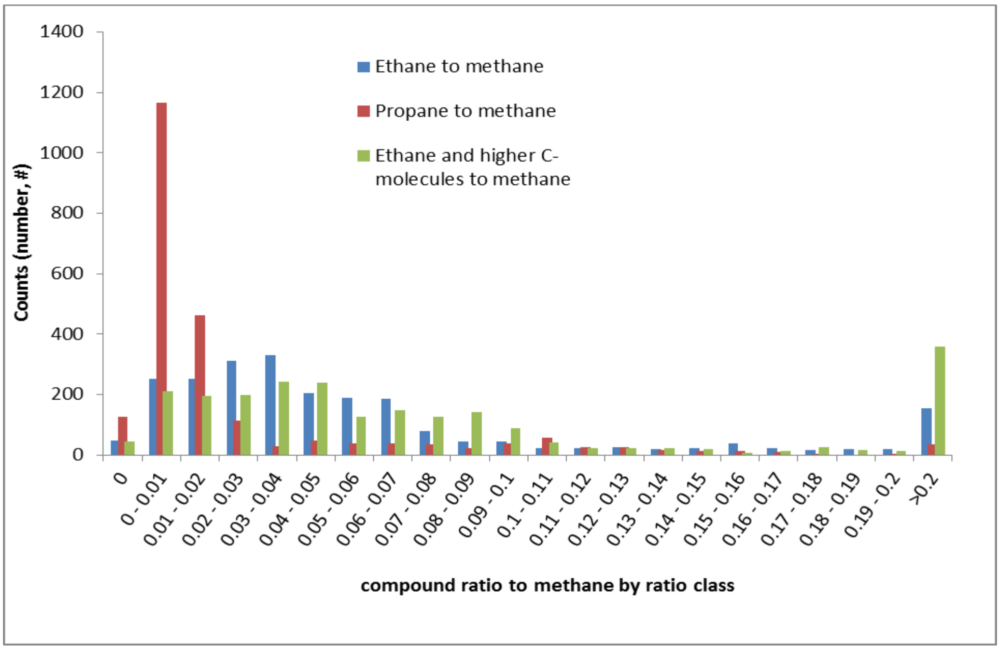

Figure 1. Frequency distribution of the ethane and propane molar fractions relative to methane, as well as the molar fraction of total hydrocarbons higher than C1 (in practice up to C7 in most cases) for all data in the TNO raw gas database.

Figure 2 shows the correlation of normalized (C1 = 1) propane (C3), butanes (C4) and pentanes (C5) molar fractions with the normalized fraction of ethane (C2). The Figure 2 shows that when the C2 fraction increases, so does the fraction of higher alkanes. For C3 to C5 reasonably robust linear dependencies on C2 are derived (Figure 2). The gas database also includes the longitude/latitude of the gas field and data on the stable isotope contents (when available), as well as the type of geological formation/reservoir and the reservoir dept.

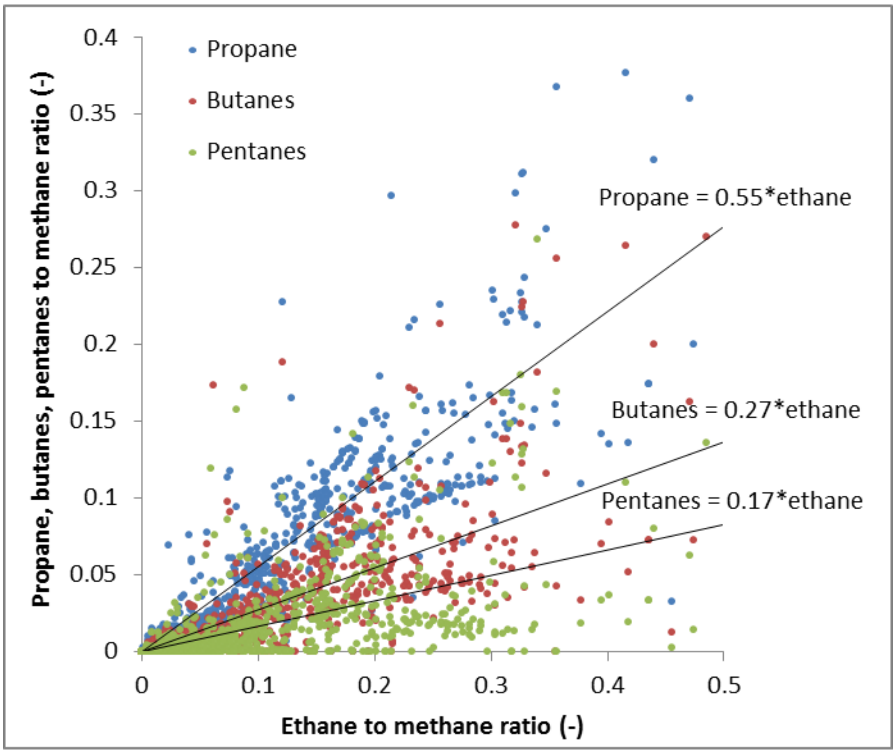

Figure 2. The correlation of propane (C3), butanes (C4) and pentanes (C5) molar fractions normalized against methane (C1 = 1) as a function of the normalized fraction of ethane (C2).

3.3 Raw shale gas

3.3.1 Impact from potential shale gas exploitation in Europe

Based on estimated reserves (by e.g. EIA 2013) eight major shale gas plays are identified in seven EU Member States. These plays are currently considered the most promising and form the basis for the proposed production scenario. Current best estimates of the risked recoverable reserves are used to assess the potential amount of gas that can be produced. Various other information sources are consulted to estimate the location, area and extent of the plays, as well as its average thermal maturity (which has important implications for the raw gas composition). The low, medium and high production scenarios are presented in Table 1. A more detailed description will be given in a next deliverable.

Table 1. Estimated shale gas production by country in a hypothetical future scenario.

Country	Play	Low production scenario 150 years (bcm)	Medium production scenario 70 years (bcm)	High production scenario 30 years (bcm)
GBR	Bowland Basin	5	10	24
POL	Lublin Basin	23	50	116
POL	Podlasie Basin			
POL	Baltic Basin			
NLD	Posidonia Shale	2	5	12
NLD	Geveric Member (Epen formation)			
DNK	Alum Shale	6	13	30
SWE	Alum Shale	2	4	9
DEU	Posidonia Shale	3	7	16
FRA	Paris Basin	23	50	116

3.3.2 Raw Shale Gas composition

There is no precise formula of natural shale gas, the main component is usually methane. Besides methane, typical composition of shale gas also includes: hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), nitrogen (N_2), and other different hydrocarbons, mainly ethane (C_2H_6), but also propane (C_3H_8), and butane (C_4H_{10}). Shale gas may also present other impurities hydrogen sulphide (H_2S), sulphur dioxide (SO_2), heavy hydrocarbons, helium (He), condensates, water, etc. Heavy liquid hydrocarbons found in shale gas include heptane, hexane, pentane, etc. These heavier hydrocarbons are separated in processing plants as liquids. Mercury may also be found in small concentrations.

Table 2. Shale gas composition at different sites and wells at Barnett in Dallas-Fort Worth area of Texas (Bullin and Krouskop 2009).

Site/Well	CH_4 (%)	C_2 (%)	C_3 (%)	CO_2 (%)	N_2 (%)
Barnett, USA/Well 1	80.3	8.1	2.3	1.4	7.9
Barnett, USA/Well 4	93.7	2.6	0.0	2.7	1.0
Marcellus, USA/Well 1	79.4	16.1	4.0	0.1	0.4
Marcellus, USA/Well 4	95.5	3.0	1.0	0.3	0.2
Antrim, USA/Well 1	27.5	3.5	1.0	3.0	65.0
Antrim, USA/Well 3	77.5	4.0	0.9	3.3	14.3

In Table 2 is shown typical shale gas composition at different sites and wells at the same reservoir. Shale gas composition may vary from area to area, depending on rocks type and formation and even wells in the same region may produce shale gas with different compositions (Bullin and Krouskop 2009). Shale gas from deposits in different areas may contain different percentages of the same basic compounds. Thus, the composition depends on the region in which the gas is originated.

On the other hand, natural shale gas found at a well has a composition different from that received by consumers due to pre-processing of the gas. The type of well that the gas comes from also affects its composition. For instance, the gas from shale gas wells is different from that obtained from oil wells or condensate wells.

This subject is further discussed in sub-chapter 3.3.3 Case Studies, where some information about USA and UK shale gas reservoirs is presented. Unfortunately, it was not possible to find information about Poland. Though some studies have been done in this country, information about Polish shale gas composition is not available.

3.3.3 Case Studies

3.3.3.1 USA

USA proved gas reserves have been increasing, mostly due to unconventional gas which includes shale, tight sands and coalbed methane. While unconventional gas proved reserves are increasing, conventional gas reserves are diminishing. In fact unconventional gas production accounts for 46% of the total USA production (Modern Shale Gas Development in the United States 2009). Shale gas reserves show a wide distribution along many USA states as shown in Figure 3.

Some of the more important shales areas, representing a large share of current and future gas production are: Barnett, Haynesville, and Fayetteville shales (in the South) and Marcellus, New Albany and Antrim (in the East and Midwest). USA annual production of shale gas has surpassed the predictions of EIA, mainly due to the high production of Barnett Shale in Texas.

However, shale gas composition is not the same all over these regions, requiring different gas processing technologies, mainly in what concerns high ethane and nitrogen contents and also other impurities like H_2S, CO_2, SO_2, etc.

Next some of the more important USA shale gas reservoirs: Barnett, Marcellus, Fayetteville, New Albany, Antrim, and Haynesville will be analysed.

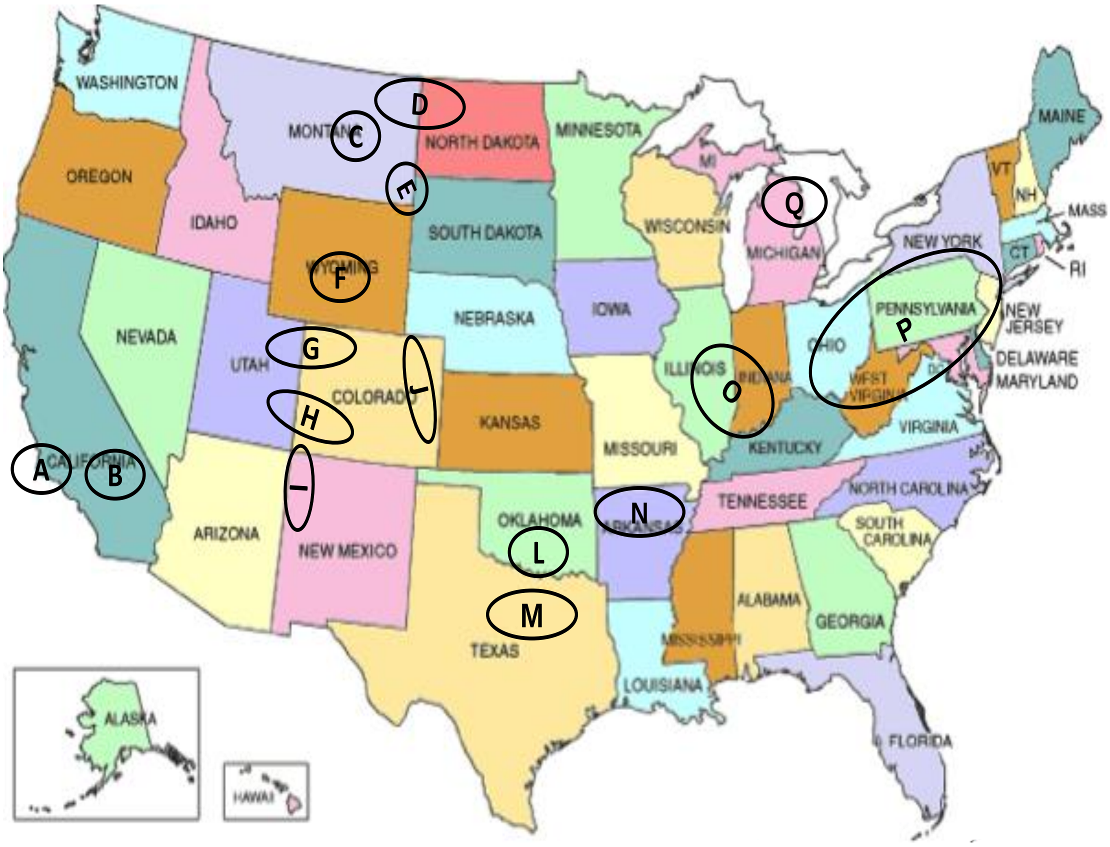

Figure 3. USA shale gas regions. A – Monterey, B – McClude, C – Bowdoin, D – Bakken, E – Cedar Creek, F – Wind River, G –Green River, H –Cane Creek, I –Lewis & Mancos, J – Niobrara, L –Woodford Caney, M –Barnett, N –Fayetteville, O - New Albany, P –Antrim, Q –Devonian (adapted from Bullin and Krouskop 2009).

Barnett Shale

The Barnett shale formation is around the Dallas-Fort Worth area of Texas and produces at depths between 1 981-2 896 m. The average production rate changes throughout the basin from $1.4x10^4$ to $11.3x10^4$ m^3/day with estimates of 8.5-9.9 m^3/ton of shale (Bullin and Krouskop 2009).

In Figure 4 are compared the typical shale gas composition at different wells at Barnett. Well 1 shows a great content of N_2, more than 7%, which requires treating to decrease it, but a more economic viable solution is the blending with another gas with more suitable composition. As shown in Figure 4 the difference between the highest (well 4) and the lowest CH_4 contents (well 1) is around 17%. This difference is much lower for C_2, around 7%. For all the other gaseous components these values are even lower between 3% for N_2 and 2% for CO_2. There is a much greater difference for CO_2, as contents between 0.3 and 2.7% were reported. There is a great increase in the amount of ethane (C_2) and propane (C_3) as the wells move west (Bullin and Krouskop 2009).

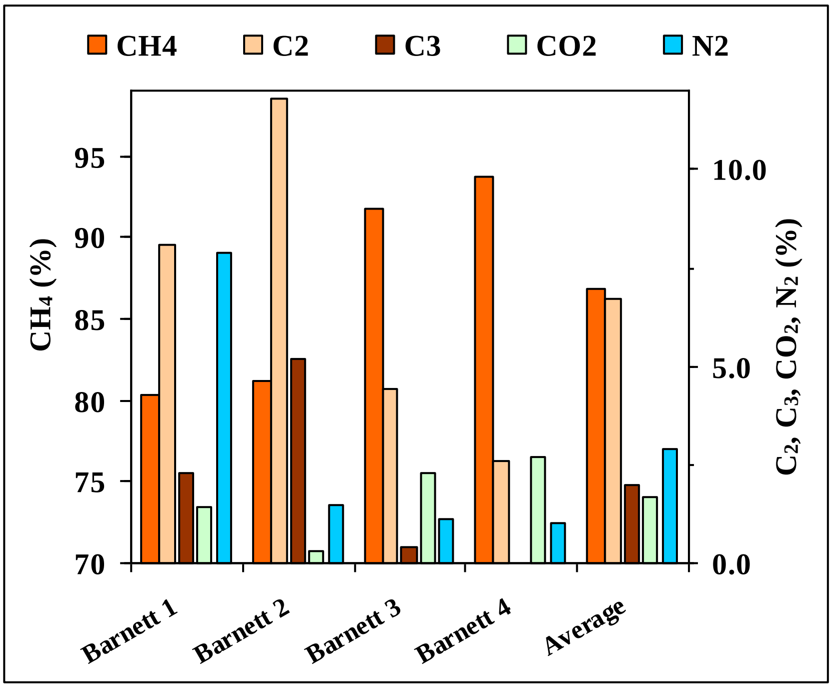

Figure 4. Variation of Barnett shale gas compositions at different wells and comparison with average composition (adapted from Bullin and Krouskop 2009).

Barnett operation includes compression, CO_2 treating with amine, cryogenic separation, and fractionation. Local regulations are wide and strict when operation occurs near urban areas, forcing the plants to move to less densely populated areas whenever possible. These regulations concern appearance (colour, landscaping, fences, and lighting) and operations (equipment height and noise level).

Marcellus Shale

The Marcellus shale reservoirs are in western Pennsylvania, Ohio, and West Virginia and have great potential. It reaches depths of 610-2 438 m^3 and 91-305 m^3. Initial production rates varied between $1.4x10^4$ to $11.3x10^4$ m^3/day with estimations of 1.7-2.8 m^3/ton of shale (Bullin and Krouskop 2009).

In Figure 5 are presented shale gas compositions at different wells. As shown in this Figure, gas is richer from east to west. The contents of CO_2 and N_2 are low, which is an advantage of Marcellus reserves. As this gas is quite dry it does not need NGL's removal for pipeline transportation. Some predictions refer that Marcellus shales could have as much gas as the Texas Barnett shale. The difference between the highest and the lowest CH_4 contents is around 20%. These differences are much higher for C_2 and C_3 concentrations, with values around 81% and 75%, respectively. There is a much greater difference for CO_2, as contents between 0.1 and 0.9% were reported.

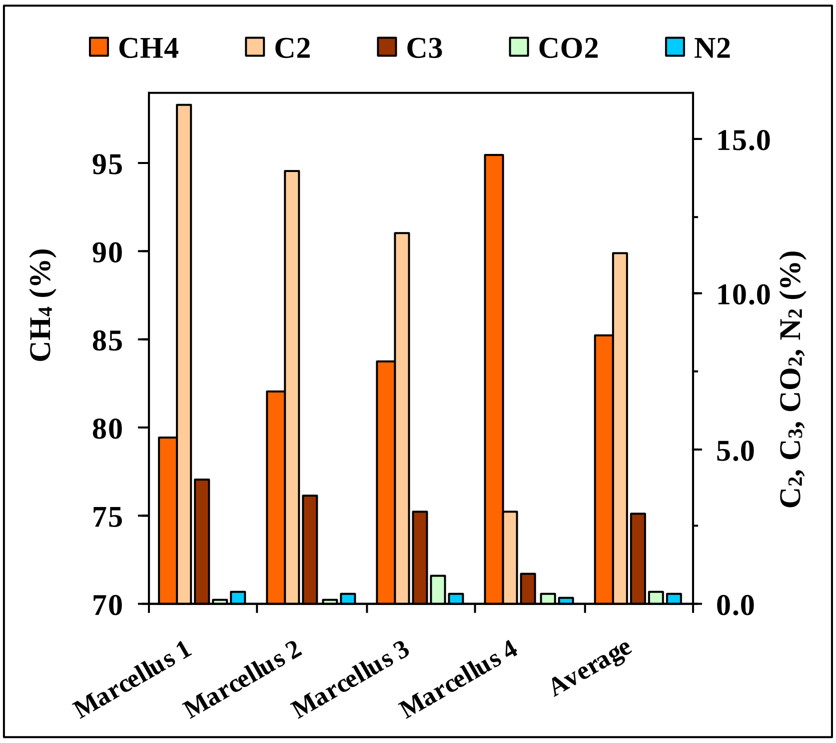

Figure 5. Variation of Marcellus shale gas compositions at different wells and comparison with average composition (adapted from Bullin and Krouskop 2009).

Fayetteville Shale

The Fayetteville shale is an unconventional gas reservoir situated on the Arkansas side of the Arkoma Basin. Shale thickness varies from 15-168 m at a depth of 457-1981 m. Initial production rates are 5 650 to 16 951 m^3/day for vertical wells and $2.8x10^4$ to 9.9 $x10^4$ m^3/day for horizontal ones. The production has increased, in 2003, to around $1.4x10^7$ m^3/day. The full scope of the Fayetteville shale is still unknown (Bullin and Krouskop 2009).

Table 3. Average shale gas composition in percentage at Fayetteville (adapted from Bullin and Krouskop, 2009).

Well	CH_4	C_2	C_3	CO_2	N_2
Average	97.3	1.0	0	1.0	0.7

In Table 3 is presented the average composition of shale gas at Fayetteville. Methane contents are quite high and the gas only requires dehydration to suit pipeline specifications.

New Albany Shale

The New Albany shale is Southern Illinois black shale that spreads through Indiana and Kentucky. It is 152-1 494 m deep and 30-122 m thick. Horizontal wells can have initial production rates of up to $5,6x10^4$ m^3/day, whilst vertical wells usually produce $7,1x10^5$ to $2,1\ x10^6$ m^3/day (Bullin and Krouskop 2009).

In Figure 6 are shown typical shale gas compositions at different wells at New Albany. CH_4 compositions of all 4 wells are quite similar to one another. In fact the difference between the highest and the lowest CH_4 is only 6%. For other gaseous components higher percentages were observed except for CO_2. The greatest variation difference between the highest and the lowest content was obtained for C_3.

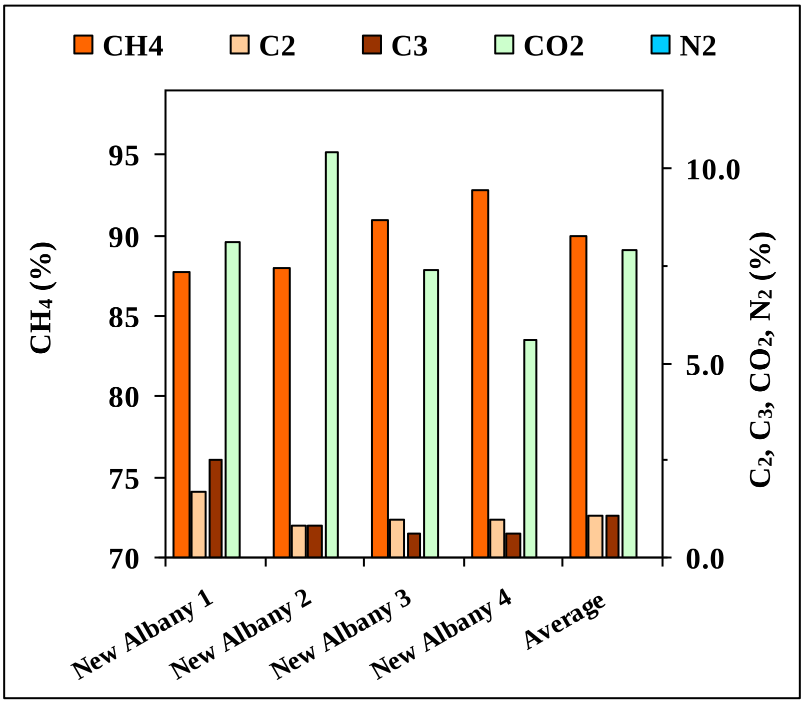

Figure 6. Variation of New Albany shale gas compositions at different wells and comparison with average composition (adapted from Bullin and Krouskop 2009).

Antrim Shale

The tax incentives of the 1980's for unconventional gas accelerated the development Antrim shale gas reservoirs in Michigan. Nowadays, there are more than 9 000 wells in Antrim that in total produce around 71 bcm (Bullin and Krouskop 2009).

The Antrim shale gas has the great advantage of being mostly biogenic, as methane is a bi-product of bacterial consumption of organic material in the shale. On the other hand, as substantial associated water is produced, central production facilities for dehydration, compression and disposal are required.

As shown in Figure 7, CO_2 content in shale gas produced at different wells vary from 0 to 9%, because CO_2 content gradually increases during a wells productive life and in some areas values around 30% may be obtained. CO_2 occurs naturally, being a byproduct of shale gas produced by desorption (Bullin and Krouskop 2009).

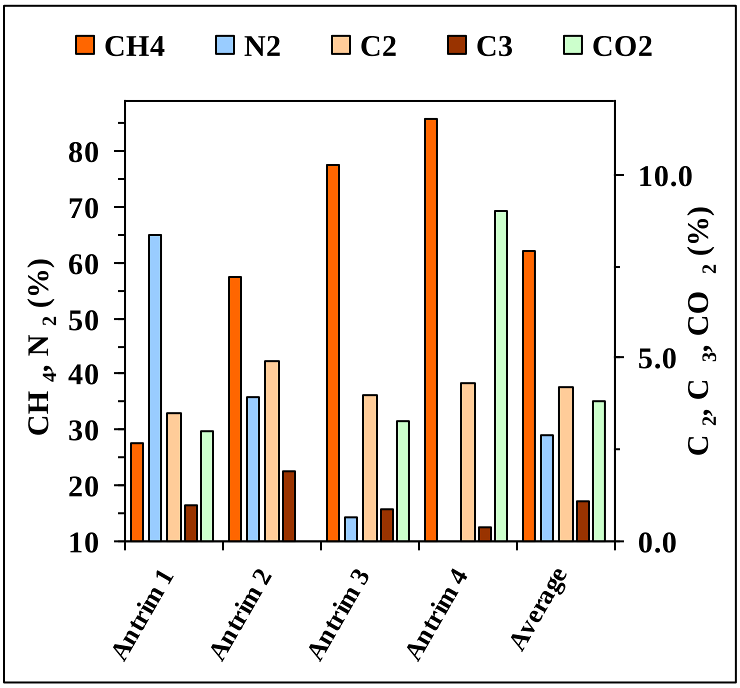

Figure 7. Variation of Antrim shale gas compositions at different wells and comparison with average composition (adapted from Bullin and Krouskop 2009).

Antrim shale gas reservoirs present great differences in gas composition depending on the well, as shown in Figure 7 the highest CH_4 content in well 4 was more than three times the lowest concentration found in well 1. Consequently, great differences were also found in N_2 contents.

Haynesville Shale

The Haynesville shale reservoirs are located in northern Louisiana and East Texas. The estimates for Haynesville show a large potential as the values are in the range from 2.8-9.3 m^3 of gas per ton of shale. The average production of each horizontal Haynesille wells is around $4.5x10^3$ m^3/day (Bullin and Krouskop 2009).

The depth is around 3 048+ m^3, being the bottom hole temperature around 177° C and the pressure between 20 and 28MPa (Bullin and Krouskop 2009). In Table 4 are shown average compositions of Haynesvilleshale gas. The relatively high contents of CO_2 require treatment with amines for its removal. The gas also needs to be treated for H_2S removal.

Table 4. Average shale gas composition in percentage at Haynesville (adapted from Bullin and Krouskop 2009).

Well	CH_4	C_2	C_3	CO_2	N_2
Average	95.0	0.1	0	4.8	0.1

The differences in shale gas composition obtained at several reservoirs are shown in Figure 8.

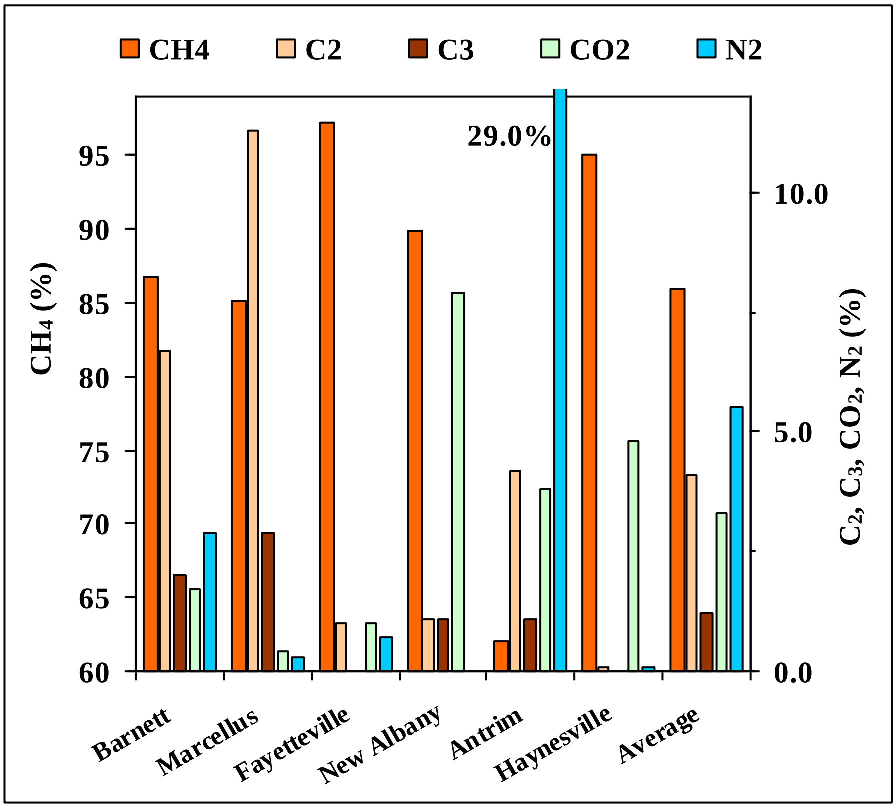

Figure 8. Variation of average shale gas compositions at different USA reservoirs (adapted from Bullin and Krouskop 2009).

The relatively high contents of CO_2 require treatment with amines for its removal. The gas also needs to be treated for H_2S removal. The average CH_4 content is around 86%, varying between 62% and 92.7%, the lowest content was found in Antrium. The second gaseous component with the highest variations is N_2, with the highest values found in Antrium. In general a low CH_4 content will correlate with a high N_2 or CO_2 content. Other gases (C_2, C_3 and CO_2) presented lower variations between the highest and the lowest contents.

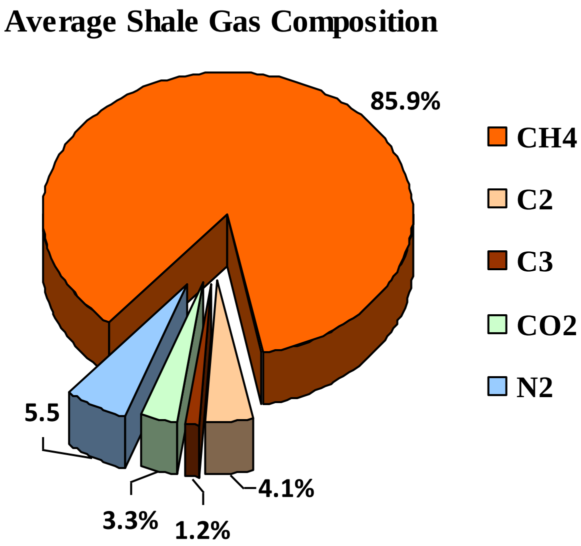

Figure 9. Average shale gas composition at different USA shale gas reservoirs (adapted from Bullin and Krouskop 2009).

Figure 9 presents the relative distribution of average shale gas composition for selected USA reservoirs. As show in this Figure, CH_4 concentration is much higher than all the others compounds. Ethane (C_2) and pentane (C_3) are also present, presenting C_3 the lowest content of gaseous hydrocarbons.

As hydrocarbons contain hydrogen and carbon, it is important to know total organic carbon (TOC) and Original hydrogen index (HI_o) values to evaluate shale quality. In the next sub-chapter (3.3.3.2 UK Case Studies) TOC and HI_o values found in USA basins will be compared to those of UK shale reservoirs whenever data is available.

3.3.3.2 UK

UK has shale gas reserves in northern, central and southern regions, Figure 10. Three shale gas resources have been investigated: the Carboniferous Bowland-Hodder shales in central Britain that was released in 2013, the Jurassic shales in the Weald Basin of southeast England, which was released in 2014 and the Carboniferous shales of the Midland Valley of Scotland also released in 2014 (Skea 2015). As UK shales geological formations are more complex than those of USA, extensive test drilling is needed to have correct data about the potentialities of shale gas.

Figure 10. UK shale gas reserves. A - Carboniferous shales of the Midland Valley of Scotland, B - Carboniferous Bowland-Hodder C - Jurassic shales in the Weald Basin of southeast England.

In the Carboniferous Bowland-Hodder shales was identified the Upper Unit with a thickness of around 150 m and the Lower Unit with 3 000 m and thus with higher potential, but also with greater uncertainty due to the higher depths. The central estimations are around 37.6 tcm (trillion cubic meters) (Skea 2015).

The Jurassic shales in the Weald Basin have shale oil potential, whose central estimates of the resource are around 4.4 billion barrels equivalent to 591 million tonnes (Skea 2015). However, no significant gas resources were identified because the shale formation did not reach the geological maturity needed to originate natural gas.

The Midland Valley of Scotland is expected to present modest quantities of shale gas and of oil. The central amount of gas is estimated to be around 2.27 tcm (Skea 2015). There is a high degree of uncertainty in the shale gas reserves due to the limited quality of the gas and geology complexity.

It is important to note that the figures related to shale gas reserves refer to the amounts present in the shale formations, though it is not known if the removal all these quantities are technical and economical viable (Skea 2015). Typical recovery percentages are between 20 and 40%. The recoverable quantities depend on reservoir geology, access to reservoirs and gas market prices.

It is not easy to find information about shale gas composition, because according to UK onshore licence terms, well data is confidential for four or five years and only after that it can be public. As mention before is important to know TOC and HI_o values to be able to estimate shale quality. For instance, for Bowland-Hodder unit in central Britain, there are only limited published data on organic carbon contents.

Table 5. UK NTS specifications (adapted from Andrews 2013).

Shale Reservoir	TOC Low Value (wt. %)	TOC High Value (wt. %)	TOC Average Value (wt. %)	HI_0 (mg/g)
Bowland-Hodder, UK	0.2	8	3	_
Barnett, USA	0.02	9.94	3.74	434
Marcellus, USA	0.41	9.58	4.67	507
Fayetteville, USA	0.71	7.13	3.77	404
Haynesville, USA	0.23	6.69	3.01	722

Shales need to be rich in organic matter and TOC values should be higher than 2%. TOC values for the upper part of the Bowland-Hodder unit are in the range from 0.2 to 8%, though most shale samples show TOC values between 1 and 3% (Andrews, 2013). Usually marine shales have higher TOC values (average around 4.5%) than non-marine shales, which have average value about 2.7%. However, two thin Namurian black shale marine bands show TOC values from 10 to 13% (Andrews, 2013). In Table 5 TOC values of Bowland-Hodder unit may be compared to those of some of the most important USA reservoirs.

Another important parameter is HI_o, it represents the amount of hydrogen relative to the amount of organic carbon. It is important to have information about HI_o, instead of present day values, HI (Andrews 2013). HI_o should be higher than 250 mg/g (Charpentier & Cook 2011), preferable in the range of 250-800 mg/g (Jarvie 2012). Only HI values are available for UK basins (Andrews, 2013). In Table 5 are also presented data HI_o) for some USA shale formation. Unfortunately, these values cannot be compared with UK ones.

Shale quality may also be predicted by the type of kerogen. Oxygen and hydrogen contents may be used to determine the type of kerogen as I, II, or III and if the rock is predisposed to have oil or gas. Type I kerogen is the highest quality and has the highest hydrogen content. Type III is the lowest quality and has the lowest hydrogen content. For a successful shale gas, the type of kerogen should be I, II, preferable II, as it indicates a marine origin (Charpentier & Cook 2011 and Jarvie 2012). Information on kerogen type is incomplete for UK basins. Type II and III kerogen were identified in various basins. Undeveloped type II kerogen can plot in the type III field when matured for gas generation (Jarvie et al. 2005).

4 MONITORING STRATEGY FOR EMISSIONS TO AIR FROM SHALE GAS EXPLOITATION

4.1 Introduction

Methane is the main component of shale gas and is a powerful greenhouse gas with a global warming potential of 28 (IPCC 2013). Complicating in identifying leakage from shale gas activities is the large amount of other CH_4 sources; cattle, landfills, wetlands. However, a unique feature of natural gas and shale gas is the presence of other hydrocarbons in the raw gas. If measured at the same time as CH_4 concentrations, the information on the accompanying hydrocarbons can potentially be used as a tracer to identify the fossil fuel gas sources from the other CH_4 sources. In this particular part of the M4Shalegas project we investigate how atmospheric monitoring could be used to detect and identify any significant leakages from a potential future shale gas industry.

4.2 Selection of hydrocarbon(s) as tracer for shale gas or natural gas leakage

Any future large scale European shale gas production in Europe will occur in a complex landscape with many different sources of methane present such as e.g. animal husbandry, wetlands and landfills. This complicates the monitoring and timely recognition of potential high methane leakage rates during shale gas production. This problem can be solved by using unique tracers such as isotopes or co-emitted (hydrocarbon) species (see e.g. Petron et al. 2012). A good example of applying the isotope ratio technique in Europe to distinguish methane sources was recently published by Röckmann et al. (2016). Isotopic analysis is however expensive and complicated. Based on a review it is concluded that the most promising tracer for shale gas methane is the co-emitted ethane, possibly in combination with propane. Ethane with a photochemical lifetime of several weeks, is essentially inert with respect to photochemical loss on time scales of transport from the sources to the location of monitors (1-2 days). In addition it is still reactive enough not to have a large background concentration (like e.g. methane). This makes ethane a suitable tracer. Examples of using ethane for natural gas plume detection are found in e.g. Petron et al. (2012) and Roscioli et al. (2015).

4.2.1 Availability of ethane baseline concentrations for remote sites in Europe

To use elevations of ethane in the atmosphere as a marker it is important to have baseline measurements. While it is possible to start the measurements shortly before a shale gas exploration activity, the availability of longer time series can be very valuable to understand the variation within the year and between years. We have explored the EMEP EBAS database for ethane measurement data. EBAS (http://ebas.nilu.no/) is a database hosting observation data of atmospheric chemical composition and physical properties. EBAS hosts data submitted by data originators in support of a number of national and international programs ranging from monitoring activities to research projects.

4.2.1.1 Data availability and seasonal patterns

For the period 1988-2014, there are twenty-six stations reporting ethane concentrations in the EBAS database. No station covers the whole period. For the years 2012/2013, fifteen stations are available. For later years fewer stations are reported in the EBAS database but this can be due to delays in reporting, so there might be more data than is available in EBAS right now.

Most stations for which data for the last five years is available are situated in Western and Central Europe (Switzerland, Germany, Czech Republic, Slovakia) with some exceptions (Great-Britain, Finland, Spain, Norway). The sampling frequency varies between 1 hour and 4 days. Most stations have a resolution of 1 day or higher. Measurements are performed using either the steel canister method or online gas chromatography. Measured concentrations in Europe range between and ppt with the highest concentrations in winter (February) and the lowest concentrations at the end of summer.

Ethane concentrations across Europe have a seasonal cycle, with the lowest concentrations (around 1000 ppt or lower) in summer and the highest (3000-4000 ppt monthly average) in winter. Concentrations of ethane fluctuate quickly. This may be due to the fluctuation of source strength or changing wind direction. These fluctuations are the most important cause of differences between years; the seasonal pattern is roughly the same for each year. To smooth out the sharp fluctuations a little, weekly averages can be used. This is a compromise between high temporal resolution to be able to identify unexpected elevations quickly and reducing the spikiness of the data. The elevation of ethane concentrations would have to persist for a longer period (e.g. a few months) to be able to say that an elevation is due to a leakage.

4.2.2 Prediction of ethane content in European shale gas

Ethane has been identified as a useful tracer for gas leakage as it is nearly always present in natural gas, comprising a significant part of the gas' content of higher hydrocarbons (C2+). Depending on the gas field its molar fraction can however vary by two orders of magnitude and this degree of variation is considered too high to be adequately characterized by only an overall average. A way to predict ethane concentrations in raw gas based on simple reservoir characteristics was sought and the parameter that has the most practical predictive value seems to be the thermal maturity of the reservoir. An alternative would be stable carbon and hydrogen isotope data but the availability of this type of data is considerably worse and the relation between stable isotope concentration and ethane content is more complex.

Thermal maturity measures the degree to which a formation has been exposed to high heat needed to break down organic matter into hydrocarbons. Depending on the temperature to which organic material has been exposed various types of hydrocarbons can be formed. The reflectance of certain types of minerals (vitrinite, R_0%) is used as an indication of Thermal Maturity.

For hydrocarbon containing source rock the R_0 for the oil preservation window ranges from 0.5 to 1.35%. Gas produced from oil-bearing source rock usually has a very high content of higher hydrocarbons (C2+) and relatively low methane content. The R_0 of the "wet" gas preservation window runs from 0.8 to 2.0%. Natural gas is considered wet if significant quantities of higher hydrocarbons in liquid form are present in the gas. Compared to associated gas produced from oil formations and condensate, wet gas has higher methane content but also still a relatively high C2+ content. The R_0 for "dry" gas preservation ranges from 1 to 3.5%. Natural gas is considered dry when it contains little higher hydrocarbons. Ethane is still present in the gas but in lower concentrations than in wet gas. Above an R_0 of 3.5% methane and higher hydrocarbon are destroyed and only coal remains. Note that the quoted R_0 ranges strongly overlap.

There have been attempts made to establish a quantitative relation between R_0 and higher hydrocarbon content although no relation is universally accepted. Berner (1989) related the relative amounts of ethane in natural gas to the thermal maturity of the sapropelic source rock according to $\%vol\ C2 = -6.3\ \ln(\%R_0) + 4.8$, but this relation seems only valid within the dry gas region (R_0 = 1.3 – 2.1%), in which ethane would vary from 0.1 to 3%. For the shale gas plays under consideration in this study average overall R_0 values are found to be either largely in the wet gas range with R_0 equal or below 1.15% (a small part of the Polish Baltic Basin, larger parts of the Podlasie and French Paris basin and almost the entire Dutch part of the Posidonia Shale), in between dry and wet gas with an R_0 of around 1.3% (Bowland and Lublin Basins and a large part of the Paris Basin), or more in the dry gas window with R_0 being above 1.5% (largest parts of the Baltic and Podlasie Basins and the entire Alum Shale, the German Posidonia and Dutch Geverik).

A histogram of the ethane to methane ratios as found in Europe in conventionally produced natural gas, based on our raw gas composition database (2000+ records) is shown in Figure 11.The units of the parameter shown on the Y-axis is chosen so that the area under the blue "curve" is proportional to the number of occurrences in the gas database, while using a logarithmic X-axis. Ethane is nearly always present in significant quantities that nevertheless can vary up to three orders of magnitude. Also indicated (in red) is what range of ethane to methane ratio we would associate with wet and dry gas, based on supplementary data on the thermal maturity of part of gas fields recorded in the gas database and various other literature sources dealing with conventionally produced natural gas.

With respect to the composition of shale gas a parallel needs to be drawn to conventional natural gas as there is only very little data available on compositions of shale gas produced in Europe. Furthermore given the high uncertainty involved when using the overall average source rock $\%R_0$ to predict average ethane content, only three indicative ethane to methane ratios have been derived for the range of R_0 observed values observed for the shale gas plays considered in this study. One value for primarily wet gas, one value for somewhat in between wet and dry gas (representing the majority of the observed ethane to methane ratios in conventional gas) and one for primarily dry gas (ethane fractions of 0.015, 0.04 and 0.1 respectively). How these indicative values compare to what is observed in Europe for conventional gas is also shown in Figure 11.

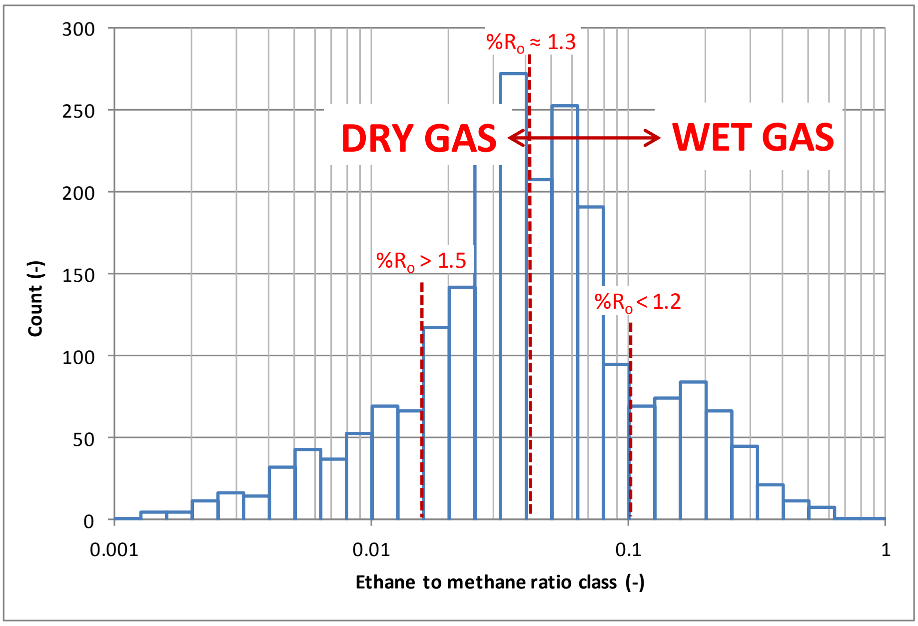

Figure 11. Histogram of the ethane to methane ratios as found in Europe in conventionally produced natural gas based on the raw gas composition database compiled by TNO (N = 2270). The vitrinite reflectance (R0%) is used as an indication of thermal maturity.

4.3 Uncertainty in leakage rates based on US data

In M4ShaleGas deliverable 15.1 (Denier van der Gon et al., 2015) top-down assessments of overall leakage rates by measuring around and / or over a large production area were discussed. Peischl et al. (2015) established top-down estimates of CH_4 leak rates using airplane flights with air masses sampling over three of the largest shale gas plays in the U.S. and quantified the net CH_4 emissions using a mass balance method. The one-day natural gas leak rates from all three shale gas plays were ranging between 0.3%–1.5% of total production. This was substantially less than previously established for several other plays. The combined shale gas plays studied by Peischl et al. (2015) accounted for over 50% of the total shale gas production in 2013 in the US and hence provide a representative range. Methane leakages of 0.25% up to ~9% of total production have been observed. Since the top-down method provides an integrated estimate, it is unknown why the loss rates vary so much between plays. Several potential reasons include 1) a trend towards cleaner operations due to implementation of green or reduced completions (REC) and, 2) the extent to which oil and gas exploration is mixed in the study area. CH_4 losses at oil fields tend to be higher because gas is not the desired commodity. Regardless of the representativeness for Europe it can be concluded that with a leakage range of 0.2-10% all possible scenarios based on available US data are covered.

4.4 Uncertain Emissions vs Composition Variety

As mentioned before, besides the raw shale gas main components (CH_4, C_2, C_3, CO_2 and N_2), other gaseous components may also be found: SO_2, H_2S, H_2, isoButane (C_4H_{10}), Oxygen (O_2), etc. (Bullin and Krouskop 2009). Mercury (Hg) and several other pollutants may also be found, although in small contents.

Shale gas composition is much affected by the shale geological formation and by the type of well that the gas comes from. Therefore, raw shale gas composition depends on the region from which the gas originates. Gas may come from fracking wells, oil wells or condensate wells. Natural gas found in oil wells is usually referred as "associated gas", being normally separated from oil. However, sometimes it may be dissolved in oil, which is not the case of shale fracking wells. Usually, gas wells produce raw gas without oil and condensate wells produce natural or shale gas with hydrocarbon condensate.

To ensure a stable quality for consumers raw shale gas needs to be processed and treated before it is injected in distribution grids. To meet pipeline, safety, environmental and quality specifications, the following compounds need to be removed: H_2S, SO_2, CO_2, N_2, heavy hydrocarbons and water. The processes used depend on the compounds to be removed and their concentrations and also on other properties of gas streams such as: temperature, pressure and flow rate. However, treated gas may still present different characteristics depending upon the origin of raw natural gas. In Figure 12 a possible diagram is presented for shale gas processing. For each process several technologies are available. The choice of the right option affects overall costs and may improve reliability, availability, maintenance and operability.

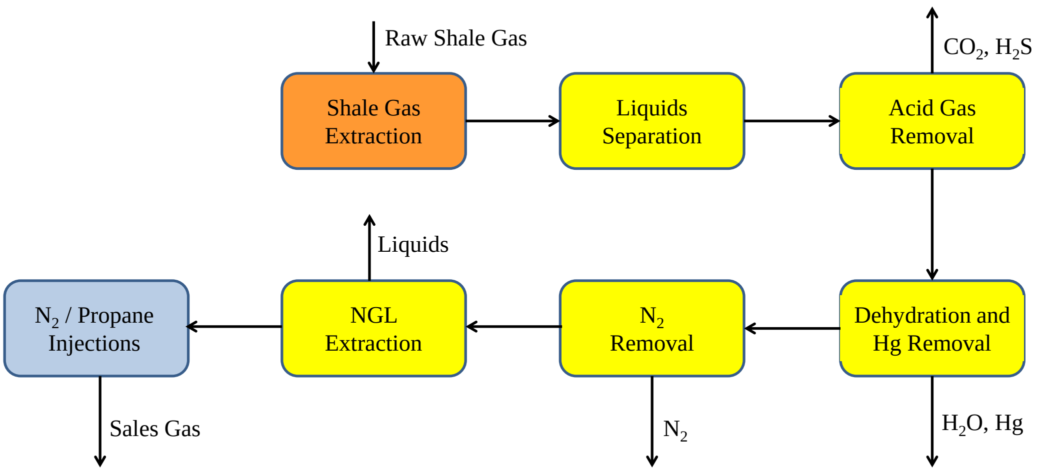

Figure 12. Possible diagram for shale gas processing (adapted from Last and Finn 2015).

H_2S and CO_2 removal is usually accomplished by absorption into aqueous amine solutions. This process is suitable for treating moderate to high concentrations of the acid-gas component for high-pressure gas streams. In some cases, an alternative is the use of physical solvents like methanol, polymer DEGP, or Selexol. When CO_2 contents are very high, as it happens in gas from CO_2 flooded reservoirs, membrane technology may be used initially for great CO_2 removals, being followed by another method to reach extremely low levels (Bullin and Krouskop 2009).

When the gas is saturated with water, dehydration is needed to increase the gas HHV and to prevent pipeline corrosion and solid hydrates formation. A glycol is usually used and its regeneration is achieved by applying heat and reducing the pressure to the water rich glycol. Another option is the use molecular sieves, being the water removed by contact with a solid adsorbent. (Bullin and Krouskop 2009). By this process water contents can be reduced to the extremely low levels needed for cryogenic separation processes.

Some countries, like UK have legislation to defined shale gas specifications. For instance in UK Natural Transmission System (NTS) specifications were defined. Raw gas needs to be treated to meet UK NTS specifications.

Shale gas is processed and treated to meet pipeline, safety, environmental and quality specifications. The key point is the production of a gas that meets each country legislation, as referred to UK (Table 6) and international rules

Table 6. UK NTS specifications (adapted from Last and Finn 2015).

Compound	**Limit**
H_2S	< = 5 mg/m3
Total Sulphur	< = 50 mg/m3
H_2	< = 0.1% (molar)
O_2	< = 0.001% (molar)
CO_2	< = 2.5% (molar)
Hydrocarbons dew point	< = 2ºC at pressure up to 85barg
Wobbe Number	47.2 to 51.42MJ/m3
Radioactivity	< = 5Becquerls /g

5 CONCLUSIONS

The lack of baseline concentrations was identified as an important knowledge gap to assess the impact of emissions to the air due to shale gas operations. Baseline observations can provide the pre-shale gas development state of the environment. Evidence from the US shows that shale gas extraction has proceeded, in most cases, without sufficient environmental baseline data. At a later stage, this makes it difficult to properly identify, quantify and characterize environmental impacts that may be associated with shale gas operations.

At present, there is the need to develop methods and data for estimating emissions from unconventional shale gas operations. Methane is identified as a compound of major concern due to its strong global warming potential and it is concluded that ‘there should be a detailed scientific research programme of methane measurement, aimed at better understanding and characterising sources and quantities of methane emissions associated with shale gas operations”.

The management of methane at unconventional gas installations will benefit from the development of new measurement and monitoring techniques and improvement of existing systems.

An assessment of potential leakage rates can be used to predict possible changes in methane and ethane concentrations in the atmosphere. By modelling these concentrations, determining the elevations and comparing those with detection limits of commercially available equipment, an assessment can be made if leakage above a certain threshold can be detected and how the detection can be optimized by the design of the monitoring network.

6 ABBREVIATIONS

BGS – British Geological Survey
C1, C2, C3, C4 – Number of carbon atoms in gases
CH_4 - Methane
CO_2 – Carbon Dioxide
EPA - Environmental Protection Agency
GHG – Greenhouse gas
H_2S - Hydrogen sulphide
N_2 – Nitrogen
NO_x- Nitrogen oxides
PM - Particulate matter
Rn - Radon
SO_x – Sulphur oxides
VOC - Volatile organic compounds

Units

bcm - billion cubic metres
mD - milidarcy
ppm – parts per million
tcm - trillion cubic metres

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