INTERNATIONAL STANDARD

ISO 20951

First edition
2019-06

Soil Quality — Guidance on methods for measuring greenhouse gases (CO_2, N_2O, CH_4) and ammonia (NH_3) fluxes between soils and the atmosphere

Qualité du sol — Recommandations sur les méthodes de mesure des gaz à effet de serre (CO_2, N_2O, CH_4) et des flux d'ammoniac (NH_3) entre les sols et l'atmosphère

Reference number
ISO 20951:2019(E)

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Fax: +41 22 749 09 47
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

Page

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/190, *Soil quality*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Greenhouse gas (GHG) emissions from soils have become a major environmental concern. Global and national emission inventories have identified soils, in particular agricultural soils, as being a major contributor to these emissions, in particular nitrous oxide (N_2O), methane (CH_4) and carbon dioxide (CO_2) related to loss of soil organic matter. Agricultural soils are also major emitters of ammonia (NH_3), which is a precursor of N_2O. Changes in soil management should take account of these emissions as part of efforts to mitigate climate change.

GHGs and ammonia fluxes from soil are complex to measure. They are variable and heterogeneous as they are governed by weather/meteorological conditions (e.g. temperature and moisture regimes), soil characteristics (e.g. soil parental material, pH, clay content, cation exchange capacity) and for managed soils by the agricultural or forestry practices (e.g. crop and wood residues management, soil tillage or no-tillage, inputs of soil conditioner and fertilizers, irrigation). These factors generally interact and their effects on GHG emissions are still poorly quantified. It results in large uncertainties for the inventories of national and global agricultural emissions. For example, Freibauer (2008)[1] has estimated an uncertainty at 80 % for European (EU27) agricultural N_2O emissions. With the reinforcement of international and regional climate policies, comparable and reliable information is needed to report on GHG emissions but also to adopt and verify mitigation options.

No standard covers the measurement of GHGs and ammonia emissions from soils. However, several measurement methods have been developed. This document provides guidance on the main methods available to quantify the exchanges of greenhouse gases (CO_2, N_2O, CH_4) and ammonia (NH_3) between soils and the atmosphere. It is intended to help users to select the measurement method or methods most suited to their purposes by setting out information on the application domain and the main advantages and limitations of each methods.

Soil Quality — Guidance on methods for measuring greenhouse gases (CO_2, N_2O, CH_4) and ammonia (NH_3) fluxes between soils and the atmosphere

1 Scope

This document gives an overview and provides guidance on the main methods available to quantify the exchanges of greenhouse gases (CO_2, N_2O, CH_4) and ammonia (NH_3) between soils and the atmosphere.

It is intended to help users to select the measurement method or methods most suited to their purposes by setting out information on the application domain and the main advantages and limitations of each methods.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.1
intrusive method
measuring method that can influence the emitting processes

3.2
mass balance approach
method based on a mass balance consisting of measuring the flux of compounds entering and leaving a volume of air above the soil surface being studied

3.3
micrometeorological method
method using analyses of the atmospheric concentration of the gas and meteorological measurements such as wind speed, wet and dry-bulb air temperatures, net radiation, and heat fluxes.

Note 1 to entry: These techniques are used for determining field-scale fluxes, and include eddy covariance, energy balance, aerodynamic and mass balance technique. They do not disturb the environmental conditions.

3.4
oasis effect
effect arising from the local environment of the field being studied and affecting emissions from a particular field depending on whether it is in an environment with a high level of emissions or a low level of emissions

Note 1 to entry: the oasis effect will only affect compounds whose fluxes result from a thermodynamical equilibrium between the surface and the atmosphere (NH_3).

4 Methods for measuring GHGs and ammonia fluxes between soil and the atmosphere

There are methods for measuring ammonia and GHG fluxes between soil and the atmosphere for a diversity of conditions and spatio-temporal resolutions (from less than an hour up to several days, from the soil sample up to several square kilometres) (this section). The main methods generally involve air sampling and determination of the concentration of the gas(es) of interest. Several concentration measurement and air sampling methods are compatible with a given flux measurement strategy (see Clause 5). The methods used and their combination depend on the purpose for which the measurements will be used, the operators' qualifications and the financial resources available (see Clause 6).

Two main strategies can be used:

a) chamber methods measuring the fluxes at source, and

b) atmospheric method used to estimate the fluxes at a distance from the source.

NOTE 1 Chamber methods are intrusive methods based on using static or dynamic flux chambers. Static and dynamic flux chambers can only quantify emissions for a small area of the source. Fluxes generally vary in time (variations in the parameters for weather and season) and in space (different soils and climatic conditions). For spatial extrapolation at field-scale, a sampling strategy using several chambers is required to reflect the variations in emissions over the area. Flux spatial structure could be determined by exploratory measurements prior to monitoring, or by assuming that flux will vary according to soil properties (e.g.: texture, organic matter content) or landscape features (e.g.: position in a slope). These methods can also be applied under laboratory conditions to determine the emissions of gases from soil samples, but hard to scale-up to field scale.

NOTE 2 Atmospheric methods are non-disruptive. The net exchange is estimated by measuring concentrations at a distance from the source together with micrometeorological measurements (e.g.: wind, air temperature). The fluxes are then estimated on the basis of these measurements, with a mass-balance approach or with models. Some of these methods are fairly difficult to implement and are highly dependent on weather conditions. Some knowledge of micrometeorology is generally required. They can be used to characterize global fluxes from heterogeneous, diffuse sources within a given area, without being able to distinguish the contribution of each particular source. In particular, atmospheric methods measure both soil and vegetation contributions, if there is active vegetation.

Table 1 presents the different methods and their main advantages and limitations.

Table 1 — The different methods and their main advantages and limitations

	Application domain	Main advantages	Main limitations
Chambers methods			
Static flux chambers	— Applicable to low fluxes — Mainly used for comparison of treatments — Applicable in field and in laboratory — Small area (~m^2) — Can be automated for monitoring dynamics over short periods — Non-reactive gases (CO_2, CH_4, N_2O)	— Easy to implement — High sensitivity even with low instrumental precision — Evaluation of spatial variability with several chambers — Most common flux measurement methods with many methodological references	— Intrusive method modifying emissions conditions. Chambers may alternate between locations (provide multiple chamber bases) to limit the impact of the chamber on the soil environment and hence emissions. — Spatial extrapolation of measurements requires a sampling strategy using several chambers with spatial and temporal extrapolation models.
Dynamic flux chambers and wind tunnels	— Comparison of treatments — Applicable in field and in laboratory — Small area (~m^2)	— Possible control of wind speed — Preferred for reactive gas such as NH_3	— Intrusive method modifying emissions conditions — Very difficult to extrapolate results to representative field emissions — The oasis effect can increase or decrease the apparent flux

Table 1 *(continued)*

	Application domain	Main advantages	Main limitations
Atmospheric methods			
Mass-balance methods	— Continuous monitoring — Real conditions — Comparison of treatment	— Easy to implement and not expensive — Non-intrusive method — Can be used for small areas (few tens of square metres)	— Need a large number of measurement points — Background concentration should be measured accurately
Inverse modelling		— Easy to implement and not expensive — Non-intrusive method — Small numbers of measurement points — Can be used to estimate emissions from several sources simultaneously, if there is a sufficient number of sensors (n+1 where n is the number of sources).	— Suitable for uniform, major emissions sources with low and fairly constant background concentrations — Not suitable for areas with hedges or scattered trees or with significant changes in surface roughness — Deployment over extended periods with changes in wind direction requires multiple measurement points to cover all wind directions.
Aerodynamic gradient	— Continuous monitoring — Real conditions — Allows measuring atmospheric deposition	— Non-intrusive method — Measures the flux from the surface directly — Can be used to monitor multiple sources	— Difficult to implement and expensive — Assumes a large uniform emitting surface
Eddy-covariance		— Applicable to large areas (>1 ha) — Non-intrusive method	— Very difficult to implement and expensive — Assumes a uniform emitting surface. Methodologies are in development to distinguish different emitting surfaces through flux footprint analysis (see for example Cowan et al. 2016[2]; Bureau et al. 2017[3]). — Requires high speed sensors for wind and gas concentrations, but method derived from eddy-covariance such as disjunct eddy-covariance (DEC) have been developed for measuring fluxes without high speed analysers — In development, for reactive gases such as NH_3 — Flux underestimation when turbulence is low, particularly during nights.

5 Concentration measurements and air sampling

5.1 General

Methods for measuring soil-atmosphere exchange of GHGs and ammonia involve the determination of gas concentrations in volumes of air. There are various methods to determine the concentrations, involving air sampling if necessary. They are characterized by the chemical species which they can detect and the associated limits of detection, the acquisition frequency, their precision, their cost and by the ease of use.

5.2 Concentration measurement methods

There are two families of concentration measurement methods (Table 2) that can be used for any type of gas targeted:

— Physical methods (absorption spectroscopy). The main characteristics of these methods are their very short response time, their sensitivity and the possibility of monitoring the concentration dynamics in real time (possibly monitoring several gases with different levels of concentration at the same time). Open path technologies exist for measuring integrated gaseous concentrations over a path directly in the atmosphere.

— Chemical methods (gas chromatography, laboratory assays, chemiluminescence). These methods are suitable for ad hoc measurements or for measurements integrated over periods from a few minutes to a few weeks. They are, therefore, less suitable for monitoring concentration dynamics. Furthermore, most of these methods are selective and cannot be used to measure several gases at the same time using the same equipment.

Annex B provides concentration measurement methods.

Table 2 — Concentration measurement methods

Method	Application domain	Advantages	Limitations
Chemical methods			
Gas chromatography	— Gaseous CO_2, CH_4, N_2O, NH_3 — Suitable with chamber and atmospheric methods, except eddy-covariance	— Technique is well understood, commercial equipment is available — High sensitivity and low limit of detection (of the order of ppm for CO_2 and ppb for N_2O, NH_3 and CH_4) — Can be used to quantify several chemical species at the same time — Can be used where there are high concentration fluctuations — Suitable with small sample volumes — Easily automated	— May be used in the field for continuous measurements but has logistical limitations and high operating costs (bottles of carrier gas, reference gases, daily intervention by operators and maintenance of ambient conditions).
Chemiluminescence	— Gaseous NH_3 — Suitable with both dynamic chamber and atmospheric methods	— High sensitivity of a few ppb for NH_3 — Fast response time (down to 0,1s) with rapid data acquisition — Particularly suitable for use with eddy covariance method	— Frequent calibration — Interference may be problematic for low concentrations in rural areas
Laboratory assay of ammonium (NH_4^+) in solution - Continuous flow analysers (CFA)	— NH_4^+ trapped in solution (passive diffusion sampler, denuders and trapping of ammonia in acid solution)	— High speed analyses (40 to 60 samples per hour) — Robust — Good reproducibility	— Allowance should be made for interference with other gases if the samples are very acidic (e.g.: having been trapped in an acid solution)
Laboratory assay of ammonium (NH_4^+) in solution - Liquid chromatography		— Can be used to assay all the major cations at the same time as ammonium — Reproducible	— Long analysis time (4 samples per hour) — Interference with other gases if the sample contains a large number of cations
Laboratory assay of ammonium (NH_4^+) in solution - Conductivity		— Easy to implement — Low cost — Small samples — Wide measurement range and low limit of detection — Good reproducibility	— Long analysis time (5 to 12 samples per hour)

[a] TDLAS : Tunable Diode Laser Absorption Spectroscopy; OA-ICOS : Off-Axis Integrated Cavity Output Spectroscopy; CRDS : Cavity Ring-Down Spectroscopy.

Table 2 *(continued)*

Method	Application domain	Advantages	Limitations
Physical methods			
Fourier-transform and photoacoustic infrared absorption spectroscopy	— Gaseous CO_2, CH_4, N_2O, NH_3 — Closed path and open path technologies — All chamber and atmospheric methods	— High sensitivity depending on the instrument and the gas (e.g. <1 ppb for N_2O and CO_2) — Can measure several compounds at the same time — Fast response time and rapid data acquisition — Standard equipment for greenhouse gases — Can be used where there are high concentration fluctuations	— Risk of interference — Sensitive to ambient conditions — Frequent calibration for some analysers but low annual drift for others
Laser absorption spectroscopy (TDLAS, OA-ICOS, CRDS)[a]		— Standard method for quantitative evaluation of trace gases — Fast response time (down to 0,1 s) with rapid data acquisition — Very high sensitivity (typically, 0,01 ppb for N_2O, 2 ppb for CH_4, 1,5 ppb for NH_3 at 1 Hz) — High selectivity and low risk of interference, in particular with Quantum Cascade Laser (QCL)	
Differential optical absorption spectroscopy	— Gaseous CO_2, CH_4, N_2O, NH_3 — Open path technologies (ambient air) — Atmospheric methods	— Fast response time (<1 s) with rapid data acquisition — Very high sensitivity (<1 ppb)	— Measurements are affected by poor visibility (ex: fog, snow), and clouds if the light source is the sun — Risk of interference

[a] TDLAS : Tunable Diode Laser Absorption Spectroscopy; OA-ICOS : Off-Axis Integrated Cavity Output Spectroscopy; CRDS : Cavity Ring-Down Spectroscopy.

5.3 Air sampling

In many cases, the determination of gaseous concentration involves sampling of a volume of air before analysis. There are various gas sampling methods which depend on the strategies adopted and the methods used to determine the concentrations.

Table 3 presents the different methods and their main advantages and limitations.

Table 3 — Air sampling methods

Method	Application domain	Advantages	Limitations
Passive diffusion samplers	— Reactive gas (NH_3) — Time-integrated measurement — Inverse modelling and mass balance (atmospheric methods)	— Easy to implement — High sensitivity for NH_3 in particular in low concentrations	— Gives an average concentration over the exposure time — Can only be used over long periods from a few hours to a few weeks — Some samplers may be affected by dust — Total cost of measurement may be close to that of an automatic analyser when measurements have to be repeated over a long period — Requires manual intervention for each measurement
Denuder tubes	— Reactive gas (NH_3) — Time-integrated measurement — Chamber methods, inverse modelling, mass balance and relaxed Eddy Accumulation (eddy-covariance derived method)	— Easy to implement — High sensitivity, can be adapted to the concentrations expected — Preferable to passive samplers for short sampling periods (from a few minutes up to about an hour) — Enables a wide variety of compounds to be collected in a relatively short sampling time	— Gives an average concentration over the exposure time — Requires manual intervention for each measurement
Trapping NH_3 in an acid solution	— NH_3 (i.e. NH_4^+ in solution) — Time-integrated measurement — Chamber methods — Inverse modelling and mass balance (atmospheric methods)	— Robust — High sensitivity — Can be adapted to the concentrations expected, and to the sampling period	— The process is time-consuming and difficult to automate — Not suitable for high temporal resolution monitoring — There may be interference from other absorbable species containing nitrogen (e.g.: volatile amines). — Requires manual intervention for each measurement

Table 3 *(continued)*

Method	Application domain	Advantages	Limitations
Continuous sampling methods for real-time analysis	— Air sample — Continuous monitoring — High temporal resolution — All chamber and atmospheric methods	— The air samples can be analysed in situ, in real time and continuously over long periods of time (high temporal resolution) — Samples can be taken from several different sampling points in succession at the same site	— It may take some time to set up or move the sampling system — The pipework needs to be protected against dust and condensation — For suction systems, there should be no leaks between the sampling point and the analyser that might dilute or contaminate the gas samples
Sampling tubes or bags	— Air sample — Delayed analysis — Static chamber method and Relaxed Eddy Accumulation (eddy-covariance derived method)	— Can be used for keeping samples of non-reactive compounds for days to weeks before analysis. — Applicable when concentration measurement is not suitable or possible in the field conditions	— Pressure fluctuations may compromise gas-tightness of the vials

Description of air sampling methods are given in Annex C.

6 Selection of the appropriate methods

Being able to quantify emissions makes it possible to compare probable emissions from various processes, estimate representative emission factors, monitor and check compliance with emission limits, etc. The methods used and their combination depend on the purpose for which the measurements will be used, the operators' expertise and the financial resources available. For example, research on the underlying processes might require a different approach than when yearly emission totals are required. As different emission measurement methods have different characteristics, an appropriate method should be selected, depending on different criteria: limit of detection and sensitivity required, field or lab measurements, maintenance and equipment costs, spatial area to cover, comparison of modalities or site monitoring. The sampling strategy should also be tailored to the gas in question. For example, soil N_2O flux has different drivers (involving biological processes) and different dynamics than ammonia (NH_3) flux (involving mainly physical and chemical processes).

Table 4 presents several published applications of flux measurement methods in relation to their purposes. Description of these methods are presented in Annex A.

Table 4 — Examples of applications of flux measurement methods in relation to their purposes

References	Flux measurement method	Purpose
de Klein and Harvey (2015)[4], Loubet et al. (2011)[5]	Static flux chambers	To measure field N_2O emissions and investigate their spatial variabilities
Minamikawa et al. (2015)[6]	Static flux chambers	To measure field N_2O and CH_4 emissions in rice paddies.
Sommer et al. (1991)[7]	Wind tunnels	To determine the influence of various factor (e.g. wind velocity, soil properties, air temperature, agricultural practices) on ammonia emission from soils in controlled conditions

Table 4 *(continued)*

References	Flux measurement method	Purpose
Laville et al. (1997)[8]; Aubinet et al. (2012)[9]; Eugster and Merbold (2014)[10]; Cowan et al. (2016)[2]	Eddy-covariance	To measure soil-atmosphere net exchange of GHG from field and investigate soil processes and agricultural practices involved.
VERA (2009)[11], Sintermann et al. (2011)[12], Carozzi et al. (2013)[13], Ferrara et al. (2014)[14]	Mass balance method, Inverse modelling	To measure ammonia emissions following manure or fertilizer spreading in field conditions
Personne et al. (2015)[15]	Aerodynamic gradient	To investigate short-time dynamics of ammonia emission

7 Minimum requirement for reporting

Reporting is important for evaluating the robustness of emission data. It is particularly crucial if they are collected for meta-analyses or intercomparison purposes, or for the calculation of emission factors. Furthermore, it is generally accepted that additional measurements are required when monitoring fluxes to interpret the results with respect to the conditions (surface temperature and humidity, incident radiation, etc).

The following minimum information should be reported:

— Experimental sites including location (e.g. latitude, longitude, altitude), soil properties (e.g. soil type, texture, bulk density, pH, organic C, available N, total N), and current and past occupations (e.g. pasture, crop, forest) and managements (e.g. fertilization, tillage, irrigation, crop protection, soil cover). Recent management can strongly affect soil-atmosphere gas exchange. For example, soil tillage and nitrogen fertilization can induce a rapid and transient increase in gaseous N emissions. Fertilizers and soil conditioner properties should be also reported (e.g. type, total N, mineral N, pH, organic C, dry matter, C:N ratio).

— Methodology including treatment details (e.g. replicates in the methodology is not spatially integrative), measurement methods (gas emission and concentration), area of the emitting surface, equipment (e.g. design, precision), duration of the monitoring, sampling scheme and method, background gas concentration.

NOTE 1 Regarding flux measurement methodology, information needs to be reported on the equipment used to estimate the variables necessary for the calculation of (1) the rate of accumulation for the chambers methods (headspace volume and air flow control/measurement devices), (2) the mass balances for the mass balance methods (wind velocity measurement device and design) and (3) the exchange coefficient for the inverse modelling, aerodynamic gradient and eddy covariance method (wind velocity measurement device and design).

NOTE 2 Regarding gas concentration measurements and air sampling, information on (1) the equipment used for gas analysis and their performances (e.g. detection limit, precision), (2) the air sampling strategy (e.g. direct or indirect, containers, continuous or sporadic, frequency) and (3) the sample manipulation and storage (e.g. duration and conditions of storage) are reported.

— Ancillary measurements including soil and weather conditions (e.g. soil water content, soil temperature, air temperature, precipitation, wind speed and direction). These data are essential to analyse and interpret the results.

— Data analysis (flux calculation method, estimation of errors, quality control).

Annex A
(informative)

Description of the flux measurement methods

A.1 Chamber methods

A.1.1 Non-steady-state or static flux chambers

A.1.1.1 General

This method is used for measuring non-reactive gas emissions at local scale usually for areas less than a square metre. Nitrous oxide (N_2O), carbon dioxide (CO_2), methane (CH_4) may be measured using static flux chambers. It is not adapted to compounds which emissions result from a thermodynamical equilibrium between the surface and the atmosphere.

A.1.1.2 Operating principles

This method estimates the fluxes from a source based on the accumulation dynamics (dC/dt) of the gases inside a sealed chamber placed on the surface of the source. The limit of detection depends on the ratio between the volume, V, and the area, A, of the chamber, the gas analyser and the integration time. The time taken for the measurement may vary from a few minutes to a few hours. For a system that is perfectly closed with no outside influences, the accumulation is close to linearity while the chamber is being used and the gas fluxes, Q, are, therefore, proportional to the accumulation slope (dC/dt or a) as shown in Formula (A.1):

$$Q = \frac{V}{A}\frac{dC}{dt} = \frac{V}{A}a \tag{A.1}$$

This method can measure both positive and negative fluxes. Depending on the type of source studied, fairly large flux chambers should be used (ground area of a significant fraction of a square metre) to take account of the spatial variability of the fluxes and a number of measurements should be taken to obtain representative values for fluxes at the scale of the source of emissions considered. Although the static flux chamber method is one of the most common flux measurement methods for which there are many methodological references (de Klein and Harvey, 2015[4]; Minamikawa et al., 2015[6]; Hutchinson and Livingston, 2002[16]; Livingston and Hutchinson, 1995[17]), it is not standardized.

A.1.1.3 Implementation

Static flux chambers are relatively easy to use depending on the concentration analysis method used (Rochette and Eriksen-Hamel, 2008[18]). Static flux chamber can be connected to an inline gas analyser for real-time analysis or uses traps for instantaneous or integrative sampling. For real-time analysis, the greenhouse gas concentrations (CH_4, N_2O, CO_2) can be detected using infrared spectroscopy. For systems with traps, the gases can also be assayed by gas chromatography. If samples are taken from the chamber for subsequent analysis, they can be stored in small pre-evacuated or flushed vials (a few ml). Chamber opening and closing can be automated to minimize manipulation, to increase the temporal resolution of the measurements and to sample specific conditions (e.g. soil temperature, rain event).

Static flux chambers are an intrusive method which changes the emission conditions at the surface of the soil, in particular by changing the turbulence, the pressure fluctuations and the differences in concentration between the soil and the atmosphere (Matthias et al., 1978[19]). Gas diffusion theory would predict that the increase inside the chamber during deployment would not be linear and some non-linear models have been proposed (Healy et al., 1996[20]). To minimize these effects and be able

to use a linear approximation, it is important to limit the measurement time, ensure that the gas is thoroughly mixed inside the chamber (e.g. fan, mixing using a sampling syringe), sink the chambers into the ground or substrate to prevent lateral diffusion so far as possible, provide a vent that will balance the pressure inside the chamber with the pressure outside and insert the chamber base into the soil at least 24 h prior to the first sampling. De Klein and Harvey (2015)[4] give recommendations on the chamber design, implementation and data treatment to maximize flux detectability and minimize any measurement artefacts.

A.1.1.4 Validation and sources of uncertainty

The measurements can be checked visually or statistically. Plotting the concentration with time enables the linearity to be checked: the coefficient of determination R^2 is widely used as an estimator and the maximum slope can also be taken into account. The level of precision of the flux measurement depends directly on the precision of the analyser and the measurement conditions (leaks, duration) and also on the estimate of the *V/A* ratio. The detection threshold of the method can be evaluated from the calculated error on the determination of the slope. It is inversely proportional to the square root of the number of measurements and depends on both the sensitivity of the analyser and the *V/A* ratio. The detection threshold can be minimized by finding a good compromise between the length for which the flux chamber is deployed, the sensitivity of the analyser and the height of the chamber.

A.1.2 Dynamic flux chambers and wind tunnels

A.1.2.1 General

Dynamic flux chambers with controlled air circulation and wind tunnels can be used for any gas. They are generally used to characterize the emissions of reactive compounds such as ammonia, for small areas (of the order of 1 square metre). They can be used to measure emissions in a laboratory, often in closely controlled conditions as well as in situ. This is a method suitable for experiments comparing different treatments.

A.1.2.2 Operating principles

A small area is swept with a controlled airflow in a tunnel enclosing the area. The airflow is imposed. It can simulate wind, one of the major factors controlling volatilization. The volatilization flow Q_S ($\mu g \cdot m^{-2} \cdot s^{-1}$) for a compound is determined from the difference in concentrations between the input and output of the tunnel, as given in Formula (A.2):

$$Q_s = q \times \frac{(C_o - C_i)}{A} \tag{A.2}$$

where

C_o and C_i ($\mu g \cdot m^{-3}$) are the concentrations of the compound of interest at the output and input of the tunnel respectively;

q ($m^3 \cdot s^{-1}$) is the airflow in the tunnel;

A (m^2) is the area covered by the tunnel.

The turbulent component of the airflow is ignored.

A.1.2.3 Implementation

Although the tunnels and wind chambers are portable, this method may be relatively difficult to implement in the field: a power supply is required for the pump. To include the effects of rain or cultivation on the land, these should either be simulated manually inside the tunnels, with the risk of not reproducing them correctly, or the tunnels can be opened automatically for some time. The tunnels can also be moved regularly across the surface being measured.

The concentrations can be assayed using inline analysers such as infrared, to measure several points at the same time over integrative periods ranging from a few hours (just after manure spreading, for example), a few days (for periods after spreading during which the fluxes are expected to be lower), to a few weeks or months.

A.1.2.4 Validation and sources of uncertainty

Positioning the tunnels or chambers directly on the emitting surface may require account to be taken of the unevenness of the distribution of the sources of emissions (e.g. manure) which may have a major effect: it is recommended that several tunnels/chambers should be used to evaluate the fluxes. Pumping air may create large pressure gradient that may strongly affect the fluxes. It is therefore highly recommended to check the pressure difference between inside and outside the tunnel/chamber. The major source of uncertainty for determining fluxes using wind tunnels or chambers is the measurement of the airflow, as was shown by Loubet et al., (1999a; 1999b)[21,22]. It is important to measure the airflow accurately, as the airflow not only has a significant direct effect on the measurement but may also affect the emissions themselves. Wind tunnels give results closer to those of the entire surface when the wind speed in the tunnels is the same as those measured outside but tend to overestimate the real fluxes due to the oasis effect.

A.2 Atmospheric methods

A.2.1 Mass-balance approaches

These methods which are based on a mass balance consist of measuring the flux of compounds entering and leaving a volume of air above the soil surface being studied.

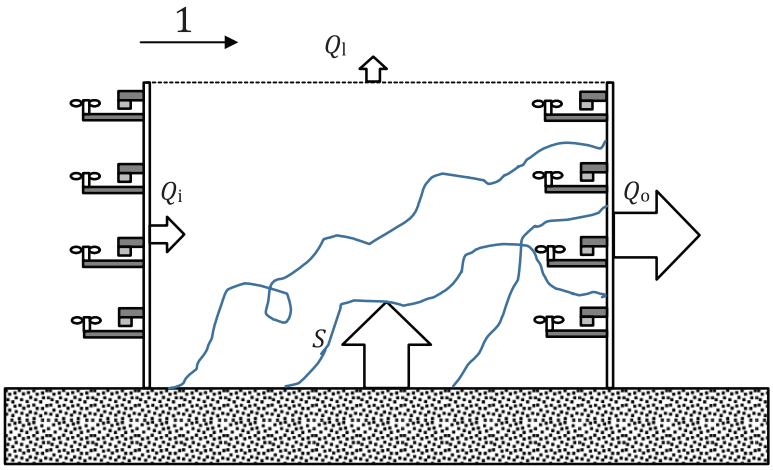
A.2.1.1 Integrated Horizontal Flux (IHF) method

A.2.1.1.1 General

The Integrated Horizontal Flux (IHF) is suitable for measuring the gaseous emissions from circular sources with a diameter from about 20 m to about 40 m. IHF has been used mainly for measuring ammonia volatilization from fields.

A.2.1.1.2 Operating principles

The method is based on mass balance by measuring the flux of compounds entering and leaving a volume of air above the surface being studied (see Figure A.1). The difference between the input flux, *F*i, and the output flux, *Fo*, from the test volume is equal to the flux emitted from the surface, *S*. The lost flux leaving the top of the test volume F_l is ignored, and should hence be minimised.



Key

1 wind

S is the emissions flux to be measured

Q_i is the input flux to the test volume (delimited by dashed lines)

Q_o is the output flux

Q_l is the lost flux through the top of the test volume

NOTE In this case, two masts measure the input and output fluxes. Each mast has an anemometer and a concentration sensor for the compound at several different heights.

Figure A.1 — Integrated Horizontal Flux method

The horizontal flux $Q_c^H(z)$ of a compound at a concentration $C(z)$ at a given height z is equal to the concentration multiplied by the wind velocity at this height $v(z)$, which, taking the means, gives Formula (A.3):

$$Q_c^H(z) = \overline{C(z), v(z)} = \bar{C}(z)\cdot\bar{v}(z) + \overline{v'c'}(z) \tag{A.3}$$

where the mean of the product is decomposed into the product of the means $\bar{C}(z)$ and $\bar{v}(z)$ plus a term $\overline{v'c'}(z)$ which represents the horizontal turbulent flux. The bars represent means over the period and the primes represent the fluctuation around the mean.

Assuming that the term representing the turbulence is negligible, the horizontal flux can be measured with an averaging concentration sensor and an anemometer. The IHF is estimated by measuring the horizontal flux at several heights, as given by Formula (A.4):

$$Q_c^{0\to\infty} = \overline{\int_0^{\infty} \bar{C}(z)\cdot\bar{v}(z)\mathrm{d}z} \sim \int_0^{z_{\max}} \bar{C}(z)\cdot\bar{v}(z)\mathrm{d}z \tag{A.4}$$

As taking measurements at great heights is neither easy nor useful, a maximum height $z_{\max}$ is set, above which the horizontal flux is considered to be negligible (approximately one tenth of the radius of the source). There are several ways of estimating the integral, either directly by summing the values or by fitting curves to the flux or concentration profiles (splines, logarithm, exponential, etc.).

Several variants of the IHF method have been developed. In general, circular plots are used for practical purposes as they measure the IHF at the centre, regardless of the wind direction. The input flux can be estimated from the background concentration for fields at some distance from the field that has been treated and a uniform vertical concentration profile is assumed.

A.2.1.1.3 Operating principles

When implementing the method, the main work involves preparing the concentration sensors if acid bubblers, denuders or passive diffusion samplers are used. The source area should be well delimited. When background concentration is used, it may be useful to have three background concentration sensors in case the wind direction changes. Wilson and Shum (1992)[23] give more information on implementation.

A.2.1.1.4 Validation and sources of uncertainty

Wilson and Shum (1992)[23] tested this method using a Lagrangian stochastic model and considered that it was accurate to about 20 %. IHF has been shown to overestimate ammonia emissions in comparison with the new standard method of inverse modelling, for volatilization after spreading manure or slurry on a field (Sintermann et al., 2012)[24]. This overestimate comes from ignoring horizontal turbulent airflow and the oasis effect which increases emissions.

A.2.1.2 The perimeter profile method

A.2.1.2.1 General

The perimeter profile method is similar to IHF and is based on mass balance. It is applied to plots by taking measurements round the outside of the plot. A few assumptions about the uniformity of the airflow can, therefore, be applied in a wide range of conditions. It can be applied for fields with a simple geometrical shape (rectangle). This method can only be used to measure emissions from plots in an environment with low concentrations. It is not suitable for small fluxes as, in this case, the method will be measuring horizontal differences in small concentrations.

A.2.1.2.2 Operating principles

The perimeter profile method is based on determining the mass balance, i.e. measuring the quantity of the compound that enters and the quantity that leaves in the airflow above the source studied: the difference between the input flux (Q_i) and the output flux (F_o) from the test volume is equal to the flux emitted from the surface (S). This method usually uses four masts on the edge of a diffuse source (Denmead et al., 1998)[25]. Measurements may be taken continuously (inline analyser) or at long intervals using sensors that integrate the concentrations over time, such as impingers and Ferm tubes. The horizontal flux is estimated in the same way as for the IHF method as the wind velocity multiplied by the concentration, at the height of the boundary layer that develops over the surface (typically 10 % of the length of the plot).

A.2.1.2.3 Implementation

Perimeter profile measurements require 4 masts supporting sampling points or sampling lines which measure the concentrations of the gas of interest at the same time as the horizontal wind speed. The source area should be well delimited, and the measurement masts should be positioned correctly. For point measurements, it is possible to use real-time, spatially integrating methods or a system similar to that used for aerodynamic gradient measurements. For measurements integrated over time, the main work involved is preparing the concentration sensors if denuders or passive diffusion samplers are used.

A.2.2 Inverse modelling

A.2.2.1 General

This method is used to estimate the fluxes of gaseous or particulate compounds emitted from a reasonably well isolated source of known geometry. This method can be used with real-time analysers or integrative passive diffusion samplers. Although this method is mainly suitable for isolated sources, it can be used to estimate emissions from a number of plots provided the sensors are well positioned (Denmead, 2008[26]; Flesch et al., 2009[27]; Loubet et al., 2010[28]; Loubet et al. 2017[29]). The dispersion models assume that the ground surfaces are uniform. This method is therefore not suitable for an

area with hedges or isolated trees or sudden changes in roughness, although Flesch et al. (2004)[30] demonstrated that the method could still be used with some disturbance.

A.2.2.2 Operating principles

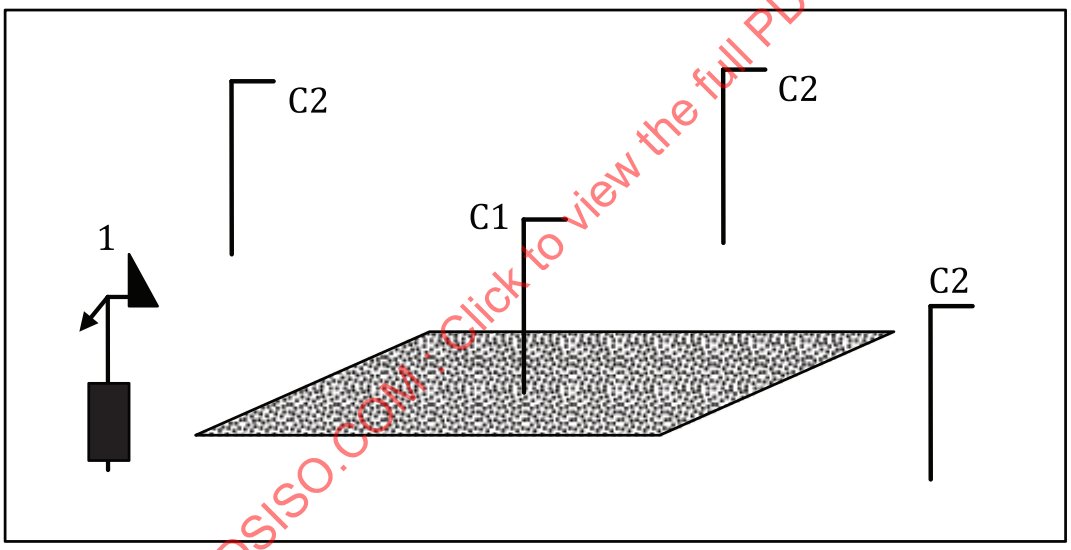
The method measures concentrations in and around the plot studied and then adjusts the source terms S_j to minimize the difference between the measured concentrations (C^i_{mes}) and the predicted concentrations (C^i_{mod}). The concentrations are predicted by Formula (A.5):

$$C^i_{\text{mod}} = \sum_{j=1}^{N} D_{ij} S_j + C_{\text{background}} \quad \text{(A.5)}$$

where

N is the number of sources;

D_{ij} is the transfer coefficient which is the concentration C^i_{mod} that would be produced by the source S_j if were the sole source equal to 1 and the background concentration $C_{\text{background}}$ were zero.



Key

1 anemometer
C1 concentration sensor
C2 background concentration

Figure A.2 — Example of configuration for estimating the emissions S1 from an isolated plot (Ferrara et al. 2014)[14]

NOTE 1 A concentration sensor C_1 is placed in the middle of the plot and three concentration sensors in the surrounding area to estimate the background concentration. A sonic anemometer is also used to characterize the turbulence in the boundary layer.

NOTE 2 In other configuration, the concentration sensor is be placed downwind of the emission site.

In practice, D is estimated using an atmospheric dispersion model. There are various models with calculation software:

— Stochastic Lagrangian models describe the trajectory of a large number of fluid parcels emitted by the sources, moving in a random walk, the concentration at a particular point being equal to the probability of the presence of these parcels at that point. Windtrax software is based on this principle (Flesch *et al.*, 2004)[30]. These models are suitable for dispersion over short distances and allow the statistics of the emissions from the sources to be estimated. The turbulence in the boundary layer is represented using the Monin-Obukhov similarity theory or based on direct measurements of the Reynolds tensor ($u_i u_j$) and heat fluxes. Windtrax is described on the Thunderbird Scientific website (http://www.thunderbeachscientific.com/) (Flesch *et al.*, 2004)[30].

— Gaussian and pseudo-Gaussian models are based on solving Euler's equations for fluid dynamics based on the conservation of mass (or based on the advection-diffusion equation). Gaussian models are based on the assumption that the wind and the diffusion coefficient are constant, whereas pseudo-Gaussian models such as FIDES are based on vertical profiles for the wind and diffusion coefficient that follow a power law ($v(z) = a\ z^p$, $K(z) = b\ z^n$). For a complete description see Loubet *et al.* (2010)[28].

These models for the concentrations at the measurement points require, at minimum, the following parameters: friction velocity (v_f^*), Obukhov length (L), aerodynamic roughness length (z_0), zero plane displacement (d), wind vector (U, V, W) and standard deviations (σ_u, σ_v, σ_w). Precise details of the geometry of the source and the position of the sensors are also required. There are various optimization methods for fitting the predictions to the measurements. Linear regression is suitable.

A.2.2.3 Implementation

For measuring emissions on a plot, the concentration measurement point should be at a height of less than one tenth of the fetch (the fetch is the distance between the measurement mast and the upwind edge of the field) to maximize the effect of the source on the sensor. It should not be too close to the ground to avoid excessive uncertainty on the height of the sensor. Loubet et al. (2017)[29] recommend in practice using heights of 50 cm above the canopy in order to reduce uncertainty in positioning the sensors close to the ground as well as avoid being too close to the roughness layer close to the canopy which is characterized by non-diffusive transfer. The background measurement points are positioned far away from the source being measured and other local sources, typically at least 300 m away. However, if the geographical situation does not allow this, they should be more than 100 m away. 3 to 4 measurement points should be used. The measurement frequency can be lower than for the measurement point on the plot. Ideally, measurements should be taken every 30 min on the plot and daily or weekly for background concentrations. However, it might be useful to characterize the background concentration dynamics first to give a more accurate assessment. For emissions with strong dynamics, such as after manure spreading, background measurements can be taken at increasing intervals (2 h, 6 h, 12 h, 24 h, 7 days, 1 month).

Another implementation is based on the use of laser open-path spectrometry, which integrates the concentration over long path length. In these methods (Flesch et al. 2004)[30], the best is to place the emitter and mirrors to cross the entire source area.

Wind measurements are best made at about 1,5 m close to the main measurement point and preferably using a 3D ultrasonic anemometer (Flesch et al. 2004)[30]. Free software is available for acquisition and calculating the turbulence parameters from the anemometer data. Standard meteorological measurements, such as solar radiation, air temperature and humidity, wind speed and direction, are useful as explicative and control variables.

A.2.2.4 Validation and sources of uncertainty

The inverse modelling method has been validated in several situations. Lagrangian models (Flesch *et al.*, 2004)[30] have been validated using controlled methane sources and have shown a bias generally less than 20 %. The FIDES model was validated for ammonia fluxes in comparison with the aerodynamic

gradient method after amendment with calcium ammonium nitrate and with manure (Loubet et al. 2010)[28] with a bias of less than 10 %.

The main source of uncertainty is the precision of the concentration measurement and of the difference between the background concentration and the concentration in the plot. For example, Loubet et al. (2010)[28] estimated that the inverse modelling method requires a resolution for the NH_3 concentration difference (C - $C_{background}$) (in µg·m^{-3}) = a·S (in µg·m^{-2}·s^{-1})/v_f* (in m·s^{-1}) where a varies between 1,2 and 4,1. A central assumption for the method is that the source and the surface are uniform, which is not often the case in practice. Other sources of uncertainty are the geometry of the source which is not easy to determine, in particular during manure spreading as the source moves with the tractor (Sintermann et al., 2011)[12], and the estimation of the turbulence parameters, z_0, v_f* and L (if not measured directly with a 3D sonic anemometer). Finally, the inverse modelling method to estimate source strength depends on a good description of atmospheric transport, which is known to be difficult under extreme stability conditions and/or low wind speeds. Flesch et al. (2004)[30] proposed filtering criteria for L and v_f* of the model output to avoid error-prone emission estimates.

A.2.3 Aerodynamic gradient

A.2.3.1 General

The aerodynamic gradient method was very popular in the second half of the 20th century for estimating the momentum, sensible heat and water vapor fluxes between the surface of the Earth and the atmosphere. It is based on a simple principle which made it a standard method for many years for measuring many other surface fluxes: CO_2, SO_2, O_3, NH_3, mercury, volatile organic compounds, nitric acid (HNO_3), pesticides, etc.

It is still used for compounds which are difficult to measure by eddy covariance, such as reactive compounds that need to be converted before analysis or for which real-time analysers are not sufficiently sensitive (NH_3, metals, pesticides, HONO, bacteria) (Honrath et al., 2002[31]; Kruit et al., 2007[32]; Milford et al., 2009[33]). The aerodynamic gradient method is also used for measuring chemical systems such as the NO-NO_2-O_3 system. The gradient method is able to estimate both the flux and the conversion rate of one chemical species to another (De Arellano and Duynkerke, 1992[34]; Duyzer et al., 1995[35]; Stella et al., 2012[36]).

A.2.3.2 Operating principles

The aerodynamic gradient method measures the vertical flux above a uniform surface. It is based on Fick's first law of diffusion whereby the flux Q (g·m^{-2}·s^{-1}) of a quantity depends on the gradient of its concentration C (g·m^{-3}) and its diffusion coefficient D (m^2·s^{-1}). For example, in the vertical direction (z) the diffusion flux is $Q = -D\,\partial C/\partial z$.

This law applies to any molecular diffusion phenomenon and has been extended to the case of turbulent diffusion in a surface boundary layer. By analogy with the molecular diffusion which depends on the thermal agitation of molecules in a gas or a liquid, a turbulent flux ($\overline{w'c'}$, where w is the vertical component of the wind (m·s^{-1}), c is the concentration and the bar represents the mean over the period and the primes denote fluctuation around the mean) can be represented by a relationship between the flux and the concentration gradient when turbulence is small for the characteristic distance of the gradient. This can be expressed as given by Formula (A.6):

$$\overline{w'c'} = -D_t \frac{\partial c}{\partial z} \tag{A.6}$$

The turbulent diffusivity D_t (m^2·s^{-1}) is well defined for the atmospheric boundary layer by Monin and Obukhov's similarity theory (Foken, 2006[37]; Kaimal and Finnigan, 1994[38]). It depends on the friction velocity u* (m·s^{-1}), characterizing the intensity of the turbulence in the boundary layer and the thermal stratification of the boundary layer, expressed in terms of the Richardson number (R_i without dimension) or the Obukhov length (L in m). Replacing D_t by a function of u* in Formula (A.6) and replacing z by $\ln(z-d)-\psi_H\left(\frac{z-d}{L}\right)$ (where Ψ_H is the effect of thermal stratification on the temperature

gradient, and d is the zero plane displacement[1] in m), gives the commonly used flux-gradient equation (Sutton et al., 1993)[39], given by Formula (A.7):

$$Q = -k \times u^* \cdot \frac{\partial c}{\partial \left[\ln(z-d) - \psi_H \left(\frac{z-d}{L} \right) \right]} \tag{A.7}$$

$$\psi_H(\zeta) = \begin{cases} -5{,}2\zeta & \zeta > 0 \\ 2\ln\left[1 + \frac{1}{2}(1-16\zeta)^{1/2} \right] & \zeta \leq 0 \end{cases} \tag{A.8}$$

where

Q is the flux;

k is the von Karman constant (k = 0,41);

ζ is the stability parameter ($\zeta = (z - d)/L$);

d is the zero plane displacement;

Ψ_H is the empirical stability correction function for scalars.

A.2.3.3 Implementation

Measurement using the aerodynamic gradient method requires at least one thermometer and a 3D sonic anemometer to measure the friction velocity u^* and estimate the Obukhov length L, as well as equipment for measuring the gas concentration for at least three heights. It is preferable to use just one analyser to take samples at the various heights to avoid any bias that might be introduced by differences in calibration between analysers. The simplest solution is to use a multiplexer to take samples from the various channels in succession. The zero plane displacement d should also be estimated. It can be estimated from the height of the ground cover and the leaf area index (LAI) (Graefe, 2004)[40], or from the wind speed gradient measured at 4 or 5 heights as described by Loubet et al.(2013)[41].

The method requires a flat uniform surface that is as large as possible, no nearby major emission sources and no nearby obstacles. The sampling heights should have geometrical spacing from the lowest just above the turbulent layer (twice the ground cover height + 10 cm) to the highest which should be within the boundary layer for the plot (one hundredth of the fetch, the size of the plot). The analysers should be calibrated regularly. All the channels should be checked at the same height regularly to ensure that there is no drift or bias in the analysis.

A.2.3.4 Validation and sources of uncertainty

The aerodynamic gradient method has been validated for heat, water and CO_2 fluxes by comparison with standard methods such as eddy covariance. For ammonia, inter-comparison tests gave a relative standard error of 20 % for high fluxes and 33 % for lower fluxes (Milford et al., 2009)[33]. The method has also been compared against relaxed eddy accumulation giving differences from 3 % to 40 % and the inverse modelling method giving differences less than 2 % (Loubet et al., 2009[42]; Loubet et al., 2010[28]). Advection error also constitutes a potential source of error, which appears when measurements are made in the vicinity (a few hundreds of metres) of a strong source (like a farm) (Loubet et al., 2009[42]).

1) The term zero plane displacement is used when the ground is covered by dense vegetation of height H. The ground height is then considered to be raised by ~0,7 H, the zero plane displacement.

A.2.4 Eddy-covariance and derived methods

A.2.4.1 Eddy covariance

A.2.4.1.1 General

Eddy covariance is a standard method for measuring fluxes emitted by a sufficiently large and relatively uniform source (typically around 10 ha and at least 1 ha). This method can be used to measure any gaseous compounds and particulates assuming that an analyser able to take high speed real-time measurements is used (5 Hz minimum, ideally 10 to 20 Hz). This method is used routinely for time series spanning several years for measuring CO_2, water and sensible heat fluxes as well as ozone. It is being extended to cover gaseous nitrogen compounds and GHGs with the advent of quantum cascade laser spectrometers (QCL) that are sufficiently sensitive for N_2O and methane and, more recently, ammonia.

A.2.4.1.2 Operating principles

Eddy covariance is used to measure the fluxes of compounds through a horizontal plane through the measurement point. The molar flux crossing this plane at each moment is equal to the product of the concentration of compound C (mol·m^{-3}) around this plane and the wind component w (m·s^{-1}) normal to the plane. Averaging this instantaneous flux over a period gives the mean flux for the period: $F = \overline{w \cdot C}$ (mol·m^{-2}·s^{-1}). To avoid errors due to lack of precision and zero drift of the sensors, the above equation is modified to include only fluctuations in wind speed and concentration around the means (w' and C', which are not affected by drift). However, several fundamental assumptions are required to define the new equation and determining C' requires high frequency concentration measurements which are rarely unbiased. Two fundamental assumptions in particular limit the application of this method:

— The airflow should be horizontally uniform and constant over a period of between 15 min and 2 h, i.e. there should be no sudden changes in meteorological conditions or airflow during this period. This condition is sometimes not met at night when gravity waves[2] may occur. It is also not met when downwind of a nearby major emissions source, such as a main road for NO_X. Further information on these aspects may be found in Mahrt (2007;2010)[43,44].

— Measurements should be taken at a frequency significantly greater than the frequency of the eddies responsible for the mass transfer and for a sufficiently long time to include the lowest frequency eddies.

It is also assumed that the flux measured at the height of the measurement point is equal to the surface flux. This is based on two hypotheses. The first is that there is no net advection below the measurement system, i.e. that the volume of air whose composition has been modified by the source or sink in the plot studied does not leave by lateral airflow without being replaced by a volume with equivalent properties (which is the case when turbulence is low and the ecosystem is not uniform over the whole of the surface and surrounding area). The second assumption is that there is no storage effect, i.e. the mass of air below the measurement mast does not act as a reservoir (which is the case during periods with very little wind). Reviews of the eddy turbulence method are available (Aubinet *et al.*, 2000[45]; Lee *et al.*, 1997[46]; Massman and Lee, 2002[47]).

A.2.4.1.3 Implementation

Eddy covariance measurements require the following equipment:

— A 3D sonic anemometer to measure the three components of the wind at a frequency greater than 20 Hz.

— A high speed real-time gas analyser with an acquisition rate at least 2 Hz to 5 Hz and ideally 20 Hz.

2) Gravity waves occur essentially above forests in boreal conditions. They are associated with thermally stratified atmospheres.

— If the analyser is not open path, a sampling system with a pump is required to transfer the air samples to the analyser. The pump should be selected to transfer the air sample sufficiently quickly to minimize chemical interactions between the compounds to be measured and the surfaces, and in particular the possible attenuation of the high frequency variations in concentration caused by drag on the walls creating artificial mixing. To achieve this, the flow should be turbulent (Reynolds number greater than 2 000 to 3 000) and the transfer time less than a few seconds. The air should be sampled below the sonic anemometer with a sampling head that should be unobtrusive to avoid affecting the wind speed measurements.

— A mast for positioning the system at a given height without affecting the wind speed measurements

— A 20 Hz or 50 Hz data logger.

The method requires a flat uniform surface that is as large as possible, no nearby major emission sources and no nearby obstacles. Analysers able take the measurements at a high frequency often require very high-power vacuum pumps and so it is usually necessary to have a connection to an electricity supply. It should be possible to access the system remotely to check the analysers. The data acquired should be archived regularly and processed by relevant software. The analysers should also be regularly calibrated automatically or manually.

A.2.4.1.4 Validation and sources of uncertainty

This is now a standard method used for CO_2, CH_4, water and sensible heat. It has been evaluated many times using both theoretical and experimental methods. However, there are very few studies comparing this method to others and there are doubts about possible biases in the method concerning the loss of high frequency information for reactive compounds such as ammonia (Ferrara *et al.*, 2012[48]; Sintermann *et al.*, 2011[12]; Whitehead *et al.*, 2008[49]).

The main source of uncertainty is the loss of high frequency information as a result of using an analyser that is not fast enough (Massman, 2000)[50]. The analyser should sample at a higher rate than the minimum required to catch the energy of the covariance signal, typically above 10 Hz (Kaimal et al. 1972[51]; Kaimal and Finnigan, 1994[38]). Non-stationarity of the turbulent flow and a variable flux footprint in a heterogeneous landscape, causing the fluxes to be unrepresentative of the targeted area, are both major sources of uncertainty but the uncertainty can be estimated using standard tests (Aubinet *et al.*, 2000)[45] and footprint models (Kljun *et al.*, 2004)[51]. Finally, low frequency variations in the fluxes due to the site's topography (rolling, flat) and the way the topography is accounted for in the data processing also introduce uncertainties (Finnigan et al. 2003)[52].

A.2.4.2 REA, DEC and vDEC

A.2.4.2.1 General

The various methods derived from eddy covariance (Relaxed Eddy Accumulation (REA), Disjunct Eddy Covariance (DEC), and Virtual Disjunct Eddy Covariance (vDEC, sometimes called DEC-MS) have the same scope of application as eddy covariance itself. They are suitable for measuring fluxes emitted by a sufficiently large and relatively uniform source (typically around 10 hectares and at least 1 hectare). These methods can, in principle, be used to measure any gaseous compounds and particulates but, unlike eddy covariance, do not require a 10 Hz to 20 Hz, real-time analyser. These methods are, therefore, used for measuring fluxes of compounds for which there are no high-speed analysers. However, they are rarely used as a routine method as they require more equipment (high speed solenoid valves, bags) and more human effort. Some of these methods based on simple samplers can be used for long-term measurements.

— The REA method described by Businger and Oncley (1990)[53]requires an analyser response of 30 min to 1 h. It has been used satisfactorily for volatile organic compounds (VOCs), particulates down to ultrafine, ammonia, nitric acid, sulfate, sulfur dioxide, methane, N_2O and pesticides.

— The DEC (Haugen, 1978)[54] and vDEC methods require analysers with a response time of a few tens of seconds per channel. These methods have been used mostly for VOCs (where 10 compounds can be scanned successively) as well as for aerosols, N_2O and NO_X.

A.2.4.2.2 Operating principles

Disjunct eddy covariance (DEC, vDEC) and eddy accumulation (EA, REA) methods are based on the same principle as eddy covariance and measure the fluxes of compounds through a horizontal plane through the measurement point. They differ from the eddy covariance method in that the sampling is conditional for the accumulation methods and at intervals greater than the system response time for disjunct methods.

The Relaxed Eddy Accumulation (REA) method is based on two fundamental assumptions:

a) the "flux-variance similarity" for a compound (Obukhov, 1960[55]; Wyngaard and Coté, 1971[56]; Wyngaard *et al.*, 1971[57]) and

b) the "scalar similarity" between the transport of different scalars (such as the temperature and the compound of interest).

The compound is sampled conditionally depending on the vertical wind component. When the wind is upwards, the air is stored in the "up" bag and when the wind is downwards, the air is stored in the "down" bag (Ruppert et al., 2006)[58]. The flux is expressed as $Q = b\sigma_w \left(\overline{C}_{\uparrow} - \overline{C}_{\downarrow} \right)$ (g·m^{-2}·s^{-1})

where

b is a proportionality coefficient,

σ_w is the standard deviation of the vertical wind component (m·s^{-1})

$\overline{C}_{\uparrow}$ and $\overline{C}_{\downarrow}$ are the concentrations in the "up" and "down" bags (g·m^{-3}).

For ideal turbulence, b is 0,627.

In practice, b is estimated for each measurement period by assuming that the same equation applies to the flux of the compound and to the heat flux. It is calculated from the covariance between the temperature and the vertical wind component $\overline{w'T'}$ and the difference between the "up" temperatures $\overline{T}_{\uparrow}$ and the "down" temperatures $\overline{T}_{\downarrow}$ $b = \overline{w'T'} / \sigma_w \left(\overline{T}_{\uparrow} - \overline{T}_{\downarrow} \right)$. The REA has an advantage over the (v) DEC methods in that the volume sampled for each sample is much larger and generally provides higher sensitivity and therefore a lower limit of detection for the fluxes.

The Disjunct Eddy Covariance (DEC) method is based on the same principle as eddy covariance. The flux is taken to be equal to the covariance of the concentration (C) and the vertical wind component w: $Q = \overline{w' \cdot C'}$. The difference is that, instead of measuring the concentration fluctuations at high speed (typically 10 Hz to 20 Hz), the concentration fluctuations are estimated by sampling air every 10 s to 30 s over a very short sampling period (0,1 s to 0,2 s). This means that the concentration of the compound can be measured using analysers with a response time of around ten seconds. As the air is sampled for a very short period, the covariance with the vertical wind component is not attenuated. Because the measurements are not continuous, subsequent processing is carried out as if it were a conventional series of covariance data which was only being analysed for 1 point in every 10 or 20 points. The covariance, however, is unaffected. There is, however, attenuation of frequencies greater than 10 Hz which should be evaluated.

The vDEC method is based on the same principle as the DEC method which takes samples over a short time interval with a shorter sampling frequency than the eddy covariance method. The difference is that there is no storage system and a high frequency analyser can be used for sequential measurements

of the concentration of several different compounds such as VOCs. The vDEC method can also be used to measure the fluxes of a compound at several different heights.

A.2.4.2.3 Implementation

The DEC or REA methods for measuring fluxes require a 3D sonic anemometer which measures the three wind components at a frequency greater than 10 Hz.

— The REA method required a concentration analyser able to analyse at least three samples in each measurement period (30 min to 2 h). The samples may be assayed in a laboratory (storage in bags, denuders or WEDD reservoirs).

— The DEC method requires a concentration analyser with an acquisition time of at least 10 s to 20 s, ideally a few seconds. It also requires a multiplexer and a complex sample storage system which can store one sample while assaying another.

— The DEC method requires a concentration analyser with the same basic acquisition frequency as the eddy covariance method (10 Hz – 20 Hz).

— The sampling systems and pump should be dimensioned to ensure that the samples are transferred rapidly to avoid attenuating the high frequency variations in the concentrations which would reduce the apparent flux.

— A mast for positioning the system at a given height without affecting the wind speed measurements.

— A 20 Hz or 50 Hz data logger.

The method requires a suitable site to minimize the limitations of the method: a flat uniform surface that is as large as possible, no nearby major emission sources and no nearby obstacles. Analysers able to take the measurements at a high frequency often require very high-power vacuum pumps and so it is usually necessary to have a connection to an electricity supply. It should be possible to connect to the Internet for the acquisition system to monitor the analysers and storage systems for vDEC and REA. The data acquired should be archived regularly and processed by the same type of software as used for standard eddy covariance. The analysers should also be regularly calibrated automatically or manually.

A.2.4.2.4 Validation and sources of uncertainty

The REA method has been validated using theoretical methods and by direct comparison for CO_2, for example, by Brut *et al.* (2004)[59]. One of the main limitations for the REA method is in the assumptions of flux-variance similarity and scalar similarity (Ruppert *et al.*, 2006)[58]. In particular, the determination of the constant *b* depends on conditional sampling which is strongly affected by variations in both the wind and the concentration (Gronholm *et al.*, 2008)[60].

The DEC method has been validated, both by sub-sampling eddy covariance measurements, and by comparing DEC and EC measurements for "inert" compounds such as CO_2 (Hoertnagl *et al.*, 2010)[61]. One limitation of the method is the maximum time between each sample: this is limited in practice by the number of data points that can be acquired during the integration period (30 min to 2 h). For flux measurements with an uncertainty of less than 10 %, studies have shown that, typically, at least 2 to 15 measurements per minute are required (Rinne *et al.*, 2008[62]; Turnipseed *et al.*, 2009[63]). Another limitation of this method is the difficulty of evaluating the effect of high frequency attenuation on the fluxes (Hoertnagl *et al.*, 2010)[61]. As the vDEC method has the same basis as the DEC method, it should be validated in the same way and has the same sources of uncertainty. However, there is an additional uncertainty in the assessment of the time lag (phase lag) between the concentration measurement and the wind measurement. This time lag should be determined (Hoertnagl et al. 2010)[61].

Annex B
(informative)

Description of the concentration measurement methods

B.1 Chemical methods

B.1.1 Laboratory assays of ammonium (NH_4^+) in solution

B.1.1.1 General

Quantitative laboratory assays of ammonium in solutions extracted from ammonia traps such as passive diffusers, denuders and impingers. Before the assay, the solution may be distilled as for the Kjeldahl method for determining total nitrogen (ISO 11261:1995)[64].

B.1.1.2 Operating principles

This subclause covers three methods for determining the concentration of ammonium in solution.

Continuous flow analysers (CFA)

The ammonium ion (NH_4^+) is assayed by continuous flow absorption spectroscopy using Berthelot's reaction (Krom, 1980). The ammonium in an alkaline solution (1) reacts with hypochlorite (ClO^-) that has been released by dichloroisocyanurate (2) to form chloramine (NH_2Cl) which then reacts with salicylate on a nitroprusside catalyst (3) at a temperature of between 37 °C and 50 °C to form a blue-green indophenol which is measured quantitatively by continuous flow spectrometry. The absorbance is measured at a wavelength of between 640 nm and 660 nm. This chemical reaction and the absorbance measurement are managed automatically by the continuous flow analyser. The intensity of the coloration is proportional to the ammonium concentration (ISO 11732:2005)[65].

Conductivity assay after separation using a semi-permeable membrane

The NH_4^+ is assayed by measuring the conductivity of deionized water which has absorbed the NH_3 passing through a semi-permeable membrane.

The sample is first mixed with NaOH (1) which converts the acid ammonium ion (NH_4^+) into its conjugate base, ammonia (NH_3). The NH_3 solution then flows across a semi-permeable membrane (impermeable to the fluid but permeable to the gas). As NH_3 can exist in both aqueous and gaseous form at the same time, it diffuses across this membrane (2) and the rest of the sample is eliminated. Deionized water flows across the membrane in the opposite direction, trapping the gaseous NH_3 and reacting with it to re-form the NH_4^+ ions (3). The conductivity of the sample is then measured and compared with that of the deionized water (4). The conductivity is proportional to the concentration of ammonium ions. The samples are taken and measured automatically.

Liquid chromatography

Liquid chromatography is used to separate the various cations of a sample using a stationary and a mobile phase. The stationary phase is a low capacity cation exchange column. Aqueous solutions of mono- or di-acids are usually used as eluents for the mobile phase (ISO 14911:1999)[66]. Methanesulfonic acid (MSA) can be used as an eluent, for example. The anions in the sample are eliminated by an anion suppressor before the cation concentration is assayed by measuring the conductivity.

B.1.2 Gas chromatography

B.1.2.1 General

Gas chromatography can be used to determine the concentrations of certain greenhouse gases (GHG) - methane (CH_4), carbon dioxide (CO_2) and nitrous oxide (N_2O) - in air samples.

B.1.2.2 Operating principles

Gas chromatography is used for gaseous compounds or compounds that may be vaporized. A gas chromatograph separates the components in the sample and measures the concentrations of the compounds separated. There are 4 basic items of equipment: an injector, the column, the oven surrounding the column and the detector. The sample is vaporized in the injector and swept by the carrier gas through the heated column. The column separates the various compounds depending on their polarity and their boiling point. The compounds that have been separated are identified and quantified by the detector.

Main detectors used with gas chromatography to detect greenhouse gases and reactive nitrogen species

Detector	Operating principle	Gases detected, limitations
Thermal conductivity detector (TCD)	Differential measurement of the resistivity of two filaments in contact with the gas to be assayed and the carrier gas	Any type of gas, simple and robust
Flame ionization detector (FID)	A hydrogen flame ionizes the molecules in the gas to be assayed; the ions are collected in an electric field	Suitable for organic compounds (e.g. CH_4).
Electron capture detector (ECD)	The carrier gas is ionized by beta particles. When electronegative analyte molecules pass through the detector, they absorb the free electrons, reducing the ionization current	Electronegative molecules such as halogen compounds and N_2O
Mass spectrometer (MS)	The molecules of the gas to be assayed are ionized and separated according to their mass-to-charge ratio (m/z). The ion streams are converted into an electrical signal	All types of compound

B.1.3 Chemiluminescence

B.1.3.1 General

Routine analysis of atmospheric gas compounds by chemiluminescence began in the 1970s, with the measurement of NO, NO_2 and terpenes. The measurement of NO by chemiluminescence is the basis for the measurement of many nitrogen compounds after capture in gaseous or liquid form and catalytic transformation (Navas *et al.*, 1997)[67]: gaseous ammonia (NH_3), nitric acid (HNO_3) and nitrous acid (HNO_2), nitrates, peroxyacetyl nitrate (PAN) and total nitrogen. Two relatively recent articles have reviewed the state of the art (Toda and Dasgupta, 2008[68]; Zhang *et al.*, 2005[69]). The method is subject to interference, which may be problematic for low concentrations in rural areas.

B.1.3.2 Operating principles

Chemiluminescence is the emission of light as a result of a chemical reaction. The light is emitted when electrons fall from an excited state, releasing energy. The effect has been known since the end of the 19th century, in particular for ozone (since 1896), and most analysis methods use chemiluminescence with ozone. This can be used to detect NO and any nitrogen compound that can be degraded to NO, such as NH_3. There are some other oxidants (e.g.: H_2O_2) which are also strongly chemiluminescent. Any chemical reaction which emits light can be used. For NO and O_3:

$NO + O_3 \rightarrow NO_2^* + O_2$

$NO_2^* \rightarrow NO_2 + light$

The light is emitted at a particular wavelength that depends on the compound (in this case NO_2^*). A sensitive photomultiplier is used to count the number of photons emitted which is proportional to the number of NO molecules that have reacted with the ozone. For measuring ammonia, a stainless steel catalyst heated to 800 °C is used in standard analysers (Mennen *et al.*, 1996)[70]. Recently a catalyst has been developed that can convert any nitrogen compound into NO (Ammann *et al.*, 2012[71]; Bruemmer *et al.*, 2013[72]; Marx *et al.*, 2012[73]).

B.2 Physical methods

B.2.1 Fourier transform and photoacoustic infrared absorption spectroscopy

B.2.1.1 General

Infrared absorption spectroscopy is used to analyse gas samples. The main gases that can be measured are methane (CH_4), carbon monoxide (CO), carbon dioxide (CO_2), ammonia (NH_3), nitrous oxide (N_2O), nitrogen monoxide (NO), nitrogen dioxide (NO_2), sulfur dioxide (SO_2), hydrogen chloride (HCl) and water (H_2O). This method can be used to analyse the concentrations of several gases simultaneously.

B.2.1.2 Operating principle

Infrared (IR) absorption spectroscopy measures the absorption of infrared radiation by a gaseous mixture. It detects the characteristic resonances of the chemical functions present in the gas, each type of chemical bond having its own set of IR absorption bands resulting from these resonances. Two main techniques are used for measuring emissions from farms using absorption spectroscopy: Fourier transform infrared spectroscopy (FT-IR) and photoacoustic infrared spectroscopy (IR-PAS).

FT-IR spectroscopy is based on the use of an interferometer which uses interference between two beams to produce a modulated beam. The modulated beam passes through the chamber with the sample to be measured where selective absorption takes place. The beam then passes into a detector which transforms the amplitude into an electric signal which is processed by Fourier transform to generate the spectrum characteristic of the sample.

Photoacoustic infrared spectroscopy excites a sample with a pulsed monochromatic light beam. The wavelength characteristics of the target gases are selected using optical filters. Some molecules in the sample absorb part of the light energy and enter an excited state and this energy is released, when they relax, as an acoustic signal which is captured by a microphone.

B.2.2 Laser absorption spectroscopy

B.2.2.1 General

Laser absorption spectroscopy covers the use of lasers to measure the concentration or quantity of a gas species by absorption spectroscopy. The target gases are greenhouse gases (CO_2, N_2O, CH_4, H_2O) and reactive gases such as NO, HCL, HNO_2, NH_3 and CO. It can also be used to make precision measurements of the concentrations of various stable isotopes of the target gases when measuring emissions from farms ($^{13}CO_2$, $^{15}N_2O$, $H_2{}^{18}O$, etc), identify the origin of natural sources or mark and then monitor the transformation or transport of a compound in the soil, plant or atmosphere.

B.2.2.2 Operating principles

Laser absorption spectroscopy is one of the oldest methods used for non-intrusive measurement of the concentrations of certain gas species. It measures the absorption of light from a light source with a well-defined spectrum along the optical path to the detector. The intensity of the light detected at a wavelength characteristic of the target gas depends on the concentration of that gas. The more

molecules in the optical path, the greater the amount of light that is absorbed (Beer-Lambert law) as given by Formula (B.1):

$$\ln\left(\frac{I_0}{I}\right)=\sigma NL \tag{B.1}$$

where

I_0 is the intensity of the incident light;

I is the intensity of the light on exit;

σ is the absorption cross-section ($cm^2 \cdot molecule^{-1}$);

N is the concentration of the gas ($molecule \cdot cm^{-3}$);

L is the length of the optical path (cm).

The absorption cross-section depends on both the target molecule and the wavelength. The choice of wavelength determines the type of molecule detected. In the near and mid infrared (IR) regions, the signature of the gas molecules is the result of the rotation-vibration resonances. It is usually used more with wavelengths from 1 µm to 12 µm. The fundamental bands are the most intense and are found in the mid infrared region (3 µm to 12 µm) and the less intense harmonic bands are found in the near infrared region (0,78 µm to 3 µm). The spectroscopic absorption parameters of these bands are given in the HITRAN (Rothman *et al.*, 2009)[74] or GEISA databases which include the line positions (wavenumber, cm^{-1}) and the broadening parameters for the pressure and temperature of the gas. To determine the concentration of the absorbing medium with precision, the absorption for a line should be measured for pressures between 10 and 100 mmHg over an extended band covering a Voigt profile corresponding to the convolution between a Gaussian profile and a Lorentzian profile.

The most common systems available on the market are Tunable Diode Laser Absorption Spectroscopy (TDLAS), Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS) and Cavity Ring-Down Spectroscopy (CRDS). Most of these use photon detectors. The performance (response time, measurement sensitivity) of these technologies now makes it possible to measure emission fluxes using micrometeorological flux gradient and eddy covariance method. However, they can also be used for real-time measurements using static flux chambers. These spectroscopes are both highly sensitive and very selective and are non-intrusive. The technology can be used for several open path (OP-TDLAS) and point monitoring approaches.

B.2.3 Differential optical absorption spectroscopy

B.2.3.1 General

Differential optical absorption spectroscopy (DOAS) is used to measure gaseous concentrations over an optical path in the atmosphere. Used together with airflow characterization methods (e.g.: tracer gas, inverse modelling, aerodynamic gradients), it can estimate emissions from livestock buildings, waste manure storage and fields (Hu et al., 2014[75]; Volten et al., 2012[76]). It can be used for GHGs (CO_2, N_2O, H_2O) as well as reactive species such as NH_3, NO, SO_2, NO_2 and O_3. The methods and procedures are described in EN.16253:2013[77].

B.2.3.2 Operating principles

Measurement by DOAS is based on the absorption of light at wavelengths that are characteristic of the target gases. Extending the Beer-Lambert law, the intensity of the light detected at a particular wavelength depends on the concentration of the target gas following Formula (B.2):

$$I_\lambda = I_{0,\lambda} \times e^{-\left(\alpha_{i,\lambda} \times C_i + \epsilon_M + \epsilon_R\right) \times L} + S(\lambda) \tag{B.2}$$

where

I_λ and $I_{0,\lambda}$ ($W \cdot sr^{-1}$) are the intensity of radiation of the wavelength λ incident on the receiver and emitted by the radiation source respectively;

$\alpha_{i,\lambda}$ ($m^2 \cdot \mu g^{-1}$) is the absorption cross-section of gas i at wavelength λ;

C_i ($\mu g \cdot m^{-3}$) is the concentration of the gas in the gaseous compound;

L (m) is the length of the optical path;

ϵ_M and ϵ_R are the extinction coefficients per unit of the optical path for particles comparable to the wavelength of the light (Mie scattering) and for air molecules and smaller particles (Rayleigh scattering).

Account should also be taken of Rayleigh scattering of solar radiation $S(\lambda)$ which causes a slight increase in the radiation measured by the detector.

More particularly, the method is based on the analysis of the rapidly varying structure of the absorption spectrum. Differentiation of Formula (B.2) with respect to the absorption cross-section $\alpha_{i,\lambda}$ defines the initial differential intensity $I_{0,\lambda}'$ corresponding to the initial intensity $I_{0,\lambda}$ after attenuation by Rayleigh scattering, Mie scattering and the low frequency component of the absorption coefficient. Account is also taken of the Rayleigh scattering of solar radiation and the attenuation in the optical system. The spectrum is usually analysed by mathematical modelling of I_λ, using Formula (B.3):

$$I_\lambda = \mathrm{P}(\lambda) \times e^{-\Sigma - \alpha_{i,\lambda}' \times C_i \times L} \tag{B.3}$$

where

$P(\lambda)$ is a polynomial describing $I_{0,\lambda}'$;

$\alpha_{i,\lambda}'$ is the differential (the rapidly varying component of the absorption) cross-section of gas i.

The mean concentration of gas C_i in the optical path is obtained by adjusting the model to the measured spectrum. DOAS can, therefore, be used to overcome the impossibility of determining the initial radiation intensity $I_{0,\lambda}'$ and take account of differential light densities of the gases studied for the whole of the spectral domain selected for analysis.

The radiation spectrum studied may vary from near ultraviolet radiation to near infrared radiation (from about 200 nm to 2 500 nm). DOAS is often used in the ultra-violet and visible light ranges as the gas absorption properties in these ranges are not very sensitive to temperature and atmospheric pressure conditions. For example, ammonia can be detected within a band from 200 nm to 230 nm.

Annex C
(informative)

Description of the air sampling methods

C.1 Passive diffusion samplers

C.1.1 General

Many different types of passive diffusion samplers have been described in scientific literature and are used by companies that provide analysis services. They all measure the mean concentration of gases over a period of time that depends on the environment, the concentration ranges being measured, and the precision required. An overview of these samplers for measuring ammonia and nitrogen dioxide can be found in Tang *et al.* (2001)[78]. They are able to measure concentrations of reactive gases such as ammonia and nitrogen dioxide but are not used to measure greenhouse gases.

C.1.2 Operating principles

All passive samplers operate on the principle of diffusion of gases along a sampler of defined dimensions onto an absorbing medium (acid, base, resin compounds) according to Fick's law. During diffusion, the gas passes from a zone with a high concentration of the gas (the ambient air being analysed) to a zone with a low concentration (the absorbing medium). The absorbing medium maintains a low concentration of the gas in the adjacent air which ensures that there is continuous diffusion. The theoretical uptake rate of a sampler is a function of the cross-sectional area, A (m^2), the length, L (m) (the distance from the mouth of the sampler to the reaction surface) and the diffusion coefficient, D ($m^2 \cdot s^{-1}$), of the gas of interest. The effective volume of air sampled, V (m^3), is determined using Formula (C.1):

$$V = D \times \frac{A \times t}{L} \tag{C.1}$$

where t is the exposure time in seconds.

The cross-section and length can be adjusted to obtain the required sampling time.

The air concentration of a pollutant, C ($\mu g \cdot m^{-3}$), can then be calculated by Formula (C.2):

$$C = \frac{(m_e - m_b)}{V} \tag{C.2}$$

where

m_e (µg) is the mass of pollutant collected on an exposed sample and m_b;

m_b (µg) is the mass of pollutant in a control sample.

There are two main types of passive diffusion sampler: tubes and badges. Tube samplers are usually vertical hollow tubes, the absorbing medium being placed at the top. The lower end of both tubes and badges may be open or capped with a permeable membrane that does not react with the gas being measured. For measuring ammonia concentrations, the absorbent is citric, phosphoric; sulfuric or tartaric acid.