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**Dottoranda**

Dott.ssa Gioia Capelli Ghioldi

**Supervisore**

Prof. Franco Tassi

**Co-supervisore**

Dott. Giancarlo Tamburello

**Coordinatore**

Prof. Sandro Conticelli

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*And the secrets of the strange days will be one with the deep's secrets;  
one with the hidden lore of the old ocean,  
and all the mystery of primal earth.*

H.P. Lovecraft, The Colour Out of Space



# Abstract

This doctoral thesis presents an integrated geochemical and methodological analysis of Unusual Geological Phenomena (UGP) in the Emilia-Romagna region, Italy. UGP represents a broad set of naturally occurring geological manifestations, often linked to deep-seated fluid circulation and CH<sub>4</sub>-rich gas seepage. The research was driven by the necessity to improve understanding of the mechanisms governing the generation, migration, and near-surface transformation of natural CH<sub>4</sub> and CO<sub>2</sub> emissions, and to refine quantification techniques for effective environmental monitoring and the estimation of regional greenhouse gas budgets. The study was fundamentally aimed at moving beyond conventional, simplified models by acknowledging and characterising the intrinsically heterogeneous nature of these manifestations in compressional sedimentary settings, thereby outlining an inherently heterogeneous regional emission framework. The investigation spanned three distinct, representative UGP sites. At Santa Maria Nuova, the study focused on diffuse soil seepage, documenting elevated CH<sub>4</sub> and CO<sub>2</sub> fluxes in the upper range of published microseepage estimates. Isotopic evidence confirmed a shallow, microbially driven system, while the integration of remote sensing vegetation metrics with ground surveys successfully linked the observed spatial pattern of high fluxes, thermal anomalies, and persistently reduced vegetation indices to intense near-surface microbial oxidation processes, providing a unique link between the geochemical flux and the biosphere footprint. The Renazzo site, characterised by substantial CH<sub>4</sub> ebullition from a shallow, structurally focused well, presented the challenge of accurately quantifying high atmospheric CH<sub>4</sub> release where established chamber flux measurement methods are limited. This was addressed by comparing two complementary chamber configurations that converged on an order-of-magnitude estimate. Furthermore, a major methodological contribution was the development of a calibrated low-cost sensor network. An Artificial Neural Network (ANN) model was successfully employed to reproduce the non-linear response of metal-oxide sensors across the full range of CH<sub>4</sub> concentrations, resulting in a stable and robust system for characterising gas dispersion and resolving spatial gradients at a small footprint. Finally, the Salse di Nirano mud pools required a tailored approach to quantify CH<sub>4</sub>-dominated ebullition. To effectively resolve the highly episodic nature of the venting, a floating-chamber workflow was implemented, utilising an event-wise approach to decompose the time series into a persistent background and a highly variable burst component. This partitioning clarified the dynamics, revealing that the burst term accounts for most of the observed flux variability. Paired multiparameter records across mud pools showed synchronous variability, supporting the view that vent behaviour is primarily mediated by a common shallow driver, locally modulated by conduit efficiency.



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## Introduction

The release of gases from deep geological formations in sedimentary basins gives rise to a wide range of surface emissions. Since ancient times, these manifestations have been linked to health beliefs or religious cults, often regarded as sacred or therapeutic phenomena. It was only much later that they became the subject of scientific investigation, initially prompted by hydrocarbon exploration, and it is precisely to petroleum research that we owe much of the current understanding of gas reservoir formation, the structural conditions that enable gas entrapment, and the geological features that promote its migration towards the surface. Within petroleum geology, the term *seepage* refers explicitly to the natural escape of hydrocarbon-rich gases, predominantly methane ( $\text{CH}_4$ ), with lesser amounts of ethane ( $\text{C}_2\text{H}_6$ ), propane ( $\text{C}_3\text{H}_8$ ), and butane ( $\text{C}_4\text{H}_{10}$ ), originating from the microbial or thermal degradation of organic matter in source rocks. Minor quantities of non-hydrocarbon gases, such as carbon dioxide ( $\text{CO}_2$ ), nitrogen ( $\text{N}_2$ ), helium ( $\text{He}$ ), and hydrogen sulphide ( $\text{H}_2\text{S}$ ), are also commonly present. It is essential to distinguish this type of seepage from geothermal or volcanic gas emissions, which are typically dominated by  $\text{CO}_2$  and  $\text{H}_2\text{O}$  vapour, with only minor hydrocarbon components (Hunt, 1996; Etiope, 2015). After its formation, the accumulation of hydrocarbons into economically significant reservoirs requires the presence of structural or stratigraphic traps, geological configurations that inhibit further migration and allow gas to concentrate. Cap rocks, such as shales or evaporites, serve as seals, confining the gases within porous reservoir rocks. The long-term persistence of such accumulations is affected by factors such as subsidence, tectonic deformation, erosion and leakage. Structures formed by compressive tectonics, including folds, thrust faults, and fracture networks, critically influence fluid flow, acting both as conduits and barriers. Their structural complexity shapes not only gas accumulations but also their potential release, giving rise to phenomena such as punctual gas seeps, mud volcanoes, and diffuse soil degassing. These features are frequently observed near fault zones or intersections, where tectonic stress enhances permeability and facilitates vertical gas migration (Osborne and Swabrick, 1997). This body of knowledge has laid the foundation for more recent investigations focused on understanding the broader spectrum of gas-related phenomena. Scientific interest has progressively expanded to encompass environmental, biogeochemical, and geohazard implications of gas migration, including its interactions with groundwater, vegetation, and seismic activity.

In Italy, the distribution of hydrocarbon seeps and their associated subsurface reservoirs is mainly localised in the foreland and foothills regions of the Apennine chain, with a particularly dense concentration in the Po Valley. This extensive sedimentary basin, the largest in Italy, has acted as a long-lived depocentre for thick sequences of marine and continental sediments rich in organic matter. Over geological time, the structural and thermal conditions within the Po Valley have favoured the

generation, entrapment, and migration of CH<sub>4</sub>-rich fluids. Within this context, the Emilia-Romagna region, situated in the northern sector of the Apennine chain and foredeep, provides an exemplary setting for studying natural gas emissions. Decades of geochemical investigations, significantly advanced by hydrocarbon exploration and drilling activities led by major energy companies such as Agip and ENI, have enabled a comprehensive characterisation of gas occurrences in the Emilia-Romagna region. A seminal study by Mattavelli et al. (1983) was the first to systematically classify natural gases in the Po Basin and its surrounding areas into three main categories: biogenic, thermogenic, and mixed origin gases. Biogenic gases, which are predominant within the Pliocene–Pleistocene sedimentary cover of the Po Plain, are generated at shallow depths and low temperatures through microbial reduction of carbonates and organic matter. This process yields methane with a notably light isotopic signature ( $\delta^{13}\text{C}$ ), reflecting its microbial origin. In contrast, thermogenic gases are produced at greater depths as a result of the thermal maturation of organic matter and are typically associated with a suite of heavier hydrocarbons. These gases are mainly concentrated along the Apennine chain, where deep structural traps and migration pathways, shaped by compressive tectonics, facilitate their accumulation and eventual migration toward the surface (Tassi et al., 2012a). Mixed gases, exhibiting intermediate isotopic features, reflect contributions from both biogenic and thermogenic processes. Among other factors, the thick accumulation of Pliocene–Pleistocene turbiditic deposits, combined with synsedimentary tectonic deformation associated with the Apennine orogeny, has created conditions conducive to a hydrocarbon-prone environment. These geological phases, marked by alternating episodes of compression, folding, and faulting, have promoted the vertical migration of CH<sub>4</sub> and other deep-sourced fluids through permeable strata and fracture networks, leading to numerous surface manifestations that have been reported since historical times. These include: (i) gas bubbling in water wells; (ii) sudden increases in groundwater temperature; (iii) ground deformation and heating; (iv) rapid fluctuations in groundwater levels; (v) fish die-offs in small lakes and canals; and (vi) sand and mud volcanoes (Bonzi et al., 2017; Ricci et al., 2023). Many of these manifestations are persistent features, as exemplified by the Salse di Nirano mud volcano field, which are sustained over long periods by continuous or episodic fluid inputs from depth. Others, in contrast, are ephemeral, emerging abruptly and vanishing within days or weeks, likely indicative of temporary pressure equilibrium shifts or transient structural reactivations. In some cases, such events appear to correlate with seismic activity. For instance, recent studies have highlighted how earthquakes can trigger abrupt changes in groundwater levels and temperatures (Capaccioni et al., 2015), soil liquefaction (Sciarra et al., 2012), or increase soil gas concentrations (Sciarra et al., 2017). Seismic events can transiently enhance rock permeability, triggering the rapid ascent of subsurface fluids along fault lines and fractured sediments. Fluid migrations often manifest as *microseepage*, the

slow and diffuse release of gases, such as CH<sub>4</sub>, from the subsurface to the surface environment. Beyond representing a direct emission pathway to the atmosphere, microseepage plays a crucial role in shaping near-surface geochemical and ecological conditions. The diffusive flux of CH<sub>4</sub> through soils not only constitutes an emission source but also influences local vegetation growth by altering soil chemistry and oxygen availability in the root zone. Elevated CH<sub>4</sub> concentrations can inhibit plant development, leading to zones of vegetation stress or dieback coinciding with areas of enhanced gas flux. A well-documented example of this phenomenon is the Terre Calde di Medolla, where diffuse CH<sub>4</sub> emissions are linked to localised ground warming (Capaccioni et al., 2015). This warming arises from the exothermic oxidation of CH<sub>4</sub> by methanotrophic bacteria within the soil. As these microbes metabolise the gas, they release heat, increasing soil temperatures above ambient levels. Moreover, this bacterial oxidation generates a significant CO<sub>2</sub> flux from the soil, adding to the overall gas emissions and further disrupting ecosystem dynamics while complicating the local emission budget. This microbial activity thus serves not only as a geochemical indicator of active CH<sub>4</sub> seepage, but also as a driver of altered thermal, chemical and ecological conditions in natural gas emission sites. The natural gas manifestations described above, such as diffuse CH<sub>4</sub> emissions, soil warming, and episodic fluid releases, often raise concern among local populations. These phenomena are frequently associated with seismic activity, and the presence of flammable gas near the surface understandably generates fears related to explosivity and safety. Such apprehensions underscore the importance of enhancing our understanding and monitoring of these gas emissions, not only from a scientific perspective but also for risk assessment and effective public communication.

Within this broader framework, the primary aim of this PhD thesis is not to provide a complete characterisation of fluid emissions at a single location, but rather to test and improve a range of investigative techniques that can be effectively applied across various geological and environmental contexts. In many real-world situations, site-specific constraints, such as land access, human activity, or environmental conditions, can limit the use of specific monitoring or sampling methods. Therefore, the research intentionally focuses on multiple case studies, each presenting unique features and challenges, to build a more flexible framework for studying unusual gas manifestations and near-surface migration phenomena. This multi-site approach allows for the comparison of methods and results, as well as the identification of common geochemical and geophysical patterns across different structural environments within the Po Plain and Apennine foredeep system. The study covers three key areas in the Emilia-Romagna region:

**Santa Maria Nuova Spallicci (FC):** This site is characterised by the diffuse soil emission of CH<sub>4</sub> across an agricultural field. A two-year monitoring campaign enabled the identification of emission hotspots where secondary processes such as microbial methane oxidation occur, producing localised

ground heating due to the exothermic nature of the reaction. Additionally, satellite-based vegetation indices such as the Ratio Vegetation Index (RVI) were applied to detect and monitor the manifestation remotely. The observed CH<sub>4</sub> flux alters plant vitality, leading to detectable anomalies in vegetation cover, an approach that may prove helpful in identifying undetected emissions in comparable environments.

**Renazzo (FE):** At this site, continuous CH<sub>4</sub> bubbling from a private water well has been documented since at least the 1950s, suggesting a persistent and possibly long-term phenomenon. The research focused on testing two methods to estimate the CH<sub>4</sub> flux released from the well (expressed in kg d<sup>-1</sup>) and evaluating the spatial dispersion of gases in the surrounding area. This was achieved using low-cost air quality sensors capable of measuring CH<sub>4</sub> and CO<sub>2</sub> concentrations. To ensure data reliability, the sensors were calibrated against reference-grade instrumentation, and a machine learning model based on artificial neural networks was developed to enhance the calibration process.

**Salse di Nirano (MO):** The Salse di Nirano mud volcano field offers a natural laboratory for investigating deep gas transport and transient fluid recharge events. A multiparametric probe measuring temperature, electrical conductivity, and mud level was installed in a CH<sub>4</sub>-bubbling mud pool to monitor temporal changes. A year-long dataset yielded a high-resolution time series that was benchmarked against a second mud pool aligned along the major structural axes of the complex. To quantify gas release, a floating extension for an accumulation chamber was deployed on four representative pools, and CH<sub>4</sub> and CO<sub>2</sub> fluxes were derived using two complementary approaches: (i) an end-to-end method based on linear concentration increase; and (ii) an event-based decomposition that treats bubbling as discrete bursts. The burst framework provided not only fluxes (separating burst and slowly varying background components) but also descriptors of degassing dynamics, including the burst frequency ( $\lambda$ , min<sup>-1</sup>) and the mean mass per burst ( $\bar{m}$ , g).

The study of these three sites reflects the complexity and heterogeneity of natural CH<sub>4</sub> emissions across geological settings. Each location is embedded in a distinct tectono-stratigraphic framework shaped by the geodynamic evolution of the Northern Apennines and the long-term subsidence history of the Po Basin. This diversity is critical for understanding how different fluid migration mechanisms interact with shallow stratigraphy, local fault networks, and surface processes. Importantly, these case studies underline the relevance of assessing natural CH<sub>4</sub> sources, which are often underrepresented in global emission inventories. The presence of sedimentary basins worldwide makes the processes observed here not only scientifically significant but also potentially common. Therefore, the methodological approaches developed in this research, spanning geochemical surveys, remote sensing, continuous monitoring, and machine learning-assisted flux estimation, can serve as flexible tools for other regions facing similar fluid emission phenomena.

Furthermore, the episodic nature and spatial unpredictability of gas release events underscore the challenges of identifying active sources and integrating them into the global methane budget. These uncertainties hinder accurate quantification of geological emissions and complicate the evaluation of their role in climate change.

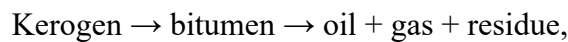
# Chapter I - Methane and Associated Gases in Sedimentary Basins

## *1.1 Origin of Hydrocarbons in Sedimentary Basins*

Gases present in sedimentary basins originate from a combination of organic and inorganic processes, driven by the progressive burial of material under increasing temperature and pressure over geological timescales. These processes include the thermal breakdown of organic matter, as well as chemical and microbial reactions, resulting in the formation of a wide spectrum of gaseous species. Among these, hydrocarbons represent a key group of compounds, organic molecules consisting solely of carbon (C) and hydrogen (H), covering a wide variety of molecular sizes and physical states. Deep hydrocarbons encompass a variety of organic constituents found in petroleum systems, including oil and gas in porous reservoirs, solid bitumen in oil sands, coal deposits, and clathrate hydrates (Tissot and Welte, 1984). The main gaseous hydrocarbons in organic geochemistry are classified as alkanes (saturated), like methane ( $\text{CH}_4$ ), ethane ( $\text{C}_2\text{H}_6$ ), propane ( $\text{C}_3\text{H}_8$ ), and butane ( $\text{C}_4\text{H}_{10}$ ); alkenes (unsaturated), cycloalkanes, and aromatic compounds. The liquid component of petroleum is a complex mixture of linear, branched, and cyclic hydrocarbons, primarily ranging from  $\text{C}_5$  to  $\text{C}_{17}$  in carbon chain length. The solid phase, on the other hand, mainly consists of heavier compounds, such as paraffin waxes, typically with carbon chain lengths from  $\text{C}_{18}$  to  $\text{C}_{40}$ . The vast structural diversity of hydrocarbons (and of many other organic and inorganic compounds in sedimentary basins) stems from carbon's remarkable chemical versatility, as it forms strong covalent bonds with itself and with other elements, enabling the formation of stable chains, rings, and complex frameworks. Importantly, carbon can occur in various oxidation states, ranging from highly reduced forms like  $\text{CH}_4$  to fully oxidised compounds such as carbon dioxide ( $\text{CO}_2$ ), highlighting its central role in both geochemical and biological cycles.

The origin of deep-seated hydrocarbons in the Earth's crust is predominantly linked to the long-term transformation of organic matter (OM). Unlike pure chemical compounds, natural OM lacks a well-defined molecular formula, as it represents a heterogeneous mixture of biomolecules derived from different biological sources. The main building blocks of life are carbohydrates, proteins, lipids (fats), and lignin, each primarily composed of C, H, oxygen (O), nitrogen (N), and sulphur (S). These biogenic macromolecules differ in structure and elemental composition; for example, carbohydrates and lignin are rich in oxygen-containing functional groups, lipids are predominantly hydrocarbons with few heteroatoms, while proteins contain notable amounts of N and S (Tissot and Welte, 1984; Hunt, 1996). As these organic materials are buried and subjected to increasing temperature and

pressure over geological time, their elemental constituents are gradually transformed, resulting in a broad spectrum of gaseous and liquid hydrocarbons, as well as other diagenetic compound products. The formation of hydrocarbon gases in sedimentary basins begins with the accumulation and burial of OM, mainly derived from marine and terrestrial organisms. This initial phase establishes the basis for a series of complex thermal and chemical transformations that ultimately produce kerogen, a term for organic matter found within sedimentary rocks. Kerogen is a complex, high-molecular-weight, insoluble organic macromolecule, formed from the degradation and recondensation of biological precursors during early diagenesis. Its heterogeneous and polymeric nature reflects the diversity of its biological origins and depositional environments. During thermal maturation under progressive burial, kerogen decomposes in high-temperature pyrolysis reactions to form lower-molecular-weight products, resulting in the following simplified reaction:



where bitumen is defined as the non-volatile organic matter soluble in organic solvents formed during initial heating. Kerogens are classified as Types I, II, III, and IV, based on their elemental composition, particularly the relative abundances of C, H, and O. These differences are commonly expressed through atomic ratios, such as H/C and O/C, which are widely used to define the compositional fields of each kerogen type on Van Krevelen diagrams (Fig. 1.1).

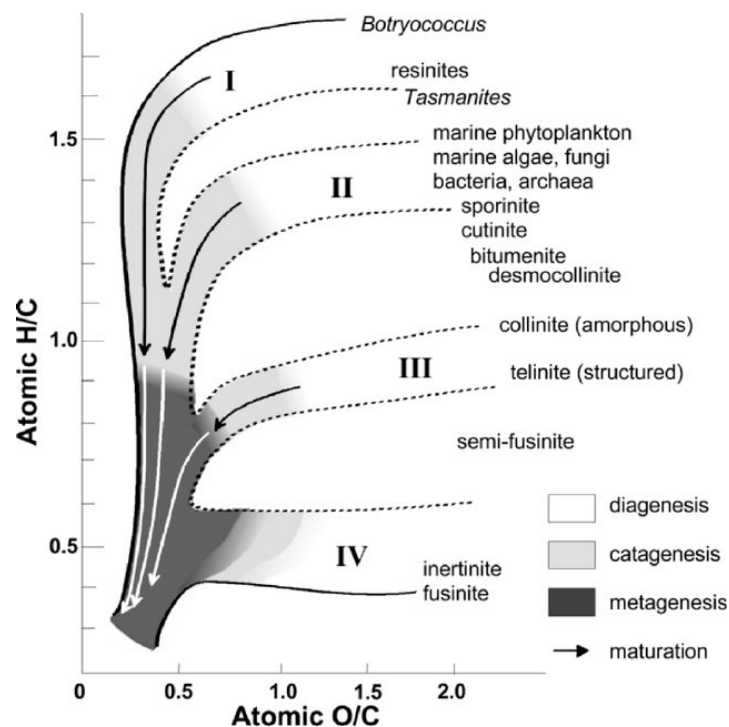


Figure 1.1. van Krevelen type diagram showing the distribution of kerogen types and some of their precursor macerals in relationship to their H/C and O/C atomic ratios (Walters, 2006). The diagram also indicates representative biological precursors.

Types I and II, which are richer in H and poorer in O, generate most of the world's oil; Type III, characterized by lower H/C and higher O/C ratios, generates primarily gas, condensates, and some waxy oil; while Type IV, with very low hydrogen content and high oxygen levels, is essentially inert and generates only minor amounts of CH<sub>4</sub> and CO<sub>2</sub> (Hunt, 1996). These atomic ratios reflect the differences in biological precursors: Type I is predominantly derived from lipid-rich algal material deposited in anoxic lacustrine environments; Type II originates from a mix of marine plankton and bacterial debris; Type III is mainly formed from terrestrial plant material rich in cellulose and lignin (humic substances); and Type IV consists of highly oxidised, inert organic matter with minimal hydrocarbon potential (Tissot and Welte, 1984; Peters and Cassa, 1994; Hunt, 1996). With progressive burial, kerogen is subjected to increasing temperature and pressure, which drive its transformation through three main stages: diagenesis (<50–60 °C), where microbial and early chemical alterations lead to kerogen formation; catagenesis (60–150 °C), the main window for oil and wet gas generation through the thermal cracking of kerogen; and metagenesis (>150 °C), where residual kerogen and bitumen break down further, yielding dry gas (primarily CH<sub>4</sub>) and residual carbon-rich material (Fig. 1.2). The transition from catagenesis to metagenesis also marks the lower threshold of metamorphism, beyond which organic matter is converted into graphite-like structures and hydrocarbon generation ceases.

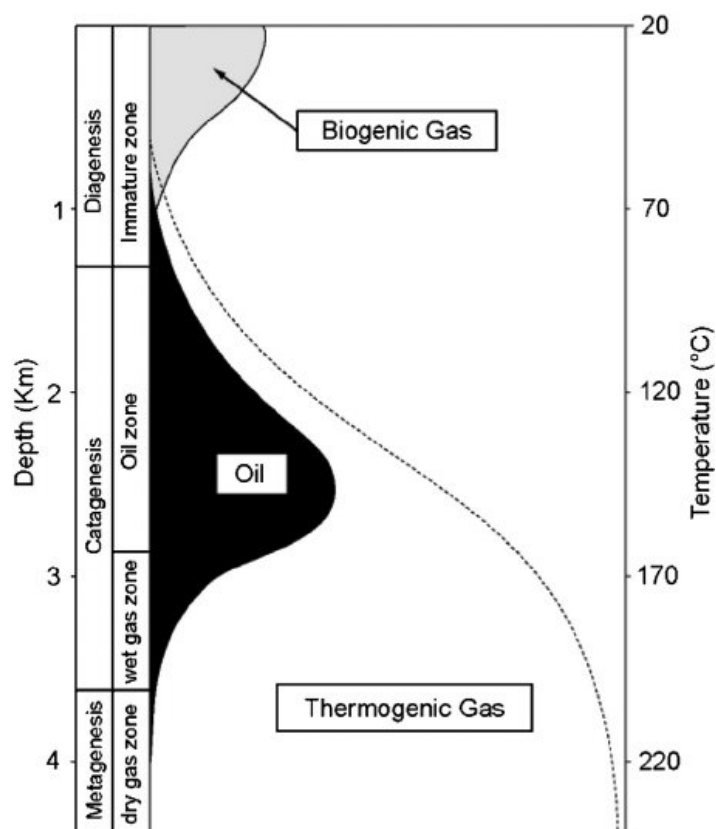
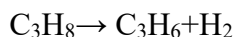
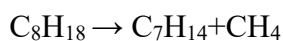


Figure 1.2. Scheme of thermal evolution of organic matter during burial (Meslé et al., 2013).



### 1.1.1 Thermogenic CH<sub>4</sub> Generation

Typically, a gas reservoir contains 70 to 100% CH<sub>4</sub>, 1 to 10% C<sub>2</sub>H<sub>6</sub>, and lower percentages of higher hydrocarbons up to hexanes, along with traces of nonanes (C<sub>9</sub>H<sub>20</sub>). As the primary component of natural gas, CH<sub>4</sub> consists of a single carbon atom bonded to four hydrogen atoms in a tetrahedral structure, making it the most chemically stable, lightest, and most volatile of the alkanes, thus representing the simplest end-member of a broader spectrum of hydrocarbons. Typically formed during the late stages of catagenesis and throughout metagenesis (>150°C), the primary chemical processes involved in thermogenic CH<sub>4</sub> generation are thermal cracking and catalytic reforming, both of which result in the degradation of complex organic compounds into simpler gaseous hydrocarbons. Thermal cracking involves the progressive breaking of molecular bonds, particularly carbon-carbon (C–C) and carbon-hydrogen (C–H) bonds, as the temperature and pressure increase with depth. Depending on the precursor material, thermal cracking is classified into *primary cracking*, when CH<sub>4</sub> is generated directly from solid OM such as kerogen (all types) and coal, and *secondary cracking*, which refers to the breakdown of liquid hydrocarbons like oil, present in source and reservoir rocks, into lighter gaseous components (Hunt, 1996). The mechanisms involved are well illustrated by two representative reactions reported by Capaccioni et al. (1993):



The first reaction, involving the rupture of a C–C bond, prevails during thermal cracking of high molecular weight hydrocarbons, while the second, involving a C–H bond, occurs preferentially when lighter hydrocarbons represent the starting material. These processes are central to the progressive enrichment of gas over oil in mature petroleum systems, as methane remains stable up to high temperatures (1030°C; Guéret et al., 1997). Rather than temperature or pressure alone, the presence of catalytic agents plays a significant role in the reforming generation of CH<sub>4</sub>. Catalytic agents are substances that increase the rate of a chemical reaction by lowering the activation energy required for the reaction to proceed. By providing an alternative reaction pathway with reduced energy barriers, catalysts enable reactions to occur more rapidly and at lower temperatures than would otherwise be possible. The concept of hydrocarbon catalytic reforming was initially developed and applied within the petroleum industry, optimised for fuel production, where processes employ catalysts such as platinum, rhenium, and other transition metals supported on alumina to facilitate key reactions, including dehydrocyclisation, isomerisation, and hydrogen transfer. These industrial catalysts enable the transformation of heavy hydrocarbons into lighter, high-value products such as high-octane

gasoline and hydrogen, typically under temperatures ranging from 450 to 550 °C (Speight, 2014). Only later were analogous catalytic effects investigated in natural systems, where minerals can play a comparable role.

In natural environments, the presence of clays (e.g., smectite, illite), metal oxides, and sulphides can activate catalytic reforming reactions (Hunt, 1979; Capaccioni et al, 1995). These mineral surfaces provide active sites that promote hydrogen transfer reactions, as dehydrogenation and isomerisation, thereby enhancing the breakdown of complex organic molecules into simpler gases at temperatures lower than those needed for purely thermal reactions, typically between 150 and 350°C, where catalytic reforming processes dominate the generation of organic gases in sedimentary basins (Capaccioni et al., 1995). An example of a catalytic reforming reaction is the metathesis of C<sub>2</sub>H<sub>6</sub>, described by Mango et al. (2009) as:



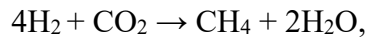
The observation that thermodynamic equilibrium is achieved among light hydrocarbons at moderate temperatures supports the predominance of catalytic reforming processes in natural gas generation (Mango et al., 2009). Complementing field remarks, laboratory experiments by Wei et al. (2018) demonstrated that heating kerogen-containing rocks at relatively low temperatures (60-100 °C) over extended periods can generate substantial amounts of CH<sub>4</sub>, alongside minor quantities of C<sub>2</sub>–C<sub>3</sub> alkanes. The CH<sub>4</sub> yields observed were several orders of magnitude higher than those predicted by traditional kinetic models, strongly suggesting that catalytic methanogenesis contributes significantly to natural gas formation even at temperatures well below the typical thermal cracking window. Clearly, the process is governed by the availability of natural catalysts, geothermal gradients, and the composition of the organic substrate.

### *1.1.2 Microbial CH<sub>4</sub> production*

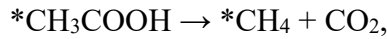
While the above-mentioned chemical processes dominate at higher temperatures and greater depths, an equally significant source of methane is microbial activity. Biogenic pathways primarily occur at shallow depths and low-temperature conditions and are carried out by methanogenic archaea, anaerobic organisms that depend on organic carbon as an electron donor to drive their metabolism. It is necessary to clarify, however, that in the literature, the term biogenic is commonly used to describe microbial CH<sub>4</sub> formed in near-surface environments. However, since all CH<sub>4</sub> derived from organic matter can technically be considered biogenic, it is more appropriate to refer specifically to *bacterial* or *microbial* CH<sub>4</sub> when indicating low-temperature production by methanogenic microorganisms.

This process primarily occurs in the water column or sediments, mainly under low-oxygen, reductive conditions ( $E_h < 200$  mV; Whiticar, 1999), and is the outcome of a complex network of microbial activities involving both syntrophic interactions and competition for key substrates (Bridgham et al., 2013). Methanogens rely on fermentation end products such as  $H_2$ ,  $CO_2$  and acetate, which are also consumed by other microbial groups that reduce inorganic terminal electron acceptors (TEAs), including nitrate ( $NO_3^-$ ), Fe (III), Mn (III/IV), and sulphate.

The relative importance of these metabolic pathways is governed by their thermodynamic favourability, with denitrification, iron and manganese reduction, and especially sulphate reduction generally outcompeting methanogenesis until these TEAs are depleted (Meronigal et al., 2004). As a result, sulphate reduction frequently suppresses  $CH_4$  production in brackish and saline environments due to the continuous supply of  $SO_4^{2-}$ . Bacterial  $CH_4$  is generated through both “carbonate reduction” and acetate fermentation, with the hydrogenotrophic reaction being a primary route



where  $CO_2$  is related to dissolved bicarbonate in water. Under anoxic conditions, fermentative bacteria decompose organic matter, producing hydrogen and  $CO_2$ . Initially,  $H$  is consumed by sulphate reducers, but once sulphate is depleted, methanogenesis becomes the dominant pathway. The net reaction for the acetate fermentation pathway is



where \* indicates the intact transfer of the methyl position to  $CH_4$  (Whiticar, 1999). In depositional environments, methanogenesis is most commonly associated in sand-shale sequences rich in continental (type III) OM and restricted to the upper ~1000 m of sediment, above which thermogenic processes begin to dominate and temperatures exceed  $50^\circ C$  (Law and Rice, 1993). The extent to which microbially produced  $CH_4$  accumulates in aquatic sediments largely depends on the sedimentation rate: in rapidly accumulating sediments,  $CH_4$  can be trapped and preserved, whereas in environments with slower sedimentation, it is more likely to be released to the overlying water or atmosphere through diffusion, ebullition (bubble transport), or advection.

The most widely accepted method for distinguishing between  $CH_4$  production processes is through the analysis of its isotopic composition, particularly the stable carbon ( $\delta^{13}C$ ) and hydrogen ( $\delta D$ ) signatures. Both are expressed via the standard  $\delta$ -notation, which quantifies the relative difference in isotope ratios between a sample and an internationally recognised standard, defined as:

$$\delta_x(\text{‰}) = \left[ \left( \frac{(R_x)_{\text{sample}}}{(R_x)_{\text{standard}}} \right) - 1 \right] \times 1000,$$

where for C isotopes, the standard is Vienna Pee Dee Belemnite (VPDB), while for H isotopes, the standard is Vienna Standard Mean Ocean Water (VSMOW).

During microbial methanogenesis, particularly via the  $\text{CO}_2$  reduction pathway, methanogenic archaea preferentially utilise lighter isotopes,  $^{12}\text{C}$  over  $^{13}\text{C}$  and  $^1\text{H}$  over deuterium ( $^2\text{H}$  or  $\text{D}$ ). This results in  $\text{CH}_4$  that is strongly depleted in heavy isotopes. Depending on the isotopic composition of the original substrate, microbially produced methane can exhibit  $\delta^{13}\text{C}$  values as low as  $-109\text{‰}$  V-PDB, and  $\delta\text{D}$  values around  $-250\text{‰}$  V-SMOW (Schoell, 1988). These signatures are typically associated with low-temperature, biologically mediated processes and differ markedly from those typical of thermogenic methane, which tends to be enriched in heavier isotopes due to less pronounced fractionation processes during high-temperature formation.  $\delta^{13}\text{C}$  values for thermogenic  $\text{CH}_4$  generally range between  $-50\text{‰}$  to  $-20\text{‰}$  V-PDB, while  $\delta\text{D}$  values fall approximately between  $-275\text{‰}$  to  $-100\text{‰}$  V-SMOW. The progressive enrichment in  $^{13}\text{C}$  is linked to the increasing maturity of the gas, gradually approaching the  $^{13}\text{C}/^{12}\text{C}$  ratio of the original OM kerogen. However, the isotopic signature of  $\text{CH}_4$  can be significantly altered by various post-genetic processes such as mixing between gases of different origins, secondary microbial modification, partial oxidation, and especially migration through the subsurface, where isotopic fractionation may occur due to diffusion or sorption effects. Methane associated with oil in petroleum reservoirs, for example, often exhibits intermediate isotopic values. Many authors report  $\delta^{13}\text{C}$  and  $\delta\text{D}$  values around  $-60\text{‰}$  and  $-200\text{‰}$ , respectively, indicating mixing between thermogenic and microbial end-members within the reservoir (Schoell, 1988). This isotopic variability is often shown in  $\delta^{13}\text{C}$  vs  $\delta\text{D}$  plots, where genetic fields help differentiate  $\text{CH}_4$  of microbial, thermogenic, and mixed origin (Fig. 1.3).

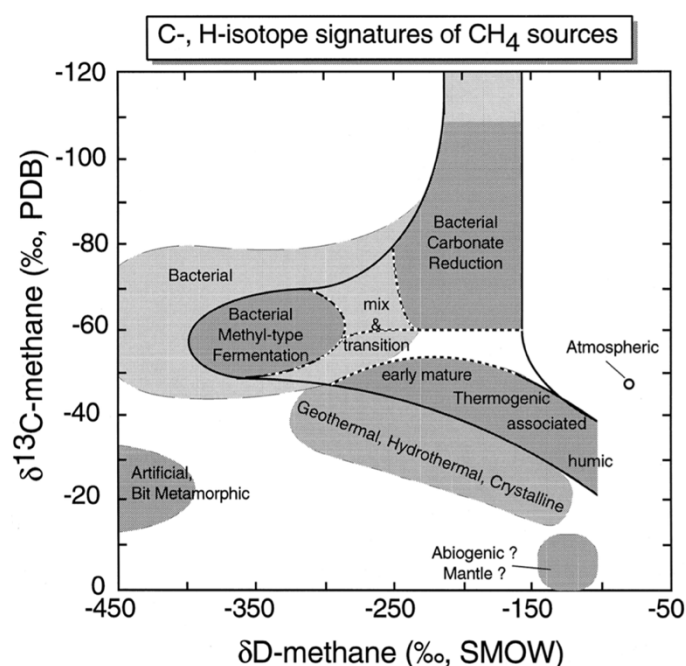
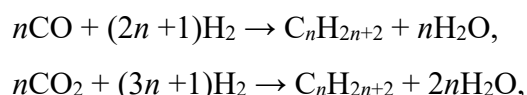


Figure 1.3. CD-diagram for classification of bacterial and thermogenic natural gas by the combination of  $\delta^{13}\text{C}$  and  $\delta\text{D}$  information (Whiticar, 1999).

### 1.1.3 Abiotic CH<sub>4</sub>

Besides being generated through the thermal or bacterial decomposition of organic matter, CH<sub>4</sub> can also be produced abiotically in various geological environments, particularly those associated with high temperatures and reducing conditions, such as volcanic and hydrothermal systems. A major abiotic pathway is represented by Fischer–Tropsch-type (FTT) reactions, in which carbon monoxide (CO) or CO<sub>2</sub> reacts with H<sub>2</sub> in the presence of metal catalysts such as iron (Fe), nickel (Ni) and cobalt (Co). The generalised FTT reactions can be represented as:



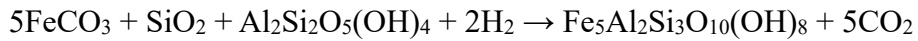
where  $n$  denotes the number of C atoms in the hydrocarbon chain (McCollom and Seewald, 2007; Etiope and Sherwood Lollar, 2013). Another well-established mechanism for abiotic CH<sub>4</sub> production is serpentinisation, a hydrothermal alteration process involving the interaction of ultramafic rocks rich in olivine with water under reducing conditions. This reaction leads to the oxidation of ferrous iron in olivine, generating H<sub>2</sub>, which can then reduce inorganic carbon species (CO or CO<sub>2</sub>) to form methane. Serpentinisation-derived CH<sub>4</sub> is commonly found in environments such as ophiolite complexes and mid-ocean ridges, where these reactions contribute significantly to the observed gas fluxes (Klein et al., 2019; McCollom and Seewald, 2013). Abiotic methane can be distinguished from microbial and thermogenic methane by its isotopic signatures and molecular composition of the mixture, often exhibiting heavy  $\delta^{13}\text{C}$  and  $\delta\text{D}$  values, and distinct hydrocarbon gas ratios (Etiope and Sherwood Lollar, 2013). Evidence for abiotic CH<sub>4</sub> has been increasingly documented across a broad spectrum of geological settings. Methane and other light hydrocarbons consistent with abiotic origins have been identified in submarine hydrothermal vents, deep-seated fracture networks within both continental and oceanic crystalline rocks, volcanic emissions, and natural gas seeps associated with serpentinised lithologies (e.g., Abrajano et al., 1990; Sherwood Lollar et al., 2002, 2008; Proskurowski et al., 2008; Etiope et al., 2018).

## 1.2. Nonhydrocarbon Constituents in Sedimentary Basins

Nonhydrocarbon gases, including CO<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>S, H<sub>2</sub>, and He, are significant components of natural gas accumulations in sedimentary basins. Their concentrations can range widely from trace amounts to nearly 100%, depending on geological context and depth. These gases originate from a variety of organic and inorganic processes, reflecting complex geochemical interactions within the subsurface.

In natural reservoirs, CO<sub>2</sub> exhibits an erratic distribution due to its multiple sources, high solubility in formation waters, and chemical reactivity. The main origins of CO<sub>2</sub> in sedimentary basins include: (i) Thermal degradation of organic matter during diagenesis and catagenesis, predominantly from continental humic material, which typically completes by the end of the oil window (Hunt, 1996).

(ii) Inorganic reactions such as the dissolution of carbonates or alteration of minerals like kaolinite, leading to CO<sub>2</sub> generation. A representative reaction (Hutcheon and Abercrombie, 1990) is:



(iii) Deep degassing from mantle or volcanic sources, including both CO<sub>2</sub>-bearing magmas and carbonate thermal decomposition in magmatic intrusions (Walker et al., 1981).

CO<sub>2</sub> concentrations tend to increase with depth due to enhanced thermal and mineralogical processes (Ceriotti et al., 2017). Additional minor contributions may derive from meteoric infiltration and atmospheric CO<sub>2</sub> dissolution at shallow levels. The isotopic composition  $\delta^{13}\text{C}$  helps distinguish thermogenic CO<sub>2</sub> from OM, which tends to be more depleted in <sup>13</sup>C compared to CO<sub>2</sub> from carbonate decomposition, while bacterial oxidation of CH<sub>4</sub> may produce CO<sub>2</sub> with highly variable  $\delta^{13}\text{C}$  values, depending on the  $\delta^{13}\text{C}$  of the CH<sub>4</sub> precursor (Whiticar, 1999; Miller et al., 2018).

Nitrogen in subsurface systems also originates from various sources, including atmospheric incorporation, mantle outgassing, and in situ generation through the oxidation of ammonia (NH<sub>3</sub>) dissolved in pore waters (Krooss et al., 1995). NH<sub>3</sub>, commonly present in basin waters, may be oxidised by contact with heavy metal oxides or oxygen-rich meteoric fluids. Nitrogen-rich gases are also found occluded in igneous rocks, indicating contributions from the mantle. Additional N<sub>2</sub> derives from the thermal breakdown of organic nitrogen compounds such as amino acids and proteins present in source rocks, as well as from atmospheric nitrogen trapped during sediment deposition. Contributions from deeper crustal sources also add to the nitrogen content, with isotopic signatures of nitrogen ( $\delta^{15}\text{N}$ ) used to discriminate its origin (Rosman and Taylor, 1998). The quantity and isotopic composition of N<sub>2</sub> ( $\delta^{15}\text{N}$ ) are often used to infer both organic and inorganic origins. However, relying solely on the isotopic ratio of a single element may be insufficient, and it is necessary to incorporate additional geochemical indicators, considering the redox conditions and thermal maturity of the source rock, which can significantly affect N<sub>2</sub> generation (Xiaobo et al., 2021). H<sub>2</sub>S in hydrocarbon reservoirs primarily forms through bacterial sulphate reduction (BSR) in anoxic environments, where sulphate-reducing microorganisms reduce SO<sub>4</sub><sup>2-</sup> while decomposing organic matter (Orr, 1974; Machel et al., 1995). This biological process operates at relatively low temperatures, typically below 80°C, and generally produces modest H<sub>2</sub>S concentrations. The activity of BSR can be enhanced under conditions such as water injection, which stimulates microbial

sulphate reduction and increases H<sub>2</sub>S levels (Cavallaro et al., 2007; Hosseiny et al., 2016). At elevated temperatures, typically above 120–150°C, thermochemical sulphate reduction (TSR) becomes the dominant mechanism, converting sulphate minerals into H<sub>2</sub>S through abiotic reactions with hydrocarbons or organic-rich components. TSR is especially prevalent in evaporitic or highly saline formations, such as carbonate reservoirs containing anhydrite, and can generate substantially higher concentrations of H<sub>2</sub>S (Nederlof et al., 2016). Additionally, H<sub>2</sub>S may be liberated by the direct thermal decomposition of organically bound sulphur in kerogen, oil, and bitumen during thermal maturation (Orr, 1974).

Due to its small molecular size and high reactivity, H<sub>2</sub> rarely accumulates in reservoirs but indicates active generation or diffusion from deeper sources. It is produced chiefly through water-rock interactions, especially serpentinisation processes where ferrous minerals oxidise and release H<sub>2</sub>, as well as through radiolysis, the radiogenic splitting of water molecules induced by natural radioactivity in volcanic or crystalline basement rocks (Lollar et al., 2006). It can also form during high-temperature organic matter maturation or migrate from mantle-derived fluids in structurally active zones (Ware et al., 1984; Toutain and Baubron, 1999). Finally, He, a noble gas, accumulates predominantly from radiogenic decay of uranium and thorium within the crustal rocks, gradually diffusing and migrating into sedimentary reservoirs, with its abundance controlled by the uranium-thorium content and the structural permeability of the basin. Minor mantle helium inputs can sometimes be distinguished based on isotopic ratios, specifically, <sup>4</sup>He originates from radioactive decay in the crust, while <sup>3</sup>He is sourced from the mantle. Consequently, low <sup>3</sup>He/<sup>4</sup>He ratios of about 10<sup>-8</sup> indicate a crustal origin, whereas higher ratios (10<sup>-7</sup> to 10<sup>-5</sup>) point to mantle-derived inputs (Mamyrin and Tolstikhin, 1984). Due to its low solubility and small size, He can easily diffuse through mineral grain boundaries and pore networks, allowing it to migrate efficiently from deep crustal sources and often accumulate in reservoirs where suitable cap rocks or structural traps can retain it. Its presence in a reservoir usually indicates a currently active source and dynamic processes.

### 1.3 Migration and Accumulation of Gases

Once generated in the source rock or accumulated in subsurface reservoirs, gases migrate through sedimentary sequences via processes that are controlled by rock physical properties, fluid-rock interactions, and the physicochemical characteristics of the gases. Migration pathways are first and foremost controlled by key rock properties such as porosity and permeability. Porosity refers to the proportion of a rock's total volume that consists of void spaces capable of storing fluids, while permeability describes the rock's ability to transmit fluids through these pore spaces, which depends on the size, shape and connectivity of the pores. Porosity can be classified into two main types: primary and secondary. Primary porosity develops during the initial sediment deposition, and it is subdivided into *intergranular* porosity (spaces between individual sediment grains) and *intragranular* porosity (spaces within the grains, e.g., fossil fragments or minerals) (Bear and Braester, 1972). Secondary porosity forms later through diagenetic processes such as dissolution, fracturing, or recrystallisation, improving pore connectivity and creating additional pathways for fluids. This is especially significant in otherwise tight formations like certain carbonates and volcaniclastic rocks (Bjørlykke, 2010). Accurately measuring porosity can be challenging due to spatial variability within formations, but it is a critical parameter alongside permeability in assessing reservoir quality. Sedimentary rocks such as sandstones and carbonates generally exhibit the best combination of porosity and permeability: well-sorted sandstones often provide high porosity and interconnected pore networks facilitating fluid flow and storage, while carbonates can develop enhanced permeability through dissolution-related secondary porosity. In contrast, shales typically have low permeability and porosity, limiting fluid migration and serving as cap rocks preserving the reservoir (Bear and Braester, 1972; Bjørlykke, 2010; L'Heureux and Fowler, 2000; Tiab and Donaldson, 2024). Migration is commonly divided into primary and secondary migration. Primary migration refers to the initial expulsion of hydrocarbons and non-hydrocarbon gases from the low-permeability source rocks into adjacent, more permeable carrier beds or sediments. It is driven mainly by overpressure generated during gas generation and involves overcoming capillary forces within very fine-grained matrices (Tiab and Donaldson, 2014). Secondary migration, referring to the movement of gases through more permeable pathways toward reservoirs, traps, or to the surface, is typically controlled by buoyancy forces and pressure gradients and relies on well-connected pore networks of fractures. Gas transport in sedimentary basins occurs through diffusion, advection, and, under specific conditions, convection (Fig. 1.4). These processes are driven by concentration, pressure, and temperature gradients, respectively, and can operate simultaneously depending on subsurface conditions.



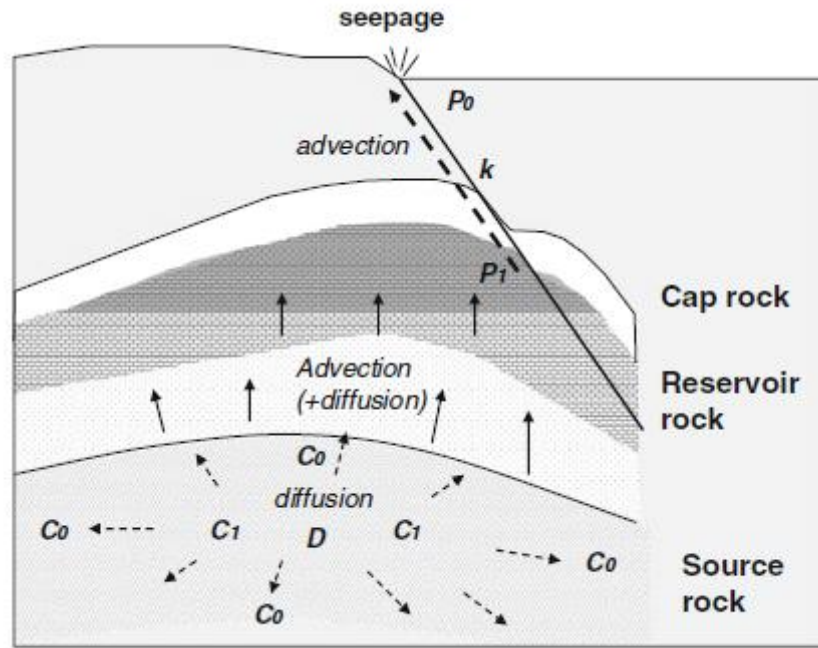


Figure 1.4. Conceptual model showing gas migration by diffusion and advection through sedimentary layers, with seepage occurring along permeable fault zones (from Etiope, 2015).

Molecular diffusion is the movement of gas molecules from areas of higher concentration to areas of lower concentration. This process becomes particularly important in low-permeability formations, such as shales or fine-grained compacted sediments, where other transport mechanisms are limited and gas migration occurs over geological timescales. Gas molecules are subject to chaotic Brownian motion, which leads to a progressive homogenisation of concentration differences. The rate at which this occurs depends on the nature of the intragranular spaces, the porosity of the rock, and on chemical interactions at the grain-fluid interface. Fick's first law quantitatively describes molecular diffusion:

$$\Phi = -D \frac{dC}{dx}$$

Where  $\Phi$  is the diffusive flux ( $\text{mol m}^{-2} \text{s}^{-1}$ ),  $D$  is the diffusion coefficient ( $\text{m}^2 \text{s}^{-1}$ ) and  $\frac{dC}{dx}$  is the concentration gradient ( $\text{mol} \cdot \text{m}^{-4}$ ). The diffusive flux occurs perpendicular to the Earth's surface and is proportional to both the diffusion coefficient and the concentration gradient. Diffusion coefficients in porous media are often lower than in free fluids due to tortuosity and porosity constraints and are further modulated by rock moisture content and compaction.

Typical diffusion coefficients for gases in water-saturated sediments range between  $10^{-10}$  and  $10^{-9} \text{ m}^2 \text{s}^{-1}$  (Tissot and Welte, 1984; Curtis, 2002). The small molecular size and low molecular weight of gases such as He and  $\text{H}_2$  result in higher diffusion coefficients, allowing them to migrate more rapidly through porous media compared to heavier gases. This is because lighter molecules move faster at a

given temperature, and their smaller size reduces the probability of being trapped within rock structures. Consequently, gases like helium can migrate upward over significant distances, even in the absence of advection, potentially reaching the surface from deep reservoirs over millions of years. Among hydrocarbons, CH<sub>4</sub>, with its small effective molecular diameter of ~0.38 nm, exhibits remarkable mobility and diffusivity, allowing it to migrate even through rocks that are effective seals for larger molecules, such as oil. Conversely, larger and heavier molecules require more favourable pore structures or must rely on advective transport mechanisms to migrate effectively. The enhanced mobility of CH<sub>4</sub>, combined with greater buoyancy (due to its high hydrogen-to-carbon ratio), makes methane capable of penetrating low-permeability formations and migrating over considerable distances. This characteristic leads to a broader spatial distribution of CH<sub>4</sub> in the subsurface compared to oil, both vertically and laterally (Hunt, 1996). Gases generated in deep or laterally extensive source rocks can diffuse through fine-grained rocks and bypass small-scale traps, reaching surface seeps or accumulating in secondary traps over time. In contrast, oil is typically confined to more discrete and geologically younger traps, where migration pathways are more limited by its viscosity and molecular size. It is important to note that although diffusion is a slow mechanism, it can be highly effective over long timescales, especially in sealed or semi-sealed systems. When reaching the surface, in dry and well-aerated soils, diffusive gas migration can span several meters, whereas in wet or highly compacted sediments, it may be restricted to just a few centimetres.

Advection refers to the bulk movement of gas through porous media driven primarily by pressure gradients within the subsurface. This transport mechanism dominates in geological formations with sufficient permeability to sustain fluid flow, especially along well-connected pore networks, natural fractures, or fault planes that act as preferential pathways (Bear, 1972; Dullien, 2012). Unlike molecular diffusion, which operates at the scale of individual molecules responding to concentration gradients, advection governs the large-scale displacement of fluid volumes responding to hydraulic pressure differences (Fetter, 1999). Advection is described by Darcy's law, which expresses the volumetric flow rate of a fluid through a porous medium:

$$q = -\frac{k}{\mu} \frac{dP}{dx}$$

Where  $q$  is the Darcy flux (m<sup>3</sup> s<sup>-1</sup>),  $k$  is the intrinsic permeability of the rock (m<sup>2</sup>),  $\mu$  is the dynamic viscosity of the fluid (Pa s) and  $\frac{dP}{dx}$  is the pressure gradient (Pa m<sup>-1</sup>) (Bear, 1972).

Porosity and permeability are, once again, pivotal factors in regulating advective transport, directly impacting the potential for pressure-driven gas migration. Methane's low viscosity and high compressibility make it particularly responsive to pressure gradients compared to liquids like oil or brine (Tiab and Donaldson, 2024). Under hydrostatic conditions at ~1220 m, its volume decreases to

about 1% of its surface volume (Duan et al., 1992), allowing substantial quantities of gas to be stored in compact form. A drop in confining pressure, such as near fractures or fault zones, can cause rapid expansion, enhancing vertical migration through buoyancy-driven transport (Pruess, 1991). This high mobility allows CH<sub>4</sub> to bypass formations that effectively seal larger molecules like oil. However, impermeable barriers such as methane hydrates, evaporites, or highly compacted clays can significantly restrict vertical gas movement by drastically reducing permeability (Zoback, 2010; Kvenvolden, 1993). In natural settings, advection rarely occurs alone but coexists with diffusive transport and other processes like dispersion. Gases may initially migrate advectively through permeable “carrier beds” (e.g., sandstones), which serve as lateral or vertical conduits, then diffuse across finer-grained, semi-permeable cap rocks or clay-rich layers (Sahimi, 2011). During natural gas formation, thermal cracking of oil increases gas volumes, potentially causing pressure buildup that may surpass the tensile strength of surrounding rocks, resulting in new or enhanced fractures. This fracturing significantly boosts permeability and, consequently, advective flow rates (Bjørlykke, 2010). The level of saturation in the formation critically affects advective flux: gas migration is more effective in unsaturated zones where gas occupies pore space preferentially, while in water-saturated formations, capillary forces, wettability, and phase interactions may hinder or redirect flow pathways (Dake, 1978). Fault zones often serve as vertical migration pathways, forming focused corridors that connect deep gas accumulations to the surface and may result in natural gas seeps if traps are absent or breached. Depending on their internal structures and pressure conditions, faults can act either as conduits or seals. When pore pressure within a fault zone exceeds the fracture gradient, microfractures open, sharply increasing permeability and enabling fluid migration both vertically and laterally across sealing layers (Grall et al., 2018). Conversely, a reduction in pressure and an increase in effective stress can close these fractures, turning the fault into a barrier to migration. The fracture networks, especially within fault damage zones, are typically anisotropic, creating preferential fluid pathways. Their ability to enhance both storage and migration is influenced by mechanical dilation during fault slip as well as chemical processes like mineral dissolution, which further increase porosity and permeability (Agosta et al., 2010). Together, these factors govern the efficiency and extent of secondary hydrocarbon migration in sedimentary basins. Although convection is generally considered a secondary transport mechanism in sedimentary basins, it can become locally significant in deep, permeable, and geothermally active settings (Bear, 1972). Convective fluid flow is driven by thermal gradients, often associated with regional geothermal heat flow or localised heat sources such as magmatic intrusions (Pruess and García, 2002). This induces density-driven circulation cells that can enhance the redistribution of gases and fluids in the subsurface. For example, convection can promote upward migration of gases by coupling thermal expansion and pressure gradients, potentially

increasing permeability by fracturing or dissolution processes. Interactions between migrating gases and mineral surfaces also play a crucial role in controlling subsurface gas transport and fate. Mechanisms such as adsorption, chemical reactions, and mineral trapping at the grain-fluid interface can slow down migration or alter the gas composition. Adsorption onto shales and organic matter can temporarily immobilise gases like CH<sub>4</sub> and CO<sub>2</sub>, with CO<sub>2</sub> showing an adsorption capacity more than 5 times greater than CH<sub>4</sub> on both reservoir shales (Nuttal et al., 2005; Kang et al., 2011) and individual mineral phases, such as illite and kaolinite, or carbon surfaces (Heller and Zoback, 2014). This process is particularly relevant to shale gas extraction and CO<sub>2</sub> sequestration, as it directly affects the fraction of gas that remains mobile. Chemical reactions can modify migrating gases through processes such as dissolution–precipitation at mineral surfaces. The dissolution of CO<sub>2</sub> into formation waters can lower pH, promoting the precipitation of carbonate minerals (e.g., calcite, dolomite) that effectively trap carbon in solid form (Xu et al., 2004; Gaus, 2010). Such reactions can permanently remove part of the gaseous phase from the migration pathway, altering both flux and composition. Mineral trapping refers more specifically to the immobilisation of gases via incorporation into newly formed or pre-existing minerals within the rock matrix. In the context of CO<sub>2</sub> storage, this is considered the most secure long-term trapping mechanism, as the gas is converted into thermodynamically stable carbonate minerals that are unlikely to remobilise under reservoir conditions (Krevor et al., 2011; Matter and Kelemen, 2009). Although slower than structural or solubility trapping, mineral trapping can progressively reduce the mobile gas fraction over geological timescales. Moreover, CO<sub>2</sub> and CH<sub>4</sub> can act as *carrier gases*, facilitating the transport of trace gases and minor species by acting as solvents or vectors, due to their particular solubility and miscibility characteristics. Trace gases like Rn and He are present in such small amounts in the subsurface that they cannot form a large enough gas domain to move advectively on their own. Instead, they must be carried by the larger volumes of carrier gases like CO<sub>2</sub> and CH<sub>4</sub> that can form a macroscopic gas flow and move upwards through the subsurface (Etiope and Martinelli, 2002). The ability of CO<sub>2</sub> to dissolve in aqueous and hydrocarbon phases enhances the mobility of dissolved components, whereas the small molecular size and high diffusivity of CH<sub>4</sub> enable it to permeate tight formations, entraining other gases through physical or chemical interactions. After migrating through sedimentary sequences, CH<sub>4</sub> and other gases can reach the surface as gas seeps, which typically localise near active faults and fault intersections, thus resulting in a loss of gas from the reservoir. Upon release, CH<sub>4</sub> transitions from a geochemical fluid to a potent atmospheric trace gas with significant climatic implications.

## *1.4 Methane in the Atmosphere*

Although chemically simple, CH<sub>4</sub> exhibits complex behaviour in the Earth's surface systems due to its physical properties, reactivity, and potent greenhouse effect. It is only sparingly soluble in water, with a solubility of approximately 22 mg/l at 25°C (Haynes, 2016), meaning that once released into aquatic systems, much of it escapes into the atmosphere unless oxidised by microbial processes. In the atmosphere, CH<sub>4</sub> possesses an average lifetime of  $12 \pm 2$  years and exhibits a global warming potential (GWP) of approximately 83 over a 20-year period and approximately 30 over a 100-year period, thereby demonstrating greater efficacy than CO<sub>2</sub> in trapping heat (IPCC, 2021). This makes it the second most important anthropogenic greenhouse gas after CO<sub>2</sub>, despite its lower concentration. According to the US NOAA (National Oceanic & Atmospheric Administration), the globally averaged CH<sub>4</sub> concentration in the atmosphere was 1,935 ppb in April 2025, which indicates an increase of over 160% from pre-industrial times, where it had an average concentration of 720 ppb (Lan et al., 2025). Methane's immediate impact on global warming is amplified by indirect effects, notably the formation of tropospheric ozone and stratospheric water vapour, both potent greenhouse agents. In the atmosphere, CH<sub>4</sub> is primarily removed through oxidation initiated by hydroxyl radicals (OH). This process begins with the reaction between CH<sub>4</sub> and OH, producing methyl radicals (CH<sub>3</sub>), which then form methylperoxy radicals (CH<sub>3</sub>O<sub>2</sub>) and follow complex pathways yielding formaldehyde (H<sub>2</sub>CO), carbon monoxide (CO), and ultimately CO<sub>2</sub>. Reactive intermediates such as hydroperoxyl (HO<sub>2</sub>) also arise and, in the presence of nitrogen oxides (NO<sub>x</sub>), drive the production of tropospheric ozone (Wuebbles and Hayhoe, 2002; Dlugokencky et al., 2011). Through these photochemical pathways, CH<sub>4</sub> oxidation influences atmospheric chemistry. The net climate forcing from CH<sub>4</sub> thus includes both direct infrared absorption and these indirect effects, making it the second-largest contributor to anthropogenic radiative forcing after CO<sub>2</sub>.

Methane emissions come from both natural and human sources. They mainly originate from anaerobic biological processes in wetlands (about 30% of emissions), agriculture (20%, especially from livestock and rice paddies), fossil fuel production and use (around 30%), and other minor sources such as biomass burning, landfills, and permafrost thawing (Saunio et al., 2025). Geogenic emissions also contribute a small but significant part to the global CH<sub>4</sub> budget, accounting for approximately 53 Tg CH<sub>4</sub> per year, about 10% of the total estimated CH<sub>4</sub> emissions (~530 Tg yr<sup>-1</sup>; EMEP/EEA, 2023). In Europe, geological CH<sub>4</sub> emissions from macroseeps, mud volcanoes, and diffuse microseepage are estimated at around 3 Tg CH<sub>4</sub> per year, making this the second-largest natural CH<sub>4</sub> source after wetlands. Despite their significance, the estimation of geogenic CH<sub>4</sub> emissions remains challenging due to the spatial heterogeneity of seepage, the overlap with biogenic sources, and the complexities of measuring diffuse fluxes (Etiope et al., 2007).

While methane's primary atmospheric sink is its oxidation by hydroxyl radicals (OH) in the troposphere, a secondary, yet ecologically important, sink occurs in soils, where methanotrophic bacteria oxidise CH<sub>4</sub> under aerobic conditions, converting it ultimately to CO<sub>2</sub>. Their activity is influenced by numerous environmental factors, including soil texture, temperature, pH, nutrient availability, and particularly moisture content, which governs oxygen diffusion into the soil. Well-drained and aerated soils, such as those found in upland forests and grasslands, tend to serve as more effective methane sinks. Conversely, waterlogged or compacted soils often demonstrate diminished oxidation capacity due to limited oxygen penetration. On a global scale, terrestrial CH<sub>4</sub> oxidation by soils is estimated to remove approximately 20–30 Tg CH<sub>4</sub> annually, accounting for about 5–10% of the total methane sink. However, this process exhibits significant spatial variability, which is influenced by land cover and climatic conditions (Dutaur and Verchot, 2007; Saunio et al., 2025). Accurately quantifying CH<sub>4</sub> emissions from all sources, encompassing both anthropogenic and natural origins, is vital for comprehending its influence within the climate system. Although targeted mitigation of anthropogenic emissions can be managed through policy initiatives and technological advancements, enhancing our understanding of natural sources, including geogenic emissions, remains equally imperative for refining global CH<sub>4</sub> budgets and forecasting future atmospheric trends.

## Chapter II – Geological, Hydrogeological, and Geochemical Setting of Methane-Rich Areas in Emilia-Romagna

### *2.1 Geofluids Distribution in Italy*

The Italian territory is home to a remarkable variety of natural geofluid emissions, reflecting its complex tectonic and geodynamic evolution. As illustrated in Figure 2.1, the peninsula can be broadly divided into two geochemical domains based on the fluid composition: a CO<sub>2</sub>-rich fluid domain in the Tyrrhenian sector, associated with extensional tectonics, and a CH<sub>4</sub>-rich fluid domain along the Adriatic side, which corresponds to compressional tectonics. This spatial distribution is not only the result of contrasting tectonic regimes but also of distinct processes of fluid generation and migration. CO<sub>2</sub> emissions in Italy originate from both shallow and deep sources. The main genetic processes include the anatexis of carbonate rocks at depths of 3–5 km, which is prevalent in areas of mantle upwelling and high heat flow, and widespread degassing from the mantle lithosphere in geodynamically active areas (Chiodini et al., 1999; Minissale et al., 1997, 2000). According to Chiodini et al. (2004), the overall CO<sub>2</sub> discharge in Italy results from a combination of these processes, with the shallow crustal component dominating in high-heat-flow zones and the mantle-derived component prevailing elsewhere. Recent estimates indicate that Italy's natural CO<sub>2</sub> emissions, comprising both concentrated volcanic emissions and diffuse soil degassing, amount to tens of millions of tons of CO<sub>2</sub> yr<sup>-1</sup> (Chiodini et al., 2004; Cardellini et al., 2014; Ricci et al., 2023). These emissions are unevenly distributed, with the highest fluxes concentrated along the Apennine belt and Tyrrhenian margin, as shown by the clustering of CO<sub>2</sub>-rich sites in Figure 2.1. In contrast, CH<sub>4</sub> emissions are more prominent within the compressional domains of the Adriatic foredeep and Po Plain, where hydrocarbon-prone sedimentary basins and active fault systems facilitate the migration of CH<sub>4</sub>-rich fluids to the surface. Local studies indicate that Italian macroseeps and mud volcanoes emit on the order of 10<sup>5</sup> tons CH<sub>4</sub> yr<sup>-1</sup>, with microseepage representing the main methane output on a regional scale (Etiope et al., 2007). Although CH<sub>4</sub> and hydrocarbons are also emitted from volcanic and geothermal systems, their fluxes are typically much lower than those from sedimentary basins. Studies such as Etiope and Milkov (2004) have shown that natural fossil methane emissions from soils and marine sediments are roughly an order of magnitude greater than those released directly from volcanic and geothermal areas.



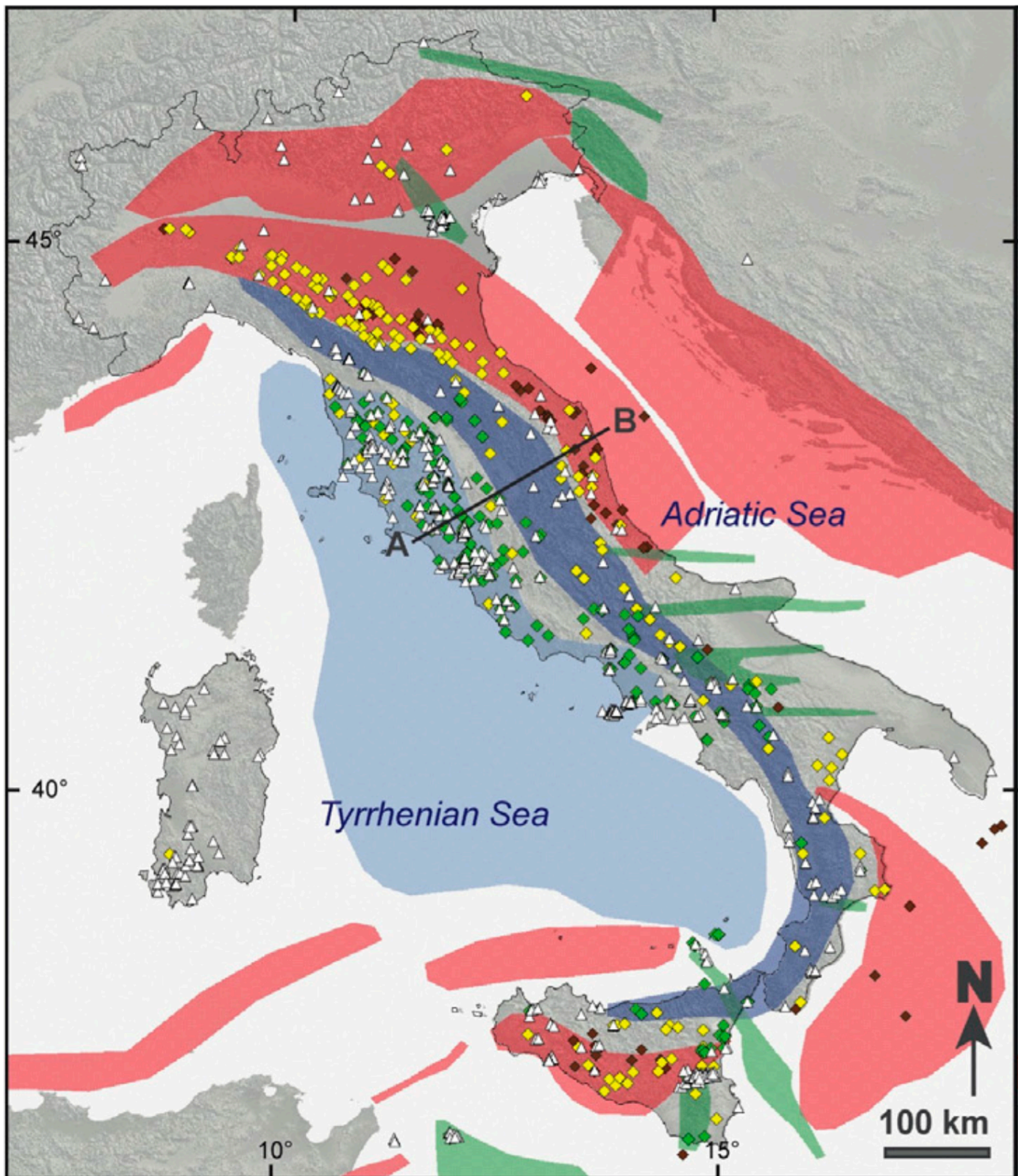


Figure 2.1. Distribution of fluid emissions in Italy and their tectonic pertinence (from Vannoli et al., 2021). The shaded areas indicate active tectonic domains. Light blue - areas of rifting and mantle upwelling; blue - post-orogenic extension; red - active contraction; green - active strike-slip. Geofluid emissions: white triangles - thermal springs having  $T > 20^{\circ}\text{C}$ ; green diamonds - natural  $\text{CO}_2$  emissions; yellow diamonds - gas seeps (mainly  $\text{CH}_4$ ); brown diamonds - mud volcanoes.



About 80% of active seeps in Italy release thermogenic methane, produced in deep reservoirs along the Apenninic sector, and their distribution closely follows the major tectonic structures and petroleum systems.

## *2.2 Gas Deposits in the Po Valley and Northern Apennines*

Most of the current geological understanding of the Po Basin's subsurface is derived from decades of hydrocarbon exploration and drilling, which have yielded extensive stratigraphic, structural, and geochemical data. These investigations have revealed a complex system of gas deposits characterised by diverse origins, migration pathways and reservoir settings. Mattavelli et al. (1983) provided a detailed classification of gases within the Po Basin, identifying three major types: bacterial, thermogenic, and mixed gases. Geological factors strictly govern the distribution and quantity of the three gas types. According to Mattavelli and Novelli (1988), approximately 82% of the natural gas is of bacterial origin, associated predominantly with Plio-Pleistocene sediments; 15% represents mixed origin gases, and only 3% is purely thermogenic, derived from pre-Pliocene formations. In terms of structural distribution, 77% of reservoirs are located in the foreland, 10% in the foothills, and 13% within the mountain chain. Bacterial gases dominate the foreland, while mixed and thermogenic types become more common in structurally complex settings. Bacterial gases are primarily produced in place within the thick sedimentary sequence of Pliocene-Pleistocene, where depths may reach up to 4,500 m (e.g., Antonella well, one of the deepest bacterial gas fields known). At intermediate depths (< 2,000 m), a full spectrum of bacterial, mixed, and thermogenic gases is observed. Notably, Messinian-age reservoirs often host mixed gases due to overlapping generation and migration processes. In contrast, all gases hosted in pre-Tertiary reservoirs are thermogenic, typically accumulating in Miocene foredeep turbiditic sequences, which serve as the principal reservoir rocks. These turbidites are effectively sealed by overlying Ligurian and Epiligurian Units, which provide the necessary cap rocks for long-term gas retention (Ricci Lucchi, 1986; Vai and Martini, 2013; Oppo et al., 2013). These foredeep reservoirs are often saturated with connate saline waters and contain a complex mixture of gas phases, indicating long-range vertical migration from deeper, more mature source zones. Structural traps are mainly associated with thrust-related anticlines and tectonic highs along the Apennine foothills—features that remain productive today. Additionally, methane-rich cold seeps, seep-carbonate buildups, and mud volcanoes have been reported within the Miocene successions of the Apennine accretionary wedge. These features are sustained by ongoing fluid migration driven by tectonic activity, where high-angle normal faults cut through the Ligurian and

Epiligurian units, providing conduits for deep-sourced fluids and gases to reach the surface (Capozzi and Picotti, 2002; Oppo et al., 2013; Coiro et al., 2021). Although natural methane seeps, such as hydrocarbon-rich springs, bubbling pools, and dry gas emissions, were historically widespread, they are now infrequent or absent in most parts of the basin. This decline is likely due to the progressive depletion of shallow, unsealed accumulations over time. In systems lacking effective cap rocks, continuous degassing over geological timescales leads to gas exhaustion, leaving behind only geochemical or mineralogical traces (e.g., carbonate crusts or oxidised zones) of formerly active seepage.

### *2.3 Regional Geological Framework*

The Emilia-Romagna region is situated in north-central Italy, bounded by the Northern Apennines to the west and by the Adriatic Sea to the east. Its northernmost sector is occupied by the Po Plain, which extends beyond the regional borders and constitutes a vast and actively subsiding foreland basin associated with the Apennine orogenic system (Fig. 2.2). The Po Plain is among the most densely populated and economically productive territories in Europe, hosting major urban and industrial areas as well as several UNESCO World Heritage Sites. Its development has been historically tied to the exploitation of strategic subsurface resources, most notably hydrocarbons, which played a crucial role in shaping the region's economic and infrastructural landscape throughout the 20<sup>th</sup> century. This intense anthropogenic activity is embedded within a geologically complex setting, where natural hazards such as seismicity, land subsidence, and flooding frequently overlap with human settlements and infrastructure (Livani et al., 2023). To comprehend the current configuration of the Po Plain and its relation to fluid migration pathways, it is necessary to consider the broader geodynamic framework of the region.

The present-day morphology of the region is the result of the Apennine orogeny, a fold-and-thrust belt formed by the convergence of the Adria microplate (associated with the African Plate) and the Eurasian Plate (Ricci Lucchi, 1986).



Figure 2.2. Geographic and tectonic setting of the Emilia-Romagna region (highlighted in brown and green) within the Italian peninsula. The brown area represents the Apennine mountain domain, while the green area corresponds to the Po Plain foredeep basin. Major thrust and fold fronts of the Southern Alps and Apennines are shown in red. The yellow line indicates the trace of the geological cross-section C–C'. Modified from the Seismotectonic Map of Emilia-Romagna (2016).

This tectonic evolution of the Apennines is marked by the following key events:

- Early Jurassic rifting led to the opening of the Piedmont-Ligurian Ocean and the development of a horst-and-graben seafloor morphology bounded by extensional faults.
- A subsequent phase of tectonic quiescence occurred around 150-155 million years ago (Mya).
- The closure of the oceanic domain began in the Late Cretaceous (approximately 88-85 Mya), culminating in the subduction of the oceanic crust during the Upper Eocene to Lower Oligocene (around 40 Mya).

- This was followed by a continental collision, initiating the development of the Apennine thrust belt, a process that continues to the present day (Boccaletti et al., 1981).

A complex series of thrusts and folds formed after the inversion of subduction polarity, shifting from a Europe-directed to an Adriatic-directed orientation, which began in the middle Eocene. This inversion was a pivotal event that caused significant rearrangement of the deep-marine units, such as the Ligurian Units, which migrated northeastward and thrust over the Mesozoic and Tertiary successions of the Adriatic foreland (Pini, 1999). These thrust sheets form a sedimentary cover that today serves as the main reservoir for fluid accumulation. Marine sedimentation then continued in satellite basins atop the Ligurian thrust sheets, resulting in the formation of the Epiligurian Units, a sequence of sedimentary deposits primarily composed of siliciclastic sediments that filled the accretionary wedge-top basins. Their composition, thickness, and layering vary significantly due to the dynamic nature of the underlying tectonic activity (Vai and Martini, 2013). Throughout the Neogene, the foreland basin migrated northeastward alongside the growth of the accretionary wedge, generating thrust faults and folds that deformed the entire margin (Ricci Lucchi, 1986). The geology of the Northern Apennine foothills is characterised by the stacking of Ligurian and Epiligurian Units over Messinian evaporites and Miocene foredeep turbidites, which themselves rest atop Mesozoic-Paleogene carbonate platforms (see Figure 2.3). The Miocene foredeep turbidites, most notably the Marnoso-Arenacea Formation, represent a thick (>4000 m) succession of deep-water siliciclastic sediments deposited in the elongate foredeep basin that developed in front of the advancing Apennine orogenic wedge. The sedimentation of these turbidites was strongly influenced by syntectonic subsidence and the progressive migration of the orogenic front, resulting in vertical and lateral facies changes that reflect the dynamic interplay between tectonics and sediment supply (Tinterri et al., 2012). These Miocene turbiditic units are of particular economic interest, as they serve as both reservoir and, locally, source rocks for hydrocarbons in the region (Oppo et al, 2013). Hydrocarbon accumulations are primarily associated with structural highs formed by thrust-related folding and faulting, and the sealing capacity of overlying evaporitic and Ligurian-Epiligurian units is a key factor in the preservation of these resources. Subsequently, the Messinian evaporites were deposited during the Messinian Salinity Crisis (5.59 – 5.3 Ma), a dramatic paleoenvironmental event triggered by the restriction of Atlantic inflow into the Mediterranean Sea, causing the basin to become hypersaline and, at times, nearly desiccated (Bice and Tavarnelli, 2022).

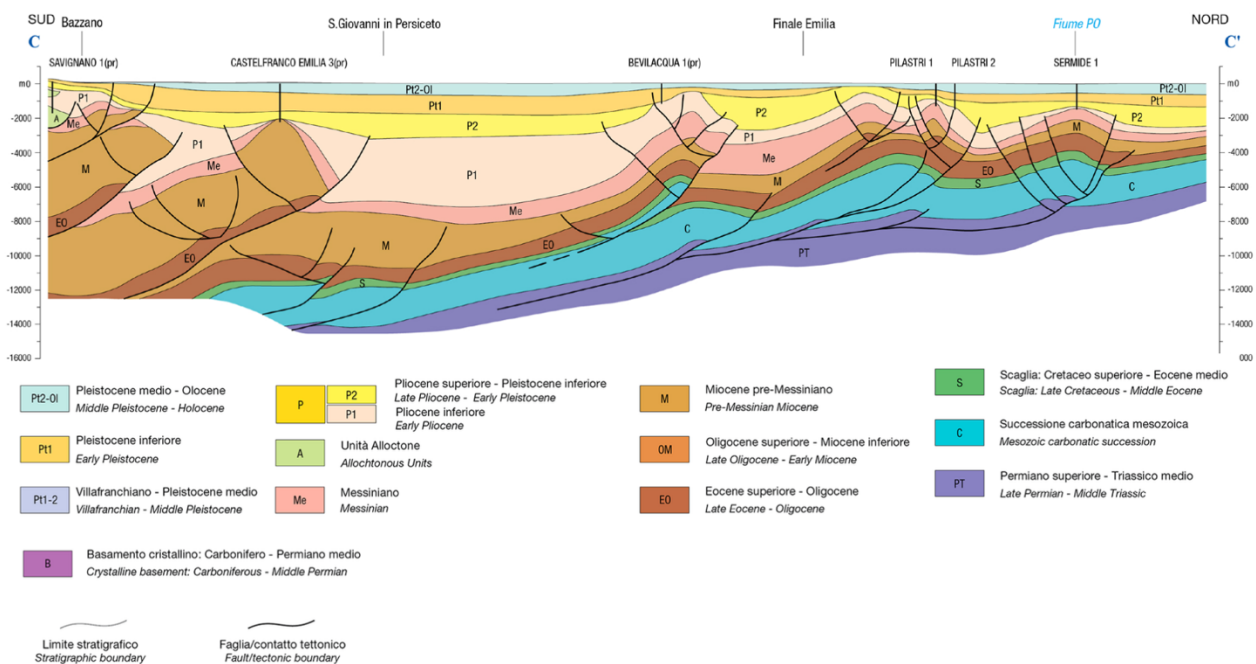


Figure 2.3. Geological cross-section C–C' (whose trace is included in Fig. 2.1) showing the sedimentary architecture of the Po Plain across the Emilia-Romagna region. Modified from the Seismotectonic Map of Emilia-Romagna (2016).

This led to the precipitation of thick sequences of evaporitic minerals (gypsum and halite primarily) in both shallow, thrust-top basins and deeper foredeep settings. This tectono-sedimentary architecture sets the stage for the Po Plain, where the sedimentary cover records the transition from marine to continental environments during the Pliocene and Quaternary. The Po Plain's subsurface preserves an almost continuous record of these younger sediments, which blanket the deformed Apennine foothill structures and document the ongoing evolution of the foreland basin system. Since the Neogene, the Po Plain has functioned as a subsiding foreland basin, with subsidence primarily driven by the tectonic load associated with the progressive accumulation of a substantial Plio–Pleistocene sedimentary succession, locally reaching thicknesses of up to 8 km. This succession is predominantly composed of terrigenous continental and fluvial deposits. The initial infilling of the basin was largely sourced from erosion related to the Alpine orogeny, which began shaping the region through thrusting and uplift in the southern Alps from the middle Eocene onward (Pieri and Groppi, 1981). Subsequently, the Apennine orogeny contributed additional sediment, with thrust systems progressively developing in the northern Apennines from the Oligocene to the early Miocene. The interplay between these two major fold-and-thrust belts, resulting from the convergence of the Eurasian and African plates, induced regional-scale flexural subsidence that governed both the

formation and the sedimentary evolution of the basin (Coward and Dietrich, 1989; Ghielmi et al., 2010; Carminati and Doglioni, 2012; Livani et al., 2023).

In the Northern Apennines, the major structures are characterised by NNE vergence (i.e., southward-dipping), affecting both the sedimentary cover and the deeper Mesozoic carbonate sequence. On a regional scale, the structural architecture of the Po Plain can be divided into distinct domains (Figure 2.4). To the north, the prominent folds of the Southern Alps contrast with the southern sector, which is defined by three main arcuate structures representing the most advanced thrust fronts of the Apennine chain: the Monferrato Arc, the Emilia Arc, and the Ferrara Romagna Arc.

These arcs are bordered on their outer side by thrust faults, which serve as the division between them and the Pedalpine monocline. The Ferrara Romagna Arc, in particular, can be further subdivided into three minor groups: the Ferrara folds, the Romagna folds, and further east, the Adriatic folds, which together constitute the proper external (and largely buried) front of the Apennines (Scrocca et al., 2007).

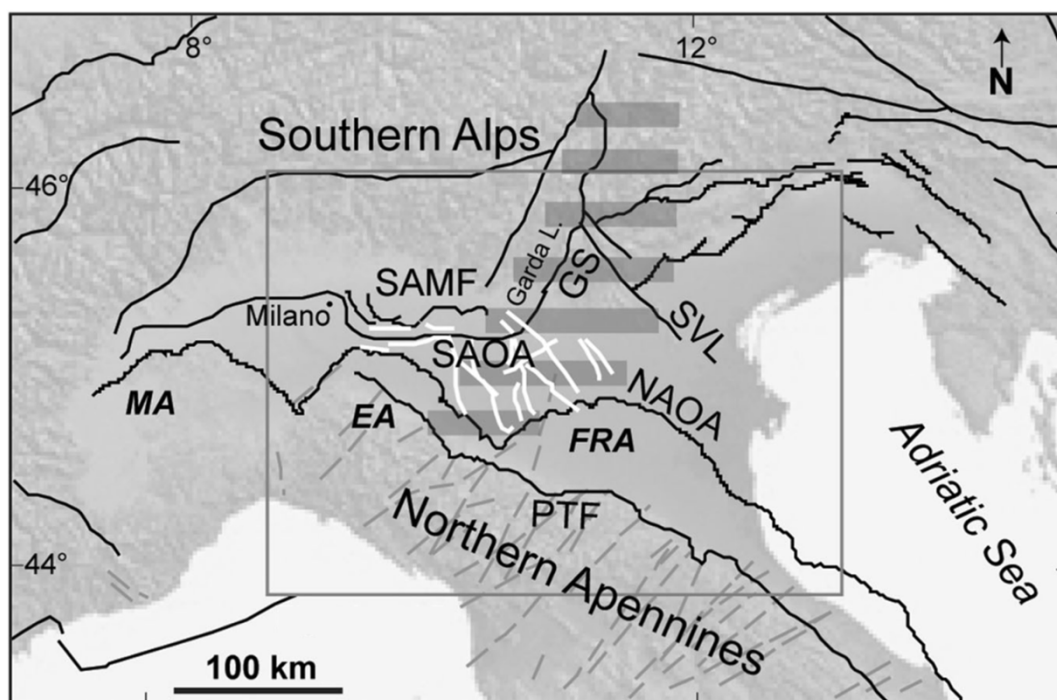


Figure 2.4 Structural sketch map of the Po Plain and surrounding regions, from Vannoli et al. (2015). Black lines indicate the main structural elements; white lines represent inherited faults; dashed lines show transverse (chain-perpendicular) structures. Grey horizontal shading marks the Trento Platform (after Cuffaro et al., 2010). Key structural features are labelled: SAMF—Southern Alps Mountain Front; SAOA—Southern Alps Outer Arc; GS—Giudicarie System; SVL—Schio-Vicenza Line; NAOA—Northern Apennines Outer Arcs; PTF—Pedeapenninic Thrust Front; MA—Monferrato Arc; EA—Emilia Arc; FRA—Ferrara-Romagna Arc.

High-angle normal faults are widespread along the Northern Apennine foothills, particularly in association with the major arcs and thrust fronts. These faults typically develop on the crests of anticlines, reflecting local extensional regimes that arise from the bending and uplift of the fold limbs. Importantly, high-angle normal faults serve as primary pathways for the upward migration of fluids, including hydrocarbons and saline waters, facilitating the formation of surface seepages and mud volcanoes. This increased permeability is a key factor in the occurrence of spontaneous gas and oil emissions observed along the foothills, as these faults penetrate the sealing Ligurian and Epiligurian cover down to the Miocene reservoirs (Picotti et al., 2009; Capozzi and Picotti, 2010; Oppo et al., 2013). The relationship between normal faulting and fluid migration highlights the dynamic evolution of the tectonic and petroleum systems in the region, as further illustrated by the distribution of major buried thrusts and inherited lineaments beneath the Po Plain (Vannoli et al., 2015).

## *2.4 Seismicity*

Although Emilia-Romagna is classified as a region of moderate seismicity, the associated hazard remains significant compared to other parts of Italy, primarily due to the high population density, widespread productive infrastructure, and the presence of historical and cultural heritage that is often structurally vulnerable. Seismic activity in the region is mainly concentrated in the foothills separating the Apennines from the plain and is associated with the NE-verging thrust system of the fold-and-thrust belt. These structures are deeply buried beneath the Po Plain due to rapid sedimentation and relatively low deformation rates, making surface evidence of their activity scarce and challenging to interpret. Nonetheless, geomorphological indicators, such as anomalies in river courses, which are manifested through both fluvial deviations and abrupt changes in the erosive activity of the watercourse, can be related to the growth of buried anticlines (Toscani et al., 2009). Figure 2.5 shows the distribution of historically and instrumentally recorded earthquakes, reported in the Parametric Catalogue of Italian Earthquakes (CPTI), highlighting the concentration of seismicity along the Apennine margin and in the Po Plain. Recent seismicity is generally low to moderate in magnitude (up to  $M_w$  5.9) and is characterised by compressive focal mechanisms.

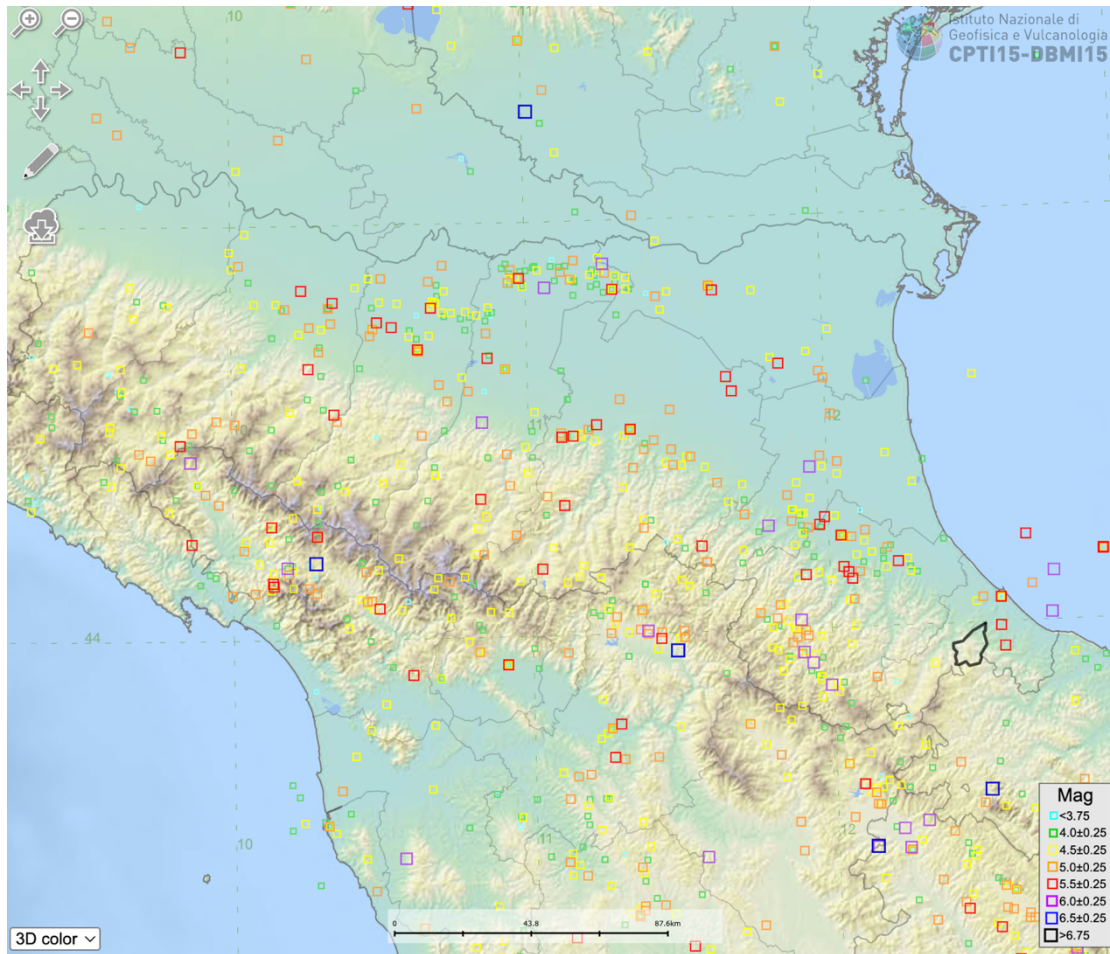


Figure 2.5. Historical seismicity in Emilia-Romagna and bordering regions (Rovida et al., 2022; available in interactive form at [https://emidius.mi.ingv.it/CPTI15-DBMI15/query\\_eq/](https://emidius.mi.ingv.it/CPTI15-DBMI15/query_eq/)). Earthquakes are represented by magnitude classes, with larger squares indicating higher magnitudes.

The Po Plain experiences both superficial (<10-12 km) and relatively deep (>15 km) earthquakes. While shallow earthquakes often produce intense but spatially constrained effects, deeper events of similar magnitude can affect wider areas, albeit with reduced peak accelerations. Additionally, the unconsolidated sedimentary fill of the Po Basin contributes significantly to the amplification of seismic waves, thereby enhancing the potential for structural damage even at moderate magnitudes. Among notable historical earthquakes in Emilia-Romagna, many have occurred in the Modena-Ferrara and Romagna areas. The Modena-Ferrara sector is associated with the Ferrara-Romagna arc, comprising the Ferrara-Romagna thrust ITCS050 and the Mirandola thrust ITCS051 (Fig. 2.6). This system is responsible for moderate to strong earthquakes, with magnitudes reaching approximately Mw 6.1 at depths between 2 and 10 km. Historical events such as the 1570 Ferrara earthquake (Mw 5.4–5.7) and the recent 2012 seismic sequence (Mw 5.9 and Mw 5.8) have been attributed to the activity of these buried thrusts (ISIDe Database, 2012; Moretti et al., 2017).



The 2012 sequence, notable for causing significant damage and fatalities, shared with the 1570 event the characteristic of comprising several potentially destructive earthquakes occurring over days to months.

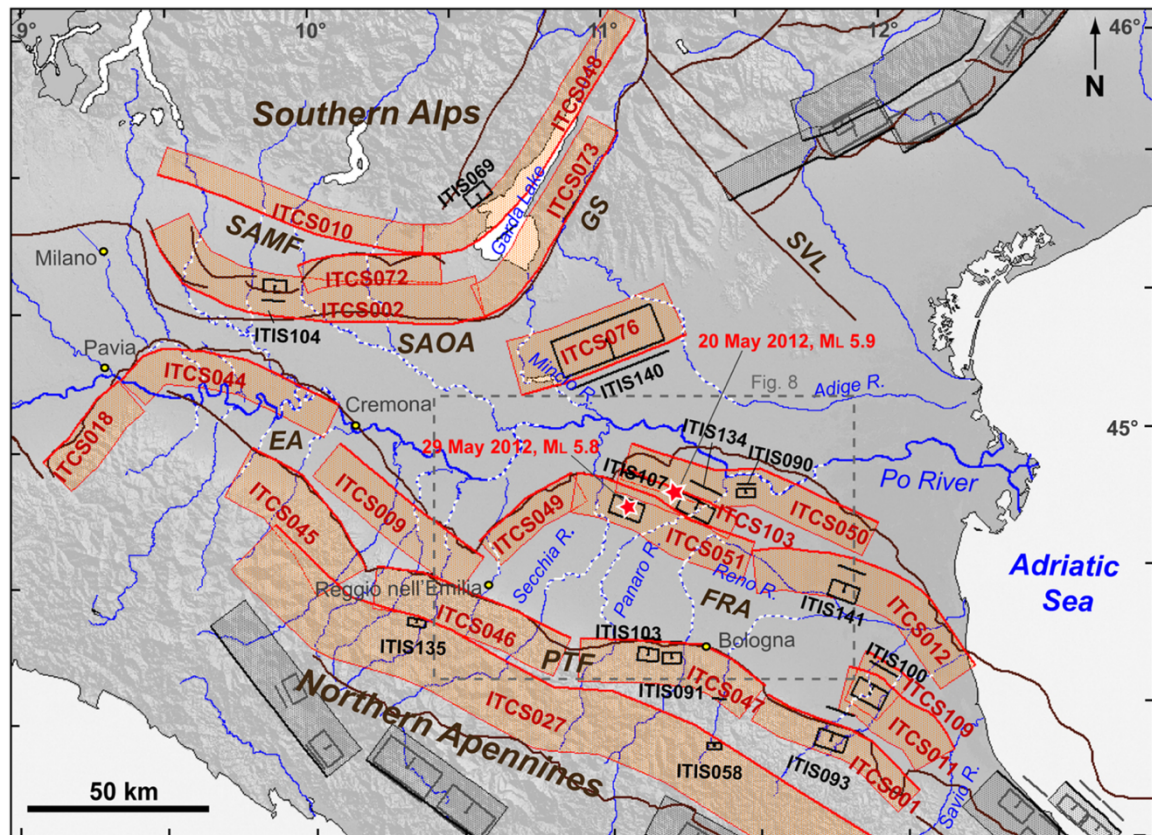


Figure 2.6. From Vannoli et al, 2015. Composite and individual sources of the Po Plain, respectively shown as red ribbons and black rectangles. Reaches of anomalous drainage are marked in white.

The Romagna area is also historically affected by a notable concentration of seismic events, including the 1688 Forlì earthquake (estimated  $M_w$  5.5), which has been associated with the eastern continuation of the Ferrara-Romagna Arc system, specifically with a distinct thrust segment (ITCS109 in Fig. 2.5). According to Vannoli et al. (2015), this segment, along with the Modena-Ferrara thrust, the Mirandola thrust, and other structures along the arc, is classified as a Group #1 fault, meaning it is among the principal active thrusts of the Alps and Apennines. These include faults located both along the foothills and at the most external fronts of the mountain chains. As such, the Ferrara-Romagna Arc represents a continuous and potentially seismogenic structural feature.

The geological characteristics of the shallow subsurface in the Po Valley make the region particularly susceptible to secondary seismic effects. In particular, the alternation of clay-rich sediments with interbedded sandy layers, especially in areas between Modena and Ferrara, favours the development of liquefaction phenomena during seismic events. These processes can lead to the ejection of sandy material at the surface, occasionally forming structures such as sand volcanoes. Such effects were

widely documented during the 2012 Po Plain earthquake sequence (Capaccioni et al., 2017; Emergeo Working Group, 2012; Moretti et al., 2013). These effects, combined with sudden temperature increases in wells and heightened soil gas concentrations documented during the 2012 sequence, indicate active fluid migration triggered by seismic activity (Capaccioni et al., 2015; Sciarra et al., 2017).

## *2.5 Hydrogeology and Hydrochemistry*

The hydrogeological framework of the Emilia-Romagna plain reflects a complex stratigraphic architecture, shaped by alternating alluvial, coastal, and marine sedimentation over the Quaternary. Historically, this shallow portion of the subsurface received limited attention outside oil exploration and water well drilling. However, basin-scale studies focused on marginal and marine deposits within the first few hundred metres of subsoil have delineated a complex multilayered aquifer system.

The classification proposed by Regione Emilia-Romagna and ENI-AGIP (1998) introduces three aquifer groups (A, B, and C), each representing genetically and temporally distinct depositional systems, bounded by regionally extensive aquitard layers (Fig. 2.7). Aquifer Group A, dating from the present to approximately 350–450 ka, is composed mainly of alluvial deposits, including coarse gravel layers from alluvial fans and finer sediments from meandering and floodplain systems of the Po River (Upper Emilia-Romagna Synthem). Sub-units (referred to as Aquifer Complexes, e.g., A0, A1, A2) reflect individual transgressive-regressive sequences, each typically underlain by a clayey basal aquitard. The organic-rich clay layer at the base of A0 (10–20 m deep) is regionally continuous and marks the shallow groundwater table across large parts of the plain. Group B, spanning roughly 350–650 ka, shows similar sedimentary facies to Group A, albeit generally deeper and with more consolidated deposits (Lower Emilia-Romagna Synthem). Aquifer Group C, spanning from ~650 ka to over 3Ma, is predominantly composed of coastal and marginal marine sediments with alternating sands and finer materials, as well as occasional gravel deposits formed by the Apennine River alluvial fans during the Lower and Middle Pleistocene.

| STRATIGRAPHIC UNITS             |                                  | DEPOSITIONAL SEQUENCES |                           | AGE (MY)       | CHRONOSTRATIGRAPHIC SCALE (MY)       | HYDROSTRATIGRAPHIC UNITS |                         |    |
|---------------------------------|----------------------------------|------------------------|---------------------------|----------------|--------------------------------------|--------------------------|-------------------------|----|
|                                 |                                  |                        |                           |                |                                      | AQUIFER GROUP            | AQUIFER COMPLEX         |    |
| EMILIANO-ROMAGNOLO SUPERSYNTHEM | UPPER EMILIANO-ROMAGNOLO SYNTHEM | Qc                     | Qc <sub>2</sub>           | ~0.12          | UPPER PLEISTOCENE-HOLOCENE<br>~0.125 | A                        | A1                      |    |
|                                 |                                  |                        |                           |                |                                      |                          | A2                      |    |
|                                 | LOWER EMILIANO-ROMAGNOLO SYNTHEM |                        | Qc <sub>1</sub>           | ~0.35<br>-0.45 | MIDDLE PLEISTOCENE                   |                          | B                       | B1 |
|                                 |                                  |                        |                           |                |                                      |                          |                         |    |
| MARINE QUATERNARY SUPERSYNTHEM  | IMOLA SANDS                      | Qm                     | Qm <sub>3''</sub>         | ~0.65          |                                      | C                        |                         | C1 |
|                                 |                                  |                        | Qm <sub>3'</sub>          |                |                                      |                          |                         | C2 |
|                                 | SANTERNO GROUP                   |                        | Qm <sub>2</sub>           | ~0.8           | ~0.89                                |                          | C3                      |    |
|                                 |                                  |                        | Qm <sub>1</sub>           | ~1.0           | LOWER PLEISTOCENE                    |                          | C4                      |    |
|                                 |                                  |                        |                           |                | ~2.2                                 |                          | MIDDLE TO LATE PLIOCENE | C5 |
| UPPER-PLIO SYNTHEM              | P2                               | ~3.3-3.6<br>~3.9       | LOWER PLIOCENE<br>MIOCENE | ~3.55          | BASAL AQUITARD                       |                          |                         |    |

Figure 2.7. Hydrostratigraphic Units and correlated stratigraphy, adapted from Regione Emilia-Romagna and AGIP-ENI (1998). Purple, yellow, and brown lines indicate discontinuity surfaces and aquitards between aquifer groups.

Flow within regional aquifers tends to be confined to stratigraphic layers, with water movement largely parallel to depositional surfaces, except within direct recharge zones. The basal aquitard beneath the plain, extending to and emerging from the Apennine-Po margin, comprises mainly low-permeability Pliocene-Pleistocene formations such as the Argille Azzurre and intra-Apennine pelites. Geochemically, waters in Group A are predominantly Ca-HCO<sub>3</sub> type, typical of shallow, recently recharged aquifers in silicate matrices, with two notable trends derived from the primary calcium bicarbonate water. One trend involves Na-Cl waters found in northeastern provinces (Reggio Emilia, Modena, Ferrara, Ravenna), originating from connate lagoonal and deltaic deposits, residual saltwater in Po delta sandy lobes, or mixing of Alpine waters with fossil saline waters related to structural complexity (e.g., the Ferrara Ridge). The second trend involves Na-HCO<sub>3</sub> waters, likely produced by ion-exchange processes involving clay minerals and feldspars, driven by CO<sub>2</sub> from organic matter decomposition, CH<sub>4</sub> transport, or thermochemical reactions. A smaller subset of waters falls within the Ca-SO<sub>4</sub> facies due to interactions with evaporitic Triassic and Messinian formations. Aquifer Group B exhibits four main geochemical facies, including Ca-HCO<sub>3</sub>, Ca-SO<sub>4</sub> (notably near the

Secchia river cone), Na-HCO<sub>3</sub>, and Na-Cl, the latter interpreted as Alpine water influence. Group C data are sparse, but available evidence suggests similar geochemical evolution pathways as the overlying units. Increased confinement and isolation from recharge areas likely lead to more reducing conditions and higher salinity. Based on their hydraulic behaviour and geochemical composition, aquifers in the region can be broadly classified into unconfined, mainly located in the southern part of the region, and confined types, which are more common in the northern areas. (Martinelli et al., 1998). Stable isotope analyses ( $\delta^{18}\text{O}$  and  $\delta\text{D}$ ) of groundwater samples collected from various wells across the region indicate a predominantly meteoric origin for all aquifer waters, including those characterised by high Na-Cl concentrations (Martinelli et al., 1998). The isotopic signatures correspond to recharge from precipitation falling at elevations between approximately 1000 and 2000 metres, consistent with inputs from both the Alpine chain and the Northern Apennines. A distinction between aquifers north of the Emilia route (which connects the main cities) shows that they are predominantly recharged by Alpine-derived precipitation with a more continental isotopic signature plotting along the Global Meteoric Water Line (GMWL). At the same time, those in the south reflect inputs influenced by Mediterranean air masses, plotting along the Mediterranean Meteoric Water Line (MMWL). Tritium ( $^3\text{H}$ ) and radiometric analyses indicate that much of the groundwater has a long residence time, in some cases exceeding 20,000 years, consistent with confined flow conditions in deeper aquifer units (e.g., Group Aquifer C).

In addition to their primary role as water reservoirs, aquifers in the Emilia-Romagna plain act as sensitive interfaces capable of recording the vertical migration of deep-seated fluids, including thermal waters, brines, and dissolved gases. The presence of high-salinity Na-Cl waters, even in relatively shallow aquifers, can be a direct indication of upward leakage or mixing with fossil brines. At the regional scale, hydraulic gradients, fault zones, and anticlinal structures may facilitate the vertical migration of fluids, especially where aquitards are locally fractured or thinned. A notable example is the Ferrara-Ravenna Ridge, a structurally complex area characterised by anomalous heat flow and geochemical-isotopic anomalies pointing to significant inputs from deep fluid sources (Martinelli et al., 1998; Italiano et al., 2012). These phenomena became especially evident and well-documented in the aftermath of the 2012 seismic sequence, when numerous anomalous events were observed across the region. Italiano et al. (2012) reported the mobilisation of deep-sourced fluids, rich in helium and isotopically heavy CO<sub>2</sub>, into overlying aquifers as a result of crustal deformation. These intrusions induced measurable shifts in water chemistry, including abrupt calcite undersaturation and changes in gas composition, particularly in CO<sub>2</sub> and CH<sub>4</sub>. Similarly, Bonzi et al. (2017) highlighted the occurrence of significant water temperature anomalies in wells throughout the Po Plain, phenomena often associated with enhanced gas emissions and interpreted as evidence of

deep fluid inputs along fault zones. These anomalies were particularly frequent in the post-seismic context, likely amplified both by increased crustal permeability and heightened public awareness leading to more frequent reporting. Although many of these observations were triggered or intensified by seismicity, persistent gas emissions and fluid anomalies have also been documented in areas far from the 2012 epicentral zone, where such manifestations appear to be perennial rather than episodic. In these contexts, monitoring wells with multiparameter probes (capable of detecting real-time changes in water level, temperature, and conductivity) become a powerful tool for identifying signals of deep fluid input. These methods allow for the early detection of subtle hydrochemical and thermal perturbations, providing critical data for understanding the dynamics of fluid migration in sedimentary basins.

## *2.6 Inventory of Geofluid Manifestations in Emilia-Romagna*

The term Unusual Geological Phenomena (UGP) was first introduced to describe a broad set of naturally occurring geological manifestations, often linked to deep-seated fluid circulation and gas seepage (Severi and Bonzi, 2014; Bonzi et al., 2017). In Emilia-Romagna, systematic data collection on UGP began in 2012 after the Emilia seismic sequence, intending to document both newly reported events and manifestations that were historically known from historical sources. During the initial half of the 20th century, geologists from Eni–Agip assembled a comprehensive dataset of spontaneous hydrocarbon manifestations for mineral exploration purposes, predating the widespread use of seismic reflection surveys. The records, covering the period from 1862 to 1959, exhibit similarities with the UGP features documented in present times. In Emilia-Romagna, 934 mapped manifestations have been identified, the majority of which (809) are described in detail in *Manifestazioni di idrocarburi nella Regione Emilia-Romagna* (Eni S.p.A., S. Donato Milanese, Technical Internal Report, vol. 2, 691 pp; Mosca, 1983). The remaining 125 are known only from their location and type, as reported on maps included in the same report. The *Geology, Soils, and Seismicity* unit of the Emilia-Romagna Geological Survey reviewed and synthesised this historical dataset, integrating it into the webGIS platform “Segnalazioni fenomeni geologici particolari e manifestazioni storiche di idrocarburi.” The database also incorporates:

- manifestations for which no detailed Eni record is available,
- 70 sites immediately outside the regional boundary, documented only by their type and location from Eni maps.



In total, 1,004 mapped manifestations have been classified into twelve types (number of occurrences in brackets):

- running water with gas (30)
- saline water and hydrocarbons (50)
- gas (209)
- gas from water wells (145)
- gas from drilling (218)
- gas and oil (98)
- gas and oil from drilling (30)
- surficial gas (29)
- oil (128)
- oil from drilling (10)
- exploratory wells (30)
- brine and hydrocarbons (27)

Most historical manifestations were georeferenced using small-scale cartography (1:200,000), implying a positional uncertainty of approximately 50–250 m. The resulting database and interactive map, accessible via the Emilia-Romagna regional geological services portal (<https://servizimoka.regione.emilia-romagna.it/mokaApp/apps/sfgp/index.html>), provide a comprehensive framework for analysing the spatial distribution and typology of hydrocarbon-related UGP in the region. From the website page, users can click on individual mapped phenomena to access detailed descriptions of the event, the location, and any inspections conducted.

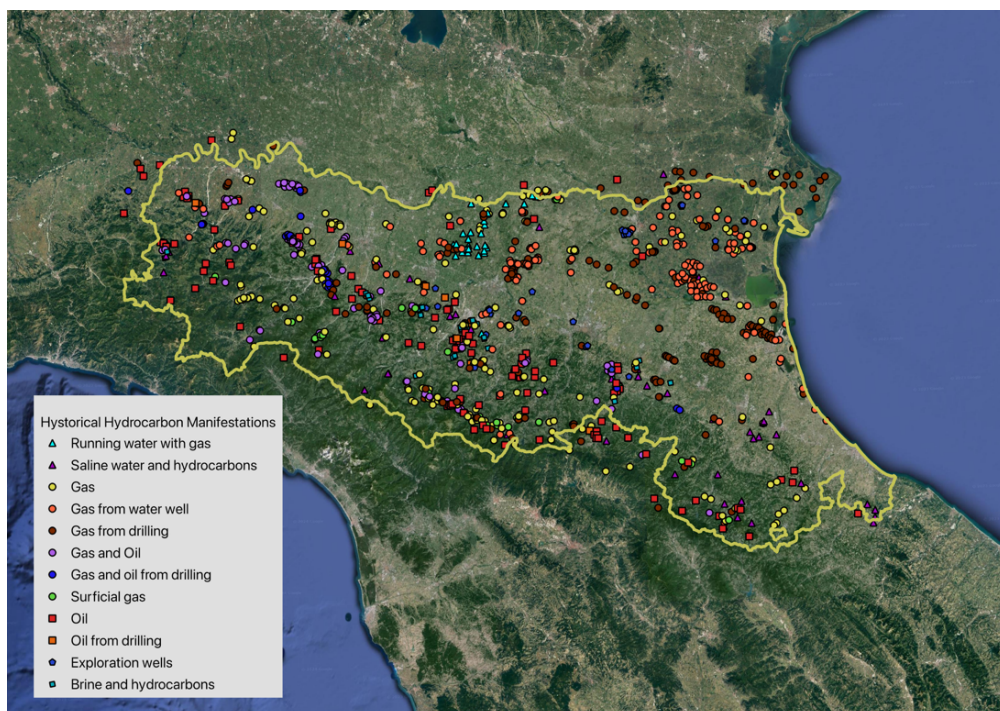


Figure 2.8. Historical Hydrocarbon Manifestations Map.

## 2.7 The Study Sites

This PhD research examines three geofluid emission sites in the Emilia–Romagna region: Santa Maria Nuova, Renazzo, and Nirano (see Fig. 2.9). Although situated within a few tens or hundreds km of each other, these sites display distinct geochemical signatures and CH<sub>4</sub> release characteristics, differing significantly in their structural settings and in the surface expression and dispersal patterns of gas discharge.



Figure 2.9. Location of the three study sites investigated in this work—Santa Maria Nuova, Renazzo, and Nirano—within the Emilia–Romagna region. Yellow lines indicate provincial boundaries; base map adapted from regional cartography.

### 2.7.1 Santa Maria Nuova

Santa Maria Nuova Spallicci is located within the Municipality of Bertinoro in the Province of Forlì-Cesena, at an elevation of 30 m a.s.l., in the hill sector of the Romagna piedmont (44°20'26"N, 12°18'36"E; Fig. 2.9, green circle).

The small village lies within an area of gentle slopes used predominantly for agriculture, surrounded by vineyards and arable fields. No bedrock formations crop out in the area; the surficial geological



units belong to the AES8 and AES8a subsynthem of the Upper Emilia–Romagna Synthem, consisting of sandy–loamy alluvial deposits dating back to the Roman and post-Roman periods (ISPRA, 2009). In the subsurface, these alluvial deposits extend to a depth of about 175 m (Emilia–Romagna Region–ENI Agip, 1998), overlying basal Middle Pleistocene coastal marine sediments, which in turn rest on progressively older marine sequences. Historically, residents and local authorities have intermittently reported gas manifestations. Notably, in July 2021, an incident was reported to the Regional Geological Survey at a private water well in Santa Maria Nuova (hereafter referred to as SMN). The well, 8.35 m deep from ground level, had accumulated CH<sub>4</sub>-rich gases above the water level. The presence of a heavy metal panel sealing the exit prevented gas dispersion into the atmosphere, allowing CH<sub>4</sub> concentrations to exceed the lower flammability limit (4.4 vol%) rapidly. When a spark from the water pump ignited the gas, the metal cover was violently blown off, although the well structure itself did not explode. In the days following the event, vigorous gas bubbling persisted in the water well, and non-dispersive infrared sensors placed at the wellhead detected hazardous CH<sub>4</sub> levels (>5 vol%). Local residents reported that similar microseepage events had occurred over the past decades, including gas bubbling in ponds during heavy rains and the interruption of excavation works due to intercepted gas pockets. The first on-site survey, conducted in May 2022 (several months after the initial report of the explosion in July 2021), found that the gas bubbling activity in the well had ceased, and the well itself was being kept open, allowing atmospheric dispersion. Measurements near the well revealed an adjacent agricultural field managed under conventional annual crop rotation, which was cultivated with barley at the time (May 2022), where circular barren patches were present (Fig. 2.10). These patterns closely resembled vegetation stress documented at the Terre Calde di Medolla site (Modena province), where CH<sub>4</sub> seepage has been shown to promote methanotrophic oxidation, resulting in elevated CO<sub>2</sub> emissions, soil heating, and persistent vegetation damage (Capaccioni et al., 2015; Sciarra et al., 2021). The combination of these surficial manifestations and the anomalous vegetation patterns prompted a comprehensive investigation of gas seepage dynamics at SMN. The study aimed to assess the spatial dispersion of soil gas fluxes after initial measurements of CH<sub>4</sub> and CO<sub>2</sub> in the barren vegetation patches carried out in May 2022. A semi-annual monitoring campaign of gas fluxes from the soil of the agricultural field was conducted over a two-year period, coupled with chemical and isotopic characterisation of soil gases. Once a thermal anomaly was detected in the field, its extent and characteristics were also evaluated. In parallel, satellite-derived vegetation reflectance and related indices were analysed to develop an approach for remotely identifying and monitoring phenomena analogous to those at SMN and the Terre Calde site of Medolla (TCM), focusing on their persistence through time using temporal series analysis. As the initial reports were linked to the nearby well, a multiparametric probe was



installed within it to record water level, electrical conductivity, and temperature, while dissolved gases and solutes in the well water were also chemically characterised.



Fig. 2.10. Satellite view of the SMN site with a drone-acquired orthomosaic (May 2022) overlaid on the agricultural field. Circular barren patches indicating vegetation stress are clearly visible within the cultivated area. The location of the July 2021 well explosion is marked with a red dot.

### 2.7.2 Renazzo

Renazzo is a small town located in the municipality of Cento, province of Ferrara, at  $44^{\circ}45'49.32''\text{N}$   $11^{\circ}17'05.64''\text{E}$  (Fig. 2.9, purple circle). The site lies at an elevation of approximately 16 m a.s.l. within the central Po Plain, in an area characterised by extremely low morphological relief. The area is underlain by up to 8 km of Plio–Pleistocene terrigenous sediments, which were deposited in the subsiding foreland of the Northern Apennines and are structurally influenced by the Ferrara arc, the easternmost segment of the Apennine fold-and-thrust belt (Bigi et al., 1992; Scrocca et al., 2007). The outcropping unit at Renazzo consists predominantly of medium to fine sands arranged in decimetre-thick beds, laterally grading into or interbedded with silty fine sands and, subordinately, clayey silts. Locally, medium to coarse sands occur in lenticular or ribbon-shaped bodies. These deposits are interpreted as channel and proximal levee sediments, representing the most recent phases of alluvial deposition in the area. Renazzo is notable for a persistent  $\text{CH}_4$  leak from a private water well, about



6 m deep from ground level, first reported to the Regional Geological Survey in March 2017 (Fig. 2.11). At the time, the emission was substantial enough to displace groundwater from the well, producing vigorous bubbling at the surface. According to the well owners, the phenomenon has been ongoing since at least the 1950s, making it a long-lived manifestation of subsurface gas migration in the area. The gas was confirmed to be  $\text{CH}_4$  by local authorities through controlled ignition tests. Given the magnitude and persistence of the emission, the site was selected for a detailed investigation as part of this study.



Figure 2.11. Location and appearance of the Renazzo well. Left: Satellite image (Google Earth) showing the position of the emitting water well relative to the town of Renazzo. Right: Photographs of the well taken in March 2017 (top) and May 2017 (bottom), documenting persistent  $\text{CH}_4$ -rich gas bubbling and water overflow.

Potential variations in physicochemical parameters of the well water associated with gas presence were monitored over two years through the deployment of a multiparametric probe. The perennial nature of the discharge also allowed for targeted experiments to estimate the gas flux from the well, considered as a point source analogous to a fumarole or vent. These experiments were conducted using different instrument configurations to enable comparative assessment. In addition, to evaluate gas dispersion in the surrounding area, a three-week monitoring campaign was undertaken using low-cost measurement stations, specifically assembled and calibrated for this purpose.

### 2.7.3 Nirano

Nirano is located within the municipality of Fiorano Modenese, province of Modena, at 44°32'10" N, 10°46'40" E, at an elevation between 140-300 m a.s.l. (Fig. 2.9, red circle). The site lies on the northern foothills of the Northern Apennines and is part of the *Riserva Naturale delle Salse di Nirano*, a protected area established in 1982 to conserve one of the most extensive mud volcano fields in the Italian peninsula. The Nirano mud volcanoes form an elliptical depression situated along an anticline ridge predominantly aligned in a typical NW–SE Apennine orientation. They develop within the Plio-Pleistocene Argille Azzurre Formation, which is primarily composed of marly-silty clays. This depression has been interpreted either as a mud volcano caldera resulting from progressive collapse due to degassing (Bonazzi and Tosatti, 1999; Bonini, 2008) or as the final stage of mud diapir evolution (Castaldini et al., 2005). Mud volcanism at Nirano represents a surface expression of deep-seated fluid migration, typically involving the expulsion of brackish connate water, gas (predominantly CH<sub>4</sub>, ~98%) and fine-grained sediments through vent structures driven by overpressure in the subsurface (Kopf, 2002; Mazzini and Etiope, 2017). Minor components include CO<sub>2</sub>, N<sub>2</sub>, C<sub>2</sub>–C<sub>10</sub> hydrocarbons, and noble gases, with isotopic data ( $\delta^{13}\text{C-CH}_4$  and  $\delta\text{D-CH}_4$ ) indicating a primarily thermogenic origin, sometimes accompanied by secondary microbial CO<sub>2</sub> and some biodegradation (Minissale et al., 2000; Etiope et al., 2007; Tassi et al., 2012a; Heller et al., 2011; Sciarra et al., 2019). Thrust faults and fractures facilitate fluid migration, linking mud volcano activity to regional tectonics and compressional processes along the NE-verging Apennine fold-and-thrust belt (Giambastiani et al., 2022). The area is seismically active, with historical earthquakes such as the Mw 6.05 event of June 5, 1501, and the 2012 Emilia sequence affecting nearby regions (Rovida et al., 2022). Historical records document the evolving morphology of the Salse di Nirano field, marked by the periodic formation of new vents and the cessation of activity in others over relatively short timescales. Mud pool F, a mud pool first reported in 1907 (Castaldini et al., 2017), displays substantial variability in size over time, reflecting the inherently dynamic behaviour of active mud volcano vents. At present, it covers an area of approximately 40 m<sup>2</sup> (De Nardo et al., 2019) and reaches a depth of 11.1 m. Unlike the main gryphons and emission points of the Reserve, mud pool F is located in a secluded forest clearing, overgrown with vegetation. Its long-term persistence is consistent with the stability of the geometric patterns defined by the alignments of emission points, predominantly oriented NW–SE (Castaldini et al., 2017), coinciding with the axis of the anticline crest underlying the Reserve. Mud pool F was selected as the focus site for assessing the dynamics of the Nirano mud volcano system, given its accessibility, stability, and representativeness of gas–water–sediment interaction processes. As part of this study, a multiparametric probe was installed within the mud pool to monitor physicochemical parameters over time. The site was monitored over an extended period



to identify potential correlations between variations in mud pool F and the broader dynamics of the Nirano system. Comparative analysis with data from another pool in the field, monitored by colleagues at INGV Milan, enabled the evaluation of differential responses of the two mud pools to deep inputs and surface environmental changes. In addition to the physico-chemical monitoring, gas release from selected mud pools was quantified using a floating extension adapted for accumulation-chamber work.



Fig. 2.12. Left: Satellite view of the Nirano mud volcano field (Riserva Naturale delle Salse di Nirano) with the location of the monitored site, Polla F. Right: Photograph of Polla F.

This setup enlarged the chamber headspace and stabilised measurements on the mud–water surface, enabling paired  $\text{CH}_4$ – $\text{CO}_2$  acquisitions at four representative pools distributed along the main structural alignments. Fluxes were derived with two complementary approaches: (i) an end-to-end treatment that converts the linear concentration increase over a selected interval into a mass flux; and (ii) an event-based decomposition tailored to stepwise, bubble-driven rises. The latter separates the total into a burst component and a slowly varying background, and yields descriptors of degassing dynamics such as the burst frequency ( $\lambda$ ,  $\text{min}^{-1}$ ) and the mean mass per burst ( $\bar{m}$ , g).

## Chapter III – Methodologies

Although the investigated sites represent distinct geological settings, the methodological approach adopted in this study follows a unified framework aimed at detecting, quantifying, and characterising CH<sub>4</sub> emissions and associated geofluids. Each method is presented by first outlining the measurement or analytical technique—whether field-based or laboratory-based—and subsequently describing the procedures used to process and interpret the resulting data. This integrated structure ensures that the instrumental setups, sampling strategies, and analytical protocols are directly linked to the computational treatments applied, which include calibration, statistical analyses, simulations, and remote sensing approaches.

### *3.1. Continuous Monitoring of Chemical–Physical Parameters*

Continuous monitoring of hydrogeological and physicochemical parameters in wells and mud pools represents a crucial approach to identifying potential signals of deep fluid migration. Variations in temperature, electrical conductivity, and water level may provide valuable indications of subsurface processes that would otherwise remain undetected. For instance, reports of unusually warm water wells, when not attributable to pump malfunction (Bonzi et al., 2017), have been interpreted as heating effects caused by the exothermic bacterial oxidation of methane rising through groundwater and reaching the wells (Ricci et al., 2023). Likewise, increases in electrical conductivity can reveal the ascent of saline waters from deeper horizons, plausibly enriched in dissolved gases. Fluctuations in water level, when not attributable to meteoric recharge, may also reflect episodes of fluid overpressure and migration from depth. The systematic acquisition of continuous time series is therefore fundamental to distinguish background variability from anomalous signals and to better constrain the dynamics of fluid flow within sedimentary basins. The chosen methodology across all three studied sites relied on the use of STS DL.WMS/GPRS/R/SDI-12 modular multi-parametric probe (Fig. 3.1). This system is specifically designed for in-field measurement of water level, temperature, and electrical conductivity, combining versatility, reliability in harsh environments, and advanced data management capabilities. The probe is equipped with:

- A pressure sensor for level measurements from 3 to 300m of H<sub>2</sub>O, with overpressure resistance up to 300% of full scale and precision  $\leq \pm 0.05\%$  FS.
- A silicon temperature sensor operating from -10 °C to +80 °C, with  $\pm 0.3$  °C accuracy.

- A four-electrode electrical conductivity sensor covering from 0  $\mu\text{S}/\text{cm}$  to 200mS/cm, with a precision within 2.5% of the measurement range. The sensor features six titanium electrodes with 4-wire technology.

The STS probe features a stainless-steel (316L/1.4435) housing with an IP68 protection to ensure resistance to submersion and flooding. It continuously monitors internal humidity, battery voltage, and housing temperature, safeguarding reliability during extended deployments. Field management is entirely wireless, using a 433MHz near-field radio interface accessed through a USB dongle connected to the computer, so the logger does not need to be opened for configuration. The integrated 4G modem supports real-time data transmission, which is sent to the INGV Palermo server and is accessible via PC or smartphone. Data logging is modular, supporting up to 230,000 entries in non-volatile memory that persists without battery power. Data are stored in industry-standard ASCII or CSV formats, readily exportable for further processing.

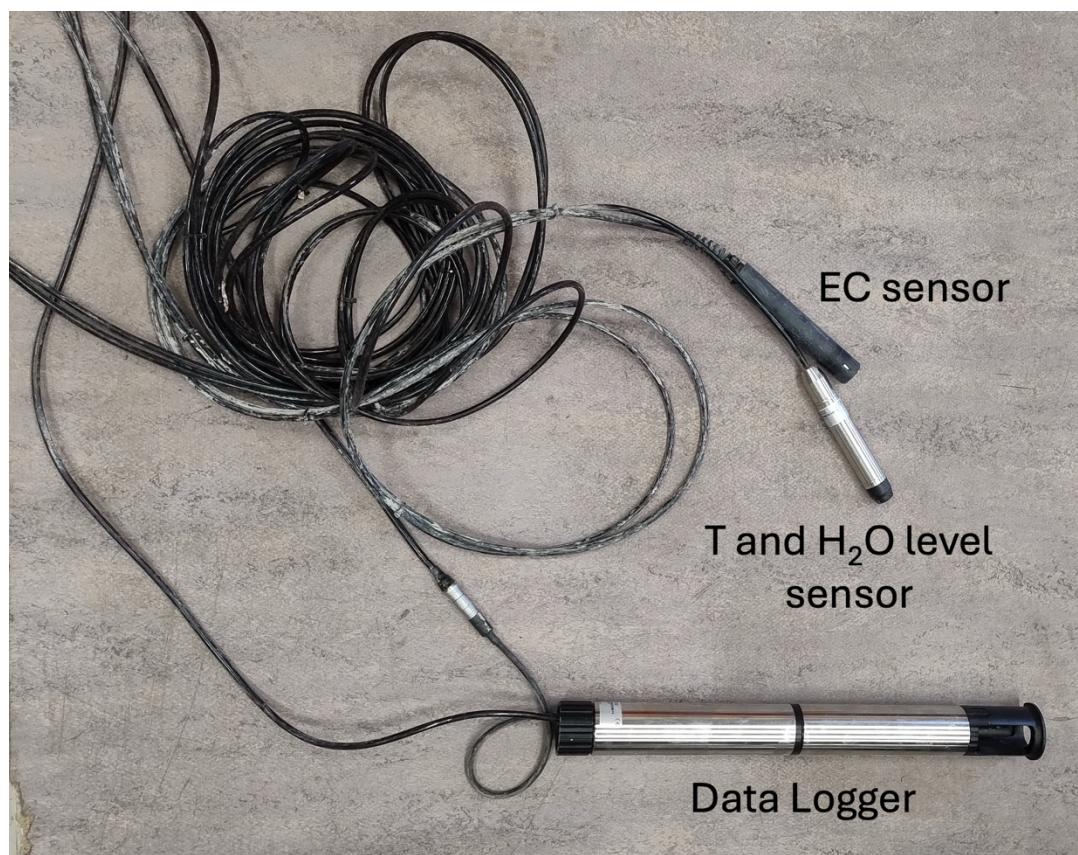


Figure 3.1. The STS DL.WMS/GPRS/R/SDI-12 multiparametric probe, with a 15 m long cable attached to the temperature and water level sensors (combined in one device), and the EC sensor.

At the SMN site, the STS probe was deployed in the well on 14 June 2023 at a depth of approximately 2.70 m (Fig.3.2a). The instrument was configured to record measurements every hour and transmit the data to the INGV Palermo server every 12 hours.



On the same date, a similar probe was installed in the Renazzo well at a depth of 4.46 m (Fig.3.2b), with identical sampling and transmission settings. At Polla F (Fig. 3.2c), the probe was installed earlier, on 3 April 2023, with an initial configuration of 10-minute sampling and data transmission every 8 hours. Due to transmission difficulties, the sampling interval was later extended to one hour. Monitoring at this site experienced several interruptions:

- from 4 April to 8 May 2023;
- from 6 June to 22 July 2023;
- from 1 August 2023 to 23 November 2024, when the probe stopped transmitting due to severe damage (the sensor cables were found cut and could not be recovered from within the mud pool);
- after its replacement on 12 January 2024, the probe functioned until 17 April 2025, when it failed again.

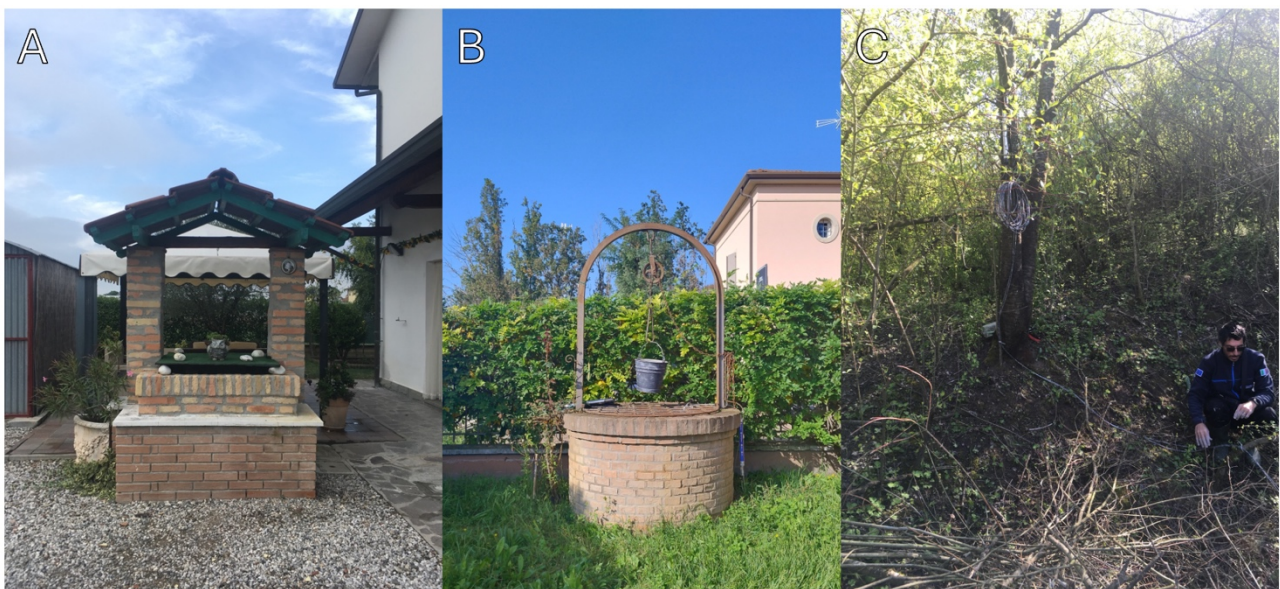


Figure 3.2. Placement of the STS probes in (A) SMN well, (B) Renazzo well and (C) at Polla F in Nirano, where the photo shows the placement of the logger-transmitter close to the mud pool.

### 3.2 *Water Sampling and Analysis*

The investigation of groundwater requires a systematic approach that integrates in situ measurements of physicochemical parameters with laboratory analyses. This methodology ensures the capture of both short-term variability and long-term hydrochemical trends. Field measurements, obtained using a multiparameter probe, offer an immediate and dependable assessment of critical indicators such as pH, oxidation–reduction potential (ORP), temperature, electrical conductivity (EC), and pressure.

These parameters are essential for delineating the physicochemical state of groundwater, evaluating potential contamination, identifying redox conditions, and constraining the geochemical environment where gas migration and water–rock interactions occur.

The Hanna HI9829 multiparameter probe is equipped with sensors for temperature, EC, ORP, pH, total dissolved solids (TDS), pressure/water level, and dissolved oxygen (DO), as well as an integrated GPS for georeferencing. Measurements include from automatic temperature compensation (pH, EC, DO) and barometric compensation (DO). The probe provides high accuracy, with  $\pm 0.02$  units for pH,  $\pm 1$  mV for ORP, and  $\pm 1\%$  of reading or  $\pm 1$   $\mu\text{S}/\text{cm}$  for EC. This configuration ensures robust and accurate *in situ* measurements that effectively complement laboratory-based chemical analyses. Groundwater samples from the SMN and Renazzo wells, as well as mud samples from Nirano, were collected on 4 April 2023. For chemical analyses, different aliquots were prepared and collected as follows:

- an unfiltered aliquot, stored in 125 ml polyethylene (PE) bottles, for the analyses of total alkalinity, labile species ( $\text{NH}_4^+$  and  $\text{NO}_2^-$ ), and major anions.
- a filtered (0.45  $\mu\text{m}$ ) and acidified (suprapur HCl) aliquot, collected in 50 ml high-density polyethylene (HDPE) bottles, for the determination of major cations;
- a filtered (0.45  $\mu\text{m}$ ) and acidified (with 4M ultrapure  $\text{HNO}_3$ ) and stored in special PE samplers (Falcon) for the analysis of minor and trace elements.

The SMN sample was analysed at the Fluid Geochemistry Laboratory of the Department of Earth Sciences, University of Florence, where the determination of major anions and cations was performed by ion chromatography (IC), which allows for accurate and simultaneous quantification of multiple ionic species in aqueous samples. IC for water matrix analysis functions by separating ions and ionisable molecules according to their charge interactions with a stationary phase composed of charged ion-exchange resins (Ahuja et al., 2021). Major ions ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) were determined by IC, using Metrohm 761 and Metrohm 861 for cations and anions, respectively. Labile species ( $\text{NH}_4^+$  and  $\text{NO}_2^-$ ) were determined by molecular absorption spectrophotometry using HACH DR/2010, while total alkalinity ( $\text{HCO}_3^-$ ) was measured via acidimetric titration with Metrohm 794 Basic Titrino, using 0.01 M HCl as titrating solution and methyl-orange as indicator. The analytical error for major components analyses is  $\leq 5\%$ . The Renazzo and Nirano samples were analysed at the Department of Environment and Prevention Sciences (DEPS), University of Ferrara, where chemical analyses on cationic species were performed using inductively coupled plasma–mass spectrometry (ICP-MS) with a Thermo Electron Corporation X series mass spectrometer (Thermo



Fisher Scientific, Bremen, Germany). Samples were appropriately diluted, filtered through 0.45  $\mu\text{m}$  PTFE syringe filters, and stabilised with a few drops of 2%  $\text{HNO}_3$ .

### *3.3 Dissolved Gas Sampling and Analysis*

Dissolved gases are a fundamental component of geochemical investigations, particularly in sedimentary basin environments, where they serve as sensitive indicators of subsurface processes. Their high mobility, combined with markedly different solubility coefficients, makes them excellent geochemical tracers capable of recording fluid–rock interactions and gas migration pathways. Most gases are only sparingly soluble in water, generally less than 60 cc per litre at equilibrium pressure (1 atm), with solubilities decreasing in the sequence  $\text{CH}_4$  (30 cc/L) >  $\text{O}_2$  >  $\text{CO}$  >  $\text{H}_2$  >  $\text{N}_2$  >  $\text{Ar}$  >  $\text{Ne}$  >  $\text{He}$  (8.7 cc/L). In contrast,  $\text{CO}_2$  is highly soluble in water, and its solubility strongly depends on temperature, pressure, salinity, and pH due to the formation of carbonate and bicarbonate species (Wiebe and Gaddy, 1940). These differences strongly influence gas behaviour during water–gas exchange and their persistence in aquifers. From a theoretical standpoint, gas solubility is governed by Henry’s law, which states that, at chemical equilibrium and constant temperature, the amount of gas dissolved in a liquid is directly proportional to its partial pressure in the vapour phase. While Henry’s constant ( $K_h$ ) is independent of pressure, it varies with temperature and salinity, adding further complexity to the interpretation of dissolved gas concentrations in natural waters. The analytical approach adopted in this study follows Capasso and Inguaggiato (1998) and relies on the equilibrium partitioning of gases between the liquid and gas phases. By measuring gas concentrations in the headspace and applying the appropriate partition coefficients for each species, the original concentrations of dissolved gases in the water can be calculated. The sampling setup consists of a glass flask with a known volume (122 cc), sealed with gas-tight rubber or Teflon plugs. The flask is completely filled with the water sample, avoiding trapped air bubbles, and then sealed. Next, 10 cc of pure Ar is injected into the flask while an equivalent volume of water is withdrawn through a needle, maintaining atmospheric pressure. The choice of carrier gas depends on the species being analysed and the capabilities of the gas chromatograph. To minimise the loss of gases such as helium through septum punctures, the flask is kept inverted until analysis. Because natural water samples may contain gases at concentrations either below or above saturation, the internal pressure of the flask is adjusted to atmospheric conditions before gas extraction. This is done by adding or removing small water volumes while the flask is connected upside down to a water-filled tube open to the atmosphere. Once the sample reaches standard temperature (25 °C) and pressure (1 atm) and is shaken for five minutes, gas is extracted for chromatographic analysis using two plastic syringes equipped with

stopcocks: one syringe injects water into the flask, while the other draws the corresponding volume of gas for analysis. The analysis were performed at the Fluid Geochemistry Laboratory of INGV Rome, where major components ( $\text{He}$ ,  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CH}_4$ , and  $\text{CO}_2$ ) were measured using a gas chromatograph (Agilent 7890) equipped with PPU and MS5A columns, associated with a MicroGC Varian 4900 (PPU column) and a dual detector system (TCD and FID), using Ar as the carrier gas. Higher hydrocarbons ( $\text{C}_2\text{H}_6$ ) were analysed with a Shimadzu 2010 GC equipped with FID and a capillary CP Poraplot column, using He as the carrier gas. The analytical precision is better than  $\pm 5\%$  for trace gases and  $\pm 10\%$  for alkanes. Only one dissolved gas sample was collected from the SMN water well on April 4<sup>th</sup> 2023. At the Renazzo site, the occurrence of gas bubbling rendered free gas sampling more suitable, whereas at Nirano, the mixture with mud prevented dissolved gas collection of dissolved gases; the methodology for free gas sampling at both sites is detailed in the subsequent section.

### *3.4 Free Gas Sampling*

At the Nirano site, free gas sampling was performed on April 4<sup>th</sup> 2023, using an inverted funnel placed directly above the visible gas emission point in the mud. Once the funnel was properly immersed in the mud, ensuring isolation from atmospheric contamination, gas was drawn using a syringe connected to the funnel via a three-way valve. The third port of the valve was connected to a 12 cc vial for gas storage. To ensure that only the collected gas entered the vial, which was initially filled with water, a two-needle system connected to the vial septum was used to progressively displace the water as the gas was injected, allowing the sample to fill the vial without air contamination. The analysis of the free gas of Nirano was performed at the Fluid Geochemistry Laboratory of INGV Rome with the instruments and analytical errors described in paragraph 3.1.3. At the Renazzo site, naturally bubbling gases from the water well were collected on 18 December 2024 using an inverted funnel connected via a three-way valve to 5 L multi-layer foil gas sampling bags (Restek). Given the inability to position the funnel directly at the water surface, which was approximately 2 meters below the wellhead, the funnel was secured in place using a rod to prevent air intrusion (Fig. 3.3). Additionally, because the silicone tubing connecting the funnel to the valve was relatively long, the gas was purged multiple times with a 100 mL syringe to ensure that only the well gas filled the connecting lines. Once this procedure was completed, the gas bags were filled. The gas collected at Renazzo was specifically sampled to be used as a calibrating mixture for  $\text{CH}_4$  and  $\text{CO}_2$  sensors in the low-cost monitoring stations, which are described in Section 3.9.



Figure 3.3 – Sampling setup at the Renazzo well.

### *3.5 Soil Gas Sampling and Analysis*

Soil gas prospecting involves the collection of gas samples from the unsaturated zone to determine the concentration of gaseous species permeating the soil pore space. This methodology was first systematised in the 1970s by the U.S. Geological Survey of Colorado (Roberts et al., 1975), which developed a standardised approach to extract interstitial gases for geochemical exploration, and was later adopted and applied extensively in Italy (Lombardi et al., 1984; Tassi et al., 2015). The principle relies on accessing the pore system of shallow soils and retrieving gases that are in equilibrium with both subsurface processes and potential upward migration of deeper volatiles. In this study, soil gas sampling was carried out in the agricultural field of SMN during two measurement campaigns, in September 2022 and April 2023. Sampling points were selected based on the results of preliminary flux surveys, which had already delineated the geometry of the gas flux anomalies. Gas samples were therefore collected both from the area showing the highest gas fluxes and from additional scattered points where no significant flux anomaly was detected, in order to provide a representative comparison. The sampling was performed by inserting a stainless-steel probe into the ground to a depth of 20–40 cm, depending on soil hardness and the possibility of penetrating the vadose zone

without reaching the saturated layer. The probe was connected to a 100 mL syringe via a PTFE three-way valve system used to store the extracted gases in 1L air sampling Supelco® bags (Figure 3.4).



Figure 3.4. Display of the stainless-steel probe inserted into the soil and connected to the three-way valve linking the syringe and sampling bags at the SMN site.

Both inorganic (He, Ne, H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>) and organic (CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>) gases were analysed at the Fluid Geochemistry Laboratory of INGV Rome by a MicroGC Varian 4900, with an analytical error <3%. The same soil gas sample bags were also used to determine the isotopic carbon ratio of both CO<sub>2</sub> and CH<sub>4</sub> (expressed as  $\delta^{13}\text{C-CO}_2$  and  $\delta^{13}\text{C-CH}_4$ , Vienna PeeDee Belemnite (VPDB) ‰), which was measured via cavity ringdown spectroscopy (CDRS) with the Picarro G2201-i instrument, with a precision within 0.16‰ for  $\delta^{13}\text{C-CO}_2$  and 1.15‰ for  $\delta^{13}\text{C-CH}_4$ .

### *3.6 Accumulation Chamber Measurements*

#### *3.6.1 Gas Fluxes from the Soil*

The accumulation chamber method, originally developed for soil respiration studies in agronomy (Parkinson, 1981) and subsequently adapted for soil degassing investigations in volcanic and sedimentary environments (Chiodini et al., 1998; Cardellini et al., 2003), is based on the principle of measuring the rate of change in gas concentration within a sealed volume placed over the emission

surface. As gases emitted from the soil enter the chamber, their concentration increases over time; by recording this temporal increase and knowing the chamber volume and footprint area, the surface flux can be calculated via the following formula:

$$F = \frac{V}{A} \cdot \frac{dC}{dt}$$

where  $F$  is the gas flux ( $\text{mol m}^{-2} \text{s}^{-1}$ ),  $V$  is the chamber volume ( $\text{m}^3$ ),  $A$  is the chamber area ( $\text{m}^2$ ), and  $\frac{dC}{dt}$  is the rate of change in gas concentration inside the chamber over time ( $\text{mol m}^{-3} \text{s}^{-1}$ ). The flux can also be expressed in mass units (e.g.  $\text{g m}^{-2} \text{day}^{-1}$ ) or in  $\text{mmol m}^{-2} \text{day}^{-1}$  by applying appropriate conversion factors based on molecular weight and time.

Gas flux measurements were conducted using a West Systems portable soil flux meter (model WS-LI820) equipped with a type B accumulation chamber. The WS-LI820 model incorporates a double-beam infrared (IR) analyser for  $\text{CO}_2$  detection, compensated for temperature variations between  $-10$  and  $45$  °C and for atmospheric pressure variations in the range of  $660$ – $1,060$  hPa. The concentration measurement range is  $0$ – $20,000$  ppm  $\text{CO}_2$ , and when used with the type B chamber (diameter  $200$  mm, height  $200$  mm, footprint area  $0.0314$   $\text{m}^2$ ), the instrument covers a flux range from  $1$   $\text{mmol m}^{-2} \text{day}^{-1}$  to  $300$   $\text{mol m}^{-2} \text{day}^{-1}$ , with an accuracy of  $\pm 25\%$  for fluxes below  $1.5$   $\text{mol m}^{-2} \text{day}^{-1}$  and  $\pm 10\%$  for higher fluxes.  $\text{CH}_4$  flux measurements were obtained using the optional WS-CH4-TLD detector, which employs Tunable Diode Laser Absorption Spectroscopy (TDLAS) coupled with a multipass Herriott cell. This configuration allows detection over a concentration range of  $0.1$  ppm to  $10\%$  v/v  $\text{CH}_4$ , corresponding to a flux range of  $0.5$   $\text{mmol m}^{-2} \text{day}^{-1}$  to  $1,000$   $\text{mol m}^{-2} \text{day}^{-1}$ , with comparable accuracy classes. All measurements were georeferenced using the system's integrated GPS receiver, which records position and elevation data during flux acquisition. Field operations were managed via the *Flux Revision* software on the supplied handheld computer, which logged concentration-time curves and automatically computed fluxes. Each flux measurement required approximately  $1$ – $2$  minutes, depending on the establishment of a stable concentration-time trend within the accumulation chamber. A clear linear increase in gas concentration, achieved when a measurable flux was present and the chamber was well sealed from the atmosphere, was necessary for reliable flux estimation. Four field campaigns were conducted between May 2022 and October 2023 at the cultivated field of SMN, roughly at six-month intervals (May 2022, September 2022, April 2023, and October 2023). During each campaign, soil  $\text{CH}_4$  and  $\text{CO}_2$  fluxes were measured within a single day of fieldwork, providing representative snapshots of emission patterns under different seasonal conditions. Measurement points were distributed over an area of approximately  $1.5$  hectares, encompassing both sectors showing visible signs of vegetation stress and areas with normal vegetation cover. Measurements were generally easier to perform on bare or sparsely vegetated soil surfaces, where



chamber placement was less constrained (Fig. 3.5). The spatial resolution ranged from 75 to 130 measurement points per campaign, primarily depending on vegetation density and field accessibility.



Figure 3.5. Example of soil gas flux measurement with the accumulation chamber at SMN during field surveys. The photo (April 2023) illustrates chamber deployment on cultivated soil under typical site conditions of sparse vegetation.

The measured fluxes of  $\text{CH}_4$  and  $\text{CO}_2$  (expressed in  $\text{g m}^{-2} \text{d}^{-1}$ ) measured at SMN were interpolated using Sequential Gaussian Simulation (sGs) on a regular  $5 \times 5$  m grid. This geostatistical approach allows the spatial variability of the fluxes to be reproduced without introducing the excessive smoothing that typically characterises deterministic interpolation methods such as ordinary Kriging. In sGs, the values at unsampled locations are estimated sequentially by drawing from the local conditional distribution. At each step, both the measured data and the values simulated at previously estimated nodes are taken into account, thus ensuring that the simulated field honours the spatial correlation structure inferred from the experimental variogram (Deutsch and Journel, 1998). This procedure generates multiple equally probable realisations of the spatial distribution, which collectively provide a statistical representation of the uncertainty associated with the interpolation. For each dataset, 200 independent simulations were performed. The results were then post-processed

to obtain representative maps of CH<sub>4</sub> and CO<sub>2</sub> fluxes, from which the total output (t d<sup>-1</sup>) was calculated by integrating the simulated values over the study area. All simulations and post-processing routines were carried out in R (R Core Team, 2025) through a custom function developed for sG simulation. The function transformed the measured flux data into normal scores in order to approximate a Gaussian distribution suitable for simulation. The spatial correlation structure was analysed and modelled by fitting experimental variograms, either through automated routines (*automap* package) or by manual parametrisation when required. The sequential Gaussian simulation was then performed using the *gstat* package, generating multiple realisations that capture the spatial variability of the fluxes. The simulated values were back-transformed to the original measurement units (e.g., g m<sup>-2</sup> d<sup>-1</sup> or mol m<sup>-2</sup> d<sup>-1</sup> depending on the dataset), and finally aggregated to produce mean maps, probability maps, and integrated estimates of the total flux. This procedure ensured that both the spatial heterogeneity of the measured fields and the associated uncertainty were explicitly taken into account.

### 3.6.2 Gas Fluxes from Mud Pools

For the Nirano mud volcanoes field, the accumulation chamber technique was adapted to account for the specific conditions of bubbling pools. A floating extension structure (54 × 54 × 60 cm), constructed from high-density EPS panels, was designed to enlarge the adequate chamber volume and ensure stability on the mud surface. The structure was equipped with a circular opening at the top, allowing the standard accumulation chamber to be securely positioned. Once deployed, the device floated on the bubbling pool, creating an enclosed headspace suitable for flux measurements (Fig. 3.6). In contrast to soil gas surveys, measurements at Nirano required longer acquisition times, up to 10 minutes. This adjustment was necessary because gas release occurred as irregular bubble bursts rather than as a continuous diffusive flux. Consequently, concentration trends displayed stepwise increases, reflecting the intermittent disruption of the mud–water interface by rising bubbles. Following field deployment with the floating chamber extension, raw measurement logs and accompanying metadata were processed to convert the in-chamber concentration increases into surface fluxes. The effective geometry of the measurement system was defined as the footprint of the floating extension ( $A = A_d$ , expressed in m<sup>2</sup>) and the total headspace volume ( $V = V_d + V_c$ , i.e., extension plus accumulation chamber, expressed in m<sup>3</sup>).





Figure 3.6. Floating extension structure for accumulation chamber measurements at Nirano. (A) Laboratory view of the high-density EPS structure designed to enlarge the chamber volume and ensure buoyancy. Field application of the modified device on bubbling mud pools at Nirano, with the accumulation chamber placed on the circular opening at the top of the structure. (B) Polla F mud Pool and (C) mud pool close to La Giunta.

Because degassing at Nirano mud pools occurred as discrete bursts, step-like increments were first identified in each acquisition. The rate of concentration increase ( $\text{ppm s}^{-1}$ ) was determined subsequently in FluxManager by marking the interval of growth; these event-wise slopes were then converted to mass flux using the ideal-gas formulation:

$$F(g\ m^{-2}d^{-1}) = \frac{pV}{RT} \frac{1}{A} \left( \frac{d\chi}{dt} \right) 10^{-6} M \times 86400,$$

where  $p$  is pressure (Pa),  $T$  temperature (K),  $A$  the footprint area,  $V$  the headspace volume,  $\chi$  the methane/carbon-dioxide mixing ratio (ppm),  $R$  the gas constant and  $M$  the molar mass. For a robust “daily equivalent” flux for each acquisition, two complementary approaches were used:

1. End-to-end estimate. After discarding the initial stabilisation (between 20-30 s), the end-to-end slope  $(\chi_{\text{end}} - \chi_{\text{start}})/\Delta t$  was used in the equation above. This is equivalent to summing all net step increments  $\Sigma \Delta \chi_i$  and normalising by the total duration  $\Delta t$ .
2. Event-based (burst) decomposition. Bursts were detected by thresholding the time derivative of the signal; for each event, the net increment  $\Delta \chi_i$  was quantified from the mean plateau concentrations before and after the step. The mass per burst was then

$$m_i = \Delta \chi_i \frac{pV}{RT} 10^{-6} M,$$

and then burst-driven flux

$$F_{burst} = \frac{\sum i m_i}{A \Delta t} \times 86400.$$

A slowly varying background component was estimated by regressing  $\chi(t)$  on time after masking short windows around detected bursts, yielding  $F_{bg}$  via the same gas-law conversion. The total flux  $F_{tot} = F_{burst} + F_{bg}$ , which is algebraically consistent with the end-to-end estimate, while additionally providing the burst rate  $\lambda$  (events  $s^{-1}$ ) and the mean mass per burst  $\bar{m}$ . For site-level summaries (e.g., Polla F, La Giunta), multiple acquisitions collected in close succession were aggregated by time-weighted averaging:

$$\bar{F}_{site} = \frac{\sum k F_k \Delta t_k}{\sum k \Delta t_k}.$$

Upscaling to the entire pool surface was not attempted unless the active bubbling fraction was independently constrained; therefore, reported fluxes are representative for the covered footprint and conservative for the pool as a whole. Uncertainties were documented by (i) the standard error of the slope (or variability of  $\Sigma \Delta \chi_i$ ), (ii) geometric uncertainty on  $V/A$ , and (iii) between-acquisition variability at each site. The  $V/A$  term typically dominates the propagated error.

### 3.7 Soil temperatures

Soil temperature measurements were carried out only at the SMN site, following the detection of thermal anomalies spatially consistent with the patterns of gas flux. During the September 2022 campaign, a drone-based thermal survey was performed using a DJI Matrice 300 UAV equipped with a Zenmuse H20T radiometric thermal sensor, flown at 60 m above ground level (Fig. 3.7a). From that campaign onward, soil temperature was systematically measured at a depth of  $\sim 10$  cm with a digital thermometer and a 20 cm Type-K thermocouple, at the same locations where soil gas flux was determined. Since the observed heating at the point of  $CH_4$  flux anomaly could have been attributed to the metabolic activity of methanotrophic bacteria, typically occurring within the 20–60 cm soil horizon, a dedicated gradient monitoring station was built up and installed in November 2023 (Fig. 3.7b), to complement discrete soil temperature surveys. This system comprised three XS Mini T1 dataloggers placed at different depths ( $\sim 66$  cm,  $\sim 20$  cm, and surface), together with a Mini TH sensor for air temperature and humidity. Unfortunately, some of the Mini T1 units malfunctioned shortly

after installation or replacement, but the deepest logger (~55 cm) successfully provided a continuous time series until November 2024, when the station was dismantled. Thermal data acquired in the field were processed through the sGs interpolation approach, producing temperature anomaly maps.



Figure 3.7. Soil temperature monitoring at the SMN site. (a) DJI Matrice 300 UAV used during the September 2022 thermal survey. (b) Gradient monitoring station installed in November 2023, comprising three XS Mini T1 dataloggers at different soil depths (~66 cm, ~20 cm, and surface) and a Mini TH sensor for air temperature and humidity measurements.

### 3.8 Methane Flux Estimation from Renazzo Well

Most of the existing literature on CH<sub>4</sub> flux quantification from wells has focused on abandoned oil and gas wells leaking to the atmosphere, where the emission pathways are typically dry conduits of limited diameter. In such cases, the most common approach is the deployment of static or dynamic flux chambers that completely enclose the small wellhead opening. Kang et al. (2014), for instance, measured CH<sub>4</sub> leakage from abandoned wells in Pennsylvania using static chambers, while Pekney et al. (2018) applied similar techniques to report daily CH<sub>4</sub> fluxes from a range of well types. Riddick et al. (2018) further employed dynamic chambers to quantify leakage rates in the order of grams per hour, and technical guidelines issued by the U.S. Department of Energy (2024) likewise recommend chamber-based approaches for detecting emissions as low as one gram per hour. These studies have established flux chamber methods as the standard for well emissions; however, they are inherently suited to small and relatively dry apertures where the entire leakage area can be sealed beneath a chamber. The conditions at the Renazzo site differ substantially from those described above. Here, CH<sub>4</sub> does not leak through a narrow conduit but rather emerges vigorously as bubbles through the

water column of an active well with a diameter of 108 cm. The resulting emission area is nearly an order of magnitude larger than those typically examined, and the presence of continuous bubbling and high humidity precludes the use of conventional closed-chamber techniques. These site-specific features required an adaptation of standard methodologies and the design of two experimental approaches tailored to the geometry and dynamics of this water-filled well. Two complementary experimental approaches were therefore designed and applied in different measurement sessions to quantify CH<sub>4</sub> emissions at the Renazzo well.

In the first configuration, M1, the WS-LI820 accumulation chamber (see Section 3.6.1 for specifications) was employed as a high-frequency gas detector, taking advantage of its one-second acquisition rate and wide dynamic range to capture methane concentrations directly above the bubbling surface without saturation. The chamber was sequentially positioned at nine locations distributed across the 108 cm circular wellhead, namely the four cardinal and four intercardinal positions as well as the centre, each measurement lasting approximately two minutes. Two dedicated field campaigns were carried out on 30 October 2024 and 15 April 2025. During these deployments, a three-dimensional ultrasonic anemometer (Delta OHM HD2003) was simultaneously mounted above the grate. This instrument measures the three components of wind velocity with an accuracy of  $\pm 0.1 \text{ m s}^{-1}$ , in addition to sonic temperature, air temperature, relative humidity ( $\pm 2\%$ ), and barometric pressure ( $\pm 0.5 \text{ hPa}$ ). This instrument was chosen over its 2D version to allow for the future development of a dispersion model (Massaro et al., 2025). The HD2003 was mounted horizontally on the grate, a setup where the vertical velocity was derived from the wind component aligned with the local vertical beneath the sensor, rather than the standard w-axis, due to the horizontal mounting arrangement. The combined acquisition of concentration and velocity allowed a spatially resolved characterisation of the plume dynamics across the well aperture. To reduce potential artefacts, the data were carefully time-synchronised, the humidity filter was maintained on the inlet line, and care was taken to minimise transient effects when relocating the chamber. This first experimental arrangement is illustrated in Figure 3.8.





Figure 3.8. Schematic of the multi-point configuration (M1) on 15 April 2025. The WS-LI820 chamber was sequentially positioned at nine locations (N, S, E, W, NE, NW, SE, SW, and Centre) over the 108-cm aperture while a horizontally mounted 3-D sonic anemometer Delta OHM HD2003 measured wind components; the vertical component aligned with the local plumes was extracted for flux estimation.

To obtain a first-order estimate of the  $\text{CH}_4$  flux, the concentration data acquired with the WS-LI820 at the nine measurement points on the wellhead (cardinal, intercardinal and central positions) were interpolated across the entire circular aperture. For each location, the one-second time series was summarised by its 25th, 50th, and 75th percentiles to mitigate the influence of transient eddies. The point values were positioned at their coordinates on the wellhead (with an effective diameter of 105 cm, incorporating a 10-cm inward offset to avoid the rim) and interpolated onto a  $100 \times 100$  grid using multilevel B-spline approximation (MBA). The resulting interpolated field was masked to the circular

aperture. Ambient background concentrations were subtracted to derive excess concentrations  $\Delta C(x, y)$  in ppm (e.g., 437 ppm for CO<sub>2</sub>; analogous values obtained from upwind records). Concentrations were then converted to mass flux using:

$$\iint_A \Delta C(x, y) \frac{M}{V_m} w_{eff} dA$$

where  $M$  is molar mass (CH<sub>4</sub> = 16.04 g mol<sup>-1</sup>; CO<sub>2</sub> = 44.01 g mol<sup>-1</sup>), and  $V_m = RT/P$  is the molar volume computed from contemporaneous temperature and pressure. The effective vertical velocity  $w_{eff}$  was obtained from the sonic anemometer mounted horizontally on the grate by keeping only time steps where the flow was near-vertical ( $|v| < 0.1$  m s<sup>-1</sup>,  $|w| < 0.1$  m s<sup>-1</sup>,  $u < 0$  upward) and taking the median  $u$ ; the sign was flipped so that upward is positive. The integral in the provided R script calculates the total daily methane emission. This is achieved by first summing the gridded  $\Delta ppm$  values over the entire aperture. This sum is then multiplied by the grid-cell area, converted from cm<sup>2</sup> to m<sup>2</sup> by dividing by 10,000. To convert the concentration to a mass concentration, the result is then multiplied by a conversion factor of  $6.55 \times 10^{-7}$  kg m<sup>-3</sup> ppm<sup>-1</sup>, which is specific to methane at approximately 25 °C and 1 atm. Next, the calculation incorporates the effective wind speed,  $w_{eff}$ , in m s<sup>-1</sup>. Finally, the result is converted to a daily emission rate in tonnes per day (t d<sup>-1</sup>) by multiplying by a factor of 86.4. This value is derived from the conversion of seconds to days (86400 s/day) and kilograms to tonnes (1/1000 kg/tonne), though the script can also report the emission in g d<sup>-1</sup> if desired. The 75th percentile maps are considered the preferred estimates because they effectively minimise the influence of short-term recirculation or downdraft events while still capturing the coherent upward plume. Conversely, the 25th and 50th percentile maps are used to establish lower-bound checks on the emissions.

The second configuration, M2, was conceived to control the geometry of the emission and to allow co-located measurements of gas concentration and flow velocity. A plastic tarp was secured tightly around the wellhead perimeter, and a central pass-through pipe connector was installed, defining a reduced emission cross-section of  $A_r = 0.009503$  m<sup>2</sup> (0.11 m diameter), through which the gas escaped freely without creating overpressure. A hot-wire anemometer (RS-8880, RS Components) was then inserted at the centre of this opening to record continuously the axial velocity of the gas (Fig. 3.9).



Figure 3.9. Reduced-aperture configuration (M2) applied on 15 April 2025 showing tarp constraining the emission to a central orifice ( $A_r$ ) while the a hot-wire probe RS-8880 measured axial velocity co-located with the chamber inlet of WS-LI820 for concentration, enabling co-registered velocity–concentration flux estimates.

This instrument is designed for low-velocity flows, with a measurement range of  $0.1\text{--}25.0\text{ m s}^{-1}$ , a resolution of  $0.01\text{ m s}^{-1}$ , and an accuracy of  $\pm 5\%$  of reading. Simultaneously, the inlet tube of the accumulation chamber, still equipped with a humidity filter, was positioned adjacent to the probe to monitor gas concentrations. Each acquisition lasted about five minutes, and repeated runs were performed on 18 March 2025 and 15 April 2025 to verify the reproducibility of the method. Data inspection focused on identifying stable plateaux in  $\text{CH}_4$  and  $\text{CO}_2$  concentration, while the velocity signal was averaged over the same time windows. For the reduced-area configuration, gas fluxes were derived by combining the velocity measurements from the hot-wire anemometer with the gas concentrations recorded by the accumulation chamber inlet. The effective emission area was defined by the circular aperture created at the centre of the plastic tarp, which in this case measured  $0.0095\text{ m}^2$ . The areal flux  $F$ , expressed in  $\text{g m}^{-2}\text{ d}^{-1}$ , was computed according to

$$F = \frac{v \cdot C \cdot M \cdot 86400}{Vm \cdot 10^6}$$



where  $v$  is the measured axial velocity ( $\text{m s}^{-1}$ ),  $C$  is the gas concentration in ppm,  $M$  is the molar mass of gas ( $\text{g mol}^{-1}$ ), and  $V_m$  is the molar volume of the gas ( $\text{m}^3 \text{mol}^{-1}$ ), calculated as  $V_m = RT/P$  ( $P$  in Pa,  $T$  in K,  $R = 8.314462618 \text{ J mol}^{-1} \text{K}^{-1}$ , where  $P$  and  $T$  are the contemporaneous pressure from the WS-LI820) and temperature (from the RS-8880). This formulation is valid for both  $\text{CH}_4$  ( $M = 16.04 \text{ g mol}^{-1}$ ) and  $\text{CO}_2$  ( $M = 44.01 \text{ g mol}^{-1}$ ), and the corresponding total daily emission ( $\text{g d}^{-1}$ ) was obtained by multiplying the areal flux by the effective cross-sectional area of the reduced aperture  $A_r$ .

### 3.9 Low-cost Monitoring Stations

In recent years, low-cost air quality sensors have gained increasing attention as a complementary approach to conventional monitoring systems. Their affordability and versatility make them attractive for dense monitoring networks, capable of providing high spatial and temporal resolution data in contexts where traditional reference stations would be economically prohibitive (IPCC, 2022; Etiope and Schwietzke, 2019). In particular, metal oxide semiconductor (MOS) sensors such as the Figaro TGS series have been widely investigated due to their potential for detecting near-background  $\text{CH}_4$  concentrations at low cost (Ponzoni et al., 2017; Biagi et al., 2024; Kiplimo et al., 2024). However, the adoption of such devices in real-world conditions remains limited by several challenges: (i) sensor-to-sensor variability, which prevents the direct comparability of measurements; (ii) environmental interferences, including strong sensitivity to temperature and humidity; (iii) cross-sensitivities to other gases; (iv) signal drift over time; and (v) inherently non-linear responses that are difficult to capture with standard calibration curves (Shah et al., 2023; Rivera-Martinez et al., 2021). For instance, manufacturers typically provide only a basic calibration based on the resistance ratio  $R_s/R_0$  (the sensor's measured resistance normalised by its baseline resistance in clean air) in controlled laboratory conditions, but this relationship quickly degrades when sensors are exposed to uncontrolled field environments (Van der Bossche et al., 2017; Collier-Oxandale et al., 2018). These limitations justify the adoption of advanced calibration approaches, including machine learning techniques, which can explicitly account for environmental dependencies and sensor-specific variability (Zimmerman et al., 2018; Mitchell et al., 2024).

### 3.9.1 Stations Architecture

These issues were addressed by designing six low-cost monitoring stations for studying gas dispersion near the Renazzo bubbling well. Each station was built around an Arduino UNO Rev3 microcontroller (Arduino, Turin, Italy), operating at 16 MHz with an ATmega328P processor and featuring a 10-bit analog-to-digital converter (ADC) for sensor signal acquisition. A custom-designed integrated circuit board (Biagi et al., 2024) facilitated sensor connectivity and power management, linking the three primary sensors to the system:

- DHT22 digital sensor (Aosong Electronics) to measure air temperature ( $-40\text{ }^{\circ}\text{C}$  to  $80\text{ }^{\circ}\text{C}$ ,  $\pm 0.5\text{ }^{\circ}\text{C}$  accuracy,  $0.1\text{ }^{\circ}\text{C}$  resolution) and relative humidity ( $0\text{--}100\%$ ,  $\pm 5\%$  accuracy,  $0.1\%$  resolution).
- Figaro NGM2611-E13 metal oxide sensor for  $\text{CH}_4$  (a pre-calibrated module based on the TGS2611-E00 element), provides an analog voltage output proportional to  $\text{CH}_4$  concentration. The manufacturer's specified detection range is 300 to 10,000 ppm, with a factory-calibrated set point at  $5000 \pm 100$  ppm  $\text{CH}_4$  in air under ambient conditions of  $20 \pm 2\text{ }^{\circ}\text{C}$  and  $65 \pm 5\%$  RH, yet the sensor has shown high accuracy for relative measurements  $< 300$  ppm (2-9 ppm, van der Bossche et al., 2017; 2-700 ppm, Bastviken et al., 2020; 0-200 ppm, Mitchell et al., 2024). Its analog signal is digitised as raw ADC counts (1-1023) by the Arduino's 10-bit ADC.
- Sensirion SCD30 (Stäfa, Switzerland) NDIR sensor for  $\text{CO}_2$ , with a concentration range of 400–10,000 ppm,  $\pm 30$  ppm accuracy, 2 s response time, and I<sup>2</sup>C communication.

Additionally, an Adafruit DS3231 Precision RTC module provided accurate timestamps via I<sup>2</sup>C interface, and a microSD card module was connected through SPI for local data storage. Each station was housed in a custom-built casing with an open bottom, protected by a fine mesh to allow airflow while preventing the entry of insects and debris (Fig. 3.10). Data acquisition was set at 0.1 Hz.

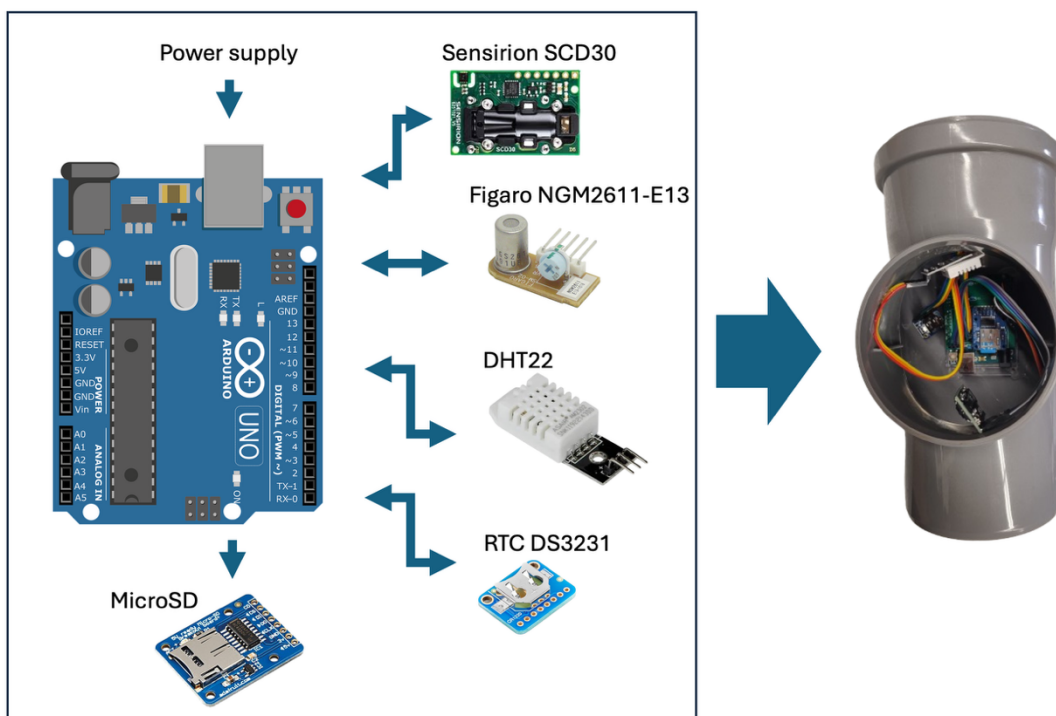


Figure 3.10. Schematic representation of the low-cost monitoring stations. Each unit is built around an Arduino UNO Rev3 microcontroller with a Figaro NGM2611-E13 CH<sub>4</sub> sensor, a Sensirion SCD30 CO<sub>2</sub> sensor, a DHT22 temperature and humidity sensor, a real-time clock (RTC) module, and an SD card for data storage. The right panel shows the internal arrangement of components within the protective casing.

### 3.9.2 Settings for Experimental Calibration of Sensors

The calibration of the low-cost monitoring stations was carried out in three successive experimental setup phases, each designed to progressively expand the range of CH<sub>4</sub> concentrations and environmental conditions represented in the training dataset. This approach was necessary because calibrations performed only under ambient atmospheric conditions are poorly transferable to field deployments such as Renazzo, where CH<sub>4</sub> levels are highly variable and may reach several orders of magnitude above background. Limiting the training set to near-atmospheric concentrations would have led to negative predictions, poor model performance, and large uncertainties at elevated levels. By combining ambient air measurements, controlled chamber experiments, and high-concentration exposures, the calibration dataset was systematically expanded to ensure that the subsequent machine learning models could reproduce the full dynamic range of sensor responses under realistic operating conditions.

### Phase 1 – Ambient calibration (July 12–23, 2024).

In the first phase, all six stations were co-located outdoors with a Picarro G2201-i analyser, used as the reference instrument, with a detection range of 1.8–500 ppm for CH<sub>4</sub> and 380–2,000 ppm for CO<sub>2</sub>. The Picarro inlet was extended with a silicone tube to sample the same air volume as the stations (Fig. 3.11A–B). Ambient CH<sub>4</sub> concentrations during this period ranged from approximately 1.9 to 3.1 ppm, reflecting typical atmospheric background levels. Synchronisation between the low-cost stations and the analyser was achieved by generating short, well-defined CO<sub>2</sub> pulses (brief manual exhalations into the inlets), which were simultaneously recorded by both instruments and allowed precise alignment of the two datasets. The resulting data formed the baseline for training an initial Random Forest (RF) model, which demonstrated high accuracy at near-background concentrations but limited predictive capacity when later deployed under the higher CH<sub>4</sub> levels at Renazzo. RF served as a non-linear ensemble baseline; ANNs were adopted for CH<sub>4</sub> due to poor RF performance at high concentrations.

### Phase 2 – Controlled environment calibration (January 8–10, 2025).

To overcome this limitation, a second calibration was conducted under controlled laboratory conditions (Fig. 3.11C–D). The stations were placed inside a sealed polystyrene crate equipped with dual inlets for the Picarro analyser and for CH<sub>4</sub>-rich gas injections. The gas mixture, which was sampled directly from the Renazzo well and collected into Restek Tedlar 5 L bags using the procedure described in section 3.1.4, was used to inject progressively higher CH<sub>4</sub> concentrations into the crate without dilution. Environmental conditions inside the crate were actively modified to broaden the calibration dataset: temperature ranged from 10 to 37 °C by alternating ambient heating with the use of ice packs, while relative humidity ranged from 32 to 86 %, regulated with wet sponges to counterbalance the dryness of injected gas (initial RH ~30%). Only Picarro CH<sub>4</sub> data ≤500 ppm were retained for this phase to remain within the analyser's linear response range. This setup allowed the inclusion of intermediate CH<sub>4</sub> concentrations and variable T–RH conditions, addressing the cross-sensitivities of the MOS sensors.

### Phase 3 – High-concentration calibration with accumulation chamber (January 15, 23, 28, 2025).

The third phase extended the calibration to very high CH<sub>4</sub> concentrations, approaching those observed at the Renazzo well (Fig. 3.11E). The stations were placed in pairs in a smaller insulated casing powered by external battery banks and connected via silicon tubes to the West Systems accumulation

chamber analysers (see section 3.1.6 for instrument specifics). Three-way valves allowed controlled gas injection, pressure regulation, and real-time monitoring of concentration peaks. Synchronisation between West System analysers and station sensors was performed manually by matching distinct CH<sub>4</sub> peaks in both datasets. This configuration enabled calibration up to ~16,000 ppm, thereby covering the full range of concentrations expected during field deployment.

Overall, these three calibration phases systematically broadened the training dataset from ambient atmospheric CH<sub>4</sub> levels to concentrations four orders of magnitude higher, under variable temperature and humidity conditions. This comprehensive dataset was fundamental for training robust machine learning models capable of accurately reproducing the sensors' non-linear responses and environmental dependencies during long-term monitoring at the Renazzo site.



Figure 3.11. Experimental calibration setups of the low-cost monitoring stations. (A–B) Phase I: collocation of all stations with a Picarro G2201-i analyser, used as reference instrument, under ambient atmospheric CH<sub>4</sub> concentrations. (C–D) Phase II: controlled enclosure tests, where the stations were exposed to CH<sub>4</sub>-enriched gas sampled from the Renazzo well, allowing calibration across intermediate concentrations under regulated temperature and humidity conditions. (E) Phase III: portable setup for exposure to high CH<sub>4</sub> concentrations, using an accumulation chamber coupled with a TLD analyser to extend the calibration range up to ~16,000 ppm.



### 3.9.3 Field Placement

Between October 30<sup>th</sup> and November 21<sup>st</sup> 2024, the six low-cost monitoring stations (S1–S6) were deployed at the Renazzo site to investigate atmospheric CH<sub>4</sub> concentrations near the well affected by persistent gas bubbling. The stations were arranged radially with respect to the well, considered the emission source, and placed at varying horizontal distances (d) to capture the spatial distribution of CH<sub>4</sub>. The relative positions and heights of the stations are illustrated in Figure 3.12.

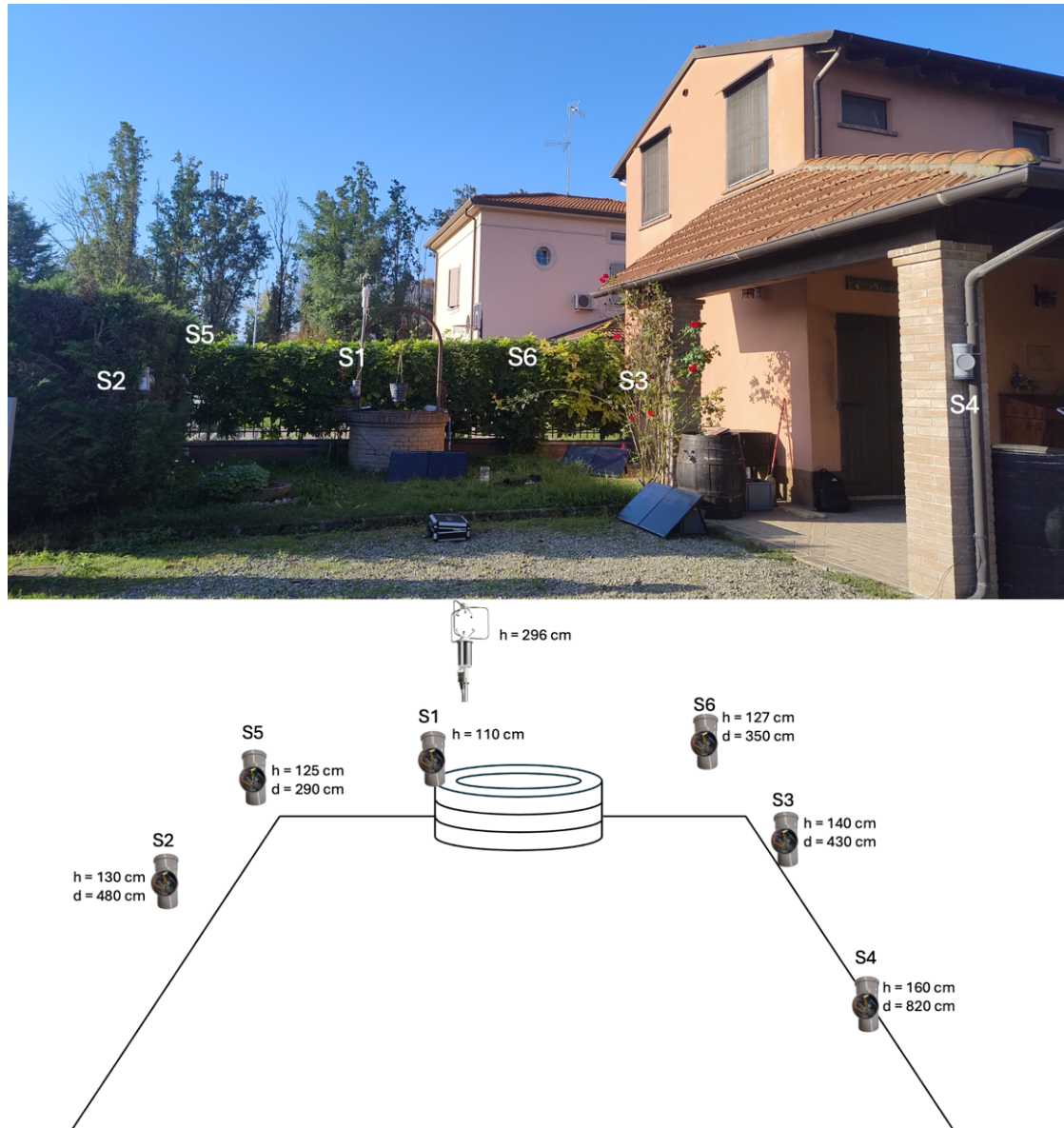


Figure 3.12. Field setup of the low-cost monitoring stations at the Renazzo site. The 3D anemometer continuously acquired data at approximately 40 Hz, including atmospheric pressure, air temperature, relative humidity, wind speed along the three orthogonal components (u, v, and w), and wind direction (0–360°). The stations were measuring at 0.1 Hz frequency and the obtained data from (CH<sub>4</sub>, CO<sub>2</sub>, T and RH) was averaged over 1-minute intervals to reduce high-frequency noise while preserving variability.



Station S1 was located closest to the well ( $d = 40$  cm, height = 110 cm), directly above the emission source. The other stations were positioned at increasing distances: S2 ( $d = 480$  cm,  $h = 130$  cm), S3 ( $d = 430$  cm,  $h = 140$  cm), S4 ( $d = 820$  cm,  $h = 160$  cm), S5 ( $d = 290$  cm,  $h = 125$  cm), and S6 ( $d = 350$  cm,  $h = 127$  cm). The stations were powered in pairs using 12V batteries connected to solar panels, ensuring autonomous functioning throughout the monitoring period. A 3D sonic anemometer (model HD2003.1) was mounted above the well at a height of 296 cm, powered by a dedicated 12V battery. Wind vectors were derived from the 3-D sonic anemometer at the wellhead and the wind direction used in all directional diagnostics follows the meteorological from-direction convention.

### 3.9.4 Neural Network Model

The calibration of the low-cost methane sensors was implemented through a supervised machine learning approach based on artificial neural networks (ANNs). Calibration of CH<sub>4</sub> and CO<sub>2</sub> sensors was initially attempted using an RF model (Biagi et al., 2024). While this approach yielded accurate results at near-background levels, it proved inadequate for the Figaro sensors when exposed to the high CH<sub>4</sub> concentrations typical of the Renazzo site, occasionally producing unrealistic outputs (including negative values). To address this issue, the calibration strategy was further developed by adopting ANN models, better suited to reproduce the non-linear response of MOS sensors under variable environmental conditions. The NGM2611-E13 CH<sub>4</sub> sensor output was read via the Arduino's 10-bit ADC (0–1023 counts, corresponding to 0–5 V). Although  $R_s/R_0$  normalisation was technically possible, it was discarded due to baseline drift and environmental dependencies (Biagi et al., 2024; Mitchell et al., 2024). Instead, raw ADC counts were directly employed as inputs for the machine learning models, preserving the intrinsic dynamics of sensor responses and avoiding the propagation of additional uncertainty. The workflow was structured into a series of steps, from data preparation to model training and post-processing of predictions (Fig. 3.13). The first step consisted of loading and cleaning the calibration datasets acquired during the three experimental phases. Time stamps were standardised into a uniform datetime format, and all missing or corrupted records were removed to avoid biases in the training process. Since the microcontroller recorded sensor outputs as 10-bit ADC counts (0–1023), these raw values were retained instead of being converted into resistance ratios ( $R_s/R_0$ ). Preliminary analyses had shown that baseline drift and environmental interferences strongly degraded  $R_s/R_0$  stability, whereas direct use of raw counts preserved the intrinsic dynamics of the sensor response. Subsequently, the data underwent type conversion and transformation. All features of interest—relative humidity (RH), temperature (T), CH<sub>4</sub> ADC counts, and reference CH<sub>4</sub>

concentrations from the analysers—were cast to 32-bit floating-point precision to ensure numerical stability during training. Given the broad dynamic range of CH<sub>4</sub> concentrations (from ~2 ppm background levels to ~16,000 ppm in chamber experiments), the target variable was log-transformed as  $\log(1 + \text{CH}_4)$ . This step reduced skewness and allowed the network to learn patterns more effectively across different scales.

Once transformed, both input features (RH, T, CH<sub>4</sub> counts) and target values ( $\log\text{-CH}_4$ ) were standardised using z-score normalisation, i.e. centring each variable by subtracting the mean and dividing by the standard deviation. Standardisation prevented variables of larger magnitude from dominating the training process and improved the efficiency of gradient descent. The fitted scaling parameters were saved to ensure consistent transformations could be applied when calibrating new datasets. The prepared dataset was then split into training and testing subsets, with 90% of the data used for model fitting and 10% reserved for independent evaluation. To further validate model robustness, a five-fold cross-validation scheme was applied within the training set, whereby the data were iteratively partitioned into training and validation folds. This procedure yielded average metrics and their variability, providing an estimate of model generalisation to unseen conditions. The ANN itself was designed as a feedforward network with three hidden layers. The first layer contained 3 neurons, followed by two larger layers of 64 and 32 neurons, respectively. All hidden layers used the ReLU (Rectified Linear Unit) activation function, chosen for its ability to capture non-linear relationships while maintaining computational efficiency. To limit overfitting and penalise overly complex models, each dense layer was regularised with an L2 penalty ( $\lambda = 0.01$ ). The final output layer consisted of a single neuron with linear activation, directly returning the calibrated methane concentration in transformed space. Training was carried out using the Adam optimiser with a learning rate of 0.0005, a batch size of 32, and 200 epochs. Adam was selected for its adaptive learning rates and good performance in non-stationary optimisation problems. The model was compiled with the mean squared error (MSE) loss function, appropriate for continuous regression tasks. At the end of training, model performance was assessed both on the cross-validation folds and on the independent test set. Evaluation metrics included MSE, mean absolute error (MAE), and the coefficient of determination ( $R^2$ ). In addition, residual analysis was performed by plotting prediction errors against predicted concentrations and by inspecting their distribution. These diagnostics ensured that no systematic bias was introduced and that errors were approximately symmetrically distributed across the concentration range. Finally, predictions were back-transformed to restore physical units. This required inverting the standardisation (multiplying by the original standard deviation and adding the mean) and reversing the logarithmic transformation ( $\text{CH}_4_{\text{calib}} = \exp(\text{CH}_4_{\text{standard}}) - 1$ ). The result was a time series of calibrated methane concentrations in ppm, which could then be compared

directly with reference measurements and applied to field monitoring datasets. Through this workflow, the ANN models successfully captured the non-linear behaviour and environmental dependencies of the MOS sensors. The calibration framework proved capable of transferring across different experimental conditions, from ambient background air to high CH<sub>4</sub> concentrations at Renazzo, thereby enabling accurate and robust long-term deployment of the low-cost monitoring stations. The complete ANN script and processing parameters are provided in Appendix A.5 to ensure reproducibility.

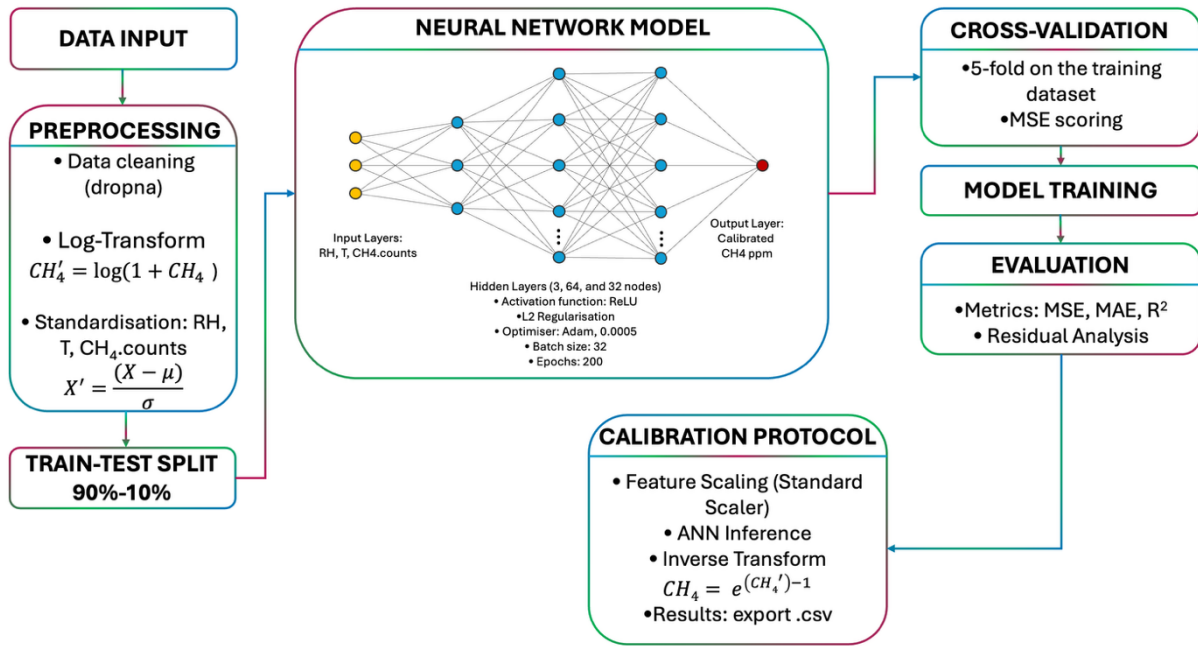


Figure 3.13. Workflow of the artificial neural network calibration model applied to low-cost CH<sub>4</sub> sensors.

### 3.10 Vegetation Anomalies and Spectral Data Processing

At SMN, field inspections during flux campaigns revealed persistent patterns of bare or sparsely vegetated patches. A retrospective screening of high-resolution imagery in Google Earth Pro confirmed that these features recur in similar positions over multiple years (Fig. 3.14), suggesting a temporally stable anomaly potentially linked to local methane seepage and ground heating, as reported for comparable sites in the Po Plain (e.g., Capaccioni et al., 2015; Sciarra et al., 2021). On this basis, a satellite-based analysis was designed to quantify the vegetation response objectively through a reflectance index. The approach exploits the contrasting spectral behaviour of vegetation in the red and near-infrared (NIR) portions of the spectrum: chlorophyll strongly absorbs red light

( $\approx 630\text{--}690$  nm), whereas leaf internal structure reflects NIR ( $\approx 760\text{--}900$  nm) (Tucker, 1979). Combining these domains enhances the separability between photosynthetically active vegetation and background soil. The Ratio Vegetation Index (RVI; Pearson and Miller, 1972) was adopted to emphasise this contrast, defined as

$$\text{RVI} = \frac{\text{NIR}}{\text{R}},$$

where R and NIR are the mean reflectances in the red and near-infrared channels, respectively. Spectral processing was conducted in Google Earth Engine (GEE), using Sentinel-2 Level-2A surface reflectance data (COPERNICUS/S2\_HARMONIZED). The image collection (January 2015–November 2023) was filtered spatially to a  $100 \times 100$  m box centred on the seepage zone and radiometrically by retaining only scenes with CLOUDY\_PIXEL\_PERCENTAGE < 20%. A QA60-based mask removed pixels flagged as clouds or cirrus (bits 10 and 11), and reflectance values were rescaled (/10,000) to the calibrated 0–1 range. The collection was then clipped to the study area. RVI was computed from bands B8 (NIR, 842 nm) and B4 (red, 665 nm); to further reduce residual cloud/shadow contamination, pixels with red reflectance < 0.1 were excluded following the Sentinel-2 cloud detector threshold. Because both B4 and B8 have 10 m spatial resolution, the resulting RVI products preserve fine-scale variability across the field. Temporal trends in vegetation stress were evaluated by averaging RVI within two circular regions of interest (radius  $\sim 30$  m): (i) the centre of the anomaly, recurrently bare or sparsely vegetated (RVI<sub>an</sub>), and (ii) a nearby reference area with nominally healthy vegetation (RVI<sub>bg</sub>). The location of these regions was guided by CH<sub>4</sub> flux maps from the initial field campaigns, delineating zones of active seepage versus unaffected vegetation.



Figure 3.14. Time-stamped Google Earth Pro imagery (2002–2022) showing the recurrence of bare/sparse vegetation patches at SMN (white dates indicate month–year). These observations motivated the satellite-based RVI analysis described in the text.

## Chapter IV – Santa Maria Nuova

This chapter presents the results of the investigations conducted at the SMN site, with an emphasis on (i) the spatio-temporal dynamics of diffuse CH<sub>4</sub> and CO<sub>2</sub> fluxes, (ii) soil-gas composition and isotopes, (iii) ground heating and vegetation responses. For clarity, the results are organised into dedicated subsections, each focusing on a specific type of measurement or analysis. The presentation of the datasets is followed by a discussion section, where the main findings are examined and compared in order to highlight temporal variations, spatial patterns, and possible controlling factors.

### 4.1 Results

#### 4.1.1 Groundwater and hydrochemical parameters

Hourly groundwater level, temperature and EC (June 2023 - August 2025; Fig. 4.1) show seasonal and recharge driven variability, without coupled salinity, temperature or phreatic excursions suggestive of deep inputs. All variations, even abrupt ones, can be reconnected to meteoric water inputs.

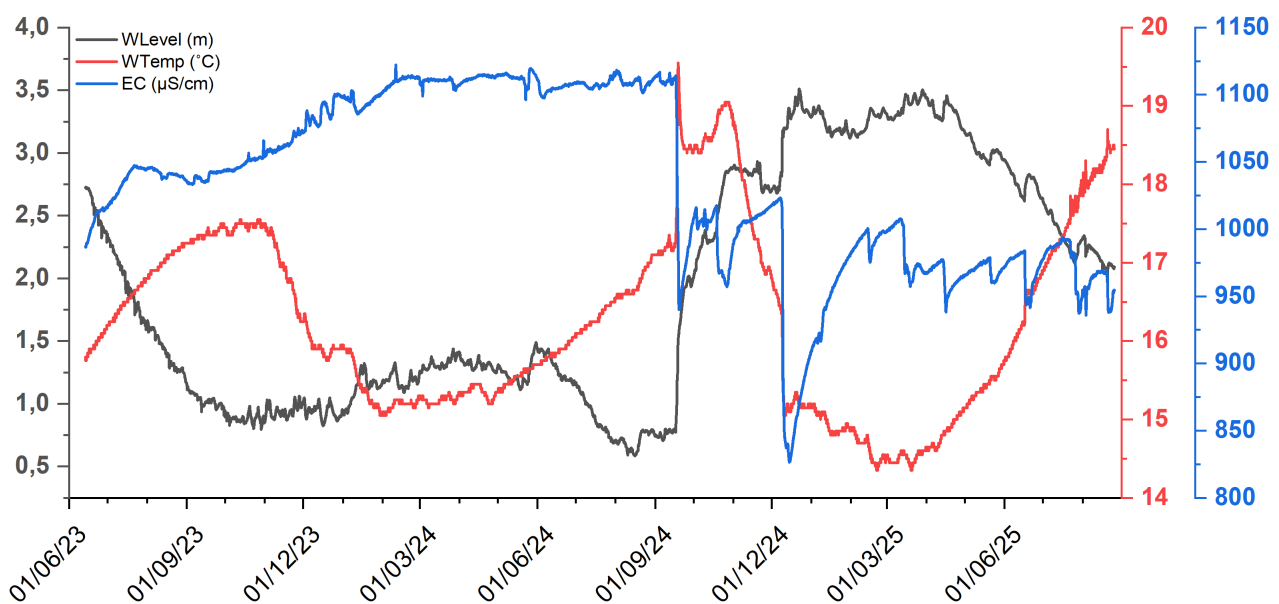


Figure 4.1. Time series of the STS probe installed at SMN well, from 14/06/2023 to 26/08/2025.



Seasonal variations were evident in water temperature, which ranged between  $\sim 14$  and  $20\text{ }^{\circ}\text{C}$ , while electrical conductivity fluctuated between  $\sim 800$  and  $1150\text{ }\mu\text{S cm}^{-1}$ . Water level showed a general declining trend over summer, followed by partial recoveries in autumn and winter. The only abrupt variations occurred in autumn 2024, corresponding to intense rainfall events, during which sharp fluctuations in all three parameters were recorded. Apart from these transient responses, the groundwater parameters did not show remarkable deviations from local background conditions. In situ measurements of groundwater parameters at the SMN well are summarised in Table 4.1. pH values remained relatively stable throughout the monitoring period, between 7.6 and 7.9. Water temperature showed modest seasonal variability, from  $14.9\text{ }^{\circ}\text{C}$  in May 2022 to nearly  $18\text{ }^{\circ}\text{C}$  in March 2023. Electrical conductivity was consistently around  $1040\text{--}1090\text{ }\mu\text{S cm}^{-1}$ , with corresponding TDS values between  $\sim 522$  and  $602\text{ mg L}^{-1}$ . Oxidation–reduction potential (ORP) exhibited a wider variability, ranging from slightly reducing conditions ( $-11.9\text{ mV}$  in October 2023) to more oxidising values ( $+119.3\text{ mV}$  in May 2022). Dissolved oxygen values, available for the first two surveys, were between 32–36%.

| Date       | pH  | T( $^{\circ}\text{C}$ ) | EC ( $\mu\text{S cm}^{-1}$ ) | TDS ( $\text{mg L}^{-1}$ ) | ORP (mV) | DO (%) |
|------------|-----|-------------------------|------------------------------|----------------------------|----------|--------|
| 2022/05/13 | 7.9 | 14.87                   | 1080                         | 540                        | 119.3    | 31.9   |
| 2022/09/19 | 7.8 | 17.03                   | 1093                         | 547                        | 30.1     | 36.3   |
| 2023/04/03 | 7.6 | 17.97                   | 1044                         | 602                        | --       | --     |
| 2023/10/19 | 7.8 | 17.33                   | 1045                         | 522                        | -11.9    | --     |

Table 4.1. Summary of *in situ* groundwater measurements at the SMN well during the monitoring campaigns (2022–2023).

Chemical analyses of major ions are available for two campaigns, April and October 2023 (Table 4.2). In both cases, the groundwater indicates a Ca–Mg– $\text{HCO}_3$  composition typical of shallow Po Plain aquifers, with bicarbonate as the dominant anion ( $687\text{--}683\text{ mg L}^{-1}$ ) and overall moderate salinity. The sample from April 2023 shows a slight cation excess, therefore direct quantitative comparison should be addressed with caution. Within this context,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  occur at comparable levels, but with a marked seasonal shift in their balance:  $\text{Ca}^{2+}$  decreases from  $113$  to  $71.4\text{ mg L}^{-1}$  between April and October, whereas  $\text{Mg}^{2+}$  remains  $\sim 81\text{--}84\text{ mg L}^{-1}$ , yielding a Ca/Mg ratio that drops from  $>1$  to  $<1$ .  $\text{Na}^+$  is stable around  $51\text{--}54\text{ mg L}^{-1}$ , and  $\text{K}^+$  remains low ( $2.6\text{--}2.7\text{ mg L}^{-1}$ ), supporting an overall moderate salinity within the bicarbonate facies.

Among minor anions,  $\text{Cl}^-$  declines from 54 to 29  $\text{mg L}^{-1}$  and  $\text{SO}_4^{2-}$  is consistently very low (3.3→2.5  $\text{mg L}^{-1}$ ).  $\text{Br}^-$  sits at 0.4–0.5  $\text{mg L}^{-1}$  and  $\text{F}^-$  near 0.9–1.0  $\text{mg L}^{-1}$ . The low  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  (0.19→0.07  $\text{mg L}^{-1}$ ;  $\text{NO}_2^-$  detected only in October at 0.23  $\text{mg L}^{-1}$ ) together with  $\text{NH}_4^+$  (1.8 → 0.13  $\text{mg L}^{-1}$  in October) point to mildly reducing conditions in the sampled horizon—conditions compatible with environments where methane is present.

| Date       | $\text{HCO}_3^-$ | $\text{F}^-$ | $\text{Br}^-$ | $\text{Cl}^-$ | $\text{NO}_2^-$ | $\text{NO}_3^-$ | $\text{SO}_4^{2-}$ | $\text{PO}_4^{3-}$ | $\text{Ca}^{2+}$ | $\text{Mg}^{2+}$ | $\text{Na}^+$ | $\text{K}^+$ | $\text{NH}_4^+$ |
|------------|------------------|--------------|---------------|---------------|-----------------|-----------------|--------------------|--------------------|------------------|------------------|---------------|--------------|-----------------|
| 2023/04/03 | 687              | 0.9          | 0.4           | 54            | na              | 0.19            | 3.3                | na                 | 113              | 80.6             | 53.5          | 2.7          | 1.8             |
| 2023/10/19 | 683              | 0.9          | 0.5           | 29            | 0.23            | 0.07            | 2.5                | 0.02               | 71.4             | 83.6             | 50.6          | 2.6          | 0.13            |

Table 4.2. Chemical analyses of the SMN water samples. All values expressed as  $\text{mg L}^{-1}$ .

Dissolved gas analysis (Table 4.3) highlighted the presence of methane as the dominant species, with concentrations of ~0.10 mmol/L (3.3 vol%), accompanied by  $\text{CO}_2$  (0.32 mmol/L, 0.8 vol%),  $\text{N}_2$  (0.49 mmol/L, 21.4%), and  $\text{O}_2$  (0.14 mmol/L, 4.8%). Trace amounts of  $\text{H}_2$  (0.41 mmol/L), He and Ne were also detected. Isotopic signatures indicated  $\delta^{13}\text{C-CH}_4 = -67\text{‰ V-PDB}$  and  $\delta^{13}\text{C-CO}_2 = -30\text{‰ V-PDB}$ .

| Date       | He       | Ne       | $\text{H}_2$ | $\text{O}_2$ | $\text{N}_2$ | $\text{CH}_4$ | $\text{CO}_2$ | $\delta^{13}\text{C-CH}_4$ | $\delta^{13}\text{C-CO}_2$ |
|------------|----------|----------|--------------|--------------|--------------|---------------|---------------|----------------------------|----------------------------|
| 2023/04/03 | 0.000003 | 0.000007 | 0.00041      | 0.14         | 0.49         | 0.10          | 0.32          | -67                        | -30                        |

Table 4.3. Major components and isotopic ratio  $\delta^{13}\text{C}$  in  $\text{CH}_4$  and  $\text{CO}_2$  of the dissolved gases in the SMN water sample. Values expressed as mmol/L and ‰ V-PDB.

#### 4.1.2 Diffuse gas emissions from the SMN field

A summary of  $\text{CH}_4$  and  $\text{CO}_2$  fluxes recorded during the 2022-2023 field campaigns, along with total output flux from the sGs simulations, is presented in Table 4.4. In May 2022,  $\Phi\text{CH}_4$  ranged from 0 to 917  $\text{g m}^{-2} \text{d}^{-1}$ , with a total estimated output of  $0.82 \pm 0.1 \text{ t d}^{-1}$ .  $\Phi\text{CO}_2$  varied between 28.2 and 308.5  $\text{g m}^{-2} \text{d}^{-1}$ , resulting in a total emission of  $1.8 \pm 0.18 \text{ t d}^{-1}$ . By September 2022,  $\text{CH}_4$  total output had significantly decreased to  $0.008 \pm 0.003 \text{ t d}^{-1}$ , with fluxes spanning from 0 to 5.8  $\text{g m}^{-2} \text{d}^{-1}$ , while  $\Phi\text{CO}_2$  ranged from 9.4 to 174.8  $\text{g m}^{-2} \text{d}^{-1}$ , with an emission of  $0.62 \pm 0.05 \text{ t d}^{-1}$ . The April 2023 campaign yielded a maximum  $\text{CH}_4$  flux of 224.4  $\text{g m}^{-2} \text{d}^{-1}$ , with an estimated total of  $0.51 \pm 0.09 \text{ t d}^{-1}$ . Meanwhile,  $\text{CO}_2$  fluxes ranged from 5.2 to 157.8  $\text{g m}^{-2} \text{d}^{-1}$ , contributing to a total emission of  $0.65 \pm 0.07 \text{ t d}^{-1}$ . In October 2023,  $\text{CH}_4$  fluxes decreased again, from 0 to 4.6  $\text{g m}^{-2} \text{d}^{-1}$ , with a total

output of  $0.005 \pm 0.002 \text{ t d}^{-1}$ .  $\text{CO}_2$  fluxes showed a wider range, from 1.9 to  $466.1 \text{ g m}^{-2} \text{ d}^{-1}$ , with an overall emission of  $0.66 \pm 0.04 \text{ t d}^{-1}$ .

| $\Phi\text{CH}_4 \text{ (g m}^{-2} \text{ d}^{-1}\text{)}$ |             |      |        |                    |                             |
|------------------------------------------------------------|-------------|------|--------|--------------------|-----------------------------|
|                                                            | Value Range | Mean | Median | Standard Deviation | Output in $\text{t d}^{-1}$ |
| May 2022                                                   | 0 – 916.9   | 25.3 | 11.6   | 51.3               | $0.75 \pm 0.1$              |
| September 2022                                             | 0 – 5.8     | 0.5  | 0.4    | 0.4                | $0.008 \pm 0.003$           |
| April 2023                                                 | 0 – 224.4   | 28.2 | 18.1   | 31.7               | $0.51 \pm 0.09$             |
| October 2023                                               | 0 – 4.6     | 0.4  | 0.2    | 0.5                | $0.005 \pm 0.002$           |

| $\Phi\text{CO}_2 \text{ (g m}^{-2} \text{ d}^{-1}\text{)}$ |              |      |        |                    |                             |
|------------------------------------------------------------|--------------|------|--------|--------------------|-----------------------------|
|                                                            | Value Range  | Mean | Median | Standard Deviation | Output in $\text{t d}^{-1}$ |
| May 2022                                                   | 28.2 - 308.5 | 73.8 | 63.8   | 35.8               | $2.18 \pm 0.18$             |
| September 2022                                             | 9.4 - 174.8  | 42.4 | 35.8   | 24.3               | $0.62 \pm 0.05$             |
| April 2023                                                 | 5.2 - 157.8  | 37.2 | 31.7   | 24.2               | $0.65 \pm 0.07$             |
| October 2023                                               | 1.9 – 466.1  | 43.9 | 26.3   | 48.3               | $0.66 \pm 0.04$             |

Table 4.4. Descriptive statistics of the soil diffuse  $\text{CH}_4$  and  $\text{CO}_2$  flux values for the 2022-2023 surveys (in  $\text{g m}^{-2} \text{ d}^{-1}$ ) and total output in  $\text{t d}^{-1}$ .

Figure 4.2 shows sGs maps (200 realisations) for  $\Phi\text{CH}_4$  and  $\Phi\text{CO}_2$ . The spatial distribution patterns indicate a persistent hotspot recurring in the south-central sectors of the agricultural field across all surveys, with seasonal amplitude changes throughout the two-year observation period.

For completeness, the individual flux measurements collected during each campaign are reported in Appendix A.1-A.4. These tables provide the raw data underlying the statistical summaries presented in Table 4.4, offering a detailed overview of the spatial variability observed at the sampling scale.

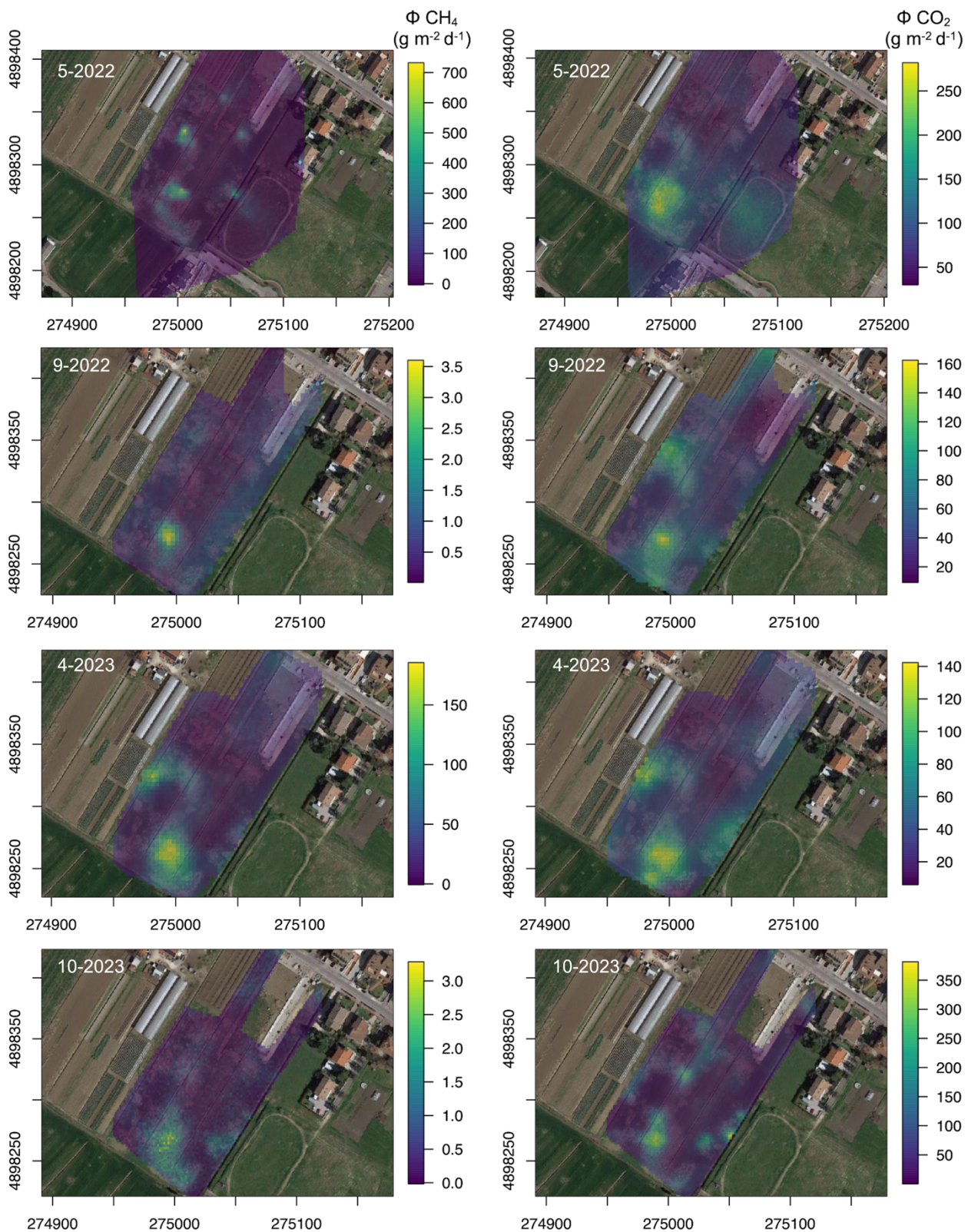


Figure 4.2. Flux distribution of  $\text{CH}_4$  and  $\text{CO}_2$  at the SMN Site during the 2022-2023 observation period. Both flux measurements were processed using Sequential Gaussian Simulation and are expressed in  $\text{g m}^{-2} \text{d}^{-1}$ .

### 4.1.3 Interstitial Soil Gases and Isotopic Data

Interstitial soil gas compositions, sampled following the procedure described in section 3.5, were analysed during two campaigns carried out in September 2022 and April 2023. The results are summarised in Table 4.5, while the location of the sampling points is shown in Fig. 4.3. In September 2022, two gas samples (22A and 22B) were collected in the southern portion of the field. Sample 22A was characterised by atmospheric-like values, with O<sub>2</sub> and N<sub>2</sub> accounting for more than 95% of the gas mixture, CH<sub>4</sub> below 0.001 vol% and CO<sub>2</sub> around 0.1 vol%. Conversely, sample 22B displayed a markedly different composition, with CH<sub>4</sub> reaching 29.8 vol%, accompanied by 6.4 vol% CO<sub>2</sub> and significantly reduced concentrations of atmospheric gases (O<sub>2</sub> = 4.7 vol%). The April 2023 survey extended the dataset to six additional sites (23A–23F). Interstitial soil gases span trace (0.95 vol% in 23A) to CH<sub>4</sub>-rich mixtures ( $\leq 54.1$  vol%, in 23E). The highest methane contents were accompanied by depleted O<sub>2</sub> levels, in some cases below 10 vol% (23D and 23E). CO<sub>2</sub> concentrations also varied, between 0.07 and 6.9 vol%. Only sample 23F, collected in the northern part of the field, showed background-like conditions, with negligible CH<sub>4</sub> (0.01 vol%) and nearly atmospheric O<sub>2</sub> and N<sub>2</sub>. The CH<sub>4</sub>/CO<sub>2</sub> ratio spanned more than two orders of magnitude, from values close to zero (22A and 23F) up to 26–54 in the CH<sub>4</sub>-rich samples (23D and 23E). Isotopic analyses of CH<sub>4</sub> revealed  $\delta^{13}\text{C}$  values ranging from  $-68\text{‰}$  to  $-78\text{‰}$  V-PDB, while CO<sub>2</sub> isotopes ( $\delta^{13}\text{C}\text{-CO}_2$ ) varied between  $-24\text{‰}$  and  $-52\text{‰}$  V-PDB, where available. Figure 4.3 indicates the points corresponding to the soil gas samples, highlighting how the gas anomalies were mainly concentrated in the southern-central sector of the field, consistent with the area where diffuse flux surveys had previously identified enhanced soil degassing.

| ID   | Date       | O <sub>2</sub><br>vol % | N <sub>2</sub><br>vol % | CH <sub>4</sub><br>vol % | CO <sub>2</sub><br>vol % | CH <sub>4</sub> /CO <sub>2</sub> | $\delta^{13}\text{C}\text{-CH}_4$<br>‰ V-PDB | $\delta^{13}\text{C}\text{-CO}_2$<br>‰ V-PDB |
|------|------------|-------------------------|-------------------------|--------------------------|--------------------------|----------------------------------|----------------------------------------------|----------------------------------------------|
| 22A  | 2022/09/23 | 19.7                    | 75.5                    | 0.00074                  | 0.09                     | 0.01                             | -61                                          | -25                                          |
| 22B  | 2022/09/23 | 4.7                     | 61.7                    | 29.78                    | 6.43                     | 4.63                             | -74.5                                        | -30                                          |
| 23A  | 2023/04/04 | 19.99                   | 78.71                   | 0.95                     | 0.07                     | 13.57                            | -72                                          | -26                                          |
| 23A* | 2023/04/04 | 19.99                   | 77.65                   | 1.03                     | 0.09                     | 11.44                            | -68                                          | -39                                          |
| 23B  | 2023/04/04 | 17.73                   | 72.57                   | 7.05                     | 1.23                     | 5.73                             | -69                                          | -35                                          |
| 23C  | 2023/04/04 | 17.74                   | 72.14                   | 7.74                     | 0.88                     | 8.80                             | -76                                          | -24                                          |
| 23D  | 2023/04/04 | 8.25                    | 59.29                   | 25.57                    | 6.88                     | 3.72                             | -68                                          | -52                                          |
| 23E  | 2023/04/04 | 6.07                    | 37.61                   | 54.08                    | 2.69                     | 20.10                            | -77.8                                        | -37                                          |
| 23F  | 2023/04/04 | 20.03                   | 78.32                   | 0.01                     | 0.15                     | 0.07                             | -72                                          | -                                            |

Table 4.5. Displays the sample ID, date, depth, chemical composition in vol%, and the CH<sub>4</sub>/CO<sub>2</sub> ratio, along with the isotopic carbon ratios of CO<sub>2</sub> and CH<sub>4</sub> expressed as  $\delta^{13}\text{C}$  ‰V-PDB for the interstitial gases at the SMN field. The analysis for sample 23A\* relates to a slightly greater depth of 35 cm.



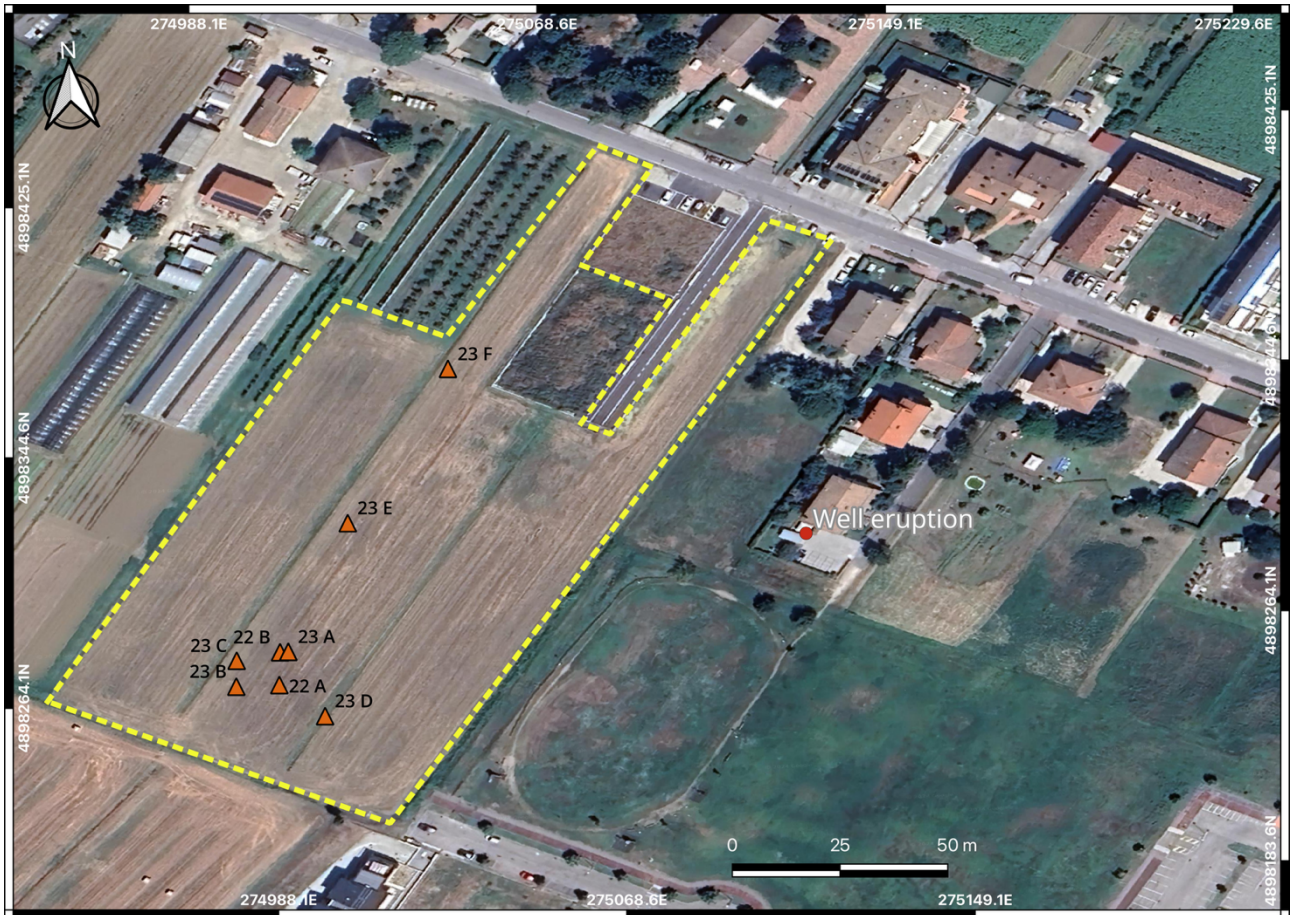


Figure 4.3. Aerial view of the SMN field and surrounding area. The yellow dashed line outlines the cultivated field where gas flux measurements were conducted. The red circle shows the location of the CH<sub>4</sub> saturated well, and orange triangles indicate the sampling points for interstitial gas.

#### 4.1.4 Soil temperature measurements

The spatial distribution of ground surface temperatures obtained through both UAV-based thermal imaging and point-based measurements during the flux campaigns is shown in Fig. 4.4. Panel (a) shows the thermal orthomosaic acquired via drone prior to the September 2022 flux campaign, where a warmer area is clearly visible in the southern-central sector of the cultivated field, where surface temperatures exceed 17 °C, contrasting with surrounding zones measuring as low as ~3 °C. Panels (b), (c), and (d) display soil temperature data collected at ~10 cm depth during the surveys conducted in September 2022, April 2023, and October 2023, respectively. In all three cases, a consistent temperature gradient is observed across the field, with relatively higher values located in the central-southern portion where vegetation appears sparser or absent. The temperature difference between warmer and cooler zones varies across the three campaigns: approximately 5 °C in September 2022 (panel b), up to 3.5 °C in April 2023 (panel c), and exceeding 10 °C in October 2023 (panel d).



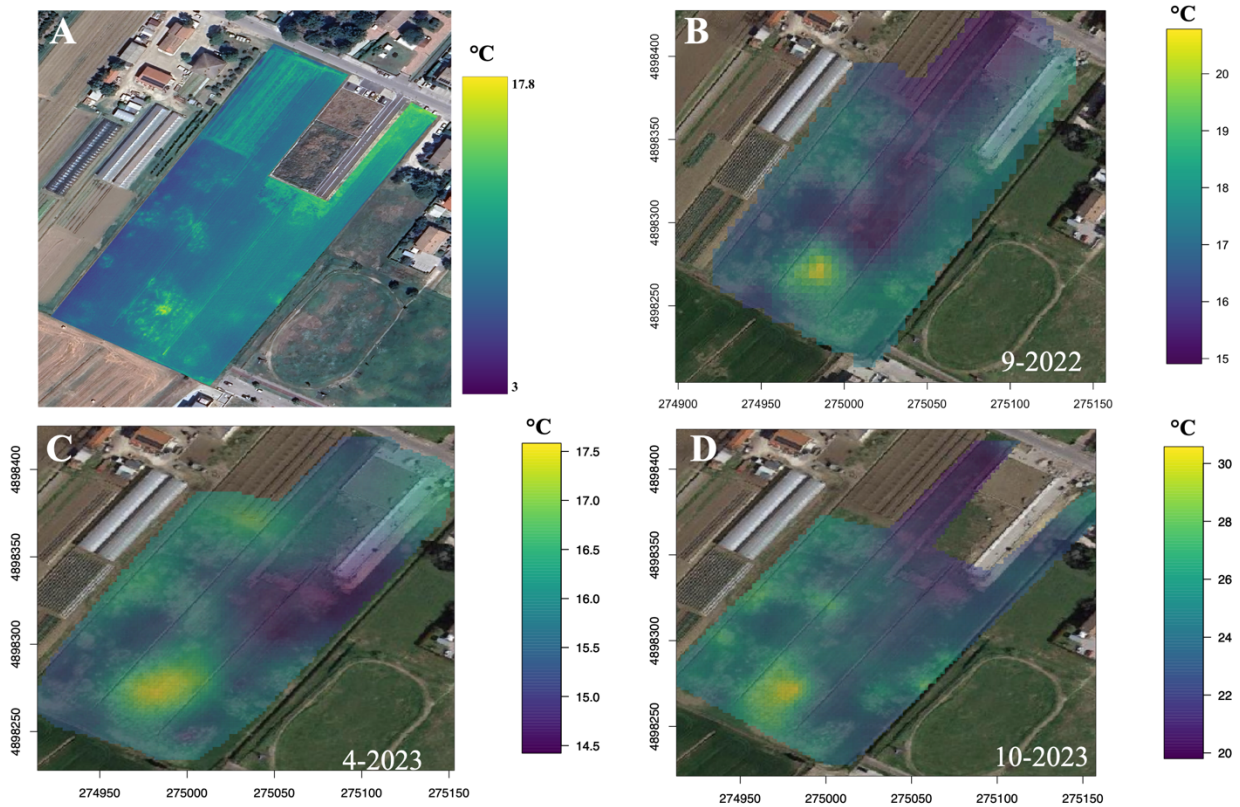


Figure 4.4. Orthomosaic image captured by the drone with a thermal camera (a) and thermal maps generated using sGs interpolation from ground measurements (b, c, and d).

The more pronounced contrast visible in the UAV-derived dataset (panel a) is further addressed in the Discussion section. The seasonal cycle of soil temperature at SMN in 2024 is illustrated in Fig. 4.5. where soil temperatures are shown vs air temperature ( $^{\circ}\text{C}$ ) and precipitation (mm) retrieved from ERA5 satellite data and WeatherUnderground.com, respectively. Surface temperatures (green line) showed strong variability, ranging from near  $0^{\circ}\text{C}$  in winter to peaks  $> 35^{\circ}\text{C}$  in summer, with sharp fluctuations driven by daily meteorological conditions and precipitation events. At 50 cm depth (red line), the seasonal trend was smoother and more attenuated, with a gradual warming from winter ( $\sim 15^{\circ}\text{C}$ ) to late summer ( $\sim 36\text{--}38^{\circ}\text{C}$ ), followed by progressive cooling towards the end of the year. Precipitation (blue bars) often produced sudden short-term drops in surface temperature, whereas the subsurface response was more buffered.

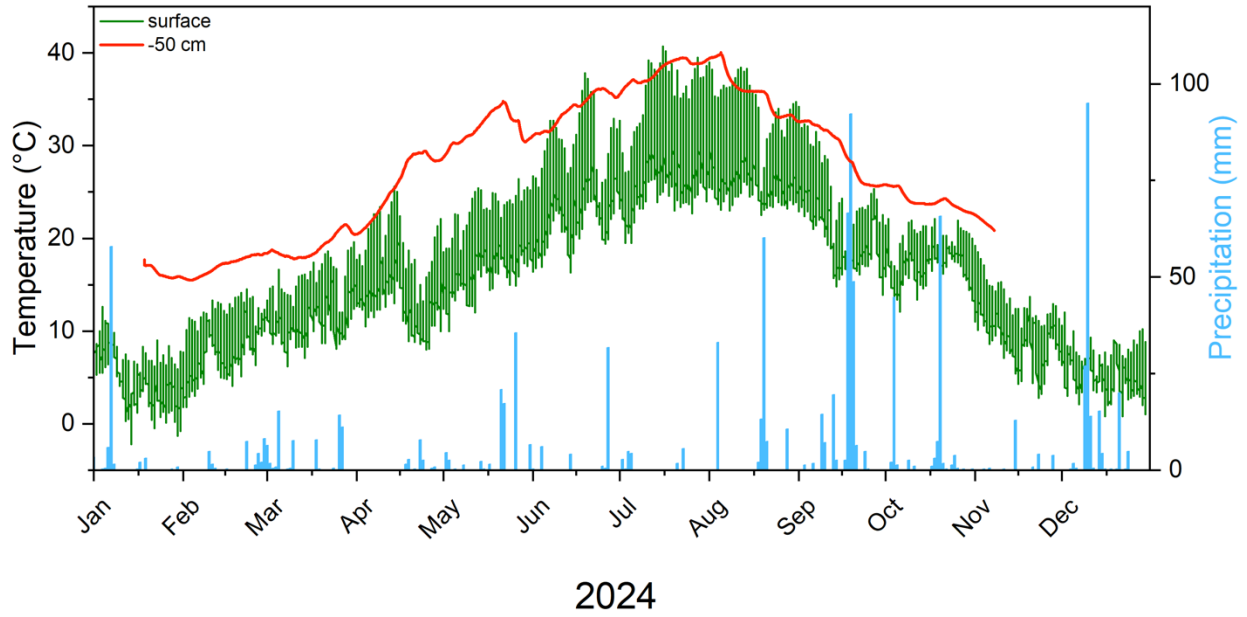


Figure 4.5. Time series of the SMN anomaly soil temperature (in red) compared with ground temperature (in green, satellite data from ERA5) and daily precipitation (in light blue, data from Weather Underground <https://www.wunderground.com/dashboard/pws/IEMILIAR241>)

#### 4.1.5 RVI Analysis

The temporal evolution of the RVI derived from Sentinel-2 satellite data for both the SMN and Medolla fields is illustrated in Fig. 4.6. The Medolla site is included in the analysis as it represents another location where vegetation stress has been observed in connection with ground heating and soil gas fluxes. At Medolla, the  $RVI_{an}$  was computed over a larger anomaly area rather than a single point, capturing a broader spatial impact. Both graphs span the period from July 2017 to May 2024. At the SMN site (upper panel),  $RVI_{bg}$  values (green circles) show a clear seasonal pattern, with sharp increases during spring and early summer each year. These peaks vary in magnitude, notably in 2019 and again between 2022 and 2023. Significantly,  $RVI_{bg}$  values display greater dispersion and variability compared to the  $RVI_{an}$  values. The  $RVI_{an}$  data (orange squares) exhibit a lower amplitude of seasonal variation throughout the series, with most values staying below 4. The contrast between  $RVI_{an}$  and  $RVI_{bg}$  is particularly evident during peak growing seasons, when  $RVI_{bg}$  reaches its highest levels, while  $RVI_{an}$  remains relatively stable or only increases moderately. Dashed vertical lines mark the four time points of the flux campaigns held in May 2022, September 2022, April 2023, and October 2023. At Medolla (lower panel), both  $RVI_{bg}$  and  $RVI_{an}$  display well-defined seasonal cycles, with higher values during vegetative periods and lower during winter months. Like at SMN,  $RVI_{bg}$  at

Medolla generally reaches higher peaks than  $RVI_{an}$ , although the two curves follow a more similar trend over time compared to SMN. Peak  $RVI_{bg}$  values often surpass 15 and reach approximately 25–27 in some years (notably in 2019 and 2020), while  $RVI_{an}$  values mostly stay below 15, even during peak growing seasons.

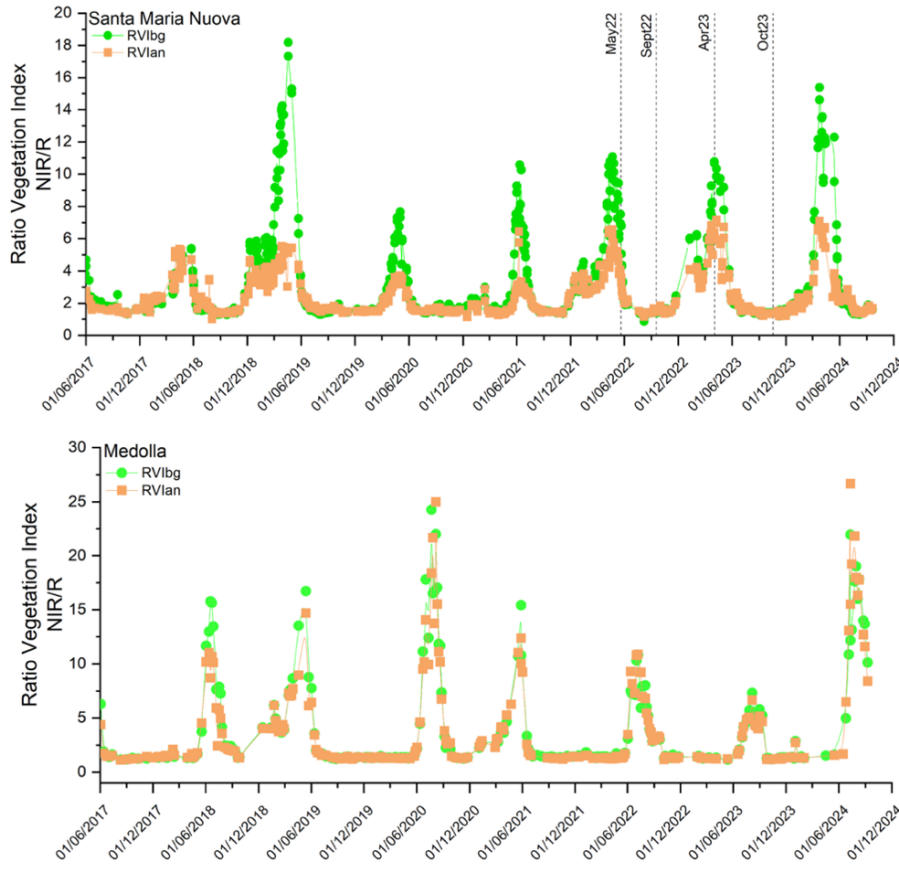


Figure 4.6. Time series of the Ratio Vegetation Index (RVI) derived from Sentinel-2 data for the SMN site (upper panel) and Terre Calde di Medolla site (lower panel) over the 2017-2024 period. At each site, RVI was calculated both over vegetated background areas ( $RVI_{bg}$ , in green) and over zones affected by  $CH_4$  seepage ( $RVI_{an}$ , in orange). The satellite images display the points from which the indices were derived. Dashed vertical lines in the SMN panel mark the dates of the four gas flux surveys conducted in May 2022, September 2022, April 2023, and October 2023.

## 4.2 Discussion

### 4.2.1 Groundwater

The SMN well, with a depth of 8.35 m from ground level, can be attributed to Group A aquifers as defined in Chapter II (Section 2.5). These shallow, recently recharged aquifers are typically characterised by Ca–HCO<sub>3</sub> water types, reflecting rapid circulation through silicate-rich matrices and strong influence of meteoric recharge. The chemical composition measured in October 2023 is consistent with this classification, showing clear HCO<sub>3</sub><sup>–</sup> dominance, with Ca<sup>2+</sup> and Mg<sup>2+</sup> as the primary cations, and minor contributions from Cl<sup>–</sup> and SO<sub>4</sub><sup>2–</sup>. Such features confirm the shallow, active recharge conditions of the aquifer. At the same time, the relatively elevated Mg<sup>2+</sup> content, coupled with the presence of dissolved CO<sub>2</sub> and CH<sub>4</sub>, suggests that this groundwater may also express the Na–HCO<sub>3</sub> trend described in Section 2.5. This trend arises from ion-exchange processes between Ca<sup>2+</sup> and Na<sup>+</sup> mediated by clays and feldspars, often promoted by CO<sub>2</sub> derived from organic matter decomposition or associated with CH<sub>4</sub> migration (Regione Emilia-Romagna and ENI-AGIP, 1998). Cl-to-Br mass ratios ( $\approx 135$  in April;  $\approx 58$  in October) are well below halite-dissolution values and do not indicate a significant evaporitic or deep brine contribution at the times of sampling. The detection of measurable CH<sub>4</sub> in dissolved gases ( $\sim 0.10$  mmol/L), accompanied by isotopic evidence of microbial origin, strengthens this interpretation. The long-term monitoring series further supports the classification of the SMN well as a shallow, recharge-dominated aquifer. Water level oscillations follow seasonal patterns of recharge and drawdown, while conductivity fluctuations remain within the typical range of Group A aquifers (800–1150  $\mu\text{S}/\text{cm}$ ). Sharp variations recorded in autumn 2024 coincided with intense rainfall events, indicating a rapid hydraulic response to meteoric inputs, again consistent with unconfined aquifers of this group. In this context, the monitoring of water level, electrical conductivity, and temperature did not reveal anomalies attributable to deep fluid inputs, such as synchronous increases in salinity, temperature, and hydraulic head. Instead, these parameters primarily reflect meteoric recharge. However, the dissolved gas composition presents a different narrative: CH<sub>4</sub> is measurable in solution ( $\sim 0.10$  mmol L<sup>–1</sup>, Table 4.3) and isotopically depleted ( $\delta^{13}\text{C}\text{-CH}_4 = -67\text{‰}$ ), pointing to a microbial origin for the gas. Concentrations well above atmospheric equilibrium, together with historical evidence of bubbling and episodic over-pressurisation at the well, indicate upward migration of microbial CH<sub>4</sub> that partially dissolves into the shallow aquifer without substantially modifying its bulk hydrochemistry, which remains characteristic of Group A aquifers.

### 4.2.2 Origin of gases

The isotopic analysis of SMN soil gases reveals a distinctly biogenic origin, with all  $\delta^{13}\text{C}\text{-CH}_4$  values below  $-60\text{‰}$  V-PDB (Table 4.5). Figure 4.7a illustrates the relationship between  $\delta^{13}\text{C}\text{-CH}_4$  and  $\delta^{13}\text{C}\text{-CO}_2$ , contextualised within the genetic fields and isotopic processes defined by Milkov and Etiope (2018). The isotopic composition of soil gases from the SMN site falls within the  $\text{CO}_2$  reduction (CR) field, indicating that  $\text{CH}_4$  is primarily generated through microbial carbonate reduction in marine sediments. This pathway favours the production of  $^{12}\text{C}$ -enriched  $\text{CH}_4$ , which is consistent with the characteristics of  $\text{CH}_4$  emissions in the area (Tassi et al., 2012a). The  $\delta^{13}\text{C}\text{-CO}_2$  values of the soil samples also provide further insights that point to other methane-related processes. While approximately half of the samples display  $^{13}\text{C}/^{12}\text{C}$  ratio values typical of  $\text{CO}_2$  sources linked to soil respiration and organic matter decomposition (e.g.  $-20\text{‰}$  to  $-30\text{‰}$  V-PDB; Amundson et al., 1998), others exhibit significantly depleted  $\delta^{13}\text{C}\text{-CO}_2$  values (e.g., 23D:  $-52\text{‰}$ , 23E:  $-37\text{‰}$ , 23A:  $-39\text{‰}$ ). Such highly negative values suggest an enhanced influence of methanotrophic activity, where the microbial oxidation of  $\text{CH}_4$  results in the transfer of the  $\delta^{13}\text{C}\text{-CH}_4$  signature to  $\text{CO}_2$  through isotopic mass balance,  $^{12}\text{C}$  being preferentially incorporated into the oxidised  $\text{CO}_2$ . Although some degree of atmospheric contamination may affect the  $\delta^{13}\text{C}$  values in certain samples (particularly in sample 22A, which is characterised by low  $\text{CO}_2$  concentrations and roughly atmospheric  $\text{N}_2$  and  $\text{O}_2$  values), the overall isotopic signatures remain consistently depleted in  $^{13}\text{C}$ . This suggests that atmospheric dilution has a limited impact on the measured isotopic composition of both gases and does not significantly bias the interpretation of their origin. Figure 4.7b further supports this interpretation by showing the relationship between  $\delta^{13}\text{C}\text{-CH}_4$  and the  $\text{CH}_4/\text{CO}_2$  ratio. The observed trend indicates that as  $\text{CH}_4/\text{CO}_2$  decreases,  $\delta^{13}\text{C}\text{-CH}_4$  becomes progressively enriched in  $^{13}\text{C}$ . For comparison, Fig. 4.7b also includes gas data from the Terre Calde di Medolla site, sourced from Capaccioni et al. (2015). Despite variations in sampling depth, these data exhibit a similar trend of increasing  $\delta^{13}\text{C}\text{-CH}_4$  values with decreasing  $\text{CH}_4/\text{CO}_2$  ratios. The extent of  $\text{CH}_4$  oxidation, however, is likely influenced by several environmental factors, including oxygen availability, temperature, soil moisture, microbial community density, soil composition, land use, and vegetation cover (Shukla et al., 2013). This interpretation aligns with the general characteristics of gas reservoirs in the Padania Plain and the southern Po River Basin, where  $\text{CH}_4$  is generated at relatively shallow depths (1.5–2 km) and lower temperatures ( $\sim 50^\circ\text{C}$ ) within the Pliocene-Pleistocene sedimentary infill of the Apennine Chain foredeep (Martinelli et al., 2012; Ricci et al., 2023).

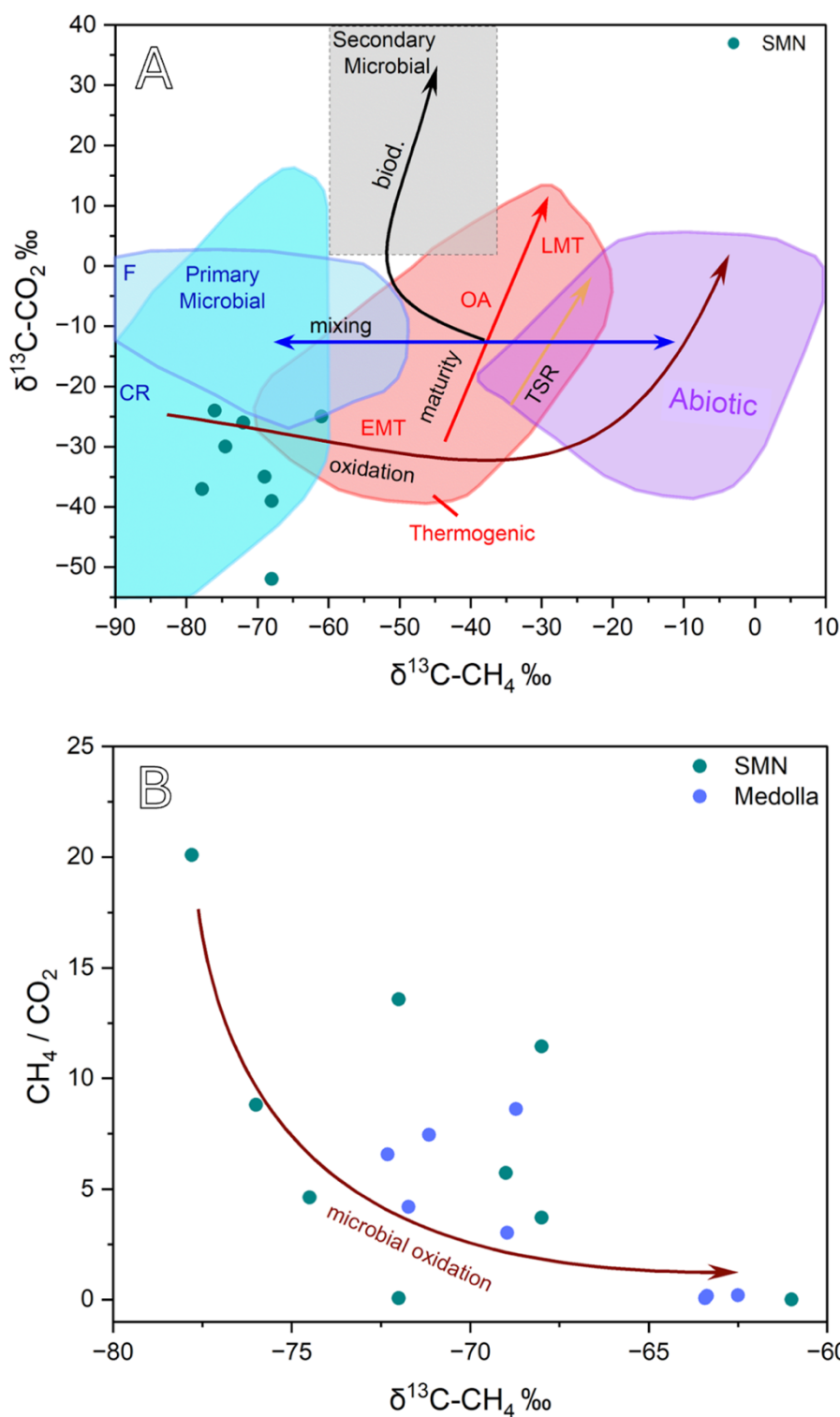


Figure 4.7. (a) SMN soil gas samples are plotted on a diagram of  $\delta^{13}\text{C}-\text{CH}_4$  versus  $\delta^{13}\text{C}-\text{CO}_2$ , which includes genetic fields and processes influencing the carbon isotopic composition of  $\text{CH}_4$  and  $\text{CO}_2$  in natural gases, as proposed by Milkov and Etiope (2018). Field acronyms denote  $\text{CO}_2$  reduction (CR), methyl-type fermentation (F), secondary microbial (SM), early mature thermogenic gas (EMT), oil-associated thermogenic gas (OA), and late mature thermogenic gas (LMT); while process acronyms represent biodegradation (biod.) and thermochemical sulphate reduction (TSR). (b) Binary diagram of  $\delta^{13}\text{C}-\text{CH}_4$  versus  $\text{CH}_4/\text{CO}_2$  ratio for the SMN soil gas samples (green) and the Terre Calde di Medolla soil gas samples (cyan) from Capaccioni et al. (2015).



These microbial gas accumulations differ from the thermogenic CH<sub>4</sub> found in the Emilian sector of the Apennines, west of the study area, where emissions display a clear thermogenic signature linked to deeper, higher-temperature formations (Tassi et al., 2012a). The geological cross-section in Fig. 4.8 (trace shown in the upper panel) shows that the marine deposits from the Pliocene to Pleistocene beneath the study area are less than 0.5 km thick. These sediments, comprising alluvial gravel and sand with interbedded clay, directly overlie Messinian clay–sand layers, as documented in the Cannuzzuola I well log (available at [www.videpi.com](http://www.videpi.com)). Since microbial carbonate reduction generally occurs in shallow, organic-rich marine sediments, the Pliocene–Pleistocene layers are a plausible zone for bacterial CH<sub>4</sub> formation. The underlying evaporitic sequence is considered an unlikely host for organic material. Instead, a deeper gas source could be related to the Marnoso-Arenacea turbidite formation, which lies at depths greater than 1 km. However, CH<sub>4</sub> from this unit, as reported by Mattavelli et al. (1983), is of mixed biogenic and thermogenic origin and typically shows a heavier carbon isotopic signature than that seen in our samples. Additionally, the cross-section highlights two reverse faults crossing the stratigraphic succession. These tectonic features may serve as preferred pathways for upward gas migration, supporting the idea that fault-controlled permeability plays a key role in channelling the emissions observed at the surface.

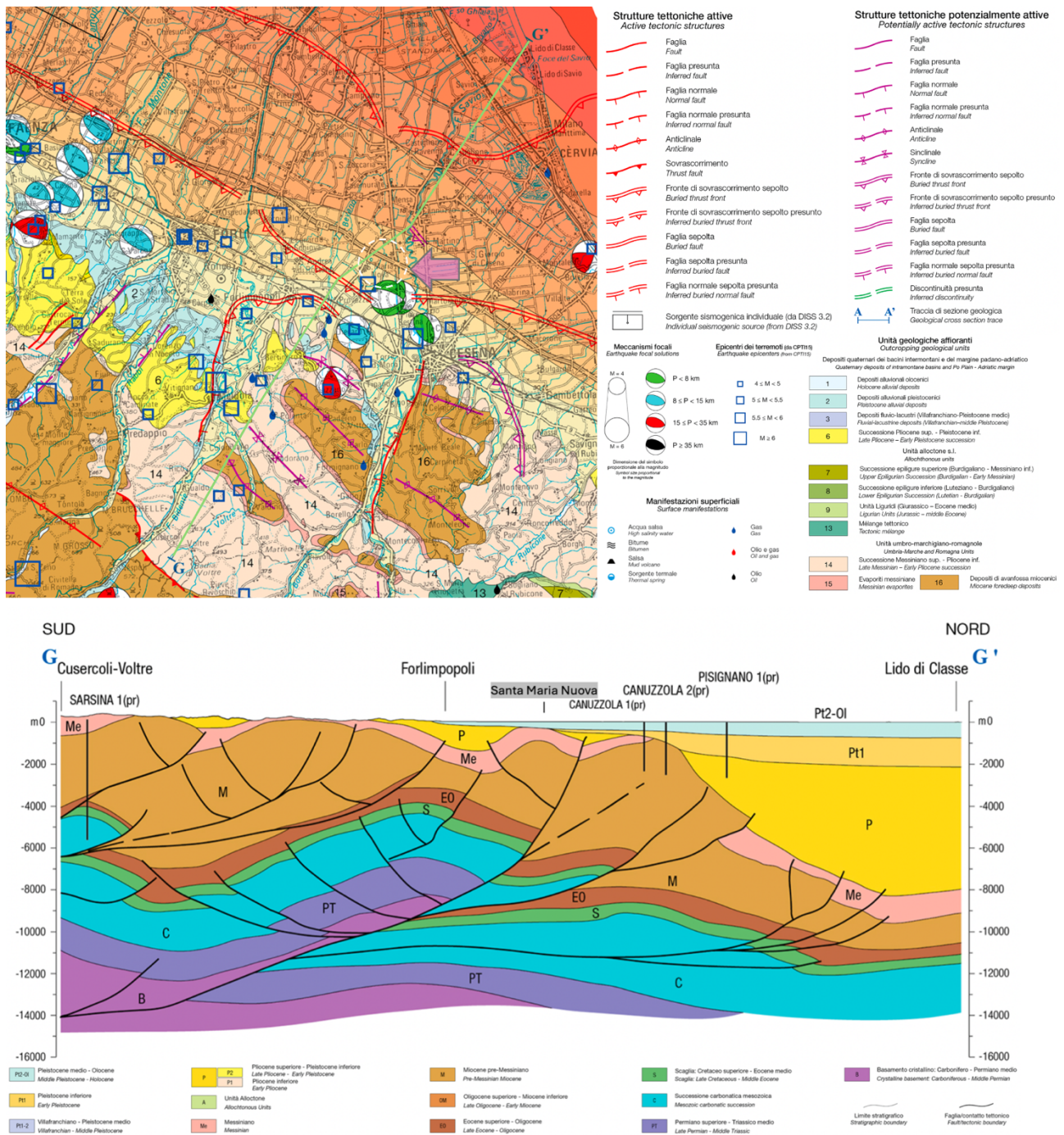


Figure 4.8. Detailed seismotectonic map (upper panel), which displays the primary tectonic structures and geological formations in the vicinity of SMN (indicated by the pink arrow and encircled in white), the locations of earthquakes along with their magnitude and depth, as well as reports of hydrocarbon manifestations, including a trace of geological cross-section G-G' (highlighted in green) that passes over the site (Emilia-Romagna Region; 2016). To view the complete map, please consult [https://mappegis.regione.emiliaromagna.it/gstatico/documenti/sismotett\\_2016/Carta\\_Sismotettonica.pdf](https://mappegis.regione.emiliaromagna.it/gstatico/documenti/sismotett_2016/Carta_Sismotettonica.pdf). Cross-section G-G', trace highlighted in green (Emilia-Romagna Region, 2016), illustrates the geological setting of the subsurface of the study area, located between Forlimpopoli and the Cannuzzuola I well.

#### 4.2.2 Spatial and temporal evolution of $\Phi\text{CH}_4$ and $\Phi\text{CO}_2$

The maps showing the spatial distribution of  $\text{CH}_4$  soil fluxes indicate a confined area south of the agricultural field with a significant anomaly, which was consistently observed throughout the two-year surveys (Fig. 4.2). During both spring campaigns (May 2022 and April 2023), the main  $\text{CH}_4$  anomaly was always accompanied by a secondary flux anomaly slightly to the west — an additional feature absent in autumn surveys. Notably,  $\text{CH}_4$  fluxes measured in spring reached values up to two orders of magnitude higher than those recorded in autumn. This recurring pattern suggests a potential seasonal control on  $\text{CH}_4$  seepage. Various factors could drive this seasonality, including soil moisture which influences soil permeability and gas transport pathways. However, further targeted investigations are required to clarify the mechanisms behind this seasonal variability. According to the Etiope and Klusman (2010) classification, high  $\text{CH}_4$  microseepage is defined as fluxes exceeding  $50 \text{ mg m}^{-2} \text{ d}^{-1}$ , medium microseepage ranges from  $5$  to  $50 \text{ mg m}^{-2} \text{ d}^{-1}$ , and low microseepage falls between  $0$  and  $5 \text{ mg m}^{-2} \text{ d}^{-1}$ . At SMN, many  $\text{CH}_4$  fluxes greatly surpassed the high microseepage level (Table 4.4), even when environmental factors inhibited the flux. The spatial distribution of  $\Phi\text{CO}_2$  mirrored that of  $\Phi\text{CH}_4$  (Fig. 4.2), consistent with both gases being produced and consumed through microbial activity. This pattern aligns with prior studies in the Terre Calde di Medolla area (Capaccioni et al., 2015), which documented a strong correlation between  $\text{CH}_4$  and  $\text{CO}_2$  fluxes at sites dominated by microbial gas generation and oxidation processes. Typical biogenic soil respiration fluxes of  $\text{CO}_2$  in similar environments, without additional sources, generally reach several tens of  $\text{g m}^{-2} \text{ d}^{-1}$  (Chiodini et al., 2008). In the anomalous spots within the study area, the observed  $\Phi\text{CO}_2$  values exceed these background levels, indicating a significant contribution from methanotrophy. To quantify the relative contributions of  $\text{CH}_4$  oxidation and background soil respiration to the total  $\text{CO}_2$  flux, the distribution of September 2022  $\text{CO}_2$  flux values was modelled using a Gaussian Mixture Model (GMM), applying the Expectation-Maximisation (EM) algorithm (as implemented in the R package *mixtools*; Benaglia et al., 2009), to fit a finite model representing two normal populations of the empirical distribution. This statistical decomposition enabled estimation of the mean and mixing fraction of each population (Fig. 4.9). The lower  $\text{CO}_2$  flux population, which is the most common, represents background soil respiration and was observed across both areas with and without  $\text{CH}_4$  anomalies. This population accounted for 69% of the total flux, while the population associated with  $\text{CH}_4$  oxidation made up the remaining 31%. The mean and standard deviation of these two components were used in a Monte Carlo simulation with 3,000 iterations to estimate the mean flux and associated uncertainty for each population. The results indicated flux values of  $143.2 \pm 26.5 \text{ g CO}_2 \text{ m}^{-2} \text{ d}^{-1}$  for the  $\text{CH}_4$  oxidation population and  $36.7 \pm 2.7 \text{ g CO}_2 \text{ m}^{-2} \text{ d}^{-1}$  for the background soil respiration population.

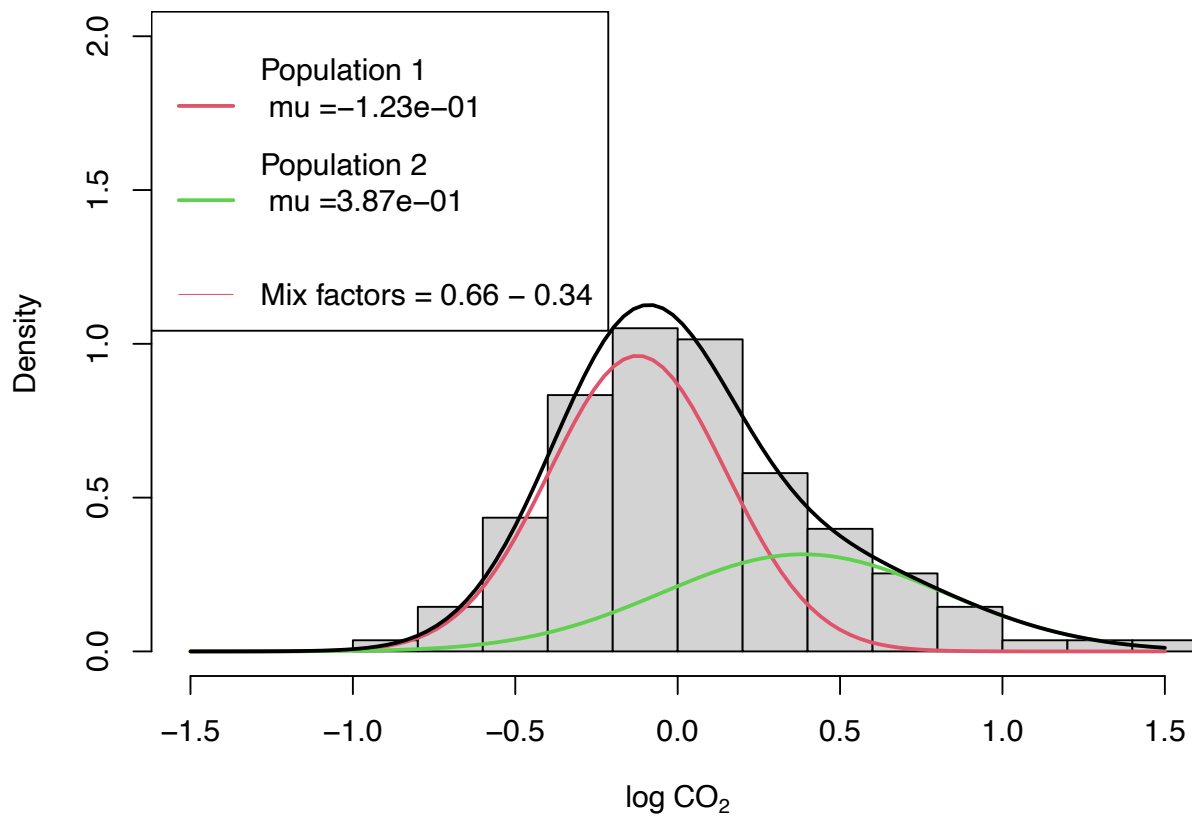


Figure 4.9. The mixing plot for the September 2022 flux campaign was created using the logarithm of CO<sub>2</sub> fluxes. The plot illustrates the proportion of the two CO<sub>2</sub> mixing factors, along with the mean value (mu) for each population: soil respiration in red and methane oxidation in green.

#### 4.2.3 Thermal Anomaly and Vegetation Health Assessment

A notable discrepancy exists between the temperature ranges recorded from the drone-derived thermal map and those obtained from ground-based measurements. (Fig. 4.4). This is primarily due to the nature of the measurements since drone imaging captures the surface temperature, while the other maps represent soil temperature at a depth of 15 cm. Additionally, the thermal emissivity coefficient ( $\epsilon$ ) is uniformly applied to the entire acquisition, disregarding the presence of materials different from the soil (e.g., cement, metal from orchard fences). Despite the thermal maps not being directly comparable, this approach enables the identification of thermal anomalies while providing spatial continuity for the temperature parameter observed across various time intervals. The highest temperatures were consistently measured at and around the main CH<sub>4</sub> emission spot, even across time (Fig. 4.5), where the exothermic oxidation of CH<sub>4</sub> to CO<sub>2</sub> generates localised heating (Capaccioni et al., 2015). Seasonal variations in ground temperature and soil moisture modulate the extent and intensity of this thermal anomaly since these environmental factors influence gas mobility and microbial growth in the soil. Upon comparing these seasonal background conditions with the thermal



imaging and in situ measurements at SMN, it becomes evident that the anomalous warm spots identified in the southern field sector cannot be ascribed to typical soil temperature dynamics. While surface soils inherently experience substantial fluctuations associated with air temperature and precipitation, the persistent thermal anomaly at SMN remained observable across various seasons, exhibiting differences of 3–10 °C relative to surrounding soils. Such a pattern exceeds the anticipated meteorological influence depicted in Fig. 4.5 and instead suggests that other processes are at play. The most plausible explanation is the exothermic oxidation of methane seeping through the soil, which locally elevates subsurface temperatures. This interpretation is supported by the spatial coincidence between the thermal anomaly, zones of enhanced methane flux, and areas of visible vegetation stress. Methane release and its subsequent oxidation to CO<sub>2</sub> by methanotrophic bacteria negatively affect plant health, often leading to reduced growth, sparse cover, or a scorched appearance near leakage zones (Davis, 1977). These impacts can be further exacerbated by altered nutrient cycling and microbial competition, which reduce the availability of nitrogen essential for plant development (Karbin et al., 2015; Chang et al., 2024). The observed oxygen depletion in three interstitial gas soil samples (22B, 23D, 23E) also indicates that oxidative methane processes could impair root respiration. Field observations (Fig. 4.10) provide visual confirmation of these patterns: the affected portions of the field show irregular and thinning vegetation cover, contrasting with adjacent unaffected areas.



Figure 4.10. Field views of the SMN anomaly area showing vegetation stress associated with methane seepage. Left: diffuse soil gas flux survey (May 2022). Centre: irregular crop growth in the anomaly sector (May 2024). Right: thinning vegetation rows in autumn (November 2024).

The negative effects on vegetation are evident in the RVI time series at SMN (Fig. 4.4), which consistently shows lower values at the anomaly site compared to surrounding areas. Seasonal fluctuations in RVI (higher in spring and summer, lower in fall and winter) reflect regular vegetation

cycles in unaffected regions. Conversely, the anomaly site demonstrates suppressed growth, supporting the idea that CH<sub>4</sub> emissions harm plant health. This vegetation vitality difference is captured through satellite-derived spectral reflectance data. Typically, an RVI < 1 indicates significant vegetation stress or sparse cover due to lower NIR reflectance compared to Red light (Richardson and Wiegand, 1977). Yet, despite expected distress from gas seepage, the anomaly RVI (RVI<sub>an</sub>) remains above this threshold, likely because the 10m resolution of Sentinel-2 averages local effects over a broader area, diluting the visible impact on vegetation. Other influences on RVI include phenological stage, as young or ageing plants show different reflectance compared to mature vegetation (Kobayashi et al., 2018). Additionally, crop rotation (i. e., barley in 2022 and fava beans in 2024) introduces species with distinct spectral traits due to variations in leaf structure and water content, further affecting RVI. Soil moisture and background reflectance are also vital; moist soils lower NIR reflectance, while dry soils increase it, potentially reducing RVI values (Polívová et al., 2022). Comparing the RVI time series at SMN and Medolla improves understanding of how vegetation reacts to gas-related stress under diverse site conditions. At both locations, the anomaly RVI consistently records lower values than the surrounding background RVI, indicating ongoing reduction in vegetation vitality near the gas seepage zones. Nonetheless, the gap between background RVI (RVI<sub>bg</sub>) and anomaly RVI (RVI<sub>an</sub>) is markedly wider at SMN (notably during the growing seasons), suggesting more intense or prolonged stress. Conversely, Medolla's vegetation shows generally stronger growth, with higher and sharper RVI peaks, even at the anomaly site, implying either less severe environmental stress or more favourable baseline conditions. The more significant vegetation decline at SMN may be associated with chronic exposure to CH<sub>4</sub> emissions, whereas at Medolla, stress appears more episodic or mitigated by local factors like soil composition, land management, or microclimate.



## Chapter V – Renazzo

The Renazzo site, situated within the municipality of Cento (province of Ferrara), constitutes a distinctive example of persistent CH<sub>4</sub> emissions emanating from a privately owned water well in the Po Plain. The persistent seepage, originating from an open and long-abandoned well, provided a valuable opportunity to examine methane dynamics in natural conditions and to evaluate innovative monitoring methodologies. This setting enabled (i) targeted experiments to quantify emission rates and (ii) deployment of a low-cost sensor network to track CH<sub>4</sub> variability. In parallel with direct flux measurements, well gas was used to calibrate sensors under field conditions, allowing an assessment of performance in situ.

### 5.1 Results

#### 5.1.1 Groundwater and hydrochemical parameters

Time series of groundwater level, temperature, and electrical conductivity (EC) at the Renazzo well are shown in Fig. 5.1.

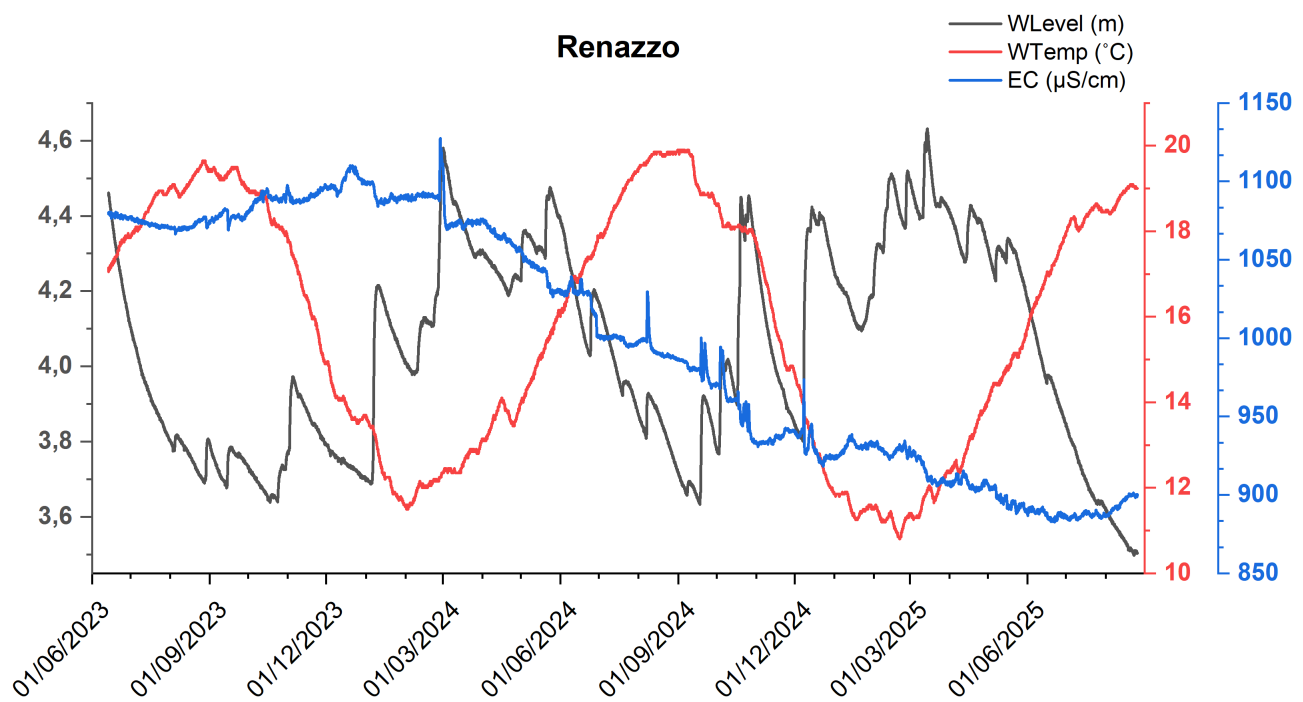


Figure 5.1. Time series of the STS probe installed at Renazzo well, from 14/06/2023 to 26/08/2025.

The water level (black line) exhibits notable seasonal fluctuations between 3.5 m and 4.5 m, with higher heads in late spring-summer, and lower heads during autumn and winter, superimposed by short-term oscillations. The water temperature (red line) follows a distinct annual cycle, peaking near 20 °C in summer and reaching ~11 °C in winter. The electrical conductivity (blue line) remains relatively stable throughout the monitoring period, ranging between 900 and 1100  $\mu\text{S cm}^{-1}$ , with a gradual decrease after mid-2024.

A single water sample from the Renazzo well was analysed by the University of Ferrara in April 2023 (Table 5.1). The dataset includes pH, temperature, electrical conductivity, and total dissolved solids, together with a partial suite of major anions and cations. Reported concentrations indicate a bicarbonate–calcium–magnesium water type, consistent with shallow aquifers in the Po Plain. However, the chemical dataset is incomplete: several analytes (e.g.  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{NH}_4^+$ ) were not determined, and the resulting ion balance does not close within acceptable limits. In particular, the discrepancy between the sum of cations and anions prevents a reliable evaluation of water composition and geochemical processes. For this reason, these data are presented here for documentation purposes only but were not considered further in the interpretation of the site.

| Date       | pH  | T(°C) | EC ( $\mu\text{S cm}^{-1}$ ) | TDS ( $\text{mg L}^{-1}$ ) |
|------------|-----|-------|------------------------------|----------------------------|
| 2023/04/04 | 8.3 | 12.9  | 990                          | 643                        |

| Date       | $\text{HCO}_3^-$ | $\text{F}^-$ | $\text{Br}^-$ | $\text{Cl}^-$ | $\text{NO}_2^-$ | $\text{NO}_3^-$ | $\text{SO}_4^{2-}$ | $\text{PO}_4^{3-}$ | $\text{Ca}^{2+}$ | $\text{Mg}^{2+}$ | $\text{Na}^+$ | $\text{K}^+$ | $\text{NH}_4^+$ |
|------------|------------------|--------------|---------------|---------------|-----------------|-----------------|--------------------|--------------------|------------------|------------------|---------------|--------------|-----------------|
| 2023/04/04 | 399              | 0.12         | n.a.          | 53            | n.a.            | n.a.            | 7                  | n.a.               | 66.5             | 53.6             | 64.9          | 13           | n.a.            |

Table 5.1. Chemical analyses of water from the Renazzo well (University of Ferrara, 04 April 2023). Values expressed as  $\text{mg L}^{-1}$ , missing analytes are indicated as “n.a.”.

### 5.1.2 Estimations of Gas Fluxes From the Well

The gas flux from the Renazzo well was quantified through the two experimental approaches described in Section 3.8. In the first configuration (M1), high-frequency  $\text{CH}_4$  measurements were combined with a three-dimensional sonic anemometer to capture both concentration and vertical velocity across the full aperture of the well. The second configuration (M2) constrained the emission geometry by reducing the outlet cross-sectional area, allowing for co-located measurements of gas concentrations and flow velocity using a hot-wire anemometer. M1 was deployed on 30 October 2024 and 15 April 2025. M2 was tested on 18 March 2025 and repeated on 15 April 2025. Tables 5.2 and 5.3 report M1 results for its two measure days and M2 results for its two days (no M1 data exist for 18 March 2025, and no M2 data exist for 30 October 2024). The overall results for  $\text{CH}_4$  flux are

summarised in Table 5.2. For M1, nine above-wellhead measurements were interpolated to a continuous concentration field and combined with vertical velocity; therefore, no single representative concentration is listed. In this case, fluxes calculated for the campaigns of 30 October 2024 and 15 April 2025 ranged between 2.8 and 7.2 kg d<sup>-1</sup>. Vertical velocities derived from the sonic anemometer were generally very low, with mean values between 0.01 and 0.07 m s<sup>-1</sup>. In contrast, M2 provided direct concentration measurements at the reduced outlet, together with velocity data from the hot-wire anemometer. Velocities in this configuration were consistently higher, ranging from 0.12 to 0.23 m s<sup>-1</sup>, reflecting the effect of geometric constraint on the gas flow. The corresponding methane fluxes ranged from 2.8 to 11.1 kg d<sup>-1</sup>, with standard deviations typically between 1.7 and 5.8 kg d<sup>-1</sup>.

| Date           | Method | Concentration (ppm) | Velocity (m s <sup>-1</sup> ) | Flux (kg d <sup>-1</sup> ) | St. Dev. |
|----------------|--------|---------------------|-------------------------------|----------------------------|----------|
| 30-10-2024     | M1     | —                   | 0.07                          | 6.9                        | —        |
| 18-03-2025     | M2     | 2.9E+04             | 0.20                          | 3.5                        | 2.8      |
| 18-03-2025     | M2     | 4.5E+04             | 0.19                          | 4.5                        | 4.1      |
| 18-03-2025     | M2     | 4.3E+04             | 0.12                          | 2.8                        | 1.7      |
| 18-03-2025     | M2     | 4.2E+04             | 0.16                          | 4.0                        | 3.5      |
| 18-03-2025     | M2     | 4.3E+04             | 0.14                          | 3.5                        | 2.6      |
| 18-03-2025     | M2     | 5.4E+04             | 0.13                          | 3.8                        | 2.5      |
| 18-03-2025     | M2     | 5.8E+04             | 0.17                          | 5.8                        | 4.5      |
| 18-03-2025     | M2     | 5.5E+04             | 0.12                          | 3.8                        | 3.2      |
| 18-03-2025     | M2     | 6.4E+04             | 0.12                          | 4.1                        | 2.2      |
| 15-04-2025 (a) | M1     | —                   | 0.05                          | 5.8                        | —        |
| 15-04-2025 (b) | M1     | —                   | 0.04                          | 5.1                        | —        |
| 15-04-2025 (c) | M1     | —                   | 0.04                          | 7.2                        | —        |
| 15-04-2025 (d) | M1     | —                   | 0.01                          | 2.8                        | —        |
| 15-04-2025     | M2     | 5.7E+04             | 0.21                          | 6.4                        | 1.9      |
| 15-04-2025     | M2     | 7.6E+04             | 0.22                          | 9.2                        | 2.0      |
| 15-04-2025     | M2     | 4.4E+04             | 0.22                          | 5.7                        | 5.8      |
| 15-04-2025     | M2     | 8.8E+04             | 0.21                          | 10.6                       | 5.5      |
| 15-04-2025     | M2     | 7.4E+04             | 0.21                          | 8.3                        | 2.4      |
| 15-04-2025     | M2     | 8.0E+04             | 0.23                          | 9.8                        | 3.7      |
| 15-04-2025     | M2     | 9.4E+04             | 0.22                          | 11.1                       | 3.2      |
| 15-04-2025     | M2     | 8.4E+04             | 0.21                          | 9.4                        | 2.7      |
| 15-04-2025     | M2     | 7.8E+04             | 0.22                          | 9.1                        | 3.4      |
| 15-04-2025     | M2     | 8.0E+04             | 0.19                          | 8.2                        | 3.1      |

Table 5.2 Results of CH<sub>4</sub> flux estimates at the Renazzo well obtained from M1 (open-aperture) and M2 (reduced-aperture) configurations, with flux values expressed as daily emissions (kg d<sup>-1</sup>). Flux standard deviation and mean concentration values (in ppm) are reported only for M2.

The spatial patterns of CH<sub>4</sub> above the well obtained with M1 are shown in Figures 5.2 and 5.3. The interpolated maps from 30 October 2024 (Fig. 5.2) show concentrations varying from well above-background levels (<500 ppm) at the margins to peaks above 4000 ppm in the eastern sector, revealing a strongly heterogeneous distribution. The three percentile maps (25th, 50th, and 75th) demonstrate how percentile selection influences the reconstructed concentration–velocity fields and,

consequently, the flux values. For M1, fluxes were computed using the 75th percentile of concentration and the 50th percentile (median) of the longitudinal velocity component, as this selection highlights the areas within the well where the majority of bubbling occurs. The four replicate acquisitions of 15 April 2025 (Fig. 5.3) confirm this heterogeneity, with fluxes ranging from 2.8 (d) to 7.2 kg d<sup>-1</sup> (Table 5.2).

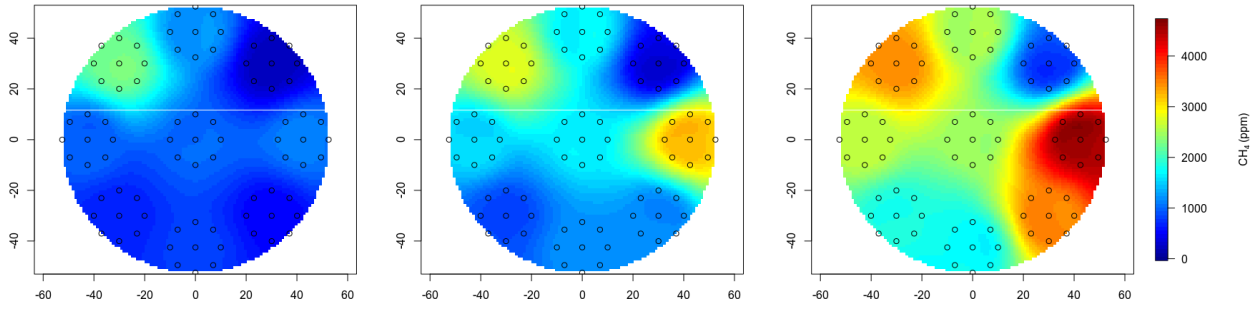


Figure 5.2. M1 interpolated CH<sub>4</sub> and w fields on 30 Oct 2024 (CH<sub>4</sub> percentiles 25/50/75).

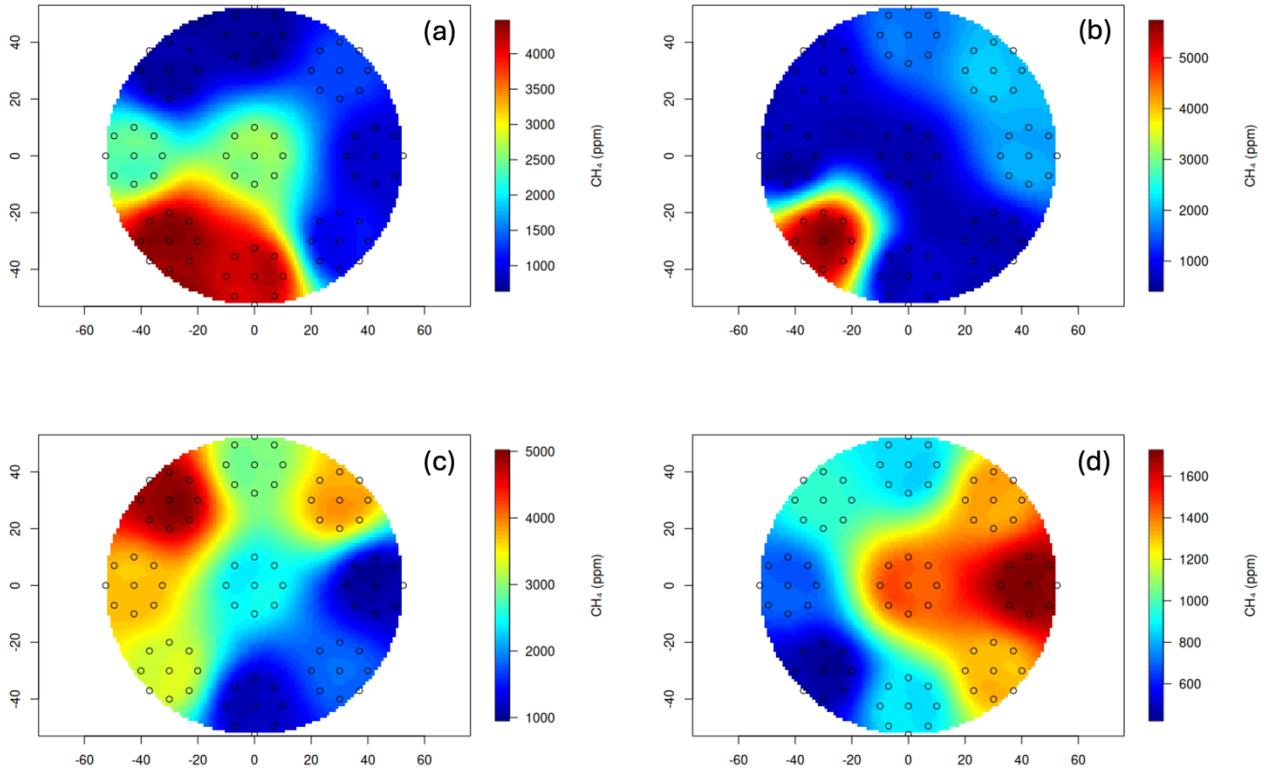


Figure 5.3. M1 interpolated CH<sub>4</sub> fields from four replicates (15 Apr 2025; 75th percentile of CH<sub>4</sub> concentration).

Both methods were also applied to compute CO<sub>2</sub> fluxes, with results reported in Table 5.3. M1 fluxes, calculated using the 75th percentile of CO<sub>2</sub> concentration, were between 0.077 – 0.384 kg d<sup>-1</sup>. For M2, outlet concentrations were  $1.0 \times 10^3$  –  $2.1 \times 10^3$  ppm, about one order of magnitude lower than for

CH<sub>4</sub>. Fluxes obtained with M2 were correspondingly smaller, ranging from 0.01 to 0.70 kg d<sup>-1</sup>. The associated standard deviations, typically on the order of 0.004 – 0.35 kg d<sup>-1</sup>, reflect both the lower signal strength and the influence of velocity variability on the estimates, which are the same as for CH<sub>4</sub> flux (0.12 – 0.23 m s<sup>-1</sup>).

| Date           | Method | Concentration (ppm) | Velocity (m s <sup>-1</sup> ) | Flux (kg d <sup>-1</sup> ) | St. Dev. |
|----------------|--------|---------------------|-------------------------------|----------------------------|----------|
| 30-10-2024     | M1     | —                   | 0.07                          | 0.372                      | —        |
| 18-03-2025     | M2     | 1.0E+03             | 0.20                          | 0.315                      | 0.155    |
| 18-03-2025     | M2     | 1.3E+03             | 0.19                          | 0.015                      | 0.007    |
| 18-03-2025     | M2     | 1.2E+03             | 0.12                          | 0.009                      | 0.004    |
| 18-03-2025     | M2     | 1.3E+03             | 0.16                          | 0.012                      | 0.006    |
| 18-03-2025     | M2     | 1.3E+03             | 0.14                          | 0.292                      | 0.152    |
| 18-03-2025     | M2     | 1.4E+03             | 0.13                          | 0.268                      | 0.160    |
| 18-03-2025     | M2     | 1.4E+03             | 0.17                          | 0.383                      | 0.290    |
| 18-03-2025     | M2     | 1.6E+03             | 0.12                          | 0.294                      | 0.190    |
| 18-03-2025     | M2     | 1.5E+03             | 0.12                          | 0.272                      | 0.135    |
| 15-04-2025 (a) | M1     | —                   | 0.05                          | 0.262                      | —        |
| 15-04-2025 (b) | M1     | —                   | 0.04                          | 0.384                      | —        |
| 15-04-2025 (c) | M1     | —                   | 0.04                          | 0.286                      | —        |
| 15-04-2025 (d) | M1     | —                   | 0.01                          | 0.077                      | —        |
| 15-04-2025     | M2     | 1.5E+03             | 0.21                          | 0.475                      | 0.120    |
| 15-04-2025     | M2     | 1.9E+03             | 0.22                          | 0.633                      | 0.135    |
| 15-04-2025     | M2     | 1.4E+03             | 0.22                          | 0.481                      | 0.347    |
| 15-04-2025     | M2     | 2.1E+03             | 0.21                          | 0.696                      | 0.058    |
| 15-04-2025     | M2     | 1.7E+03             | 0.21                          | 0.539                      | 0.137    |
| 15-04-2025     | M2     | 1.9E+03             | 0.23                          | 0.652                      | 0.233    |
| 15-04-2025     | M2     | 2.1E+03             | 0.22                          | 0.691                      | 0.189    |
| 15-04-2025     | M2     | 1.9E+03             | 0.21                          | 0.588                      | 0.165    |
| 15-04-2025     | M2     | 1.9E+03             | 0.22                          | 0.614                      | 0.225    |
| 15-04-2025     | M2     | 1.9E+03             | 0.19                          | 0.529                      | 0.202    |

Table 5.3. Results of CO<sub>2</sub> flux estimates at the Renazzo well obtained from M1 (open-aperture) and M2 (reduced-aperture) configurations, with flux values expressed as daily emissions (kg d<sup>-1</sup>). Flux standard deviation and mean concentration values (in ppm) are reported only for M2. Axial velocities matched the Table 5.2 M1 and M2 values.

### 5.1.3 Evaluation of Calibration Models for Low-cost CH<sub>4</sub> and CO<sub>2</sub> sensors

The training datasets (approximately 16,700 records per station) included the acquisition timestamp (for synchronisation), environmental covariates measured by the DHT22 sensor (air temperature,  $T(\text{dht})$ , and relative humidity,  $RH(\text{dht})$ , the raw CO<sub>2</sub> readings from the Sensirion SCD30 (already expressed in ppm), and the raw 10-bit ADC counts from the Figaro NGM2611-E13 methane sensor. For comparative tests with tree-based methods, the ratio  $R_s/R_0$  was calculated, where  $R_s$  is the instantaneous sensor resistance and  $R_0$  is the minimum resistance value considered representative of background conditions, following the NGM2611-E13 guidelines.

Reference concentrations of CO<sub>2</sub> and CH<sub>4</sub> from the WS-LI820 and the Picarro analysers served as targets for the machine learning models. For each station, CH<sub>4</sub> reference data were grouped into three concentration ranges (<10 ppm, 10-500 ppm and > 500 ppm). Across stations, 94.6-95.8% of the records fall in the low range, 4.1 – 5.3% in the intermediate range and only 0.04-0.13% in the high range, documenting the strong imbalance towards near-background conditions and the rarity of very high anomalies. The operative ranges covered by each station's training dataset are presented in Table 5.4.

|                                                 | <b>S1</b>      | <b>S2</b>      | <b>S3</b>      | <b>S4</b>      | <b>S5</b>      | <b>S6</b>      |
|-------------------------------------------------|----------------|----------------|----------------|----------------|----------------|----------------|
| <b><i>T</i>(dht) range (°C)</b>                 | 5.3 - 36.1     | 5.3 - 37.1     | 5.3 - 37.3     | 5.3 - 38.5     | 5.3 - 35.9     | 5.3 - 36.8     |
| <b><i>RH</i> (dht) range (%)</b>                | 32.4 - 86.2    | 32 - 85.4      | 29.1 - 85.5    | 21.9 - 85.5    | 30.4 - 85.4    | 32.3 - 85.5    |
| <b>CO<sub>2</sub> concentration range (ppm)</b> | 406 - 2087     | 424.6 - 2882   | 442.3 - 2748.6 | 504.3 - 3020.3 | 436.3 - 2365   | 497.5 - 3621   |
| <b>CH<sub>4</sub>_counts range</b>              | 28 - 455       | 26.3 - 513     | 30 - 513       | 16.5 - 533     | 29.5 - 508     | 28 - 477       |
| <b>Rs/R0</b>                                    | 0.05 - 1       | 0.06 - 1       | 0.06 - 1       | 0.06 - 1       | 0.05 - 1       | 0.05 - 1       |
| <b>CO<sub>2</sub>_reference (ppm)</b>           | 413.3 - 1987.5 | 413.3 - 1987.5 | 413.3 - 1944.7 | 413.3 - 1944.7 | 413.3 - 1944.7 | 413.3 - 1944.7 |
| <b>CH<sub>4</sub>_reference (ppm)</b>           | 1.9 - 12945.3  | 1.9 - 12945.3  | 1.9 - 16856    | 1.9 - 16856    | 1.9 - 15403    | 1.9 - 15403    |

Table 5.4. Ranges (minimum-maximum) of the variables included in the training datasets for gas sensor calibration of the six stations (S1-S6). Temperature (*T*dht, °C) and relative humidity (*RH*dht, %) are measured by the DHT22. CO<sub>2</sub> concentration is derived from the station's SCD30 output. CH<sub>4</sub>\_counts represent the raw Figaro NGM2611-E13 counts. Rs/R<sub>0</sub> is the resistance ratio normalised to the station-specific minimum (background). *CO<sub>2</sub>\_reference* and *CH<sub>4</sub>\_reference* are the reference channels used for calibration, measured by the WS-LI820 and Picarro analysers.

The temperature ranged from 5.3 °C to 38.5 °C (S4). The minimum value (5.3 °C) was observed across all stations because, in Phase II, the final step utilised a single T/RH sensor (from S1) while all CH<sub>4</sub> sensors were positioned within the same casing. The maximum temperature values are consistent across stations, ranging from 36 °C to 38.5 °C. Relative humidity spans similar intervals across stations (~ 30% – 86%), with the sole notable exception of S4, which recorded a lower minimum of 21.9% (~7-10 percentage points below the other stations; minima elsewhere 29.1 – 32.4%), while upper bounds remained comparable. For the CO<sub>2</sub> sensor (SCD30), station-wise ranges differ substantially, with the lowest minimum measured by S1 (406 ppm), whereas the highest minima were recorded at S4 (504 ppm) and S6 (498 ppm). The largest maxima are observed at S6 (3621 ppm) and S4 (3020 ppm), while S1–S2 and S3–S5 remain below approximately 2900 ppm and 2750 ppm, respectively. Minimum CH<sub>4</sub> raw counts cluster around 26-30 for almost all stations, except S4, which recorded a value of 16.5.



Maximum CH<sub>4</sub> raw counts vary widely, according to the different peak CH<sub>4</sub> concentrations reached during Phase III of calibration (see Section 3.9.2). Regarding reference channels, *CH<sub>4</sub>\_reference* exhibits clear pairwise maxima consistent with the calibration logistics of two stations per run in the sealed case, with the highest CH<sub>4</sub> concentration of 16,856 ppm measured for S3-S4 calibration. Accordingly, the reference ranges for CO<sub>2</sub> show slightly higher maxima for S1–S2 (413.3–1987.5 ppm) compared to S3–S6 (413.3–1944.7 ppm). Rs/R<sub>0</sub> spans 0.05–1.00 overall (0.06–1.00 for S2–S4), consistent with the manufacturer’s baseline definition. The datasets produced for each station were used as training data for machine learning Random Forest (RF) and Artificial Neural Network (ANN) models. Model inputs for calibration were defined a priori and differ by pollutant and model. For CO<sub>2</sub>, calibration relied on the RF algorithm, using the SCD30 CO<sub>2</sub> signal (ppm) together with *T*(dht) and *RH*(dht) to account for potential cross-sensitivities and environmental dependencies. For CH<sub>4</sub>, the same RF model was tested using the Rs/R<sub>0</sub> ratio, *T*(dht) and *RH*(dht) to produce a calibrated concentration output. Conversely, the resistance ratio Rs/R<sub>0</sub> was not used in the ANN model due to baseline drift instability under variable environmental conditions; instead, it used raw ADC counts (CH<sub>4</sub>\_counts) with *T*(dht) and *RH*(dht) as predictors. The performance statistics of the two machine learning (ML) models tested for calibration of CO<sub>2</sub> and CH<sub>4</sub> sensors are shown in Table 5.5.

|                 | Station | RMSE_ppm | MAE_ppm | MAPE  | R <sup>2</sup> | Model |
|-----------------|---------|----------|---------|-------|----------------|-------|
| CH <sub>4</sub> | S1      | 9.30     | 0.87    | 2.68  | 0.993          | ANN   |
|                 | S1      | 8.51     | 1.43    | 33.71 | 0.999          | RF    |
|                 | S2      | 75.14    | 3.02    | 3.23  | 0.860          | ANN   |
|                 | S2      | 18.23    | 1.83    | 25.59 | 0.996          | RF    |
|                 | S3      | 73.26    | 4.80    | 3.30  | 0.975          | ANN   |
|                 | S3      | 69.21    | 4.72    | 23.57 | 0.954          | RF    |
|                 | S4      | 49.06    | 2.94    | 3.14  | 0.969          | ANN   |
|                 | S4      | 34.72    | 2.87    | 33.70 | 0.988          | RF    |
|                 | S5      | 5.33     | 0.39    | 2.46  | 0.977          | ANN   |
|                 | S5      | 85.16    | 3.66    | 7.26  | 0.938          | RF    |
|                 | S6      | 17.96    | 1.26    | 2.46  | 0.882          | ANN   |
|                 | S6      | 15.82    | 1.76    | 12.27 | 0.997          | RF    |
| CO <sub>2</sub> | S1      | 24.57    | 10.54   | 2.11  | 0.972          | RF    |
|                 | S2      | 19.77    | 9.74    | 1.82  | 0.982          | RF    |
|                 | S3      | 31.14    | 22.87   | 4.73  | 0.954          | RF    |
|                 | S4      | 37.43    | 15.07   | 2.83  | 0.933          | RF    |
|                 | S5      | 23.32    | 12.83   | 2.53  | 0.974          | RF    |
|                 | S6      | 21.07    | 13.89   | 2.78  | 0.980          | RF    |

Table 5.5. Performance metrics of RF and ANN models for CH<sub>4</sub> and CO<sub>2</sub> calibration across the six monitoring stations. Metrics include RMSE, MAE, MAPE and R<sup>2</sup> for the test sets.

Metrics are computed on the held-out test set and reported in the original units (RMSE, MAE in ppm;  $R^2$  dimensionless). MAPE (mean absolute percentage error) is also noted, computed only for values  $> 1$  ppm (to avoid division by near-zero and to emphasise performance during non-background episodes). RMSE/MAE provide absolute error magnitudes, while MAPE complements them with a level-normalised view that is most informative during high concentration excursions.  $\text{CH}_4$  test-set errors show RMSE ranging from 8.5 to 85.16 ppm for RF (minimum at S1, maximum at S5) and from 5.33 ppm to 75.14 ppm for ANN (minimum at S5, maximum at S2). MAE varies from 1.43 ppm (S1) to 4.72 ppm (S3) for the RF model, while for the ANN, it varies from 0.39 ppm (at S5) to 4.80 ppm (S3). Despite comparable absolute errors at some stations, ANN systematically provides the lowest percentage errors in the above-background phases: MAPE (calculated for  $y > 1$  ppm) is narrow between  $\sim 2.5$ – $3.3$  % for all stations, while RF ranges between  $\sim 7$ – $34$  %. The  $R^2$  values for RF are high and very compact (0.938–0.999), while for ANN they show a wider range (0.882–0.993). For  $\text{CO}_2$  only the RF metrics are shown, as the model performed consistently across stations. To establish the baseline performance of the RF across stations, Fig. 5.4 shows the RF-calibrated SCD30 concentration tracking the Picarro reference over the full ambient range, reproducing the diel modulation and synoptic drift with small residuals. The test-set metrics of Table 5.5 confirm this visual impression:  $R^2$  spans from 0.933 at S4 to 0.982 at S2, with S6 (0.980), S5 (0.974) and S1 (0.972) close to the upper bound. The RMSE varies from 19.77 ppm (S2) to 37.43 ppm (S4), while the MAE extends from 9.74 ppm at S2 to 22.87 ppm at S3. The MAPE extends from 1.82% at S2 to 4.73% at S3, while the other stations cluster around 2.1–2.8%. Given this consistency and the relatively compact dynamic range of  $\text{CO}_2$  in Phase I co-location, RF provides an adequate and robust solution for  $\text{CO}_2$  sensors in this dataset, and it is retained as the calibration model.

Although these summary metrics provide valuable insights, they do not definitively determine the optimal model choice for  $\text{CH}_4$  at Renazzo. Firstly, the indicators integrate heterogeneous regimes, namely, near-background levels punctuated by brief excursions, rendering cross-station comparisons susceptible to the relative frequency of each regime. Secondly, coefficients of determination for RF are consistently high across stations, yet absolute and percentage error metrics vary with level, potentially resulting in inconsistent rankings. Consequently, the metric panel presented in Table 5.5 remains inconclusive regarding the preferred model for operational calibration. To resolve this, a targeted diagnostic on the Phase I ambient co-location dataset compared ANN and RF calibrated  $\text{CH}_4$  against the Picarro reference. Figure 5.5 shows 72-hour excerpts for each station, where : the left column juxtaposes the reference  $\text{CH}_4$  concentration (Picarro) with the  $\text{CH}_4$  calibrated by the two ML models (ANN and RF); the right column depicts the same time window with only Picarro and ANN to highlight the fidelity of the ANN calibration. Across all stations, the ANN reconstruction closely

follows the diel variability and transient fluctuations captured by the reference, accurately reproducing both the timing and amplitude of peaks and troughs with minimal offset. In contrast, the RF series exhibits noticeably larger deviations at local maxima and minima and tends to underestimate sharper excursions during dynamic periods, resulting in a less accurate representation within the ambient concentration range. This time-series evidence is consistent with the percentage-error behaviour summarised in Table 5.5 ( $\text{MAPE} \approx 2.5\text{--}3.3\%$  for ANN vs  $\approx 7\text{--}34\%$  for RF for  $y > 1$  ppm) and provides a decisive, station-wise visual confirmation. On this basis, ANN was adopted as the preferred calibration model for  $\text{CH}_4$  at Renazzo, whereas RF remained the chosen solution for  $\text{CO}_2$ , for which it performed robustly across stations.

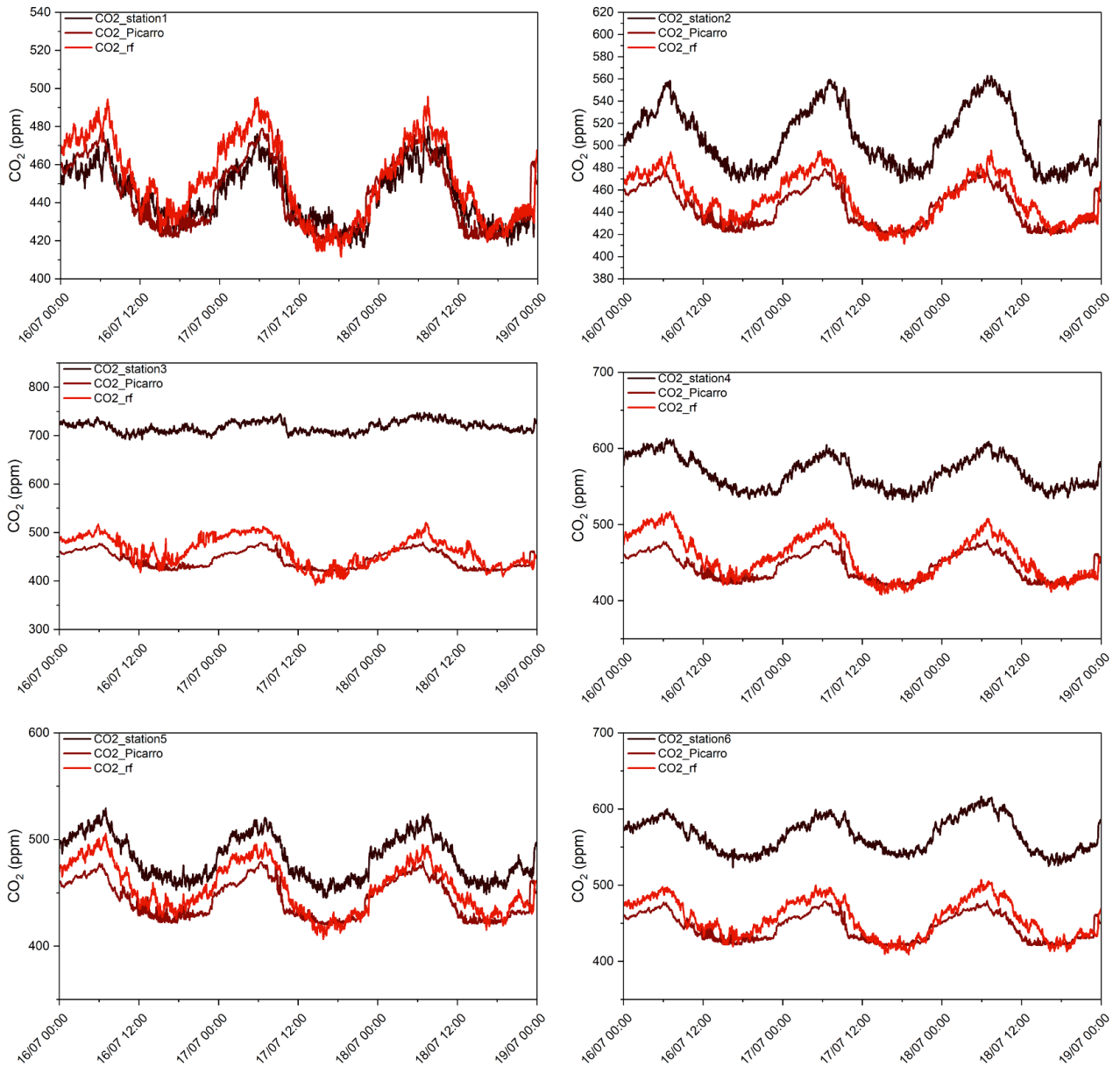


Figure 5.4. Time-series comparison of  $\text{CO}_2$  (ppm) during Phase-1 co-location. Each panel shows station signal, RF-calibrated output, and Picarro reference; RF reproduces diel and synoptic variability with small residuals across all stations.

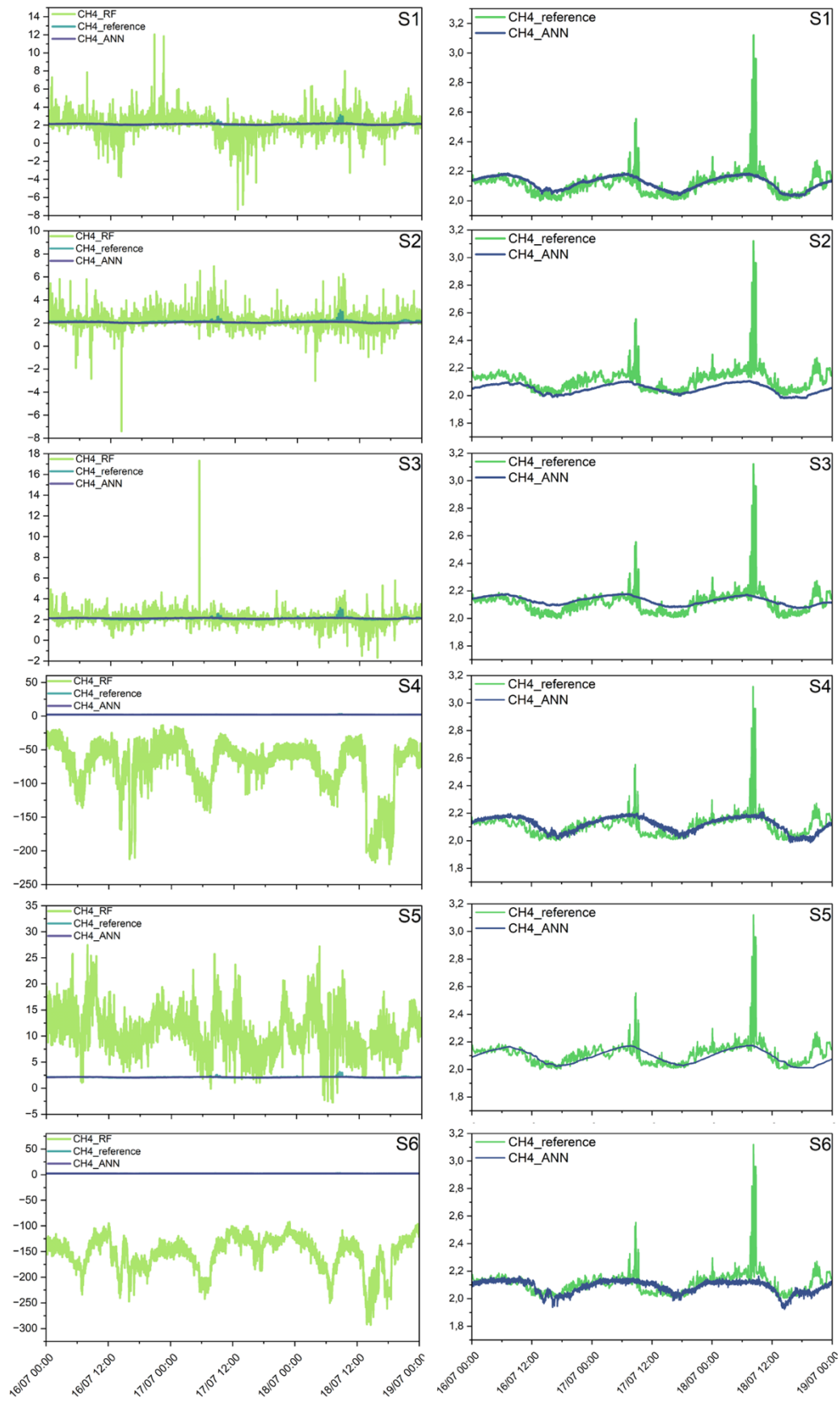


Figure 5.5. Time-series comparison of  $\text{CH}_4$  (ppm) over representative 72-h windows during Phase I co-location. Left:  $\text{CH}_4$ \_Reference, ANN-calibrated  $\text{CH}_4$ , and RF-calibrated  $\text{CH}_4$ , Right: Picarro and ANN only, emphasising ANN fidelity during excursions.

### 5.1.4 Measurement Campaign and Datasets at Renazzo

All stations logged at 10-s resolution, while the HD2003 3-D anemometer operated at ~35 Hz (0.028–0.029 s), and all series were then averaged to 1-min values with NA removed. Because each sensor requires a stabilisation period after installation, the Start times reported in Table 5.6 mark the beginning of the analysis window rather than the physical deployment time. Between 30 October and 21 November 2024 (~22 days), each station produced ~31.3–31.5 k one-minute records, equivalent to roughly 522–525 hours of data. Additionally, the anemometer yields 31,543 records (525.71 h).

| Station       | Start          | End            | Duration (d hh:mm) | Duration (h) | N (records to 1 min) | Distance from well (cm) | Position |
|---------------|----------------|----------------|--------------------|--------------|----------------------|-------------------------|----------|
| <b>S1</b>     | 30/10/24 14:00 | 21/11/24 11:05 | 21 d 21:05         | 525.08       | 31501                | 50                      | SW       |
| <b>S2</b>     | 30/10/24 14:00 | 21/11/24 10:49 | 21 d 20:49         | 524.82       | 31483                | 480                     | SSE      |
| <b>S3</b>     | 30/10/24 16:27 | 21/11/24 11:00 | 21 d 18:33         | 522.55       | 31363                | 430                     | E        |
| <b>S4</b>     | 30/10/24 14:00 | 21/11/24 10:55 | 21 d 20:55         | 524.92       | 31487                | 820                     | SSE      |
| <b>S5</b>     | 30/10/24 14:42 | 21/11/24 11:01 | 21 d 20:19         | 524.32       | 31469                | 290                     | SSW      |
| <b>S6</b>     | 30/10/24 14:36 | 21/11/24 11:02 | 21 d 20:26         | 524.43       | 31461                | 350                     | NNE      |
| <b>HD2003</b> | 30/10/24 14:02 | 21/11/24 11:08 | 21 d 20:30         | 525.71       | 31543                | 0                       | –        |

Table 5.6. Monitoring window, duration, and one-minute record counts for stations S1–S6 and the HD2003 anemometer at Renazzo, together with station–well geometry (distance from the bubbling well and bearing). Start/End refer to the analysis window after sensor stabilisation and 1-minute aggregation.

Small gaps are present, and they occur during short maintenance operations, specifically when power was temporarily disconnected to download data on 14 November 2024 and to replace the batteries supplying the solar-powered units, and these interruptions are limited to a few minutes. Apart from these brief service windows, the acquisition proceeded continuously and without malfunctions. The table also reports the station–well geometry, with distances from the bubbling well ranging from 50 cm for S1 (e.g., the closest to the well) to 820 cm for S4, and bearings SW, SSE, E, SSE, SSW, NNE. The anemometer is listed at 0 cm and no position since it is co-located at the wellhead (Fig. 3.12).

All pollutant concentrations are reported post-calibration with the machine-learning models described earlier, and all series were aggregated to 1-min values. Table 5.7 summarises the distribution of CH<sub>4</sub> and CO<sub>2</sub> for each station using the minimum, interquartile range (IQR), mean, median, maximum, standard deviation (SD) and median absolute deviation (MAD). CH<sub>4</sub> distributions differ markedly among stations. S1 shows the largest central tendency and variability, with a median of 207.7 ppm (IQR 46.3–270.8 ppm), a mean of 175.2 ppm, and a maximum of 688.2 ppm (SD 125.72, MAD 153.77). At the other end, S2 and S4 present low medians and narrow IQRs—2.3 ppm with 2.2–2.3

ppm and 2.2 ppm with 2.0–2.3 ppm, respectively, together with small dispersions (S2: SD 0.91, MAD 0.05; S4: SD 17.53, MAD 0.16) and maxima of 83.7 ppm (S2) and 334.5 ppm (S4). S6 shows intermediate values, with a median of 8.9 ppm (IQR 5.3–14.5 ppm), a mean of 11.0 ppm, and a maximum of 104.7 ppm (SD 8.42, MAD 6.40). S3 and S5 sit slightly above background values, with medians around 3.1 ppm and 2.9 ppm, respectively, with moderate spreads (S3 IQR 2.5–5.6 ppm, SD 5.83, MAD 1.34; S5 IQR 2.25–4.5 ppm, SD 6.11, MAD 1.07) and maxima of 121.4 ppm (S3) and 157.9 ppm (S5).

|                 |                         | Min      | IQR             | Mean   | Median | Max    | SD     | MAD    |
|-----------------|-------------------------|----------|-----------------|--------|--------|--------|--------|--------|
| CH <sub>4</sub> | S1                      | 1.95     | 46.3 - 270.8    | 175.2  | 207.7  | 688.2  | 125.72 | 153.77 |
|                 | S2                      | 2.09     | 2.2 - 2.3       | 2.3    | 2.3    | 83.7   | 0.91   | 0.05   |
|                 | S3                      | 1.85     | 2.5 - 5.6       | 5.3    | 3.1    | 121.4  | 5.83   | 1.34   |
|                 | S4                      | 1.94     | 2 - 2.3         | 3.5    | 2.2    | 334.5  | 17.53  | 0.16   |
|                 | S5                      | 2.09     | 2.25 - 4.5      | 4.6    | 2.9    | 157.9  | 6.11   | 1.07   |
|                 | S6                      | 2.07     | 5.3 - 14.5      | 11.0   | 8.9    | 104.7  | 8.42   | 6.40   |
| CO <sub>2</sub> | S1                      | 374.9    | 478.8 - 506.2   | 490.7  | 494.1  | 570    | 26.05  | 20.02  |
|                 | S2                      | 443.4    | 547.4 - 575.2   | 557.9  | 561.6  | 727.7  | 26.97  | 20.62  |
|                 | S3                      | 322.5    | 423.2 - 449.4   | 431.8  | 438.9  | 488.3  | 32.35  | 19.27  |
|                 | S4                      | 398.8    | 490.6 - 522.5   | 503    | 509    | 639.2  | 30.31  | 22.54  |
|                 | S5                      | 437.7    | 485.1 - 510.7   | 498.4  | 497.4  | 575.8  | 20.83  | 18.98  |
|                 | S6                      | 426.6    | 486.2 - 518.8   | 502.5  | 504.4  | 843.1  | 26.91  | 24.17  |
| HD2003          | P (hPa)                 | 991.5    | 1018.4 - 1023.4 | 1018.7 | 1021   | 1028.4 | 7.8    | 3.7    |
|                 | T (°C)                  | -1.8     | 6.905 - 11.790  | 9.4    | 9.3    | 23     | 4.3    | 3.6    |
|                 | (%)                     | 22.1     | 82.9 - 98.6     | 89.14  | 94.64  | 100    | 12.70  | 7.35   |
|                 | u (m s <sup>-1</sup> )  | -1.2596  | 0.106 - 0.893   | 0.54   | 0.41   | 4.2    | 0.56   | 0.52   |
|                 | v (m s <sup>-1</sup> )  | -1.55529 | - 0.017 - 0.56  | 0.27   | 0.22   | 3.0    | 0.44   | 0.42   |
|                 | w (m s <sup>-1</sup> )  | -0.53587 | - 0.010 - 0.02  | -0.04  | -0.04  | 0.6    | 0.10   | 0.10   |
|                 | wd (degrees)            | 0.0604   | 223.05 - 268.48 | 243.45 | 241.31 | 359.9  | 60.69  | 31.98  |
|                 | ws (m s <sup>-1</sup> ) | 0.0012   | 0.28 - 1.07     | 0.74   | 0.58   | 5.0    | 0.58   | 0.53   |

Table 5.7. Descriptive statistics (Min, IQR, Mean, Median, Max, SD, MAD) for 1-minute calibrated concentrations of CH<sub>4</sub> and CO<sub>2</sub> are reported for stations S1–S6, with units in ppm. Meteorological variables from the HD2003 sensor are also included in their native units: pressure (P) in hPa, temperature (T) in °C, relative humidity (RH) in %, wind components (u, v, w) and wind speed (ws) in m s<sup>-1</sup>, and wind direction (wd) in degrees. The u and v variables represent the horizontal wind components, while w is the vertical component.



For CO<sub>2</sub>, the medians range from 438.9 ppm to 561.6 ppm. S2 exhibits the highest central values (median 561.6 ppm, IQR 547.4–575.2 ppm, mean 557.9 ppm) and reaches a maximum of 727.7 ppm (SD 26.97, MAD 20.62). S6 records the largest maximum, 843.1 ppm, while its central tendency is near 504–505 ppm (median 504.4 ppm, IQR 486.2–518.8 ppm, mean 502.5 ppm). S4, S5, and S1 cluster close to 500 ppm medians (S4 509.0 ppm, S5 497.4 ppm, S1 494.1 ppm), with IQRs of 490.6–522.5 ppm, 485.1–510.7 ppm, and 478.8–506.2 ppm, respectively; their maxima are 639.2 ppm (S4), 575.8 ppm (S5), and 570.0 ppm (S1). S3 shows the lowest central values (median 438.9 ppm, IQR 423.2–449.4 ppm, mean 431.8 ppm) and a maximum of 488.3 ppm (SD 32.35, MAD 19.27). The 3D anemometer HD2003 statistics show that pressure centres around a median of 1021 hPa (IQR 1018.4–1023.4 hPa, range 991.5–1028.4 hPa), temperature around 9.3 °C (IQR 6.905–11.790 °C, range –1.8–23 °C), and relative humidity around 94.64% (IQR 82.9–98.6%, range 22.1–100%). The 1-min wind speed has a median of 0.58 m s<sup>–1</sup> (IQR 0.28–1.07 m s<sup>–1</sup>, maximum 5.0 m s<sup>–1</sup>), while wind direction has a median of 241.31° (IQR 223.05–268.48°). The 1-min means of the wind components are  $u = 0.54 \text{ m s}^{-1}$  (median 0.41 m s<sup>–1</sup>),  $v = 0.27 \text{ m s}^{-1}$  (median 0.22 m s<sup>–1</sup>) and  $w = -0.04 \text{ m s}^{-1}$  (median –0.04 m s<sup>–1</sup>).

Figure 5.6 shows the calibrated CH<sub>4</sub> concentrations at each monitoring station, arranged by closeness to the Renazzo well. A dotted line at 2 ppm indicates the atmospheric CH<sub>4</sub> background. This visualisation offers a comprehensive overview of the temporal dynamics of the gas throughout the monitoring period. Because S1 sits within ~0.5 m of the source, it exhibits dense sequences of short-lived bursts. To suppress burst aliasing while preserving the underlying trend, a 30-minute rolling median was used at S1, whereas a 10-minute window sufficed for the other stations, where plume interceptions are rarer and more isolated. The S1 series shows the largest absolute levels and amplitude, with broad, non-periodic oscillations spanning most of the window, with the underlying values spanning from ~2 ppm up to ~688 ppm (Table 5.7). S5 remains near the ~2 ppm background for long stretches, punctuated by short, quasi-regular bursts that recur through the period, with a one-minute maximum of ~158 ppm. S6 maintains a moderate baseline on which broader, longer-lived increases are superimposed, particularly in the second half of the window, reaching ~105 ppm in the one-minute data (Table 5.7). S3 hovers close to the background with aperiodic departures that become denser towards the end of the record, up to ~121 ppm on a one-minute basis (Table 5.7). S2 (480 cm) is nearly flat around ~2–2.5 ppm, interrupted by isolated transients in the first days of November and again around 19 November. S4 (820 cm) stays close to background values for almost the entire window, with a brief cluster of transients during the night of 14 November and a single pronounced spike reaching ~334 ppm in the one-minute series (Table 5.7). A common feature across S5, S6, and S3 is the intensification of transient activity after the night of 10 November until 21 November.

The time series of CO<sub>2</sub> concentrations for all six stations is displayed in Fig. 5.7 using unsmoothed, raw data. All stations consistently exhibit a recurring diurnal pattern in CO<sub>2</sub> concentrations over the monitoring period. Concentrations typically peak during the night and then decrease during the day, with the amplitude of this daily fluctuation visible across all stations. Occasional, isolated crests are visible at the very start of some records (notably S6, S2, and S4) and coincide with the acquisition onset.

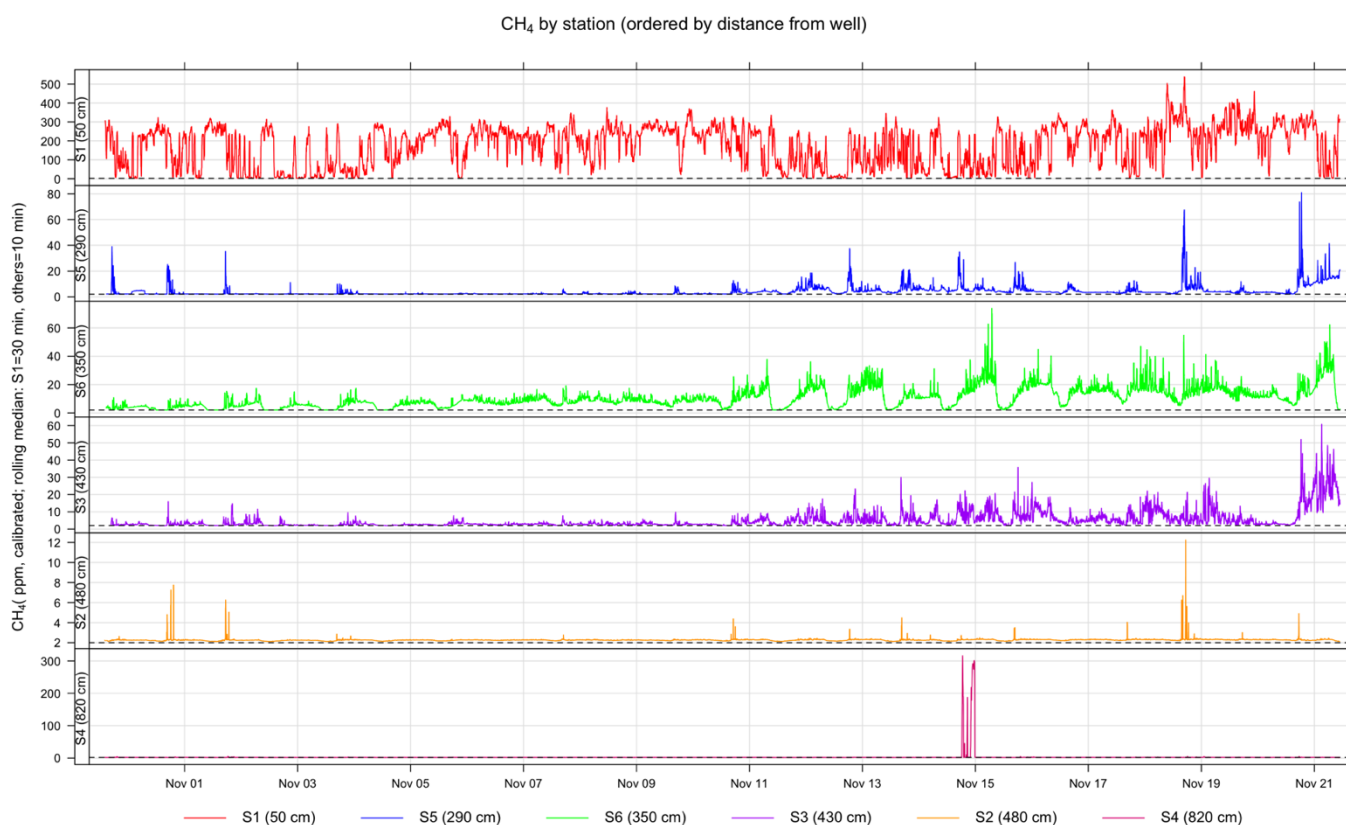


Figure 5.6. One-minute calibrated CH<sub>4</sub> (ppm) for stations S1–S6, shown as small multiples ordered by distance from the bubbling well.

These points were retained in both figures and statistics, but they are flagged as potential stabilisation artefacts rather than geochemical signals. The CO<sub>2</sub> diurnal cycle is characterised by central values clustered within two groups: a lower range of approximately 440–505 ppm and a higher range of 505–562 ppm. The series from station S2 is notably centred at a higher level than all other stations, with a median of 561.6 ppm compared to a median of 438.9 ppm at S3. Between 5 and 10 November, the diel amplitude is reduced across all stations, yielding comparatively flat cycles on those days. Overall, the CO<sub>2</sub> time series does not display the narrow, spike-like transients seen in CH<sub>4</sub>; instead, they vary smoothly around their station-specific centres, with the ranges reported in Table 5.7.

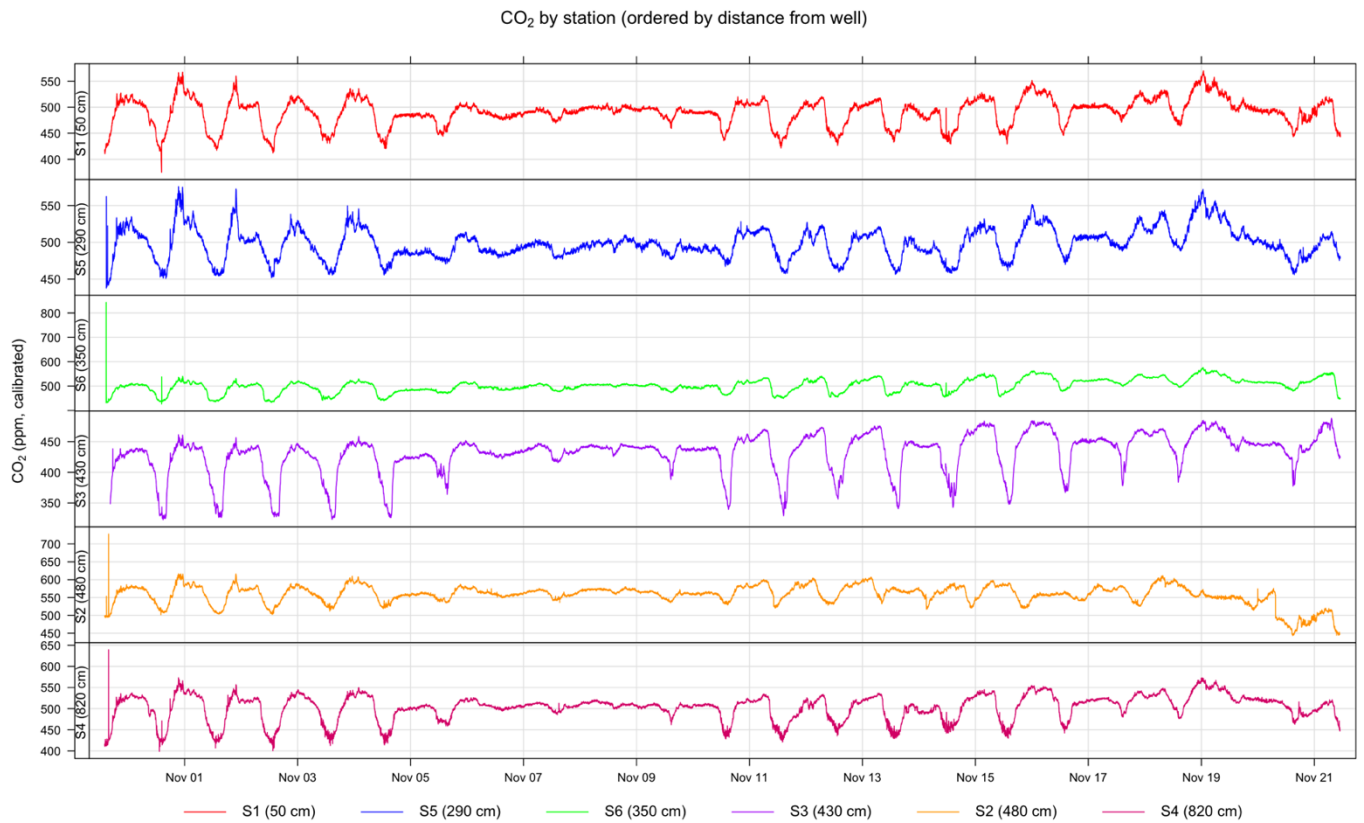


Figure 5.7. One-minute calibrated CO<sub>2</sub> (ppm) for stations S1–S6, shown as small multiples ordered by distance from the bubbling well.

## 5.2. Discussion

### 5.2.1 Groundwater time series

The Renazzo well displays coherent hydrochemical variability over the June 2023–August 2025 record (Fig. 5.1). Water level varies between ~3.5 and 4.5 m, with multi-month oscillations characterised by higher heads in late winter–early spring and minima in late summer. Superimposed, short-lived excursions, most notably a sharp rise around March 2024 and renewed peaks in early 2025, suggest episodic recharge or operational transients affecting the well. Groundwater temperature exhibits an annual range of approximately 9 °C, peaking in late summer and reaching minima in winter, with a rapid cooling in early November 2024, indicative of the infiltration of cold meteoric water and an efficient hydraulic connection with the shallow aquifer.

EC ranges from  $\sim 880\text{--}1,120\text{ }\mu\text{S cm}^{-1}$  with a net downward trend through the series, punctuated by step-like decreases in late 2024 and mid-2025. Taken together with the head dynamics, this behaviour is consistent with progressive freshening driven by recharge and mixing with less mineralised waters, typical of shallow unconfined aquifers (Martinelli et al., 1998). Periods of elevated water level generally coincide with lower EC, whereas falling heads in late summer–autumn tend to coincide with higher or stabilised EC, reflecting dilution–concentration effects; deviations from this inverse co-variation (e.g., declining level yet decreasing EC in mid-2024) likely reflect changes in recharge routing, or transient connections to fresher flow paths. Overall, the time series depicts a thermally responsive, hydraulically dynamic shallow system where seasonal recharge controls temperature and head, while EC mainly reflects mixing and dilution rather than in-situ production/consumption of geochemical processes.

These patterns provide an important context for interpreting gas occurrence at the site: colder, high-head, low-EC phases mark enhanced meteoric recharge and greater oxygen delivery (favouring  $\text{CH}_4$  oxidation), whereas warm, low-head periods imply reduced dilution and potentially greater propensity for gas accumulation and episodic release. To assess the role of meteorological forcing, the groundwater record was compared with daily mean air temperature ( $^{\circ}\text{C}$ ) and daily precipitation (mm) from the nearest weather station ICENTO24 at <https://www.wunderground.com/weather/it/cento/ICENTO24> (Fig. 5.8).

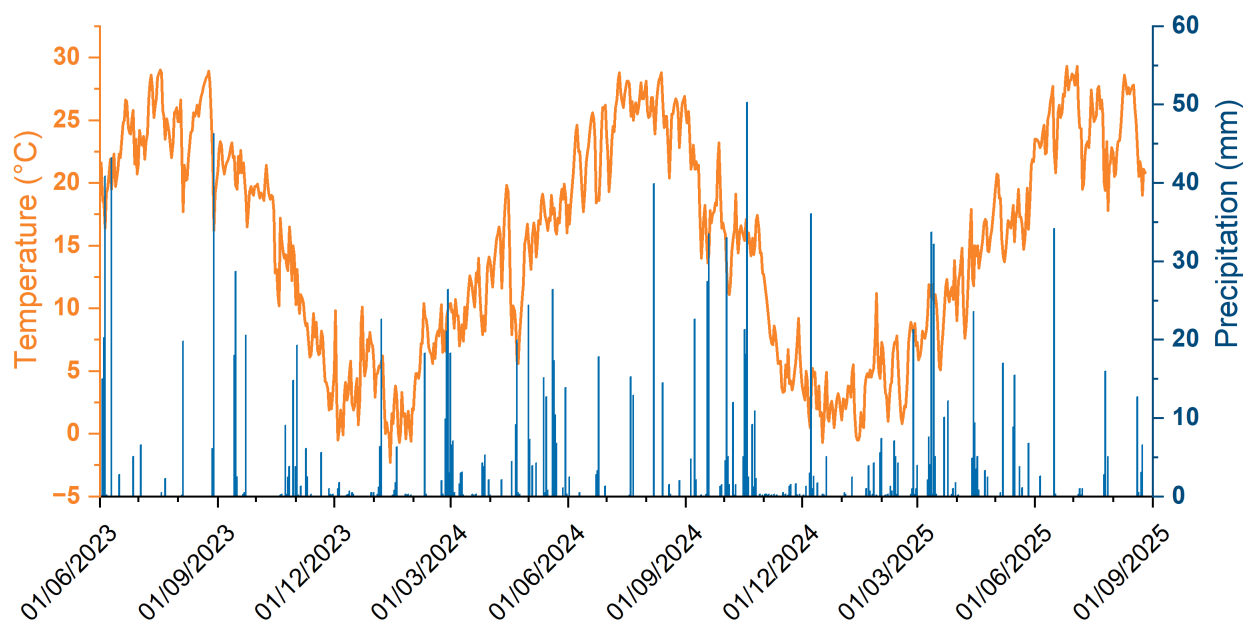


Figure 5.8. Daily air temperature (orange, left axis) and precipitation (blue, right axis) from the nearest Weather Underground station (ICENTO24) to Renazzo, June 2023–September 2025.

Groundwater temperature exhibits a close correlation with air temperature, displaying synchronous peaks during summer and troughs in winter.

An abrupt cooling event in early November 2024 coincides with a sharp decline in air temperature and a rainy spell, consistent with infiltration of cold meteoric water and effective exchange with the shallow aquifer. Precipitation events are followed, within a few days, by step-like increases in water level and decreases in electrical conductivity, indicating dilution during recharge. Throughout the observation period, there is no evidence of (i) winter-time positive thermal anomalies separate from air temperature, (ii) sustained increases in conductivity coinciding with rising water levels, or (iii) persistent phase shifts between groundwater temperature and air temperature, i.e., phenomena that would suggest upward advection of warm, saline fluids. The hydro-chemical variability at the Renazzo well is most parsimoniously explained by meteoric recharge and seasonal heat exchange within a shallow, sedimentary aquifer. Aside from the persistent CH<sub>4</sub> bubbling, the record shows no independent signatures of upward input from deeper fluids (e.g., thermal or salinity anomalies decoupled from meteorology). The ebullition is consistent with quasi-steady release of gas accumulated in shallow, organic-rich horizons, with its intensity modulated by recharge-driven pressure changes. The single hydrochemical analysis indicates a bicarbonate–Ca–Mg facies typical of shallow Po Plain aquifers (Orecchia et al., 2022), but the ion balance does not close; therefore, it is not used for process inference beyond documenting the context.

### 5.2.2 Gas Fluxes from the Well

The two complementary experimental configurations converged on CH<sub>4</sub> emissions in the order of a few to  $\sim 10$  kg d<sup>-1</sup> (Table 5.2). The multi-point, open-aperture arrangement (M1), which combined high-frequency concentration measurements with the 3-D sonic anemometer and integrates over the 108-cm wellhead, yielded fluxes between 2.8 and 7.2 kg CH<sub>4</sub> d<sup>-1</sup> across acquisition percentiles and replicate maps, with very small vertical velocities on average ( $\approx 0.01$ – $0.07$  m s<sup>-1</sup>). In contrast, the reduced-aperture setup (M2), which geometrically constrains the outflow through a 0.0095 m<sup>2</sup> orifice and co-locates concentration with a hot-wire velocity probe, produced consistently higher axial velocities ( $\sim 0.12$  –  $0.23$  m s<sup>-1</sup>) and total releases of 2.8 – 11.1 kg d<sup>-1</sup>, as expected from Bernoulli's principle whereby forcing a similar volumetric flow through a smaller cross-section increases jet speed. These ranges overlap and agree in order of magnitude, supporting the robustness of the kg d<sup>-1</sup> emission level despite different flux geometries and averaging strategies. The systematic discrepancy is consistent with M1 being biased downward due to (i) recirculation and intermittent downdrafts over the broad, water-covered aperture, which dilutes and redirects the upflow, (ii) turbulence advects the emerging plume laterally and irregularly, and (iii) the relatively slow, point-by-point sampling

cannot always intersect the plume at the same location. In addition, adopting a conservative percentile for the vertical wind component further depresses the M1 estimate. Conversely, M2 may be biased upward if the tarp more persistently concentrates the plume compared to the natural, spatially heterogeneous emission field. Nevertheless, both datasets demonstrate vigorous ebullition-driven degassing, which is inconsistent with “minor leak” regimes.

Methodological choices stabilised the estimates, including the percentile-based summaries (25th/50th/75th) to suppress transient eddies in M1, the strict time-synchronisation of velocity and concentration, and the explicit gas-law conversions using contemporaneous T and P. For both approaches, uncertainty is dominated by the geometry (V/A or effective cross-section), and short-term plume intermittency, treating these with percentile envelopes and replicate acquisitions provides an internally consistent uncertainty bracket for site-level reporting.

Comparing the CH<sub>4</sub> flux estimates from this study with values reported in the existing literature is rather challenging, as the latter primarily focuses on gas leaks from abandoned oil and gas wells (Kang et al., 2014; 2016), a phenomenon governed by significantly different channel geometries, depths, and emission rates. Direct emission studies of abandoned hydrocarbon wells typically report mean CH<sub>4</sub> emission orders of magnitude lower than at Renazzo. In Pennsylvania, static-chamber measurements across 19 wells found a mean of 0.27 kg CH<sub>4</sub> d<sup>-1</sup> per well, with a long-tailed distribution, but most sites are in the grams-per-hour regime (Kang et al., 2014). Subsequent work in the U.S. and U.K. reported typical unplugged-well emission factors around a few grams per hour (e.g., ~3.2 g h<sup>-1</sup> median for unplugged vs ~0.1 g h<sup>-1</sup> for plugged wells in West Virginia; Riddick et al., 2018), again far below the order of magnitude fluxes retrieved from the Renazzo well. Additional surveys corroborate that while rare “super-emitters” exist, the central tendency for abandoned/decommissioned wells remains <1 kg d<sup>-1</sup> (Boothroyd et al., 2016). Measurement guidelines from U.S. federal programs likewise calibrate method sensitivity around ≥ 1 g h<sup>-1</sup> (0.024 kg d<sup>-1</sup>), reflecting the expectation that most targets are relatively weak sources compared to Renazzo (U.S. Department of Interior, 2023). In this context, the Renazzo well acts differently to a typical leaking hydrocarbon wellhead, as it is not actually a wellhead of that type. The active water column and large aperture promote continuous bubble release and “plume” coherence, producing integrated emissions in the 2.8–11.1 kg d<sup>-1</sup> range that exceed the median levels documented for abandoned oil/gas wells by roughly one or two orders of magnitude (Kang et al., 2014).

Bubble-mediated CH<sub>4</sub> transfer (ebullition) dominates emissions in many shallow waters and engineered impoundments, but typical areal fluxes, reported via floating chambers, traps, or sonar, are usually tens to a few hundreds of mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup> on seasonal averages, with strong spatiotemporal intermittency and localised “hot spots” (Wik et al., 2013). Even where ebullition surges during warm



periods or low water tables, integrated daily releases scaled to sub-square-meter patches seldom approach kilograms per day unless the emission area is large or gas is hydrologically focused (Männistö et al., 2019). The Renazzo configuration is precisely such a focusing structure: a ~1 m-diameter, water-filled conduit tapping gas-charged strata, which channels ebullition through a confined aperture. This geometry explains why the integrated wellhead flux far exceeds “background” lake or pond ebullition scaled to similar footprints, aligning instead with local seep or mud-volcano behaviours where gas delivery is structurally focused.

The regional reports of gas-bearing wells and bubbling groundwater in Emilia-Romagna (Bonzi et al., 2015) document CH<sub>4</sub>-rich fluids rising along shallow pathways, sometimes accompanied by thermal anomalies when oxidation is significant (Capaccioni et al., 2015). These occurrences provide an apt analogue for the Renazzo mechanism, though quantitative flux data are rarely available at the wellhead scale.

The kg d<sup>-1</sup> CH<sub>4</sub> flux, together with persistent ebullition and the absence of independent hydrochemical indicators of deep fluid input, indicates a shallow, gas-charged system that efficiently migrates into the wellbore with limited oxidation in the near-source water column; this interpretation is consistent with the hydrogeological framework reconstructed from water level, temperature, and electrical conductivity time series. For large, water-covered apertures, the two measurement strategies are best viewed as complementary: open-aperture mapping (M1) preserves native plume heterogeneity and supports spatial integration, whereas the controlled-orifice co-location (M2) improves concentration-velocity measurement at the expense of some artificial focusing. Combining both approaches and bracketing outcomes with percentile-based envelopes alongside geometry-related uncertainty yields defensible reporting ranges. In magnitude, the Renazzo well behaves as a powerful source when compared with abandoned-well leakage datasets (kg d<sup>-1</sup> rather than the ~0.03–0.3 kg d<sup>-1</sup> typical range). Yet, it remains mechanistically aligned with ebullition-dominated seep systems in which structure funnels gas through a confined surface. Uncertainties are governed primarily by geometry (effective V/A or cross-section), short-term intermittency (clusters of bubble bursts versus lulls), and humidity effects at inlets. The reported ranges already incorporate these effects through replicate acquisitions and percentile integration, but an explicit uncertainty budget propagating geometry bounds together with percentile spread would formalise the current bracketing. Where feasible, independent checks, such as a short-duration hood test over a floating ring with transient mass balance, or a rigid mass-flow-meter chamber validated against recent intercomparisons, would further constrain potential method bias for water-surface point sources.

The CO<sub>2</sub> flux estimates (Table 5.3) obtained with the two approaches (M1 and M2) are consistent in order of magnitude, mirroring the convergence observed for CH<sub>4</sub> and reinforcing the robustness of the methodology across different flux geometries. Absolute CO<sub>2</sub> fluxes are markedly lower than the CH<sub>4</sub> releases, yet the concentration fields display a systematic excess above background, with Q3 values of the interpolated maps clustering around ~450–600 ppm across all acquisitions (Fig. 5.9).

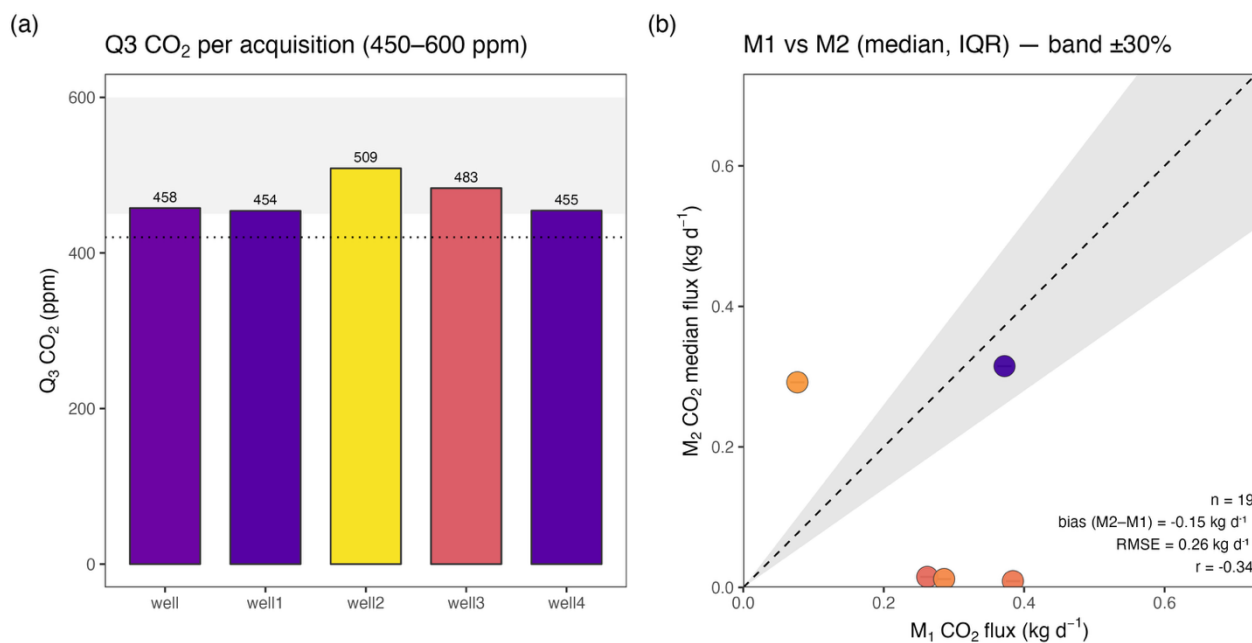


Figure 5.9. (a) Q3 CO<sub>2</sub> per chamber acquisition within the 450–600 ppm band (values above bars; dotted line = across-acquisition median). (b) Median CO<sub>2</sub> flux from methods M1 vs M2 (IQR as dispersion); dashed 1:1 line and shaded ±30% agreement band; inset: n, bias (M<sub>2</sub>–M<sub>1</sub>), RMSE, r.

This pattern indicates limited but persistent in-situ oxidation of a fraction of the rising methane within the near-source water column and at the air–water interface, without evidence for an additional deep CO<sub>2</sub> input. The comparatively small CO<sub>2</sub> flux relative to CH<sub>4</sub> implies short residence times of bubbles and modest oxidative conversion before emission to the atmosphere, in line with the hydrogeological context and the observed stability of the ebullition regime. Agreement between M1 (spatially integrated, plume-heterogeneity preserved) and M2 (co-located C–v, plume focusing) for CO<sub>2</sub> further supports the interpretation that geometry and averaging strategy bracket, rather than determine, the reported magnitude.

The CO<sub>2</sub> fields mapped around the Renazzo well show coherent, spatially structured enrichments that persist across acquisitions and broadly co-locate with the methane plume core (Fig. 5.10). Despite differences in scale among surveys, the highest CO<sub>2</sub> anomalies consistently occur along the preferential outflow quadrant identified for CH<sub>4</sub>, while the central, well-mixed water lens remains closer to background. This pattern is compatible with limited in-plume oxidation of rising methane combined with rapid ventilation at the water surface, rather than with a distinct deep CO<sub>2</sub> source feeding the conduit (Hanson and Hanson, 1996; Reeburgh, 2007; Bastviken et al., 2008).

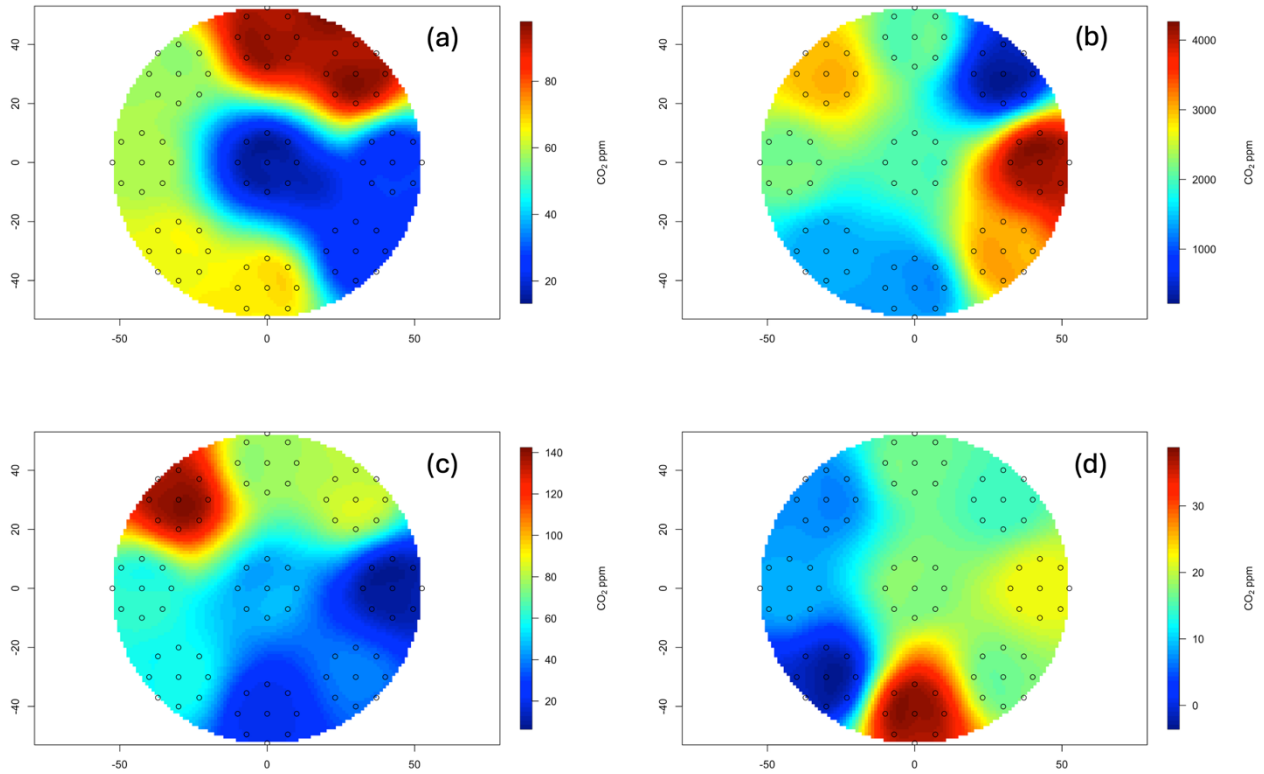


Figure 5.10. M1 interpolated CO<sub>2</sub> fields from four replicates (15 Apr 2025; 75th percentile of CO<sub>2</sub> concentration).

The joint analysis of instantaneous concentrations confirms a tight within-acquisition co-variation between CH<sub>4</sub> and CO<sub>2</sub> (Fig. 5.11). Linear fits yield positive slopes for all campaigns, indicating that where CH<sub>4</sub> accumulates, CO<sub>2</sub> also increases above ambient levels.

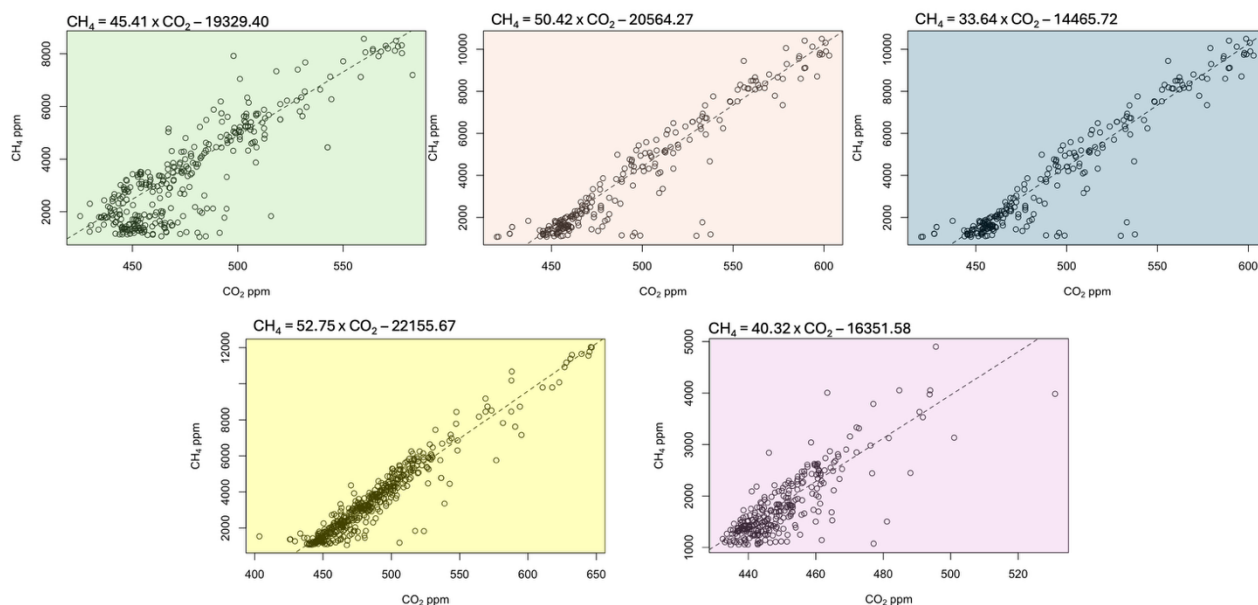


Figure 5.11. Scatterplots of CH<sub>4</sub> (ppm) versus CO<sub>2</sub> (ppm) for individual acquisition sets with M1 configuration; each panel shows ordinary least-squares fit (dashed) with the regression equation at top.

This co-variation is expected when bubbles rise through a shallow water column: dissolved CH<sub>4</sub> is partly oxidised by methanotrophs and CO<sub>2</sub> accumulates within the same micro-plume before being stripped to the atmosphere, while the remainder of the CH<sub>4</sub> escapes ebullitionally with limited residence time (Leifer & Patro, 2002; McGinnis et al., 2006; Reeburgh, 2007). The slopes vary among acquisitions, reflecting changing hydrodynamic mixing and bubble residence times, so they are not interpreted stoichiometrically but as a diagnostic of co-located production and transport. The agreement in magnitude, together with the spatial co-location of anomalies and the CH<sub>4</sub>–CO<sub>2</sub> co-variation, supports an interpretation in which CO<sub>2</sub> at the wellhead is generated primarily by near-source oxidation of CH<sub>4</sub> within a shallow, well-ventilated system (Bastviken et al., 2004; Reeburgh, 2007; Etiope & Klusman, 2010). Consistently, the carbon isotopic composition of the Renazzo gas used for sensor calibration ( $\delta^{13}\text{C-CH}_4$  of -65.3 ‰ V-PDB and  $\delta^{13}\text{C-CO}_2$  of -20.2 ‰ V-PDB) indicates a microbial origin for both species. This biogenic signature aligns with previous observations at the site, where the gas is reported to consist almost entirely of CH<sub>4</sub> (90.1 %) of biogenic origin, a composition that is coherent with methanogenesis in the shallow Pliocene-Pleistocene sediments of the Po Plain (Ricci et al., 2023). Together, these lines of evidence point to a near surface, microbially sourced CH<sub>4</sub> plume with local oxidation producing the observed CO<sub>2</sub> at the wellhead.

### 5.2.3 Evaluation of Machine Learning Models

The calibration strategy relied on two complementary machine-learning approaches configured according to sensor physics and available covariates. For CO<sub>2</sub>, the RF model was adopted using the SCD30 signal in ppm together with air temperature and relative humidity from the DHT22, to control for environmental dependencies. For CH<sub>4</sub>, two alternatives were tested: an RF model built on the resistance ratio  $R_s/R_0$  plus T and RH, and an ANN that instead used the raw 10-bit ADC counts from the Figaro methane sensor with the same environmental covariates. The choice to exclude  $R_s/R_0$  from the ANN and use counts directly stemmed from the observed instability of baseline-normalised ratios under variable ambient conditions, which introduced drift and degraded transferability (e.g. Biagi et al., 2024; Mitchell et al., 2024). Raw counts better preserved the sensor dynamics across regimes. These modelling choices are consistent with the methodological framework outlined in Chapter III and with the implementation choices in the ANN pipeline (log1p transform of the reference, standardisation of features and target, L2-regularised dense layers, cross-validation, and explicit back-transformation to ppm for output calibration). The training data covered wide and partially non-uniform operating ranges across stations, with temperature spanning ~5–38.5 °C and RH clustering mostly between ~30–86%, and with markedly different maxima in both SCD30 CO<sub>2</sub> and Figaro CH<sub>4</sub> channels depending on the calibration phases. These differences are material because the metrics computed on held-out test sets integrate heterogeneous regimes, namely long background intervals punctuated by short excursions. Accordingly, model performance was evaluated with level-aware metrics in addition to absolute errors. For CH<sub>4</sub>, the RF and ANN models achieved high coefficients of determination overall, yet diverged in error structure. On the test sets, RF yielded compact  $R^2$  values ( $\approx 0.94$ – $0.999$ ) but wider spreads in RMSE/MAE and, crucially, larger percentage errors during above-background conditions, with MAPE ranging roughly 7–34%. The ANN displayed similarly high  $R^2$  at several stations but achieved consistently lower level-normalised errors in the same regimes, with MAPE  $\approx 2.5$ – $3.3\%$  for  $y > 1$  ppm. Because  $R^2$  for tree-based models remained high even where local extrema were under-represented, the absolute/relative error panels, though informative, were not decisive alone. This motivated a targeted diagnostic on the Phase-1 ambient co-location dataset, where minute-resolved references exist and it is compared with the calibrated output from both models. The 72-h excerpts in Fig. 5.4 show that the ANN reconstruction reproduces diel variability and sharp transients with minimal timing and amplitude offset, whereas RF tends to flatten local maxima and minima and underestimates rapid excursions, especially within the ambient range most relevant for operational use. On that basis, the ANN was retained as the preferred calibration for CH<sub>4</sub> throughout the Renazzo deployment. The ANN configuration adopted in the code base underpins these outcomes: the target was transformed via log1p, features and target were

standardised, training used an L2-regularised multilayer perceptron with Adam optimisation, and performance was reported in both scaled space and original units after rigorous inverse transformation. Robust per cent metrics were computed after excluding near-zero denominators ( $y \leq 1$  ppm) and complemented by sMAPE, with model artefacts checked by residual diagnostics. This design mitigated heteroscedasticity across regimes and stabilised learning when excursions were sparse. For CO<sub>2</sub>, the RF solution proved adequate and consistent across stations, as tested by Biagi et al (2024). Test-set  $R^2$  ranged from  $\sim 0.93$  to  $\sim 0.98$  with RMSE typically  $\sim 20$ – $37$  ppm and MAPE around  $\sim 2$ – $5\%$ , indicating that the SCD30 sensor, once corrected for T and RH, can be calibrated reliably with a tree-based model in the explored operating envelope. Given the stability of CO<sub>2</sub> diel cycles during monitoring and the lower dynamic range relative to the CH<sub>4</sub> bursts at Renazzo, adopting RF for CO<sub>2</sub> ensured robust performance with limited computational complexity and straightforward interpretability of variable importance.

A comparison with recent literature clarifies why the calibration strategy at Renazzo adopted different model families for CH<sub>4</sub> and CO<sub>2</sub>. Biagi et al. (2024) co-located low-cost stations with a CRDS reference and calibrated them using Linear Forest Regression with  $R_s/R_0$  for the CH<sub>4</sub> channel, along with environmental covariates (T, RH). Their models yielded robust test performance (CO<sub>2</sub> and CH<sub>4</sub>  $R^2$  up to  $\approx 0.98$  and  $\approx 0.94$ , respectively), demonstrating that tree-based ensembles can provide accurate reconstructions when the calibration and application domains are well covered by the training data and the concentration span remains relatively compact in practice. The approach explicitly included temperature and humidity to control environmental dependencies and treated  $R_s/R_0$  as the primary CH<sub>4</sub> feature, an arrangement well suited to the co-location regime reported. This picture is consistent with broader evidence that model form and performance depend critically on the operative concentration range. Mitchell et al. (2024) calibrated the NGM2611-E13 across 0–200 ppm with  $>50$  k datapoints and showed that models accounting for T–RH interactions achieve very high accuracy within that bounded regime (RMSE  $\approx 5$  ppm;  $R^2 \approx 0.997$ ), while simpler or range-mismatched formulations either underperform or overfit and can misrepresent transients when transferred beyond the conditions seen in calibration. They further note that co-deployment calibrations weighted toward “typical” field concentrations may be poorly conditioned for high excursions if those are under-represented during training, underscoring the importance of distributional match between training and application. Kiplimo et al. (2024) reach a complementary conclusion from a different angle: conventional  $R_s/R_0$ -based algorithms can be brittle at near-background levels because results hinge on an accurately determined  $R_0$  and on sufficient signal-to-noise in the resistance channel; humidity sensitivity and sensor-to-sensor variability further complicate transferability. They therefore advocate machine-learning mappings from raw resistance



with T and RH to mixing ratio, showing that an RF regressor can recover analyser-like distributions over background to  $\sim 100+$  ppm releases when the training set spans that range. These findings highlight both the utility of ML for MOS calibration and the risks of relying on ratio-based linearisations when SNR is low or environmental effects are strong. These methodological nuances align with the practical choices made at Renazzo. The CH<sub>4</sub> record spans multiple magnitude orders, from near-ambient backgrounds to elevated bursts, so the concentration distribution is more heterogeneous than in narrow-range laboratory or short co-location exercises. In such conditions, a log-scaled target coupled with a flexible function class improved amplitude fidelity across regimes and reduced level-dependent errors, whereas tree ensembles trained on imbalanced data tended to smooth local extrema and under-reconstruct rapid excursions within the ambient–low-ppm band that dominates the time series. This behaviour is consistent with the strong imbalance of the Renazzo training set, where high-concentration excursions represent only a very small fraction of the records (see Sect. 5.1.3). It also agrees with the literature consensus that models calibrated on narrow, single-order-of-magnitude spans can excel in-range but become less reliable when the operative domain broadens without commensurate training coverage, particularly for MOS sensors whose response is temperature- and humidity-dependent and whose selectivity is intrinsically limited (e.g., Mitchell et al., 2024; Furuta et al., 2022; Kiplimo et al., 2024; Ponzoni et al., 2017). For CO<sub>2</sub>, by contrast, the operative dynamics at Renazzo are comparatively gentle and quasi-stationary around diel variability, and the SCD30 channel exhibits a high-quality, linearisable signal in the explored envelope. In this setting, a Random Forest with T and RH covariates provides station-consistent accuracy with limited complexity, in line with the outcomes reported by Biagi et al. (2024) for their co-located CO<sub>2</sub> calibrations. Finally, because the calibrated concentrations underpin subsequent flux interpretation, it is worth recalling the cautionary perspective from fence-line studies: even with proper calibration, low-cost networks can detect and, under suitable deployment and modelling, quantify emissions, but uncertainties grow when attempting high-frequency emission estimates or when the sensor signal is weak relative to environmental noise (Riddick et al., 2022). Robust calibration across the relevant concentration/humidity/temperature envelope, therefore, remains a prerequisite for credible downstream flux analyses.

#### 5.2.4 Gas Dispersion Near the Renazzo Well

The three-week deployment of the low-cost station network delineates a heterogeneous CH<sub>4</sub> field centred on the well and modulated by wind pathways within the courtyard (Fig. 5.6), alongside a comparatively homogeneous CO<sub>2</sub> evolution across all stations (Fig. 5.7). When stations are ordered by distance from the source, CH<sub>4</sub> shows a clear spatial gradient: sustained enrichment and frequent

excursions at the wellhead location (S1, S6, S3 and S5), fading rapidly to background with only episodic peaks at the peripheral sites (S2 and S4).

In contrast, CO<sub>2</sub> maintains coherent diel patterns at all stations, with daytime depressions and nocturnal build-up that vary in amplitude according to local siting but preserve the same phase relations, indicating that the dominant controls are micro-meteorological rather than source-proximity effects. Figure 5.12 shows the station-wise CH<sub>4</sub> polar plots (using the 95th percentile) over the site orthophoto, with CH<sub>4</sub> concentrations conditioned on wind speed and direction, as measured by the 3-D anemometer at the well. Throughout, wind direction follows the meteorological “from direction” convention, and the mean wind vectors used in the conditioning are derived from the 3-D sonic anemometer installed above the well. Because the same anemometer dataset drives the directional conditioning for all stations, the angular “imprint” (i.e., the distribution of available wind sectors and speeds) is common across panels. What distinguishes one station from another is the strength of the CH<sub>4</sub> response within that shared wind field. Consequently, the modal enhancement sector at a given node should coincide with the bearing from that station back toward the well, potentially rotated by several tens of degrees, where courtyard geometry channels the flux. Near-ground sources typically peak at low to moderate wind speeds, with higher speeds enhancing dilution (Carslaw et al., 2006).

At Station 1, located slightly SW from the source, the polar plot exhibits a broad, intense ridge in the W–WSW sector at low to moderate wind speeds, indicating that CH<sub>4</sub> is preferentially elevated when the wind comes from the E-NE toward the sensor, precisely along the station to well line. Minor rotations of the lobe around NE (tens of degrees) are compatible with gas flux deflection around nearby structures. Station 2 shows that the concentration peaks are narrow and centred near N-NNW at low wind speeds, consistent with short advective events, while weakening at higher wind speeds indicates dilution. A slight sectoral shift towards NW or NNE is plausible due to channelling along the fence where S2 and S5 were placed. Station 3, positioned to the E of the well, shows a weaker maximum in the WSW–W sector, implying impacts when the wind carrying air from the well arrives through the courtyard gaps toward S3, with a modest angular offset that is compatible with building wake deflection in the courtyard. Station 4, the most remote, presents only a faint sectoral response, in keeping with its essentially background time series and the rarity of downwind alignment. The single large excursion observed in the record is consistent with a transient period of winds from WSW-WNW that would transport the plume along a narrow corridor. At Station 5, the polar plot aligns with a clear NNE–E ridge, mirroring the repeated short-lived enhancements seen in the time series under evening slow wind flows from that quadrant. In contrast, rapid falloffs at higher wind speeds indicate dilution or plume displacement away from the fence wall. Station 6, to the NNE of the well, is impacted when winds are from S–SSW, i.e., from the source side toward the station, with

a mixture of directional peaks and a smoother background that suggests alternating periods of direct advection along the S-SSW corridor and brief recirculation episodes. This ensemble of polar maps read against the orthophoto makes the directional link between station peaks and the well explicit. When a station lies downwind of the source in a given sector, the polar surface develops a ridge in that sector. In contrast, stations off the advective path remain near background despite the same angular conditioning. In the following subsections, these directional diagnostics are cross-referenced to the station-wise time-series panels to substantiate the event timing and the sectoral alignment at each location.

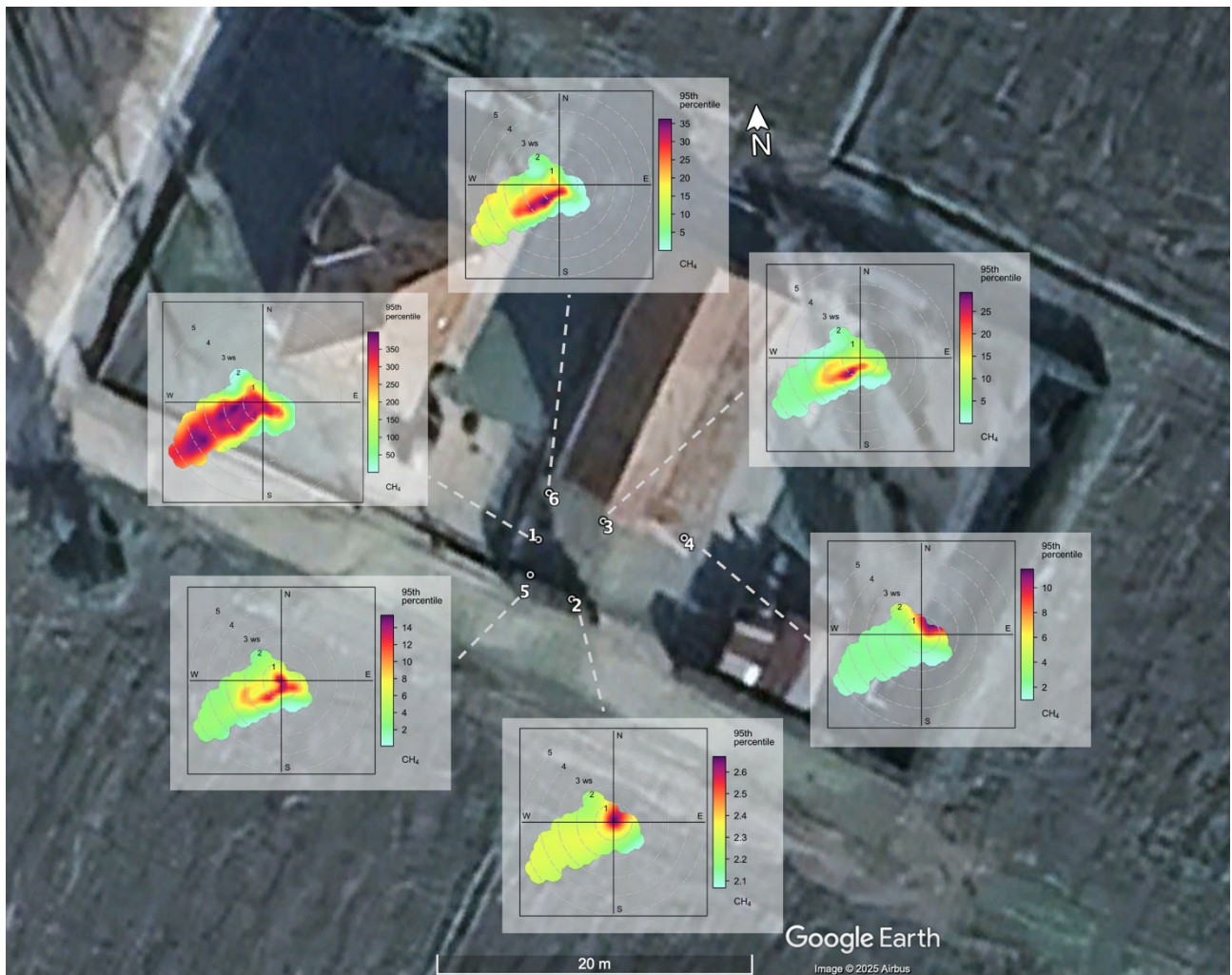


Figure 5.12. Station-wise CH<sub>4</sub> p95 polar plots over the site orthophoto.

CH<sub>4</sub> concentrations at S1, closest to the well, remain persistently elevated with frequent excursions, while the 30-minute median exposes a multi-day undulation onto which diurnal variability is superimposed (Fig. 5.13, upper panel). The diurnal and weekday composites (Fig. 5.13, middle row) indicate a gentle morning rise and late-afternoon increase that repeat across days, suggesting meteorological control rather than episodic operations.

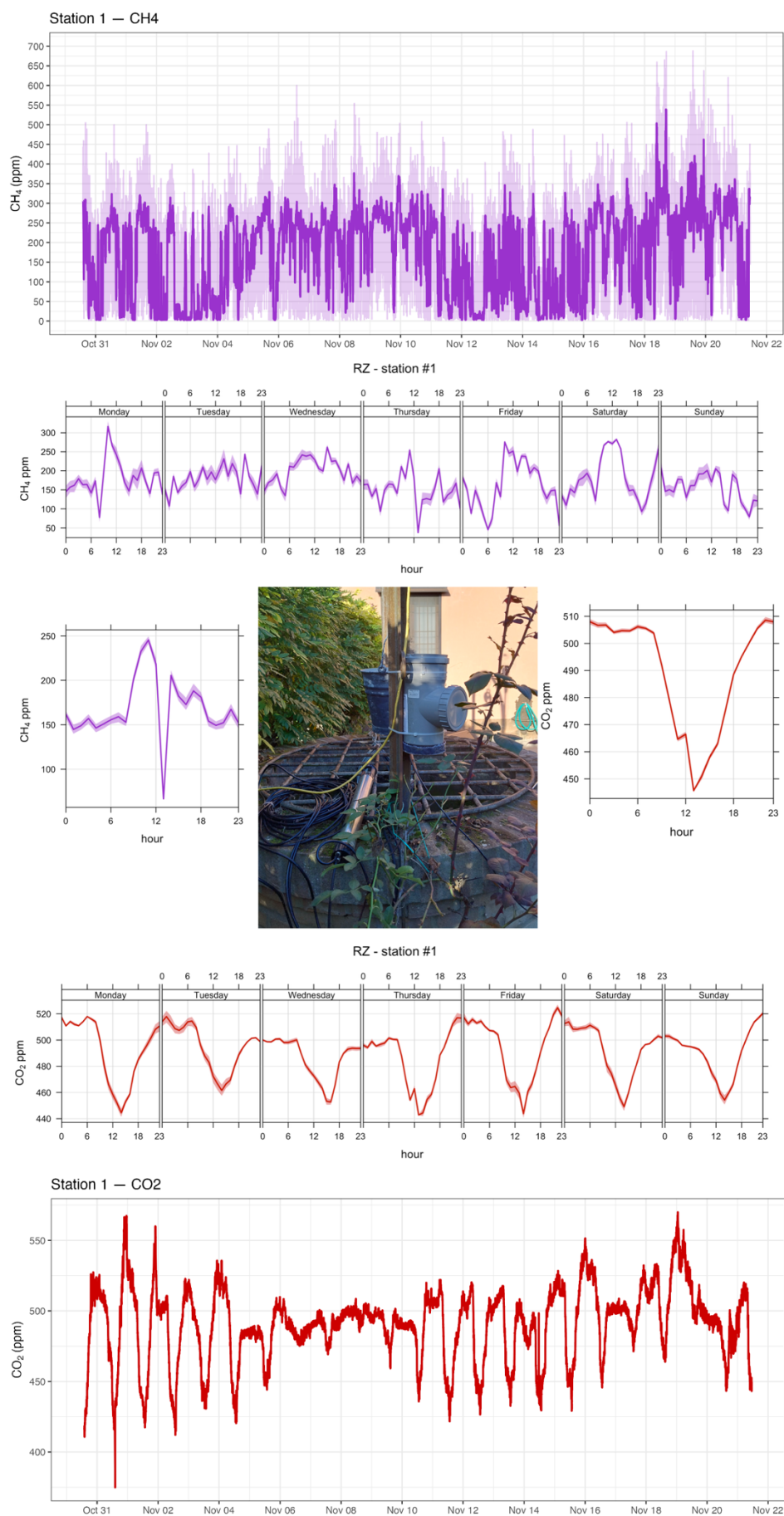


Figure 5.13. Station 1 CH<sub>4</sub> and CO<sub>2</sub> time series and relative diurnal/weekday composites.

The corresponding CO<sub>2</sub> record fluctuates around 460–520 ppm, with a pronounced daytime minimum and nocturnal build-up (Fig. 5.13, lower panels), consistent with photosynthetic uptake and nighttime accumulation in a semi-enclosed setting (Weber and Weber, 2008; Imasu and Tanabe, 2018; Munassar et al., 2025). Away from the well, Stations 2 and 4 remain close to background for most of the deployment, with CH<sub>4</sub> expressed primarily as short, advective excursions rather than as a persistent diurnal cycle (Figs. 5.14 and 5.16a, upper panels). Their diurnal medians stay in the 2.2–2.6 ppm range and exhibit weak weekday structure (Figs. 5.14 and 5.16a, middle rows), confirming that elevated values are episodic. CO<sub>2</sub> at both nodes preserves a regular diel pattern, with depressed daytime levels and nocturnal build-up (Figs. 5.14 and 5.16a, lower rows), indicating micro-meteorological control instead of proximity to the CH<sub>4</sub> source. These time-series features are consistent with the faint, narrow p95 sectors in the polar montage (Fig. 5.12) for S2 and S4, where only infrequent downwind alignment with the well produces detectable CH<sub>4</sub>. Stations 5 and 2 deserve particular attention because they sit along the same outer fence wall of the courtyard and display recurrent CH<sub>4</sub> peaks around ~18:00 in the time-variation plots (Figs. 5.14 and 5.17, middle rows). A plausible interpretation is that the early-evening transition in the boundary layer, when convective mixing collapses and flow becomes more weakly forced, recurrently steers the near-surface wind into the N–NNE/NNW corridor that connects the well to this wall, while turbulence and dilution simultaneously decrease. Under such conditions, the plume is intermittently channelled along the frontage wall, leading to short, repeatable concentration increases at both S5 and S2. This reading is consistent with their directional plots (Fig. 5.12), which show modal enhancement sectors from N–NNE for S5 and N–NNW for S2 at low-to-moderate speeds, i.e., precisely the sectors that advect air from the well towards that side of the enclosure. A secondary explanation, periodic site activity around that time, cannot be excluded a priori, yet the directional coherence across stations argues for a primarily meteorological gating rather than a localised operational trigger.

Station 3 shows the lowest daytime CO<sub>2</sub> minima across the network, reaching about 350 ppm (Fig. 5.15, lower panels). Its siting within the vegetation canopy and near a sun-exposed sector likely enhances daytime removal by photosynthesis and promotes vertical ventilation, both of which depress local CO<sub>2</sub> relative to the other nodes. The CH<sub>4</sub> record at S3 tends to approach background around midday (Fig. 5.15, upper/middle rows). This behaviour is best explained by enhanced dilution under a deeper, better-mixed daytime boundary layer rather than by chemical loss: the principal tropospheric sink for methane is OH oxidation with a characteristic lifetime of months to years, far too slow to imprint a midday minimum on the timescales observed here. In other words, the midday easing of CH<sub>4</sub> at S3 reflects mixing and advection, while the strong CO<sub>2</sub> diel signature reflects canopy biophysics and local ventilation.

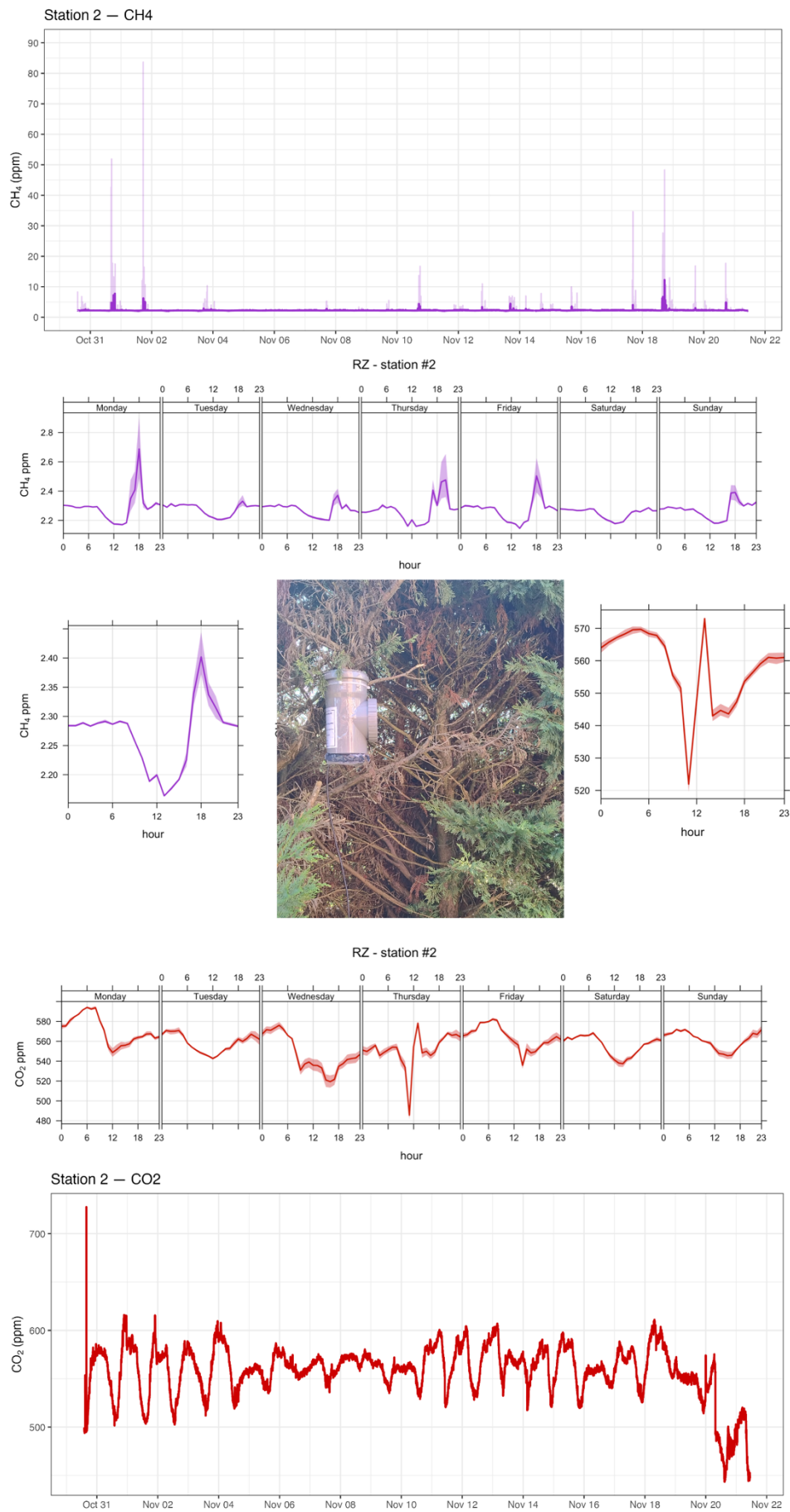


Figure 5.14. Station 2 CH<sub>4</sub> and CO<sub>2</sub> time series and relative diurnal/weekday composites.



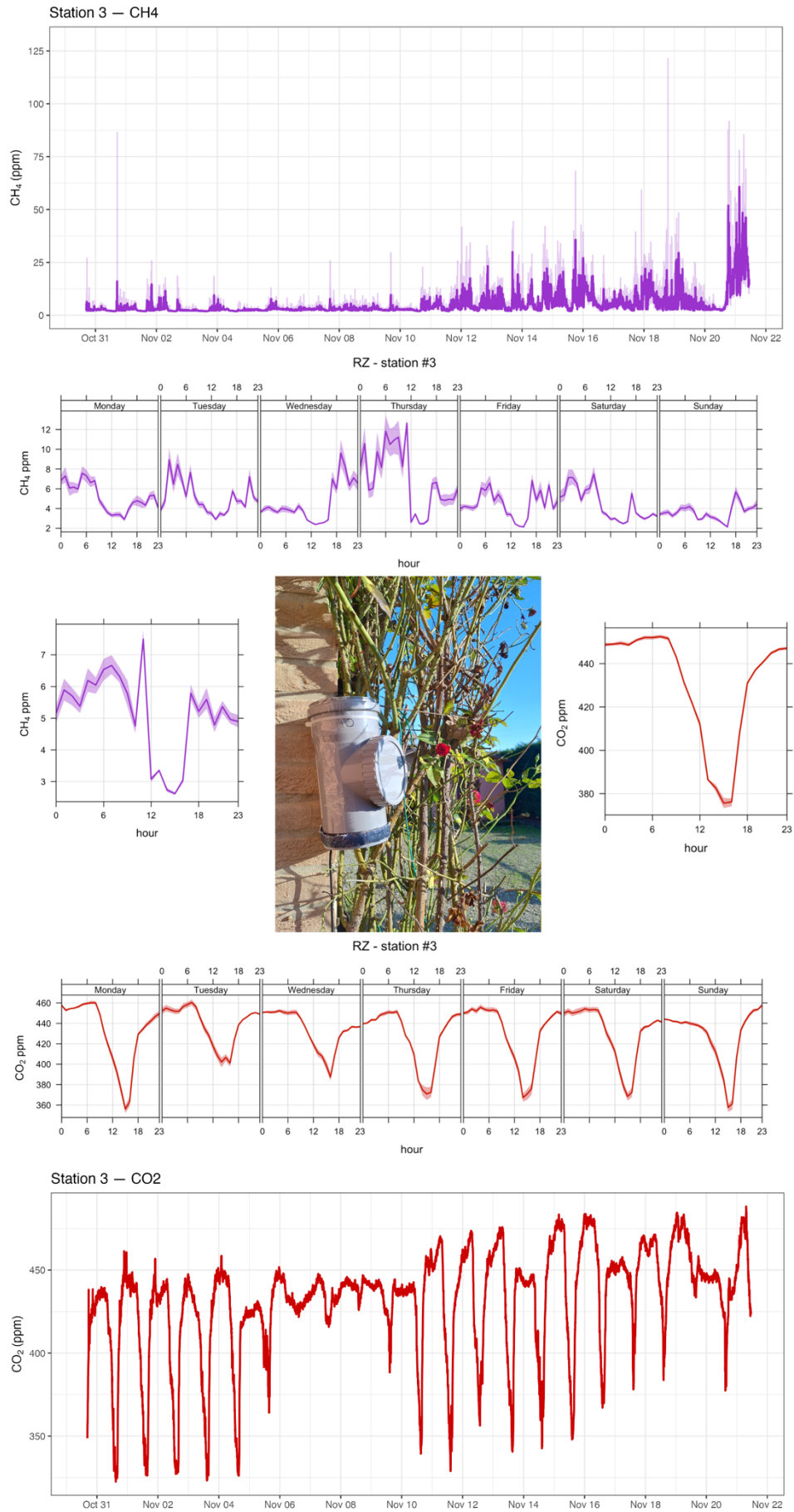
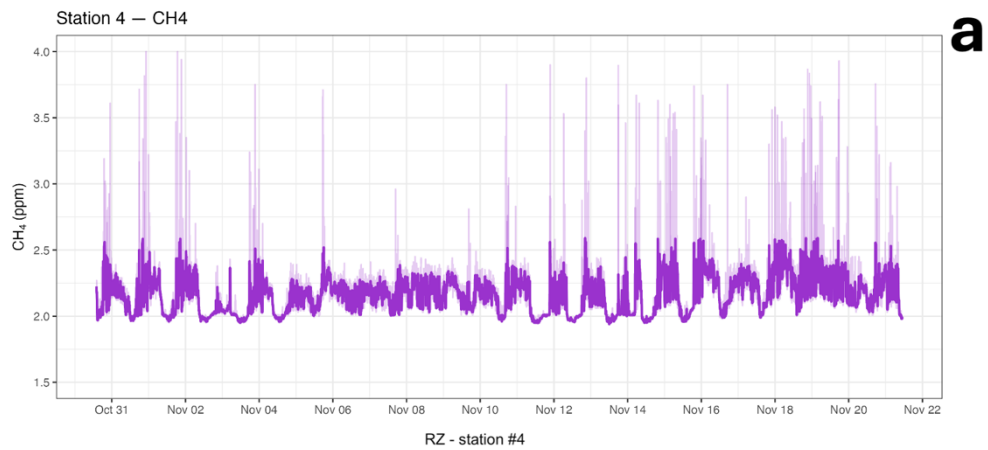
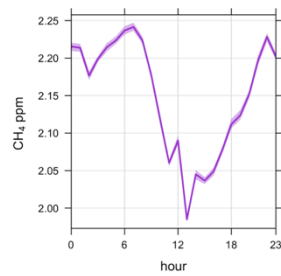
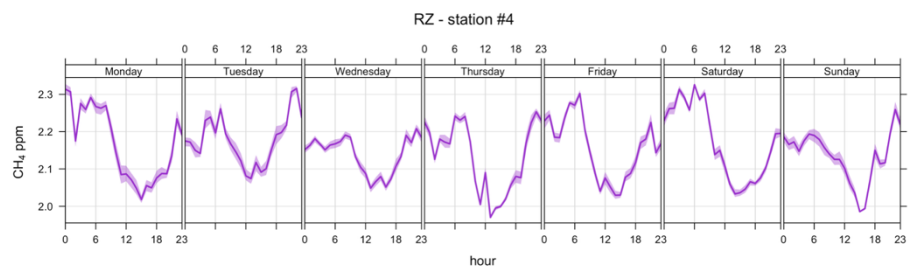


Figure 5.15. Station 3 CH<sub>4</sub> and CO<sub>2</sub> time series and relative diurnal/weekday composites.

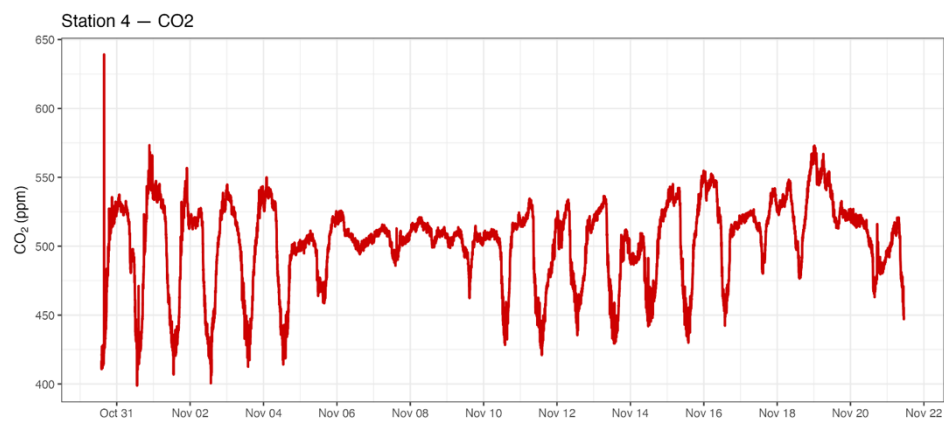
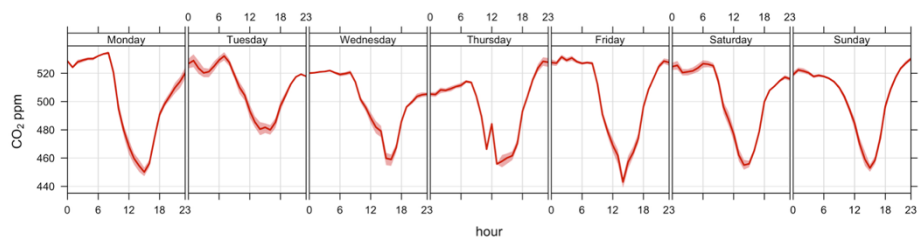
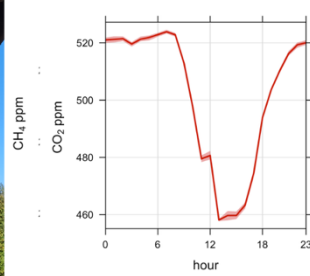
Station 4, the most remote station from the well, is dominated by background conditions but contains a single, very large excursion during the night of 14 November that masks day–night oscillations at the chosen y-axis scale (Fig. 5.6). To recover the diel behaviour without losing the information on the rare outlier, the S4 time-series panel was replotted after an IQR-based visual capping (Fig. 5.16a). This graphical cleaning leaves the underlying dataset unchanged for all analyses and summary statistics, while it prevents the single large spike on the night of 14 November (21:40–23:50) from suppressing the day–night structure on the y-axis. With the IQR-scaled view, CH<sub>4</sub> at S4 is seen to remain near background (median  $\approx 2.1$ – $2.3$  ppm) with weak but regular diel modulation (Fig. 5.16a, top), while CO<sub>2</sub> preserves the expected daytime minima and nocturnal build-up (Fig. 5.16a, bottom), in line with the interpretation for distant stations. The anomalous enhancement itself is retained and examined separately (Fig. 5.16b). The zoomed CH<sub>4</sub> trace shows a smooth rise from  $\sim 21:52$  and a plateau close to 300 ppm that collapses shortly after midnight. The concurrent polar plot, conditioned on the event window, indicates winds from W–NW, i.e., the upwind sector expected to advect air from the well toward S4 given the site geometry. Speeds during the event fall predominantly in the low-to-moderate range, consistent with reduced dilution, precisely the wind-speed dependence typically reported for near-ground plumes in bivariate polar plots. This combination of sector and speed corroborates a transient advective origin for the event rather than a persistent local source. The absence of comparable excursions at the other stations that would have been downwind under W–NW flow (notably S3 and S6; Fig. 5.6) and the rapid return to background further support a short-lived alignment of the flux along the long fetch from the well to S4.



**a**



RZ - station #4



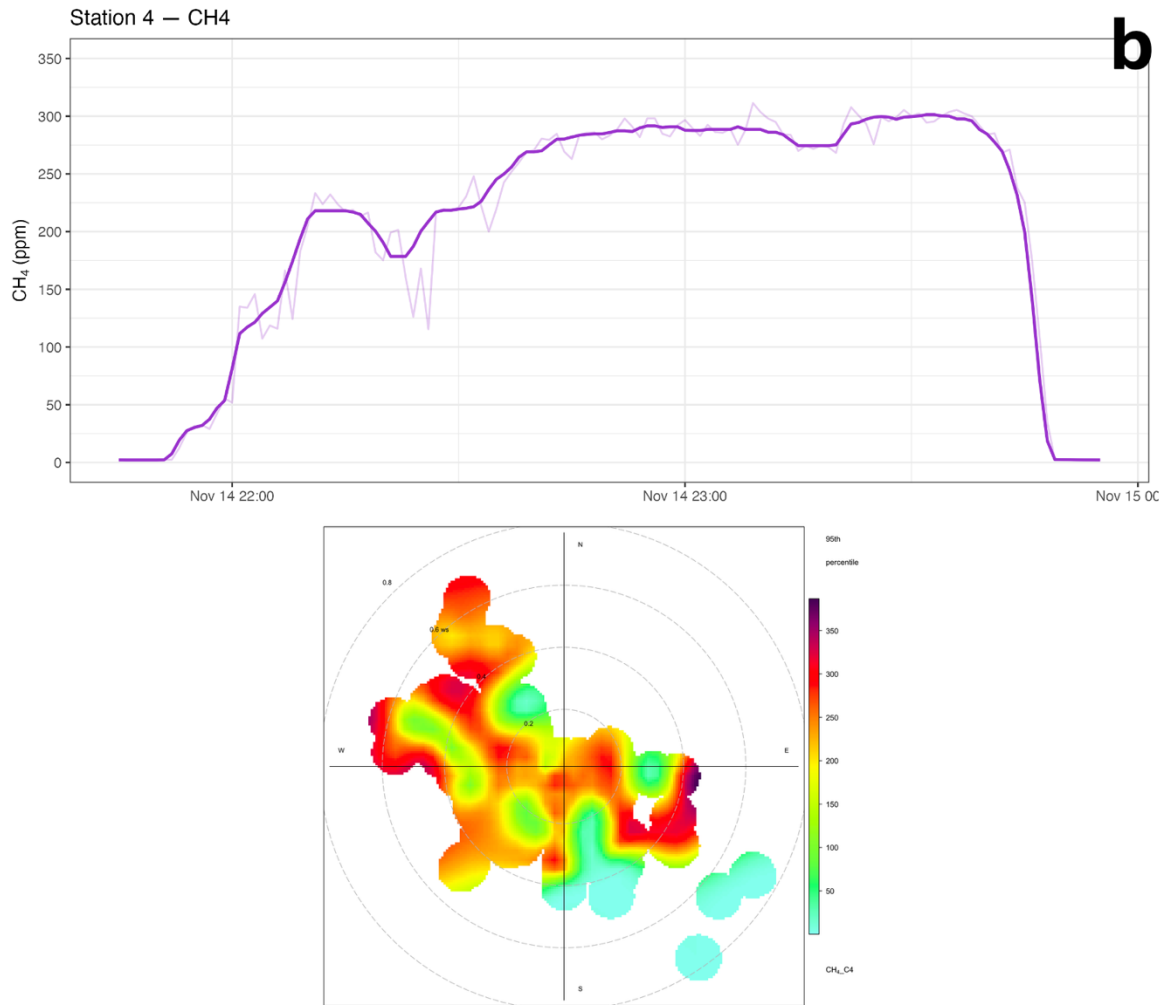


Figure 5.16. (a) Station 4 CH<sub>4</sub> time series and diurnal/weekday composites after IQR-based visual capping to preserve the diel structure (top and middle). CO<sub>2</sub> time series and weekday composites (lower panel). (b) Zoomed CH<sub>4</sub> time series at S4 (top) and event-window polar plot (bottom).

Station 6 exhibits behaviour intermediate between background and persistent influence. CH<sub>4</sub> remains close to background around local noon, rising more frequently during morning and evening stability (Fig. 5.18, upper/middle rows), and CO<sub>2</sub> shows the robust diel cycle typical of the other nodes (Fig. 5.18, lower panels). This pattern matches its polar plot (Fig. 5.12), where enhancements concentrate for S–SSW winds at lower speeds, again indicating a directional, weakly ventilated pathway from the well. Across S2, S5, and S6 the 4–6 November stability episode manifests as a damping of the CH<sub>4</sub> day–night range and a flattening of the CO<sub>2</sub> cycle, visible at all stations, in step with high surface pressure and reduced wind variability during that interval. The concurrence of reduced turbulence and the evening recurrence at S2/S5 underscores that methane variability at the outer stations is gated by advection under specific sectors and modulated by the local mixing state, whereas CO<sub>2</sub> is primarily governed by canopy-scale exchange and nighttime accumulation.

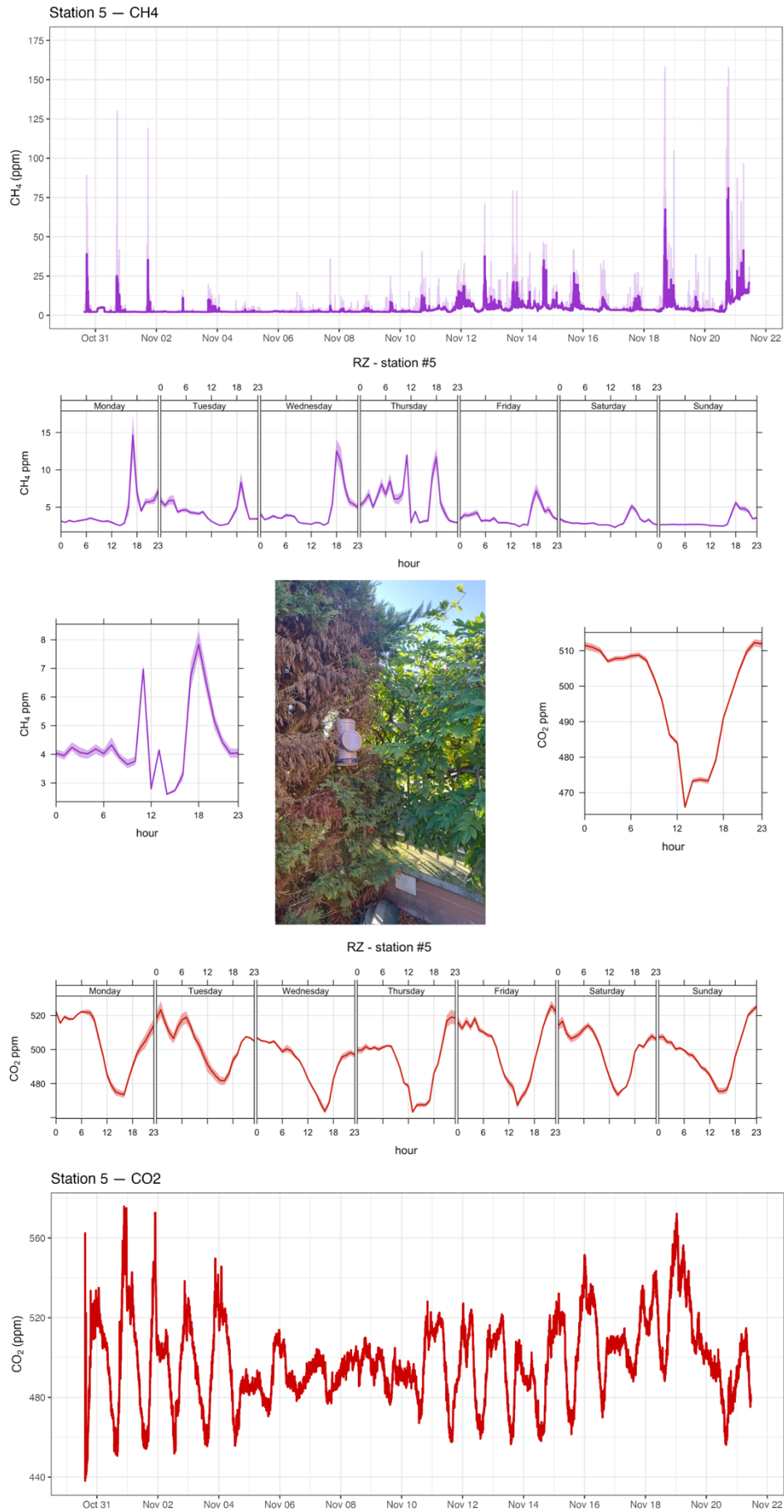


Figure 5.17. Station 5 CH<sub>4</sub> and CO<sub>2</sub> time series and relative diurnal/weekday composites.

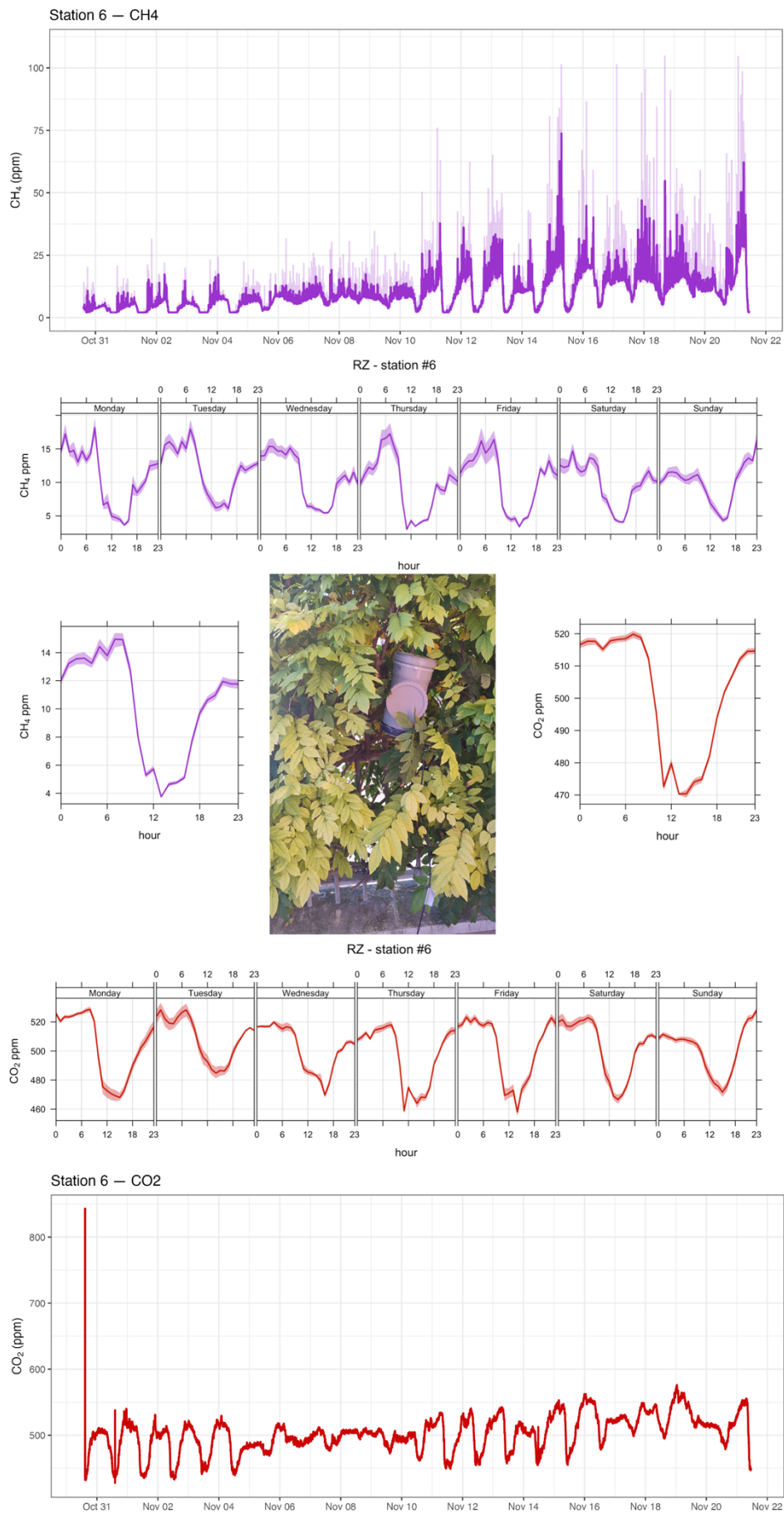


Figure 5.18. Station 6 CH<sub>4</sub> and CO<sub>2</sub> time series and relative diurnal/weekday composites.



Together with the on-source behaviour at S1, this set of time-series panels (Figs. 5.13–5.18) and the directional assortment (Fig. 5.12) delineates a consistent picture: a dominant near-field emitter at the well, a plume that becomes detectable along preferred corridors during low-to-moderate winds, most evidently in the early evening along the S5–S2 wall, and otherwise a rapid return to background under stronger ventilation. Despite the very high in-well concentrations, the dispersion regime observed during deployment did not result in hazardous plume buildup within the courtyard. Between 6 and 9 November, gases and meteorology jointly indicate a phase of persistent atmospheric stability. Across all stations the CO<sub>2</sub> diel cycle is dampened (daytime minima are shallow or absent and nocturnal build-up weakens) while CH<sub>4</sub> variability is suppressed, with fewer and smaller enhancements away from the well and only short, intermittent excursions at the more impacted nodes (S5–S6, and marginally S1). The anemometer series (Fig. 5.19) corroborates this regime: the temperature range compresses from  $\approx 10$  °C to only a few degrees and relative humidity remains high with limited daytime drying. Such co-evolution of T and RH is characteristic of a shallow, stably stratified boundary layer under anticyclonic control, in which the evening transition collapses the convective mixed layer and a surface-based inversion forms and persists, thereby reducing mixing depth and turbulent exchange (Piringer and Baumann-Stanzer, 2024; van de Wiel et al., 2012). With the mixing-layer height (MLH) depressed, vertical dilution of conservative scalars is strongly curtailed—a canonical boundary-layer result that explains both the damping of the CO<sub>2</sub> cycle and the selective, advection-gated appearance of CH<sub>4</sub> (Wagner and Schäfer, 2017). Chemistry does not offer a competing mechanism on these timescales: the primary CH<sub>4</sub> sink by OH is far too slow to shape sub-daily variations (Stull, 2012). The shaded window in Fig. 5.19 therefore provides the physical context for the “flattening” seen in the gas records: dispersion during 6–9 November was controlled by a persistent inversion/stability episode, with advection along preferred corridors still determining when methane is detectable, but overall variability in both gases markedly reduced by weak ventilation and low MLH.

Anemometer — Temperature and Relative Humidity  
 Shaded = atmospheric inversion episode (6–9 Nov)

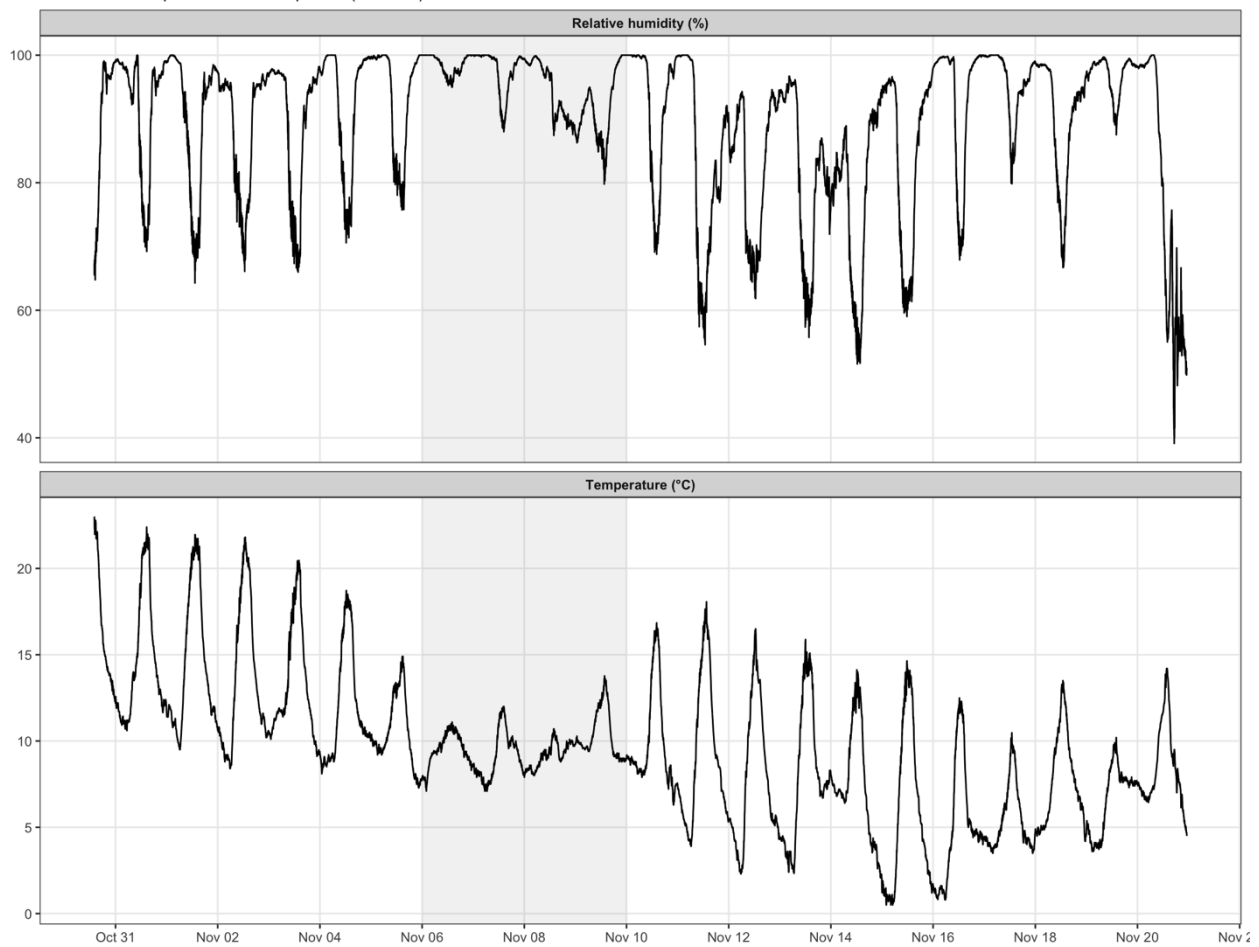


Figure 5.19. Time series of relative humidity (top) and air temperature (bottom) from the wellhead anemometer.

## Chapter VI – Nirano

The Salse di Nirano mud-volcano field lies along the Pede-Apennine margin of the Northern Apennines, within an elliptical depression developed in the Plio–Pleistocene Argille Azzurre Formation and aligned with the regional NW–SE structural grain. Gas discharge focuses at conical edifices and bubbling pools (Fig. 6.1), where fluid ascent is guided by thrusts and fractures associated with the fold-and-thrust belt (Bonini et al., 2007; Castaldini et al., 2017). Emitted gases are CH<sub>4</sub>-dominated, with isotopic signatures indicating a prevailing thermogenic component and subordinate microbial contributions (Etiope et al., 2007; Oppo et al., 2017), while the liquid phase consists primarily of brackish connate waters in combination with mud. In addition, the area is seismically active, providing a natural laboratory to explore how deep-fluid pressurisation and tectonic forcing modulate surface emissions. This chapter targets two complementary goals: (i) to characterise the temporal variability of mud-column properties to evaluate the relative roles of environmental drivers versus deep perturbations;

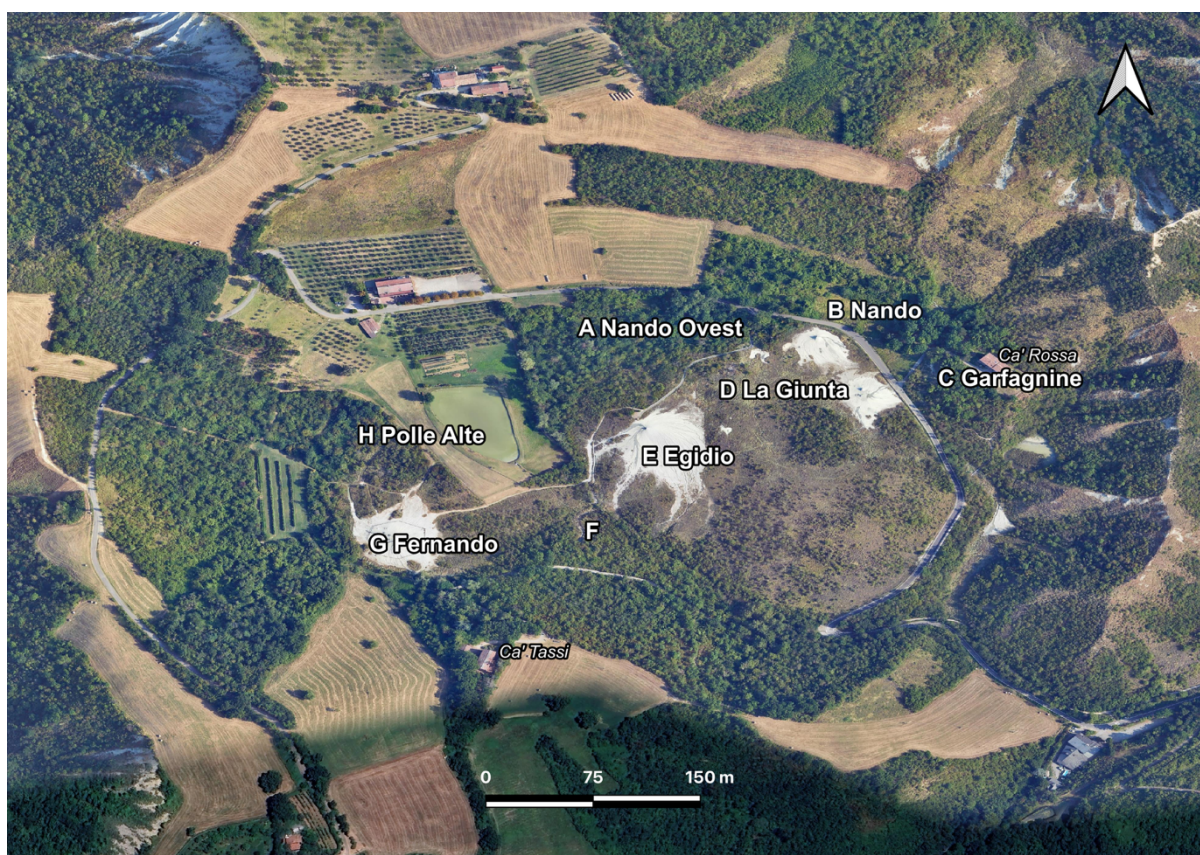


Figure 6.1. Positioning of the main mud volcanoes and mud pools of the Salse di Nirano Natural Reserve.

(ii) to quantify CH<sub>4</sub> and CO<sub>2</sub> fluxes from bubbling pools under realistic field conditions using a purpose-built floating extension for accumulation-chamber measurements (Section 3.6.2), thereby providing robust, footprint-scale fluxes addressing burst-dynamics.

## 6.1 Results

### 6.1.1 Mud Pool Monitoring

The temporal series for mud pool F, shown in Fig. 6.2, covers the period from April 24 2023 (shortly after installation), to November 15, 2024. As described in Section 3.1, the subsequent data, collected after the sensor was damaged and replaced, represents a time series too short for a meaningful interpretation within this study. The STS probe data is presented alongside meteorological information produced by the INGV (Milano) weather station, installed nearby mud pool La Giunta in the same timeframe.

Mud temperature (green line) ranges from 7.1 °C to 17.6 °C, with a clear seasonal trend that mirrors air temperature measurements (sky blue line in the lower panel). Mud level varies between 2.17 m and 2.37 m relative to the local datum, with the most extended near-constant interval occurring 9 May–6 Jun 2023 (29 days) at ~2.18 m. Electrical conductivity spans from 995  $\mu\text{S cm}^{-1}$  to 13,826  $\mu\text{S cm}^{-1}$ . In April–June 2023, EC remains high, with daily medians around 9100–9800  $\mu\text{S cm}^{-1}$ . Through October–December 2023, it decreases to monthly medians of 7770, 5590, and 4370  $\mu\text{S cm}^{-1}$ , and further to ~2270  $\mu\text{S cm}^{-1}$  by March 2024. A prolonged low-variability plateau is observed 6 May–9 June 2024 (35 days) within 2112–2210  $\mu\text{S cm}^{-1}$ , after which EC reaches its pointwise minimum (995  $\mu\text{S cm}^{-1}$  on 31 Jul 2024). This period is followed by a sharp rise during August 2024: the largest one-day increase in the daily median is +9653  $\mu\text{S cm}^{-1}$  on 28 Aug 2024, with the daily-median maximum of 12 521  $\mu\text{S cm}^{-1}$  on 29 Aug 2024 (instantaneous maximum 13 826  $\mu\text{S cm}^{-1}$  late on 28 Aug). Large day-to-day decreases also occur in early September 2024 (e.g., -8098  $\mu\text{S cm}^{-1}$  on 7 Sep 2024). Monthly medians stabilise around 4340–5760  $\mu\text{S cm}^{-1}$  in September–October 2024, and near 4360  $\mu\text{S cm}^{-1}$  in November 2024.

Additionally, a set of vertical profiles was acquired at mud pool F using the STS probe (Fig. 6.3), logging one measurement every 8 s during a continuous downcast, which is reflected by the high density of points. Mud temperature increases quasi-monotonically with depth, indicating a weak conductive gradient and limited vertical mixing in the lower part of the column. Electrical conductivity (EC) shows lower and more scattered values in the upper metres, followed by a progressive increase and stabilisation at depth.

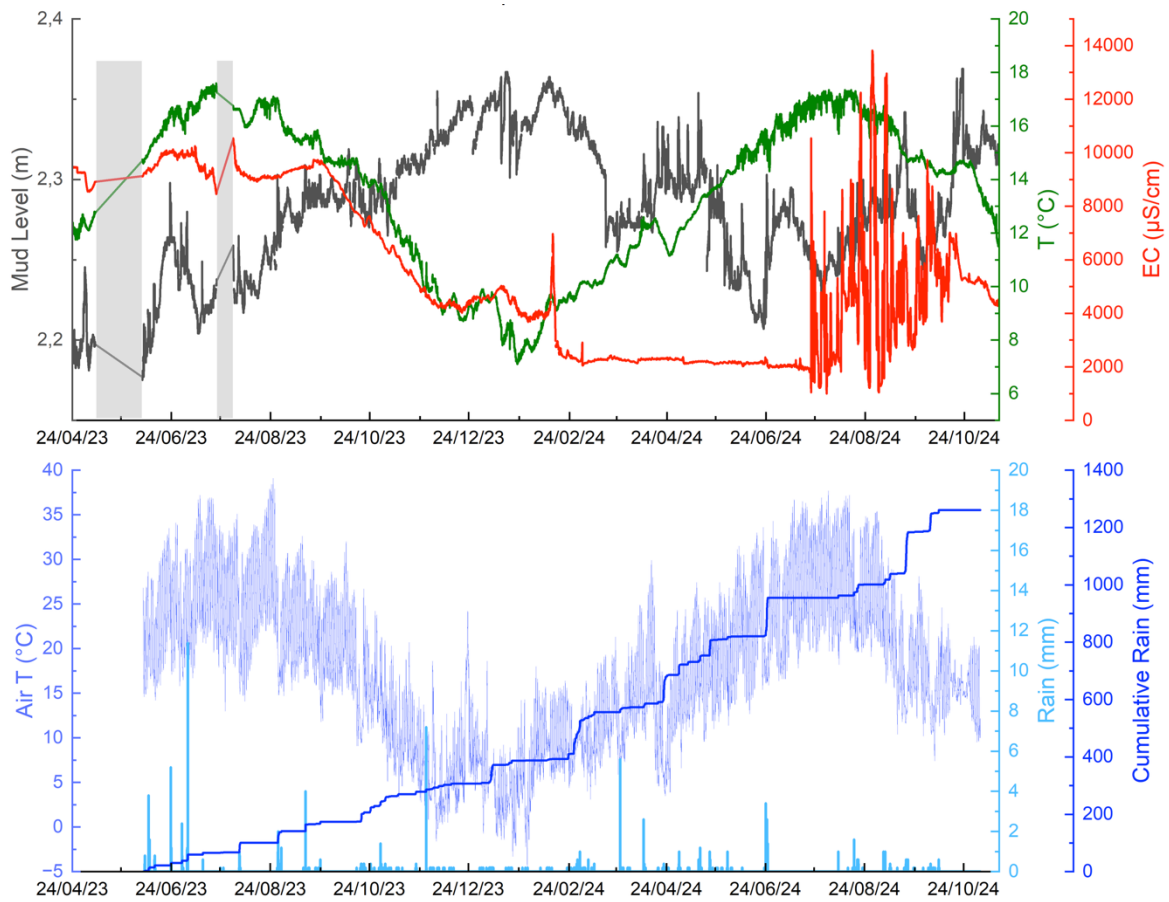


Figure 6.2. Time series of the STS probe installed at mud pool F in Nirano, from 24/04/2023 to 15/11/2024 (upper panel); lower panel displays air T (°C), daily precipitation (mm) and cumulative rain (mm) acquired from the weather station installed near mud pool La Giunta by INGV Milano.

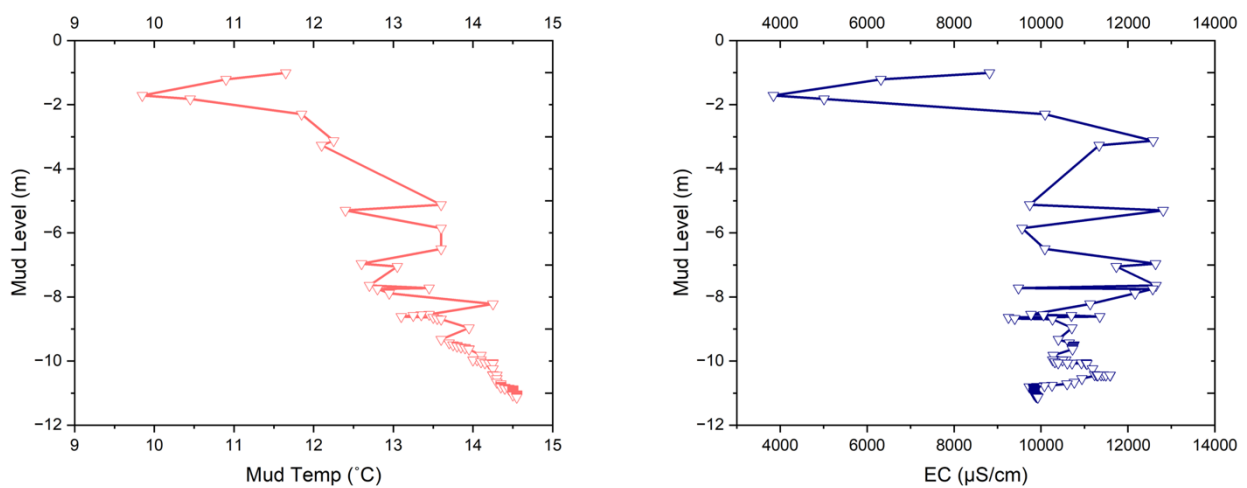


Figure 6.3. Vertical profiles of mud temperature (left) and electrical conductivity (right) in pool F measured with the STS probe.

### 6.1.2 Bubbling Gas Analysis

The analysis of the bubbling gas collected at La Giunta on 4 April 2023 is reported in Table 6.1. For readability, the same composition expressed as per cent of total (normalised to 100% by volume of the reported sum) is: CH<sub>4</sub> 94.1%, N<sub>2</sub> 3.4%, O<sub>2</sub> 1.4%, CO<sub>2</sub> 1%, C<sub>2</sub>H<sub>6</sub> 0.04%; noble gases and H<sub>2</sub> occur at trace levels (He 0.001%, Ne 0.001%, H<sub>2</sub> 0.0002%). The analytical sum of the raw abundances is 1,006624.44 ppmv, where the difference from 1,000000 ppmv reflects rounding and reporting precision.

| He   | Ne  | H <sub>2</sub> | O <sub>2</sub> | N <sub>2</sub> | CH <sub>4</sub> | CO <sub>2</sub> | C <sub>2</sub> H <sub>6</sub> | δ <sup>13</sup> C-CH <sub>4</sub> | δ <sup>13</sup> C-CO <sub>2</sub> |
|------|-----|----------------|----------------|----------------|-----------------|-----------------|-------------------------------|-----------------------------------|-----------------------------------|
| 14.9 | 9.2 | 2.2            | 14554.2        | 34571.8        | 947324.6        | 9738.3          | 409.2                         | -47                               | 21                                |

Table 6.1. Chemical and isotopic composition of the free gas collected at mud pool La Giunta. Values expressed as ppmv for concentrations and ‰ V-PDB for δ<sup>13</sup>C of CH<sub>4</sub> and CO<sub>2</sub>.

### 6.1.3 Gas Fluxes from Mud Pools

The locations of the mud-pool measurements are shown in Figure 6.4. Four pools were targeted: the pool close to the Fernando cone (MP Fer), the non-bubbling pool near La Giunta (MP n-LG), La Giunta pool (MP LG), and pool F (MP F). Fourteen acquisitions were collected over two campaigns, yielding two records at MP n-LG (NIR1–NIR2), one at MP LG (NIR3), two at MP Fer (NIR8–NIR9), and nine at MP F (NIR4–NIR7 and NIR10–NIR14). The corresponding metadata are listed in Table 6.2. Acquisition duration (Δt<sub>acq</sub>) spans 138–664 seconds, the longest at NIR1 (664 s) and the shortest at NIR4 (138 s). Chamber-side temperature during measurements ranges 295.7–302.8 K (values already converted to Kelvin for the gas-law calculation) with a minimum at NIR4 and a maximum at NIR14, while pressure ranges 980.6–996 hPa (minimum at NIR10, maximum at NIR4). Replicates at MP F cover two campaigns (June and August) and provide repeated observations under comparable geometry.

All acquisitions used the floating extension designed explicitly for bubbling pools (Section 3.6.2): a high-density EPS frame (approximately 54 × 54 × 60 cm) providing buoyancy and an upper circular port for the accumulation chamber. Flux conversion follows the chamber geometry adopted, i.e. the footprint area  $A = Ad = 0.292 \text{ m}^2$  and headspace volume  $V = Vd + Vc = 0.181 \text{ m}^3$  (extension plus chamber). As described in Section 3.6.2, time series in bubbling pools are characterised by stepwise concentration increases due to bubble bursts (Fig. 6.5). Consequently, acquisition times were set to several minutes to capture multiple events.



For each record and gas ( $\text{CH}_4$ ,  $\text{CO}_2$ ), fluxes were computed from the in-chamber concentration growth using the ideal-gas formulation and the above  $V/A$  geometry, with analysis windows documented alongside the results. Where applicable, both the end-to-end slope over the selected interval and the burst-decomposition metrics defined in section 3.6.2 were derived on the same acquisitions and are reported in the following tables and figures.



Figure 6.4. Location of the mud pools investigated for chamber measurements. The upper panel shows the aerial overview with the 14 acquisition sites; lower panels: (b) MP Fer (pool near the Fernando cone), (c) MP LG and MP n-LG (La Giunta pool and the nearby non-bubbling pool), (d) MP F. Coordinates are approximate and intended for site identification.

| date       | acq_id | mud pool | $\Delta t_{\text{acq}}$ (s) | T (K) | P (hPa) |
|------------|--------|----------|-----------------------------|-------|---------|
| 06-06-2023 | NIR1   | MP n-LG  | 664                         | 301.2 | 994.4   |
| 06-06-2023 | NIR2   | MP n-LG  | 244                         | 301.2 | 994.5   |
| 07-06-2023 | NIR3   | MP LG    | 528                         | 301.2 | 995.9   |
| 07-06-2023 | NIR4   | MP F     | 138                         | 295.7 | 996     |
| 07-06-2023 | NIR5   | MP F     | 279                         | 296.5 | 995.9   |
| 07-06-2023 | NIR6   | MP F     | 356                         | 296.5 | 995.9   |
| 07-06-2023 | NIR7   | MP F     | 237                         | 298   | 995.6   |
| 07-06-2023 | NIR8   | MP Fer   | 301                         | 296.8 | 993.2   |
| 07-06-2023 | NIR9   | MP Fer   | 478                         | 297.7 | 993.3   |
| 01-08-2023 | NIR10  | MP F     | 270                         | 301.5 | 980.6   |
| 01-08-2023 | NIR11  | MP F     | 204                         | 301.3 | 984.6   |
| 01-08-2023 | NIR12  | MP F     | 285                         | 301.5 | 984.5   |
| 01-08-2023 | NIR13  | MP F     | 369                         | 302   | 984.3   |
| 01-08-2023 | NIR14  | MP F     | 424                         | 302.8 | 984.5   |

Table 6.2. Acquisition metadata for mud-pool measurements: date, identifier (acq\_id), mud pool, acquisition duration ( $\Delta t_{\text{acq}}$ ), chamber-side temperature (T) and pressure (P).

End-to-end fluxes derived from the linear concentration increase selected with the *Flux Revision* software are reported in Table 6.3. For each acquisition and gas, the slope ( $\text{ppm s}^{-1}$ ) is the user-selected regression coefficient over the stated time window  $\Delta t$  (s), with the accompanying  $R^2$  referring to that regression.

At the non-bubbling mud pool near La Giunta (NIR1–NIR2),  $\text{CH}_4$  slopes are approximately  $0.13 \text{ ppm s}^{-1}$  over  $\Delta t = 198\text{--}551 \text{ s}$  ( $R^2 = 0.778\text{--}0.933$ ), yielding fluxes of  $4.3\text{--}4.4 \text{ g m}^{-2} \text{ d}^{-1}$ .  $\text{CO}_2$  slopes range from  $0.03\text{--}0.06 \text{ ppm s}^{-1}$  with  $\Delta t = 207\text{--}569 \text{ s}$  ( $R^2 = 0.934\text{--}0.947$ ), giving  $2.6\text{--}5.2 \text{ g m}^{-2} \text{ d}^{-1}$ . At La Giunta mud pool (NIR3), the single acquisition shows a  $\text{CH}_4$  slope of  $1.35 \text{ ppm s}^{-1}$  over  $427 \text{ s}$  ( $R^2 = 0.808$ ), corresponding to  $46.4 \text{ g m}^{-2} \text{ d}^{-1}$ , while the  $\text{CO}_2$  slope is  $0.07 \text{ ppm s}^{-1}$  over  $365 \text{ s}$  ( $R^2 = 0.974$ ), corresponding to a flux of  $6.5 \text{ g m}^{-2} \text{ d}^{-1}$ . The mud pool near the Fernando cone (NIR8–NIR9) yielded  $\text{CH}_4$  slopes ranging  $32.7\text{--}61.8 \text{ ppm s}^{-1}$  with  $\Delta t = 226\text{--}298 \text{ s}$  ( $R^2 = 0.679\text{--}0.910$ ), with corresponding fluxes of  $1,133.2\text{--}2,136.3 \text{ g m}^{-2} \text{ d}^{-1}$ .  $\text{CO}_2$  slopes are  $0.28\text{--}0.53 \text{ ppm s}^{-1}$  over  $\Delta t = 224\text{--}297 \text{ s}$  ( $R^2 = 0.702\text{--}0.924$ ), with fluxes between  $26.3\text{--}50.1 \text{ g m}^{-2} \text{ d}^{-1}$ . At mud pool F (NIR4–NIR7 and NIR10–NIR14),  $\text{CH}_4$  slopes span  $3.1\text{--}290 \text{ ppm s}^{-1}$  with  $\Delta t = 73\text{--}276 \text{ s}$  ( $R^2 = 0.009\text{--}0.975$ ), corresponding to fluxes between  $104.4\text{--}10,120.3 \text{ g m}^{-2} \text{ d}^{-1}$  across the nine acquisitions.  $\text{CO}_2$  slopes are  $0.19\text{--}1.5 \text{ ppm s}^{-1}$  over  $\Delta t = 75\text{--}261 \text{ s}$  ( $R^2 = 0.093\text{--}0.954$ ), matching fluxes  $17.5\text{--}141.2 \text{ g m}^{-2} \text{ d}^{-1}$ .

| acq_id | CH <sub>4</sub> (ppm s <sup>-1</sup> ) | Δt (s) | R <sup>2</sup> | CH <sub>4</sub> (g m <sup>-2</sup> d <sup>-1</sup> ) | CO <sub>2</sub> (ppm s <sup>-1</sup> ) | Δt (s) | R <sup>2</sup> | CO <sub>2</sub> (g m <sup>-2</sup> d <sup>-1</sup> ) |
|--------|----------------------------------------|--------|----------------|------------------------------------------------------|----------------------------------------|--------|----------------|------------------------------------------------------|
| NIR1   | 0.13                                   | 551    | 0.933          | 4.3                                                  | 0.06                                   | 569    | 0.947          | 5.2                                                  |
| NIR2   | 0.13                                   | 198    | 0.778          | 4.4                                                  | 0.03                                   | 207    | 0.934          | 2.6                                                  |
| NIR3   | 1.35                                   | 427    | 0.808          | 46.4                                                 | 0.07                                   | 365    | 0.974          | 6.5                                                  |
| NIR4   | 290                                    | 73     | 0.975          | 10120.3                                              | 1.5                                    | 75     | 0.954          | 141.2                                                |
| NIR5   | 50.2                                   | 138    | 0.784          | 1746.5                                               | 0.3                                    | 131    | 0.829          | 28.8                                                 |
| NIR6   | 55.7                                   | 276    | 0.775          | 1937.1                                               | 0.29                                   | 253    | 0.777          | 27.9                                                 |
| NIR7   | 33.4                                   | 158    | 0.838          | 1157.7                                               | 0.24                                   | 150    | 0.876          | 23.1                                                 |
| NIR8   | 32.7                                   | 226    | 0.91           | 1133.2                                               | 0.28                                   | 224    | 0.924          | 26.3                                                 |
| NIR9   | 61.8                                   | 298    | 0.679          | 2136.3                                               | 0.53                                   | 297    | 0.702          | 50.1                                                 |
| NIR10  | 3.8                                    | 174    | 0.417          | 130.8                                                | 0.19                                   | 163    | 0.093          | 17.5                                                 |
| NIR11  | 110.5                                  | 163    | 0.888          | 3741.4                                               | 0.66                                   | 139    | 0.866          | 61.0                                                 |
| NIR12  | 3.1                                    | 150    | 0.009          | 104.4                                                | 0.21                                   | 210    | 0.517          | 19.3                                                 |
| NIR13  | 32.1                                   | 208    | 0.476          | 1083.4                                               | 0.26                                   | 224    | 0.542          | 24.5                                                 |
| NIR14  | 63.4                                   | 260    | 0.912          | 2134.7                                               | 0.41                                   | 261    | 0.905          | 38.2                                                 |

Table 6.3 End-to-end fluxes from linear concentration trends selected in Flux Manager. For each acquisition and gas the table lists the slope (ppm s<sup>-1</sup>), the time interval used for regression (Δt), the coefficient of determination (R<sup>2</sup>), and the flux converted with the floating-chamber geometry (g m<sup>-2</sup> d<sup>-1</sup>).

In Figure 6.5, CH<sub>4</sub> and CO<sub>2</sub> concentration time series are shown for one representative acquisition per mud pool (MP Fer, MP n-LG, MP LG, and MP F). Each trace exhibits the step-like pattern typical of bubbling pools, with discrete upward jumps superimposed on more gradual segments. The shaded selections indicate the intervals used for burst decomposition, corresponding to bubble onsets identified by abrupt increases in the in-chamber concentration. For each panel, CH<sub>4</sub> and CO<sub>2</sub> are displayed side-by-side to document that the two gases do not always show similar patterns. As a result, the selected windows for CH<sub>4</sub> and CO<sub>2</sub> may differ in timing and duration, reflecting the distinct step occurrences used in the event-wise quantification. In line with the step-like behaviour illustrated in Figure 6.5, each bubble rise is treated as a discrete event.

For every event, the net concentration change is obtained as the difference between the post-event and pre-event plateaux, computed over short windows bracketing the jump ( $\Delta\text{ppm} = \text{mean\_after} - \text{mean\_before}$ ). Each  $\Delta\text{ppm}$  is converted to mass per burst  $m_i$  (g) using the ideal-gas factor for the measurement headspace. The burst component of the flux is then obtained by summing the event masses and normalising by the chamber footprint and by the selected analysis duration, yielding  $\sum m_i / (A \times \Delta t)$  in g m<sup>-2</sup> d<sup>-1</sup>. A slowly varying background is estimated by regressing concentration against time on “clean” segments between events (short masks applied around each step); the



resulting slope, expressed in  $\text{ppm s}^{-1}$ , is converted to a background flux with the same gas-law factor and geometry.

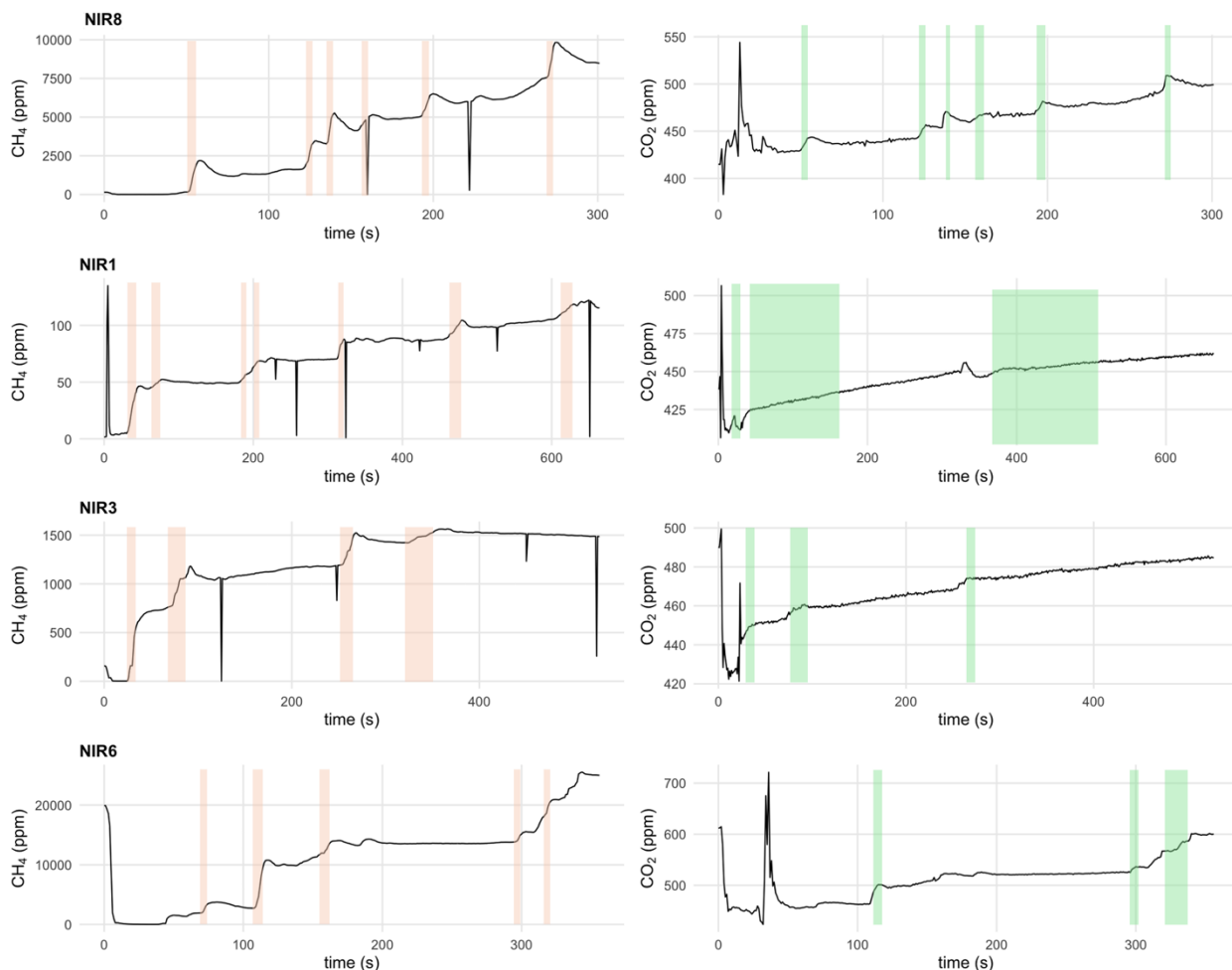


Figure 6.5. Representative CH<sub>4</sub> and CO<sub>2</sub> time series for one acquisition at each mud pool- Shaded bands indicate the analysis window used in the burst method.

The total flux for the acquisition is the sum of the burst and background contributions. In addition, two descriptive event metrics are retained: the burst rate  $\lambda$  ( $\text{events min}^{-1}$ ) and the mean mass per burst  $\bar{m}(\text{g})$ . The table listing the burst selections (start times and durations) for each acquisition is provided in Appendix A.6-A.7. Following the step-like pattern shown in Figure 6.4, event-based fluxes have been calculated and are listed in Tables 6.4 and 6.5 for CH<sub>4</sub> and CO<sub>2</sub>, respectively.

| acq_id | n bursts | $\lambda \text{ min}^{-1}$ | $\bar{m} \text{ (g)}$ | F_burst<br>( $\text{g m}^{-2} \text{ d}^{-1}$ ) | F_bg<br>( $\text{g m}^{-2} \text{ d}^{-1}$ ) | F_total<br>( $\text{g m}^{-2} \text{ d}^{-1}$ ) |
|--------|----------|----------------------------|-----------------------|-------------------------------------------------|----------------------------------------------|-------------------------------------------------|
| NIR1   | 7        | 0.7                        | 0.002                 | 6.2                                             | 4.1                                          | 10.3                                            |
| NIR2   | 4        | 1                          | 0.001                 | 4.1                                             | 4.7                                          | 8.9                                             |
| NIR3   | 4        | 0.7                        | 0.05                  | 164.7                                           | 78.7                                         | 243.4                                           |
| NIR4   | 4        | 3.2                        | 0.63                  | 10115.3                                         | 7586.6                                       | 17701.9                                         |
| NIR5   | 5        | 1.5                        | 0.38                  | 2921.9                                          | 2179.5                                       | 5101.4                                          |
| NIR6   | 5        | 1.2                        | 0.49                  | 2905.1                                          | 1603                                         | 4508.1                                          |
| NIR7   | 3        | 1.6                        | 0.21                  | 1571.5                                          | 1268.3                                       | 2839.8                                          |
| NIR8   | 6        | 1.6                        | 0.17                  | 1324.6                                          | 1121.9                                       | 2446.5                                          |
| NIR9   | 3        | 0.8                        | 0.94                  | 3491.7                                          | 648.1                                        | 4139.7                                          |
| NIR10  | 2        | 2.9                        | 0.02                  | 314.5                                           | -680.2                                       | -365.7                                          |
| NIR11  | 5        | 1.9                        | 0.41                  | 3873.6                                          | 4280.8                                       | 8154.5                                          |
| NIR12  | 1        | 6                          | 0.16                  | 4615.1                                          | 0                                            | 4615.1                                          |
| NIR13  | 4        | 2.1                        | 0.56                  | 5805.1                                          | 1384                                         | 7189.1                                          |
| NIR14  | 4        | 1.4                        | 0.60                  | 4280.5                                          | 1624.7                                       | 5905.2                                          |

Table 6.4. Event-based CH<sub>4</sub> flux metrics. For each acquisition: number of bursts (n), event rate ( $\lambda$ ,  $\text{min}^{-1}$ ), mean burst mass (g), burst component of the flux (F\_burst), background component (F\_bg), and total flux (F\_total), all in  $\text{g m}^{-2} \text{ d}^{-1}$  for flux terms. Negative values are reported as computed from the selected time windows.

| Acq_id | n bursts | $\lambda \text{ min}^{-1}$ | $\bar{m} \text{ (g)}$ | F_burst<br>( $\text{g m}^{-2} \text{ d}^{-1}$ ) | F_bg<br>( $\text{g m}^{-2} \text{ d}^{-1}$ ) | F_total<br>( $\text{g m}^{-2} \text{ d}^{-1}$ ) |
|--------|----------|----------------------------|-----------------------|-------------------------------------------------|----------------------------------------------|-------------------------------------------------|
| NIR1   | 3        | 0.3                        | 0.005                 | 7.9                                             | -3.9                                         | 3.9                                             |
| NIR2   | 1        | 0.7                        | 0.002                 | 7.9                                             | 0                                            | 7.9                                             |
| NIR3   | 3        | 0.7                        | 0.004                 | 13.6                                            | 7.7                                          | 21.3                                            |
| NIR4   | 4        | 3.2                        | 0.01                  | 170.9                                           | 156.8                                        | 327.7                                           |
| NIR5   | 3        | 1.1                        | 0.009                 | 48.1                                            | 27.2                                         | 75.3                                            |
| NIR6   | 3        | 0.8                        | 0.01                  | 41.6                                            | 13                                           | 54.6                                            |
| NIR7   | 3        | 1.6                        | 0.004                 | 27.4                                            | 24                                           | 51.4                                            |
| NIR8   | 6        | 1.6                        | 0.003                 | 26.6                                            | 26.7                                         | 53.3                                            |
| NIR9   | 2        | 0.5                        | 0.03                  | 68                                              | 12.7                                         | 80.8                                            |
| NIR11  | 5        | 1.9                        | 0.007                 | 65.1                                            | 70.8                                         | 135.8                                           |
| NIR12  | 1        | 0.3                        | 0.02                  | 32.2                                            | 0                                            | 32.2                                            |
| NIR13  | 3        | 1.6                        | 0.01                  | 74.3                                            | 50.2                                         | 124.5                                           |
| NIR14  | 4        | 1.4                        | 0.01                  | 72.2                                            | 33.8                                         | 106                                             |

Table 6.5 Event-based CO<sub>2</sub> flux metrics. Same structure as Table 6.4: n,  $\lambda$  ( $\text{min}^{-1}$ ), mean burst mass (g), F\_burst, F\_bg, and F\_total ( $\text{g m}^{-2} \text{ d}^{-1}$ ).

At mud pool n-LG (NIR1-NIR2), the event-based flux computation for CH<sub>4</sub> identified 4-7 events per acquisition, with event rates  $\lambda = 0.7 - 1.0 \text{ min}^{-1}$  and mean burst masses  $\bar{m}$  between 0.001 – 0.002 g. The corresponding burst fluxes were 6.2 and 4.1 g m<sup>-2</sup> d<sup>-1</sup>, while the background component ranged from 4.1 to 4.7 g m<sup>-2</sup> d<sup>-1</sup>, yielding total fluxes of 10.3 and 8.9 g m<sup>-2</sup> d<sup>-1</sup> for the two acquisitions, respectively (Table 6.4). MP LG's single record lists 4 events, with a rate of 0.7 min<sup>-1</sup> and  $\bar{m}$  of 0.05 g. The flux calculations yielded 164.7 g m<sup>-2</sup> d<sup>-1</sup> and 78.7 g m<sup>-2</sup> d<sup>-1</sup> for the burst sum and background, respectively, while the total flux is 243.4 g m<sup>-2</sup> d<sup>-1</sup>. At MP Fer (NIR8-NIR9), 3-6 events were detected per acquisition, with event rates  $\lambda$  between 0.8 and 1.6 min<sup>-1</sup> and mean burst masses of 0.17 – 0.94 g. The burst component (F<sub>burst</sub>) ranged from 1324.6 to 3491.7 g m<sup>-2</sup> d<sup>-1</sup> and the background component from 648.1 to 1121.9 g m<sup>-2</sup> d<sup>-1</sup>, giving total fluxes of 2446.5 and 4139 g m<sup>-2</sup> d<sup>-1</sup>. At MP F, repeated measurements resulted in an event rate of 1.2 – 6 per minute, with  $\bar{m}$  between 0.02 – 0.63 g. The computed fluxes cover 314.5 – 10115.3 g m<sup>-2</sup> d<sup>-1</sup> for the burst sum and -680.2 – 7586.6 g m<sup>-2</sup> d<sup>-1</sup> for background. The total flux ranges between -365.7 – 17701.9 g m<sup>-2</sup> d<sup>-1</sup>. The negative total flux occurs only for the NIR10 acquisition, where the background term resulted in a negative and higher magnitude.

At MP n-LG, the event-based fluxes computed for CO<sub>2</sub> (Table 6.5) are 7.9 g m<sup>-2</sup> d<sup>-1</sup> for the burst sum in both acquisitions. The background flux ranges from -3.9 to 0 g m<sup>-2</sup> d<sup>-1</sup>, with a total flux of 3.9 – 7.9 g m<sup>-2</sup> d<sup>-1</sup>. The event rate  $\lambda$  spans from 0.3 – 0.7 min<sup>-1</sup>, with a mean mass of 0.002 – 0.005 g. MP LG sole acquisition shows 3 events with rate  $\lambda$  of 0.7 min<sup>-1</sup> of 0.004 g mean burst mass, with a burst flux of 13.6 g m<sup>-2</sup> d<sup>-1</sup> and a background flux of 7.7 g m<sup>-2</sup> d<sup>-1</sup>, giving a total flux of 21.3 g m<sup>-2</sup> d<sup>-1</sup>. The MP Fer acquisitions report 2 to 6 events, with a rate  $\lambda$  of 0.5 – 1.6 min<sup>-1</sup>, with a  $\bar{m}$  between 0.003 and 0.03 g. The resulting burst fluxes span from 26.6 to 68 g m<sup>-2</sup> d<sup>-1</sup> with background values of 12.7 – 26.7 g m<sup>-2</sup> d<sup>-1</sup>, giving total fluxes of 53.3 – 80.8 g m<sup>-2</sup> d<sup>-1</sup>. Finally, at MP F, the repeated records yield 1 – 5 events, with a  $\lambda$  of 0.3 – 3.2 min<sup>-1</sup> and mean burst mass between 0.004 to 0.02 g. The corresponding burst fluxes range from 27.4 to 170.9 g m<sup>-2</sup> d<sup>-1</sup>, while background and total fluxes span from 0 to 156.8 g m<sup>-2</sup> d<sup>-1</sup> and from 32.2 to 327.7 g m<sup>-2</sup> d<sup>-1</sup>, respectively.



## 6.2 Discussion

### 6.2.1 Mud Pools Dynamics

At Mud Pool F, the STS probe recorded mud level, temperature, and EC within the upper ~2–3 m of the column from April 2023 to November 2024. The temperature and level display smooth oscillations that track the seasonal cycle of air temperature and precipitation, as expected for a sensor placed in the shallow part of the column, where atmospheric coupling is efficient and barometric forcing is negligible (Giambastiani et al., 2022). Against this slowly varying baseline, EC exhibits the most substantial departures from seasonality and thus the most diagnostic signal of changes in feeding and mixing with deeper fluids. The independent vertical profiles acquired with the same probe show that temperature increases uniformly with depth, and EC is lower and more variable in the upper metres but higher and more stable below, indicating a mixing-prone surface cap overlying a more saline, less buffered layer. This structure explains why EC at mud pool F can undergo large excursions when the relative contributions of shallow dilution and more profound brine shifts are considered.

A parallel record was acquired by researchers from INGV (branch of Milan) from the mud pool La Giunta using a CDT probe at a 1-minute acquisition frequency over the same time window from April 2023 to November 2024 (Fig. 6.6). The sensor was immersed at a fixed depth of ~9.5–10.5 m within the mud column. Four self-consistent measurement intervals (A–D) were defined, separated by occasional maintenance events that required repositioning of the sensor. The time series provides mud level, temperature, and electrical conductivity (EC) suitable for side-by-side comparison with mud pool F. Including this record enables a side-by-side assessment of synchronous versus site-specific behaviours across two distinct mud-pool structures within the same mud volcano system at Nirano, thereby strengthening the interpretation of common drivers and local modulators.

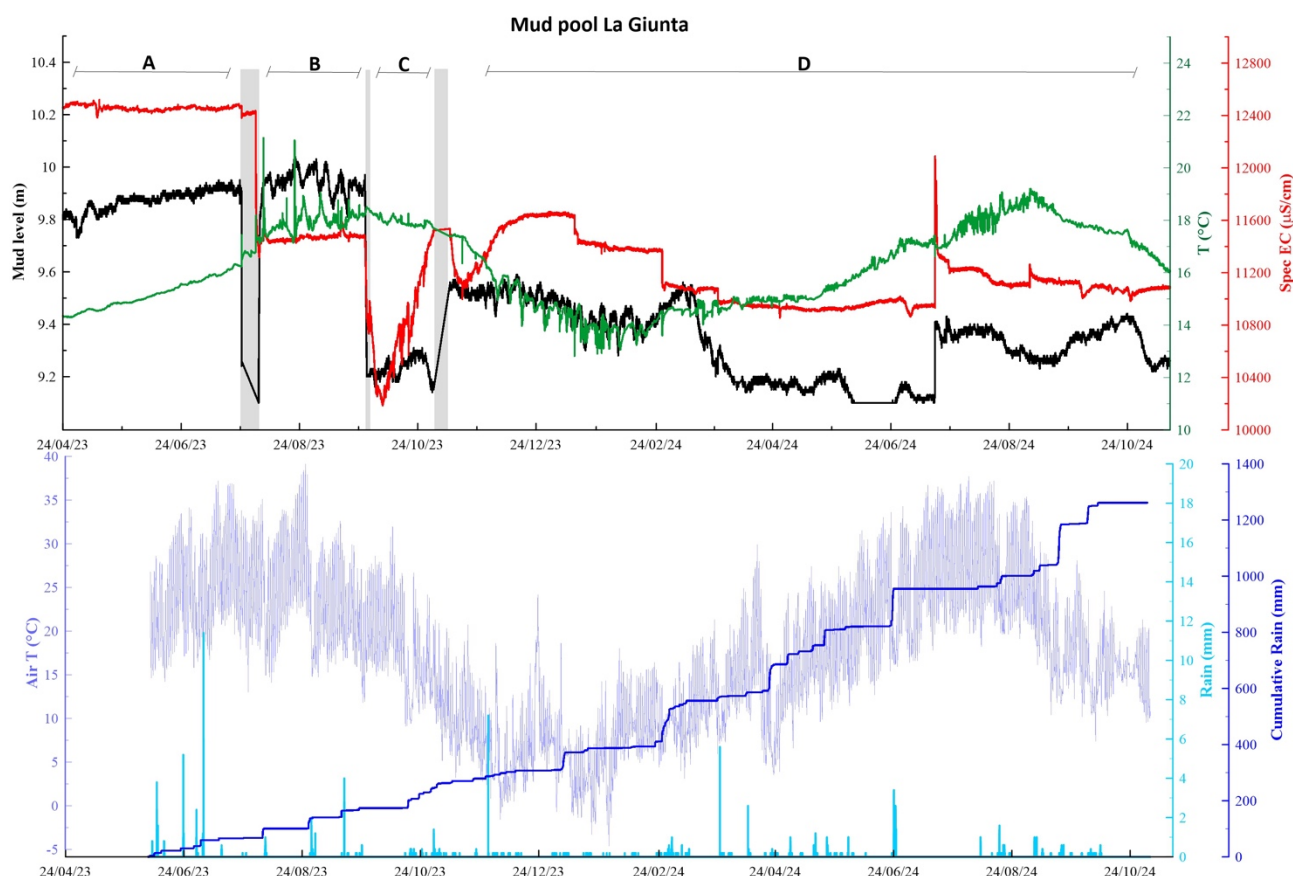


Figure 6.6. Time series for the La Giunta mud pool, including mud level, temperature and EC, with same comparing panel for meteorological parameters as Fig. 6.2. This figure and its data is explicitly credited to the INGV-Milano monitoring programme.

Because La Giunta’s mud column is substantially thicker than at mud pool F, thermal extrema occur later and with smaller amplitude consistent with greater volumetric buffering, with level changes remaining modest and step-like. Mud level at both sites shows modest changes, with intense rainfall inducing short-lived level drops attributed to near-surface dilution effects. Overall, thermal and level series provide a slowly varying baseline upon which EC variations are superimposed. EC emerges as the most diagnostic parameter for identifying changes in the feeding and mixing of the mud column. Three phases recur in both records during 2024: (i) a late February decrease; (ii) a stable, low variability phase from March to early July; and (iii) a mid to late July increase. While the timing is almost synchronous, the amplitude is strongly site dependent: mud pool F exhibits changes an order of magnitude larger than La Giunta, indicating a shared trigger modulated by local pathways, mixing efficiency with shallow meteoric inputs, and column geometry. The 2024 EC “crisis”, with a sequence of late-winter drop, spring plateau, and summer surge, is co-expressed at both mud pools but with contrasting magnitudes and buffering periods. At mud pool F, the late-February transition includes a transient spike followed by a dramatic EC drop and, after a quiescent plateau in spring, a high-

variability episode from late July through early autumn with extreme excursions up to  $13826 \mu\text{S cm}^{-1}$ . La Giunta shows the same phase pattern but with delayed, smaller shifts and more subdued variability. The coupled behaviour supports a field-wide fluid uprising in the feeding system, which reaches each structure through ascent paths of varying transmissivity and shallow mixing, with mud pool F acting as the more responsive and less buffered node. The different sampling cadences do not bias these interpretations, as minute-scale measurements at La Giunta resolve into transient EC spikes that are aliased in the hourly record at mud pool F. However, the three-phase structure and the magnitude contrast persist at daily aggregation, demonstrating that the key dynamics operate on multiple day to week time scales. Thus, cross-site synchrony in timing and site-specific differences in amplitude are robust features of the system. Integrating the comparative time series analysis with the structural and hydrogeologic framework proposed by Giambastiani et al. (2022) for Nirano refines the interpretation of the three-phase 2024 evolution observed at mud pools F and La Giunta. In the conceptual model of Giambastiani et al. (2022, Fig. 6.7), ascending fluids migrate along fault-related fractures and damage zones and then accumulate within small, shallow aquifers encased in the Argille Azzurre Formation (FAA) at roughly 5–30 m depth. When overpressure exceeds the tensile strength of the seal, fluids are released upward through fracture or pipe-like conduits to feed mud pools and gryphons. This shallow aquifer “buffer” transmits field-wide perturbations with almost synchronous timing, while local conduit geometry, transmissivity, and gas–liquid ratio modulate amplitude and volatility at each outlet, precisely the pattern expressed by the strong EC swings at mud pool F versus the muted response at La Giunta.

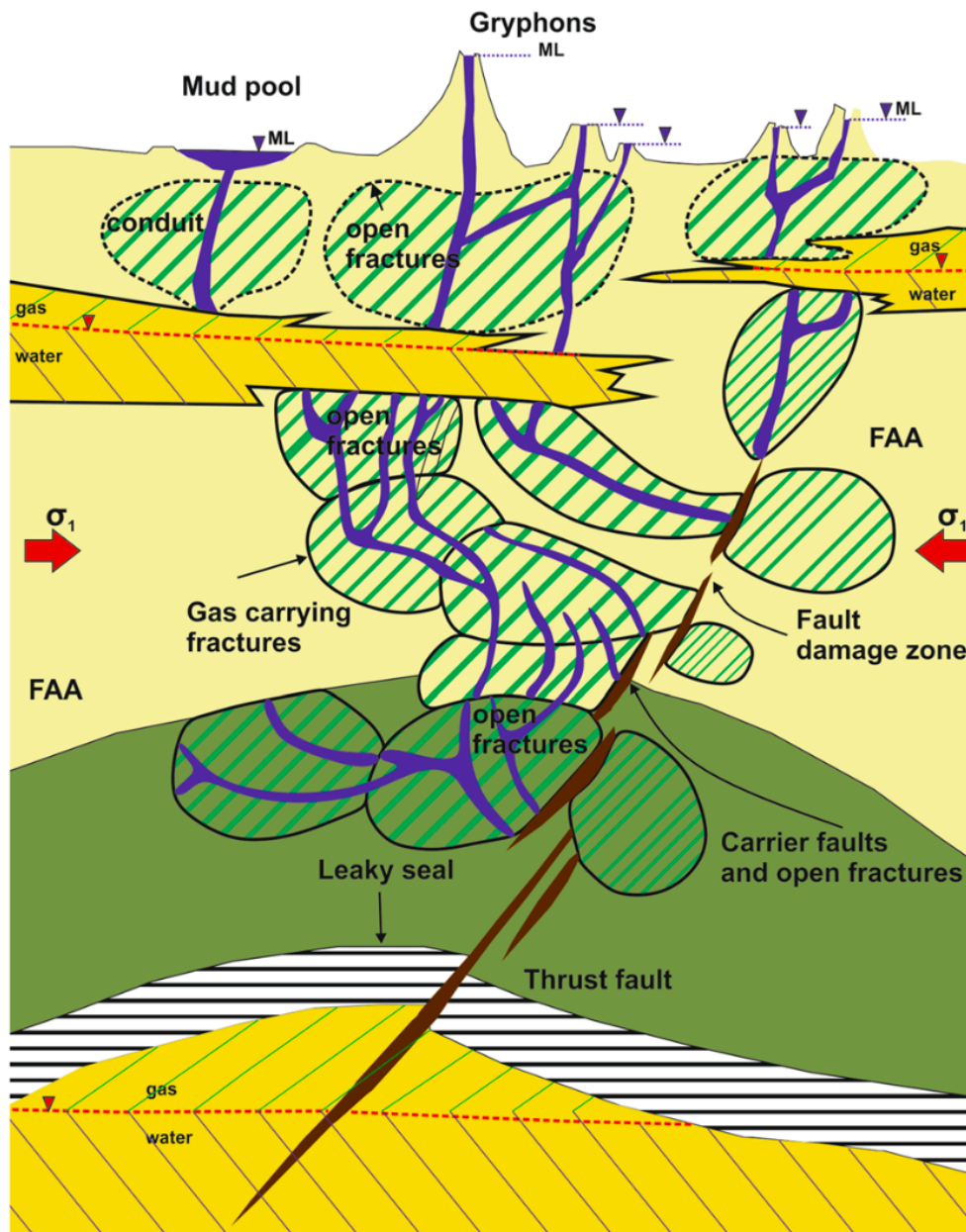


Figure 6.7. Conceptual model (not to scale) of fluid pathways at the Nirano mud volcano field (after Giambastiani et al., 2022). Near-surface conduits occur within ~0.5-5 m (locally up to 15 m). Shallow aquifers hosted in the FAA lie at ~5-30 m depth, whereas the deeper feeding system involves carrier faults and reservoirs within the Marnoso-Arenacea at ~1.5 km depth (Bonini, 2008).

The amplitude contrast between the two mud pools is consistent with different volumetric buffering and mixing efficiency along their shallow pathways. Where effective storage is small and pathways are highly transmissive, modest changes in shallow aquifer pressure or composition generate disproportionately large EC excursions at the surface, behaviour expressed by mud pool F. In contrast, a thicker, more capacious column damps the same perturbation, as it shows at mud pool La Giunta. This interpretation accords with the structural framework proposed for Nirano, in which variable,

transient conduits intermittently connect FAA-hosted shallow aquifers to surface vents. Mud level dynamics and eruption style depend on gas–liquid ratio and conduit geometry, naturally yielding common timing but site-specific amplitudes (Giambastiani et al., 2022). Mud pool F vertical profiles indicate a mixing-prone surface cap over a more saline, buffered layer sampling the shallow reservoir. Within this framework, the late-February EC drop marks a dilution or pressure reset in the shallow aquifer, the spring plateau reflects a steady storage–release, and the mid/late-summer surge records renewed supply and/or permeability changes along seal bypass corridors. The NW–SE vent alignment above a blind-thrust anticline focuses these pathways, while the weak barometric efficiency documented for Nirano supports a minor role for atmospheric forcing relative to internally driven pressure variations. Taken together, the time series, the vertical structure of mud pool F, and the Giambastiani et al. (2022) model converge on a single mechanism: field-wide perturbations of rising fluids are buffered in shallow aquifers and relayed upward through fracture controlled conduits, synchronising timing across mud pools, with mud pool F’s thin, easily entrained cap amplifying the response compared with the more buffered La Giunta column.

### 6.2.2 Mud Pool Gas Origin

According to Table 6.1, the mud pool La Giunta free-gas sample is CH<sub>4</sub>-dominated,  $\approx 94.1\%$ , with minor amounts of N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, and trace levels of C<sub>2</sub>H<sub>6</sub>, He, Ne, and H<sub>2</sub>. This pattern matches published datasets for Northern Apennine mud volcanoes, where CH<sub>4</sub> is the most abundant species and small but non-zero C<sub>2</sub><sup>+</sup> fractions persist even after migration and near-surface processes (Minissale et al., 2000; Etiope et al., 2007; Tassi et al., 2012a and b). In contrast, strictly microbial gases in the region are typically poor in C<sub>2</sub><sup>+</sup> at the vent; thus, the presence of C<sub>2</sub>H<sub>6</sub>, albeit at low abundance, suggests a thermogenic contribution to the emitted gas at La Giunta mud pool. The comparatively elevated O<sub>2</sub> in Table 6.1 is higher than expected for pristine seep gases and is best explained by air entrainment during sampling and/or interaction with air-saturated meteoric water, which dilutes hydrocarbon percentages without altering the genetic reading based on stable isotopes. The  $\delta^{13}\text{C-CH}_4$  value of  $-47\text{‰}$  plots within the thermogenic field characteristic of Apenninic gases. This composition is consistent with the established CH<sub>4</sub>-rich group from this region, for which  $\delta^{13}\text{C-CH}_4$  typically ranges between  $-39.6$  to  $-47.5 \text{‰}$  and the associated  $\delta^{13}\text{C-CO}_2$  exhibits a commonly positive signature, up to  $>+30\text{‰}$  (Mattavelli et al., 1983; Minissale et al., 2000; Etiope et al., 2007; Tassi et al., 2012a and 2012b). These intervals, widely documented for the Emilia Apennines, reflect thermogenic CH<sub>4</sub> generated at depth and a CO<sub>2</sub> component influenced by thermal degradation (decarbonation) and/or carbonate dissolution within sedimentary sequences (Minissale et al., 2000;

Tassi et al., 2012b). Altogether, and using only the analytes available in Table 6.1, the La Giunta free gas is most parsimoniously interpreted as thermogenic-dominated (or thermogenic-leaning mixed) CH<sub>4</sub> vented through fracture-controlled pathways typical of the Northern Apennines mud-volcano belt.

### 6.2.3 Mud Pool Gas Fluxes

The enhanced chamber measurements document a wide dynamic range of CH<sub>4</sub> fluxes across the investigated pools (Tables 6.3–6.5). The two calculation routes applied to the chamber data, end-to-end (E2E) conversion and the burst plus background (Burst+Bg) method, return broadly consistent magnitudes for CH<sub>4</sub> fluxes across sites, with a near-linear relationship when matched by acquisition (Fig. 6.8). The comparison indicates that E2E fluxes are systematically comparable to, or slightly lower than, Burst+Bg totals, whereas the relation between E2E and the burst only component exhibits larger scatter. This behaviour is expected in mud bubbling pools, as stepwise events dominate the mass balance, but small baseline drifts and plateaux contribute non negligibly to daily equivalent rates and are captured by E2E and by the “+Bg” term.

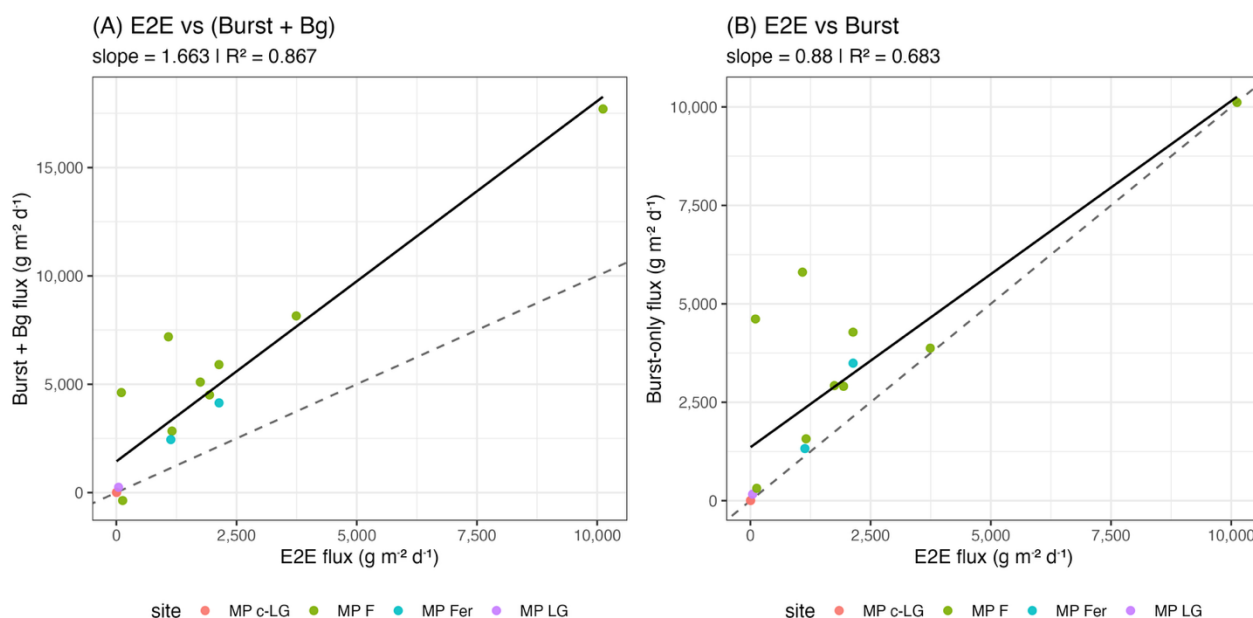


Figure 6.8. CH<sub>4</sub> flux estimates comparison: E2E vs Burst+Bg fluxes by acquisition (left) and E2E vs Burst-only flux).



To explain the negative background fluxes reported for both CO<sub>2</sub> and CH<sub>4</sub> in Tables 6.4 and 6.5, the diagnostic plots in Fig. 6.9 show how the chosen guard and inter-burst concentration drift shape the background fit. In these plots, the yellow bands mark the intervals excluded from the background fit (the  $\pm$ guard mask around each burst), red bands delimit the burst windows that are integrated, black points are the samples retained to estimate the background slope, and the green line is the linear background fit. The guard (here 6 s) is chosen to remove the influence of the burst's leading and trailing edges on the background estimate, so if the guard is too small, residual tails contaminate the fit. If the guard is too large, little signal remains, and the slope uncertainty increases. With this setting, the background slope is fitted on “quiescent” segments between burst windows within the selected duration  $\Delta t_s$ . Under strongly ebullitive conditions, the gas concentration commonly declines between bursts, due to minor headspace ventilation or entrainment, and turbulence is induced by bubbling, and/or dilution by exchange with fresher mud water (Giambastiani et al., 2022). In such cases, the green fit exhibits a negative slope (ppm s<sup>-1</sup>) and once converted to flux, this yields  $F_{bg} < 0$ . If the integrated burst mass over  $\Delta t_s$  is small relative to this negative background contribution, the total  $F_{tot} = F_{burst} + F_{bg}$  can become slightly negative (as illustrated for CH<sub>4</sub> at NIR10). This does not imply net uptake by the footprint; rather, it is a methodological artefact produced by signals composed of narrow peaks separated by downward drifting inter event segments. The windowed representation makes this behaviour explicit and, consequently, supports the use of E2E as the primary flux magnitude metric, while the burst calculation remains valuable to quantify event frequency ( $\lambda$ ) and mean mass per event, which describe emission dynamics.

CO<sub>2</sub> fluxes are consistently lower than those of CH<sub>4</sub>, as it is a minor constituent of the free gas (Table 6.1) and, unlike CH<sub>4</sub>, a substantial fraction remains retained in the mud–water phase. Owing to its higher solubility and acid–base buffering (CO<sub>2</sub>–HCO<sub>3</sub><sup>-</sup>–CO<sub>3</sub><sup>2-</sup>), less CO<sub>2</sub> is available to escape as free gas during short chamber deployments. Moreover, ebullition is typically CH<sub>4</sub>-dominated due to the lower density and greater buoyancy of CH<sub>4</sub>, which favours rapid ascent of bubbles, while CO<sub>2</sub> partitions preferentially into solution and is only partially co-transported (Mattavelli et al., 1983; Mattavelli and Novelli, 1988; Martinelli et al., 2012). As a result, the CO<sub>2</sub> concentration time series and event counts do not necessarily track those of CH<sub>4</sub> (Fig. 6.5). These processes may explain why CO<sub>2</sub> concentrations and event counts do not always mirror those of CH<sub>4</sub> and why CO<sub>2</sub> fluxes remain comparatively small at Nirano, though consistent with observations from Apenninic mud-volcano systems.

### Background Diagnostics and Burst Windows

Yellow: Mask excluded from the fit ( $\pm$ guard) | Red: Burst Windows | Black Dots/Green Line: Data/Background Fit

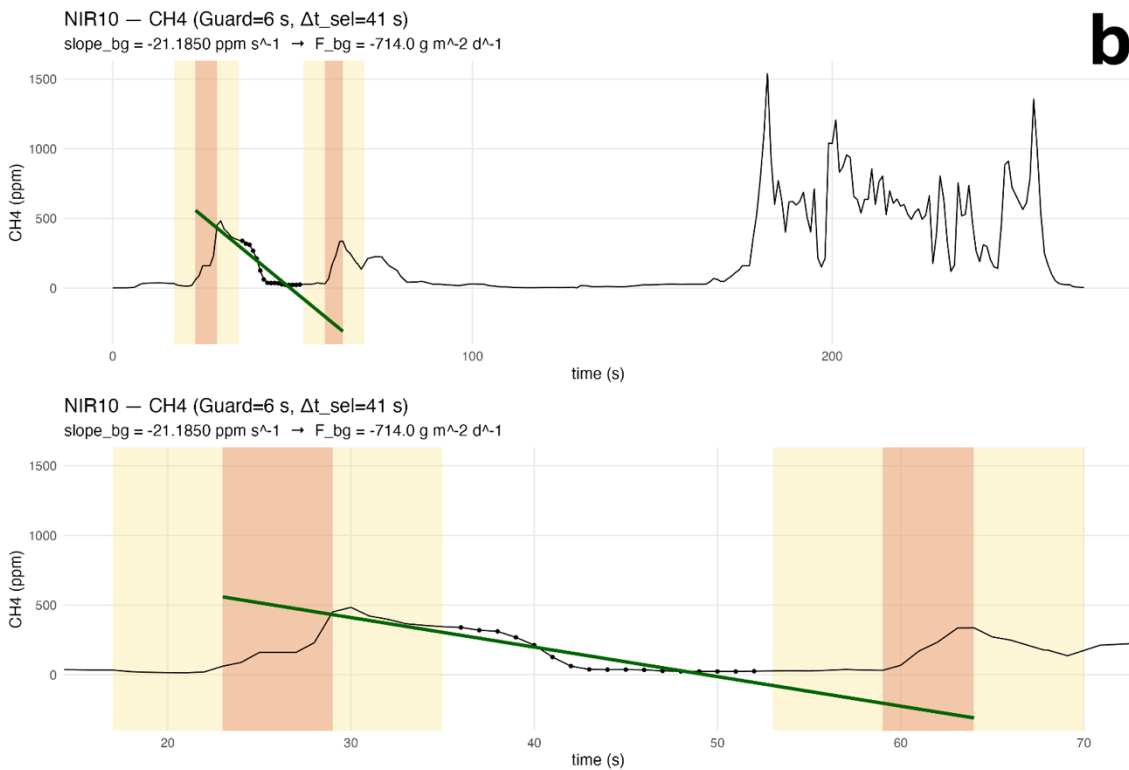
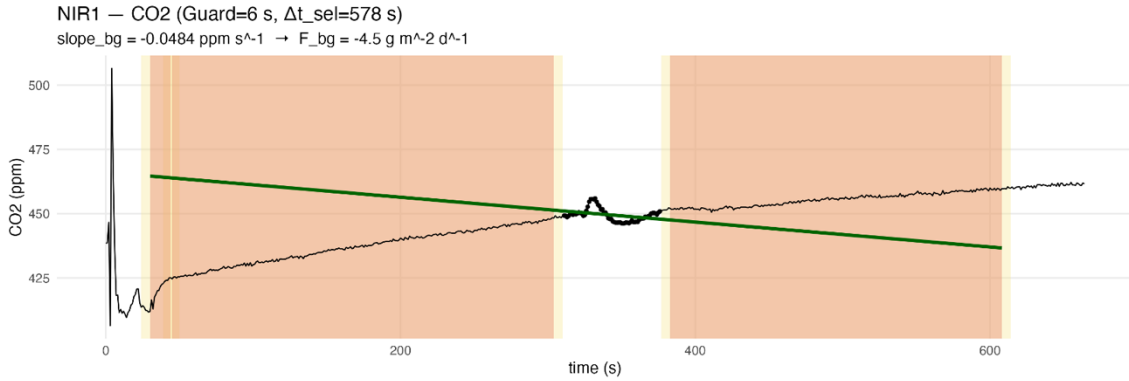


Figure 6.9. Background fit diagnostics for negative fluxes: acquisition NIR1 for CO<sub>2</sub> (upper panel) and acquisition NIR10 for CH<sub>4</sub> (lower panel).

Using E2E fluxes as the reference metric, the Nirano pools separate cleanly by magnitude in Fig. 6.10a, where MP F exhibits the highest CH<sub>4</sub> emissions, MP Fernando is intermediate, MP LG is substantially lower, and the non-bubbling pool adjacent to La Giunta is near the measurement floor. Fig. 6.10b demonstrates that these differences are not artifacts of sampling effort, as neither the number of replicates nor the cumulative acquisition time per site controls the site medians or spreads. When placed in context, the Nirano values align with published ranges for mud-volcano degassing in sedimentary settings. Field-scale “emission factors” reported for Italian seeps and mud volcanoes are typically  $\sim 10^2$ – $10^6 \text{ t km}^{-2} \text{ y}^{-1}$  (Etiope and Milkov, 2004), with areal outputs dominated by macro-

seeps near vents and pervasive microseepage on surrounding flanks. In this study, chamber measurements at bubbling mud pools purposefully target the most focused discharge zones and therefore yield small-footprint areal fluxes that can approach or exceed the upper envelope of field-averaged factors, consistent with near-vent ebullition rather than diffuse leakage (Etiope et al., 2007).

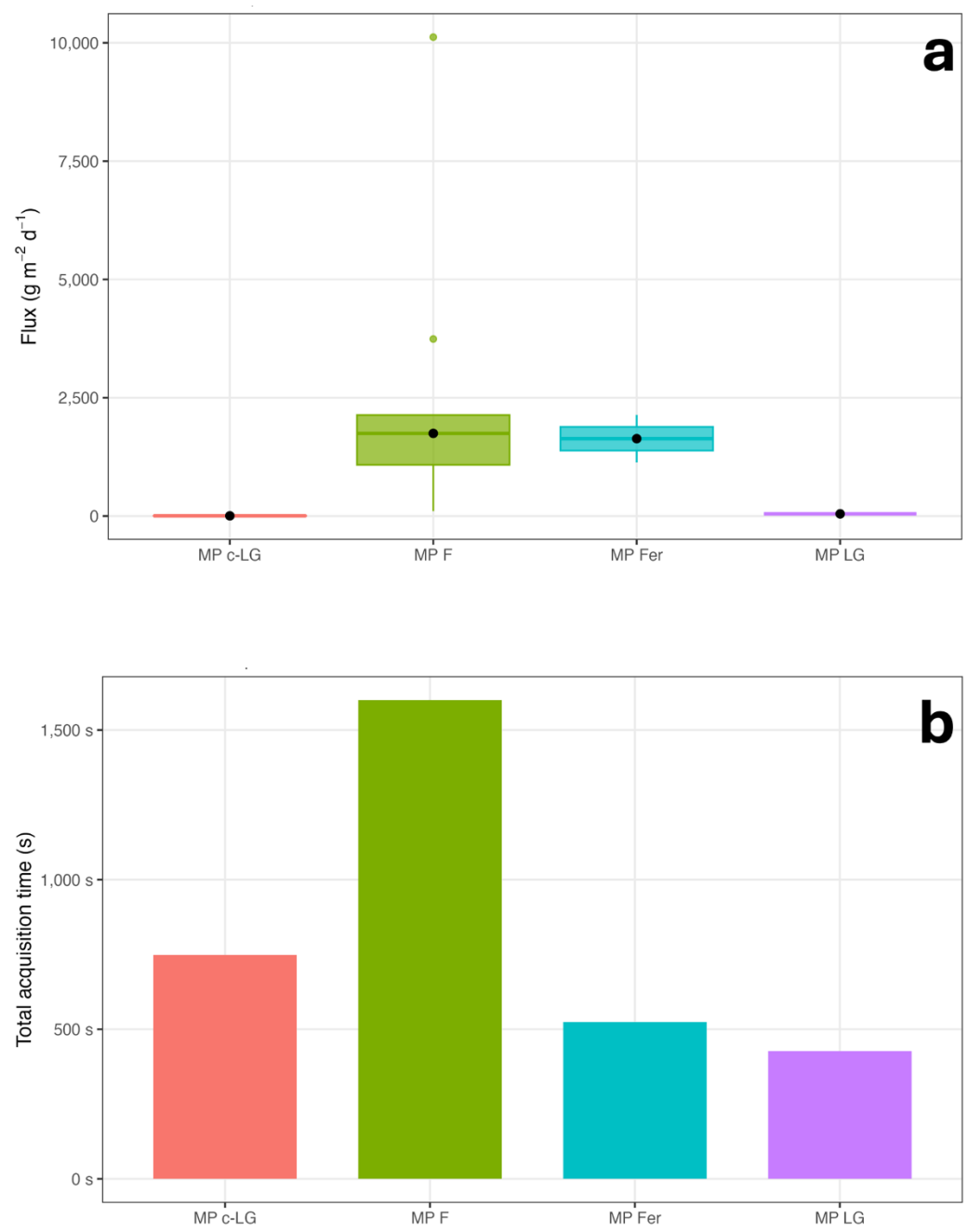


Figure 6.10. Box plot of CH<sub>4</sub> fluxes by site (with medians and spread, panel a); acquisition duration by site (panel b).

The comparatively low values at mud pool La Giunta and the near-zero flux at the non-bubbling pool fall within the microseepage domain documented in Italy and elsewhere (order  $10^2$ – $10^5$  mg m<sup>-2</sup> d<sup>-1</sup>), whereas the highest values at mud pool F reflect direct ebullitive discharge during burst-rich intervals, a behaviour repeatedly observed at active mud-volcano fields (Etiope et al., 2007). These patterns are consistent with Italian measurements that distinguish vent outputs (from individual vents and bubbling pools) from diffuse soil flux in Sicily, where quiescent single-vent emissions range from ~0.01 to 6.8 kg d<sup>-1</sup> and surrounding soil fluxes from ~ $10^2$  to  $10^4$  mg m<sup>-2</sup> d<sup>-1</sup>, and with areal totals on the order of hundreds of tonnes per year over kilometre scale fields (Etiope et al., 2002). Comparable orders of magnitude have been reported in eastern Romania, where vents reach up to ~28 t y<sup>-1</sup> and diffuse fluxes span ~ $10^2$ – $10^5$  mg m<sup>-2</sup> d<sup>-1</sup> with area-integrated outputs of ~ $10^3$  t y<sup>-1</sup>, and in Azerbaijan, where quiescent vents range from <1 to hundreds of t y<sup>-1</sup> and specific areal emissions are ~ $10^2$ – $10^3$  t km<sup>-2</sup> y<sup>-1</sup> (Etiope and Milkov, 2004; Etiope et al., 2004). At the global scale, synthesised onshore and shallow-water estimates indicate mud volcanoes contribute at least ~6–9 Mt y<sup>-1</sup> of methane to the atmosphere, underscoring that the Nirano magnitudes are characteristic of focused near vent degassing within the broader seepage spectrum (Hong et al., 2013). Taken together, the Nirano ranking and variance structure in Fig. 6.10 are best explained by differences in conduit transmissivity and near-surface buffering/mixing, while the literature comparison confirms that the observed magnitudes are consistent with mud-volcano emissions documented in Italy and other hydrocarbon-prone basins.

## Chapter VII – Concluding Remarks

This thesis investigated methane-rich Unusual Geological Phenomena (UGP) at three sites in Emilia-Romagna: Santa Maria Nuova, Renazzo, and Nirano, within a broadly shared sedimentary framework. All three areas belong to the Po Plain and its Apennine margin and are underlain by similar successions of fine-grained marine to continental deposits. What differentiates them is not the regional stratigraphy, but the local structural configuration, the thickness and architecture of the shallow sedimentary cover, and the way these factors control fluid pathways and pressure conditions. Against this common geological background, the sites express markedly different gas seepage styles, ranging from diffuse soil microseepage to structurally focused bubbling wells and burst-dominated mud pools. Taken together, the three case studies indicate that a flexible but conceptually unified approach can be applied to characterise UGP dynamics across diverse manifestations.

At Santa Maria Nuova, CH<sub>4</sub> migration is expressed as diffuse soil degassing across an agricultural and residential area, where matrix permeability, microbial activity, and shallow aquifer processes interact to shape the spatial and temporal patterns of degassing. Accumulation-chamber measurements captured microseepage fluxes that fall within the upper range of values reported for natural seepage fields, while continuous monitoring of groundwater level, temperature, and electrical conductivity showed seasonally modulated responses consistent with recharge and shallow circulation. Within this context, the supersaturated well that originally drew attention to the site acts primarily as an interceptor of rising gas rather than a deep-rooted conduit. Isotopic data and interstitial soil-gas profiles converge to indicate dominantly biogenic CH<sub>4</sub> subjected to bacterial oxidation at this site. The combination of diffuse flux and thermal mapping, multiparametric time series, and vegetation-index anomalies highlights a system in which microbial generation and consumption of methane, modulated by hydrological conditions, control the emergence and evolution of the phenomenon at the surface.

Renazzo, by contrast, exemplifies a structurally focused configuration in which CH<sub>4</sub>-charged fluids from shallow horizons are funnelled into an abandoned water well. The result is a persistently bubbling water column feeding a cold, continuous degassing system that, during the monitoring period, displayed consistently stable bubbling intensity under a range of hydrological and micrometeorological conditions. The hydrogeological record depicts a shallow aquifer that responds to recharge and seasonal heat exchange, without independent signatures of ascending warm, saline fluids. Within this hydrogeological framework, the well behaves as a highly efficient collector and emitter of gas accumulated in the surrounding sediments. Quantification of the CH<sub>4</sub> flux required

dedicated measurement strategies, because applying the diffusive flux formulation (based on a quasi-linear increase of headspace concentration under diffusion-controlled conditions) is not appropriate for a metre-scale, water-filled aperture dominated by turbulent, channelled ebullition. Two complementary configurations were therefore developed: an open-aperture setup (M1) combining high-frequency CH<sub>4</sub> measurements with a 3-D sonic anemometer to reconstruct concentration–velocity fields over the wellhead, and a reduced-aperture setup (M2) constraining the outlet cross-section and coupling pointwise concentration with hot-wire velocity. M1 relies on the assumption that the native plume geometry above the wellhead can be sampled with minimal perturbation, whereas M2 assumes that the imposed constriction, while altering the flux pattern, produces a more tractable jet suitable for co-located measurements. Despite these different premises, both configurations converged on the same order of magnitude for the methane flux, in the range of a few to about 10 kg d<sup>-1</sup>, well above typical values for many abandoned wells and comparable to structurally focused natural seeps. This convergence supports the emission estimates and illustrates how a careful treatment of geometry and plume heterogeneity can yield robust results even under challenging conditions. The Renazzo site also provided the development and testbed for a calibrated low-cost monitoring network. A set of Arduino-based stations equipped with MOS CH<sub>4</sub> sensors, CO<sub>2</sub> sensors, and meteorological probes was deployed radially around the well, and an artificial neural network (ANN) calibration strategy was implemented to reproduce the strongly non-linear response of the MOS sensors across the observed concentration range, combining the abundant near-background conditions recorded during ambient co-locations with smaller subsets of intermediate and high values obtained in controlled chamber experiments. The ANN approach was explicitly designed to overcome the limitations previously encountered with Random Forest calibration at high concentrations and was able to provide stable, physically plausible CH<sub>4</sub> estimates across varying environmental conditions. These results indicate that low-cost, ANN-calibrated sensor networks can be used to characterise CH<sub>4</sub> dispersion around focused emission sources at temporal and spatial resolutions that would be impractical with laboratory-grade analysers alone. Such networks are inherently scalable and cost-effective, making them practical tools for routine surveillance around wells, landfills, industrial facilities, or natural seepage sites embedded in inhabited or agricultural landscapes.

At Nirano, seepage is hosted within a mud-volcano field developed in the Argille Azzurre Formation along the Pede-Apennine margin. Here, CH<sub>4</sub>-dominated fluids reach the surface through conduits feeding gryphons and mud pools aligned along structural trends. The focus of this work was a set of mud pools, including Mud Pool F, where degassing is governed by episodic ebullition rather than continuous diffusion. This degassing style poses a challenge to the standard linear-flux interpretation of chamber data, which assumes smooth, monotonic concentration increases in a porous soil matrix



dominated by diffusive transport. In water- and brine-rich muds, gas can be retained in dissolved form until local saturation is exceeded, after which it escapes as bubbles, producing step-like concentration jumps in the headspace. To address this, a floating extension was designed to support the accumulation chamber on the mud–water interface and enlarge the headspace, and an event-based analytical workflow was implemented. Time series of CH<sub>4</sub> and CO<sub>2</sub> measured within the modified chamber were decomposed into discrete bubble events and a slowly varying background. For each acquisition, burst frequency and mean mass per burst were estimated, and the corresponding contributions to total flux were quantified. The results show that the burst component accounts for most of the variability in CH<sub>4</sub> release, and that different pools exhibit synchronous changes consistent with a common shallow driver, upon which local conduit efficiency is superimposed. By explicitly separating burst-driven and background degassing, this approach provides a more physically meaningful description of mud-pool emissions and offers a framework that can be exported to other systems dominated by ebullition, such as lakes, reservoirs, or additional mud-volcano fields.

Collectively, the three case studies contribute to a more nuanced understanding of CH<sub>4</sub>-rich UGP in the Po Plain. Rather than being isolated phenomena, these manifestations are expressions of a wider, regionally coherent system in which CH<sub>4</sub> is generated, stored, and released along structural and stratigraphic discontinuities, and then modified by shallow processes. Within this framework, the integration of high-frequency monitoring with geochemical indicators revealed dynamics that would remain invisible under traditional, low-resolution approaches. Short-lived degassing bursts, abrupt changes in plume structure, and seasonally modulated anomalies in temperature and vegetation status emerge clearly only when time-resolved gas measurements, hydrogeological records, and independent proxies such as remote-sensing indices are analysed together. This multi-parameter perspective goes beyond many earlier studies of CH<sub>4</sub> seepage in foredeep settings, which typically relied on punctual flux surveys or limited sets of tracers, and illustrates the additional explanatory power gained by combining diverse datasets under a coherent interpretative scheme.

A recurring element emerging from the three sites is the importance of coupling concentration and flux measurements with hydrogeological and geochemical information in order to distinguish background variability from true anomalies and to link surface manifestations to subsurface processes. Dissolved-gas chemistry, soil gases, aquifer parameters, temperature time series and continuous gas records, when interpreted jointly, allow the origin, pathways, and near-surface transformation of methane to be constrained more robustly than through any single dataset. This is particularly relevant in a basin such as the Po Plain, where shallow biogenic production, inherited thermogenic components and microbial oxidation can all influence CH<sub>4</sub> signatures within a relatively

narrow depth range, and where natural seepage and human activities co-exist within the same agricultural and industrial landscape.

The case studies further clarify how measurement strategies must be adapted to the seepage regime, and how much of their success depends on the physical assumptions used to interpret the data. Accumulation chambers work reliably in diffuse soil-gas fields such as Santa Maria Nuova, where fluxes are relatively steady over the duration of a measurement and the soil surface provides a well-defined interface. In advective or ebullitive systems like Renazzo and Nirano, the same linear diffusive formulation becomes inadequate and motivated the development of open- and reduced-aperture plume-mapping configurations and of a floating-chamber, event-based workflow. Comparison of these approaches shows that floating chambers with extended headspace are well suited to quantifying bubble-driven fluxes but say little about three-dimensional plume geometry, that sonic-anemometer mapping captures the native heterogeneity above large apertures but requires unobstructed access to the plume, that hot-wire measurements in constrained geometries yield accurate velocities at the expense of a non-native flow field, and that low-cost sensor networks and multiparametric probes provide dense spatio-temporal coverage and hydrogeological context but depend on robust calibration and cannot alone resolve fluid origin. Used in combination, these complementary tools offer a more complete and resilient picture of UGP behaviour than any single method applied in isolation.

Beyond the methodological comparison, the results underline the practical usefulness of these approaches and point to possible developments and applications in densely used territories. In rural and peri-urban contexts like Santa Maria Nuova and Renazzo, where houses, roads and cultivated fields are in direct proximity to methane-emitting structures, the ability to quantify emissions and track their variability provides an evidence base for risk assessment, infrastructure safety and land-use planning, turning “bubbling” wells or diffuse seepage into measurable source terms that can enter local and regional inventories. The coupling of microseepage and groundwater observations with vegetation indices at Santa Maria Nuova suggests that remote-sensing indicators of plant stress, interpreted together with ground-based flux and gas data, could support low-cost surveillance of agricultural land and the early detection of CH<sub>4</sub>-related anomalies similar to those documented at Santa Maria Nuova and Medolla, while at Renazzo the ANN-calibrated low-cost network shows how similar systems could be deployed around wells, landfills or industrial facilities to detect emerging CH<sub>4</sub> anomalies at scales and costs unattainable with laboratory-grade instruments alone. In protected settings such as the Nirano mud-volcano field, improved quantification of mud-pool emissions and their temporal variability can inform geosite management, visitor safety and the refinement of regional methane budgets, and the same event-based approach could be extended to lakes, reservoirs

and other ebullition-dominated environments. Looking ahead, a more systematic treatment of uncertainties for wellhead and mud-pool fluxes, targeted modifications to instrumental setups (for example optimising chamber geometries, combining sonic and hot-wire anemometry, or integrating additional environmental sensors into low-cost networks), and the integration of periodic isotopic sampling and thermal or vegetation-index imaging with continuous concentration time series would all help to improve comparability between sites and to scale these methods from site-specific studies to basin-wide assessments. These developments would increase the value of UGP monitoring for environmental agencies, local authorities and industrial operators responsible for managing methane emissions in complex rural, industrial and inhabited landscapes.

Although Santa Maria Nuova, Renazzo and Nirano differ in local structure, seepage geometry and near-surface dynamics, the results indicate that they can be investigated within a unified conceptual and methodological framework. By adapting measurement strategies to the specific characteristics of each system and by combining high-resolution monitoring with geochemical interpretation and advanced data processing, the study provides operational tools that are transferable to other seepage contexts, while at the same time refining our understanding of how CH<sub>4</sub>-rich UGP are generated, channelled and expressed at the surface in this sector of the Po Plain. In turn, these tools offer a practical basis for interpreting and managing CH<sub>4</sub> emissions in landscapes where the subsurface and human activities are tightly intertwined.

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## Web sources

WebGIS platform - Emilia Romagna Region

<https://servizimoka.regione.emilia-romagna.it/mokaApp/apps/sfgp/index.html>

Italian Earthquake Database - INGV

[https://emidius.mi.ingv.it/CPTI15-DBMI15/query\\_eq/](https://emidius.mi.ingv.it/CPTI15-DBMI15/query_eq/)

Seismotectonic Map of Emilia - Romagna

[https://mappegis.regione.emiliaromagna.it/gstatico/documenti/sismotett\\_2016/Carta\\_Sismotettonica.pdf](https://mappegis.regione.emiliaromagna.it/gstatico/documenti/sismotett_2016/Carta_Sismotettonica.pdf)

Real-Time Weather Data - Underground

<https://www.wunderground.com/dashboard/pws/IEMILIAR241>

<https://www.wunderground.com/weather/it/cento/ICENTO24>

ViDEPI – Valorisation of Italian Deep Exploration Data

<https://www.videpi.com/videpi/cessati/pdf.asp>

# Appendix

Appendix A.1. Santa Maria Nuova soil flux campaign data from May 2022.

| Point | Long     | Lat      | $\Phi\text{CO}_2$ | $\text{CO}_2 \text{ R}^2$ | $\Phi\text{CH}_4$ | $\text{CH}_4 \text{ R}^2$ |
|-------|----------|----------|-------------------|---------------------------|-------------------|---------------------------|
| 1     | 12.18541 | 44.20330 | 39.07             | 0.998                     | 0.00              | 0                         |
| 2     | 12.18549 | 44.20310 | 37.25             | 0.996                     | 0.00              | 0                         |
| 3     | 12.18531 | 44.20318 | 29.10             | 0.998                     | 0.00              | 0                         |
| 4     | 12.18510 | 44.20325 | 31.53             | 0.999                     | 0.00              | 0                         |
| 5     | 12.18516 | 44.20339 | 51.98             | 0.999                     | 0.00              | 0                         |
| 6     | 12.18548 | 44.20326 | 2.96              | 0.956                     | 197.45            | 0.78                      |
| 7     | 12.18548 | 44.20328 | 51.10             | 0.566                     | 551.78            | 0.582                     |
| 8     | 12.18530 | 44.20355 | 42.65             | 0.998                     | 0.00              | 0                         |
| 9     | 12.18539 | 44.20368 | 45.42             | 0.998                     | 0.00              | 0                         |
| 10    | 12.18551 | 44.20355 | 49.91             | 0.998                     | 0.00              | 0                         |
| 11    | 12.18538 | 44.20395 | 20.84             | 0.996                     | 8.44              | 0.997                     |
| 12    | 12.18528 | 44.20388 | 88.81             | 0.999                     | 43.42             | 0.997                     |
| 13    | 12.18525 | 44.20378 | 34.28             | 0.998                     | 0.00              | 0                         |
| 14    | 12.18476 | 44.20349 | 124.99            | 0.999                     | 455.54            | 0.999                     |
| 15    | 12.18475 | 44.20343 | 103.95            | 0.997                     | 0.56              | 0.957                     |
| 16    | 12.18469 | 44.20350 | 36.20             | 0.998                     | 0.62              | 0.992                     |
| 17    | 12.18513 | 44.20373 | 13.28             | 0.998                     | 0.00              | 0                         |
| 18    | 12.18533 | 44.20296 | 103.60            | 0.999                     | 0.00              | 0                         |
| 19    | 12.18518 | 44.20302 | 42.65             | 0.997                     | 0.00              | 0                         |
| 20    | 12.18494 | 44.20321 | 21.55             | 0.864                     | 0.00              | 0                         |
| 21    | 12.18471 | 44.20298 | 258.12            | 0.998                     | 665.34            | 0.999                     |
| 22    | 12.18437 | 44.20273 | 198.84            | 0.998                     | 0.00              | 0                         |
| 23    | 12.18410 | 44.20260 | 41.77             | 0.894                     | 41.83             | 0.92                      |
| 24    | 12.18477 | 44.20212 | 1.92              | 0.957                     | 0.00              | 0                         |
| 25    | 12.18475 | 44.20257 | 62.41             | 0.999                     | 0.00              | 0                         |
| 26    | 12.18484 | 44.20412 | 35.56             | 0.993                     | 0.00              | 0                         |
| 27    | 12.18453 | 44.20380 | 133.61            | 0.999                     | 239.00            | 0.997                     |
| 28    | 12.18449 | 44.20365 | 20.33             | 0.996                     | 0.00              | 0                         |
| 29    | 12.18427 | 44.20394 | 23.45             | 0.999                     | 12.32             | 0.999                     |
| 30    | 12.18441 | 44.20389 | 30.29             | 0.993                     | 0.00              | 0                         |
| 31    | 12.18394 | 44.20375 | 27.01             | 0.994                     | 2.43              | 0.992                     |
| 32    | 12.18379 | 44.20355 | 62.85             | 0.996                     | 52.19             | 0.994                     |
| 33    | 12.18356 | 44.20326 | 96.69             | 0.999                     | 344.54            | 0.998                     |
| 34    | 12.18500 | 44.20325 | 449.34            | 0.99                      | 59.16             | 0.993                     |
| 35    | 12.18530 | 44.20366 | 34.25             | 0.997                     | 0.01              | 0.053                     |
| 36    | 12.18423 | 44.20403 | 79.44             | 0.996                     | 0.00              | 0                         |
| 37    | 12.18363 | 44.20324 | 31.49             | 0.994                     | 0.11              | 0.954                     |
| 38    | 12.18362 | 44.20323 | 63.20             | 0.974                     | 0.10              | 0.95                      |
| 39    | 12.18361 | 44.20321 | 181.28            | 0.997                     | 71.91             | 0.998                     |
| 40    | 12.18361 | 44.20321 | 169.70            | 0.998                     | 6.49              | 0.999                     |
| 41    | 12.18360 | 44.20319 | 89.69             | 0.984                     | 0.83              | 0.995                     |
| 42    | 12.18360 | 44.20318 | 237.74            | 0.997                     | 187.35            | 0.999                     |
| 43    | 12.18359 | 44.20317 | 139.16            | 0.998                     | 0.17              | 0.97                      |
| 44    | 12.18357 | 44.20317 | 46.52             | 0.997                     | 0.19              | 0.966                     |
| 45    | 12.18355 | 44.20316 | 625.38            | 0.993                     | 98.00             | 0.996                     |
| 46    | 12.18357 | 44.20316 | 113.85            | 0.996                     | 0.06              | 0.765                     |
| 47    | 12.18356 | 44.20320 | 38.71             | 0.988                     | 0.06              | 0.84                      |
| 48    | 12.18359 | 44.20322 | 143.30            | 0.998                     | 38.00             | 0.995                     |
| 49    | 12.18360 | 44.20322 | 50.00             | 0.998                     | 0.22              | 0.988                     |
| 50    | 12.18361 | 44.20323 | 75.70             | 0.997                     | 2.50              | 0.998                     |

|     |          |          |        |       |         |       |
|-----|----------|----------|--------|-------|---------|-------|
| 51  | 12.18363 | 44.20320 | 233.25 | 0.999 | 311.18  | 0.999 |
| 52  | 12.18363 | 44.20321 | 28.20  | 0.994 | 0.39    | 0.944 |
| 53  | 12.18362 | 44.20321 | 290.95 | 0.997 | 106.22  | 0.998 |
| 54  | 12.18365 | 44.20320 | 17.60  | 0.967 | 1.07    | 0.42  |
| 55  | 12.18411 | 44.20254 | 95.77  | 0.981 | 114.16  | 0.987 |
| 56  | 12.18402 | 44.20265 | 135.59 | 0.993 | 85.75   | 0.995 |
| 57  | 12.18392 | 44.20267 | 89.96  | 0.998 | 12.38   | 0.993 |
| 58  | 12.18384 | 44.20269 | 78.38  | 0.998 | 34.29   | 0.997 |
| 59  | 12.18381 | 44.20269 | 96.29  | 0.996 | 0.27    | 0.889 |
| 60  | 12.18378 | 44.20278 | 216.84 | 0.997 | 24.69   | 0.994 |
| 61  | 12.18375 | 44.20280 | 372.37 | 0.997 | 109.14  | 0.998 |
| 62  | 12.18376 | 44.20278 | 46.91  | 0.996 | 0.54    | 0.878 |
| 63  | 12.18381 | 44.20286 | 454.18 | 0.997 | 299.31  | 0.997 |
| 64  | 12.18378 | 44.20291 | 118.39 | 0.999 | 5.06    | 0.999 |
| 65  | 12.18378 | 44.20292 | 155.84 | 0.997 | 0.33    | 0.965 |
| 66  | 12.18383 | 44.20297 | 534.72 | 0.998 | 217.98  | 0.992 |
| 67  | 12.18390 | 44.20294 | 170.19 | 0.998 | 34.12   | 0.992 |
| 68  | 12.18392 | 44.20294 | 261.16 | 0.999 | 510.55  | 0.998 |
| 69  | 12.18396 | 44.20293 | 186.69 | 0.997 | 239.64  | 0.993 |
| 70  | 12.18386 | 44.20288 | 350.45 | 0.997 | 36.83   | 0.998 |
| 71  | 12.18397 | 44.20276 | 48.23  | 0.999 | 12.49   | 0.998 |
| 72  | 12.18399 | 44.20286 | 54.88  | 0.999 | 0.00    | 0     |
| 73  | 12.18406 | 44.20291 | 327.13 | 0.998 | 38.70   | 0.997 |
| 74  | 12.18412 | 44.20300 | 189.07 | 0.998 | 345.82  | 0.999 |
| 75  | 12.18410 | 44.20303 | 81.07  | 0.991 | 0.00    | 0     |
| 76  | 12.18401 | 44.20305 | 244.70 | 0.999 | 63.20   | 0.999 |
| 77  | 12.18389 | 44.20308 | 238.67 | 0.998 | 12.08   | 0.996 |
| 78  | 12.18383 | 44.20308 | 192.59 | 0.999 | 0.00    | 0     |
| 79  | 12.18395 | 44.20312 | 67.95  | 0.996 | 3.60    | 0.997 |
| 80  | 12.18399 | 44.20317 | 42.67  | 0.995 | 0.00    | 0     |
| 81  | 12.18404 | 44.20317 | 95.85  | 0.996 | 0.01    | 0.105 |
| 82  | 12.18413 | 44.20318 | 78.03  | 0.999 | 2.02    | 0.999 |
| 83  | 12.18413 | 44.20328 | 106.86 | 0.999 | 0.07    | 0.395 |
| 84  | 12.18414 | 44.20335 | 170.01 | 0.995 | 9.12    | 0.999 |
| 85  | 12.18422 | 44.20337 | 78.69  | 0.998 | 8.80    | 0.998 |
| 86  | 12.18418 | 44.20341 | 325.59 | 0.998 | 163.45  | 0.999 |
| 87  | 12.18425 | 44.20343 | 21.23  | 0.997 | 0.00    | 0     |
| 88  | 12.18411 | 44.20347 | 127.36 | 0.996 | 149.56  | 0.998 |
| 89  | 12.18401 | 44.20343 | 314.89 | 0.983 | 544.24  | 0.99  |
| 90  | 12.18407 | 44.20350 | 260.28 | 0.993 | 1124.40 | 0.992 |
| 91  | 12.18413 | 44.20357 | 20.64  | 0.992 | 0.14    | 0.958 |
| 92  | 12.18402 | 44.20336 | 26.01  | 0.998 | 0.09    | 0.905 |
| 93  | 12.18386 | 44.20303 | 198.49 | 0.999 | 151.40  | 0.999 |
| 94  | 12.18395 | 44.20302 | 190.12 | 0.998 | 426.82  | 0.995 |
| 95  | 12.18406 | 44.20300 | 418.05 | 0.998 | 747.62  | 0.996 |
| 96  | 12.18388 | 44.20281 | 540.00 | 0.999 | 134.37  | 0.998 |
| 97  | 12.18474 | 44.20262 | 42.81  | 0.996 | 0.00    | 0     |
| 98  | 12.18480 | 44.20269 | 62.41  | 0.997 | 0.00    | 0     |
| 99  | 12.18486 | 44.20282 | 120.41 | 0.999 | 162.16  | 0.998 |
| 100 | 12.18484 | 44.20286 | 302.83 | 0.994 | 42.46   | 0.993 |
| 101 | 12.18519 | 44.20320 | 38.13  | 0.998 | 0.00    | 0     |

Appendix A.2. Santa Maria Nuova soil flux campaign data from September 2022.

| Point | Long     | Lat      | $\Phi\text{CO}_2$ | $\text{CO}_2 \text{ R}^2$ | $\Phi\text{CH}_4$ | $\text{CH}_4 \text{ R}^2$ | note | Soil Temp |
|-------|----------|----------|-------------------|---------------------------|-------------------|---------------------------|------|-----------|
| 1     | 12.18395 | 44.20289 | 432.52            | 0.999                     | 196.65            | 0.999                     | none |           |
| 2     | 12.18393 | 44.20265 | 110.22            | 1.000                     | 0.15              | 0.962                     | none |           |
| 3     | 12.18405 | 44.20277 | 202.58            | 0.999                     | 0.04              | 0.43                      | 17   |           |
| 4     | 12.18413 | 44.20287 | 132.57            | 0.997                     | 0.00              | 0.002                     | 16   |           |
| 5     | 12.18420 | 44.20299 | 9.86              | 0.995                     | 0.00              | 0                         | 14   |           |
| 6     | 12.18427 | 44.20312 | 10.44             | 0.988                     | 0.00              | 0                         | 13.4 |           |
| 7     | 12.18436 | 44.20325 | 10.21             | 0.985                     | 0.00              | 0                         | 13.6 |           |
| 8     | 12.18444 | 44.20340 | 6.36              | 0.966                     | 0.00              | 0                         | 14.6 |           |
| 9     | 12.18456 | 44.20351 | 16.76             | 0.990                     | 0.00              | 0                         | 14   |           |
| 10    | 12.18465 | 44.20364 | 36.87             | 0.996                     | 0.00              | 0                         | 17.2 |           |
| 11    | 12.18455 | 44.20365 | 32.57             | 0.997                     | 0.00              | 0                         | 16.9 |           |
| 12    | 12.18443 | 44.20357 | 26.67             | 0.996                     | 0.00              | 0                         | 14.4 |           |
| 13    | 12.18432 | 44.20345 | 13.92             | 0.998                     | 0.00              | 0                         | 14.4 |           |
| 14    | 12.18423 | 44.20333 | 15.67             | 0.995                     | 0.00              | 0                         | 15.8 |           |
| 15    | 12.18414 | 44.20324 | 125.40            | 0.995                     | 0.00              | 0                         | 16.2 |           |
| 16    | 12.18407 | 44.20312 | 15.14             | 0.989                     | 0.00              | 0                         | 15.1 |           |
| 17    | 12.18399 | 44.20303 | 55.18             | 0.998                     | 0.00              | 0                         | 18   |           |
| 18    | 12.18394 | 44.20295 | 158.84            | 0.999                     | 3.67              | 0.983                     | 31.6 |           |
| 19    | 12.18391 | 44.20296 | 63.27             | 0.999                     | 0.00              | 0                         | 17.7 |           |
| 20    | 12.18387 | 44.20299 | 78.72             | 0.998                     | 0.00              | 0                         | 16.2 |           |
| 21    | 12.18390 | 44.20295 | 252.96            | 0.999                     | 43.12             | 0.998                     | 24   |           |
| 22    | 12.18395 | 44.20292 | 89.41             | 0.997                     | 0.00              | 0                         | 22.9 |           |
| 23    | 12.18398 | 44.20299 | 469.92            | 0.999                     | 2.12              | 0.999                     | 26.9 |           |
| 24    | 12.18403 | 44.20299 | 91.87             | 0.997                     | 0.00              | 0                         | 18   |           |
| 25    | 12.18398 | 44.20298 | 249.52            | 0.997                     | 0.89              | 0.995                     | 20.6 |           |
| 26    | 12.18397 | 44.20297 | 35.59             | 0.999                     | 0.11              | 0.968                     | 18.4 |           |
| 27    | 12.18388 | 44.20291 | 30.98             | 0.998                     | 0.00              | 0                         | 16.4 |           |
| 28    | 12.18385 | 44.20286 | 266.73            | 0.999                     | 10.30             | 0.998                     | 18.2 |           |
| 29    | 12.18378 | 44.20278 | 56.36             | 0.998                     | 0.00              | 0                         | 17.2 |           |
| 30    | 12.18379 | 44.20274 | 18.16             | 0.997                     | 0.00              | 0                         | 15.4 |           |
| 31    | 12.18362 | 44.20279 | 10.69             | 0.989                     | 0.00              | 0                         | 13.9 |           |
| 32    | 12.18375 | 44.20287 | 352.35            | 0.999                     | 8.45              | 0.999                     | 19   |           |
| 33    | 12.18375 | 44.20295 | 145.20            | 1.000                     | 0.00              | 0                         | 18.5 |           |
| 34    | 12.18381 | 44.20299 | 858.00            | 0.999                     | 23.72             | 0.999                     | 19.2 |           |
| 35    | 12.18390 | 44.20312 | 103.05            | 0.998                     | 0.62              | 0.992                     | 17.8 |           |
| 36    | 12.18398 | 44.20322 | 20.42             | 0.997                     | 0.00              | 0                         | 14.3 |           |
| 37    | 12.18410 | 44.20333 | 27.52             | 0.994                     | 0.00              | 0                         | 15.9 |           |
| 38    | 12.18418 | 44.20345 | 437.49            | 0.998                     | 25.71             | 0.996                     | 22.6 |           |
| 39    | 12.18426 | 44.20353 | 17.64             | 0.992                     | 0.00              | 0                         | 15   |           |
| 40    | 12.18428 | 44.20360 | 24.31             | 0.996                     | 0.00              | 0                         | 14.9 |           |
| 41    | 12.18439 | 44.20375 | 310.55            | 0.999                     | 2.11              | 0.999                     | 18.6 |           |
| 42    | 12.18450 | 44.20384 | 22.85             | 0.997                     | 0.00              | 0                         | 15.3 |           |
| 43    | 12.18460 | 44.20394 | 18.88             | 0.998                     | 0.00              | 0                         | 15.3 |           |
| 44    | 12.18468 | 44.20405 | 36.58             | 0.998                     | 0.00              | 0                         | 14.6 |           |
| 45    | 12.18474 | 44.20419 | 22.39             | 0.997                     | 0.00              | 0                         | 14.2 |           |
| 46    | 12.18489 | 44.20428 | 35.00             | 0.998                     | 0.00              | 0                         | 14.9 |           |
| 47    | 12.18496 | 44.20438 | 22.81             | 0.992                     | 0.00              | 0                         | 13.7 |           |
| 48    | 12.18503 | 44.20437 | 23.69             | 0.996                     | 0.00              | 0                         | 14.3 |           |
| 49    | 12.18497 | 44.20427 | 24.73             | 0.996                     | 0.00              | 0                         | 14   |           |
| 50    | 12.18483 | 44.20414 | 17.23             | 0.995                     | 0.00              | 0                         | 14.7 |           |

|     |          |          |         |       |         |       |      |
|-----|----------|----------|---------|-------|---------|-------|------|
| 51  | 12.18479 | 44.20407 | 11.61   | 0.982 | 0.00    | 0     | 14.5 |
| 52  | 12.18471 | 44.20396 | 18.52   | 0.993 | 0.00    | 0     | 14.2 |
| 53  | 12.18454 | 44.20383 | 16.51   | 0.989 | 0.00    | 0     | 14.3 |
| 54  | 12.18451 | 44.20373 | 22.52   | 0.995 | 0.00    | 0     | 14.4 |
| 55  | 12.18443 | 44.20389 | 15.73   | 0.997 | 0.00    | 0     | 14.8 |
| 56  | 12.18434 | 44.20378 | 67.98   | 0.996 | 0.00    | 0     | 16.3 |
| 57  | 12.18425 | 44.20366 | 50.60   | 0.995 | 0.00    | 0     | 15.9 |
| 58  | 12.18419 | 44.20357 | 35.70   | 0.996 | 0.00    | 0     | 15.7 |
| 59  | 12.18406 | 44.20343 | 79.29   | 0.996 | 0.00    | 0     | 17.2 |
| 60  | 12.18414 | 44.20353 | 147.27  | 0.997 | 0.24    | 0.986 | 19.8 |
| 61  | 12.18399 | 44.20335 | 26.99   | 0.997 | 0.00    | 0     | 14.9 |
| 62  | 12.18390 | 44.20325 | 30.69   | 0.993 | 0.00    | 0     | 14.5 |
| 63  | 12.18380 | 44.20313 | 37.28   | 0.997 | 0.00    | 0     | 15.6 |
| 64  | 12.18375 | 44.20304 | 32.00   | 0.998 | 0.00    | 0     | 14.8 |
| 65  | 12.18363 | 44.20290 | 23.94   | 0.999 | 0.00    | 0     | 16.1 |
| 66  | 12.18358 | 44.20285 | 46.38   | 0.998 | 0.00    | 0     | 14.5 |
| 67  | 12.18349 | 44.20290 | 212.48  | 0.998 | 0.17    | 0.968 | 19   |
| 68  | 12.18354 | 44.20296 | 61.42   | 0.997 | 0.00    | 0     | 17.6 |
| 69  | 12.18361 | 44.20305 | 26.11   | 0.995 | 0.00    | 0     | 15.4 |
| 70  | 12.18370 | 44.20315 | 25.37   | 0.996 | 0.00    | 0     | 16.6 |
| 71  | 12.18381 | 44.20328 | 14.05   | 0.995 | 0.00    | 0     | 15.7 |
| 72  | 12.18390 | 44.20340 | 16.29   | 0.997 | 0.00    | 0     | 15   |
| 73  | 12.18399 | 44.20352 | 31.03   | 0.999 | 0.00    | 0     | 17.5 |
| 74  | 12.18406 | 44.20361 | 84.44   | 0.998 | 0.00    | 0     | 17.4 |
| 75  | 12.18415 | 44.20372 | 48.18   | 0.998 | 0.00    | 0     | 18.5 |
| 76  | 12.18423 | 44.20381 | 31.26   | 0.997 | 0.00    | 0     | 17.6 |
| 77  | 12.18433 | 44.20392 | 21.11   | 0.994 | 0.00    | 0     | 16.5 |
| 78  | 12.18422 | 44.20394 | 32.85   | 0.997 | 0.00    | 0     | 15.5 |
| 79  | 12.18409 | 44.20386 | 33.75   | 0.998 | 0.00    | 0     | 15.9 |
| 80  | 12.18400 | 44.20378 | 26.66   | 0.995 | 0.00    | 0     | 16.2 |
| 81  | 12.18403 | 44.20381 | 201.08  | 0.991 | 13.60   | 0.988 | 21   |
| 82  | 12.18392 | 44.20366 | 29.04   | 0.997 | 0.00    | 0     | 16.4 |
| 83  | 12.18382 | 44.20357 | 124.08  | 0.998 | 0.00    | 0.004 | 18   |
| 84  | 12.18380 | 44.20352 | 99.48   | 0.998 | 0.00    | 0     | 17.6 |
| 85  | 12.18379 | 44.20341 | 185.50  | 0.997 | 0.00    | 0     | 17.7 |
| 86  | 12.18366 | 44.20330 | 63.27   | 0.998 | 0.00    | 0     | 16.7 |
| 87  | 12.18356 | 44.20327 | 62.13   | 0.997 | 0.00    | 0     | 16.7 |
| 88  | 12.18357 | 44.20322 | 13.57   | 0.993 | 0.00    | 0     | 16   |
| 89  | 12.18344 | 44.20310 | 12.54   | 0.995 | 0.00    | 0     | 16.2 |
| 90  | 12.18336 | 44.20296 | 46.07   | 0.997 | 0.00    | 0     | 15.9 |
| 91  | 12.18395 | 44.20299 | 1389.08 | 0.997 | 2280.89 | 0.998 | 35   |
| 92  | 12.18424 | 44.20255 | 38.21   | 0.998 | 0.00    | 0     | 17   |
| 93  | 12.18432 | 44.20265 | 37.31   | 0.999 | 0.00    | 0     | 18   |
| 94  | 12.18441 | 44.20274 | 26.82   | 0.998 | 0.00    | 0     | 17.5 |
| 95  | 12.18451 | 44.20284 | 62.66   | 0.999 | 0.00    | 0     | 17.4 |
| 96  | 12.18457 | 44.20293 | 47.70   | 0.999 | 0.00    | 0     | 17.4 |
| 97  | 12.18468 | 44.20304 | 67.54   | 0.999 | 0.00    | 0     | 17.5 |
| 98  | 12.18477 | 44.20314 | 88.18   | 0.999 | 0.00    | 0     | 18.1 |
| 99  | 12.18484 | 44.20324 | 46.68   | 0.999 | 0.00    | 0     | 16.5 |
| 100 | 12.18492 | 44.20335 | 44.70   | 0.999 | 0.00    | 0     | 16.5 |
| 101 | 12.18502 | 44.20347 | 39.05   | 0.997 | 0.00    | 0     | 18.1 |
| 102 | 12.18508 | 44.20359 | 39.68   | 0.998 | 0.00    | 0     | 17.1 |
| 103 | 12.18517 | 44.20370 | 34.47   | 0.998 | 0.00    | 0     | 16.9 |
| 104 | 12.18526 | 44.20382 | 60.59   | 0.997 | 0.00    | 0     | 18   |
| 105 | 12.18536 | 44.20391 | 94.29   | 0.999 | 0.00    | 0     | 18.2 |
| 106 | 12.18544 | 44.20405 | 84.92   | 0.999 | 0.00    | 0     | 19.4 |
| 107 | 12.18491 | 44.20349 | 19.68   | 0.997 | 0.00    | 0     | 18   |
| 108 | 12.18483 | 44.20340 | 30.21   | 0.998 | 0.00    | 0     | 17   |
| 109 | 12.18476 | 44.20328 | 46.38   | 0.996 | 0.00    | 0     | 18.1 |
| 110 | 12.18466 | 44.20316 | 23.25   | 0.998 | 0.00    | 0     | 17.3 |
| 111 | 12.18457 | 44.20306 | 33.19   | 0.992 | 0.00    | 0     | 16.9 |
| 112 | 12.18447 | 44.20296 | 42.70   | 0.998 | 0.00    | 0     | 16.7 |

|     |          |          |        |       |       |       |      |
|-----|----------|----------|--------|-------|-------|-------|------|
| 113 | 12.18441 | 44.20289 | 43.94  | 0.995 | 0.00  | 0     | 20.8 |
| 114 | 12.18439 | 44.20284 | 78.98  | 0.998 | 0.00  | 0     | 19.7 |
| 115 | 12.18430 | 44.20273 | 59.58  | 0.999 | 0.00  | 0     | 16.3 |
| 116 | 12.18415 | 44.20261 | 74.54  | 0.995 | 0.00  | 0     | 18.6 |
| 117 | 12.18412 | 44.20256 | 163.86 | 0.997 | 0.00  | 0     | 17   |
| 118 | 12.18399 | 44.20261 | 161.48 | 0.996 | 0.00  | 0     | 18.6 |
| 119 | 12.18337 | 44.20239 | 96.32  | 0.997 | 0.89  | 0.995 | 21.6 |
| 120 | 12.18339 | 44.20238 | 144.76 | 0.999 | 0.61  | 0.995 | 20.3 |
| 121 | 12.18344 | 44.20235 | 59.75  | 0.997 | 0.00  | 0.005 | 19.3 |
| 122 | 12.18347 | 44.20238 | 28.06  | 0.996 | 0.00  | 0     | 19   |
| 123 | 12.18343 | 44.20240 | 92.05  | 0.998 | 0.00  | 0     | 20   |
| 124 | 12.18337 | 44.20243 | 156.07 | 0.999 | 10.21 | 0.998 | 20.8 |
| 125 | 12.18342 | 44.20246 | 32.12  | 0.998 | 0.00  | 0     | 17.8 |
| 126 | 12.18335 | 44.20241 | 66.57  | 0.995 | 0.00  | 0     | 19.6 |
| 127 | 12.18331 | 44.20238 | 50.91  | 0.999 | 0.00  | 0     | 18.9 |
| 128 | 12.18376 | 44.20286 | 88.70  | 0.994 | 0.00  | 0     | 20.2 |
| 129 | 12.18384 | 44.20297 | 118.67 | 0.998 | 0.00  | 0     | 21   |
| 130 | 12.18393 | 44.20308 | 54.65  | 0.999 | 0.00  | 0     | 19.7 |
| 131 | 12.18405 | 44.20273 | 50.25  | 0.997 | 0.00  | 0     | 18   |
| 132 | 12.18417 | 44.20286 | 46.20  | 0.996 | 0.00  | 0     | 18.2 |
| 133 | 12.18425 | 44.20298 | 48.14  | 0.994 | 0.00  | 0     | 17.2 |
| 134 | 12.18434 | 44.20309 | 62.17  | 0.995 | 0.00  | 0     | 16.7 |
| 135 | 12.18446 | 44.20320 | 56.67  | 0.996 | 0.00  | 0     | 16.8 |
| 136 | 12.18455 | 44.20331 | 41.07  | 0.995 | 0.00  | 0     | 16.6 |
| 137 | 12.18465 | 44.20342 | 33.47  | 0.994 | 0.00  | 0     | 17   |
| 138 | 12.18476 | 44.20355 | 37.78  | 0.997 | 0.00  | 0     | 18.3 |
| 51  | 12.18479 | 44.20407 | 11.61  | 0.982 | 0.00  | 0     | 14.5 |
| 52  | 12.18471 | 44.20396 | 18.52  | 0.993 | 0.00  | 0     | 14.2 |



Appendix A.3. Santa Maria Nuova soil flux campaign data from April 2023.

| Point | Long     | Lat      | $\Phi\text{CO}_2$ | $\text{CO}_2 \text{ R}^2$ | $\Phi\text{CH}_4$ | $\text{CH}_4 \text{ R}^2$ | note | Soil Temp |
|-------|----------|----------|-------------------|---------------------------|-------------------|---------------------------|------|-----------|
| 1     | 12.18507 | 44.20435 | 8.18              | 0.894                     | 5.52              | 0.983                     |      | 16        |
| 2     | 12.18497 | 44.20432 | 35.77             | 0.998                     | 28.84             | 0.993                     |      | 14.3      |
| 3     | 12.18483 | 44.20415 | 15.71             | 0.945                     | 0.05              | 0.808                     |      | 15.3      |
| 4     | 12.18473 | 44.20400 | 4.49              | 0.964                     | 0.00              | 0.002                     |      | 14.7      |
| 5     | 12.18454 | 44.20381 | 17.78             | 0.847                     | 0.45              | 0.989                     |      | 16.7      |
| 6     | 12.18445 | 44.20375 | 18.88             | 0.991                     | 0.01              | 0.067                     |      | 15.6      |
| 7     | 12.18434 | 44.20356 | 23.36             | 0.998                     | 0.00              | 0.031                     |      | 15.7      |
| 8     | 12.18422 | 44.20345 | 58.08             | 0.998                     | 10.47             | 0.999                     |      | 16.4      |
| 9     | 12.18415 | 44.20333 | 65.12             | 0.994                     | 66.08             | 0.996                     |      | 16.9      |
| 10    | 12.18405 | 44.20323 | 21.47             | 0.996                     | 0.01              | 0.321                     |      | 14.7      |
| 11    | 12.18396 | 44.20315 | 46.64             | 0.977                     | 2.86              | 0.988                     |      | 15.5      |
| 12    | 12.18390 | 44.20306 | 32.43             | 0.994                     | 0.11              | 0.917                     |      | 15.8      |
| 13    | 12.18384 | 44.20299 | 82.72             | 0.999                     | 121.58            | 0.998                     |      | 17.8      |
| 14    | 12.18378 | 44.20291 | 68.20             | 0.999                     | 33.04             | 0.999                     |      | 16.5      |
| 15    | 12.18369 | 44.20281 | 31.06             | 0.999                     | 0.00              | 0.03                      |      | 14.6      |
| 16    | 12.18387 | 44.20276 | 26.71             | 0.999                     | 14.36             | 1                         |      | 16.6      |
| 17    | 12.18385 | 44.20286 | 125.40            | 0.999                     | 580.65            | 0.999                     |      | 17.7      |
| 18    | 12.18398 | 44.20292 | 92.84             | 0.995                     | 301.55            | 0.995                     |      | 18.9      |
| 19    | 12.18404 | 44.20302 | 66.44             | 0.996                     | 59.03             | 0.999                     |      | 18.2      |
| 20    | 12.18418 | 44.20316 | 17.20             | 0.999                     | 0.02              | 0.148                     |      | 17.9      |
| 21    | 12.18426 | 44.20329 | 18.70             | 0.998                     | 0.00              | 0.014                     |      | 15.3      |
| 22    | 12.18438 | 44.20344 | 6.64              | 0.991                     | 0.00              | 0.006                     |      | 14.4      |
| 23    | 12.18450 | 44.20354 | 4.75              | 0.987                     | 0.02              | 0.286                     |      | 14.4      |
| 24    | 12.18461 | 44.20353 | 8.71              | 0.994                     | 0.00              | 0.063                     |      | 14.2      |
| 25    | 12.18477 | 44.20339 | 29.83             | 0.999                     | 0.00              | 0.002                     |      | 14.8      |
| 26    | 12.18455 | 44.20313 | 38.24             | 0.999                     | 0.00              | 0.075                     |      | 14.7      |
| 27    | 12.18440 | 44.20299 | 31.11             | 0.999                     | 0.00              | 0.015                     |      | 13.6      |
| 28    | 12.18426 | 44.20280 | 16.98             | 0.999                     | 0.00              | 0.004                     |      | 14.4      |
| 29    | 12.18415 | 44.20269 | 214.72            | 1                         | 96.08             | 0.999                     |      | 13.3      |
| 30    | 12.18404 | 44.20265 | 25.30             | 0.998                     | 34.00             | 0.995                     |      | 16.5      |
| 31    | 12.18395 | 44.20273 | 82.28             | 0.998                     | 46.36             | 0.997                     |      | 15.6      |
| 32    | 12.18410 | 44.20287 | 108.68            | 0.999                     | 89.82             | 1                         |      | 17.2      |
| 33    | 12.18422 | 44.20301 | 9.59              | 0.997                     | 0.00              | 0.029                     |      | 18.8      |
| 34    | 12.18434 | 44.20316 | 17.20             | 0.991                     | 0.42              | 0.995                     |      | 14.6      |
| 35    | 12.18446 | 44.20331 | 6.38              | 0.974                     | 0.00              | 0.037                     |      | 14.8      |
| 36    | 12.18442 | 44.20389 | 5.24              | 0.885                     | 0.00              | 0                         |      | 18.6      |
| 37    | 12.18430 | 44.20374 | 11.53             | 0.96                      | 0.00              | 0                         |      | 15.6      |
| 38    | 12.18420 | 44.20359 | 13.29             | 0.995                     | 0.00              | 0                         |      | 14.2      |
| 39    | 12.18409 | 44.20348 | 54.56             | 0.995                     | 74.27             | 0.986                     |      | 16.1      |
| 40    | 12.18399 | 44.20334 | 7.61              | 0.92                      | 0.00              | 0.037                     |      | 13.8      |
| 41    | 12.18386 | 44.20319 | 10.21             | 0.979                     | 0.00              | 0.001                     |      | 14.4      |
| 42    | 12.18372 | 44.20305 | 7.57              | 0.956                     | 0.00              | 0.138                     |      | 14.8      |
| 43    | 12.18399 | 44.20294 | 31.72             | 0.995                     | 50.37             | 0.993                     |      | 18        |
| 44    | 12.18357 | 44.20292 | 9.72              | 0.987                     | 0.00              | 0                         |      | 15.1      |
| 45    | 12.18351 | 44.20281 | 21.47             | 0.992                     | 0.00              | 0.023                     |      | 14.9      |
| 46    | 12.18339 | 44.20288 | 59.84             | 0.996                     | 44.27             | 0.998                     |      | 15.7      |
| 47    | 12.18348 | 44.20302 | 36.83             | 0.998                     | 0.00              | 0.187                     |      | 14.2      |
| 48    | 12.18364 | 44.20322 | 30.62             | 0.999                     | 31.60             | 0.999                     |      | 16        |
| 49    | 12.18357 | 44.20315 | 19.45             | 0.946                     | 0.00              | 0.011                     |      | 14.7      |
| 50    | 12.18376 | 44.20341 | 331.76            | 0.998                     | 654.43            | 0.997                     |      | 17.3      |
| 51    | 12.18390 | 44.20354 | 53.68             | 0.999                     | 28.55             | 0.998                     |      | 17.7      |
| 52    | 12.18401 | 44.20371 | 9.68              | 0.888                     | 0.00              | 0.131                     |      | 16.1      |
| 53    | 12.18414 | 44.20385 | 2.35              | 0.77                      | 0.00              | 0.149                     |      | 16.3      |
| 54    | 12.18421 | 44.20395 | 14.21             | 0.997                     | 0.07              | 0.751                     |      | 16.4      |
| 55    | 12.18382 | 44.20331 | 26.22             | 0.996                     | 0.00              | 0                         |      | 14.7      |
| 56    | 12.18417 | 44.20261 | 5.59              | 0.962                     | 0.48              | 0.929                     |      | 18        |

|    |          |          |        |       |        |       |      |
|----|----------|----------|--------|-------|--------|-------|------|
| 57 | 12.18435 | 44.20270 | 20.99  | 0.982 | 0.00   | 0.013 | 16   |
| 58 | 12.18444 | 44.20285 | 69.96  | 0.989 | 57.90  | 0.997 | 16.8 |
| 59 | 12.18453 | 44.20297 | 33.88  | 0.995 | 0.00   | 0.007 | 15   |
| 60 | 12.18462 | 44.20308 | 90.20  | 0.992 | 106.18 | 0.984 | 16.9 |
| 61 | 12.18475 | 44.20321 | 29.17  | 0.99  | 0.00   | 0.199 | 14.8 |
| 62 | 12.18487 | 44.20338 | 28.82  | 0.989 | 0.00   | 0.009 | 13.6 |
| 63 | 12.18497 | 44.20350 | 25.26  | 0.962 | 0.00   | 0     | 13.6 |
| 64 | 12.18510 | 44.20363 | 31.50  | 0.986 | 0.00   | 0.036 | 14   |
| 65 | 12.18519 | 44.20376 | 36.61  | 0.994 | 0.00   | 0.002 | 14.6 |
| 66 | 12.18529 | 44.20388 | 24.64  | 0.981 | 0.09   | 0.532 | 16.2 |
| 67 | 12.18538 | 44.20401 | 19.27  | 0.991 | 0.27   | 0.926 | 16.8 |
| 68 | 12.18546 | 44.20411 | 36.48  | 0.997 | 0.00   | 0.135 | 17.2 |
| 69 | 12.18460 | 44.20326 | 13.02  | 0.99  | 0.00   | 0.002 | 13.5 |
| 70 | 12.18459 | 44.20344 | 2.46   | 0.594 | 0.00   | 0.098 | 14.4 |
| 71 | 12.18383 | 44.20269 | 488.40 | 0.993 | 81.32  | 0.992 | 15.8 |
| 72 | 12.18367 | 44.20276 | 19.80  | 0.995 | 0.00   | 0.35  | 14.5 |
| 73 | 12.18409 | 44.20257 | 4.93   | 0.777 | 0.00   | 0.257 | 15   |

Appendix A.4. Santa Maria Nuova soil flux campaign data from October 2023.

| Point | Long     | Lat      | $\Phi\text{CO}_2$ | $\text{CO}_2 \text{ R}^2$ | $\Phi\text{CH}_4$ | $\text{CH}_4 \text{ R}^2$ | note | Soil Temp |
|-------|----------|----------|-------------------|---------------------------|-------------------|---------------------------|------|-----------|
| 1     | 12.18504 | 44.20434 | 236.28            | 0.996                     | 0.733             | 0.983                     |      | 24.5      |
| 2     | 12.18498 | 44.20433 | 16.50             | 0.96                      | 0.001             | 0                         |      | 20.5      |
| 3     | 12.18490 | 44.20424 | 31.77             | 0.988                     | 0.001             | 0.123                     |      | 19        |
| 4     | 12.18497 | 44.20421 | 39.64             | 0.981                     | 0.001             | 0                         |      | 19.3      |
| 5     | 12.18489 | 44.20412 | 27.76             | 0.998                     | 0.001             | 0                         |      | 20        |
| 6     | 12.18482 | 44.20417 | 18.08             | 0.992                     | 0.001             | 0                         |      | 19.8      |
| 7     | 12.18474 | 44.20408 | 26.71             | 0.991                     | 0.002             | 0                         |      | 19.4      |
| 8     | 12.18482 | 44.20404 | 13.46             | 0.992                     | 0.001             | 0                         |      | 19.8      |
| 9     | 12.18475 | 44.20395 | 19.62             | 0.995                     | 0.001             | 0.015                     |      | 20.2      |
| 10    | 12.18466 | 44.20399 | 22.13             | 0.996                     | 0.002             | 0.002                     |      | 20.2      |
| 11    | 12.18459 | 44.20391 | 22.62             | 0.984                     | 0.001             | 0.001                     |      | 20.5      |
| 12    | 12.18468 | 44.20387 | 18.13             | 0.982                     | 0.001             | 0.004                     |      | 21.3      |
| 13    | 12.18463 | 44.20379 | 26.71             | 0.992                     | 0.001             | 0.001                     |      | 20.8      |
| 14    | 12.18454 | 44.20382 | 22.48             | 0.991                     | 0.000             | 0                         |      | 20.6      |
| 15    | 12.18447 | 44.20375 | 24.29             | 0.991                     | 0.001             | 0.027                     |      | 21.3      |
| 16    | 12.18456 | 44.20371 | 18.96             | 0.993                     | 0.001             | 0                         |      | 21.7      |
| 17    | 12.18468 | 44.20365 | 5.98              | 0.943                     | 0.001             | 0.198                     |      | 22.5      |
| 18    | 12.18478 | 44.20362 | 17.73             | 0.988                     | 0.002             | 0.012                     |      | 21.1      |
| 19    | 12.18489 | 44.20355 | 12.50             | 0.991                     | 0.001             | 0.255                     |      | 21.2      |
| 20    | 12.18501 | 44.20351 | 13.29             | 0.95                      | 0.001             | 0.011                     |      | 22.7      |
| 21    | 12.18506 | 44.20357 | 17.60             | 0.99                      | 0.001             | 0                         |      | 23.4      |
| 22    | 12.18511 | 44.20365 | 9.55              | 0.936                     | 0.001             | 0.06                      |      | 23.3      |
| 23    | 12.18519 | 44.20371 | 18.26             | 0.995                     | 0.001             | 0.319                     |      | 21.7      |
| 24    | 12.18524 | 44.20381 | 16.10             | 0.984                     | 0.001             | 0.003                     |      | 21.5      |
| 25    | 12.18534 | 44.20384 | 7.17              | 0.962                     | 0.001             | 0.039                     |      | 21.7      |
| 26    | 12.18539 | 44.20394 | 74.36             | 0.995                     | 0.001             | 0.003                     |      | 24.6      |
| 27    | 12.18546 | 44.20401 | 59.40             | 0.986                     | 0.300             | 0.941                     |      | 26.2      |
| 28    | 12.18551 | 44.20398 | 33.53             | 0.99                      | 0.002             | 0.002                     |      | 26.2      |
| 29    | 12.18543 | 44.20391 | 75.24             | 0.998                     | 0.001             | 0.275                     |      | 23.8      |
| 30    | 12.18537 | 44.20385 | 16.72             | 0.983                     | 0.001             | 0.025                     |      | 22.8      |
| 31    | 12.18531 | 44.20379 | 7.44              | 0.897                     | 0.001             | 0.06                      |      | 22.8      |
| 32    | 12.18525 | 44.20370 | 14.34             | 0.985                     | 0.002             | 0.015                     |      | 22.3      |
| 33    | 12.18520 | 44.20361 | 27.10             | 0.997                     | 0.001             | 0.02                      |      | 23.5      |
| 34    | 12.18513 | 44.20356 | 17.69             | 0.994                     | 0.001             | 0.072                     |      | 23        |
| 35    | 12.18507 | 44.20348 | 17.20             | 0.99                      | 0.001             | 0.155                     |      | 22.4      |
| 36    | 12.18501 | 44.20341 | 12.50             | 0.952                     | 0.002             | 0.002                     |      | 22.6      |
| 37    | 12.18495 | 44.20332 | 8.32              | 0.981                     | 0.001             | 0.013                     |      | 22.8      |
| 38    | 12.18491 | 44.20324 | 8.45              | 0.966                     | 0.001             | 0.081                     |      | 22.4      |
| 39    | 12.18483 | 44.20319 | 15.05             | 0.993                     | 0.001             | 0.075                     |      | 22.9      |
| 40    | 12.18477 | 44.20312 | 344.08            | 0.994                     | 0.529             | 0.96                      |      | 30        |
| 41    | 12.18470 | 44.20304 | 24.64             | 0.997                     | 0.001             | 0.084                     |      | 24        |
| 42    | 12.18466 | 44.20296 | 1416.80           | 0.997                     | 50.526            | 0.998                     |      | 33.8      |
| 43    | 12.18458 | 44.20291 | 19.80             | 0.974                     | 0.002             | 0.099                     |      | 23        |
| 44    | 12.18454 | 44.20282 | 10.38             | 0.975                     | 0.001             | 0                         |      | 22.5      |
| 45    | 12.18447 | 44.20276 | 12.67             | 0.984                     | 0.001             | 0.053                     |      | 22.2      |
| 46    | 12.18440 | 44.20268 | 27.24             | 0.99                      | 0.001             | 0.5                       |      | 22.1      |
| 47    | 12.18435 | 44.20259 | 13.82             | 0.978                     | 0.001             | 0.006                     |      | 22.8      |
| 48    | 12.18425 | 44.20253 | 26.71             | 0.996                     | 0.001             | 0.017                     |      | 23.1      |
| 49    | 12.18416 | 44.20255 | 21.52             | 0.994                     | 0.002             | 0.14                      |      | 23.1      |
| 50    | 12.18420 | 44.20265 | 69.96             | 0.998                     | 0.002             | 0                         |      | 23.8      |
| 51    | 12.18426 | 44.20271 | 13.51             | 0.91                      | 0.001             | 0.189                     |      | 22.7      |
| 52    | 12.18434 | 44.20279 | 9.94              | 0.901                     | 0.001             | 0.029                     |      | 23.2      |
| 53    | 12.18440 | 44.20284 | 28.16             | 0.996                     | 1.166             | 0.99                      |      | 26.8      |
| 54    | 12.18446 | 44.20292 | 75.68             | 0.992                     | 0.363             | 0.978                     |      | 26.5      |
| 55    | 12.18451 | 44.20298 | 16.50             | 0.983                     | 0.001             | 0.018                     |      | 23        |
| 56    | 12.18457 | 44.20305 | 26.75             | 0.984                     | 0.001             | 0.005                     |      | 23        |
| 57    | 12.18463 | 44.20312 | 12.58             | 0.935                     | 0.001             | 0.002                     |      | 22.8      |
| 58    | 12.18467 | 44.20317 | 12.54             | 0.974                     | 0.001             | 0                         |      | 22.5      |

|     |          |          |        |       |        |       |      |
|-----|----------|----------|--------|-------|--------|-------|------|
| 59  | 12.18475 | 44.20323 | 7.26   | 0.877 | 0.001  | 0     | 22.8 |
| 60  | 12.18480 | 44.20331 | 11.84  | 0.816 | 0.001  | 0.043 | 23.4 |
| 61  | 12.18483 | 44.20340 | 12.76  | 0.975 | 0.001  | 0.056 | 22.7 |
| 62  | 12.18492 | 44.20342 | 7.96   | 0.946 | 0.002  | 0     | 22.4 |
| 63  | 12.18482 | 44.20346 | 12.23  | 0.958 | 0.001  | 0     | 22.1 |
| 64  | 12.18476 | 44.20338 | 29.70  | 0.988 | 0.001  | 0.375 | 22.5 |
| 65  | 12.18470 | 44.20330 | 26.84  | 0.992 | 0.001  | 0     | 22.5 |
| 66  | 12.18463 | 44.20322 | 5.94   | 0.941 | 0.001  | 0     | 22.7 |
| 67  | 12.18458 | 44.20316 | 7.92   | 0.939 | 0.002  | 0.044 | 22.4 |
| 68  | 12.18452 | 44.20308 | 12.32  | 0.949 | 0.001  | 0     | 23.9 |
| 69  | 12.18447 | 44.20301 | 10.38  | 0.943 | 0.001  | 0.093 | 23.7 |
| 70  | 12.18442 | 44.20294 | 506.00 | 0.997 | 21.173 | 0.998 | 28.5 |
| 71  | 12.18433 | 44.20288 | 141.24 | 0.999 | 0.001  | 0     | 24.2 |
| 72  | 12.18426 | 44.20282 | 16.68  | 0.995 | 0.001  | 0.058 | 22.1 |
| 73  | 12.18420 | 44.20274 | 21.82  | 0.982 | 0.001  | 0.003 | 23.3 |
| 74  | 12.18417 | 44.20264 | 86.68  | 0.989 | 2.518  | 0.99  | 25.6 |
| 75  | 12.18411 | 44.20258 | 94.60  | 0.996 | 1.351  | 0.991 | 27.9 |
| 76  | 12.18400 | 44.20264 | 29.26  | 0.996 | 0.002  | 0     | 23.8 |
| 77  | 12.18408 | 44.20271 | 9.11   | 0.879 | 0.002  | 0     | 23.1 |
| 78  | 12.18413 | 44.20278 | 10.30  | 0.986 | 0.001  | 0.437 | 21.7 |
| 79  | 12.18417 | 44.20286 | 7.30   | 0.892 | 0.001  | 0.121 | 22.5 |
| 80  | 12.18426 | 44.20292 | 12.94  | 0.974 | 0.001  | 0.008 | 21.6 |
| 81  | 12.18429 | 44.20299 | 9.42   | 0.96  | 0.001  | 0.009 | 22   |
| 82  | 12.18436 | 44.20307 | 13.38  | 0.961 | 0.001  | 0     | 23.8 |
| 83  | 12.18444 | 44.20311 | 11.70  | 0.962 | 0.001  | 0     | 22.4 |
| 84  | 12.18451 | 44.20321 | 15.36  | 0.977 | 0.001  | 0.308 | 22.2 |
| 85  | 12.18455 | 44.20328 | 9.94   | 0.916 | 0.001  | 0     | 21.9 |
| 86  | 12.18459 | 44.20336 | 17.29  | 0.986 | 0.001  | 0.557 | 22.5 |
| 87  | 12.18462 | 44.20344 | 8.18   | 0.953 | 0.001  | 0     | 21.5 |
| 88  | 12.18470 | 44.20352 | 18.88  | 0.986 | 0.001  | 0     | 21.4 |
| 89  | 12.18458 | 44.20358 | 53.68  | 0.993 | 0.001  | 0     | 21.5 |
| 90  | 12.18452 | 44.20350 | 17.86  | 0.962 | 0.001  | 0     | 22.7 |
| 91  | 12.18444 | 44.20342 | 7.92   | 0.884 | 0.001  | 0.257 | 23.2 |
| 92  | 12.18440 | 44.20334 | 2.38   | 0.609 | 0.001  | 0     | 22.5 |
| 93  | 12.18433 | 44.20329 | 1.64   | 0.344 | 0.001  | 0.533 | 22.5 |
| 94  | 12.18429 | 44.20322 | 19.49  | 0.945 | 0.001  | 0     | 23.6 |
| 95  | 12.18424 | 44.20314 | 14.65  | 0.953 | 0.001  | 0     | 23.6 |
| 96  | 12.18418 | 44.20308 | 9.24   | 0.909 | 0.001  | 0     | 23.3 |
| 97  | 12.18414 | 44.20301 | 19.67  | 0.973 | 0.001  | 0.005 | 23.2 |
| 98  | 12.18408 | 44.20294 | 12.67  | 0.964 | 0.002  | 0     | 24.1 |
| 99  | 12.18404 | 44.20287 | 21.21  | 0.953 | 0.110  | 0.726 | 25.4 |
| 100 | 12.18398 | 44.20280 | 14.08  | 0.966 | 0.001  | 0     | 25.4 |
| 101 | 12.18391 | 44.20273 | 42.42  | 0.966 | 0.411  | 0.984 | 29.4 |
| 102 | 12.18380 | 44.20275 | 68.64  | 0.992 | 0.133  | 0.821 | 27   |
| 103 | 12.18388 | 44.20283 | 123.64 | 0.998 | 0.057  | 0.562 | 28   |
| 104 | 12.18394 | 44.20287 | 197.12 | 0.985 | 0.241  | 0.866 | 31.4 |
| 105 | 12.18398 | 44.20293 | 226.16 | 0.995 | 9.127  | 0.997 | 34.6 |
| 106 | 12.18404 | 44.20297 | 20.68  | 0.994 | 0.127  | 0.904 | 28.9 |
| 107 | 12.18410 | 44.20304 | 5.98   | 0.812 | 0.002  | 0.054 | 23   |
| 108 | 12.18417 | 44.20311 | 2.79   | 0.829 | 0.001  | 0.028 | 23.8 |
| 109 | 12.18419 | 44.20318 | 4.62   | 0.666 | 0.001  | 0     | 23.4 |
| 110 | 12.18425 | 44.20325 | 6.64   | 0.89  | 0.001  | 0.34  | 22.2 |
| 111 | 12.18428 | 44.20334 | 23.72  | 0.989 | 0.001  | 0.006 | 23.1 |
| 112 | 12.18434 | 44.20346 | 51.92  | 0.993 | 0.001  | 0.072 | 23.4 |
| 113 | 12.18440 | 44.20352 | 75.24  | 0.99  | 0.001  | 0.03  | 23.8 |
| 114 | 12.18449 | 44.20362 | 35.60  | 0.987 | 0.001  | 0.008 | 23.4 |
| 115 | 12.18438 | 44.20369 | 36.43  | 0.994 | 0.001  | 0     | 22.3 |
| 116 | 12.18432 | 44.20363 | 47.52  | 0.978 | 0.001  | 0.009 | 23.2 |
| 117 | 12.18427 | 44.20356 | 33.88  | 0.994 | 0.001  | 0.006 | 23.7 |
| 118 | 12.18423 | 44.20348 | 38.32  | 0.993 | 0.001  | 0     | 23.3 |
| 119 | 12.18416 | 44.20339 | 475.20 | 0.999 | 0.074  | 0.327 | 32.2 |
| 120 | 12.18410 | 44.20333 | 40.96  | 0.998 | 0.001  | 0.005 | 25   |

|     |          |          |        |       |       |       |      |
|-----|----------|----------|--------|-------|-------|-------|------|
| 121 | 12.18405 | 44.20327 | 20.02  | 0.962 | 0.002 | 0.504 | 23.4 |
| 122 | 12.18398 | 44.20320 | 5.41   | 0.824 | 0.001 | 0.289 | 23.5 |
| 123 | 12.18394 | 44.20313 | 126.72 | 0.998 | 0.162 | 0.797 | 26.5 |
| 124 | 12.18387 | 44.20306 | 146.96 | 1     | 0.001 | 0.006 | 29.8 |
| 125 | 12.18382 | 44.20299 | 89.32  | 0.999 | 0.001 | 0.035 | 27.6 |
| 126 | 12.18376 | 44.20292 | 257.84 | 0.999 | 0.158 | 0.793 | 28.7 |
| 127 | 12.18369 | 44.20284 | 14.12  | 0.987 | 0.001 | 0.021 | 27.7 |
| 128 | 12.18360 | 44.20287 | 8.49   | 0.946 | 0.001 | 0.037 | 22.2 |
| 129 | 12.18367 | 44.20294 | 84.04  | 0.989 | 0.407 | 0.948 | 25.9 |
| 130 | 12.18374 | 44.20302 | 6.42   | 0.774 | 0.002 | 0     | 23.3 |
| 131 | 12.18375 | 44.20307 | 18.96  | 0.957 | 0.001 | 0.02  | 23.4 |
| 132 | 12.18383 | 44.20316 | 22.79  | 0.935 | 0.001 | 0.021 | 23.5 |
| 133 | 12.18387 | 44.20322 | 0.81   | 0.306 | 0.001 | 0.069 | 23.2 |
| 134 | 12.18392 | 44.20327 | 3.58   | 0.066 | 0.001 | 0     | 23.7 |
| 135 | 12.18401 | 44.20337 | 9.99   | 0.732 | 0.001 | 0.026 | 23.1 |
| 136 | 12.18408 | 44.20345 | 78.76  | 0.998 | 0.358 | 0.957 | 30   |
| 137 | 12.18414 | 44.20351 | 9.94   | 0.918 | 0.001 | 0.017 | 23   |
| 138 | 12.18421 | 44.20360 | 2.26   | 0.181 | 0.002 | 0.421 | 22.1 |
| 139 | 12.18427 | 44.20370 | 73.48  | 0.998 | 0.002 | 0     | 24.8 |
| 140 | 12.18433 | 44.20378 | 139.04 | 0.997 | 0.001 | 0     | 26.2 |
| 141 | 12.18423 | 44.20381 | 14.70  | 0.915 | 0.001 | 0.043 | 23.4 |
| 142 | 12.18417 | 44.20375 | 11.62  | 0.745 | 0.001 | 0     | 24.2 |
| 143 | 12.18409 | 44.20368 | 6.64   | 0.903 | 0.001 | 0.011 | 23   |
| 144 | 12.18405 | 44.20360 | 11.66  | 0.677 | 0.001 | 0.188 | 23.3 |
| 145 | 12.18398 | 44.20356 | 13.99  | 0.989 | 0.001 | 0.296 | 23.2 |
| 146 | 12.18392 | 44.20347 | 41.89  | 0.996 | 0.002 | 0     | 26.2 |
| 147 | 12.18385 | 44.20340 | 7.26   | 0.835 | 0.001 | 0.006 | 23   |
| 148 | 12.18382 | 44.20331 | 1.58   | 0.247 | 0.001 | 0.026 | 22.3 |
| 149 | 12.18374 | 44.20327 | 3.79   | 0.845 | 0.001 | 0     | 23.3 |
| 150 | 12.18369 | 44.20317 | 4.80   | 0.804 | 0.001 | 0.031 | 24.1 |
| 151 | 12.18362 | 44.20311 | 9.02   | 0.847 | 0.001 | 0.181 | 24.5 |
| 152 | 12.18356 | 44.20304 | 0.95   | 0.171 | 0.001 | 0.098 | 24   |
| 153 | 12.18349 | 44.20296 | 31.90  | 0.996 | 0.001 | 0.8   | 26.3 |
| 154 | 12.18338 | 44.20299 | 9.68   | 0.871 | 0.001 | 0     | 24   |
| 155 | 12.18343 | 44.20305 | 5.19   | 0.673 | 0.002 | 0     | 24   |
| 156 | 12.18348 | 44.20312 | 0.46   | 0.038 | 0.001 | 0     | 23.5 |
| 157 | 12.18358 | 44.20321 | 118.36 | 0.986 | 0.097 | 0.639 | 30   |
| 158 | 12.18365 | 44.20329 | 54.56  | 0.993 | 0.001 | 0.104 | 23.6 |
| 159 | 12.18374 | 44.20338 | 68.20  | 0.994 | 0.001 | 0.014 | 29   |
| 160 | 12.18380 | 44.20345 | 26.09  | 0.99  | 0.001 | 0     | 30.5 |
| 161 | 12.18387 | 44.20353 | 24.68  | 0.982 | 0.001 | 0.256 | 24.1 |
| 162 | 12.18398 | 44.20361 | 12.72  | 0.936 | 0.150 | 0.701 | 26.4 |
| 163 | 12.18397 | 44.20369 | 2.82   | 0.62  | 0.001 | 0     | 25.4 |
| 164 | 12.18406 | 44.20380 | 5.02   | 0.404 | 0.001 | 0     | 24.4 |
| 165 | 12.18413 | 44.20385 | 35.64  | 0.98  | 0.117 | 0.707 | 27.3 |

Appendix A.5 Complete Python source code for training the ANN model and for the subsequent calibration of the Figaro NGM2611-E13 sensor's raw data. Templates illustrating the required structures of the datasets for the training and calibration phases are also included.

```

from sklearn.model_selection import train_test_split, KFold, cross_val_score
from sklearn.preprocessing import StandardScaler
from tensorflow.keras.layers import Input, Dense
from tensorflow.keras.models import Sequential, load_model
from tensorflow.keras.optimizers import Adam
from tensorflow.keras.regularizers import l2
import joblib
import matplotlib.pyplot as plt
import numpy as np
import pandas as pd
import seaborn as sns
from sklearn.metrics import mean_squared_error, mean_absolute_error, r2_score,
mean_absolute_percentage_error

# =====
# 1. Load and preprocess data
# =====
data = pd.read_csv("/Volumes/SANDISK/INGV/Test Lcs - AC/NN dataset/C1.csv", sep=",",
header=0) # Attention: remember to modify with your directory!!
data["date"] = pd.to_datetime(data["date"], format="%Y-%m-%d %H:%M:%S")
data = data.dropna()

# 2. Convert columns to float32
float_columns = ['RH', 'T', 'CH4.counts', 'CH4']
for col in float_columns:
    data[col] = data[col].astype(np.float32)

# 3. Logarithmic transformation of reference CH4
data['CH4'] = np.log1p(data['CH4'])

# 4. Scale the features
scaler_standard = StandardScaler()
scaler_standard_ch4 = StandardScaler()

# 5. Apply scaling
data[['RH', 'T', 'CH4.counts']] = scaler_standard.fit_transform(data[['RH', 'T',
'CH4.counts']])
data[['CH4']] = scaler_standard_ch4.fit_transform(data[['CH4']])
print(data)

# 6. Prepare X (features) and y (target)
X = data[['RH', 'T', 'CH4.counts']].values
y = data['CH4'].values

# 7. Data split into 90% training and 10% test
X_train, X_test, y_train, y_test = train_test_split(X, y, test_size=0.1, shuffle=True)

# 8. Save processed data and scalers
data.to_csv("C1_test_norm.csv", index=False) #Remember to change Station name
joblib.dump(scaler_standard, 'scaler_standard.joblib')
joblib.dump(scaler_standard_ch4, 'scaler_standard_ch4.joblib')

# =====

```

## # 9. Neural Network Architecture with L2 Regularizer

```
# =====
```

```
def create_model(input_shape):
    model = Sequential(
        [
            Input(shape=input_shape), # Use Input(shape) here
            Dense(3, activation="relu", input_shape=input_shape,
kernel_regularizer=l2(0.01)),
            Dense(64, activation="relu", kernel_regularizer=l2(0.01)),
            Dense(32, activation="relu", kernel_regularizer=l2(0.01)),
            Dense(1, activation="linear")
        ]
    )
    model.compile(optimizer=Adam(learning_rate=0.0005), loss="mse")
    return model
```

## # 10. 5-fold Cross-Validation

```
kfold = KFold(n_splits=5, shuffle=True, random_state=42)
mse_scores = []

for train_index, val_index in kfold.split(X_train, y_train):
    X_train_fold, X_val_fold = X_train[train_index], X_train[val_index]
    y_train_fold, y_val_fold = y_train[train_index], y_train[val_index]

    model = create_model((X_train_fold.shape[1],))
    model.fit(X_train_fold, y_train_fold, epochs=200, batch_size=32, verbose=0)

    y_val_pred = model.predict(X_val_fold).flatten()
    mse = mean_squared_error(y_val_fold, y_val_pred)
    mse_scores.append(mse)

print(f"Mean MSE (Cross-Validation): {np.mean(mse_scores)}")
print(f"MSE Standard Deviation (Cross-Validation): {np.std(mse_scores)}")
```

## # 11. Test Set Evaluation Model

```
model_test = create_model((X_train.shape[1],))
model_test.fit(X_train, y_train, epochs=200, batch_size=32, verbose=0)
```

## # 12. Save Model

```
model_test.save('model_counts_C1.keras')
print(f"Model saved as {'model_counts_C1.keras'}")
```

```
# =====
```

## # 13. Test Set Model Evaluation (Scaled/Log space)

```
# =====
```

```
y_pred = model_test.predict(X_test).flatten()
mse = mean_squared_error(y_test, y_pred)
mae = mean_absolute_error(y_test, y_pred)
mape = mean_absolute_percentage_error(y_test, y_pred)
r2 = r2_score(y_test, y_pred)
print(f"MSE: {mse}")
print(f"MAE: {mae}")
print(f"MAPE: {mape}")
print(f"R2: {r2}")
```

## # 14. Metrics in original units (ppm) without retraining

```
def inverse_transform_ch4(z_scaled, scaler):
    """
```



```

z_scaled: target array in scaled space (StandardScaler di log1p(CH4)).
Returns CH4 in ppm: expm1( z_std_inv ).
"""

```

```

z_std_inv = z_scaled * scaler.scale_[0] + scaler.mean_[0]
return np.expm1(z_std_inv)

```

#### # 15. Inversion for test set

```

y_test_ppm = inverse_transform_ch4(y_test, scaler_standard_ch4)
y_pred_ppm = inverse_transform_ch4(y_pred, scaler_standard_ch4)

```

#### # 16. Metrics in ppm

```

mae_ppm = mean_absolute_error(y_test_ppm, y_pred_ppm)
rmse_ppm = np.sqrt(mean_squared_error(y_test_ppm, y_pred_ppm))
r2_ppm = r2_score(y_test_ppm, y_pred_ppm)

```

#### # Robust MAPE: ignores denominators ~0 (es. < 1 ppm)

```

mask = y_test_ppm > 1.0
if np.any(mask):
    mape_ppm = 100 * np.mean(np.abs((y_pred_ppm[mask] - y_test_ppm[mask]) /
y_test_ppm[mask]))
    ape = 100 * np.abs((y_pred_ppm[mask] - y_test_ppm[mask]) / y_test_ppm[mask])
    mape_p95 = np.percentile(ape, 95)
else:
    mape_ppm, mape_p95 = np.nan, np.nan

```

#### # sMAPE (symmetric Mean Absolute Percentage Error) to assess the accuracy of forecasting models

```

smape = 200 * np.mean(
    np.abs(y_pred_ppm - y_test_ppm) / (np.abs(y_pred_ppm) + np.abs(y_test_ppm) + 1e-9)
)

```

```

print("\n=== Test set metrics in ORIGINAL ppm ===")
print(f"MAE_ppm: {mae_ppm:.3f} ppm")
print(f"RMSE_ppm: {rmse_ppm:.3f} ppm")
print(f"R2_ppm: {r2_ppm:.3f}")
print(f"MAPE_ppm (y>1 ppm): {mape_ppm:.2f}% | APE p95: {mape_p95:.2f}%")
print(f"sMAPE: {smape:.2f}%")

```

#### # (optional) save as CSV

```

pd.DataFrame({
    'metric': ['MAE_ppm', 'RMSE_ppm', 'R2_ppm', 'MAPE_ppm(y>1)', 'APE_p95', 'sMAPE'],
    'value': [mae_ppm, rmse_ppm, r2_ppm, mape_ppm, mape_p95, smape]
}).to_csv('C1_ann_metrics_test_ppm.csv', index=False)

```

#### # 17. Train Set Model Evaluation

```

y_train_pred = model_test.predict(X_train).flatten()
mse_train = mean_squared_error(y_train, y_train_pred)
mae_train = mean_absolute_error(y_train, y_train_pred)
mape_train = mean_absolute_percentage_error(y_train, y_train_pred)
r2_train = r2_score(y_train, y_train_pred)

```

```

print("=== Train Set ===")
print(f"MSE: {mse_train}")
print(f"MAE: {mae_train}")
print(f"MAPE: {mape_train}")
print(f"R2: {r2_train}")

```

#### # Train metrics in ppm

```

y_train_ppm = inverse_transform_ch4(y_train, scaler_standard_ch4)
y_train_pred_ppm = inverse_transform_ch4(y_train_pred, scaler_standard_ch4)

```

```

mae_train_ppm = mean_absolute_error(y_train_ppm, y_train_pred_ppm)
rmse_train_ppm = np.sqrt(mean_squared_error(y_train_ppm, y_train_pred_ppm))
r2_train_ppm = r2_score(y_train_ppm, y_train_pred_ppm)

mask_tr = y_train_ppm > 1.0
if np.any(mask_tr):
    mape_train_ppm = 100 * np.mean(np.abs((y_train_pred_ppm[mask_tr] -
y_train_ppm[mask_tr]) / y_train_ppm[mask_tr])))
else:
    mape_train_ppm = np.nan

print("\n=== Train set metrics in ORIGINAL ppm ===")
print(f"MAE_ppm: {mae_train_ppm:.3f} ppm")
print(f"RMSE_ppm: {rmse_train_ppm:.3f} ppm")
print(f"R2_ppm: {r2_train_ppm:.3f}")
print(f"MAPE_ppm (y>1 ppm): {mape_train_ppm:.2f}%")

# (optional) save as CSV
pd.DataFrame({
    'metric': ['MAE_ppm', 'RMSE_ppm', 'R2_ppm', 'MAPE_ppm(y>1)', 'APE_p95', 'sMAPE'],
    'value': [mae_ppm, rmse_ppm, r2_ppm, mape_ppm, mape_p95, smape]
}).to_csv('C1_ann_metrics_train_ppm.csv', index=False)

```

#### # 18. Residual Analysis

```

residuals = y_test - y_pred
plt.figure(figsize=(10, 5))

plt.subplot(1, 2, 1)
sns.scatterplot(x=y_pred, y=residuals)
plt.axhline(y=0, color='r', linestyle='--')
plt.xlabel('Predicted Values')
plt.ylabel('Residuals')
plt.title('Residuals vs Predicted Values')

plt.subplot(1, 2, 2)
sns.histplot(residuals, kde=True)
plt.xlabel('Residuals')
plt.ylabel('Frequency')
plt.title('S1 Residuals Distribution')
plt.savefig('CH4_counts_S1_ResidualsDistribution, dpi=300)

plt.show()

```

#### # Residual Analysis ppm

```

residuals_ppm = y_test_ppm - y_pred_ppm
plt.figure(figsize=(10, 5))

plt.subplot(1, 2, 1)
sns.scatterplot(x=y_pred_ppm, y=residuals_ppm)
plt.axhline(y=0, color='r', linestyle='--')
plt.xlabel('Predicted Values')
plt.ylabel('Residuals (ppm)')
plt.title('Residuals vs Predicted Values')

plt.subplot(1, 2, 2)
sns.histplot(residuals, kde=True)
plt.xlabel('Residuals')
plt.ylabel('Frequency')
plt.title('S1 Residuals Distribution (ppm)')

```

```
plt.savefig('CH4_counts_S1_ResidualsDistribution_ppm', dpi=300)

plt.show()
```

```
# =====
# MODEL APPLICATION - calibration of field data, RENAZZO example
# =====

# 1. Upload the dataset that you want to calibrate
calib_file_path = "/Volumes/SANDISK/INGV/RENAZZO/Centraline
gas/20241030_20241121/RNN/centr1_dati_medie_1min.csv" #remember to change the
directory!
calib_data = pd.read_csv(calib_file_path)
calib_data["date"] = pd.to_datetime(calib_data["date"], format="%Y-%m-%d %H:%M:%S")
calib_data.info()

# 2. Conversion to float32
calib_data['RH'] = calib_data['RH'].astype(np.float32)
calib_data['T'] = calib_data['T'].astype(np.float32)
calib_data['CH4.counts'] = calib_data['CH4.counts'].astype(np.float32)
calib_data.info()

# 3. Pre-processing (uploads the saved scalers)
scaler_standard = joblib.load('scaler_standard.joblib')
scaler_standard_ch4 = joblib.load('scaler_standard_ch4.joblib')
calib_data[['RH', 'T', 'CH4.counts']] = scaler_standard.transform(calib_data[['RH',
'T', 'CH4.counts']])

# 4. Calibration
# Uploads the saved model
input_columns = ['RH', 'T', 'CH4.counts']
model_calib = load_model('model_counts_C1.keras')
y_calib = model_calib.predict(calib_data[input_columns]).flatten()

# 5. Reversing standardisation and logarithmic transformation
mean_CH4 = scaler_standard_ch4.mean_[0]
std_CH4 = scaler_standard_ch4.scale_[0]
y_calib_standard = (y_calib * std_CH4) + mean_CH4
y_calib_original = np.exp(1/y_calib_standard)

# 6. Displaying and saving results
plt.figure(figsize=(12, 6))
plt.plot(calib_data['date'], y_calib_original)
plt.savefig('CH4_counts_C1_REN.png', dpi=300)
plt.show()

# 7. Exporting calibrated data files
results = pd.DataFrame({'date': calib_data['date'], 'CH4_calibrated':
y_calib_original})
results.to_csv('CH4_counts_REN_C1.csv', index=False)
print("Calibration completed. Results saved as CH4_counts_REN_C1.csv") # Pay attention
to filename/station number
```

### Training Dataset lookalike

| date                | RH   | T    | CH4.counts | CH4  |
|---------------------|------|------|------------|------|
| 2024-07-12 13:24:00 | 51.1 | 31.6 | 55.5       | 2.02 |
| 2024-07-12 13:25:00 | 51.3 | 31.6 | 55.5       | 2.02 |
| 2024-07-12 13:26:00 | 51.2 | 31.6 | 55.7       | 2.02 |
| 2024-07-12 13:27:00 | 51.1 | 31.6 | 55.7       | 2.03 |
| 2024-07-12 13:28:00 | 51.2 | 31.7 | 55.5       | 2.02 |
| 2024-07-12 13:29:00 | 51.0 | 31.7 | 55.0       | 2.02 |

### Calibration dataset lookalike

| date                | RH   | T    | CH4.counts |
|---------------------|------|------|------------|
| 2024-10-30 12:27:00 | 58.2 | 29.6 | 74.25      |
| 2024-10-30 12:28:00 | 58.2 | 29.6 | 136.3      |
| 2024-10-30 12:29:00 | 58.5 | 29.7 | 149.7      |
| 2024-10-30 12:30:00 | 58.8 | 29.8 | 157.0      |
| 2024-10-30 12:31:00 | 57.1 | 29.8 | 112.3      |
| 2024-10-30 12:32:00 | 56.5 | 29.8 | 117.0      |
| 2024-10-30 12:33:00 | 56.9 | 29.8 | 85.5       |

Appendix A.6 Burst selections (start times and durations) and mean concentration of plateau pre and post for CH<sub>4</sub> fluxes.

| acq_id | date     | burst_start_s | burst_dt_s | pre_mean_p<br>pm | post_mean_p<br>pm | $\Delta$ _ppm | left_s | right<br>s | m_i_g  |
|--------|----------|---------------|------------|------------------|-------------------|---------------|--------|------------|--------|
| NIR1   | 06/06/23 | 31            | 14         | 4.3              | 44.9              | 40.6          | 31     | 627        | 0.005  |
| NIR1   | 06/06/23 | 60            | 14         | 46.0             | 51.9              | 5.9           | 31     | 627        | 0.001  |
| NIR1   | 06/06/23 | 181           | 25         | 49.1             | 68.3              | 19.2          | 31     | 627        | 0.002  |
| NIR1   | 06/06/23 | 215           | 7          | 67.4             | 68.0              | 0.6           | 31     | 627        | 0.000  |
| NIR1   | 06/06/23 | 312           | 9          | 70.1             | 85.4              | 15.2          | 31     | 627        | 0.002  |
| NIR1   | 06/06/23 | 458           | 21         | 87.4             | 99.9              | 12.5          | 31     | 627        | 0.001  |
| NIR1   | 06/06/23 | 608           | 19         | 105.3            | 119.1             | 13.8          | 31     | 627        | 0.002  |
| NIR2   | 06/06/23 | 8             | 6          | 124.2            | 126.6             | 2.5           | 8      | 241        | 0.0003 |
| NIR2   | 06/06/23 | 32            | 7          | 126.6            | 129.0             | 2.3           | 8      | 241        | 0.0003 |
| NIR2   | 06/06/23 | 66            | 15         | 129.7            | 133.8             | 4.1           | 8      | 241        | 0.0005 |
| NIR2   | 06/06/23 | 180           | 13         | 136.3            | 155.6             | 19.3          | 8      | 241        | 0.0022 |
| NIR2   | 06/06/23 | 231           | 10         | 152.1            |                   |               | 8      | 241        |        |
| NIR3   | 06/07/23 | 24            | 14         | 2.5              | 712.7             | 710.3         | 24     | 355        | 0.082  |
| NIR3   | 06/07/23 | 71            | 10         | 735.7            | 1137.3            | 401.6         | 24     | 355        | 0.046  |
| NIR3   | 06/07/23 | 254           | 14         | 1137.3           | 1479.5            | 342.3         | 24     | 355        | 0.040  |
| NIR3   | 06/07/23 | 326           | 29         | 1423.5           | 1560.8            | 137.4         | 24     | 355        | 0.016  |
| NIR3   | 06/07/23 | 18            | 16         | 429.9            | 451.2             | 21.3          | 18     | 261        | 0.007  |
| NIR4   | 06/07/23 | 46            | 5          | 43.1             | 4213.4            | 4170.3        | 46     | 120        | 0.491  |
| NIR4   | 06/07/23 | 74            | 5          | 5084.3           | 13363.9           | 8279.7        | 46     | 120        | 0.975  |
| NIR4   | 06/07/23 | 88            | 6          | 11396.4          | 15206.7           | 3810.3        | 46     | 120        | 0.449  |
| NIR4   | 06/07/23 | 105           | 15         | 16511.5          | 21697.9           | 5186.4        | 46     | 120        | 0.611  |
| NIR5   | 06/07/23 | 61            | 22         | 67.7             | 4755.8            | 4688.1        | 61     | 256        | 0.551  |
| NIR5   | 06/07/23 | 93            | 3          | 4128.3           | 5648.6            | 1520.3        | 61     | 256        | 0.179  |
| NIR5   | 06/07/23 | 112           | 10         | 5517.4           | 8222.2            | 2704.8        | 61     | 256        | 0.318  |
| NIR5   | 06/07/23 | 211           | 16         | 9167.5           | 15327.2           | 6159.7        | 61     | 256        | 0.723  |
| NIR5   | 06/07/23 | 252           | 4          | 15605.8          | 16908.7           | 1302.9        | 61     | 256        | 0.153  |
| NIR6   | 06/07/23 | 70            | 6          | 1551.0           | 3611.2            | 2060.1        | 70     | 322        | 0.242  |
| NIR6   | 06/07/23 | 108           | 9          | 2937.4           | 9958.9            | 7021.5        | 70     | 322        | 0.825  |
| NIR6   | 06/07/23 | 158           | 6          | 10994.3          | 13756.7           | 2762.5        | 70     | 322        | 0.324  |
| NIR6   | 06/07/23 | 297           | 4          | 13770.0          | 16100.3           | 2330.3        | 70     | 322        | 0.274  |
| NIR6   | 06/07/23 | 309           | 13         | 14864.2          | 21730.5           | 6866.3        | 70     | 322        | 0.806  |
| NIR7   | 06/07/23 | 52            | 8          | 28.8             | 1974.3            | 1945.5        | 52     | 168        | 0.227  |
| NIR7   | 06/07/23 | 99            | 7          | 2131.9           | 4298.6            | 2166.7        | 52     | 168        | 0.253  |
| NIR7   | 06/07/23 | 162           | 6          | 4615.9           | 5770.0            | 1154.1        | 52     | 168        | 0.135  |
| NIR8   | 06/07/23 | 51            | 7          | 37.3             | 1458.5            | 1421.1        | 51     | 275        | 0.166  |
| NIR8   | 06/07/23 | 121           | 6          | 1616.4           | 4103.3            | 2486.9        | 51     | 275        | 0.291  |
| NIR8   | 06/07/23 | 136           | 3          | 2976.8           | 4361.6            | 1384.8        | 51     | 275        | 0.162  |
| NIR8   | 06/07/23 | 154           | 8          | 4722.9           | 4899.4            | 176.5         | 51     | 275        | 0.021  |
| NIR8   | 06/07/23 | 194           | 5          | 4930.8           | 6088.5            | 1157.7        | 51     | 275        | 0.135  |
| NIR8   | 06/07/23 | 271           | 4          | 7098.9           | 9031.4            | 1932.6        | 51     | 275        | 0.226  |
| NIR9   | 06/07/23 | 189           | 2          | 2414.9           | 9432.4            | 7017.5        | 189    | 428        | 0.819  |
| NIR9   | 06/07/23 | 378           | 5          | 10867.1          | 13557.3           | 2690.2        | 189    | 428        | 0.314  |
| NIR9   | 06/07/23 | 418           | 10         | 13457.4          | 27887.4           | 14430.0       | 189    | 428        | 1.684  |
| NIR10  | 08/01/23 | 23            | 6          | 36.0             | 248.1             | 212.1         | 23     | 64         | 0.024  |
| NIR10  | 08/01/23 | 59            | 5          | 26.2             | 196.7             | 170.5         | 23     | 64         | 0.019  |
| NIR11  | 08/01/23 | 25            | 4          | 48.2             | 1942.7            | 1894.5        | 25     | 181        | 0.216  |
| NIR11  | 08/01/23 | 47            | 3          | 1943.5           | 5350.4            | 3406.9        | 25     | 181        | 0.389  |
| NIR11  | 08/01/23 | 56            | 4          | 3010.0           | 6660.2            | 3650.3        | 25     | 181        | 0.417  |
| NIR11  | 08/01/23 | 81            | 13         | 6887.0           | 13820.9           | 6933.9        | 25     | 181        | 0.792  |
| NIR11  | 08/01/23 | 170           | 11         | 16888.0          | 18854.5           | 1966.5        | 25     | 181        | 0.225  |
| NIR12  | 08/01/23 | 108           | 10         | 9977.0           | 11341.0           | 1364.0        | 108    | 118        | 0.156  |
| NIR13  | 08/01/23 | 125           | 11         | 596.1            | 8035.9            | 7439.8        | 125    | 239        | 0.848  |
| NIR13  | 08/01/23 | 136           | 7          | 689.7            | 6614.9            | 5925.2        | 125    | 239        | 0.675  |
| NIR13  | 08/01/23 | 173           | 9          | 5965.8           | 8217.9            | 2252.1        | 125    | 239        | 0.257  |

|       |          |     |    |         |         |        |     |     |       |
|-------|----------|-----|----|---------|---------|--------|-----|-----|-------|
| NIR13 | 08/01/23 | 221 | 18 | 8383.1  | 12360.1 | 3977.0 | 125 | 239 | 0.453 |
| NIR14 | 08/01/23 | 235 | 7  | 2899.2  | 8322.1  | 5422.9 | 235 | 401 | 0.617 |
| NIR14 | 08/01/23 | 247 | 8  | 4345.7  | 8977.8  | 4632.0 | 235 | 401 | 0.527 |
| NIR14 | 08/01/23 | 296 | 14 | 8483.3  | 13731.7 | 5248.4 | 235 | 401 | 0.597 |
| NIR14 | 08/01/23 | 335 | 5  | 13712.1 | 13470.1 | -242.0 | 235 | 401 |       |
| NIR14 | 08/01/23 | 393 | 8  | 13718.9 | 19506.8 | 5787.9 | 235 | 401 | 0.658 |

Appendix A.7. Burst selections (start times and durations) and mean concentration of plateau pre and post for CO<sub>2</sub> fluxes.

| acq_id | date     | burst_start_s | burst_dt_s | pre_mean_p<br>pm | post_mean_p<br>pm | $\Delta$ _ppm | left_s | right_s | m_i_g |
|--------|----------|---------------|------------|------------------|-------------------|---------------|--------|---------|-------|
| NIR1   | 06/06/23 | 30            | 14         | 417.0            | 425.8             | 8.8           | 30     | 608     | 0.003 |
| NIR1   | 06/06/23 | 45            | 259        | 419.5            | 449.4             | 29.8          | 30     | 608     | 0.009 |
| NIR1   | 06/06/23 | 383           | 225        | 450.4            | 460.1             | 9.7           | 30     | 608     | 0.003 |
| NIR2   | 06/06/23 | 13            | 87         | 460.2            | 467.5             | 7.3           | 13     | 100     | 0.002 |
| NIR3   | 06/07/23 | 65            | 25         | 451.7            | 459.3             | 7.6           | 18     | 261     | 0.002 |
| NIR3   | 06/07/23 | 253           | 8          | 467.9            | 474.1             | 6.2           | 18     | 261     | 0.002 |
| NIR4   | 06/07/23 | 46            | 8          | 440.8            | 461.1             | 20.3          | 46     | 120     | 0.007 |
| NIR4   | 06/07/23 | 74            | 5          | 462.4            | 507.9             | 45.5          | 46     | 120     | 0.015 |
| NIR4   | 06/07/23 | 88            | 6          | 496.6            | 533.9             | 37.3          | 46     | 120     | 0.012 |
| NIR4   | 06/07/23 | 105           | 15         | 525.6            | 554.6             | 29.0          | 46     | 120     | 0.009 |
| NIR5   | 06/07/23 | 61            | 17         | 513.6            | 541.3             | 27.6          | 61     | 223     | 0.009 |
| NIR5   | 06/07/23 | 112           | 10         | 547.7            | 564.4             | 16.7          | 61     | 223     | 0.005 |
| NIR5   | 06/07/23 | 214           | 9          | 576.2            | 613.5             | 37.3          | 61     | 223     | 0.012 |
| NIR6   | 06/07/23 | 108           | 8          | 463.1            | 496.9             | 33.8          | 108    | 322     | 0.011 |
| NIR6   | 06/07/23 | 297           | 4          | 525.5            | 540.8             | 15.3          | 108    | 322     | 0.005 |
| NIR6   | 06/07/23 | 309           | 13         | 533.4            | 577.5             | 44.2          | 108    | 322     | 0.014 |
| NIR7   | 06/07/23 | 52            | 8          | 430.9            | 443.3             | 12.4          | 52     | 168     | 0.004 |
| NIR7   | 06/07/23 | 99            | 7          | 445.8            | 458.0             | 12.2          | 52     | 168     | 0.004 |
| NIR7   | 06/07/23 | 162           | 6          | 462.4            | 471.2             | 8.8           | 52     | 168     | 0.003 |
| NIR8   | 06/07/23 | 49            | 8          | 428.1            | 437.8             | 9.7           | 49     | 275     | 0.003 |
| NIR8   | 06/07/23 | 121           | 6          | 441.5            | 461.7             | 20.2          | 49     | 275     | 0.006 |
| NIR8   | 06/07/23 | 136           | 3          | 453.9            | 461.2             | 7.3           | 49     | 275     | 0.002 |
| NIR8   | 06/07/23 | 154           | 8          | 463.6            | 467.2             | 3.5           | 49     | 275     | 0.001 |
| NIR8   | 06/07/23 | 194           | 5          | 467.8            | 476.7             | 8.9           | 49     | 275     | 0.003 |
| NIR8   | 06/07/23 | 271           | 4          | 488.0            | 501.7             | 13.7          | 49     | 275     | 0.004 |
| NIR9   | 06/07/23 | 189           | 10         | 451.2            | 504.2             | 52.9          | 189    | 428     | 0.017 |
| NIR9   | 06/07/23 | 378           | 5          | 523.9            | 480.0             | -43.9         | 189    | 428     |       |
| NIR9   | 06/07/23 | 418           | 10         | 548.0            | 666.5             | 118.5         | 189    | 428     | 0.038 |
| NIR11  | 08/01/23 | 23            | 4          | 436.1            | 448.9             | 12.8          | 23     | 181     | 0.004 |
| NIR11  | 08/01/23 | 47            | 3          | 448.7            | 473.0             | 24.3          | 23     | 181     | 0.008 |
| NIR11  | 08/01/23 | 56            | 4          | 458.4            | 479.3             | 20.9          | 23     | 181     | 0.007 |
| NIR11  | 08/01/23 | 81            | 13         | 480.9            | 518.1             | 37.2          | 23     | 181     | 0.012 |
| NIR11  | 08/01/23 | 170           | 11         | 539.6            | 555.1             | 15.5          | 23     | 181     | 0.005 |
| NIR12  | 08/01/23 | 29            | 210        | 435.9            | 508.7             | 72.9          | 29     | 239     | 0.023 |
| NIR13  | 08/01/23 | 125           | 11         | 437.1            | 476.0             | 38.9          | 125    | 239     | 0.012 |
| NIR13  | 08/01/23 | 136           | 7          | 436.8            | 466.8             | 30.0          | 125    | 239     | 0.009 |
| NIR13  | 08/01/23 | 221           | 18         | 488.8            | 511.4             | 22.5          | 125    | 239     | 0.007 |
| NIR14  | 08/01/23 | 235           | 7          | 448.7            | 480.2             | 31.5          | 235    | 401     | 0.010 |
| NIR14  | 08/01/23 | 247           | 8          | 461.1            | 484.6             | 23.5          | 235    | 401     | 0.007 |
| NIR14  | 08/01/23 | 296           | 14         | 481.9            | 520.1             | 38.2          | 235    | 401     | 0.012 |
| NIR14  | 08/01/23 | 394           | 7          | 520.7            | 557.1             | 36.4          | 235    | 401     | 0.011 |

