

Measuring Air Pollutant Concentrations and Fluxes



Benjamin Loubet, Dominique Baisnée, Mathieu Cazaunau, Audrey Fortems-Cheiney, Raluca Ciuraru, Cathy Clerbaux, Jean-François Doussin, Gaëlle Dufour, Cristian Focsa, Christian George, Valérie Gros, Mélynda Hassouna, Jean-Luc Jaffrezo, Julien Kammer, Patricia Laville, Abdelwahid Mellouki, Maurice Millet, Denis Petitprez, Etienne Quivet, Nathalie Redon, Roland Sarda-Esteve, Stéphane Sauvage, Gaëlle Uzu, Éric Villenave, and Nora Zannoni

Estimating agriculture's contribution to air pollution and global warming is needed to understand and limit its impact on the environment and climate. It is even a legal obligation. But it is equally important to estimate the capacity of practices to mitigate these emissions and to characterize atmospheric deposition and the impacts of air pollutants on agroecosystems. This chapter presents methods for measuring air pollutant concentrations and exchange fluxes at the soil-vegetation-atmosphere interface.

B. Loubet (✉) · R. Ciuraru · J. Kammer · P. Laville
ECOSYS, INRAE, Thiverval-Grignon, France
e-mail: benjamin.loubet@inrae.fr; raluca.ciuraru@inrae.fr; patricia.laville@inrae.fr

D. Baisnée · R. Sarda-Esteve
LSCE, CEA, Gif-sur-Yvette, France
e-mail: dominique.baisnee@lsce.ipsl.fr; roland.sarda-estev@lsce.ipsl.fr

M. Cazaunau · G. Dufour
LISA, CNRS, Créteil, France
e-mail: mathieu.cazaunau@lisa.u-pec.fr; gaelle.dufour@lisa.u-pec.fr

A. Fortems-Cheiney · J.-F. Doussin
LISA, Université Paris-Est-Créteil, Créteil, France
e-mail: audrey.cheiney@lisa.ipsl.fr; jean-francois.doussin@lisa.ipsl.fr

C. Clerbaux
LATMOS, CNRS, Paris, France
e-mail: cathy.clerbaux@latmos.ipsl.fr

C. Focsa
PhLAM, Université de Lille, Lille, France
e-mail: cristian.focsa@univ-lille.fr

Agriculture's contribution to air pollution is mainly estimated via emission factors or sometimes models, which may take into account practices and climate (see chapters “[Modelling Exchanges: From the Process Scale to the Regional Scale](#)” and “[Establishing a Diagnosis: Inventorying, Monitoring and Assessing](#)”). To establish these models and emission factors, emission measurements are required that must be representative of climate, soil and regional practices. Measurements are also needed to identify the agricultural contribution to air pollution and extrapolate the results into the future. However, existing measurements in the agricultural sector are

C. George

IRCELYON, CNRS, Villeurbanne, France

e-mail: christian.george@ircelyon.univ-lyon1.fr

V. Gros · N. Zannoni

LSCE, CNRS, Gif-sur-Yvette, France

e-mail: valerie.gros@lsce.ipsl.fr

M. Hassouna

SAS, INRAE, Rennes, France

e-mail: melynda.hassouna@inrae.fr

J.-L. Jaffrezo

IGE, CNRS, Grenoble, France

e-mail: jean-luc.jaffrezo@univ-grenoble-alpes.fr

A. Mellouki

ICARE, CNRS, Orléans, France

e-mail: mellouki@cnrs-orleans.fr

M. Millet

ICPEES, Université de Strasbourg, Strasbourg, France

e-mail: mmillet@unistra.fr

D. Petitprez

Physico-Chimie de l'Atmosphère, Université de Lille, Lille, France

e-mail: denis.petitprez@univ-lille.fr

E. Quivet

LCE, Aix-Marseille Université, Marseille, France

e-mail: etienne.quivet@univ-amu.fr

N. Redon

CERI EE, IMT Lille Douai, Douai, France

e-mail: nathalie.redon@imt-lille-douai.fr

S. Sauvage

SAGE, IMT Lille Douai, Douai, France

e-mail: stephane.sauvage@imt-lille-douai.fr

G. Uzu

IGE, IRD, Grenoble, France

e-mail: gaelle.uzu@ird.fr

É. Villenave

EPOC, Université de Bordeaux, Pessac, France

e-mail: eric.villenave@u-bordeaux.fr

still very fragmented: even for ammonia, which is probably the most characteristic compound of agricultural emissions, there are very few data measured in the field in France (Hafner et al. 2018). Furthermore, the methods used can be controversial (Sintermann et al. 2012). For N_2O , another compound that is typical of agriculture, the usually small spatial extent of measurement methods makes it difficult and uncertain to extrapolate data to larger spatial and temporal scales. For compounds such as BVOCs and HONO, data on agricultural sites are almost non-existent. Thus, there is still a strong need today to measure the fluxes of pollutants between agroecosystems and the atmosphere.

This chapter provides an overview of the main methods for measuring atmospheric concentrations and pollutant fluxes in relation to agriculture as discussed in chapter “[The Main Pollutants and Their Impacts on Agriculture, Ecosystems and Health](#)”. The compounds addressed here are emitted by agricultural activities. Nitrogen compounds (mainly gaseous) are discussed first, and include greenhouse gases such as N_2O or pollutants such as ammonia. BVOCs, including methane, and pesticides (which are semi-volatile organic compounds, Textbox 1) are also covered. Additionally, some compounds have an impact on the biosphere, especially agroecosystems. These include primary compounds emitted directly from specific sources as well as so-called “secondary” compounds that are produced by chemical reactions in the atmosphere, namely ozone and particulate matter.

This chapter not only looks at current methods for measuring concentrations and fluxes, but also at methods for attributing the origin of atmospheric compounds to sources of agricultural origin and methods for understanding the reactive mechanisms in the atmosphere that lead to the formation of aerosols and ozone. This makes it possible to assess the impacts of agriculture-related compounds on human health and the environment. At the end of the chapter, an overview is given of emerging techniques for measuring pollutants and greenhouse gases that will soon help scientists better characterize agricultural emissions and the impacts of air pollution on agriculture. Readers who want to learn more should read the ADEME report “Measuring Emissions from Livestock Farming: Greenhouse Gases, Ammonia and Nitrogen Oxides” (Hassouna and Eglin 2016), which deals with these compounds specifically as well as with methods that apply to all types of compounds.

1 Methods for Measuring Families of Chemical and Biological Compounds in the Atmosphere

The atmospheric pollutants emitted by agriculture or having an impact on crops or livestock cover a variety of gaseous or particulates compounds (chapter “[The Main Pollutants and Their Impacts on Agriculture, Ecosystems and Health](#)”). Measuring these compounds involves a wide range of techniques, most of which use methods established over decades (aqueous chemistry, gas chromatography, chemiluminescence, spectroscopy, weighing, microscopy, optical counting). However, improvements and more widespread use of these techniques has enabled the development of

Textbox 1 Measuring Airborne Pesticides

Understanding the effects of agriculture on air quality requires large-scale measurement campaigns that, for semi-volatile pollutants such as pesticides, are complex and costly. Concentration levels cover a fairly wide range, from a few $\text{pg} \cdot \text{m}^{-3}$ away from application to a few $\mu\text{g} \cdot \text{m}^{-3}$ over the source (Guiral et al. 2016). Currently, no online analytical system is available and operational to assess air contamination from these substances (it should be noted, however, that the latest generation PTR-MS analysers offer interesting and promising prospects for the future; see Vesin et al. 2012). The most common sampling systems in France use a pumping system (which flowrates differ depending on the system) to trap compounds: a filter captures them in the particulate phase while a solid adsorbent (PUF, XAD) traps them in the gaseous phase (ANSES 2017). The compounds are then extracted with organic solvents and subsequently analysed in the lab. However, the ability of these systems to separate the gaseous and particulate phases is biased due to volatilization of pesticides from the particles trapped on the filter towards the downstream gas adsorbent. The sampling time with this type of system most often varies between one and 7 days. For concentration measurements over shorter time steps (a few hours), low-flow samples on Tenax adsorbents can also be used. The trapped compounds can then be thermally desorbed, improving the quantification limits. These adsorbents are generally used for monitoring emissions from volatilization (Bedos et al. 2006).

To monitor pesticide concentrations in the atmosphere on a large scale, passive sampling is an interesting alternative method because of its simplicity (light, easy to install, no energy source required) and low cost. The principle consists in sampling the ambient air by a “diffusive” flux through a gas-permeable membrane and capturing the compound on a trapping system (e.g. filter impregnated with an adsorbent). These techniques are commonly referred to as “diffuse sampler”, “passive sensor” or “integrative sampling techniques”. These techniques are currently used with ammonia (Sutton et al. 2001) and NO_2 (Tang et al. 2001). These samplers are used for persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs), organochlorine pesticides (OCs) and polycyclic aromatic hydrocarbons (PAHs). Studies on pesticides using these sensors are beginning to be published in the United States and France (Levy 2016). One limitation of these methods is the durability of the adsorbents and efforts must be made to accurately determine the sampled air volume.

multi-component measurements. Notable examples include the contribution of quantum cascade laser diodes in the field of spectroscopy as well as flight time methods and controlled ionization modes such as proton transfer in mass spectrometry. Table 1 lists the most important compounds in agriculture and provides the existing analytical methods for each with the corresponding bibliographic

Table 1 Overview of methods for measuring the most relevant gaseous and particulate compounds for agriculture

Family	Compound	Concentrations in agricultural areas	Fluxes on agricultural canopies	Measurement methods	References
Nitrogenous species	NO _x	0.1 to 200 ppb	-0.3 to 2 nmol m ⁻² s ⁻¹	Chemiluminescence Ultraviolet-visible spectroscopy (UV-vis)	Villena et al. (2012) Fuchs et al. (2010)
	NH ₃	0.1 to 1000 ppm	-10 to 200 nmol · m ⁻² · s ⁻¹	Chemiluminescence Denuder and conductivity	Marx et al. (2012) Von Bobrutzki et al. (2010)
				Infrared (IR) spectroscopy	Von Bobrutzki et al. (2010)
	HNO ₃	0.01 to 5 ppb	-0.001 to -0.25 nmol · m ⁻² · s ⁻¹	Mass spectrometry	Sintermann et al. (2011)
				Denuder and chromatography	Nemitz et al. (2004)
			Passive diffusion sampler	Zbieranowski and Aherne (2012)	
			Mass spectrometry IR spectroscopy	Le Breton et al. (2014)	
Sulphur species	HONO	10 to 1000 ppt	-0.1 to 0.2 nmol · m ⁻² · s ⁻¹	Spectroscopy	Barnes and Rudziński (2013)
				Chemical conversion	Laufs et al. (2016)
			Denuder and chromatography	Huang et al. (2002)	
			Mass spectrometry	Barnes and Rudziński (2013)	
	SO ₂	0.1 to 20 ppb	-0.001 to -1 nmol · m ⁻² · s ⁻¹	UV and IR spectroscopy Mass spectrometry	Kürten et al. (2011)
	H ₂ SO ₄		Mass spectrometry	Kürten et al. (2011)	
	DMS		Chromatography	Borrás et al. (2016)	
	H ₂ S		Chromatography	Borrás et al. (2016)	

(continued)

Table 1 (continued)

Family	Compound	Concentrations in agricultural areas	Fluxes on agricultural canopies	Measurement methods	References
Volatile organic compounds	Oxygenated VOCs	1 ppt to 50 ppb	1 to 1000 $\text{nmol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$	Chromatography	Karl et al. (2005)
	Terpenes			Mass spectrometry	Apel et al. (2008) Abis et al. (2018)
Radicals	OH, NO ₃			Spectroscopy	Fuchs et al. (2012)
Ozone	O ₃	1 to 200 ppb	-30 to 5 $\text{nmol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$	Mass spectrometry	Fuchs et al. (2012)
				UV-vis and IR spectroscopy	Hoffman et al. (1995)
				Chemiluminescence	Gusten et al. (1992)
SVOCs	PAH			Electrochemistry	
	Pesticides	0.01 to 1000 ppt	0.001 to 2 $\text{nmol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$	Chromatography Chromatography/MS, MS/MS, ECD, FID etc.	Bedos et al. (2006)
PCB				Chromatography	
Hydrochloric acid	HCl	0.1 to 200 ppt	-0.0001 to 0.01 $\text{nmol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$	Denuder and chromatography	Nemitz et al. (2004)
Carbon monoxide	CO	1 to 2 ppm		NIR and IR spectroscopy	Catoire et al. (2015)
				Electrochemistry	Mead et al. (2013)
Greenhouse gases	CH ₄	1800 to 1900		Chromatography	Miller (2004)
				NIR and IR spectroscopy	Goopy et al. (2011)
	CO ₂	300 to 1000 ppm		NIR and IR spectroscopy	Guimbaud et al. (2011)
				Mass spectrometry	White et al. (2002)
	N ₂ O	300 to 5000 ppb		Chromatography	Rapson and Daeres (2014)
				NIR spectroscopy	Kang et al. (2014)

Aerosols	PM2.5	5 to 50 $\mu\text{g} \cdot \text{m}^{-3}$	1 to 500 $\text{ng} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$	Optical counters	Liu and Daum (2000)
	PM10	5 to 120 $\mu\text{g} \cdot \text{m}^{-3}$	1 to 2000 $\text{ng} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$	Weighing Microscopy Spectroscopy Thermo-optics Mass spectrometry	McMurry (2000) Moosmüller et al. (2009) Pöschl (2005) Jayne et al. (2010) Canagaratna et al. (2007)
Viruses and bacteria	Viruses	...-15,000 cells·m ⁻³		Chromatography Microscopy	Herrero et al. (2010) Griffin (2007)
	Bacteria			Culture and impactor	Grinshpun et al. (1994) Helin et al. (2017)
Pollens and spores		0-5000 nb·m ⁻³		Impactor Microscopy	Grinshpun et al. (1994) Griffin (2007)
				HPAEC PAD BATTERY PACK WIBS	Sarda-Estève et al. (2014) Lassar et al. (2014)

SVOCs Semi-volatile organic compounds, NIR Near-infrared, PILS Particle-Into Liquid Sampler, HPAEC High-performance anion-exchange chromatography, PAD Pulsed electrochemical detection, WIBS Wideband integrated bioaerosol sensor

references as well as an estimate of the ranges of concentrations and fluxes encountered in the environment. This table is however not intended to be exhaustive as the methodologies are rapidly improving.

2 Methods for Measuring Emission and Deposition of Air Pollutants

For the current purposes, a flux is a quantity expressed in moles or mass exchanged vertically per unit area of the ground and per unit time between a surface and the atmosphere. This flux results either from a process of production or consumption of the compound in the ground or in the canopy (such as respiration or photosynthesis) or from a physicochemical equilibrium (such as cuticular adsorption of a pollutant or volatilization). Surface-atmosphere fluxes also result from a combination of molecular or Brownian diffusion processes in the boundary layer of elements located at the surface (soil, plant), and turbulent diffusion, a process that dominates when far from these objects. The vertical diffusive flux is then the product of diffusivity (which varies with altitude) multiplied by the concentration gradient between the surface and the atmosphere. Thus, if there is no turbulence (no wind), there is no turbulent diffusivity and the exchange flux becomes negligible (molecular diffusion is a very inefficient mixing process). A compound present in greater quantity at the surface than in the atmosphere has a net flux directed upward (emission, positive flux by convention) and vice versa (dry deposition, negative flux by convention) (Fig. 1).

2.1 *Measuring Fluxes Between the Biosphere and the Atmosphere*

Emission and deposition fluxes between land surfaces and the atmosphere are often broken down into several categories. This is especially true for deposition, which is divided into dry deposition (diffusive flux of gases and very fine particles) and wet deposition (deposition due to rain) (chapter “[Mechanisms of Pollutant Exchange at Soil-Vegetation-Atmosphere Interfaces and Atmospheric Fate](#)”). This section will not cover wet deposition, which is basically measured by rainfall measurement and rain chemical analysis. Interested readers should refer to Krupa (2002) for a review of existing methods. Several flux measurement methods have been developed since the 1960s: first for heat, water, CO₂ and momentum fluxes, and later for other compounds.

To measure a flux in the soil-vegetation-atmosphere continuum, there are two categories of methods: chamber methods, which consist of enclosing the part of the ecosystem being studied in a chamber; or non-invasive micrometeorological methods, where measurements are made in the open air above the ecosystem.

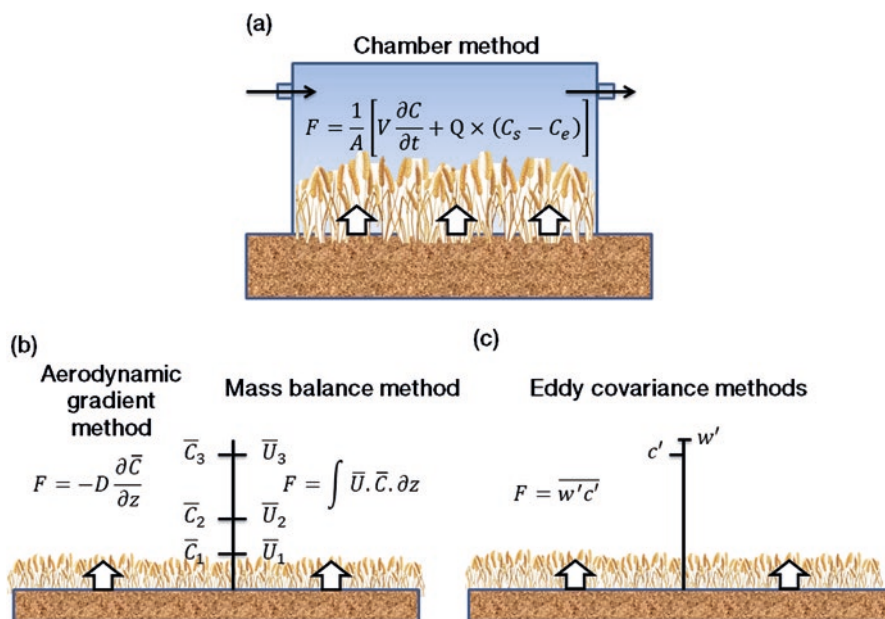


Fig. 1 Principle of the main methods used for measuring a pollutant flux over an ecosystem (a) chambers, (b) aerodynamic gradient and mass balance, and (c) eddy covariance. C is the concentration of the compound, U the horizontal component of the wind speed, W the vertical component of the wind, D the turbulent diffusivity, z the height above ground, t the time, V the volume of the chamber and A its surface on the ground. C_e is the concentration at the inlet of the chamber, C_s the concentration at the outlet. The horizontal bars indicate a time average, and the prime, a deviation from the average. ∂ is the derivation operator

Chamber methods include static and dynamic chambers. Static chambers consist in enclosing a surface and measuring the increase in concentration over time, which is proportional to the flux. In dynamic chambers, the air in the chamber is renewed with a constant airflow of either free air or filtered air. The flux is then proportional to the difference in concentration between the inlet and outlet. Chamber methods have the advantage of being more sensitive than micrometeorological methods and therefore require less accurate analysers to measure the same flux. On the other hand, they have the disadvantage of disrupting the environment of the ecosystem to be measured, and especially radiation, temperature and humidity. This makes them less representative of real-world conditions, particularly for compounds in thermodynamic equilibrium with the surface turbulence, (such as ammonia). Due to their small size, they are also more sensitive to the spatial variability of emissions, which can be very high.

Micrometeorological methods include (Fig. 1):

- Mass balance methods, which consist in calculating the balance of the horizontal fluxes entering and leaving a virtual volume including the source. The horizontal flux is estimated as the product of the concentration of the compound multiplied

by the horizontal wind speed. These methods have been the most widely used to estimate ammonia emissions.

- Aerodynamic gradient methods, which consist in estimating the flux as the product of the vertical concentration gradient and turbulent diffusivity, in accordance with Fick's Law. The method is therefore based on measuring the vertical concentration gradient above the ecosystem by sequential measurements on a single sensor or several sensors. The turbulent diffusivity is estimated from wind speed and air temperature gradient measurements or turbulence measurements.
- Eddy covariance methods, which consist in "counting" the rising and falling molecules, are based on high-frequency measurement of the vertical wind component and compound concentration. These methods, which are becoming standard today, will be detailed later in this chapter.

Micrometeorological methods assume that the flux measured a few meters above the surface is equal to the flux at the surface. This is not necessarily the case if there are sinks or sources of the molecule of interest, especially from photochemical or heterogeneous reactions in situ in the air column between the surface and the measuring height. For example, for O_3 , NO_x and BVOCs, corrections must be made to evaluate the surface fluxes from the fluxes measured at a certain height above (Stella et al. 2012; Vuolo et al. 2017).

Each method is suited to a given scale and has both advantages and disadvantages. The chamber method has a very low detection threshold and is relatively cheap, but it requires a long residence time (typically a few minutes), which can then modify the environmental conditions (temperatures, radiation) at the surface, make the chemical reactions significant and therefore bias the measurements. This method is also not always representative (square meter scale) of the flux at the field scale because of the spatial and temporal variability of some processes. The mass balance method is less sensitive, but it does not disrupt the observed system. However, it is only suitable for small sources (several dozen to a few hundred square meters), because the plume emitted by the source must be integrated over its entire height. This method is also sensitive to the ratio between the background concentration and the concentration over the source. The aerodynamic gradient method (detailed in Textbox 2) has a relatively low detection threshold and is suited to scales ranging from one to several dozen hectares, but it requires very good resolution between measurement levels and therefore a high analyser accuracy. The use of a single analyser with a level switching system is suitable provided that the signal is not too unsteady and therefore does not change from one level to another. The eddy covariance method is now the standard, because it is based on a direct measure of the flux. It is appropriate at the same scales as the gradient method and requires a good measurement resolution. It is not very sensitive to zero drifts and is suitable for long-term measurements, but it requires fast analysers. This is the standard method in 2019.

2.2 The Eddy Covariance Method and its Derivatives

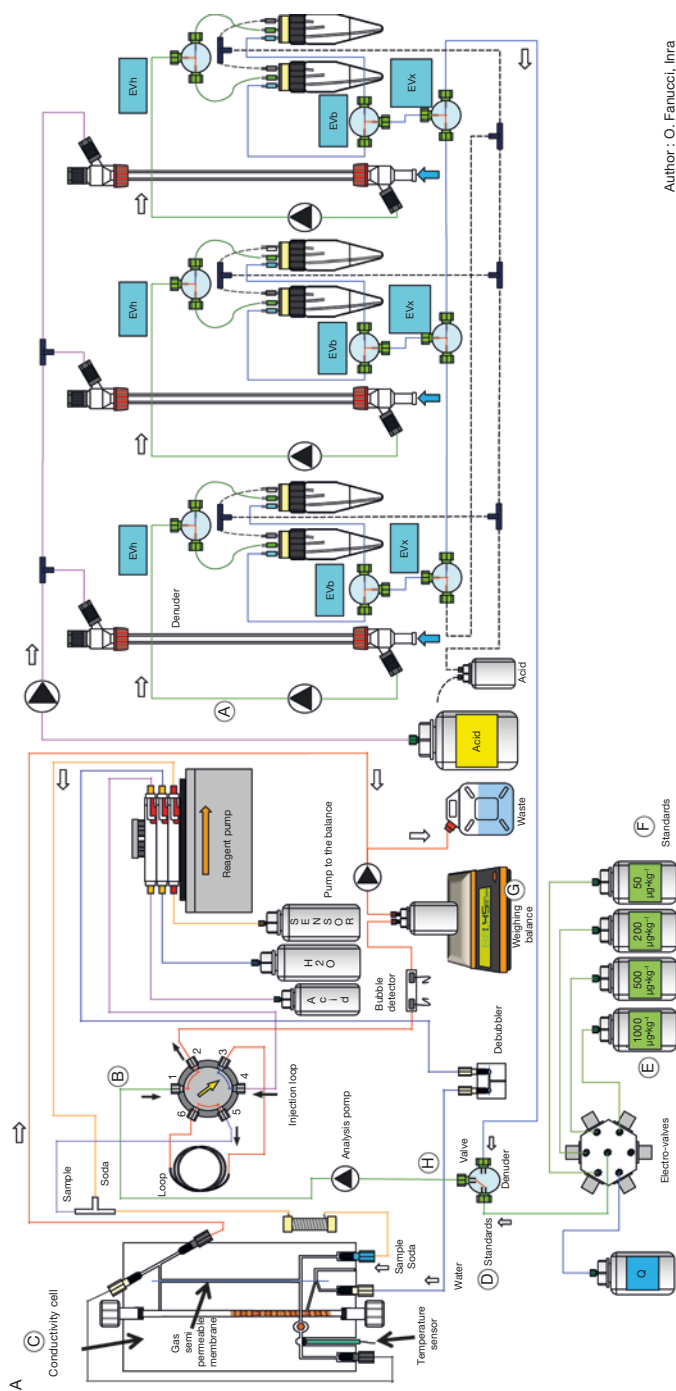
The principle of measuring a vertical flux by eddy covariances involves counting the molecules that cross the horizontal plane at the measuring point over a given period. Indeed, the quantity of molecules crossing this plane at any given time is equal to the product of the concentration of compound C ($\text{mol} \cdot \text{m}^{-3}$) multiplied by the component of the normal wind speed at this plane W ($\text{m} \cdot \text{s}^{-1}$). If this instantaneous “flux” is averaged over time, it gives the average flux F ($\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$) over the period:

$F = \overline{wc}$ (where the bar indicates a time average). In order to avoid errors due to sensory inaccuracies and zero drifts, the above equation can be developed to show only fluctuations in wind speed and concentration around the means (w' and c' are not affected by drifts). It has thus been established that $F = \overline{w'c'}$ (Aubinet et al. 2000). However, several fundamental assumptions are necessary for the establishment of this law, and the determination of what requires high-frequency concentration measurement is rarely unbiased. Two fundamental hypotheses in particular will limit its application. First, the flux must be homogeneous horizontally (so that $\overline{w} = 0$) and stationary (so that c' and w' are normally distributed) over a period of 15 min to 2 h, i.e. that there are no sudden variations in climate or airflow during these periods. Readers wishing to explore these concepts further should refer to Mahrt (2010). Second, the measurement must be made at a higher frequency (typically 10 to 20 Hz) than the frequency of the vortices that carry the mass and over a

Textbox 2 ROSAA: An Analyser Developed by INRAE to Measure Ammonia Fluxes

The Robust and Sensitive Ammonia Analyser (ROSAA), developed by INRAE, measures ammonia concentrations on six channels simultaneously every 30 min. Ammonia is first captured in mini-denuders (A) through which a slightly acidic solution runs with a controlled air flow in the opposite direction. The resulting solution is stored in tanks before injection (B) for analysis by conductivity and membrane separation (C). A series of solenoid valves (D) allows the selection of samples and standards (E) as well as quality control (F). A weighing balance (G) measures the quantity of liquid contained in each tank, while a bubble detector (H) controls the injection (Fig. 2).

The graphs of Fig. 3 illustrate the measurement of ammonia fluxes between an agricultural field and the atmosphere. These graphs show an ammonia emission sequence (fluxes are positive when they correspond to emission) following the incorporation of fava beans (*Vicia faba* family) into the soil on 22 May 2014, followed by rainfall on 25 May 2014 in a plot of the Agricultural Research Centre in Rutigliano in southern Italy. Ammonia emissions were observed following the rainfall, which brought moisture to the usually dry soil of the region, and thus allowed soil microorganisms to break down the fava bean residues and use ammonium.



Author : O. Fanucci, Inra

Fig. 2 (a) Operating diagram of the ROSAA analyser (© Olivier Fanucci, INRAE, in Loubet et al. 2012), and (b) photo of the denuders during an experiment carried out in India in 2017 (© Céline Décuq, INRAE)



Fig. 2 (continued)

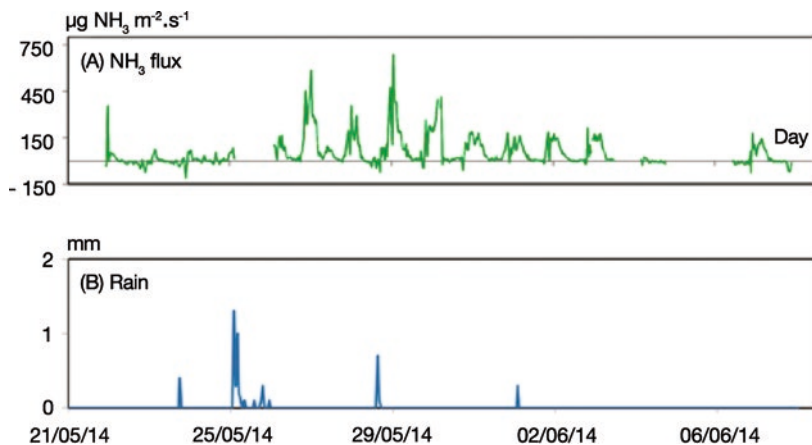


Fig. 3 Field measurements of ammonia volatilization using the ROSAA system following the incorporation of fava beans on May 22, 2014 (a) and hourly precipitation (b)

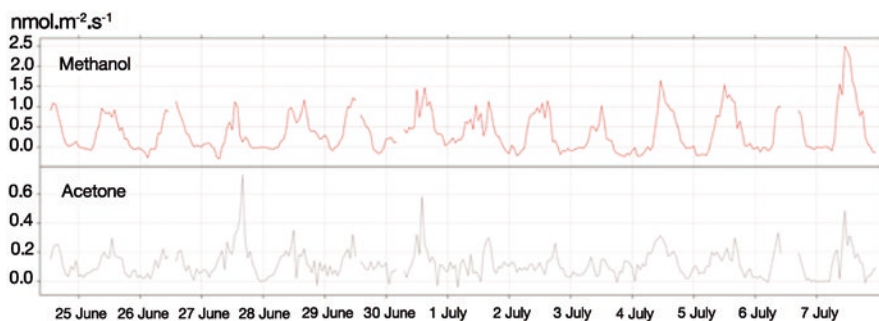


Fig. 4 Example of VOC fluxes measured by the eddy covariance method with a PTR-Qi-TOF-MS (Proton Transfer Reaction-Quadrupole interface Time-Of-Flight Mass Spectrometer) on a wheat plot in 2016 (Grignon ICOS field site). Positive values indicate emissions

sufficient duration to include the vortices at the lowest frequencies. Abundant literature is available on the eddy covariance method (see, for example, Baldocchi, 2003). An example of BVOC flux measurement by Eddy-covariance and PTR-MS is shown in Fig. 4.

There are many derivatives of the eddy covariance method to deal with the constraints of analysers that cannot measure at such high frequency or that successively measure a large number of compounds (like mass spectrometers). These include the Relaxed Eddy Accumulation (REA) method, which consists in capturing the gas to be analysed according to the sign of the vertical wind component in two containers (bags, pistons etc.) that are then analysed every 5–30 min; (Hensen et al. 2009) the Disjunct Eddy Covariance (DEC) and Virtual Disjunct Eddy Covariance (vDEC)

methods, which consist in sampling the air every 1–10 s for a duration of about 100 milliseconds and then analysing these samples (Rinne et al. 2001; Karl et al. 2002).

The eddy covariance method is a standard method today for CO₂, water and sensible heat fluxes. It has been evaluated many times using theoretical or practical approaches (Ueyama et al. 2012). Nevertheless, there are only a limited number of studies comparing this method with other techniques, and there are still important issues regarding the possible bias of the eddy covariance method and its derivatives, particularly due to high-frequency signal losses associated with a sampling system or analyser that is too slow (Massman 2000). This question is crucial for reactive or highly soluble compounds such as ammonia, which are adsorbed and desorb on sampling tubes (Whitehead et al. 2008). The non-stationarity of the flux and the footprint (area where the flux is originating from) of the measured flux are also a source of significant uncertainty, but can be identified by standard tests (Aubinet et al. 2000) and footprint models (Kljun et al. 2015). Finally, the low-frequency component of the flux related to the topography of the site (hilly, flat) and the way in which this topography is taken into account in the data processing can also create uncertainties.

2.3 Measuring Emissions from Livestock Buildings

Although this book does not focus on emissions from livestock buildings, this short section highlights the key elements for measuring emissions from these systems. Indeed, on a livestock farm, a large part of the nitrogen excreted by the animals (variable according to production and farming conditions) is volatilized in the livestock buildings in gaseous form (mainly ammonia) (Peyraud et al. 2012). Over the past 20 years, scientists have helped develop methods for measuring emissions from livestock buildings (Hassouna et al. 2016). These methods can be divided into three categories and separated according to certain metrological characteristics such as instruments, target gases, diversity of measurements, recording duration and continuity, cost, complexity, compartmentalization and environmental disturbance.

The first category includes “at source” emission measurement methods, which rely on the quantification of flowrates and concentrations for closed sources (non-intrusive, global methods), or methods that rely on the use of static or dynamic chambers (intrusive and local). The at-source methods are derived from those used in industry and are particularly suitable for so-called “ducted” emission measurements, such as in dynamically ventilated buildings with chimneys (Zong et al. 2015). Chamber methods had to be developed to study “surface” emissions such as those from slurry pits (Balsari et al. 2007) or cattle stall exercise areas (Baldini et al. 2016). Coupled with extrapolation models, they provide access to emissions from effluent.

The second category concerns the so-called “indirect” methods, which are used to estimate emissions at a distance from sources without disrupting their operation (non-intrusive, global methods). Emissions are estimated from measurements of

concentrations at a distance from the source combined with micrometeorology. Fluxes are then estimated from these measurements and dispersion models used to calculate the dispersion coefficients (McGinn et al. 2016). These techniques are quite burdensome to implement: they are highly dependent on weather conditions (especially wind direction) and are not suitable for recording emission dynamics over a breeding cycle. Finally, if they are used to characterize the emission at a surface with heterogeneous and diffuse emission sources, emissions specific to each source cannot be easily determined.

The third category involves strategies based on mass balances of volatile compound elements such as carbon and nitrogen. These methods are not based on a direct measurement of emissions, but on an estimate based on the evolution over time of element stocks. They are easier to implement than the methods described above. However, they do not provide access to emission values sorted by chemical species (N-NH₃, N-N₂O, N₂, C-CH₄ and C-CO₂), nor temporal kinetics related to technical parameters (agronomical or zootechnical) or climate variations. The accuracy of mass balances will depend on the technical and zootechnical information available, but also on the characterization of the effluents, and in some cases on the duration of the period in question for which the calculations are made (Hassouna et al. 2016).

These methods follow advances in measurement equipment and require adaptations, such as to take into account the variability of livestock systems. For some, there are detailed protocols that have been the subject of national or international consensus to move towards standardization (de Klein and Harvey 2012).

3 Source Apportionment Methods

The methods presented in the two previous sections make it possible to directly measure the fluxes of identified compounds emitted from, or deposited to, agricultural systems. This section focuses on two methods that can be used to both identify and quantify the contribution of agricultural sources to air pollution. The first method (measuring the oxidative capacity of the atmosphere) quantifies the impact of agricultural sources on air pollution and thus identifies gaps in knowledge about the compounds that are emitted. The second method can be used to attribute the origin of the pollution measured at a particular point and thus to quantify the share of agriculture in this pollution.

3.1 *Identifying Missing Sources by Measuring OH Reactivity*

Among the air pollutants emitted from different sources (whether natural or anthropogenic, including agricultural emissions), the VOC chemical family cannot be exhaustively characterized. Indeed, recent studies suggest that there are more than

10^4 – 10^5 VOCs present at trace levels in the atmosphere (Goldstein and Galbally 2007). Even if increasingly sophisticated measurement methods can be used to focus on the most significant VOCs, it is essential to ensure that compounds potentially important for atmospheric chemistry are not ignored, as they are not measured by existing techniques. One method for this diagnosis is the so-called “OH reactivity measurement”. Indeed, the OH hydroxyl radical is the main oxidant in the troposphere and the main sink for the vast majority of VOCs (as well as other species such as methane or carbon monoxide). By measuring the total OH reactivity and comparing it with that calculated from the sum of the reactivity of the individually measured compounds (see equation below, where X_i represents any compound reacting with OH and k_i is the associated kinetic constant), it is thus possible to verify that all compounds important for atmospheric OH reactivity are well measured.

$$\text{Reactivity} = \sum_i k_{i(\text{X+OH})} [X_i] \quad (1)$$

The difference between measured and calculated reactivity, if significant, is called missing reactivity. Studies carried out over the last 10 years show significant missing reactivity (up to 80%) in many environments, particularly in ecosystems that emit biogenic compounds (Nölscher et al. 2016), thus potentially in managed ecosystems as well.

Different methods have been developed for measuring total OH reactivity (which also represents the inverse of OH lifetime) and are described in the recent publication by Yang et al. (2016). Among them, the Comparative Reactivity Method (CRM) is particularly suitable for teams specialising in VOC measurements, since it uses instruments common in the atmospheric chemistry community (e.g. PTR-MS, gas chromatography) as detectors. Developed in the late 2000s by Sinha et al. (2008), this method is based on the injection of a tracer (not existing in the real atmosphere, but reacting with OH according to a known kinetic constant) into a glass reactor where OH radicals are artificially produced. The alternative injection of zero air and ambient air (the reactive species of which will react with OH) into the reactor will allow the reactivity of the ambient air to be calculated by difference.

This CRM method has been deployed several times in the field and for the first time on an agricultural crop (wheat and rapeseed) as part of the ADEME-COV3ER project (collaboration between the Laboratory for Sciences of Climate and Environment – LSCE at CNRS and the EcoSys Unit at INRAE) in spring 2016 and 2017 (Bsaibes et al. 2020). Figure 5 shows that in an environment dominated by isoprene emissions, a good recovery of measured and calculated daytime reactivity was observed. However, there was a lack of reactivity during certain periods, which could be due to unmeasured species linked to, among other things, the oxidation of biogenic compounds (Zannoni et al. 2016). The measurement of OH reactivity is therefore an important contribution to VOC source characterization, particularly those that are very poorly documented, such as agricultural sources.

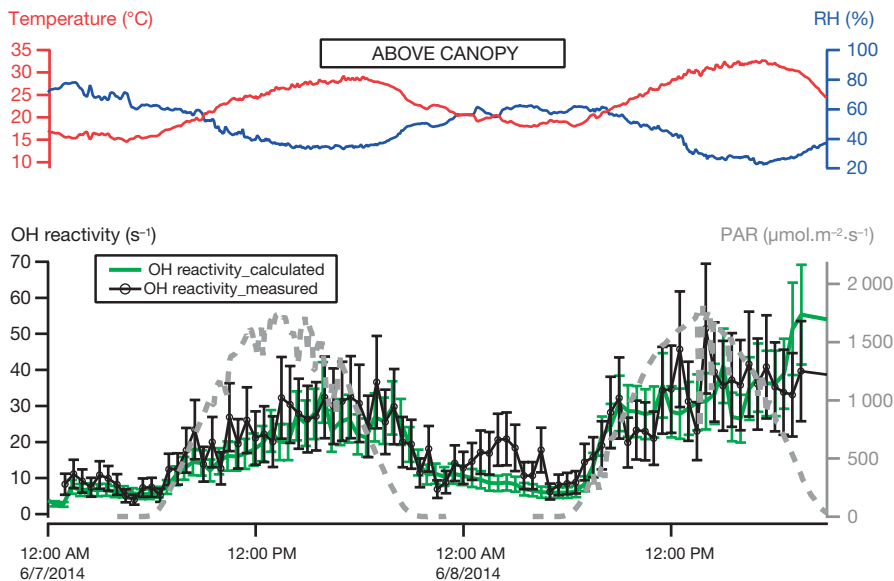


Fig. 5 Total measured OH reactivity (in black) and calculated OH reactivity (in green) at the Haute-Provence Observatory in June 2014, for a forest of downy oak trees. Atmospheric conditions – temperature, relative humidity (RH) and photosynthetic radiation (PAR) – are also reported (Zannoni et al. 2016) (under Creative Commons 4.0 license)

3.2 Source Apportionment by Positive Matrix Factorization and Isotopy

Several families of complementary mathematical models can be used to identify and estimate the contributions of the various pollutant emission sources to the air composition (referred to here as source attribution): dispersion models known as “source-oriented” using source emissions based on inventories, and so-called “receptor-oriented” models, based on concentration measurements at a site. Receptor-oriented models attempt to identify source signatures based on measurements of chemical compounds observed in the ambient environment (the study site). The most commonly used receptor models are the Chemical Mass Balance (CMB) model, which requires a very good knowledge of the chemical profiles of the sources at emission, but can be applied to a single sample; and the Positive Matrix Factorization (PMF) model, which do not require this detailed knowledge a priori, but do require a large number of samples. Over the past decade, the number of studies using receptor-oriented models has increased steadily. In order to harmonize source apportionment methodologies using these models, a guide was created in 2014 by various actors as part of a European undertaking (Belis et al. 2014). In addition, a comparative exercise to apply these models to the same dataset (chemical composition of suspended particulate matter) was organized in 2016 at European

level in order to assess the potential dispersion of the results. The Delta-SA tool was thus developed and made available online for the evaluation of source apportionment models.¹

PMF models (Paatero and Tapper 1993) are based on the principle of mass conservation. The mass balance of each of the selected chemical species present for each of the samples at the receiving site must then be calculated:

$$x_{ij} = \sum_{k=1}^p g_{ik} f_{kj} + e_{ij} \quad (2)$$

where x_{ij} is the concentration of species j in sample i , g_{ik} the contribution of source k to sample i , f_{kj} the concentration of species j for source k , e_{ij} the residual portion, not explained by the model, and p the number of emission sources. To be physically interpretable, the non-negativity of factors is a constraint integrated into the calculations. By its principle of resolution (minimization of the residual portion by least squares point by point), the results of the PMF are quantitative (for primary species with low reactivity). This model also incorporates the uncertainties of all observations to account for the level of confidence attributed to the concentration data.

This method therefore performs factor analysis by decomposing a data matrix, corresponding to measured concentrations, of size $n \times m$, where n is the number of samples and m the number of chemical species, into two matrices: one corresponding to the contributions of emission sources p (called factors) for each sample n , of size $n \times p$, and the other corresponding to source profiles (chemical composition), of size $p \times m$. This approach therefore deconvolves into different factors by combining in each factor mass fractions of each of the chemical species, whose concentrations change over time in a similar way. Geochemical knowledge (factor composition, identification of tracers, adequacy with seasonal cycles or known specific episodes, etc.) can be used to assign a source or emission process signature to each of the factors a posteriori.

PMF models are mainly applied to particle speciation. The methodology also applies to deposition, persistent organic pollutants (POPs, PAHs, etc.), VOCs and particle size distribution. Particular attention should be paid to the potential reactivity of species (especially for gases), since the principle of mass conservation of a species between source and receptor may no longer be respected. Nevertheless, this approach has been used to qualitatively identify signatures from sources or processes (see, for example, Sauvage et al. 2009).

The success of these approaches is based on an appropriate experimental strategy. The first factor is the representativeness of the study site. The choice of species is also important and should include specific tracers for the sources. It may be interesting to combine different information such as gas and aerosol speciation, or to consider auxiliary data such as micrometeorological parameters. In all cases, the number of observations should be sufficient to discern co-variations of species and identify signatures from sources.

¹<http://source-apportionment.jrc.ec.europa.eu/>

There are several PMF variants (PMF/ME-2 SoFi, EPA PMF 5.0) and developments of these models are ongoing. Figure 6 provides an example of the results of research in the Arve Valley in the French Alps, which takes advantage of these opportunities (Chevrier 2016).

As far as the authors of this book are aware, there is currently no PMF-type study identifying a specific agricultural source factor using these techniques. There are likely many reasons for this. First, agricultural sources are very diverse, and their chemical profiles are equally variable, not well known and poorly characterized by specific tracers. For sources that could be well identified (such as pesticide sprays), there is no dedicated PMF study that integrates analyses of these molecules. Second, species such as crustal dust (typical in tillage) are also emitted from other sources, which hinders the development of a well-identified agricultural factor. Finally, since a significant share of agricultural emissions is also present in gaseous form, a PMF approach would require a combination of gaseous and particulate species, which is

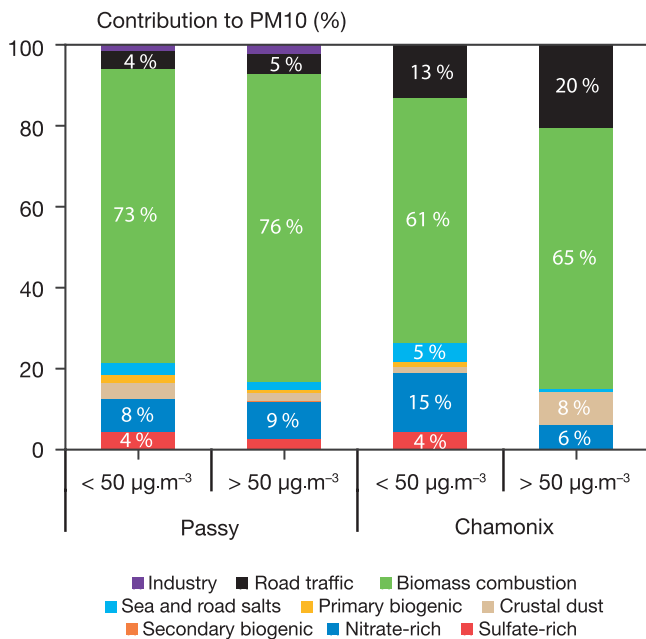


Fig. 6 Example of a source apportionment result for an environment with a low impact from agriculture.

Contributions of sources to PM10 in winter for two sites in the Arve Valley (French Alps), estimated by a PMF/ME-2 source-receptor modelling approach. The data were obtained between November 2013 and October 2014. The dataset integrates aethalometer measurements and data from radiocarbon analysis. Winter averages (winter 2013–2014) are presented for cases excluding pollution episodes ($\text{PM}_{10} < 50 \mu\text{g}\cdot\text{m}^{-3}$) and during pollution episodes ($\text{PM}_{10} > 50 \mu\text{g}\cdot\text{m}^{-3}$). These results show that the biomass combustion source is the main source in winter in these environments, and that its share increases during episodes when the $50 \mu\text{g}\cdot\text{m}^{-3}$ threshold is exceeded

still not well developed at present and requires special precautions (such as simultaneous measurements, homogeneity of datasets, potential species reactivity). Finally, these models are currently yielding very interesting and promising results for the study of sources related to agricultural activities, given recent analytical developments and access to new tracer molecules as well as the development and harmonization of the models used.

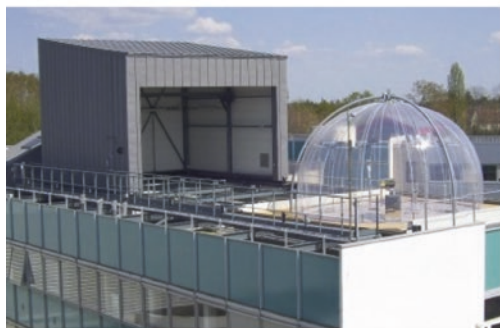
4 Methods for Measuring Atmospheric Compound Reactivity

The previous section described the methods for identifying the origin of a given pollutant and diagnosing a current or past situation. This section discusses methods to characterize the impact of one or more primary pollutants on chemical reactions and subsequently the level of air pollution. This information can ultimately be used to prioritize the emissions for which action must be taken to reduce air pollution. This information is also crucial in order to evaluate the effectiveness of emission reduction measures through atmospheric chemistry models. For example, Pozzer et al. (2017) show that a 50% reduction in ammonia emissions in Europe and North America without a simultaneous reduction in nitrogen oxide emissions from transport leads to a limited decrease (~10%) in PM_{2.5} concentration. Another example shows that the effect of insect attacks on conifers in Europe would lead to the emission of highly reactive organic compounds leading to a significant increase in PM_{2.5} concentrations (Bergstrom et al. 2014). These two studies clearly demonstrate the importance of reactivity measurements of gaseous or particulate atmospheric compounds in predicting the impact of climate change and agricultural uses and practices on air quality.

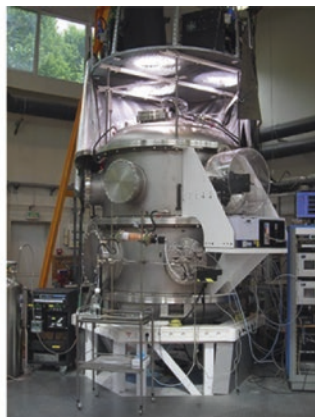
4.1 Measuring Atmospheric Compound Reactivity in Atmospheric Simulation Chambers

As indicated in the introduction to this chapter, the aim here is to understand physicochemical processes in order to be able to describe and simulate changes in the atmosphere and the impact of the biosphere on it. While it may sound straightforward, this is a rather complex undertaking. Very specific facilities such as atmospheric simulation chambers are necessary to understand the full complexity of the atmosphere. These large-volume reactors recreate controlled conditions in the laboratory similar to those actually present in the ambient air (Fig. 7).

Atmospheric simulation chambers are enclosures with walls made of Teflon, quartz, pyrex or stainless steel. These facilities are equipped with the most modern tools and analytical instrumentation for gas and aerosol metrology, such as infrared



Atmospheric simulation chamber
« HELIOS », Orléans



Atmospheric simulation chamber
« CESAM », Paris-Créteil

Fig. 7 Photos of the CESAM and HELIOS simulation chambers

and ultraviolet spectroscopic methods, mass spectrometry, chromatography (gas and liquid) or specific analysers for gases and particles. Performing studies in an atmospheric simulation chamber consists in injecting the reagents to be studied into the chambers and monitoring their temporal change as well as that of the products from their degradation. Atmospheric oxidants are either injected directly into the chamber with the reagents (as is the case with ozone), or produced in situ through chemical reactions (nitrate radicals – NO_3) or through photolysis (hydroxyl radicals – OH). Atmospheric simulation chambers can use solar radiation as a source of irradiation (e.g. HELIOS in Orléans, France; EUPHORE in Valencia, Spain) or lamps to simulate solar radiation (e.g. CESAM in Paris, France).

Isoprene (2-methylbuta-1,3-diene) is the most emitted BVOC worldwide, with estimated global annual emissions ranging between 440 and 660 Tg C (Guenther et al. 2006). Isoprene is an unsaturated species, which means it has $\text{C}=\text{C}$ double bonds, like nearly all biogenic species. Once injected into a simulation chamber (such as those shown in Fig. 7), the chemical conversion mechanism of this compound can be studied in the presence of the various atmospheric oxidants (O_3 , OH , NO_3 etc.) and the reaction products. Isoprene reacts rapidly with the OH radical by bonding to one of the unsaturated carbons. In addition to kinetic studies, atmospheric simulation chamber work has identified the main primary products of isoprene degradation, i.e. methacrolein (MACR), methyl vinyl ketone (MVK), formaldehyde (HCHO) and 3-methylfuran (3-MF), which were found in the outdoor atmosphere (e.g. Karl et al. 2009), demonstrating the ability of simulation chambers to reproduce real environments.

As with any tropospheric VOC oxidation process, the photo-oxidation of isoprene in the presence of sufficient nitrogen oxide (NO_x) leads to the formation of significant amounts of ground-level ozone at the regional scale (Wiedinmyer et al.

2001). Additionally, since the majority of oxidation products from the photo-oxidation of isoprene are volatile, isoprene had been thought for years to not contribute significantly to the formation of secondary organic aerosols in the troposphere (Pandis et al. 1991). However, several studies on natural sites (Claeys et al. 2004) and monitoring of measurements in atmospheric simulation chambers (Boge et al. 2006) have confirmed the significant contribution of isoprene to secondary atmospheric organic aerosols.

The reactivity of pesticides in the atmosphere has been the subject of many studies in atmospheric simulation chambers. Thus, determinations of reaction rate constants have shown that a large proportion of pesticides could react with OH radicals and that this process represents a potentially important sink for pesticides in the troposphere. Solar photolysis also appears to be an important degradation process, especially for active substances such as trifluralin and chloropicrin, for which this process is the dominant atmospheric sink. Gaseous and particulate reaction products have been detected in some studies, suggesting photolysis degradation mechanisms for these chemical species.

Simulation chambers are facilities with a range of tools that can provide the knowledge necessary for parameterizing chemical reactions in numerical simulations of atmospheric chemistry. They are therefore an essential link in the knowledge chain to understand the change in air quality in response to changes in primary pollutant emissions from agriculture that are related to changes in agricultural uses and practices and agroecosystem responses to climate change.

4.2 Measuring Atmospheric Compound Reactivity Under Outdoor Conditions

The previous section covered the existing means to characterize atmospheric compound reactivity in the laboratory. However, the complexity of the atmospheric composition exceeds what can be simulated under controlled conditions. This is why it is important to measure also this reactivity in situ.

A direct reactivity measurement method consists in estimating the flux divergence of a compound between two measurement heights. This estimate gives the quantity of compound produced or consumed during its transport between the two levels. This is shown by Finco et al. (2018) for NO and ozone. In some cases, it may also be possible to compare the measurements with a physical transfer model. Large differences between model outputs and observations may be interpreted as a result of chemical reactions (Lamaud et al. 2009; Kammer et al. 2019).

Another measure of field reactivity is the direct use of atmospheric simulation chambers described in the previous section in the field. As in the laboratory, the compounds are exposed to a known amount of ozone, OH radicals or NO₃. Observation of the decrease in OH radicals, ozone and reactive gases then makes it

possible to directly assess reactivity in the real atmosphere and the potential for aerosol formation (e.g. Lambe et al. 2011).

Reactivity can also occur on longer time scales. Indeed, if the less reactive compounds are weakly oxidized in the near field, they will react during their transport in the atmosphere. Thus, the older an air mass is, i.e. the farther from the source, the more oxidized it will be: this is called ageing of the air mass. The age of an air mass can therefore be evaluated by comparing the ratio between two compounds of different reactivity, whose source ratios are known. For example, in the context of an anthropogenic air mass, the larger the ratio between benzene and toluene, the older the air mass will be (Gelencsér et al. 1997). To assess the ageing of an aerosol population, the methodology consists in looking for tracers of advanced reactivity, such as the presence of organosulfur compounds or compounds of high molecular weight, or the oxidation state of particulate organic matter (e.g. Kristensen et al. 2016).

It should be noted that, despite its importance, there are currently very few reactivity measurements for the agriculture sector. There is therefore a real need to develop this type of field experiments in order to better characterize the impact of agriculture on air quality and climate.

4.3 Pesticide Reactivity on Aerosols

The majority of commonly used pesticides are semi-volatile organic compounds and are therefore often associated with atmospheric particles. The study of heterogeneous reactivity is important, as the transformation kinetics of pesticides in the particulate phase may be slower than in the gaseous phase (Socorro et al. 2016). The field of investigation is vast, because the adsorption medium (origin, specific surface area, pore size, hydrophobicity etc.) plays an important role in reactivity. Today, while most studies are conducted on mineral particles such as silica, quartz, kaolinite and Arizona sand (Socorro et al. 2015), there are also studies using organic media (Wang et al. 2012) or even plant media such as apple leaves (Sleiman et al. 2017). The compound is deposited on the medium by various methods (liquid-solid adsorption, gas-solid adsorption, in situ formation). The compound-coated particles are then exposed to light or atmospheric oxidants (ozone, OH and NO₃ radicals) in the presence or absence of moisture. Second-order constants and the half-life time of products are determined from changes in concentrations of particles, radicals and reaction products. The kinetic constants obtained can sometimes vary by several orders of magnitude depending on conditions such as the type of substrate characteristics, humidity, the recovery rate of the pesticide on the aerosol, as well as due to experimental designs or the calculation method. The modelling of these processes is still in the development phase. More studies will be required to produce indisputable references (Socorro et al. 2017).

5 Future Measurement Methods

The previous sections presented existing methods to characterize emissions from agricultural land and the potential for the formation of secondary pollutants. This chapter explores recent technological developments that show a strong potential to better assess agricultural sources of air pollutants and the impact of air pollution on agricultural land. These include remote sensing of ammonia and particulate matter, as well as inverse modelling to constrain emissions through spatialized measurements. Meanwhile, advances in measurement techniques, such as mass spectrometry and spectroscopy, are enabling scientists to measure more compounds in smaller concentrations at a faster rate and using smaller instruments.

5.1 Remote Sensing of Ammonia Concentrations

Besides pesticides, ammonia is the most characteristic atmospheric compound of intensive agriculture activities. Its lifetime in the atmosphere is short and its concentration is therefore highly variable spatially. Remote estimates of NH_3 concentration in the atmosphere from space have only been possible in recent years (Coheur et al. 2009). They provide a spatial coverage that cannot be achieved by conventional sensors but which is essential for assessing the impact of agriculture on air quality. To date, five on-board atmospheric sounders can measure ammonia: the American AIRS/AQUA and CrIS/Suomi-NPP sounders (in orbit since 2002 and 2011) and the family of three IASI sounders (Clerbaux et al. 2009) on board the European Metop-A, Metop-B, and Metop-C platforms (launched in 2006, 2012, and 2018), which combine good spectral resolution, good spatial coverage, and allow the production of global scale maps (Fig. 8). These instruments all use infrared radiation emitted by the Earth's surface, and record the modulations of the signal as it passes through the atmosphere. Since each atmospheric gases have a specific spectral signature, the concentration of a given gas in the measured atmospheric column can be deduced by analyzing the signal received by the satellite. This compound absorbs, in a particular spectral region, the atmospheric window, located between 8 and 12 μm , which is transparent to infrared radiation (except for an intense absorption band associated with ozone around 10 μm). Therefore, even if its atmospheric concentration is relatively low compared to other gases, the absorption spectrum of ammonia is very clearly visible and allows its concentration to be measured and emission fluxes to be derived using ad hoc inversion models (see section "Source evaluation by inverse modelling: ammonia"). In recent years, successive versions of the processing algorithm that extracts concentrations from the luminances observed by IASI have been developed and continuously improved, and validated with

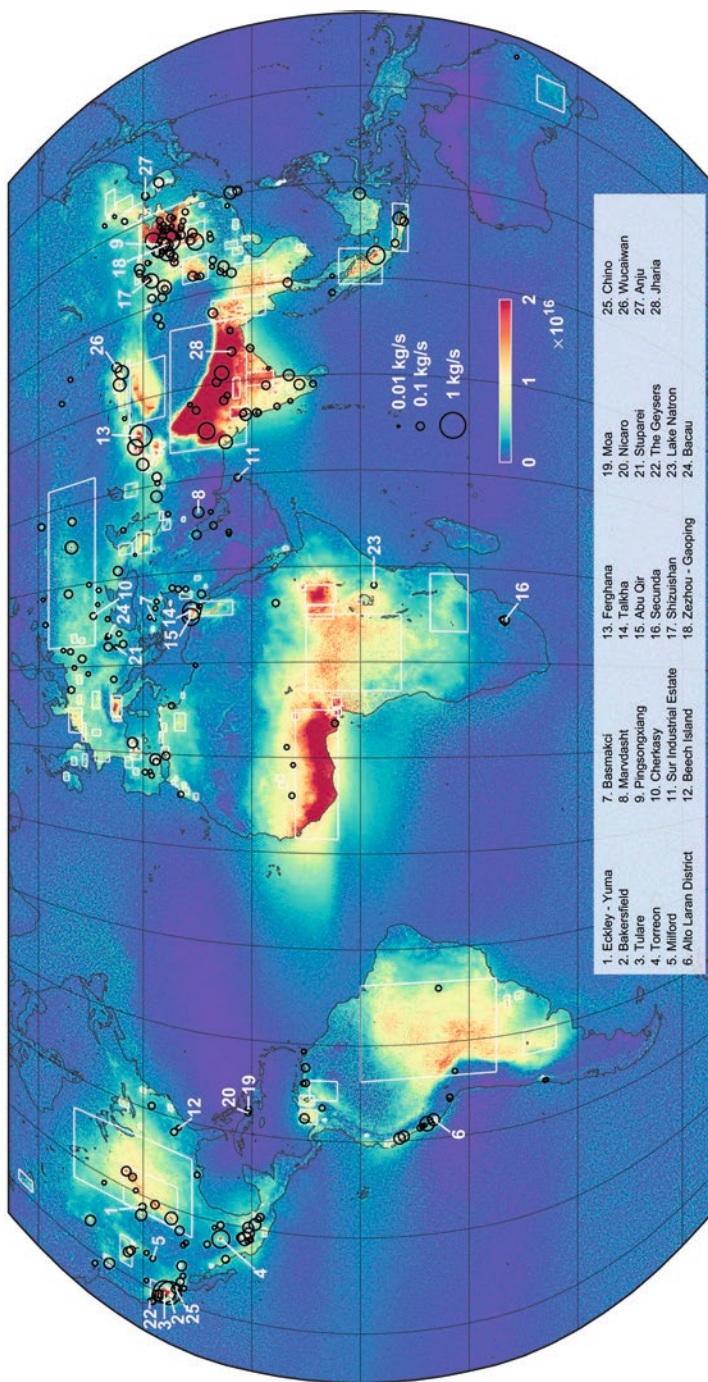


Fig. 8 Mapping of the ammonia content of the tropospheric column (colour scale in molecules per square centimetre) and ammonia emission hot spots (circles in kg ammonia per second) estimated by inverse modelling. (From Van Damme et al. 2018)

existing in situ measurements (e.g. Van Damme et al. 2018). Daily measurements since the launch of the IASI mission are available via the AERIS² database.

5.2 *Remote Sensing of Aerosols by Infrared Spectrometry*

Agriculture contributes to the emission of primary and secondary aerosols. Remote sensing of aerosols is providing information on their size, concentration in number, and chemical or mineralogical composition (e.g. Mishchenko et al. 2004). Recent work (e.g. Clarisse et al. 2013) shows that infrared observations ($400\text{--}4000\text{ cm}^{-1}$) from high spectral resolution spectrometers (AIRS, IASI or Tanso-FTS) can be used to detect mineral particles emitted during intense episodes such as desert storms. They have several advantages: they can offer observations during the day and at night, are sensitive to the types of particles, and can simultaneously provide the gaseous phase concentrations. However, the determination of aerosol parameters (size, concentration in number, shape, chemical composition) remains challenging and time-consuming, but above all is highly dependent on the quality of the optical properties of these aerosols available in the databases (e.g. Thomas and Gaultier 2009).

Indeed, two distinct processes occur during the interaction between a light beam and a particle: absorption and diffusion. The absorption phenomenon is closely related to the particle's chemical composition while the diffusion phenomenon depends on the particle's shape and size. Only a few teams carried out these experiments on particles in the form of suspended aerosols, making it possible to characterize these processes and derive mathematical models for the inversion of satellite data (Hubert 2017). However, it is by combining different instrumental remote sensing techniques (several spectral ranges, active or passive detection, using the viewing axis or the off-axis) that aerosols could be characterized and their sources identified in the future.

5.3 *Source Evaluation by Inverse Modelling: Ammonia*

One way to check ammonia emissions assessments by spatial inventories is to use inverse modelling methods that have developed over the past two decades. These methods, which use atmospheric observations to constrain emissions, are potentially very effective to complement traditional approaches. The development of satellite observations and the improvement in their quality over the past decade have contributed significantly to the early success of these alternative methods, namely by providing information on regions that are poorly documented by in situ

²www.aeris-data.fr; https://en.aeris-data.fr/?noredirect=en_GB

measurements (see previous section “Remote sensing of ammonia concentrations”). The Bayesian approach of seeking the most likely spatial and temporal distribution of fluxes taking into account a priori fluxes, observations, the model, and associated errors is the most widely used. It was first applied on a global scale for low-reactive compounds (CO_2 , CH_4 , CO), and later for more reactive compounds to constrain emissions of NO_x (Miyazaki et al. 2017), SO_2 (Huneeus et al. 2013) and some biogenic and anthropogenic VOCs (e.g. Stavrou et al. 2015). At the regional level, NO_x emissions were mainly studied from tropospheric NO_2 columns (e.g. Mijling et al. 2013). A recent study showed the potential of IASI observations to determine agricultural ammonia emissions by combining them with the CHIMERE chemical transport model (Fortems-Cheiney et al. 2016). In particular, this study showed the possibility of restoring, with satellite observations, the daily ammonia emissions during the targeted fertilizer application period and thus improving the model’s ability to simulate ammonia and particulate ($\text{PM}_{2.5}$) concentrations during the pollution peaks. The application of inverse methods on a regional scale is expected to become more widespread using future satellite instruments such as TROPOMI and IASI-NG and should make it possible to move towards finer spatial resolutions and to constrain new species with greater precision. It should be noted that these inverse methods are also used to estimate ammonia emissions in the field at much smaller scales (Loubet et al. 2010, 2018) using local concentration measurements and turbulent dispersion models.

5.4 Mass Spectrometry

One of the important points for characterizing emissions of pollutants from agriculture concerns how the concentrations of the compounds in question are measured. Mass spectrometry is a technique that is rapidly progressing and can be used to quantify an ever-increasing number of compounds in ever smaller concentrations. This method is especially essential for pesticides and BVOCs.

Mass spectrometry (alone or in combination with pre-separation methods, e.g. chromatography, electrophoresis, ion mobility) is a highly sensitive, high-resolution and selective technique. Mass spectrometer performance is generally characterized by its mass limit (devices up to 10^6 Dalton are now available); resolution (ability to separate ions with very close mass to charge ratios, the best performance being $\sim 10^{-6}$ from the mass of the measured ion); accuracy of the m/z scale (currently in the ppb/ppm range for the best instruments); and sensitivity (ability to detect small quantities, often in the attomole/ppb amounts). There is a wide variety of mass spectrometry devices available on the market or developed in research laboratories, especially with regard to ionization sources (ionization by electronic impact, photoionization, chemical or proton transfer ionization, electron fogging, etc.) and analyzers (quadrupole, ion trap, time-of-flight, ion cyclotron resonance – Fourier transform, electrical and magnetic sectors, Orbitrap).

In the gaseous phase, VOC measurement by proton transfer mass spectrometry (PTR-MS) with soft chemical ionization (based on the transfer of a proton from the hydronium ion H_3O^+ to the VOC to be analysed) has been identified as the most robust method, due in particular to its rapid response, high sensitivity, and absence of reactions of H_3O^+ with the main air constituents (Ellis and Mayhew 2013). In the field of soft chemical ionization (Chemical Ionization Mass Spectrometry, CIMS), other reactants (NO^+ , O_2^+ , O^- , O_2^- , OH^- , NO_2^- , NO_3^- , iodine, acetate, etc.) to achieve charge transfer to the molecule to be analysed have been proposed to detect a wider range of compounds, not only those with a higher proton affinity than water. In recent years, PTR-MS has been successfully used to study emissions from various sources related to agriculture and agricultural practices (Park et al. 2013; Bachy et al. 2018). It has also identified VOC emissions from livestock (Yuan et al. 2017; Feilberg et al. 2015) and from different types of compost (Abis et al. 2018). There continues to be significant innovation in PTR-MS techniques or more generally CIMS (Laskin et al. 2018). These include miniaturization efforts, coupling with chromatography or ion mobility for isomer separation, or the use of special inlet modules for simultaneous analysis of the gaseous and particulate phases.

With regard to the analysis of the condensed phase of the atmospheric aerosol, there are two categories of techniques: offline approaches, in which the particles are deposited on a substrate which is then analysed by the mass spectrometer, and online analyses, where the particles are injected directly (often using aerodynamic lenses for size selection) from the atmosphere to the high vacuum of the mass spectrometer for real-time analysis on individual particles or a set of particles. Individual particle approaches (Single Particle Mass Spectrometry, SPMS) use an optical detection module for size selection (typically 0.1–3 μm) and one or more lasers for particle vaporization (ablation) and ionization of the vaporized material (Murphy 2007). This method is extremely useful for classifying particles according to their type and origin, but remains affected by significant fragmentation, due to the high power densities required for ablation and ionization with a single laser. Very recent developments seek to overcome these limitations (e.g. Passig et al. 2017). Mass spectrometry techniques for the online chemical analysis of atmospheric aerosols are becoming increasingly important for a wide range of agriculture-related emissions: detection of trace pesticides on individual particles (Barker et al. 2010); characterization of aerosols generated during grass mowing (Drewnick et al. 2008); and emissions from plants (Kiendler-Scharr et al. 2009), trees (Faiola et al. 2015), algae (May et al. 2018) and soil and litter (Faiola et al. 2014).

5.5 *Infrared Spectrometry for Ground-Level Measurements*

Infrared absorption spectroscopy is a recognized, but still under development, non-invasive method of measurement and observation. It is widely used for monitoring air pollution and greenhouse gases (Cui et al. 2012). There are many optical methods. They are differentiated by both source and detector. They can use coherent light such as lasers or non-coherent sources such as lamps or light-emitting diodes

(LEDs), which cover wider spectral range. In the near-infrared, a revolution is still underway with distributed feedback (DFB) laser diodes. Initially developed for near-infrared fiber-based telecommunications, they have been extended to measure molecules in the gaseous phase (Spott et al. 2016). These particularly robust sources operate at room temperature in the near-infrared between 1 and 2.7 μm . For the mid-infrared, alternative semiconductor sources have emerged, and are significantly better than lead salt diodes: these are the quantum cascade lasers (QCLs) that operate continuously and in a singular frequency, but which are still expensive, especially for models operating at room temperature.

The light transmitted by a medium of length L illuminated with an intensity I_0 follows an exponential decay law known as the Beer-Lambert law, $I = I_0 e^{-\alpha L}$, with $\alpha(\lambda) = n \sigma(\lambda)$ (expressed in cm^{-1}) the absorption coefficient of the gas directly depending on the wavelength λ , considered as a function of the effective absorption cross-section $\sigma(\lambda)$ ($\text{cm}^2 \cdot \text{molecule}^{-1}$) and the concentration n of the molecular species considered. Measuring a very low concentration therefore implies very good sensitivity on the absorbance measurement α , but also a choice of wavelength for which $\sigma(\lambda)$ is high. Optimizing the signal-to-noise ratio of I and I_0 is therefore extremely important, but it is equally important to increase the path of the light through the sample as much as possible. One method is to use multi-pass cells, which are used in many compact commercial devices, but their sensitivity is limited to around 10^{-8} cm^{-1} (e.g. Aerodyne QCL, Pitt et al. 2016). The resonant cavity technique, known as cavity enhanced absorption spectroscopy (CEAS), can be compared to an absorption amplifier (O'Keefe et al. 1999). Another way to measure cavity absorption losses is to measure the lifetime of photons in the cavity. This is called cavity ring down spectroscopy (CRDS) (see, for example, Nakaema et al. 2011). The lifetime is measured by simply switching off the laser source when the cavity contains enough photons; the cavity then empties exponentially. The resonance damping time depends on the reflectivity of the mirrors and the absorption $\alpha(\lambda)$. This technique is currently used by the manufacturer Picarro (Picarro Inc., Santa Clara, California, USA). Other manufacturers use the signal transmitted by the cavity directly, such as Los Gatos Research (LGR, San Jose, California, USA) or AP2e (AP2e ProCeas, Aix-en-Provence, France).

Many chemical species absorb in the near- and mid-infrared. These are of course the main greenhouse gases (CO_2 , N_2O , CH_4 , H_2O), but also other more reactive molecules that may have an interest for air quality. Current spectrometers are capable of detecting a light intensity attenuation of 10^{-9} ; the detection threshold by species will depend on the intensity of their absorption lines and possible interference with other species. Table 2 shows, for example, the detection limits that can be reached for different molecules depending on the wavelength chosen.

Table 2 Example of detection limits that can be reached for different molecules in 1 s

Species	CO_2	H_2S	NH_3	CO	CH_4	H_2O	HCl	C_2H_4	HF	NO, NO_2	N_2O
Detection limit at 1 Hz (ppb)	300	100	1	1	1	1	1	50	0.2	0.1	0.1
λ (nm)	1600	1604	2326	2326	2326	1390	1742	1620	1297	410	4464

5.6 *Connected Sensors*

Mini-sensors, which were once known for their low sensitivity and reserved for specific applications (e.g. workplace monitoring), have recently undergone unprecedented development leading to smaller, cheaper, potentially high-performance and increasingly connected devices. In the field of air quality, these mini-sensors can measure in near-real time (resolution of a few minutes or better) the concentrations of various gaseous and particulate pollutants including carbon monoxide, ozone and nitrogen oxides. However, it should be noted that many interferences are associated with this technique, which requires suitable correction algorithms. Sensitivity and accuracy are key challenges for mini-sensors, because – as a recent study by the Joint Research Centre (Ispra, Italy) on nitrogen oxide sensors showed – many of them do not adapt their performance to concentration levels and the variability of compounds in “real” atmosphere. For particulate pollutants, different types of sensors have been developed. Portable micro-aethalometers can measure a black carbon equivalent and have already been used in several studies (e.g. Reche et al. 2014).

The use of these technologies in the field of pollution in rural areas is still marginal for the time being, but significant developments are expected in the coming years, with the emergence of sensors to measure compounds related to agricultural emissions. The main targets are ammonia (NH_3) and small secondary particles (diameter $< 2.5 \mu\text{m}$), such as ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$), ammonium nitrate (NH_4NO_3) or ammonium chloride (NH_4Cl). Micro-sensors based on intrinsically conductive polymers developed in recent years would provide an appropriate response to this problem. They are very efficient compared to their competitors, with a detection limit of around a few ppb (compared to 1 ppm for electrochemical cells), a measurement range over several orders of magnitude of concentrations, and finally an instant, reversible and interference-free response (Wojkiewicz et al. 2017). Research laboratories have also received requests to develop sensitive sensors likely to meet specific rural pollution measurement needs, such as the detection of hydrogen sulphide or particulate ammonium nitrate.

5.7 *Moving Towards Measuring Health Impacts*

Air pollution has deleterious effects on health, as discussed in more detail in chapter “[The Main Pollutants and Their Impacts on Agriculture, Ecosystems and Health](#)”, particularly on the cardiopulmonary system (WHO 2016). One of the exposure pathways is through the lungs after inhalation of reactive oxygen species (ROS) transported or generated by atmospheric particulate matter (PM) as well as by some oxidizing gaseous species. Oxidative stress is defined as an imbalance in antioxidants involved in the immune system’s defences, caused by the oxidative species absorbed. In the lungs, this leads to cellular damage and is the root cause of multiple pathologies such as asthma or bronchitis. While scientists are continually learning

more about the complex mechanisms governing the appearance of diseases, the regulatory indicator for issuing health alerts during particulate events only takes into account PM mass. However, a large part of PM mass has low toxicity. Conversely, some species such as transition metals and organic compounds contribute little to the total particulate concentration, but have high reactivity and toxicity.

Thus, the intrinsic ability of atmospheric species to generate ROS in a biological environment, also known as oxidative potential (OP), is a rapidly developing indicator for its relevance in predicting the harmfulness of air pollutants. This indicator incorporates heterogeneities in particle size, composition and surface area and is a promising alternative to simple PM mass concentration measurements currently in use for regulation or used in the majority of epidemiological studies (Kelly and Fussell 2012). Over the past decade or so, several *in vitro* and *in vivo* methods have been developed to measure the PO of particulate matter. *In vivo* methods consist in measuring oxidative stress biomarkers directly in the blood or urine (glutathione, cytokines, ...). *In vitro* methods consist of depositing particles on pulmonary epithelial cells and measuring the expression of markers of cellular inflammation. Because of their specificity to certain types of ROS or to certain PM components, there is no current consensus on the biochemical test that is most representative of actual health effects, and the scientific community is moving towards combinations of several methods.

No studies are currently focused specifically on the effects of agricultural emissions on health, but this area could be of interest given the concern on pesticide emissions and potentially primary biogenic species from agriculture.

5.8 Real-Time Detection, Identification and Quantification of Particles of Atmospheric Primary Biological Aerosols

Primary biological aerosol particles (PBAPs) are composed of dead or living organisms (algae, bacteria, and viruses), bioparticles (pollens, fungal spores) and various fragments (plants, excretion products). Agriculture is a major contributor to these particulate emissions. Bioaerosols range in size from a few nanometers to about 100 micrometers. They are involved in climate regulation based on their physical and chemical properties. More specifically, they can lead to cloud and precipitation formation by acting as condensation nuclei causing the formation of ice crystals, snow and water droplets (Fröhlich-Nowoisky et al. 2016).

To document bioaerosol variability in the atmosphere, they must be collected, counted and identified. Bioaerosol collection devices are based on inertial forces such as impactors or non-inertial sampling methods such as filtration or passive deposition. Generally, enumeration and identification are then carried out in the laboratory by growing cultures on selective nutrient media and observations by optical microscopy. For the collection and identification of particles larger than 10 μm such as pollens and fungal spores, the most commonly used device is the Hirst-type

volumetric sensor by Lanzoni (Grinshpun et al. 1994). A known volume of air is sucked in and particles are impacted on an adhesive strip attached to a rotating cylinder, allowing sampling over 7 days. After exposure, the strip is analysed under an optical microscope (Thibaudon et al. 2013).

The optical or chemical detection of atmospheric microorganisms in real time is a significant challenge in analytical physical chemistry. Optical detection devices are based on counting isolated particles and their induced fluorescence to distinguish particles having a biological activity (Crawford et al. 2015). The chemical detection system is based on a technique for collecting and dissolving atmospheric aerosols (Particle-Into-Liquid Sampler, PILS) coupled with high-performance liquid chromatography, with mass spectrometric detection (HPLC-MS) targeting cellular metabolites. Optical methods are simple to implement, but allow quantification without differentiation of bioaerosols, while the PILS-HPLC-MS method allows quantification and differentiation of moulds and fungal spores in the atmosphere (Sarda-Estève et al. 2014). Among the optical detection instruments tested, the Wideband Integrated Bioaerosol Sensor (WIBS) proved to be the most efficient (Lassar et al. 2014).

Today, the different approaches to detecting, identifying and quantifying the presence of bioaerosols in the air are evolving. Ongoing research to improve the sensitivity, specificity and quantification of bioaerosols will soon make it possible to offer simple and effective instruments for setting up measurement networks.

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