

Metrology and Monitoring of Gases Transfer (CO and CH) Processes within the System of Geosphere and Biosphere

Didi Adisaputro

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Par Didi ADISAPUTRO

Metrology and Monitoring of Gases Transfer (CO₂ and CH₄) Processes within the System of Geosphere and Biosphere

Sous la direction du Philippe de DONATO et du Laurent Saint ANDRE

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Rapporteurs :

Bernard LONGDOZ- Professeur - Université de Liège, Belgique.Didier BONIJOLY- Ingénieur, Expert Indépendant

Présidente: :

Marie Odile SIMONNOT - Professeur- EMPP, Nancy, France

Examinateurs:

Eric GAUCHER	- Docteur -Universität Bern, Switzerland
Catherine Galy	- Dr, Ingénieur – ANDRA, Bure, France
Philippe de DONATO	- Directeur de Rechercher, CNRS, Nancy, France
Laurent Saint ANDRE	- Directeur de Recherche - INRAE, Nancy, France

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List of Abbreviations and Symbols

ANOVA	Analysis of Variance
CRDS	Cavity Ring-Down Spectroscopy
CH ₄	Methane
CO_2	Carbon Dioxide
EC	Eddy Covariance
FTIR	Fourier Transform Infrared
GC	Gas Chromatography
GPP	Gross Primary Productivity
H ₂ O	Water
N_2	Nitrogen
NEE	Net Ecosystem Exchange
PCA	Principal Component Analysis
Reco	Ecosystem Respiration
Rg	Global Radiation
SOM	Soil Organic Matter
SWC	Soil Water Content
Та	Air Temperature
Tsoil	Soil Temperature
u*	Friction Velocity
VPD	Vapor Pressure Deficit
χc	CO ₂ mole fraction

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Résumé

Ce travail de recherche s'inscrit dans le prolongement de différentes études conduites notamment dans le cadre du pilote de Capture Transport et Stockage du CO₂ (pilote Total CCS, Lacq- Rousse, France) relatives au suivi des mécanismes de transfert des gaz (CO2 et CH4) dans les compartiments Géosphère/Biosphère/Atmosphère. De ces études, il était ressorti que l'évolution de la fraction molaire de CO₂ (xc) dans le sous-sol karstique du plateau du Jurançon était négativement corrélée aux battements de la nappe phréatique située à -45m via des mécanismes de dissolution/dégazage. Cependant, il n'est pas encore clair si cette relation existe dans l'écosystème forestier, qui représente importante de l'échange de CO_2 atmosphérique. Dans ce contexte, cette thèse se concentre sur la surveillance des échanges gazeux et de leurs processus de transport au sein de la zone critique, entre le sous-sol (-6 m), le sol (-1 m) et le couvert végétal (+50m). Nous avons développé et mis en place un système de surveillance géochimique in situ en puits dédiés pour le suivi continu de la fraction molaire de CO₂ dans le sous-sol et le sol couplé à un système de surveillance micrométéorologique utilisant une tour de flux préétablie dans l'écosystème forestier (Montiers, Région Lorraine, France). Au cours des périodes d'étude allant de Juin 2018 à Décembre 2020, l'écosystème a agi comme un puits de carbone net avec une moyenne annuelle des paramètres d'échange d'écosystème net (NEE), de productivité primaire brute (GPP) et de respiration de l'écosystème (Reco) de -453±122 gC m-2y-1, -1468 ±109 gC m-2y-1, et 1052 ±88 gC m-2y-1 respectivement. L'échange de carbone, les données météorologiques et les facteurs environnementaux durant les épisodes de sécheresse ont été comparés aux données de référence à long terme enregistrées durant les années allant de 2014 à 2017. Contrairement à certaines recherches précédentes où les paramètres NEE et Reco ont diminué parallèlement pendant les épisodes de sécheresse, les données enregistrées sur site ont montré que le paramètre Reco est plus sensible à la sécheresse que le paramètre NEE, ce qui a entraîné une augmentation significative de l'échange net au sein de l'écosystème. Ainsi, durant les périodes de séchesses d'été et d'automne (2018-2019), le paramètre de respiration de l'écosystèem (Reco) a diminué de 20 %, et 26 % par rapport aux années de référence (2014-2017). Les traitement statistique des données comparées sous-sol/sol/couvert végétal, montre des preuves empiriques solides que la turbulence du vent, mesurée au travers du paramètre de vitesse de frottement (u*) joue un rôle important dans la variabilité des concentrations de CO_2 dans les sols même jusqu'à des profondeurs de -6m, ce qui n'avait jamais été établi. Nous supposons que cela pourrait être dû aux effets de pompage de la pression qui diminue la fraction molaire de CO2 dans le sol lors de fortes turbulences et augmente le stockage du CO2 dans les sols profonds lors de faibles turbulences. Cette étude a aussi démontre le rôle de l'hydromètrie du sol sur ces processus d'échanges. En effet, en périodes humides, la perméabilité est considérablement réduite ce qui diminue la diffusion et l'advection moléculaires.

Cette étude a également révélé une forte influence biotique sur la production de CO_2 . Les valeurs de $\delta^{13}C_{CO2}$ dans le sous-sol de notre site peuvent être attribuées à la respiration et à la décomposition des plantes en C3. Ces origines biologiques du CO_2 du sol entraine très probablement des augmentations de la densité de l'air ce qui conduit à faire migrer le CO_2 stocké vers les couches plus profondes du sol par le biais d'un mécanisme de percolation gravitationnelle. La relation des gaz du sous-sol souligne également que les composants biogéniques dominent les origines et le processus de contrôle du CO_2 du sous-sol alors que le processus géochimique joue un rôle insignifiant.

Mots-clés : Surveillance géochimique des gaz, CO₂, NEE, Vitesse de frottement, Hétérotrophe.

Abstract

This study is a continuation of our previous geochemical monitoring finding at the injection wells of Rousse 1 (Total CCS pilot, Lacq- Rousse, France) where it was identified that the soil CO₂ mole fraction (χc) evolution in subsoil was negatively correlated with the level of the water table and the CO₂ sources were attributed to the CO₂-rich aquifers. However, it is still unclear whether this relationship exists in the forest ecosystem, representing a significant proportion of the CO₂ atmospheric budget. For this reason, this thesis focuses on monitoring the gas exchange and its main driver of the transport process between soil (-1 m), subsoil (-6 m), and biosphere. We developed and implemented an in-situ geochemical monitoring system for continuous monitoring of CO₂ mole fraction in the subsoil coupled with a micrometeorological monitoring system using a pre-established flux tower in the forest Ecosystem (Montiers, Lorraine Region, France). This soil gas measurement infrastructure combining borehole measurement with micrometeorological measurement offers great possibilities for long-term in-situ and continuous gas monitoring to derive the vertical distribution of CO_2 . Thus, this infrastructure allowed the observation of the temporal dynamics in soil-gas CO₂ research. During the study periods, the ecosystem acted as a net carbon sink with a mean annual NEE, GPP, and Reco of -453±122 gC m-2y-1, -1468 ±109 gC m-2y-1, and 1052 ±88 gC m-2y-1 consecutively. The Carbon exchange, climate, and environmental drivers during the drought episodes were compared with long-term reference data recorded from 2014 to 2017. In contrast with some previous research where GPP and Reco parallelly decreased during the drought episodes, our site showed Reco is more sensitive to drought than GPP, resulting in a significant increase in Net Ecosystem exchange. Reco decreased by 20%, and 26% were found in Summer and Autumn (2018-2019) relative to the reference years (2014-2017). This study shows strong empirical shreds of evidence that wind turbulence plays a significant role in driving the deep soil CO₂ concentration. We hypothesize that this could be due to pressure pumping effects where it decreases the CO₂ molar fraction in the soil during high turbulence and increases the CO₂ storage in deep soil during low turbulence. This study also demonstrates that permeability significantly reduced during wet periods diminishing molecular diffusion and advection. This study also revealed a strong biotic influence on CO₂ production. The $\delta^{13}C_{CO2}$ values in our site subsoil can be attributed to the respiration and decomposition of the C3 plants. These biological origins of soil CO_2 are highly likely to increase air density resulting in gravitational percolation that leads the CO_2 stored in a deeper layer of soil. The relationship of subsoil gases also emphasizes that biogenic components dominate the origins and controlling process of subsoil CO_2 while the geochemical process plays an insignificant role.

Keywords: Geochemical Gas Monitoring, CO₂, NEE, Friction velocity, Heterotroph.

Chapter 1: General Introduction

1.1. Global Carbon cycle

Intergovernmental Panel on Climate Change (IPCC), along with more than 200 countries, has agreed to limit the global temperature rise below 2 °C during a COP21 meeting in France 2015. To achieve this goal, the two greenhouse gasses of CO₂ and CH₄ have become a significant concern. CO₂ consists of the triatomic molecule in a linear structure, including carbon and oxygen atom, which has a positive charge of +0.592 and a negative charge of -0,296, respectively. The vibrational modes that involve bend (667 cm⁻¹, n2 mode) and antisymmetric stretch (2349 cm⁻¹, n3 mode) are the two atomic motions responsible for the greenhouse effects of CO₂ (Styring, Quadrelli and Armstrong, 2014). CO₂ is widely known for its infra-red activity that absorbs and emits infrared radiation. The CO₂ is responsible for nearly 75% of total greenhouse effects than CH₄, NO₂, and f-gaseous combined. Although CO₂ absorbs and traps infrared radiation much lower than the other greenhouse gas previously mentioned, the concentration of CO₂ in the atmosphere is highly abundant. The most recent data of CO₂ measured by the observation of Loa Laboratory Hawaii in 2018 shows the constant increase of monthly mean CO₂ at 408.35 ppm (NOAA ESRL, 2018)

The second most significant contributor to the greenhouse effect is Methane (CH₄), with approximately 16% of total greenhouse effects or total radiative forcing, which is currently measured at 1.7 μ mol mol⁻¹ in the atmosphere (Serrano-Silva *et al.*, 2014; Pratt and Tate, 2018). CH₄ is a tetrahedral molecule that also has two vibrational modes under direct interaction with infrared light. These IR-active vibrational modes are associated with changes in their bond dipole moments and only occur when a change in individual C-O and C-H bond dipoles is undergone (D. Meliga and S. Z. Lavagnino, 2016). CH₄ is one of the most predominant hydrocarbons in the earth's atmosphere. It is 21 times more potent per molecule on a 100-year time horizon regardless of its fewer abundances in the atmosphere (Smeets *et al.*, 2009). The global atmospheric methane (CH₄) almost reaches 1800 ppbv due to the growing net CH₄ is less significant (Tate, 2015). It is widely known that current estimations of any sink and source magnitudes in the CH₄ global budget have been significantly uncertain. Moreover, the scientific controversy over both the direction and the importance of forests and the atmosphere is unavoidable (Smeets *et al.*, 2009).

It is widely known that the increase of CO₂ and CH₄ molar fraction in the atmosphere, causing an increase in the greenhouse effect and the consequent global warming. The rise of the concentration occurs due to the imbalance state of gas exchange between sources and sinks (Sánchez-Cañete, 2013). The carbon gases are exchanged between some reservoirs, including the ocean, atmosphere, lithosphere, and biosphere. Thermogenic sources that include the combustion of fossil fuel, the cement industry, geological and industrial processes represent most of the perturbation of climate change. However, biogenic sources and sinks also play a significant role in the land-atmosphere exchange of these gasses. Land biogenic greenhouse gas (GHG) mainly originated from animals, plants, and microbial communities, which constantly fluctuate, driven by natural and anthropogenic perturbations (Tian *et al.*, 2016).

Carbon is transported at different natural rates of exchange (fluxes), varying from relatively short time scales (photosynthesis) to long time scales (fossil fuels formation) (Sánchez-Cañete, 2013). It is a widely held view that the primary producer fixes the carbon dioxide and further is released into the atmosphere by utilizing the fixed energy. Carbon is also stored in living biomass, sediment, and peat for different lifespans. Besides CO₂, CH₄ is also produced in some anoxic environments (Juutinen, 2004; Kim, 2013). The transfer gas between the terrestrial ecosystem represents a significant proportion of the CO₂ atmospheric budget (Angert et al., 2015). In 2008, it was estimated that more than 350 PgCO₂yr⁻¹ were released from the soil to the atmosphere.

1.2. Scientific Context of the Thesis: DEEPSURF Project

This thesis project is one part of the IMPACT DEEPSURF scientific research program funded by the *Plan d'Investissement d'Avenir (PIA)* and supported by Lorraine Université d'Excellence (LUE) that is also part of I-Site (Initiatives of Science, Innovation, Territories, and Economy). DEEPSURF project gathers around 80 researchers from 12 laboratories of the Université de Lorraine. It also unifies 9 French state-controlled entities of an industrial nature (EPIC) and six local companies. This project aims to answer some significant challenges of the 21st century, mainly related to the energy transition and resources management, by using a scientific and technical approach to fulfill the energy needs while at the same time preserving the water resources and maintaining the biodiversity of the subsoil, soil, and vegetation by enhancing the current knowledge regarding the complex environments and their interactions that can drive the public policy to achieve sustainable development goals. It is also highly relevant to the H2020 issues, the National Low Carbon Strategy (SNBC), the National Research Strategy (SNR), the ANR, and the Regional Strategy (MEP Valley). This thesis mainly focuses on the dynamics of the subsoil, soil, vegetation cover, and atmosphere. The scientific questions will cover the gas transfer between the compartment ranging from the subsoil to the atmosphere. Therefore, it is possible to assess the impact and the associated risks on the ecosystems caused by the land-use changes and understand the economic feasibility and public perception of this spatial planning project.

This research project supports the DEEPSURF project by enhancing our knowledge regarding the environment and its interaction. It is a collaboration project between the University of Lorraine involving various partners, including INRAE (*l'Institut National de Recherche pour l'Agriculture, l'Alimentation et l'Environnement*), ANDRA (*Agence Nationale pour la Gestion des Déchets Radioactifs*) SOLEXPERTS, and INERIS. More specifically, this research project mainly focuses on metrology, monitoring, and modeling of gas transfer of (CO₂ and CH₄) in the compartment of the geosphere and biosphere. This research project is carried out in situ, continues, and deported monitoring of the gas across compartment including subsoil (-6 m), soil (1 m), vegetation cover (up to 40m), and the atmosphere. This project aligns with the DEEPSURF project studying the gas transfer within the critical zone, mainly CH₄ to the future possible extraction of CBM (Coal Bed Methane) in the Lorraine basin by employing a vast geochemical and isotopic database relative to the concentration and flows with the critical zone.

Considering this research project's complexity, the data will be incorporated into the various partners focusing on multidiscipline tasks. As for the University of Lorraine (The laboratory of Georesources), the work focuses on the temporal evolution of CO_2 , and CH_4 concentration and isotopic composition in the aquifers, subsoil, and soil, employing continuous monitoring in dedicated well ranging from 0 to 20 meters depth. The monitoring of the CO_2 and CH_4 flow using the eddy covariance method is conducted with the support of the INRAE and ANDRA. The semi-hourly flows of CO_2 and their variability between the ecosystem and the atmosphere using the eddy covariance (EC) method (Aubinet, Vesala and Papale, 2012b). This approach allows assessing the biosphere carbon balance and its contribution to the wide range of scale from local to global. The specific gas concentration and flow can provide us with the observation column's comprehensive exchange model. This research project's overall result can be used as the baseline for the future exploitation of CBM (Coal Bed Methane) in the Lorraine region. Detection, quantification, and modeling of various gas species in the

biosphere, geosphere, and atmosphere boundary layer are considered some of the most critical elements for monitoring geological storage.

This study is also a continuation of our previous geochemical monitoring finding at the injection wells of Rousse 1 (Total CCS pilot, Lacq- Rousse, France), where it was identified that the soil CO₂ mole fraction (χ c) evolution in subsoil was negatively correlated with the level of the water table and the CO₂ sources were attributed to the CO₂-rich aquifers. However, it is still unclear whether this relationship exists in the forest ecosystem, representing a significant proportion of the CO₂ atmospheric budget. Furthermore, the monitoring site of the field campaign, known as Montiers site, is situated in northeastern France in the Meuse department, representing the soil representative's diversity ranging from calcic and superficial soils to acidic and deep soil there are homogenous and mature beech trees grow. Further detail related to the geochemical characteristics and the site's vegetation cover is provided in **Chapter 3**.

1.3. Aims of the thesis

Understanding the gas exchange between terrestrial ecosystems and the atmosphere requires robust long-term measurements at various temporal scales. This research aims to understand the complex interaction of the geosphere, biosphere, and atmosphere regarding the gas exchange between those compartments, mainly CO₂ and CH₄. Therefore, the overall result of this research project can be used as the baseline of the future exploitation of CBM (Coal Bed Methane) or the monitoring of geological storage sites. To achieve those aims, four specific objectives need to be executed as follows.

- 1. To develop and field test the subsoil gas monitoring system.
- 2. To continuously measure the soil gas concentration and auxiliaries data and define gas exchange's main physical drivers in a deep soil layer (-6 m).
- To quantify interannual variability of the Net Ecosystem Exchange over contrasting climatic conditions and management practice and determine the variability's main driving factors.
- 4. To determine the subsoil CO₂ storage dynamics compared to the ecosystem respiration and estimate the CO₂ and CH₄ origins based on depth-dependent and seasonal variation.

1.4. Chapters Structure

This doctoral thesis is divided into five main chapters.

Chapter 1 has provided a general introduction and the literature review about Greenhouse gasses dynamic and measurement in the soil, mainly CO_2 and CH_4 . An accurate and precise measurement technique of the subsoil CO_2 is fundamental to better understanding better the gas transfer process between the geosphere, biosphere, and atmosphere.

Chapter 2 has explained the metrological experiment starting with the basic knowledge of gas analyzers along with calibration technique and laboratory cross-validation.

Chapter 3 (wells measurements) is mainly devoted to measurements of gases in dedicated wells while emphasizing the importance of the soil zone and above the water table. It is marginally influenced by the atmospheric conditions and has been widely applied to create a CO_2 baseline for a wide range of geological storage applications. This study shows strong empirical evidence that wind turbulence plays a significant role in driving deep soil CO_2 concentration. We hypothesize that this could be due to pressure pumping effects where it decreases the CO_2 molar fraction in the soil during high turbulence and increases the CO_2 storage in deep soil during low turbulence. This study also demonstrates that permeability is significantly reduced during wet periods diminishing the non-diffusive transport process. Part of this chapter was published in Applied Science, (*Appl. Sci. 2021, 11, 1753. https://doi.org/10.3390/app11041753*)

To better understand long-term carbon balance in our monitoring site, in **Chapter 4** (eddy covariance measurements), long-term (six years) eddy covariance measurements of carbon and water fluxes under contrasting management practice, and climatic conditions are provided. In contrast with most EC sites in Central and Northern Europe, GPP (Gross Primary Productivity) and Reco (Ecosystem Respiration) concurrently declined. Our site increased its carbon sink capacity during the drought episode, demonstrating an overall decrease in NEE (Net Ecosystem Exchange),

Having determined the effects of soil ventilation and NEE variation and characterizing their driving variables, there is a strong need to define soil gas origins. **Chapter 5 (Borehole-EC Measurement)**. This study provides strong empirical evidence that subsoil ventilation significantly contributed to the NEE. This study also revealed a substantial biotic influence on

 CO_2 production. The $\delta 13C_{CO2}$ and soil gases ratio values in our site subsoil can be attributed to respiration and decomposition of the C3 plants. These biological origins of soil CO_2 are highly likely to increase air density resulting in gravitational percolation that leads the CO_2 stored in a deeper layer of soil.

Chapter 6 is based on a cross-comparison and interpretation of all the recorded data, providing a general synthesis and a comprehensive outlook regarding this research project's overall results.

1.5. CO₂ and CH₄ Dynamic in Critical Zone

One of the most essential zones determining the gas exchange rate is called the critical zone, where a holistic framework integrates the studies of air, soil, rock, water, and biological sources in the near-surface of the terrestrial ecosystem. These permeable layers represent complex and heterogeneous processes from the top of the tree to the aquifers' bottom (Lin, 2010). The gas exchange within a critical zone represents a significant part of the CH₄ and CO₂ atmospheric budget. The figure below describes the process involved in the CO₂ transfer process.



Fig 1. (A) The schematic processes diagram of soil gas CO_2 in a critical zone (Hasenmueller *et al.*, 2015) and (B) CO_2 and CH₄ production and consumption in soil (Dalal and Allen, 2008).

Fig 1 demonstrates that various processes are driving the soil atmosphere pCO_2 , which includes i) The production of CO_2 by the soil microbes, ii) The diffusion of the CO_2 downward to the groundwater or upward to the atmosphere, iii) the mineral dissolution causing the CO_2 degassing or drawdown to pore-fluids, iv) advection of DIC (Dissolved Organic Carbon) containing fluid out or into the system, v) advection of the carbon dioxide into air-filled soil pore spaces. Soil pCO2 distribution was also found to be varied predictably with the topographic position.

The CO₂ efflux (F_{soil}) commonly refers to soil respiration (Rs) from the surface of the soil to the atmosphere, which may come from multiple sources, including respiration of the root system (Rr), respiration of the soil fauna, and CO₂ production from non-biological source (Rn). Although both terms, Fsoil and Rs, are used interchangeably, several findings have challenged this assumption. Some argued that respired CO₂ might be dissolved in soil solutions (Xu and Shang, 2016; Sánchez-Cañete, Barron-Gafford, and Chorover, 2018). The high soil pCO_2 was found in a wet and deep level in swale slopes and valleys. Meanwhile, the low level of soil pCO_2 was found in dry and shallow levels in planar slopes and ridges (Hasenmueller *et al.*, 2015).

The CO₂ gas exchange can be categorized into three types consisted of (i) soil respiration, which includes root and microbial respiration, (ii) ecosystem respiration involving aboveground plant respiration, and (iii) Net Ecosystem Exchange [NEE], which is the differences between photosynthesis and ecosystem respiration where the positive values reveal the soil as a source and negative value indicate a CO₂ sink. As for methane, it is naturally originated from microorganisms belonging to the domain archaea when anoxic microsites are formed. Methanotrophy (oxidation of CH₄) and methanogenesis (production of CH₄) are two biogenic processes driving the concentration, especially in the soil compartment (Oertel *et al.*, 2016). Three main possible transport mechanisms rule temporal and spatial variations of CH₄ along the concentration gradient, ii) the release due to ebullition (CH₄ contained in the bubbles), iii) plant mediated-transport. Meanwhile, the CH₄ originating from anthropogenic sources results from agriculture, waste, energy, and industrial activity (Serrano-Silva *et al.*, 2014).

1.5.1. Humidity

The anaerobic condition is strictly required by the CH₄ producing bacteria, which correlate positively with the soil's water content. Besides, the soil acts as a sink of CH₄ during this aerobic condition (Smith *et al.*, 2003; Gao *et al.*, 2015; Oertel *et al.*, 2016). The soil organic matters strongly affect the moisture content that further has a proportional effect on soil CH₄ oxidation and its retention in the soil. The activity of the methanotrophs is affected by the moisture content by controlling the diffusion of the gas in and through the soil (Hiltbrunner *et al.*, 2012; Tate, 2015). The distribution of grain size in the soil also affects the amount of moisture occupied in the soil.

Moreover, the emission of the gasses produced aerobically is fostered when the soil has a high proportion of large pores that retain less water and more oxygen (Van Der Weerden, De Klein and Kelliher, 2010). Meanwhile, The CH₄ formation emitted during anaerobic conditions is more extensive in the soil whose dominant fine pore (Dutaur and Verchot, 2007). It also promotes the N₂O formation during a similar anaerobic condition (Gu *et al.*,

2013). During the warm period, the Lower CO_2 emission was identified in the sandy soils compared with the fine-textured soils (Dilustro *et al.*, 2005).

The higher soil emission was found in the unstable soil aggregates because C and N are more available for soil microbes (Kögel-Knabner *et al.*, 2010). Precipitation contributes to the evolution of gas emission from the soil, also known as the Birch effect (Birch, 1958). Driven by the availability of readily decomposable material and renewed mineralization, the soil emission rises within minutes or hours of precipitation. Within the next few days, the level of emission returns to the baseline (Ludwig *et al.*, 2001; Borken and Matzner, 2009). Nonetheless, this Birch effect decrease as it has a more intensive wet-dry cycle (Borken and Matzner, 2009). The decomposition of the soil organic matter has been widely reported to be influenced by high solar radiation. Also known as the photodegradation process, ultraviolet light stimulates a direct breakdown of organic matter to CO_2 occurs mainly during the low moisture season (Brandt, Bonnet, and King, 2009; Yanni, Suddick and Six, 2015)

1.5.2. Temperature

The effect of the soil temperature on the CO_2 outgassing has been calculated since the early 1990s. For instance, Silvola et al., (1996) have concluded that temperature is the most critical factor controlling the outgassing of CO_2 from the soil. Based on the laboratory experiment, Moore and Dalva (1993) found that the CO₂ emission from the peat soil was increased more than doubled when the temperature was increased from 10 to 23 °C. The sensitivity factor of Q10 is widely used to describe the dependency of gas emissions from the soil, both biological and chemical, with the temperature change of 10°C (Berglund, Berglund and Klemedtsson, 2010) as well as an increase of the depth (Tang et al., 2003). The rise of the soil temperature causes higher soil emissions and respiration rates due to the increase of microbial metabolism. Besides, soil respiration rates affecting CH₄ and N₂O emissions are forced by increasing soil temperature, leading to the decrease of O₂ concentration in the soil (Butterbach-Bahl et al., 2013; Oertel et al., 2016). During the field measurement campaign, even though the soil respiration rate showed an exponential increase with the temperature (Tang et al., 2003), it is difficult to distinguish the degree of moisture and temperature contribution due to their overlapping effects (Fang and Moncrieff, 2001). The rates of CH₄ oxidation tend to rise with the soil temperature due to its association with the enzymatic process. The higher exchange of CH₄ at high altitudes is found due to rapid warming. This exchange occurs mainly from a switch between CH₄ oxidation and loss with soil thawing (Serrano-Silva *et al.*, 2014; Tate, 2015). Nonetheless, in less extreme environments, the soil temperature does not play a significant role in controlling CH₄ oxidation

1.5.3. Soil pH Values

The changes in soil bacteria community can be indicated by the pH value changes that are often subject to more intensive management practice, for instance, lime and fertilizer application (Lauber *et al.*, 2008; Tate, 2015). Even though, in general, acidic soil conditions lead to lower soil emission, the optimal pH value to optimize CH₄ production (Methanogenesis) is ranging from a pH value of 4 to 7. In contrast, the oxidation of CH₄ is usually identified over various pH values between 2.5 to 8 (Oertel *et al.*, 2016). However, pH is suspected to be a less crucial controlling variable because, in some studies where most soils exhibit a soil pH's value of 6, the consumption of atmospheric CH₄ is frequently high and observed at various pH values. It is almost certain that over time methanotrophic communities in a different ecosystem can accommodate a broad range of soil pH (Tate, 2015). As for the CO₂, the most massive emission was identified at neutral pH-values (Cuhel *et al.*, 2010; Oertel *et al.*, 2016). Moreover, insignificant correlations were found between the emission of NO and N₂O and pH value (Pilegaard *et al.*, 2006; Oertel *et al.*, 2016)

1.5.4. Nutrients

It is a widely held view that nutrient plays an essential role in the microbial and respiratory process. The sources range from natural N and C available in the soil, atmospheric deposition, and manure or fertilizer (Oertel *et al.*, 2016). The emission of CO₂ and CH₄ are mostly positively correlated with the C/N ratio (Shi *et al.*, 2014). However, the CH₄ production might be decreased in the presence of Fe³⁺, Mn⁴⁺, SO₄^{2-,} and NO³⁻ acting as electron donors, especially in (sub)tropical soils and paddy fields (Oertel *et al.*, 2016). On the contrary, the N₂O emission is negatively correlated with the C/N-ratio (Pilegaard *et al.*, 2006). Generally, the increase of soil N content results in higher soil respiration and higher NEE. Nonetheless, the amount of Carbon (C) is restricted, causing limited influence on soil respiration. The application of N fertilizer also affects the enormous sensitivity on soil respiration relative to the soil moisture and reversal effects again soil temperature (Peng *et al.*, 2011).

1.5.5. Exposure and Air Pressure

The site exposure that may consist of the elevation, morphological position, and the plant cover affects the soil emission indirectly by influencing soil temperature. Besides, the lower air pressure encourages more significant soil emission due to reduced counter-pressure on the soil (Reicosky *et al.*, 2008; Oertel *et al.*, 2016). It is a widely held view that the CO_2 dissolution and ventilation process plays a significant role in storing a large amount of CO_2 for more than 50000 ppm of CO_2 in subsurface cracks, pores, and cavities. Furthermore, it has the most significant effect on limestone and karst soil and can be transferred to the atmosphere. The impact of wind speed and wind gustiness on subsurface gas vertically and horizontally has been simulated experimentally. It is indicated that the gas transport near the wind-exposed surface is considerably affected by wind speed and wind gustiness (Poulsen, Furman, and Liberzon, 2018). However, it is unclear whether this happens on the deep layer of soil (greater than 6 m). Previous research conducted in the CCS Total pilot, Lacq-Rousse, France, on the monitoring and modeling aspects showed that the soil CO_2 concentration at the deep layer of soil was negatively correlated with changes in the piezometric level groundwater in seven seasonal cycles. Specifically, the fluctuation is caused by CO_2 dissolution or release process by the perched water table acting as a pump

1.5.6. Land Use Changes

The land-use change plays a significant role in GHG emissions from the soils, especially when the land covered with the vegetation (forests, grass, peatlands) is converted into agricultural land. 30% to 35% of the soil carbon occupying the top 7 cm of the soil will be lost during the first 30 years after the land-use change (Degryze *et al.*, 2004; Oertel *et al.*, 2016). Land-use changes generally affect the quantity and the quality of the organic matter that further proportionally changes the general population of microbial biomass, including methanotroph communities and smaller methanogen. Typically, the soil organic matter changes also influence soil properties, including water retention and soil fertility. It indirectly affects the methanotroph community's activity and the oxidation of CH₄ (Tate, 2015).

1.5.7. Stand and Plant types

The tree type and vegetation age affect soil respiration. The young spruce forest was found to have the highest soil respiration rate than 10-,15-,31-, and 47-year-old stands (Saiz *et al.*, 2006). The decrease of soil respiration is mainly caused by lower sufficient root biomass as the stand age. However, the lower root respiration decrease is compensated with higher microbial respiration due to the abundance of organic matter (Saiz *et al.*, 2006). Similar results of higher soil respiration in the younger forest were also found for pine stands, fir stands, and poplar plantations. Vegetation is also found to affect CH₄ emission and is positively correlated with net ecosystem productions. The elevated concentrations in the

atmosphere can also affect the concentration of CO_2 in the soil due to higher root mass. The vegetation covers lower the temperature of the soil due to its leaf area and related shade.

Moreover, the soil moisture increases are caused by decreased stomata opening time, promoting N₂O and CH₄ emission (Kim, 2013). Meanwhile, the study on the CH₄ consumption rate in response to the stand type is scarce. Generally, According to 13 studies, tropical forest consumes less CH₄ with $-2.75 \pm 0.42 \mu$ mol CH₄ m² h⁻¹ while the temperate forest was found to be higher at $-3.42 \pm 0.44 \mu$ mol CH₄ m² h⁻¹ (Base on 18 studies) (Dalal and Allen, 2008). Coniferous forest soils demonstrate, on average lower consumption rate compared with deciduous forest soil. Regrowth and fertilized forests show lower CH₄ consumption than undisturbed forests (Oertel *et al.*, 2016).

Plant type consisting of C3 and C4 plants is widely regarded as the most crucial factors affecting the isotopic composition of soil gases, as shown in Fig 2. Isotopic composition is also an essential tool to distinguish the source of CO_2 and CH_4 , whether it is biogenic or inorganic, where the former tends to be isotopically lighter than the former.



Fig 3. Stable carbon isotopes in soil between C3 and C4 pathway due to pedogenic carbonate, respiration, and soil organic matter (Nordt and Holliday, 2017).

C3 plant signature (Calvin cycle) is predominantly produced by warm-season grasses where the δ^{13} C values are ranging from about -35 % to -20 % (Bowling, Pataki and Randerson, 2008) with an average of -13 % (Nordt and Holliday, 2017). C4 plant signature, on the other hand, averages at-27 ‰ (Nordt and Holliday, 2017). Furthermore, a combination of C3 and C4 (Hatch–Slack, -19% to -9%) results in photosynthesis pathway δ^{13} C mean from -27%and -13% (Zhu *et al.*, 2019). Further detail regarding the measurement and analysis method of soil gases isotopic composition is provided in Chapter 5.

1.5.8. Hydrobiogeochemical Processes

Multiple processes are considered as geochemical factors influencing the gas exchanges, including but not limited to.

- a. During the precipitation process in which the carbon dioxide is dissolved in the rainwater, carbonic acid is formed that further is dissolved slowly by rocks and transported to the ocean by the river. It contributes to the CO₂ influx around 0.3 GtCyr⁻¹ and occurs due to corrosive action during the dissolution of the outcropping silicate and carbonate minerals (Beaulieu *et al.*, 2012). The CO₂ is released back to the atmosphere during the metamorphism of limestone at depth in orogenic belts and subduction zone in the relatively long geologic time scale.
- b. In the biomineralization process, some organisms, for instance, fungi, lichens, and cyanobacteria can modify calcite dissolution and precipitation, contributing to the CO₂ gas exchanges. Cailleau, Braissant, and Verrecchia (2004) have also studied the Iroko tree (*Milicia excelsa*) related to its ability to accumulate mineral carbon as calcium carbonate (CaCO₃). Since the carbonate accumulation involves only Ca-carbonate-free and atmospheric CO₂ sources, the system is regarded as a net carbon sink
- c. The erosion processes can indirectly affect the amount of organic carbon in the soil due to the transport of particles by air or water (Boix-Fayos *et al.*, 2009; Wang *et al.*, 2017)
- d. Besides molecular diffusion, the advective CO₂ transport has a great magnitude on the CO₂ gas exchange. The CO₂ penetration of wind into subsoil is possible due to pores, cracks, and cavities in the soil (Sanchez-Cañete *et al.*, 2011a). In addition, dissolved CO₂ from the groundwater can also be discharged to surface water bodies contributing to the terrestrial and atmospheric exchange(Jurado *et al.*, 2018).

1.5.9. Measurement methods for gas exchange

The study related to the gas exchange between the atmosphere and terrestrial ecosystem began in the 1980s by von Caemmerer and Farquhar (1981), focusing on the small covered areas, studying the relationship between photosynthesis and the gas exchange of leaves. This research area further was extended to the regional networks at the end of the 1980s. For instance, Running and Coughlan (1988), have also studied the forest ecosystem's modelizations, called FOREST-BGC, taking into account carbon, water, and nitrogen cycles through a forest ecosystem for regional application. The CO₂ and CH₄ soil emissions can be measured directly in the field and the laboratory (Oertel et al., 2016). The field measurement is preferred since it preserved the biological and physical interaction within the soil. In this context, the most widely used methods are (i) chambers method (soil-air interface) (Angert et al., 2015; Hoffmann et al., 2015; Pokryszka et al., 2017; Sánchez-Cañete, Barron-Gafford and Chorover, 2018), (ii) micro-meteorological eddy covariance method (vegetation interface) (Eder et al., 2015; Barba et al., 2017; Klosterhalfen et al., 2019) and (iii) the gradient method (subterranean gas transport) (Maier and Schack-Kirchner, 2014; Sánchez-ca and Kowalski, 2014; Angert et al., 2015; Phillips et al., 2016; Sánchez-Cañete, Barron-Gafford and Chorover, 2018; Y. Wang et al., 2018). The data produced by these methods are further calculated with empirical and process-oriented models (Oertel et al., 2016). However, each method and stage differs significantly in the scale of applicability, observation scale, assumptions, and limitations (Maier and Schack-Kirchner, 2014). The study continues until now, where carbon exchanges are measured in different ecosystems that primarily rely on the eddy covariance technique (EC) (Sánchez-Cañete, 2013). A more detailed explanation of each technique is explained in Chapters 3 and 4.

Chapter 2: Metrology

Metrology for the in-situ quantitative measurement of CO2 and CH4 concentrations in soil and subsoil.

Didi Adisaputro ^{1,2,3,*}, Philippe De Donato ¹, Laurent Saint-Andre ², Odile Barres ¹, Catherine Galy ⁴, Gilles Nourrisson ², Médéric Piedevache ⁵, and Marion Derrien ⁵

- ¹ GeoRessources Laboratory, Université de Lorraine, CNRS, BP 70239, 54506 Vandœuvre-lès-Nancy, France;
- ² INRAE, UR BEF, Centre de Nancy, 54280 Champenoux, France;
- ³ Institut Teknologi Sumatera, 35365 Way Huwi, Lampung, Indonesia
- ⁴ ANDRA, 55290 Bure, France;
- ⁵ Solexperts France, 17 av de la Forêt de Haye, 54500 Vandoeuvre lès Nancy, France;

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Resume

Il est largement admis qu'une mesure précise et continue du CO₂ du sol et du sous-sol est très importante pour mieux comprendre le processus de transfert de gaz entre la géosphère, la biosphère et l'atmosphère. La mesure des ces concentrations repose avant tout sur une calibration fine en laboratoire, des capteurs utilisés. Pour cela, ce travail décrit une technique d'étalonnage spécifique appliquée en laboratoire pour la mesure quantitative des gaz du soussol à l'aide d'un spectromètre infrarouge portable connecté à une cellule à gaz à faible trajet optique (1 = 5 cm) et à résolution modérée (1 cm-1). Les concentrations de gaz ont été validées de manière croisée en combinant un spectromètre infrarouge portable, une spectroscopie à anneau de cavité, une chromatographie en phase gazeuse et des capteurs NDIR de faible puissance. Les courbes d'étalonnage par spectroscopie infrarouge à transformée de Fourier (FTIRS) du CO₂ ont été établies dans une plage de concentration allant 100 à 60 000 ppm. De la même manière, les courbes d'étalonnage par FTIRS du CH4 ont été établies dans la plage de concentration allant de 50 à 5000 ppm. Dans ces conditions de mesures en faible réolution (Res =1cm⁻¹) les lois de proportionalités entre l'aire d'une bande (A) et sa concentration (C_{CO2}, C_{CH4}) sont du type polynomiales à savoir : C_{CO2}= $-0.0286A^{3} + 4.67A^{2} + 450A - 2.17(R^{2} = 1)$ et CCH4 = $-1.06A^{3} + 39.4A^{2} + 1130A -$ 1.13 ($R^2 = 0.9999$). Même si pendant les mesures de terrain, la concentration de CH₄ a toujours été inférieure à la limite de sensibilité de notre capteur IR (<5 ppm), elle était toujours détectable avec une analyse ex-situ de micro-GC. Le bon accord entre les différentes valeurs de concentration données par les différents capteurs utilisés (FTIRS, Non Dispersive infared Sensor - NDIR, Gas Chromatography - GC et Cavity Ring Down Spectroscopy - CRDS) valide l'utilisation d'un seul capteur IR sur le terrain, limitant ainsi les consommations d'énergie tout en simplifiant le dispositif expérimental. Une telle stratégie de surveillance pour la mesure des gaz offre de grandes possibilités de surveillance à long terme pour dériver la distribution verticale du CO₂ et du CH₄ ainsi que pour aider à créer des données empiriques sur les flux de gaz à partir du sous-sol sur plusieurs cycles saisonniers.

Abstract

It is a widely held view that accurate and continuous measurement of the subsoil CO₂ is fundamental to understand better the gas transfer process between the geosphere, biosphere, and atmosphere. This work describes a specific calibration technique applied in the laboratory for quantitative subsoil gas measurement using a portable infrared spectrometer connected to a gas cell with low path optical (1 = 5 cm) and moderate resolution (1 cm^{-1}) . Gas concentrations were cross-validated by combining portable infrared spectrometer, cavity ringdown spectroscopy, gas chromatography, and low-power NDIR sensors. The FTIR calibration curves of CO₂ have been established in the range of 100 to 60,000 ppm. Similarly, the FTIR calibration curves of CH₄ were created in the range of 50 to 5000 ppm fit a simple polynomial fitting on $C_{CO2} = -0.0286A^3 + 4.67A^2 + 450A - 2.17(R^2 = 1)$ and $C_{CH4} =$ $-1.06A^3 + 39.4A^2 + 1130A - 1.13$ ($R^2 = 0.9999$), where C_{CO2} and C_{CH4 are} the CO₂ and CH₄ concentration and A is a unit area of absorbance band consecutively. Even though CH₄ concentration under 5 ppm was always below the sensibility limit of our IR sensor during the field test, it was still detectable with a micro-GC ex-situ analysis. The excellent agreement of CO₂ concentration derived from FTIR, NDIR, GC, and CRDS justifies using a single IR sensor in the field, resulting in low energy consumption and less complexity. Such a monitoring strategy for gas measurement offers great long-term monitoring possibilities to derive CO₂ and CH₄'s vertical distribution and help create empirical gas fluxes data from the subsoil.

2.1. Fundamental and Instrumental Generalities: Application to Gas Studies

The accurate and continuous measurement of the gas exchange between the geosphere, biosphere, and atmosphere is essential to detect any slight increase of atmospheric CO_2 and CH_4 (Frey *et al.*, 2015). Several factors are known to influence the precision and accuracy of greenhouse gas measurement, including the analyzer's quality, the calibration strategy, and the experimental protocol.

2.1.1. FTIR Spectroscopy (FTIRS)

The term Infrared (IR) refers to electromagnetic radiation that falls in the region spanning from 0.7 μ m to 1000 μ m. The so-called mid-IR that falls in the region between 2.5 μ m to 25 μ m (4000 to 400 cm-1) is considered the most helpful region for analyzing and identifying chemical functional groups (Larkin, 2011). spectroscopy is widely viewed as very reliable in molecular studies for analyzing quantitatively and qualitatively. It can be used for understanding the interaction of IR radiation and samples that can be either solid, liquid, or gas by measuring the frequency and intensity of IR absorption (Maria, 2012; Mitsuo, 2014).

The discovery of interferometers by Albert Michelson and the Fourier mathematical equation by Lord Rayleigh leads to a massive breakthrough in IR spectroscopy. Known as FTIR (Fourier Transform Infrared) spectrophotometer, it allows the measurement and the calculation of the IR spectrum (Naseska, 2016). It is based on the idea of the radiation interferences between two beams to generate interferograms, a function of the path line change of the two-beam signal derived using the mathematical method of Fourier-transformation (Stuart, 2004). Some significant advantages of using FTIR are (i) a small number of the optical element; (ii) Excellent sensitivity and stability, (iii) fast data collection and near real-time operation, (iv) low maintenance (Doyle, 1992; Naseska, 2016). However, in terms of its operating condition, FTIR spectroscopy has some limitations, including (i) only recognizing heteronuclear gases, (ii) low resolution (1 cm⁻¹) that requires specific laboratory calibration for every single gas, (iii) it is superimposed by the presence of impurities (Smith, 2011; Taquet *et al.*, 2013)

There are generally some significant components of the FTIR that includes; (i) an Infrared beam source, (ii) a Michelson Interferometer consisting of a beam splitter and a compensating plate, and (iii) optical elements. The difference in path length between the two arms is intentionally varied mechanically. It produces the interferogram, which is transmitted optical intensity that rises to a time-dependent. Principally, the spectral point's power can be identified by bypassing the electrical signal obtained by the infrared radiation detector through the electronic filter. At the same time, the complete spectrum can be determined by applying various filter frequencies. This processing time, nowadays, is shortened by performing a Fourier transformation using a digital computer. Hence, the composite spectrum can be yielded directly from the instrument, the source, and the sample along the optical path (Doyle, 1992). The schematic diagram of the FTIR is provided in *Fig 4*.



Fig 4. The schematic diagram of the Classic Michelson interferometer. Adapted from Stuart (2004, p.19)

FTIR's approach relies on the fact that most of the molecules absorb infrared radiation on which the concentration of the sample is proportional to the absorption intensity. Therefore, the sample's concentration can be determined using pre-constructed calibration curves (Maria, 2012; Frey *et al.*, 2015). The FTIR calibration for gas analysis, mainly CO₂ and CH₄, has been carried out by (CAILTEAU, 2008; TAQUET, 2012; Frey et al., 2015; Hase et al.

The portable FTIR spectrometers (version alpha) manufactured by Bruker were used in this research project. It would be calibrated to measure the precise and continuous observation of the CO_2 and CH_4 . Besides its portable size, another outstanding factor distinguishes the Alpha Bruker FTIR Spectrometers from other FTIR devices on the market. Instead of using the classical Michelson type of interferometers, the Alpha Bruker FTIR utilizes ROCK SOLID interferometers. The use of a simple Michelson interferometer that depends on the flat mirrors is practically prone to mirror tilt resulting in a decrease in the stability, resolution, and spectral quality. This problem occurred since the light returning to the beam splitter must be accurately recombined. This problem, however, can be resolved by using an approach called dynamic alignment. The ROCK SOLID Interferometer integrates a dual pendulum arrangement in which each consists of retroreflective cube corner mirrors. The mechanism of a wear-free pivot and the comparison between those techniques that are illustrated in *Fig 5* prevents mirror tilt and avoid mirror shear.



Fig 5. The ROCKSOLID Interferometer (1. Beam splitter, 2. Cube Corner reflectometer, 3. Wear-free pivot mechanism) [a] The Optical Comparison between the Flat mirror and Retroreflecting Cube Corners. Adapted from Bruker Optik GmbH (no date, p.1)

The FTIR Bruker alpha utilizes a permanently aligned ROCKSOLID interferometer that enables low polarization effects and relatively large energy throughput. Moreover, the spectrometer's resolution defines the degree of the ability of an instrument to distinguish peaks that are close together. If the peak changes between two spectra are 32 cm-1, the minimum resolution needed is 32 cm-1, which is considered a low solution. The influence of FTIR resolution on spectral is provided in Fig 6.

[b]


Fig 6. The comparison between the spectrum of water vapor measured at a resolution of 0.5 cm⁻¹ (top) and the spectrum of water vapor was measured at a resolution of 32 cm⁻¹ (bottom). Adapted from Smith (2011, p.36).

Nonetheless, there is a significant trade-off between resolution and noise level where the high resolution of measurement produces a high level of noise. Smith (2011) has recommended 8 or 4 cm⁻¹ for solid and liquid states and 2 cm⁻¹ or higher for samples in a gas state. Besides, the higher accuracy of the FTIR is needed to show the absorption spectrum because of the rotational vibration,

Although FTIR is widely used to analyze organic chemistry qualitatively, the band intensities and path length can also measure the quantity since they are highly correlated to the sample's concentration through the BEER-Lambert Law be seen in the equation below.

$$A = \epsilon IC$$
 Equation 2.1.1

A is the absorbance, ε is the molar absorptivity in L/(mol cm), l is the length of the path (cm), and C is the concentration of the sample moles/L. It is expected that the function will be in linear dependence format, $A = slope \times C + offset$. According to the equation, the number and range of the IR (Infrared) spectrum are highly dependent on the range of the standard gas concentration. If the absorbance of the known standard gas series is measured, a plot of the function of the absorbance against the concentration can be generated using least-square analysis.

2.1.2. Cavity Ring-Down Spectroscopy (CRDS)

Compared with conventional spectroscopy, Cavity Ring-Down Spectroscopy (CRDS) is considered to have higher sensitivity. The measurement is based on the absorption rate instead of the magnitude of absorption on which the light circulates an optical cavity with a high Q factor (Berden, Peeters, and Meijer, 2000; Lehmann, Berden, and Engeln, 2009). It detects even very weak transitions and trace species (Jong, 2012). The other advantages of using CRDS are the very long effective path length that

can be done in stable optical cavities. Secondly, the fluctuation of light source intensity has little effect on intrinsic sensitivity. (Berden, Peeters and Meijer, 2000). In the last decade, there is some evidence to suggest that the CRDS approach is potent in gas-phase spectroscopy both for the measurement of trace amount containing strong absorption species and a large concentration of weak absorption species (Crosson, 2008). The Schematic diagram of the CRDS is provided in **Fig 7**.



Fig 7. The schematic diagram of the CRDS measurement system. Adapted from Saad, Kuramoto, and Zare (2009, p.1)

The principal mechanism of CRDS starts with a small (35 cc) optical resonator cavity containing the gas sample that receives the light from a tunable semiconductor diode laser. After the laser completes the build-up, the light will circulate in the cavity traveling more than 20 km. There are three mirrors inside the cavity on which the photodetector located behind each mirror identifies the light intensity. A laser pulse is intentionally trapped in an optical cavity wherein the presence of scattering and absorbing compound the intensity of the trapped laser pulse decays exponentially (Jong, 2012). The decay time, also known as cavity ring-down time, is inversely proportional to the losses inside the cavity. The rate of absorption is determined by measuring this cavity ring-down time, resulting in an absolute scale of the losses in which introducing the sample causes a shorter ring-down time due to more extensive cavity loss (Lehmann, Berden, and Engeln, 2009). It is a widely held view that the CRDS can provide high absorption intensity with noise equivalent absorption limits of ~10⁻⁹ - 10⁻¹¹ cm⁻¹ Hz⁻¹, which further allows detection of the gas concentration as low as parts-per-trillion depending on the details of the optical scheme and target species (McHale, Hecobian, and Yalin, 2016).

2.1.3. Gas Chromatography (GC)

Gas Chromatography (GC) is one of the most widely-used analytical methods for identifying and quantity measurement of the organic substances in much-advanced research worldwide (Sparkman,

Penton and Kitson, 2011; Mohd, 2012). Chromatography is a separation technique parting the samples' components into two samples, including a stationary bed with a relatively large surface area and a gas spreading gradually through the stationary bed (McNair and Miller, 2009). Thus, this technique allows the mass spectra of individual compounds obtained for qualitative purposes and quantitative information in the same compound (Sparkman, Penton and Kitson, 2011). There are some majors advantages to using GC analysis on the complex mixture, which includes: (1) excellent resolution shown by symmetric and sharp peaks, (2) high reproducibility and repeatability, (3) High accuracy and high precision, and (4) minimum catalytic and thermal decomposition especially for sensitive sample component (Al-Bukhaiti et al., 2017). The analyzed mixture may be either a solid, a liquid, or a gas in which one of the requirements is that the sample components be stable, have a vapor pressure around 0.1 Torr at operating condition, and interact with column material and the mobile phase (Grob and Barry, 2004). The critical parts of a GC can be seen in Fig 8, which includes a gas source as the mobile phase, an inlet for delivering the sample to the column. The column where separations were taking place; an oven is acting as a thermostat for the column; a detector for registering the presence of chemical data in the column effluent; and a data system to display and proceed the chromatogram (Eiceman, 2006).



Fig 8. The Simplified Block Diagram of Gas Chromatograph. Adapted from Eicemen (2006, p.1)

The time taken from injection to emergence, also known as the Retention Time (Rt), varies between substances under given conditions. It also depends on the volatility of the substance and the column's temperature, length, and diameter. Some methods for detecting and measuring the individual component have been developed. The most common type of detector is thermal conductivity (TCD). It measures changes in heat conduction and thermal ionization (FID), which measures pyrolysis changes. TCD and FID have approximate limit detection of 10⁻⁵ to 10⁻⁶ gs⁻¹ and 10⁻¹² gs⁻¹. As for data processing, most modern chromatographic instruments are equipped with integrated hardware and software to estimate peak areas of analyte substances (Al-Bukhaiti *et al.*, 2017).

2.2. Laboratory Gases Analysis

The detailed description of gas analyzers, gas standard preparation, and calibration technique is extensively described in this section. The works include leakage tests, cross-validation, and reproducibility test. These metrology protocols were done to allow a monitoring campaign in Montiers-sur-Saulx.

2.2.1. Gas Analyzers and Gas standard Preparation

Commercially available FTIR alpha produced by Bruker optic alpha was first calibrated in the laboratory of Georesources at the University of Lorraine and used throughout the monitoring campaign in Montiers-sur-Saulx. This IR spectrometer is equipped with RockSolidtm interferometer, which is currently considered very stable and permanently aligned. Equipped with a standard KBr beam splitter makes it possible to analyze a sample in the region between 375 to 7500 cm⁻¹. It has a slightly better spectral resolution compared with standard FTIR. Moreover, it has wavenumber accuracy and precision <0.05 cm⁻¹ and <0.0005 cm⁻¹ respectively at 2000 cm⁻¹. The default company setting was used throughout this metrological experiment. The FTIR alpha Bruker's data output is the IR absorption spectrum transformed into an interferogram spectrum integrating a range of bands specifying the identified gas in a unit area. Furthermore, the illustration of the main metrological experimental apparatus is provided in *Fig 9*.



Fig 9. Real view and schematic diagram of experimental devices used for CO₂ gas calibration: A) schematic diagram of gas circulation, B) realistic view, and C) gas standard mixing diagram.

Some gas analyzers were also employed to cross-validate standard gas and collected gases sample. Therefore, the reproducibility of the gases measurement results can be maintained across the devices, which include a) GC-TCD, b) a low-power NDIR sensor engineered by Solexperts allowing the continuous monitoring of CO₂; c) CP-4900 Micro-Gc (Gas Chromatography) manufactured by Varian BV where a six levels calibration was carried out for each gas of interest including Ar, O₂, N₂, CH₄, and CO₂ at INRAE laboratory, and d) G2201-i Greenhouse Gas Analyzer (Picarro Inc., Santa Clara, CA, USA)



Fig 10. The realistic view of gas analyzers includes a) GC-TCD, b) NDIR, c) CP-4900 Micro-GC, and d) Cavity Ring-down Spectroscopy G2201-i.

As shown in **Fig** *10*, GC-TCD and CRDS gas analyzers were pre-calibrated and utilized to cross-validate the gas standard. Single reference gas was supplied by Air Liquide S.A. and certified with a relative uncertainty of 2%. The various mixture of binary gas of CO₂, N₂, Ar, and CH₄ was produced using an on-site customized gas standard preparation system of AlyTech GasMixTMby (mixing, diluting, and injecting single references gas standard). It has a dimension of $42 \times 22 \times 46$ cm (L×W×H) connected through Swagelok 1/8" with the error of less than 2% of the flow over the scale. The gas standard was controlled in the provided software interface allowing the user to define the gas concentration and flow rate.

The sub-soil gas measurement depends heavily on NDIR and FTIR due to its simplicity and low power consumption. This measurement system is supported by ex-situ gas laboratory analysis using a CRDS analyzer and *CP-4900 Micro-GC*. CRDS G2201-i measures H2O, CO2, and CH4 concentrations and isotopic ratios of those gases. The default setting of the CRDS G2201-I was used throughout the experiment. It can also measure CO₂ and its isotopic composition up to 4000 ppm with measurement intervals of 3 to 5 seconds. To obtain considerable accuracy, the sample pressure that was introduced should be no more than 1.315 atm. Moreover, a more detailed explanation of FTIR and CP-4900 Micro-G's calibration technique is given in the following subchapter.

2.2.2. Calibration Strategy

Fig 9 illustrates the complete design of the FTIR calibration setup, including FTIR Bruker Alpha ($[22\times33\times26 \text{ cm } (w \times d \times h)]$, gas cell, and the gas cylinder. There are four valves, including some connections manufactured by Swagelok, regulating the flow of the gas. A needle valve was also installed to introduce the gas slowly and accurately to the apparatus system. The FTIR internal compartment is also equipped with extraordinary support to align with the IR beam emerging from the interferometer perfectly. The gas cell on both windows is made of IR grade Calcium Fluoride (CaF₂) because it protects the cell from the deterioration caused by moisture presence. It is also considered nearly transparent on wave numbers of 900-5500 cm⁻¹.

Furthermore, the gas pressure inside the cell is measured using a built-in piezoresistive-based pressure gauge manufactured by Keller. It can handle pressure ranging from 1 bar to 1 kbar with a 0.01-1% accuracy. A PFEIFFER vacuum model MVP 015-2used in this apparatus was also used mainly during the measurement of references. The other major component of this apparatus is the gas cell consisting of some sub-components proven to be leak-free (*Fig 11*). The performances of this apparatus were tested at different constant room temperatures $(22^{\circ}C)$.



Fig 11. The leak testing in 15 minutes time scale

Leak testing is one of the critical stages in this experiment considering the interdependent parts' apparatus. The leak testing was carried out within 15 minutes timeframe in near-vacuum conditions resulting in 0.002 bar left in the system after design improvement representing a small fraction of the atmospheric pressure. Considering the total atmospheric pressure is dedicated well, ranging from 0.950 to 1.050 bar, the pressure introduced in the

calibration experiment is at 1 ± 0.002 . This argument has been previously proven in a study conducted by Cailteau *et al.*, (2011). The temperature is negligible because the gas's temperature in the borehole, especially at -6 m, is relatively stable. Calibration is done by calculating the total absorption area under the curve of known gas standards. This peak integration method can be done using OPUS 6.5 software and follows a protocol that is provided as follow;

- 1. The cylinder is filled with the known gas concentration (CO₂ and CH₄) that have been diluted with N_2 using AlyTech GasMixTM LiqMix.
- 2. The gas mixture was then verified using Picarro CRDS, measuring the CO_2 and CH_4 concentration and water vapor. Picarro CRDS also measured the ambient air condition during the measurement of the IR absorption spectrum.
- 3. The apparatus in *Fig* 9 was vacuumed up to 0.002 bar to create the baseline of measurement. The subtraction of atmospheric CO_2 is much needed because its concentration is in the range of known standard gas, in which the atmospheric CO_2 contributes to the inner component of the FTIR spectrometer.
- 4. The apparatus was filled with the prepared standard gas up to 1 ± 0.04 bar.
- Fourier Transformation transfers the absorption spectrum into a single channel spectrum. It is also called the ranges that further represent the absorption intensity based on the sample's wavelength, as shown in *Fig 12*.



Fig 12. Infrared spectra of 3000 ppm of CO₂ (a) and 1800 ppm of CH₄ (b). For CO₂: frequency range for v3 area calculation (1). For CH₄: frequency range for v4 area calculation (2) and frequency range for v3 area calculation (3).

The figure above shows the absorption spectra of CO_2 and CH_4 at the concentration of 3000 ppm and 1800 ppm, respectively. Since the CH_4 that will be encountered on the field is most likely less than 10 ppm, the CH_4 calibration protocol is considered straightforward where only 2800-3200 cm⁻¹ (v3) fundamental band is used and neglecting the v2. Meanwhile, considering our monitoring site's karstic environment, the CO_2 molar fraction in the soil might reach 10% (Kim *et al.*, 2019). Therefore an analytical approach of the calibration strategy that has been developed by Cailteau *et al.* (2011) should be taken into consideration;

1. As for the low concentration of < 1% CO₂, the analysis is performed where the significant bounce exists, located at 2350 cm⁻¹ (v₃) [2400; 2220]. The subtraction of atmospheric CO₂ is

always required since the atmospheric CO_2 is considered significant relative to the gas sample. The spectra are provided in *Fig 12*.

- 2. For the > 1% CO2 concentration, the analysis is carried out with a combination of v_2 located at 3610 cm⁻¹ [3660; 3460] that can be written as $2v_2+v_1$. At this band combination, the atmospheric CO₂ concentration can be neglected. However, since the absorption spectra of CO₂ at this band overlap with CO₂, there is a strong Need to subtract the water vapor's contribution at the spectrum.
- 3. The third band combination of CO₂ is located at 4980 cm⁻¹ [5020; 4900] using the formula of $v_1+2v_2+v_3$ when the v1 and v2 are fully saturated.

Nonetheless, in our case, even at the 6% CO₂ gas standard, v2 has not been fully saturated. This finding makes the CO₂ molar fraction quantification more straightforward and robust by only relying on the fundamental band of v2 and eliminating the need for water vapor subtraction. Furthermore, the CP-4900 Micro-GC was calibrated in the INRAE laboratory by the person in charge using standard manufacturer protocols. A six-level calibration was carried out for each gas of interest, including Ar, O₂, N₂, CH₄, and CO₂. The Micro-GC calibration was established without taking into account the presence of H₂O (dry condition). The calibration of CO₂ and CH₄ by Micro-GC will also be provided in the calibration curve results. Unlike the other two gas analyzers, the CRDS G2201-I was already calibrated, and the default setting was used throughout the experiment, where the CO₂ operational range is 100 - 4,000 ppm. Unlike the in-situ FTIR measurement, Micro-GC and CRDS need to be normalized using ideal gas law considering the pressure and temperature from the borehole and once it was analyzed in the laboratory. In this work, the error value sources are divided into two groups: Firstly, those resulting from the manufacturer's optical measurement uncertainty and secondly, from the experimental error associated with reproducibility.

2.3. Results

2.3.1. Calibration results of CO₂ and CH₄

The calibration curve of CO₂ was reproduced after minimizing and eliminating all the external factors that may contribute to the uncertainty and reproducibility of the data set. It consists of 11 measurement points on which the measurements were repeated three times with new references IR absorption spectrum for each point. It is also a combination of three different measurement instruments: Picarro CRDS G2201-i Analyzer, Gas Chromatography, and gas standard produced by Air LiquideTM. The graph is shown in Fig 13.



Fig 13. A) FTIR calibration curve of CO_2 with a polynomial model fitting ranging from 100 ppm to 60000 ppm (6%) with the resolution of 1 cm⁻¹ and (B) Micro-GC calibration curve of CO_2 with a linear model fitting ranging from 700 ppm to 230000 ppm (23%).

It is generally observed in the scatter plot of the bivariate data above that the relationship between CO_2 concentration and the absorbance area is highly positively correlated. FTIR ranges from 100 ppm with the area of CO_2 bond (Abs) of 0.22 to 60000 ppm with an average Abs of 94. For Micro-GC, the lowest Abs was 65000, and the highest Abs was 23x10⁷. The procedure of CH₄ calibration also follows the section that is provided in Section 2.3.2.



Fig 14. A) FTIR calibration curve of CH₄ with a polynomial model fitting ranging from 100 ppm to 60000 ppm (6%) with the resolution of 1 cm⁻¹ and (B) Micro-GC calibration curve of CO₂ with a linear model fitting ranging from 700 ppm to 230000 ppm (23%).

The highest CH₄ concentration tested in the FTIR is 5000 ± 99 ppm, with an average absorbance area of 0.046 ± 0.024 . The lowest concentration tested was 44 ± 4.05 ppm, with an average absorbance area (Abs) of 3.97 ± 0.012 with a Y-intercept of -1.13. The CH4 fits with the linear model fitting with R² of 1. The residual error for both CH₄ and CO₂ FTIR calibration curves is provided in

Table 1.

Table 1. The residual error and the adjusted R² of the two polynomial model fitting of CO₂ And CH₄ (Resolution: 1 cm⁻¹).

CO ₂ (100 to 60000 ppm)	Residuals by Section							Residual Standard Error Adjust			
	Min	1Q	Median	3Q	Max			57.84 on 15 degrees of			
	-81.94	-18.07	-3.33	7.58	109.58	-		freedom	1		
CH ₄ (50 . to 5000 ppm)	Residuals by Data Points						Residual Standard Error Adjusted R				
	1	2	3	4	5	6	7	17.62	0.0000		
	-5.97	21.23	-19.23	7.76	-3.4	-1.4	1	- 17.02 on 5 degrees of freedom	0.9999		

The CO₂ and CH concentration and the unit area have a large goodness fit of linear correlation with R^2 of 1 and 0.9999. In addition, it is also essential to understand how the lower resolution of FTIR at 4 cm⁻¹ is compared with 1 cm⁻¹. The comparison of the polynomial model fitting is provided in *Fig* 15. Since the FTIR measurement with a resolution of 1 cm⁻¹ and 4 cm⁻¹ are visually identical with a polynomial model, the linear model fitting was applied for both resolutions.



Fig 15. The Comparison of calibration curves in polynomial fitting between resolution FTIR of 1 cm⁻¹ and 4 cm⁻¹.

Even though FTIR measurement with a resolution of 1 cm-1 and 4 cm-1 is visually identical, the model fitting intercepts each other at the lower and higher values. In other words, one of the curves is more linear than the other and can be tested using a linear model fitting *Table 2*.

FTIR Resolution	Equation	Adjusted R ²		
1 cm ⁻¹	Y = 640x-781	0.987		
4 cm ⁻¹	Y= 650x-1351	0.976		

Table 2. The linear fitting comparison between FTIR resolution of 1 cm⁻¹ and 4 cm⁻¹.

Table 2. demonstrates that a resolution of 4 cm⁻¹ has a slightly lower determination index compared with 1 cm⁻¹ at 0.976 and 0.987, respectively. A previous work confirms that the calibration equation does not precisely follow beer-lambert law, especially if measured using low resolution. Since the gas state poses vibrational and rotational transitions that are often thin (FWHM [Full width at half maximum] < 0.2 cm⁻¹), the entire spectral line can only be detected in a very high resolution around 0.1 cm⁻¹. The absorbance area derived from FTIR does not precisely match the sum of all the theoretical spectral lines of vibration rotation. Therefore, a three-degree polynomial model fitting fits better than the linear model fitting. Furthermore, considering our application of this gas is for CO₂ subsoil monitoring. The longer scanning time resulting in lower temporal resolution, the 3-degree polynomial is deemed acceptable for producing a calibration curve.

2.3.2. Cross-Validation

Even though the purpose of this work is mainly to establish calibration curves, it is also essential to identify the on-field performance of gas analyzers that further can be used as preliminary guidelines to better execute the monitoring campaign to understand how the performance of some of the gas analyzers relative to FTIR, the CO_2 concentration derived using NDIR, Micro-GC, and CRDS were compared in (*Fig 16*)



Fig 16. Comparison of CO₂ concentration measured using FTIR (n=40), NDIR (n=36), GC (n=3), and CRDS (n=1).

Fig 16 demonstrates a good correlation between the FTIR relative to NDIR (R^2 :0.9449), Micro-GC (R^2 :0.9994), and CRDS, indicating that the NDIR gives coherent measurements context. This comparison result justifies using a single IR sensor in the field, resulting in less complexity and energy consumption, along with ex-situ laboratory analysis for other trace gases measurement and isotopic composition.

2.4.Intermediate Conclusion

The metrological experiment was designed to create new calibration curves of FTIR, evaluate the calibration curves, and test the applicability of CO2 and CH4's calibration curves. This experiment has raised important questions about the different resolutions that will help establish a greater degree of understanding about the non-linearity of the absorption spectra in a subsoil gas measurement application where the CO₂ molar fraction is less than 6%. The quantification of CO₂ concentration using this calibration technique is considered very simple since it only considers the CO₂ vibrational mode at the wavelength of 2400 cm-1 (v3). Although CH₄ concentration was always below our IR sensor's sensibility limit, it was still detectable with micro-GC analysis at 0.72-5.97 ppm. The high-frequency data hold many interesting features that are not captured in synoptic data sets and will be helpful for tuning our understanding of soil carbon. This soil gas measurement technique combining FTIR, NDIR, and laboratory analysis offers great possibilities for long-term in-situ and continuous monitoring to derive the vertical distribution of CO₂ and CH₄ and help build the baseline of natural gas exchange in the Lorraine region. The good agreement of CO₂ concentration derived from FTIR, NDIR, GC, and CRDS justifies using a single IR sensor in the field, resulting in low energy consumption and less complexity. If necessary, the system can run a high-frequency measurement since it takes less than one minute to run 16 scan analyses. The high-frequency data hold many interesting features that are not captured in synoptic data sets and will be helpful in tuning our understanding of soil carbon.

Above Canopy Turbulence Effects on the Subsoil CO₂ Dynamics in Temperate Deciduous forest

Didi Adisaputro ^{1,2,3,*}, Philippe De Donato ¹, Laurent Saint-Andre ², Odile Barres ¹, Catherine Galy ⁴, Gilles Nourrisson ², Médéric Piedevache ⁵, and Marion Derrien ⁵

- ¹ GeoRessources Laboratory, Université de Lorraine, CNRS, BP 70239, 54506 Vandœuvre-lès-Nancy, France;
- ² INRAE, UR BEF, Centre de Nancy, 54280 Champenoux, France;
- ³ Institut Teknologi Sumatera, 35365 Way Huwi, Lampung, Indonesia
- ⁴ ANDRA, 55290 Bure, France;
- ⁵ Solexperts France, 17 av de la Forêt de Haye, 54500 Vandoeuvre lès Nancy, France;

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Resume

Les études sur l'influence de la turbulence du vent sur la dynamique du CO₂ dans le sous-sol ont principalement porté sur la couche supérieure du sol (-6m à -1m). À cet égard, ces travaux soulignent l'importance de la zone biologiquement inactive du sol et située au-dessus de la nappe phréatique, où elle est légèrement influencée par les conditions atmosphériques. Ils ont été largement appliqués pour créer une base de référence pour le CO₂ dans un large éventail d'applications de stockage géologique. Ce travail décrit un système de surveillance spécifique en puits dédiés qui a été mis en place dans un écosystème forestier (Montiers, France). Les données mesurées in situ, avec des intervalles de mesure relativement courts (de 30 min à 1H), ont été collectées par le biais de deux complétions placées dans des puits dédiés à 1 m et 6 m de profondeur, couplées à des mesures micro météorologiques au-dessus de la canopée Les concentrations de gaz ont été déterminées en combinant un spectromètre (50m). infrarouge portable et des capteurs NDIR de faible puissance. Les données auxiliaires, notamment la température, la pression, la teneur en eau du sol, les précipitations et la vitesse de frottement se produisant au-dessus de la canopée, ont été enregistrées simultanément. La stratégie de surveillance dans cette étude pour la mesure des gaz combinant la méthode des gradients, la FTIR et la NDIR, offre de grandes possibilités de surveillance à long terme pour dériver la distribution verticale du CO₂ et du CH₄ ainsi que pour aider à créer des données empiriques sur les flux de gaz du sous-sol. Notre étude montre que le CO₂ mesuré à 1 m profondeur est constamment inférieur au CO₂ mesuré à 6 profondeurs, allant de 1000-70000

ppm à -1 m et oscillant entre 10000-60000 ppm à -6m. Les valeurs de χc à -1 m étaient au plus bas en hiver 2019 et au plus haut en été en juin 2020. Par comparaison, la variation saisonnière de χc à -6m est quelque peu différente puisque les maximas ont été atteints à la fois en été et en hiver. Cependant, on observe que la diminution de χc coïncide avec une augmentation de la vitesse de friction (u*) avec une relation linéaire très prononcée surtout pendant les périodes sèches avec une valeur de coefficient de corrélation (R²) voisine de 0,6. Cette étude montre des preuves empiriques solides que la turbulence du vent joue un rôle important dans la variabilité des concentrations de CO₂ dans les sols et cela jusqu'à des profondeurs de -6m.. Ces variations semblent dû aux effets de pompage en lien avec les variations de pression entre le sol et l'atmosphère. Ce déséquilibre de pression contribue à diminuer la fraction molaire de CO₂ dans les couches plus profondes du sol lors des épisodes de faibles turbulences atmosphériques, c'est dire des faibles valeurs de u*. Cette étude démontre également que la perméabilité aux gaz est considérablement réduite pendant les périodes humides, ce qui diminue le processus de transport non diffusant.

Abstract

Studies on the influence of wind turbulence on subsoil CO2 dynamics have mainly focused on the top layer of soil. In this regard, this work emphasizes the importance of the biologically inactive soil zone and above groundwater table where it is marginally influenced by the atmospheric conditions and has been widely applied to create a CO₂ baseline for a wide range of geological storage applications. This work describes a specific monitoring system implemented in a forest ecosystem (Montiers, France). Data measured in situ, with relatively short measurement intervals, were collected through two completions placed in dedicated wells at 1 m and 6 m depth coupled with micrometeorological measurement above the canopy. Gas concentrations were determined by combining a portable infrared spectrometer and low-power NDIR sensors. Auxiliaries data, including temperature, pressure, soil water content, precipitation, and friction velocity, occurred above the canopy recorded simultaneously. This study's monitoring strategy for gas measurement combining gradient method, FTIR, and NDIR offers great long-term monitoring possibilities to derive the vertical distribution of CO₂ and CH₄ and help create empirical gas fluxes data for the subsoil. Our study shows that χc measured at 1 m depth is constantly lower than CO₂ measured in 6 depth ranging from 1000-70000 ppm at -1 m and 10000-60000 ppm at -6m. The χc at -1 m was at the lowest in winter 2019 and highest in summer 2020.

Meanwhile, the seasonal variation of χc at -6m is somewhat unclear since the maxima were reached in summer and winter. However, an increase of hourly Temperature at 1 m depth inevitably leads to higher soil respiration rates with an R² of 0.88. Nonetheless, this factor related to biological activity cannot fully explain the variation. The decrease in χc also coincides with an increase in friction velocity, especially during dry periods with an R² of 0.68. This study shows strong empirical evidence that wind turbulence plays a significant role in driving deep soil CO₂ concentration. We hypothesize that this could be due to pressure pumping effects where it decreases the CO₂ molar fraction in the soil during high turbulence and increases the CO₂ storage in deep soil during low turbulence. This study also demonstrates that gases permeability is significantly reduced during wet periods diminishing the non-diffusive transport process.

Keywords Subsoil Gases · Baseline Monitoring · Forest

3.1. Introduction

The gas exchange between the atmosphere and terrestrial ecosystem represents a large proportion of CO₂ and CH₄ atmospheric budgets (Angert et al., 2015). Soil CO₂ budget and efflux due to land-use change averaged globally from 2009-2018 were estimated at 5496-8793.6 PgCO₂yr⁻¹ and 5.49 PgCO₂yr⁻¹ respectively (Friedlingstein et al., 2019), as for the comparison the emission due to fossil fuel combustion and the cement industry is around 33.4 PgCO₂yr⁻¹ (Oertel et al., 2016). Adequate and trustworthy monitoring strategies of natural gas exchange will help to understand the local variability of gas concentration in the soil in anticipation of the CO₂ injection (Taquet et al., 2013; Schacht and Jenkins, 2014) and to promote public acceptance (Schlömer, Möller and Furche, 2014). Generally, GHG (Greenhouse gasses) emissions from the soils are measured in both laboratories and directly in the field (Oertel et al., 2016). The most widely used approaches in this context are chambers methods (soil-air interface) (Angert et al., 2015; Hoffmann et al., 2015; Pokryszka et al., 2017; Sánchez-Cañete, Barron-Gafford, and Chorover, 2018), micro-meteorological eddy covariance method (vegetation-atmosphere interface) (Aubinet, Vesala and Papale, 2012a; Eder et al., 2015; Barba et al., 2018; Klosterhalfen et al., 2019) and the gradient method (subsoil gas transport) (Maier and Schack-Kirchner, 2014; Sánchez-ca and Kowalski, 2014; Angert et al., 2015; Phillips et al., 2016; Sánchez-Cañete, Barron-Gafford and Chorover, 2018; Y. Wang et al., 2018)

It is a widely held belief that the soil CO₂ molar fraction (χ c) generally increases with the rise of the depth, from the near-atmospheric layer up to a few meters below the topsoil. The CO₂ molar fraction (χ c) below 20 cm for most soil types is between 0.2 and 4% (Rose, Hawkes and Webb, 1979). Meanwhile, the χ c above 10% are generally found in the active geothermal area with a significant pressure gradient transport instead of the solely diffusive process (Pearce *et al.*, 2004; Camarda *et al.*, 2007). Although molecular diffusion plays a substantial part in soil CO₂ emission, the physical component such as soil ventilation is highly porous surface layers. Advective CO₂ transport involving wind speed, friction velocity, or pressure is also essential (Maier and Aubinet, 2011). The porous soil structure is continually changing due to so many factors, including water gains and losses, soil redistribution, changes in matrix structure because of the earthworms, and deformation due to compaction (Nawaz and Bourrié, 2013). Some studies reported that the CO₂ dissolution and ventilation process plays a significant role in storing and releasing a large amount of CO₂ in subsurface cracks, pores, and cavities (Sánchez-cañete *et al.*, 2016; M Maier *et al.*, 2017; Laemmel *et al.*, 2019)

There was substantial evidence from previous works that soil gas transport in the unsaturated zone was predominantly affected by the water table variations. A study focusing on the monitoring and modeling aspects in the CCS (Carbon Capture Storage) Total pilot plant on Lacq-Rousse, France, shows that the soil xc was negatively correlated with changes in the piezometric level (Monne et al., 2015). Specifically, the fluctuation is caused by the CO₂ dissolution or release process by the perched water table acting as a pump. There was also a strong indication of the seasonal condition affecting the variability of the χc in the soil (Monne et al., 2015). Sanchez-Cañete et al. (2011) have studied the variation of subterranean CO_2 molar fraction (χc) within the depth of 1.5 m. It was found that the molar fraction (χc) of CO₂ was predominantly caused by pressure variations instead of biological or wind influences (Tate, 2015). However, the driving mechanisms of carbon dynamics in a forest ecosystem are still uncertain. Such studies cannot be conducted in the laboratory because the natural soil profile primarily consists of active Rhizophora-producing and consuming methane, plant-soil interactions, and spatial interaction (M Maier et al., 2017). To construct a reliable baseline of natural gas exchange and study its transport and production, the monitoring should be performed in long-term continuous monitoring with relatively short measurement intervals (Schlömer, Möller, and Furche, 2014). However, this approach has been considered economically unfeasible and complex. Therefore, there is a strong need to develop an economic and robust continuous soil gas measurement that does not need complex maintenance as well as complemented by remote data logging.

While most of the works regarding the monitoring of soil CO_2 focus on the top layer up to one meter, this work emphasizes the importance of the biologically inactive soil zone and above the water table where it has marginally influenced by the atmospheric conditions. This location has been widely applied to create a CO_2 baseline for a wide range of geological storage applications, including but not limited to the CCS (Carbon Capture and Storage) monitoring programs (Schloemer *et al.*, 2013; Schlömer, Möller and Furche, 2014). Our improved understanding of this zone will advance geological storage monitoring applications. Therefore, the main objective of this study was two-fold. Firstly, to field test a specific flow system equipped with a membrane probe to continuously measure the soil gas concentration and auxiliaries data regardless of the water saturation conditions and understand the main physical drivers of gas exchange in a deep soil layer (-6 m).

3.2. Materials and Methods

3.2.1. Study site description

The geochemical monitoring was conducted in a dedicated site located in Montiers, the integrated site, to study the forest functioning system where a flux tower, 355m apart from the borehole (*Fig 17*). The Montiers site covers about 73 ha with an altitude varying from 340 and 386 m, with an average slope of 4.25% (Kirchen *et al.*, 2017). It is situated in Northeastern France in the Meuse department representing the soil representative's diversity ranging from calcic and superficial soils to acidic and deep soil where there are homogenous and mature beech trees. The stand of the studied forest consists of 89% beech (*Fagus sylvatica L*), 6% maple (Acer pseudoplatanus L.), 5% other deciduous trees, including whitebeam, ash, oak, hornbeam, and wild cherry, with an average tree height of 25 m and average density of 800 stems/ha (Kirchen *et al.*, 2017).



Fig 17. A vertical section of the soil profile of Tithonian limestone surmounted by vlaginian sediments. On the surface, borehole measurement and a lattice tower (FT) were constructed within the distance. 355 m.

The dystric cambisol lies on the Valanginian layer to around 200 cm of the depth with a pH of 4.9 at the surface and 5.1 at a depth of 45-60 cm. The Cationic Exchange Capacity (CEC) ranged from 0.9-6.7 cmolc kg⁻¹ up to a depth of 60 cm of the vertical section. Sandy and clayey passages were found in the lower soil layer indicating the textural and structural heterogeneity caused by the complex sedimentary source material. The calcareous bedrock mainly consisted of calcium carbonate and a few amounts of clay minerals. The calcareous bedrock is surrounded by the weathered layer rich in clays due to decarbonization. However, the surmounting detrital sediments are considered far more complicated due to heterogeneous deposition and cross-stratification containing silt, clay, coarse, sand, and iron oxide nodules (Calvaruso *et al.*, 2017; Kirchen *et al.*, 2017). The chemical properties of the soil in Montiers site are provided in **Table 3**.

Parent material		Element (i	Element (in % of dry soil)									
		SiO ₂	Al_2O_3	Fe ₂ O ₃	K ₂ O	MgO	CaO	P_2O_5	Na ₂ O	MnO		
Calcareous bedrock	Total	2.34	0.68	0.25	0.14	0.51	54.63	0.05	0.04	0.01		
	Clay minerals	63.13	17.10	4.86	3.87	1.66	0.29	0.21	0.12	0.01		
Detrital sediments		52.91	13.37	23.64	0.80	0.49	0.14	0.41	0.13	0.20		

Table 3. Chemical properties of the soil in the Montiers site. Adapted from (Calvaruso et al., 2017)

The deciduous forest has been known to rely on a considerable amount of rainfall (800-1400 mm per year) and can survive freezing winter down to -20° C as well as warm summer up to low 30°C (Baldocchi *et al.*, 2005) on which our site receives on average 1100 mm per year. The annual scale of the variation is significantly similar among the soil temperature, air temperature, and net radiation with the range of the monthly average of 2.2°C to 17.7 °C, -1.1°C to 21.6°C, 8.21 wm⁻² to 665.8 wm⁻² Respectively. The pattern across the soil temperature, air temperature, air temperature, and net radiation are unsurprisingly followed a seasonal pattern

with the highest in July and the lowest in February. Also, the precipitation is found to be intense in January, May, August, and December.

3.2.2. In-situ Subsoil Gases and Auxiliaries Data Measurements

In-situ gas measurement was executed in the boreholes dedicated to investigating soil-gas concentration in the unsaturated zone with a different depth of 1 m and 6 m. Those boreholes were drilled on 3 June 2019 using a geotechnical rig capable of performing rotary drilling in a remote location. The borehole consists of a perforated pipe and a permanent well fitted with drilling tubes *Fig 18*. shows the subsoil measurement system composed of three main parts, including completion (A), gas circulation module (B), and calibrated FTIR Bruker Alpha (C), with an additional GC analysis for cross-validating purposes. This configuration was subject to previous research (De Donato et al., 2011; Monne et al., 2015) applied to the carbon storage site. It was deployed in the shallows well at a depth of 1 m and 6 m and located about 50 meters from the weather station, measuring the monitoring field's environmental driver and meteorological conditions. This well is dedicated to recording the gas phase's geochemical properties in the subsoil, which operates continuously and simultaneously with a log data station.



Fig 18 Monitoring concept for simultaneous and continuous gas measurement, including Schematic diagram (i) and realistic view (ii) of monitoring infrastructure. The Schematic diagram describes in more detail the process flow, which includes completion/ boreholes (A), the circulation module (B), and calibrated FTIR Bruker Alpha with an additional GC sensor (C) for cross-validating. The circulation module consists of 1) temperature sensor, 2) pressure sensor, 3) water trap, 4) fluxmeter, 5) packer pressure, 6) borehole temperature indicator, 7) atmospheric temperature sensor, 8) atmospheric pressure sensor, 9) CO₂ NDIR sensor, and 10) Soil moisture sensor.

The completion (A) consists of three significant subparts: chamber, packer, and circulation lines. The collection chamber is one of the most critical components that allows continuous gas sampling in the soil using an electric pumping system and a manual sampling port. The length and the diameter of the collection chamber are 60 cm and 50 mm respectively. The packer made of an annular inflatable device of 64 mm long prevents any interferences with the ambient atmospheric gases by fully isolating the collection chamber. The circulation module consists of two stainless steel lines, which are 4 mm in diameter allowing the gas to be transferred to the sensor and reintroduced into the borehole. The other two lines are equipped with pressure and temperature sensor. The gas flow module permits the gas sample's transportation from the sensor's completion and controls all parameters associated with the fluids flow (pressure, temperature, and flow). The gas circulation module B) was installed equipped with a) circulation pump with a flow rate of 20 ml/min allowing the extraction and reintroduction of the gas in the collection chamber; b) a water trap ensuring the control of the potentially liquid water in the circuit by trapping the moisture and redirect its flow; c) the flow meter and a pressure sensor measuring the flow rate and the pressure of the gas sample inside of the circulation module; d) Sample cells connected in parallel to the gas circuit allowing samples of gas for laboratory analysis without causing the ambient atmospheric gases to enter the system; e) Various types and sizes of valves; and f) an inlet and an outlet to FTIR Bruker Alpha. Since the monitoring site had no access to grid power, three batteries with a total capacity of 300 Ah were used to supply the monitoring system's power.

The subsoil gas was collected using a collection chamber via the pump at the rate of 20 mL/min. It operated for 10 minutes every hour to allow well-mixed gas in the system and conserve energy consumption. The gas passed through temperature, pressure, and NDIR sensor before it was analyzed hourly through the IR gas cell and re-injected to the borehole's collection chamber. For every follow-up visit for replacing the battery, some gas samples were also collected to be cross-validated with Gas Chromatography. Subsoil gas spectra were recorded using FTIR for 16 scans over the range of 5000 to 600 cm⁻¹ with a spectral resolution of 1 cm⁻¹. The Opus software allows the integration of the various processing, including a continuous recording of the spectra, eliminating the H2O fingerprints, and calculating χc . Even though the water condensation can occur inside the gas circuit, it only interferes strongly with the combination band of 3609 cm⁻¹ (Fig 20). Therefore, an additional correction is unnecessary since it does not interfere with the fundamental vibrational mode of CO₂ at 2400 cm⁻¹. The data collected and recorded are automatically uploaded and synchronized to the online platform of Mission OS once the internet network is available. The obtained field data were further processed using open-source statistical computing and graphics software (R Core Team, 2020).

3.2.3. Micrometeorological Measurement

An eddy covariance tower was used to measure the χc , Soil Temperature (TS), Air Temperature (TA), net radiation, friction velocity (u*), Soil Water Content (SWC), Friction velocity, and precipitation. It was built at the end of 2012 and constructed at the height of 45 m above the ground.





Fig 19. The Flux Tower is located in the middle of a broadleaved deciduous forest; a) The picture was taken in Winter 2019 and b)in summer 2020. Sub figure C) indicates the layout of sensors and pieces of equipment installed on the flux tower.

It also allows the continuous measurement of the wind's speed and direction at 35 m height (around 10m above forest canopy) using six 3D sonic anemometers (HS-50 Gill, Hampshire, UK) with a sampling rate of 10 Hz, and data were analyzed per 30 min interval. In this site, the wind direction is dominated by the South and Southwest. Measurement period. This flux tower is also supported with the meteorological which includes a) air temperature and moisture sensor installed at six different levels (HMP155, Vaisala, Vantaa, Finland), b) global radiation sensors (pyranometer, CMP21, Kipp & Zonen, Delft, Netherlands), c) soil moisture sensors at two stations and multi-depth. The annual time series of environmental drivers and χc in 2018 showed that the monthly mean χc is highest in March with 431 ppm and the lowest in June at 401 ppm. The scale of the variation is significantly similar among the soil temperature, air temperature, and net radiation with the range of the monthly average of 2.2°C to 17.7 °C, -1.1°C to 21.6°C, 8.21 wm⁻² to 665.8 wm⁻² respectively. The pattern across the soil temperature, air temperature, and net radiation are unsurprisingly followed a seasonal pattern with the highest in July and the lowest in February. Also, the precipitation is found to be intense in January, May, August, and December. pSense hand-held instrument was also used to measure atmospheric CO₂, temperature, and rh.

3.2.4. Principal Component and Wavelet Analysis

In order to understand the cross-relationship between the different measuring data, principal component and wavelet analysis were used in this work. It is a widely held view that relying too much on univariate analysis is dangerous because any existing covariation with other variables is neglected, resulting in ignored principal features. However, the linear combination of the two original variables as one new variable could replace the original one that will turn out to be essential in Principal Component Analysis (PCA). (Bro and Smilde, 2014). PCA is one of the oldest and most widely used multivariate analyses to reduce the data set's dimensionality. There are many interrelated data and retain as much as possible the variation present in the data set. The dimensional reduction is achieved by transforming the data set into a new set of principal component analysis variables. Furthermore, it is ordered so that most of the variation present in all of the original variables can be retained (Jolliffe, 2002). To compute, extract, visualize, and interpret PCA results, the FactoMineR, and factoextra packages were used using R studio (R Core Team, 2020).

The wavelet analysis allows the observation of high frequency and low-frequency data with sufficient resolution and periods. Also known as the Morlet wavelet transform (Morlet et al., 1982) reveals the brief information of phenomena challenging to observe when the data is

provided in conventional time series. The Morlet wavelet transform of a time series (x_t) is described in **Equation 3.2.1** where the time series convolution (τ) with a set of "wavelet daughters" generated by the "wavelet mother" (Ψ), by translation in time by τ and scaling by s (Rösch and Schmidbauer, 2018).

$$W_x(\tau, s) = \sum_t x_t \frac{1}{\sqrt{s}} \Psi^* \left(\frac{t - \tau}{s}\right)$$
 Equation 3.2.1

The daughter wavelet position is defined by the localizing time parameter (τ) that is shifted by the increment of the time (δ t), also identified as time resolution. The set scale choice (s) defines the wavelet coverage of the time series in the frequency domain, where the scale value is a fractional power of 2. The equation used to generate wavelet power is also known as time-frequency wavelet energy density, as shown in **Equation 3.2.2**. Furthermore, the wavelet coherence between two-time series (*xt*) and (*yt*) was computed in **Equation 3.2.3** following a previously developed approach (Torrence and Webster, 1999).

$$P_{x}(\tau, s) = \frac{1}{s} \times |W_{x}(\tau, s)|^{2}$$
Equation 3.2.2
Coherence = $\frac{|S \times W_{xy}|^{2}}{S \times P_{x} \times S \times P_{y}}$ Equation 3.2.3

The concept of wavelet coherence requires smoothing of the cross-wavelet spectrum and the normalizing individual wavelet power spectra (Torrence and Compo, 1998). Where smoothing operator (S) is determined as $S(W(\tau, s)) = (S_{scale}(S_{time}(W(\tau, s))))$. S_{time} and S_{scale} , represent smoothing in time and smoothing along wavelet scale axis. More detail description of the wavelet approach might refer to previous study (Torrence and Compo, 1998). R software (R Core Team, 2020)equipped with the 'WaveletComp' package (Version 1.1) was used in this work (Rösch and Schmidbauer, 2018).

3.2.5. In-situ Subsoil Gases Measurement

Fig 20 shows a typical infrared profile of gas coming from the borehole at 6 m depth, where only the absorption bands of CO₂ and H₂O are visible. These monitoring stations have shown that the monitoring of soil χc can be maintained long-term without grid power. After deployment, there were follow-up visits to change the batteries every month before December 2019 and every week after December 2019. Still, cumulatively these equated to only a few

days of fieldwork. During the deployments, the average power consumption for two days of continuous and simultaneous measurements was roughly 300 A. This includes the power demand from a laptop, FTIR, auxiliary sensors, and circulation module (pumps). Nonetheless, the advantages outweighed the drawback of its power consumption, where the other actively IR gas interfinger can be identified individually.



Fig 20 Typical infrared profile of soil gas from the 6 m borehole (Time: 20:03 on 16/10/2019). Interferences weak bands of H₂O_{vapour} are also visible on the spectrum at the low and high-frequency ranges.

The FTIR calibration was considered very simple, considering the CO_2 vibrational mode at the wavelength of 2400 cm⁻¹. The high-frequency data hold many exciting features that are not captured in synoptic data sets and will be useful for tuning our understanding of soil carbon. With this study, this monitoring infrastructure was considerably successful in terms of survivability and management. In continuously accessible power, the system could record and store high-frequency measurements (< 1 min). There is also an opportunity to reduce power consumption by eliminating an FTIR Bruker alpha and a laptop while relying only on low power consumption, an IR sensor, and a data logger.

3.2.6. Seasonal, Daily, and Hourly Variations

The long-term monitoring was done to evaluate our monitoring facility's performance and observe seasonal and daily variations. The micrometeorological measurement was executed from summer to winter (19/July/2019 to 23/July/2020). The subsoil measurement system of CO₂ using FTIR started on 23 July 2019, sustaining approximately two days of continuous measurement on each visit due to power supply limitations. Meanwhile, the auxiliaries data

both from the subsoil monitoring system and lattice tower which include soil temperature at various depths (**Fig 21. a**), air pressure at different depths (**Fig 21. b**), Soil Water Content (SWC) (**Fig 21. c**), precipitation (**Fig 21. c**), CO₂ molar fraction (χ c) at 1 and 6 m depth (**Fig 21.d**), and friction velocity (**Fig 21.d**) were measured continuously and simultaneously during monitoring periods.



Fig 21. Time-series graph showing the daily max of temperature at various depths (35 m, 0m, -1 m, and -6 m) (a), the daily average of atmospheric pressure at 35 m, 0 m, and -6 m (b), Soil Water Content (SWC) (c), precipitation (c), CO₂ molar fraction (χ c) at 1 and 6 m depth (d), and friction velocity (d).

Overall, during the monitoring periods, the atmospheric temperature ranges from -2° C to 38°C (**Fig 21**. a). The variation of atmospheric temperature is significantly higher above the ground ranging from -2° C to 42°C, and is highly affected by the daily variation. It was also

clearly seen that the deeper the soil layer, the less daily and seasonal fluctuation where the temperature at -1 m and -6 m was found at 4.98-19.80 °C and 9.73-11.13 °C respectively. The atmospheric temperature at 35 meters shows a clear seasonal pattern that was the highest in summer 2019 at 38°C, and it started to decline significantly during the Autumn. The significant fluctuation is unsurprisingly identified on atmospheric temperature followed by shallow soil temperature (0m), subsoil temperature at -1m, and -6 m consecutively. The diurnal atmospheric temperature variations are also considered significant. Meanwhile, the borehole temperature at -1 m and -6 m shows less variation with a constant slow increase or decrease ranging from 4.98-19.80 °C and 9.73-11.13 °C respectively in summer and winter.

Even though there is a small difference in magnitude between the atmospheric and soil-air pressure (-6 m) around 150 mbar, the general pattern over the monitoring periods is similar. The daily average of atmospheric pressure (35 m and 0 m) and soil-air pressure (-6 m) shows a visually similar general pattern (Fig 21. b). The atmospheric pressure at the highest altitude at 35 m shows the lowest value, followed by soil air pressure at 6 m depth and soil interface (0 m) consecutively. However, we notice a significant difference from 10/2019 until 11/2019 with the variation of the atmospheric pressure and soil air pressure of (0 m: 0.028 -0.049) and (-6 m: 0.022 - 0.053) bar. The trend of the soil air pressure becomes similar to the atmospheric pressure. The atmospheric ranges from 990 to 1008 bar in the summer and 975 to 1026 bar in the winter. The soil air pressure at -6 m fluctuates from 992 to 1008 bar in the summer and 966 to 1017mbar in the winter. The daily average of soil water content (Fig 21. c) demonstrates a clear relationship with precipitation, temperature, and very pronounced seasonal variation. The lowest SWC occurred in summer at around 0.1 (10 %), with some spikes due to the rainfall episodes. However, this increase in SWC of approximately 0.2 lasted only around five days after the rainfall. During the winter, SWC remained high at around 0.4 due to more frequent rain and low temperatures. A slight reduction of SWC was identified from January to February due to less frequent rain events. However, it only reduced the SWC by around 5%.

In *Fig* 21.*d*, the daily CO₂ molar fraction (χ c) at -1 and -6 m along with friction velocity (u*) above the canopy are provided. The χ c generally increases as the depth, from the near-atmospheric layer up to a few meters to the subsoil layer. Our study shows that χ c measured at 1 m is constantly lower than CO₂ measured in 6 m depth ranging from 1000-70000 ppm at -1 and 10000-60000 ppm at -6m. The χ c at -1 m was at the lowest in winter and highest in summer in June 2020. Meanwhile, the seasonal variation of χ c at -6m is somewhat unclear

since the maxima were reached in summer and winter. However, it can be seen that the rise of χc at -6 m depth is coincident with falling u* and a decrease in SWC due to the absence of rainfall. The seasonal variation of u* is also unpronounced. It is found to be low during summer and higher during winter, with an exception in early December 2019 to the end of February 2020. These results emphasize the significance of seasonal variation and the importance of intraday spikes of short-term variation. To further see the correlation between variables, the correlation matrix is provided in **Fig 22**.



Fig 22 Heat map based on correlation matrix between daily CO₂ molar fraction (-1m and -6m) (χc), Soil Water Content (SWC), u* (friction velocity), Temperature_(max) (T, at -6 m and 0 m), soil air pressure (-6m), air pressure (p), and precipitation (P).

The heatmap based on hourly data between observed variables from 1 June 2019 to 23 July 2020 shows that the influence of temperature m on subsoil CO₂ concentration at -6 m was pronounced with R of 0.94 (T_{soil} at -1m) and 0,83 (T_{soil} at 0m). The CO₂ concentration at -6 m was also weakly inversely correlated with atmospheric pressure at 0 m (R: -0.59), soil-air pressure at -6 m (R: -0.48), SWC (R: -0.50), and soil temperature at -6m (R: -0.59). However, a strong correlation between temperature and soil CO₂ does not extend to the shallower depth of -1 m. Pearson's CO₂ concentration at -1 m with soil temperature at -1 m and 0 m were - 0.36 to 0.14 consecutively. This relatively low correlation is most likely due to time window measurement inconsistency. While all temperature data were measured hourly during the monitoring campaign, χc at -1 m was measured only once every visit during midday. Furthermore, the heat map demonstrates a pronounced pattern between soil temperature at

various depths and SWC with R more significant than -0.7, except for soil temperature at -6 m. To better understand the driving mechanism of CO_2 concentration at -6 m during dry and wet periods and weather correlation between subsoil CO_2 concentrations extends to seasonal timescales, Principle Component Analysis (PCA) and time series of hourly data corresponding to observed variables are provided in *Fig 23*



Fig 23. The Principal Component Analysis (PCA) of hourly data during the monitoring time window from 19/09/2019 to 23/07/2020 (Left) and a comparison between hourly u* and CO₂ during a single visit (right). The data separated into wet (SWC > 20%) (a) and dry periods (SWC \leq 20%) (b).

Fig 23 focuses on a principal component analysis (PCA) and hourly variations of CO₂ molar fraction (χc) at 6 m depth auxiliaries data to define which variable contributes most. The color affected the different parameters refers to the significance of the variables (cos²) expressed between 0 (bad defined) and 1 (well defined). It can be seen from PCA that CO₂ at 6 m depth during low SWC (*Fig 23*. b) is inversely correlated with u* with cos² above 0.75.

A graph showing intraday variation firmly confirms the inverse relationship with identical rises and falls on the right side. The χc at 6 m depth decreased by more than 10000 ppm, following an increase of u,* from 0.2 m/s to 0.8 m/s. However, this pattern does not apply in observation during the wet period (*Fig 23.* a) where PCA fails to define the relationship between CO₂ at -6m with other variables and the intraday graph on the right side does not indicate a pronounced negative correlation pattern. However, it is noticeable that even during wet periods, a significant increase of u* to 1.45 m/s led to decreases in CO2 values at -6m dropping from 27000 ppm to 25000 ppm.

3.3.Discussion

3.3.1. CO₂ molar fraction dynamics

Our forest site's soil CO2 concentrations are comparable with a study conducted previously under similar conditions ranging between 774 ppm and 6521 ppm at 1 m depth (Jochheim, Wirth and von Unold, 2018). It is almost that CO₂ concentration and fluxes vary depending on physicochemical properties, soil cover types, and climatic conditions. However, the CO₂ change between forest land and grassland is similar to approximately 100 to 1300 mg CO_2 m² h⁻¹ than barren land and cropland (Oertel et al., 2016). The ranges of CO₂ concentration measured at the grassland in Kyushu Island, Japan was around 1300-8700 ppm (0.1 m depth), 2500-10800 ppm (0.2 m depth), 4200-13200 ppm (0.3 m depth), and 5800-16500 ppm (1.0 m depth) (Salmawati, Sasaki and Yuichi, 2017). It has also been reported that the Soil CO₂ concentration measured at a depth of 0.3 m in the South-Moravian region was around 5000 to 8000 ppm (Faimon and Lang, 2018). A study conducted in a temperate forest located Shale Hills Critical Zone Observatory, Pennsylvania, US, reported that the CO2 concentration reached up to 50000 ppm at a depth of 150 cm attributed to the greater root respiration depth partly due to higher macroporosity of sandstone lithologies (Hodges et al., 2019). The CO₂ concentration above 10% is generally found in the active geothermal area with a significant pressure gradient transport instead of the solely diffusive process (Pearce et al., 2004; Camarda *et al.*, 2007). Some studies suggest a strong positive correlation between χc and Temperature (Delogu et al., 2016; Oertel et al., 2016; Faimon and Lang, 2018), where temporal CO₂ concentration is affected by soil temperature on a biweekly basis (Jochheim, Wirth and von Unold, 2018). Our work demonstrates that CO₂ and Temperature are positively correlated at 1 and 6 m depth. In a temperate forest, Temperature is considered as the primary driver of heterotrophic soil respiration, releasing CO₂ as organisms decompose Soil Organic Carbon (SOC) (Lloyd and Taylor, 1994; Kätterer et al., 1998; Raich, Potter and Bhagawati, 2002). However, soil temperature effects toward heterotrophic respiration are rather complicated (Buysse *et al.*, 2013). It might also indirectly affect the microbial, substrate quantity, and substrate availability on a daily to annual basis (52,53). On minutes to an hourly basis, it might also influence the enzyme activity produced by bacteria and fungi(M.Willey, 2008).

Furthermore, most of the studies carried on in the forest soil mainly focused at a depth of 0 to 1 meter, where the soil CO_2 production is often a correlation to biological activity is more instantaneous. Very little data are available on the evolution of the CO_2 concentration in the deepest layers of the soil. In the present study, the abiotic drivers' relationship, including SWC and u*, is further explored and provided in **Fig 22**.

3.3.2. Analysis of Wind Turbulence and Soil moisture Content

Several periods with high and low friction velocity were detected during the monitoring period (**Fig 24**) where the relationship between friction velocity and soil CO₂ concentration at -6m is very pronounced, especially during dry periods with R² of 0.6 where SWC is less than $0.2 \text{ m}^3/\text{m}^{-3}$ $CO_2 = -14882u * + 55066$. However, this relationship does not extend during wet periods where SWC is above $0.2 \text{ m}^3/\text{m}^3$.



Fig 24. The relationship between hourly CO₂ molar fraction (χc) at 6m depth and friction velocity (u*) above the canopy for different levels of SWC: SWC<0.2 (red, p<0.0001), SWC between 0.2 to 0.3 (purple, p=0.35), SWC between 0.3 to 0.4 (blue, p=0.33), and SWC> 0.4 (green, p=0.144).

This finding acts as empirical evidence of subsoil ventilation and the importance of advection in gas transport processes where the decrease of χc coincides with high u* that fits with the linear model (Coefficients: b[0] 55066, b[1] -14882, R²:0.68) (**Fig 24**). Some previous works

focusing on soil CO₂ dynamics have reported the influence between γc and u^{*} (Maier and Aubinet, 2011; Roland et al., 2013; Sánchez-cañete et al., 2016). Our site's lower soil consists of sandy and clayey passages caused by the complex sedimentary source material. The calcareous bedrock mainly consisted of calcium carbonate and a few clay minerals surrounded by the weathered layer rich in clays due to decarbonization. It is a widely held view that limestone's solubility in weak acid and limestone results in karst forming processes. It has been previously studied that the karst system stores a large amount of CO₂ underground, which later was emitted during windy days, and filled quickly during low wind speed through cracks and fissures (Roland et al., 2013). Even though some sinkholes in our site are visible, this hypothesis needs further investigation to understand the rate and magnitude of calcite dissolution. This study also demonstrates that the subsoil's permeability is most likely reduced during wet periods diminishing molecular diffusion and advection. The lower the SWC value, the more enormous the potential for ventilation to remove CO₂ from the soil as suggested by previous works in a karstic environment (Sanchez-Cañete et al., 2011b; Roland et al., 2013). High friction velocity (u*) has also coincided with high temperature. It is widely known that the increase of CO2 efflux leads to higher respiration rates known as temperature sensitivity (Q10), which is related to biological activity cannot fully explain the variation. Instead, the CO2 fluctuation is likely due to Pressure Pumping Effects (PPE), where the soil acts as a semi-permeable membrane storing and releasing CO_2 (Laemmel et al., 2017, 2019; Mohr et al., 2017). Besides, the lower air pressure encourages the larger soil emission due to reduced counter-pressure on the soil (Reicosky et al., 2008; Oertel et al., 2016) To test our hypothesis regarding pressure pumping effects generated in a deep layer of soil, time series of hourly pressure fluctuation at various depth, friction velocity, and the temperature is provided in figure Fig 25.





Fig 25. Half-hourly wavelet-based analysis from 17 June to 23 July 2020 which include (a) wavelet power spectrum of (a.1) temperature at 35 m, (a.2) friction velocity (u*), (a.3) air pressure at 35 m, and (a.4) air pressure difference (Δp) between 35 m and -6 m. Moreover, wavelet coherence analysis (b) shows statistical significance of multivariate of (b.1) temperature at 35 m over u* and (b.2) Δp over u*. In part, a reddish area and black lines represent high wavelet power levels. In part b, a red area with white contour lines demonstrates a high correlation with significance levels of more than 5% in part b. Arrows represent a multivariate phase-locked angle relationship where horizontal arrows pointing left (phase angle: 180°) indicate that two wavelet series are out of phase and horizontal arrows pointing right (phase angle : 0°) suggest that two wavelet series are in phase. A white shaded area indicates that edge effects influence the time series.

Friction velocity (u*) and temperature (35 m) recorded from 17 June to 23 July 2020 ranged from 0 m/s-1m/s and 10° -28°C, respectively. Wavelet power analysis of temperature and u* (**Fig 25.a.1,2**) demonstrates a strong diurnal scale as expected, shown by maximum power wavelet at periods of 24 (24 hours). Wavelet power levels of u* in periods of 24 hours were slightly higher with 3.33 compared to temperature with 2.87. As for the air pressure, even though the pressure above the canopy (35 m), soil-air interface pressure (0 m), soil-air

pressure (-6m) shows different values of magnitude, the general patterns are similar; therefore, a wavelet power analysis was employed only to the air pressure at 35 m. In contrast with the temperature (35 m) and u*, the air pressure at 35 m shows little or no daily variations. Instead, the wavelet power levels of air pressure at 35 m Fig 25.a.3) were significant at the region of 128 (5 days) with only 1.74, which was also found in a wavelet power analysis of temperature (35 m). What is striking in the wavelet power analysis is that the pressure difference (Δp , 35 m, and -6 m) provide in Fig 25.a.4 shows strong daily fluctuation shown by dominant periods of 24 hours similar to temperature (35 m) and u*. However, these data should be interpreted carefully since the pressure sensor's resolution was only 0.002 bar and could not detect smaller pressure fluctuation. The pressure fluctuation in the frequency ranging from 0.01 Hz–0.1 Hz is highly dependent on the above canopy wind speed (Mohr et al., 2016). In other words, the pressure dynamics that might be generated from pressure pumping effects due to wind turbulence above the canopy must be further investigated. According to Wavelet coherence analysis, the temporal correlation between the temperature at 35 m over u* [Fig 25.b.1] and Δp (35 m and -6m) over u* [Fig 25.b.2] demonstrated substantial variation, especially at daily scale with time lags of temperature (35 m) and Δp (35 m and -6m) over u* ranged from 2 to 4 hours. Besides the temperature, Δp between soil air interface and soil-air is highly likely to promote the contraction and expansion of the air stored in soil pores, cracks, and fissures, which play a significant role in regulating the vertical transport and gas storage suggested by previous works (Tillman and Smith, 2005; Laemmel et al., 2019; Moya et al., 2019). Nonetheless, propagation of atmospheric pressure fluctuations into the subsurface has been known to promote the air's migration in moderately permeable materials up to 10 m depth and even greater depth in a fractured rock system (Massmann and Farrier, 1992; Parker, 2003; Kuang, Jiao and Li, 2013). However, most works on assessing the PPE and wind turbulence CO₂ focus on the top layer up to one-meter depth; our work provides empirical evidence of a strong partial relationship on a deeper soil layer (6 m).

3.4. Conclusion

We describe the calibration technique, observational setup of the measurement campaign, aspects of the data analysis, and Instrument field analysis of the recorded time series of soil gases and auxiliaries data within the study area. This soil gas measurement infrastructure combining borehole measurement with micrometeorological measurement offers excellent possibilities for long-term in-situ and continuous gas monitoring to derive the vertical
distribution of CO₂. Thus, this infrastructure allowed the observation of the temporal dynamics in soil-gas CO₂ research. Relatively short-term events could be monitored, notably those associated with pressure and Temperature at a deep soil layer, which is difficult to measure using a conventional method. Besides, the long term data set of soil gas baseline will contribute to understanding better the influence of short-term events, including (i) spikes of short term events, (ii) magnitudes of change caused by the suspected driving variables, (iii) the duration of the changing circumstances, and (iv) Indirect variables influencing these short term events. Such a metrology approach will contribute to the definition of good practice for the state of studies related to subsoil CO₂ molar fraction in conjunction with the soil-air pressure and Temperature. Even though this approach has been applied to the forest ecosystem, it can be extended to any other natural or anthropic system.

Furthermore, this study shows strong empirical shreds of evidence that the increase of temperature leads to higher respiration rates, which is further, produced CO_2 stored in deep soil layers. However, this factor related to biological activity cannot fully explain the variation. We hypothesize pressure pumping effects also play a role, especially during dry summer. The decreases of CO_2 molar fraction in the subsoil coincided with high turbulence, resulting in increased CO_2 storage in deep soil during low turbulence. This study also demonstrates that permeability significantly reduced during wet periods diminishing molecular diffusion and advection. This highlights the importance of spatial and temporal dynamics of deep soil CO_2 dynamics that reach a value of up to 100 times larger than atmospheric CO_2 . This empirical evidence also challenges the current assumption that PPE's influence is only significant on a topsoil layer. However, it is still uncertain whether this strong relationship is site-specific or not since it is highly likely that the soil porosity, soil texture, stand type, and canopy height play roles. As flux tower establishment expands, there is a strong need to apply borehole measurement underneath to understand better the relationships between friction velocity and subsoil CO_2 dynamics on various sites.

Increasing Net CO₂ Uptake During the European Drought 2018-2019 in Beech Forest, North-Eastern France

Didi Adisaputro ^{1,2*}, Philippe De Donato ¹, Laurent Saint-Andre ², Catherine Galy ³

² INRAE, UR BEF, Centre de Nancy, 54280 Champenoux, France;

³ ANDRA, 55290 Bure, France;

Resume

La mesure du flux de carbone à long terme est nécessaire pour mieux comprendre la réaction d'un écosystème naturel dans des conditions climatiques changeantes. Dans cette étude, la technique de covariance des tourbillons a été utilisée pendant six années consécutives pour déterminer les réponses des échanges forêt-atmosphère aux épisodes de sécheresse dans la hêtraie, dans le nord-est de la France. La période de 2014 à 2019 comprend deux années consécutives exceptionnellement sèches (2018-2019) indiquées par un indice normalisé de précipitation-évapotranspiration significativement bas, accumulé sur 3 mois (SPEI-3, 2018=-2,252, 2019=-2,224). Contrairement à la plupart des sites les valeurs d'eddy covariance (EC) en Europe centrale et du Nord, de productivité primaire brute (GPP) et de respiration de l'écosystème (Reco) ont diminué simultanément, ce qui a entraîné une augmentation des valeurs d'échange net de l'écosystème (NEE), notre site a augmenté sa capacité de puits de carbone pendant l'épisode de sécheresse. De plus, la diminution du paramètre NEE était due à une baisse des valeurs du paramètre Reco plutôt qu'à une augmentation de la productivité primaire brute (GPP). Les valeurs de Reco, mesurées en été et en automne 2018-2019, ont diminué de 20 % et 26 % par rapport à celles mesurées lors des années de référence (2014-2017). Les valeurs décroissantes du Reco ont coïncidé avec une baisse de la teneur en eau du sol (SWC, -57 %) et une hausse de la température du sol (T_{soil}) (+15 %). Il est fort probable que les différents écosystèmes en fonction de leur localisation géographique au sein de la zone d'étude, réagissent différemment à des variations climatiques locales, en particulier ceux situés à la limite du domaine de l'extrême sécheresse. Ces bases de données combinées

¹ GeoRessources Laboratory, Université de Lorraine, CNRS, BP 70239, 54506 Vandœuvre-lès-Nancy, France;

météorologiques et de flux de CO₂ peuvent être utilisées pour mieux comprendre et prévoir la réponse future de l'écosystème forestier au changement climatique.

Abstract

Long-term carbon flux measurement is necessary to better understand the landscape response under changing climatic conditions. In this study, the eddy covariance technique was employed for six consecutive years to determine forest-atmospheric exchange responses to drought episodes in the beech forest in North-Eastern France. The period from 2014 to 2019 includes two consecutive unusually dry years (2018-2019) indicated by significantly low Standardized Precipitation-Evapotranspiration Index accumulated over three months (SPEI-3, 2018=-2.252, 2019=-2.224). In contrast with most of the EC sites in Central and Northern Europe where GPP (Gross Primary Productivity) and Reco (Ecosystem Respiration) concurrently declined, that lead to an overall increase in NEE (Net Ecosystem Exchange), our site increased its carbon sink capacity during the drought episode. It is almost certain that the combination between high GPP at the beginning of the year and low Reco at the end of the year results in high net CO₂. However, the decrease of NEE was mostly influenced by the decline of Reco rather than increased GPP. Reco decreased by 20% and 26% in Summer and Autumn (2018-2019) relative to the reference years (2014-2017). The decreasing values of Reco coincided with falling SWC (-57%) and rising soil temperature (Ts) (15%). It is highly likely that different ecosystems and regions respond differently to a changing climate, especially those situated at the edge of the domain of extreme drought. Such CO₂ flux and meteorological data can be used to better understand and predict the forest ecosystem's future response to changing climate.

4.1. Introduction

The eddy covariance method has been widely applied in many areas of carbon and water fluxes measurement, including but not limited to the primary forest ecosystem (Grace *et al.*, 1996; Curtis *et al.*, 2002; Dennis D. Baldocchi, 2003; Hayek *et al.*, 2018), crops (Chi *et al.*, 2016; Anderson *et al.*, 2017), shrublands (Eder *et al.*, 2015; Valayamkunnath *et al.*, 2018), desserts (Eder *et al.*, 2015; Ma *et al.*, 2017; Valayamkunnath *et al.*, 2018). The vast majority of global carbon in terrersterial ecosystem are stored in semi-arid biomes and forest (Dixon *et al.*, 1994; Pan *et al.*, 2011; Poulter *et al.*, 2014) where the seasonal variability of these ecosystems are strongly influenced by the interactions plant physiology and climate(Granier *et al.*, 2008).

It is a widely held view that evapotranspiration (ET) and NEE are two significant fluxes exchanged between terrestrial vegetation and the atmosphere. The latter consists of three components: GPP (fluxes-gross photosynthesis) and ecosystem respiration (autotrophic and heterotrophic respiration). These components' variability is driven by interconnected biotic and abiotic factors, including temperature, water availability, radiation, vapor pressure deficit, pests, and anthropogenic (van Dijk, Dolman and Schulze, 2005; Granier et al., 2008; Yi et al., 2010). However, the relationship between these variabilities and GPP is somewhat complicated. Photosynthesis can either be promoted or reduced by sunlight, humidity, clouds, and excessive rain or drought (Jung et al., 2010; Seneviratne et al., 2010). A drier year tends to increase photosynthesis up to a point where the stomatal closure occurs due to high VPD (Reichstein et al., 2007; Wolf et al., 2016). On the other hand, the wetter year is associated with a lower photosynthesis rate due to a lower amount of received radiation (Zeri et al., 2014). The soil and plant respiration tend to decline if the soil water content is too low or too high and is highly associated with the rhizosphere's carbon inputs (Baldocchi, 2008). Furthermore, the temperature may affect positively or negatively both GPP and Reco. GPP responds to a change in temperature in a non-linear relationship where it may increase GPP up to a point where it is intolerable for the vegetation (Reichstein et al., 2005; Richardson et al., 2010). while, Temperature will increase the Reco given sufficient soil water content Reco (Xu and Qi, 2001; Atkin et al., 2005; Wen et al., 2006; Jassal et al., 2008).

A large number of long-term eddy-covariance studies in the temperate deciduous forest have been carried out for the last few decades (Urbanski *et al.*, 2007; Granier *et al.*, 2008; Pilegaard *et al.*, 2011; Wilkinson *et al.*, 2012; Shao *et al.*, 2014; Froelich *et al.*, 2015; Herbst *et al.*, 2015; Novick *et al.*, 2015; Sulman *et al.*, 2016). The interannual variation of the flux (\pm 100 gC m⁻² y⁻¹) in the temperate and deciduous forest is relatively large compared with the other climate and functional types such as evergreen, semiarid, and crops (Baldocchi, Chua and Reichstein, 2018). Even though the driving mechanisms of seasonal variation are already well known, a relatively small alteration in climate variables may lead to a disproportionate change in extreme frequency, altering the precipitation, temperature, and other weatherdriven phenomena (Seneviratne *et al.*, 2010).

2018 and 2019 have been the driest year at the eddy covariance (EC) site (Montiers-sur-Saulx, France) for more than a decade with SPEI (Standardized Precipitation and Evaporation Index) of 2.25 and 2.24 consecutively. As a comparison, the extreme drought in 2003 was - 2.52 (Beguería *et al.*, 2014). The drought epicenter was identified in Central and Northern

Europe, where forests and crops were rarely exposed by high water deficits and hot summer (Peters *et al.*, 2020). The terrestrial carbon exchange's sensitivity toward the drought episodes in Europe has been studied using multiple EC sites comparing the 2018 drought to the 2016 reference data. High temperature indirectly aggravated drought impacts on GPP by 10 % for the forest ecosystem (Fu *et al.*, 2020). The results demonstrated that high temperature-induced increases in VPD and decreases in SWC aggravated drought impacts on GPP. However, long-term and site-specific EC analysis will undoubtedly help better understand the ecosystem's response to climate variations and extremes. Also, most current studies heavily rely on chrono-sequences, which are applied across massive geographical regions that do not take into account soil and vegetation cover type (Baldocchi, Chua and Reichstein, 2018).

Thus, considering high uncertainty in interannual variability and more frequent extreme event, this work aims to determine the effects of contrasting climate on beech forest over six years periods with some objective as follow : (1) Quantify interannual variability of the fluxes; (2) calculate the change of GPP and Reco during the drought episodes; (3) Determine the main driving factors of the variability; and (4) Identify the ability of satellite-derived index of vegetation state in detecting the variability due to drought and thinning.

4.2. Materials and Methods

4.2.1. The Fundamental of Eddy Covariance Technique

For the last decades, the gas exchange from a specific compartment to the atmosphere has been measured by this EC technique. EC depends on multiple meteorological conditions because they affect the footprint, temporal, and spatial homogeneity. It has significant advantages in providing a long-term investigation of gasses exchange by offering non-intrusive measurements that integrate a large footprint (Aubinet, Vesala, and Papale, 2012b). The atmosphere contains a turbulent atmosphere downward and upward moving air carrying along with trace gas such as CO₂ and CH₄ (Dennis D Baldocchi, 2003). The eddy covariance (EC) methodology allows the quantification of energy and mass exchanges between the atmosphere and the surface of the earth by relying mainly on wind speed and tracer concentration that enables capturing turbulent motions at a particular time-scale (Aubinet, Vesala, and Papale, 2012b; Arriga *et al.*, 2017). A turbulent flux (F) of a quantity through the interface can be determined by the product of covariance between the measurement of vertical velocity (w) and the trace gas concentration (c) that is represented in Equation 4.2.1. Where $\binom{\rho_c}{\rho_a}$ is defined as the mixing ratio of a trace gas in air:

$$F = \overline{\rho_a ws}$$
 Equation 4.2.1

The vertical flux is driven by atmospheric turbulence as eddies of different wind speed transport the gas upward and downward. The fluctuation values of w and s are measured in a period of interval and further processed using the Reynolds decomposition resulting means and deviations indicated by overbar and prime. The yielded equation is provided as follow:

$$F = \overline{(\bar{\rho}_a + \dot{\rho}_a)(\bar{w} + \dot{w})(\bar{s} + \dot{s})}$$
 Equation 4.2.2

Furthermore, the parentheses are opened, and since the average deviation from the mean is zero, the variables that include $\overline{\rho_a}\overline{w}\dot{s}$, $\overline{\rho_a}\dot{w}\overline{s}$, and $\dot{\rho}_a\overline{w}\overline{s}$ are excluded from the equation. then yields:

$$F = \left(\overline{\rho}_a \overline{w} \overline{s} + \overline{\rho}_a \overline{w} \overline{s} + \overline{w} \overline{\rho}_a \overline{s} + \overline{s} \overline{\rho}_a \overline{w} + \overline{\rho}_a \overline{w} \overline{s}\right)$$
Equation 4.2.3

Moreover, the crucial assumption is made for conventional eddy covariance in which the fluctuation of the air density is assumed to be zero due to its negligibility. Hence, $\overline{w}\overline{\rho}_{a}\dot{s}, \overline{s}\overline{\rho}_{a}\dot{w}, and \overline{\rho}_{a}\dot{w}\dot{s}$ are eliminated from the equation. However, this assumption is not applicable in a mountain ridge where the wind strongly flows over the mountain ridge,

resulting in a large fluctuation of the density (ρ 'w'). However, when eddy covariance is used conventionally over vast and flat spaces, this assumption is reasonable because the change of density can be assumed negligible (Burba and Anderson, 2010). Another assumption is also taken into account where there is no divergence or convergence due to the mean vertical flow is assumed negligible for horizontal homogeneous terrain. Hence $\bar{\rho}_a \bar{w} \bar{s}$ is also out of equation then yields:

$$F \approx \overline{\rho}_a \overline{\dot{w}} \dot{s}$$
 Equation 4.2.4

Equation 4.2.4 for the eddy flux shows that the change is approximately equal to the mean air density and the mean covariance between vertical wind speed and the mixing ratio of substances 'c' in the air. The empirical formula for measuring the Carbon Dioxide flux is given in the following equation:

$$F_c = \dot{w}\dot{\rho_c}$$
 Equation 4.2.5

Equation 4.2.5 for CO₂ and CH₄ flux then is applied. The w and c need to be measured at the same point and quick enough to prevent the variability influenced by the atmospheric turbulence. Eddy covariance depends on the turbulent air flows to calculate the Net Ecosystem Exchanges (NEE). The flux data collected on top of the tower above the forest was taken in rapid succession (10-20 Hz) and was assessed semi-hourly. Aside from the gas analyzer that can be open-path or close, the EC instrumentation also consists of a 3-dimensional anemometer positioned near the anemometer. Even though the distances should be chosen to be as small as possible, strong NEE somehow avoids the wind distortion. The so-called Footprint (FP) representing the area around the measurement point is essential in the EC technique. It spatially integrates fluxes from a place that extends upwind of the tower. Even though the measurement height influences the footprint's size, some other factors such as upwind topography, wind speed, and surface layer stability also contribute significantly (Launiainen, 2011).

Even though the fundamental principle of the EC is relatively straight forward, there are some common technical and methodological challenges, including (1) Underestimation of the small scale of turbulence due to inadequate frequency response of the sonic anemometer and gas analyzer; and (2) The low-frequency flux also might be caused by the incorrect choice of the averaging time. Therefore co-spectral correction needs to be employed to solve the problem (Dennis D Baldocchi, 2003; Launiainen, 2011; Barba *et al.*, 2017). While the Methodological

challenges include (1) Misinterpretation of the ecosystem response and directional differences in measured flux due to non-ideal measurement where horizontal homogeneity is limited; (2) The stable mass balance during the night is incorrectly calculated because the EC cannot detect vertical and horizontal advection and storage below the measurement height; and (3) currently there is no uniform methodology for measuring, post-processing, quality screening, data gap-filling regardless the recent advancement (Launiainen, 2011). Nonetheless, it is a widely held view that EC's benefit for detecting turbulent of the whole ecosystem-atmosphere flux outweigh its limitation. Thus, it is not only successful in seeing whole-ecosystem response but also for estimating annual and seasonal balance.

4.2.2. Instrumentation and Measurements

The primary measurement platform is a flux tower built at the end of 2012 and constructed at a height up 45 m above the ground to record the Net Ecosystem Exchange (NE). It also allows the continuous measurement of the wind's speed and direction at 35 m height (around 10m above forest canopy). It is equipped with an enclosed infra-red CO₂/H₂O gas analyzer (IRGA, Li-7200, LI-COR, Lincoln, NE USA) and six 3D sonic anemometers (HS-50 Gill, Hampshire, UK). The amount of CO₂ stored in the air between the EC system and the soil surface is measured at different heights along the flux tower spanning from 5, 10, 15, 25, 35, and 45 meters. Hence, this system allows the calculation of CO₂ absorption or accumulation in and below the forest canopy. The eddy covariance tower is also supported by the meteorological which includes a) air temperature and moisture sensor installed at six different levels (HMP155, Vaisala, Vantaa, Finland), b) global radiation sensors (pyranometer, CMP21, Kipp & Zonen, Delft, Netherlands), c) photosynthetically active radiation sensor (BF5, Delta-T Devices Ltd., Cambridge, England), and d) shortwave and longwave radiation sensors both incident and reflected components (a net radiometer, CNR4, Kipp & Zonen, Delft, Netherlands).

4.2.3. Data Processing

The NEE values are the sum between Fc (CO₂ flux) and storage flux measured using the EC system and CO₂ profile system consecutively. The EddyFlux software (EddySoft, Meteotools, MPI, Jena) was used to calculate the CO₂ flux (Fc) following a protocol recommended in the literature (Aubinet *et al.*, 1999). Furthermore, data postprocessing was executed in three steps, which include: 1) data quality assessment by removing low-quality data associated with malfunction and out of range spikes; 2) data was processed using an outlier detection algorithm following a protocol from literature (Papale *et al.*, 2006); 3) rejecting the night time flux data with friction velocity (u*) under the threshold (from 0.18 to 0.34 m s⁻¹) which was

applied according to the moving point test (Papale *et al.*, 2006). Furthermore, incorrect fluctuations in energy fluxes and CO_2 were rejected according to the moving median for further spikes identification, which consists of a) separating the data into a residual and smooth part and b) manually rejecting entire incorrect data. This leads to the first set of preprocessed NEE data as shown in *Fig 26*. Then, the gap-filling technique was executed using a marginal distribution sampling algorithm that takes into account meteorological data and the covariation between fluxes as well as temporal auto-correlation of fluxes (Reichstein *et al.*, 2005).



Fig 26. The fingerprint of NEE from 2014 to 2019 represents all of the data available for gap-filling purposes.

This flux gap-filling method consists of three levels of operation, including a) using meteorological data (Rg, Ta, and VPD) as a reference to obtain mean value with a similar

meteorological condition within seven days time frame and might be prolonged to 14 days window; b) using the same approach but only relying on Rg to define the mean value of similar meteorological condition within the seven-day window; and c) if the meteorological and radiation data unavailable, the gaps are filled with a mean value in the last hour taking considering a diurnal variation of every variable. In case the gaps have not been filled after these three levels of operation, the same procedure is applied considering a larger time frame.

Flux partitioning for of NEE into GPP and Reco was also carried out, where Reco is estimated from night-time and extrapolated to daytime following a protocol provided in the literature (Reichstein *et al.*, 2005) were on the night-time periods:

$$NEE = Reco$$
 Equation 4.2.6

And for the daytime periods:

$$NEE = Reco - GPP$$
 Equation 4.2.7

Nighttime fluxes were adjusted in relation to T_{air} where, the dependence of Reco on temperature (Lloyd and Taylor, 1994) was used to adjust nighttime fluxes through the following equation:

$$Reco = Reco_{ref} \times \exp\left(E_0 \times \left(\frac{1}{T_{ref} - T_0}\right) - \left(\frac{1}{T_{air} - T_0}\right)\right) \qquad \text{Equation 4.2.8}$$

Where R_{eco} (µmol m⁻² s⁻¹) is is a combination of respiration rates from the autotrophic and heterotrophic component, Reco_{ref} is the respiration rate at reference temperature T_{ref}(10°C), E0 (308.56 kJ mol⁻¹) is the activation energy, and T0 is the baseline temperature (-42.02 °C). The entire postprocessing steps were executed using R software (Wutzler *et al.*, 2018; R Core Team, 2020)

4.2.4. The flux footprint

A two-dimensional parameterization model was used to estimate the flux footprint (Kljun *et al.*, 2015) run on R software (R Core Team, 2020). Even though parameterization is considered robust and valid for various heights and boundary-layer conditions, it is not valid for low friction velocity (u*> 0.1 m s-1). Therefore, the model was executed for daylight conditions only. The operation requires some data, which include a) flux tower height (45m),

b) canopy height (26 m), surface friction velocity (u^*), mean wind speed (m s⁻¹), wind direction, Obukhov length (m), and standard deviation of the vertical wind speed.

4.2.5. Drought Index and Vegetation State

The SPEI was calculated using a difference between precipitation and reference evapotranspiration also known as climatic water balance. It is also considered as reliable to measure drought severity compared with solely using precipitation data since climatic water balance compares the atmospheric evaporative demand (ET0) with water availability (P (Beguería et al., 2014). The Standardized Precipitation Evapotranspiration Index (SPEI) has been widely used in numerous climatology and hydrology studies (Pearce et al., 2004; Borken and Matzner, 2009; Um et al., 2016; Vicca et al., 2016; Prabnakorn et al., 2018; R. Wang *et al.*, 2018). This multiscalar drought index is used to identify the anomaly in terms of its onset, magnitude, and drought conditions relative to its normal conditions. SPEI-3 (Standardized Precipitation Evapotranspiration Index accumulated over three months) Index with 0.5° spatial resolution (Beguería et al., 2014) was used In this work. The main drivers of the observed temporal and spatial variability of carbon exchange (GPP, Reco, and NEE) are not only radiation and temperature but also leaf area (van Dijk, Dolman and Schulze, 2005). Therefore, we also gathered LAI (Leave Area Index) from Moderate Resolution Imaging Spectroradiometer (MODIS) (MOD15A253) with 8-day composites at 500 m spatial resolutions. Enhanced Vegetation Index (EVI) was also used to determine the vegetation state response to the interannual fluxes variability and anomalies induced by drought. EVI has been studied to detect a reduction in GPP following drought (Vicca et al., 2016). This estimation of area-average aboveground biomass was derived from the MOD13Q1 product with sixteen-day composites at 250 m spatial resolution from 2014 to 2020.

4.3. Results

4.3.1. Seasonal variations in environmental variables

The climatic conditions in our site vary from year to year (

Fig 27). The coldest month is identified in January 2017 with a daily average of Ta at -1.576 °C. The warmest periods were identified in July 2018 and July 2019, with a monthly average of Ta at 21.6°C and 20.8°C consecutively.



Fig 27. (a) Time series of daily carbon flux (NEE, Reco and GPP, $gCm^{-2} day^{-1}$; (b) rainfall, mm month⁻¹; soil water content (SWC); (c) daily average of soil temperature (Ts) and air temperature (Ta) (d) the daily average of photosynthetically active radiation (PPFDmax, μ molm⁻²s⁻¹) and vapor pressure deficit (VPD, kPa); and (e) SPEI-3 (standardized precipitation evapotranspiration index over three years cumulative)

The monthly average of Ta and Ts was also unsurprisingly at the highest in July 2018 and July 2019 at 17.72 and 18.69. Combine with low precipitation in the summer of 2018 and 2019, resulting in low Soil Water Content (SWC) under 0.1 (10%) for four consecutive months from July-October in 2018 and June-September 2019. Even though the SWC could not be measured, the SPEI-3 (three years cumulative) was used as a proxy were showed that the summer 2018 and summer 2019 are the lowest. This lowest index below -2 did not return to 0 even after relatively wet periods in winter 2018. Furthermore, the highest VPD (Vapor Pressure Deficit) is found in July 2019 and July 2018 at 5.25 kph and 3.78 kph consecutively. During summer periods, the monthly average of PPFD (Photosynthetic Photon Flux Density)

is highest in June 2019 at 544 mol Photon $m^{-2} s^{-1}$ and the lowest in August 2014 at 88.302 mol Photon $m^{-2} s^{-1}$. Summer 2014 is also considered the coldest summer with a monthly average temperature at 15.39 °C and relatively low VPD at 1.7 kph.

4.3.2. Variations of Carbon Exchange

During the study periods, the ecosystem acted as a net carbon sink with mean annual NEE, GPP, and Reco of -453 ± 122 gC m⁻²y⁻¹, -1468 ± 109 gC m⁻²y⁻¹, and 1052 ± 88 gC m⁻²y⁻¹



Fig 28 shows a bibliographical compilation showing how these carbon exchange values compared to long-term studies on the other EC sites in the deciduous broadleaved forest.





Fig 28. Annual carbon flux, including NEE (Net Ecosystem Exchange), GPP (Gross Primary Productivity), and Reco(Ecosystem Respiration) in a deciduous broadleaved forest. These include our site (FR-MsS) (France-Montiers, n = 6 years), FR-Hes (France, Hesse, n=10 years) (Granier *et al.*, 2008), US-HFEMS (Massachusetts-Harvard Forest, n = 13 years) (Urbanski *et al.*, 2007), DK-Sor (Denmark-Soroe, n = 13 years) (Pilegaard *et al.*, 2011), JPN-TKY (Japan-Takayama, Saigusa *et al.*, 2005, n=10 years) UK-SI (UK-Straits Inclosure, n = 12) (Wilkinson *et al.*, 2012), US-MOZ (Missouri-Ozarks, n = 5 years) (Shao *et al.*, 2014), CA-Cbo (Canada-Ontario-Borden, n = 18 years) (Froelich *et al.*, 2015), DE-Hai (Germany-Hainich, n=7 Years) (Herbst *et al.*, 2015), US-Dk2 (North Carolina-Duke Forest, n=8 years) (Novick *et al.*, 2015), and US-MMS (Indiana-Morgan-Monroe, n = 13 years) (Sulman *et al.*, 2016).

In comparison to the previous studies that have conducted long-term monitoring (> 5 years) in a temperate forest, our site (FR-MsS) is the fourth largest net carbon sink. Also, Since FR-MsS and FR-Hes are relatively close, influenced by almost similar climatic conditions, and have identical stand types (*Fagus sylvatica L*), It is evident that NEE, GPP, and Reco are in a similar range at around 400 gCm⁻²y⁻¹, 1400 gCm⁻²y⁻¹ and 1000 gCm⁻²y⁻¹ Consecutively. However, interannual variation of NEE among the EC sites that differ in climate and available type is considerably high with a mean of SD at around 100 gC m⁻² y. However, it is also important to note that the recording year between sites differs. It has been widely known that climatic conditions play a significant role in regulating carbon exchange and storage. Further detail regarding the interannual variation in FR-MsS is provided in *Fig 29*.



Fig 29. Annual Net Ecosystem Exchange (NEE), Gross Primary Production (GPP), and Ecosystem Respiration (Reco) for the four years of measurements at Montiers site.

The forest ecosystem of Montiers was always a sink for carbon interannually, with the lowest NEE identified in 2016 with -297 gCm⁻²y⁻¹. The NEE significantly increased (negatively) from 2017 to 2019 with -602 gCm⁻²y⁻¹ and -633 gCm⁻²y⁻¹ consecutively (note: there are no data NEE data at the end of 2017 due to technical issues). The increases in NEE from 2018 to 2019 are primarily attributed to falling Reco rather than increasing gross primary productivity (GPP). These years also coincide with the driest and warmest years during the study periods (*Fig* 21). Daily cumulative of GPP, Reco, and NEE varies seasonally from time-series data. *Table 4* shows cumulative seasonal fluxes, including cumulative P, average SWC, Ts_(max), and Ta_(maximum) during the study periods.

Table 4. Seasonal Variation of NEE (Net Ecosystem Exchange), RE (Ecosystem Respiration), GPP (Gross Primary Productivity), P (Precipitation), SWC (Soil Water Content), Ts (Soil Temperature), and Ta (Air Temperature) from 2014 to 2019.

Veen	Period	NEE	RE	GPP	Р	SWC	Ts	Та
rears			(g C m ⁻² Season ⁻¹)			(%)	(°C)	(°C)
2014	Winter			-	-	-	-	-
	Spring	78	318	-397	12	-	-	23.1
	Summer	-446	5 385	-830	336	-	-	30.7
	Autumn	1	304	-303	195	-	-	23.3
2015	Winter	14	4 125	-11	230	-	-	12
	Spring	85	5 312	-397	199	-	-	24.6
	Summer	-409	408	-818	101	-	-	33.9
	Autumn	-10	255	-265	217	-	-	21.5
2016	Winter	107	124	-17	253	0.26	7.9	13.7
	Spring	1	285	-284	287	0.26	14.6	18.7
	Summer	- <mark>4</mark> 01	480	-882	192	0.18	21.6	33.4
	Autumn	-2	2 237	-239	185	0.12	19.5	28.9
	Winter	96	112	-15	122	0.22	7.06	15.1
2017	Spring	376	5 226	-215	163	0.21	17.2	29.2
2017	Summer	- 13	3 383	-797	303	0.15	20.27	31.8
	Autumn			-	-	-	-	-
2018	Winter				-		-	-
	Spring	32	2 225	-357	287	0.24	16.73	25.6
	Summer	- 525	327	-853	150	0.08	22.44	34
	Autumn	-77	7 212	-290	100	0.07	18.31	27.3
2019	Winter	85	120	-35	261	0.21	10.02	19.7
	Spring	<mark>-14</mark> 1.7	331	-417	187	0.2	18.3	24.9
	Summer	- 554	4 331	-885	73	0.06	25.95	37
	Autumn	58	3 179	-237	248	0.15	21	26

The seasonal categorization considers a winter with data in December previous year and as expected, the ecosystem is always a carbon source during the winter with a NEE of 100.5 g C m⁻² Season⁻¹. Overall the ecosystem act as a carbon sink during the summer periods with an average seasonal cumulative NEE of 458 g C m⁻² Season⁻¹. Nonetheless, during autumn and spring, the ecosystem's role is somewhat unclear and interchangeably from a source to sink of carbon. The ecosystem acted as a low carbon source during the Spring season in 2017 (3.76 g C m⁻² Season⁻¹) and 2016 (1 g C m⁻² Season⁻¹). Furthermore, What is striking from *Table 4* is that the ecosystem significantly increases its capacity in sinking carbon during Autumn 2018 (-77 g C m⁻² Season⁻¹) and 2019 (-58 g C m⁻² Season⁻¹) and Autumn 2018 (327 and 212 gC m⁻² Season⁻¹) and 2019 (331 and 179 gC m⁻² Season⁻¹). These periods coincide with the driest and warmest periods during the observational periods and probably for the last few decades based on the SPEI-12 index (Beguería *et al.*, 2014). To better understand the degree of influence of Temperature and SWC toward GPP and Reco variation, a comparison of monthly variation is provided in **Fig 30**.



Fig 30. Yearly comparison of average monthly data from 2014 to 2020 between Gross Primary Productivity (GPP) (a), Reco (Ecosystem Respiration) (b), Air Temperature Maximum $(Ta_{(max)})$ (c), and Soil Water Content Average (SWC) (d).

It can be clearly seen in **Fig 30** that the peak period of GPP in 2014, 2015, 2018, and 2019 which were detected in June, differed from the observation periods of 2016 and 2020, which fell in July and May consecutively. The peak was shifting in 2016 corresponded with the monthly average of SWC that remained steady (~29%) from January to June and slowly decreased to September. The peak periods' shifting can be attributed to the early or late growing season (Froelich *et al.*, 2015). Unlike the other years, the peak of GPP in 2017 is somewhat unclear, since it reached 278 gC m⁻² month⁻¹ in June, decreased to 238 gC m⁻² month⁻¹, and increased by 42 gC m⁻² month⁻¹ in August. However, it is clear that the drop in GPP in July coincided with the decline in Temperature. Moreover, Reco in 2018 and 2019 was identified continuously as the lowest from July to October, corresponding to the lowest SWC during the same periods. What is also striking from **Fig 30** is an increase of Reco parameter in February and March 2020 by ± 50 gC m⁻² month⁻¹ compare to the mean of Reco from 2014-2019. These bursts of Reco might be attributed to the decreasing SWC due to the absence of rainfall shown in

Fig 27. In order to verify the finding, the data were also plotted cumulatively on a monthly basis is provided in Fig 31.



Fig 31. Yearly comparison of monthly data from 2014 to 2020 between cumulative Gross Primary Productivity (GPP) (a) and cumulative Reco (Ecosystem Respiration).

Fig 31 further confirms that the GPP was started to increase significantly during the spring (May) in 2018, 2019, and 2020. Meanwhile, as for the Reco, the monthly accumulation was extremely low from the beginning of the autumn. It is very likely that the combination between high GPP at the beginning of the year and low Reco at the end of the year results in increased net CO₂ uptake in the dry years (2018-2019). To further investigate the relationship between carbon exchange components and environmental variables, a Principal Component Analysis (PCA) was carried out to center variance-scaled monthly and seasonally (GPP, RECO GPP, RE, ETa, Ta, Ts, u*, VPD, Ta, Ts, Rg, LE, EVI, SPEI-3, P, SWC, and RH). Results are provided in **Fig 32** for the first two dimensions of principal component components (PC; eigenvalues >1, 72.7% (Monthly) 74.3% (Seasonally).



Fig 32. Biplot displaying principal component analysis monthly (left) and seasonally (right) from 2014 to 2019. It shows the first two dimensions of principal component and cos2 value applied to Net Ecosystem Exchange (NEE), Gross Primary Productivity (GPP), Ecosystem respiration (Reco), Friction Velocity (u*), Vapour Pressure Deficit (VPD), Air Temperature (Ta), Soil Temperature (Ts), Global Radiation (RG), Latent Heat Flux (LE), Enhanced Vegetation Index (EVI), Standardised Precipitation-Evapotranspiration Index accumulated over three months (SPEI-3), "Precipitation (P), Soil Water Content (SWC), and Air Humidity (RH)

The monthly and seasonal PCA shows a similar general pattern. However, it is clear that the biplot shown seasonally separates more pronounced SPEI-3, P, and SWC, which in turn are poorly correlated due to its angle between vectors approximately 90° from the rest of the variables. The direct relationship between NEE and GPP negatively correlated with RG, LE, TA, PPFD, and VPD is very pronounced both seasonally and monthly due to its angle close to 0° or 180°. In addition, these variables are also identified in the first dimension that can explain more than 58% of the variation and are very well defined with cos2 more than 0.8. It is also evident that the GPP is strongly negatively correlated with Rg.

4.3.3. Vegetation State

To better understand the canopy dynamic in regulating the carbon exchange and its response to the heatwave and drought, the vegetation state derived from the Moderate Resolution Imaging Spectroradiometer (Modis) was used (

Fig 27). It is plotted alongside the daily average of gross primary productivity (green line).



Fig 33. The Variation of vegetation state using (a) EVI (Enhanced Vegetation Index) and (b) LAI (Leaf Area Index) from 2014 to 2017.

From 2014 to 2019, EVI varied from 0.2 (January 2015) to 0.9 (May 2018), and LAI varied from 0 to 9.243 (May 2019). The canopy dynamic followed a distinct pattern: EVI peaked in early summer (around May) (

Fig 27. a), and LAI peaked in early summer (around June) (

Fig 27.b) and then consistently reduced until the new leaves emerged the upcoming year. Neither a late nor an earlier leaf flush were detected during the study periods. Furthermore, EVI and LAI indicated that the start and the end of the growing season are visually similar between 2014 to 2019. However, a steep slope of decreasing EVI was detected in 2018. It is also almost certain that the lengthy and heavy drought had little influence on the Satellitebased EVI and LAI estimates. Since a similar general pattern of EVI, LAI, and GPP is detected, these variables' linear relationship is further investigated in *Fig 34*.



Fig 34. Seasonal relationship between Enhanced Vegetation Index (EVI) (left) and Leaf Area Index (LAI) (right) on Gross Primary Production over six years periods (2014-2019)

It is clear from *Fig 34* that the linear relationship between EVI and GPP is slightly stronger ($R^2 = 0.8714$) compared with the linear relationship between LAI and GPP ($R^2 = 0.6810$). Moreover, it is conspicuous that EVI is distinctly able to detect ecosystem photosynthetic activity in all seasons except in the summer.

4.3.4. Thinning and Fluxes

Management practice of stand thinning was applied in our Montiers site massively by the French National Forestry Office (ONF). The operation is executed every 7 years, reducing above-ground biomass by approximately 40×10^3 Kg ha⁻¹ (Turpault *et al.*, 2018). However, the thinning operation was only carried out in early March 2020 (winter), 10 years after the last thinning in winter 2009–2010 (Heid *et al.*, 2018). EVI and LAI used as a proxy vegetation state after thinning operation in 2020 (red square) are provided in figure *Fig 35*.



Fig 35. The monthly average of Enhanced Vegetation Index (EVI, left) and Leave Area Index (LAI, right) derived from MODIS (see method) from 2014 to 2020.

The thinning operation has been known for decreasing LAI (Vesala *et al.*, 2005; Granier *et al.*, 2008). However, this was not found in our site that used LAI derived from remotely sensed data. Undetected change in LAI might be due to the low spatial resolution of the LAI index (500 m). LAI was the second-highest in April and May 2020 at around 2.2 and 3.5 consecutively. Even though EVI in 2020 was constantly second of the lowest compared to the other years, it was preferably used to quantify the vegetation greenness. Even though there was a substantial soar of Reco in February and March 2020 by ± 50 gC m⁻² month⁻¹ compare to the mean of Reco from 2014-2019 **Fig 30**. These bursts of Reco might be attributed to the decreasing SWC due to the absence of rainfall shown in

Fig 27. As for GPP, Thus, thinning reduced neither GPP nor Reco.

4.4. Discussion

4.4.1. Soil and atmospheric dryness across the years

On our site, the 2018 and 2019 drought and heatwave are visible from the SPEI-3. These two years (SPEI-3, 2018=-2.252, 2019=-2.224) have been the driest periods since the last severe drought in 2003 with SPEI-3 of -2.525. The values are consistent with SWC measured from 2016 to mid-2020, which reached a minimum for two consecutive years in 2018-2019 (19% decrease). Concurrently, increasing temperature and declining precipitation were detected compared to the previous four years, 2014-2017. The comparison between VPD in 2018-2019 and the references years (2014-2017) also indicated the ecosystem atmosphere was unusually drier (

Fig 27) with an increase of annual average by 34%. The drought in 2018 was also identified as even more severe in Central and North Europe (Peters *et al.*, 2020). The massive scale of drought and heatwave is due to large scale, complex and rare phenomena involving synoptic situations, the interaction of land-atmosphere, and modulated by long-term warming trends (Mueller and Seneviratne, 2012; Quesada *et al.*, 2012; Miralles *et al.*, 2014; Drouard, Kornhuber and Woollings, 2019).

4.4.2. Ecosystem Respiration Responses

It is evident that the increase in net ecosystem uptake (NEE) during the drought episodes is due to decrees in Reco rather than an increase in GPP. Reco in winter and spring 2019-2020 was detected in a similar range compared with reference years (2015-2018) with a small decrease of 0.2 to 2.5 % consecutively. However, significant Reco decreased by 20%, and

26% were found in Summer and Autumn relative to the references years. The decreasing values of Reco coincided with falling SWC (-57%) and rising soil temperature (Ts) (15%).

SWC and Temperature have been known to significantly limit Reco (Xu and Qi, 2001; Atkin *et al.*, 2005; Wen *et al.*, 2006; Jassal *et al.*, 2008). The Reco reduction can be attributed to reducing both microbial soil respiration and plant respiration due to diminishing substrates (Burton *et al.*, 1998; Borken *et al.*, 2006). Even though the high temperature is highly likely to promote root and microbial respiration up to a point, water limitations might prevent this from occurring. Nonetheless, it is apparent that both microbial and root respiration could sustain the process during the early stage of drought (Spring) since they may still have access to water stored in cold-wet winter. Further investigation regarding the heterotrophic and autotropic respiration response during drought episodes should be done. Our results are also consistent with a previous finding (Fu et al., 2020) where Reco was significantly reduced during drought episodes in *Table 5*.

Table 5. Comparison of changes in CO_2 fluxes (summer) and environmental drivers in summer 2018 and 2016 between our EC site (FR-MsS) and EC site from the literature (Fu *et al.*, 2020) in the deciduous broadleaved forest, which includes air temperature (Ta), Vapour Pressure Deficit (VPD), Soil Water Content (SWC), Photosynthetic Photon Flux Density (PPFD), summer Gross Primary Productivity (GPP), summer Net Ecosystem Exchange (NEE), and summer Ecosystem Respiration (Reco).

Country	Site	ΔТа	ΔVPD	ΔSWC	APPFD	ΔGPP	ΔΝΕΕ	ΔReco
Country		(°C)	(hPa)	(%)	(µmol m=2s=1)	gC season ⁻¹ m ⁻²		
Czechia	CZ-Stn	1.4	1.6	-6 <mark>.5</mark>	18	32	-19	13
Germany	DE-Hai	1.8	3.8	-7.1	44	-416	204	-212
Germany	DE-HoH	1.6	2.8	-8.1	5	-88	-25	-113
France	FR-Hes	1.7	3.4	-6 <mark>.</mark> 4	60	32	63	95
France	FR-MsS	1.2	1.2	-4.1	26	29	-124	-153
Denmark	DK-Sor	1.8	3.1	-1.9	58	-375	0	-375

Reco at our EC site (FR-MsS) decreased by -153 gC season⁻¹m⁻² in summer 2018 compared with summer 2016. The highest decrease was identified in DK-Sor's site with 375 gC season ⁻¹m⁻². while the site of FR-Hes experienced an increase in soil respiration of 95 gC season ⁻¹m⁻². What is striking from this comparison is that the most considerable change in NEE was found in our site with -124 gC season ⁻¹m⁻². In contrast with other sites where most flux measurements indicated that the GPP and Reco decreased simultaneously. This study showed that negative sensitivity applied only to Reco rather than GPP, resulting in a significant increase in carbon use efficiency. It is almost certain that our EC site was at the edge of the domain of the extreme drought shown by the lowest Δ Ta and Δ VPD of 1.2 °C and 1.2 hPa consecutively while Central and Northern Europe increased by up to 1.8 °C and 3.8 hPa consecutively. The other forests positioned in similar conditions receiving less rain and more heat are likely to have a larger carbon use efficiency.

4.4.3. Gross Primary Productivity Response

The results show that the ecosystem exhibited more positive sensitivity to an increased temperature, where GPP was higher in 2018 and 2019 than in previous years. However, it is still similar to a GPP value in 2014 and 2015, around 1500 GPP (gC m⁻² y⁻¹). It is almost certain that the increase of GPP in 2018 and 2019 can be attributed to the rise of light/radiation due to its strong relationship with GPP ($R^2 = 0.77$). Prolonged periods of low SWC under 10% in 2018 and 2019 coupled with low rainfall can also be associated with less cloudy days, thus more intense light received by the ecosystem promoting more photosynthesis (Baldocchi, Chua and Reichstein, 2018). However, the relationship between these variabilities and GPP is somewhat complicated. Photosynthesis can either be promoted or reduced by sunlight, humidity, clouds, and excessive rain or drought (Jung et al., 2010; Seneviratne et al., 2010). Increases in Ta might also indirectly affects GPP through ET (Evapotranspiration), VPD, and SWC. (Jung et al., 2010; Seneviratne et al., 2010). The increase in temperature is also detected in 2018-2019, up to 15% increase compared to reference years (2014-2017). It has been known that GPP's response to change in temperature is a non-linier relationship. However, excessive heat that leads to high VPD has also been known to promote stomatal closure (Reichstein et al., 2007; Wolf et al., 2016) and browning, which were not detected both from GPP measured in EC and Satellite-based EVI and LAI. An increase of GPP by 63 gC season⁻¹m⁻² in summer 2018 compared with summer 2016 was found at our EC site.

4.5. Intermediate Conclusion

Long-term (6 years) carbon balance components (NEE, GPP, and Reco) in the beech forest, North-Eastern France, are presented. During the study periods, the ecosystem acted as a net carbon sink with a mean annual NEE, GPP, and Reco of -453 ± 122 gC m⁻²y⁻¹, -1468 ± 109 gC $m^{-2}v^{-1}$, and 1052 ±88 gC $m^{-2}v^{-1}$ consecutively. This work investigated how 2018 and 2019 drought episodes affected carbon exchange in a deciduous temperate forest ecosystem. The Carbon exchange, climate, and environmental drivers during the drought episodes were compared with long-term reference data recorded from 2014 to 2017. In contrast with some previous research where GPP and Reco parallelly decreased during the drought episodes, our site showed Reco is more sensitive to drought than GPP, resulting in a significant increase in net ecosystem exchange. Reco decreased by 20%, and 26% were found in Summer and Autumn (2018-2019) relative to the reference years (2014-2017). The decreasing values of Reco coincided with falling SWC (-57%) and rising soil temperature (Ts) (15%). It is almost certain that both microbial and root respiration could sustain the process during the early stage of drought (Spring) since they may still have access to water stored in cold-wet winter. We hypothesize that the mature forest with deeper root access water is stored in a deep layer of soil that helps to sustain the photosynthesize activity while reducing the microbial respiration rate The significant reduction of Reco reduction in the summer might be attributed to the decrease of both microbial soil respiration and plant respiration due to diminishing substrates. It is also clear that there were bursts of CO₂ emission when dry soils were rewetted by rainfall after the dry season. Furthermore, the lengthy and strong drought had little effect on the satellite-derived LAI (Leaf Area Index) and EVI (Enhanced Vegetation Index). In other words, there is no noticeable reduction of vegetation cover and browning. Even though less severe drought was detected on our site compared with Central and North Europe, likely, different ecosystems and regions respond differently to a changing climate, especially those situated at the edge of the domain of the extreme drought. As predicted, drought and heatwaves will be more frequent in the future. It is unclear whether prolonged, repeated, and more severe drought and heatwave episodes will have a similar effect on carbon exchange.

Subsoil CO₂ Ventilation and Subsurface Removal: Evidence from Eddy Covariance, Soil CO₂ storage, δ13C, and Gas Composition Analysis

Didi Adisaputro ^{1,2,*}, Philippe De Donato ¹, Laurent Saint-Andre ², Gilles Nourrisson ², Odile Barres ¹, Catherine Galy ³, Gilles Nourrisson ², Médéric Piedevache ⁴, and Marion Derrien ⁴

- ¹ GeoRessources Laboratory, Université de Lorraine, CNRS, BP 70239, 54506 Vandœuvre-lès-Nancy, France;
- ² INRAE, UR BEF, Centre de Nancy, 54280 Champenoux, France;
- ³ ANDRA, 55290 Bure, France;
- ⁴ Solexperts France, 17 av de la Forêt de Haye, 54500 Vandoeuvre lès Nancy, France;

Resume

L'abondance du CO_2 du sous-sol et la teneur en eau du sol dans la forêt tempérée à feuilles caduques créent des conditions favorables à son élimination du sous-sol par des processus bio-hydro-géochimiques. Cependant, la ventilation du CO₂ présent dans le sous-sol et son élimination du sous-sol dans la zone vadose sont insuffisamment étudiées par rapport au sol sus-jacent. Cette étude vise à déterminer les processus de contrôle de la dynamique de stockage du CO₂ dans le sous-sol. Dans cette étude, le stockage du CO₂ dans le sous-sol a été estimé et mesuré à -1 m, et à -6 m au travers d'un forage dédié, et le Reco (Ecosystem Respiration) a été calculé en utilisant la technique de covariance des tourbillons décrite dans les chapitres précédents. Le rapport des gaz et l'analyse de la composition isotopique du CO₂ ont été utilisés pour distinguer la source de CO₂. Les tendances saisonnières montrent que la diminution du stockage du CO₂ dans le sous-sol (0-6 m de profondeur) de 2,3 à 1,2 mol de $CO_2 \text{ m}^{-2}$ a coïncidé avec une augmentation du Reco de 0,2 à 0,5 mol de $CO_2 \text{ m}^{-2} \text{ d}^{-1}$ pendant une vitesse de frottement (u*) exceptionnellement élevée à 1,8 m/s. Bien que la concentration de CO₂ dans le sous-sol à 6 m de profondeur ait été constamment plusieurs fois supérieure à la concentration de CO₂ à 1 m de profondeur, elle est plus réduite sur la valeur du δ^{13} C. Les résultats mettent en évidence une variation linéaire (R^2 de 0,68) de la valeur de $\delta^{13}C$ du CO_2 du sol variant ainsi de -25,9 ‰ à -20,485 ‰ avec une intersection à l'origine (C_{CO2}=0 ppm) de 25,09 qui peut être considérée comme le $\delta^{13}C$ de fond de notre écosystème forestier.

L'origine de cette évolution peut être attribuée à la décomposition des matières organiques du sol et à la respiration des racines des plantes en C3 entrainant ainsi une augmentation en C^{13} . Sur notre site, la recharge et le rejet de CO_2 modifient les valeurs de $\delta^{13}CO_2$. Ainsi, plus la concentration de CO₂ dans le sol entre -1 et -6m sera élévée, plus basse sera la valeur de $\delta^{13}CO_2$ et inversement. La diminution de $\delta^{13}CO_2$ dans le sol à une profondeur est caractéristique d'une période d'activité biologique dominée par la production de CO₂ dans le sol alors qu'une augmentation de $\delta^{13}CO_2$ correspond à un dégazage du CO_2 vers l'atmosphère par un mécanisme de diffusion se produisant principalement lorsque la vitesse de friction est élevée. L'étude des variations saisonnières montre que la respiration anaérobie est prépondérante durant les périodes estivales, comme le montre les valeurs de ARQ>1, où la respiration dépasse la diffusion dans les pores sol-air. En hiver et au printemps (ARQ<1), ont constate une dissolution considérable du CO_2 consécutivement à l'arrivée, dans le sol, de l'eau de pluie s'est produite. Cependant, sur notre site, où le pH du sol est inférieur à 6, la dissolution ultérieure du CO_{2aq} en H_2CO_3 , HCO_3^- , CO_3^{2-} est négligeable. Ces résultats nous aideront à mieux comprendre le rôle de la dynamique du stockage naturel du CO₂ dans les mécanismes influençant les variations de NEE et la manière dont ce stockage peut être intégré dans les différents modèles de procédés de gestion des écosystèmes forestiers

Abstract

The abundance of subsoil CO₂ and soil water content in the temperate deciduous forest creates favorable subsurface removal conditions by bio-hydro-geochemical processes. However, CO₂ ventilation of the subsoil and subsurface removal in the vadose zone are inadequately studied compared to overlying soil. This study aims to determine the controlling processes of sub-soil CO₂ storage dynamics. In this study, subsoil CO₂ storage was estimated and measured at -1 m, and -6 m from the borehole, and Reco (Ecosystem Respiration) was calculated using the eddy covariance technique. The gas ratio and stable isotopic composition analysis were employed to distinguish the source of CO₂. The seasonal trends show that the decrease of subsoil CO₂ storage (0-6 m depth) from 2.3 to 1.2 mol CO₂ m⁻² coincided with an increase of Reco from 0.2 to 0.5 mol CO₂ m⁻² d⁻¹ during exceptionally high Friction Velocity (u*) at 1.8 m/s. Although the subsoil CO₂ concentration at 1 m depth, it is more depleted in δ^{13} C. The δ^{13} C of soil CO₂ ranged from -25.9 ‰ to -20.485 ‰, and the keeling plot between CO₂ concentration and δ^{13} C shown in R² of 0.68 and intercept of 25.09 (δ 13C background), which can be

attributed to the decomposition of soil organic matters and root respiration of C3 plants. In our site, soil CO₂ concentration was inversely correlated with δ^{13} CO₂. The decrease in soil δ^{13} CO₂ at any given depth indicates a period dominated by soil CO₂ production. The increase of δ^{13} CO₂ is related to the external factors during the outgassing to the atmosphere through diffusion (i.e., during high friction velocity). The seasonal variation shows that anaerobic respiration contributes significantly during the summer, shown by ARQ>1, where the respiration outpaces the diffusion in soil-air pores. In the winter and spring (ARQ<1), considerable CO₂ dissolution of rainwater occurred. However, in our site, where the soil pH is below 6, further dissolution of CO_{2aq} into H₂CO₃, HCO₃⁻, CO₃²⁻ is negligible. These results will help to improve our understanding of the role of CO₂ storage dynamics in the NEE and how it can be incorporated into the process-based ecosystem model.

5.1. Introduction

The variability of Reco, GPP, and NEE is driven by interconnected biotic and abiotic factors (van Dijk, Dolman and Schulze, 2005; Granier *et al.*, 2008; Yi *et al.*, 2010). Moreover, Ecosystem respiration (Reco), consists of various components (Barba *et al.*, 2018) that can be described as $R_{eco} = R_{soil} + R_L + R_w + C_W + SV + PD$. Where R_L (leaves), R_W (woody tissue), CW (Carbonate Weathering), SV (Subterranean Ventilation), and PD (Photo-degradation) are a combination of biogenic and non-biogenic sources. It is a widely held view that Soil respiration (Rsoil) is the biggest component of R_{eco} . The CO₂ efflux (F_{soil}) commonly refers to soil respiration (Rsoil) from the surface of the soil to the atmosphere, which may come from multiple sources, including respiration of the root system (Rr), respiration of the soil fauna, and CO₂ production from non-biological source (Rn). Although both terms, Fsoil and Rs, are used interchangeably, several findings have challenged this assumption. Some argued that respired CO₂ might be dissolved in soil solutions that can be attributed to the dissolution in water, biological activities, and chemical reactions (Roland *et al.*, 2013; Angert *et al.*, 2015; Oertel *et al.*, 2016; Laemmel *et al.*, 2019).

One of the most effective ways to measure or monitor the soil's gas emission is through the Flux Chamber (FC) deployment that was first introduced by Chiodini *et al.*, 1998. Because of its portability, simplicity, low costs, and low power consumption, closed chamber systems are widely employed to measure the Net Ecosystem Exchange (NEE) in the soil (Hoffmann *et al.*, 2015). However, this measurement approach promising high-temporal frequency measurements of R_{soil} is typically carried out at a few locations assumed to represent the whole ecosystem (in both patterns and magnitudes) but may underrepresent the spatial

variability of R_{soil} (Barba et al., 2017). A previous study (Pokryszka et al., 2017) has reported that within the last 20 years of studies measuring a wide range of ecosystems that i) The natural flow of CO₂ is highly dependent on seasonal variations rather than the other parameters where it was identified that the flow was highest in summer and lowest in winter; ii) The CO₂ efflux on the natural site are ranging from 0 to 6 cm³ min⁻¹ m⁻² in winter and from 3 to 20 cm³ min⁻¹ m⁻² in summer; iii) The insignificant flow of CH₄ on drained soils where CH₄ efflux was ranging from 0.1 cm³ min⁻¹ m⁻² for the highest point values and less than 0.04 cm³ min⁻¹ m⁻². However, the differences in chamber operational handling and data analysis reported in the other literature are subject to different uncertainty sources (Oertel et al., 2016). The data processing procedure is a significant source of uncertainty of obtained results (Hoffmann et al., 2015). Furthermore, unlike the Gradient-Based Method (GM), it is difficult to distinguish the CO₂ and CH₄ contribution from the soil to the atmosphere, especially in the near-surface, since the leaks and natural variations can significantly affect the data. Besides, the gas exchange might also be affected by the photosynthesis, biodegradation, root respiration, and organic carbon content in the soil, in which the degree may vary depending on the physical properties of the soil such as temperature, the moisture content, nutrients, and soil pH value (Oertel et al., 2016).

As for methane, it is naturally originated from microorganisms that belong to the domain Archaea when anoxic microsites are formed. Methanotrophy (oxidation of CH₄) and methanogenesis (production of CH₄) are two biogenic processes driving the concentration, especially in the soil compartment. Three main possible transport mechanisms rule temporal and spatial variations of CH₄ production within the critical zone, which include i) diffusion of dissolved CH₄ along the concentration gradient, ii) The release due to ebullition (CH₄ containing bubbles), iii) plant mediated-transport. Meanwhile, the CH₄ originating from anthropogenic sources results from agriculture, waste, energy, and industrial activity (Serrano-Silva *et al.*, 2014). As for the methane, wetlands are the primary source of methane, while there was insignificant CH₄ efflux in the forest land, grassland, barren land, and cropland. Emission rates vary widely (0.1–6950 μ mol CH₄ m⁻² h⁻¹), with the average grassland CH₄ emission rate was below 3 μ mol m⁻² h⁻¹.

The Carbon-isotopic composition (δ^{13} C) of soil CO₂ efflux has widely been employed to evaluate the soil carbon-cycling process (Kayler *et al.*, 2010; Goffin *et al.*, 2014; Delogu *et al.*, 2016; Maurer *et al.*, 2016; Rao *et al.*, 2017) thus provides valuable insight into plant-soil carbon metabolism, and respiratory carbon sources at different temporal and spatial scales (Kayler et al., 2010). Two essential processes drive the soil respiration and carbon isotopic signature: the production of the ¹³CO₂ and ¹²CO₂ by the soil (P) and their transport from its source to the atmosphere (Goffin *et al.*, 2014). The total CO_2 production can be divided into the heterotrophic component due to saprophytic microorganisms feeding on organic matter and an autotrophic part due to mainly root respiration (Delogu et al., 2016). Partitioning can be accomplished due to the fact that these components differ in their natural isotope abundance (Goffin *et al.*, 2014). Even though Rs and δ^{13} Rs are assumed to be solely driven by its production, physical processes such as rain events, wind pumping, and atmospheric pressure fluctuation are contributing factors (Fassbinder, Griffis and Baker, 2012). A Chamber system used for measuring the gas concentration can also be coupled with an isotopic ratio analyzer of C and O species combined with a cascade laser-based spectrometer (Fassbinder, Griffis and Baker, 2012; Oertel et al., 2016). In addition, some studies have also successfully integrated the isotopic ration analyzer with the gradient method (Goffin et al., 2014, 2015; Delogu et al., 2016). Even though isotopic composition was too small and very fluctuating, It was promisingly reported in a study using gradient methods that Rs differed significantly across vertical stratification while the production of δ^{13} varied insignificantly. There were two parameters highly affecting the temporal variation of Rs that was found in the most productive horizon, which include temperature and Soil Water Content (SWC) without visible & 13P climatic dependence was visible (Goffin et al., 2014). The strong correlation of PCO₂ and between -10 to -20 cm depth the canopy inherent water use efficiency (IWUE) measured the day before, arguing a connection between canopy activity and soil autotrophic production (Delogu et al., 2016). There is also a strong need to consider the CO₂ transport caused by turbulent advection and dispersion, especially at the top of the soil (Goffin et al., 2014; Delogu et al., 2016).

Even though carbonate weathering and subsequent outgassing from soil water is a minor abiotic component of the R_{eco} , Soil CO₂ flux due to C leaching out of the soil plays a significant role (Schindlbacher *et al.*, 2015, 2019). Jurado et al. (2018) conducted research related to the generation of greenhouse gasses (GHGs) in the groundwater primarily related to the hydrogeological and geochemical processes, containing 0 micrograms/ liter to 17.1 micrograms per liter of CH₄ and 1769 to 100514 ppm of the partial pressure of CO₂. It is also found that the groundwater is oversaturated with CO₂ and CH₄ due to the equilibrium process. One of the most important findings of this research is that the outgassing of the CO₂ and methane is much lower with only 27 kg CO₂ ha⁻¹y⁻¹ than GHG emissions from the

agricultural soils and emissions generated by fossil fuels. The aquifer's effects on the soil's atmospheric gas level are similar to monitoring campaigns using onsite cavity Raman spectroscopy conducted by Torsten (2017). It was generally observed that the gas atmosphere near the surface level is predominantly driven by aerobic microbial activity.

Meanwhile, aquifers and soil/rock properties highly determine the atmospheric gases in the deeper subsurface layer. One of the most critical findings in this research is that water's lateral transport plays a vital role in CO_2 and O_2 gas exchange. The aquitards between aquifers have lower oxygen content, which is highly likely caused by hindered diffusion of the gases from above and below—the seasonal observation results in a difference of groundwater levels at the border of aquifers and aquiclude. The paper also suggested that more extensive modeling is required to interpret the complex interaction of biological, physical, and chemical processes.

Even though a fair understanding of the GHG exchange between the pedosphere and the atmosphere has been achieved by these soil-air interface studies, the knowledge of the CO_2 and CH₄ production/consumption pattern in the soil profile is still very limited numbers. As previously discussed, it is mostly assumed that soil surface effluxes of CO_2 , CH₄ are instantaneous soil emissions and neglect subsurface removal due to bio-hydro-geochemical processes. The quantity of CO_2 and CH₄ in the soil, including air-filled soil pores and soil solution, can be several times the daily soil-surface efflux (Martin Maier *et al.*, 2017; Y. Wang *et al.*, 2018). Hence, it is a prerequisite to accurately predict the CO₂ and CH₄ dynamic within soil profile using Gradient-Based Method (GM) to have detailed knowledge of subsurface CO₂ and CH₄ fluxes (Y. Wang *et al.*, 2018). Therefore, the objective of this chapter is 1) to analyze the subsoil CO₂ storage dynamics in comparison to the ecosystem respiration, 2) to identify the main drivers of CO₂ and CH₄ by measuring its isotopic composition and gas composition ratio.

5.2. Materials and Methods

5.2.1. CO₂ storage calculation

The CO₂ continuous measurement was carried out using a methodology and data provided in **Chapter 3**. Some assumptions were applied to calculate CO₂ storage up to 6-meter depth since only CO₂ concentration from topsoil (-1m) and subsoil (-6 m) could be obtained during the observation periods. Furthermore, soil porosity and soil water content need to be

considered in estimating CO_2 storage. Therefore, the physicochemical properties of the soil that have been measured from the previous work were used. Soil porosity (%) was calculated using Equation 5.2.1Where particle density is constant at 2.65 g cm⁻³.

Soil porosity =
$$100 - \left(100 \times \left(\frac{Bulk \ Density}{Particle \ Density}\right)\right)$$
 Equation 5.2.1

Table 6. Physicochemical properties of a studied soil (Dystric Cambisol) include a bulk density (g.cm³), soil porosity (%), Soil Water Holding Capacity (SWCHC), and pH_{water} and textural distribution in g kg⁻¹(clay: <2 lm, fine silt: 2–20 lm, coarse silt: 20–50 lm, fine sand: 50–0.2 mm, coarse sand: 0.2–2 mm). Adapted from (Calvaruso et al., 2017; Kirchen et al., 2017)

Depth	B. density	Soil	SWHC	pHwater	Clay	F. sılt	C. silt	F. sand	C. sand
		Porosity			-				
cm	g cm ⁻³	%	mm				g kg-1		
0-5	0.98	63	8.2	4.9	255	281	160	185	121
5 15	0.04	64	16.5	1 9	245	276	167	10/	121
5-15	0.94	04	10.5	4.0	243	270	102	104	151
15-30	1.23	53	22.7	4.8	268	280	161	170	115
30-45	1.36	48	22.6	4.9	306	262	150	161	119
45-60	1.45	45	18.1	5.1	355	229	126	166	141

The variations of soil porosity and soil water holding capacity in *Table 6* were used to estimate CO_2 storage for the first 60 cm calculating using **Equation 5.2.2**. a constant profile of Soil Water Content (SWC) and soil porosity was assumed to be homogenous up to 6 m depth. This procedure was required to consider the Physicochemical characteristics of each horizon. The CO_2 mole fraction at 6 m depth was interpolated linearly to the CO_2 mol fraction at 1m depth (Tang *et al.*, 2003). This linear interpolation was also applied for temperature and pressure.

CO₂ total storage from 0m to -6m (S_{total}, mol CO₂ m⁻²) was estimated as a sum of CO₂ in the air-filled pore space (ϵ , m³ air m⁻³ bulk soil) and CO₂ in the water-filled pore space (θ , m³ H₂O m⁻³ bulk soil) by a summation of discrete soil strata of the thickness of the first 6 m (Δz) 6 m (Maier *et al.*, 2010).

$$S_{Total} = \sum_{i=0}^{n} S^{i} = \sum_{i=0}^{n} \left(S^{i}_{water} + S^{i}_{air} \right), \qquad \text{Equation 5.2.2}$$

Where S^{i}_{water} and S^{i}_{air} described the CO₂ storage in the water-filled pores and air-filled pores of stratum *i* (mol CO₂ m⁻² bulk soil) with n (total number of strata). The formula for calculating S^{i}_{water} and S^{i}_{air} are provided in **Equation 5.2.2** and **Equation 5.2.3**, respectively.

$$S^{i}_{air} = \frac{P^{i}_{CO_{2}}}{R T^{i}_{air}} \varepsilon^{i} \Delta z,$$
 Equation 5.2.3

With $P^{i}{}_{CO_{2}}$ is the pressure of CO₂ (Pa), R is a gas constant (8.3136 J mol⁻¹ K⁻¹), and T_{air} is soil air temperature (K). As for $S^{i}{}_{water}$, perfect mixing of the soil solution and thermodynamic equilibrium between soil solution and soil air was assumed.

$$S^{i}_{water} = c^{i}_{CO_2} \theta^{i} \Delta z = P^{i}_{CO_2} K_s \theta^{i} \Delta z$$
 Equation 5.2.4

In which, $c_{CO_2}^i$ is the concentration of CO₂ in the soil solution (mol m⁻³) could be calculated from K_s which is the solubility of CO₂ (µmol Pa⁻¹ m⁻³) and $P_{CO_2}^i$. In experimental sites with pH above 7, the different DIC species (Dissolve Organic Carbon) such as CO_{2aq}., H₂CO₃, HCO₃⁻, CO₃²⁻ need to be considered. However, on our site, where the soil pH is below 6, K_s Corresponds to henry's law constant since a further dissolution of H₂CO₃ is negligible. K_s was calculated with an assumption of thermodynamic equilibrium within the CaCO₃-CO₂-H₂O-system (Lindsay, 1979). Moreover, since K_s value is temperature dependence, it was further calculated using temperature-sensitivity functions to derive the dissociation constants and Henry's law constant (Sander, 2015) using **Equation 5.2.5**.

$$K_{s} = K^{\circ}{}_{s} \exp\left(\frac{d(\ln(K_{s}{}^{i}))}{d\left(\frac{1}{T^{i}}\right)}\right) \left(\frac{1}{T^{i}} - \frac{1}{298.15 K}\right)$$
Equation 5.2.5

 K°_{s} is Henry's law constant for solubility in water at 298.15K is $3.4 \times 10^{-4} mol m^{-3} Pa^{-1}$ where the temperature dependence of equilibrium constants can be described mainly using the van 't Hoff equation.

$$\left(\frac{d(\ln(K_s^{\ i}))}{d\left(\frac{1}{T^i}\right)}\right) = \frac{-\Delta_{sol}H}{R} = 2400 K$$
 Equation 5.2.6

In which Δ_{sol} H is the enthalpy of dissolution, equates to a constant of 2400 K once divided by a gas constant. It is almost certain that the assumption of perfect mixing is inaccurate since the CO₂ concentration in Intra-aggregate space is generally higher than the adjacent macropores because of the relatively slow velocity of gas diffusion in water (Sierra, Renault and Valles, 1995). Nonetheless, considering the availability of recorded data, the calculation of Soil CO₂ storage using this approach appeared to be most appropriate.

5.2.2. Ecosystem Respiration and Flux Footprint

Ecosystem respiration was estimated from night-time and extrapolated to daytime following a protocol provided in the literature (Reichstein *et al.*, 2005). More detail regarding the Reco estimation is provided in Chapter 4. Moreover, An accurate estimate of the flux footprint before comparing soil efflux and ecosystem efflux leads to better and more precise interpretation (Phillips *et al.*, 2016). The flux footprint was estimated using a two-dimensional parameterization model (Kljun *et al.*, 2015) executed on R software (R Core Team, 2020) (*Fig 36*).). The parameterization required inputs of a) flux tower height (45m), b) canopy height (26 m), surface friction velocity (u*), mean wind speed (m s⁻¹), wind direction, Obukhov length (m), and standard deviation of the vertical wind speed.



Fig 36. (a) Flux Footprint estimated using a two-dimensional parameterization model of the flux tower on the monitoring site includes subsoil (borehole) estimated in daylight condition in June 2019. (b) soil sequences, including Alocrisol, Brunisol, Calcisol, and Rendisol (Calvaruso *et al.*, 2017). (C) Illustration and vertical section of the soil characteristic and the flux footprint.

The flux footprint model in **Fig 36** was calculated half-hourly and estimated at daylight in June 2019 because this parameterization model is not valid to be applied for low friction velocity ($u^* > 0.1 \text{ m s}^{-1}$). Nonetheless, it is clear that the borehole area contributed to the flux

footprint, thus validating a cross-data analysis between data measurement on borehole and flux tower.

5.2.3. Soil Gases Sampling and Analysis

A gas sampling at each depth of 1 m and 6 m was done on the site of Montiers on a weekly basis. A more detailed description and construction of the gas samplers are provided in Chapter 3. Briefly, soil gas samplers at -6 m well were part of the circulation module. The pump runs for at least 5 minutes before the sampling occurs to ensure the air inside the circulation module and borehole was in equilibrium and homogenous. As for the -1 m borehole, the pump was used to create vacuum conditions in the gas sampler before introducing the soil gas to prevent interferences from ambient air. Stainless steel tubing and mini cylinders (volume = 50 mL) manufactured by Swagelok were used to extract and transport soil gases. Before the ex-situ analysis, the soil gas sample was analyzed in-situ using FTIR Bruker alpha to measure the CO₂ concentration. Then, subsoil gas samples were analyzed ex-situ using CP-4900 micro Gas-Chromatography (Agilent) at Unité Biogéochimie des Ecosystèmes Forestiers (BEF, INRAE). Before analyses, A three levels calibration was carried out for each gas of interest, including Ar, O₂, H₂, N₂, CH₄, and CO₂. The GC analysis did not consider the presence of H₂O (dry condition). It has also been normalized where the Temperature and the laboratory's pressure were adjusted. The standard gas was analyzed continuously until the uncertainty is less than 5%. The measurement concentration was then expressed in ppmv for a more straightforward interpretation and consistency.

Isotopic composition is an essential tool to distinguish the source of CO_2 and CH_4 , whether it is biogenic or inorganic, where the former tends to be isotopically lighter than the former. The stable carbon isotopic ratio of the gas phases is expressed in the equation **Equation 5.2.2**.

$$\delta^{13}C = \left[\frac{(13C/12C)_{sample}}{(13C/12C)_{standard}} - 1\right] \times 10^3$$
Equation 5.2.7

Where $\delta^{13}C$ (‰), relative to Peedee belemnite, was measured using Cavity Ring-down Spectroscopy (G2201-i, Picarro Inc., Santa Clara, CA, USA) described in **Chapter 2** using CO₂-CH₄ simultaneous mode with an error less than 0.16 ‰. Since the CO₂ operational range (0-4000 ppm) was much lower than the CO₂ concentration in the field, the sample was diluted with N₂ (CO₂<100 ppb) using an apparatus provided in *Fig 37*. Data were collected at a higher frequency, of more than 1 Hz, and expressed on VPDB (VPDB, Vienna Pee Dee Belemnite) scale.



Fig 37. A set of apparatus systems used for diluting gas samples consists of gas standard, pump, mixing cylinder, and **Hydraulics**

The diluting cylinder volume (*Fig 37*) was 1640 mL, and the range of CO_2 concentration from the field was 10000 to 54000 ppm. Therefore, filler with a diameter of 7.1 cm and height ranging from 3 to 10 cm were used to produce CO_2 concentration with the operational range of CRDS. Even though this dilution did not change CO_2 and CH4's isotopic composition, the procedure altered CO_2 and CH4 concentration. Thus, the sample gas composition was analyzed using the micro-GC described in **Chapter 2** before the dilution procedure.

5.3.Results

5.3.1. Ecosystem Respiration, CO₂ Storage, and Environmental Driver Dynamics

The soil, subsoil, and micrometeorological data were measured simultaneously and hourly from summer 2019 to winter 2020, as provided in **Fig 38**.


Fig **38.** Time-series graph showing a daily average of ecosystem respiration (Reco, mol CO₂ m² d⁻¹) and CO₂ storage (mol CO_{2⁻²}), the daily max of temperature at various depth (Tmax, °C), the daily average of Soil Water Content (SWC, m³/m³), precipitation (mm day⁻¹), friction velocity (u*, m s⁻¹), Photosynthetically Active Radiation (PPFD, μ molm⁻²s⁻¹) and Vapor Pressure Deficit (VPD, kPa)

Overall, Reco in summer was higher than in winter where the accumulative of ecosystem respiration (Reco) was ranging from 0.7 mol CO₂ m⁻² d⁻¹ during the summer period (17 June 2019) to as low as 0.02 CO₂ m⁻² d⁻¹ during the winter (**Fig 38**.a). The highest monthly cumulative of Reco was also identified in June 2019 with 16.2413 mol CO₂ m⁻² month⁻¹ while it was only 10 mol CO₂ m⁻² month⁻¹ in June 2020. The decline coincided with the decrease of T_{max} (**Fig 38**.b), PPFD (Photosynthetically Active Radiation), and VPD (Vapor

Pressure Deficit) (**Fig 38**.e). As for total CO₂ storage up to 6-meter depth, the maximum values were found in winter and summer. However, the dissolved CO₂ in soil-water space dominated the total CO₂ storage in wet winter, where it was found to be the opposite during the dry summer.

These results emphasize not only the significance of CO_2 in soil-air space but also soil-water space. Similar to seasonal trends of χc , the maxima and minima of total CO_2 (**Chapter 3**) storage was reached both in winter and summer with 2.3 and 2.7 mol CO_2 m⁻² respectively. Moreover, the decline of total CO_2 storage coincided with the increase of Reco, as occurred on 27 November 2019, 10 February 2020, and 13 June 2020. What is striking is the increased Reco rate on 10 February 2020, which corresponded to an unusually high friction velocity of 1.8 m/s and was followed by declining CO_2 storage by around 1 mol CO_2 m⁻². In general, the temperature was profoundly influenced by the daily variation, where the more in-depth the soil layer, the fewer variations were found. The temperature range at -1 m and 66 m was 4.98-19.80 °C and 9.73-11.13 °C consecutively (**Fig 38**.b). Meanwhile, the highest variation was unsurprisingly found above the soil/ vegetation covers ranging from -2°C to 42°C.

As for the Soil Water Content (SWC) (**Fig 38**.c), the lowest value occurred in summer at around 0.1 (10 %) with some spikes due to the rainfall episodes. However, this increase in SWC of about 0.2 lasted only around five days after the rainfall. During the winter, SWC remained high at approximately 0.4 due to more frequent rain and low temperatures. A slight reduction of SWC was identified from January to February due to less frequent rain events. However, it only reduced the SWC by around 5%. Furthermore, the daily average friction velocity (u*) was relatively higher during the winter (0.7 m/s) than in summer (0.4 m/s). Exceptionally high u* was identified on 10 February with a daily mean of 1.8 m/s as shown in (**Fig 38**.e) also show that the early summer 2019 was higher and more fluctuated than in the early summer of 2020. PPFD and VPD reached up to 654 μ mol Photon m⁻² S⁻¹ and 3.7 kPa consecutively in 2019.

It was also found that hourly CO_2 storage variations (mol) might reach more than ten times higher than Reco's rate, which indicated that the hourly change in CO_2 molar fraction could not be directly defined as a change in CO_2 storage. Instead, the high concentration of CO_2 moved upward and downward due to falling and increasing pressure. The variation of total CO_2 storage only varies with CO_2 at different SWC, temperature, and pressure (see **Chapter** **5.2.1**). Thus, the hourly CO₂ molar fraction was used to compare the ecosystem respiration to avoid bias. Even though the seasonal variation shows that the dropped in CO₂ storage coincided with an increase of Reco, the hourly relationship was less pronounced. The R² between CO₂ concentration and Reco varies from 0.02 on 3/12/2019 to 0.7693 on 6/7/2020. The low R² of 0.02 was found during low Reco (± 1 mol CO₂ m⁻² hour⁻¹) and high SWC (37%), while the high R² of 0.7693 was identified during high (± 1 mol CO₂ m⁻² hour⁻¹). However, it is clear that even though the R² varies significantly, the increase of Reco was followed by the decrease in CO₂ molar fraction since ten out of 12 graph shows a negative slope. To determine the origin of the CO₂ stored in the soil and the contribution of CH₄ consumption and production, the stable isotope analysis is provided in *Fig* 39 and *Fig* 40.



Fig **39.** Keeling plot of the CO₂ stable isotope (δ^{13} C) (a) and time series of change in the isotopic composition of CO₂ (b). Square points represent data taken from -6 m, and triangle points are the data measured from -1 m.

The δ^{13} C of soil CO₂ ranged from -26 ‰ to -20.485 ‰ (*Fig* **39.a**) with a very pronounced seasonal pattern (*Fig* **39.b**), depleted δ^{13} C_{CO2} during the winter and enriched δ^{13} C_{CO2} during the summer. The CO₂ concentration at 6 m depth was generally higher than 1 m depth, and it was found to be more depleted in δ^{13} C as reported by a previous study (Cherkinsky, Brecheisen and Richter, 2018). However, based on ANOVA (Analysis of variance), the seasonal effect on variation is highly significant (<0,001) compared to the slight impact of

depth (0.01), and about 60 % of the residuals are comprised between -1,34 delta13C and + 1,34 delta13C. A mixing line was drawn on the keeling plot to define a natural background of δ^{13} C, where a strong correlation with R² of 0.68 and intercept of -25.09 was identified. The intercept values have been widely used as a natural background of δ^{13} C_{CO2} (Rouchon *et al.*, 2011; Garcia-anton *et al.*, 2014; Rillard *et al.*, 2015; Kim *et al.*, 2019), which falls into the C3 plant signature (Calvin cycle) where the δ^{13} C values are ranging from about -35 ‰ to -20 ‰ (Bowling, Pataki and Randerson, 2008). However, a combination of C3 and C4 (Hatch–Slack, -19‰ to -9‰) results in photosynthesis pathway δ^{13} C mean from -27‰ and -13‰ (Zhu *et al.*, 2019). As for the isotopic composition of CH₄, the time series plot is provided in *Fig* 40.



Fig 40. Figure showing plot of CH₄ concentration and stable isotope (δ^{13} C) (a) and time series of change in the isotopic composition of CH₄ (b). Square points represent data taken from -6 m, and triangle points are the data measured from -1 m.

Moreover, *Fig* 40.a demonstrates that the mean of $\delta^{13}C_{CH4}$ ranged from -64 ‰ to -25 ‰ with an unpronounced seasonal pattern. Since a relatively small concentration of soil CH₄ was detected (1 to 3 ppm), the $\delta^{13}C_{CH4}$ had significant uncertainty values up to 20 ‰ compared to its mean. However, it is clear that the overall general pattern shows that CH₄ concentration was lower in concentration and lighter in 6 m depth than 1 m depth. It is most likely caused by more active methanotrophic CH₄ production in the shallower layer of soil, leading to higher CH4 concentration and depleting in $\delta^{13}C_{CH4}$. It is consistent with previous findings where the CH₄ is might be fractionated due to production, oxidation, and transport (Whiticar, 1999; Krueger *et al.*, 2002; Zhu *et al.*, 2019). Firstly, during the CH₄ production, methanotrophic bacteria prefer to consume ${}^{12}C_{CH4}$; secondly, during the oxidation, methanotrophic bacteria utilize faster the ${}^{12}C_{CH4}$; thirdly, the ${}^{12}C_{CH4}$ is transported more quickly than ${}^{13}C_{CH4}$.

5.3.3. Relationship between soil CO₂ and other gas compositions

A geochemical-based-process method is often used to identify underground gas leakage and identify soil gas origin (Romanak *et al.*, 2012, 2013; Beaubien *et al.*, 2013; Schacht and Jenkins, 2014; Gal *et al.*, 2019). It is achieved by examining the relationship between some major fixed gases (CO₂, CH₄, O₂, and N₂) (**Fig 41**) with an assumption where the primary production of CO₂ in the vadose zone is either aerobic bacterial respiration (CH₂O + O₂ = CO₂ + H₂O) or oxidation of methane (CH₄ + 2O₂ = CO₂ + 2H₂O) (Romanak *et al.*, 2012, 2013). In this work, we use this approach to estimate the CO₂ due to carbonate weathering (Anderson *et al.*, 2017) and subterranean ventilation (Sanchez-Cañete *et al.*, 2011b).



Fig 41. The subsoil gas ratio of CO2, O2, Ar, and N2 at -1 m (red) and -6 m (blue) was measured weekly during daytime periods. (a) CO₂ and O₂ relationship with R² of 0.9618 and slope of -1.8. (b) The ratio between CO₂/Ar and O₂/Ar with R² of 0.88 and slope of 0.14. (c) Geochemical relationship between N₂/O₂ and CO₂ with the R² of 0.688 and slope of 0.38. (d) The ratio between CO₂ and N₂, indicating Enriched or depleted N₂.

The CO₂ and O₂ relationship (**Fig 41**.a) are strongly negatively correlated. It also indicates that the monitoring site's process combines both aerobic bacterial respiration and oxidation of methane justified by the slope of regression line -1.819. The slope suggests that every formation of 1 CO₂ mole induces 1-2 O₂ mole conversion, with more tendency toward methane oxidation than aerobic respiration. CO₂/O₂ ratio gases taking into account the concentration of Ar shown in **Fig 41.b**, further provided evidence of soil respiration coupled with CO₂ diffusion (Bergel *et al.*, 2017). The variation of CO₂ was also followed by a constant ratio of N₂/O₂, indicating that CO₂ input is solely biogenic (**Fig 41.c**). In the N₂-CO₂ diagram (**Fig 41.d**), the soil N₂ concentration was constant and within the range of atmospheric N₂ regardless of CO₂ molar fraction since there was neither deep input of CO₂ nor dissolution CO₂. All plots on this natural ecosystem, both at - 1m and -6 m, unsurprisingly have an approximate N_2 composition as the atmosphere and N_2 concentration of more than 76.4%, with -6 m slightly enriched in N_2 .

Apparent respiratory quotient (ARQ) has been recently used to understand biotic controls on soil gases better using simultaneous CO_2 and O_2 (Angert *et al.*, 2015; Sánchez-Cañete, Barron-Gafford and Chorover, 2018; Hicks Pries *et al.*, 2019a; Hodges *et al.*, 2019). It has also been found that up to 33% of Rsoil was emitted directly to the atmosphere, whereas 67% of Rsoil was removed by subsurface processes, indicated by the ARQ at 0.3 (Sánchez-Cañete, Barron-Gafford and Chorover, 2018). Some argued that respired CO_2 might be dissolved in soil solutions that can be attributed to the dissolution in water, biological activities, and chemical reactions. The estimation of ARQ is provided in **Fig 41**.



Fig 42. Plot of soil CO₂ and O₂ and theoretical slope governed by diffusion and aerobic respiration (green line). Point color corresponds to seasons, and the point shape indicates the depth of gas samples. The fitted regression of all data is provided in the black line and the dotted black line (95% confident interval). Point fall above the theoretical line has an ARQ value of more than one, and point fall below the theoretical line has an ARQ value of less than 1.

Hodges *et al.* (2019) has extensively described some scenarios when ARQ is not equal to 1. the ARQ < 1 can be attributed to the 1) abiotic or chemolithoautotrophic oxidation, 2) carbonate weathering, 3) Dissolution of CO₂ gas in soil water, 4) silicate weathering, and lignin or lipid mineralization. While ARQ > 1 corresponds to 1) heterotrophic activity, 2) degassing of CO₂-rich soil water, 3) carbonates precipitation, and 4) mineralization of mineral acid. In **Fig 41**, It is clear that the ratio between CO₂ production and O₂ consumption does follow the theoretical slope of 0.76. However, the regression line of all data in our site demonstrates an intercept of -16.69, resulting in a high proportion of the data having an ARQ of more than 1. A similar finding has been reported in a temperate forest with a slope of -0.8 to -0.58 and a y-intercept of 12.17 to 16.77 (Hodges *et al.*, 2019). This means the processing controlling subsoil CO_2 in our site was not solely diffusion and aerobic metabolism using carbohydrate (i.e., ARQ = 1, slope = -0.76).

5.4.Discussion

Our data demonstrate that soil CO_2 storage, stable isotopic composition, and gas ratio analysis varied by depth and seasonally. Also, the change in soil CO_2 storage corresponded to the change in Reco. However, these results are expected based on previous studies (Maier *et al.*, 2010; Sánchez-Cañete, Barron-Gafford and Chorover, 2018). This study is important and notable since this is the first study to combine the EC technique, borehole measurement, isotopic analysis, and gas ratio analysis.

5.4.1. Change in Soil CO₂ storage Due to Subsoil Ventilation

At the ecosystem levels, a study employing the EC (eddy covariance) method has been conducted to calculate CO₂ fluxes at the site of Montiers. The research also shows that CO₂ flux varies significantly hourly, daily, and seasonally. The lowest CO₂ flux was observed during mid-day in the summer due to a higher photosynthesis rate inside the EC system's footprint area. Overall, Reco in summer was higher than in winter, where accumulative ecosystem respiration (Reco) ranged from 0.7 mol $CO_2 \text{ m}^{-2} \text{ d}^{-1}$ during the summer period (17 June 2019) to as low as $0.02 \text{ CO}_2 \text{ m}^{-2} \text{ d}^{-1}$ during the winter. This study further demonstrates friction velocity (u*) plays a significant role in affecting soil CO₂ storage. The decline in subsoil CO₂ storage, high u*, and high Reco was concurrent during the observation periods. The decrease of subsoil CO₂ storage (0-6 m depth) from 2.3 to 1.2 mol CO₂ m⁻², coincided with an increase of Reco from 0.2 to 0.5 mol CO_2 m⁻² d⁻¹ during exceptionally high u* at 1.8 m/s. We hypothesize that during the calm day (low u*), CO₂ remains in the subsoil due to gravitational percolation resulting from a higher density. Even though the daily accumulative of Reco values corresponded very well with the day-to-day dynamics of soil CO2 storage, Reco's hourly accumulative cannot explain the change of soil CO₂ storage. We hypothesize that the change in subsoil CO₂ storage does not always translate into ventilation induce soil. It is instead of falling and increasing pressure that causes soil air to be expanded and contracted. Ventilation and expansion of soil-air are possible due to soil properties that are semipermeable, especially during dry summer. Similar studies in different ecosystems have also reported a strong correlation between soil CO₂ and wind speed (Takle et al., no date; Jassal et al., 2005; Sanchez-Cañete et al., 2011a; Mohr et al., 2016, 2017; Maier, Mayer and Laemmel, 2019). A more detailed discussion about the u* influence on subsoil gas concentration is provided in Chapter 3.

Nonetheless, comparing the borehole measurement and eddy covariance technique should be carried out carefully since it has been widely reported that even though the CO₂ fluxes measured using a method of EC and flux chamber followed a similar general pattern, there was a discrepancy between both values on which the EC accounted between 39 and 52% of soil chamber fluxes (Barba et al., 2017). Even though R_{soil} is expected to be the most significant component of R_{eco}, it is still a fraction. Theoretically, it has to be smaller than Reco (i.e., Reco> Rsoil) at annual, seasonal, daily, or sub-daily scales (Phillips et al., 2016). Reco(Ecosystem Respiration) was not consistently higher than R_{soil} (Soil Respiration) daily to annual scales across different ecosystems. It is caused by some issues, including a) nighttime measurements of Net Ecosystem Exchange (NE), where it is calm and stable, advection may be predominant, causing CO₂ produced near the ground can be transported laterally and undetected by the EC tower (b) R_{soil} measurements (e.g., outside of flux footprint), and (c) the interpretation of the functional relationships of the fluxes with temperature (i.e., Q10) (Dennis D Baldocchi, 2003; Barba et al., 2017). However, in this study, it is almost certain that the comparison is representatively shown by pronounces time-series variation between the daily average of Reco and CO₂ storage. It is due to the fact that we have chosen homogenous stands and soil characteristics coupled with Footprint calculation half-hourly.

In addition, the key findings of this study are, firstly, the importance of soil-water CO_2 storage that was more significant compared to soil-air CO_2 storage during wet seasons. It might explain the low coefficient relationship between u* and CO_2 mole fraction in subsoil since most of the subsoil CO_2 gas is dissolved in the water and not readily available for ventilation. Secondly, the production of CO_2 by biological respiration in the soil is accumulated until the condition is favorable for CO_2 outgassing through relatively slow diffusion and rapid advection due to subsoil ventilation. Thirdly, the interpretation of the data measured using borehole should be done with caution since it has been widely reported that CO_2 flux measured at the ecosystem undervalued the soil CO_2 efflux.

5.4.2. Controlling Processes on Subsoil CO₂ in Temperate Forest

It is a widely held view that bio-hydro-geochemical processes play an essential role in controlling the CO_2 dynamic in the critical zone. There is a strong need to understand better the dynamic of CO_2 storage, CO_2 production, and CO_2 loss. The calcareous bedrock mainly consisted of calcium carbonate and a few amounts of clay minerals in our site. It is surrounded by the weathered layer rich in clays due to decarbonization. A widely held view is that limestone's solubility in weak acid and limestone results in karst forming processes. It has

also been previously studied that the karst system stores a large amount of CO_2 underground, which later was emitted during windy days and filled quickly during low wind speed through cracks and fissures (Roland *et al.*, 2013). However, CO_2 in the soil is mainly driven by two distinct sources, including respiration of plants primarily through roots and decomposition of organic matters by soil microorganisms, where the plant contribution of CO_2 produced by the plant is more significant during early growing seasons (Amundson, 1998).

The $\delta 13C$ values of the subsoil CO₂ showed a distinct seasonal pattern, with the highest values occurring in early winter and the lowest summer values. It was in agreement with monitoring in a karstic environment with heavy $\delta 13C$ and low CO₂ concentration (Spötl, Fairchild and Tooth, 2005). A mixing line was drawn on the keeling plot (Keeling, 1958) to define a natural background of δ^{13} C where it was identified at -25.09 ‰. The δ^{13} C_{CO2} values in our site subsoil are likely due to the decomposition of soil organic matters and root respiration of C3 plants reported from previous studies (Amundson, 1998; Garcia-anton et al., 2014; Zhu et al., 2019). The 1 m depth was identified to be isotopically heavier in our site than the 6 m depth. It is previously reported using steady-state production models coupled with diffusion that the isotopic composition of soil CO₂ shows a gradual change typically as an increase of depth where the isotopic composition becomes closer to the biological's depth source (Pla et al., 2017). In our site, recharge and discharge of soil CO₂ can be identified where the soil CO₂ concentration was inversely correlated with δ^{13} CO₂. The decrease in soil δ^{13} CO₂ at any given depth indicates a period dominated by soil CO₂ production. The increase of $\delta 13CO_2$ is related to the external factors during the outgassing to the atmosphere through diffusion (i.e., during high friction velocity).

As for the CH₄, It is a widely held view that soil may act as a source or a sink for CH₄, where the former mainly occurs in the wetland (organic-rich soil and anoxic condition) and the latter in upland (well-drained and oxic condition) (Le Mer and Roger, 2001). However, it has been reported that forestland accounted for the second-highest flux rate after wetland and grassland (Oertel *et al.*, 2016). Even though the CH₄ concentration found in -1 m is slightly higher than a sub-atmospheric concentration (i.e., <c. 1.8 ppm), the site most likely acts as a net methane sink due to the low concentration of CH₄ found in -1m (The interface between the atmosphere and the deeper layer of soil). In addition, the abundance of CH₄ at -1m can be explained by the depletion of O₂ concentration (**Fig 41**.a,c) that leads to slightly anoxic conditions promoting the methanogenesis process. It is most likely caused by more active methanotrophic CH₄ production in the shallower layer of soil, leading to higher CH₄ concentration and depleting in $\delta^{13}C_{CH4}$. It is consistent with previous findings where the CH₄ is might be fractionated due to production, oxidation, and transport (Whiticar, 1999; Krueger *et al.*, 2002; Zhu *et al.*, 2019). Firstly, during the CH₄ production, methanotrophic bacteria prefer to consume ¹²C_{CH4}; secondly, during the oxidation, methanotrophic bacteria utilize faster the ¹²C_{CH4}; thirdly, the ¹²C_{CH4} is transported more quickly than ¹³C_{CH4}.

Even though the isotopic composition and soil gas ratio analysis clearly indicated that the CO₂ is coming from biogenic sources. Further investigation was carried out to define the exact sources and controlling processes of subsoil CO2. On our site, the ARQ was lower during summer (ARQ<1) than winter/spring (ARQ>1). the ARQ < 1 during wet winter and early growing season can mainly be attributed to the CO_2 dissolution. It has been proven in this study that the CO_{2aq} were predominantly exhibited the soil-water during wet winter. O₂ was reported to be less soluble than CO₂ (Hoagland *et al.*, 2017; Li *et al.*, 2018) in water resulting in a change in O₂/CO₂ ratio. This is consistent with a finding where it was reported that considerable CO₂ dissolution in rainwater occurred in saline/alkaline soil (Ma et al., 2013). Although the δ^{13} C value of CO₂ efflux coming from carbonate has been reported around -25.8 ‰ in a temperate forest (Schindlbacher et al., 2015), which fall at the same range as our CO₂ isotopic composition background (-25.09 ‰), the acidic soil and subsoil cannot support a formation of carbonates weathering accounted for a negligible fraction of CO_2 loss. In our site, where the soil pH is below 6, further dissolution of CO_{2aq} into H₂CO₃, HCO₃⁻, CO₃ 2⁻ is negligible (Lindsay, 1979). Also, the DIC leaching has been reported very weak at around 5.3 ± 2 gC m⁻² year⁻¹ (Siemens, Kaiser and Walmsley, 2011) in a temperate forest.

The weathering from forest soil with carbonate bedrock has been reported at around 2-5% of total annual gasses loss from the soil or around 20 ± 2 gC m⁻² year⁻¹ (Schindlbacher *et al.*, 2019). Besides the fact that the carbonate weathering occurs in a prolonged reaction, our site's lower soil consists of sandy and clayey passages caused by the complex sedimentary source material in our area that has been widely known for transporting water at a prolonged rate. This most likely prevents dissolved CO₂ in the soil-water pore from being transported to the groundwater. It has also been reported that the Fe oxidation is responsible for a seasonal pattern that caused the ARQ < 1 in a temperate forest (Sánchez-Cañete, Barron-Gafford and Chorover, 2018). Oxidation of reduced iron formed during times of considerable soil moisture and local anaerobic condition inside soil aggregate in highly acidic soils has also been reported where the ARQ was unexpectedly low of less than 0.7 (Angert *et al.*, 2015).

Silicate weathering might also contribute to the ARQ<1 in the soil. However, the degree of contribution is still uncertain.

Moreover, the ARQ > 1 that was found during the growing seasons can be attributed to the increased biological respiration in the soil, such as the root system (Rr) and non-biological source (Rn). It is most likely this significant increase in biological respiration outpace the supply of O₂ through diffusion from the soil surface. Due to thermodynamic favorability and resource availability, heterotrophic micro-organisms within the rhizosphere may switch to respiration using a different oxidized species. This effect is more pronounced when the soil air is exhibited by water, which reduces the diffusion coefficient significantly, limiting O₂ supply to the soil aggregates occurring in late growing seasons (W. H. Patrick and Jugsujinda, 1992; Hodges et al., 2019). The higher ARQ in summer (0.9) compared to the winter (0.7) has also been reported where it is hypothesized that root respiration fueled by oxidized substrates play a significant role during the growing season, while microbial necromass dominated the production of CO₂ by reducing substrate such as lipids and protein in the winter (Hicks Pries et al., 2019b). We acknowledge distinguishing the controlling process and origin of C using both the concentration and isotopic composition must be carried out carefully since various factors such as soil characteristics and climate variability may hinder the interpretation. In addition, since the measurement of $\delta 13C$ was carried out noncontinuously for approximately one year, the intra-daily variations and interannual variations might not be well represented.

5.5. Conclusion

This study demonstrated that by integrating eddy covariance with soil gas monitoring techniques, such as carbon-13 isotope analysis (CO_2 and CH_4) and gas ratio analysis, the regulating mechanisms governing subsoil CO_2 storage dynamics may be successfully determined. This work offers compelling empirical evidence that subsurface ventilation is critical in regulating a considerable quantity of CO_2 trapped subsurface that was subsequently discharged during windy days and rapidly filled during low friction velocity. Additionally, this research demonstrated a significant biotic effect on CO_2 generation. The 13CCO₂ concentrations in the subsoil at our location may be ascribed to the C3 plants' respiration and degradation. These biological sources of soil CO_2 are very likely to raise air density, which results in gravitational percolation, which transports the CO_2 to a deeper layer of soil. Additionally, the link between subsoil gases demonstrates that biogenic components dominate

the origins and governing processes of subsurface CO₂, while geochemical processes play a minor role. Due to adverse circumstances, the ARQ variation suggested that the subsurface removal was insignificant (e.g., acidic soil). The seasonal fluctuation indicates that anaerobic respiration plays a substantial role during the summer, as shown by ARQ>1, when respiration exceeds diffusion in soil-air pores. During the winter and spring, precipitation dissolved a significant amount of CO₂. However, additional dissolution of CO_{2aq} into H₂CO₃, HCO₃⁻, CO₃²⁻ is minimal at our location, where the soil pH is less than 6. Automated, in-situ, and long-term monitoring approaches should be developed to investigate further and better understand this study's findings

Chapter 6: General Discussion and Conclusion

It is well understood that increasing the molar proportion of CO_2 and CH_4 in the atmosphere causes an increase in the greenhouse effect and, as a result, global warming. The imbalanced condition of gas exchange between sources and sinks causes the concentration to rise. The CO_2 atmospheric budget includes a considerable amount of transfer gas between terrestrial ecosystems (Angert et al., 2015). More than 350 PgCO₂ yr⁻¹ was anticipated to be transferred from the soil to the atmosphere in 2008. Despite this, due to the intricacy of the regulatory processes, the temporal fluctuation of gas exchange inside the critical zone remains unknown.

Although the study of soil CO_2 dates back to the nineteenth century Although the study of soil CO_2 dates back to the nineteenth century (Boussingault and Levy, 1853), some research questions remain unanswered, such as:, some research questions remain unanswered, such as 1) How to acquire a representative baseline of subsoil CO_2 and its variability for geological storage application, 2) Does the CO_2 concentration in the forest subsoil is negatively correlated with changes in the water table?; 3) How do the drought dynamics affect the gas exchange in the terrestrial ecosystem and how is the performance of Satellite-derived index in detecting those periods?; 4) What is the role of Subsoil CO_2 ventilation in the net ecosystem respiration of a karstic temperate Forest?.

From the metrological perspective (first research question), we have applied the borehole measurement system in the forest ecosystem to monitor the subsoil CO_2 dynamics. This apparatus has previously been used to monitor geological storage sites (Pironon *et al.*, 2013; Taquet *et al.*, 2013). In a subsoil gas measurement application where the CO_2 molar fraction is less than 6%, the quantification of CO_2 concentration using this calibration technique is considered very simple since it only considers the CO_2 vibrational mode at the wavelength of 2400 cm-1 (v3). Although CH₄ concentration was always below our IR sensor's sensibility limit, it was still detectable with micro-GC analysis at 0.72-5.97 ppm. This experiment has generated important questions concerning the various resolutions, which will aid in gaining a better understanding of the absorption spectra's non-linearity. The high-frequency data hold many interesting features that are not captured in synoptic data sets and will be useful for tuning our understanding of soil carbon. This soil gas measuring approach, which combines FTIR, NDIR, and laboratory analysis, does indeed have a lot of potential for long-term in-situ and continuous monitoring to determine the vertical distribution of CO₂ and CH₄ and assist

establish a baseline of natural gas exchange in the Lorraine area. The excellent agreement of CO_2 concentrations determined from FTIR, NDIR, GC, and CRDS in the field warrants the use of a single IR sensor in the field, resulting in lower energy consumption and reduced complexity. Adequate and reliable natural gas exchange monitoring systems would surely aid in understanding the local fluctuation of gas concentration in the soil.

Secondly, most of the research carried on in the forest soil mainly focused on 0 to 1-meter depth; Little do we know about the CO_2 dynamics at the deeper layer of the soil that the water table might influence. This deep soil zone where is marginally influenced by the atmospheric conditions is a widely used location to create a CO_2 baseline for a wide range of geological storage applications. Nonetheless, the water table could not be observed from -1 m and -6 m boreholes. However, this study shows strong empirical shreds of evidence that wind turbulence plays a significant role in driving the deep soil CO_2 concentration from the Borehole measurement. We hypothesize that this could be due to pressure pumping effects. It decreases the CO_2 molar fraction in the soil during high turbulence and increases the CO_2 storage in deep soil during low turbulence provided in *Fig 44*.



Fig 43. Schematic diagram of CO_2 gas transport between subsoil and vegetation cover during dry periods. The first scenario (left) shows a relatively calm condition with no turbulence above the canopy resulting in a low transport process driven by PPE (Pressure Pumping Effects. The second scenario (right) shows more turbulence above the canopy enhancing soil gas transport.

This research also shows that during rainy seasons, gas permeability decreases, reducing molecular diffusion and advection. It emphasizes the significance of spatial and temporal dynamics of deep soil CO_2 dynamics, which can be 100 times greater than air CO_2 . This empirical finding also calls into question the commonly held belief that PPE's impact is limited to the top layer of soil. However, it is unclear if this strong association is site-specific, as soil porosity, soil texture, stand type, and canopy height are all likely to play a role. As the number of flux towers grows, there is a greater demand for borehole measurements to better understand the links between friction velocity and subsurface CO_2 dynamics at diverse locations.

Long-term and site-specific EC studies will surely contribute to better understanding the ecosystem's response to climatic changes and extremes, which is the third research question. Furthermore, the majority of current research relies largely on chrono-sequences, which are

applied across vast geographical regions without taking into account soil and vegetation cover type. (Baldocchi, Chua and Reichstein, 2018). From Long-term (6 years) Flux tower monitoring, During the study periods, the ecosystem acted as a net carbon sink with mean annual NEE, GPP, and Reco of -453 ± 122 gC m⁻²y⁻¹, -1468 ± 109 gC m⁻²y⁻¹, and 1052 ±88 gC m⁻²y⁻¹ consecutively. This work investigated how 2018 and 2019 drought episodes affected carbon exchange in a deciduous temperate forest ecosystem.

Droughts and heatwaves will become more common, as expected. It's uncertain if longer, more frequent, and more severe droughts and heatwaves would have a comparable impact on carbon exchange across the landscape. 2018 and 2019 have been the driest year at Eddy Covariance (EC) site (Montiers-sur-Saulx, France) for more than a decade with SPEI of 2.25 and 2.24 consecutively. As a comparison, the extreme drought in 2003 was -2.52 (Beguería *et al.*, 2014). The drought epicenter was identified in Central and Northern Europe, where forests and crops were rarely exposed by high water deficits and hot summer (Peters *et al.*, 2020). During drought events, carbon exchange, climate, and environmental causes were compared to long-term reference data collected from 2014 to 2017, with the yearly mean shown in *Fig 44*.

In contrast to prior studies that found GPP and Reco declined in synch during droughts, our site revealed Reco is more drought-sensitive than GPP, resulting in a substantial rise in Net Ecosystem Exchange. In comparison to the reference years, Reco fell by 20% in the summer and by 26% in the autumn (2018-2019). (2014-2017). Reco was dropping at the same time that SWC was decreasing (-57%) and soil temperature (Ts) was rising (15%). Both microbial and root respiration are almost assured to be able to keep the process going during the early stages of drought (Spring), since they may still have access to water conserved throughout the cold, rainy winter. We hypothesize that in mature forests with deeper root access, water is retained in a deep layer of soil, allowing photosynthetic activity to continue while microbial respiration rates are reduced. Due to depleting substrates, the large fall in Reco reduction in the summer might be attributable to a decrease in both microbial soil respiration and plant respiration. It's also obvious that when dry soils were rewetted by rainfall following the dry season, there were bursts of CO₂ release. Furthermore, the severe and prolonged drought had minimal impact on the LAI (Leaf Area Index) and EVI (Ecological Value Index) calculated from satellite data (Enhanced Vegetation Index). That is, there is no discernible decrease in vegetation cover or browning. Even though our location experienced less severe drought than Central and North Europe, various ecosystems, and places, particularly those on the margin of the extreme drought domain, are expected to behave differently to a changing climate. Drought and heatwaves will become more frequent in the future, as projected. It's unknown if longer, more frequent, and more severe droughts and heatwaves would have a comparable effect on carbon exchange.



Fig 44. Schematic diagram of CO_2 gas exchange between aquifers, subsoil, vegetation, and atmosphere during the study periods. The Reco (Ecosystem Respiration), NEE (Net Ecosystem Exchange), and GPP (Gross Primary Productivity) were quantified using eddy covariance Data (2014-2019), and DIC Leaching is estimated based on Gas ratio Analysis, isotopic composition, and literature review.

In response to the last research topic, this thesis contributes to advancing scientific understanding on the driving mechanism of subsurface CO₂ storage and exchange, as well as the impact of drought on the Net Ecosystem Exchange. This study revealed that integrating eddy covariance with soil gas monitoring techniques, such as carbon-13 isotope analysis and gas ratio analysis, may substantially reveal the governing processes of sub-soil CO₂ storage dynamics (*Fig 44*). This work gives solid empirical evidence that subsurface ventilation is important in controlling a considerable quantity of CO₂ underground, which is later discharged on windy days and swiftly filled on low friction days. This study also revealed a strong biotic influence on CO₂ production. The $\delta 13C_{CO2}$ values in our site subsoil can be

attributed to the C3 plants. ARQ variation indicated that the subsurface removal was insubstantial due to unfavorable conditions (e.g., acidic soil). The seasonal fluctuation reveals that anaerobic respiration plays a larger role in the summer, as seen by ARQ>1, when respiration outpaces diffusion in soil-air pores. Rainwater dissolved a significant amount of CO_2 in the winter and spring. , further dissolution of CO_{2aq} into H₂CO₃, HCO₃⁻, CO₃²⁻ is negligible in our site, where the soil pH is below 6. The connection of subsurface gases also shows that biogenic components dominate the origins and governing mechanism of subsoil CO_2 , whereas geochemical processes play a minor role. To understand the spatial variance surrounding the flux tower, multiple boreholes are required. To investigate further and better comprehend the findings of this study, automated, in-situ, and long-term monitoring systems should be implemented.

This research project has examined a wide range of existing studies of the gas transfer process within the system of soil and vegetation cover. It can be concluded that; 1) the design and implementation of methods will contribute to a better understanding of the carbon balance; 2) this work makes a significant contribution to the understanding of the response of natural systems to climatic disturbances (impacts of droughts on the forest system) and; 3) it also completes the in-situ CO_2 measurement protocol necessary to establish the baseline of the gas exchange and origin of a natural ecosystem before the introduction of any disturbance. However, this research topic might be further be expanded for advancing the state of the science and to clarify uncertainties. The Perspectives on future research include.

- a) The continuous measurement of CO₂ subsoil which relies on power sources therefore can eliminate uncertainty and minimize data loss.
- b) The need for water table measurement to investigate whether its effects on subsoil gases concentration (CO₂ and CH₄) are significant.
- c) Additional subsoil CO₂ measurement coupled with Eddy covariance tower in another location
- d) The continuous measurement of soil gas composition (CO₂, N₂, CH₄) and isotopic composition.

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Annex

7.1 Installation of Borehole Instrument

éomonit	oring d	Précision	SOL	EXPERTS
s	Rapp /stèm	oort d'installation e de mesure des forage lite de Montiers-sur-Saulx (55	d'un gaz en	
		<u>Rédacteur :</u> M.DERRI <u>Approbateur :</u> V.NAVEL	EN OT	
		FRA-244		01/10/2019
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Date	Version	Commentaires		
				Solexperts France SARL 10 altee de la torêt de la Reine 54500 Vandœuvre-tes-Nancy Tel +33 (0)3 83 94 04 55 Fax +33 (0)3 83 94 03 58 Info@foolexperts.fr www.solexperts.com

SOLEXPERTS

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FRA-244 Installation d'un système de mesure des gaz_site de Montiers-sur-Saulx (55)

Introduction

Le projet de recherche DEPPSURF s'inscrit dans le cadre de la labélisation I-site (Initiatives Science – Innovation – Territoires – Économie) de l'Université de Lorraine via le Plan d'Investissement d'Avenir.

Le but du projet est de contribuer à répondre scientifiquement et techniquement aux grands défis du 21ème siècle, notamment la transition énergétique, gestion des besoins énergétiques et préservation de la ressource en eau et de la biodiversité.

Plus spécifiquement, le projet DEEPSURF se concentre sur les changements d'usage du sol et du sous-sol. Les questions scientifiques portent :

 sur les transferts de matière (liquides aqueux ou hydrocarbonés, solutés, gaz y compris de toxiques) entre compartiments depuis le sous-sol jusqu'à l'atmosphère,

- sur l'impact et les risques associés, sur les écosystèmes de ces nouveaux usages,

 - sur l'évaluation économique et la perception sociétale de ces projets d'aménagement du territoire (source Georessource).

Solexperts, dont la spécificité est l'étude du sous-sol, intervient dans le projet pour mettre en place des forages qui permettent d'étudier les échanges gazeux avec ce dernier.

Deux sites d'études ont été sélectionnés situés dans une forêt domaniale à proximité de Montiers sur Saulx (55).

Le présent rapport expose la mise en place de 4 forages en juin 2019 et leur instrumentation avec des systèmes de mesure des gaz en forage en juillet 2019 (planning en Annexe A).

1 Description des forages

Deux sites d'étude ont été sélectionnées dans la forêt domaniale de Montiers-sur-Saulx, MEUSE (55) repérés sur la Figure 1.

FRA-244 Installation d'un système de mesure des gaz_site de Montiers-sur-Saulx (55)



Figure 1 : Localisation des forages et des sites d'étude à Montiers-sur-Saulx (source : Georessource)

1.1 Site N°1 (forages 1 et 3)

Sur le site N°1, deux forages ont été implantés dont les principales caractéristiques sont regroupées dans le Tableau 1.

Identifiant	Forage 1	Forage 3			
Longueur forage [m]	1 m	<u>6m</u>			
Tubage	De 0 à 0.5 m : Tube plein De 0.5 à 0.95 m : Crépine	De 0 à 5 m : Tube plein De 5 à 6 m : Crépine			
Diamètre tubage [mm]	40 mm	140 mm			
Niveau statique [m]					
Technique utilisée pour forer	Tarière manuelle	Tarière mécanique (forage réalisé par GEOTEC)			

Tableau 1 : Caractéristiques des forages 1 et 3 implantés sur le site Nº1

La Figure 2 montre l'implantation des forages 1 et 3.

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Figure 2 : Photographie des forages 1 et 3

FRA-244 Installation d'un système de mesure des gaz_site de Montiers-sur-Saulx (55)

				Ec	Date : 05/06/2019 chelle : 1/100				
-	1	ravaux	de sondages	Υ:					
Affa	ire : 1	9/04169	NANCY	Z :	n				
Cote	Prof.			Coupe Indicative		Eau	Outi	Equipement	
-	10	CAP YOUR		terre végétate			-		
				argile brune rougeåtre		NEANT	TAR @140	Piezometre	
000								RANK I II	
Pose	d'un pi	ezometre	se longueur 6.00m di	ametre 65/90mm crépiné de 5.00m à 6.00m avec protection	de tête				

La Figure 3 présente la coupe du forage et la lithologie (source : Geotec).

Figure 3 : Coupe lithologique forage 3 réalisé par Geotec



1.2 Site N°2 (forage 2 et piézomètre 2)

Sur le site N°2, deux forages ont été implantés dont les principales caractéristiques sont regroupées dans le Tableau 2.

Identifiant	Forage 2	Piézomètre 2
Longueur forage [m]	0.65 m	0.65 m
Tubage	De 0 à 0.55 m : Tube plein De 0.55 à 0.65 m : Crépine	De 0 à 0.55 m : Tube plein De 0.55 à 0.65 m : Crépine
Diamètre tubage [mm]	40 mm	40 mm
Niveau statique [m]	020	12
Technique utilisée pour forer	Tarière manuelle	Tarière manuelle

Tableau 2 : Caractéristiques du forage 2 et du piézomètre 2 implantés sur le site N°2

La Figure 4 et la Figure 5 montrent l'implantation du forage 2 et du piézomètre 2.



Figure 4 : Photographie du forage 2

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Figure 5 : Photographie du piézomètre 2

2 Instrumentation des forages

2.1 Description des équipements

- 2.1.1 Site 1 : forages 1 et 3
 - Forage 1

Le forage 1 est équipé d'un intervalle de mesure de 0.4 m (entre 0.55 à 0.95 m de profondeur). Une entrée en tête de forage permet les prélèvements et/ou analyses. Le forage est équipé d'un capteur de température.

L'Annexe B présente le système installé dans le forage.

Forage 3

Le forage 3 est équipé d'une complétion munie d'un obturateur définissant une chambre de mesure de 1 m (entre 5 à 6 m de profondeur). Ce forage possède un capteur de niveau d'eau et un capteur de température.

L'Annexe C présente le système installé dans le forage.

Les paragraphes suivant détaillent les éléments qui composent la complétion.

2.1.1.1 Obturateurs

L'obturateur a une longueur d'ancrage de 1 m, le diamètre externe des obturateurs non ancrés est de 52 mm. La gomme est composée de gomme naturelle et le corps d'acier inoxydable.

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2.1.1.2 Intervalle

L'intervalle mesure 1 m. Il est situé de 5 à 6 m dans le forage, ce qui correspond à la partie crépinée.

2.1.1.3 Tiges

Des tiges en p.v.c. sont placées pour permettre l'installation de la complétion en forage.

2.1.1.4 Unité de contrôle

L'unité de contrôle montée en surface comprend (voir schéma :

- · Ligne obturateur : pour l'ancrage des obturateurs, avec manomètre de contrôle.
- Ligne intervalle pression : capteur de pression (gamme 0-100 bar, précision 0.1% FS)
- · Lignes pour réaliser les analyses sur le spectromètre infra rouge
- · Un logger SDLG qui permet d'acquérir les données

L'unité de contrôle est protégée dans un boîtier posé sur le sol de la cabane livrée et installée le 23/07/2019 avec l'équipe de Georessource. Une attention particulière sera portée pour cet équipement pour éviter l'endommagements du dispositif, la rupture de ligne, le dévissement de raccords... (Figure 6).



Figure 6 : photographie de l'équipement dans la cabane

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Figure 7 : Schéma des forages 1 et 3 et de l'unité de contrôle

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Figure 8 : Photographie de l'unité de contrôle

2.1.2 Site 2 (Forage 2 et piézomètre 2)

Forage 2

Le forage 2 est équipé d'un intervalle de mesure de 0.1 m (entre 0.55 à 0.65 m de profondeur). Une entrée en tête de forage permet les prélèvements et/ou analyses. L'Annexe D présente le système installé dans le forage.

Piézomètre 2

Le piézomètre 2 est crépiné de 0.55 à 0.65 m de profondeur, non équipé, fermé par un bouchon.

L'Annexe E présente le système installé dans le forage.

2.2 Planning de l'installation

Le planning des opérations est détaillé en Annexe A.

2.3 Liste capteurs et raccordement centrale d'acquisition

Le Tableau 3 dresse la liste des différents capteurs monitorés grâce au logger SDLG et leur valeur initiale le 24/07/2019 à 11h08.

Туре	Capteur	Valeur	Unité

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	PRE_Mb	0.974	bar		
ssion	PRE_forage3	1.005	bar		
Pres	PRE_Packer	13.423	bar		
	Pre_atm	1006	bar		
•	TEM_forage3	15.882	°		
iratu re	TEM_forage1	18.316	°c		
Tempé	TEM_armoire	21.100	°C		
-	TEM_Pompe3	21.5979	°C		

Tableau 3 : liste des différents capteurs installés et valeurs initiales

FRA-244 Installation d'un système de mesure des gaz_site de Montiers-sur-Saulx (55)

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Annexe

FRA-244 Installation d'un système de mesure des gaz_site de Montiers-sur-Saulx (55)

Annexe A : Tableau du déroulement des différentes étapes du chantier

						_	
03/06/19	10:00	10:45	Forage N'3	FRA-244	MD.VO. API	PMD	Arrivée sur site
							Visite de site en attendant les foreurs
03/06/19	10:45	12:00	Forage N'3	FRA-244	MD.VO. API	INS	Mse en place machine
							Implantation du forage : emplacement désigné par Laurent Saint André (INRA)
03/06/19	12:00		Forage N'3	FRA-244	MD, VO, API	INS	Forage : 6 m (1 passe diamètre 100 mm, puis 140 mm) tarrière
							Mise en place du plezomètre (diam : 80/90 mm)
03/06/10	12:00	14:00	Econom MED	EDA 244	MELLIO ARI	_	Cote fond equipement : -6m
03/00/15	13.00	14.00	Forage N a	F104-244	ND, VO, AP1	100	céle Tube dels : 4.0 6/m (ser report au sol) 40.53 m (ser report à la margelle)
							const métalique : + 0,61m (par rapport au sol) +0,55 m (par rapport a la margelle)
	<u> </u>					-	Grader: -6.6.4.70 m
03/06/19	14:00		Forage N°3	FRA-244	MD, VO, API	NS	Arole : -4 70 à 4 20 m
03/06/19	14:40	16:30	Eorane N°3	FRA.244	MD.VO. API	STD	Eoreurs sont allès chercher du ciment (non prévu dans leur liste matériel)
03/06/19	16:30	18:00	Forage N'3	FRA-244	MD.VO. API	NS	Ciment : - 4.20 à +0.06m
03/06/19	18:00		Forage N°3	FRA-244	MD.VD. API	PMD	Rangement matériel et Départ du site
13/06/19	9:15					PMD	Arrivée sur site
13/06/19	9:15	10:00	Forage N'1	FRA-244	MD,VO	INS	transport du matériel puis creusement et mis en place forage N°1 (1m)
13/06/19	10:30	11:00	Forage N°2	FRA-244	MD,VO	PMD	rangement du matériei et mise en place de ce dernier sur le deuxième site
13/06/19	11:00	13:00	Forage N°2	FRA.244	MD.VO	NS	creusement du forage N°2 : roche à 85 cm de profondeur
13/06/19	12:30	13:30	Plézomètre N°2	FRA-244	MD,VO	NS	creusement du plézomètre N°2 : roche à 65 cm de profondeur
							Appel P.De Donatto + L. Saint-André pour décision profondeur forage :
13/06/19	14:00		Plézomètre N'2	FRA-244	MD,VO	PMD	les deux forages seront crépinés de 50 à 60 cm (10cm de crépine),
13/06/19	14:30	15:00	Plézomètre N°2	FRA-244	MD,VO	INS	Mise en place des forages à la côte souhaitée
13/06/19	15:00	15:30	Plézomètre N'2	FRA-244	MD,VO	PMD	Rangement du matériel
23/07/19	09:00			FRA-244	MD,VO	PMD	Rdv Castorama Houdemont pour récupération cabane avec carnion Solexperts
23/07/19	9:45	11:00		FRA-244	MD,VO	PMD	Trajet jusqu'au site N°1 (forage 1 et 3)
23/07/19	11:00	11:15		FRA-244	MD,VO	PMD	Matériel
							installation du système dans le forage avant construction cabane, repose au fond du forage en attendant
23/07/19	11:15	12:12	Forage N°3	FRA-244	MD,VO	100	ancrage
23/07/19	12:15	18:30		FRA-244	MD,VO	INS	Montage de la cabane
23/07/19	18:30	19:45		FRA-244	MD,VO	PMD	Départ du site, trajet du retour
24/07/19	8:00	9:15		FRA-244	MD	PMD	Départ de Nancy vers le site N°1
24/07/19	9:15	10:00	Forage N°3	FRA-244	MD	INS.	Préparation du matériei
24/07/19	10:00	11:30	Forage N'3	FRA-244	MD	INS	Connexion de l'armoire + ancrage du packer
24/07/19	10:50	11:15	Forage N°3	FRA-244	MD	INS	Essale envoie de données : ok
24/07/19	11:30	13:00	Forage N°3	FRA-244	MD	INS	Branchement du spectro
24/07/19	14:00	15:30	Forage N*3	FRA-244	MD	NS	Mesures spectro
24/07/19	14:30		Forage N°2	FRA-244	MD	NS	Instrumentation forage 2
24/07/19	15:30			FRA-244	MD	PMD	Rangement matériei et Départ du site

Annexe B : Layout Forage 1

	FRA-244 : Deensurf											
Borehole	Forage N°1			ret	: Deepsurr	Date	140	3/2019	Reponsable	MD		
Sorehole Depth	0,95 m	Direction	vertical descendant	Diamétre forage	40 mm	Parjet	rn.	A-244	Localization	Site 1		
in Or Capter	Membrane Lmembrane 4.membrane ur de température	L	inez		Type d'équiper nombre et long	ment, (preur n	00 10 nm mm	Depth	Comments: Référence : l (0	Niveau du so m)		
					Bouchon Tube plein	1-	33 25 33 25	0,00				
					Tube crépiné P	VC 1"	33 25	0,55	I			
INTERVAL			I		1 tube* 10 (cm						

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				FRA	-244 : Deep	surf						
ihole	Forage N*3		vertical	Reference point	noi	Dam			1403/2019	ē	Responsible	MD
hale	6,00 m	Direction	des centilant	Diamitre Iorage	140 mm	Projet			1104-204		Localitation	Sile 1
N	Annibearse	a de cancier	Lives		Type d'équip	errard,	OD	<i>i</i> D	Léquipt	Depth	Comments:	
h_ Out	membrane membrane				nombre at lo	guer	JUNIT.	min	128	m	Référence : I (0	liveau du si m)
Capitor	Packer				Demière ra	longe	60	51	687	87,00	Haut du tube	ga:+87 cm
					1 00	50 cm					0451.500	
					Tiges de ra	longe	00	51	637		Capot :	+ 53 cm
					2 thilorges	199 cm						
				ľ.								
Ť					pláce ferralis o	(15 cm			249	151		
char				I	Packe gomme de 1	12 cm	52					
					piece de Tube crép	/A on Nhê				5,00		
INVAL					1 tube 2	"1m	60	51			Tube or	pinë 1m
		a	1		Marcala		-		40			

Annexe C : Layout Forage 3

FRA-244 Installation d'un système de mesure des gaz_site de Montiers-sur-Saulx (55)



	Annexe D : Layout forage 2										
Formular TESTING PLAN FOR PACKER SYSTEM											
	FRA-244 : Deepsurf										
Borehole	forage N°2		vertical	Reference point	sol	Date	14/0	3/2019	Ausponsable	MD	
Borehole Depth	0,65 m	Direction	descendant	Diamètre forage	40 mm	Projet	-	A-244	Localization	Site 2	
Capter	Membrane _membrane it_membrane ir de température	لل	hez		Type d'équiper nombre et long Bouchon	nent, jueur	00 10 mm mm 33 25	Depth	Comments: Référence : ()	Niveau du sol 0 mj	
			1		1 tube 50 c	m	35 25		1		
INTERVAL					Tube crépi 1 tube* 10 c	né cm	33 25	0,55			
	End Borehole				Bouchon			0,65	1		

Annexe E : Layout piézomètre 2

Formula TEST	Formular TESTING PLAN FOR PACKER SYSTEM											
	FRA-244 : Deepsurf											
Borehole	Borehole Piézométre N°2 vertical			Reference point	sol	Date	14/03/2019		/2019	Responsable	MD	
Borehole Depth	1,00 m	Direction	descendant Diamétre forage		40 mm	Projet		FRA	-244	Localization	Site 2	
Capter	Membrane Lines In_membrane Out_membrane Capteur de température				Type d'équiper nombre et long	nent, jueur	OD mm I	D mm	Depth m	Comments: Référence :	Niveau du sol 0 m)	
					Bouchon		33	25	0,00			
					Tube pleir	ı	33	25				
					1 tube 50 c	m						
INTERVAL					Tube crépir 1 tube* 10 c	nê Im	33	25	0,55			
	End Borehole			2003	Bouchon				0,65			

FRA-244 Installation d'un système de mesure des gaz_site de Montiers-sur-Saulx (55)

7.2. Percentage of filtered and missing data from flux tower

2019

Percentage of filtered data NEE LE Н VPD RG Tair Tsoil rН Ustar 2019 8.24342068 7.512702 14.11201 5.21208 6.34241 2.197865 7.518411 7.518411 7.506993 NEE 2019 2019 å Fingerprint at yourSiteID: NEE (umolm-2s-1) Nov e Fingerprint at yourSiteID: NEE_uStar_f (umolm-2s-1) đ Nov ö Sep Sep Aug Aug 3 3 5 10 -30 -20 -10 0 Mav -30 -20 -10 0 10 Aay NEE NEE_uStar_f Apr Mar f 5 0 2 4 6 8 10 12 14 16 18 20 22 24 0 2 4 6 8 10 12 14 16 18 20 22 24 LE 2019 2019 Dec Fingerprint at yourSiteID: LE_f (Wm-2) Dec Fingerprint at yourSiteID: LE (Wm-2) Nov Nov Oct ö Sep Sep Aug Aug Jul Ę Jun Ę May 0 200 400 600 -400 -200 May 0 200 400 600 -400 -200 LE_f Apr LE Apr Mar Mar Feb Feb Jan Jan 5 0 2 4 6 8 10 12 14 16 18 20 22 24 0 2 4 6 8 10 12 14 16 18 20 22 24

Н





Fingerprint at yourSiteID: H_f (Wm-2)



Rg



2019



Fingerprint at yourSiteID: Rg_f (Wm-2)



T air







0 2 4 6 8 10 12 14 16 18 20 22 24













Fingerprint at yourSiteID: Tsoil_f (degC)



VPD







Fingerprint at yourSiteID: VPD_f (hPa)



0 1000 2000 3000 4000 5000 VPD_f

Percentage of filtered data

	NEE	LE	Н	Rg	Tair	Tsoil	rH	VPD	Ustar
Count	4452	3361	4591	1360	438	576	473	696	1224
Percentage	25.41096	19.18379	26.20434	7.762557	2.5	3.287671	2.699772	3.972603	6.986301

NEE

















100 200 300 400 500 LE_f





















rH







Fingerprint at yourSiteID: rH_f (%)



Fingerprint at yourSitelD: Tair_f (degC)

Percentage of filtered data

	NEE	LE	Н	Rg	Tair	Tsoil	rH	VPD	Ustar
Count	4040	1247	1084	929	368	49	360	369	542
Percentag	23.05936	7.11758	6.187215	5.302511	2.100457	0.27968	2.054795	2.106164	3.093607

NEE























Tsoil







40 60 80 100 rH_f

rΗ



Percentage of filtered data

	NEE	LE	Н	Rg	Tair	Tsoil	rH	VPD	Ustar
Count	638	602	841	937	452	669	491	464	492
Percentag	3.641553	3.436073	4.800228	5.348174	2.579909	3.818493	2.802511	2.648402	2.808219

NEE









LE



Fingerprint at yourSiteID: LE (Wm-2)

2016





Н





























Tsoil

Dec

Nov

ođ

Sep Aug

R

Ę

May

Apr

Mar

Feb

Jan



Fingerprint at yourSiteID: Tsoil_f (degC)



rΗ





Fingerprint at yourSiteID: rH_f (%)

30 40 50 60 70 80 90 100 rH_f

Percentage of filtered data

	NEE	LE	Н	Rg	Tair	Tsoil	rH	VPD	Ustar
Count	676	689	940	946	530	17520	301	544	554
Percentag	3.858447	3.932648	5.365297	5.399543	3.025114	100	1.718037	3.105023	3.1621

NEE







2015





LE



2015





Н







0 2 4 6 8 10 12 14 16 18 20 22 24

Fingerprint at yourSiteID: H_f (Wm-2)






200 400 600 800 1000 0 Rg_f

Tair







Tsoil

rΗ









VPD

2014

Percentage of filtered data

	NEE	LE	Н	Rg	Tair	Tsoil	rH	VPD	Ustar
Count	3046	1844	2009	1019	690	17520	751	683	1714
Percentag	17.38584	10.52511	11.46689	5.81621	3.938356	100	4.28653	3.898402	9.783105

NEE



LE



Н



Rg





Fingerprint at yourSiteID: Rg_f (Wm-2)



Tair









Tsoil

rH







Jan

2014

5 0 2 4 6 8 10 12 14 16 18 20 22 24 Fingerprint at yourSiteID: rH_f (%)



7.3. Half-hourly Measurement of Borehole and Flu (2019-2020)



19/9/2019 (Q3)





Hours









24

0



. 36

. 48



12/9/2019 (Q3)

















12/3/2019 (Q3)





















12/17/2019 (Q3)

















12/20/2019 (Q3)

















- Temperature at -1 m

1/6/2019 (Q3)



















1/21/2019 (Q3)



















02/24/2019 (Q3)











-- Air Temperature-- Temperature at -6 m

(CO2 vs CO2 air)



06/30/2020 (Q3)











0

Air Temperature --- Temperature at -6 m





07/6/2020 (Q3)











(CO2 vs CO2 air)



07/14/2020 (Q3)











12

--- Air Temperature --- Temperature at -6 m

0

24

36

48

(CO2 vs CO2 air)



07/21/2020 (Q3)











-- Air Temperature-- Temperature at -6 m

(CO2 vs CO2 air)

