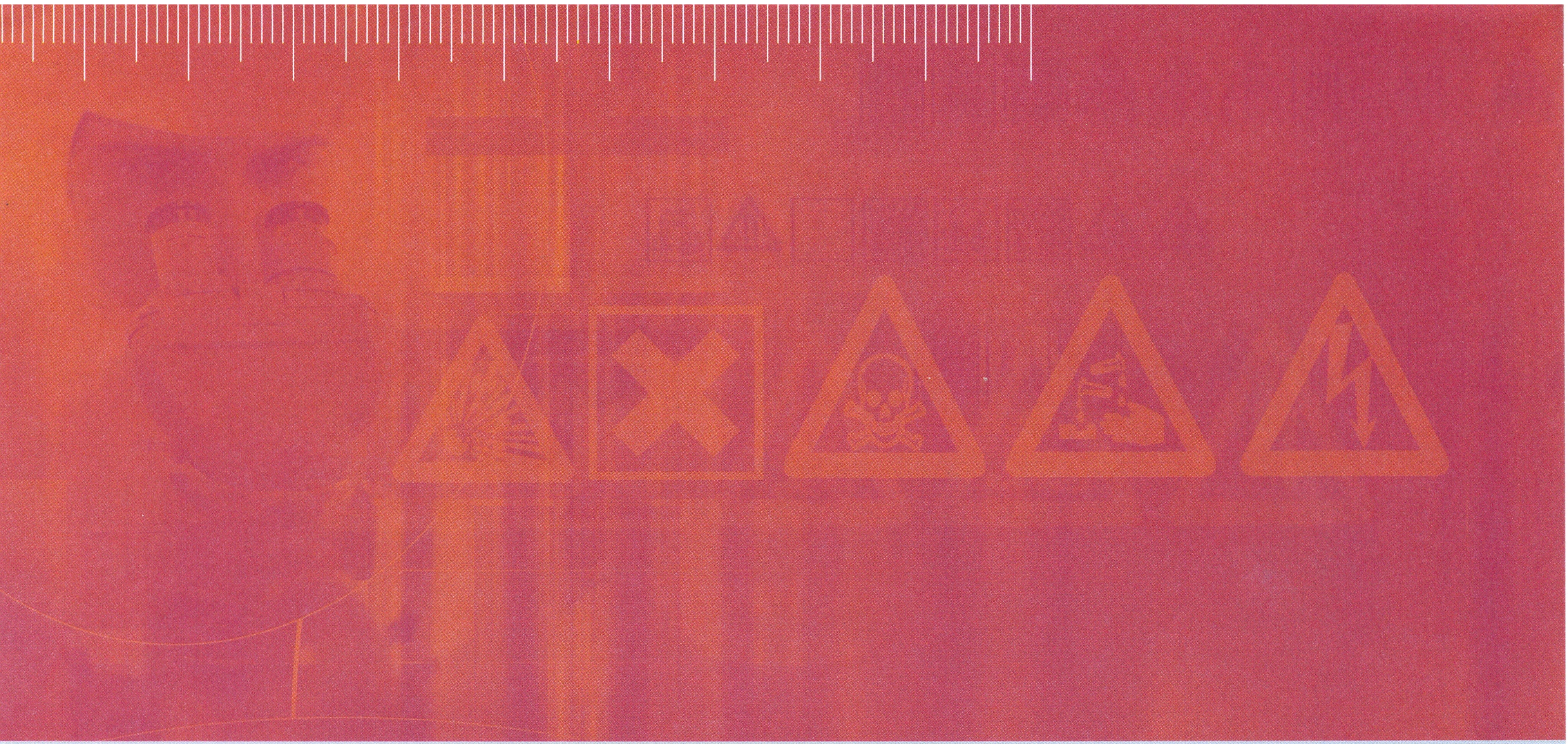

STUDY REPORT 04/06/2019

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Reference values of naturally occurring biogenic CO_2 and CH_4 fluxes from soils

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Reference values of naturally occurring biogenic CO_2 and CH_4 fluxes from soils

Ground and Underground Risks Division

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SUMMARY

Methane and carbon dioxide are naturally emitted by soils as products of different, mainly biological, processes. These emissions are usually low, but vary significantly in time and space. There is still very limited quantitative data regarding the natural biogenic flux of soil gas in France.

However, it is important to know the CH_4 and CO_2 flux levels usually observed in sites that are considered natural and unpolluted, in order to distinguish these natural biogenic emissions from possible anomalies. These may be of anthropogenic (post-mine, caused by contamination, landfills, city gas leak, etc.) or natural origin (mainly geological origin).

From the experimental data acquired by Ineris over 20 years, we analyzed naturally occurring biogenic CO_2 and CH_4 emissions. On one hand, it confirmed that there is no significant flux of CH_4 from soils that are normally drained and, on the other hand, that there is a generalized presence of a natural, largely measurable, flux of CO_2 in almost all normally drained soils.

The natural flux of CO_2 undergoes generalized and very pronounced seasonal variations. On average, emission was clearly strongest in summer and weakest in winter. It is intermediate in spring and fall. Seasonal variations are on average stronger than the influence of other specific parameters of the studied sites (climate zone, land use, geology, pedology, etc.).

Ranges of normal values, average values, low limits, high limits, and the most frequent values for specific configurations were established from statistically processed data. For example, the most probable CO_2 flux ranges on natural sites are respectively from 0 to 6 $cm^3\ min^{-1}\ m^{-2}$ in winter and 3 to 20 $cm^3\ min^{-1}\ m^{-2}$ in summer. The higher thresholds that mark an abnormally high flux, corresponding to a natural or anthropogenic anomaly, were respectively evaluated at 12 $cm^3\ min^{-1}\ m^{-2}$, for winter times 30 $cm^3\ min^{-1}\ m^{-2}$, for summer times.

Practical recommendations were also made to lead to professional standards for in situ measurement of gaseous emissions from soil.

The study's results can be used as reference data for natural emissions, needed to evaluate non-biogenic phenomena, particularly the “mine gas” hazard. They can also be used outside of the mining and post-mining context: impact linked to industrial pollution of soils, impact of underground storage, landfills, etc.

KEYWORDS

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gas, soil, flux, biogenic, CH_4, CO_2, *in situ* measurements,

REGION

Metropolitan France

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1. INTRODUCTION

Methane and especially carbon dioxide are naturally emitted by soils as products of different, mainly biological, processes in the shallow biosphere. There is usually a small quantity of gas emitted, but it significantly varies in space and time.

There is still very limited quantitative data regarding the natural biogenic flux of soil gas in France. According to our feedback, there is no reference database made on the topic.

It is however important to know the CH_4 and CO_2 flux levels usually observed on sites that are considered natural and unpolluted (natural background), in order to be better able to distinguish these natural emissions from possible anomalies of anthropogenic, post-mining origin, caused by pollution, related to a landfill waste, a gas leak, septic tank biogas leaks, etc.

The same goes for identifying and defining natural gas anomalies, which can also have a multitude of origins (shallow geochemical system, volcanic, crustal, etc.).

Ineris has acquired a significant number of experimental data for research programmes (ANR[1], RFCS[2], etc.), works carried out by the government and state agencies as well as internal programs. From this dataset, Ineris has proposed to establish a reference of naturally occurring CO_2 and CH_4 in order to reach:

- An evaluation of a reference range of normal (*i.e.* classically observed) values, with the establishment of average values, low limits, high limits, and the most frequent values;
- A definition of the main characteristics of the gas flux, according to the environmental parameters identified as the most important.

The results obtained can have two main purposes:

- Reference values of natural emissions established complete and update the methodological guide for evaluation of the post-mining gas hazard published by Ineris in 2015 (Pokryszka et al., 2015);
- The database created can also be used outside of the mining and post-mining context, for example to assess the impact linked to soil pollution or even the impact of other soil and subsoil uses (underground storage, landfill, etc.).

This study has been performed as a part of a technical support programme funded by the Ground and Underground Bureau (B3S) of the French Ministry of Ecological and Sustainable Transition, with a contribution from the European project RFCS MERIDA.

Note: The Ineris data taken into account in the analysis only correspond to local diurnal emissions, measured directly at the soil's surface. The fluxes are expressed in $cm^3\ min^{-1}\ m^{-2}$ in standard temperature and pressure (STP). For CO_2: $1\ cm^3\ min^{-1}\ m^{-2}{}_{STP} = 0.033\ mg\ s^{-1}\ m^{-2}$. For CH_4: $1\ cm^3\ min^{-1}\ m^{-2}{}_{STP} = 0.012\ mg\ s^{-1}\ m^{-2}$.

[1] French National Agency for Research

[2] Research Fund for Coal and Steel

2. ESSENTIAL BIBLIOGRAPHICAL INFORMATIONS [3]

2.1 GENERAL INFORMATION ON THE BIOGENIC EMISSION OF CO_2 AND CH_4 FROM SOILS

Most soils naturally emit a rather significant quantity of naturally occurring gas. These are primarily CO_2 and, to a lesser degree, CH_4. A soil's natural emission of carbon dioxide is commonly called "soil respiration". Emitted carbon dioxide originates from biological and chemical processes. The respiration of plant roots and their associated biological components, as well as the decomposition of organic matter by microorganisms and soil fauna are biogenic sources of carbon dioxide in soil (Ryan et al., 2005).

The intensity of CO_2 production in soils is therefore highly connected to the local environmental and biological context. In principle, it is much more intense in vegetated areas with soils rich in organic matter than in arid areas where the soil is poor.

The mechanisms of methane production in soil are very complex. Indeed, the shallow biosphere harbors at the same time bacterial populations that produce methane by decomposing organic material without oxygen (anaerobic methanogenic bacteria) and bacteria that oxidize methane into carbon dioxide (aerobic methanotrophic bacteria). These two microbial activities are both opposing and inter-dependent. At the soil-atmosphere interface, the biologically occurring methane flux is the result of the competition between the phenomena of production and consumption of this gas (Roger et al., 2003).

Flooded or submerged soils (rice paddies, wetlands, estuary soils, peatlands, etc.) are conducive to methane emission. Overall, more methane is produced in the anaerobic layers of these soils than it is oxidized in the aerobic overlying strata.

Conversely, soils that are normally water drained consume most or all of any methane produced in the deepest, wettest, and least-oxygenated layers. Soils of this kind therefore show an overall low to nonexistent CH_4 flux toward the atmosphere.

Note that on certain natural sites, CO_2 and CH_4 fluxes of biological origin must be linked to emissions of geological origin. However, for CO_2 fluxes in temperate climates, emissions of biogenic origin represent an overwhelming majority, outside very specific geological sectors. These specific sectors are mainly areas affected by gas emissions from major geologic faults through hydrothermal activity, volcanic activity, or even a significant geochemical anomaly. These sectors are relatively well-known in France.

2.2 CO_2 FLUX

According to the best available references, in Europe's temperate climates, the annual average CO_2 flux observed in a classic normal environment (grasslands, forests, agricultural areas) fall within a range of approximately 0.5 to 3 $cm^3\ min^{-1}\ m^{-2}$ (von Arnold et al., 2005). Locally, this flux can be much stronger, but rarely exceeds 5 $cm^3\ min^{-1}\ m^{-2}$.

[3] This chapter is partly a result of the bibliographical summary performed beforehand by Ineris as a part of "Sentinelle" programme (Lafortune, 2009), supported by French National Agency for Research (ANR).

In areas of North America with a temperate climate, the annual average fluxes found at the surfaces of grassland, agricultural field and forest type areas, fall within around 1.5 and 2.5 $cm^3\ min^{-1}\ m^{-2}$ (Raich and Schlesinger, 1992). However, measurements on some sites reached monthly averages exceeding 5 $cm^3\ min^{-1}\ m^{-2}$.

This Raich and Schlesinger study demonstrated also a strong influence of the annual climatic cycle on the intensity of CO_2 emissions. Maximum fluxes were consistently observed in summer and minimum fluxes in winter. An example of this seasonal change is shown in figure 1.

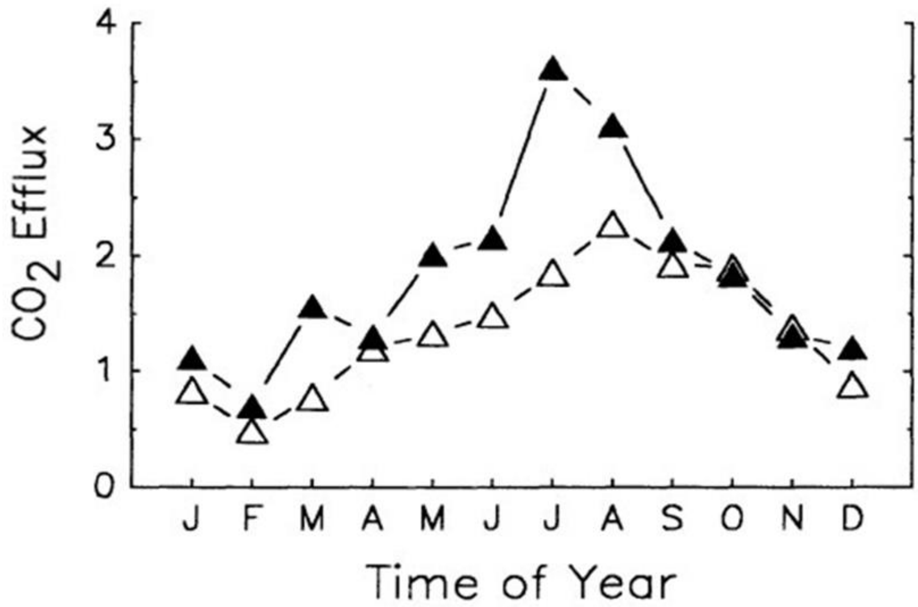

Figure 1. Monthly CO_2 flux in gC day $^{-1}m^{-2}$ measured over two years on the soil of a coniferous forest in the United States, (Raich and Schlesinger, 1992, modified) [4]

This annual variation of biological activity producing CO_2 in soils, linked to seasonal climatic conditions, is mentioned in other bibliographical sources (Kiefer and Amey, 1992; Bajracharya et al. 2000)

The flux ranges observed respectively in European (von Arnold et al., 2005) and North American (Raich and Schlesinger, 1992) conditions are very similar.

2.3 CH_4 FLUX

In European climate conditions, there is a usually very weak methane flux of biological origin from a **normally water drained soil**, usually lower than 0.1 $cm^3\ min^{-1}\ m^{-2}$, for the maximum one-off values, and lower than 0.04 $cm^3\ min^{-1}\ m^{-2}$, for average values drawn from several measurements carried out on larger surfaces (von Arnold et al. 2005).

Outside anomalies of geological origin (e.g. deep gas migrations), CH_4 fluxes on natural sites can locally exceed 0.1 $cm^3\ min^{-1}\ m^{-2}$, but only in very particular areas that are very humid and rich in organic materials, like peatlands, muddy or estuary soils, rice paddies, etc. (Ryan et al., 2005).

[4] For CO_2 and CH_4: 1 gC $day^{-1}\ m^{-2}$ equals 1,3 $cm^3\ min^{-1}\ m^{-2}{}_{STP}$

3. USED MEASUREMENT TECHNIQUE

All measurements taken into account in this study were carried out using the specific accumulation chamber coupled with external gas recirculation (CARE) developed and patented by Ineris (Ineris, 1998). Ineris has used this method for nearly 25 years and has tested it in real conditions on a multitude of sites with widely varying characteristics (natural sites, landfills, mines, post-mining sites, polluted soils, underground storage, geological anomalies, etc.).

A comprehensive description of the method and its applications is available in several documents and specific publications (Pokryszka 1996; Ineris, 1996; Pokryszka and Tauziède, 2000; Pokryszka et al., 2010). Here you will find essential information and characteristics.

3.1 PRINCIPLE

The CARE method can be categorized as an intermediary technique between the static principle and the dynamic principle. It is a **method for directly measuring the gas flux locally emitted at the surface of the soil**. These principles are presented in figure 2.

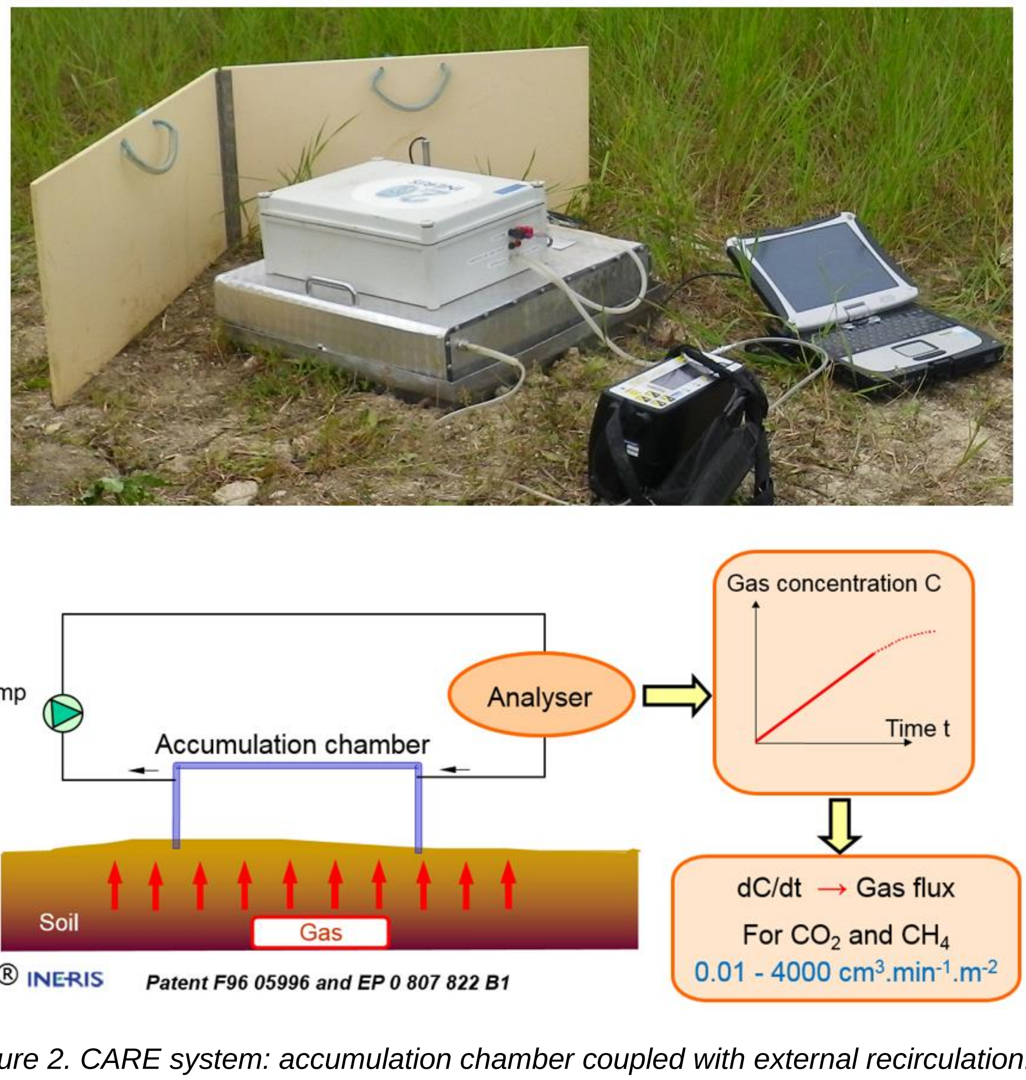

Figure 2. CARE system: accumulation chamber coupled with external recirculation. Principle of the method patented by Ineris.

The method comprises using an enclosure (chamber) to cover a certain ground surface area (0.25 m^2) in a practically sealed manner, without significantly modifying the gas migration conditions. This operation creates an “accumulation” effect that forms the basic phenomena for measuring the local gas flux. The gas released by the covered surface accumulates in the confined atmosphere inside the chamber that is initially made up of air and that is practically free of the gas to be measured (CO_2 or CH_4).

We then note a progressive rise in the average gas concentration inside the chamber. Initially, this rise is almost proportional to the accumulation time and can be taken to be a linear function of time (see figure 2).

In the Ineris method, it is this part of the phenomena that is observed and used to deduce the local gas flux. In standard conditions, the measurement itself (apart from the set-up of the device) lasts about 3 minutes.

For each placement of the chamber, the measurements provide the local flux values emitted by the covered surface. They are expressed in units of volume (or mass) of a given gas by unit of time and by unit of the ground surface area.

For each measurement point, the flux measurements are paired with the local atmospheric pressure and temperature conditions in order to be able to express the gas flux values observed in standard pressure and temperature conditions (STP) or even to be able to express them in units of mass.

This is necessary to be able to account for the changes in ambient conditions from one point to another and particularly to be able to compare the results obtained on the different points or areas or even to compare these results with other data (earlier measurements, bibliographical data, etc.).

3.2 METROLOGICAL VALIDATION OF THE METHOD

In the method’s developmental phase, its metrological characteristics were verified and validated on a test bench and *in situ*.

For methane, the metrological validity of the Ineris method was checked and confirmed as a part of an inter-comparison programme of the different methods, performed under the auspices of French Environment and Energy Management Agency (ADEME) on a laboratory test bench and on a real site (Pokryszka and Jodart, 1994; Savanne et al., 1995; ADEME, 1997; Savanne et al., 1997).

The metrological validation of the device currently used for measuring the CO_2 flux was finalized in ANR’s CO_2 programme “GeoCarbon Monitoring” (Pokryszka and Charmoille, 2008; Pokryszka et al., 2010).

3.3 SCOPE OF THRESHOLDS AND MEASUREMENTS

For both CO_2 and CH_4, the method makes it possible to perform the measurements in a wide range of fluxes going from very low values (around 0.01 to 0.1 $cm^3\ min^{-1}\ m^{-2}$) up to extremely strong emissions of around 4,000 $cm^3\ min^{-1}\ m^{-2}$. It is also possible to get a reasonable estimation of even stronger fluxes.

The lower detection and measurement thresholds are very low and adapted to each gas. For CO_2, the standard measurement threshold is 0.1 $cm^3\ min^{-1}\ m^{-2}$, a value that is well below the usual level of biogenic emissions observed in

European climate conditions (see chapter 2). The device also makes it possible to detect a flux (or a change in a flux) at a weaker level, around 0.05 $cm^3\ min^{-1}\ m^{-2}$ with, however, greater uncertainty.

For methane, the device allows for even more refined observation, because the lower measurement threshold is 0.02 $cm^3\ min^{-1}\ m^{-2}$ and the detection threshold can be estimated at 0.01 $cm^3\ min^{-1}\ m^{-2}$ or even less. These two thresholds are adapted to the normal level of natural methane emission of biological origin on the surface of the soil, which is usually much lower than the carbon dioxide flux.

3.4 PRECISION AND REPEATABILITY

The precision of CH_4 and CO_2 flux measurements was tested on test benches in the laboratory, during the method's metrological validation phase.

In the respective ranges of the most commonly found fluxes on the field for both gases (0 to 400 $cm^3\ min^{-1}\ m^{-2}$, for methane and 0 to 3,000 $cm^3\ min^{-1}\ m^{-2}$, for carbon dioxide), on average there was no more than $\pm$ 5% difference between the real fluxes and the fluxes measured by the device (Pokryszka and Jodart, 1994; Savanne et al. 1995; Pokryszka and Charmoille, 2008).

The results obtained in the laboratory were confirmed in the actual conditions on the field (landfills for household waste and sites that naturally emit gas), in various meteorological conditions.

Many tests performed *in situ* enabled us to determine that, regardless of the flux level measured for both gases, the relative deviation between the measurements and an average value of a series of measurements are rather limited and do not exceed 10 %. This spread of measured values includes possible natural changes due to the gas flux itself between the different measurements. It can therefore be considered as the method's maximum inaccuracy when used normally *in situ*.

3.5 PRACTICAL CHARACTERISTICS OF THE METHOD

The CARE device used to measure is relatively simple and easy to handle. One measurement takes about 5 to 10 minutes including the time to setup the chamber.

Then you can multiply the number of measurements taken over a given time over a limited area. Depending on the site-specific difficulties and the time needed to move between the different measurement locations, it is possible to take 20 to 60 separate measurements per day.

There is also an automated version of the method (DAMEG device) which allows to monitor the changes in the gas flux over time on a given location (INPI, 2018). After being installed, the DAMEG device autonomously performs repeated measurements at an adjustable frequency, without an operator being present, with sufficient energy autonomy to last several days, even over a week.

4. DATA AND SITES TAKEN INTO ACCOUNT

4.1 DATA ORIGINS

Ineris has measured gas emissions at the soil/air interface for over 25 years. For the most part, these measurements have been done using the CARE method presented above in chapter 3.

Most often, measurements are performed to diagnose the sites affected by abnormal gas emissions, or potentially affected sites, which must be recognized due to former industrial activity. In most cases, these are sites located at the surface of former underground mines.

As a part of these assessments, comparative measurements are often taken from nearby natural sites that are outside of the sectors that might be affected by anthropogenic emissions.

The feedback from the different diagnoses performed over time demonstrates the need to have structured reference data on gas emissions of natural sites based on their characteristics, as well as the variations of this emission over time.

For this reason, specific measurements were taken between 2007 and 2014, as part of an Ineris internal study and also as part of an ANR research programme (ANR Sentinelle, 2013). Around fifteen sites were chosen on which to perform periodical soil gas flux measurements. They were located in varied geological contexts. The choice of locations also took into account the main biological contexts and the major climate zones.

On each of these sites, Ineris performed 8 to 10 exploratory measurement campaigns for natural CO_2 and CH_4 fluxes. Their objective was to start building a reference database in the climate, geological, and biological conditions in France.

Moreover, some experiments performed *in situ* as a part of the research programmes (ANR, RFCS, etc.) also needed data on soil gas emission, for instance, to establish the initial geochemical baseline of the studied sites (ANR Sentinelle, ANR CIPRES, etc.).

The results of these various measurements acquired between 1995 and 2016 were collected and are an initial source of data for this study.

Some of the results obtained before have already been published (de Donato et al., 2010; ANR Sentinelle, 2013; Lafortune et al., 2013; Pokryszka et al., 2014; Gombert et al., 2014; Gal et al., 2014; Total, 2015, etc.). They were included in this study.

4.2 DATA SELECTED FOR THE ANALYSIS AND THEIR NATURE

The database created for this study contains the results selected from all of the measurements of soil gas fluxes performed by Ineris between 1995 and 2016. The data were chosen according to their representativeness and their consistency with the study's objectives.

In addition to seeking the most variable configurations possible, both of the following criteria were imposed when selecting sites:

- Absence or negligible contribution of anthropogenic emissions linked to former industrial activity, soil pollution, and of natural emissions of geologic origin;
- The availability of data obtained over at least two measurement campaigns, performed at the same locations and at least in two different periods of the year. The objective is here to assess the role of seasonal variations in gas production in soils and in gas transfers at the soil/atmosphere interface.

The sites selected for final data analysis, their location, and their main characteristics are presented in table 1. The spread of the data available between seasons, as well as the acquisition framework of these data are also described in the table.

The choice and definition of the characteristics of the sites presented in table 1 are explained and discussed in chapter 5.

The data selected come from all the following origins, in unequal proportions, as mentioned above (see table 1):

- specific measurements meant for the acquisition of reference data. A large part of these data (around 75%) were selected from sites A, C, D, E, F, H, J, K, L, M, N, Q, T, V, W and X;
- one-off measurements were performed on the natural sites for comparing with diagnosed neighboring post-mining sites that are affected or potentially affected by abnormal gas emissions: sites G, I, N, O, R and S. They contribute to about 15% of the database;
- measurements performed when establishing the initial geochemical baseline and the monitoring of experimental sites: P and U;
- one-off measurements performed to diagnose or recognize sites potentially affected by abnormal gas emissions (sites B and G). For these sites, the data taken into account correspond only to the locations without any significant anthropogenic influence.

When establishing the database, the values known to have been acquired in extreme meteorological conditions that can obviously disturb the soil gas emissions (very strong wind, heavy rainfall, frost, snow covering, etc.) were excluded. Measurements made on abnormally humid or water-saturated surfaces were also eliminated.

Site label	Name of site	Localisation (French department number)	Land cover			Geological context	Climate zone	Measurements repartition between the seasons				Data origin
			Prairies & grasslands	Forests & woods	Fields & vegetable patches			Winter	Spring	Summer	Fall	
A	Villers-Cotterêts	2	✓	✓	✓	Sedimentary: carbonates	Oceanic	✓	✓	✓	✓	1, 2
B	Manosqe Nord	4	✓	✓		Sedimentary: carbonates	Mediterranean		✓		✓	1, 3
C	Reims La Veuve	15	✓	✓	✓	Sedimentary: carbonates	Oceanic	✓	✓	✓	✓	1, 2
D	Vierzon	18	✓	✓	✓	Sedimentary: carbonates	Oceanic	✓	✓	✓	✓	1, 2
E	Uzerche	19	✓	✓	✓	Metamorphic	Continental	✓	✓	✓	✓	1, 2
F	Poupry	28	✓	✓	✓	Sedimentary: carbonates	Oceanic	✓	✓	✓	✓	1, 2
G	Grand Combe	30	✓	✓	✓	Sedimentary: Carboniferous	Mediterranean	✓		✓		4
H	Brion	36	✓	✓	✓	Sedimentary: carbonates	Oceanic	✓	✓	✓	✓	1, 2
I	La Motte d'Aveillans	38	✓	✓		Sedimentary: Carboniferous	Continental	✓	✓	✓	✓	4
J	La Ferté St Aubin	45	✓	✓	✓	Sedimentary: detrital	Oceanic	✓	✓	✓	✓	1, 2
K	Montfaucon	46	✓	✓	✓	Sedimentary: carbonates	Continental	✓	✓	✓	✓	1, 2
L	Audun le Roman	54	✓	✓	✓	Sedimentary: carbonates	Continental	✓	✓	✓	✓	1, 2
M	Verdun	55	✓	✓	✓	Sedimentary: detrital	Continental	✓	✓	✓	✓	1, 2
N	Etzling	57	✓	✓	✓	Sedimentary: detrital	Continental	✓	✓	✓	✓	1, 2, 3
O	Freyming-Cocheren	57	✓	✓	✓	Sedimentary: detrital	Continental	✓	✓	✓		1, 3
P	Catenoy	60	✓			Sedimentary: carbonates	Oceanic		✓	✓	✓	2
Q	Verneuil en Halatte	60	✓	✓	✓	Sedimentary: carbonates	Oceanic	✓	✓	✓	✓	1, 2
R	Brassac	63	✓		✓	Sedimentary: Carboniferous	Continental	✓		✓	✓	4
S	Messeix	63	✓			Metamorphic Sedimentary: Carboniferous	Continental	✓		✓		4
T	Gan Sud	64	✓	✓	✓	Sedimentary: detrital	Oceanic	✓	✓	✓	✓	1
U	Jurançon Sud	64	✓	✓	✓	Sedimentary: detrital Sedimentary: carbonates	Oceanic	✓	✓	✓	✓	1, 2
V	Lacommande	64	✓	✓	✓	Sedimentary: detrital	Oceanic	✓	✓	✓	✓	1
W	Pau Nord	64	✓	✓	✓	Sedimentary: detrital	Oceanic	✓	✓	✓	✓	1
X	Le Fraisse	87	✓	✓	✓	Volcanic	Continental	✓	✓	✓	✓	1, 2

Table 1. Characteristics of the selected measurement sites
**1: Ineris own measurements, 2: Ineris measurements for ANR research programmes, 3: Ineris measurements for the French Administration, 4: Ineris measurements for Geoderis*[5]

It should be noted that, for most sites, there is a rather substantial amount of available measurements. They cover the 4 seasons of the annual cycle and are repeated for two years in a row or more.

Considering the characteristics of the selected sites and the measurements, we can conclude that the data analyzed respect both of the following principles:

- They are only diurnal gas fluxes, measured directly at the soil surface,
- In principle, these fluxes are of biological or mostly biological origin.

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[5] Geoderis is a public interest group dedicated to expertise related to post-mining risks.

5. PARAMETERS CONSIDERED IN THE STUDY

5.1 POTENTIAL FACTORS OF INFLUENCE

There are numerous and complex origins and processes of gas production in the shallow biosphere as well as the mechanisms of gas exchange between the soil and the atmosphere. Therefore, there are a plethora of factors that influence gas emissions from soils.

Depending on their type and the time horizon of their influence, they can be categorized, in a very simplified manner, into two families:

- Generalized or long-term influence factors.

  This family includes, in particular, all the environmental, biological, climatic, geological, pedological, etc. factors that determine the nature of the soils and determine the development and evolution of biological life in the soil and on the surface,

- Local or short- and medium-term influence factors.

  This includes mainly the local meteorological factors that influence gas transfer from soils. It can also temporarily modify the normal cycle of biological activity in some soils. These factors include, in particular, variation in atmospheric pressure, changes in ambient temperature (in the day/night cycle and in the day), sunlight, rain, wind, snow, frost, etc. All these factors can mutually interact. In addition, for the most part, they can act in two directions, meaning they can amplify or, conversely, slow down gas exchanges between the soil and the atmosphere, depending on the direction and magnitude of their change.

The list is obviously not exhaustive. Indeed, some specific local characteristics of a given site can also influence the flux both long-term (for example a local micro-climate or a seasonal fluctuation in groundwater) and short-term (for example, the presence of a very permeable soil or a major fracture in the bedrock inducing thermal effects).

5.2 FACTORS CONSIDERED IN THE DATA ANALYSIS

The characteristics of the sites and available data made it possible to consider the factors that are in principle the most relevant, that can influence the gas flux generally or on the long-term, namely:

- The seasons of the annual climate cycle,
- The general climate context (climate zones),
- The land cover that determines the biological context,
- The general geological context of the shallow underground,
- And, partially, the sites' pedological context.

5.2.1 SEASONS

Seasonal limits were taken based on their climatological definition proposed by Météo-France (www.meteofrance.fr/publications/glossaire): "Spring in the North hemisphere traditionally covers the months of March, April, and May; summer: June, July, and August; fall: September, October, and November; winter: December, January, and February. Respectively, summer and winter become the hottest and coldest quarters of an annual cycle in temperate zones"

To avoid an arbitrary decision, the available data were categorized following this definition, based on the date the measurements were taken and independent of the meteorological conditions observed on site.

5.2.2 LAND COVER

The three main kinds of land cover selected for the analysis are, respectively:

- Prairies and grasslands,
- Forests and woods,
- Fields and vegetable patches.

This choice follows the classic approaches listed in scientific literature. Furthermore, these are the most prevalent biological contexts found in Metropolitan France, so the most frequently found *in situ* during the measurement campaigns.

5.2.3 GENERAL CLIMATE CONTEXT OF THE SECTOR

The general climate context of the measurement sites was defined by cross-analyzing many bibliographical data. There were some disparities between the interpretation, classification, and scope of the different climate zones of Metropolitan France (www.meteofrance.fr; Joly et al., 2010; Houot, 2003; www.meteonature.com; www.alertes-meteo.com, etc.)

Figure 3 presents, as an example, two versions of the territory distribution between the different climate zones considered in the analysis.

To simplify the interpretation of data, 3 major climate zones were selected according to the zoning proposed by Houot (figure 3; Houot, 2003):

- Oceanic zone, including oceanic and degraded oceanic climates,
- Continental zone, including the continental climates, degraded continental climates, and mountain climates,
- Mediterranean zone, including Mediterranean and degraded Mediterranean climates.

The sites were classified based on their respective geographic positions. Ultimately, 3 climate classifications are represented in the database, but unequally. Indeed, only 2 sites belong to the Mediterranean climate zone (see table 1).

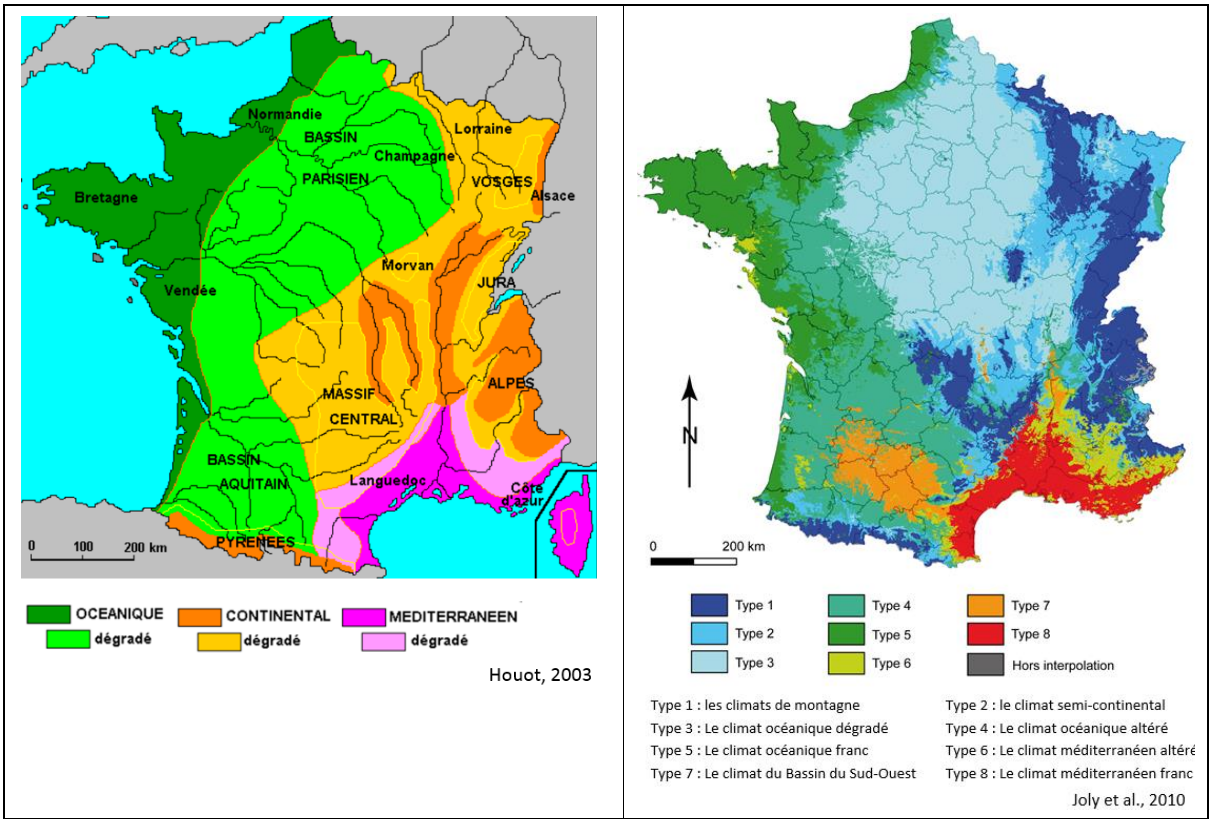

Figure 3. Climate zones in France

5.2.4 GENERAL GEOLOGICAL CONTEXT OF THE SHALLOW UNDERGROUND

The analysis performed looked at the general geological context of the shallow underground of the studied sites. This context was established using available geological maps (infoterre.brgm.fr). Depending on their position, the sites were classified based on the 3 major geological context categories: sedimentary, metamorphic, and volcanic.

As you can see in table 1, a majority of the sites are located in the sedimentary context. Only 3 sites out of the 24 available are found in different geological contexts: 1 in the plutonic context and 2 others in the metamorphic context (one of which only partially).

Therefore, to refine the analysis, we divided the classification of the sites in the sedimentary context. It was indeed possible to distribute the data by the 3 relatively homogeneous sub-categories that each contains enough sites and data to perform a statistical analysis, namely:

- A sub-category of detrital sedimentary geology,
- A sub-category of carbonate sedimentary geology,
- A sub-category of Carboniferous sedimentary formations.

Note that in this last sub-category, there are also detrital and carbonate rocks. However, it is unique in including coal seams and other rocks containing organic matter (shale and carbonaceous sandstone). These rock formations are known to contain natural gases (mainly CH_4 and CO_2) and to be able to produce CO_2 by oxidizing the carbon-rich material.

Therefore, it was useful to separately analyze the Carboniferous geology sites to see whether they had a different level of gas emission (in this case, higher) compared to the sites that did not have coal deposits in their underground.

We also note that, depending on the measurement point position, the selected sites S and U in table 2 are simultaneously affected by two different geological contexts. This particular feature was considered in the analysis

5.2.5 PEDOLOGICAL CONTEXT

We attempted to define the pedological context of the sites studied by using the available maps and guidelines (INRA, 1998; AFES, 2009). This endeavor was quite tedious, because many studied sectors could have soils of various kinds. The results obtained a wide spread of data, with at least 9 soil categories present.

For some categories, there was so little available data that it made the statistical analysis difficult and inconclusive at this stage (see chapter 7.5).

5.3 NON-ANALYZED FACTORS

The factors not analyzed were only those acting locally or on the short- and medium-term.

The main objective of the study is to identify general trends, so variability in fluxes related to minor effects were not prioritized.

In addition, this analysis would have been very tedious and would have needed an enormous amount of additional data that are probably very hard to find, with ultimately a very small probability of getting a relevant result, from a practical perspective. Indeed, overall, there is a substantial amount of data on gas fluxes and a large number of sites were analyzed. Likewise, the measurements making up this data were taken in highly variable climate and meteorological conditions and, for more sites, several times.

We can conclude that on the analysis time scale (from three months to several years), local short-term influences mitigate or mutually offset the large amount of data processed or, in any case, that the influence of the factors in question is much lower than long-term factors.

We furthermore recall that the measurements taken in extreme meteorological conditions that could obviously have short-term effects on gas fluxes (heavy rain, frost, snow cover, etc.) were excluded from the analysis. Measurements performed on abnormally humid or water-saturated surfaces were also eliminated.

This helped reduce the variability of the values within the database that might be linked to the influence of local and short-term factors.

6. RESULTS: CH_4 FLUX

The numerous measurement campaigns performed on all the sites selected for this study never showed, on normally water drained soils, natural methane fluxes exceeding 0.1 $cm^3\ min^{-1}\ m^{-2}$.

These results, obtained in the biological environments of agricultural fields, prairies-grasslands or forest-woods confirm the literature findings cited in chapter 2.

On a normally drained soil, CH_4 fluxes exceeding the 0.1 $cm^3\ min^{-1}\ m^{-2}$ threshold are thus considered abnormally high.

7. RESULTS: CO_2 FLUX

7.1 ALL DATA

Table 2 below presents the main statistical parameters of the population analyzed of over 2,650 local CO_2 fluxes measured on all the 24 sites selected for the study.

The table also shows similar statistical parameters obtained when collecting the values following the 4 seasons of the annual climate cycle. This part will be discussed in detail in the next chapter.

Parameter	Unit	All data	Winter	Spring	Summer	Fall
sites number	-	24	22	21	23	21
measurements number	-	2674	744	532	684	714
minimum value	$cm^3\ min^{-1}\ m^{-2}$ (STP)	0,0	0,0	0,0	1,0	0,0
maximum value	$cm^3\ min^{-1}\ m^{-2}$ (STP)	26,4	10,4	21,5	26,4	25,6
median value	$cm^3\ min^{-1}\ m^{-2}$ (STP)	4,8	2,3	4,3	9,0	5,9
mean value	$cm^3\ min^{-1}\ m^{-2}$ (STP)	5,8	2,7	4,9	9,3	6,4
standard deviation	$cm^3\ min^{-1}\ m^{-2}$ (STP)	4,1	1,8	3,2	4,3	3,6
variation coefficient	%	71%	67%	64%	46%	56%
zero values number	-	33	19	9	0	5
5th percentile	$cm^3\ min^{-1}\ m^{-2}$ (STP)	0,8	0,3	1,0	3,3	1,2
3rd quartile	$cm^3\ min^{-1}\ m^{-2}$ (STP)	8,3	3,7	6,8	11,7	8,4
95th percentile	$cm^3\ min^{-1}\ m^{-2}$ (STP)	13,6	5,8	11,1	17,5	12,5
99th percentile	$cm^3\ min^{-1}\ m^{-2}$ (STP)	19,4	8,7	15,9	21,5	17,8

Table 2. Main statistical parameters of the population analyzed of local CO_2 fluxes

The data analysis shows that a largely measurable and significant or even very significant CO_2 flux was observed on all of the sites explored, regardless of their context and the period of the year. There was a very low, even negligible, number of measurements across the data that showed undetectable (considered zero) emissions (1.2 % of the population).

Thus, for the whole population analyzed, the CO_2 flux values fall within a range going from 0 to 26.4 $cm^3\,min^{-1}\,m^{-2}$, with an average of 5.8 $cm^3\,min^{-1}\,m^{-2}$. The standard deviation of the population is 4.1 $cm^3\,min^{-1}\,m^{-2}$, which gives a rather high variation coefficient of 71%.

The median value is 4.8 $cm^3\,min^{-1}\,m^{-2}$ and is significantly lower than the average (5.8 $cm^3\,min^{-1}\,m^{-2}$). This suggests an asymmetric frequency distribution, with a larger distribution in stronger values (see chapter 7.6).

This is demonstrated by the 3rd quartile and 95th percentile. Indeed, a quarter of the values exceeds 8.3 $cm^3\,min^{-1}\,m^{-2}$ (3rd quartile) and 5% of the values exceed 13.6 $cm^3\,min^{-1}\,m^{-2}$ (95th percentile).

A 1% fraction of the data fall between 19.4 $cm^3\,min^{-1}\,m^{-2}$ (99th percentile) and the maximum value of the population is 26.4 $cm^3\,min^{-1}\,m^{-2}$.

7.2 CO_2 WITH REGARD TO THE ANNUAL CLIMATE CYCLE

Despite the wide variability in CO_2 emissions mentioned in the preceding chapter, there is a clear overall trend observed according to the seasons of the annual climate cycle.

This trend is graphically illustrated in figure 4 and confirmed by the statistical parameters given in table 2.

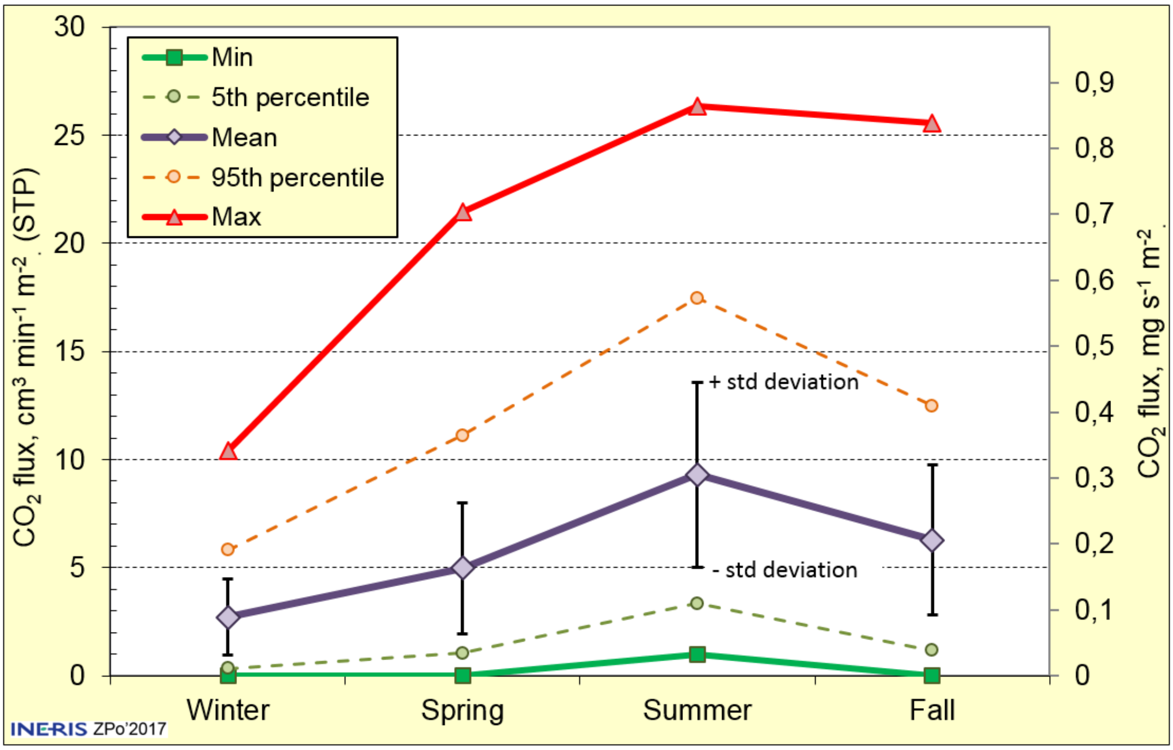

Figure 4. Changes in CO_2 flux between the seasons of the annual climate cycle.

On average, CO_2 emission is highest in summer (average value of 9.3 $cm^3\,min^{-1}\,m^{-2}$) and lowest in winter (average value 2.7 $cm^3\,min^{-1}\,m^{-2}$). It is intermediate in spring and fall. The average ratio between summer and winter is around 3.5. It can vary between 2 and 5, mainly depending on the land cover context (biological context) of the sites studied. Fluxes in fall are on average slightly stronger than in the spring.

The Student's t-test shows that, despite the wide variability of values within each respective sub-population, the differences among all the average seasonal values are significant, with a confidence level above 99%.

The maximum fluxes follow the same trend as the respective average values of the 4 seasons. Undetectable fluxes were infrequently observed, mostly in winter (2.5% of this category values), but also occasionally in spring and fall. No undetectable (zero) flux was observed in the summer on a normally water drained soil.

This marked change in CO_2 emission correlated to the annual seasonal cycle confirms the findings of the studies mentioned above in chapter 2. However, the general level of CO_2 fluxes observed in the Ineris experimental data is significantly higher compared to bibliographical data corresponding to comparable environmental and climate conditions. The ratio is 2 to 3 for the annual average, depending on the case.

A deeper literature review would be needed to clarify this gap. It could be due, for example, to the differences between the measurement methods used or the difference between the biosphere horizons in which the measurements were taken[6].

7.3 CO_2 WITH REGARD TO LAND COVER

Table 3 shows the main CO_2 flux statistical parameters obtained after the distribution of data across all seasons, based on the three main kinds of land cover selected for the analysis: prairies and grasslands, forests and woods, fields and vegetable patches.

To be able to compare them, similar values obtained for all the measurements analyzed are also shown.

Figure 5 graphically illustrates the average, maximum, and minimum values of the flows obtained for these three data sub-populations.

These presentations of the results show that the CO_2 fluxes would be on average higher in prairie and grassland type environments, lowest in fields and medium in forests and woodlands. There are relatively limited differences between the average values of the three sub-populations analyzed. However, the Student t-test shows that these differences are clearly significant, with a confidence level above 99%.

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[6] The Ineris data taken into account only correspond to local diurnal fluxes, measured directly at the soil's surface, without influence of photosynthesis. To measure gas fluxes in the soil, the "global" methods are frequently used that supply the average fluxes of a larger surface (several thousand m^2 to several tens of km^2) measured in the atmosphere above the vegetation. The effect of photosynthesis can strongly reduce measured diurnal CO_2 fluxes.

In some cases, the data cited in the literature comprise, without being clearly mentioned, the diurnal and nocturnal gas fluxes, which can have very different respective levels.

Parameter	Unit	All data	prairies & grasslands	forests & woods	fields & vegetable patches
sites number	-	24	24	21	20
measurements number	-	2674	1669	677	328
minimum value	$cm^3 min^{-1} m^{-2}$ (STP)	0,0	0,0	0,0	0,0
maximum value	$cm^3 min^{-1} m^{-2}$ (STP)	26,4	26,4	19,7	22,8
median value	$cm^3 min^{-1} m^{-2}$ (STP)	4,8	5,7	4,1	3,2
mean value	$cm^3 min^{-1} m^{-2}$ (STP)	5,8	6,4	5,1	3,9
standard deviation	$cm^3 min^{-1} m^{-2}$ (STP)	4,1	4,3	3,7	3,5
variation coefficient	%	71%	66%	72%	89%
zero values number	-	33	17	8	8
5th percentile	$cm^3 min^{-1} m^{-2}$ (STP)	0,8	0,9	1,0	0,3
3rd quartile	$cm^3 min^{-1} m^{-2}$ (STP)	8,3	9,1	6,9	5,2
95th percentile	$cm^3 min^{-1} m^{-2}$ (STP)	13,6	14,1	12,8	11,8
99th percentile	$cm^3 min^{-1} m^{-2}$ (STP)	19,4	20,7	17,3	16,3

Table 3. Main statistical parameters of local CO_2 fluxes from soils with different land cover

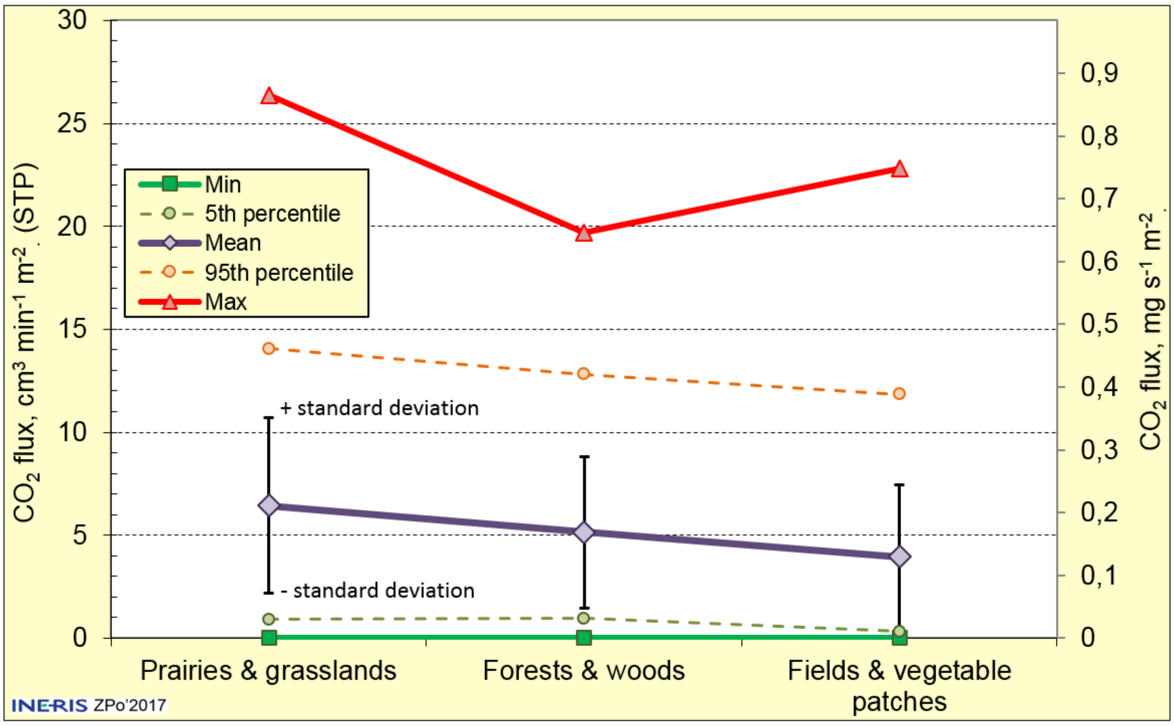

Figure 5. Average, maximum, and minimum CO_2 flux values from soils with different land cover

Note that the 3rd quartile as well as the 95th and 99th percentiles consistently follow the trend observed in the average values.

This is not entirely the case for the maximum values, since it is a much more random indicator and less representative of the preceding parameters. They still stay within a rather consistent range (19.7 to 26.4 $cm^3\ min^{-1}\ m^{-2}$). We also note that undetectable (zero) fluxes were observed in all 3 biological context categories.

To take into account the seasonal influence and biological factors at the same time, we performed a cross-analysis with a distribution of values between the 3 types of land cover selected and the 4 seasons of the annual climate cycle.

Figure 6 illustrates the results of this analysis. We observe that, regardless of the kind of land cover, the average fluxes follow the very pronounced seasonal changes, which has already been demonstrated in the analysis of the whole population (see chapter 7.2). This seasonal effect far outweighs the influence of the biological characteristics of the measurement sites.

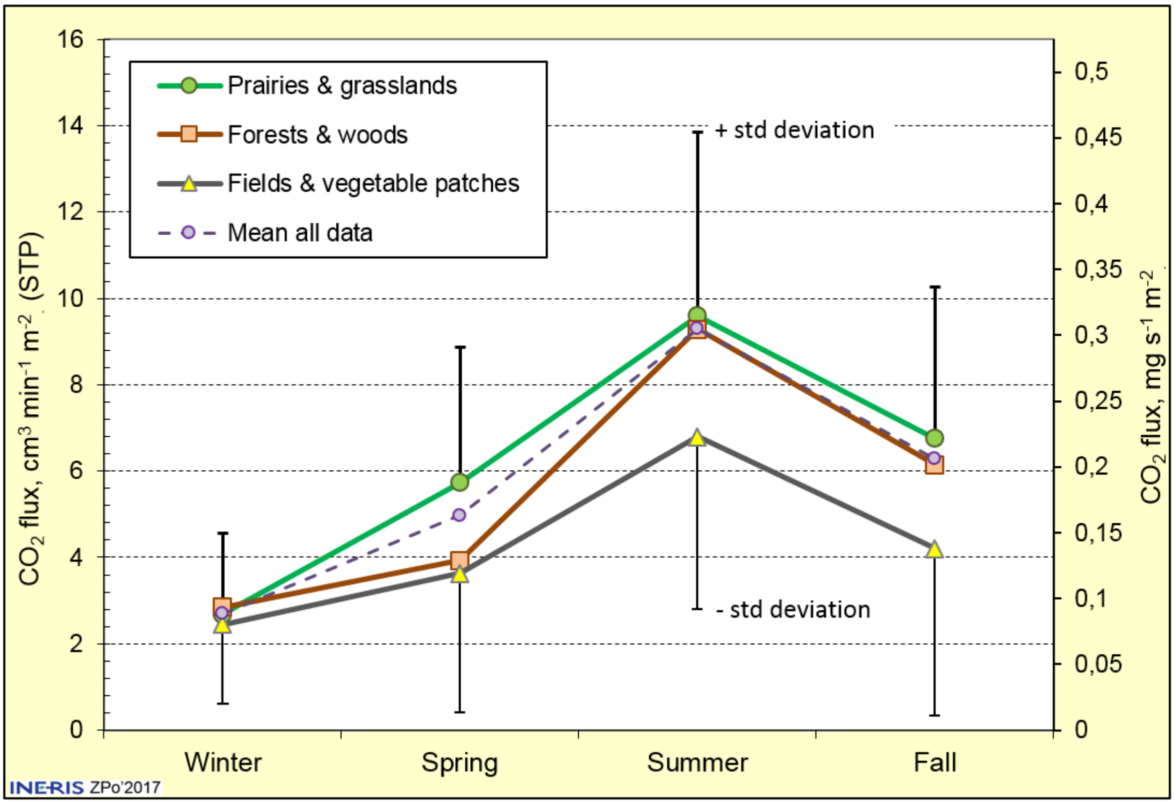

Figure 6. CO_2 flux change as a function of the kind of soil cover and the seasons

Note: The standard deviations correspond respectively to the extreme average values obtained for each season.

However, the relationships demonstrated above between the average fluxes of the 3 kinds of land cover are visible and overall respected, excepted for the winter averages which differ very little among them.

Note that, regardless of the season, the average fluxes observed in the fields and vegetable patches are always lower compared to the two other analyzed categories. There is a particularly large difference in summer and fall measurements.

Each kind of land cover also has a wide spread of values. This spread expressed in table 3 by rather high variability coefficients (66% to 89%) and illustrated in figure 6 by a very significant spread of the ranges determined by the associated standard deviations respectively to the extreme average values obtained for each season.

7.4 CO_2 FLUX WITH REGARD TO THE GENERAL CLIMATE CONTEXT

The main statistical parameters of CO_2 fluxes derived from an analysis of data broken down into sub-categories based on the general climate of the measurement sites are presented in table 4.

To facilitate their comparison, similar values obtained for all the measurements analyzed are also shown.

Figure 7 graphically illustrates the average, maximum, and minimum values of the fluxes obtained respectively for the three data sub-populations.

Parameter	Unit	All data	Climate zone		
			Oceanic	Continental	Mediterranean
sites number	-	24	12	10	2
measurements number	-	2674	1849	579	246
minimum value	$cm^3\,min^{-1}\,m^{-2}$ (STP)	0,0	0,0	0,0	0,0
maximum value	$cm^3\,min^{-1}\,m^{-2}$ (STP)	26,4	26,4	22,9	21,0
median value	$cm^3\,min^{-1}\,m^{-2}$ (STP)	4,8	5,1	4,1	4,9
mean value	$cm^3\,min^{-1}\,m^{-2}$ (STP)	5,8	6,0	5,2	5,7
standard deviation	$cm^3\,min^{-1}\,m^{-2}$ (STP)	4,1	3,9	4,3	4,6
variation coefficient	%	71%	64%	83%	80%
zero values number	-	33	21	10	2
5th percentile	$cm^3\,min^{-1}\,m^{-2}$ (STP)	0,8	1,1	0,6	0,5
3rd quartile	$cm^3\,min^{-1}\,m^{-2}$ (STP)	8,3	8,4	7,1	8,0
95th percentile	$cm^3\,min^{-1}\,m^{-2}$ (STP)	13,6	13,1	13,6	15,0
99th percentile	$cm^3\,min^{-1}\,m^{-2}$ (STP)	19,4	17,7	21,5	19,5

Table 4. Main statistical parameters of local CO_2 fluxes with regard to climate zones

Unlike the influence of the biological context's, here we see that the average fluxes from the 3 climate zones differ little among them. The values fall within a limited interval (5.2 to 6.0 $cm^3\,min^{-1}\,m^{-2}$) and diverge little from the general average of all the data analyzed (5.8 $cm^3\,min^{-1}\,m^{-2}$).

The Student t-test shows that, depending on the case, the differences between the averages are not significant or very close to statistical significance.

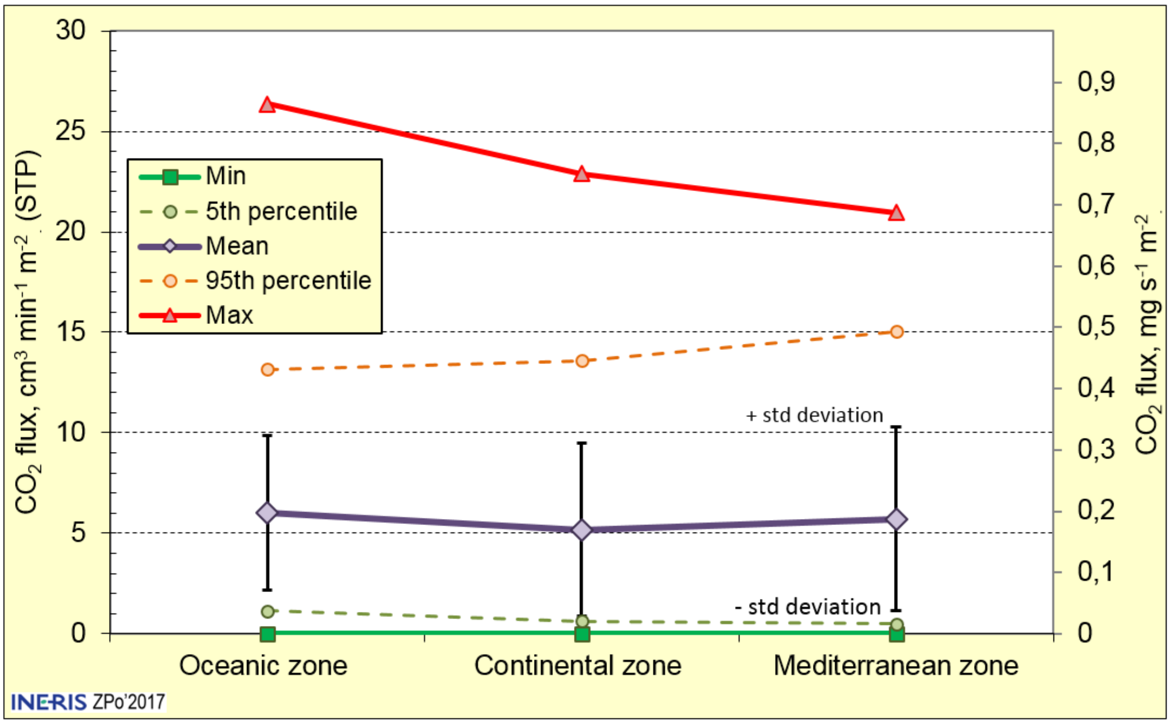

Figure 7. Average, maximum, and minimum CO_2 flux values with regard to the climate zone of the sites studied

Note that all average values by climate zone are consistent despite a great dispersion of values within each respective population.

This dispersion is indeed important, as the high values of the coefficient of variation shown in table 4 (values from 65% to 84%). It is also graphically illustrated in figure 7 by a large span in the standard deviation with regard to the average respective values.

Note that the maximum values do not entirely follow the trend found for the average values, but they stay within a rather uniform range. The same goes for the 3rd quartile as well as the 95th and 99th percentiles. Zero fluxes were observed in all climate zones.

To take into account the seasonal influence and the role of the general climate of the studied sites at the same time, we performed a cross-analysis with a distribution of values between the 3 climate contexts selected and the 4 seasons of the annual climate cycle. Figure 8 illustrates the results of this analysis.

We observe that, regardless of the climate zone of the measurement sites, the average fluxes follow the very pronounced seasonal changes for the whole of the population (see chapter 7.2). This seasonal influence largely outweighs the influence of the general climate of the sites studied.

As observed for all of the data, regardless of the season, there are few outlying averages of the respective climate sub-populations established for a given season with regard to this season's average value.

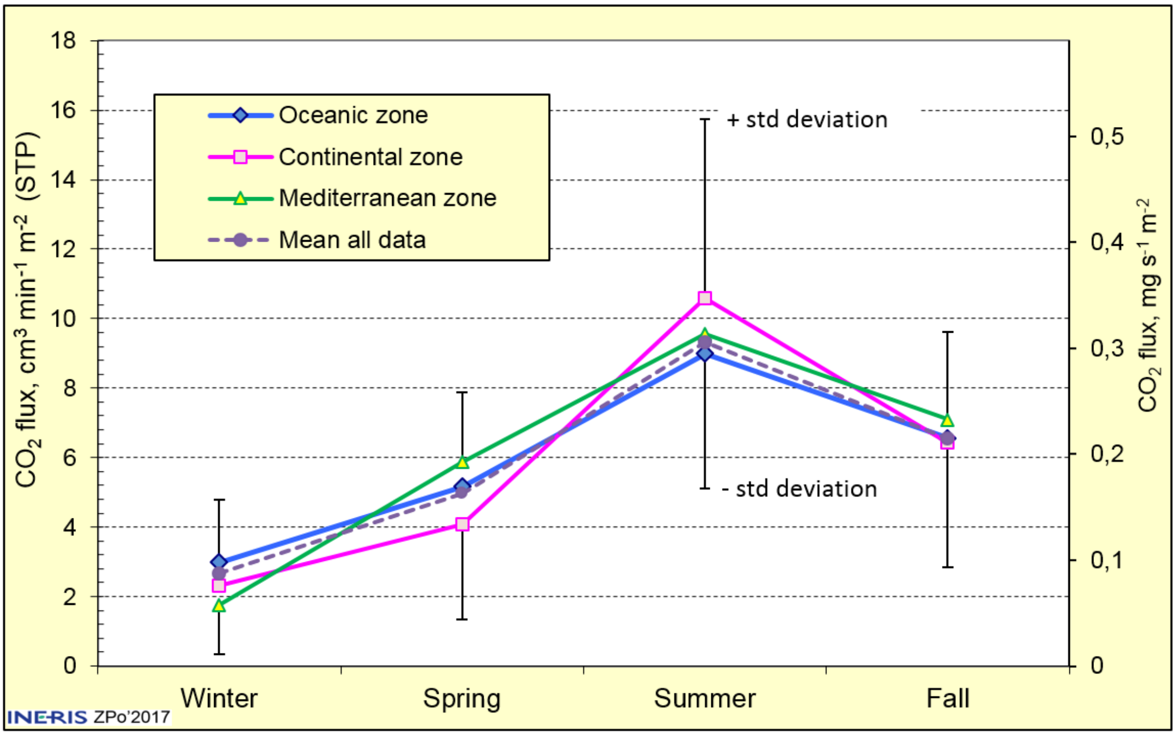

Figure 8. CO_2 flux change as a function of the climate zones and the seasons

Note: The standard deviations correspond respectively to the extreme average values obtained for each season.

These results suggest that, for the three climate zones considered, all belonging to the temperate climate family, their particular features do not seem to have a significant influence on the CO_2 emission from soils.

In any case, any influence of the general climate in the sector of the sites studied is much weaker than the changes in gas emissions caused by the annual seasonal cycle.

7.5 CO_2 FLUX VS GEOLOGICAL AND PEDOLOGICAL CONTEXTS

The main statistical parameters of CO_2 obtained from the breakdown of data across all seasons, based on the general geological context of the measurement sites' subsoils are presented in table 5.

The similar values relating to all the available data are also shown there for comparison.

Figure 9 graphically illustrates the average, maximum, and minimum values of the fluxes obtained respectively for the five geological contexts considered.

Parameter	Unit	All data	Geological context				
			Sedimentary			Metamor-phic	Volcanic
			Carbonate	Detrital	Carboniferous		
sites number	-	24	11	8	3	2	1
measurements number	-	2674	1101	1045	405	77	46
minimum value	$cm^3 min^{-1} m^{-2}$ (STP)	0,0	0,0	0,0	0,0	0,0	0,0
maximum value	$cm^3 min^{-1} m^{-2}$ (STP)	26,4	25,6	26,4	22,8	22,9	11,7
median value	$cm^3 min^{-1} m^{-2}$ (STP)	4,8	5,6	4,2	4,5	3,1	3,7
mean value	$cm^3 min^{-1} m^{-2}$ (STP)	5,8	6,2	5,3	5,8	6,7	4,1
standard deviation	$cm^3 min^{-1} m^{-2}$ (STP)	4,1	3,7	3,7	4,8	6,7	3,0
variation coefficient	%	71%	60%	71%	83%	100%	74%

Table 5. Main statistical parameters of local CO_2 fluxes with regard to the general geological contexts of the sites studied

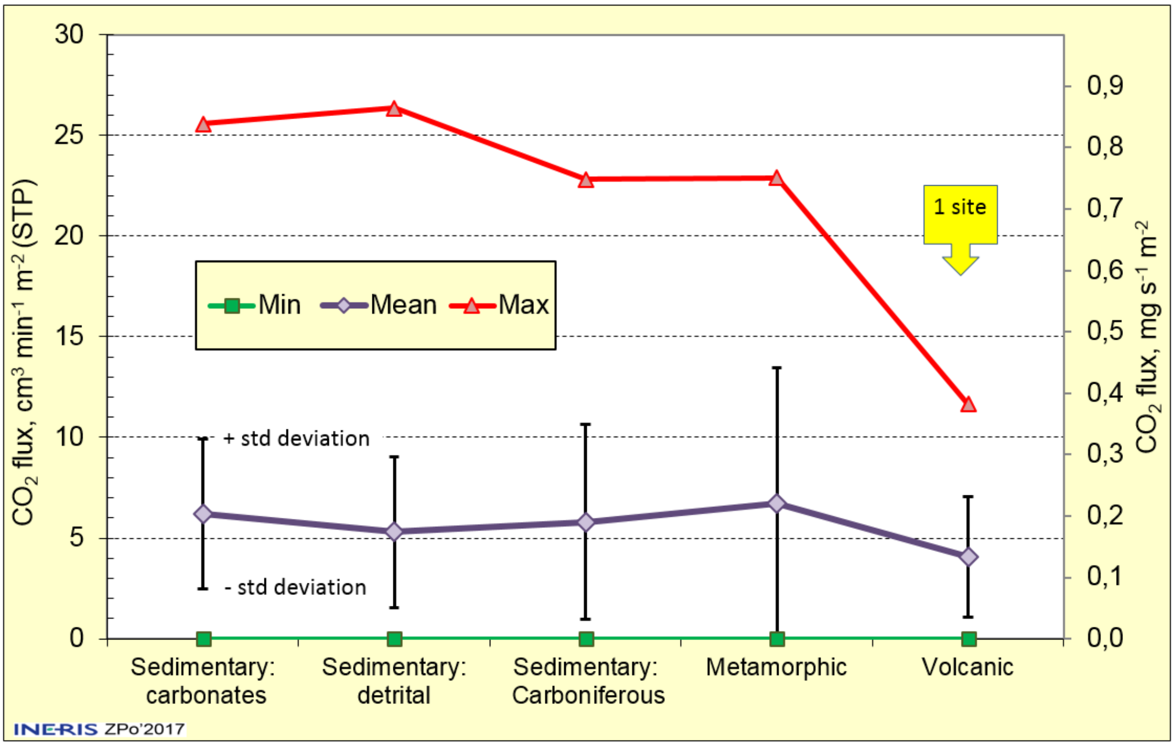

Figure 9. Average, maximum, and minimum CO_2 flux values with regard to the general geological context of the sites studied

Conclusions cannot easily be drawn from the results obtained because the metamorphic and volcanic contexts are not well represented compared to the three sub-categories of the sedimentary context. Depending on the case, the number of values available within these two categories is 5 to 20 times smaller than in the 3 sedimentary sub-contexts (table 5).

Apart from this, we observe that the average fluxes from the 5 geological contexts do not differ much among them. The values fall within an interval varying from 4.1 to 6.7 $cm^3 min^{-1} m^{-2}$.

If we focus on the three sub-categories of the sedimentary context, there are weak variations between the averages (values from 5.3 to 6.2 $cm^3 min^{-1} m^{-2}$). From a statistical perspective, the differences between these averages are, if there are some, not significant, or border significance, with a confidence level of 99%.

The differences between the respective averages of the 3 well-represented populations in the database (3 sedimentary sub-categories) and the 2 other poorly represented ones (volcanic and metamorphic contexts) could not be tested due to insufficient statistical representativity of the latter two populations.

We also note that undetectable fluxes were observed in all geological categories. The maximum values were high and rather uniform among the categories except for the plutonic context. However, there are not enough available values in this geological context to draw any reliable conclusions.

The cross-analysis that considers both the geological context and the seasons could only be done for the first two sub-categories of the sedimentary context, since there was not enough representative data available for the 3 other contexts to analyze them by season.

The results are presented in figure 10. Seasons are again the strongest influence here.

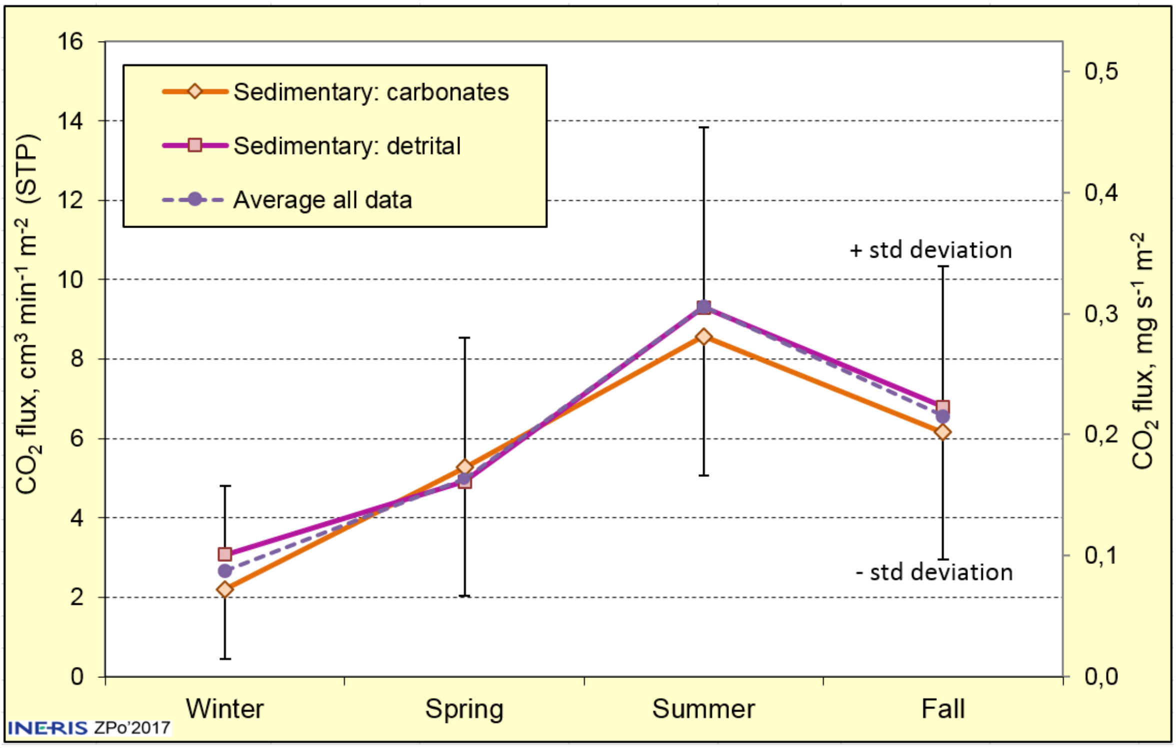

Figure 10. CO_2 flux change based on geological context and seasons

Note: The standard deviations correspond respectively to the extreme average values obtained for each season.

With regard to the pedological context influence, the number of possible situations is very large and there is not enough available data to perform a correct statistical analysis. There are not enough measurements taken and they are too spread out among the different soil categories in the analyzed sites.

As a result, there is no statistically justified general hypotheses proposed at this stage for the relationships between CO_2 fluxes and soil types. This point can be looked at more deeply when there is more data.

We recall however that the study concerns an overall moderate climate and targets 3 specific categories of land cover: prairies and grasslands, forests and woods, fields and vegetable patches. In principle, this implies that the soils in the selected sites have enough meteoric water, are biologically active and are thick and fertile enough to exploit agriculturally or to not limit the natural vegetation development.

We can thus assume that, within the limits defined in this study, the pedological context of the selected sites does not have an overall major influence on the production of carbon dioxide in the soil, nor on its emission at the surface.

The results of the partial analysis, which was performed with the available data, seem to suggest this. Indeed, for the three categories of the best represented soils (brunisol, leached soils and fluviosol), there was no major difference identified in the average values and the spread of the values within each sub-population.

In addition, for all these soil categories, the average CO_2 fluxes consistently follow the seasonal changes. Seasonal changes are again the strongest influential factor.

7.6 FREQUENCIES AND THEIR DISTRIBUTION

Figure 11 presents the frequency distribution for the whole population analyzed of the 2,674 values of CO_2 fluxes. It is very asymmetric and bimodal.

The asymmetry of the frequencies, already reported in the initial data analysis (see chapter 7.1), is demonstrated by a large number of outlying high values compared to the average value (positive or right skew).

Indeed, even if the majority of the fluxes remain lower than 20 $cm^3\,min^{-1}\,m^{-2}$ (99% of the population), there is a certainly small but significant number of values falling between 20 and 25 $cm^3\,min^{-1}\,m^{-2}$ (around 0.8% of the population) and even some isolated values between 25 and 27 $cm^3\,min^{-1}\,m^{-2}$. No measurements exceed the 27 $cm^3\,min^{-1}\,m^{-2}$ threshold.

The bimodality of the frequency distribution is characterized by the presence of a main mode m_1 to around 3.5 $cm^3\,min^{-1}\,m^{-2}$, falling in the range of lower to average values and a secondary mode m_2 to around 9.5 $cm^3\,min^{-1}\,m^{-2}$, appearing in the higher to average value range (figure 11).

This bimodality is mainly linked to the overlap in summer measurements (average to high values) with the winter ones (overwhelmingly low values).

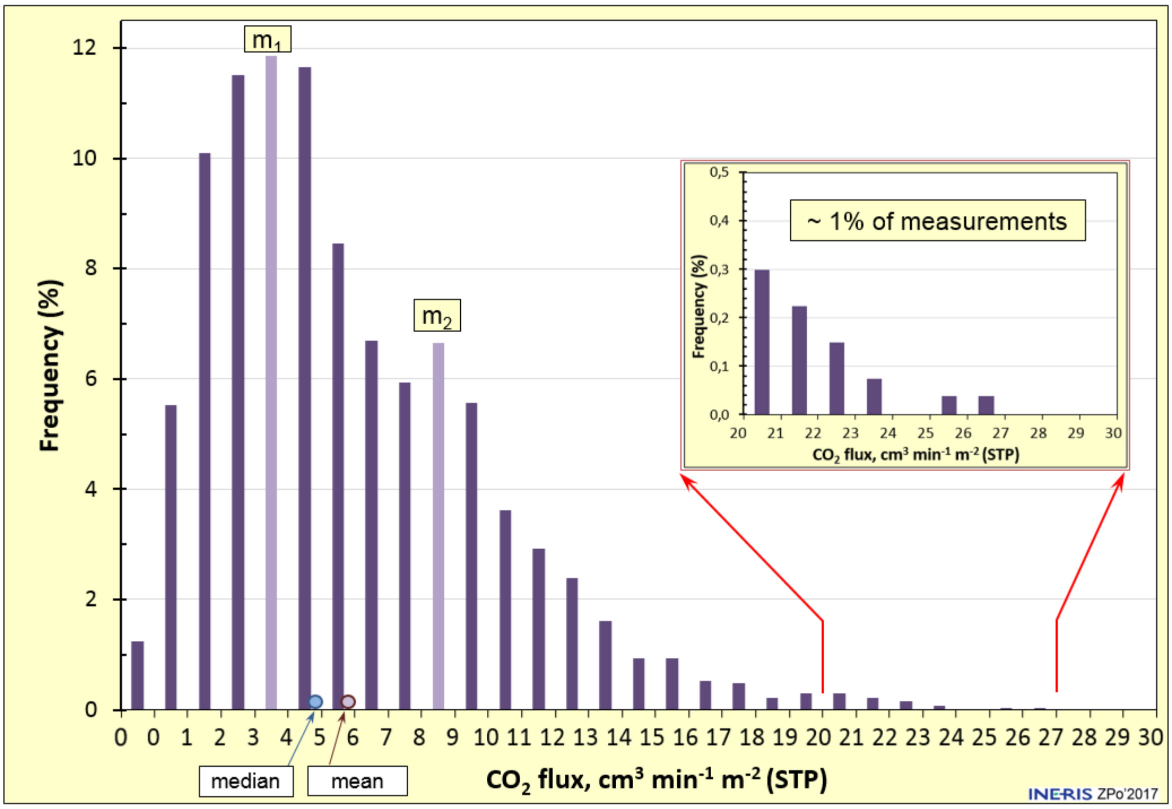

Figure 11. Frequency distribution for the whole analyzed population of CO_2 fluxes.

This led us to perform the rest of the frequency analysis by distributing the data by the 4 seasons of the annual climate cycle. Indeed, this parameter clearly appears to be the strongest influence on the variability of the CO_2 flux.

Processing the data this way makes the respective distributions monomodal (figure 12). They remain asymmetric, with a larger distribution in the higher values (right skew).

Looking at these distributions in a normal asymmetric distribution model (Azzalini, 1985; Sicard, 2013), trying to identify the likely threshold values can be very useful for practical application.

The results of this analysis are presented in table 6. The most interesting part in practical terms is to estimate the most probable flux intervals for each season.

This is done for the two confidence levels usually used in statistical data processing: 95% and 99%. To simplify the analysis, the calculated thresholds were rounded by 0.5 $cm^3\ min^{-1}\ m^{-2}$.

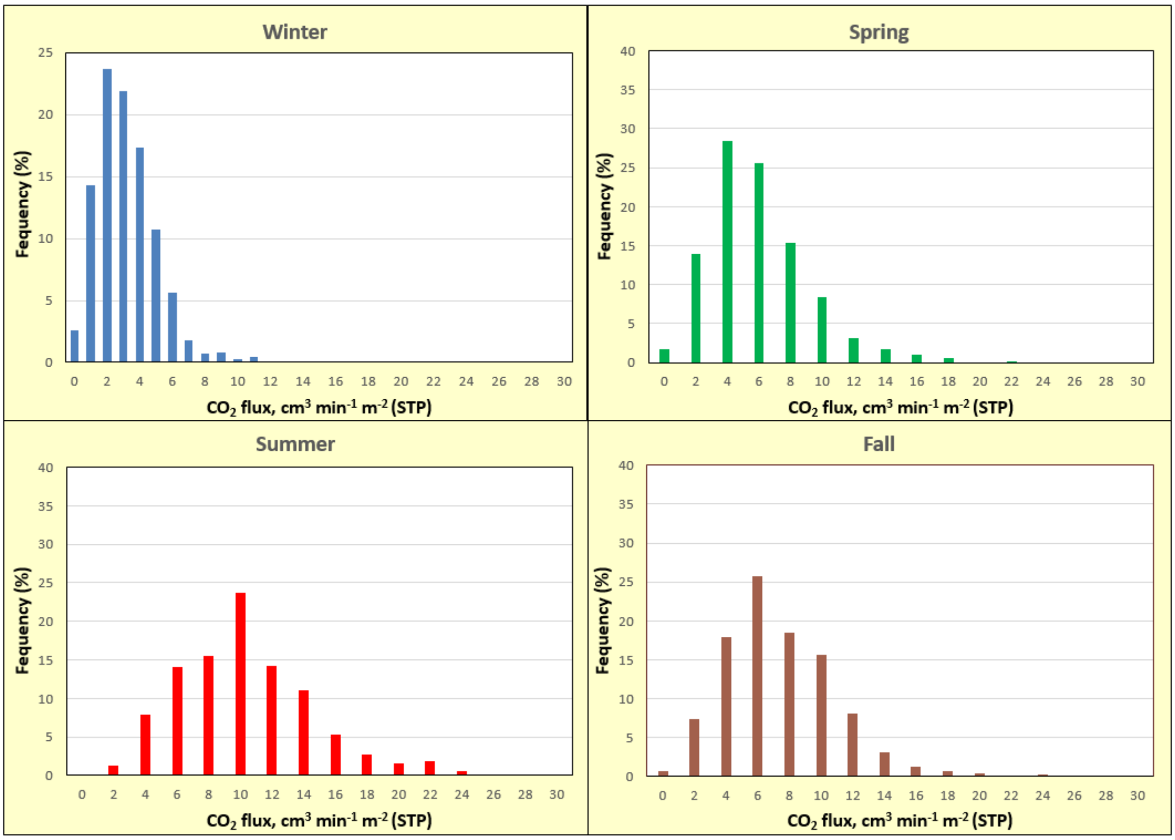

Figure 12. CO_2 flux frequency distribution with the spread of data by seasons of the annual climate cycle

Parameter	Unit	Winter	Spring	Summer	Fall
mode = m	$cm^3\ min^{-1}\ m^{-2}$ (STP)	1,5	4	9,5	5
number of values < m	-	216	234	336	281
number of values > m	-	528	298	348	433
standard deviation of values < m	$cm^3\ min^{-1}\ m^{-2}$ (STP)	0,5	1,1	2,0	1,4
standard deviation of values > m	$cm^3\ min^{-1}\ m^{-2}$ (STP)	1,5	2,8	3,3	3,0
confidence interval 95%	$cm^3\ min^{-1}\ m^{-2}$ (STP)	0,5 à 4,5	2 à 9,5	5 à 15,5	2,5 à 11
confidence interval 99%	$cm^3\ min^{-1}\ m^{-2}$ (STP)	0 à 6	1 à 12,5	3 à 19,5	1 à 14

Table 6. Statistical parameters of local CO_2 fluxes by season, obtained by applying a normal asymmetric distribution model

These results are graphically represented in figure 13. We can observe that the most probable flux ranges clearly differ between winter and summer.

The respective confidence intervals at 95% of these two seasons are completely separate. The confidence intervals at 99% very partially overlap and only in the respectively highest value ranges in winter and the lowest in summer.

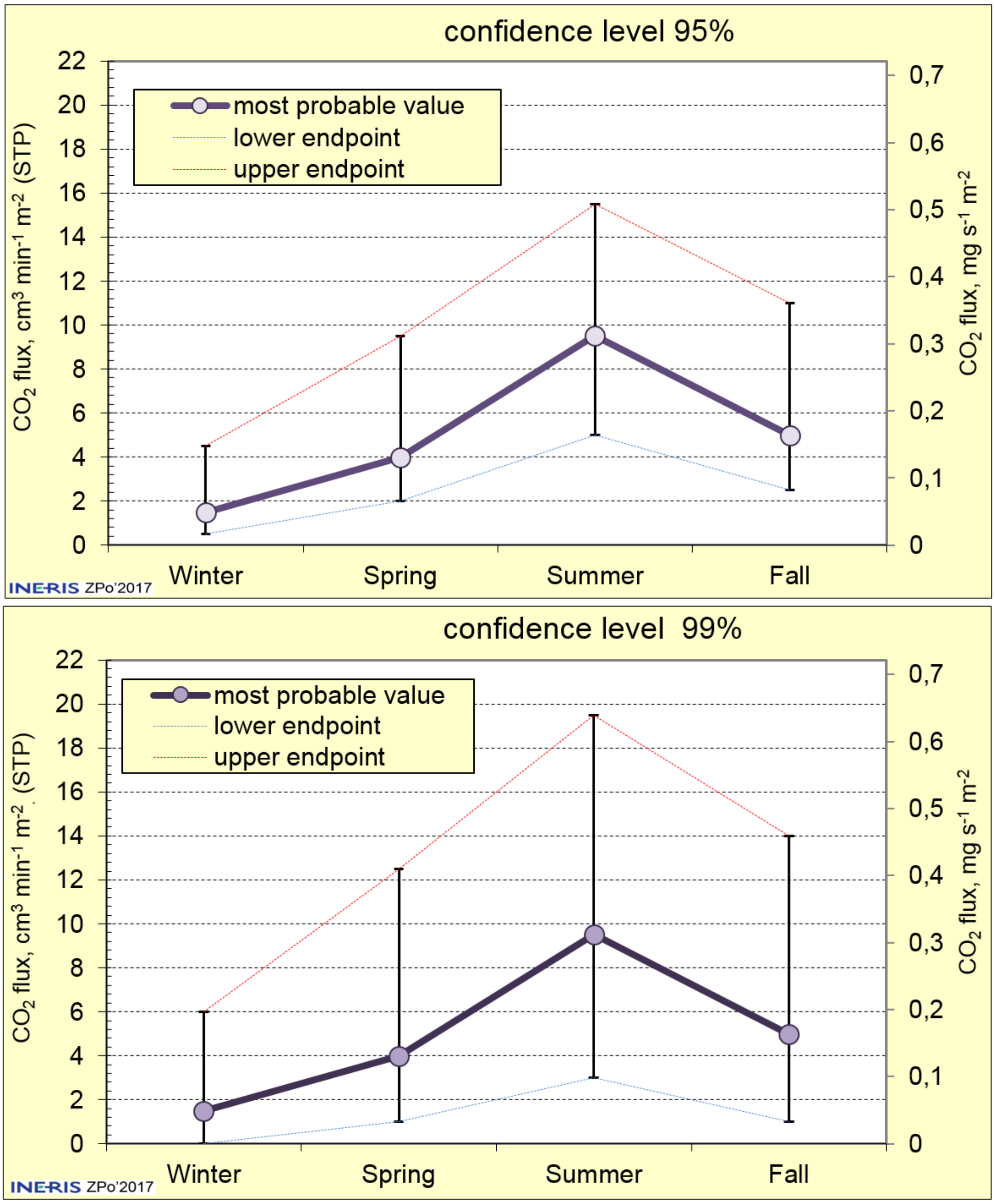

Figure 13. Intervals of the most probable values of local CO_2 fluxes by season, estimated with two confidence levels: 95% and 99%.

The most probable flux ranges obtained respectively for spring and fall logically present intermediate values, with rather spread out overlapping zones, compared to the winter and summer ranges. The intervals of the most probable values for these two seasons are furthermore very similar.

If we summarize the extreme values presented in table 6, we can deduce that the most probable annual value ranges fall between around 0 and 20 $cm^3\ min^{-1}\ m^{-2}$, with a 99% confidence level.

8. CONCLUSIONS AND RECOMMENDATIONS

8.1 OVERALL CONCLUSION

The natural biogenic CO_2 and CH_4 fluxes values selected for the study were measured on the three most prevalent land cover categories in metropolitan France: prairies and grasslands, forests and woods, fields and vegetable gardens. They come from sites presenting in principle “normal” geological and pedological characteristics, without any detected geological and geochemical anomalies.

For CH_4 emission from soils, there were no measurements of natural fluxes observed exceeding 0.1 $cm^3\ min^{-1}\ m^{-2}$. Therefore, there is very little natural methane emission. These results confirm the literature data acquired by the measurements taken in comparable conditions.

The following characteristic information emerged for CO_2 emission for all of the seasons of the annual climate cycle:

- Its flux usually falls between 0 and 20 $cm^3\ min^{-1}\ m^{-2}$,
- fluxes falling between 20 and 25 $cm^3\ min^{-1}\ m^{-2}$ are rare,
- fluxes falling between 25 and 27 $cm^3\ min^{-1}\ m^{-2}$ were exceptionally observed, only in summer or early fall conditions,
- fluxes exceeding 27 $cm^3\ min^{-1}\ m^{-2}$ were never observed.

The generalized and very pronounced seasonal variations of CO_2 emission were observed on all the sites studied. On average, emission was clearly stronger in summer and weaker in winter. It is intermediate in spring and fall.

Overall, seasonal variations largely outweigh the influence of other parameters characterizing the monitored sites: climate zone, biological, geological, or pedological context.

There is a very clear general distinction in the CO_2 emission level between winter and summer. Table 7 below summarizes the difference between these two seasons. It indicates the value ranges of the measured fluxes, scaled on the frequency with which they were found *in situ*.

CO_2 flux values	Unit	Winter	Summer
mean	$cm^3\ min^{-1}\ m^{-2}$ (STP)	2,7	9,7
usually observed		0 à 6	3 à 20
rarely observed		6 à 9	20 à 25
exceptionally observed		9 à 11	25 à 27
never observed	For CO_2 : 1 $cm^3\ min^{-1}\ m^{-2}$ (STP) = 0,033 $mg\ s^{-1}\ m^{-2}$	> 11	> 27

Table 7. Summary of characteristic ranges of CO_2 flux determined from winter and summer data

The ranges of the values presented in table 7 were determined in the following manner:

- The ranges of the usual values correspond, rounded off, to the confidence intervals at 99% in table 6,
- The thresholds separating the rare high value range with that of the exceptional values are drawn from the respective values of the 99th percentile (table 2) and the results of the frequency analysis performed in chapter 7.6,
- the thresholds of the value ranges never found are based on the maximum values observed *in situ* respectively in winter and summer (see table 2), rounded to the nearest whole number.

The following conclusions were drawn on the influence of other potentially significant factors:

- When we stay within the temperate climate conditions, the specific climate zone of studied site does not seem to significantly influence CO_2 emission from the soil,
- The general geological characteristics of the sites studied do not seem to have considerable influence on CO_2 emission. In any case, any influence of the geological context is much weaker than that of seasonal variations,
- The land cover type played some role even if this factor's influence is, overall, minor compared to the seasonal changes of gas fluxes from soils. The data show that the CO_2 fluxes are on average smaller in fields and vegetable patches compared to forest/wood and prairie/grassland environment types, especially in summer and fall.

The influence of the pedological context, which has not sufficiently studied, due to the incomplete data with respect to the subject's complexity, must also be considered. Nevertheless, the results of the partial analysis that was able to be performed suggest that, for the three land cover categories considered in the study, the pedological factor does not have a strong influence. In any case it is much weaker than the effect of seasonal variations.

8.2 RECOMMENDATIONS

When surveying sites or assessing the gas emissions from soil, the following factors should be given priority consideration:

- the season of the annual climate cycle,
- the type of land cover that determines the site's general biological context,
- the kind of soil and its humidity,
- the change in the local short-term meteorological conditions in order to avoid situations that make the measurements taken non-representative (water-saturated soils, snow cover or frost, strong change in atmospheric pressure, violent wind, etc.).

The studies should be performed in winter and/or summer, which corresponds to the characteristic periods of the biological activity of the soils, respectively low and high.

Indeed, in many cases, it is useful, or even necessary, to perform repeated measurements at the same location performed during these two seasons, to take into account the seasonal changes of the gaseous flux and temperature effects on the transfer of gas between the soil and the free atmosphere (for example, the thermal drought effect).

For CO_2 emissions, the following **reference values** are proposed, with a distinction for measurements in summer and winter conditions.

For **summer** measurements:

- Fluxes between **3 and 20 cm^3 min^{-1} m^{-2}** are considered **usual,**
- Fluxes between **20 and 25 cm^3 min^{-1} m^{-2}** are considered very high and comprise the **upper limit of normal emissions,**
- Fluxes between **25 and 30 cm^3 min^{-1} m^{-2}** are considered **suspicious and can be a sign of an anomaly** of natural[7] or anthropogenic origin,
- Fluxes **exceeding 30 cm^3 min^{-1} m^{-2}** are considered abnormally high and correspond to an **anomaly** of natural or anthropogenic origin.

For **winter** measurements:

- Fluxes between **0 and 6 cm^3 min^{-1} m^{-2}** are considered **usual,**
- Fluxes between **6 and 9 cm^3 min^{-1} m^{-2}** are considered very high and comprise the **upper limit of normal emissions,**
- Fluxes between **9 and 12 cm^3 min^{-1} m^{-2}** are considered **suspicious and can be a sign of an anomaly** of natural or anthropogenic origin,
- Fluxes **exceeding 12 cm^3 min^{-1} m^{-2}** are considered abnormally high and correspond to an **anomaly** of natural or anthropogenic origin.

Figure 14 graphically illustrates the reference values proposed.

[7] These are often emissions of geologic origin from major faults or those relating to hydrothermal activity, former volcanic activity or even a local geochemical anomaly (see chapter 2.1). It could also be an anomaly of biological origin, for example due to the decomposition of a large accumulation of natural organic waste.

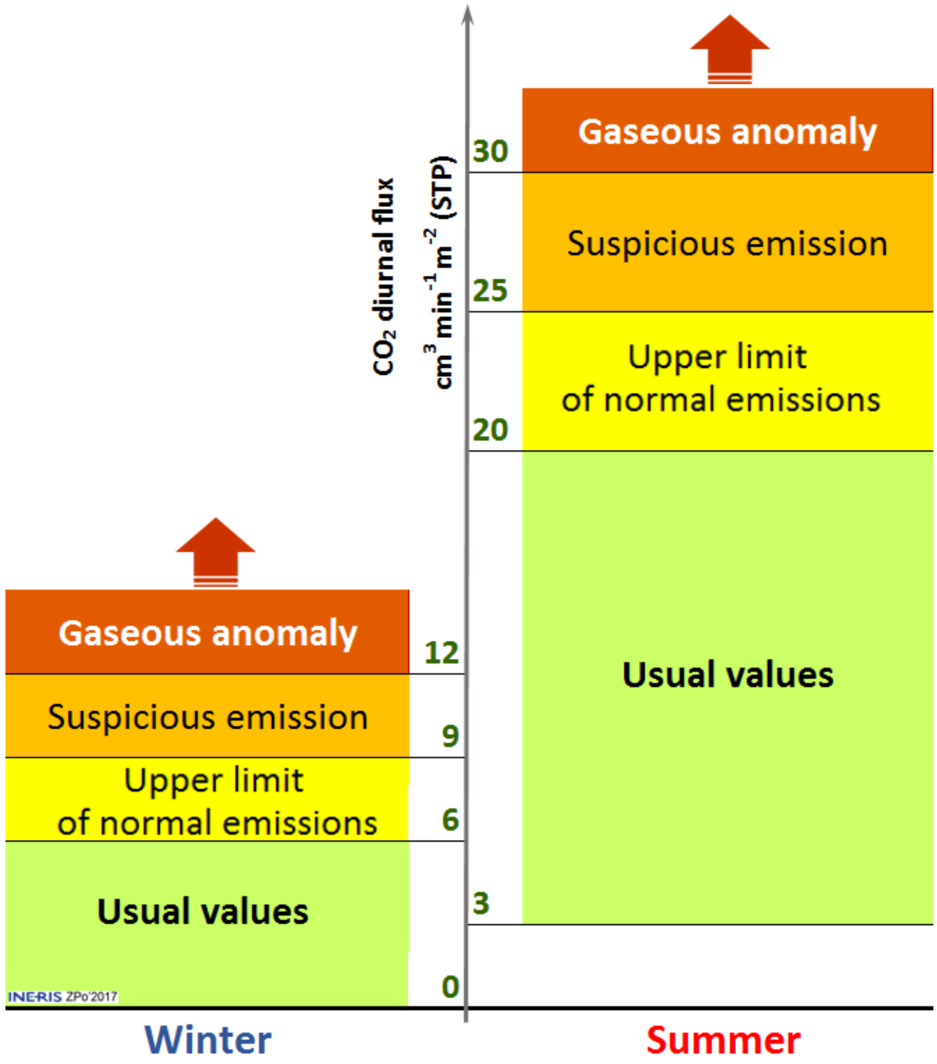

Figure 14. Graphic representation of the reference values CO_2 flux from soils

The thresholds that determine the usual range limits and the upper limits of the emissions considered as normal are drawn from the ranges in table 7.

The anomaly thresholds of 30 $cm^3\ min^{-1}\ m^{-2}$ in summer and 12 $cm^3\ min^{-1}\ m^{-2}$ in winter correspond to the maximum values of CO_2 fluxes founded respectively in summer and in winter, plus 10% for maximum theoretical inaccuracy of the measurement method in the *in situ* conditions (see chapter 3.4).

The criteria proposed above for summer conditions can also be applied to spring and fall, especially when the meteorological conditions are similar to the summer.

Winter criteria should be applied outside of the obvious meteorological anomaly periods (e.g. excessively high temperatures lasting over one week) that could lead to a temporary increase in biological activity of the vegetation and surface soil

Likewise, these criteria might have to be revised and adapted for measurements on particular sites that have very mild and humid local microclimates, thus making them conducive to year-long biological activity.

For CH_4 emissions, regardless of the context of the site studied and the measurement period, any flux exceeding **0.1 $cm^3\ min^{-1}\ m^{-2}$**, on a normally drained soil is considered **suspicious and indicative of a potential gaseous anomaly**.

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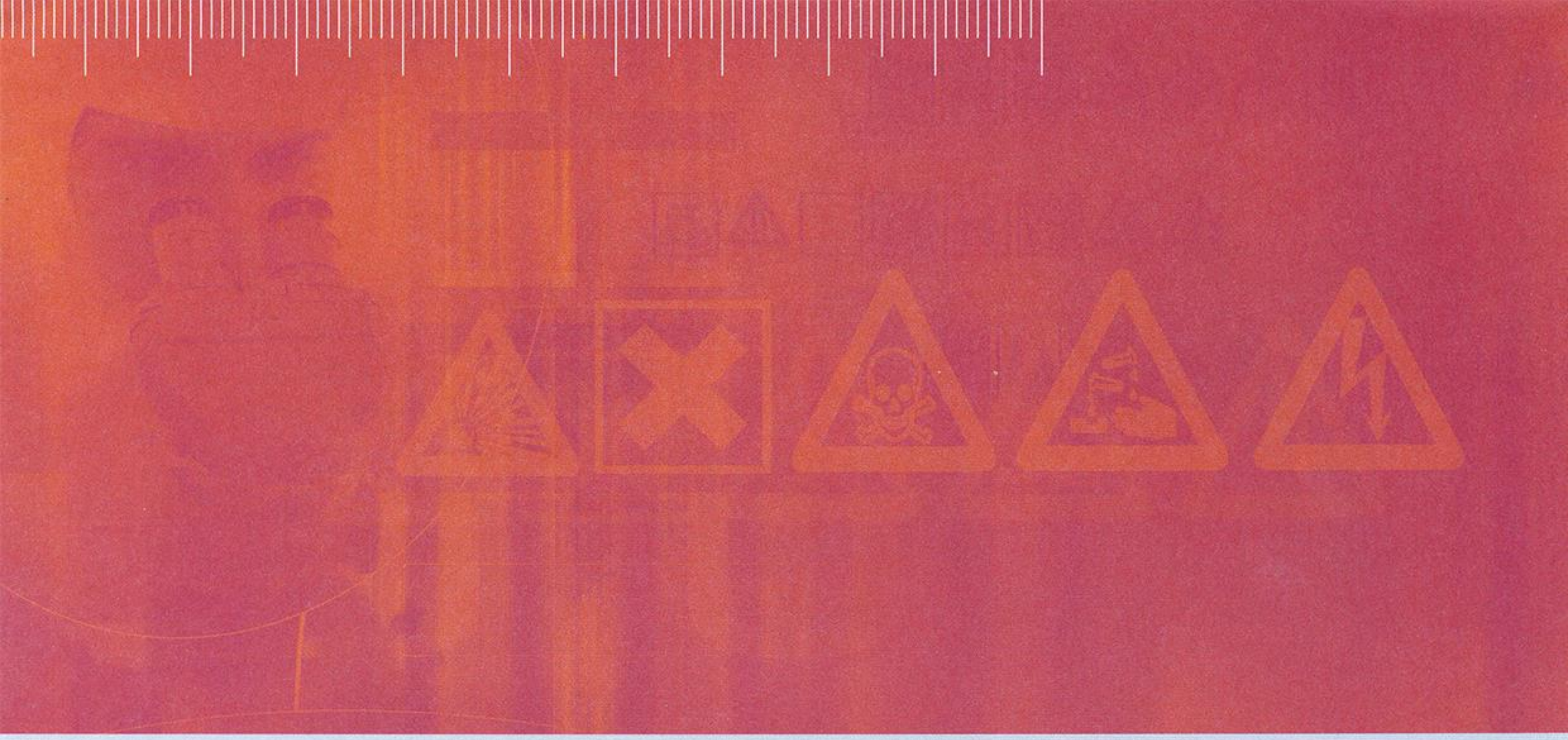

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