Project Acronym and Title:

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

Physicochemical parameters to assess the harmfulness of flowback water and waste relevant to shale gas operations

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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

Exploration of hydrocarbon deposits, regardless of their type, are connected with the generation of waste, which may have varying environmental effects. Such wastes may pose a serious risk to the surrounding environment and public health because they usually contain numerous potentially toxic chemicals and high levels of total dissolved solids (TDS). During shale gas operations two major types of waste are generated: (a) waste connected directly with the drilling operations and subsequent reservoir tests i.e., extractive wastes and (b) wastes connected with drilling rig operations, delivery of services, and presence of employees on the drill site.

Waste associated with exploration of unconventional hydrocarbon deposits (both drilling wastes and flowback water) is composed of a mixture of organic and inorganic materials, the qualitative and quantitative composition of which changes widely over time, depending on numerous factors such as, for example, depth and construction of the hole, type of drilled rock formations, chemical reactions between the rock and the fluid, the time fluid remains in the borehole and chemicals used in technological process. The proper determination of the range of physicochemical parameters, which should be designated in waste samples, is very important. Information gained from detailed chemical analyses of drilling chemicals, drilling wastes, and flowback water can be used to manage shale gas-related wastes more appropriately, develop treatment methods, source it, and assess the relative environmental and health risk.

Little information is publicly available about the qualitative and quantitative composition of waste generated during exploration of unconventional hydrocarbon deposits. Characterization of waste connected with shale gas operations has been reported in the literature in various degrees of detail. This report collects available information on designated physicochemical parameters in this type of waste. The review has shown that the most designated physicochemical parameters, to varying degrees, in samples of drilling waste and flowback water are pH, conductivity, total suspended solids (TSS), total dissolved solids (TDS), inorganic anions, metals, total organic carbon (TOC), dissolved organic carbon (DOC),

chemical oxygen demand (COD), biochemical oxygen demand (BOD) and organic compounds, including hydrocarbons and surfactants. In addition, in flowback water samples, the concentration of natural radioactive isotopes is designated. The contents of determined parameters and components are different depending on the areas and shales, and quality of chemicals used in drilling and fracturing.

Evaluation of waste generated during exploration of unconventional hydrocarbon deposits, in terms of harmfulness to the environment, should be carried out both based on the study of physicochemical parameters and the analysis of the composition of the fluid used in hydraulic fracturing. The range of physicochemical parameters initially proposed within the project, which should be designated in the waste generated during shale gas operations, include designation of pH, conductivity, total organic carbon (TOC), chemical oxygen demand (COD), biochemical oxygen demand (BOD), metals (including heavy metals), inorganic anions, hydrocarbons (including mono- and polycyclic aromatic hydrocarbons), phenol index and alcohols.

TABLE OF CONTENTS

Page

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) 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 makes 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

Overview of the literature reports regarding the scope of determined physicochemical parameters of waste generated during exploration and identification of unconventional hydrocarbon deposits in order to evaluate their potential impact on the environment. Compilation of preliminary guidelines for determining the physical and chemical parameters allowing an assessment of the harmfulness of waste generated during shale gas operations.

1.3 Aims of this report

The aim of this report is to present information regarding designated physicochemical parameters in waste generated during shale gas operations, relevant to determining harmfulness of this waste. A properly selected range of designated physicochemical parameters for drilling waste and flowback water will allow for selecting appropriate treatment options and identifying its source in cases of environmental contamination, and thus will contribute to reducing risks for the environment and human health.

2 CHARACTERISTICS OF WASTES GENERATED DURING SHALE GAS OPERATIONS

Exploring of hydrocarbon deposits, regardless of their type, are associated with the generation of waste, the harmfulness of which to the natural environment varies and depends largely on the type of materials and chemicals used in the process. Due to environmental and economic aspects, some of the used fluids are subjected to the processes of water treatment and re-used, while the remaining waste must be managed in a manner consistent with the requirements of relevant legislation. The challenge of efficient waste management for years now has been in the spotlight of environmental policy of the European Union, whose main priority in this regard is in the first place preventing waste generation, than re-using, recycling and recovering of waste, when its generation can not be prevented and as a last solution - landfill disposal.

Proper management of waste from shale gas operations is particularly important. Firstly, it results from the fact that large amounts of waste are generated during such operations. Secondly, it is related to the characteristics of generated waste, including its impact on the environment and human health, that in Europe are not well known.

During the exploration of unconventional hydrocarbon deposits type and amount of particular waste depends on the stage of the works, which can be divided into four consecutive stages, i.e.:

- preparation/ realization stage (preliminary and installation work),
- function/ operating stage, specifying: phase of drilling / drilling works and phases of special treatments / hydraulic fracturing (extraction intensification)
- decommissioning stage (decommissioning of facilities at the drilling rig and remediation of the site) and
- seismic survey.

At each of these stages different types of waste will be generated and before drilling it is not possible to determine the exact quantity and quality of waste. However, waste generated during the exploration of gas from shale formations can be divided into two main types:

- waste directly connected with drilling operation and subsequent reservoir tests, i.e. extractive wastes (cuttings, spent mud, reservoir waters, flowback water and deposits or sludge from flowback water tanks or treatment installations),
- waste connected with drilling rig operation, delivery of services, presence of employees on the drill site, etc. (municipal wastes, construction wastes, rigging up and rigging down wastes, wastes that are produced in association with drilling rig operation, e.g. adsorbents, cleaning materials, oils and lubricants, filtration materials, etc.).

The waste generated during drilling includes chemicals used for preparation and adjustment of drilling mud, oil derivatives, corrosion inhibitors, products of mud component decomposition, biocides, surfactants, reservoir fluids in the form of brine water and crude oil and completion and hydrocarbon flow stimulation chemicals. It should be noted that the detailed composition and properties of the waste depend mainly on the type of drilling fluid used during drilling. During piping installation in the borehole, casing's column cementation and treatments of deposits' stimulation, small amounts of other types of waste are also generated, like cement slurry leftovers and post-reaction fluids after stimulation jobs. During deposit stimulation the main type of generated waste is post-treatment fluid, returning from the borehole. This post-treatment fluid contains substances which were used to prepare the fracturing fluid. Such fluid may also contain components lixiviated from the rock subjected to stimulation, such as heavy metals, inorganic anions, radioactive elements or hydrocarbons (*News service of Polish Geological Survey: Waste management – part 1*).

Waste generated during exploration of hydrocarbon deposits are typically characterized by a high water content (30-40% in the case of drillings, 70-90% in the case of used drilling fluid and 99.9% in flowback fluid). This type of waste has liquid, semi-liquid or solid consistency, form of a sludge or slime and thixotropic properties. It is also characterized by a high pH value (sometimes even higher than 11), high content of chloride ions (up to 100,000 mg/l), and sodium and potassium, while the content of dissolved solids can be up to 200,000 mg/kg. In this waste high levels of environmentally harmful substances can also be present, including heavy metals (e.g. Pb, Cr, Cd, Cu, Zn, Mn, Fe) and petroleum derivatives (greases, oils and lubricants). In addition, wastes generated during the shale gas operations may contain other materials used to prepare drilling or technological fluids, and products of their decomposition and reaction between the components (e.g. corrosion inhibitor, biocides, alkalis, acids, surface active agents, compounds having a reduction potential). The content of radioactive isotopes in the waste from the drilling phase is low and comparable to the average content of radioactive isotopes in the soil (*Starzycka, 2012; Starzycka, 2014*).

It is estimated that the average amount of waste (drillings and used drilling fluid) generated during drilling of a single exploratory borehole of conventional crude oil and natural gas in Poland varies from 2,500 to 6,000 Mg (Megagram) (in the case of shallower boreholes it is up to 2,000 m, the amount of drilling waste is about 0.4 m^3 per 1 m of drilling; in the case of deeper boreholes it can reach up to 0.8 m^3 per 1 m of drilling, including excavated material (drillings) from 0.2 to 0.3 m^3) (*Starzycka, 2012*). The amount of generated waste and their properties vary for each borehole and depend on well depth and construction, type of rock being drilled, drilling technology, mud type, mud management methods and number of special procedures (e.g. hydraulic fracturing). The amount and properties of waste connected with hydraulic fracturing is difficult to assess because of the large number of factors which may influence on these. Among the factors influencing the quality and quantity of waste generated during hydraulic fracturing are: volume, compositions and properties of stimulation fluids, number and kind of procedures made, type of rock subjected to stimulation, presence of reservoir fluids, chemical reactions between the rock and fluids, total time of fluid presence in the rock mass, flowback water volume, approach to flowback water treatment and possibility to reuse the flowback water in subsequent procedures. Such a large number of variable factors means that the amount of waste generated during hydraulic fracturing varies widely.

There is little available information on the amount of waste generated during shale gas operations. It is also very important, however, to be aware of the fact that a single well can generate millions of liters of waste, representing a mixture of formation brine and injected hydraulic fracturing fluids. From the data available for Poland it is visible that in the years 2010-2012 total 95,251 Mg of wastes were generated as a result of the exploration and identification of unconventional hydrocarbon deposits (given number concerns only the quantity of mining waste, directly connected to the exploration and identification of unconventional hydrocarbons, classified as drilling fluids and other drilling wastes). For one exploratory borehole drilled for gas from shale formations the average number of 3,490 Mg of waste was generated in 2010, 2,832 Mg in 2011 and 2,116 Mg in 2012. The average amount of waste in 2010-2012 generated for one exploratory borehole was 2,442 Mg (*News service of Polish Geological Survey: Waste management – part 1*). Table 1 summarizes available information on the amount of produced or anticipated waste connected with exploration of unconventional hydrocarbon deposits in Poland.

Table 1. The amounts of mining waste produced or anticipated in the areas of shale gas operations (*based on Konieczyńska et al., 2011; Ścisłowicz and Dziubek, 2011; Ścisłowicz et al., 2012*).

No.	Name of the borehole	Type of waste	Amount of waste [Mg, unless otherwise specified]	
			single borehole	total
1.	Łebień LE-2H[1)]	solid waste containing mainly high-silica sand (proppant)	-	7.90
		waste of a more liquid consistency, including the sludge from surface tank, in which the purified fluid was collected	-	86.4
2.	Oleśnica[2) 3)]	mining waste generated during drilling process	5,750	34,500
		mining waste generated during special treatments (hydraulic fracturing in vertical section of the shale formation)	1,200 – 2,000	7,200 – 12,000
		mining waste generated during special treatments (hydraulic fracturing in horizontal section of the shale formation)	9,000	54,000
		mining waste generated during special treatments (hydraulic fracturing in vertical section of sandstone formations)	600 – 1,000	3,600 – 6,000
		hazardous waste (except for mining waste	104	624
		non-hazardous waste (except mining waste)	151	903
		municipal waste	20.0	120
3.	Brześć Kujawski	post-fracturing fluid - liquid waste	-	925[4)] 1,800 – 2,300 [m^3] [6)]
		drilling fluid and drilling fluid sludge	-	1,500 – 1,800[5)]
		drilling fluid - solid waste	-	3,879[4)]
		drilling fluid - liquid waste	-	1,497[4)]
		proppant (sand) after the fracturing process - solid waste	-	64.9[4)]
		drillings/ output	-	70.0 [m^3] [5)]

[1)] Data refer to the actual amount of generated waste.

[2)] Data refer to forecasted amount of waste.

[3)] In the case of Oleśnica a single hole is the sum of vertical and horizontal section, and total = projected vertical hole + 1 optional horizontal section and 5 optional holes (vertical section + 1 horizontal section).

[4)] According to the data for borehole with a depth of 4,500 m.

[5)] According to the data for borehole with a depth of 1,200 – 1,500 m.

[6)] According to the data for borehole with a depth of 4,400 m.

Table 2 shows the total amount of waste generated in Poland (in 2009-2013) related to exploration and exploitation of conventional and unconventional hydrocarbons, classified as drilling fluids and other drilling wastes.

Table 2. The amount of mining waste generated in Poland in 2009-2013 during exploration and exploitation of conventional and unconventional hydrocarbons (based on *News service of Polish Geological Survey: Waste management – part 1; Sprawozdanie z realizacji krajowego planu gospodarki odpadami 2014 [The report on the implementation of the National Waste Management Plan 2014], 2015*).

No.	Year	The amount of mining waste generated globally [Mg]	The amount of generated waste connected with shale gas operations [Mg]
1.	2009	84,520	no data available
2.	2010	131,518	10,470
3.	2011	81,600	33,984
4.	2012	no data available	50,797
5.	2013	53,800	no data available

Apart from the waste directly connected with the exploration and identification of unconventional hydrocarbon deposits, classified as drilling fluids and other drilling wastes, within the drilling rig other waste is also generated. This type of waste is typical for the industry using machines (e.g. waste containing oil and engine lubricants) and connected with drilling rig operation, presence of employees on the drill site and running supplementary works (e.g. plastics, packaging, filters, sorbents, metal scraps, municipal waste, etc.). Table 3 presents main groups of waste generated during drilling proceeds, together with the estimated number of individual waste groups (*Macuda, 2010; Otawa and Skomudek, 2015*).

Table 3. Main types of waste generated during exploration and exploitation of hydrocarbon deposits (based on *Macuda, 2010; Otawa and Skomudek, 2015*).

No.	Type of waste	The amount of generated type of waste [Mg]
1.	used drilling fluid, drillings	2,849
2.	plastics waste	0.37
3.	used oils	0.50
4.	oil cleaning	0.10
5.	fluorescent tubes and other waste containing mercury	0.030
6.	welding waste and spent electrodes	0.020
7.	iron and steel scrap	1.00
8.	waste from treatments stimulating inflow of the reservoir fluid to the borehole	238

Waste generated in the process of hydraulic fracturing should be tested for physical and chemical properties, and the results of this research should be available to the public. Ignorance of the actual characteristics of the waste constitutes a risk of their improper treatment or management by facility, storage facilities and waste disposal operators.

The main feature that makes the further use of mining waste difficult is high water content and the resulting consistency of the waste (colloidal and sludgy in the case of mining waste and liquid in the case of postoperative fluid). Another difficulty is that chemical composition of the waste (e.g. high and variable contents of heavy metals and salts of some alkali elements in the form of chlorides, sulphates or hydrogen carbonates) is highly variable and difficult to predict. Safe disposal and handling of these waste can be improved by understanding their origin and characteristics.

3 PHYSICOCHEMICAL PARAMETERS FOR WASTES FROM SHALE GAS OPERATIONS – LITERATURE DATA

The exact determination of quality of the waste generated during exploration and identification of unconventional hydrocarbon deposits is very important. Knowledge of the content of particular chemical substances in this type of wastes, especially hazardous substances, allows further sound management of such wastes and contributes to minimizing their negative impact on the environment and human health. It should be noted that regardless of the type of generated mining waste, a further way of their management should be done in accordance with the applicable laws and issued decisions.

The qualitative composition of waste (both drilling and flowback water) generated during the shale gas operations changes widely over time, depending on numerous factors such as, for example depth and construction of the hole, the type of drilled rock formations, chemical reactions between the rock and the fluid and the time fluid remains in the borehole. Usually in the case of the post-fracturing fluid, content (concentration) of the individual components increases, the longer fluid remains in the borehole. This chapter also contains available information on the quality of drilling waste and flowback water generated during shale gas operations, covering both the scope of physicochemical parameters designated in this type of wastes, and identified contents of particular chemicals. It should be added that there is little available information on this topic.

3.1 Physicochemical parameters for wastes from shale gas operations – USA

There is only little literature information available on the qualitative composition of waste generated during exploration of unconventional hydrocarbon deposits in the United States. Despite environmental concerns and a dynamic regulatory framework, Marcellus flowback and produced water have been infrequently characterized. Information on the chemical composition of additives used in hydraulic fracturing fluid is available through an online chemical disclosure registry (*FracFocus, www.fracfocus.org*), but public information on flowback and produced water constituents is sparse. The existing literature analyses data from a small number of wells or reports summary statistics obtained from oil and gas operators (*Shih et al., 2015; Thacker et al., 2015; Vengosh et al., 2014*). Summary of the most frequently designated physicochemical parameters along with the reported values for the post-fracturing fluid samples from Marcellus deposit are shown in Table 4, and from Barnett deposit in Table 5. Values of determined parameters are given as a range of minimum and maximum values for each parameter reported in the literature. Collected values of individual parameters are for illustration only, since the value of the parameter or the content of a given component changes not only depending on the used fracturing fluid or location and nature of the geological formation, but also changes depending on how long the fluid remains in the geological formation. Usually concentrations of most inorganic components of flowback water (Cl, Br, Na, K, Ca, Mg, Sr, Ba, Ra, Fe, Mn, total dissolved solids, and others) increase with time from a well after hydraulic stimulation.

Table 4. Summary of designated physicochemical parameters in flowback water post-fracturing fluid samples from Marcellus deposit in Pennsylvania (based on *Akob et al., 2016; Ferrer and Thurman, 2015; Granops et al., 2013; Haluszczak et al., 2013; Hayes, 2009; Hayes, 2011; Kargbo et al., 2010; Rahm, 2011; Shaffer et al., 2013; Shih et al., 2015; Zhang et al., 2016; Ziemkiewicz, 2013*).

No.	Designated parameter	Range of changes of designated parameter[1)]	Range of changes of designated parameter[2)]	Range of changes of designated parameter[3)]	Range of changes of designated parameter[4)]	Unit
1.	pH	5.8-7.2	4.9-6.8	5.1-11.6	-	---
2.	Specific Conductance	79.5-470	6.8-710	11.0-178	0.064-480	mS/cm
3.	Total Suspended Solids (TSS)	10.8-3,220	17.0-1,150	-	-	mg/l
4.	Total Dissolved Solids (TDS)	38,500-238,000	3,010-261,000	7,520-197,000	2.80-390,000	mg/l
5.	Total Alkalinity	48.8-327	26.1-121	29.0-939	-	mg/l
6.	Acidity	<5.00-447	<5.00-473	-	-	mg/l
7.	Hardness	5,100-55,000	630-95,000	-	-	mg $CaCO_3$/l
8.	Turbidity	2.30-1,540	10.5-1,090	-	-	NTU
9.	Chloride (Cl^-)	26,400-148,000	1,670-181,000	390-105,000	18.0-200,000	mg/l
10.	Sulphate (SO_4^{2-})	2.40-106	<10.0-89.3	<5.00-420	1.00-1,700	mg/l
11.	Bromide (Br^-)	185 – 1,190	15.8-1,600	<2.20-613	0.24-3,300	mg/l
12.	Nitrate-Nitrite (NO_3^- and NO_2^-)	<0.10-1.20	<0.10-0.92	-	-	mg/l
13.	Fluoride (F^-)	<0.05-17.3	<0.05-50.0	-	-	mg/l
14.	Bicarbonate (CO_3^-)	29.8-162	-	-	-	mg/l
15.	Cyanide, Total	<10.0-72.1	<10.0	-	-	µg/l
16.	Total Phosphorus	<0.01-2.50	<0.10-2.20	-	-	mg/l
17.	Total Sulphide	<3.00-5.60	<3.00-3.20	-	-	mg/l
18.	Aluminium (Al)	ND-47.2*	0.15-0.91	-	0.010-860	mg/l
19.	Antimony (Sb)	ND-47.2**	-	-	-	µg/l
20.	Arsenic (As)	ND-124	-	-	-	µg/l
21.	Barium (Ba)	21.4*-13,900	76.0-13,600	4.00-6,270	0.061-12,000	mg/l
22.	Beryllium (Be)	ND	-	-	-	µg/l

No.	Designated parameter	Range of changes of designated parameter1)	Range of changes of designated parameter2)	Range of changes of designated parameter3)	Range of changes of designated parameter4)	Unit
23.	Boron (B)	3.14*-97.9	2.70-3,880	-	-	mg/l
24.	Cadmium (Cd)	ND-9.60**	-	-	-	µg/l
25.	Calcium (Ca)	1,440*-23,500*	204-14,800	100-17,900	16.0-40,000	mg/l
26.	Chromium (Cr)	ND-152	-	-	0.84-2,200	µg/l
27.	Cobalt (Co)	ND	-	-	-	µg/l
28.	Copper (Cu)	ND-4,150	-	-	6.50-18,000	µg/l
29.	Iron (Fe)	21.4-180	14.0-59.0	-	0.073-1,400	mg/l
30.	Lead (Pb)	ND-606	-	-	-	µg/l
31.	Lithium (Li)	10.6-153	4.00-202	-	0.018-630	mg/l
32.	Magnesium (Mg)	135-1,550	22.0-1,800	-	0.25-3,700	mg/l
33.	Manganese (Mn)	0.88-7.04	1.20-8.40	0.28-29.4	0.010-73.0	mg/l
34.	Mercury (Hg)	ND-0.24*	-	-	-	µg/l
35.	Molybdenum (Mo)	ND-147**	-	-	6.80-2,000	µg/l
36.	Nickel (Ni)	ND-187**	-	-	5.00-3,200	µg/l
37.	Potassium (K)	48.9**-2,430	8.00-1,010	4.00-5,240	0.074-5,000	mg/l
38.	Selenium (Se)	ND	-	-	-	µg/l
39.	Sodium (Na)	10,700-65,100	1,100-44,100	1,210-37,800	8.00-82,000	mg/l
40.	Strontium (Sr)	345-4,830	46.0-5,350	6.00-3,570	0.063-7,900	mg/l
41.	Thallium (Tl)	ND-24.6**	-	-	-	µg/l
42.	Tin (Sn)	ND-25.7**	-	-	-	µg/l
43.	Titanium (Ti)	ND-313**	-	-	-	µg/l
44.	Zinc (Zn)	0.07*’**-2.93*	0.07-0.14	-	0.003-17.0	mg/l
45.	Ammonia nitrogen (NH_4^+)	29.4 - 199	3.70-359	-	-	mg/l
46.	Total Kjeldahl Nitrogen	38.0 - 204	5.60-261	-	-	mg/l
47.	Total organic carbon (TOC)	3.70-388	1.20-509	-	-	mg/l

No.	Designated parameter	Range of changes of designated parameter[1)]	Range of changes of designated parameter[2)]	Range of changes of designated parameter[3)]	Range of changes of designated parameter[4)]	Unit
48.	Dissolved organic carbon (DOC)	30.7-501	5.00-695	-	-	mg/l
49.	Chemical oxygen demand (COD)	195-17,700	228-21,900	-	-	mg/l
50.	Biochemical oxygen demand (BOD)	37.1-1,950	2.80-2,070	-	-	mg/l
51.	Total recoverable phenolics	<0.01-0.31	<0.01-0.31	-	-	mg/l
52.	Ra^{226}	-	-	40.0-5,830	0.067-17,000	pCi/l
53.	Ra^{228}	-	-	0.00-710	0.00-2,600	pCi/l
54.	U	-	-	0.00-93.0	0.00-170	pCi/l

1) Range of changes based on *Granops et al., 2013; Hayes, 2009; Hayes, 2011;* samples taken after five days of fracturing.

2) Range of changes based on *Haluszczak et al., 2013; Hayes, 2009; Hayes, 2011;* samples taken after fourteen days of fracturing.

3) Range of changes based on *Haluszczak et al., 2013.*

4) Range of changes based on *Shih et al., 2015;* data obtained on the basis of statistical analysis of available information from 160 samples (39 samples of drilling waste, 58 samples of produced water, 61 samples of flowback and 2 samples labelled as “supply water”) examined in 2009-2011.

- means that during the literature review no information on the subject was encountered.

ND - not detected.

* Estimated concentration for analyte detected between the method detection level and the reporting limit.

** Analyte was also detected in the method blank for that sample.

Table 5. Summary of the most frequently designated physicochemical parameters in post-fracturing fluid samples from Barnett deposit; samples taken after five days of fracturing (based on *Hayes, 2011*).

No.	Designated parameter	Range of changes of designated parameter	Unit
1.	pH	6.6-8.0	---
2.	Alkalinity	238-1,630	mg/l
3.	Total suspended solids (TSS)	36.8-253	mg/l
4.	Total dissolved solids (TDS)	23,600-98,900	mg/l
5.	Total organic carbon (TOC)	9.50-99.1	mg/l
6.	Biochemical oxygen demand (BOD)	92.6-1,480	mg/l

Analysis of the data included in Table 4 and Table 5 revealed that the composition of flowback water in terms of parameters such as pH, alkalinity, total dissolved solids, total organic carbon and other parameters from general water characterization does not differ from the range reported for conventional produced waters. In the post-fracturing fluid, dominant cations are sodium and calcium while among anions chloride predominates. Trace metals of toxicological concern were present at low levels. In the analysed fluid samples volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) were also determined. Among volatile organic constituents, approximately 96% of these constituents were found at non-detectable levels and 0.5% were above 1 ppm. The data indicate that the constituents above 1 ppm are those that are a normal part of produced waters associated with natural gas operations (such as xylenes, toluene and naphthalene). Among the semi-volatile organic compounds, more than 98% of all determinations were at non detectable levels and 0.03% of these constituents were above 1 ppm (*Hayes, 2009; Hayes, 2011*). Flowback water contains concentrations of Ra226, Ra228, Ba and other constituents far higher than drinking water limits. Improper disposal of the flowback water can lead to unsafe levels of these and other constituents in water, biota and sediment from wells and streams (*Haluszczak et al., 2013*). Statistical analysis carried out by Shih et al. (*Shih et al., 2015*) revealed that Cl, Na, Ca, Sr, Ba, Mg, and Br were the primary constituent ions in the samples from Marcellus deposits, with typical median concentrations of hundreds to 10s-of-thousands of mg/l.

Analysis of the physical and chemical parameters were also performed for the post-fracturing fluid samples from the Denver–Julesburg (DJ) basin in Colorado (*Lester et al., 2015*) and from operations in West Texas (*Thacker, 2015*). In the first case the water quality data was translated to propose effective treatment solutions tailored to specific reuse goals. Analysis included bulk quality parameters, trace organic and inorganic constituents, and organic matter characterization. The aim of testing samples from hydraulic fracturing operations in West Texas was to develop and apply many modern analytical techniques to characterize the properties of the flowback water samples from the site with small amount of available data on the quality of waste (especially liquid) generated during shale gas operations. The results of values determination for individual parameters were collected in Table 6.

Table 6. The results of physicochemical parameters determination for flowback water sample from the Denver–Julesburg (DJ) basin in Colorado (based on *Lester et al., 2015*).

No.	Designated parameter	Value of designated parameter	Range of changes of designated parameter	Unit
1.	pH	6.8	6.5-8.0	---
2.	Conductivity	-	21.3-152	mS/cm
3.	Total suspended solids (TSS)	360	-	mg/l
4.	Total dissolved solids (TDS)	22,500	-	mg/l
5.	Total organic carbon (TOC)	-	8.60-200	mg/l
6.	Alkalinity	150	-	mg $CaCO_3$/l
7.	Acetic Acid	1,600	-	mg/l
8.	n-Butyric acid	19.0	-	mg/l
9.	Propionic acid	33.0	-	mg/l
10.	Chloride (Cl^-)	13,600	9,000-75,100	mg/l
11.	Sulphate (SO_4^{2-})	1.30	199-2,600	mg/l
12.	Bromide (Br^-)	87.2	15.9-851	mg/l
13.	Cyanide, Total	0.055	-	mg/l
14.	Sulphide	0.31	-	mg/l
15.	Aluminium (Al)	0.064	-	mg/l
16.	Arsenic (As)	0.067	-	mg/l
17.	Barium (Ba)	8.54	3.48-15.4	mg/l
18.	Beryllium (Be)	-	0.15-0.27	mg/l
19.	Boron (B)	3.11	-	mg/l
20.	Calcium (Ca)	524	-	mg/l
21.	Caesium (Cs)	0.073	-	mg/l
22.	Chromium (Cr)	0.058	1.35-2.33	mg/l
23.	Cobalt (Co)	-	2.46-4.14	mg/l
24.	Copper (Cu)	0.29	6.47-8.56	mg/l
25.	Iron (Fe)	81.4	2.34-14.9	mg/l
26.	Lithium (Li)	3.52	-	mg/l
27.	Magnesium (Mg)	106	-	mg/l
28.	Manganese (Mn)	1.47	-	mg/l
29.	Molybdenum (Mo)	-	2.13-5.06	mg/l
30.	Nickel (Ni)	0.042	3.06-4.78	mg/l
31.	Potassium (K)	101	-	mg/l
32.	Rubidium (Rb)	0.23	-	mg/l
33.	Silicon (Si)	19.7	-	mg/l
34.	Sodium (Na)	6,944	-	mg/l
35.	Strontium (Sr)	60.3	16.0-418	mg/l
36.	Titanium (Ti)	0.028	1.40-4.16	mg/l
37.	Vanadium (V)	0.12	3.44-4.51	mg/l
38.	Zinc (Zn)	0.051	1.00-2.04	mg/l
39.	Zirconium (Zr)	-	6.64-8.76	mg/l
40.	Ammonia Nitrogen (NH_4^+)	24.7	-	mg/l

No.	Designated parameter	Value of designated parameter	Range of changes of designated parameter	Unit
41.	Acetone	16,000	-	µg/l
42.	2-Butanone	240	-	µg/l
43.	Xylenes, total	30.0	-	µg/l
44.	Dissolved organic carbon (DOC)	590	-	mgC/l
45.	Chemical oxygen demand (COD)	1,218	-	mg/l
46.	Biochemical oxygen demand (BOD)	1,100		mg/l
47.	Total recoverable phenolics	1.40	-	mg/l
48.	1.4-Dioxane	60.0	-	µg/l
49.	2-Methylphenol	150	-	µg/l
50.	3&4 methylphenol	170	-	µg/l
51.	2-Methylnaphthalene	4.00	-	µg/l
52.	Dimethyl phthalate	15.0	-	µg/l
53.	Phenanthrene	3.00	-	µg/l
54.	Pyrene	0.90	-	µg/l
55.	Butyl benzyl phthalate	4.20	-	µg/l
56.	Bis(2-ethylhexyl) phthalate	29.0	-	µg/l
57.	Phenol	830	-	µg/l
58.	2,4-Dimethylphenol	790	-	µg/l

- Means that during the literature review no information on the subject was encountered.

Data analyses in Table 6 shows that the flowback water sample from the Denver–Julesburg (DJ) basin in Colorado contained salts, metals and high concentration of dissolved organic matter. Toxic heavy metals were either not detected in the flowback water sample or detected at relatively low concentrations (<1.00 mg/l). The organic matter comprised fracturing fluid additives such as surfactants and high levels of acetic acid. The high concentration of acetic acid in the flowback water sample is probably the result of anaerobic microbial degradation of the fluid's biopolymers down-hole (*Olsson et al., 2013*). Acetic acid can also be naturally found in formation water from biogenic gas deposits, as an intermediate substrate for acetoclastic methanogenesis (*Dahm et al., 2013*). It should be added that among the numerous designated volatile and semi-volatile organic compounds, only those listed in the table occurred in quantities above the limit of determination or above 1.00 mg/l (*Lester et al., 2015*).

3.2 Physicochemical parameters for wastes from shale gas operations – Europe and Poland

In Europe, similarly to the United States, there is still little available information on the quality of waste generated during shale gas operations (drilling waste and flowback water). It is the information about the qualitative composition of waste generated during the exploration of unconventional hydrocarbon deposits that is very important for the selection of appropriate technical methods and measures that could be applicable for waste treatment, recycling and/or disposal. The discussion on the environmental impact of the storage, transport, and disposal of waste from hydraulic fracturing operations, is among other relevant issues, a matter of concern in Europe.

Table 7 shows data on the quality of post-fracturing samples from three locations in Germany (Damme 3, Buchhorst T12 and Cappeln Z3a). The values of determined parameters are given as a range of minimum and maximum values for samples from all three locations (*Olsson et al., 2013*).

Table 7. Summary of designated physicochemical parameters in flowback water samples from three locations in Germany (Damme 3, Buchhorst T12 and Cappeln Z3a) (based *on Olsson et al., 2013*).

No.	Designated parameter	Range of changes of designated parameter	Unit
1.	Chloride (Cl^-)	7,010-115,140	mg/l
2.	Sulphate (SO_4^{2-})	4.00-1,100	mg/l
3.	Acetate	110-480	mg/l
4.	Formate	37.0-190	mg/l
5.	Barium (Ba)	0.00-593	mg/l
6.	Calcium (Ca)	612-22,000	mg/l
7.	Chromium (Cr)	0.30	mg/l
8.	Iron (Fe)	23.0-500	mg/l
9.	Lead (Pb)	0.30-55.0	mg/l
10.	Lithium (Li)	4.00-50.0	mg/l
11.	Magnesium (Mg)	72.0-2,170	mg/l
12.	Manganese (Mn)	1.00-38.0	mg/l
13.	Nickel (Ni)	1.00	mg/l
14.	Potassium (K)	52.0-7,510	mg/l
15.	Sodium (Na)	3,200-44,800	mg/l
16.	Strontium (Sr)	21.0-1,720	mg/l
17.	Zinc (Zn)	0.30-290	mg/l

The analysis highlighted an increase of chloride concentrations up to saturation limit over the time. High salinity concentrations were used as indicator for estimating the percentage of hydraulic fracturing fluid and formation water in flowback water. In the flowback water, the detected acetate and formate were probably degradation products of polymers and very likely are reliable indicators of hydraulic fracturing fluid concentrations in flowback water. Additionally, most of the investigated fluids were extremely salty or saturated (*Olsson et al., 2013*).

In 2015, a report entitled *The environment and shale gas exploration. Results of studies on the soil-water environment, ambient air, acoustic climate, process fluids and wastes* was published in Poland *(Środowisko i prace rozpoznawcze dotyczące gazu z łupków; wyniki badań środowiska gruntowo-wodnego, powietrza, klimatu akustycznego, płynów technologicznych i odpadów [The environment and shale gas exploration. Results of studies on the soil-water environment, ambient air, acoustic climate, process fluids and wastes]*, *2015*). This report was prepared at the request of the Ministry of Environment by three research units: The Polish Geological Institute - National Research Institute, AGH University of Science and Technology and Gdańsk University of Technology. The report was prepared within the framework of the project *Evaluation of the environmental risks of the process of exploration, identification and extraction of unconventional hydrocarbon deposits*. The aim of the report was to determine the impact on the environment and people of works related to exploration of unconventional hydrocarbon deposits, including a detailed analysis of the potential and actual impacts on individual elements of the environment, in particular: the atmosphere, site surface area, soil, surface and groundwater. The report contains the results of comprehensive research conducted in the area of drilling for gas from shale formations located in Pomeranian Voivodeship (Lubocino, Stare Miasto, Wysin, Gapowo) and Lublin Voivodeship (Syczyn and Zawada). This report also includes results of physicochemical research of drilling waste and post-fracturing fluids from the aforementioned locations.

3.2.1 Drilling wastes

Drilling wastes tested in the cited work were characterized by dark color, in shades of black and earthy to grey and graphite and from black through brown to rust with grey-blue discoloration, and their texture was mostly muddy and loamy (with the exception of samples from Gapowo - 1A, which were quite loose, with a tendency to local micro agglomeration).

Table 8 shows the results of physicochemical parameter designations for drilling waste samples from exploration of unconventional hydrocarbon deposits in Poland. The table shows the results obtained for the solid phase of drilling waste (total content of a given component in the waste is designated) and the leaching tests results (the amount of ingredient, which may enter the environment as a result of washing out of the waste, is designated). Conducted leaching tests were designed to determine the potential impact of generated drilling wastes on the environment and the potential possibilities for their storage and use.

Table 8. Summary of designated values of physicochemical parameters (as total content component in waste or leached from waste) in drilling waste samples from drilling for gas from shale formations in Poland (based on *Środowisko i prace rozpoznawcze dotyczące gazu z łupków; wyniki badań środowiska gruntowo-wodnego, powietrza, klimatu akustycznego, płynów technologicznych i odpadów [The environment and shale gas exploration. Results of studies on the soil-water environment, ambient air, acoustic climate, process fluids and wastes], 2015*).

No.	Designated parameter		Pomeranian Basin (Lubocino, Stare Miasto, Wysin and Gapowo)		Lublin Basin (Syczyn i Zawada)	
			total content	**leachable form**	**total content**	**leachable form**
			[mg/kg DW]		[mg/kg DW]	
1.	**Metals**	Antimony (Sb)	0.03-10.0	$2.90\cdot10^{-2}$-0.11	0.05-0.05	$4.20\cdot10^{-2}$-$6.10\cdot10^{-2}$
2.		Arsenic (As)	2.10-14.7	$1.28\cdot10^{-2}$-0.13	7.50-9.00	$4.64\cdot10^{-2}$-$5.90\cdot10^{-2}$
3.		Bar (Ba)	455-2,836	$1.40\cdot10^{-2}$-0.76	877-2,516	$3.40\cdot10^{-2}$-$7.49\cdot10^{-2}$
4.		Beryllium (Be)	0.40-2.60	$2.80\cdot10^{-4}$-$3.09\cdot10^{-3}$	0.84-2.80	$6.56\cdot10^{-4}$-$8.50\cdot10^{-4}$
5.		Boron (B)	0.50-33.1	$1.97\cdot10^{-2}$-$6.20\cdot10^{-2}$	5.00-16.9	$2.53\cdot10^{-2}$-$4.00\cdot10^{-2}$
6.		Chromium (Cr)	31.8-95.4	$7.60\cdot10^{-4}$-$5.33\cdot10^{-3}$	40.1-64.2	$2.88\cdot10^{-3}$-$3.40\cdot10^{-3}$
7.		Tin (Sn)	3.00-24.7	$4.70\cdot10^{-3}$-$6.63\cdot10^{-2}$	2.50-8.50	$2.56\cdot10^{-3}$-$1.00\cdot10^{-2}$
8.		Zinc (Zn)	53.4-189	$2.56\cdot10^{-2}$-$8.70\cdot10^{-2}$	90.6-313	$3.49\cdot10^{-2}$-$4.50\cdot10^{-2}$
9.		Aluminium (Al)	18,370-48,113	$5.85\cdot10^{-3}$-1.12	25,825-38,418	0.53-0.56
10.		Cadmium (Cd)	0.10-0.40	$1.30\cdot10^{-3}$-$5.28\cdot10^{-2}$	0.40-5.30	$8.60\cdot10^{-4}$-$5.90\cdot10^{-3}$
11.		Cobalt (Co)	6.40-19.3	$2.80\cdot10^{-3}$-$9.02\cdot10^{-3}$	9.30-11.9	$4.70\cdot10^{-3}$-$1.20\cdot10^{-2}$
12.		Lithium (Li)	18.6-31.5	-	25.1-29.8	-
13.		Magnesium (Mg)	8,432-29,969	-	17,450-22,698	-
14.		Manganese (Mn)	377-1,448	$1.39\cdot10^{-3}$-0.34	363-411	$2.80\cdot10^{-3}$-$5.54\cdot10^{-3}$
15.		Copper (Cu)	27.6-106	$1.15\cdot10^{-4}$-$1.80\cdot10^{-2}$	50.8-58.6	$1.00\cdot10^{-3}$-$7.40\cdot10^{-3}$
16.		Molybdenum (Mo)	0.20-5.20	$4.10\cdot10^{-3}$-$8.20\cdot10^{-2}$	6.10-10.9	$7.70\cdot10^{-3}$-$9.80\cdot10^{-3}$
17.		Nickel (Ni)	27.5-71.3	$1.20\cdot10^{-3}$-$1.20\cdot10^{-2}$	41.2-61.0	$2.60\cdot10^{-3}$-$7.25\cdot10^{-3}$

No.	Designated parameter		Pomeranian Basin (Lubocino, Stare Miasto, Wysin and Gapowo)		Lublin Basin (Syczyn i Zawada)	
			total content	leachable form	total content	leachable form
			[mg/kg DW]		[mg/kg DW]	
18.		Lead (Pb)	5.80-91.5	$5.50\cdot10^{-3}$-$3.84\cdot10^{-2}$	13.5-14.3	$2.08\cdot10^{-2}$-$3.40\cdot10^{-2}$
19.		Potassium (K)	6,794-22,248	3.20-17,400	9,801-16,763	189-2,179
20.		Mercury (Hg)	0.02-0.30	$2.20\cdot10^{-5}$-$3.80\cdot10^{-2}$	0.03-0.20	$<10^{-6}$-$4.60\cdot10^{-2}$
21.		Selenium (Se)	0.10-1.80	$8.70\cdot10^{-2}$-2.05	0.10-1.80	1.41-1.60
22.		Sodium (Na)	1,948-44,987	365-23,585	2,784-3,067	692-1,432
23.		Silver (Ag)	0.00-0.60	$2.81\cdot10^{-4}$-$7.90\cdot10^{-3}$	0.10	$2.73\cdot10^{-3}$-$3.10\cdot10^{-3}$
24.		Strontium (Sr)	87.7-582	$2.41\cdot10^{-2}$-0.39	137-237	$8.10\cdot10^{-2}$-0.12
25.		Thallium (Tl)	0.10-2.30	$2.30\cdot10^{-2}$-0.11	0.20-2.50	$1.81\cdot10^{-2}$-$4.40\cdot10^{-2}$
26.		Titanium (Ti)	4.70-115	$1.10\cdot10^{-4}$-$1.83\cdot10^{-3}$	36.0-51.1	$5.36\cdot10^{-4}$-$3.60\cdot10^{-3}$
27.		Vanadium (V)	47.4-119	$3.20\cdot10^{-3}$-$2.20\cdot10^{-2}$	64.2-231	$9.30\cdot10^{-3}$-$5.02\cdot10^{-2}$
28.		Calcium (Ca)	20,209-62,543	241-3,206	42,527-47,479	200-281
29.		Iron (Fe)	20,812-66,476	$7.00\cdot10^{-3}$-0.15	33,343-37,150	$8.68\cdot10^{-2}$-0.14
30.		Ammonium Nitrogen (NH_4^+)	37.6-267	2.60-55.0	134-155	<0.25-7.20
31.		Bromine, bromides (Br)	-	4.90-509	-	2.20-6.70
32.	Anions	Chlorides (Cl^-)	-	1,469-44,676	-	1,418
33.	Anions	Fluorides (F^-)	29-698	12.0-264	112-192	10.1-58.4
34.	Anions	Sulphates (SO_4^{2-})	-	51.3-466	-	18.6-124
35.		Hydrogencarbonates (HCO_3^-)	-	610-6,834	-	959-2,746
36.		Total dissolved solids (TDS)	-	7,029-78,921	-	5,306-8,310
37.		Phenol index	<0.5-0.80	<0.01-0.50	1.40-7.00	0.20-1.70

No.	Designated parameter		Pomeranian Basin (Lubocino, Stare Miasto, Wysin and Gapowo)		Lublin Basin (Syczyn i Zawada)	
			total content	**leachable form**	**total content**	**leachable form**
			[mg/kg DW]		[mg/kg DW]	
38.		Total organic carbon (TOC)	3,058-34,241	510-6,880	39,325-40,650	6,370-9,380
39.		Dissolved organic carbon (TOC)	1,113-7,736	430-6,360	7,548-10,190	5,780-7,280
40.		Surfactants (anionic)	9.00-64.6	<0.20-6.90	34.3	4.20-8.40
41.		Chemical oxygen demand (COD)	7,950-89,032	1,080-17,200	108,400-110,229	18,180-24,400
42.		Gasoline (total)	3.25-211	1.94-29.4	8.84-182	8.78-18.2
43.		Mineral oils (total)	99.8-1,541	4.08-97.0	359-623	184-236
44.	**Hydrocarbons**	Aliphatic	212-1,591	6.15-107	480-629	197-242
45.		Aromatic	1.08-70.2	0.65-9.80	2.93-60.6	-
46.		Total	214-1,616	7.19-113	541-632	203-245
47.	**Polycyclic aromatic hydrocarbons (PAHs)**	Naphthalene	<0.001-0.018	$<10^{-5}$-0.009	<0.001	$<10^{-5}$-0.012
		Acenaphthene	<0.001-0.018	$<10^{-5}$-$8.70\cdot10^{-4}$	0.005-0.082	$<10^{-5}$
		Fluorene	<0.001-0.012	$<10^{-5}$-$8.80\cdot10^{-4}$	<0.001-0.022	$<10^{-5}$-0.002
		Phenanthrene	<0.001-0.109	$<10^{-5}$-$2.80\cdot10^{-3}$	0.019-0.374	$<10^{-5}$-0.001
		Anthracene	<0.001-0.004	$<10^{-5}$-$2.60\cdot10^{-4}$	0.002-0.006	$3.00\cdot10^{-5}$-$6.00\cdot10^{-5}$
		Fluoranthene	<0.001-0.016	$<10^{-5}$-$5.20\cdot10^{-4}$	<0.001-0.20	$<10^{-5}$-$7.80\cdot10^{-4}$
		Pyrene	<0.001-0.018	$<10^{-5}$-$5.60\cdot10^{-4}$	<0.001-0.080	$<10^{-5}$-$6.90\cdot10^{-4}$
		Benzo(a)anthracene	0.008-0.446	$<10^{-5}$-0.001	0.017-0.438	$<10^{-5}$-0.002
		Chrysene	0.003-0.065	$<10^{-5}$-$4.50\cdot10^{-4}$	<0.001-0.079	$<10^{-5}$-$5.20\cdot10^{-4}$
		Benzo(b)fluoranthene	<0.001-0.012	$<10^{-5}$-$3.50\cdot10^{-4}$	<0.001-0.018	$<10^{-5}$-$2.90\cdot10^{-4}$
		Benzo(k)fluoranthene	<0.001-0.009	$<10^{-5}$-$2.30\cdot10^{-4}$	<0.001-0.009	$<10^{-5}$-$2.50\cdot10^{-4}$

No.		Designated parameter	Pomeranian Basin (Lubocino, Stare Miasto, Wysin and Gapowo)		Lublin Basin (Syczyn i Zawada)	
			total content	**leachable form**	**total content**	**leachable form**
			[mg/kg DW]		[mg/kg DW]	
		Benzo(a)pyrene	<0.001-0.014	$<10^{-5}$-2.40	<0.001-0.016	$<10^{-5}$-$1.80\cdot10^{-4}$
		Dibenzo(ah)anthracene	<0.001-0.005	$<10^{-5}$-$1.20\cdot10^{-4}$	<0.001-0.009	$<10^{-5}$-10^{-3}
		Benzo(ghi)perylene	<0.001-0.016	$<10^{-6}$-0.012	0.020-0.024	$<10^{-5}$-$1.30\cdot10^{-4}$
		Indeno(1,2,3,c,d)pyrene	<0.001-0.014	$<10^{-6}$-$2.20\cdot10^{-4}$	<0.001-0.008	$<10^{-4}$
48.		pH reaction	pH			
			7.49-8.43		8.55-9.65	
49.		Conductivity	[mS/cm]			
			15.6-5,600		7.68-11.3	
50.		Acid-neutralizing capacity (ANC)	[mg $CaCO_3$/kg s.m.]			
			10.0-5,600		73.0-3,750	

< Indicates results below the limit of determination.

- Indicates no available data/ no designation.

DW- Dry Weight (Dry Basis)

Data analysis in Table 8 shows that the content of particular organic and inorganic components (total content and the amount of substance leached from waste), and the values of designated parameters vary widely. Changes can be observed both in the results obtained for samples of drilling waste from a given basin and samples from different basins (Pomeranian and Lublin). Samples representing the Pomeranian basin contain a wider range of metal concentrations (e.g., aluminium, iron, calcium, magnesium, sodium and potassium) than samples from southern Poland (Lublin). In Lublin basin on the other hand, total organic carbon and dissolved organic carbon are present in much larger quantities. Samples from this basin are also characterized by a higher rate of chemical oxygen demand. The sum of hydrocarbons contained in the sample from the Pomeranian basin varies between 214–1,616 mg/kg DW, and in the sample from Lublin basin varies between 541–632 mg/kg DW. Differences demonstrated in the characteristics of drilling waste from different boreholes can be associated not only with the conditions of resource properties, but also the type of drilling fluid used for drilling.

Whereas performed leaching tests showed that in analysed drilling wastes both from the Pomeranian basin and the Lublin basin chlorides, fluorides, solid soluble compounds and soluble organic carbon and selenium exceeded permissible limit in relation to permissible limits set out in the Polish legislation of waste disposal in landfills for inert waste and landfills for other waste than hazardous and inert. In some cases (e.g., the drilling waste from Pomeranian basin) the allowable limits have been exceeded for the content of soluble organic carbon and chlorides for purposes of waste storage at landfills for hazardous waste.

Toxicity and ecotoxicity tests were also carried out for drilling waste. These tests showed that tested waste is toxic to tested organisms (bacterium *Vibrio fischeri*, crustacean *Heterocypris incongruens* and mustard plant *Sinapis alba*), but the level of ecotoxicity was decreasing with the dilution of samples (*Środowisko i prace rozpoznawcze dotyczące gazu z łupków; wyniki badań środowiska gruntowo-wodnego, powietrza, klimatu akustycznego, płynów technologicznych i odpadów [The environment and shale gas exploration. Results of studies on the soil-water environment, ambient air, acoustic climate, process fluids and wastes], 2015*).

3.2.2 Flowback water

The report entitled *The environment and shale gas exploration. Results of studies on the soil-water environment, ambient air, acoustic climate, process fluids and wastes* also presented research results of chemical parameters of fluids after hydraulic fracturing (*Środowisko i prace rozpoznawcze dotyczące gazu z łupków; wyniki badań środowiska gruntowo-wodnego, powietrza, klimatu akustycznego, płynów technologicznych i odpadów [The environment and shale gas exploration. Results of studies on the soil-water environment, ambient air, acoustic climate, process fluids and wastes], 2015*). In this case, the scope of analysis of determinations of inorganic components was narrower than for drilling waste. Table 9 shows research results of concentrations of elements washed from fractured formation and testing results of organic content in flowback water samples from drilling for gas from shale formations in Poland.

Table 9. Research results of concentrations of elements washed from fractured formation and testing results of organic content in flowback water samples from drilling for gas from shale formations in Poland (based on *Środowisko i prace rozpoznawcze dotyczące gazu z łupków; wyniki badań środowiska gruntowo-wodnego, powietrza, klimatu akustycznego, płynów technologicznych i odpadów [The environment and shale gas exploration. Results of studies on the soil-water environment, ambient air, acoustic climate, process fluids and wastes], 2015*).

No.	**Designated parameter**		**Pomeranian Basin (Lubocino, Stare Miasto and Gapowo)**	**Lublin Basin (Syczyn i Zawada)**
			[mg/l]	[mg/l]
1.	**Metals**	Arsenic (As)	$5.52\cdot10^{-3}$-1.10	-
2.		Bar (Ba)	$1.28\cdot10^{-3}$-16.0	0.14-59.5
3.		Boron (B)	$5.82\cdot10^{-3}$-0.49	$3.36\cdot10^{-2}$-0.60
4.		Caesium (Cs)	$1.61\cdot10^{-3}$-20.8	0.11-54.6
5.		Zinc (Zn)	-	$6.79\cdot10^{-4}$-$2.02\cdot10^{-2}$
6.		Aluminium (Al)	$1.52\cdot10^{-2}$-2.36	$3.00\cdot10^{-3}$-$3.06\cdot10^{-2}$
7.		Yttrium (Y)	-	$8.18\cdot10^{-5}$-$1.93\cdot10^{-4}$
8.		Cadmium (Cd)	$7.70\cdot10^{-3}$-$1.20\cdot10^{-2}$	$1.94\cdot10^{-4}$-$3.64\cdot10^{-3}$
9.		Cobalt (Co)	-	$6.16\cdot10^{-4}$-$3.01\cdot10^{-3}$
10.		Lithium (Li)	-	$5.66\cdot10^{-5}$-0.60
11.		Magnesium (Mg)	-	0.93-3.39
12.		Potassium (K)	3.28-86.7	1.67-13.2
13.		Selenium (Se)	$4.19\cdot10^{-2}$-40.6	-
14.		Sodium (Na)	0.84-602	16.7-305
15.		Silver (Ag)	$1.13\cdot10^{-2}$-$3.04\cdot10^{-2}$	-
16.		Strontium (Sr)	$8.80\cdot10^{-4}$-17.3	0.56-23.5
17.		Titanium (Ti)	-	$5.97\cdot10^{-5}$-$3.66\cdot10^{-4}$
18.		Uranium (U)	-	$1.69\cdot10^{-3}$-$1.93\cdot10^{-2}$
19.		Calcium (Ca)	0.23-200	2.64-37.0
20.		Iron (Fe)	-	$5.27\cdot10^{-3}$-1.34
21.		Phenol index	0.02-0.79	0.02-1.20
22.		Total organic carbon (TOC)	115-1,090	131-853
23.		Dissolved organic carbon (TOC)	99-919	105-1,193
24.		Surface-active substances (anionic)	0.68-25.7	0.50-16.0
25.		Chemical oxygen demand (COD)	307-6,230	554-5,920
26.		Gasoline (total)	0.04-56.1	2.57-35.5
27.		Mineral oils (total)	0.42-332	0.45-112
28.	**Hydrocarbons**	Aliphatic	0.46-418	4.64-135
29.		Aromatic	0.02-18.7	0.86-11.9

No.	Designated parameter		Pomeranian Basin (Lubocino, Stare Miasto and Gapowo)	Lublin Basin (Syczyn i Zawada)
			[mg/l]	[mg/l]
30.		Total	0.49-427	6.73-146
31.	**Polycyclic aromatic hydrocarbons (PAHs)**	Naphthalene	$<5.00\cdot10^{-6}-2.86\cdot10^{-4}$	$1.00\cdot10^{-5}-6.50\cdot10^{-4}$
		Acenaphthene	$6.00\cdot10^{-5}-1.38\cdot10^{-4}$	$<5.00\cdot10^{-6}-3.20\cdot10^{-4}$
		Fluorene	$<5.00\cdot10^{-6}-4.60\cdot10^{-5}$	$<5.00\cdot10^{-6}-2.60\cdot10^{-4}$
		Phenanthrene	$4.30\cdot10^{-5}-2.31\cdot10^{-4}$	$1.10\cdot10^{-5}-1.35\cdot10^{-4}$
		Anthracene	$1.90\cdot10^{-5}-8.79\cdot10^{-5}$	$<5.00\cdot10^{-6}-5.60\cdot10^{-5}$
		Fluoranthene	$<5.00\cdot10^{-6}-1.46\cdot10^{-4}$	$<5.00\cdot10^{-6}-1.00\cdot10^{-4}$
		Pyrene	$2.40\cdot10^{-5}-1.16\cdot10^{-4}$	$<5.00\cdot10^{-6}-5.40\cdot10^{-5}$
		Benzo(a)anthracene	$<5.00\cdot10^{-6}-3.82\cdot10^{-4}$	$<5.00\cdot10^{-6}-4.30\cdot10^{-5}$
		Chrysene	$10^{-4}-8.70\cdot10^{-5}$	$<5.00\cdot10^{-6}$
		Benzo(b)fluoranthene	$<5.00\cdot10^{-6}-3.60\cdot10^{-5}$	$<5.00\cdot10^{-6}-1.00\cdot10^{-4}$
		Benzo(k)fluoranthene	$<5.00\cdot10^{-6}-2.00\cdot10^{-5}$	$<5.00\cdot10^{-6}$
		Benzo(a)pyrene	$<5.00\cdot10^{-6}-6.10\cdot10^{-5}$	$<5.00\cdot10^{-6}$
		Dibenzo(ah)anthracene	$<1.00\cdot10^{-5}$	$<1.00\cdot10^{-5}$
		Benzo(ghi)perylene	$<5.00\cdot10^{-6}-3.30\cdot10^{-5}$	$<5.00\cdot10^{-6}-2.10\cdot10^{-4}$
		Indeno(1,2,3,c,d)pyrene	$<1.00\cdot10^{-5}$	$<1.00\cdot10^{-5}$

< Indicates results below the limit of determination.

- No increased concentration was detected.

As it is known, the chemical composition of the fracturing fluid is highly variable in terms of both quality and quantity. Content of the individual elements in flowback water is a result of both the fluid composition and the nature of rock into which fluid is injected. Clearly elevated levels of certain elements in the flowback water as compared to their content in the fracturing fluid may indicate that they pass to technological fluid in the process of contact with the rock (*Środowisko i prace rozpoznawcze dotyczące gazu z łupków; wyniki badań środowiska gruntowo-wodnego, powietrza, klimatu akustycznego, płynów technologicznych i odpadów [The environment and shale gas exploration. Results of studies on the soil-water environment, ambient air, acoustic climate, process fluids and wastes], 2015*).

Tested flowback waters from different boreholes in Poland are characterized by a great diversity in terms of the content of organic components and showed toxic properties in respect of tested organisms (*Środowisko i prace rozpoznawcze dotyczące gazu z łupków; wyniki badań środowiska gruntowo-wodnego, powietrza, klimatu akustycznego, płynów technologicznych i odpadów [The environment and shale gas exploration. Results of studies on the soil-water environment, ambient air, acoustic climate, process fluids and wastes], 2015*).

For all tested samples, i.e. samples of drilling waste and flowback water, research and analysis of the concentration of natural radioactive isotopes were also carried out. The analysis, carried out in terms of impact on the environment and human health, of used drilling fluids and drilling waste, indicated a slightly elevated (but still within the range of natural variability) concentrations of ^{40}K and ^{226}Ra in comparison to the world average content in the soil. Also the concentration of the isotope ^{228}Th in the studied waste was low, equal to the average natural concentration of this isotope in the environment. Concentrations of natural radioactive isotopes in post-fracturing fluids were slightly higher than in the fracturing fluids but still within the range of their natural concentration in the environment (*Środowisko i prace rozpoznawcze dotyczące gazu z łupków; wyniki badań środowiska gruntowo-wodnego, powietrza, klimatu akustycznego, płynów technologicznych i odpadów [The environment and shale gas exploration. Results of studies on the soil-water environment, ambient air, acoustic climate, process fluids and wastes], 2015*).

Table 10 and Table 11 contain the available information on the designated physicochemical parameters in post-fracturing fluids from boreholes in Łebień in Lubocino, respectively.

Table 10. Summary of physicochemical parameters determined in flowback water samples from borehole in Łebień (based on *Granops et al., 2013; Klimkiewicz and Korczak, 2012; Starzycka, 2012; Starzycka, 2014*).

No.	**Designated parameter***	**Range of changes of designated parameter**	**Unit**
1.	pH	5.73-7.47	---
2.	Conductivity	11.9-123	mS/cm
3.	Chlorides (Cl^-)	3,800-48,000	mg/l
4.	Sulphates (SO_4^{2-})	<5.00-150	mg/l
5.	Bromides (Br^-)	25.0-500	mg/l
6.	Nitrates (NO_3^-)	0.40-7.10	mg/l
7.	Fluorides (F^-)	0.50-6.10	mg/l
8.	Hydrogencarbonates (HCO_3^-)	166-509	mg/l
9.	Calcium (Ca)	318-7,568	mg/l
10.	Boron (B)	2.50-40.1	mg/l
11.	Bar (Ba)	5.30-218	mg/l
12.	Potassium (K)	51.0-536	mg/l
13.	Sodium (Na)	1,685-22,596	mg/l
14.	Strontium (Sr)	25.8-857	mg/l
15.	Iron (Fe)	2.40-23.4	mg/l
16.	Ammonium nitrogen (NH_4^+)	9.00-159	mg/l
17.	Total organic carbon (TOC)	11.0-129	mg/l
18.	Phenol index	<2.00-20.0	mg/l
19.	Surface-active substances (anionic)	<0.50-31.0	mg/l
20.	Total alkalinity	136-417	mg $CaCO_3$/l

* In flowback water samples elements such as Hg, Li, Be, Al, Co, Ni, Cu, Rb, No, Ag, Cd, Sn, Sb, Pb and U were also determined; however only minor levels or traces of aforementioned elements were discovered.

Table 11. Summary of the physicochemical parameters designated in the average flowback water sample from borehole in Lubocino (based *on Granops et al., 2013*).

No.	Designated parameter*	Value of designated parameter	Unit
1.	pH	6.00	---
2.	Total suspension	168	mg/l
3.	Chlorides (Cl^-)	9,833	mg/l
4.	Sulphates (SO_4^{2-})	71.6	mg/l
5.	Boron (B)	4.1	mg/l
6.	Bar (Ba)	20.6	mg/l
7.	Potassium (K)	403	mg/l
8.	Sodium (Na)	5,330	mg/l
9.	Nickel (Ni)	0.30	mg/l
10.	Iron (Fe)	68.1	mg/l
11.	Ammonium nitrogen (NH_4^+)	22.2	mg/l
12.	Nitrogen (Kjeldahl method)	71.5	mg/l
13.	Total organic carbon (TOC)	1,680	mg/l
14.	Chemical oxygen demand (COD)	4,903	mg/l
15.	Biochemical oxygen demand (BOD)	2,416	mg/l
16.	Phenol index	0.09	mg/l
17.	Surface-active substances (anionic)	5.97	mg/l
18.	Surface-active substances (non-ionic)	89.1	mg/l
19.	Substances extracted with petroleum ether	37.5	mg/l

* In flowback water sample elements such as Co, Be, Ag, V, Mo, Tl, Ti, Se were also determined; however only minor levels or traces of aforementioned elements were discovered.

Flowback water from the Łebień borehole was characterized by variable chemical composition (depending on the time in which it returned to the surface) and values of selected parameters in successive lots of tested fluid varied within wide limits (Table 10). The first lots of flowback water were characterized by lower levels of each determined parameters. The longer fluid was in the borehole, the higher was the concentration of individual components in flowback water (*News service of Polish Geological Survey: Waste management – part 2*). It is worth noting that the post-fracturing fluid from Lubocino was characterized by much higher organic carbon content than the fluid from Łebień but it remained in correlation with the level of contamination pointed out by indicators COD and BOD.

3.3 Physicochemical parameters for wastes generated during shale gas operations – short recapitulation based on the literature data

Review of available information regarding the range of designated physicochemical parameters in waste (drilling waste and flowback water) showed that the range of designated parameters is wide and varied. The range of designated physicochemical parameters not only changes depending on the type of tested waste (drilling waste, flowback water), but also on the location of the borehole. Basic physical parameters are designated (typically pH and conductivity) and many organic and inorganic compounds. Among the inorganic components designated in this type of waste metals should be primarily mentioned, including heavy metals and anions (most frequently chlorides and sulphates). Determined organic parameters are primarily hydrocarbons (aliphatic and aromatic), phenol index, and total and dissolved organic carbon (TOC and DOC). However, despite such a wide range of research of physicochemical parameters, there is no guidance speaking on what basis these parameters have been chosen for tests. In such a situation it is difficult to evaluate whether the extent of the research is sufficient and takes into account the designation of all ingredients that may have harmful effects on the environment. Detailed assessment of a range of tests of physicochemical parameters and designated values for individual parameters will be carried out in the next stage of the project.

The review carried out within the framework of the project showed that the amount of publicly available detailed information on the test results of waste generated during shale gas operations is small and selective. There is also no information available on the amount of mining waste generated during exploration and identification of unconventional hydrocarbon deposits.

Chemical composition of drilling waste and flowback water is highly variable in terms of both qualitative and quantitative. A major impact on the content of individual components in the waste and fluid has not only the composition of the drilling waste and flowback water, but also the type of rock. Waste generated during exploration of unconventional hydrocarbon deposits is not inert and often has toxic properties. Therefore, determination of appropriate range of physicochemical parameters, which should be determined in this type of waste, is very important. Only properly selected scope of testing, including all components that could have a negative impact on the environment, along with the proper process of purification or disposal of such waste, guarantee safety for humans and the environment.

Waste connected with shale gas operations should not enter in an unpurified form into the environment, even unintentionally, e.g. as a result of failure. Post-fracturing fluids should be used on site for further treatments whereas the transport of such waste to other locations for reuse or to mining waste disposal facilities should be in accordance with waste transport procedures.

4 PHYSICOCHEMICAL PARAMETERS ALLOWING AN EVALUATION OF HARMFULNESS OF WASTE FROM SHALE GAS OPERATIONS

Waste generated in hydraulic fracturing may contain components of the fracturing fluid, remnants of drilling fluid, hydrocarbons, natural salines leached from rock and components of the rock. It is estimated that, after fracturing, up to 30% (*Kidder et al., 2011*) of the fluid volume (occasionally it can be even 80% (*Karakulski et al., 2012*)) used in the procedure returns to the surface as a liquid waste which only partially can be used in the next step (this possibility is limited because of the increasing salinity of the fluid and the loss of its key properties). The remaining waste should be managed in accordance with the requirements of applicable legislation and limiting any possible negative impact on the environment and the health of people. To ensure proper management of waste, its harmfulness to the environment and human health should be specified, along with indicating harming properties of substances or groups of substances because they determine the choice of how to deal with the waste.

Choosing a set of necessary analytical tests for waste produced during shale gas operations, to determine its harmfulness and appropriate management should be based on the following procedure:

- STAGE I - establishing a list of substances which occurrence in the waste is expected (based on the available data mainly on the quality of materials used in drilling and fracturing fluids),
- STAGE II - performing preliminary tests confirming the presence of these substances (if possible), and
- STAGE III - carrying out detailed research and analysis to identify the concentration of selected harmful substances.

It should be added that due to difficulties in obtaining full and detailed data on the qualitative and quantitative composition of drilling and fracturing fluids (for commercial reasons companies that carry out drilling provide only aggregate consumption of drilling mud materials and in the case of fracturing fluids - maximum content of a given component) it may be necessary to extend the range of study of physicochemical parameters depending on the available data.

Information that has been gathered so far, both on the basis of analysis of literature reports, as well as the experiences of Oil and Gas Institute - National Research Institute (*Król et al., 2013*), shows that the waste generated during exploration and exploitation of gas from shale formations may contain:

- acids and organic and inorganic substances dissolved in water, e.g.: anions
- (Cl^-, SO_4^{2-}, Br^-, F^-), cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, Sr^2+, NH_4^+), methanol, isopropanol, ethylene and diethylene glycol, 2-butoxyethanol,
- substances insoluble in water,
- hydrocarbons C_6–C_{35}, including mononuclear aromatic hydrocarbons (BTEX) and polycyclic aromatic hydrocarbons (PAHs),
- metals such as: bar (Ba), cadmium (Cd), lead (Pb), molybdenum (Mo), antimony (Sb), chromium (Cr), zinc (Zn), copper (Cu), nickel (Ni), aluminium (Al), vanadium (V), arsenic (As), cobalt (Co), selenium (Se), iron (Fe) and mercury (Hg).

Therefore, in the initial stage (STAGE II), the following physicochemical parameters in the generated waste should be designated:

- pH - allows to determine whether the waste contains substances that cause a significant change in pH of the environmental elements; low values of this parameter indicate the presence of acids in the waste and similarly, high values indicate the presence of hydroxides; moreover, a pH equal or less than 3 and equal or more than 11.5 shows irritant waste, while pH equal or less than 2 and equal or more than 12.5 shows caustic waste; caustic or irritant waste may be hazardous,
- conductivity - increased value of this parameter indicates the electrolyte content in waste and the necessity of performing a test for anions (mainly chlorides),
- the dry residue and content of dissolved substances - these two parameters are important for a general characterization of waste, they also indicate the salinity and presence of suspensions,
- chemical oxygen demand (COD (Cr)) - indirectly determines the sum of all reducers in the waste (total organic content and easily oxidizable inorganic components); high values of COD (Cr) indicate a significant organic load in the waste (including significant hydrocarbon content), resulting in significant consumption of oxygen in the environment;
- biochemical oxygen demand (BOD) - this parameter is indirectly used to determine the organic matter degradable through a biochemical process, and
- content of total organic carbon (TOC) - this parameter indicates the content of organic carbon compounds in the analysed waste.

Then, on the basis of analysis of initial results and analysis of the composition of fracturing fluid, a range of specific tests should be defined. Literature sources and the experience gained during many years of research and evaluation of harmfulness of waste generated during exploration and exploitation of hydrocarbons from conventional deposits, militate in favour of carrying out specific tests, which should include determination of:

- chloride ions (or sulphides, bromides, fluorides),
- sodium (Na), potassium (K), calcium (Ca), magnesium (Mg) and strontium (Sr),
- ammonium ions (or total nitrogen),
- aluminium and total iron,
- toxic heavy metals: barium (Ba), cadmium (Cd), lead (Pb), molybdenum (Mo), antimony (Sb), total chromium (Cr), zinc (Zn), tin (Sn), copper (Cu), nickel (Ni), vanadium (V), arsenic (As), cobalt (Co), selenium (Se), mercury (Hg)
- suspensions,
- hydrogencarbonate ions (HCO_3^-),
- sulfide / sulfide sulfur,
- gasoline hydrocarbons (C_6-C_{12}),
- mineral oil (hydrocarbons C_{12}-C_{35}),
- mononuclear aromatic hydrocarbons (BTEX) - benzene, toluene, ethylbenzene and xylene,
- polycyclic aromatic hydrocarbons (PAHs), including benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene and indeno (1,2,3-cd)pyrene,
- phenol index,

- methanol, isopropanol, glycols, 2-butoxyethanol, depending on the composition of the fracturing fluid.

In addition to the presented scope of research of physicochemical parameters it is also advisable to designate the density of waste (which facilitates, if necessary, conversion of test results), and the ignition/ spontaneous combustion temperature of waste (which allows to determine whether a waste is hazardous because of its flammability). In the waste generated during shale gas operations the content of anionic and non-ionic surface-active substances should be monitored, due to low levels of allowable concentrations of these substances in groundwater. In addition, this type of waste should be subjected to toxicological and ecotoxicological tests.

The above-mentioned range of research of waste generated during shale gas operations (post-fracturing fluids and drilling waste) also contains parameters that can be used to determine whether the produced waste can be considered as inert waste, in accordance with the Directive 2006/21/EC of the European Parliament and of the Council of 15 March 2006 on the management of waste from extractive industries and amending Directive 2004/35/EC (*Directive 2006/21/EC*) and Commission Decision 2009/359/EC of 30 April 2009 completing the definition of inert waste in implementation of Article 22(1)(f) of Directive 2006/21/EC of the European Parliament and the Council concerning the management of waste from extractive industries (*Commission Decision 2009/359/EC*).

The content of anions (Cl^-, SO_4^{2-}, Br^-, F^-) and cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, Sr^{2+}, NH_4^+) indicates the salinity of the waste. Salts are components of fracturing and drilling fluids, they are also present in deposit waters and may be leached from the rock. Metals with the exception of barium (barium sulphate is a component of drilling fluids) may appear in waste generated during shale gas operations mainly due to leaching from rocks but they can also be components of the deposit waters. In post-fracturing waste it is difficult to avoid the presence of hydrocarbons (gasoline, mineral oil, and mono- and polycyclic aromatic hydrocarbons), if waste is generated due to works related to opening out and exploiting of hydrocarbon deposits. Furthermore, different types of hydrocarbons can be components of fracturing fluid and greases and oils used during exploration and exploitation works. The presence of organic compounds such as methanol, isopropanol, ethylene and diethylene glycol, 2-butoxyethanol or phenol, depends on the composition of fluid for hydraulic fracturing. Decision on the designation of their contents should be made individually, based on the analysis of the composition of a given fluid.

Table 12 shows the classification of chemical harmfulness that should be designated during the ongoing assessment of harmfulness of the waste associated with shale gas operations (drilling waste and post-fracturing fluids). Classification was based on the Annex VI of the Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006 (CLP Regulation) (*Regulation (EC) No 1272/2008*). Table 12 does not include cations and heavy metals selected for determination of anions waste, due to the fact that they are part of composition of different salts or rocks. Accordingly, the assessment of their harmfulness should be carried out individually for each borehole on the basis of previously mentioned Annex VI.

Table 12. The harmfulness of chemicals that should be designated during the ongoing assessment of harmfulness of drilling waste and post-fracturing fluids (based on *Regulation (EC) No 1272/2008*).

No.	Chemical name	Index No	CAS number	CLP Classification[1)]	
				Hazard Class and Category Code(s)	**Hazard Statement Code(s)**
1.	**benzene**	601-020-00-8	71-43-2	Flam. Liq. 2 Carc. 1A Muta. 1B STOT RE 1 Asp. Tox. 1 Eye Irrit. 2 Skin Irrit. 2	H225 H350 H340 H372** H304 H319 H315
2.	**toluene**	601-021-00-3	108-88-3	Flam. Liq. 2 Repr. 2 Asp. Tox. 1 STOT RE 2* Skin Irrit. 2 STOT SE 3	H225 H361d*** H304 H373** H315 H336
3.	**ethylbenzene**	601-023-00-4	100-41-4	Flam. Liq. 2 Acute Tox. 4*	H225 H332
4.	**xylene - a mixture of isomers**	601-022-00-9	1330-20-7	Flam. Liq. 3 Acute Tox. 4* Acute Tox. 4* Skin Irrit. 2	H226 H332 H312 H315
5.	**o-xylene**		95-47-6		
6.	**p-xylene**		106-42-3		
7.	**m-xylene**		108-38-3		
8.	**gasoline**	649-421-00-7	64742-31-0	Asp. Tox. 1	H304
9.	**mineral oil**	649-485-00-6	90640-91-8	Carc. 1B	H350
10.	**benzo[a]pyrene**	601-032-00-3	50-32-8	Carc. 1B Muta. 1B Repr. 1B Skin Sens. 1 Aquatic Acute 1 Aquatic Chronic 1	H350 H340 H360-FD H317 H400 H410
11.	**benzo[k]fluoranthene**	601-036-00-5	207-08-9	Carc. 1B Aquatic Acute 1 Aquatic Chronic 1	H350 H400 H410
12.	**methanol**	603-001-00-X	67-56-1	Flam. Liq. 2 Acute Tox. 3* Acute Tox. 3* Acute Tox. 3* STOT SE 1	H225 H331 H311 H301 H370**
13.	**isopropanol**	603-117-00-0	67-63-0	Flam. Liq. 2 Eye Irrit. 2 STOT SE 3	H225 H319 H336

No.	Chemical name	Index No	CAS number	CLP Classification 1)	
				Hazard Class and Category Code(s)	Hazard Statement Code(s)
14.	**ethylene glycol**	603-027-00-1	107-21-1	Acute Tox. 4	H302
15.	**diethylene glycol**	603-140-00-6	111-46-6	Acute Tox. 4	H302
16.	**2-butoxyethanol**	603-014-00-0	111-76-2	Acute Tox. 4* Acute Tox. 4* Acute Tox. 4* Eye Irrit. 2 Skin Irrit. 2	H332 H312 H302 H319 H315
17.	**phenol**	604-001-00-2	108-95-2	Muta. 2 Acute Tox. 3* Acute Tox. 3* Acute Tox. 3* STOT RE 2* Skin Corr. 1B	H341 H331 H311 H301 H373** H314

1) symbols and indications are explained in Table 13 and 14.

„*, **, ***„ – see CLP Regulation, Annex VI, Part 1, point 1.2.

Table 13. Hazard class and category codes.

Hazard Class	Hazard Class and Category Code
Flammable liquid	Flam. Liq. 2
	Flam. Liq. 3
Acute toxicity	Acute Tox. 3
	Acute Tox. 4
Skin corrosion/irritation	Skin Corr. 1B
	Skin Irrit. 2
waste generated during drilling includes	Eye Irrit. 2
Respiratory/skin sensitization	Skin Sens. 1
Germ cell mutagenicity	Muta. 1B
	Muta. 2
Carcinogenicity	Carc. 1A
	Carc. 1B
Reproductive toxicity	Repr. 1B
	Repr. 2
Specific target organ toxicity — single exposure	STOT SE 1
	STOT SE 3
Specific target organ toxicity — repeated exposure	STOT RE 1
	STOT RE 2
Aspiration hazard	Asp. Tox. 1
Hazardous to the aquatic environment	Aquatic Acute 1
	Aquatic Chronic 1

Table 14. Hazard statement codes.

Hazard statement codes	
H225	Highly flammable liquid and vapour
H226	Flammable liquid and vapour
H301	Toxic if swallowed
H302	Harmful if swallowed
H304	May be fatal if swallowed and enters airways
H311	Toxic in contact with skin
H312	Harmful in contact with skin
H314	Causes severe skin burns and eye damage
H315	Causes skin irritation
H317	May cause an allergic skin reaction
H319	Causes serious eye irritation
H331	Toxic if inhaled
H332	Harmful if inhaled
H336	May cause drowsiness or dizziness
H340	May cause genetic defects (state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard)
H341	Suspected of causing genetic defects (state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard)
H350	May cause cancer (state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard)
H360FD	May damage fertility. May damage the unborn child
H361d	Suspected of damaging the unborn child
H370	Causes damage to organs (or state all organs affected, if known) (state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard)
H372	Causes damage to organs (or state all organs affected, if known) through prolonged or repeated exposure (state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard)
H373	May cause damage to organs (or state all organs affected, if known) through prolonged or repeated exposure (state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard)
H400	Very toxic to aquatic life
H410	Very toxic to aquatic life with long lasting effects

Analysis of the data included in Table 12 shows that waste generated during exploration and exploitation of gas from shale formations may contain chemical substances dangerous for the environment, toxic or very toxic to aquatic organisms, which may cause long-term negative effects in the aquatic environment. This type of waste can also contain substances dangerous to health and life of humans, causing genetic damage, cancer or organ damage.

Also individual components, included in the total dissolved solids (TDS), like calcium, magnesium, sodium, potassium, sulphates, chloride, and even barium, cadmium, and copper may cause process inhibition in activated sludge and nitrification, and anaerobic digestion processes in publicly owned treatment works (POTW) (*Jack et al., 2014*).

However, the final evaluation of the waste associated with shale gas operations in terms of harmfulness to the environment should be carried out both on the basis of physicochemical parameters proposed tests results, and on the basis on the analysis of the fluid composition used in hydraulic fracturing. The evaluation should aim at acquiring the most detailed information on the qualitative and quantitative composition of fracturing fluid or, if this is not possible, at least accurate data about all appropriate measures in hydraulic fracturing. Knowledge of the composition of a fluid used in hydraulic fracturing is very important because:

- each time on its basis should be modified the scope of waste testing,
- designation of all fluid components is not always possible (e.g., due to lack of analytical methods or incorrect sensitivity of the method, unreasonable cost). In such a situation, during the evaluation of adverse effects of waste, it can be assumed that the level of a given substance in the waste is equivalent to its level in the fluid, provided that it is a substance whose concentration can significantly increase e.g., due to dissolution of rock. On the other hand, it should be noted that substance concentration adopted for the waste and analogous to the fluid can be overstated, since the fluid components during hydraulic fracturing may undergo various changes (e.g., degradation, oxidation, reduction), and their concentration in the resulting waste may be lower than in the fracturing fluid.

The suggested range of research of physicochemical parameters, which can be supplemented by the designation of additional parameters resulting from the composition analysis of hydraulic fracturing fluid, will be assessed by laboratory analysis of real samples of waste (post-fracturing fluids and, if possible, drilling waste) in the next stage of the project. On the basis of the obtained results of testing real samples, a range of the proposed designations of physicochemical parameters for this type of waste will be verified and an analysis will be carried out to test the harmfulness of waste generated during shale gas operations.

5 RECAPITULATION AND CONCLUSIONS

Exploration of hydrocarbon deposits, regardless of their type, are connected with generation of waste and potentially with adverse environmental effects which may vary and depend largely on the type of materials and chemicals used in the process. The quality of generated waste is also affected by the location and nature of the geological formation and the time span the fluids remain in the borehole.

Wastes generated during shale gas operations can be divided into two main types: (a)waste directly connected with drilling operation and subsequent reservoir tests i.e., extractive wastes and (b) wastes connected with drilling rig operation, delivery of services, presence of employees on the drill site.

Waste associated with the exploration of unconventional hydrocarbon deposits is a mixture of organic and inorganic materials, many of which are components of fracturing fluids. Qualitative composition of this type of waste (both drilling and flowback water) changes widely over time, depending on numerous factors such as, for example, depth and construction of the borehole, type of drilled rock formations, chemical reactions between the rock and the fluid, the time fluids remain in the borehole and chemicals used in technological process. In the this case, the proper determination of the range of physicochemical parameters, which should be designated in waste samples, is very important. Detailed knowledge of waste qualitative composition should contribute to better waste management and enable the selection of appropriate treatment options and identification of its source in cases of environmental contamination, and thus to reduction of the risk posed by the waste to the environment and human health.

Little information is publicly available about the qualitative and quantitative composition of waste generated during exploration and identification of unconventional hydrocarbon deposits. Characterization of waste connected with shale gas operations has been reported in the literature in various degrees of detail. Only a few papers, mainly in the last decade, have reported the identification of organic compounds in flowback and produced waters.

In the USA, the most frequently designated physicochemical parameters of the post-fracturing fluid samples are pH, conductivity, total suspended solids (TSS), total dissolved solids (TDS), inorganic anions, metals, total organic carbon (TOC), dissolved organic carbon (DOC), chemical oxygen demand (COD), biochemical oxygen demand (BOD) and organic compounds. Test results show that flowback water is usually characterized by a high content of sodium ions (up to 82,000 mg/l) and chloride ions (up to 200,000 mg/l),and thus the content of total dissolved solids may also be high (even up to 390,000 mg/l). In addition, other components such as barium, strontium, magnesium, calcium, iron, sulphate, bromide and other noxious inorganic constituents are found in flowback water. In flowback water organic compounds are also designated, but their content is very low. Flowback water may also contain surfactants (*Thurman et al., 2014*).

In Europe in drilling wastes generated during exploration of unconventional hydrocarbon deposits are determined parameters such as pH, conductivity, metals, inorganic anions, total dissolved solids (TDS), total organic carbon (TOC), dissolved organic carbon (DOC), hydrocarbons including polycyclic aromatic hydrocarbons and surface active substances (anionic). Tests results show that, depending on the location of the deposit and chemicals used in drilling, drilling waste may contain high levels of metals such as aluminium, iron, calcium, magnesium, sodium and potassium, or may have a high content of total organic carbon and hydrocarbons. A similar range of physicochemical parameters was designated in flowback water samples. In addition, in fluid samples concentration of natural radioactive isotopes was determined. In this case, the tested samples were usually characterized by a high content of sodium ions and chloride ions. Contents of the rest designated components varied depending on areas and shales, and quality of fluid used in hydraulic fracturing.

The range of designated physicochemical parameters of the waste generated during shale gas operations appears to be quite broad but not all parameters are always determined for each deposit. There are also no guidelines stating what range of parameters should be determined so that the generated waste does not endanger the environment and human health. Final evaluation of waste generated during exploration of unconventional hydrocarbon deposits in terms of harmfulness to the environment should be carried out both on the basis of the study of physicochemical parameters, and the analysis of the composition of the fluid used in the hydraulic fracturing.

The range of physicochemical parameters initially proposed within the project, which should be designated in the waste generated during shale gas operations, includes designation of pH, conductivity, total organic carbon (TOC), chemical oxygen demand (COD), biochemical oxygen demand (BOD), metals (including heavy metals), inorganic anions, hydrocarbons (including mono- and polycyclic aromatic hydrocarbons), phenol index and alcohol. In the next stage of the project, this range of physicochemical parameters tests will be assessed and verified by laboratory analysis of real samples of waste. Analysis of the impact of waste generated during shale gas operations on the environment is also planned to be carried out.

6 REFERENCES

Akob, D.M., Mumford, A.C., Orem, W., Engle, M.A., Klinges, J.G., Kent, D.B., Cozzarelli, I.M. (2016) Wastewater Disposal from Unconventional Oil and Gas Development Degrades Stream Quality at a West Virginia Injection Facility, Environ. Sci. Technol., 50, p. 5517−5525.

Commission Decision 2009/359/EC of 30 April 2009 completing the definition of inert waste in implementation of Article 22(1)(f) of Directive 2006/21/EC of the European Parliament and the Council concerning the management of waste from extractive industries.

Dahm, K.G., van Straaten, C.M., Munakata-Marr, J., Drewes, J.E. (2013) Identifying well contamination through the use of 3-d fluorescence spectroscopy to classify coalbed methane produced water. Environ. Sci. Technol. 47, p. 649–656.

Directive 2006/21/EC of the European Parliament and of the Council of 15 March 2006 on the management of waste from extractive industries and amending Directive 2004/35/EC (Official Journal 11.04.2006 UE L 102 with later amendments).

Ferrer, I., Thurman, E.M. (2015) Chemical constituents and analytical approaches for hydraulic fracturing waters, Trends in Environmental Analytical Chemistry, 5, p. 18–25.

Granops, M., Firlit, Z., Michelc, M.M., Granops, J. (2013) Oczyszczanie ścieków (płynu zwrotnego) powstających po szczelinowaniu hydraulicznym [Treatment of wastewater (flowback water) after hydrofracturing], Przem. Chem., 92, 5, 675.

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, p. 55–61.

Hayes, T. (2009) Sampling and analysis of water streams associated with the development of Marcellus shale gas, Final Report, Gas Technology Institute. Website: https://www.bucknell.edu/script/environmentalcenter/marcellus/default.aspx?articleid=14, accessed in July 2016.

Hayes, T. (2011) Characterization of Marcellus Shale and Barnett Shale Flowback Waters and Technology Development for Water Reuse, Gas Technology Institute. Website: https://www.epa.gov/hfstudy/characterization-marcellus-and-barnett-shale-flowback-waters-and-technology-development, accessed in July 2016.

Jack, R., Kondratyuk, T., Stolz, J. (2014) Analysis of Flowback Water from Marcellus Unconventional Gas Extraction Using IC and ICP-OES, PITTCON™ Conference & Expo.

Karakulski, K., Gryta, M., Morawski, A., Mozia, S. (2012) Oczyszczanie wód z procesu wydobycia gazu zwanego łupkowym [Water purification after a process of shale gas extraction], Przem. Chem. 91, nr 10, 2011.

Kargbo, D.M., Wilhelm, R.G., Campbell, D.J. (2010) Natural gas plays in the Marcellus shale: challenges and potential opportunities. Environ. Sci. Technol 44, p. 5679-5684.

Kidder, M., Palmgren, T., Ovalle, A., Kapila, M. (2011) Treatment options for reuse of frac flowback and produced water from shale, World Oil Online, 232(7), p. 95–97.

Klimkiewicz, A., Korczak, K. (2012) Technologiczne i środowiskowe aspekty wykorzystywania wody w procesie wydobycia gazu łupkowego [Technological and environmental aspects of water use in the extraction of shale gas], Research Reports Mining and Environment, 3, p. 43-54.

Konieczyńska, M., Woźnicka, M., Antolak, O., Janica, R., Lichtarski, G., Nidental, M., Otwinowski, J., Starzycka, A., Stec, B., Wróbel, G., Potrykus, R., Gdaniec Rohde, B., Włodarski, T. (2011) Badania aspektów środowiskowych procesu szczelinowania hydraulicznego wykonanego w otworze Łebień LE-2H, Raport końcowy [Study of the environmental aspects of the process of hydraulic fracturing performed in Łebień LE-2H borehole, Final Report].

Król, A., Krasińska, A., Kukulska-Zając, E., Dobrzańska, M., Holewa, J., Szlęk, M. (2013) Odpady wydobywcze – weryfikacja metodyki badawczej i sposobu oceny szkodliwości [Extractive waste - verification of research methodology and method for assessing the harmfulness], Oil and Gas Institute – National Research Institute, Krakow.

Lester, Y., Ferrer, I., Thurman, E.M., Sitterley, K.A., Korak, J.A., Aiken, G., Linden, K.G. (2015) Characterization of hydraulic fracturing flowback water in Colorado: Implications for water treatment, Science of the Total Environment, 512–513, p. 637–644.

Macuda J. (2010) Środowiskowe aspekty potencjalnej produkcji gazu ziemnego z niekonwencjonalnych złóż [Environmental aspects of the potential production of natural gas from of unconventional deposits], Przegląd Geologiczny, vol.58, nr 3.

News service of Polish Geological Survey (http://infolupki.pgi.gov.pl/pl), sub-page “Waste management – part 1” (http://infolupki.pgi.gov.pl/pl/srodowisko/gospodarka-odpadami-czesc-1-0), visited in July 2016.

News service of Polish Geological Survey (http://infolupki.pgi.gov.pl/pl), sub-page “Waste management – part 2” (http://infolupki.pgi.gov.pl/pl/srodowisko/gospodarka-odpadami-czesc-2), visited in July 2016.

Olsson, O., Weichgrebe, D., Rosenwinkel, K.H. (2013) Hydraulic fracturing wastewater in Germany: composition, treatment, concerns. Environ. Earth Sci. 70, p. 3895–3906.

Otawa, A., Skomudek, W. (2015) Aspekty logistyczne poszukiwania i wydobywania gazu łupkowego w Polsce [Logistical aspects of shale gas exploration and extraction in Poland], Logistyka 6/2015.

Rahm, D. (2011) Regulating hydraulic fracturing in shale gas plays: the case of Texas, Energ. Policy 39, p. 2974-2981.

Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labeling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006 and its subsequent amendments (Official Journal of the European Union, L 353/1).

Shaffer, D.L., Arias Chavez, L.H., Ben-Sasson, M., Romero-Vargas Castrillon, S., Yip, N.Y., Elimelech, M. (2013) Desalination and reuse of high-salinity shale gas produced water: drivers, technologies, and future directions, Environ. Sci. Technol 47, p. 9569-9583.

Shih, J-S., Saiers, J.E., Anisfeld,S.C., Chu, Z., Muehlenbachs,L.A., Olmstead, S.M. (2015) Characterization and Analysis of Liquid Waste from Marcellus Shale Gas Development, Environ. Sci. Technol., 49, p. 9557−9565.

Sprawozdanie z realizacji krajowego planu gospodarki odpadami 2014 za okres od dnia 1 stycznia 2011r. do dnia 31 grudnia 2013r. [The report on the implementation of the National Waste Management Plan 2014 for the period from 1 January 2011 until 31 December 2013], 2015, Ministerstwo Środowiska [Ministry of the Environment]. Website: https://www.mos.gov.pl/, accessed in July 2016.

Starzycka, A. (2012) Środowiskowe i prawne aspekty zagospodarowania odpadów powstających w trakcie poszukiwania, rozpoznawania i wydobycia gazu z łupków [Environmental and legal aspects of waste generated during exploration, identification and extraction of shale gas], Poznań.

Starzycka, A. (2014) Gospodarka odpadami powstającymi podczas poszukiwania węglowodorów ze złóż niekonwencjonalnych [Waste generated during exploration of hydrocarbons from unconventional deposits], warsztaty „Gospodarka wodna i gospodarka odpadami w procesie poszukiwania i wydobycia węglowodorów ze złóż niekonwencjonalnych" [workshop "Water and waste management in the process of exploration and extraction of hydrocarbons from unconventional deposits"], Gdańsk.

Ścisłowicz, W., Bogacz, B., Dziubek, K., Góra, S., Płocica, K., Rychlewski, Ł., Szwedo, R., Tott, M., Urbańczyk, M. (2012) Poszukiwanie i rozpoznawanie złóż gazu ziemnego i ropy naftowej w obszarze „Oleśnica" – zmiana koncesji nr 37/2011/p [Identification and exploration of natural gas and crude oil in "Oleśnica" - change of a license No. 37/2011/p], Raport o oddziaływaniu na środowisko przedsięwzięcia [Report on the environmental impact of the project].

Ścisłowicz, W., Dziubek, K. (2011) Poszukiwanie i rozpoznawanie złóż ropy naftowej i gazu ziemnego w obrębie obszaru koncesyjnego Brześć Kujawski [Exploration and identification of oil and natural gas deposits within the concession area of Brześć Kujawski], Karta informacyjna przedsięwzięcia [Project Information Sheet].

Środowisko i prace rozpoznawcze dotyczące gazu z łupków; wyniki badań środowiska gruntowo-wodnego, powietrza, klimatu akustycznego, płynów technologicznych i odpadów [The environment and shale gas exploration. Results of studies on the soil-water environment, ambient air, acoustic climate, process fluids and wastes], 2015, praca zbiorowa na zlecenie Ministerstwa Środowiska [collective work commissioned by the Ministry of the Environment]. Website: http://www.gdos.gov.pl/gaz-z-lupkow, accessed in July 2016.

Thacker, J.B., Carlton, D.D.,Jr., Hildenbrand, Z.L., Kadjo, A.F., Schug, K.A. (2015) Chemical analysis of wastewater from unconventional drilling operations. Water, 7, p. 1568−1579.

Thurman, E.M., Ferrer, I., Blotevogel, J., Borch, T. (2014) Analysis of Hydraulic Fracturing Flowback and Produced Waters Using Accurate Mass: Identification of Ethoxylated Surfactants, Anal. Chem., 86, p. 9653−9661.

Vengosh, A., Jackson, R.B., Warner, N., Darrah, T.H. Kondash, A. (2014) A critical review of the risks to water resources from unconventional shale gas development and hydraulic fracturing in the United States. Environ. Sci. Technol., 48, p. 8334−8348.

Zhang, X., Sun, A.Y., Duncan, I.J. (2016) Shale gas wastewater management under uncertainty, Journal of Environmental Management, 165, p. 188-198.

Ziemkiewicz, P.F. (2013) Characterization of Liquid Waste Streams fom Shale Gas Development, AGH Drilling, Oil, Gas, 30, 1, p. 297-310.

