REVIEW ARTICLE

Why and how terrestrial plants exchange gases with air

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ABSTRACT

This work is intended as a review of gas exchange processes between the atmosphere and the terrestrial vegetation, which have been known for more than two centuries since the discovery of photosynthesis. The physical and biological mechanisms of exchange of carbon dioxide, water vapour, volatile organic compounds emitted by plants and air pollutants taken up by them, is critically reviewed. The role of stomatal physiology is emphasised, as it controls most of these processes. The techniques used for measurement of gas exchange fluxes between the atmosphere and vegetation are outlined.

INTRODUCTION

The Earth's atmosphere and the vegetation layer covering its surface (the phytosphere) are not isolated from each other. A number of physical and chemical processes occur at the atmosphere/phytosphere (or more simply, air/plant) interface, and these profoundly influence both air and plants. As a first example, the current atmospheric chemical composition has been completely modified in past geological times due to the emergence of photosynthetic vegetation on the continents about three billion years ago (Levine 1985). The primitive Earth's atmosphere, the composition of which was mainly determined by outgassing of the primitive Earth, was probably dominated by water vapour (H_2O), carbon dioxide (CO_2), molecular nitrogen (N_2), some methane (CH_4) and ammonia (NH_3). Molecular oxygen (O_2) was present only as a trace gas, and was formed by photolysis of CO_2 and H_2O. When photosynthetic plants spread out over the continents, a massive release of O_2 took place, favouring the development of respiring animals. A steady state was then reached, with a mean O_2 molar fraction of about 21%.

Photosynthesis is a biochemical process that has been known for more than two centuries, and was first discovered in Priestley's experiment (1771) and then studied by Lavoisier. The Dutch physiologist Moleschott (1851) rightly wrote: ''The field on which wheat grows feeds us. But when we cross a forest, we feed it with the CO_2 we exhale.'' This sentence summarizes in a concise way the environmental and biogeochemical equilibrium existing between photosynthetic plants and respiring animals, which continuously exchange O_2 and CO_2 with each other through the atmosphere. So, it is not exaggerated to say that plants, but also animals, profoundly influence the composition of the atmosphere. However, photosynthesis and respiration are far from being the only gas exchange processes between air and vegetation. Water vapour, which is an important atmospheric chemical, is continuously released to air by plants through evapotranspiration. This process has been described by Penman (1948), Monteith (1981) and many others. The mass fractions of water

vapour in the atmosphere are highly variable according to place and time, ranging roughly between 0 and 0.04, depending on a number of environmental and meteorological factors. The water vapour mass fraction (or specific humidity) has an essential influence on weather and climate by participating in the hydrological cycle.

A number of other gaseous substances are exchanged between air and plants in both directions: from plant to air (hereafter referred to as upward) and *vice versa* (downward). An array of volatile organic compounds (VOC), as byproducts of metabolism, are released to air by plants in significant amounts, estimated at 1200 Tg of carbon per year (Guenther *et al.* 1995). Among these, isoprene (C_5H_8) is by far the most important, as its global emission rate probably exceeds 500 Tg·year^{-1} (Wiedinmyer *et al.* 2006), outweighing the sum of all VOCs emitted through human activities around the world (ranging from 130 to 160 Tg·y^{-1}; Butler *et al.* 2008).

Besides photosynthetic vegetation, other organisms soil microorganisms or marine algae like emit substances like methane (CH_4), nitrous oxide (N_2O) and dimethylsulfide (DMS, or CH_3-S-CH_3). Methane, first identified in air by Migeotte (1948), is mostly emitted from the soil in anaerobic conditions, as in rice paddies; it is also released from faecal matter produced by livestock. Methane is a powerful greenhouse gas. Since both worldwide rice production and world livestock are directly related to human population, the increase in CH_4 concentration in air is exponential (Khalil *et al.* 2007). DMS, first discovered in ocean waters by Lovelock *et al.* (1972), is produced by marine algae as a byproduct of their metabolism, and participates in the sulphur cycle, contributing to the formation of sulphate aerosols, which have consequences on the atmospheric radiation balance and hence on climate. The substances mentioned in this paragraph are not strictly speaking emitted by photosynthetic terrestrial vegetation, and thus will not be treated in this review, but they deserve to be mentioned because of their role in the global climate system.

Chemical atmosphere/vegetation exchange can also occur from air to plant, mainly consisting of the uptake of CO_2 (Jones 1992) and various air pollutants (Omasa *et al.* 2002a) by plants. The main pollutants that can penetrate plant tissues are ozone (O_3), nitrogen oxides (NO_x), ammonia (NH_3) and sulphur dioxide (SO_2). Deposition of aerosol particles can also play an indirect role in air/plant gas exchange processes, especially when hygroscopic salts are deposited on leaves and absorbed by deliquescence water vapour evaporated from the stomata, thus modifying the stomatal aperture (Burkhardt *et al.* 2001a,b; Eichert & Burkhardt 2001). Only gaseous exchange, however, is treated in this review.

From a more general perspective, both emission and uptake of chemical substances from and into vegetation can be seen as a part of global environmental processes, described as global environmental change (Graedel & Crutzen 1993). This includes not only climate change, which involves physical variables such as temperature, wind, humidity, precipitation regime, *etc.*, but also the change in chemical composition of the atmosphere, nowadays often called "chemical climate". A synthesis of this change at European scale can be found in Slanina (1997), and at global scale in Brasseur *et al.* (2003). But see also the IPCC reports (*e.g.* Climate Change 2007).

The exchange of gases between air and terrestrial vegetation is part of a vaster system known as global biogeochemical cycling, in which chemical substances are exchanged between the different reservoirs present on planet Earth: atmosphere, oceans, biosphere and lithosphere. Molecular oxygen, water, CO_2 and many other substances are present in these reservoirs in variable quantities (expressed *e.g.* in mol) and are transferred from one to another with characteristic times (days, years, millions of years) and fluxes (mol per unit time, the area being integrated over the whole Earth surface). Global cycling has been extensively studied, both through modelling and observations (Bolin & Cook 1983; Fung *et al.* 1991; Keeling *et al.* 1993; Siegenthaler & Sarmiento 1993; Bender *et al.* 1998). In these processes, oxygen plays a crucial role, both in molecular form (as O_2) and as an element entering into the composition of many substances (water, CO_2, O_3, oxygenated organics). The main scope of the present review is not, however, a synthesis of global cycling, about which abundant literature can be found (Wigley & Schimel 2000; Jorgensen & Fath 2008; Miller 2008). Gas exchange between atmosphere and terrestrial plants, where this work is focused on is a subsystem of global cycling.

THE ROLE OF STOMATA

Stomata are microscopic pores present on the surface of leaves, constituting organs that permit gaseous substances to penetrate or leave plant tissues. The stomatal aperture is physiologically regulated in such a way as to control the quantity of gaseous matter transiting through them (Meidner & Mansfield 1968; Jarvis & Mansfield 1981; Zeiger *et al.* 1987; Omasa *et al.* 2002a; Shimazaki *et al.* 2008). Environmental conditions such as light, temperature, humidity, soil water content, CO_2 and air pollutant concentrations influence stomatal regulation, directly or indirectly. Since evaporation of liquid water uses heat, it causes cooling. If stomata are more open, more water is evaporated, resulting in lowering of the temperature. Opening the stomata is thus used by the plant to reduce foliar temperature to protect leaves from excessive heating due to the absorption of sunlight. This constitutes the thermal regulation mechanism. When the intercellular concentrations of CO_2 are sufficient for optimal photosynthesis, stomata close in order to save water (hydrological regulation). Stomatal closure typically occurs in drought conditions. A conflict between the need to reduce foliar temperature by opening the stomata and the need to reduce water use by closing them may appear in conditions of excessive drought and heat. In such cases, stomata tend to close to save water, but thermal regulation is inhibited and the leaves become too hot. The plant

then becomes stressed and, if conditions worsen, this may lead to the death of leaves.

Air pollutants may take advantage of the stomatal aperture to enter leaves. The more stomata are open, the greater are the quantities of air pollutants entering plant tissues. The role of stomata is described in great detail in Zeiger *et al.* (1987). The leaf-scale stomatal conductance for water vapour (g_{sw}) can be estimated using the multiplicative model developed by Jarvis (1976) and further developed by Emberson *et al.* (2000):

$$g_{sw} = g_{max} \cdot f_{age} \cdot f_{light} \cdot f_{temp} \cdot f_{VPD} \cdot f_{SMD} \qquad (1)$$

where the maximum stomatal conductance of a plant species (g_{max}) is modified as a function of plant development (f_{age}), light availability (f_{light}), air temperature (f_{temp}), vapour pressure deficit (f_{VPD}) and soil moisture deficit (f_{SMD}). All f functions range between 0 and 1 (LRTAP Convention 2004). A microscopic picture of stomata is shown in Fig. 1.

PHOTOSYNTHESIS AND RESPIRATION

Photosynthesis and respiration provide an important contribution to exchange processes between atmosphere and vegetation (Monteith & Unsworth 1990; Jones 1992). They involve three chemical species: O_2, CO_2 and H_2O. These processes have been known for a long time, as noted in the introduction, and play an essential role not only in plant physiology, as they ensure the survival of plants, but as regulators of atmospheric composition. For example, if vegetal biomass dramatically decreased as a consequence of a badly managed environment, the atmospheric concentration of O_2 would decrease with unpredictable consequences for the reign of animals and mankind. Vegetation also absorbs CO_2 and tends to counteract the increase of this gas in the atmosphere.

TRANSPIRATION

The release of water vapour through stomata critically depends on stomatal aperture, which generally undergoes a daily cycle, opening after sunrise, decreasing in the afternoon, and having a tendency to remain closed during the night. According to some recent work, however, stomata might remain open during the night in particular conditions (Dawson *et al.* 2007). This cycle is modulated by environmental conditions, like water supply, intensity of sunlight and wind speed. When the latter is strong, stomata close in reaction to the stress that has appeared.

Extending the theory introduced by Penman (1948) to describe evapotranspiration, Monteith (1981) used the resistance analogy to parameterise the role of surface elements that are responsible for this process by introducing the surface resistance r_s expressed in s m^{-1}. When vegetation completely covers the surface, the surface resistance is equal to the stomatal resistance, because the entire water vapour flux uses the stomatal pathway. The quantity of water vapour evaporated to the atmosphere per unit area and time is then expressed by the Penman–Monteith (PM) equation, where both water vapour flux and stomatal resistance appear. The PM equation is widely used in the field of agrometeorology. Inverting the equation permits the calculation of the stomatal resistance for evaporation if all other parameters are known. The PM equation contains parameters such as measured radiative and ground heat fluxes, temperature and humidity, and other quantities appearing in the equation (aerodynamic and laminar resistances) are accessible through parameterisations (Hicks *et al.* 1987; Garland *et al.* 1988; Massman 1993).

As far as chemical exchange between air and vegetation is concerned, the PM approach is very useful as the stomatal resistance for water vapour can be used to deduce the stomatal resistances for other chemical substances penetrating or leaving the stomata. Subsequently the fluxes of these substances through the stomata can be obtained. This can be done since stomatal resistances for different gases, *i.e.* the resistances against the diffusive transfer of these gases through the stomatal cavity are proportional to each other because the fluxes are laminar inside the stomatal cavity. Hence, the fluxes obey the laws of molecular diffusion and are characterised by a diffusive coefficient, which is constant for a given gas, but its value depends on the nature of the gas. The resistance against diffusive transfer is defined by
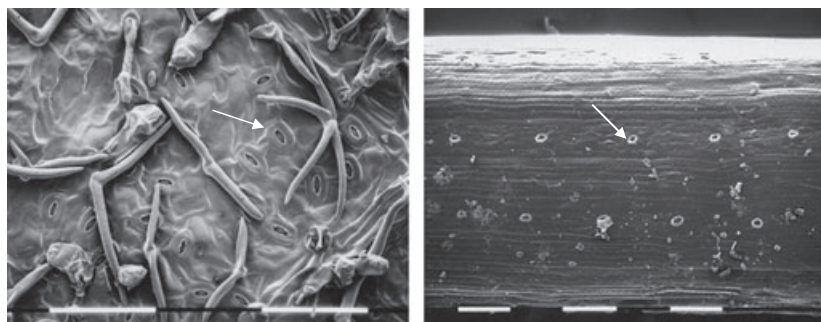

Fig. 1. Microscope view of stomata (arrow) of *Castanea sativa* (left) and *Pinus halepensis* (right). White bar = 100 μm.

$$r \equiv \int_{z_1}^{z_2} \frac{dz}{D_i}, \qquad (2)$$

where z is a spatial coordinate of the system where the diffusion process occurs, and D_i is the molecular diffusion coefficient for the gaseous i-labelled substance. Since D_i is independent from any space coordinate but depends on the nature of the diffusing substance only, we can easily integrate equation (2) over the spatial coordinate, assuming a spherical shape for the stomatal cavity. We thus obtain a simple expression for the stomatal resistance for gaseous substance i

$$r_s = \frac{z_2 - z_1}{D_i}, \qquad (3)$$

where we see that resistances are inversely proportional to molecular diffusion coefficients. Thus, if we want to know the stomatal resistance for a substance like O_3, we can relate it to the stomatal resistance for water vapour through the proportion

$$\frac{r_{O_2}}{r_{H_2O}} = \frac{D_{H_2O}}{D_{O_3}} \qquad (4)$$

We can see from the above developments that knowledge of the stomatal resistance for water vapour, *e.g.* through the application of the PM approach, is essential for studying the transfer of any gaseous substance through the stomata.

EMISSION OF VOCs

Volatile organic compounds (VOCs) constitute an important group of substances released by plants to the atmosphere. Emission of VOC species like essential oils or leaf oils has been known for a long time (Guenther 1949; Simonsen 1953). Rasmussen (1970) established that isoprene (C_5H_8), which is emitted by many plant species worldwide, is produced in a biochemical process and is not part of the composition of leaves. This compound plays an important role in atmospheric chemistry as it participates in a number of reactions producing O_3 (Trainer *et al.* 1987; Jacob & Wofsy 1988). It reacts with the OH radical, reducing the oxidising capacity of the atmosphere (Ehhalt *et al.* 1991) and increasing its ''cleaning'' capacity for air pollutants. Other VOC species are mono- and sesquiterpenes, such as α- and β-pinene, camphene, Δ-3 carene, sabinene, limonene, α- and β-phellandrene, thuyene and myrcene. Plants also emit alkanes (n-hexane), alkenes (ethylene), arenes (toluene), aldehydes (formaldehyde, acetaldehyde, etc.), ketones (acetone, camphor, 2-methyl-5-heptene-2-one, butanone), ethers (1,8-cineole), alcohols (methanol, linalool) and carboxylic acids (formic, acetic). Overviews of worldwide VOC emissions from vegetation and their role in the global atmospheric system can be found in

Brasseur *et al.* (2003), Wiedinmyer *et al.* (2004) and Loreto *et al.* (2008).

Biogenically emitted VOCs are byproducts of physiological activity. Not all of their production and emission mechanisms are fully explained, and they can differ considerably from each other. Some of these substances are synthesised inside the chloroplasts and related to photosynthesis; while others are produced as defences against stressors. Decaying and drying vegetation also produces VOCs. Plant growth hormones and floral scents can also be emitted (Hewitt 1999). The emission fluxes depend only partly on stomatal aperture, but also on the rates of synthesis of the substance emitted, which, in turn, depend on availability of the precursors.

Production of isoprene inside the leaves may play a protective role against the damaging effect of drought (Sharkey & Loreto 1993), heat (Loreto & Sharkey 1990) and O_3 (Loreto & Velikova 2001).

Emission rates of isoprenoids (isoprene and monoterpenes) from leaves are functions of both sunlight intensity and temperature, as shown *e.g.* by Guenther *et al.* (1991, 1993). These authors made use of systems called cuvettes or enclosures in which portions (leaves or branches) of plants were confined in order to directly measure amounts of emitted substances. These measurements led to the development of parameterisations that were subsequently used in modelling (Thunis & Cuvelier 2000).

UPTAKE OF AIR POLLUTANTS

It has been known for more than 30 years that air pollutants can penetrate plant tissues and damage them (Omasa *et al.* 2002a). The mechanism of stomatal uptake of air pollutants was first studied by O'Dell *et al.* (1977), as a molecular diffusion process inside the stomatal cavity. Subsequent work (Omasa *et al.* 2000, 2002a,b) demonstrated that pollutant uptake is not simply controlled by this diffusive process but also by leaf metabolism. Pollutant solubility in water does not seem to play an important role. Other authors, like Pasqualini *et al.* (2002), Grulke *et al.* (2007) and Fares *et al.* (2008), also studied stomatal uptake experimentally, as explained later.

Kerstiens & Lendzian (1989) and Van Hove *et al.* (1999) showed that the penetration of most pollutants through the cuticle can be considered as negligible since the cuticle is covered by waxes that constitute a barrier against stressors. Among air pollutants, O_3 is now recognised as responsible for most of the damage to vegetation. Damage by O_3 to agricultural crops has been estimated in many modelling studies (*e.g.* Legge *et al.* 1995; Krupa *et al.* 1998; Simpson *et al.* 2007) and is very important at global scale (Van Dingenen *et al.* 2009). The role of stomata in favouring O_3 uptake by leaves is illustrated in Fig. 2, showing a microscope view of cells subjected to O_3 damage. This damage is visualised by a dye reacting with hydrogen peroxide (H_2O_2) molecules formed after the oxidation processes initiated by O_3 (Faoro & Iriti 2009). The damage is visible on cells surrounding the stomata.
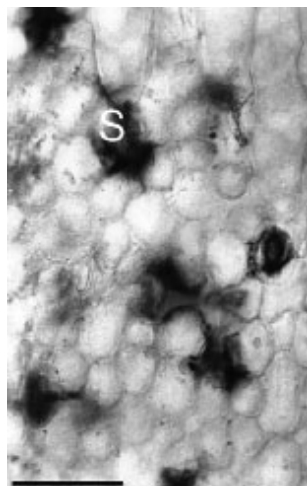
Fig. 2. Microscope view of ozone-damaged onion leaf cells near the stomata (S) (Faoro & Iriti 2009). The brownish colour of cells surrounding the stomata is due to precipitates formed by reaction between the 3,30-diaminobenzidine (DAB) stain and the peroxidation product H_2O_2. Bar = 100 μm.

Using 3D cell-level chlorophyll fluorescence imaging. Endo & Omasa (2007) also showed that O_3-induced inhibition occurs in cells immediately located under the epidermal cells.

The damaging effect of O_3 to vegetation is related to its oxidising capacity and its high reactivity. After diffusion through stomatal cavities, O_3 reaches the cell walls and is rapidly decomposed. Other oxidants such as hydroxyl radicals (OH), more generally known as reactive oxygen species (ROS), are formed and damage membranes, proteins and chorophylls (Haberer *et al.* 2007). Plants have developed defence mechanisms consisting mostly in producing antioxidant molecules, such as ascorbate, which serve as electron donors and reduce ROS. Obviously, the efficiency of the defence mechanisms is limited by the availability of antioxidants and by the quantity of O_3 reaching the cells.

Besides O_3, the main air pollutants that have damaging potential are mainly sulphur oxides, nitrogen oxides (NO_x) and NH_3. The damaging action of sulphur compounds on plants was studied by Thomas (1951) and subsequently by many authors. The action of these pollutants is complex, as both adverse and beneficial effects may arise, since sulphur can be used for plant growth (De Kok *et al.* 1998). A similar effect can be ascribed to the uptake of NO_x, which can be used by plants to synthesise amino acids when absorbed at low atmospheric concentrations (Yoneyama *et al.* 2002). Nitrogen dioxide (NO_2) is the most abundant NO_x species. It dissolves in extracellular water and is converted into nitrite and nitrate ions, which participate in protein build up. At higher atmospheric NO_2 concentrations, however, damage occurs. Exchange of NH_3 between air and plants has been studied by Farquhar *et al.* (1980), Sutton *et al.* (1995)

and many others. The flux of NH_3 is bidirectional, so that a compensation point exists. Plants have very different responses to NH_3, and the problem becomes more complicated by the very inhomogeneous distribution of concentrations of this species in air. Strong concentrations are observed in the case of presence of farms and use of fertilisers (Mattsson *et al.* 2009). Phytotoxic concentrations of NO_x and NH_3 occur only very close to their emission sources (Bytnerowicz *et al.* 1998).

FLUXES AND METHODS OF DETERMINATION

Chemical exchange between air and vegetation is best quantified by the flux of the chemical species exchanged. This quantity can be expressed in units of quantity of matter (mol) or mass (kg) per unit area and time. Fluxes can be positive (upward, emission) when directed to the atmosphere, or negative when directed to the plant (downward, uptake). Their determination is not straightforward but several methods exist, some are observational and others computational. Flux measurement methods are essentially divided into two categories: *in situ* (with enclosures or cuvettes) and micrometeorological (or aerodynamic).

Determining the flux of air pollutants through the stomata into leaves by *in situ*, leaf-level gas exchange measurements is the first step before upscaling to the tree, stand and landscape level. The following discussion is focused on O_3 for clarity, as much work has been carried out on this substance and since it is the most important stressor for vegetation, but similar features characterise other air pollutants, such as nitrogen and sulphur oxides. Ozone is extremely reactive, and direct measurements of its fluxes are thus challenging. Leaf-level O_3 flux is usually calculated using a mass-balance approach from the difference between O_3 concentration at the chamber inlet and outlet, multiplied by air flow rate and subtracted from the chamber sink strength for O_3 deposition (Omasa *et al.* 1979a; Skärby *et al.* 1987; Havranek & Wieser 1994; Matyssek *et al.* 1995; Wang *et al.* 1995; Pasqualini *et al.* 2002; Wieser 2002; Grulke *et al.* 2007). By this approach, stomatal uptake cannot be distinguished from other O_3 sink processes, unless measurements are also carried out after stomatal closure (Grulke *et al.* 2007). Cuticular deposition (adsorption and decomposition) of O_3, however, is very small compared to that of open stomata (Omasa *et al.* 1979b; Pleijel *et al.* 2004; Grulke *et al.* 2007; Fares *et al.* 2008). The water vapour surrogate method is thus being used to calculate stomatal O_3 uptake on the basis of direct measurements of stomatal conductance for water vapour, the diffusion coefficient of water vapour against that of O_3, and difference among the mole fractions of O_3 in air outside and inside the leaf (Wieser *et al.* 2008). This method assumes that the O_3 flux through the cuticle is negligible (Kerstiens & Lendzian 1989) and O_3 concentrations inside the leaf approach zero (Laisk *et al.* 1989; Moldau *et al.* 1990), given the rapid decomposition of O_3 into oxidative derivatives in the apoplast (Runec-

kles 1992). In general, stomatal O_3 fluxes derived from gas exchange measurement are in agreement with assessments based on the chamber inlet/outlet approach (Wieser *et al.* 2008). In addition, boundary layers are destroyed by leaf-level gas exchange assessments, which may strongly affect O_3 uptake (Wieser *et al.* 2003). Since transpiration and O_3 flux into the tree crown are coupled through stomatal regulation, sap flow measurement of crown transpiration has been suggested for assessing stomatal O_3 flux at the tree level (Wieser *et al.* 2008). The sap-flow assessment may then be combined with micrometeorological techniques.

The micrometeorological methods are based on the analysis of turbulent motion of lower air layers in contact with vegetation. Air transports chemical substances upward and downward by means of turbulent eddies. Molecules of the transported substances are like passengers on a train (the air motions). The vertical flux F_i of species i in a turbulent medium is governed by a Fick-like diffusion law (Fick 1855), which can be written as

$$F_i = K(z)\frac{\partial C_i}{\partial z} \qquad (5)$$

where $K(z)$ is the turbulent diffusion coefficient, C_i the local concentration of the species i and z is the height above ground level (a.g.l.). Contrary to the molecular diffusion coefficient, which is independent of space and time but depends on the nature of the transported gas, the turbulent diffusion coefficient depends on space and time but not on the nature of the gas. Equation (5) is the basis for a first method of measurement of vertical fluxes, called the vertical gradient method. It consists in measuring concentrations of the gas at several heights a.g.l. in order to calculate their vertical gradient. The turbulent diffusion coefficient can be calculated since there are various parameterisations available in the literature (Dyer & Hicks 1970; Dyer 1974).

Another micrometeorological method is the so-called eddy covariance technique, based on calculation of the covariance of the vertical component w of the wind vector and of the concentration of the substance under consideration, both measured at very high sampling frequency. This method was introduced by Scrase (1930) for momentum, and later by Swinbank (1951) for water vapour fluxes. It was then applied to various gaseous substances (Desjardins 1972; Delany *et al.* 1986; Baldocchi *et al.* 1988; Hicks & Matt 1988; Foken *et al.* 1995). The covariance is expressed by

$$F_i = \overline{w'C_i'} \qquad (6)$$

where the primed quantities represent fluctuations around the time-averaged value of the corresponding variable, and the overbar stands for the time-averaging process. The eddy covariance technique is generally considered as the most reliable micrometeorological flux determination method as it does not suffer from artifacts or biases. However, this method presents two main disadvantages: its use is delicate and it requires fast-response chemical sensors, which only exist for a few gases. Nevertheless, fluxes of CO_2, O_3 (Delany *et al.* 1986; Hicks *et al.* 1987; Massman 1993; Lamaud *et al.* 1994; Gerosa *et al.* 2003; Cieslik 1998, 2004, 2009; Affre *et al.* 2000 and many others), NOx (Wesely *et al.* 1989; Coe & Gallagher 1992; Stocker *et al.* 1993), NH_3 (Famulari *et al.* 2004), N_2O and CH_4 (Fowler *et al.* 1995; Di Marco *et al.* 2004), isoprene (Guenther & Hills 1998) and some others have been successfully obtained by this method. An example of results obtained with the eddy covariance method is shown in Fig. 3, where O_3 fluxes measured during 4 days of May 2003 over an onion field in northern Italy (Gerosa *et al.* 2007) are represented.

A third micrometeorological method, the eddy accumulation technique, sometimes quoted as "conditional sampling", was mainly developed by Businger & Oncley (1990) for CO_2 and CH_4 and subsequently used for a number of other gases (Baker *et al.* 1992; Darmais *et al.* 2000; Myles *et al.* 2007), is a kind of compromise between the two previously described methods. It consists in accumulating air in two containers according to the direction (up- or downward) of the vertical wind during a certain
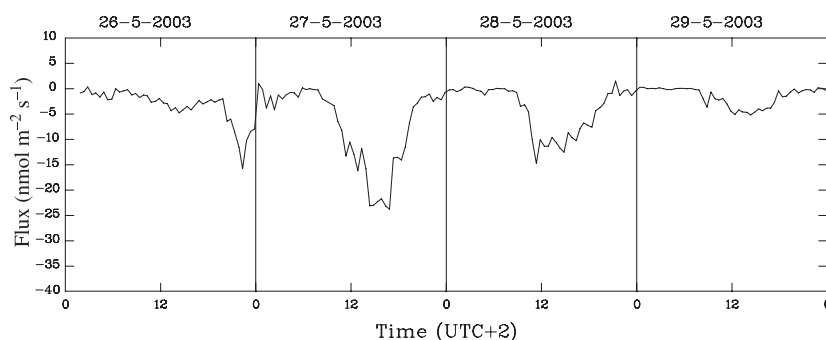

Fig. 3. Vertical total ozone fluxes recorded during a measuring campaign conducted over an onion field near Voghera (northern Italy) in May 2003.

time interval (generally 30 min); the content of the containers is subsequently analysed to obtain the concentrations of the gases for which the flux is measured. The flux is then given by

$$F = b\overline{w}(C_+ - C_-) \tag{7}$$

where b is an empirical coefficient, w is the vertical wind; C_+ and C_- are the concentrations measured in the two containers. This technique is easier to use in the field than the eddy covariance technique. It does not require fast-response sensors and the measurement is made at one single level, unlike the gradient technique, which needs measurement at different levels. It is thus especially adapted for the measurement of fluxes of VOC species (see *e.g.* Graus *et al.* 2006).

CONCLUDING REMARKS

The interactions between the chemical composition of the atmosphere and vegetation are an evident fact. The concentrations of major components of the atmosphere, like O_2, water vapour and CO_2, are strictly related to the presence of vegetation at the surface of the Earth, and any modification of the vegetal cover has consequences on these concentrations. Conversely, changes in concentrations of these substances have consequences on the state of vegetation and not only on climate. Besides these "main" substances, a number of chemical species, often called "minor atmospheric species", are exchanged between plants and the atmosphere in both directions and, in spite of their low atmospheric concentrations they can have an important influence on both atmospheric chemistry and vegetation health. Many organic substances are produced by vegetation, released in the air and influence air chemistry; air pollutants penetrate plant tissues and cause deleterious effects on plant health. Due to increasing emissions of various man-made substances, the atmospheric composition is changing. For example, ozone concentrations are increasing around the world; this reduces plant growth and consequently carbon sequestration. This process hinders policies aimed at fighting global warming (Sitch *et al.* 2007). Another important example is the role of isoprene, emitted by plants, and influencing atmospheric photochemistry at global scale by interacting with various air pollutants. The interactions between air pollutants, climate change and vegetation are often neglected by decision-makers. Air/vegetation interactions are bidirectional and their study is complex, being highly nonlinear and causing feedbacks. These studies are thus important to preserve the quality of both air and biosphere.

The quantities of gases exchanged between the atmosphere and terrestrial plants are enormous and most of these substances use the stomatal pathway. But at single-stoma level, the quantities exchanged are minute. This causes technical difficulties for measurements, increasing uncertainties in the assessment of exchanged quantities at

global level, and constitutes a major challenge for future research in this field. Another difficulty is how to relate these very different scales to each other and thus solve the upscaling problem.

The gas exchange processes between terrestrial vegetation and the atmosphere are an essential component of the global atmosphere/biosphere/lithosphere system and also interact with the climate system. A considerable amount of knowledge has been accumulated on this theme since the discovery of photosynthesis. Remaining unknowns are related to differences in spatial and temporal scales involved and technical problems in measurement. More interdisciplinarity is also needed to obtain a global depiction of gas exchange, since the phenomena are of a biological, chemical and physical nature.

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