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**SECURE – Subsurface Evaluation of Carbon capture  
and storage and Unconventional risks**

**GUIDELINES FOR COMMON STRATEGIES IN GAS  
STORAGE AND EXPLOITATION BASELINE  
ASSESSMENT AND MONITORING**

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## Public introduction

Subsurface Evaluation of CCS and Unconventional Risks (SECURE) is gathering unbiased, impartial scientific evidence for risk mitigation and monitoring for environmental protection to underpin subsurface geoenergy development. The main outputs of SECURE comprise recommendations for best practice for unconventional hydrocarbon production and geological CO<sub>2</sub> storage. The project is funded from June 2018–May 2021.

The project is developing monitoring and mitigation strategies for the full geoenergy project lifecycle, by assessing plausible hazards and monitoring associated environmental risks. This is achieved through a program of experimental research and advanced technology development that includes demonstration at commercial and research facilities to formulate best practice. We will meet stakeholder needs; from the design of monitoring and mitigation strategies relevant to operators and regulators, to developing communication strategies to provide a greater level of understanding of the potential impacts.

The SECURE partnership comprises major research and commercial organisations from countries that host shale gas and CCS industries at different stages of operation (from permitted to closed). We are forming a durable international partnership with non-European groups; providing international access to study sites, creating links between projects and increasing our collective capability through exchange of scientific staff.

## Executive report summary

The report presents an overview of baseline assessment and environmental monitoring on three selected study sites, comprising a CO<sub>2</sub> pilot injection site, an acid gas storage site and a gas seeping site as natural analogue of gas leakage from shale gas formations. This work outlines and discusses the options for monitoring methodologies and identifies the components of an appropriate baseline assessment using the examples of the various sites. Key findings with focus on spatial criteria of the deployed monitoring methodologies and generic requirements for the baseline assessment are given.



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# 1 Introduction

The efficient and cost-effective utilization of unconventional and sustainable energy resources has been required with decreases in conventional hydrocarbon resources (Streich et al., 2010). The unconventional hydrocarbon resources include natural gas from shale formations (shale gas), natural gas from coal seams (coalbed methane) and crude oil from shale formations or other formations with low permeability (tight oil or shale oil). Shale gas, especially, is considered the unconventional fossil fuel with the most significant development potential in Europe (EU Parliament, 2014). Concurrently, carbon capture and storage (CCS) has been developed worldwide as an intermediate perspective option for the successful transition to the low-carbon economy and reduce the environmental impact of exploiting fossil energy resources (Liebscher et al., 2013; Streich et al., 2010). The CCS technology aims to capture, transport, and permanently store carbon dioxide (CO<sub>2</sub>) underground in order to avoid its emission into the atmosphere. It has been considered as a key technology for the decarbonisation of the global energy system and can be applied to power generation and industrial production (Budinis et al., 2018; Wallquist et al., 2010).

Despite the successful implementation of several gas storage and exploitation operations, pilot and commercial projects, there is still concern about the potential detrimental impacts on the environment and human health. To minimize environmental impact and provide public assurance, a scientifically credible and robust monitoring program at the geological reservoir and an environmental impact assessment of any plausible leakage even at the surface are required to be performed during the all project life cycle (Ajayi et al., 2019; Blackford et al., 2015). Although the subsurface technologies, CCS and gas exploitation from unconventional reservoirs, have a different spatial and temporal scale of the potential gas and brine migration, both technologies utilize deep-lying geological formations. It may induce similar impacts via similar pathways, including induced seismicity, detrimental fluid migration, and displacement of brine solutions (Hough, 2018). Various monitoring experiences exist from the gas storage and exploitation sites, environmental baseline monitoring programs, and also natural analogue sites. These previous experiences are of great importance because the methodological and technical background can be comparable with the monitoring strategy for future geoenery projects (Baumann, 2013).

This deliverable report aims to give an overview of baseline and monitoring techniques and technical lessons learned from existing gas storage and exploitation project sites at various operation stages from the permission to abandonment. The monitoring methods obtained from the natural resource survey and environmental monitoring will also be included. The study sites are 1) Ketzin CO<sub>2</sub> storage site (DE), 2) Borzęcin acid gas storage (PL), and 3) French Subalpine gas seepage site (FR) (see Figure 1). Here, the detailed monitoring results will not be presented. Instead, the key messages obtained from the projects will be addressed. Finally, common baseline and monitoring strategies will be outlined by assessing the plausible hazards and understanding the techniques evaluated at the sites. The output will be applicable to the other demonstration projects providing criteria for stable and reliable monitoring.

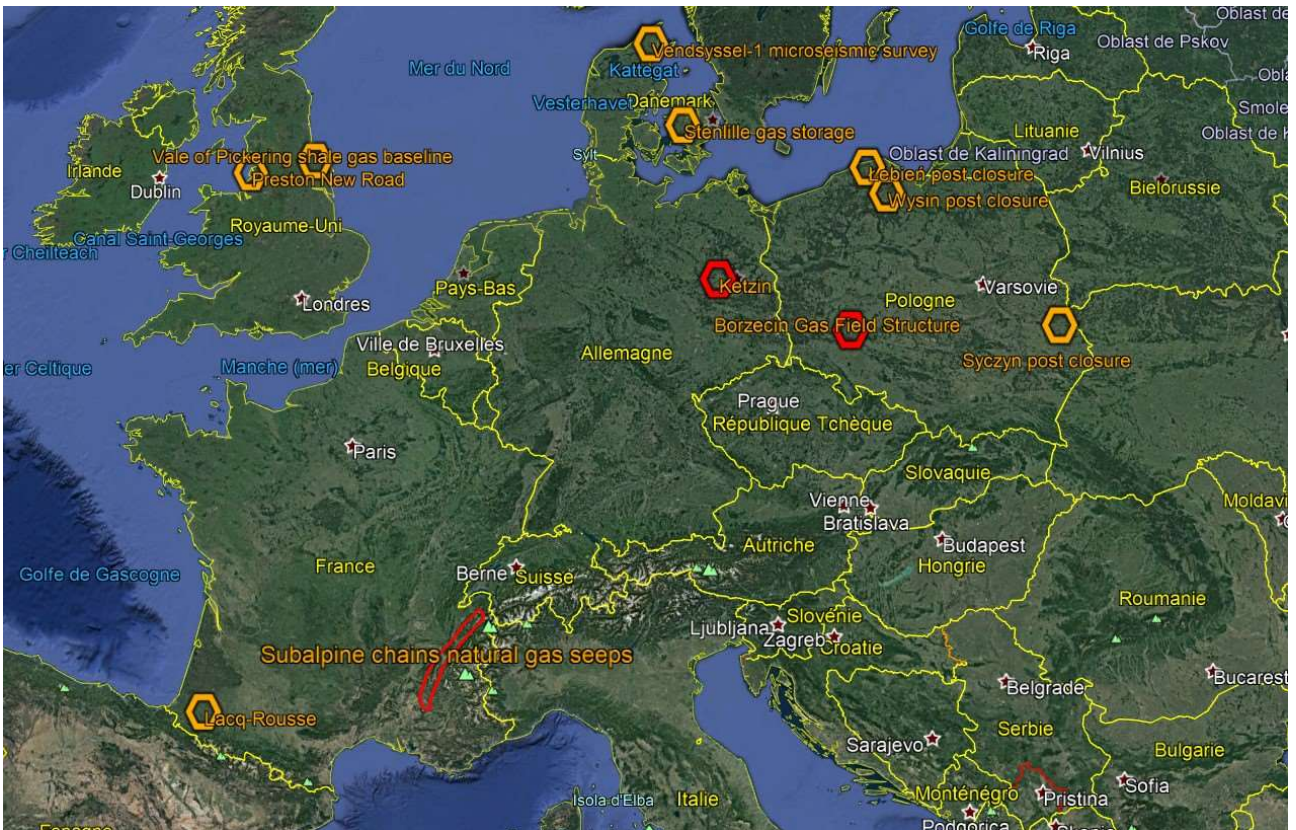


Figure 1 European study sites for WP3, in red: Study sites investigated in this report.



## 2 Monitoring methodology for gas storage and exploitation from unconventional reservoirs

In the ten years since publication of the IPCC 2005 report on CCS, considerable progress has been made in measurement, monitoring and verification (MMV), as the review of Jenkins et al. (2015) has determined. Numerous technologies have been adapted and implemented to demonstrate containment, conformance, and no environmental impact at test sites and field projects under investigation. Some years later, an updated screening by Jenkins (2020) showed that a shift towards commercial utilization has altered the context of MMV. Some particular methods and monitoring systems in certain areas have been more rapidly developed than others, driven by cost requirements or demands for quantification of CO<sub>2</sub> leakage. Examples are the seismic surveying based on optical fibre technology (DAS) and acoustic surveillance techniques for the marine ecosystem.

Appropriate monitoring should be performed in spatial and time scales. The obtained information should be compared with the baseline measurement before the project starts with repeated measurement, during operation/exploitation, and after site abandonment to evaluate the induced changes (Ajayi et al., 2019). In general, monitoring techniques can be divided spatially into atmospheric monitoring, near-surface monitoring, and subsurface monitoring (Brown et al., 2009). The atmospheric monitoring includes satellite remote sensing. The near-surface monitoring includes soil gas analysis and water analysis. For the subsurface monitoring, geophysical and geochemical techniques are used to derive relevant properties of the subsurface reservoir and the confining strata. Comparing to the surface monitoring, the subsurface monitoring techniques cover a wide range of scales with different resolutions for the derived properties (Baumann, 2013). On a temporal basis, monitoring can be classified as injection phases and post-injection phase, or in the case of shale gas resources in exploration, drilling (vertical-horizontal), hydraulic fracturing (multiple), exploitation, closure and post-closure. In this work, we limit ourselves to discussing monitoring on a spatial basis.

The suitability of different monitoring tools and their combination has been evaluated at the selected study sites (see **Table 1**). These sites cover a wide range of suitable geological formations for gas storage and exploitation purposes. The first two study sites in **Table 1** are the full-lifecycle sites, and the third is a natural analogue to develop, compare, and identify the most appropriate monitoring methods. Briefly, the Ketzin pilot site (DE) for geological storage of CO<sub>2</sub> is the first demonstration project for geological on-shore CO<sub>2</sub> storage in Europe, and injection was accompanied by a comprehensive operational monitoring program (Liebscher et al., 2013). The Borzęcin injection project (PL) is a full-scale acid gas reinjection process of practical value into the original gas reservoir, and the acid gas sequestration process has been monitored for the injected gas migration in the water layers and to the gas cap (Lubaś et al., 2020). In the survey area in the French Subalpine Chains (FR), soil gas monitoring has been performed on natural hydrocarbon gas seeps from organic-rich shales as a natural analogue of gas leakage from shale gas formations (Gal et al., 2019a).





**Table 1 Monitoring tools applied to gas storage and for natural gas exploitation from unconventional reservoirs for selected study sites of Figure 1.**

	<b>Ketzin CO<sub>2</sub> storage</b>	<b>Borzecin Acid gas storage</b>	<b>French Alps (CO<sub>2</sub>/CH<sub>4</sub>)</b>
	Full-life cycle storage		Survey areas
Seismic survey	x		
Gas monitoring	x	x	x
Fluid sampling	x		
Groundwater monitoring	x	x	
Temperature-pressure profiling	x		
Injected waste loads and characteristic		x	
Well-integrity monitoring	x	x*	

\*well casing corrosion monitoring

## 2.1 SUBSURFACE MONITORING

### 2.1.1 Well-integrity monitoring

Well-integrity is one of the most crucial issues for the long-term and integral for safe gas storage (Zemke et al., 2017). During the injection phase, cement and casing material integrity is vital to ensure sustainable injection processes. For the post-injection phase, the well integrity is the most essential for any proper and safe long-term abandonment of the well (Wipki et al., 2016). For example, the well is likely to be a potential migration pathway for leakage, and the corrosion may trigger unexpected geochemical and geophysical changes (Duguid et al., 2017).

Pulsed neutron gamma logging (PNG), magnetic induction defectoscopy (MID), and video inspection can be applied to the well-integrity monitoring program. The PNG logging uses controlled neutron bursts, which interact with the nuclei of the surrounding borehole and formation. Due to collision with these neutrons, atoms from the surrounding environment emit gamma rays (Baumann, 2013). It provides information on potential changes in fluid composition in the very near well-bore area and a hint for upward CO<sub>2</sub> infiltration of the cement (Baumann et al., 2014; Wipki et al., 2016). This technique is widely used in oil and gas fields, giving detailed information about possible changing saturation conditions due to production or injection operations (Baumann et al., 2014; Liu et al., 2018). The MID is an advanced logging method for non-destructive testing and has the great advantages that it can be operated in gas-filled boreholes and provides information also for outer casing (Zemke et al., 2017). MID is an electromagnetic downhole logging technique that records magnetization decays induced by high-power electromagnetic pulses that can penetrate through multi tubulars, providing information about pipe condition that was not previously available. The measurements reflect the well sketch and the position of the downhole tools (such as collar, casing shoes, packers, and valves). They can be used to determine the thickness of the tubing and casing in wells and detect various damages such as corrosion, deformation, cracks, fractures, and/or holes in the pipe string. (Zemke et al., 2017). Finally, the video camera inspection can visualize corrosion effects as the camera descends to the casing while continuously filming. Using this inspection, the inner casing surface can be screened (Gawel et al., 2017).



## 2.2 NEAR-SURFACE MONITORING

### 2.2.1 Soil gas monitoring

Soil gas monitoring is a set of shallow-focused monitoring techniques that may include the monitoring of gas concentrations in the soil, gas flux measurements at the soil/atmosphere interface and gas concentrations in the atmosphere, with a large set of sensors and monitoring equipment (Jenkins *et al.*, 2015). The techniques of soil gas or ground gas monitoring encompass a large spectrum of species of interest, with specific focus on CO<sub>2</sub> for Carbon Capture and Storage applications (e.g. Klusman (2011)) and on CH<sub>4</sub> for Shale Gas applications (e.g. Lowry *et al.* (2020)). Soil gas monitoring techniques have been widely used in CCS applications and to a lesser extent in Shale Gas applications. One of the key issues to consider using soil gas monitoring is to understand how human activities can affect the natural systems and subsequently the natural variations that gas species may have in the soil (Teasdale *et al.*, 2014). Meteorological conditions have indeed a strong influence on gas emissions and large variabilities can be induced by these natural processes as demonstrated since a long time with one of the first gas species ever monitored; radon gas (Kovach, 1946). To overcome part of these natural-induced variabilities, attribution techniques have been developed such as the process-based approach (Romanak *et al.*, 2012), which is useful not only to monitor baseline conditions but also to assess the integrity of a storage site throughout its lifetime including post-closure monitoring (Gal *et al.*, 2019; Shao *et al.*, 2019).

In the framework of SECURE, soil gas monitoring techniques have been used at some hydrocarbon gas seeps located in the Alpine chain. These investigations were mostly relying on two established monitoring techniques. The first technique is the monitoring of soil gas concentrations at 1 m depth in the soil, a depth where the effect of atmospheric dilution becomes negligible Hinkle, 1994. Some species were directly quantified in the field using gas detectors (CO<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>) and other species (like N<sub>2</sub> and alkanes from C<sub>2</sub> to C<sub>6</sub>) were monitored by gas chromatography on samples (Gal *et al.*, 2018a). Sampling also enables further isotopic determination in the laboratory on CO<sub>2</sub> and CH<sub>4</sub>. The second technique is the monitoring of the CO<sub>2</sub> and CH<sub>4</sub> flux emitted at the surface of the soil into the atmosphere, using the accumulation chamber technique, with external recirculation (Gal *et al.*, 2018). These two techniques are robust techniques used in a variety of contexts and applications for decades so that the limitations on the measuring procedures are well constrained, and they are constantly being improved thanks to technological advances on sensors. Complementary investigations were performed using more recent technologies, namely Unmanned Aerial Vehicles (UAV), with specific sensing capacities, to benefit from quicker acquisitions over far larger areas (Jordan *et al.*, 2021). Routine soil gas and soil flux monitoring techniques give indeed accurate information but they are labor-intensive if we aim at getting a good evaluation of concentrations and fluxes even over relatively small areas. For example, the investigations reported by Gal *et al.* (2018) were performed over grids of 1 m to 2 m spacing and some days are required to investigate a 20x20 m area.

Soil gas monitoring can be used as a tool for detection of gas leakage from natural or artificial gas storage reservoirs whose natural confinement might have been compromised through exploitation and/or injection boreholes (Schout *et al.*, 2019). Also, reservoir pressure changes (stress and/or relaxation due to gas production, injection of fluids in hydraulic fracturing operations or enhanced hydrocarbon recovery, CO<sub>2</sub> sequestration or other substances storage) might impact a confinement integrity or even trigger tectonic mass movements. As an effect of the latter, migration pathways along fractures and faults may be opened, especially for buoyancy-driven gas migration. Unfortunately, it is not easy to assess or predict where such induced migration paths may be opened and thus where the migrating gases can show up in the soil gas composition.

However, well-documented boreholes (which may not be the case for a quite substantial number of legacy oil and gas wells decommissioned in the past worldwide without any stored records) can be subjected to soil gas composition monitoring as an auxiliary method<sup>1</sup> for detecting gas leakage caused by well integrity failure in operating wells and as the main technique for assessing leakage of decommissioned wells. Note however, that depending on soil conditions and the depth where a well casing has been cut off within decommissioning operations, leaking gas flux may be dispersed in a near-surface zone so that the highest gas concentrations

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<sup>1</sup> Detection and quantification of gas leakage caused by well integrity failure is typically assessed at the wellhead by a sustained casing pressure (SCP) measurements (Bruffatto *et al.*, 2003; Lackey *et al.*, 2017), surface casing vent flow (SCVF) method (Dusseault *et al.*, 2014; Watson and Bachu, 2009) or visual observation of leaking gas bubbles.



can be diverted from the original well location point. Thus, the surficial scanning of gas flux needs to be conducted in the vicinity of well locations, e.g. as proposed by Schout et al. (2019), on a spiral pattern. When collecting gas from a certain depth into gas flux chambers placed on a ground surface, due to the mentioned dispersion, significant differences in gas concentrations were detected between the samples taken from different depths at the same point (Schout, 2019). Samples for laboratory concentration and isotope measurements collected directly from a certain depth by soil gas samplers should follow regular arrays starting at the well location (Koniecznyńska & Macuda, 2015, Koniecznyńska et al., 2018, Sechman et al., 2015). It is important to follow the same methodology and to keep the same depth of samples collection to be able to compare long-term observation results.

It needs to be emphasized that in case of long-term industrial activities (like in the Borzęcin gas mine and acid gas injection plant described further in this report) there may not be sufficient baseline observations of soil gas due to a lack of available measurements and legal requirements at the start of a project. Also, in the future, technological development will possibly bring about better methods for soil gas monitoring and improve the use of data acquired this way. Assuming that the time scale needed for observations in underground projects is and will be very long, the researchers must remember to adjust the results interpretation to a changing methodology, try to cooperate as close as possible with the site operators and make sure that obtained monitoring results are comparable over time. This needs a thorough documentation of the techniques used both for field measurements and sampling and for laboratory analyses.

### 2.2.2 Groundwater monitoring

Leakage of gases from underground natural or artificial accumulations can also be assessed based on results of gas concentrations in groundwater. It is noticeable that the interest in measuring dissolved methane concentrations in aquifers increased with the exploitation of unconventional gas resources, though possibility of gas migration towards the surface is not restricted to these resources – simply the awareness of the problem became more common with the shale gas development controversy. However, the research started mainly because examples in the North American shale gas development have shown the importance of establishing a stringent pre-production baseline for tracking changes in groundwater gas content along with gas production activities (Bell, 2017).

Dissolved gas content and isotopic composition monitoring in groundwater has been used for possible gas leakage detection in many locations of hydrocarbons prospection and exploitation (e.g. Osborn et al., 2011; Van Stempvoort and Jaworski, 1995, Koniecznyńska et al., 2015). However, in case of hydrocarbons as well as any other accumulated gases in the subsoil (naturally or artificially injected) the ability to detect leakage using groundwater monitoring strongly depends on the distance between the leakage point and the groundwater sampling location (Jackson et al., 2013, Molofsky et al., 2011), the direction and velocity of groundwater flow and the occurrence of microbial methane oxidation (Schout et al., 2017; Van Stempvoort et al., 2005). Even with detailed recognition of these parameters (which is still quite rare in particular for industrial sites) the problem with determination of actual gas migration path, same as in a soil gas monitoring, still remains the main shortage for proper observation points localization. In many cases known from the literature the observations of groundwater chemistry and gas content were conducted within a certain radius from hydrocarbons producing wells as exclusive strategy to define leakage points, neglecting groundwater flow direction and velocity. A similar approach was implemented in the phase of baseline determination on Polish shale gas exploration sites (Koniecznyńska et al., 2015), as there was no time for detailed modelling of groundwater dynamics below those sites. For the same reason, only existing water wells were used at this stage. Furthermore, it was assumed that no previous activities related to conventional hydrocarbon exploitation led to thermogenic gas accumulations in groundwater.

Gas migrating along natural or artificial pathways, to reach the surface can occur via several groundwater layers. For effective leakage mitigation, the deeper it is detected, the better. Thus, the monitoring of deep saline aquifers overlying gas reservoirs according to e.g. model-predicted migration paths would seem better early warning tool than the most usual observations of actual usable fresh groundwater. But not only costs of constructing deep monitoring wells but also difficulties in proper samples collection from pressured aquifers limit the use of this kind of observations for gas leakage detection. The difficulties are related to possible dissolved gas concentration shifts along with a pressure and temperature changes while samples are collected



and transported. Downhole sampling techniques like those used for the reservoir fluids themselves may be appropriated in such cases.

In shallow fresh groundwater the risk of failures in gas content analysis due to improper sampling technique seems to be less critical. A series of experiments conducted in the SECURE project on sampling of groundwater from a depth of some meters to some tens meters with use of different water abstraction tools (peristaltic and impeller submersible pumps as well as a discrete interval sampler) showed no significant differences between samples taken with each method. Initial differences in the results of methane and carbon dioxide composition in samples stored for longer than one week were observed which might have been caused either by not sufficiently tight sample containers or bacterial activity in the collected water. Addition of a biocide to a consecutive series of samples proved the latter cause. Detailed discussion on shortages and implemented methods of groundwater sampling and gas content analysis can be found in the SECURE D3.8 report of long-term post-operational monitoring of Ketzin (CCS) and Polish (shale gas) sites.



## 3 Environmental baseline monitoring programs for the gas storage and exploitation of unconventional reservoirs

### 3.1 KETZIN CO<sub>2</sub> STORAGE SITE, GERMANY

The Ketzin CO<sub>2</sub> site was initiated in 2004 to evaluate and develop methods for CO<sub>2</sub> storage monitoring (Martens et al., 2014; Würdemann et al., 2010). Between 2008 and 2013, about 67 kt of CO<sub>2</sub> were injected into saline aquifers. After the successful injection, the site was permanently closed, and all monitoring programs were ended in 2017. The Ketzin site provides a unique opportunity to work on data from all phases of the storage life cycle, from permission to abandonment. Compared to the baseline and operational data, only limited data from post-injection monitoring exist. The post-injection monitoring data are required for storage validation, model calibration, and long-term evaluation of monitoring strategies (Michael et al., 2010). The experience from the Ketzin site has been beneficial for other demonstration projects. It can be used to establish best practice guidelines.

#### 3.1.1 Location and geologic setting

The Ketzin site is located about 25 km west of Berlin, Germany, and has been used for gas storage since 1964. The site is situated on the southern flank of an anticlinal structure, and the anticline hosts the sandstones of the Triassic Stuttgart Formation. The Stuttgart Formation is lithologically heterogeneous, consisting of sandstone, alternating with muddy rocks. The sandstones vary in thickness between 15 and 30 m (Förster et al., 2006) and are present at a depth range of 620-650 m. The Stuttgart Formation is sealed by thick cap rocks of the Weser Formation (up to 165 m thick clay- and mud-stone) (Norden and Frykman, 2013).

#### 3.1.2 Drilling and well completion and CO<sub>2</sub> injection

A total of five wells had been installed including three deep observation wells (Ktzi 200, Ktzi 202, and Ktzi 203), one deep injection/observation well (Ktzi 201), and one shallow observation well (P300). The five wells are now abandoned and back-filled. Four are deep wells of about 700-800 m depth and one a relatively shallow well of about 445 m. The wells Ktzi 200, Ktzi 201, and Ktzi 202 were drilled in 2007 prior to the start of CO<sub>2</sub> injection, and the shallow well P300 was drilled in 2011 to monitor the integrity of the storage and to trace fluctuations of natural geogenic CO<sub>2</sub> outside the storage reservoir. The last well Ktzi 203 was completed in 2012 to gain rock cores from the cap rock and reservoir. An injection facility was built in 2008.

The injected CO<sub>2</sub> predominantly had a purity of >99.9%, and only from May to June 2011, 1.515 kt CO<sub>2</sub> with a purity of >99.7% was injected. The gas consisted of CO<sub>2</sub> with traces of N<sub>2</sub>, He, and CH<sub>4</sub> (Liebscher et al., 2013). After the injection of 67 kt CO<sub>2</sub>, the site entered into the post-injection phase. In parallel, the abandonment phase was prepared by conducting a staged abandonment of the observation well Ktzi 202 in 2013 with additional material investigations. The observation well Ktzi 202 was fully cemented and abandoned in 2015, not available anymore for post-injection monitoring, and all other wells were finally abandoned in 2017. More detailed information can be found in Prevedel et al. (2014).

#### 3.1.3 Multidisciplinary monitoring concept at the Ketzin site

A multidisciplinary monitoring concept has been applied at the Ketzin site (Wipki et al., 2016). The monitoring concept targets the storage complex, the overburden, the surface, and the wellbores. The well-integrity and tightness of the cap rock are monitored by pressure-temperature measurements. Hydraulic and geochemical impact on the formation water was assessed through well P300 (Wiese et al., 2013), and the surface was monitored by CO<sub>2</sub> soil flux measurements and groundwater fluid sampling (Zimmer et al., 2011b). A detailed summary of monitoring techniques conducted at the Ketzin site is given in Martens et al. (2014).

All monitoring methods are applied either on permanent or a periodic basis. Except for above-zone monitoring through well P300, which was drilled in 2011, baseline measurements for all methods were performed prior to starting of CO<sub>2</sub> injection. Geophysical and geological baseline information was integrated with a geological 3D-



model for the Ketzin pilot site, regularly updated based on new monitoring data. Using this static model, numerical simulations based on a history-matched dynamic model were used to predict site behaviour (Wipki et al., 2016). The four deeper wells were completed according a smart casing concept (Prevedel et al., 2009), comprising cables for distributed temperature sensing (DTS) and heating experiments, 45 electrodes (Vertical Electrical Resistivity Array VERA; apart from well Ktzi 203), pressure and temperature (p-T) gauges. The above-zone monitoring is achieved by the well P300 with two pressure sensors and a U-tube fluid sampling system for pressure and fluid monitoring of the indicator horizon (Martens et al., 2014). The monitoring and sampling methods installed in each wellbore are listed below:

- 1) Ktzi 200 : observation well (~800 m depth) ; DTS, VERA, p-T, wireline p
- 2) Ktzi 201 : injection/observation well (~750 m depth) ; DTS, VERA, p-T
- 3) Ktzi 202 : observation well (~750 m depth) ; DTS, VERA, p-T, riser tube sampling
- 4) Ktzi 203 : observation well (~700 m depth) ; DTS, p-T, core sampling
- 5) P300 : shallow observation well (~450 m) ; Above-zone monitoring, U-tube system, p-T

### 3.1.4 Well-integrity monitoring and assessment of CO<sub>2</sub> impacts on the reservoir geochemistry by geochemical modelling

#### 3.1.4.1 WELL-INTEGRITY MONITORING RESULTS

The well-integrity monitoring program was started after the CO<sub>2</sub> injection and continued until well abandonment in summer 2017. The different well inspection techniques, PNG, MID, and video camera inspection, were applied since the beginning of injection on a biannual to an annual basis (Zemke et al., 2017). The dates of the well-integrity monitoring campaigns within the life-cycle of the Ketzin site are displayed in Figure 2. The PNG logging was started in July 2008, just after the start of the CO<sub>2</sub> injection (June 2008), and then performed annually. The first MID measurements of the three deep wells Ktzi 200, 201, and 202 took place in October 2009 and then served as the baseline for the repeated measurement campaigns. The baseline for the later drilled well Ktzi 203 took place in 2013. Video camera inspection started in October 2009 and continued until final well abandonment. Through the PNG logging, monitoring results did not provide any evidence for CO<sub>2</sub> infiltration into the casing cement or even leakage to higher strata through the casings, and data from the MID showed casing thickness within reported production tolerance for the used casing materials. The effects of some degree of corrosion on the inner surface and slight surface erosion, such as scratches from the regular logging tool operations, could be seen on the microscopic scale from the video camera inspection. However, no pitting or surface corrosion of the casings on the macroscopic scale was observed (Schmidt-Hattenberger et al., 2018).



**Figure 2 Post-injection well integrity monitoring (month/year) with the completed storage cycle of the Ketzin CO<sub>2</sub> storage site from (Schmidt-Hattenberger et al., 2018)**

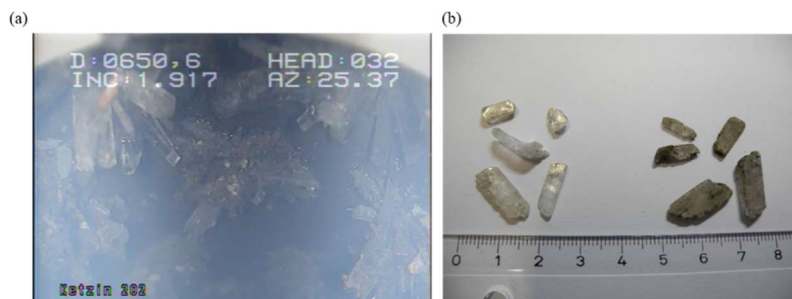
Well-integrity measurements, therefore, show no well integrity issues. In 2013, well Ktzi 202 was partly cemented and abandoned in the reservoir section up to a depth of 521 m after the general integrity of the



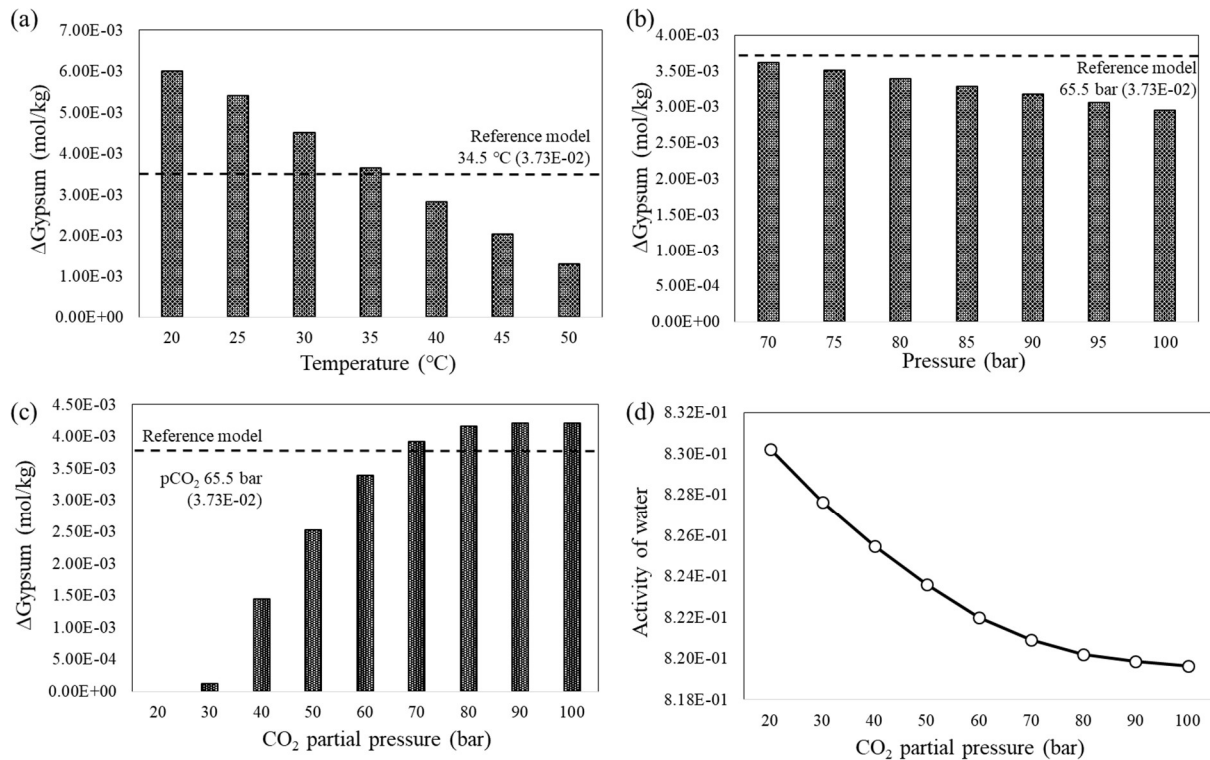
casing, and casing cement had been proved. The integrity of this stage 1 cementation had been monitored by a gas membrane sensor within well Ktzi 202 that allowed probing of the in-well gas composition to detect any potential CO<sub>2</sub>. After the integrity of Stage 2 cementation had been proven, well Ktzi 202 was finally cemented and abandoned in 2015. Integrity monitoring of the other wells was continued until the final abandonment of all wells by summer 2016 (Wipki et al., 2016). Additional information on the well-integrity monitoring can be found in e.g. Wipki et al. (2016), Baumann et al. (2014), Zemke et al. (2017), and Schmidt-Hattenberger et al. (2018).

### 3.1.4.2 ASSESSMENT OF CO<sub>2</sub> IMPACTS ON THE RESERVOIR GEOCHEMISTRY BASED ON THE FIELD OBSERVATION

In October 2011, crystal precipitation was observed in the observation well Ktzi 202 during the video camera inspection. The colourless prismatic crystals were observed at the well perforation holes with an inward growing direction in a bottom filter screen at a depth of 650-651m (Figure 3). The crystals were sampled and investigated by X-ray diffractometry (XRD) in 2012. The phase content analysis showed that the crystals are pure gypsum (CaSO<sub>4</sub>\*2H<sub>2</sub>O). Based on the video camera inspection and XRD analysis, no indication of other mineral precipitation occurred, and only gypsum precipitation was defined.



**Figure 3 (a) Screenshot camera inspection (from the observation well Ktzi202 in Oct 2011 at a depth of 650.6m). The fibrous gypsum and gypsum needles in the well perforation holes grow perpendicular to the well. (b) Samples in the laboratory before and after ultrasonic cleaning (right and left, respectively). The samples are colorless to white and have a monoclinic crystal system.**



**Figure 4 Gypsum precipitation changes due to the  $\text{CO}_2$  intrusion as a function of (a) reservoir temperature, (b) hydrostatic pressure, and (c), (d) imposed of the  $\text{CO}_2$  partial pressure. Modeled gypsum and sulfate concentration changes were calculated using PHREEQC (v 3.4) Appelo *et al.*, 2014 and the Pitzer database which recently incorporated  $\text{CO}_2$  and fugacity in the code.**

The geochemical assessment of the potential mineral precipitation was conducted within the SECURE project by a combined analysis of field observation and modelling evaluation (Jang *et al.*, in prep). The geochemical modelling results showed that the gypsum solubility decreases with increasing reservoir  $\text{CO}_2$  concentration, and a large amount of potential gypsum precipitation can be expected due to the reservoir temperature and pressure drops in the Ketzin sulfate-rich formation fluid (Figure 4) upon post-closure. These results highlight the importance of the baseline assessment, including formation fluid composition and mineralogy, before the operation starts, since the potential mineral precipitation may change the physical properties with an increase or a decrease in the porosity and permeability and drive the well-clogging and loss of  $\text{CO}_2$  injectivity during the injection phases.

It is necessary to investigate the exact geochemical impact of the  $\text{CO}_2$  injection and avoid the potential for false positive and false negative signals. Such false-positive (natural variability misinterpreted as anomalies) and false-negative (missed anomalies) signals are related to the concentration of the considered ion species and mineral dissolution/precipitation in the reservoir, as indicators due to the impact of  $\text{CO}_2$ -induced reactions.

For example, the uncertainties in the parameters (as e.g., due to missing or erratic baseline measurements) are possibly propagated to the geochemical interpretation, which may lead to a false interpretation of the concentration and distribution of the generated  $\text{CO}_2$ , further controlled by the migration processes and trapping mechanisms, and eventually, buffered by mineral- $\text{CO}_2$ -fluid interactions.

The conclusive message is that an appropriate baseline assessment and subsequent monitoring is required to minimize the probability of false identifications so that a better prediction of the potential mineral precipitation can be achieved.





### 3.1.5 Lessons learned and real-life experience

#### 3.1.5.1 BASELINE ASSESSMENT OF THE FLUID COMPOSITION IN THE RESERVOIR

The baseline assessment is a prerequisite for monitoring gas and fluid leakage and associated environmental impacts. Understanding the potential altering of fluid composition caused by CO<sub>2</sub> storage is crucial for a successful and safe CO<sub>2</sub> storage project (Li et al., 2018). Unfortunately, Ketzin brine solutions before CO<sub>2</sub> injection are only available at the observation well Ktzi 202 in 2008 (Würdemann et al., 2010), and post-injection brine solutions were obtained from the injection/observation well Ktzi 201 in 2014, one year after finishing the five-year CO<sub>2</sub> injection period (Martens et al., 2015). No direct baseline composition is available for well Ktzi 201. However, the main constituent trends continue between the pre-injection brine (Ktzi 202) and the post-injection brine (Ktzi 201), as shown in detail in Jang et al. (in prep.). The latter manuscript presents geochemical modelling work based on Ketzin baseline and monitoring data and is submitted to Environmental Earth Science by the end of the SECUREproject. The paper focuses on the assessment of potential mineral precipitation as consequence of CO<sub>2</sub> injection-influenced geochemical equilibrium of the reservoir fluid. Injected CO<sub>2</sub> dissolves into the reservoir brine and lowers the brine pH. Subsequently, acid-induced reactions may occur, namely dissolution of primary minerals and precipitation of secondary minerals.

Moreover, above-zone monitoring was conducted through the shallow observation well P300 (at a depth of about 450m). The hydraulic conditions, temperature, water chemistry, gas geochemistry, and carbon isotope analysis were investigated using a tubing inserted inside the well with pressure sensors and a U-tubing sampling system. Because the well P300 was drilled in 2011, there is no baseline information regarding the above-zone before the CO<sub>2</sub> injection starts. Wiese et al. (2013) investigated the hydraulic and geochemical impact on the formation fluid, and the fluid composition was compared to the literature values instead, such as formation fluid of the Exter Formation in the context of geothermal boreholes in the North-East German Basin. The research reported that the observed formation fluid and gas concentration gained by U-tubing sampling are similar to those observed in formation fluids prior to the CO<sub>2</sub> injection; an impact of the CO<sub>2</sub> reservoir was not detectable.

#### 3.1.5.2 CO<sub>2</sub> SOIL FLUX MEASUREMENTS AND LI-COR MULTIPLEXER

The Li-COR multiplexer system applied for the CO<sub>2</sub> soil flux measurements (Zimmer et al., 2011b) is constructed in such a way that it automatically and continuously records data from eight measuring chambers without maintenance.

Errors occurred due to malfunction of the humidity and infrared sensors in each of the sampling chambers. In this case, the Li-COR multiplexer device switched off automatically. Furthermore, the clogging of the connection hoses by leaves or the activity of animals led to the interruption of the measurements. During frost and high humidity in the winter months, the mechanics of the sampling chambers occasionally froze. All interruptions led to a stop in data recording and consequently to gaps in the data series.

#### 3.1.5.3 CO<sub>2</sub> SOIL FLUX MEASUREMENTS AND LI-COR SURVEY SAMPLING SYSTEM

For a better accessibility, most of the sampling positions are located next to agricultural roads and fields. Therefore, an influence of agriculture activities cannot be ruled out. Fertilisation could either increase or decrease the activity of soil organisms and also have an effect on the root respiration of the plants. Tillage can either loosen or compact the structure of the soil, which can lead to increased outgassing or to the retention of soil CO<sub>2</sub>. All of the effects described can lead to changes and distortions in the natural soil CO<sub>2</sub> production and flux to the atmosphere. LI-COR system (automated system) without daily maintenance, technical problems (failure of sensors or clogging of the chamber by e.g., animals or leaves) have caused gaps in the data series.

### 3.2 BASELINE ASSESSMENT AND MONITORING STRATEGY FOR ACID GAS STORAGE (BORZECIN ACID GAS STORAGE)

The Borzęcin site is a natural gas producing mine in western Poland. The mine belongs to the Polish Oil and Gas Company (PGNiG) and except for a constant gas production, the Operator owns a license for acid gas injection and liquid mine waste injection into the reservoir structure. The detailed description of site history and research activities conducted on the site can be found in the [SECURE D2.2 Report](#) on effects of long-term



sequestration process in the Borzęcin structure – observation evidence of the injected gas migration and possible leakage.

The long-term acid gas sequestration has been carried out in the Borzęcin structure since 1996. The Borzęcin injection project was the first full scale acid gas reinjection process of practical value carried out on a running production of natural gas from a conventional deposit. The acid gases, produced together with natural gas and recovered in a chemical process, are being reinjected into the water-bearing zone underlying the gas cap, from which the natural gas is constantly produced.

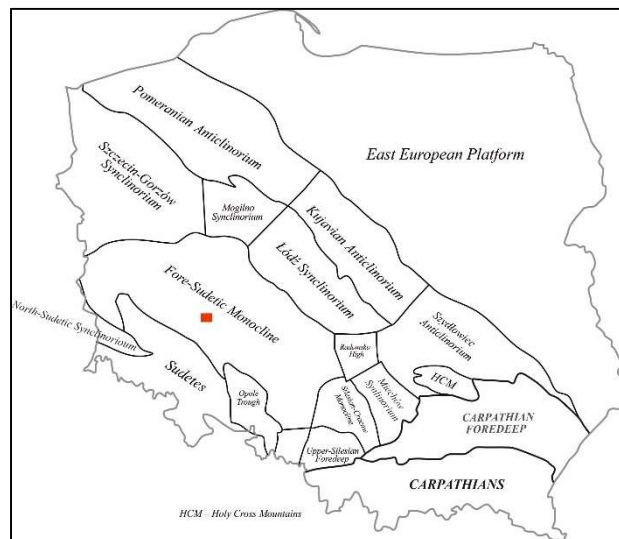
In the last century middle 90ies the sequestration of acid gases was a quite new technology in the world of oil and gas industry. Within other projects already in progress by that time, the gases were not injected into the exploited field, but into selected structures that met the conditions of storage. The Borzęcin project was then an innovation on a global scale, also in the area of reservoir engineering. It required the performance of detailed simulations with the assumption that it was possible to rationally reconcile the simultaneous recovery of the gas and back injection of acid gases into the water-bearing zone, and it would have been in accordance with applicable laws and the principles of rational exploitation. The challenge was also to inject an aggressive mixture of H<sub>2</sub>S and CO<sub>2</sub>, similar e.g. to those injected during the Zama Field Validation Test in Canada in 2005-2009 period (Global CCS Institute - <https://co2re.co/FacilityData>). It is necessary to emphasize the positive attitude of the District Mining Office that approved the implementation of such an innovative solution.

The Borzęcin installation is considered to be a unique experimental plant which has allowed to investigate the acid gas sequestration process for 24 years of its operation and possibly a few more years to come. Unlike other large reservoirs, the small capacity of the onshore Borzęcin structure enables an effective control and analysing the detailed mechanisms of the sequestration process in a short-term scale.

Additionally, in the beginning the 21st century, the Borzęcin mine obtained a license for an injection of mining liquid waste from drilling operations and liquid waste from dehumidification and gas purification into the same reservoir.

### 3.2.1 Location and geological setting

The Borzęcin site is located in South-West Poland within the southern part of Fore-Sudetic Monocline (Figure 5) and comprises a conventional natural gas reservoir exploited since the year 1976 (Olszewska and Mularczyk, 2012).

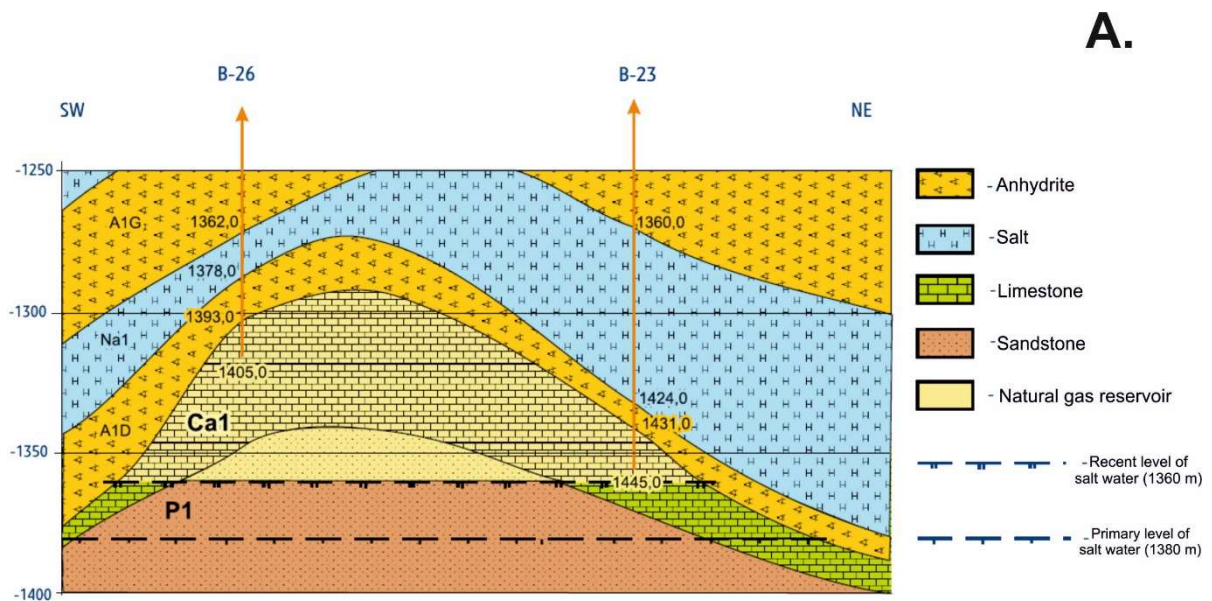


**Figure 5 The localization of the Borzęcin site (marked by the red rectangle) in the background of the tectonic subdivision of Poland (Karnkowski, 2008).**

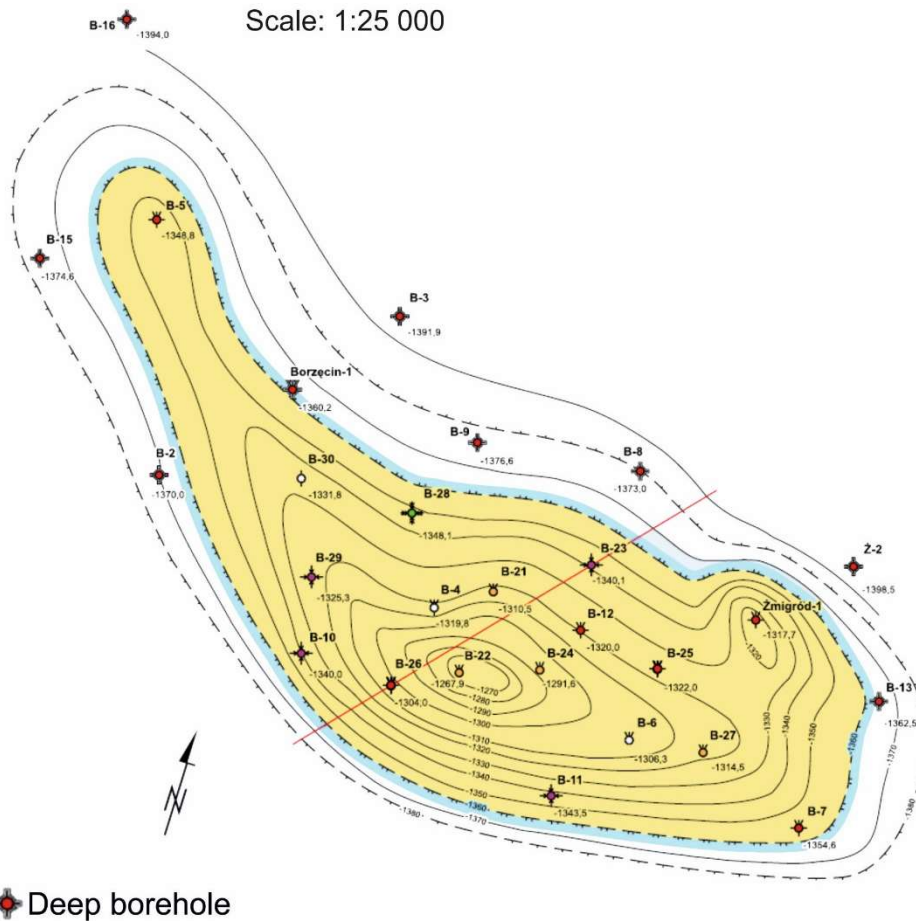
The hydrocarbon accumulation was discovered within the hydrodynamically connected layers of Upper Rotliegend and Basal Limestone (Zechstein) within a depth range from 1268 m to 1380 m (Lubaś et al., 2012;



Pleśniak et al., 2017; Figure 6). The lower, Rotliegend part of the reservoir is built of aeolian facies represented by sandstones of different grain sizes with clay-carbonate or clay-iron bearing cement (Jarzyna et al., 2009; Pleśniak et al., 2017). The upper part of the Rotliegend formation exhibits good reservoir properties, with average effective porosity equal to ca. 10%, and a wide range of permeability values from several to over a thousand mD (Jarzyna et al., 2009). The upper, Zechstein part of the investigated reservoir constitutes a reef facies, represented by organogenic limestones and dolomites (Raczyński et al., 2017). The gas-bearing level within this unit is characterized by respectively high values of permeability (up to 150 mD, Peryt et al., 2010) and porosity (in the range from 2 to 18%). The reservoir rocks are sealed by thick layers of salts and anhydrites (Olszewska and Mularczyk, 2012; Figure 7). The whole hydrocarbon system consists of a level of salt water and natural gas, entrapped in a structural trap, which is a top of WNW–ESE striking brachyanticline (Lubaś and Szott, 2010; Olszewska and Mularczyk, 2012; Figure 7).



**Figure 6** The geological setting of the Borzęcin deposit: **A.** The profile of the hydrocarbon system of the investigated site located within the Permian layers, scale 1:25 000 (Olszewska and Mularczyk, 2012).



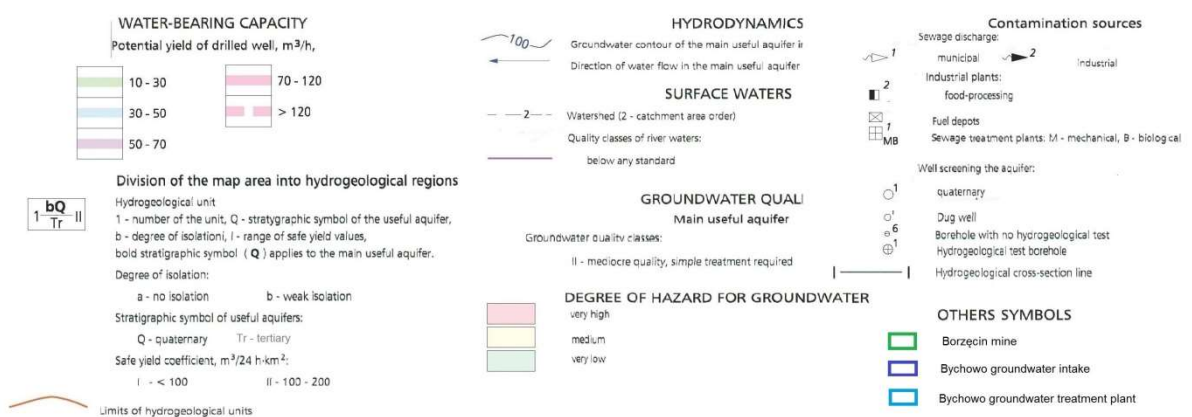
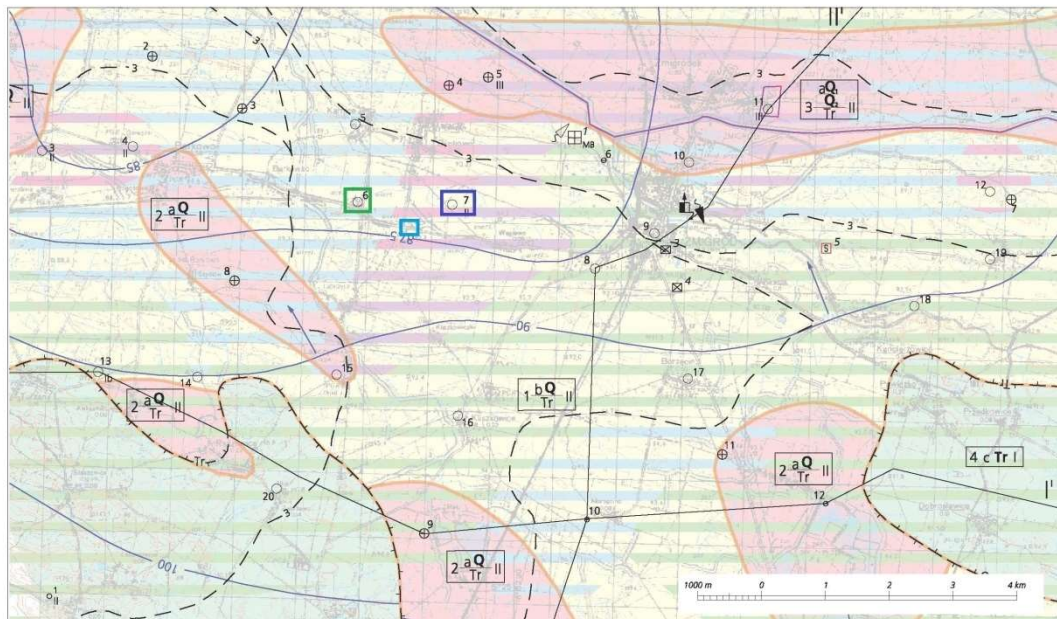
**Figure 7 The geological setting of the Borzęcin deposit: B the structural map of the Basal Limestone comprising the upper parts of reservoir rocks with drilled boreholes.**

### 3.2.1.1 GROUNDWATER

The main potable aquifer used in the area of the Borzęcin gas mine is located in Quaternary sediments in a depth interval starting from some meters up to 60 m (Figure 8, Figure 9). Below the depth of 100 m there is a Tertiary fresh water system consisting of 2, locally 3 water-bearing layers. The main groundwater flow direction in the region is towards N-W. Deeper groundwater layers, including water horizons underlying the gas-bearing strata in Rotliegend sandstones and Zechstein limestones and aquifers in Triassic and Jurassic sediments are brines.

Quaternary groundwater in the vicinity of the Borzęcin mine is mainly of  $\text{HCO}_3$  - Ca type with increased levels of iron as specific constituent (Figure 10). According to some mentions in local administration policy documents (IME Consulting, 2004) a classification of groundwater quality as third class (according to Polish legal regulations on water quality relevant for that time) is caused, apart from increased iron concentration, by the occurrence of  $\text{H}_2\text{S}$  and concentration of strontium as well as a level of total hardness. Unfortunately, it is not possible to confront the information on  $\text{H}_2\text{S}$  presence with any publicly available direct chemical analysis results.

The security of the quality of the Quaternary aquifer is especially important as about 2 km to the East from the Borzęcin gas mine are located the water wells of groundwater intake for several local counties and the treatment and pump station for local potable water supply network is installed about 1 km to the South-East from the mine. Water quality in local supply system is annually controlled by the sanitary inspection to ensure a sufficient water treatment.



**Figure 8 The Borzęcin gas mine on the Hydrogeological Map of Poland 1:50 000, sheet 690 - Żmigród (Wojciechowska, 1998).**

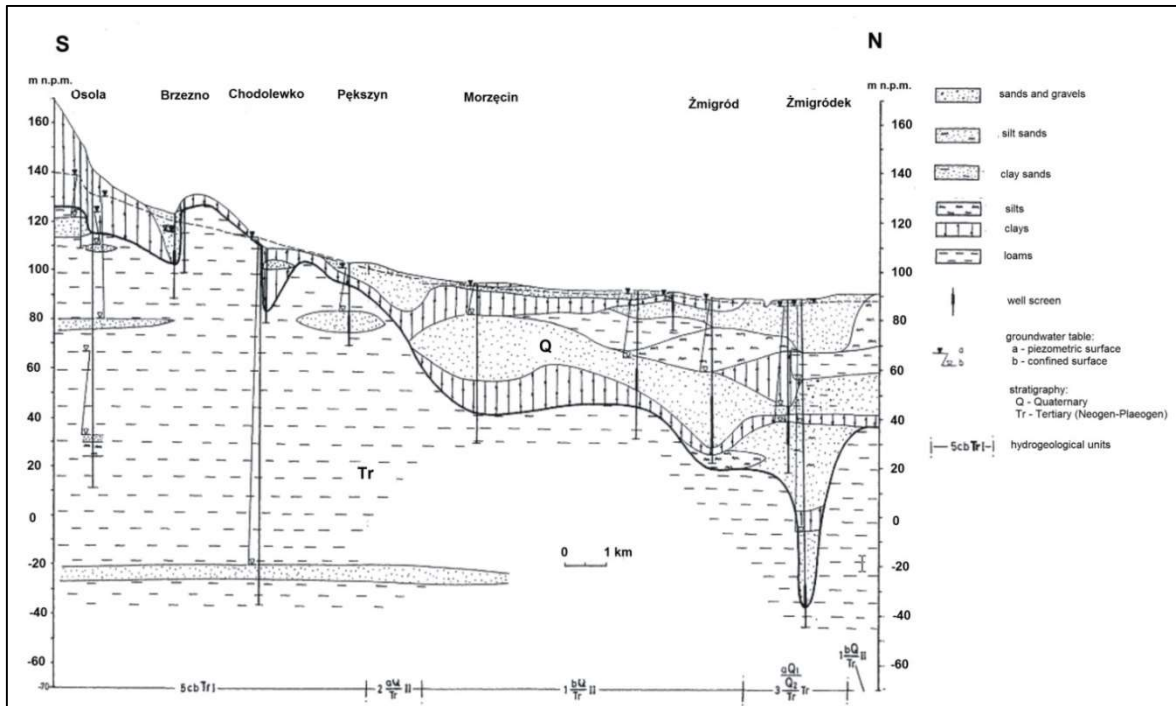


Figure 9 The hydrogeological cross-section through the Borzęcin mine area (Wojciechowska, 1998).

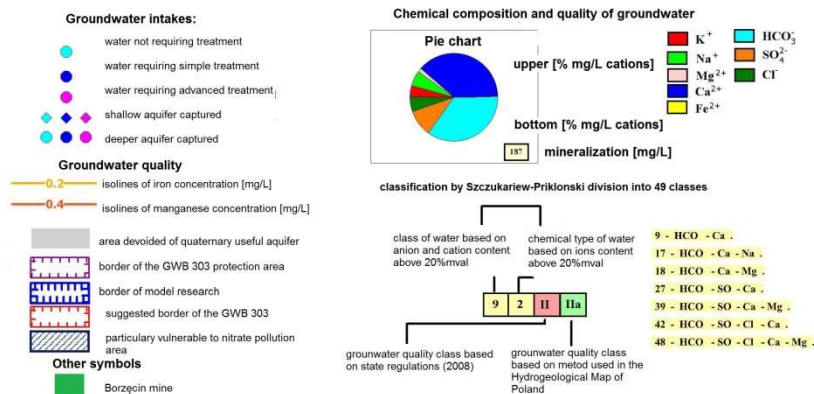
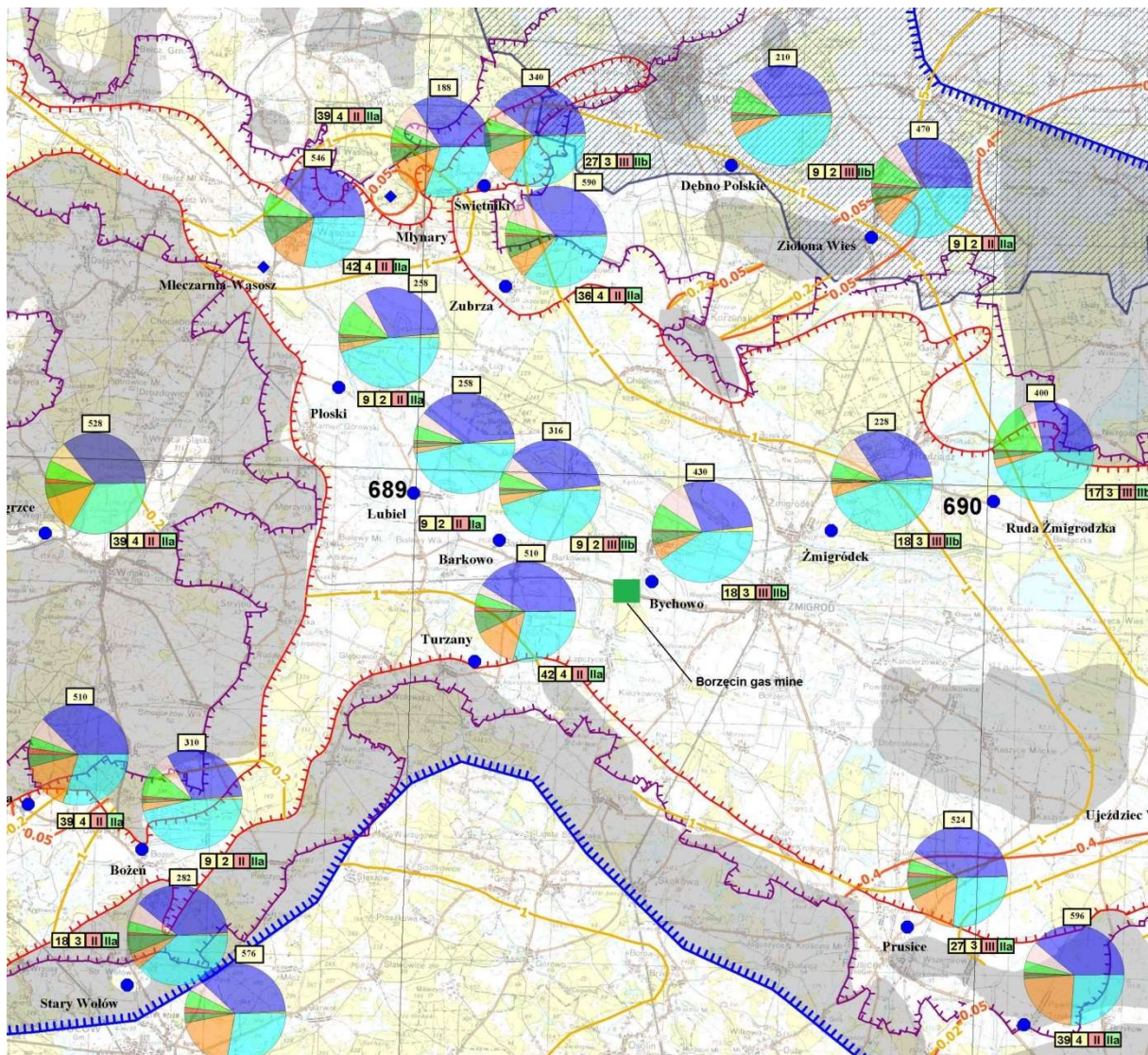


Figure 10 The hydrogeochemical map of quaternary aquifer in the area of the Borzęcin mine (Wojciechowska et al., 2011).



### 3.2.2 Drilling and well completion and injection history

The production phase in the Borzęcin mine started from one borehole - Żmigród-1 located in the NE part of the reservoir structure (see Figure 7). Exploited natural gas contained 64% of methane, a relatively high amount of nitrogen (32%), and a mix of helium (0.17%), carbon dioxide (0.07%), and hydrogen sulphide (0.04%). In the next stage, the PGNiG company launched a sweetening installation, which enabled the removal of H<sub>2</sub>S and thereby the selling of exploited gas. At the time of putting the installation into operation (the year 1977), the exploitation was conducted by seven boreholes till the year 1982 when borehole B-7 was flooded out and excluded from further production. In the years 1984 – 1987, the mine was expanded by an additional ten production wells (B-21 - B-30), from which one turned out to be dry (B-28). Later on, in 1985 and 1987, two other boreholes (B-10 and B-11) stopped producing due to too high water-gas ratio. The increasing number of wells enabled the maintenance of steady production for ten years (1977 – 1987). Later on, however, the underlying and/or surrounding aquifers caused relatively fast water flooding of the producing wells and consequently reduction of the gas production (Lubaś et al., 2020; Olszewska and Mularczyk, 2012).

The drop of reservoir pressure and depletion of the exploitable resources led to a plan of closing the mine in the first decade of the 21st century (Pleśniak et al., 2017). To avoid this scenario and to reduce the H<sub>2</sub>S, the mine operator installed an injection plant for acid gas (Olszewska and Mularczyk, 2012) after the exploitation of 67% of available gas resources (Lubaś, 2007). At this point, in the year 1996, the injection phase started. In the injection phase, the products of the gas sweetening (H<sub>2</sub>S and CO<sub>2</sub>) have been injected back to the underlying, water-bearing zone of the reservoir structure, beneath the original gas cap. To achieve this goal, well B-28 (located in the northern part of the reservoir, Figure 7) was converted from a producer into an injector (Lubaś, 2007; Lubaś et al., 2020). During the first 16 years of work, 700 tonnes of H<sub>2</sub>S and 3400 tonnes of CO<sub>2</sub> were injected into the reservoir rocks within the Borzęcin field (Olszewska and Mularczyk, 2012) and by July 2019 the total amount of both was almost doubled (information from INiG).

During the years of the gas production, the consecutive wells have been watered out and removed from the exploitation process: B-23 in 1997, B-26 in 1999, B-25 in 2000, B-31 in 2001, B-12 in 2003, B-29 in 2003, B-6 in 2007, and finally B - 24 in 2013 (Lubaś et al., 2020). Recently, the remaining gas resources are exploited only by four boreholes: B-21, B-22, B-24, and B-27. Wells B-10, B-11, B-23, B-29 have been converted into injectors of produced water and liquid waste.

### 3.2.3 Baseline assessment and Interdisciplinary monitoring

Injection of acid gases into the Borzęcin reservoir is conducted alongside continuous natural gas production from the same reservoir. The concept of injecting the acid gases coming from sweetening of produced gas was developed due to increasing requirements for commercial gas supply quality and possible environmental threats coming from storage and disposal of acid gases removed from produced natural gas. Prior to the injection phase (before 1996) the main environmental hazards were associated with surface activities. Depleting pressure in the reservoir did not support leakage possibility, even if well integrity loss was not identified as a leakage hazard by that time.

Prior to the injection phase the observations focused mainly on reservoir conditions. First sampling and measurements of reservoir fluids were carried out when the gas field was being developed (1969-70) and subsequently during the production phase, when new wells were drilled (1987). Based on those measurements a dynamic numerical model of the structure was developed and calibrated with production and injection rates data and downhole and wellhead pressure monitoring measurements. It is considered as a tool for assessment and prediction of the reservoir behaviour and leakage probability.

Within the Borzęcin field, several monitoring strategies are in use:

1. Bottom-hole sampling and chemical characterization of reservoir fluids - water and gas. One of the monitoring strategies involves the sampling of brine underlying the gas cap to follow the migration path of the injected acid gas. The samples of the reservoir water (so-called PVT – pressure, volume, temperature samples) are obtained by the downhole samplers driven down to the well bottom. The sampler is lowered at the desired depth, and the sampled fluid is hermetically closed within the isolated chamber, preventing changes in pressure and temperature. Taking such samples allows for the determination of the composition of gas dissolved/dispersed in the reservoir water (Lubaś et al., 2020). First sampling was carried out when the gas field was being developed (1969-70) and subsequently





during the production phase, when new wells were drilled (1987) and gas resources and reserves were being reassessed, before acid gas injection started. In the frame of the SECURE project the fluids survey was repeated by the INiG in the B-4 and B-6 wells drilled in 1969-70 and the B-21, B-24 and B-27 wells drilled in 1987.

2. Changes in the isotope composition, on which a pilot program was conducted in 2009-2015. Reservoir gases are a mixture showing a wide variability in the isotopic composition, depending on certain physio-chemical factors that accompany the formation of the individual phases forming the deposit. This system is dramatically disrupted by the exploitation of the deposit and the injection of acid gases (also liquids from outside the Borzęcin deposit). The isotopic distinction associated with the above processes and the migration of phases in the reservoir causes spatial and temporal variability in the isotopic composition of the test system to appear. Injected gases have their own unique isotopic characteristics of hydrogen and carbon, which is caused i.a. by a number of processes accompanying the separation of acid gases and their migration and mixing. This, and the availability of nearly 30 deep boreholes covering the reservoir, gives a unique opportunity to quantitatively track the rate and directions of gas migration in the reservoir, as well as to show possible leaks. With a large amount of data, it may be possible to perform an isotopic mass balance and indicate the places and size of a leak (Lubaś et al., 2020; Pleśniak et al., 2017).
3. Soil gas analysis. To determine the possible leakage pathways and the impact of the injected acid gas into the reservoir, within the Borzęcin site also some measurements of soil gas composition have been carried out. Within 2 sampling campaigns in 2018 and 2019, gas samples were collected from the monitoring wells installed at the distance ca. 35 meters from the production wellheads. The gas was sampled from the depth of 2 meters with use of glass pipettes and a vacuum pump (Lubaś et al., 2020).
4. Monitoring of potable aquifer (required by conditions of the injection license). The observation wells have been constructed to enable sampling and physico-chemical analysis of the water from the potable aquifer. Broad scope of parameters are observed annually to make sure the quality of this water layer is not adversely affected by mine activities (PGNiG data, 2020).
5. Measurements of corrosion of injecting wells - measurements of integrity profile performed in the injectors systematically every 2 years. The analysis of the composition of the acid gases injected are also carried systematically on samples taken from the injection installation (Lubaś et al., 2020).
6. Due to legal requirements on waste disposal, analysis of composition of injected liquid mine waste are performed and their quantitative results are stored on monthly manner with a summary reported annually.

### 3.2.4 Current monitoring research

In the years 2018-2019 the Polish Oil and Gas Institute (INiG) attempted to evaluate the effects of long-term CO<sub>2</sub>-H<sub>2</sub>S sequestration process in the Borzęcin (Poland) reservoir structure. Various tests and analyses were performed on downhole, as well as surface samples of reservoir fluids, collected from selected wells of the Borzęcin reservoir. The results aimed at identifying the propagation and intensity of acid gas migration within the reservoir and potential leakage pathways towards the ground surface. Some of the tests such as soil gas or gas from downhole brine degassing analyses have never been conducted before, providing additional information on the safety of geological storage of acid gases within the Borzęcin structure.

#### 3.2.4.1 DEEP GROUNDWATER

Because of full hydrodynamic communication within the Borzęcin hydrocarbons trap, the underlying water zone and gas-bearing zone remain in equilibrium. Water underlying the gas reservoir remains naturally saturated with natural gas. The acid gases, injected by the B-28 well to the flooded layer, partly dissolve in formation water adjacent to the well. The gas volumes, which did not dissolve in water, can remain in the aquifer in the form of immobile dispersed bubbles. Having exceeded the critical gas saturation of the brine, the mixture of acid gases will gravitationally migrate upwards the reservoir and will penetrate to the gas zone leading to gradually mixing with the reservoir gas. Composition changes of gas produced by individual production wells and the occurrence of increased CO<sub>2</sub> and/or H<sub>2</sub>S concentrations provide information on the

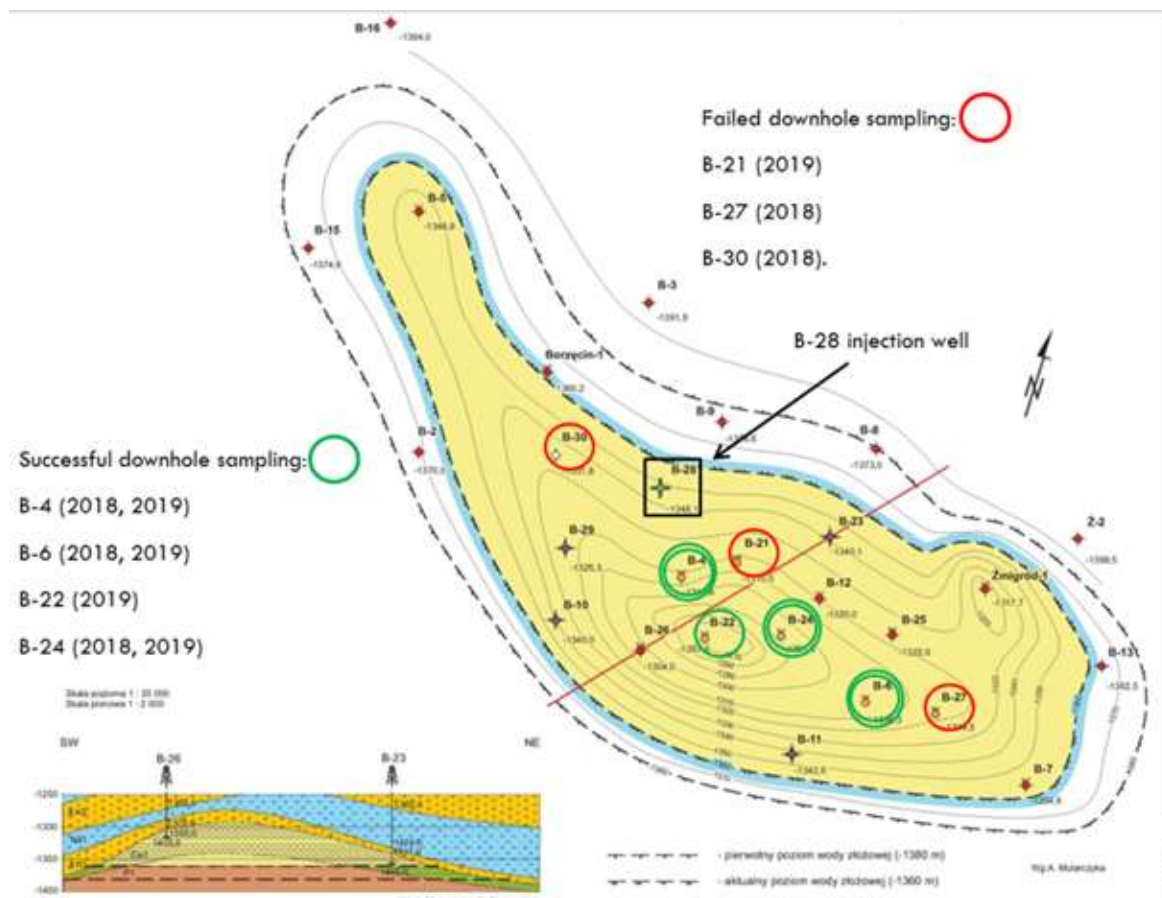


propagation of acid gases plume in the gas zone of the Borzęcin sequestration structure. For a proper migration analysis within the aquifer, bottom-hole samples of reservoir water saturated with gas were collected. The sampler, after lowering to a preset depth was hermetically closed and the fluid (gas/oil/water) remained isolated in its chamber preserving the pressure and temperature at the moment of sampling, hence in-situ reservoir conditions.

The collecting of bottom-hole samples from the Borzęcin sequestration structure was carried out in two series. The first was performed in September 2018 on productive wells: B-4, B-27, B-6, B-30 and B-24. The second series took place in July 2019 and comprised wells: B-21, B-22, B-24, B-4 and B-6 (Lubaś, J. et al., 2020). Despite attempts, no bottom-hole samples from wells B-21, B-27 and B-30 were obtained because of the lack of water at the preset depth of sampler's driving. The attempts to drive it to the maximum safe depth determined previously by the drift mandrel with an overflow bailer did not help. Samples of reservoir water saturated with gas were successfully collected from wells B-4, B-6, B-22 and B-24. Table 2 presents a summary of the different stages of reservoir water bottom-hole sampling. Figure 11 presents the location of wells on the map of Borzęcin reservoir.

**Table 2: Bottom-hole sampling summary (Lubaś et al., 2020)**

Well number	Well status	Sampling date	Blow-out risk	Drift depth (m b.g.l.)	Tubing shoe depth (m b.g.l.)	Sampling depth (m b.g.l.)	Sampling result	Gas in water saturation [Nm <sup>3</sup> /m <sup>3</sup> ]
B-4	producing	4.09.2018	yes	1435	1396	1425	Positive	0.63
						1428	Positive	0.66
	producing	17.07.2019	no	1430	1396	1425	Negative	-
						1428	Positive	0.29
B-6	closed	6.09.2018	no	1443	1398	1438	Positive	0.33
						1441	Positive	0.32
	closed	18.07.2019	no	1443	1398	1438	Positive	0.20
						1441	Positive	0.21
B-21	producing	15.07.2019	yes	1431	1435	cancelled	Negative	-
B-22	producing	16.07.2019	no	1420	1419	1417	Positive	0.62
						1420	Positive	0.60
B-24	closed	7.09.2018	no	1330	1341	1327	Positive	0.25
						1330	Positive	0.18
	closed	17.07.2019	no	1330	1341	1327	Positive	0.17
						1330	Positive	0.27
B-27	producing	5.09.2018	yes	1399	1395	cancelled	Negative	-
B-30	closed	6.09.2018	no	1415	1424	cancelled	Negative	-



**Figure 11 Bottom-hole sampling of Borzęcin reservoir (Lubaś et al., 2020).**

### 3.2.4.2 CHANGES IN THE ISOTOPE COMPOSITION

The isotope composition of the produced gas was analysed in 2009-2015 years on a larger scale (Pleśniak et al., 2017) and in 2018-2019 in the framework of the SECURE project (Lubaś et al., 2020). As part of the isotope analyses, the values of carbon ( $\delta^{13}\text{C}$ ) in methane, ethane, propane and carbon dioxide, deuterium ( $\delta\text{D}$ ) in methane, and nitrogen ( $\delta^{15}\text{N}$ ) in molecular nitrogen were determined. In 2018, samples were taken from the B-4, B-6 and B-24 and in 2019 – from B-4, B-21, B-22 and B-27 wells.

Analysis of the isotope composition of carbon in methane ranged from 35.9‰ to 34.4‰ (average 35.1‰), in ethane from 30.57‰ to 30.1‰ (average 30.2‰), in propane from 26.4‰ to 26.0‰ (average 26.2‰), and in carbon dioxide from 17.58‰ to 3.71‰ (average 10.4). The isotope composition of hydrogen in methane was in the range of: 133.5÷ 106.9 ‰ (average 118.4 ‰), while the isotope composition of nitrogen ranged from - 0.4 to 5.2 ‰ (average 3.4 ‰) (Lubaś et al., 2020).

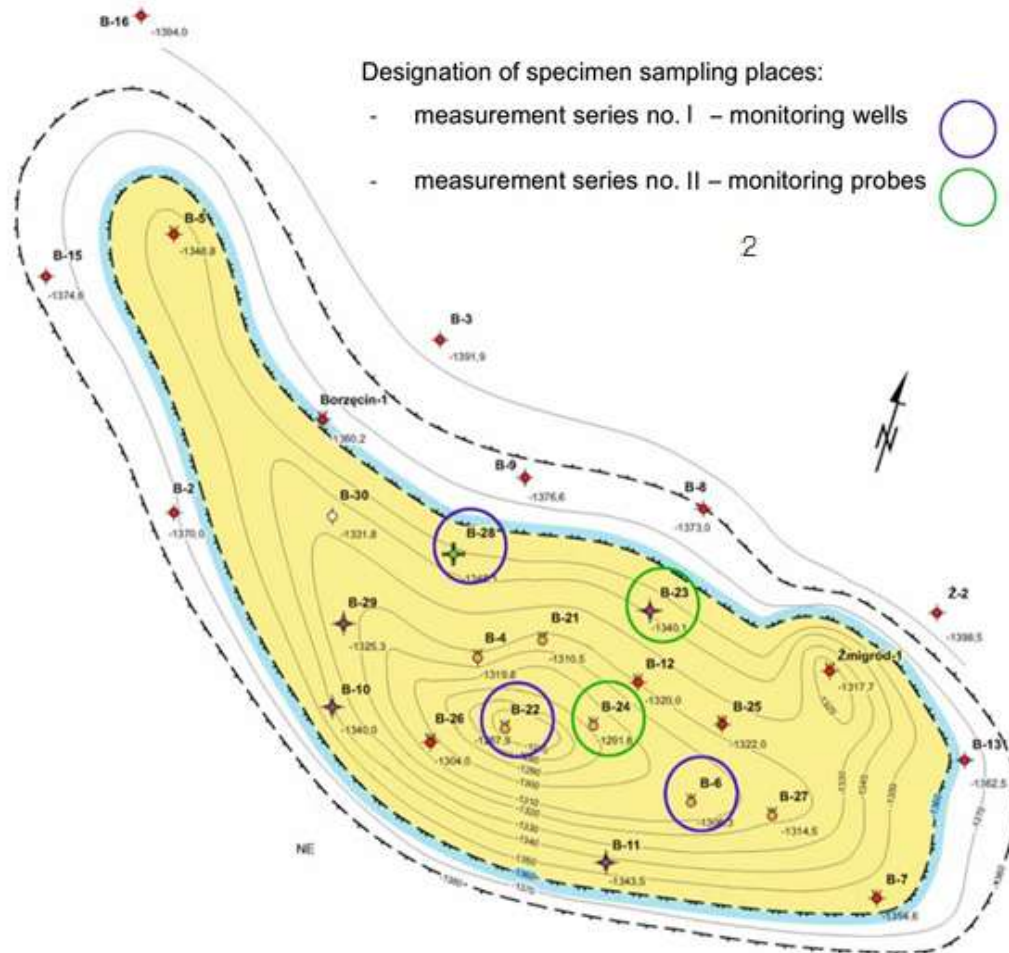
Based on the survey it was found that the isotope composition of carbon in methane, ethane and propane appeared to be unchanged and independent of the type of gas sample drawn and the time of sampling. The differences in the extreme values of carbon isotope composition in methane were about 1.5‰ (approximately 4%), and in ethane and propane, ca. 0.4 ‰ (approximately 1.5%). The variability in the carbon isotope composition was noticeable in case of carbon dioxide. The changes in the isotope composition of hydrogen in methane were also noticeable. The hydrogen in the extracted gas samples was enriched in a heavier isotope, the deuterium, similarly to gas samples from brine degassing taken in 2019 (Lubaś et al., 2020).

### 3.2.4.3 SOIL GAS

The monitoring of soil gas was conducted in the two sampling campaigns in 2018 (B-6, B-22 and B-28) and 2019 (B-23 and B24) (Figure 12). A total of four measurements series were made. During the first 3 measurements series (I stage), the gas samples were collected from the monitoring wells installed at the distance ca. 35 meters from the production wellheads. The gas was sampled from the depth of 2 meters with use of glass pipettes and a vacuum pump (Lubaś et al., 2020). Whereas, during last (fourth) measurement



series (II stage), 18 driven-in monitoring probes were deployed, each with a 1 m depth, 9 units per well around the two wells (B-23 and B24). The measuring points were located within approx. 25 m and 50 m distances from the wells and at the wells themselves. The soil gas samples from the installed probes were drawn into glass bulbs (Lubaś et al., 2020).



**Figure 12 Location of wells in the area of the Borzęcin natural gas reservoir with soil gas sampling sites indicated (Lubaś et al., 2020).**

Based on both stages results, no uncontrolled leakage and migration upward of injected acid gases into the soil gas was detected (Lubaś et al., 2020.). The low methane concentrations found in some samples are a consequence of natural processes occurring in the soil. The CO<sub>2</sub> levels observed (0.05% - 2.09%) should therefore be assumed to be absolutely normal for the type of area, which is also supported by literature data. Moreover, the lack of even trace amounts of hydrogen sulphide (H<sub>2</sub>S) in the samples examined authenticate no acid gases releases from the reservoir.

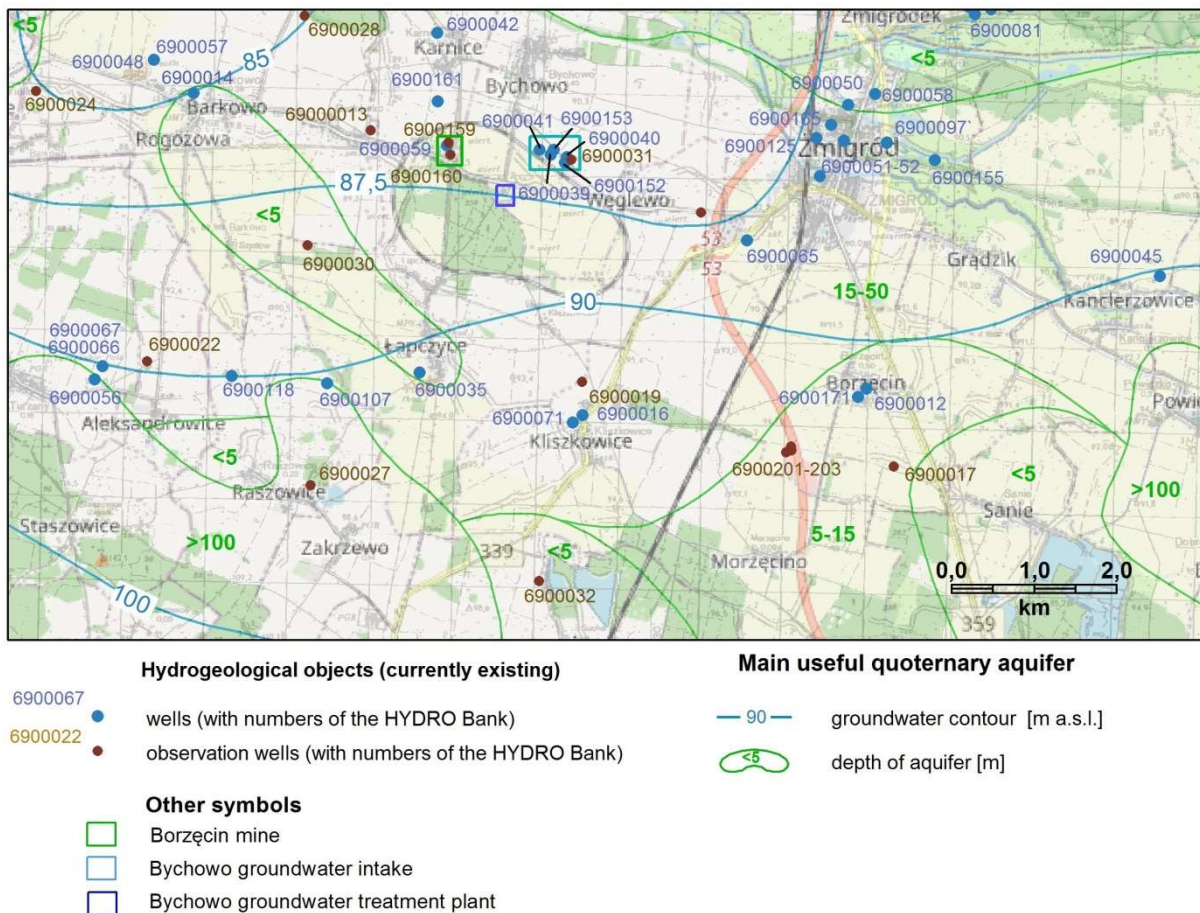
Whereas, the high level of methane (approx. 2.5%) and, in particular, the presence of higher hydrocarbons near the producing wellheads might indicate gas releases from the reservoir, most probably along casing and cementing (Lubaś et al., 2020).

#### 3.2.4.4 SHALLOW GROUNDWATER MONITORING

Groundwater monitoring is carried out on a basis of Ministry of Environment injection licence condition. The monitoring was conducted based on three wells - two shallow observation wells: 6000159 and 6000160 on Figure 13 (one in the Quaternary groundwater inflow into the mine area and the other in the water outflow) and the S-1 (shown as 6900059 on Figure 13) water well. The B-30 borehole was also included into the monitoring network requested by the injection licence condition. The measurement series were conducted twice a year (spring and autumn) except for the B-30 well, where testing was conducted every 10 days in accordance with



schedule of required periodic pressure measurements. The observed parameters included: pH, electrical conductivity, total dissolved solids (TDS), total organic carbon (TOC), chemical oxygen demand (COD), BTEX (volatile organics), hydrocarbons (including mono- and polycyclic aromatic hydrocarbons), hydrogen sulphide, total hardness, mineral oil index, dissolved oxygen, ammonia nitrogen, fluoride, chloride, nitrite nitrogen, nitrate nitrogen, phosphate, sulphate, sulphide, arsenic, cadmium, calcium, copper, chromium, iron, lead, magnesium, manganese, mercury, nickel, sodium, zinc (source: PGNiG, 2020).



**Figure 13** The location of hydrogeological boreholes and conditions of the main useful aquifer in the Borzęcin mine area according to the Hydrogeological Map of Poland 1:50 000 (Wojciechowska, 1998).

### 3.2.4.5 TUBING CORROSION MEASUREMENTS

During the injection process the metal tubing in the well are exposed to a risk of corrosion. The measurements of the corrosion profile were being performed in the injecting well from 2002 until 2018 (nine series each 2 years). Based on this analysis, the corrosion rate was determined as a function of depth - the corrosion rate increases with the tubing depth and reaches the maximum value of 0.18 (+/-0.02) mm/year. From this value and thickness of tubing wall (8.6 mm), the probability of the tubing full penetration can be determined as a function of time (Lubaś et al., 2020.).

### 3.2.4.6 SIMULATION MODEL AS MONITORING RESULTS COMPRISING AND PREDICTION TOOL

Based on the geological model of Borzęcin the dynamic simulation model of the structure was constructed. It is considered as a tool for assessment and prediction of the leakage probability. The model was calibrated based on historical production data (gas production and injection rates, bottom hole pressures and water-gas ratios of the producing wells, CO<sub>2</sub> concentration of gas produced by individual wells) (Lubaś et al., 2020.).

The dynamic model was used for simulation of a forecast assumption. The simulation of the injection phase was performed for the next 20 years that was followed by a 100 years relaxation phase. In this case the whole



amount of the produced CO<sub>2</sub> and H<sub>2</sub>S is assumed to be re-injected back to the water-bearing zone of B-28 as it has been done so far. According to simulation results, the production rate and the consequent injection rate in the analysed forecast are relatively small, the modelled estimates of basic reservoir parameters (pressures and saturations) at the end of the injection phase (2039) do not differ significantly from those at the end of the historical activities (2019). Greater changes of the reservoir parameters can be expected at the end of the relaxation phase (estimated for 2139) (Lubaś et al., 2020.).

### 3.2.5 Lessons learned from Borzęcin experience

At the Borzęcin site, prior to the injection phase, the main environmental hazards were associated with surface activities of gas production and its sweetening treatment. Depleting pressure in the reservoir did not enhance leakage probability, even if well integrity loss was not identified as a leakage hazard by that time. Prior to the injection phase, the observations focused mainly on reservoir conditions. First sampling and measurements of reservoir fluids were carried out when the gas field was being developed (1969-70) and subsequently during the production phase, when new wells were drilled (1987). Based on those measurements a dynamic numerical model of the structure was developed and calibrated with production and injection rates data and downhole and wellhead pressure monitoring measurements. It is considered as a tool for assessment and prediction of the reservoir behaviour and leakage probability.

As part of the SECURE project the fluids survey was repeated by the INiG in the B-4 and B-6 wells drilled in 1969-70 and the B-21, B-24 and B-27 wells drilled in 1987. Various tests and analyses were performed on downhole, as well as surface samples of reservoir fluids. The results aimed at identifying the propagation and intensity of acid gas migration within the reservoir and potential leakage pathways towards the ground surface. Some of the tests which have never been conducted before, provide additional information on the safety of geological storage of acid gases within the Borzęcin structure (Lubaś et al. 2020).

However, due to long time between baseline observations during the site development stage and technological progress, the scope of laboratory measurements in brine samples and gas samples was not always consistent with those done in the past. Moreover, in particular wells, due to local conditions, the samples were not always collected from the same depth range within the reservoir horizon (source: PGI CBDG database on [geoportals.gov.pl/otwory](http://geoportals.gov.pl/otwory)).

The underground storage of acid gases, produced water and occasionally liquid mining wastes, despite their important role in the reduction of CO<sub>2</sub> (or other gases) emission to the atmosphere, is not free from operational risk. The gathered experience in the Borzęcin field enabled the operator to identify two potential hazards:

1. Leakage risk. One of the gas leakage risk factors is the possibility of exceeding the formation breakdown (fracturing) pressure during the injection process. After an injection of acid gases, the pore pressure of reservoir formation might get higher than the breakdown pressure, causing a generation of the induced fractures, creating the pathways for fluid migration outside the previously sealed reservoir (Szott et al., 2020). The next type of leakage risk is related to losing the sealing integrity of the caprock due to possible changes in wettability level. The change of wettability during the injection of CO<sub>2</sub> may lead to a decrease in capillary entry pressure. Then, assuming the pressure of the CO<sub>2</sub> phase is high enough to displace the water in the caprock, the capillary leakage may occur (Farokhpour et al., 2013, Lubaś et al., 2020).
2. Problem of casing column corrosion and loss of well integrity. An injection of acid gas containing CO<sub>2</sub> and H<sub>2</sub>S with a high partial pressure increases a temperature within the aquifer accelerating the corrosion process. Widely used standards indicate that the values of partial pressure exceeding 0.21 MPa for CO<sub>2</sub> and above 0.34 kPa for H<sub>2</sub>S define a highly corrosive environment. In the case of the Borzęcin site, the mentioned values are equal to 3.6 MPa if CO<sub>2</sub> is injected into the water zone and 1.8 MPa if the H<sub>2</sub>S is injected into the reservoir. Thus, the environment within the reservoir seems to be highly corrosive. Despite the performed measurements indicated the actual corrosion of the steel infrastructure within the Borzęcin site is much lower than expected (Stopa et al., 2006), this hazard should not be neglected.

In order to verify environmental pollution risk related to a potential hazard of gas leakage as a result of acid gas injection into aquifers, the following studies were carried out in Borzęcin:

1. shallow groundwater quality monitoring – (3 observation wells, twice a year);
2. bottom-hole sampling of reservoir fluids (water saturated with gas) including:
  - chemical composition of gas



- isotopic composition of gas
  - reservoir water analysis
  - PVT analysis
3. soil gas analysis in the vicinity of wellheads
  4. tubing corrosion measurements and analysis.

Moreover, in the 90ies of the last century, long-term laboratory studies were performed on the samples of the typical cement slurry composition also used in the B-28 – injection well (Lubaś et al. 2020).

In the case of the Borzęcin mine, based on so far gained experience, it is recommended:

1. To continue groundwater monitoring in accordance with the current guidelines. In addition, methane and carbon dioxide dissolved in water need to be observed. Furthermore, the results of observations should be publically available for all interested parties and for administration.
2. To continue soil gas monitoring around all existing wellheads. The schedule and observed parameters need to be defined to enable comparability of monitoring series and trends observation.
3. To continue PVT and reservoir fluids chemical analyses in a time schedule relevant to observed changes dynamics.
4. To continue observations of the temporal and spatial variability in the isotope composition in gases sampled directly from the deposit reservoir, based on which further study on behaviour of individual system phases dynamics would be conducted, which may contribute to predictions for future system development.
5. To continue tubing corrosion measurements with the current schedule of each 2 years.
6. To implement cement integrity tests in the wells which is exposed to carbonate corrosion. Such studies have not been conducted so far.
7. To continue simulation model studies with implementation of all acquired reservoir parameters monitoring results and well integrity tests factor addition. If possible – enrich the modelling studies with the conclusions derived from individual phases isotope observations.

### 3.3 HYDROCARBON GAS SEEPS (CH<sub>4</sub>+CO<sub>2</sub>) FRENCH SUBALPINE CHAINS (FR)

As is customary in CCS studies, performing some monitoring on naturally leaking hydrocarbon sites (natural analogues) helps in defining tool capabilities for the detection of leakage and evaluating the best-suited methods for doing so. In the case of hydrocarbon leakage, the main species of interest is CH<sub>4</sub>, a molecule that can be easily monitored directly in the field using e.g. infrared sensors. The parallel is direct with CCS studies focused on CO<sub>2</sub>, which can be analysed using similar technologies. In the CCS context, attention must be paid on the origin of the CO<sub>2</sub> gas phase because a large number of sources can contribute to the CO<sub>2</sub>-budget in the soil, with biologically mediated production in the soil, interaction with minerals or the presence of atmospheric air contributing to the presence of CO<sub>2</sub>. This is why attribution methods have been developed to better assess the production mechanisms of soil CO<sub>2</sub> (Romanak *et al.*, 2012). In the case of hydrocarbons, attention must be also paid to the origin of CH<sub>4</sub>. The atmospheric contribution to the CH<sub>4</sub> budget is generally very low as the mean CH<sub>4</sub> concentration is still below 2 ppm ([https://esrl.noaa.gov/gmd/ccgg/trends\\_ch4/](https://esrl.noaa.gov/gmd/ccgg/trends_ch4/)). Methane can be produced by microbial activities in the soil as the end product of the anaerobic decomposition of organic matter. Under aerobic conditions, CH<sub>4</sub> is mineralized to carbon dioxide by methanotrophic bacteria (Topp & Pattey, 1997). Therefore, because of the oxidation of CH<sub>4</sub> in CO<sub>2</sub>, the monitoring cannot be focused on the sole CH<sub>4</sub> gas phase and has to include considerations on the CO<sub>2</sub> gas phase. This is why the investigations done in the French subalpine chains have included soil gas concentration and gas flux measurements on both the CH<sub>4</sub> and the CO<sub>2</sub> gas phases.

Four sites were investigated in 2019, from North to South: Rochasson, Fontaine Ardente du Gua, Molières-Glandaz and Jonchiers. These four sites are emplaced in black shales formations from the Callovian-Oxfordian period. Previous investigations in these sites are reported by Gal et al. (2018, 2019a). These sites are all naturally leaking sites are either known for millenaries (Fontaine Ardente du Gua) or only recently reported (Rochasson). Most of them are in pristine conditions, with the exception of the Fontaine Ardente du Gua. Trials of gas exploitation were conducted in the late nineteenth century at this site and borehole drilling was done in the late twentieth century. Nowadays, the main emission point corresponds to a former wellhead that was



destroyed but diffuse leakage still occurs close to this emission point (Gal et al., 2018). Investigations conducted at the Fontaine Ardente du Gua site are thus comparable with investigations around a wellbore in leakage situation. This offers the possibility to compare different emission conditions.

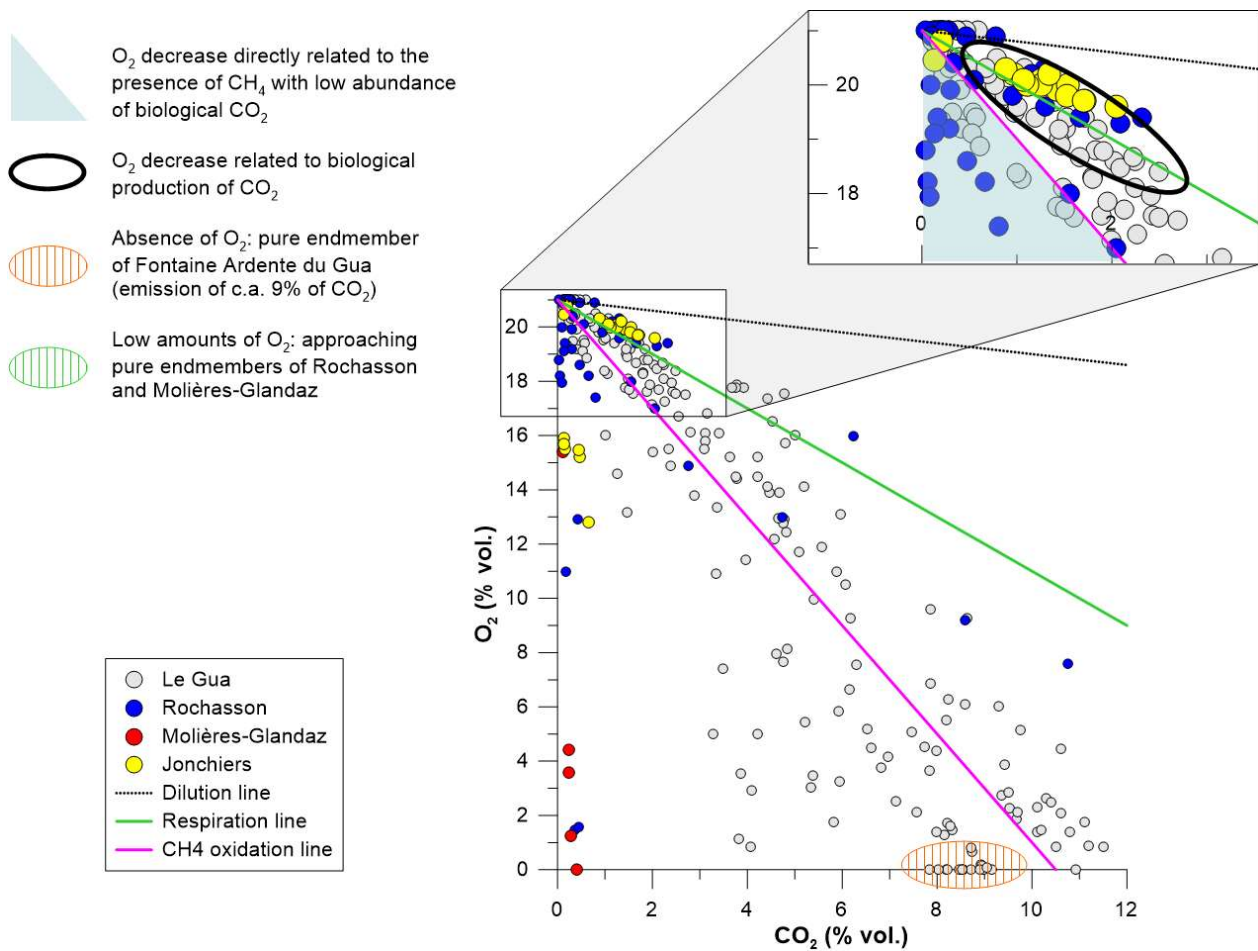
The compositions of the gas phase emitted at the main gas seep at each location are reported in **Error! Reference source not found.** Methane is the dominant gas species. Two main features distinguish the gas of the Fontaine Ardente du Gua from the gas of the other gas seeps: the richness in CO<sub>2</sub> and the low abundance of heavier alkanes.

**Table 3 Gas composition of the deep endmember for each of the four monitored sites; composition is recalculated from residual atmospheric contamination (O<sub>2</sub> concentration set to zero); balance is N<sub>2</sub> plus minor amounts of Ar±He.**

<i>Data in % vol.</i>	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>10</sub>	C <sub>5</sub> H <sub>12</sub>
Fontaine Ardente du Gua	9	88	0.07	-	-	-
Rochasson	0.4	95	1.9	0.3	0.07	0.003
Molières-Glandaz	0.3	94	2.4	0.4	0.06	0.006
Jonchier	1.7	96	0.8	0.2	0.05	0.006

In the framework of environmental baseline monitoring, an important aspect when considering natural analogues in leakage situation, is to be able to determine where and when the measurements depart from natural behaviour (biologically mediated processes) and enter a domain of possible influence of gas leakage from the ground. A classical approach, coming from the CCS world, is to use the process-based approach Romanak *et al.*, 2012. An example is given in **Figure 14**. In the case of CH<sub>4</sub> emissions, this approach is not the best suited but it can give some information. The first is that some of the measurements follow the respiration line; this indicates that, even in narrow perimeters around emissive structures, it is possible to monitor soil gases from soil formations not affected by leakage. The second is that, especially in the case of Fontaine Ardente du Gua, the CO<sub>2</sub>-O<sub>2</sub> relation may lead to erroneous observations. If referred to **Figure 14**, most of the CO<sub>2</sub>/O<sub>2</sub> data fall close to the CH<sub>4</sub> oxidation line. This is not the case as evidenced in **Figure 15** for the CO<sub>2</sub>-CH<sub>4</sub> relation. A large set of the data is indeed characterized by high CH<sub>4</sub> concentrations (>10%) with variable amounts of CO<sub>2</sub>. In such a case, the decrease of the O<sub>2</sub> concentrations simply results from dilution of the O<sub>2</sub>+N<sub>2</sub> pool existing in the soil by the degassing CH<sub>4</sub>+CO<sub>2</sub> deep endmember. For Molières-Glandaz, and to a lesser extent Jonchiers and Rochasson, the CO<sub>2</sub>-O<sub>2</sub> relation is less informative, only suggesting a rapid decrease of the O<sub>2</sub> concentration with no increase of the CO<sub>2</sub> concentration. This is related to the poorness of the gas phase in the latter gas (Table 3).

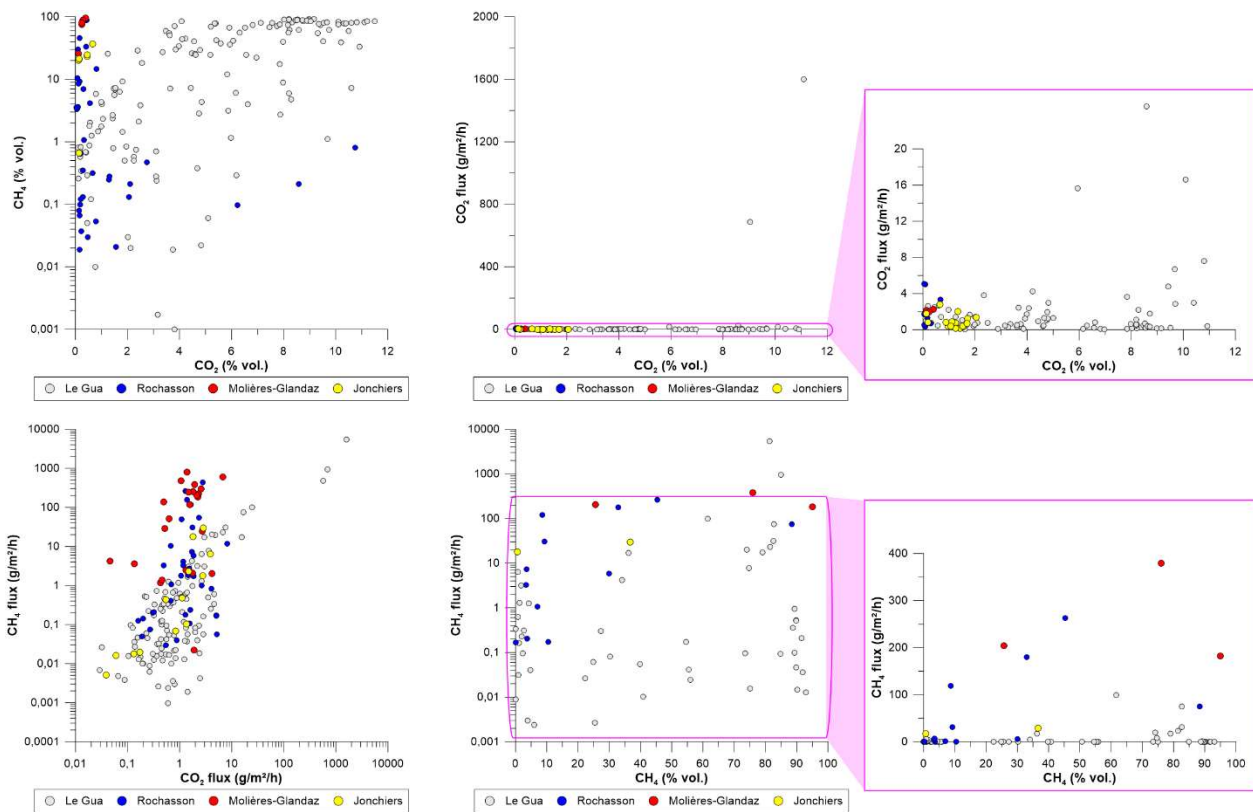




**Figure 14 CO<sub>2</sub>-O<sub>2</sub> scatter plot.**

Another parameter to consider when a leak is established is to determine the strength of the gas efflux to the atmosphere. Some information is reported in **Figure 15**. There is a large range of variation for the CH<sub>4</sub> flux to the atmosphere, ranging from low values (0.001 g/m<sup>2</sup>/h, i.e. the instrumental detection limit) to very high fluxes approaching or exceeding 100 g/m<sup>2</sup>/h, a value characteristic of the macro-seep category (Etiopie, 2015). In normally drained soils, the CH<sub>4</sub> flux is generally lower than 0.0017 /m<sup>2</sup>/h von Arnold *et al.*, 2005 so that any of the measurements points to the existence of anomalous areas, with increasing emission towards the main emission points Gal *et al.*, 2018a; Gal *et al.*, 2019. By comparison, most of the CO<sub>2</sub> fluxes are below the reported maximum emissions in soils, ranging from 2.4 to 3.6 g/m<sup>2</sup>/h depending on the season Pokryszka *et al.*, 2019 and may consequently be considered as non-anomalous. The CO<sub>2</sub> fluxes measured close to the main emission points at Fontaine Ardente du Gua do not follow this rule and are anomalous in relation with the CO<sub>2</sub> richness of the gas.

In the case of baseline monitoring, and apart from specific areas (e.g. wetlands), any detection of CH<sub>4</sub> flux at values greater than 0.002 g/m<sup>2</sup>/h may suggest that further characterization and understanding needs to be done. On the contrary, in shale gas applications, the monitoring of CO<sub>2</sub> fluxes may not be very informative.



**Figure 15** From top to bottom and from left to right: CO<sub>2</sub>-CH<sub>4</sub> scatter plot; CO<sub>2</sub> – CO<sub>2</sub> flux scatter plot; CH<sub>4</sub> – CH<sub>4</sub> flux scatter plot; CO<sub>2</sub> flux – CH<sub>4</sub> flux scatter plot.

Another lesson from studies on natural analogues is the existence, or absence, of a relationship between the concentration of a gas species measured in the soil and the flux at the soil/atmosphere interface of this species. These relations are reported in Figure 15 for CO<sub>2</sub> and CH<sub>4</sub>. Confirming the absence of CO<sub>2</sub> supply from depth, there is no relation between the CO<sub>2</sub> concentration and the CO<sub>2</sub> flux for Rochasson, Molières-Glandaz and Jonchiers. There may be some tendency of relation between concentration and flux for Fontaine Ardente du Gua, being constrained by two points of very high fluxes. At lower CO<sub>2</sub> fluxes, the relation is less straightforward and the influence of soil formations, in the context of an area with anthropized – or at least reworked – soils, may induce poor correlation, as well as the presence of biologically mediated CO<sub>2</sub> in the soil, which modifies the CO<sub>2</sub> flux.

As the abundance of CH<sub>4</sub> in soils is by far lower, such influence of near-surface production of CH<sub>4</sub> should be much lower. As reported in Figure 15, the relation between concentration and flux is not as expected. A large part of the strong increases in CH<sub>4</sub> concentration in the soil is not related with enhanced emissions to the atmosphere. Only a small number of measurements point to a coupling between concentration and flux. This may be related to a bias in the data acquisitions because some of the main gas seeps (Fontaine Ardente du Gua, Molières-Glandaz) could not be investigated for soil gas concentration measurements, in the absence of soil covering the shale formations. This may also suggest that the heterogeneity of the soil formations, where existing, may influence the strength and the pattern of the degassing.

The results of these investigations at some hydrocarbon gas seeps in France are in line with the results reported elsewhere in the world (e.g. Etiope, 2015 and references therein) and also with the results obtained from CO<sub>2</sub> emitting natural analogues (e.g., Annunziatellis *et al.* (2008) and Schütze *et al.* (2012)). The patterns of the degassing structures are often small to very small, these patterns may experience geometrical changes with time and the vents may experience strong changes in their emission rates even over short time scales (e.g. Boudoire *et al.* (2017); Gal *et al.* (2018b)). This makes leakage detection still challenging over wide areas using ground-based techniques, explaining the interest in monitoring techniques allowing a larger coverage. These methods can be ground-based (e.g., Feitz *et al.* (2014) and Lowry *et al.* (2020)) or operated from the sky (e.g. Emran *et al.* (2017) and Villa *et al.* (2016)) but these techniques have their own drawbacks (e.g. Deventer *et al.*, 2019; Fox *et al.*, 2019; and Golston *et al.*, 2018). For baseline acquisitions, a combination of



airborne and ground-based monitoring techniques, associated with an in-depth understanding of the signal attribution, is thus recommended in the perspective of the ability to monitor/detect changes when a site enters into exploitation/use.

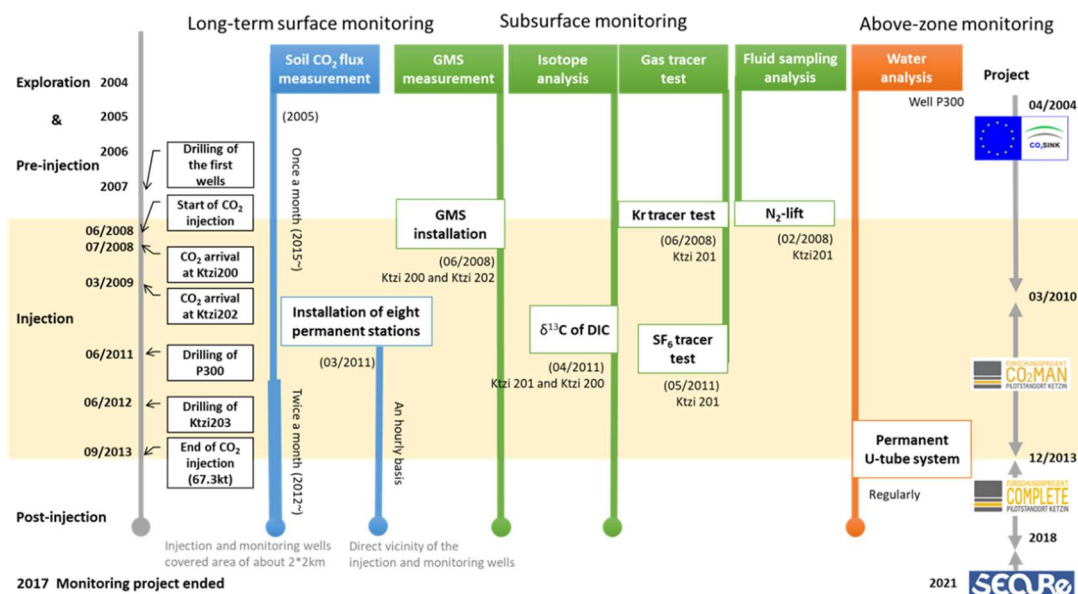


## 4 Guidelines for common strategies in gas storage and exploitation from unconventional reservoirs baseline assessment and monitoring

The baseline assessment is an essential phase in the preparation for drilling and for control and monitoring of the injection activities. The information of the baseline study, including geology, pilot seismic testing, reservoir modelling, laboratory experiments on rock samples, and surface and subsurface fluid geochemistry, form the scope of this study Förster *et al.*, 2006. The results serve as a baseline for comparison with analysis during and after injection of CO<sub>2</sub> to identify potential leakage of CO<sub>2</sub> from the storage reservoir at depth. Thus, the data form the basis for risk assessment in the post-drilling phase of the project. At the Ketzin site, for all multi-disciplinary monitoring methods, with the exception of a few methods that were added later on by project partners, baseline assessment and monitoring took place, as displayed in **Figure 16** for the whole set of geochemical investigations.

Although the baseline geology benefited from the previous exploration and the operation of a gas-storage facility at the Ketzin site, the database is not comparable in terms of quality, frequency, and consistency to databases available from exploration and exploitation of oil and gas fields in other areas.

In conclusion, CO<sub>2</sub> injection into saline aquifers requires thorough exploration and baseline investigations covering several disciplines of geoscience, including geology, geophysics, mineralogy, and geochemistry. These disciplines need to provide data for the engineering and the risk assessment of CO<sub>2</sub> injection, which, in turn, heavily depend on integrated modelling and updating existing subsurface static geological and dynamic flow models Förster *et al.*, 2006.



**Figure 16** Geochemical monitoring concept at the Ketzin storage site.

As gas storage activities and hydrocarbon production especially from unconventional resources are long term activities and their impact on subsurface can last long after industrial processes on the surface are finished, the technology development both in monitoring measurements and interpretation of results needs to be foreseen and all the changes in monitoring scope and schedule ought to be introduced gradually to ensure adjustment of all trends observations to new types of results and approaches.



There is a strong need of close cooperation between industry and researchers planning and conducting both baseline studies and further monitoring activities. A possibility to connect the observations results with an industrial process is crucial for proper interpretation of phenomena observed in the environment. On the other hand, results obtained from all observation systems ought to be reported both to the site operator and controlling bodies to ensure that any adverse changes cause will be identified and best possible counteractions will be undertaken in order to minimize an impact and further risk.

Public availability of environmental monitoring results of large-scale subsurface projects like underground gas storage or unconventional hydrocarbons resources exploitation may help to gain citizens trust to such projects as well as increase public awareness creating tools for a civil society aims achievement.



## 5 Conclusions and recommendations

Talking about underground storage of CO<sub>2</sub>, as well as any other gas mixture one must remember that these are activities which operational phase can last for tens of years and completion of which does not mean that all induced processes in the subsurface have also stopped.

This long timeframe that has to be taken into account when above-mentioned activities are considered can cause substantial inconsistencies both in baseline assessment and long-term monitoring scope and measurements technique and legal requirements of environmental impact assessment and process monitoring.

With regard to the state of the art in CO<sub>2</sub> storage monitoring, Jenkins (2020) reported new opportunities in measurement, monitoring and verification (MMV), and that impressive examples of progress in certain technological directions have been developed. The review also stated field projects continue to be vital to progress, because many of the developments in the MMV originate from field data.

It needs to be noted that research programs both for baseline assessment prior to any underground activity commencing and further operational and post-operational monitoring are relatively easy to be established within a scope of particular projects and their financing as long as we consider scientific projects and programs for pilot or demonstration cases. It is far more difficult to work with real life projects operated by an industry, when on-site access is restricted and activities in many cases depend on economy and market rules. If a baseline assessment is not clearly required by legal regulations or at least decisions that are in charge, there is always a threat that there will not be enough time to conduct all necessary observations which need in many cases last years and require appropriate infrastructure for observations (like e.g. properly located and screened groundwater observations wells). The same refers to operational environmental monitoring – if not legally required or required by name not by a defined scope and frequency, it may appear improper or insufficient. All large-scale subsurface activities likely to have a significant environmental impact need to be sufficiently regulated in terms of requirements for baseline assessment and process monitoring. The financing sources for such activities must be defined and if not conducted by a subject independent from an investor, need to be supervised by adequate knowledgeable institutions.

All mentioned above also refers to post-operational phase monitoring which in the best cases is usually limited to particular industry presence on site. Every legal entity which takes the liability must be aware of needs for further observations derived from particular case study and this requires to be stated in adequate regulations. It will be worth to think about financing sources for long term post-operational monitoring, special risk-based insurance system and/or state liability.

It is also important to understand that the monitoring itself is not a mitigation or remediation tool. Certain actions need to be pre-defined in case of any adverse effect identified by the observations results. This has been also concluded by a scientific literature review of shale gas environmental impacts (Costa et al., 2017), which noted that future research efforts should focus on mitigation techniques as well as standardization practices to enable a more precise comparison between studies or procedures in order to establish a wider, stronger consensus on environmental impacts of shale gas exploration and exploitation.

It is highly recommended to disclose the results of environmental monitoring to the public, which can stimulate public engagement and contribute to wide education, thus help in creation of informative society. Such practice can build better society trust in the industrial initiatives and give the society a proper knowledge about the environment which they live in.

### 5.1 KETZIN

The Ketzin pilot site provides an example of observing the complete life cycle of a CO<sub>2</sub> storage facility, from site assessment, injection operation, post-operation, closure, post-closure until the transfer of liability back to authorities. Within the framework of the geological characterisation for preparing the CO<sub>2</sub> storage, it was necessary to draw on the legacy data from the time of the former town gas/natural gas storage (1964–2000). Here, the difficulty of referring to measurement data from old observation techniques already became first apparent. Much of the legacy data was only available in analogue form or in 2D output, and most of the data had to be digitised first. During the 13 years of scientific observation at the Ketzin CO<sub>2</sub> pilot site (2004–2017), great importance was attached to using the same techniques and registration methods for all surface and subsurface observations. However, it became clear to the responsible scientists that due to the progressive development of monitoring methods and the availability of more complex evaluation procedures over more



than a decade, the same problem would arise again if in the distant future, eventually within the framework of another storage project, the connectivity to an existing data archive had to be elaborated again in the same manner as at the Ketzin beginning.

## 5.2 BORZEÇIN

The Borzeçin mine case is a good example of long-lasting operations which started nearly 50 years ago as conventional gas accumulation exploitation. With time, an acid gas injection was added which contributed to gas recovery to some extent. Later, a produced water and liquid mining waste disposal was established in the same reservoir structure. It is hard to determine what ought to be considered as baseline conditions for each of these activities and accordingly which legal regulations and standards should be adopted. Moreover, observation techniques with regard both to possible parameters and detection ability have evolved over these 50 years in a way that measurements taken at the beginning of the site development may not be comparable with the ones being done at present and for many research possibilities at present there are simply no reference values from the past.

## 5.3 FRENCH ALPS CHAIN

The use of natural analogues of gas leaks revealed a new, pertinent strategy for environmental baseline assessment and leak detection. Fortunately, gas leaks at industrial sites are rather rare and in general remediation attempts are undertaken as soon as the leak is detected. For these reasons it is difficult to test and develop monitoring techniques on real-world industrial sites. On the other hand, natural gas seeps, in particular macro-seeps in the definition of Etiope (2015), may have similar characteristics as industrial leaks in terms of gas types and flow rates. In the case of the Fontaine Ardente seep, both gases relevant for CCS and unconventional gas development, CO<sub>2</sub> and CH<sub>4</sub> are present and the yearly flow rate at the main vent is significant (18 tons of CH<sub>4</sub> and 5.5 tons of CO<sub>2</sub>, Gal et al., 2018). This allows testing gas monitoring techniques under the conditions prevailing around a localized gas leak e.g. in the immediate vicinity of a leaking well. On the other hand, diffuse gas seeps, as encountered around the main vent, are typical for the natural geochemical background of gas-bearing formation (shales) and provide ideal testing conditions for natural baseline strategies and monitoring techniques at different spatial scales. Multiscale measurements from local (soil gas concentration and flow measurements with different techniques, IR-spectroscopy, laser-based systems) to regional (e.g. airborne or satellite measurements) are recommended both for baseline definition and for monitoring. Local measurements are indispensable for obtaining reliable data and for calibrating large-scale measurements e.g. airborne but they cannot easily be used for systematic measurements with a representative coverage of larger areas. Here, the laser techniques developed in SECURE revealed efficient in terms of measurement speed and, in consequence, costs. Their use on airborne systems is a promising way to further increase coverage, in particular for baseline assessment. A second lesson learnt from the work conducted on the French subalpine natural analogues is the importance of secondary natural processes leading to modifications of gas concentrations and flow and ratios between the target gases (CO<sub>2</sub> and CH<sub>4</sub>) and background gases (e.g. O<sub>2</sub> and N<sub>2</sub>). Such processes have to be considered (e.g. through geochemical fingerprinting techniques) when defining the natural background but also when investigating possible leaks. Last but not least, natural analogues are long-lived phenomena (in the case of the Fontaine Ardente its lifetime is at least two millenaries) so that long-term monitoring techniques could be tested: natural archives, e.g. tree rings (see deliverable D 4.7) can be used to assess the chronology of leakage. Also, the microbial adaptation to the enhanced natural gas flows can be considered as complete so that the investigation of microbial testing methods is facilitated (report D4.7).



## 6 References

- Annunziatellis, A., Beaubien, S. E., Bigi, S., Ciotoli, G., Coltella, M., and Lombardi, S., 2008, Gas migration along fault systems and through the vadose zone in the Latera caldera (central Italy): Implications for CO<sub>2</sub> geological storage: *International Journal of Greenhouse Gas Control*, v. 2, no. 3, p. 353-372.
- Appelo, C. A. J., Parkhurst, D. L., and Post, V. E. A., 2014, Equations for calculating hydrogeochemical reactions of minerals and gases such as CO<sub>2</sub> at high pressures and temperatures: *Geochimica et Cosmochimica Acta*, v. 125, p. 49–67.
- Bell R.A., Darling W.G., Ward R.S., Basava-Reddi L., Halwa L., Manamsa K., Ó Dochartaigh B.E., 2017. A baseline survey of dissolved methane in aquifers of Great Britain, *Science of the Total Environment* 601–602 (2017) 1803–1813, <https://doi.org/10.1016/j.scitotenv.2017.05.191>
- Boudoire, G., Di Muro, A., Liuzzo, M., Ferrazzini, V., Peltier, A., Gurrieri, S., Michon, L., Giudice, G., Kowalski, P., and Boissier, P., 2017, New perspectives on volcano monitoring in a tropical environment: Continuous measurements of soil CO<sub>2</sub> flux at Piton de la Fournaise (La Réunion Island, France), v. 44, no. 16, p. 8244-8253.
- Brufatto, C., Cochran Aberdeen, J., Lee Conn David Power, S., Zaki Abd Alla El-Zeghaty, S., Fraboulet, B., Griffin, T., James Trevor Munk, S., Justus Santa Cruz, F., Joseph Levine, B.R., Montgomery, C., Murphy, D., Pfeiffer Houston, J., Tiraputra Pornpoch, T., Rishmani Abu Dhabi, L., 2003. From mud to cement—building gas Wells. *Oilf. Rev.* 62–76.
- Costa, D., Jesus, J., Branco, D., Danko, A., Fiúza, A., 2017. Extensive review of shale gas environmental impacts from scientific literature (2010–2015), *Environ Sci Pollut Res* (2017) 24:14579–14594, <https://doi.org/10.1007/s11356-017-8970-0>
- Deventer, M. J., Griffis, T. J., Roman, D. T., Kolka, R. K., Wood, J. D., Erickson, M., Baker, J. M., and Millet, D. B., 2019, Error characterization of methane fluxes and budgets derived from a long-term comparison of open- and closed-path eddy covariance systems: *Agricultural and Forest Meteorology*, v. 278, p. 107638.
- Dusseault, M., Jackson, R., 2014. Seepage pathway assessment for natural gas to shallow groundwater during well stimulation, in production, and after abandonment. *Environ. Geosci.* 21, 107–126. <https://doi.org/10.1306/eg.04231414004>.
- Emran, B. J., Tannant, D. D., and Najjaran, H., 2017, Low-Altitude Aerial Methane Concentration Mapping, v. 9, no. 8, p. 823.
- Etiopie, G., 2015. *Natural Gas Seepage The Earth's Hydrocarbon Degassing*, Springer. ed. ISBN 978-3-319-14601-0
- EU Parliament, 2014. Communication from the Commission to the European Parliament, The Council, The European Economic and Social Committee and the Committee of the Regions - On the exploration and production of hydrocarbons (such as shale gas) using high volume hydraulic fracturing in the EU. [https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:52014DC0023R\(01\)&from=EN](https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:52014DC0023R(01)&from=EN)
- Faber J., 2007: EIA report of KZG Borzęcin installation modernisation for reservoir waste disposal. (Raport oddziaływania przedsięwzięcia na środowisko dla modernizacji KZG Borzęcin z przystosowaniem instalacji do składowania odpadu w złożu - in Polish).
- Farokhpoor, R., Akervol, I., Torsæter, O., Bjørkvik, B.J.A., 2013. CO<sub>2</sub> capillary entry pressure into flow barrier and caprock, in: SINTEF. Presented at the International Symposium of the Society of Core Analysts, Napa Valley, California.
- Feitz, A., Jenkins, C., Schacht, U., McGrath, A., Berko, H., Schroder, I., Noble, R., Kuske, T., George, S., Heath, C., Zegelin, S., Curnow, S., Zhang, H., Sirault, X., Jimenez-Berni, J., and Hortle, A., 2014, An assessment of near surface CO<sub>2</sub> leakage detection techniques under Australian conditions: *Energy Procedia*, v. 63, p. 3891-3906.
- Förster, A., Norden, B., Zinck-Jørgensen, K., Frykman, P., Kulenkampff, J., Spangenberg, E., Erzinger, J. r., Zimmer, M., Kopp, J. r., Borm, G. n., Juhlin, C., Cosma, C.-G., and Hurter, S., 2006, Baseline characterization of the CO<sub>2</sub>SINK geological storage site at Ketzin, Germany: *Environmental Geosciences*, v. 13, no. 3, p. 145-161.
- Fox, T. A., Barchyn, T. E., Risk, D., Ravikumar, A. P., and Hugenholtz, C. H., 2019, A review of close-range and screening technologies for mitigating fugitive methane emissions in upstream oil and gas: *Environmental Research Letters*, v. 14, no. 5, p. 053002.
- Gal, F., Kloppmann, W., Proust, E., and Humez, P., 2018a, Gas concentration and flow rate measurements as part of methane baseline assessment: Case of the Fontaine Ardente gas seep, Isère, France: *Applied Geochemistry*, v. 95, p. 158-171.





- Gal, F., Leconte, S., and Gadalia, A., 2018b, The “Escarot” gas seep, French Massif Central: CO<sub>2</sub> discharge from a quiescent volcanic system – Characterization and quantification of gas emissions: *Journal of Volcanology and Geothermal Research*, v. 353, p. 68-82.
- Gal, F., Pokryszka, Z., Labat, N., Michel, K., Lafortune, S., and Marblé, A., 2019, Soil-Gas Concentrations and Flux Monitoring at the Lacq-Rousse CO<sub>2</sub>-Geological Storage Pilot Site (French Pyrenean Foreland): From Pre-Injection to Post-Injection, v. 9, no. 4, p. 645.
- Golston, L. M., Aubut, N. F., Frish, M. B., Yang, S., Talbot, R. W., Gretencord, C., McSpirtt, J., and Zondlo, M. A., 2018, Natural Gas Fugitive Leak Detection Using an Unmanned Aerial Vehicle: Localization and Quantification of Emission Rate, v. 9, no. 9, p. 333.
- Hinkle, M. E., 1994, Environmental conditions affecting concentrations of He, CO<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub> in soil gases: *Applied Geochemistry*, v. 9, no. 1, p. 53-63.
- IME Consulting, 2004. Programme of environmental protection for town and county Żmigród (Program Ochrony Środowiska dla Miasta i Gminy Żmigród), 2004, IME CONSULTING WROCŁAW (in Polish)
- Jackson, R.B., Vengosh, A., Darrach, T.H., Warner, N.R., Down, A., Poreda, R.J., Osborn, S.G., Zhao, K., Karr, J.D., 2013. Increased stray gas abundance in a subset of drinking water wells near Marcellus shale gas extraction. *Proc. Natl. Acad. Sci.* 110, 11250–11255. <https://doi.org/10.1073/pnas.1221635110>
- Jarzyna, J., Puskarczyk, E., Bała, M., Papiernik, B., 2009. Variability of the Rotliegend sandstones in the Polish part of the Southern Permian Basin - permeability and porosity relationships. *Ann. Soc. Geol. Pol. Vol. 79, No 2*, 13–26.
- Jenkins, C., 2020. The State of the Art in Monitoring and Verification: an update five years on. *International Journal of Greenhouse Gas Control* 100, 103118. <https://doi.org/10.1016/j.ijggc.2020.103118>
- Jenkins, C., Chadwick, A., and Hovorka, S. D., 2015, The state of the art in monitoring and verification—Ten years on: *International Journal of Greenhouse Gas Control*, v. 40, p. 312-349.
- Jordan, C., Rochelle, C., Gal, F., Proust, E., Maunoury, A., Pineau, F., Donnat, L., Dubucq, D., and Credoz, A., 2021, Report on applicability of UAV technology for monitoring large-scale sites and the impact of remote sensing on decisions of baseline.
- Karnkowski, P.H., 2008. Regionalizacja tektoniczna Polski-Niż Polski. *Przegląd Geol.* Vol. 56, 895–903.
- Klusman, R. W., 2011, Comparison of surface and near-surface geochemical methods for detection of gas microseepage from carbon dioxide sequestration: *International Journal of Greenhouse Gas Control*, v. 5, no. 6, p. 1369-1392.
- Koniecznyńska M., Adamczak-Biały T., Brodecki A., Brzezińska A., Janica R., Dziekan-Kamińska E., Fajfer J., Feldman-Olszewska A., Felter A., Frydel J., Głuszyński A., Gryczko-Gostyńska A., Jarosiński M., Joźwiak K., Kordalski Z., Kowalewski T., Kijewska S., Lichtarski G., Lidzbarski M., Lipińska O., Mikołajków J., Nidental M., Otwinowski J., Pasierowska B., Pergół S., Podhalańska T., Roman M., Rosowiecka O., Sobień K., Starzycka A., Stec B., Śliwiński Ł., Waksmundzka M., Woźnicka M., Dzieńiewicz M., Guzy P., Izydor G., Konopka E., Kotarba m., Kowalski T., Lewkiewicz-Kotysa A., Macuda J., Nagy S., Sechman H., Bernaciak M., Grzelak W., Janicki W., Korkosz A., Kozak k., Kudłak B., Męcik M., Zabiegała B., 2015, *The Environment and Shale Gas Exploration*. Generalna Dyrekcja Ochrony Środowiska (General Directorate for Environmental Protection), ISBN 978-83-62940-97-4, 188 p.
- Koniecznyńska M., Brodecki A., Janica R., Kowalewski T., Joźwiak K., Lichtarski G., Lipińska O., Lidzbarski M., Otwinowski J., Nidental M., Śliwiński Ł., Warumzer R., Wołkiewicz W., Woźnicka M., Sechman H., Guzy P., Twaróg A., Rams-Pietraszewska J., Dzieńiewicz P., Kotarba M., Kowalski T., 2018 - „Środowisko i prace rozpoznawcze dotyczące gazu z łupków” - Sprawozdanie z prac wykonanych podczas realizacji przedsięwzięcia pt.: „Wykonanie badań dla oceny aktualnego stanu środowiska naturalnego na 7 poligonach badawczych, gdzie prowadzono prace poszukiwawcze za gazem z formacji łupkowych” w ramach umowy nr 394/2017/Wn-07/FG-go-dn/D z dnia 27.12.2017 r.(in Polish)
- Koniecznyńska M., Macuda J., 2015, Environmental Impact of exploration from unconventional gas deposits in Poland. *Ecological Chemistry and Engineering. S (ECOL CHEM ENG S.)* 2015, 22(4), pp:703-717.
- Kovach, E. M., 1946, Diurnal variations of the radon-content of soil-gas, v. 51, no. 1, p. 45-55.
- Lackey, G., Rajaram, H., Sherwood, O.A., Burke, T.L., Ryan, J.N., 2017. Surface casing pressure as an indicator of well integrity loss and stray gas migration in the Wattenberg Field, Colorado. *Environ. Sci. Technol.* 51, 3567–3574. <https://doi.org/10.1021/acs.est.6b06071>.
- Lowry, D., Fisher, R. E., France, J. L., Coleman, M., Lanoisellé, M., Zizzeri, G., Nisbet, E. G., Shaw, J. T., Allen, G., Pitt, J., and Ward, R. S., 2020, Environmental baseline monitoring for shale gas



- development in the UK: Identification and geochemical characterisation of local source emissions of methane to atmosphere: *Science of The Total Environment*, v. 708, p. 134600.
- Lubaś, J., 2007. Pionierskie doświadczenia Polski w zakresie sekwestracji dwutlenku węgla. *Przegląd Geol.* 55, 663–665.
- Lubaś, J., Szott, W., 2010. 15-year experience of acid gas storage in the natural gas structure of Borzęcin – Poland. *Nafta-Gaz R.* 66, nr 5, 333–338.
- Lubaś, J., Szott, W., Jakubowicz, P., 2012. Effects of Acid Gas Reinjection on CO<sub>2</sub> Concentration in Natural Gas Produced from Borzęcin Reservoir. *Nafta-Gaz R.* 68, nr 7, 405–410.
- Lubaś, J., Szott, W., Łętkowski, P., Gołabek, A., Miłek, K., Rychlicki, A., Warnecki, M., Wojnicki, M., Kuśnierczyk, J., Szufflita, S., Biały, S., 2020. Report on effects of long-term sequestration process in the Borzęcin structure – observation evidence of the injected gas migration and possible leakage. Deliverable 2.2, SECURE 2020.
- Molofsky, L.J., Connor, J.A., Farhat, S.K., Wylie, A.S., Wagner, T., 2011. Methane in Pennsylvania water wells unrelated to Marcellus shale fracturing. *Oil Gas J.* (December 5), 54–67.
- Olszewska, K., Mularczyk, A., 2012. KZG Borzęcin (in Polish). *Pol. Gór. Naft. Gazow.* SA W Warszawie Oddz. W Zielonej Górze.
- Osborn, S. G., Vengosh, A., Warner, N. R., Jackson, R. B., 2011. Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing. *PNAS*, <https://doi.org/10.1073/pnas.1100682108>
- Peryt, T.M., Geluk, M.C., Mathiesen, A., Paul, J., Smith, K., 2010. Zechstein, in: *Petroleum Geological Atlas of the Southern Permian Basin Area*. EAGE Publications, pp. 123–147.
- Pleśniak, Ł., Orion-Jędrysek, M., Jakubiak, M., Bucha, M., Krajniak, J., Matuszewicz, M., Kufka, D., Matyasik, I., Janiga, M., Lojen, S., Zigon, S., 2017. Ocena migracji składników gazu ziemnego w złożu Borzęcin na podstawie wyników analiz izotopów trwałych wodoru i węgla (in Polish with English summary). *Nafta-Gaz R.* 73, nr 1. <https://doi.org/10.18668/NG.2017.01.03>
- Pokryszka, Z., Adelise, F., Farret, R., Lafortune, S., Michel, E., and Rupasinghe, S., 2019. . Reference values of naturally occurring biogenic CO<sub>2</sub> and CH<sub>4</sub> fluxes from soils, INERIS Report DRS-19-164646-00273A INERIS Report DRS-19-164646-00273A
- Raczyński, P., Peryt, T.M., Strobel, W., 2017. Sedimentary and environmental history of the Late Permian Bonikowo Reef (Zechstein Limestone, Wuchiapingian), western Poland. *J. Palaeogeogr.* 6, 183–205. <https://doi.org/10.1016/j.jop.2017.05.001>
- Regulation of Ministry of Environment of 23<sup>rd</sup> July 2008 on criteria and method of groundwater state assessment, *Journal of Laws* 2008.143.896 (Rozporządzenie Ministra Środowiska z dnia 23 lipca 2008 r. w sprawie kryteriów i sposobu oceny stanu wód podziemnych, Dz.U.2008.143.896), in Polish.
- Romanak, K. D., Bennett, P. C., Yang, C., and Hovorka, S. D., 2012, Process-based approach to CO<sub>2</sub> leakage detection by vadose zone gas monitoring at geologic CO<sub>2</sub> storage sites, v. 39, no. 15.
- Schmidt-Hattenberger, C., Jurczyk, C., Liebscher, A., Möller, F., Norden, B., Prevedel, B., Wiese, B. U., Zemke, K., & Zimmer, M. (2018). Post-injection monitoring and well abandonment results of the Ketzin test site – an essential part for transfer of liability. In 14th International Conference on Greenhouse Gas Control Technologies, Melbourne. Available at SSRN: <https://ssrn.com/abstract=3365957>
- Schout G., Griffioen J., Hassanizadeh S.M., Cardon de Lichtbuer G., Hartog N., 2019 – “Occurrence and fate of methane leakage from cut and buried abandoned gas wells in the Netherlands”, *Science of the Total Environment* 659 (2019) 773–782, <https://doi.org/10.1016/j.scitotenv.2018.12.339>
- Schout, G., Hartog, N., Hassanizadeh, S.M., Griffioen, J., 2017. Impact of an historic underground gas well blowout on the current methane chemistry in a shallow groundwater system. *Proc. Natl. Acad. Sci.* 115 (201711472). <https://doi.org/10.1073/pnas.1711472115>.
- Schütze, C., Sauer, U., Beyer, K., Lamert, H., Bräuer, K., Strauch, G., Flechsig, C., Kämpf, H., and Dietrich, P., 2012, Natural analogues: a potential approach for developing reliable monitoring methods to understand subsurface CO<sub>2</sub> migration processes: *Environmental Earth Sciences*, v. 67, no. 2, p. 411-423.
- Sechman H., Dzieńiewicz M., Kotarba M., Guzy P., Koniecznyńska M., Lipińska O., 2015, Wyniki powierzchniowych badań geofizycznych w rejonie odwiertów ukierunkowanych na poszukiwanie i udostępnianie gazu ze złóż niekonwencjonalnych. *Przegląd Górniczy*, T. 71, no. 10, pp. 68-80 (in Polish).
- Shao, H., Ussiri, D. A. N., Patterson, C. G., Locke, R. A., Wang, H., Taylor, A. H., and Cohen, H. F., 2019, Soil gas monitoring at the Illinois Basin – Decatur Project carbon sequestration site: *International Journal of Greenhouse Gas Control*, v. 86, p. 112-124.



- Stopa, J., Lubaś, J., Rychlicki, S., 2006. Underground storage of acid gas in Poland - experiences and forecasts. Presented at the 23rd World Gas Conference, Amsterdam.
- Szott, W., Łętkowski, P., Gołabek, A., Miłek, K., 2020. Modelling of the Long-Term Acid Gas Sequestration and Its Prediction: A Unique Case Study. *Energies* 13, 4701. <https://doi.org/10.3390/en13184701>
- Teasdale, C. J., Hall, J. A., Martin, J. P., and Manning, D. A. C., 2014, Ground Gas Monitoring: Implications for Hydraulic Fracturing and CO<sub>2</sub> Storage: *Environmental Science & Technology*, v. 48, no. 23, p. 13610-13616.
- Topp, E., and Pattey, E., 1997, Soils as sources and sinks for atmospheric methane, v. 77, no. 2, p. 167-177.
- Van Stempvoort, D., Maathuis, H., Jaworski, E., Mayer, B., Rich, K., 2005. Oxidation of fugitive methane in ground water linked to bacterial sulfate reduction. *GroundWater* 43, 187–199.
- Villa, T. F., Gonzalez, F., Miljevic, B., Ristovski, Z. D., and Morawska, L., 2016, An Overview of Small Unmanned Aerial Vehicles for Air Quality Measurements: Present Applications and Future Prospectives, v. 16, no. 7, p. 1072.
- von Arnold, K., Nilsson, M., Hånell, B., Weslien, P., and Klemedtsson, L., 2005, Fluxes of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O from drained organic soils in deciduous forests: *Soil Biology and Biochemistry*, v. 37, no. 6, p. 1059-1071.
- Watson, T.L., Bachu, S., 2009. Evaluation of the potential for gas and CO<sub>2</sub> leakage along wellbores. *SPE Drill. Complet.* 24, 115–126. <https://doi.org/10.2118/106817-PA>.
- Wojciechowska R., 1998 – Mapa hydrogeologiczna Polski w skali 1:50 000, ark. Żmigród (690). PIG-PIB, Warszawa.
- Wipki, M., Ivanova, A., Liebscher, A., Lüth, S., Möller, F., Szzybalski, A., Wiese, B. U., & Zimmer, M. (2016). Monitoring Concept for CO<sub>2</sub> Storage at the Ketzin Pilot Site, Germany – Post-injection Continuation Towards Transfer of Liability. *Energy Procedia*, 97, 348–355. <https://doi.org/10.1016/j.egypro.2016.10.017>
- Wojciechowska R., Brytan P., Mżyk S., Śliwka R., 2011 – Dokumentacja hydrogeologiczna określająca warunki hydrogeologiczne w związku z ustanawianiem obszarów ochronnych Głównego Zbiornika Wód Podziemnych nr 303 Pradolina Barycz-Głogów (E). PROXIMA, Wrocław.