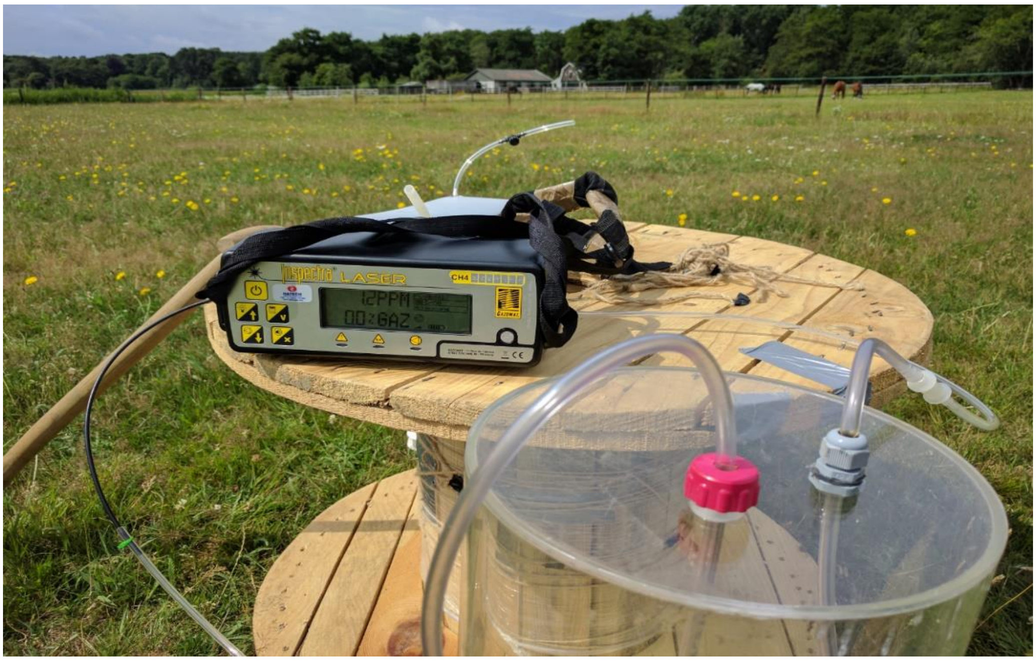

Methane leakage from abandoned gas wells in the Netherlands, reality or fiction?

Master Thesis

Water Sciences and Management

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Summary

A number of studies performed in the U.S. and Canada has proved that methane leakages from abandoned gas wells exist. The leakages pose environmental and safety risks as they represent a non-negligible amount of methane emitted in the atmosphere. IPCC inventories on gas emission considered as nulle the emitted methane from abandoned gas wells. Methane is a potent greenhouse gas 30 times stronger than carbon dioxide in the atmosphere. Methane in groundwater aquifer favors the risk of contamination of pollutants. Because the Netherlands is an important gas-producing country, this makes the question relevant whether or not methane leakages from abandoned wells occurs in the Netherlands as well. Therefore, this research aims at detecting: (1) the methane flux emissions of a selected number of abandoned gas wells, (2) the evidence of high methane emitter, and (3) the source of the emitted methane, i.e. biogenic or thermogenic.

29 abandoned gas wells were investigated in the Netherlands during July 2017 in order to identify the presence of any leakages. In this research, a field work monitoring campaign has been performed. As a first step, a screening measurement was performed in a circle of approximately 16 meters radius for 24 wells locations, excluding 5 others wells because of obstacles on sites (e.g. presence of ditches, ponds or invasive vegetation). Secondly, two sets of flux measurements (one at the surface and one at one meter depth) were performed at the controls and at the exact X-Y coordinates of the wells using the static chamber method for the 29 wells selected. Finally, the isotopic analysis of 35 samples was monitored at IMAU laboratories (Utrecht University) using the δ13C and δD ratios as references.

The concentration screening method in a 16 meters radius circle used to identify evidences of high fluxes at the surface has proved to be inefficient as high fluxes were detected independently from the results of the screening. Only one decommissioned well located at Monster (MON-02) had a significant high flux (40,026 mg/(hr.m^2)) of methane. Further analysis of the isotopic composition for this site revealed the presence of thermogenic gas, confirming the hypothesis of leakage for this well. Three other wells have shown methane fluxes above 100 mg/(hr.m^2), for which only one has been performed at ground surface. The application of a linear model to time series of methane concentrations for a spot showed a better fit of the flux estimates for the measurements performed at one meter depth compared to those at the surface. The outcomes of the isotopic analysis showed the existence of two main biogenic groups differing for their δD ratios: primary biogenic methane that became altered in their isotopic composition due to partial oxidation. Considering the abundant presence of peat in the Netherlands, a comparison with the regional occurrence of the shallow Holocene Nieuwkoop Formation (which is by definition composed of peat) did not allow any reliable conclusion on the origin of the two groups of biogenic methane.

The presence of one well with a high flux of thermogenic methane (MON-02) out of 29 investigated makes the Netherlands a country subject to leakages. Considering further research, the circled screening method performed is not recommended for leakage identification. However, performing the methane measurements at one meter depth is an efficient way to detect fluxes.

Acknowledgments

While leading a master thesis research project as this one has shown to be full of uncertainties and changes, I would like to thank prof. Jasper Griffioen and Gilian Schout for their full support in my educational progress. Their inputs are greatly appreciated as they helped keeping my self-confidence during this project. Their availabilities and their critical mindsets were a major plus in the progression of my research and knowledges on the issue of methane emission from abandoned gas wells. This master thesis was also an opportunity to learn the principle of GIS, for which Gilian showed a tremendous amount of help and patience. Last but not least, I must recognize I had a great pleasure during the month of July 2017 performing my very first field work campaign as it was the opportunity for me to discover the marvelous Dutch landscape.

Contents

1. Introduction

1.1 Scope of the study

Natural gas represents an important part of the world's energy supply and, globally, is expected to be even more necessary during the next decades as energy needs are likely to grow (Ratner et al. 2013). Used as primary combustible to heat our houses for instance, natural gas is currently an unavoidable resource in our daily life. Stemming from the deep sub-surface of the Earth, natural gas is the product of the degradation of organic matter after photosynthesis, and is composed predominantly of methane (Schoell, 1980). It is commonly agreed that the beginning of gas extraction practices refer to the latter half of the 19th century (Olah, 2005).

While natural gas resources have been considerably depleted during the last decades, a growing energy demand remains in developed countries with a western-oriented consumption. In parallel, we must recognize that those countries have been undertaking numerous actions towards a more environmental friendly energy transition since the last 20-25 years (Kivimaa et al., 2017).

The reinforcement of conventional and unconventional gas extraction practices is a strategy that has been developed to maintain the current level of natural gas consumption. This strategy may represent an opportunity for nations to reduce their reliance on energy import, that subsequently would increase their economic independency. Furthermore, this strategy is economically affordable, increasing the favorable consent of economic leaders. As illustration, more than half of the gas consumption in the US relied on natural gas extraction in 2015 (EIA, 2016).

Although the on-going intensive drilling of gas wells will allow more economic power, scientists in particular and people in general are concerned about their environmental impacts (Vidic et al., 2013; Entrekin et al., 2011). Typically, both water and air quality issues must be considered.

Water quality is threatened because of the increase of aquifer vulnerability nearby the drilling sites. While the methane itself is not hazardous for the aqueous environment, its presence in the aquifer can have an important influence on the presence of iron, manganese, aluminum and arsenic in shallow drinking water aquifers (Molofsky et al., 2016).

Furthermore, methane is known as actively contributing to the greenhouse gas (GHG) effect. The GHG potential of methane in the atmosphere is estimated to be 30 times higher than carbon dioxide (Princeton University, 2014). Albeit methane is found in significant lower amount than carbon dioxide in the atmosphere, it does contribute to the GHG effect as methane has proved to be responsible for 20 percent of the global warming effect by generating ozone in the troposphere (Kirschke et al., 2013). Methane emission from gas wells has been a topic of scientific interests as 3.6 to 7.9 percent of methane is lost in the atmosphere during each extraction procedure of natural gas (Howart et al., 2011). Moreover, Kang *et al.*

(2016) estimated that the methane emitted from abandoned wells represent 5 to 8 percent of the total annual anthropogenic emission in Pennsylvania. Even after abandonment, methane can still be emitted from a few high emitter wells (Kang et al., 2016). It is mostly the result of some forms of well integrity failures caused by numerous factors.

The Netherlands possesses a large amount of oil and gas reservoirs mainly located in the northeastern part of the country (Fig. 1). Millions of wells have been drilled for natural gas extraction since 1940s and many of them have been abandoned. The abandonment procedure of gas wells is an important topic of interest for this research because leakages can appear with the years and result in the release of methane in the groundwater as well as in the atmosphere (Caulton et al., 2014; Rivard et al. 2014). The Marcellus shale in Pennsylvania was the topic of a study led by Osborn *et al.* (2011) and high methane concentrations were observed in nearby water wells. The leakage of methane to the groundwater and the atmosphere can be the result of mechanical failures of the cement inside the well due to an improper abandonment procedure (Davies et al., 2014; King & King, 2013).

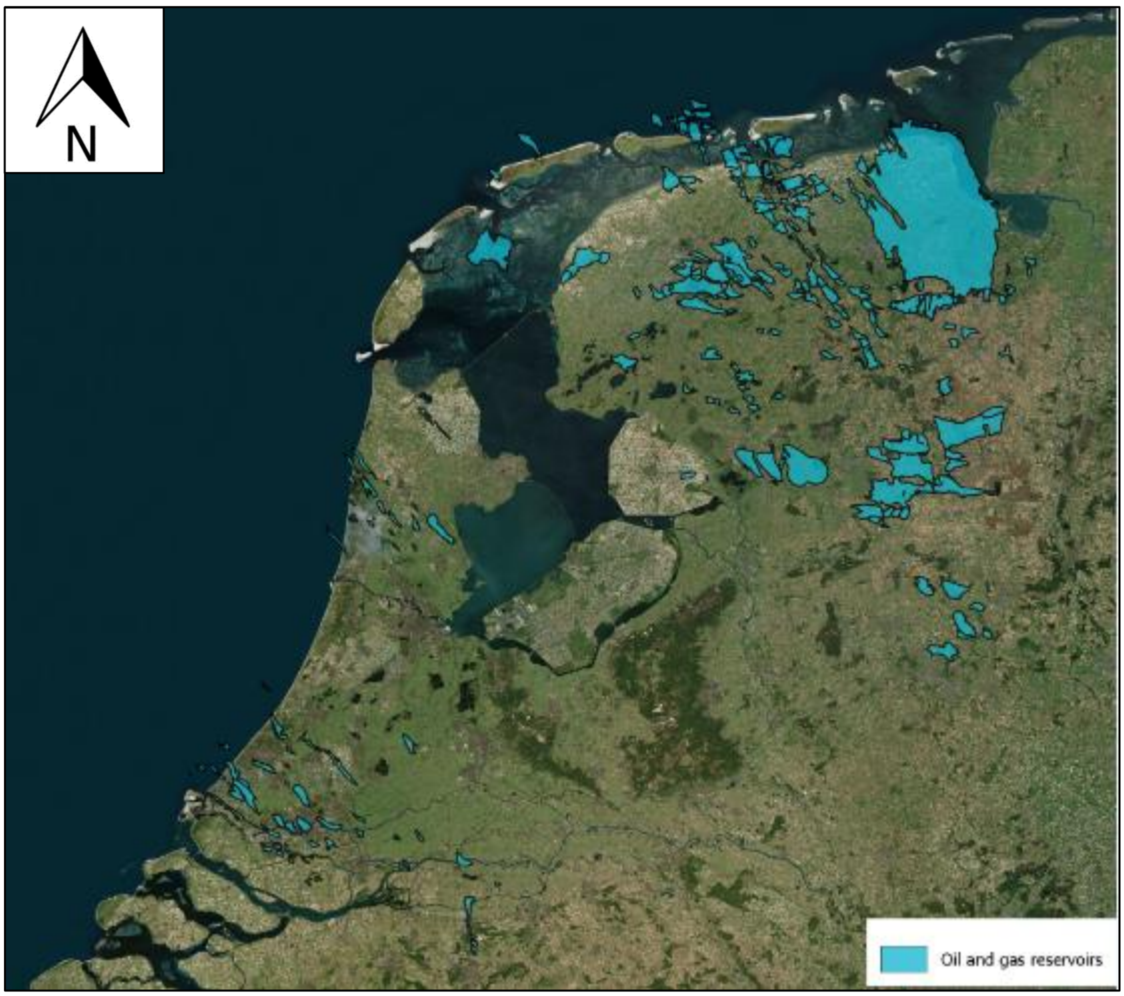

FIGURE 1: DUTCH ON-SHORE OIL AND GAS FIELDS LOCATIONS LARGELY DOMINATED BY THE GIANT GRONINGEN FIELD IN THE NORTHEASTERN REGION OF THE COUNTRY (SOURCE OF LOCATIONS GAS FIELDS: DINOLOCKET, 2017)

A few papers have pointed out the correlation between the presence of abandoned wells and the presence of methane in groundwater: first, methane concentrations are expected to increase with proximity to the nearby extraction wells (Osborn et al., 2011). Second, a strong correlation exists between the aerobic and anaerobic conditions of the soil and the presence of methane in groundwater (Cahill et al., 2017). Last, Vidic *et al.* (2013) suggest that low oxygen conditions, such as in presence of methane, can enhance processes including the dissolution of arsenic and iron, and reduction of sulfites and sulfates by bacteria.

1.2 Gas extraction in the Netherlands

A driving force of the Dutch economic market has been the natural gas extraction that started in 1959 with the discovery of the Groningen gas field and lasts until now (De Jager and Geluk, 2007). From 1959 on, the Dutch economy has been driven by this new economically favorable energy supply. In 2014, natural gas fulfilled 40% of the total energy use in the Netherlands (CBS, 2015 cited by Perlaviciute et al., 2017).

The immensity of the Groningen gas field has been a key element in the economic growth of the Netherlands in the sixties and seventies and the gas sector remains an important factor of the Dutch economic growth. However, a governmental decision has aimed to limit the annual gas production from the Groningen field to 27 billion cubic meters (bcm) (CBS, 2015). The *Centraal Bureau voor de Statistiek* (CBS) reported a more modest economic growth than the usual for 2016 mainly caused by the decision to reduce exports of natural gas (CBS, 2016).

While the gas sector is still a major economical ressource, political efforts towards a more environmental friendly economy are observed in the Netherlands (Bosman et al., 2014). The emergence of renewable energy has pushed the Dutch gas sector to change the entire gas economy and to seek for more sustainable alternatives in terms of energy production. Typically, the energy agenda set by the Dutch government has set a step by step plan until 2050 in order to ensure an energy transition towards more renewable resources. By 2020, renewable energy must be the source of 14% of the total energy production. By 2023, renewable energy must represent 16% of the total Dutch energy production (Ministry of Economic affairs, 2016).

An additional reason for the Dutch government to lower the activity of gas extraction is the much more intense seismic activity observed in the region of Groningen. Discovered in 1959, the Groningen gas field was one of the 10 largest gas resources in the world with a production potential expected to last until 2080. In the region concerns arose due to the intensive extraction activities inducing earthquakes, contributing to current debates questioning risk mitigations. Recurrent earthquakes events have been observed in the region of Groningen since the last 5 years (Perlaviciute et al., 2017). Major debates appeared since 2012 because of the multiple occurrence of earthquakes and more specifically since the Huizinge earthquake that has been recorded to shake with a 3.2 magnitude on the Richter scale. Therefore, much more attention towards policies implementation from the Dutch government are observed with more considerations for safe energy production.

A natural gas resource is defined as “the volume of natural gas that can be produced from discovered gas accumulations in the subsurface”. On January 1st 2016, among 477 gas accumulations existing in the Netherlands, 253 are in production and 82 are abandoned.

Globally, the Netherlands possesses the largest European gas resource in Groningen and the country contains the largest number of small fields. The Dutch total gas volume in 2012 was 4500 bcm of which the Groningen field contained 2750 bcm (Kombrink et al. 2012). Although all the gas extracted from those fields can be easily comparable, it differs in terms of their level of nitrogen. The higher is the nitrogen content, the lower is the calorific value. In terms of use, the appliances must be adapted to the calorific value of the gas extracted. It is typically observed with the Groningen gas field and the surrounding country, i.e. Belgium, Germany and the northern part of France, where most of the heating and cooking equipment mainly rely on this gas and are adapted to the low calorific value of the Groningen gas field.

1.3 Scientific contribution and gap of knowledge

A current regulation bans the practice of drilling activities for conventional and unconventional, i.e. shale gas, extraction in the Netherlands until 2023. The Dutch government wishes to establish an inventory of the risks for water resources before taking any decisions on the future methods of gas extraction. Furthermore, the decommissioning of wells and the related infrastructures represent a significant part of total expenditure of oil and gas infrastructure maintenance in the Netherlands. As reported by *Energy Beheer Nederland* (EBN) in 2015, the expenditure for decommissioned oil and gas infrastructure amounts to 6.7 billion Euros. Therefore, this proposed research may support better consideration for oil and gas well abandonment procedures.

While most of the previous studies have been performed in the U.S., no research provide evidences on leakage of abandoned gas wells in the Netherlands. As described above, the Netherlands is a large natural gas producer where numerous gas wells have been drilled and abandoned. Data on GHG emission as well as groundwater quality deterioration are required in order to assess the effects associated to the abandonment of gas wells.

1.4 Research questions and objectives

The main research question of this proposal was:

Are leakages of abandoned gas wells in the Netherlands a reality or a fiction?

In this research, two sets of sub-questions are answered:

1. Based on literature:

    a) How many abandoned gas wells exist in the Netherlands?

    b) Why does the Netherlands have a high potential for methane leakages from abandoned wells?

2. Based on field monitoring research and literature:

a) Are there any evidences of methane leakage from a selected number of abandoned wells in the Netherlands?

b) Can methane leakages be identified at the surface?

c) Are there any high methane emitters?

d) What is the isotopic composition of the gas emitted near abandoned wells?

e) Does the methane emitted from abandoned wells can be related to the abundance of peat occurring in the Netherlands?

The specific objective of this research is to investigate evidences of high fluxes of methane from abandoned gas wells in the Netherlands. By realizing a series of measurements of methane fluxes and an isotopic analysis for a set of selected wells, the current research will identify:

1) The methane fluxes of a selected number of abandoned gas wells.
2) The evidence of high methane emitter.
3) The source of the emitted methane, i.e. biogenic or thermogenic.

2. Contextualization

2.1 General insights on wells abandonment

The term of well abandonment is technically characterized by the fact that the well has been cut-off, sealed and buried (Boothroyd et al., 2016). The purpose of the abandonment procedure is to prevent pressure build-up from the subsurface. It is necessary to isolate hydrocarbons according to geological constraints such as pressure. Several thousands of meters are drilled and pressure forces are likely to cause damages on the casings. Typically, the abandonment procedure requires the down hole and surface abandon plug. Proper abandonment procedures or measures equalize the pressure along the well so that failures do not appear in the cement casings. The plugging of the well is the most important aspect of the abandonment operation (Nicot, 2009). Two main purposes of the plugging operation are (1) the isolation of fresh water and other natural resources and (2) the prevention of cross contamination. The quality of the abandonment procedure of gas wells depends mainly on the technology used at the time the methods have been applied.

The different types of plugging well methods are important for gas well abandonment. Recurrent issues in the plugging techniques are the cracking or shrinking in the cement casing and the long-term corrosion behavior of abandoned plugs (Yamaguchi et al., 2013). Three main plugging techniques can be distinguished:

- The balanced cement plug method: using the principle of balanced hydrostatic in both extremities of the cement string (Fig. 3), it is the most common plugging method for abandonment. In this method, the hydrostatic pressure in the end of the drilling string is the same as the hydrostatic pressure in the annulus of the cement string. A recurrent problem with this method is the potential cement contamination.
- The dump bailor system consists of a measured amount of cement that is lowered in the wellbore through a wireline (Fig. 3). Mainly used at shallow depth, it can also be used at the desired plug depth although deeper depth requires a larger cement receptor which is limited most of the time.
- The two-plug method is named as two plugs because of the presence of two cement plugs. The main advantages of this method are (1) its high level of accuracy for the required depth of the plug as well as (2) a limited potential for cement contamination. The technique aims at pulling above the cement till the desired plugging depth. Figure 4 explains the different steps of the technique.

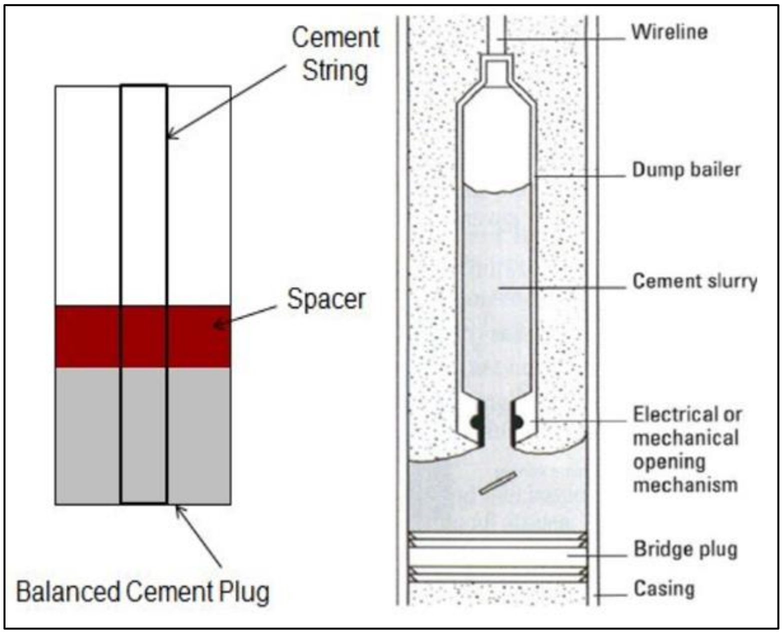

FIGURE 3: SCHEME OF THE BALANCED CEMENT PLUG SYSTEM (LEFT) (DRILLINGFORMULAS, 2017) AND THE DUMP BAILOR SYSTEM (RIGHT) (GLOBALCCSINSTITUTE, 2017)

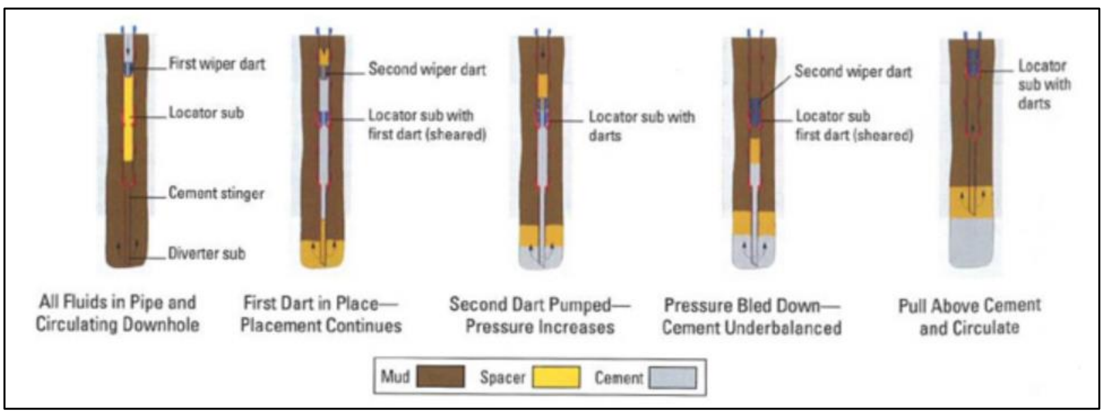

FIGURE 4: SCHEME OF THE TWO-PLUG METHOD FROM NELSON AND GUILLOT (2006) (GLOBALCCSINSTITUTE, 2017)

The maintenance of well bore integrity has been of interest due to the high potential contamination of the soil and aquifers (King et King, 2013; Jackson et al., 2013). The results of the studies led by Davies et al. (2014) demonstrated that 7 possible paths for oil and gas leakages can be identified (Fig. 2). They consist of (1) between the cement and the rock formation, (2) between the casing and the surrounding cement, (3) between the cement plug and the casing or the production tubing, (4) through the cement plug, (5) through the cement between the casing and the rock formation, (6) across the cement outside and of the casing and then between the cement and the casing, (7) along a sheared bore. Although different causes can be attributed to those pathways, they are not relevant in this current research.

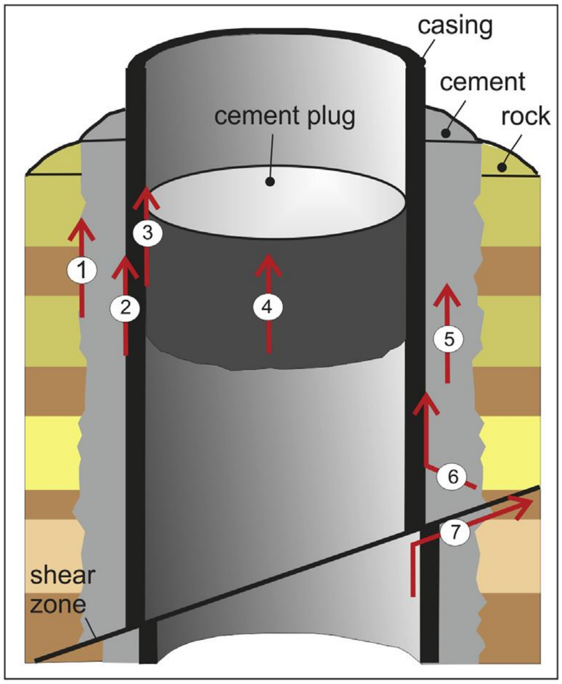

FIGURE 2: THE SEVEN SUBSURFACE ROUTES FOR WELLBORE FAILURES (DAVIES ET AL., 2014)

Causes of well failure can be associated to the aspect of well integrity, which is referring to the zonal isolation of liquids and gases (King and King, 2013). In relation to the well integrity failures, each attribute of a well can be considered as the origin of a leakage.

The loss of both wellbore integrity and effective permeability is a phenomenon highlighted in several reports as well as its influence on the contamination of nearby aquifers (Boothroyd et al.2016, Kang et al. 2015, Cooper, 2009). The main concern of well leakages is the loss of their integrity caused by fatalities due to cement shrinking and cracks of the channels (Dusseault et al., 2000, Jackson, 2014). In the observed literature, the age of the well, the well type, the plugging status and the depth are recurrent attributes influencing the occurrence of methane leakages. All four factors are the most cited in recent research papers. Geological features are also recurrently mentioned as mechanisms causing failures - typically because of reservoir compaction during the production processes (Davies et al., 2014). It turns out that a pressure gradient exists between the inside the wellbore and the outside of the well, thus allowing powerful flow of gas.

2.2 Legislation

The new Mining law (Mijnbouw WW) as effective on January 1st 2003, recognized different licenses for exploration and exploitation of oil and gas reserves both for the onshore and offshore. With this law, additional licenses are required for underground storage, mining and pipelines. The data acquainted during exploration and production are confidential for a period of 5 years (Wong et al., 2007).

Apart from having environmental consequences, the abandonment of oil and gas infrastructures represents a relative important part of the financial investment of the Netherlands government. The current shift for more safe and environmental friendly practices leads to more investment in the decommissioning practices of oil and gas infrastructures as well as geothermal energy production. In addition, energy transition is required when considering the remaining lifetime of the Groningen field expected to last for the next 20 years. Thus, a masterplan for decommissioning and reuse of oil and gas infrastructure has been set and aims at more sustainable management of oil and gas infrastructure in the Netherlands. Ten topics have been identified which are presented in Fig. 5. The main vision for this plan is to provide "safe, efficient and effective Dutch decommissioning market, continually reducing costs and minimizing residual footprint" (EBN, 2016)

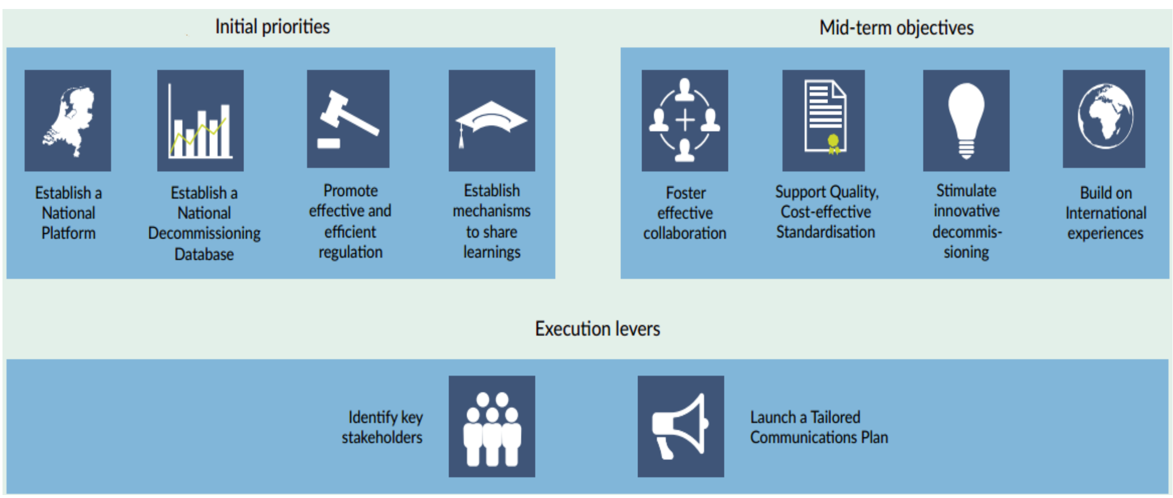

FIGURE 5: DECOMMISSIONED PLAN STRATEGY FROM 2015 (EBN, 2016)

The regulatory requirements concerning well abandonment procedures vary from country to country. Recurrent observed regulations deal with the plugging and the sealing of the well. As mentioned in the above, the plugging of the well remains the main cause of leakages. A study led by Kuip *et al.* (2011) presents an overview of the abandoned well regulations in 11 countries and states across Europe, Asian Pacific and North America. A comparison of the regulation is provided below which treats more specifically the requirements for plug lengths and positions.

The abandonment procedure for oil and gas wells in the Netherlands follows the Mining Legislation and the Working Conditions Regulation. As displayed in Tab. 1, the Dutch regulation prescribes a length of the cement plug varying between 50 and 100 meters while the minimum extension above and below the casing shoe, i.e. the transition zone between uncased and cased section, is respectively 100 and 50 meters. The comparison with the other states shows that the main distinction appears in the minimum plug length requirements between European and non-European countries. A minimum length of the cement in European countries is 100 meters, while in the non-European countries considered, the minimum length is significantly lower, varying between 60 and 15 meters.

TABLE 1: ABANDONED WELL REGULATIONS AND REQUIREMENTS FOR SEVERAL EUROPEAN AND NON-EUROPEAN COUNTRIES (KUIP ET AL., 2011)

			Option	Minimum length [m]	Minimum extension above / below casing shoe [m]		Comment
					above	below	
Denmark			Either	100	50	50	
			Or	50	50	0	+ Mechanical plug within 50 m from deepest casing shoe
Norway			Either	100	50	50	
			Or	50	50	0	+ Mechanical plug inside deepest casing
The Netherlands			Either	100	100	0	
			Or	50	50		+ Mechanical plug
United Kingdom				30	30	0	
Australia							
	Western Australia			60			
Canada	Alberta			15 + *	15	*	* Depends on formation
China				30			If borehole has no gas, oil or water-bearing strata
Japan				30			Minimum of two 30 m plugs required
USA	API			30	15	15	
	Alaska			60	30	30	
	California	Onshore		30	15	15	
		Offshore	Either	**	30	**	** Plugged from total depth
			Or	60	30	30	
	Texas			30	15	15	Only if aquifers are protected

2.3 Thermogenic and biogenic methane

In this section, an explanation of the phenomena and processes in the formation of methane is provided as well as a clarification on the isotopic composition of hydrocarbons in the subsurface.

The Dutch subsurface of the earth can be distinguished into the shallow subsurface (down to 500 m deep) and the deep subsurface (deeper than 500 meters). As a primary constituent of life on Earth, carbon (C) in the subsurface is ubiquitous. From the carbon dioxide of the atmosphere, the carbon element is indirectly restituted to the soil through the methane molecule (CH_4) in the subsurface. The carbon cycle gathers the processes in which the carbon element is distributed in the three major reservoirs that are terrestrial, oceanic and atmospheric (Cole et al., 2007). The formation of hydrocarbons such as gas and oil is the result of multiple biological processes made possible by photosynthesis at the surface and by chemical energy in the subsurface (Trevors, 2002). Although onshore and offshore hydrocarbons can be differentiated in the subsurface, this current research deals only with the hydrocarbon formed in the onshore subsurface.

The understanding of carbon formation is of significant importance in the current research because of its crucial role in the determination of methane sources. The formation of methane is mainly associated to two important mechanisms: while one refers to the chemical reduction (or degradation) of organic matter by micro-organisms, the other refers to the compression and heating of the organic matter. They are named "biogenic" methane and "thermogenic" methane respectively (Hitchman et al., 1989). In the subsurface, most of the carbon is captured in the microstructure of the coal which is later transformed into methane (Wong et al., 2007). In a dynamic environment such as the earth subsurface, the pressure, the temperature and depth affect the capacity of the coal to produce methane (Fig. 6).

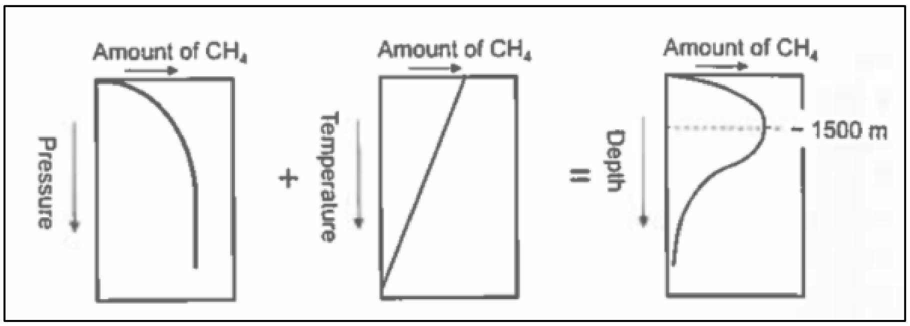

FIGURE 6: METHANE FORMATION AND INFLUENCING FACTORS IN THE SUB-SURFACE (WONG ET AL. 2007)

Deeper analysis suggests that those two distinct types of methane (i.e. biogenic or thermogenic) differ at molecular scale, and more specifically in their isotopic composition. While considering carbon in nature, we can identify carbon as one element being quite tremendously abundant in the environment. This approach contrasts with the consideration of carbon at molecular scale. In the carbon molecule, several types of carbon co-exist called isotopes. Those isotopes are qualified to be either stable or unstable and their proportion into the carbon element are different and associated to the condition of their formation in the subsurface.

In scientific context, carbon and hydrogen are used because of the stability of their isotopes. In chemistry, isotopes are qualified as "stable" when they do not decay over time. The carbon and the hydrogen elements have both two main isotopes, respectively $^{12}C/^{13}C$, $^{1}H/\ ^{2}H$ while the occurrence of ^{12}C and ^{1}H in a molecule of C and H represent 99.9 % of the molecule. In contrast, ^{13}C and ^{2}H are stable isotopes. The variation of C and H isotopes in methane can be expressed using the following ratios $^{13}C/^{12}C$ and $^{2}H/^{1}H$ in permil (‰), and noted respectively $\delta 13C\text{-}CH_4$ and $\delta D\text{-}CH_4$.

$\delta 13C\text{-}CH_4$ and $\delta D\text{-}CH_4$ have their own composition range, which is of interest for the current study. Table 2 presents the typical range of composition of both isotopes in the case of biogenic and thermogenic sources:

TABLE 2:TYPICAL ISOTOPIC RANGE COMPOSITION FOR THERMOGENIC AND BIOGENIC METHANE (WHITICAR ET AL., 1986; KANG ET AL. 2014; STOLPER ET AL. 2015)

	Biogenic (‰)	Thermogenic (‰)
δ13C-CH_4	-110 to -60	-40 to -20
δD-CH_4	-400 to -260	-200 to -150

Even though δ13C-CH_4 is commonly used in the methane source identification as tracer, δD-CH_4 can be additionally useful for CH_4 types as well (Whiticar, 1999). While it is not exclusively the case, thermogenic methane is enriched in δ13C-CH_4 compared to the biogenic one. The isotopic composition of both types of methane is highly correlated to the conditions of formation such as temperature, pH and oxygen concentration (Whiticar, 1999).

In this current study, the isotopic identification will be essentially used to determine the formation pathways in the methane cycle occuring for both thermogenic and biogenic origins. The use of δ13C/δD diagram such as the one dislayed in Fig. 7, allows a more detailed identification of the type of biogenic methane that is considered. Typically, two types of biogenic methane pathways stemming from either the acetate fermentation or the reduction of carbone dioxyde exist. The production of biogenic methane in the acetate fermentation process is closely link to the presence of organic matter in anaerobic condition such as peatlands (Bryant, 1979). In the current research, both thermogenic and biogenic pathways are considered because methane leaking from abandoned gas wells could be either thermogenic or biogenic. Note that the term microbial in Fig. 7 is refered as biogenic.

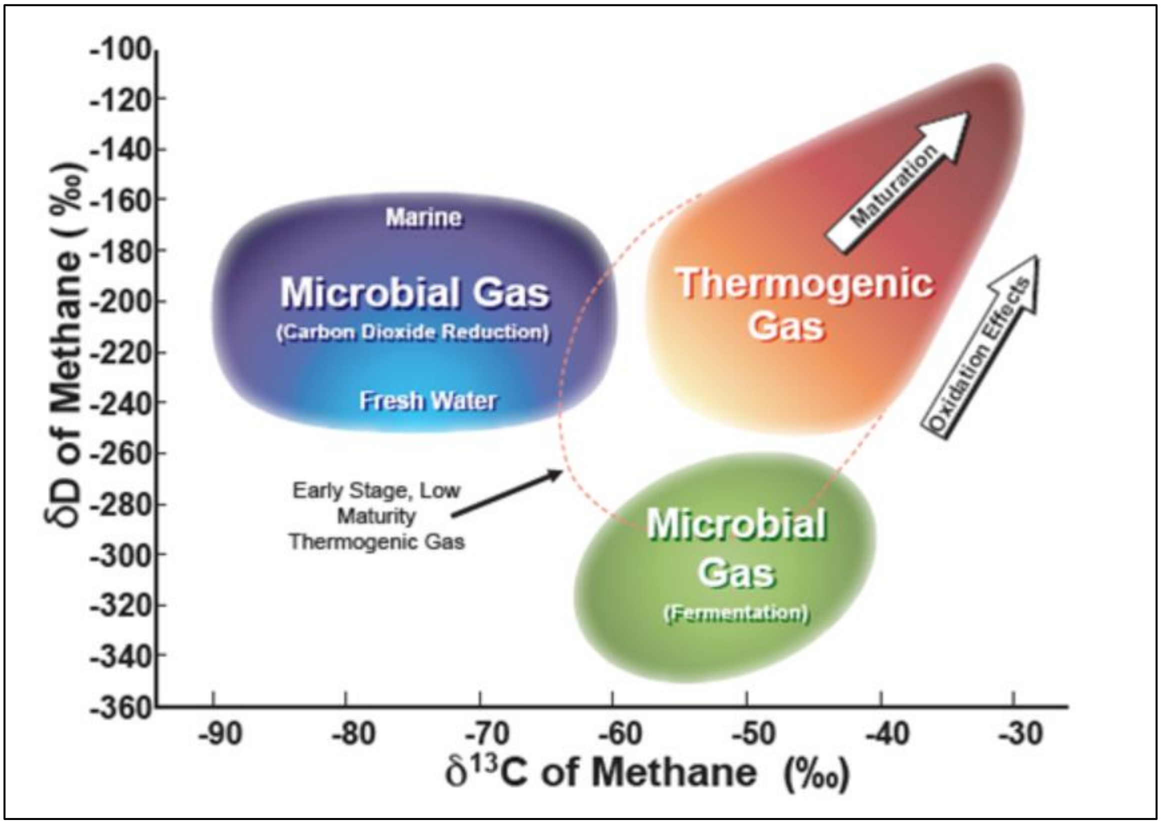

FIGURE 7: δ13C/δD DIAGRAM REPRESENTING THE TYPICAL GROUPINGS OF HYDROGENS IN FUNCTION OF CARBON ISOTOPES (RATONBASINWATERSHED, 2017)

2.4 Study area

Petroleum geology background in the Netherlands

The Netherlands is recognized as a gas country dominated by the well-known Groningen gas field. Located on the Central European Basin System, the Netherlands is more specifically positioned on the northern part of the Variscan deformation front (Nelskamp, 2011). The geological build-up of the Netherlands is characterized by a succession of sedimentary layers originating from three main eras, which are namely from the most recent to the oldest: the Cenozoic, Mesozoic and Paleozoic.

The variety of hydrocarbon fields starts from the middle of the Paleozoic and has been distorted by additional periods of structuration (Wong et al., 2007). The presence of gas plays, which consist of a cluster of gas fields, is dominated by the Rotliegend play formed by a succession of sedimentary layers composed of (1) the thick Upper Carboniferous in the Westphalian succession, (2) the Rotliegend reservoir sandstones, and (3) the seal of Zechstein salt (Wong et al., 2007). Other important gas reservoirs are located in the Triassic play. Figure 8 presents the lithostraphic column across geological time accompanied with the hydrocarbon systems in the Netherlands.

When comparing the oil and gas reserve volumes in the Dutch subsurface, gas remains by far the largest. While the oil system is almost entirely contained in the Mesozoic, the gas system is predominantly included in the Paleozoic hydrocarbon system. Not shown in Fig. 8, the Upper Permian Zechstein salt is an important sedimentary rock of the Dutch subsurface as it provides a seal between the oil and gas systems (Zhang et al., 2013). It is a large salt deposit in the northeastern German Basin and can attain 1 km thickness (Wong et al., 2007). More generally, salt deposits in the Netherlands occur within the Permian and the Triassic. Geologically, the Upper Permian Zechstein played a key role in the formation of hydrocarbons as its presence in the subsurface can influence the maturity of the source rock intervals (Wong et al., 2007).

The Upper Carboniferous with the Westphalian coals and the Carbonaceous shales is the main source for gas production in the Dutch subsurface. The source rock where the gas is contained affects the nitrogen content of the gas as well as the δ13C-CH_4 composition (see section 2.3). The nitrogen content is a gas quality criteria used by gas industries. The level of nitrogen content differs from one source rock to another and can vary from zero to several percent. Those variations in nitrogen content can be the result of the differences of the heat-flow and burial histories of the hydrocarbons (Wong et al., 2007).

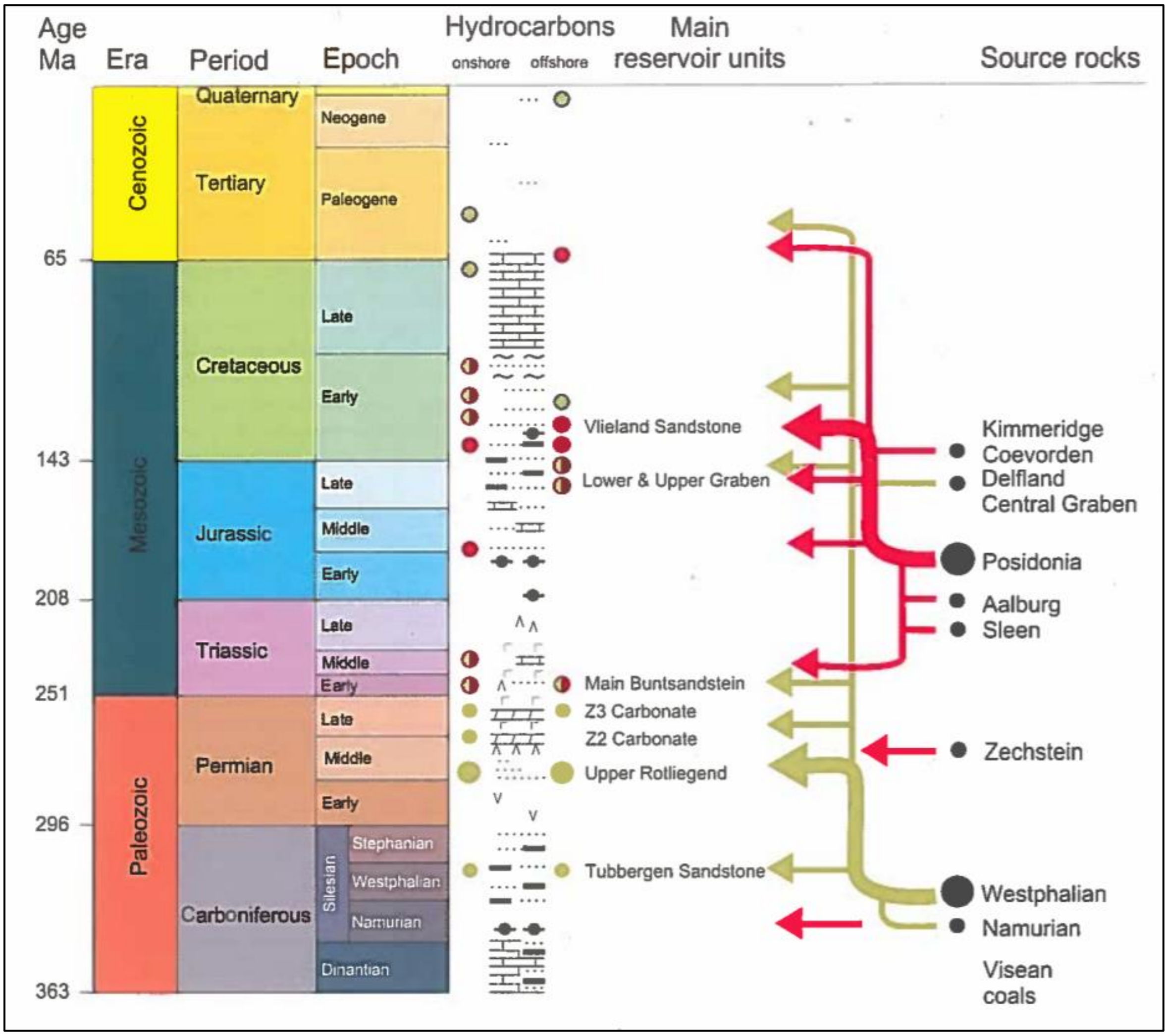

Figure 8: Geological time and hydrocarbon origins in the Netherlands (Wong et al., 2007)

The Dutch subsurface is extensively covered by a layer of peat, as being one of the main characteristics of the country (Fig. 9). For a long time, peat was used as a fuel where it was rapidly replaced by coal in the beginning of the 19st century. Peat was also used to manufacture the bedding for horses and cattle and is nowadays used for the production of peat garden and potting soil (Gerding et al., 2015). Peat can be defined as the accumulated organic matter resulting from a slow degradation process of the vegetation and characterized as a favorable condition for methane production. Due to a higher level of groundwater in peatlands, the oxygen is penetrating less deep than in other mineral soils. In those areas, methane generation is favored near the surface as a result of the absence of reducible oxides and little or no reducible sulphate. The Dutch situation enhances methane oxidation processes as a result of the important number of regions where the groundwater is anthropogenically lowered by water management measures and where the oxic zone in the unsaturated zone, i.e. above groundwater level, is enhanced. Therefore, soil drying effects imposed during drier periods render peatlands and wetlands an important natural source of methane emission (Hendriks et al., 2009).

The Dutch peat growth starts during the stratigraphic interval of the Holocene as a result of the rise of the groundwater during this epoch (Zagwijn, 1986). The Holocene is recognized as being the most recent geological unit starting 11.7 ka ago till now. Typically, the start of the Holocene epoch is characterized by the end of the last glacial period, namely the “Recent” or “Post-glacial” (Walker, 2012). In the Netherlands, the Holocene deposits are mainly present in the coastal barrier and the coastal plain. The coastal barrier is bounded in the southwest by the Scheldt and in the North by the tidal inlets of the Wadden Sea. The coastal plain is defined as the area covering half of the country and consist mainly of clay and peat (Rondeel et al., 2002).

Low and high peat can be distinguished in the Netherlands and mostly refer respectively to the lowlands (e.g. northern Groningen, Friesland, Noord-Holland, Zuid-Holland) and higher areas (e.g. Drenthe, eastern Groningen, Noord-Brabant) of the country. Note that most of the peat present nowadays in the country would be flooded in the absence of dikes, highlighting the influence of man on the geographical settings of the country (Dinoloket, 2017).

The most extensive regional existence of Holocene peat is the geologically classified Nieuwkoop Formation (Fig. 9). Within the Nieuwkoop Formation, several units are observed, which are namely the Griendtsveen, the Hollandveen, the Basic and the Flevomeer. The thickness of the Nieuwkoop formation is generally estimated to be less than 0.5 meter to 4 meters thick with a possible range varying between 0.1 meter to 8 meters in some regions. The lower limit of the Formation is characterized by a very fine to moderate coarse sand, i.e. 105 to 300 μm (being part of the Boxtel Formation), which renders the boundary clear and sharp. The upper limit is regularly delimited at the ground level - justifying the interest for the current study – or as a relatively thin coverage of fluvial or marine deposits of the Holocene. (Dinolocket, 2017)

As mentioned earlier, the organic matter is mainly oxidized by bacteria leading to biogenic methane emissions in organic media such as peat soils. Scientific observations have also provided the evidence that other factors such as soil temperature, porosity, pH, soil conductivity may contribute actively to the molecular composition of the emitted methane from peatlands (Hendricks, 2010). Having an important influence on the rate of the emission, molecular diffusion and soil respiration are two important contributing processes where their study is out of scope of the current subject. An important proportion of the Dutch gas wells might penetrate shallow peat layers when considering the geographical settings of the gas field regions and that of the Nieuwkoop Formation region (Overlay Fig. 1 and 9).

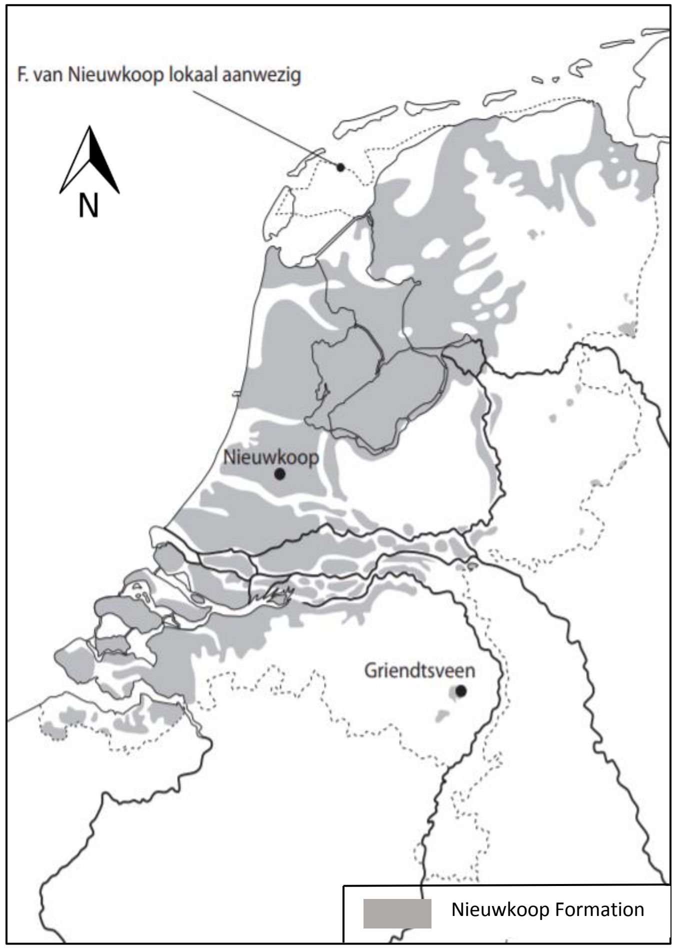

FIGURE 9: EXTEND OF THE NIEUWKOOP FORMATION (DINOLOCKET, 2017)

3. Methodology

3.1 Data collection

A high sensitive methane leak detector portable using laser spectroscopy was used to detect methane concentration (Fig. 10). The detector allows the detection of low methane concentrations below 1 ppm. The device is used for both screening of the sites and the flux measurements with the static chamber method as explained below.

FIGURE 10: METHANE DETECTOR USED DURING THE EXPERIMENT (STIEBER, 2017)

3.1. Sites selection and description

In order to obtain a series of matching wells for our study, a few steps were needed to be taken before performing the actual measurements. The database provided by NLOG were used to select the final wells considered. While NLOG provides the data for 6426 wells in total including 4333 onshore and 2093 offshore in the Netherlands, only 36 boreholes were selected. The following step-by-step procedure describes how the selection of 36 wells was undertaken from the 6422 wells offered by the NLOG database.

Step 1: only the abandoned gas wells were selected.

Step 2: among the different types of intended wells function, not only the wells for gas production were selected, but also the wells for gas exploration as they may also have a potential for leakages.

Step 3: we found that different types well shapes exist. In order to find any influences related to the shapes of the wells, vertical and deviated wells were selected.

Step 4: a visual inspection on satellites imagery from Google earth was undertaken. This step aimed at verifying the feasibility of the access and the feasibility of the use of the static chamber. Therefore, the wells located in green areas such as prairies, grasslands and clear forests were targeted.

3.3 Screening of the site

A 1 meter diameter wooden spool is placed at the X-Y coordinates of the well. Attached to a 15-20 meters rope, the experimenter turns around the wooden spool until he will reach the end of the rope. At every round, the distance to the wooden spool is diminished by 1 meter (See Fig. 11). An average of 154 concentration measurements was recorded per well in an area of approximately 800 square meters except for 5 wells for which only half of the area was screened because of the presence of multiple ditches, lakes and other obstacles on sites.

FIGURE 11: PHOTOGRAPHY OF THE PRACTICER MEASURING METHANE CONCENTRATION IN A 16 METERS RADIUS CIRCLE, THE WOODEN SPOOL BEING LOCATED AT THE EXACT X-Y COORDINATES OF THE WELL (PHOTO TAKEN IN JULY 2017)

Connected to a GPS marker, the path of the practicer was directly recorded. One screening lasted approximately 45 to 60 minutes to complete the entire circle. In case of higher methane concentration records, the exact location was marked and later measured with the static chamber method and the flux was determined later on. A supplementary static chamber measurement was performed as a control at the first screening measurement location, i.e. 16 meters away from the known coordinates of the well.

3.4 Static chamber measurements and fluxes calculations

A gas capture system in a Perspex glass cylinder as shown in Fig. 12 was used to measure the methane flux.

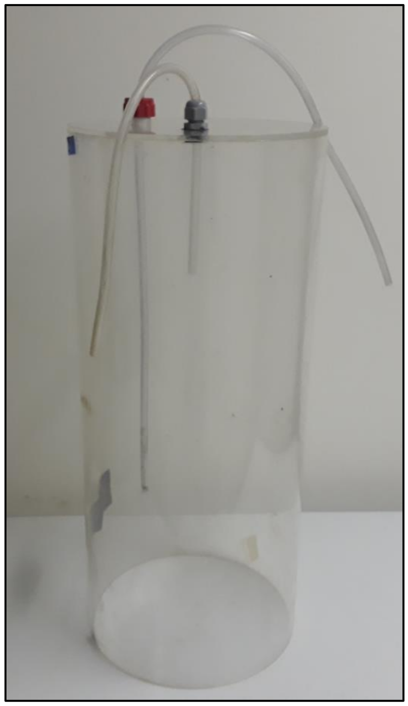

FIGURE 12: THE STATIC CHAMBER USED FOR THE EXPERIMENT

Two or more methane flux measurements with the static chamber method were performed per site:

- At the original well location where there are potential fluxes. They are presented in the appendixes as WELLNAME_1. Note that the indices "H" stands for the measurement performed at one meter depth.
- At the control locations, i.e. 16 meters offset from the coordinates of the abandoned well, which was the first methane measurement performed during the screening procedure.
- At the high emission locations during the screening. When a high methane emission was observed during the screening of the site, a marker was placed. Later, the static chamber method was employed at the exact location of the marker. The coordinates of those specific locations were recorded and reported together with the concentration time series on the fieldwork template (See Appendix 1).

Once connected to the methane detector, a first set of methane concentration over time was recorded between 5 and 10 minutes in order to determine the flux. A second set of measurements was recorded after drilling a 1 meter hole of approximately 10 centimeters diameter in order to identify the potential influence of methane oxidation in the soil. Similarly, a 5 to 10 minutes record was needed to perform this second set of measurements. Finally, the coordinates of each flux measurement locations with the static chamber were recorded in order to have the exact location of the measurements.

From the methane concentrations captured in the chamber, the methane fluxes were obtained using the ideal gas law formula, i.e.:

$$PV = nRT$$

where P is the atmospheric pressure of the location, V represents the volume of air in the static chamber, n is the number of mole in the volume of air considered (i.e. the chamber), R and T are respectively the gas constant and the temperature of the site during the measurements.

The flux of methane is calculated once in the chamber and then converted in flux in the atmosphere through a linear regression. Then, the correlation coefficient is determined between the change of mass of methane in the chamber and the time.

A two steps approach to obtain the fluxes was used as followed:

- $M = c * V$

where M is the mass of methane in the static chamber, c is the concentration in the chamber and V is the volume of the static chamber.

- $\frac{dM}{dt} = F$

where M is the mass of methane in the static chamber, t is the time and F is the flux.

The determination of the correlation coefficient allowed the determination of the linear interdependency between the two variables. If the coefficient was 1 or close to 1, there was a strong positive correlation between the two variables. In that case, when one variable moved positively, the other one also moved positively. If the correlation was comprised between -0.1 and 0.1, the two variables were not correlated and none relationship exist. If the coefficient was -1 or closed to -1, the variables moved in the opposite direction and were therefore correlated negatively.

3.5 Sampling and isotopic detection

At each well and control locations at one meter depth, a gas sample was collected in the Tedlar bags with the vacuum box system shown on Fig. 13. The lung sampler system allowed air collection avoiding possible air contamination in the sample.

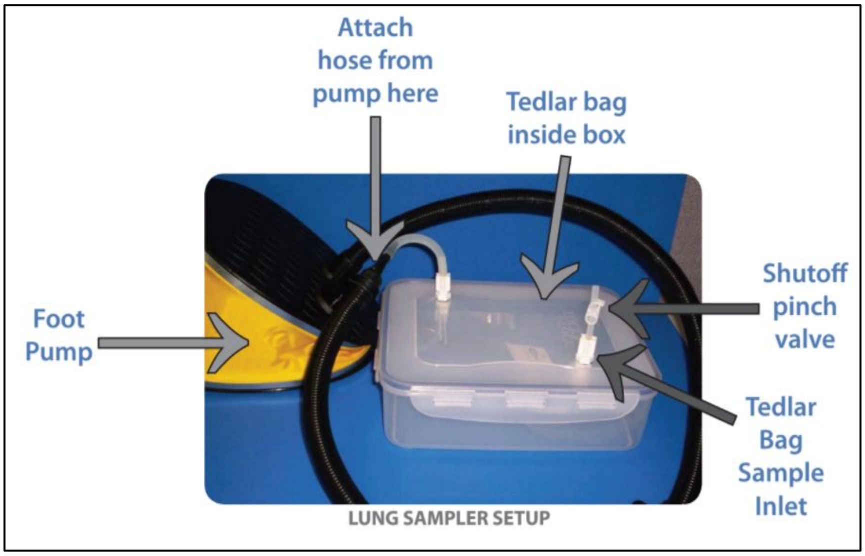

FIGURE 13: GAS SAMPLING SYSTEM USED DURING THE EXPERIMENTATION (CASLAB, 2017)

The analysis of the two methane isotopes values, i.e. δ13C-CH_4 and δD-CH_4, was identified at the IMAU laboratory at Utrecht University. The amount of sampled gas was adjusted to yield the same amount of CH_4 for each measurement. An atmospheric air sample was analyzed as a control for the isotopic detection.

4. Results

4.1 Campaign in the Netherlands

From June 26nd to July 27th 2017, the methane measurements campaign for abandoned gas wells was performed. Out of 39 wells targeted for the measurements:

- 24 wells were studied with the full measurement (i.e. screening measurements, flux measurements with the static chamber method and isotopic identification). See Appendixes 2 to 25 for each site were the screening was performed.
- 5 wells were investigated for which the screening measurements could not be carried out because of the on-site restrictions mainly caused by the land-use of restricted areas. However, the flux measurements with the static chamber method and isotopic identification were performed for those wells.
- 10 were planned for investigations but could not be carried out as a result of restrictions of the sites accessibility.

Remark 1: Only 36 wells was targeted after a step-by-step selection described earlier. During the field work, some wells were found very close to the planned ones. This was the case especially in the province of Friesland, were an important density of wells occurs.

Remark 2: In Fig. 14, only 23 investigated wells with the full measurements (in red dots) are visible because AKM-07 is hidden by AKM-10. Refer to the Appendix 3 for the details of the location of the two wells.

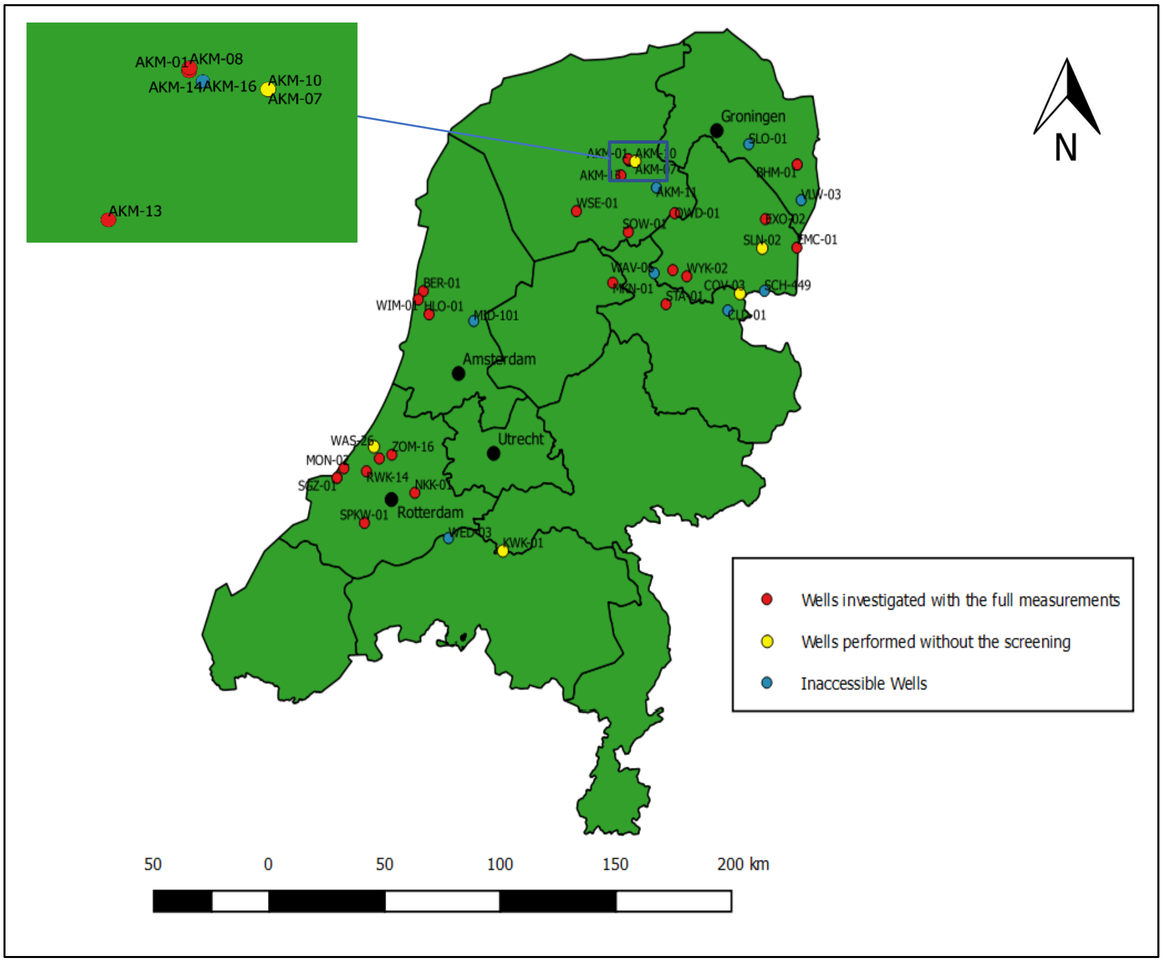

FIGURE 14: MAP OF THE ABANDONED GAS WELL SITES INVESTIGATED IN JULY 2017

4.2 Sites screening

4.2.1 The 16 meters radius circle

In the following Table 3, is calculated:

- The number of measurements per square meters in a 16 meters radius circle
- The number of covered square meters per measurement
- The mean and the standard deviation of the above two parameters

TABLE 3: OBSERVATION OF THE SCREENING MEASUREMENTS

Well	Date of measurements	Number of measurements during screening	Number of measurements per square meter assuming 803 m^2 circle	Number of covered square meters per measurement
AKM-01	25/07/2017	145	0.181	5.52
AKM-07	19/07/2017	186	0.233	4.30
AKM-08	25/07/2017	141	0.176	5.67
AKM-13	25/07/2017	148	0.185	5.41
BER-01*	11/07/2017	125	0.313	3.20
BHM-01*	26/07/2017	117	0.293	3.42
EMC-01	26/07/2017	141	0.176	5.67
EXO-02	29/06/2017	228	0.285	3.51
HLO-01	15/07/2017	157	0.196	5.10
LED-02*	5/07/2017	140	0.350	2.86
MKN-01	27/07/2017	167	0.209	4.79
MON-02	3/07/2017	174	0.218	4.60
NKK-01	10/07/2017	162	0.203	4.94
OWD-01	19/07/2017	147	0.184	5.44
RWK-14	27/07/2017	135	0.169	5.93
SGZ-01	3/07/2017	199	0.249	4.02
SOW-01	21/07/2017	125	0.156	6.40
SPKW-01	6/07/2017	141	0.176	5.67
STA-01*	17/07/2017	150	0.375	2.67
WIM-01	11/07/2017	140	0.175	5.71
WSE-01	22/07/2017	142	0.178	5.63
WYK-30*	18/07/2017	102	0.255	3.92
WYK-02	18/07/2017	192	0.240	4.17
ZOM-16	4/07/2017	200	0.250	4.00
		Mean	0.226	4.69
		Standard Deviation	0.06	1.06

*Wells for which half of the area was screened because of the presence of ditch and barriers.

The mean and the standard deviation of the measurements per square meters are 0.226 and 0.06, respectively. Considering those figures, we found a good homogeneity in the monitoring set-up especially when observing the standard deviation. The area of the circle has been calculated accordingly with the exact distance of the rope between the wooden spool and the first screening measurements. Note that for 5 wells, namely LED-02, BER-01A, STA-01, WYK-30 and BHM-01, the 16 meters radius circle has not been entirely screened because of the sites restrictions (i.e. ditches, ponds, vegetation). For those wells, references can be provided. In the calculation involved in Table 3, half of the area of the circle has been considered for those five wells.

In parallel, we calculated the mean and standard deviation for the number of covered square meters per measurement: 4.69 and 1.06 m^2 respectively. Considering the given mean, there was a relative good probability to find any subsidiary evidences of leakages within the area of the circle. The standard deviation shows a good uniformity in the measurements. It is worth to mention that there is an even better probability to find evidences of leakages nearby the well, as the density of the measurements was increased when approaching the well, as seen in Fig. 15 and 16.

Out of the 24 wells screened, the methane concentrations recorded was in the range of the atmospheric methane concentration, reasonably estimated at 1.8 ppm. Out of the 24 wells, two of them showed methane emissions higher than 2.5 ppm, namely AKM-08 and NKK-01 (See Appendixes 4 and 14).

One might expect that the methane concentration is higher when approaching the well in case of leakages. The results of the screening have not shown higher concentration at the vicinity of the well except for only two of the them, namely HLO-01 and SOW-01 (Fig. 15 and 16). Therefore, higher fluxes are expected for those wells. When considering the latter results, the screening method did not provide evidences of higher fluxes for those two wells.

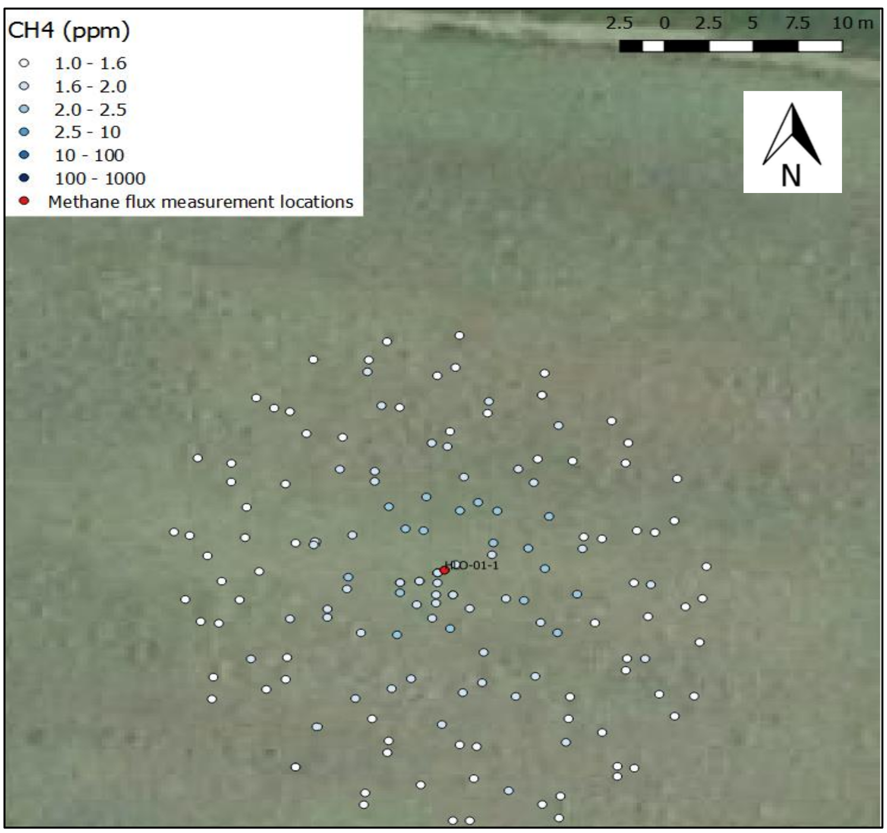

FIGURE 15: SCREENING OF THE HLO -01, LOCATED IN HEILO

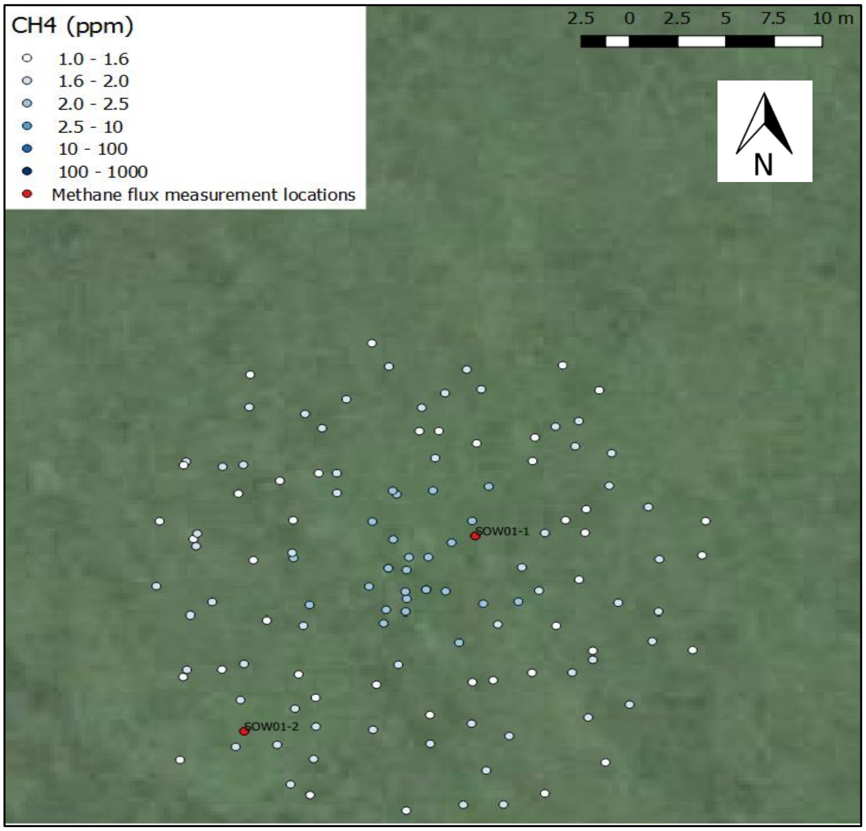

FIGURE 16: SCREENING OF SOW-01, LOCATED IN WESTSTELLINGWERF

4.2.2 High intermittent methane concentrations

High methane concentrations were measured at a limited amount of specific locations in the area of the circle, generally for a short period of time close to 3 seconds. An example of a screening measurement where high concentrations were measured was NKK-01 (Fig. 17). Potential high fluxes have been identified at NKK01-3 and NKK01-4 marked in red dots. The observations showed that when it is the case, the value of methane concentrations then slowly go back to the normal, i.e. the atmospheric value. Wherever such an observation was made, a static chamber method was systematically performed at the exact location of the observation. However, the measurement with the static chamber at those specific places have shown no particular high methane fluxes. Those intermittent methane leakages can be reasonably assumed to be the result of local intermittent microbial activities occurring at the very shallow depth of ground surface, but not related to the presence of wells.

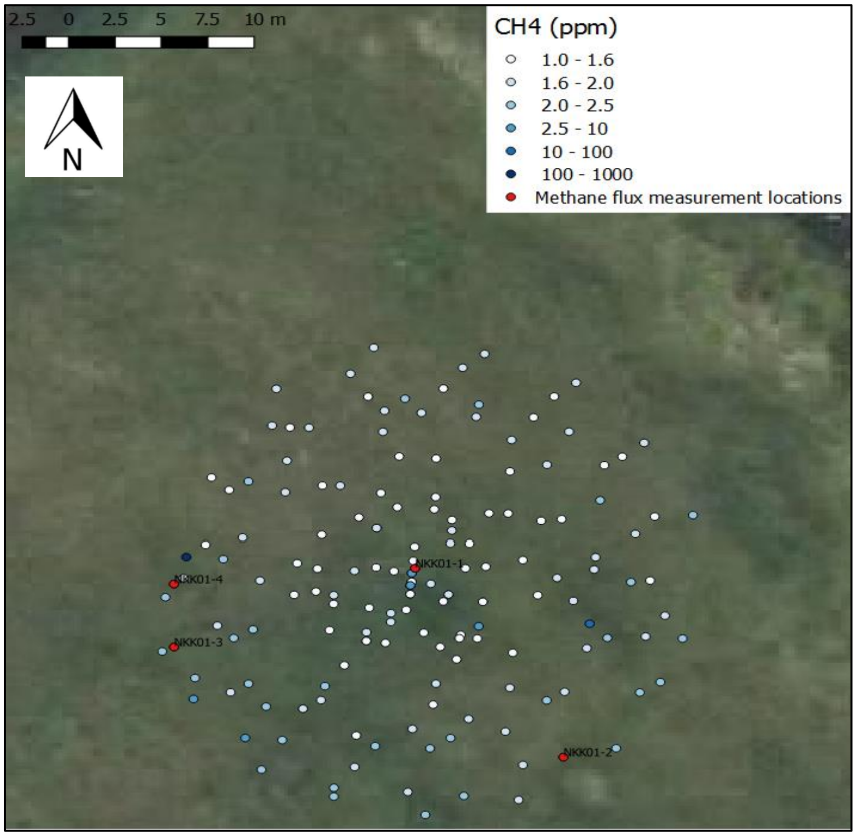

FIGURE 17: SCREENING OF NKK-01, LOCATED IN NIEUWERKERK AAN DEN IJSSEL

The homogeneity of the low values of methane concentration reflects the fact that the screening method used do not allow to draw reliable conclusions on the occurrence of leakages from the wells. While the Table 3 have shown that the 16 meters radius circle used was reliable, however it will turn out to be inefficient for the detection of leakages.

4.3 Methane flux measurements with the static chamber method

In a first subsection, an overview of the range of the R^2 and the methane fluxes is first presented in function of the two conditions of measurements (either at the surface or at one meter depth). In a second subsection, the results of the R^2 and fluxes performed at ground surface and at one meter depth are compared and analyzed. In the last subsection, the methane fluxes are evaluated in function of the two isotopes mentioned earlier (see section 2.3), i.e. δ13C and δD.

The important finding of this section is the occurrence of 4 wells that are emitting more than 100 mg/(hr.m^2) of methane, that will be qualified as “high emitter” in the rest of this report. Those are namely MON-02, NKK-01, BER-01A and AKM-08. However, MON-02 showed to be an isolated case because of the significant higher flux observed at this well.

4.3.1 Distribution of the fluxes and R^2 at one meter depth and at ground surface

Out of 123 methane flux measurements, 61 were measured at 1 meter depth and 62 were measured at ground surface. The distributions of the methane emission and the correlation coefficient of the time-series are both compared in the case where the measurements were performed at one meter depth and at the surface (See Fig. 18). The observations of the fluxes show that six measurements have a flux above 100 mg/(hr/m^2), that are MON02-1H, NKK01-2, NKK01-2H, NKK01-4H, AKM08-2H and BER01A-2H, involving the wells MON-02, NKK-01, AKM-08 and BER01A. A striking observation is that one out of the six measurements is performed at ground surface (NKK01-2). Note that in order to obtain readable values on the box plots in Fig. 18a and 18b, the outliers MON02-1H and NKK01-2 in are discarded.

45 measurements out of the 61 carried out at 1 meter depth are positive (73%) while 25 are positive (40%) out of 62 measurements at ground surface. Comparison between Figs 18c and 18d illustrates that the R^2 are in overall higher for the measurements performed at 1 m depth than those performed at ground surface. The average R^2 for one meter depth and ground surface measurements are 0.6 and 0.3, respectively. Confirmed on the illustration in Fig. 18a and 18b, we can see that the methane fluxes measured at one meter depth are generally much larger than those measured at the surface. In general, we observe that the higher is the fluxes, the higher is the R^2. The next section will confirm this trend at one meter depth.

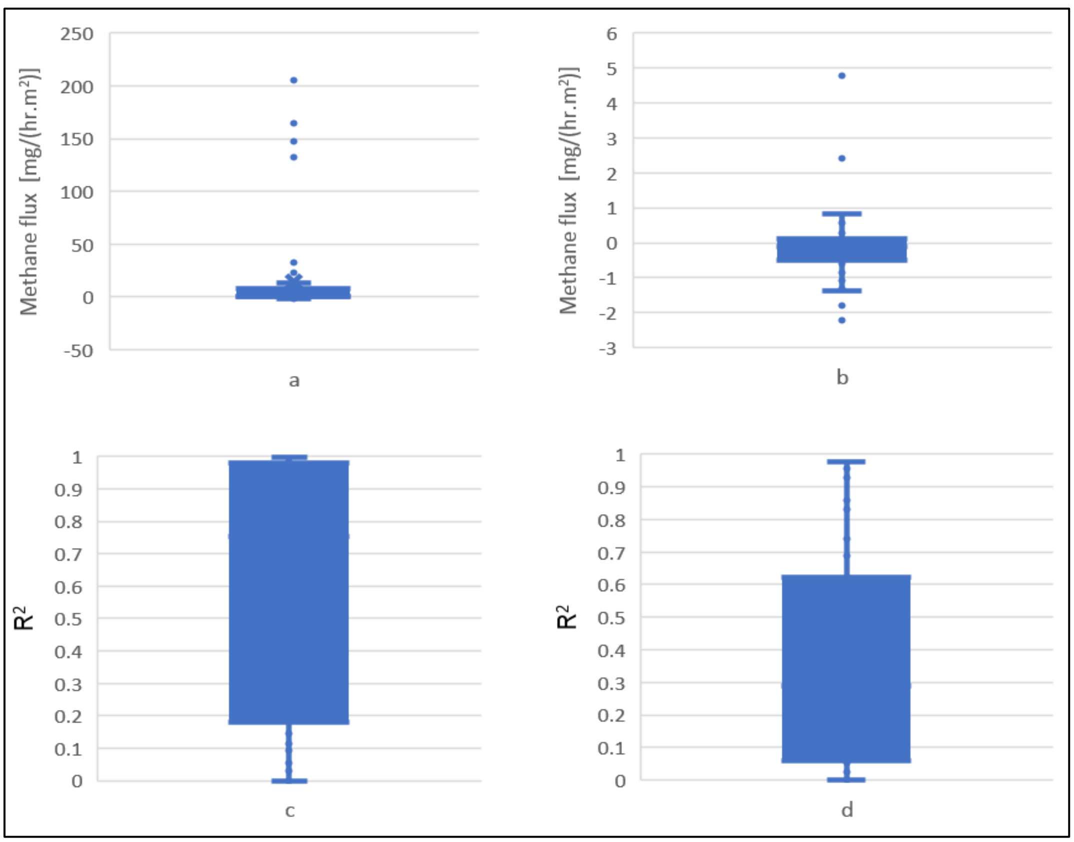

FIGURE 18: METHANE FLUX DISTRIBUTION AT ONE METER DEPTH IN a AND C (61 MEASUREMENTS); CORRELATION COEFFICIENT AT GROUND THE SURFACE IN B AND D (62 MEASUREMENTS)

4.3.2 Variation of the methane fluxes in function of the R2 at one meter depth and at ground surface

In this research, the methane fluxes variations over the time with a R^2 greater or equal to 0.8 are considered as reliable flux measurements. At 1 meter depth, 28 out of the 61 measurements show a R^2 equal or greater than 0.8, or 46%. At the ground surface, 8 out of the 62 measurements have a R^2 equal or greater than 0.8, or 12% (Fig. 19). Clearly, there is higher fluxes when the measurements are performed at one meter depth. Figure 19 shows the variation of the flux and the related correlation coefficient for two different sets of measurements: the left plot displays the variation for the 28 measurements performed at 1 meter depth with a R^2 equal or greater than 0.8. The right plot displays the situation for the 8 measurements performed at ground surface with a R^2 equal or greater than 0.8. A significant difference in the order of magnitude between the two plots is observed. When considering the R^2 as a criteria of reliability for good flux estimates, the observation of the difference shows that the measurements performed at one meter depth are more reliable than at the surface.

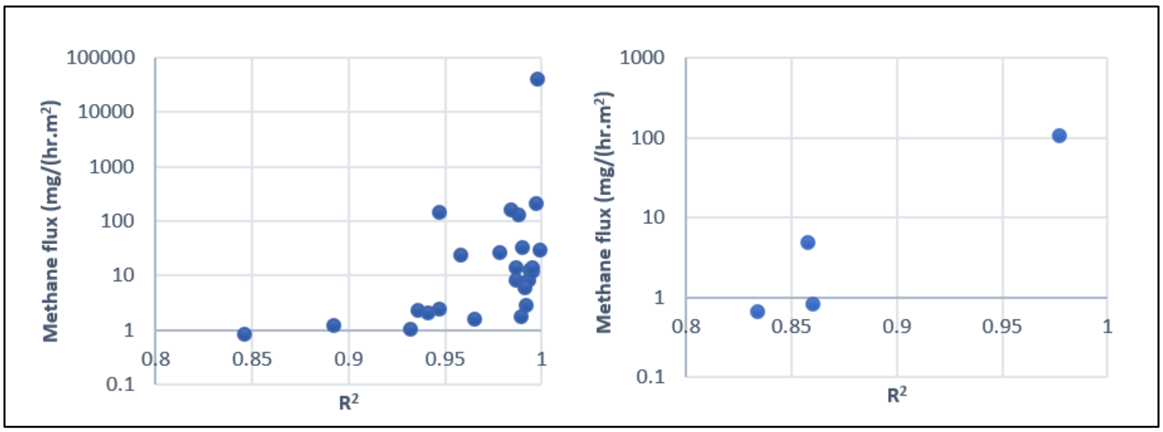

FIGURE 19: COMPARED METHANE FLUXES VARIATION IN FUNCTION OF R^2 AT ONE METER DEPTH (LEFT) AND AT THE SURFACE (RIGHT)

Three examples of methane flux measurements with the static flux chamber method are displayed in Fig. 20, 21 and 22. The first example is the case of a methane flux measurement with a high correlation coefficient (WSE01-2H). The second example illustrates a measurement with high methane flux emission and also high correlation coefficient (MON02-1H). The third example is the case where the flux is nearly zero (EMC01-1). For this example of measurement, the correlation coefficient also showed to be zero, leading to the conclusion that a low correlation coefficient is generally reflecting the absence of fluxes.

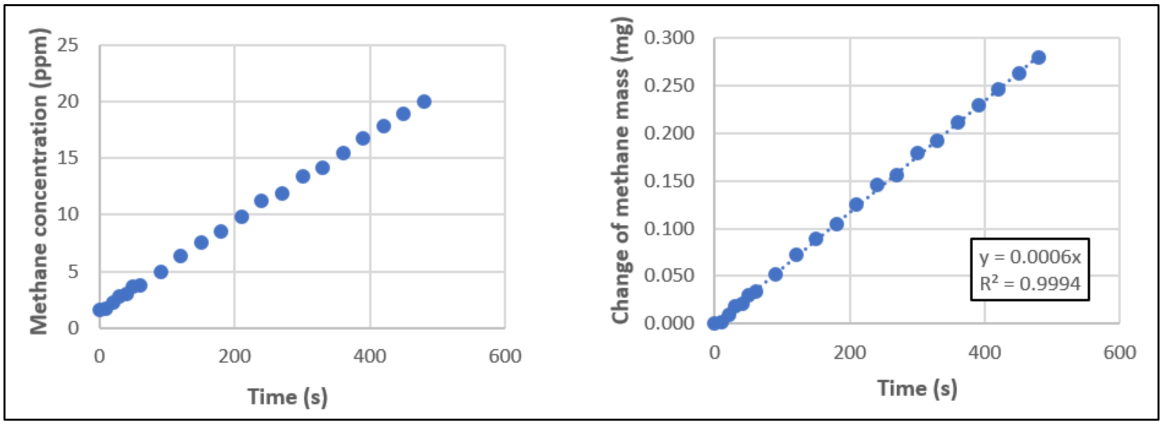

FIGURE 20: VARIATION OF METHANE CONCENTRATION (LEFT) AND THE MASS OF METHANE (RIGHT) IN THE CHAMBER IN FUNCTION OF TIME FOR THE MEASUREMENT WSE01-2H

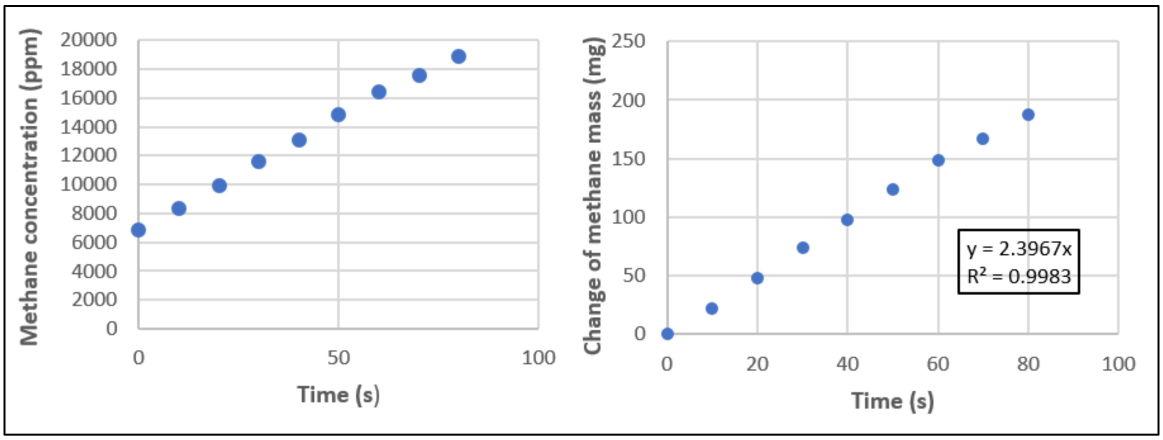

FIGURE 21: VARIATION OF METHANE CONCENTRATION (LEFT) AND THE MASS OF METHANE (RIGHT) IN THE CHAMBER IN FUNCTION OF TIME FOR THE MEASUREMENT MON02-1H

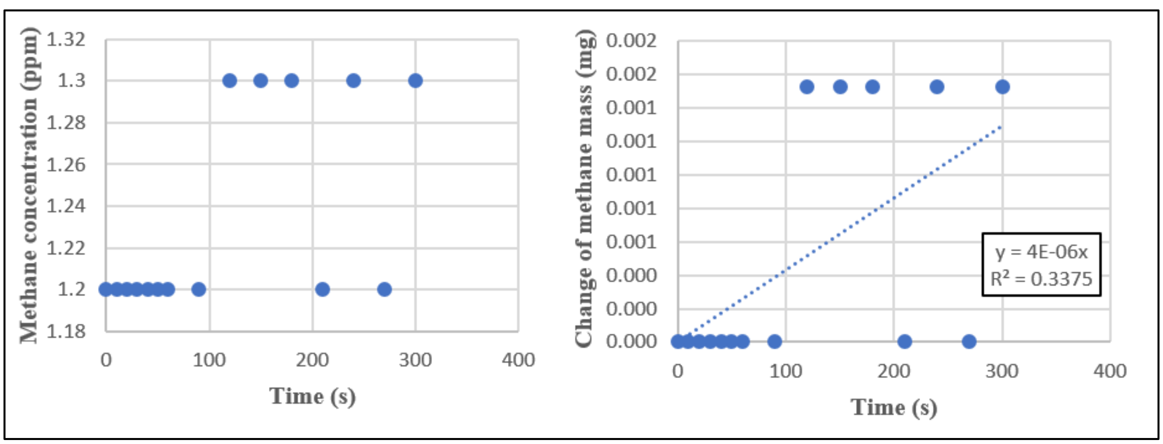

FIGURE 22: VARIATION OF METHANE CONCENTRATION (LEFT) AND THE MASS OF METHANE (RIGHT) IN THE CHAMBER IN FUNCTION OF TIME FOR THE MEASUREMENT EMCO1-1

4.3.3 Fluxes at the wells and at the controls

In this section, we determine whether the fluxes observed at the exact well coordinates is subjected to higher fluxes performed at the control locations. After selecting the measurements performed at the wells and at the controls including those performed at the surface and those performed at one meter depth, we obtained 19 pairs “control-well” of fluxes that can be plotted on a logarithmic scale. As observed in Fig. 23, the plot presents the logarithmic values of the measurements performed at the well locations on the y-axis and at the control measurements on the x-axis. A trendline in dark is plotted as a reference (1:1 line) to show the case where the fluxes at the well location are equal to the fluxes at the control locations. The plot shows more dots located below the reference line than above, 13 and 5 respectively. Note that MON-02 is not counted because the flux measured at the control (M0N02-2H) is negative. We notice that the size of the fluxes are higher at the controls than at the well location, surprisingly. This shows a relative low chance of methane leakages from the well except for MON-02.

Note 1: The measurements performed at Monster have shown significant higher fluxes when approaching the well. The fluxes at the control and at the well location were 40,026. 64 and -1.455 mg/hr/m^2 respectively. When considering the striking value for MON02-1H, it is remarkable that no flux differences were noticed at the well location and at the control during the screening of MON-02 (see Appendix 13).

Note 2: The comparison of fluxes at the controls and the well locations for the fluxes higher than 100 mg/hr/m^2 has shown that BER01A had flux at the well 83 times higher than the flux at the control, located at one meter depth. The other high emitters detected, i.e. NKK01 and AKM08, shows higher values at the controls.

Note 3: In section 4.2.1, the screening of the circle has shown higher concentration when approaching the wells for HLO-01 and SOW-01. The fluxes with the static chamber method have shown a positive flux for the measurement HLO01-1H where 11.645 mg/hr/m^2 of methane was emitted. In contrast, all the flux measurements performed at SWO-01 have shown negative values.

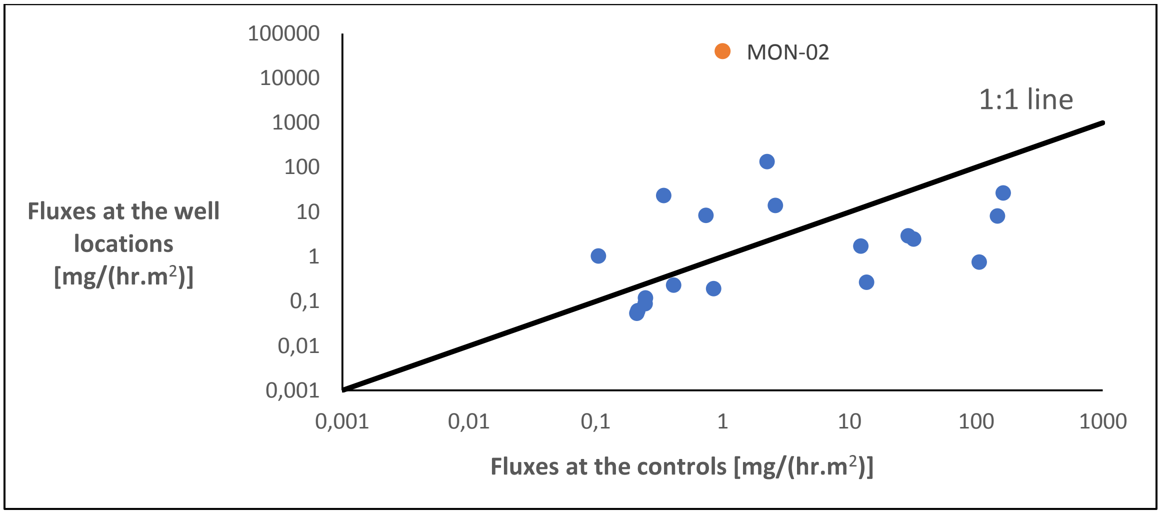

FIGURE 23: COMPARISON OF THE FLUXES AT THE EXACT WELL LOCATIONS IN FUNCTION OF THE FLUXES AT THE CONTROLS FOR 20 DIFFERENT SCREENED WELLS INCLUDING MON-02

4.3.4 Variation of the flux in function of the isotopes

In the following, the flux is compared with the δ13C-CH_4 and the δD-CH_4 analyses (Fig. 24 and Fig. 25, respectively). The value of the atmospheric sample is also displayed on the charts as a comparative value. In order to confirm the accuracy of the atmospheric sample, a comparison with a relevant study led by Rice *et al*., 2015 was performed. Our experimental sample showed a value for δ13C and δD of -48.53 ‰ and -91.2 ‰ respectively. It confirmed the consistency of our experimental sampling for the atmospheric value since the value found by the authors were -47.4 +/- 0.1 ‰ and -94+/-2 ‰ for δ13C and δD respectively. Note that in the following, δ13C-CH_4 and δD-CH_4 are expressed in ‰ relative to the standards Vienna Pee Dee Belemnite (VPDB) and Vienna Standard Mean Ocean Water (VSMOW) respectively.

The values of δ13C-CH_4 are varying between -46.86 and -78.54 ‰ (VPDB) with a flux ranging from 0.053 to 164.58 mg/hr/m^2 (Fig. 24). Only one measurement (MON02-1H) shows a higher value of δ13C-CH_4 combined with a significantly higher flux, -26.64 ‰ (VPDB) and 40026, 64 mg/hr/m^2 respectively. Methane is enriched in δ13C-CH_4 for low fluxes closed to the atmospheric value. Measurements for which high fluxes (above 100 mg/hr.m^2) were detected are displayed on Fig. 24. The measurement for HLO01-1H is also displayed as a result of the higher concentration at the well location observed during the screening measurements. The measurement for the well SOW-01 is not plotted as it showed negative fluxes.

From these observations, little or no chance of leakages are confirmed for the wells AKM-08, BER01-A, NKK-01, HLO-01 and SOW-01. However, the striking value of the fluxes for MON-02 is confirmed by a high δ13C-CH_4 value comprised in the thermogenic range (Refer to Table 2).

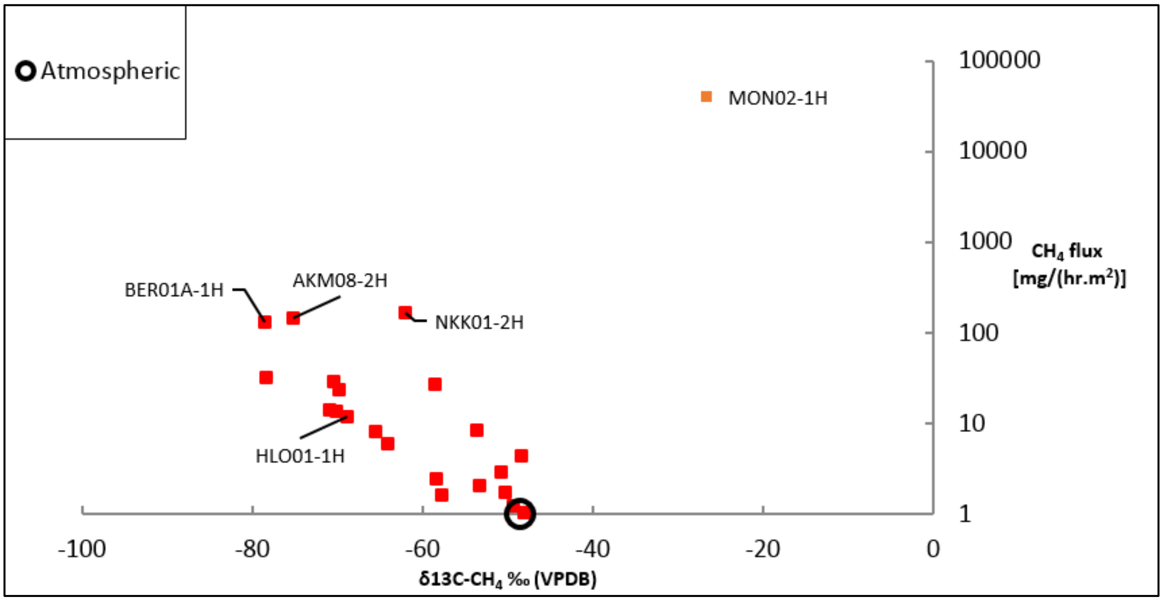

FIGURE 24: VARIATION OF METHANE FLUX IN FUNCTION OF δ13C-CH4

A similar pattern to the Fig. 24 can be observed on Fig. 25: we observe higher fluxes for lower δD-CH_4. However, two major groups can be clearly distinguished. Similar to the δ13C-CH_4 ‰ (VPDB) variation plot (Fig. 24), an outlier can be clearly observed at -149.7 ‰ (VSMOW) that refers to the MON02-1H measurement. A group of samples is observed in blue dots and ranges from -228.5 to -299.8 ‰ (VSMOW) for δD-CH_4 with higher fluxes. Another group in green dots ranges between -117.6 and -157.1 ‰ (VSMOW) for δD-CH_4 with values close to atmospheric value of δD-CH_4 and with relative low fluxes.

When comparing the range of values for δD-CH_4 between Fig.25 and Fig.7, the two groups observed do not fall into the theoretical boundaries of biogenic methane presented in Fig. 7, i.e. biogenic group from fermentation and biogenic group from CO_2 reduction.

The high flux emitters (i.e. HLO-01, AKM-08, NKK-01, BER01A), and the well with a higher concentration at the well location (i.e. HLO-01) showed that their Deuterium isotope values are much lower compared to the measurement of MON-02.

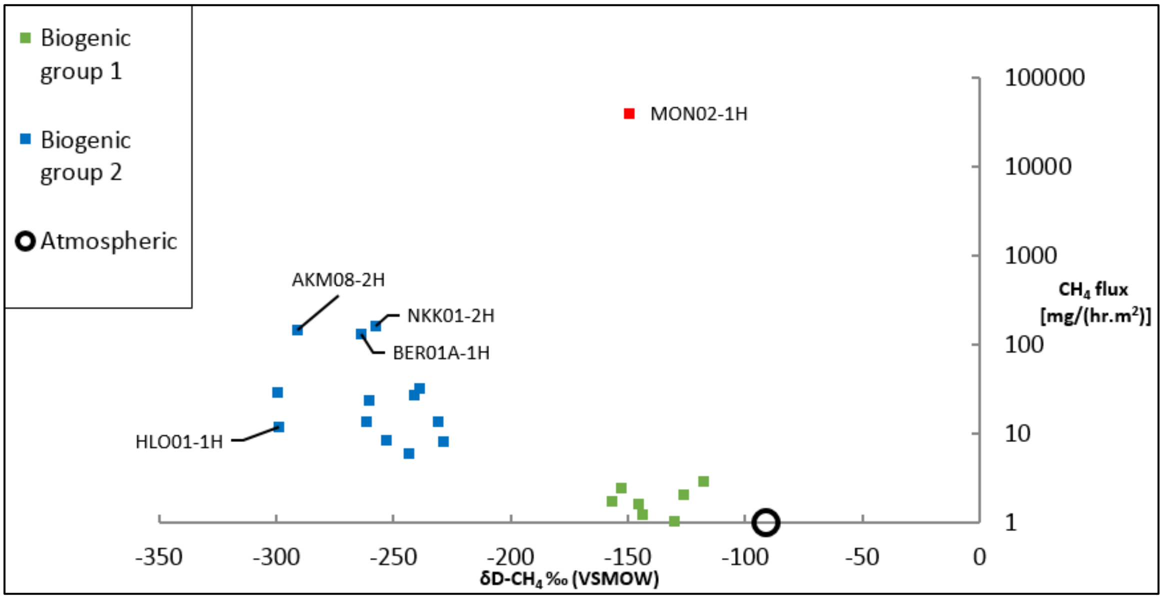

FIGURE 25: VARIATION OF METHANE FLUX IN FUNCTION OF δD-CH4

4.4 Methane source identification

In this section, the isotopic composition of 35 samples representing 28 different wells are plotted in a δ13C/δD diagram displayed in Fig. 26. Plotted in black dots are the values for the typical Dutch isotope composition of natural gas reservoirs as taken from the NLOG database record.

The graph shows similar distinctions in the isotopic values with the plot in Fig. 7. MON02-1H shows good similarities with the isotopic value of Dutch gas reference (MON-03) plotted in yellow, confirming that the methane emitted is from thermogenic origin.

A distinction of two main groups can be observed within the samples although the comparison with Fig. 7 cannot result to reliable conclusion on the origin of those two biogenic groups. In the next section of this chapter, we assume that this difference is caused by the presence of peat.

The high emitters considered in the study (i.e. above 100 mg/(hr.m^2)) are having low values for both δ13C-CH_4 and δD-CH_4, except for the measurement performed at SOW-01. The low flux of SOW-01explain its location close to the atmospheric sample.

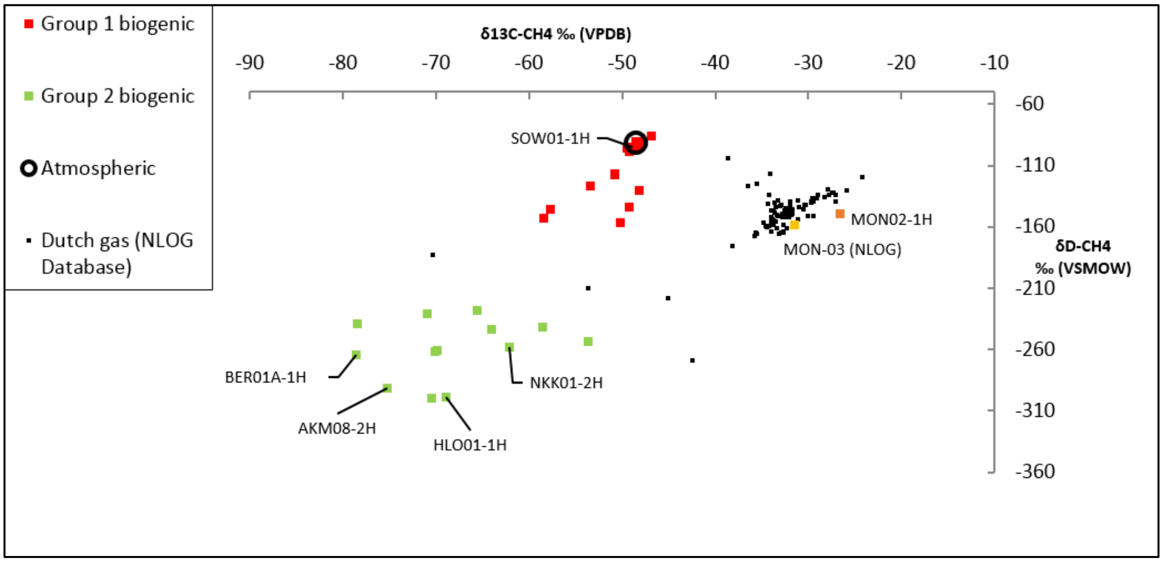

FIGURE 26: δ13C/δD DIAGRAM OF 34 SAMPLES FOR 28 WELLS (GROUP 1 AND 2), ONE ATMOSPHERIC SAMPLE AND 93 DIFFERENT GAS WELLS RESERVOIRS (SOURCE: NLOG) INCLUDING MONSTER

4.5 Biogenic and fluxe differentiation: presence of the Nieuwkoop Formation

This section aims at clarifying the causes explaining the occurrence of the observed difference between Group 1 and Group 2. The comparison with Fig. 7 could not identify clearly the origin of those two types of biogenic methane. I assume that the Nieuwkoop Formation can explain both the occurrence of 2 types of biogenic methane and the presence of high flux.

Table 4 displays the classification of the measurements associated to the Groups 1 and 2. Group 1 refers to 21 samples for 20 different well locations. Group 2 refers to 13 samples for 11 different wells locations.

As discussed earlier in the report, peat is ubiquitous in the Netherlands, and notably characterized by the presence of the Nieuwkoop Formation. Because the occurrence of peat has a high potential in methane emission, I wonder whether the presence of the Nieuwkoop Formation plays an important role in (1) the occurrence of two biogenic groups observed in Fig. 26 and (2) in the sizes of the observed methane fluxes.

When observing the wells belonging to the Group 1 in red dots (Fig. 27), 2 out of 16 wells are located within the Nieuwkoop Formation. 7 out of 11 wells belonging to the Group 2 in green dots are located in the Nieuwkoop Formation area.

Note 1: As observed in Table 4, some wells belong to the two groups, namely BER01A, BHM-01, SGZ-01 and WSE-01.

Note 2: MON-02 are not considered in the counting as I am interested in the biogenic differentiation exclusively.

TABLE 4: MEASUREMENTS AND WELL NAMES FOR THE TWO DIFFERENTIATED GROUPS OF BIOGENIC METHANE

Measurement name Group 1	Well name Group 1	Measurement name Group 2	Well name Group 2
AKM01-1H	AKM-01	AKM07-1H	AKM-07
BER01A-3H	BER01A	AKM08-1H	AKM-08
BHM01-1H	BHM-01	AKM08-2H	AKM-08
EMC01-1H	EMC-01	AKM10-1H	AKM-10
EXO2-1H	EXO-02	AKM13-1H	AKM-10
KWK01-1H	KWK-01	BER01A-1H	BER01A
LED02-1H	LED-02	BHM01-2H	BHM-01
MKN01-1H	MKN-01	HLO01-1H	HLO-01
OWD01-1H	OWD-01	NKK01-1H	NKK-01
RWK14-1H	RWK-14	NKK01-2H	NKK-01
SGZ1-1H	SGZ-01	SGZ01-2H	SGZ-01
SLN02-1HR	SLN-02	SPKW01-1H	SPKW-01
SOW01-1H	SOW-01	WSE01-2H	WSE-01
STA01-1H	STA-01		
WAS26-1H	WAS-26		
WIM01-1H	WIM-01		
WSE01-1H	WSE-01		
WYK02-1H	WYK-02		
WYK02-2H	WYK-02		
WYK30-1H	WYK-30		
ZOM16-1H	ZOM-16		

As observed in Fig. 27, most of the wells are located at the limit of the Nieuwkoop Formation, rendering more difficult the analysis of the location of the wells. Considering those results, it is hardly possible to conclude on the influence of peat on the biogenic differentiation observed. The affiliation of some measurements to both groups for some wells (see Note 1) requires further analysis of the isotopic composition for those specific wells.

Regarding the effect of peat on the sizes of the fluxes, the results cannot explain the observed high emitters highlighted in a blue circle on Fig. 27. Typically, MON-02 and NKK-01 can be clearly distinguished outside and inside of the Nieuwkoop Formation, respectively. However, the locations of AKM-08 and BER-01A are not clearly distinguishable whether they are located within the Nieuwkoop Formation or not.

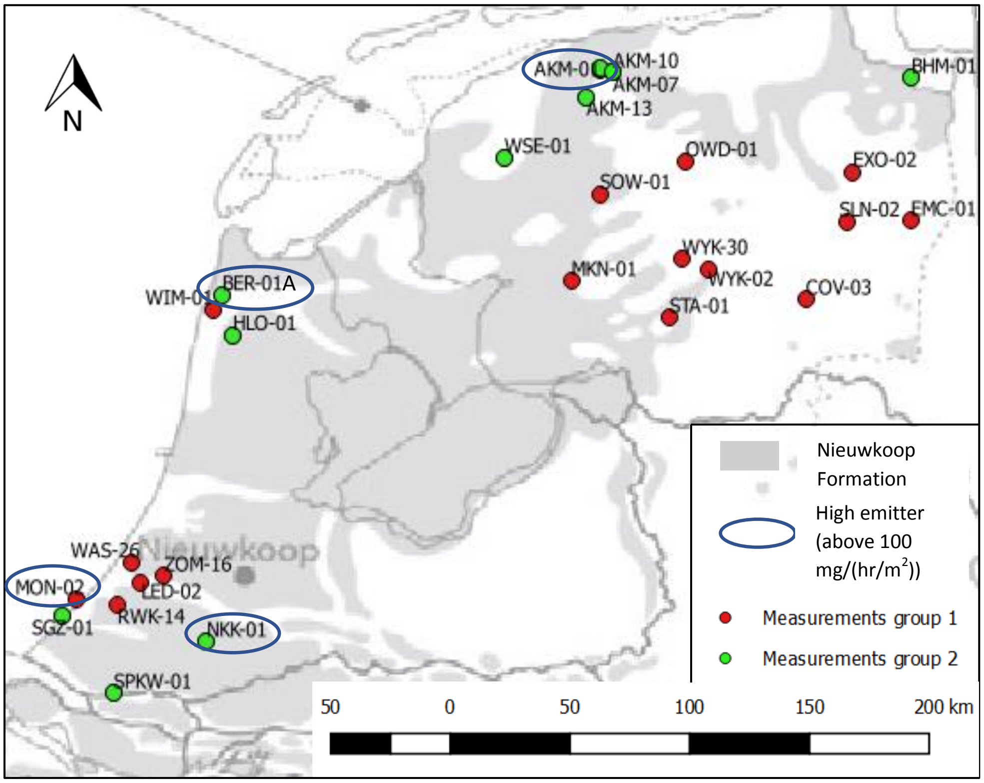

Figure 27: Group 1 (in red) and group 2 (in green) locations within the Nieuwkoop Formation (Nieuwkoop map source: Dinolocket, 2017)

5. Discussion

In this section, the issue considering the observed difference of methane will be largely discussed as it is one of the key finding of the current research. It will be followed by a discussion on the limitation of the static chamber method as well as an extrapolation of the results to a larger scale.

5.1 Flux measurements at ground surface and at 1m depth

The results of the research have shown that high fluxes were detected mainly at one meter depth. Therefore, the set of measurements performed at one meter depth was of a crucial importance when considering the results. The high fluxes measured at Monster (MON-02) would not have been detected without performing the static chamber measurements at one meter depth. Other studies such as Boothroyd *et al.* (2016) and Townsend *et al*. (2016), have not carried out methane measurements at depth. In consequence, they may have neglected the effect of the one meter soil (or more for deeper unsaturated zones) for methane leakages at wells, and more specifically the effect of oxidation at shallow depth.

The different plots displayed in the results use logarithmic scales because of the significant flux differences in the results. When considering the presence of small and negative fluxes in our study, one may realize that the absolute values are low and I assume that they reflect analytical noise around the atmospheric background value. They do not represent an important finding regarding the overall objective of the current study as high fluxes are targeted exclusively. In addition, the current study aims at finding the leakages and therefore, only high fluxes are of interests by considering only the measurements with the R^2 greater or equal to 0.8.

During the fluxes measurements at one meter depth, methane fluxes is measured. We had considered the emitted methane at the bottom of the drilled hole. However, methane is also emitted from the internal sides. The hole drilled can be readably schematized to a 1 meter cylinder with a 5 centimeters radius. The surface area of the internal surface is 3,140 cm^2. Considering that surface, the flux measured is not entirely stemming from the bottom of the hole but also from the internal sides. Too little research has performed the same type of measurements; hence comparisons of the findings cannot be established. However, I believe that the focus of the current research cannot be altered by this notice as methane leakages from abandoned wells would be still identified. The consideration for this limitation would alter the accuracy of the results but not the overall conclusion.

5.2 Methane oxidation effect

The difference of fluxes observed between the two sets of measurements can be explained by the mechanisms of soil oxidation. The process of methane oxidation is defined as being the soil capable to transform CO_2 into methane and captured mainly in the roots of the vegetation. The inhibiting effect of oxidation on methane emission is widely recognized as considerable. In the study led by Oonk *et al.* (2015), the considerable capacity of methane oxidation is highlighted. In the study, about 20 to 35 $kg.^{-1}$ was almost entirely oxidized while methane oxidation is reported to be closely dependent on the gas temperature as well as the ambient air temperature. Other variables may affect the oxidation of methane:

soil moisture and temperature are predominant factors influencing methane oxidation in the soil (De Visscher & Van Cleemput). In our study, several days was rainy and some measurements was following light rainfalls. The amount of vegetation is increasing the oxidation effect (Abichou et al., 2015); A threshold soil thickness is observed for methane oxidation according to the model performed by Yao et al., 2015. In this current research, methane oxidation is inhibited by the presence of peat and therefore increase methane emission from the soil. Although no conclusion could have been made on the potential of the Nieuwkoop Formation on the isotopic nature of the samples, oxidation is an important aspect to explain the occurrence of two types of biogenic methane. The hypothesis is that methane could have been partly oxidized at some well locations although it is not clear from our results whether this difference of oxidation level is directly related to the presence of peat.

5.3 Limitations of the static chamber method

Improper sealed equipment may occur in our method during the handling of the sampling system, i.e. the vacuum sampling box, when connecting the inlet and outlets. Minor leakages can trigger sample contamination or losses. During the screening of the sites, it was rainy during several days. Some measurements were performed the day or the hour after a rainy episode. As it goes with the rain, pressure and temperature change. Using a laser spectroscope, moisture, pressure and temperature are factors that are likely to affect the sensitivity of the tunable diode absorption contained in the methane detector.

5.4 Extrapolation of the results to the Netherlands

The results of the current study show that one well out of the 29 studied is leaking thermogenic methane. In the Netherlands, 2273 on-shore gas wells exist including abandoned, producing, plugged and side-tracked. This results in questioning on the amount of leaking gas wells in the Netherlands considering the probability of occurrence of leakages and the amount of potential leaking wells. The probability of occurrence of leakages remains relatively low while the amount of potential leaking wells can be considered as high because of the high number of wells present in the Netherlands. While considering the quite considerable occurrence of peat as a typical feature of the Netherlands and the results of our study, the occurrence of peat is an important and thorough aspect involved in the detection of the leakages since peatlands are an important environmental source of biogenic methane. Although methane oxidation of soils have been already studied, further research on the nature of methane emitted from peatlands could provide better understanding.

6. Conclusions

While mostly performed in the U.S., the study of methane leakages from abandoned gas is currently the subject of important debates among the scientific communities. The Netherlands should be part of those debates because of the important contribution of gas production in the economy of the country. The current research investigated whether methane leakages from abandoned gas wells in the Netherlands is a reality or a fiction. A field work campaign performed in July 2017 shows that methane leakages exist in the Netherlands. Out of 2,652 abandoned gas wells existing in the Netherlands, 29 wells have been investigated in this report. The results have shown that one well is an emitter of thermogenic methane and, therefore, must be considered as a leaking well. Based on literature and field monitoring research, further details of the research project show that:

- A thorough screened methodology involving a 16 meters radius circle was performed for 24 wells location. The screening of the well was intended to show whether methane fluxes could be detected at the surface or not. The screening detected very low concentrations of methane at the surface close to the atmospheric concentration. Typically, two sites (HLO-01 and SOW-01) showed higher concentrations close to the exact well locations. The latter measurements did neither show significant high fluxes nor methane from thermogenic origin that could prove the occurrence of leakages. The presence of a buried well at 3 meters deep could have enhanced the formation of artificial pathways where biogenic gas can emit. Similarly, intermittent high methane concentrations were observed at very specific location during most of the screenings and low methane fluxes were detected.

- The flux measurements performed at one meter depth with a static chamber method generally indicated higher fluxes of methane than at the surface. Typically, the well MON-02 located at Monster shows significant higher fluxes reaching 40,026 mg/[hr.m^2] at one meter depth. It is a tremendous finding in this current research as many other scientific papers underestimated the effect of one meter soil layer on the flux sizes.

- Three additional high fluxes (greater than 100 mg/[hr.m^2]) were detected including NKK-01, AKM-08 and BER-01A although the flux measurements with a static chamber method did not show higher fluxes at the well location except for BER-01A for which the fluxes at the well where 83 times higher than at the controls. However, the isotopic analysis did not confirm any occurrence of thermogenic methane for any of those 3 wells.

- The isotopic analysis shows no affiliation to the presence of two main biogenic methane groups stemming either from the acetate fermentation or the CO_2 reduction processes. The results have shown that the presence of the Nieuwkoop Formation is not influencing the origin of the biogenic methane, as well as the size of the fluxes. Oxidation effect in a 1 meter soil layer may play a major role.

The presence of the giant Groningen gas field has made the Netherlands a gas country. The efforts made by the Dutch government to reinforce the decommissioning and reuse of gas wells is a prominent start for the shift towards more environmental practices, as both air and water are involved in this important issue of gas leakages.

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Notice: websites were accessed in the period of June to November 2017

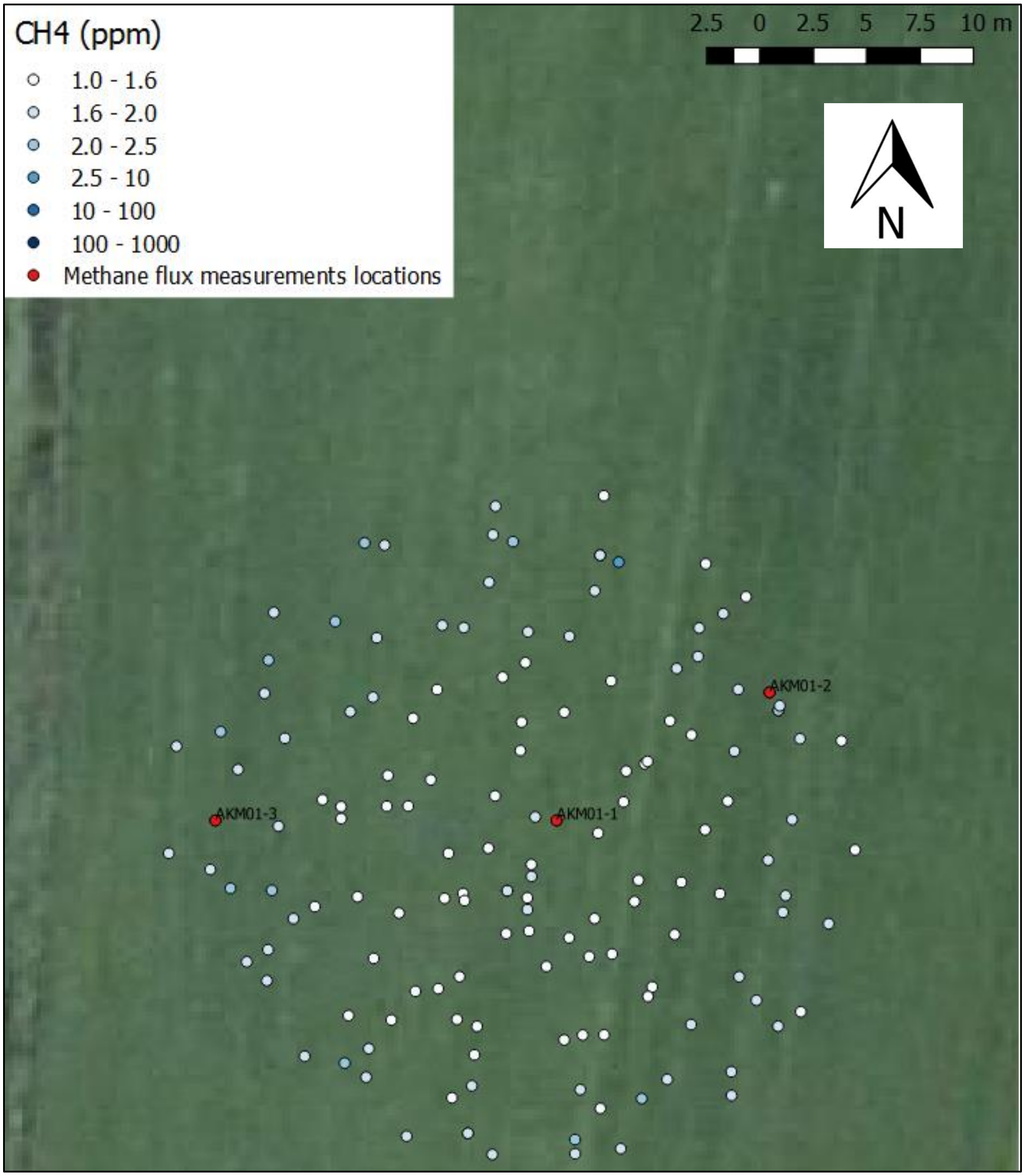
Appendixes

Appendix 1: Fieldwork template

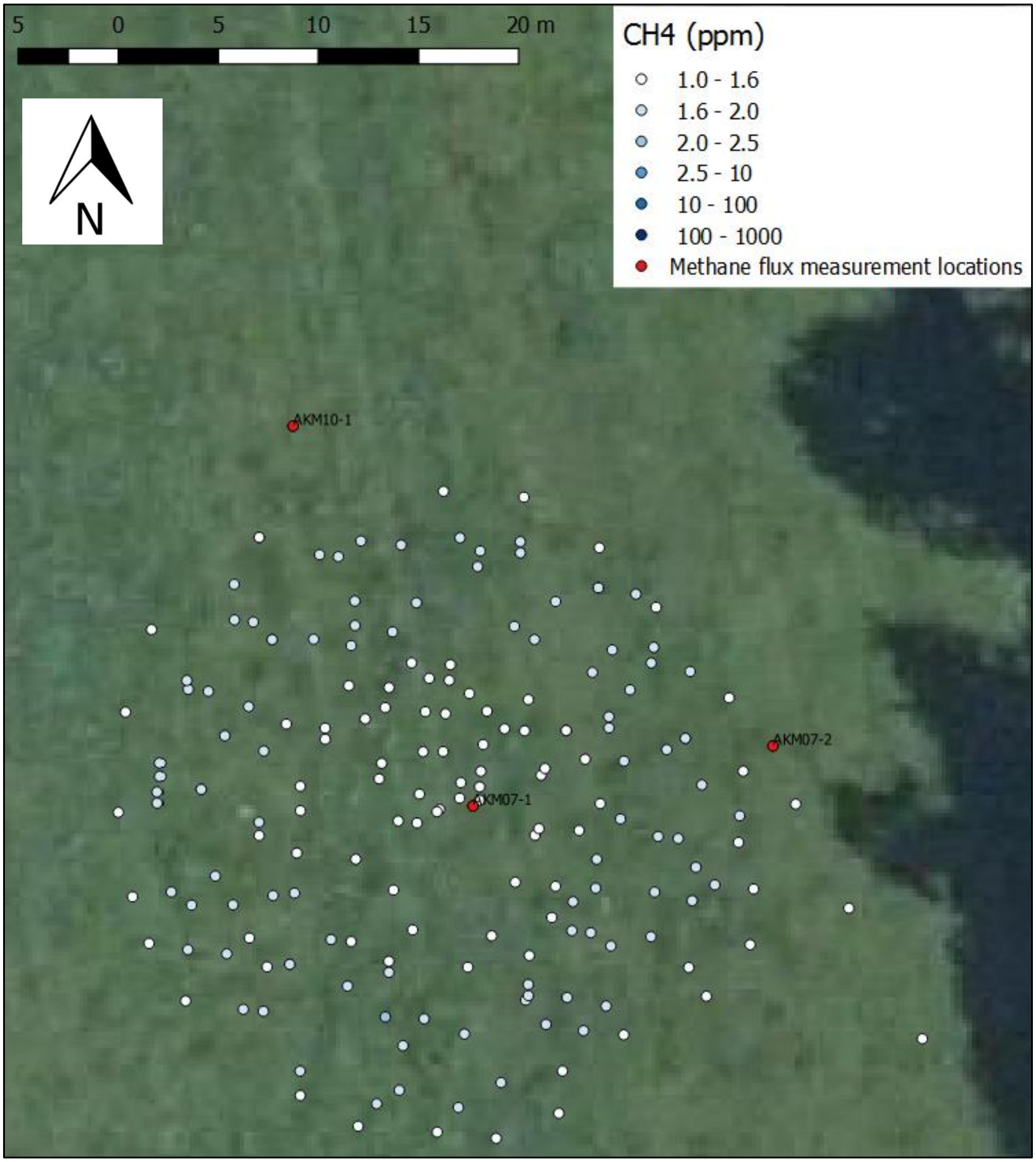
ID:	Date:
Inspectra laser Calibation: ppm	Pressure: Humidity: Temperature: Wind: km/h Present type of weather conditions: Past type of weather conditions:

Static flux measurements					
ID:		ID:		ID:	
time		time		time	
Time (s)	CH_4 (ppm)	Time (s)	CH_4 (ppm)	Time (s)	CH_4 (ppm)

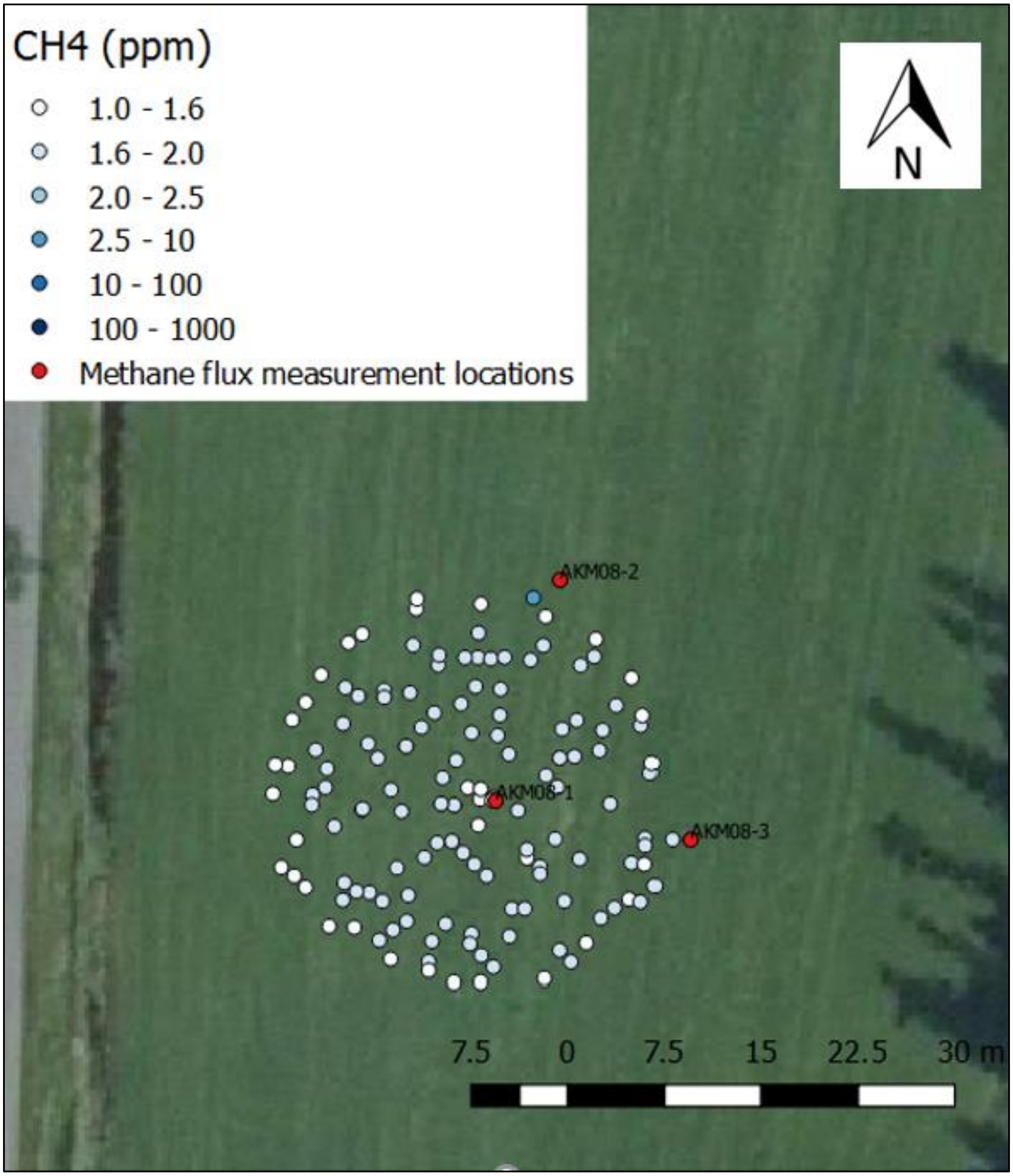
Appendix 2: Appendix AKM-01



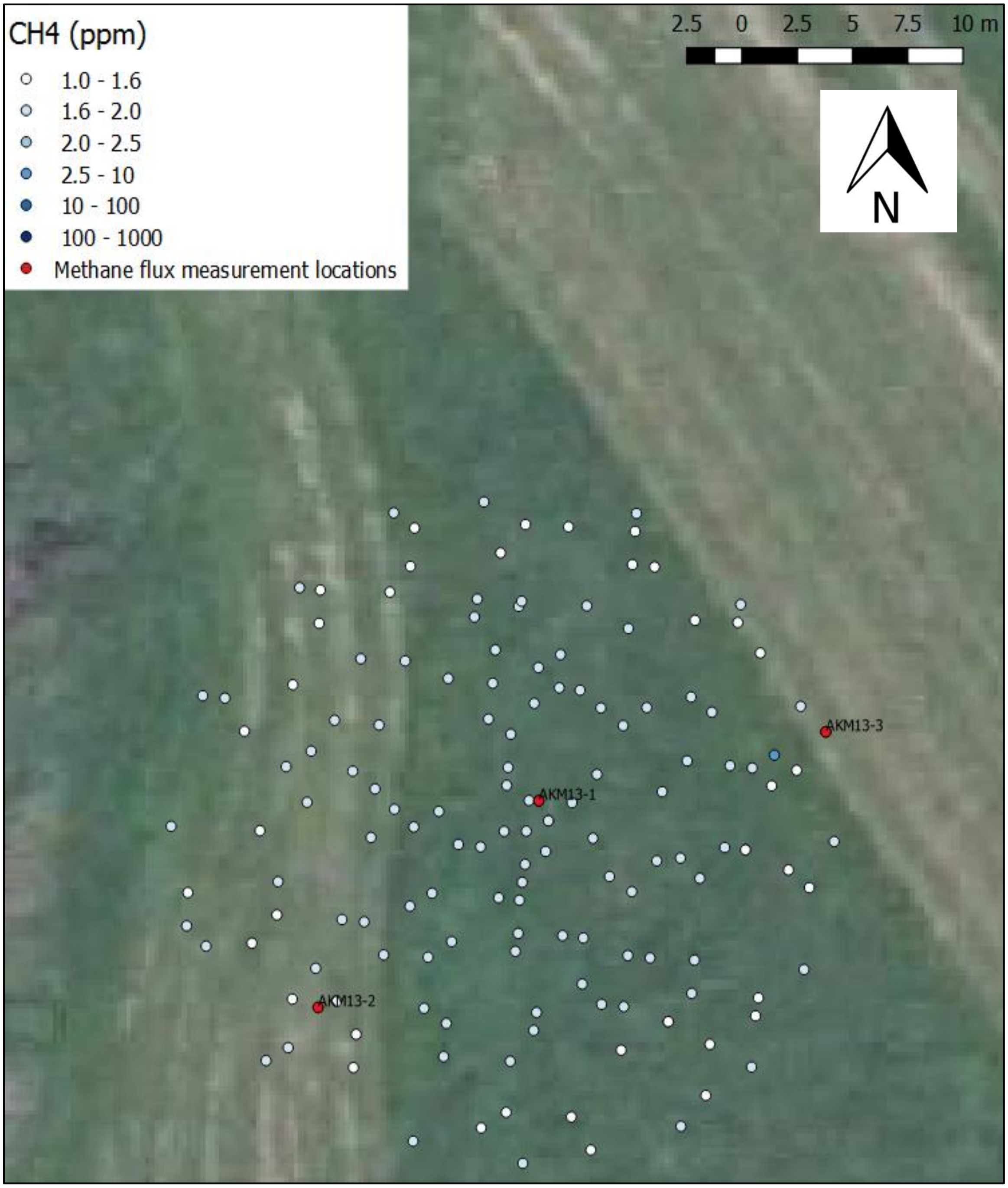
Appendix 3: Screening AKM-07



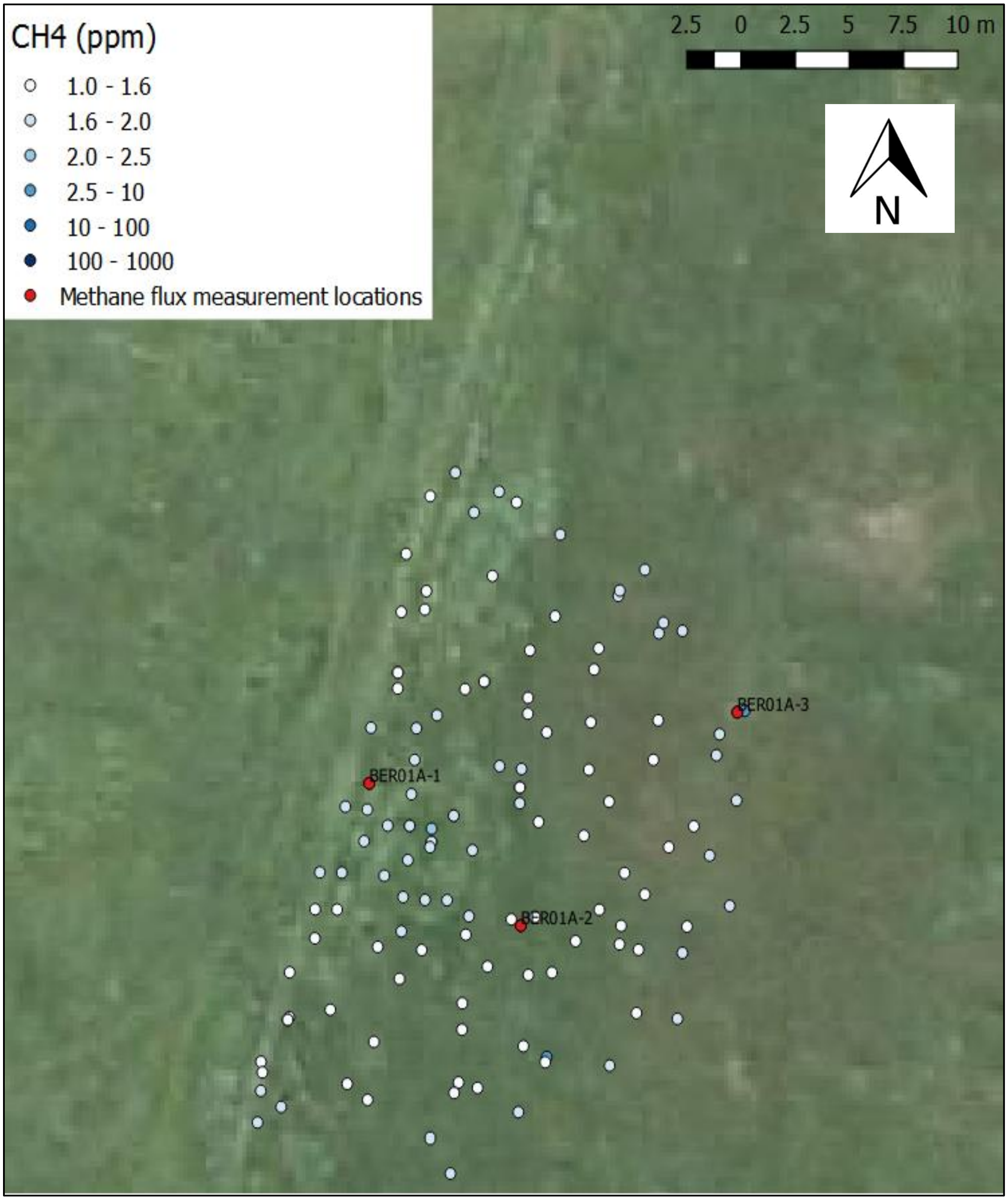
Appendix 4: Screening AKM-08



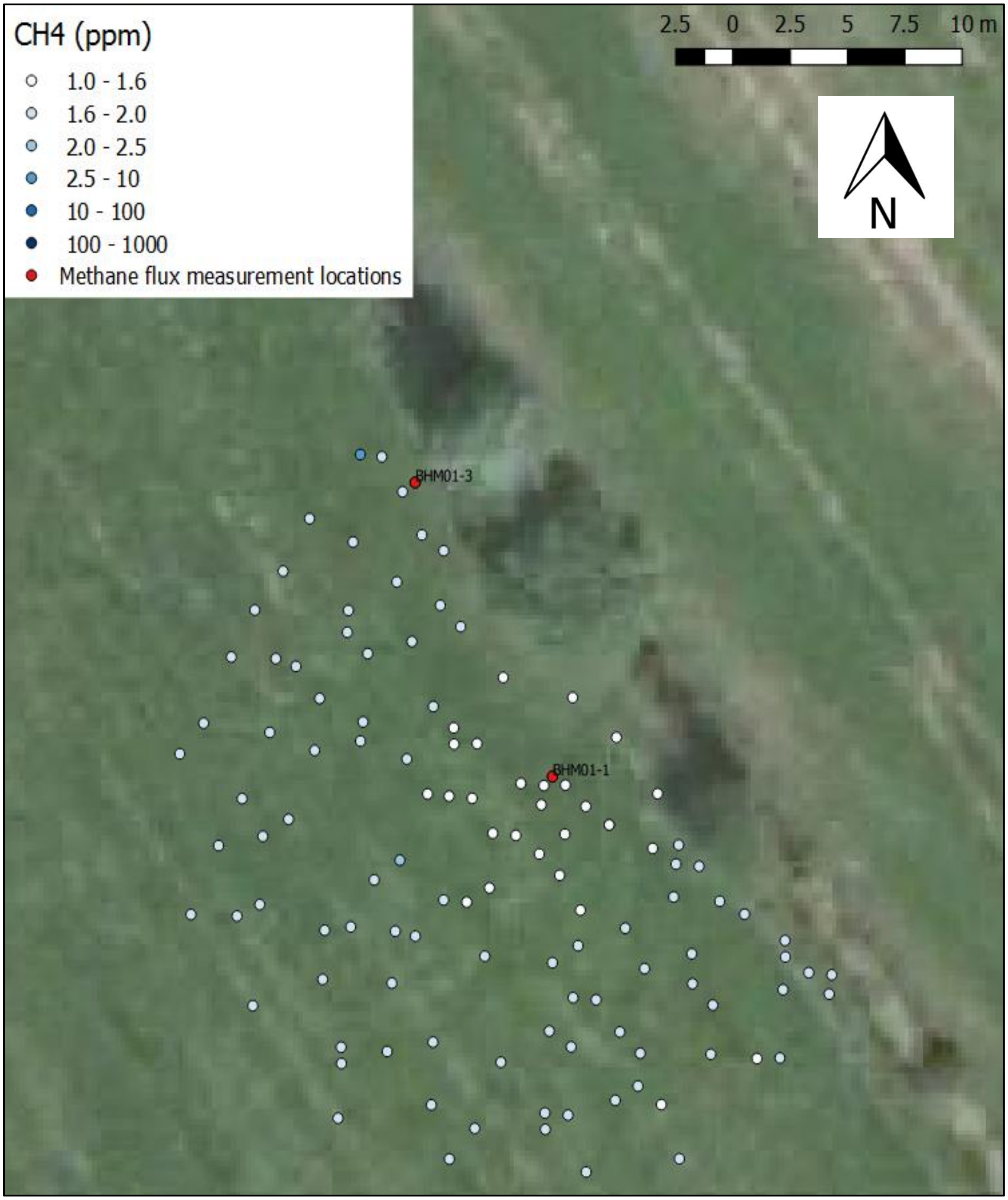
Appendix 5: Screening AKM-13



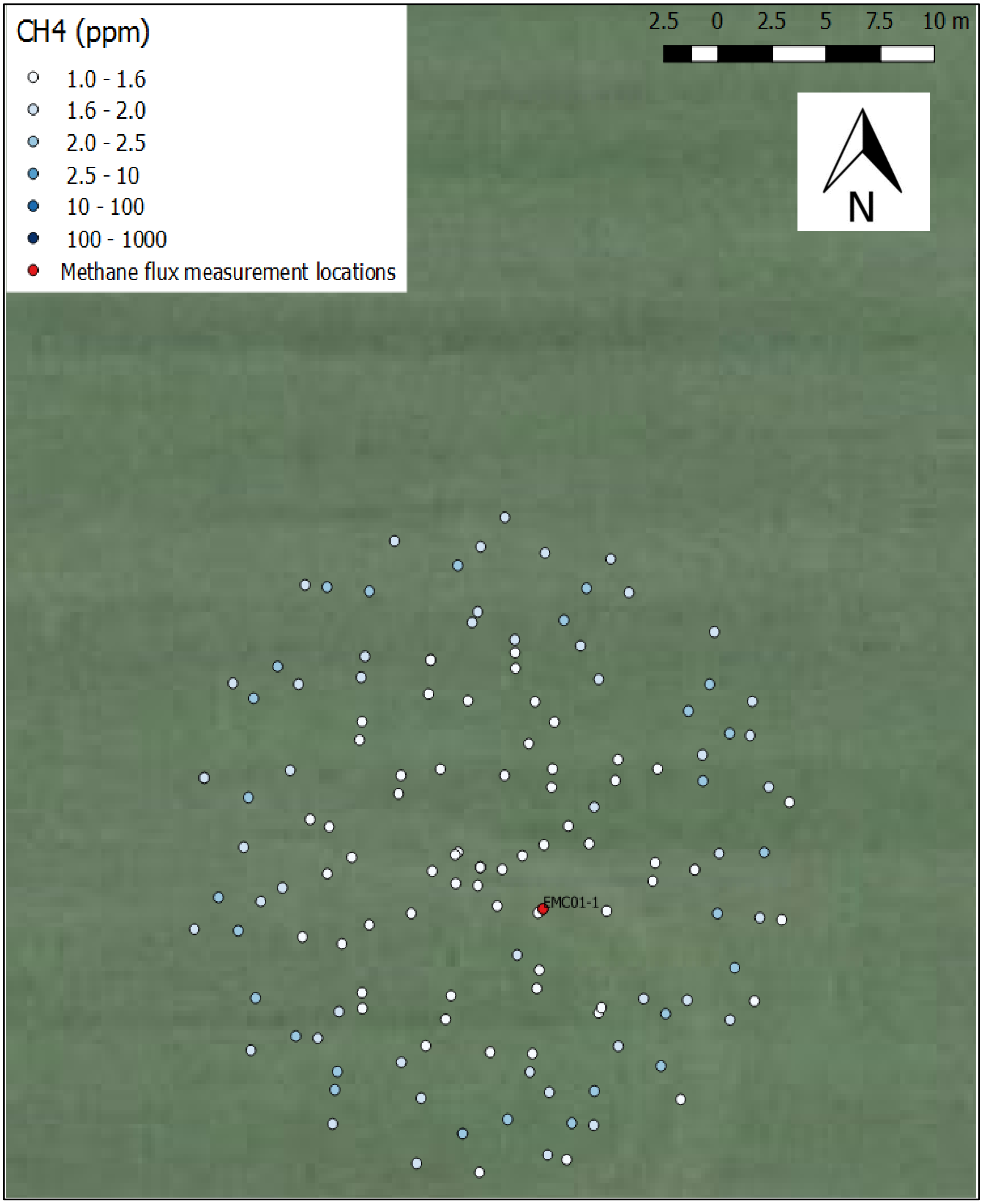
Appendix 6: Screening BER-01A



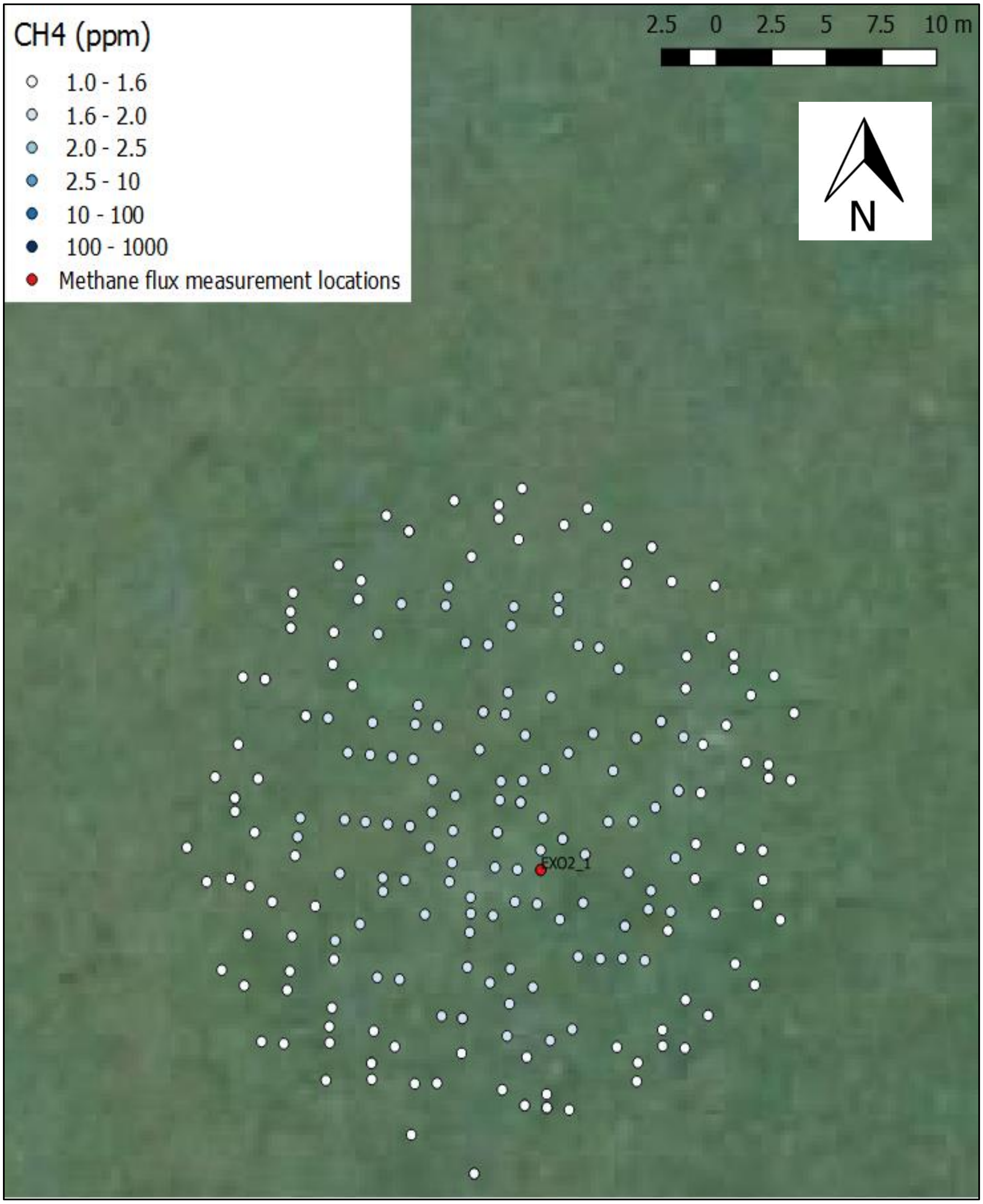
Appendix 7: Screening BHM-01



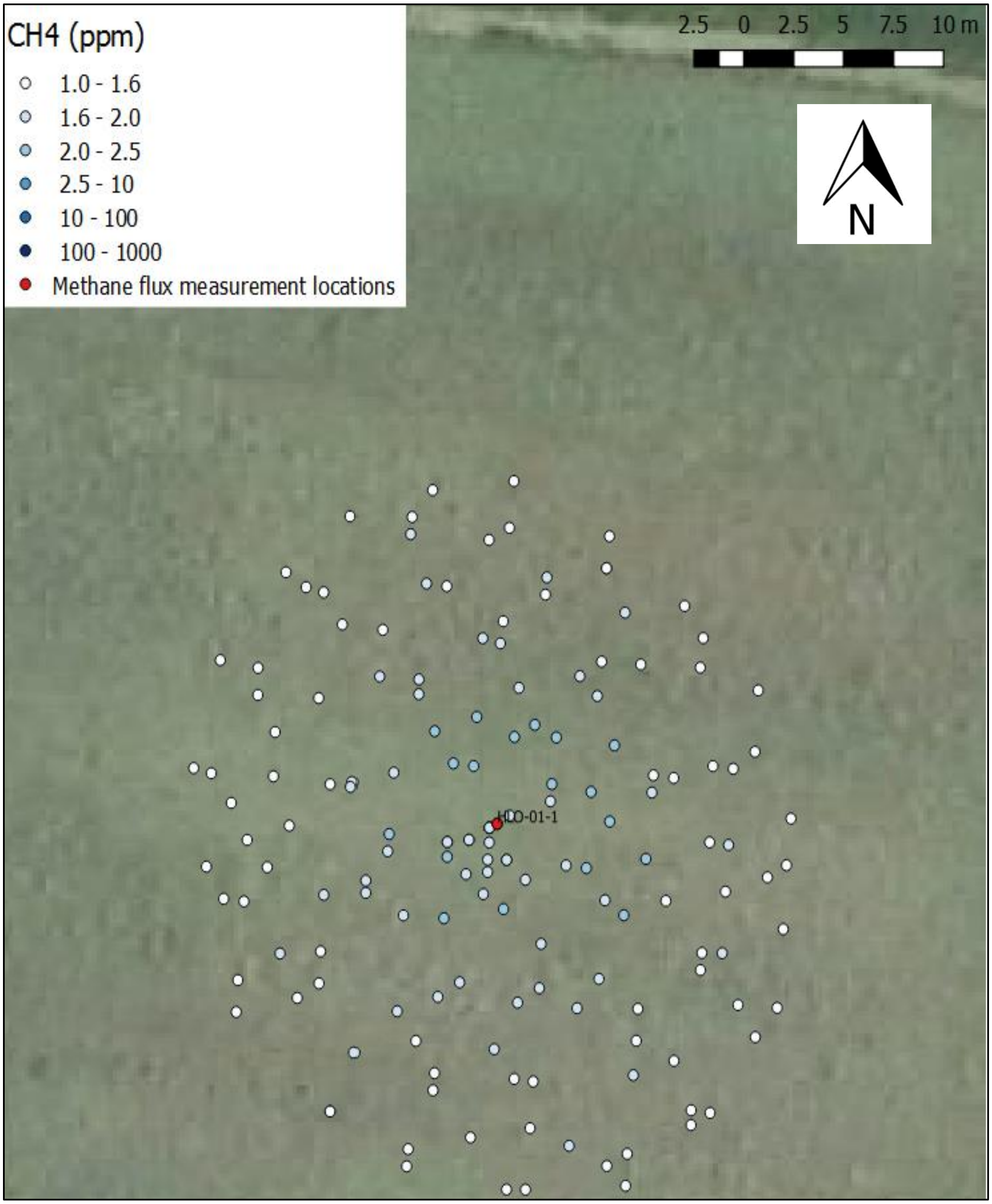
Appendix 8: Screening EMC-01



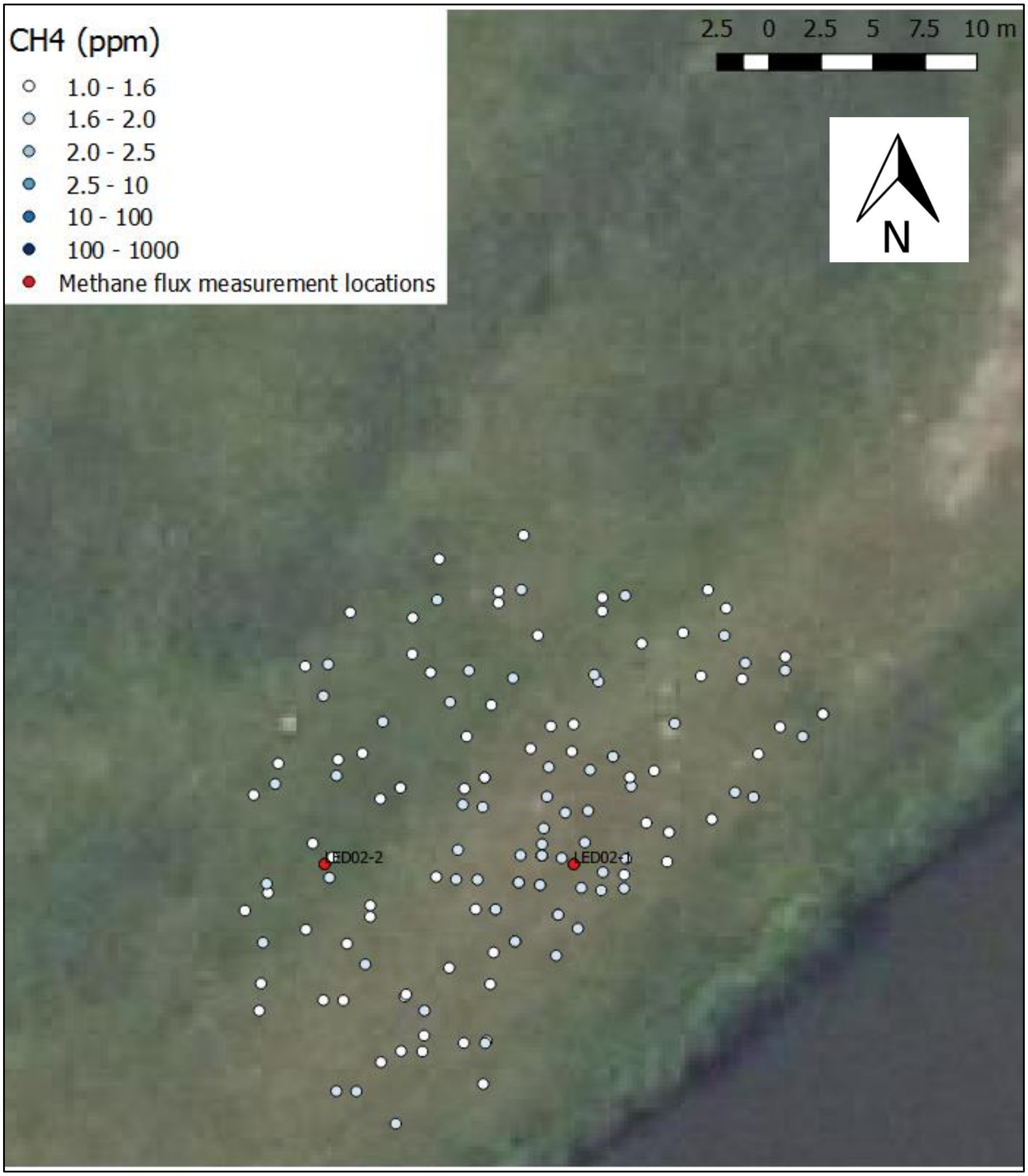
Appendix 9: Screening EXO-02



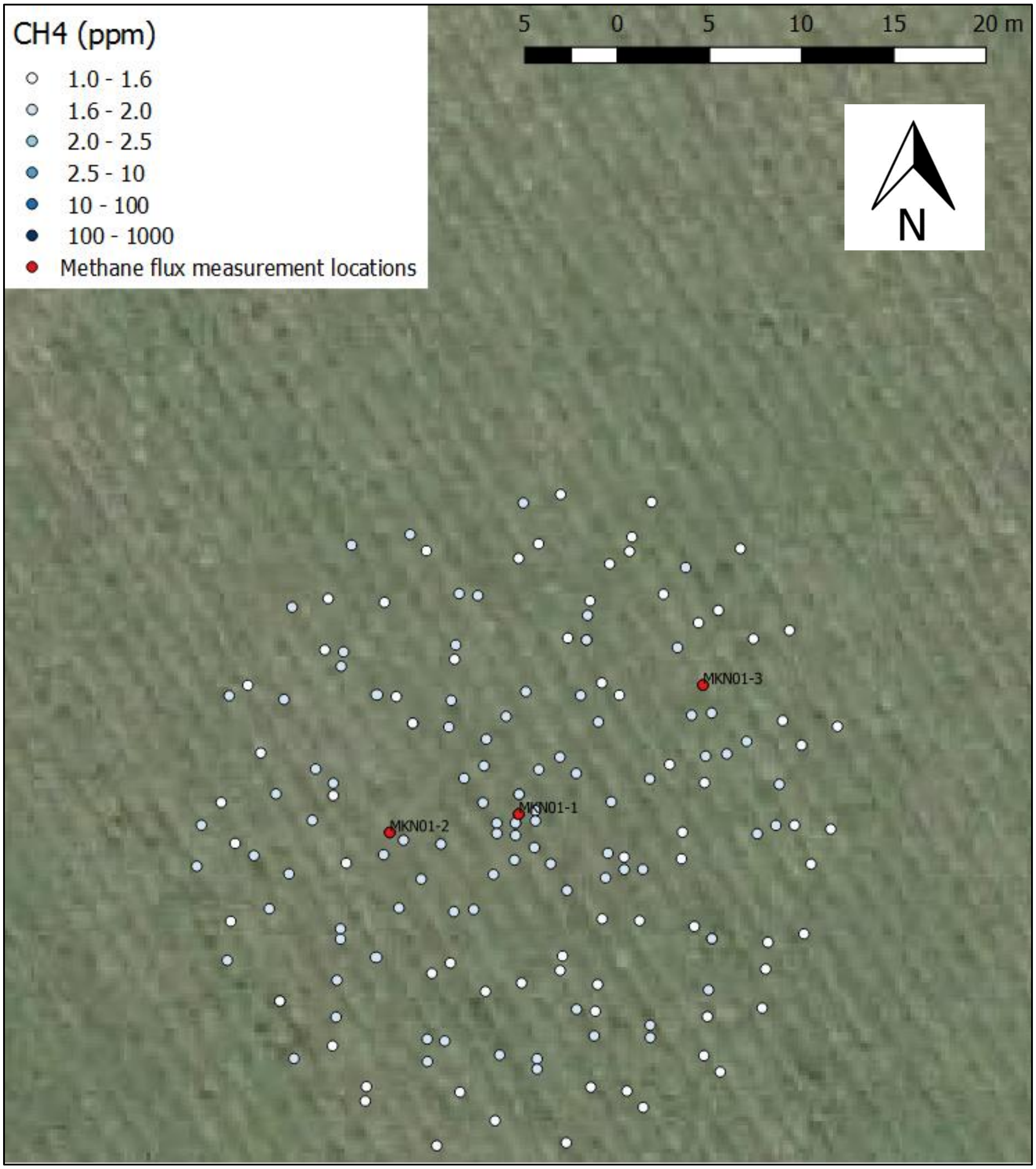
Appendix 10: Screening HLO-01



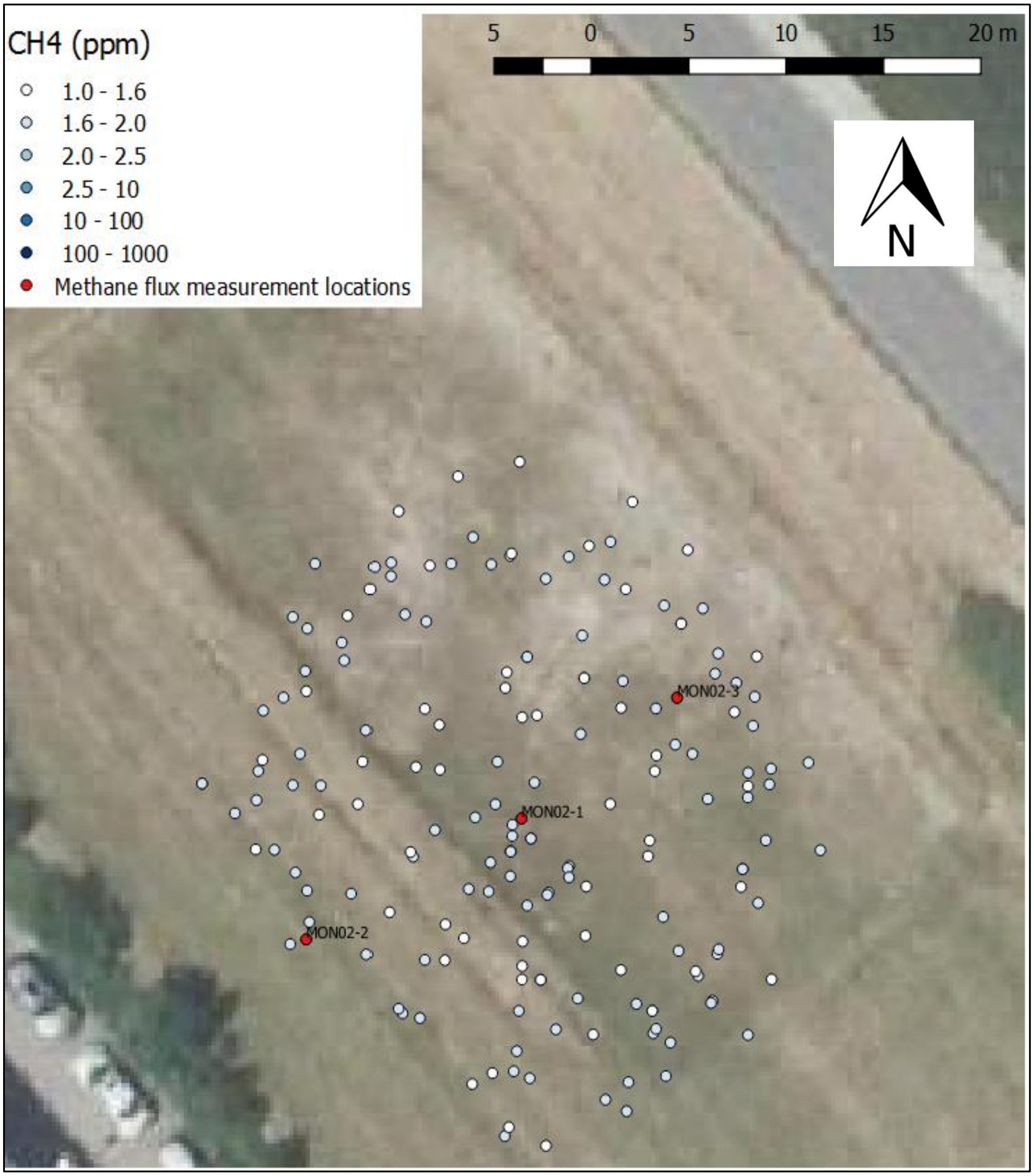
Appendix 11: Screening LED-02



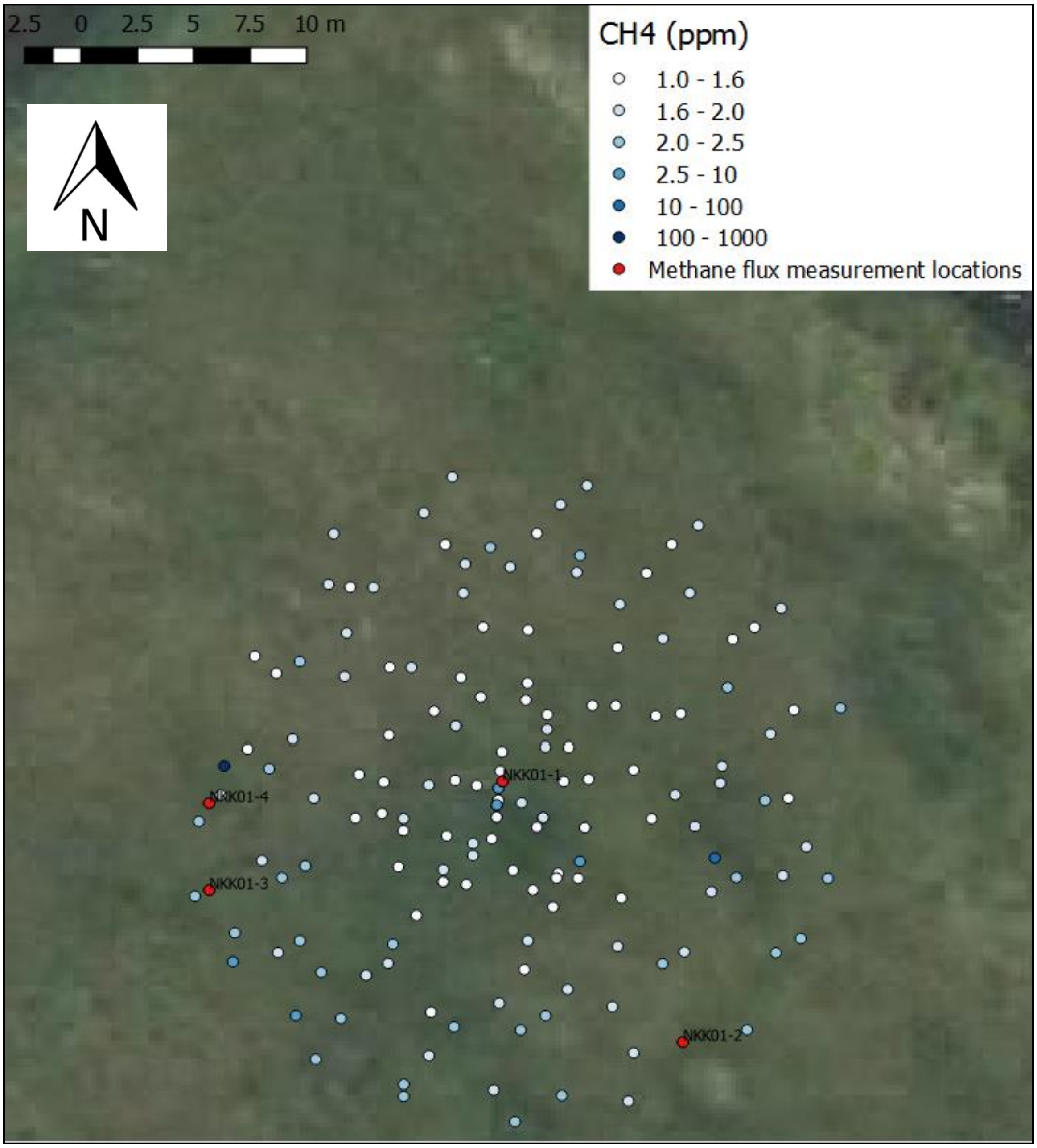
Appendix 12: Screening MKN-01



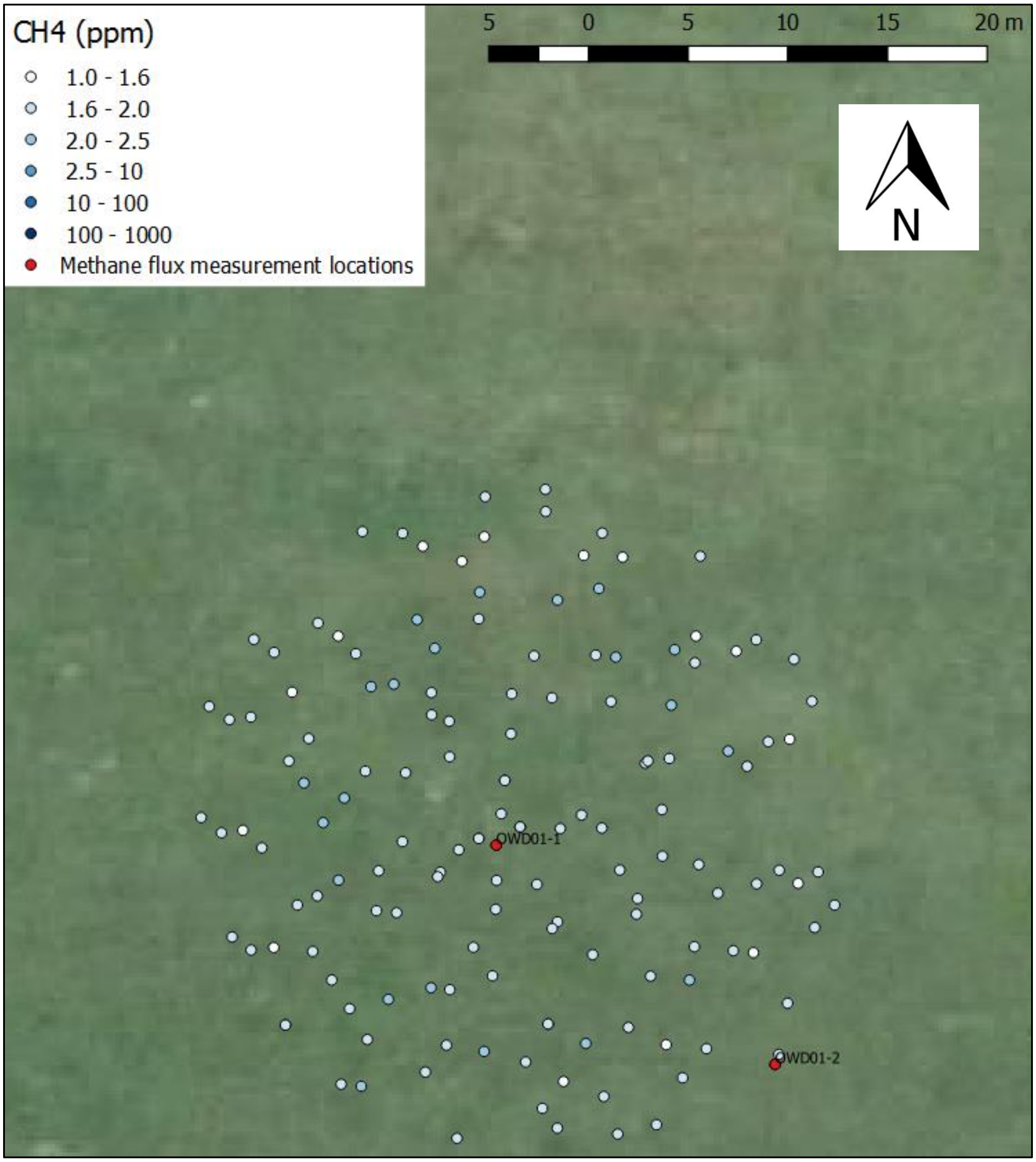
Appendix 13: Screening MON-02



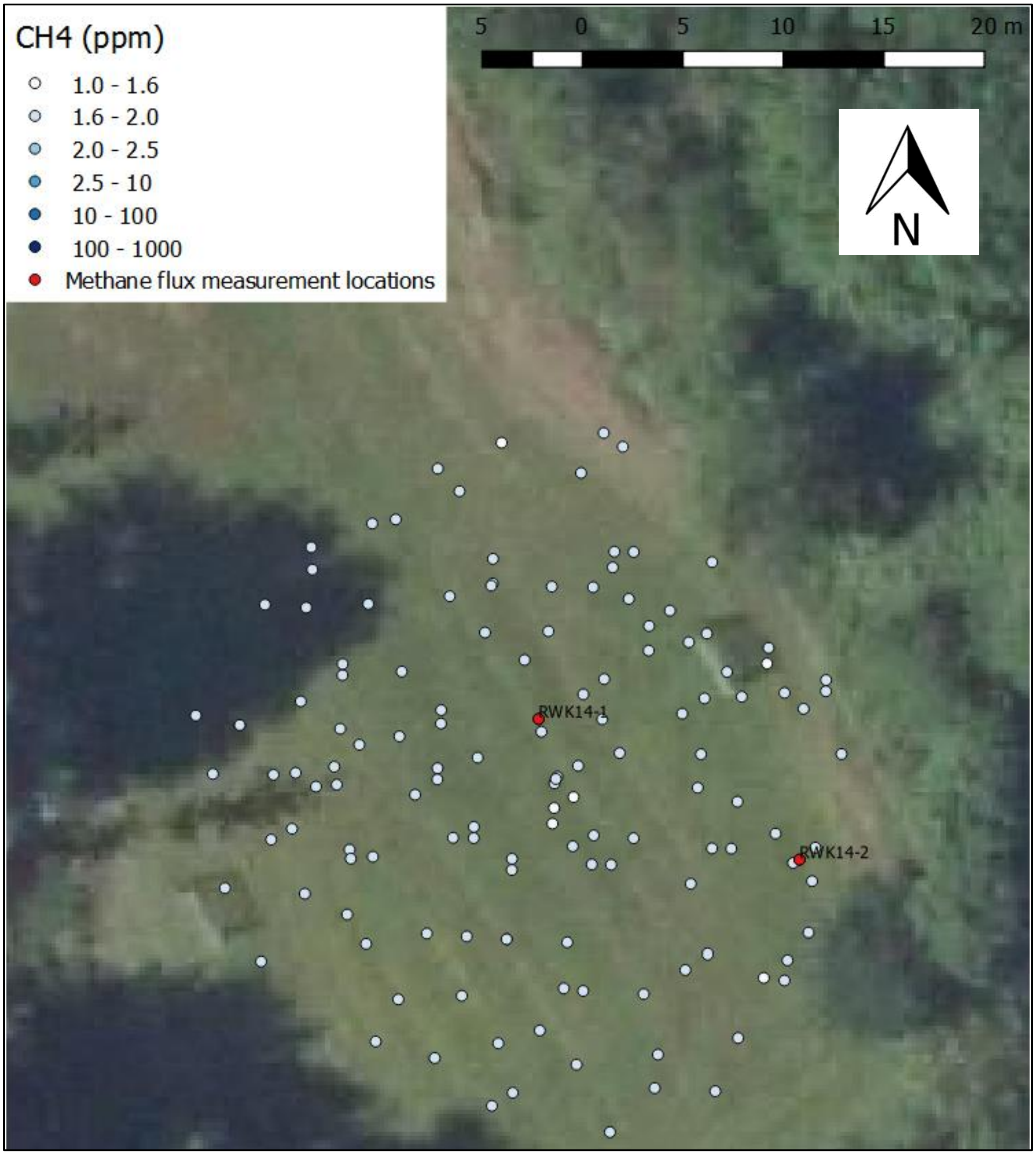
Appendix 14: Screening NKK-01



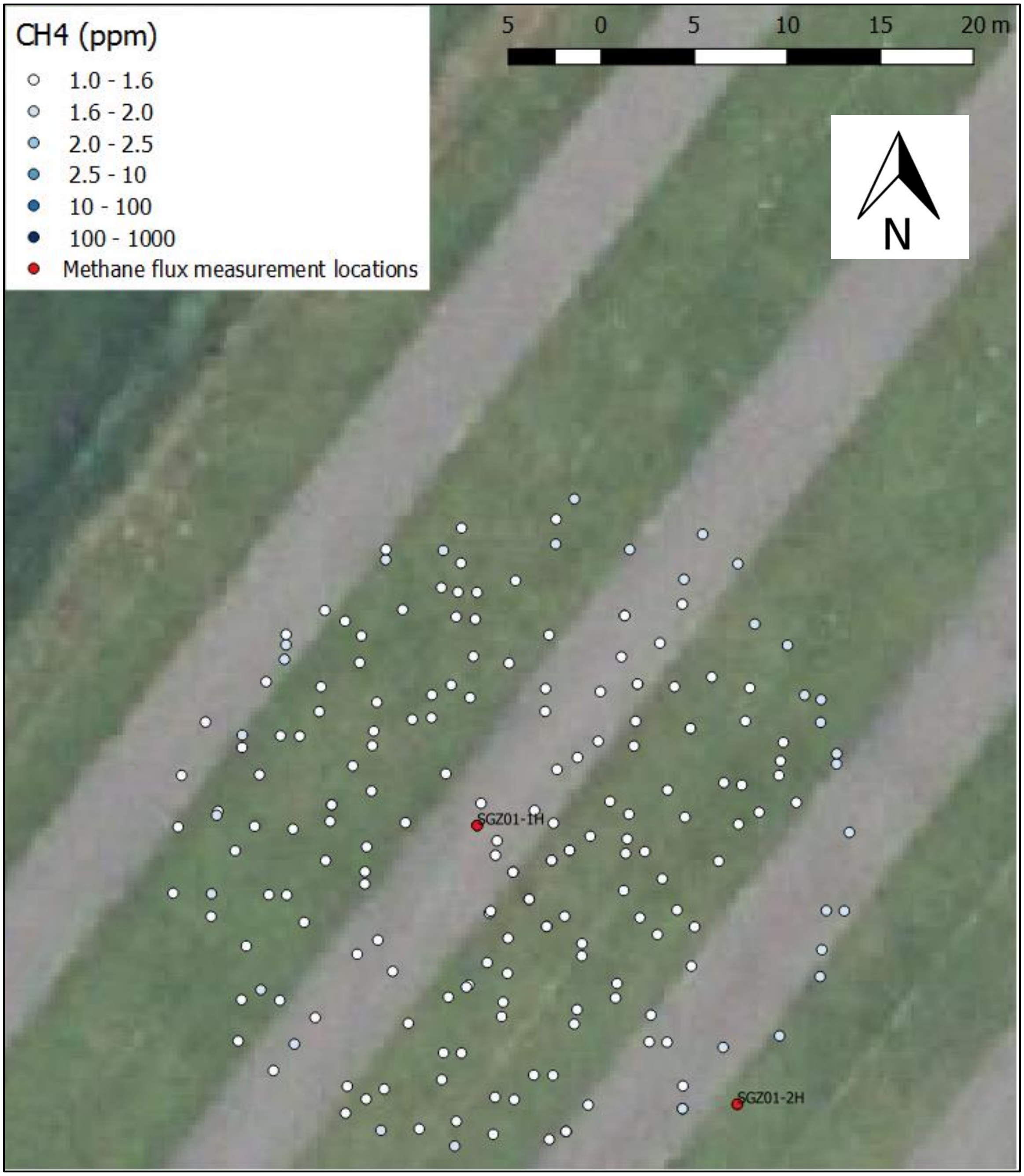
Appendix 15: Screening OWD-01



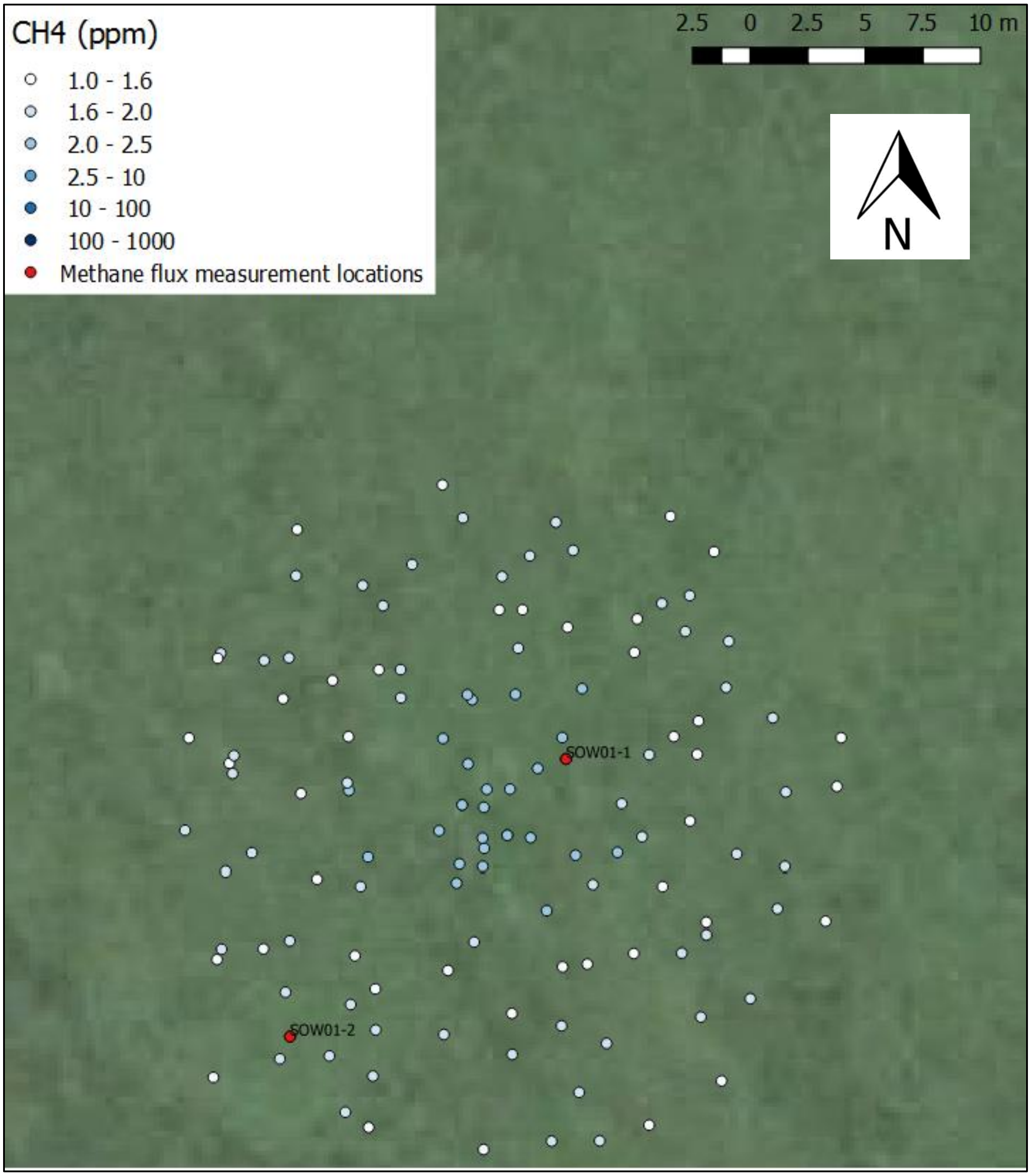
Appendix 16: Screening RWK-14



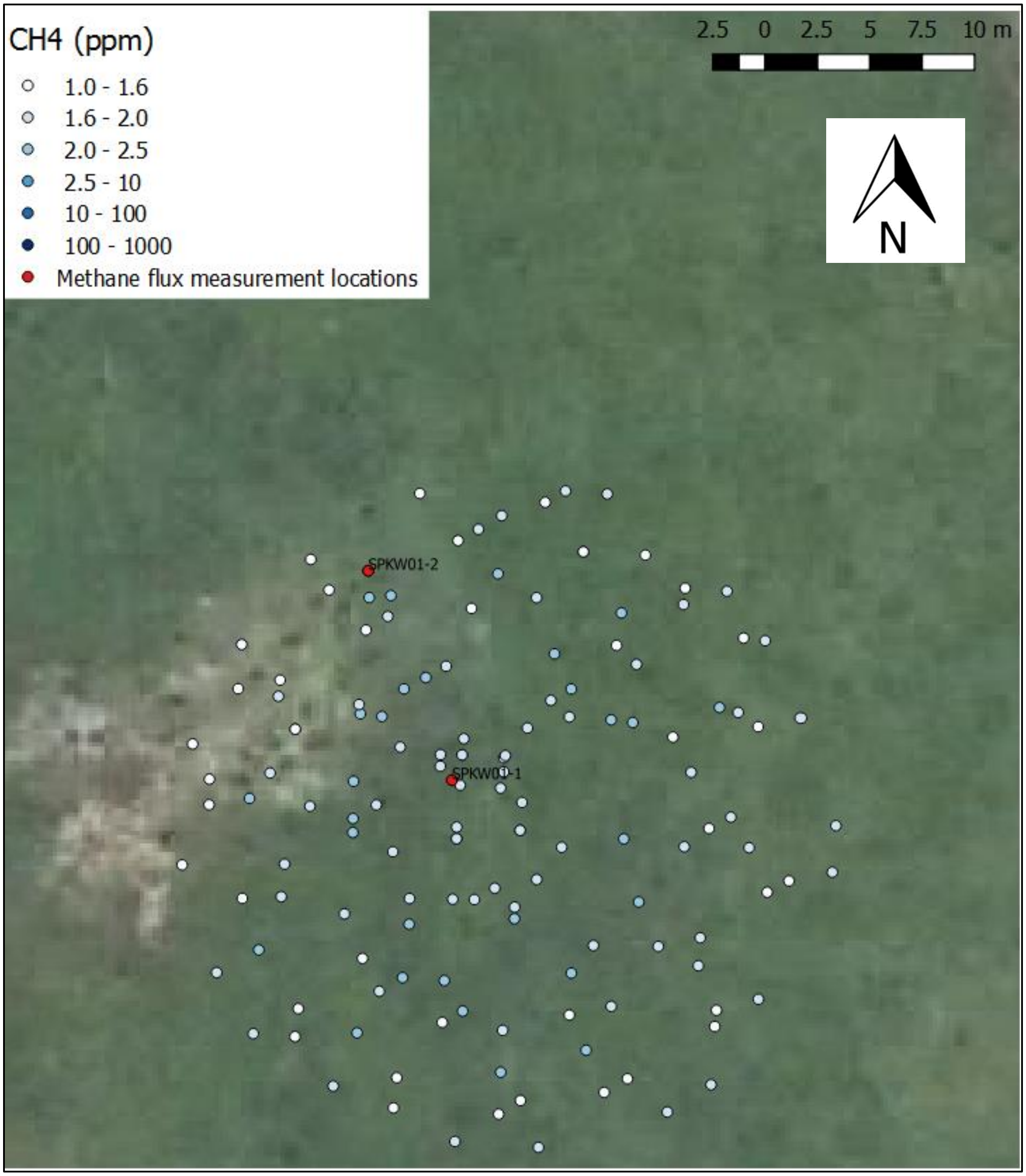
Appendix 17: Screening SGZ-01



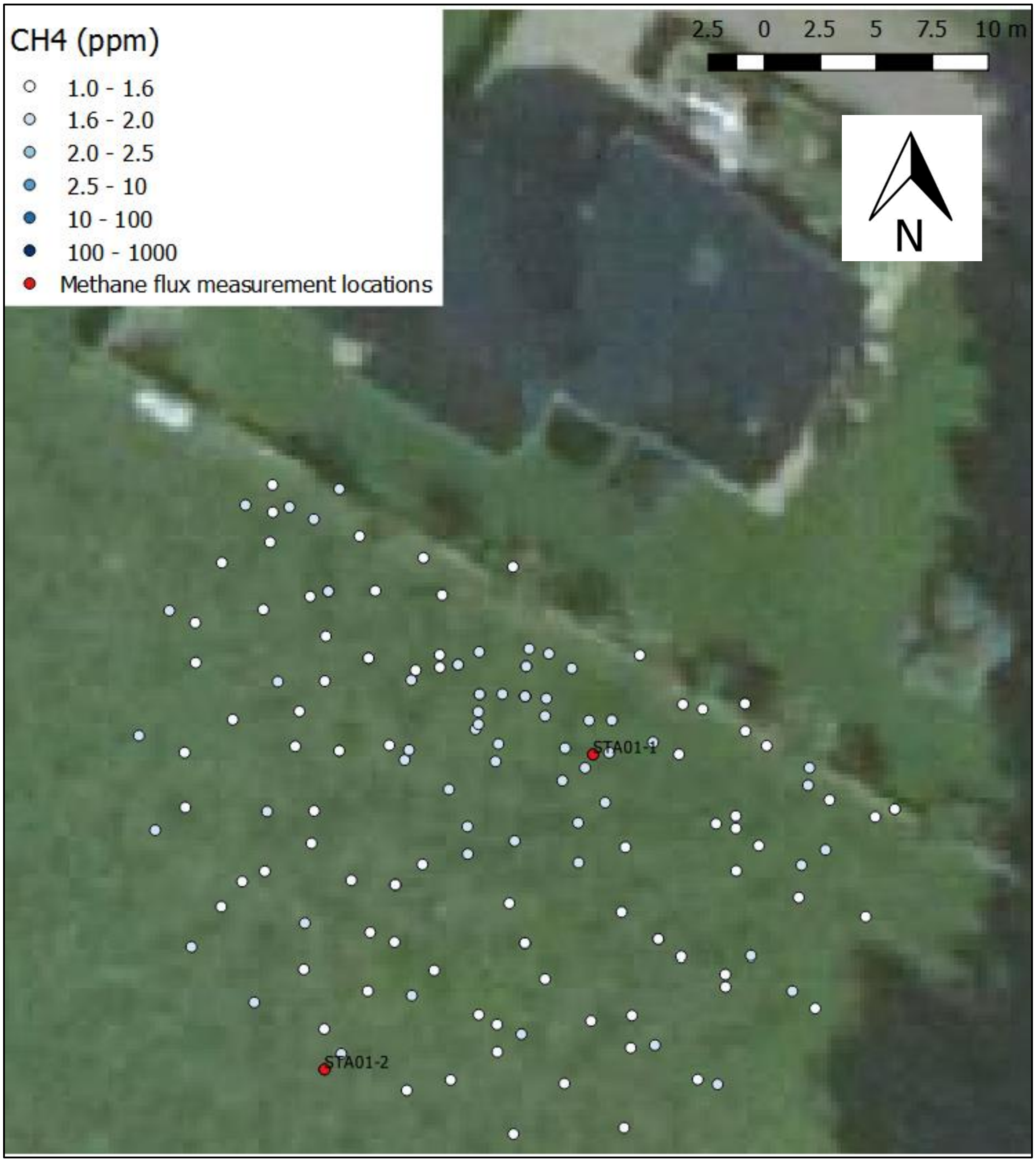
Appendix 18: Screening SOW-01



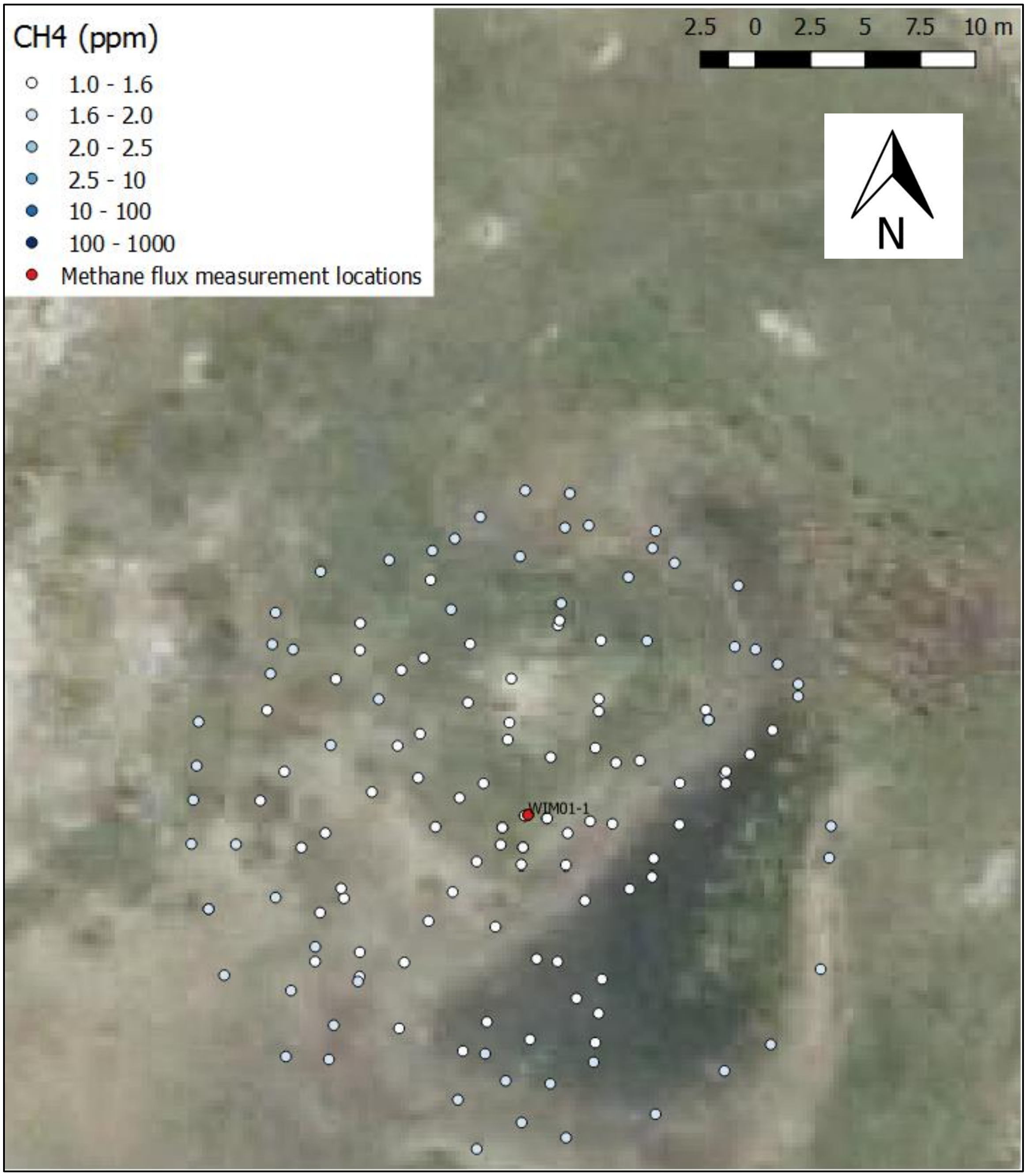
Appendix 19: Screening SPKW-01



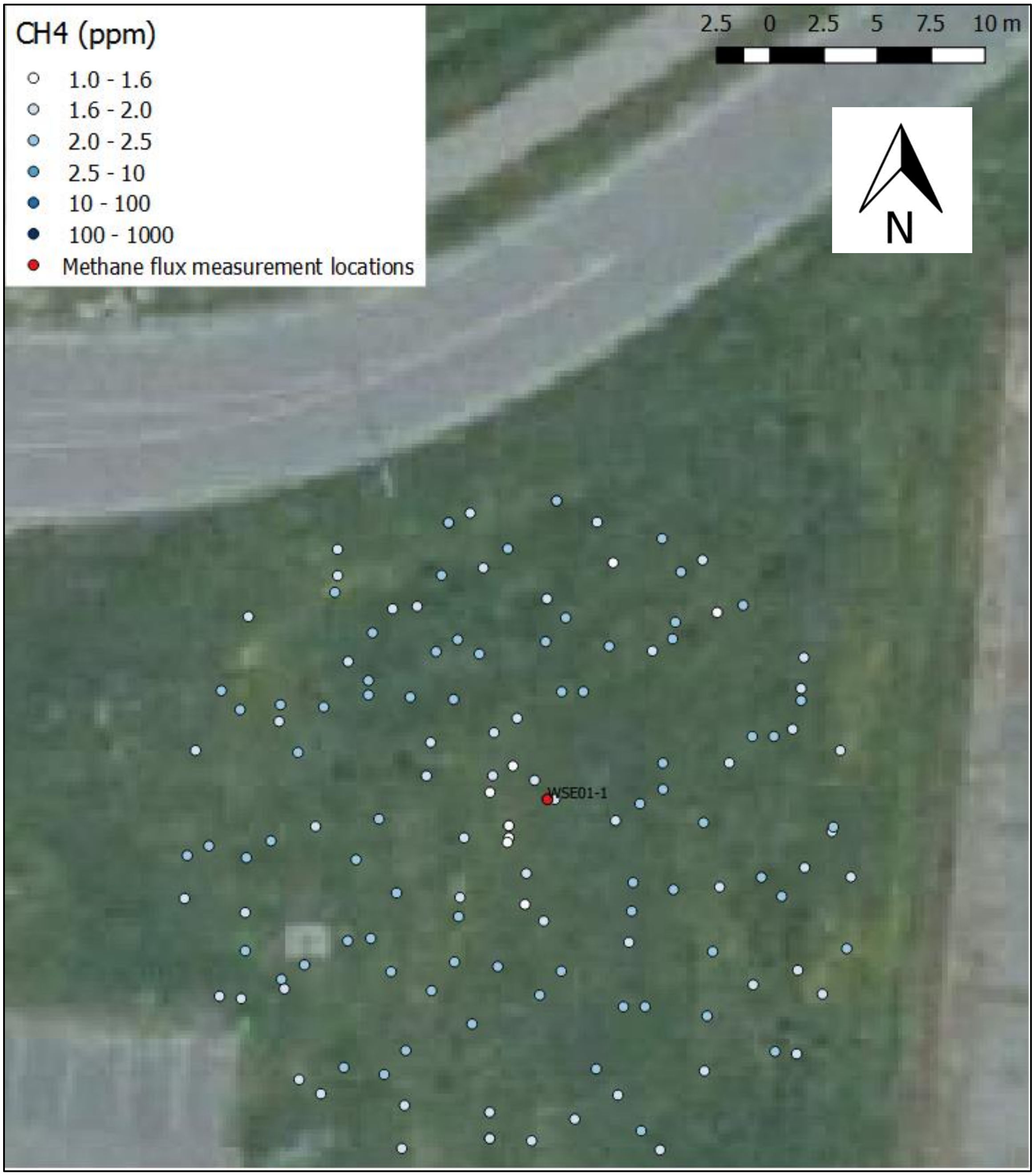
Appendix 20: Screening STA-01



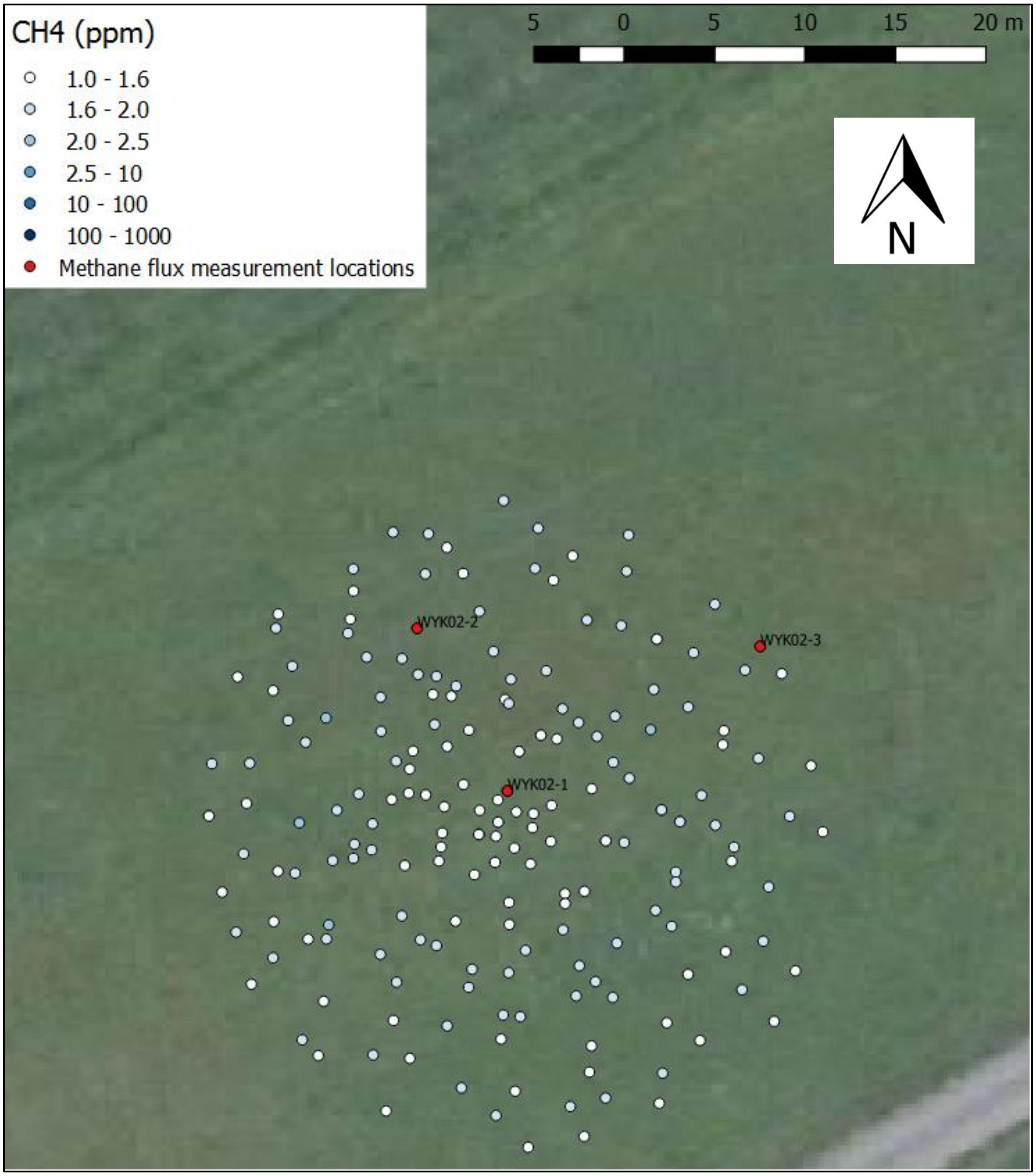
Appendix 21: Screening WIM-01



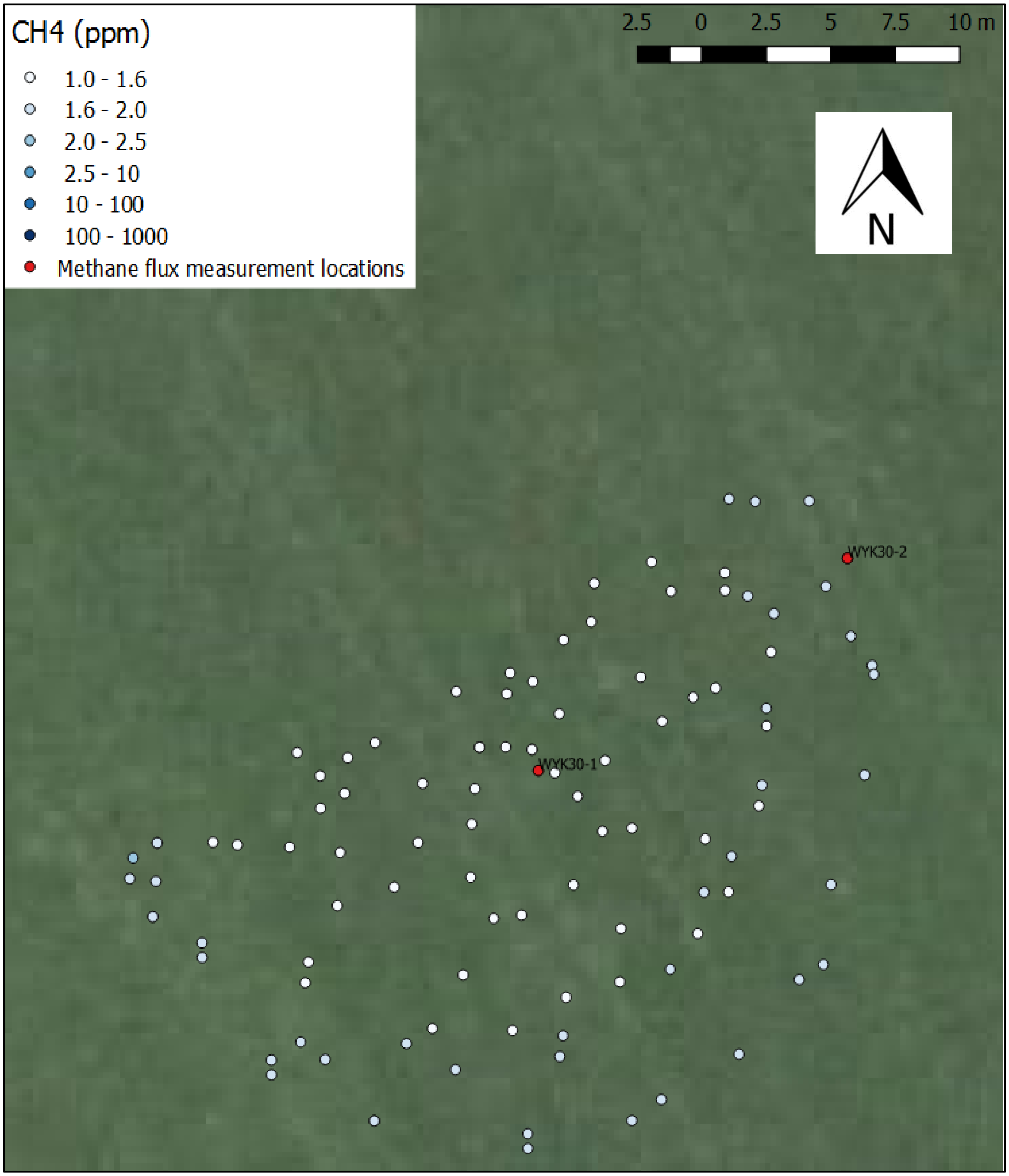
Appendix 22: Screening WSE-01



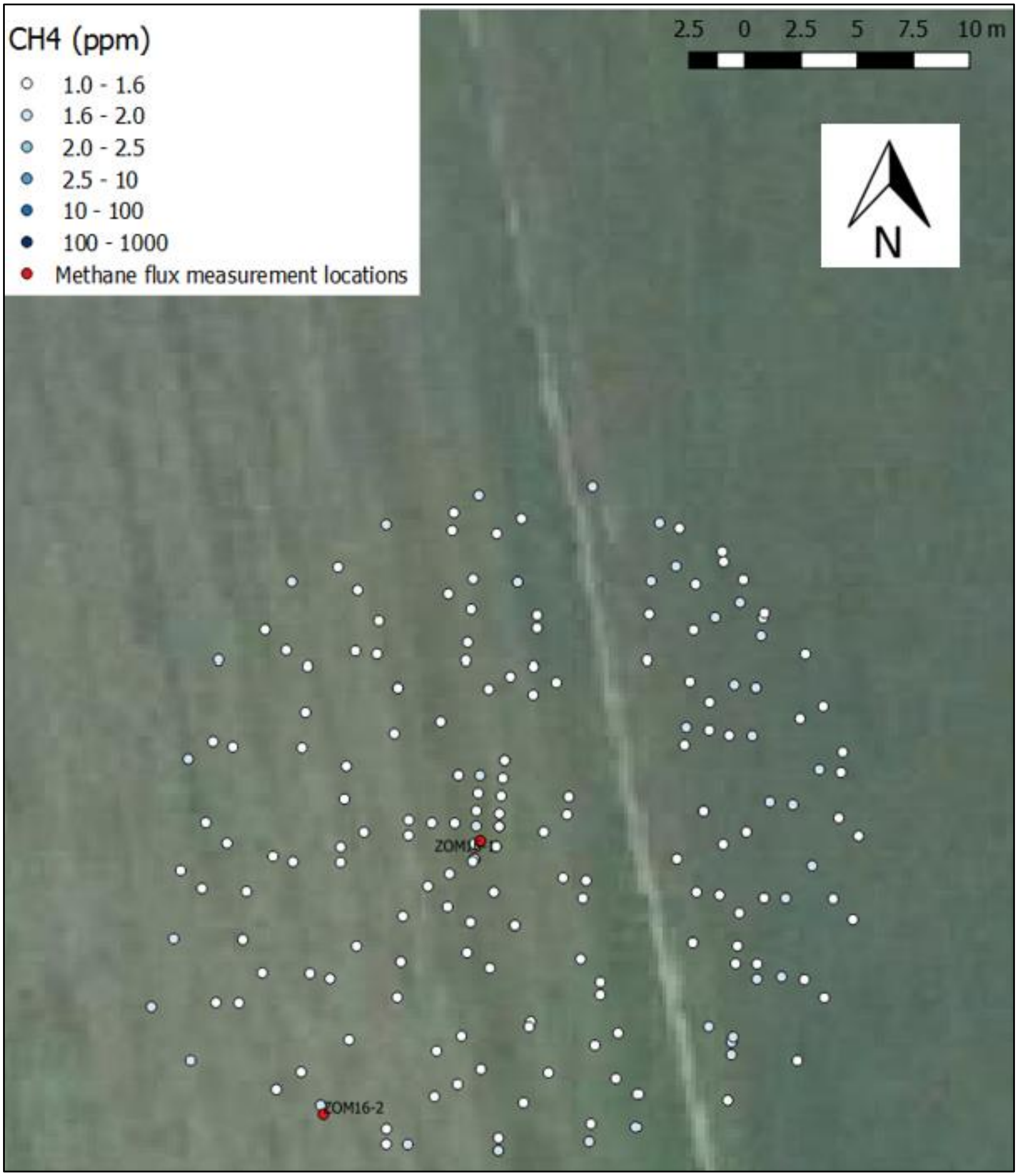
Appendix 23: Screening WYK-02



Appendix 24: Screening WYK-30



Appendix 25: Screening ZOM-16



Appendix 26: Information on the 29 well studied

Well name	X Rijksdriehoek	Y Rijksdriehoek	Starting Date	End date	Well purpose	Well status	Well shape	Lithostratigrafic code
AKM-01	194966	570782	11-05-1965	19-07-1965	Exploration of hydrocarbon	Abandoned	Vertical	DCCR
AKM-07	198039	569992	28-07-1977	04-09-1977	Development of hydrocarbon	Abandoned	Deviated	ZE
AKM-08	194977	570911	09-06-1977	24-07-1977	Development of hydrocarbon	Producing/Injecting	Deviated	ZE
AKM-10	198030	570011	08-05-1978	24-05-1978	Development of hydrocarbon	Technically failed and sidetracked	Deviated	N
AKM-13	191830	564543	12-01-1980	05-03-1980	Exploration of hydrocarbon	Abandoned	Vertical	DC
BER-01	106219	519289	03-12-1964	10-12-1964	Exploration of hydrocarbon	Abandoned	Vertical	NUCT
BHM-01	268161	568788	18-11-1971	20-03-1972	Exploration of hydrocarbon	Abandoned	Vertical	DCDT
COV-03	243376	518327	15-11-1949	19-09-1950	Development of hydrocarbon	Abandoned	Vertical	DCDT
EMC-01	268029	536284	04-04-1978	13-11-1978	Exploration of hydrocarbon	Unknown	Deviated	UNDEF
EXO-02	254409	547452	13-09-1972	31-10-1972	Exploration of hydrocarbon	Technically failed and sidetracked	Deviated	UNDEF
HLO-01	108710	510208	11-01-1965	20-03-1965	Exploration of hydrocarbon	Abandoned	Vertical	DC
KWK-01	140676	417615	27-06-1988	03-09-1988	Exploration of hydrocarbon	Abandoned	Deviated	DCDH
LED-02	87180	453807	09-10-1957	28-10-1957	Exploration of hydrocarbon	Abandoned	Vertical	SLDNR
MKN-01	188265	522539	19-06-1983	03-08-1983	Exploration of hydrocarbon	Abandoned	Deviated	DCCR
MON-02	71825	449956	09-03-1982	09-05-1982	Exploration of hydrocarbon	Abandoned	Deviated	RBSHR
NKK-01	102556	440363	08-08-1958	29-09-1958	Exploration of hydrocarbon	Abandoned	Vertical	ATWDM
OWD-01	215114	549778	11-11-1993	31-12-1993	Exploration of hydrocarbon	Abandoned	Deviated	DCCU
RWK-14	81586	448769	17-09-1956	02-11-1956	Development of hydrocarbon	Abandoned	Vertical	SLDNR
SGZ-01	68816	446222	15-11-1996	03-01-1997	Exploration of hydrocarbon	Technically failed and sidetracked	Deviated	UNDEF
SLN-02	253025	536090	02-11-1965	06-12-1965	Exploration of hydrocarbon	Abandoned	Vertical	RBMVC
SOW-01	195004	542398	23-12-1962	25-02-1963	Exploration of hydrocarbon	Abandoned	Vertical	DCCR
SPKW-01	80727	428571	11-07-1992	29-08-1992	Exploration of hydrocarbon	Abandoned	Deviated	RBMVU
STA-01	211342	514163	05-01-1950	03-03-1950	Exploration of hydrocarbon	Technically failed and sidetracked	Vertical	UNDEF
WAS-26	84832	458395	21-02-1961	28-02-1961	Development of hydrocarbon	Technically failed and sidetracked	Vertical	N
WIM-01	104051	516001	09-11-1963	01-02-1964	Exploration of hydrocarbon	Abandoned	Vertical	DC
WSE-01	172538	550566	13-03-1987	12-04-1987	Exploration of hydrocarbon	Abandoned	Vertical	DC
WYK-02	220334	525057	05-04-1951	10-06-1951	Exploration of hydrocarbon	Abandoned	Vertical	RNRO
WYK-30	214295	527490	09-04-1988	22-04-1988	Evaluation of hydrocarbon	Producing/Injecting	Vertical	RBSHM
ZOM-16	92594	455259	07-01-1965	02-02-1965	Development of hydrocarbon	Abandoned	Deviated	SLDNR