

Mechanisms of Pollutant Exchange at Soil-Vegetation-Atmosphere Interfaces and Atmospheric Fate



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The presence in the atmosphere of the pollutants identified in chapter “[The Main Pollutants and Their Impacts on Agriculture, Ecosystems and Health](#)”, their concentration levels and their residence time depend on a series of various processes (physical, chemical, physicochemical, biological). This chapter describes the basic mechanisms and main factors involved to shed light on their interactions (Chapter “[Necessary Integrative Approaches](#)”) and provide a comprehensive overview of the origin and fate of these compounds in the atmosphere and at the interfaces. These concepts are necessary to understand the context and various choices that can be made in terms of measurements (Chapter “[Measuring Air Pollutant Concentrations and Fluxes](#)”), modelling (Chapter “[Modelling Exchanges: From The Process Scale To The Regional Scale](#)”) or levers for action (Chapter “[Reducing the Impacts of Agriculture on Air Quality](#)”).

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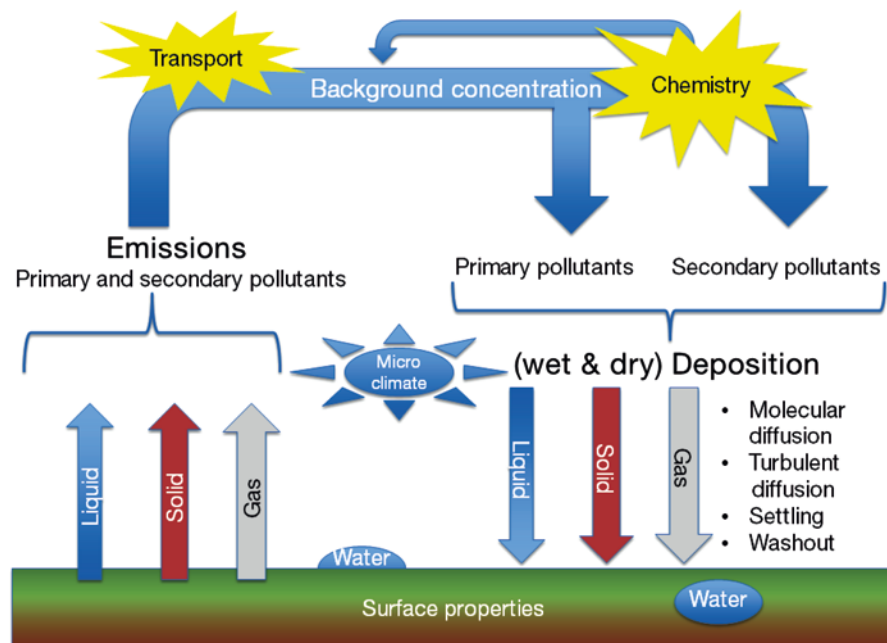


Fig. 1 Processes that determine the presence and concentration level of pollutants in the atmosphere. Emission and deposition of pollutants from plants (green) and soils (brown)

Air pollutants are classified as one of two types of pollutants: primary, which are emitted directly from agricultural activities or natural systems, transported and then deposited; or secondary, which result from physicochemical transformations in the atmosphere. Accordingly, this chapter describes, as schematized in Fig. 1, the processes at the origin of:

- pollutant emissions released directly into the atmosphere (primary pollutants) or precursors of secondary pollutants, including the identification of their determinants and their specific characteristics;
- their atmospheric transport at different spatial scales;
- the atmospheric chemistry in which these compounds are involved; and
- the various deposition routes.

For the sake of clarity, this chapter first looks at emission and deposition processes, even if in many cases exchanges are bi-directional. The mechanisms are also differentiated by type (physical, chemical, physicochemical, biological), although the processes are often interdependent (some fall within the field of multiphase chemistry, which lends a certain complexity to the system).

A certain degree of background knowledge about the state of the environment the pollutants evolve in and the exchange surfaces is necessary to understand the environmental fate of the pollutants. For example, when considering the soil, it is essential to know its water, thermal, chemical and biological status. For leaf

surfaces, their functioning (e.g. stomatal opening) and surface characteristics (e.g. developed surface, temperature, humidity, presence of liquid water) must be known in order to ultimately study the behaviour of chemical pollutants at this interface. Thus, the pedoclimatic and ecophysiological factors of interest for agricultural pollution are briefly described in the appendix to this chapter, with information given on the radiative, energy, water and thermal transfers as well as the biological functioning of plants and soil as well as on the effect of agricultural practices on these local conditions.

1 Emissions

This section examines the primary emissions of gaseous and particulate compounds. The formation of secondary pollutants (O_3 , secondary aerosols) is detailed in the section on atmospheric chemistry.

1.1 *Gaseous Compounds: Sources and Sinks*

Gaseous compounds are released into the atmosphere when compounds present in gaseous form at the emitting surface-atmosphere interface are transferred. The surface concentration of these compounds depends on different interacting processes: physicochemical, biological and physical. For the biological compartment (plants, animals, etc.), physicochemical processes coexist with biological processes, the limits of which are not always clearly defined. Finally, depending on the processes, various factors influence the intensity as well as the temporal and spatial evolution of emissions. For more information on these processes, refer to Calvet et al. (2005), or Schwarzenbach et al. (1993).

1.1.1 Physicochemical and Chemical Processes

The gaseous phase concentration of a compound depends on the different physicochemical equilibria (as illustrated by Fig. 2 for plant protection products). The resulting state changes apply to either pure liquid or solid substances or those dissolved in water. This means they can take place at the soil-atmosphere or leaf-atmosphere interface as well as in the soil itself at the liquid-air or liquid-soil interfaces within each pore of air in the soil, which are filled with water to varying degrees. Soil is a complex network of interconnected pores, due to the spatial arrangement of solid particles, which are filled with water or air, and in which microorganisms and their resources are heterogeneously distributed. As a reminder, the gaseous phase concentration resulting from the equilibrium between air and a pure substance, whether solid or liquid, is directly deduced from the saturated

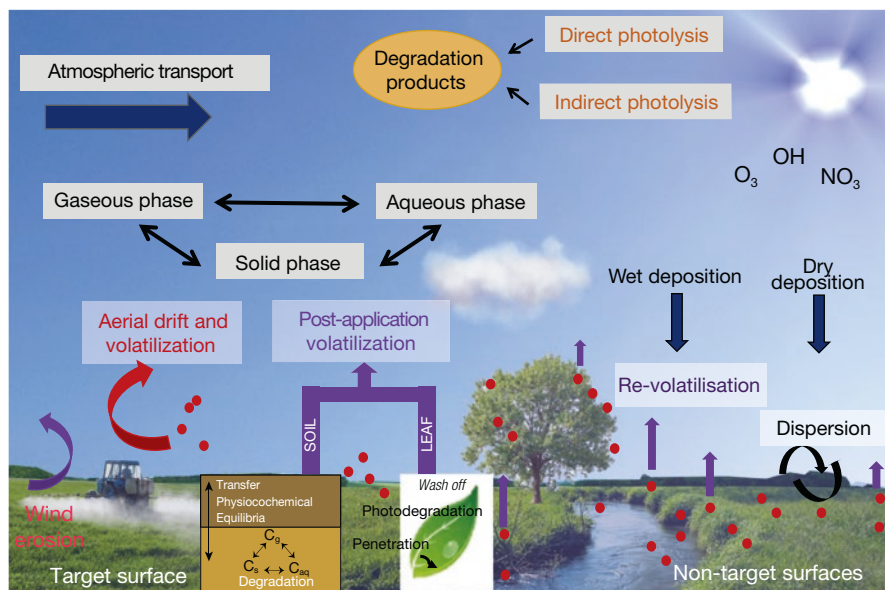


Fig. 2 Fate of plant protection products after application to a target surface (soil or crop): transfer pathways to the atmosphere (by drift, volatilization from soil or leaves and wind erosion), atmospheric fate (physicochemical equilibrium, transformations, transport) and deposition pathways (dry and wet) (Adapted from Socorro 2015)

vapour pressure of the compound P_{vap} (Pa), a specific characteristic of the compound, and exponentially depends only on temperature (according to the Clausius-Clapeyron equation). The physicochemical equilibrium between the aqueous phase in which the compound is solubilized and the gaseous phase is described using a specific partition coefficient, the Henry's law constant K_H , which reflects the tendency of a compound to pass through the air from the aqueous phase and vice versa. K_H is defined by the ratio at a time t between the compound partial pressure in the atmosphere and its concentration in the aqueous phase. K_H is generally estimated by the ratio between the saturation vapour pressure in the gaseous phase and the solubility in the aqueous phase (S_w). It is also specific to each compound. K_H depends on the temperature where equilibrium takes place. A key uncertainty concerns the determination of both P_{vap} and K_H . Refer to Sander's synthesis (2015) for the different expressions of the Henry's law constant.

Pollutants can interact with surfaces such as mineral or organic solids in the soil or leaf cuticle via adsorption phenomena or chemisorption, which are chemical reactions with organic constituents. For example, negatively charged clay complexes in the soil provide adsorption sites for ammonium ions in solution, correlating this process with the soil's cation exchange capacity (CEC). However, ammonium competes for adsorption sites with other soil cations (namely Ca^{2+} , Mg^{2+} , Na^+ and K^+ ions). An organic input such as livestock effluent, a solid organic matter that is generally negatively charged, also constitutes an adsorption matrix of

ammonium ions in solution with its own CEC, which depends on the characteristics of organic matter and the exchange surfaces. With pesticides, it is commonly considered that the adsorption process takes place mainly from the aqueous phase towards the organic matter (Hamaker and Thompson 1972), and to a lesser extent in clays for ionisable pesticides. Adsorption is described by adsorption isotherms which, when linear, can be expressed using an adsorption-desorption distribution coefficient, K_d . However, on the soil surface, during drying conditions the adsorption of the compound may occur from its gaseous phase into the air from the soil pores to the mineral solid matrix, notably via van der Waals forces (Goss 2004). The importance of this adsorption from the gaseous phase depends on the specific partition coefficient of the pesticide, and the properties and conditions of the soil, in particular the specific surface area of the mineral matrix available for adsorption. It also depends on the water content of the soil, which determines the proportion of this surface covered by water molecules, which impede adsorption of poorly water-soluble substances such as pesticides.

With regard to physicochemical equilibria with the leaf surface, an atmospheric chemical compound can be exchanged with the plant either via the cuticle or the stomata. This section focuses on cuticular exchanges; stomatal exchanges will be covered in the section on biological processes, although some may be related to physicochemical processes. For example, when a pesticide is applied to a crop canopy (Fig. 2), it may be found on all or only part of the leaf surfaces. It is often assumed that there is an essentially cuticular atmosphere-plant exchange, with adsorption depending on the compound (and, in the case of PPPs, on the formulation), on the chemical composition of the cuticle, and on the wettability of the surfaces, which affects the foliar penetration of pesticides. The adsorption intensity appears to be highly correlated with the compound's K_{ow} (octanol/water partition coefficient) due to the dependency of adsorption on the compound's lipophilicity (Lichiheb et al. 2016), as shown in the example in Fig. 3. As for nitrogen compounds, cuticular exchanges take place mainly during the deposition of the compound. Note that the exchanges of nitrogen compounds via stomata are bidirectional (see "Biological processes" section).

In addition, the emitted quantities of ammonia or pesticides with an acid or basic functional group depend on their chemical dissociation. This reaction corresponds to the equilibrium between the protonated species (acid) and the deprotonated species (base) of the compound formalized by the dissociation constant K_a defining the concentration ratio between the acid and basic forms of the compound in an aqueous medium. This process is pH and temperature dependent.

These are the physicochemical equilibrium processes, but equilibrium is not always reached, and adsorption/desorption kinetics can take place. In addition, depending on the oxidizing or reducing condition of the soil, oxidation-reduction (redox) reactions of the compounds may occur. These are reactions characterized by transfers of an electron between components. Reduction reactions occur within hydromorphic sites, while oxidation reactions occur in aerated locations. For nitrogen compounds, the oxidation of soil ammoniacal nitrogen produces nitrates, while the reduction of nitrates produces ammonium. For organic compounds such as

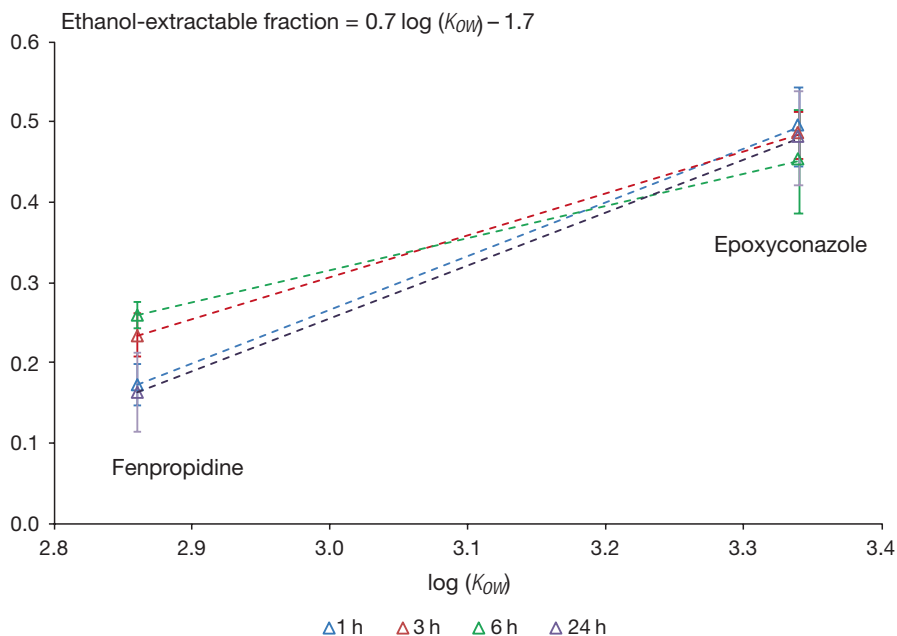


Fig. 3 Dependence of the adsorption of active ingredients of plant protection products (pure fenpropidin, pure epoxyconazole) on the cuticular surface of wheat leaves (assimilated by the ethanol-extractable fraction of the compound) with the octanol/water partition coefficient K_{ow} . The blue, red, green and purple dotted lines represent this relationship 1 h, 3 h, 6 h and 24 h after application, respectively (from Lichiheb et al. 2016)

pesticides, the reduction reaction depends on the presence or absence of functional groups that can be reduced (e.g. nitroaromatic or sulfoxide groups). It should be noted that redox reactions may have biological origins (e.g. catalysis of enzyme systems).

Finally, the concentrations of compounds available for emission depend on abiotic degradation processes, whether they occur on the surface or in soil or plant matrices. One example is pesticide hydrolysis, which is the reaction between the organic molecule with a hydrolysable functional group and a water molecule, or photo-degradation, which can occur at the surface (Richard et al. 2015).

1.1.2 Biological Processes

A number of biological processes cause atmospheric emissions of nitrogen compounds, biogenic volatile organic compounds (BVOCs), methane (CH_4) and pesticides.

1.1.2.1 Nitrogen Compounds

These biological processes can be direct sources of nitrogen compounds: for example, mineralization produces ammoniacal nitrogen involved in the volatilization of NH_3 . These processes can also contribute upstream to increasing the total nitrogen content of the soil or plant compartments and thus constitute indirect sources of gaseous compound emissions: this is the case of biological nitrogen fixation. Finally, they can be a source for one gaseous compound and at the same time a sink for another compound. One example of this is nitrification, a process through which ammoniacal nitrogen is consumed and converted into nitric nitrogen; the higher the nitrification, the more the volatilization of NH_3 decreases, but the more nitric nitrogen is available for denitrification. The main reactions of the nitrogen cycle are detailed below (Fig. 4).

Biological fixation, essentially carried out by bacteria living in symbiosis with leguminous plants, transforms atmospheric nitrogen N_2 , an essential but inert

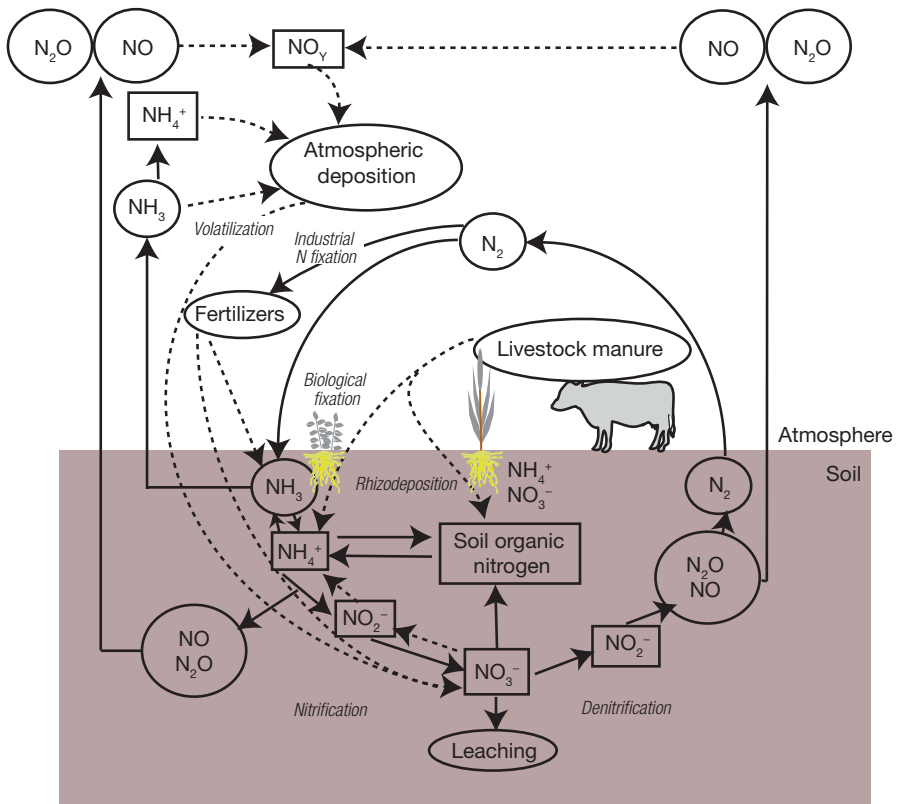


Fig. 4 The nitrogen cycle (Richard et al. 2019) illustrates the complexity and sequencing of the processes involved, as well as the variability of the forms involved in atmospheric emissions (dotted arrows: nitrogen inputs to the agricultural system)

compound in the atmosphere (78%), into so-called reactive nitrogen (Nr), which can be assimilated by all living organisms. Lightning also produces smaller amounts of NO through oxidation of N₂.

The assimilation of mineral nitrogen can only be achieved by autotrophic organisms: plants, fungi and certain bacteria. Microbial organization, or immobilization, is the biological process of mineral nitrogen assimilation by microorganisms, which leads to the formation of organic nitrogen in microbial biomass, and therefore in the soil. Mineral nitrogen absorption by plant roots is generally from the nitrate form, before its assimilation into organic nitrogen as part of the plant biomass. Heterotrophic organisms (especially animals, and including humans) cannot assimilate nitrogen in mineral form, but ingest nitrogen directly in organic form (plants, other animals, etc.).

Nitrogen in organic form returns to the mineral form after excretion or the death of the organism, via degradation of organic matter and mineralization of organic compounds. Mineralization is thus the reverse process of microbial organization, and produces the two mineral forms: nitric nitrogen (NO₃⁺), which is the oxidized form, and ammoniacal nitrogen (NH₃/NH₄⁺), which is the reduced form. Following a series of physicochemical equilibria as described above, ammoniacal nitrogen can be found in gaseous form and cause the volatilization of ammonia (NH₃), which is one of the entry routes for an active and polluting form of nitrogen into the atmosphere.

Ammoniacal nitrogen is consumed by the nitrification reaction, the biological oxidation of ammonium (NH₄⁺) into nitrate (NO₃⁻) in two successive steps: first, the oxidation of ammonium to nitrite (NO₂⁻), and then the oxidation of nitrites to nitrates. Nitrification is a competing reaction with ammonia volatilization following nitrogen fertilization. Since nitric nitrogen is consumed during the process in comparable quantities and over comparable time scales, nitrification is accompanied by biogenic emissions of nitrogen monoxide (NO) and nitrous acid (HONO), as well as a smaller proportion of nitrous oxide (N₂O). These reactions are carried out by specific bacteria. Nitrification is highly dependent on environmental conditions, particularly the rate of oxygenation: it only occurs under aerobic conditions. Microflora activity is optimal at pH values from 6.9 to 9 and temperatures between 20 °C and 36 °C. Additionally, some compounds may slow down or block these reactions, such as high levels of ammonium or nitrite, or nitrification inhibitors. In the event of a sudden increase in ammoniacal nitrogen in the substrate, the gradual growth of the bacterial populations causing this reaction leads to a latency phase that can range from a few days to a few weeks.

Denitrification is a key element of the nitrogen cycle by which reactive forms are transformed back to inert N₂ by reducing nitrate through intermediate forms, nitrites (NO₂⁻), gaseous nitrogen oxides (NO, NO₂, N₂O₅ and others) and nitrous oxide (N₂O). When it is only partial (total denitrification means all nitrate ions are transformed into N₂), it is accompanied by biogenic emissions of N₂O in particular, and NO to a lesser extent. This reaction is carried out by a large number of bacteria and fungi. It occurs when microorganisms lack of oxygen, i.e. under anaerobic reducing conditions, typically for water-filled soil porosity rates above 60%. Denitrifying

activity is low at low temperatures and is optimal at temperatures of 60 °C to 65 °C and pH levels between 6 and 8.

Nitrogen uptake by plant roots is preferentially via the nitric form, although plants also absorb ammoniacal nitrogen. Partition depends on the availability of both forms, the type of plant and soil conditions. An increase in pH and low temperatures promote the assimilation of the ammonia form, whereas it can become toxic at high temperatures. It should be noted that nitrate, which is highly mobile in the soil unlike ammonia, is subject to leaching into groundwater or surface water, where it contributes to the degradation of water quality.

NH₃ exchanges between the plant and the atmosphere happen through a flow via the stomata (while cuticular exchanges occur with previously deposited NH_x), a flux which is directly proportional to the difference in NH₃ concentration in the canopy air and in the air of the substomatal cavity (Fig. 5). The NH₃ concentration in the air of this substomatal cavity, also known as the “stomatal compensation point, χ_s ”, results from the thermodynamic balance between NH₃ in the gaseous and aqueous phases, and from the chemical balance between NH₄⁺ and H⁺ ions in the apoplast (Γ , the ratio between the concentrations of the latter two ions, is called the “emission potential”) (Massad et al. 2008; Schjoerring 1997). The ratio between χ_s and the aqueous NH₃ concentration in the apoplast is temperature dependent, while the ratio between the aqueous NH₃ concentration in the apoplast and the NH₄⁺ ion concentration depends on the apoplast pH. Absorption by the roots modifies not only the ammonium concentrations in the apoplast, but also the pH. Ammonium is constantly generated in leaf cells by various processes, the most important being nitrate reduction, photorespiration, protein renewal and lignin biosynthesis (Joy 1988; Leegood et al. 1995). The assimilation of NH₄⁺ into leaf cells occurs mainly via the glutamine synthetase (GS) and glutamate synthase (GOGAT) cycle (Leegood et al.

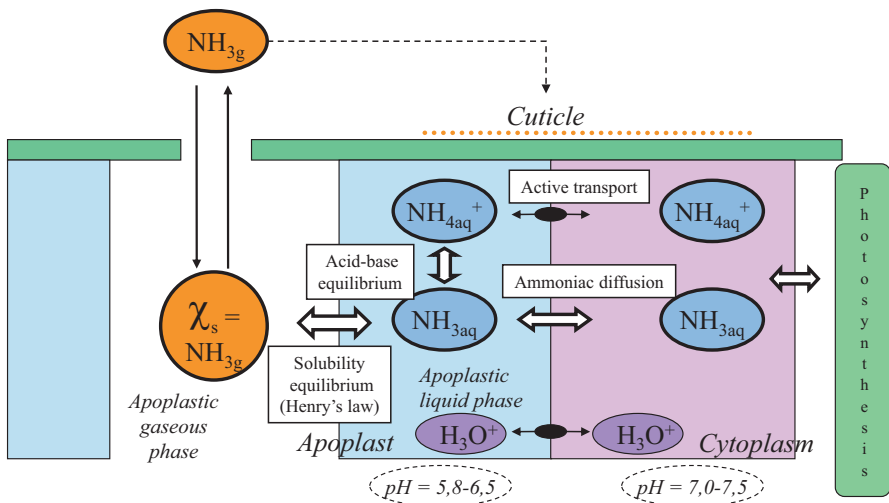


Fig. 5 Physicochemical balances and biological control of NH₃ stomatal exchanges

1995). NH_4^+ ion concentrations in foliar apoplast vary according to the intensity of all these processes (Husted and Schjoerring 1996; Schjoerring 1997). Stomatal ammonia exchanges between the plant and the atmosphere vary according to a variety of factors such as (i) the phenological stage, with atmospheric ammonia absorption generally observed during the growth phase, and emissions generally observed during the remobilization phase of assimilates from roots and leaves to reproductive organs and during the senescence phase; (ii) hydric status, which controls the stomata aperture and therefore the transfers between the substomatal cavity and the atmosphere; (iii) nitrogenous nutrition, which controls the nitrogen content of the substomatal cavity; (iv) the type of the ions taken up by the roots, with plants that more readily absorb the ammoniacal form having higher emissions than plants that absorb the nitric form.

1.1.2.2 Volatile Organic Compounds

Biogenic volatile organic compounds (BVOCs) are synthesized within plant cells according to mechanisms closely associated with their metabolism. Despite their structural and functional diversity, all isoprenoids (including terpenes) originate from the five precursor carbons of isopentenyl diphosphate (IPP) and dimethylallyl diphosphate (DMAPP), which can be converted by the isopentenyl diphosphate:dimethylallyl diphosphate isomerase (IDI) enzymes. Plants use two different pathways to synthesize these compounds. The mevalonic acid pathway (MVA) synthesizes IPP in cytosol, while the methylerythritol-4-phosphate pathway (MEP) provides both IPP and DMAPP in organelles (Bouvier et al. 2005; Rodríguez-Concepción and Boronat 2015). These BVOCs are therefore secondary metabolites whose role for the plant is not yet fully understood, although the signal role under stress conditions of some of them is currently a much-researched subject (Maffei 2010). Additionally, once synthesized, these molecules can undergo further modifications under the action of other enzymes, leading to a considerable number of compounds produced within the plant (Fig. 6).

Non-methane volatile organic compounds (NMVOCs) also originate from organic waste products (e.g. manure). While nitrogen compound emissions are relatively well documented, much less research has been done on BVOC emissions from manure. These studies, which focused on emissions during the various stages of waste composting, showed that various types of compounds can be released depending on the origin of the waste (Brinton 1998).

Livestock production, from building or grazing excretion to field application, storage, and composting and spreading of manure, is also a source of VOCs (Feilberg et al. 2015; Houot et al. 2014). Some of these VOCs, together with ammonia and H_2S , are sources of odour nuisance. Of all VOC sources, livestock has been estimated to be the main source of aliphatic amines in the atmosphere, with trimethylamine (TMA) being the main emitting compound. The interaction between faeces and urine in animal production systems is the main source of agricultural TMA emissions. Excreted urine contains large amounts of urea and TMA-N-oxide, which

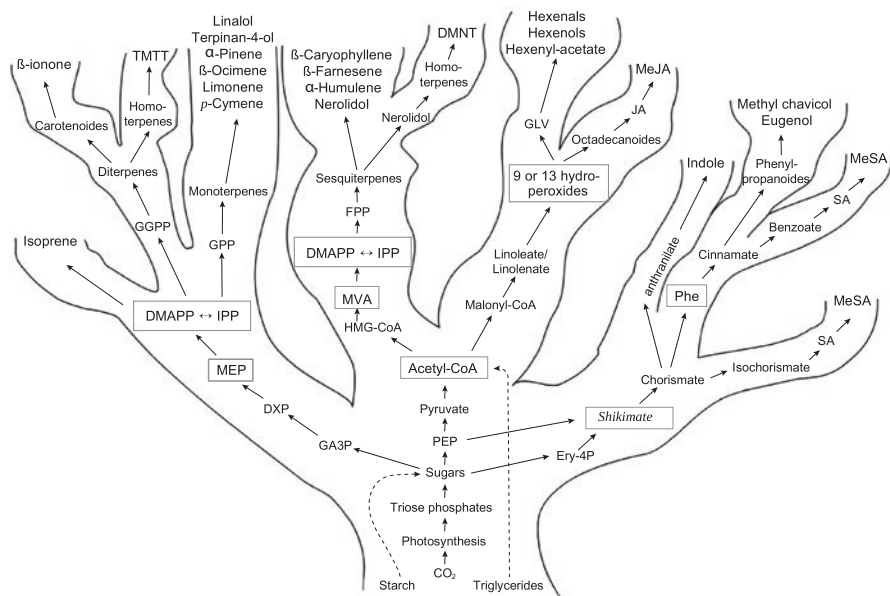


Fig. 6 Illustration of the multitude and complexity of VOC emissions from plants. Different biochemical pathways are involved according to Maffei (2010) (under Creative Commons 4.0 license). DMAPP: dimethylallyl-pyrophosphate; DMNT: 4,8-dimethylnoma-1,3,7-triene; DXP: deoxyxylulose-5-phosphate; Ery4P: erythrosis-4-phosphate; FPP: farnesyl-diphosphate; GA3P: glyceraldehyde-3-phosphate; GGPP: geranylgeranyl-pyrophosphate; GPP: geranyl-diphosphate; IPP: isopentenyl-diphosphate; JA: jasmonic acid; MEP: 2-C-methyl-D-erythritol 4-phosphate; MeJA: methyl jasmonate; MeSA: methyl salicylate; TMTT: 4,8,12-trimethyletrideca-1,3,7,11-tetraene; MVA: mevalonic acid; PEP: phosphoenolpyruvic acid; SA: salicylic acid; HMG-CoA: 3-hydroxy-3-methyl-glutaryl-coenzyme A; Phe: phenylalanine

are transformed into NH_3 and TMA, respectively, through the enzymatic activity of microbes in the faeces (Sintermann et al. 2014). Measurements on pig farms have shown a wide variety of VOCs, with more than 300 compounds identified in the air and sewage lagoons (Schiffman et al. 2001). Acids, alcohols, aldehydes, amides, amines and aromatic compounds are among the main classes of VOCs identified.

Soil microorganisms are also important actors in VOC production, either by breaking down soil organic matter or in response to stimuli in communication processes with other organisms in their environment. Thus, their production depends on the quantity and quality of organic matter in the soil as well as on biotic or abiotic parameters (e.g. pH, soil moisture, temperature, presence of manure) (Abis et al. 2018; Potard et al. 2017).

Methane (CH_4) emissions are the result of two antagonistic and correlated microbiological reactions, methanogenesis and methanotrophy. Methanogenesis is the gross production of methane (and CO_2) in soil by microorganisms using organic molecules for energy supply via methane fermentation in a strict anaerobic environment, i.e. by complete mineralization of the available organic matter. Four

specialized microbial populations break down complex organic molecules into simple compounds (given by a reaction $C_6H_{12}O_6 \rightarrow 3 CO_2 + 3 CH_4$). Methanogenic soils are typically flooded soils such as rice fields, swampy areas, estuary soils or tropical mangroves, but they also include landfills and compacted areas of formerly flooded soils. Conversely, methanotrophy is the gross consumption or oxidation of methane by methanotrophic bacteria which produces CO_2 and H_2O . There are two types of oxidation of CH_4 in soils: the first, known as “high affinity”, occurs at CH_4 concentrations similar to those in the atmosphere and for soils with low NH_4^+ content. It is apparently ubiquitous in aerobic soils, which explains why formerly flooded cultivated soils are natural sinks of atmospheric CH_4 outside the fertilization period. The second, called “low affinity”, occurs at higher CH_4 concentrations. It is characteristic of methanotrophic bacteria present in soils with a pH over 4.4 and which use CH_4 as the only source of C and energy. The availability of O_2 is the limiting factor for their activity. Methanogenic and methanotrophic microorganisms are found in all soils, thus ensuring the coexistence of the two reactions when there are simultaneous anoxic and well-oxygenated zones in the same soil. The main situations favouring the emission of CH_4 from agricultural soils are submergence and the use of organic fertilizers or crop residues, thus providing a carbonaceous substrate for methanogenic bacteria (Thangarajan et al. 2013). Finally, temperature affects microbial activity, which is highest between 37 °C and 48 °C, resulting in the highest emissions.

1.1.2.3 Plant Protection Products

With regard to xenobiotics such as active ingredients in PPPs present on the surface of treated leaves, their volatilization depends on the amount of compounds available on the surface that evolves according to this volatilization as well as on the processes of penetration (including adsorption), photodegradation and rain washout. Regarding penetration, after the compounds diffuse through the cuticle, they must pass through the cell wall to the cytoplasm, which is an aqueous compartment. As such, the effectiveness of cell penetration depends on the compound’s solubility in water. However, co-formulants used with the active ingredient can significantly modify its behaviour: some, by ensuring better spreading of the solution on the surface of the leaves by lowering surface tension, facilitate their penetration and/or adsorption by producing a thin layer at the large surface interface, thus promoting their action. A study of the effect of organosilicone adjuvants of acifluorfen and bentazone in velvet leaves as cited by Leistra (2005) showed that the penetration of the formulated product is 88% over a period of 15 min, while that of the pure product is less than 5%. The experimental laboratory study by Lichiheb et al. (2015) confirmed the dependence of penetration on water solubility, and noted the effect of co-formulants on adsorption and penetration processes. Once inside the leaf cells, the fraction of compounds that has penetrated can be distributed to the plant’s different compartments.

Observations have been used to estimate half-life times of the compounds in plants, depending on the plant species, their stage of development and the compounds' physicochemical properties (pKa and pH of the plant compartment in question). Bromilow and Chamberlain (1991) proposed a simplified diagram showing the pKa/log K_{ow} combinations to describe the different types of transport of un-ionized pesticides and weak acids within the plant. Thus, highly lipophilic compounds (log K_{ow} > 4) appear to be non-systemic, those with a log K_{ow} between -0.5 and 4 would circulate preferentially in the xylem, and un-ionized compounds with a log K_{ow} < 0 and a pKa > 6 (weak acids) would circulate both in the xylem and in the phloem. However, at present, despite the many existing studies to assess the fate of pesticides in plants, our knowledge remains fragmented due to the lack of analysis of the different processes involved and their interactions. There are also pesticide sink processes in soil, such as mineralization or root absorption.

1.1.3 Physical Processes

The gaseous phase concentration available at the surface for atmospheric transfers also depends on physical transfer processes within the soil compartment or the canopy. In the soil, the main compound transfers are:

- *in the aqueous phase* by convection and hydrodynamic dispersion: Convection involves a flow proportional to the flow velocity of the fluid multiplied by the concentration of the aqueous phase. Hydrodynamic dispersion is the result of the combination of molecular diffusion (Fick's Law) in the moving liquid phase and the spatial variation of the velocity of water movement in the poral space. This dispersion implies a flux proportional to the concentration gradient. The soil is a porous medium with complex porous spaces, consisting of pores of very different shapes and sizes (see references in Calvet 2013). Transport phenomena therefore do not occur in the same way throughout the entire volume of a soil. A direct coupling between water and heat transfers is required (see Appendix). In addition, in soils subject to preferential transfers, this rapid transfer route should be considered.
- *in the gaseous phase* by molecular diffusion in the poral space occupied by air (gas convection in the soil is not significant due to very small pressure gradients).
- *associated with the solid phase* (minerals, organic matter) *or living organisms*: a displacement of the solid phase used as an adsorption support or via the movements of earthworms. There may also be a displacement of adsorbed compounds on soil particles, either by infiltration under very dry conditions followed by precipitation, or during cultivation practices involving soil mixing.

In the plant itself, there may also be compound transport processes. These were described in the section on biological processes, as they are closely tied to the physiological functioning of the plant.

In the case of methane, soil-atmosphere exchanges depend on the transfer conditions between the production area and the atmosphere, or between the atmosphere

and the consumption area. The transfer from the soil to the atmosphere is a diffusion process: thus, methane produced in an anaerobic zone can be consumed during its transfer to the atmosphere if it passes through an aerobic zone. In the case of flooded soils, it also occurs in the form of bubbles or mainly through the parenchyma of aquatic plants. Another pathway is the plant itself, which acts as a “funnel” for methane produced in the soil; this artefact led to the conclusion that the plants themselves were sources of methane (Keppler et al. 2006), which turned out to not be true (Nisbet et al. 2009).

Emissions towards the atmosphere resulting from surface concentrations of compounds are based on diffuse and convective physical transport processes detailed in the “Atmospheric transport” section. Generally speaking, emission dynamics are highly dependent on climate forcing, and primarily on incident radiation, which, by warming the surface, increases convective exchanges and the saturated vapour pressure of the compound in the vicinity of the surface and intensifies water evaporation, which will foster compound concentration on the soil surface. Secondly, wind speed facilitates the turbulent compound transport (see “Atmospheric Transport” section) by shearing the air flow in relation to the surface roughness. Finally, precipitation in most cases favours infiltration into the ground and thus reduces the concentration of pollutants on the surface. It should be noted, however, that low intensity precipitation, which does not generate infiltration, nevertheless rewets the soil, which can lead to the volatilization of compounds subject to adsorption from their gaseous phase to the soil matrix when the soil is dry. Pollutant fluxes also depend on the concentration gradient established between the emitting surface and the ambient atmosphere.

1.2 Particles

1.2.1 Physical Processes

The processes of primary particle emission are similar to those driving gaseous emission. However, given the heavier weight of some of these pollutants, their emission is often associated with specific mechanisms (wind, erosion, abrasion, leaching, etc.). Particulate pollutants or aerosols are classified according to their size using the metric particulate matter (PM_x), where x corresponds to the maximum diameter in micrometres. Particles can be solid (e.g. dust, crustal particle) or liquid (droplets). Due to physicochemical processes in the atmosphere, including secondary particle formation, the particle size distribution in the atmosphere is traditionally trimodal, which corresponds to three main modes of formation. The first mode is coarse and solid particles between 3 and 5 µm, which corresponds to mechanical processes. Next is an accumulation mode, which partially corresponds to wet deposition between 0.1 and 1 µm. The last is the nucleation mode around 0.02 µm. These three main modes of particle size distribution are more or less represented depending on the source and the environment.

Emissions of primary particulate matter of agricultural origin are linked to livestock activities and field activities (Faburé et al. 2011). Emissions from livestock farming depend on the animal species, their physiology and age, feeding characteristics and the way manure and transhumance are managed. In livestock housing, these emissions depend on ventilation, land cover management (Haeussermann et al. 2008), cleaning and manure and excreta. In general, climatic conditions (outdoor or indoor) play an important role in animal activity and emissions. Concerning field activities, emissions (other than those related to agricultural machinery use) are mainly due to soil preparation activities such as ploughing; (direct) sowing, including abrasion in seed drills of seed treatments likely to generate concentrated pesticide dust; crop treatment; harvesting; management of residues from previous harvests and burning of crop residues; and storage, treatment, drying and transport operations for harvests.

As a result, particulate matter from agriculture consists of compounds of essentially mineral crustal origin and organic origin such as organic fertilizers, plant and animal matter, microorganisms and pesticides through drift (Faburé et al. 2011). Drift is defined as the “quantity of plant protection product that is carried out of the sprayed (treated) area by the action of air currents during the application process” (ISO 22866:2005).¹ The main factors influencing drift are the size of the drops (which depends on the type of atomizer or nozzle, the pressure and physicochemical properties of the spray mixture), the speed and direction of the air assistance and atmospheric conditions (including wind speed and direction and atmospheric stability).

In addition, the suspension, saltation (bouncing of particles on the ground) and creeping (sliding and rolling) of soil particles (Pye 1987) – where wind causes particles to move from the ground into the atmosphere – are known collectively as wind erosion. It should be noted that soil particles can be suspended in the atmosphere by rain via splashing raindrops, which leads to crustal particles. These processes depend on crop structure, moisture, soil roughness, leaf area index (LAI), wind speed and precipitation.

1.2.2 Biological Processes

Bioaerosols (bacteria, spores, pollen grains, seeds) are almost always present in the air. These particles are formed on or by plants, sometimes in relatively complex and specialized biological structures (e.g. pollen anthers, spore-producing structures). There are many different kinds and they are specific to the plant or type of fungal spore. Thus, the release of bioaerosols depends on these structures. These plant organs have diverse dehiscence mechanisms. They may be active, where bioaerosols are literally propelled into the atmosphere by bellows mechanisms; mixed, where the action of surface water allows the dissolution of mucilage containing spores, for example; or passive, where the action of factors outside the plant is

¹ <https://www.iso.org/obp/ui/#iso:std:iso:22866:ed-1:v1:en>

required for particle suspension. These factors include mainly (1) wind (anemophilous release), which acts on bioaerosol-producing surfaces with some mechanisms shared with soil erosion physics, (2) rain, where droplets hit surfaces and propel spores and bacteria into splash droplets (Huber et al. 2006), and (3) plant movement by the action of wind, rain, agricultural machinery or animals.

Accordingly, the characteristics and concentrations of bioaerosols are highly variable, depending on time of day, weather and season, geographical location and proximity to sources (depending on the species, the maximum dispersal distance often varies from 10 to 500 m, and is around 50 m for many shrubs or grasses) (Nathan et al. 2002). The specific characteristics of biotic particles (size, mass, shape, water content, viability) play a major role in their aerodynamic behaviour, dispersal ability and survival, which determine their invasion and/or infection capacity (Aylor 2017).

2 Atmospheric Transfers

The atmosphere is divided into several layers that are rather clearly demarcated by an increasing or decreasing vertical gradient in air temperature. In the troposphere, the thermal gradient is generally negative as altitude increases, with the occasional occurrence of near-surface inversions. These conditions of atmospheric stability or instability have a strong impact on the atmospheric dispersion of pollutants emitted at the surface and on the thickness of the atmospheric layers (a particularly important factor in determining the concentration of pollutants in the atmosphere). For particular meteorological conditions (e.g. nocturnal radiative deficit of surfaces, see Appendix), the temperature gradient can be reversed, leading to a significant reduction in the thickness of the layer closest to the ground and thus to a high accumulation of pollutants. Moreover, these layers are characterized by different transfer processes that are decoupled to varying degrees. The following paragraphs will discuss the differences between vertical and horizontal transfers. For a more detailed description of the atmospheric compartment, refer to Triplet and Roche (1996) or Delmas et al. (2005).

2.1 Vertical Transfers

All the processes presented thus far determine the level of concentration of the compound in the gaseous phase on the surface (soil or leaf), i.e. the quantity available for atmospheric transfer. This transfer takes place in the atmospheric compartment, which is characterized by a viscous and compressible fluid: “the air” moving above the Earth’s surface. In fluid mechanics, the concept of boundary layer is used to represent the area in which flow is influenced by the presence of an obstacle; with respect to the atmosphere, this is the Earth’s surface. This layer is characterized by

a wind speed gradient that tends towards zero on an obstacle surface (for more details, see Seinfeld and Pandis 2016; Stull 1988). Next is the planetary boundary layer (PBL), also known as the atmospheric boundary layer (ABL), which ranges from 1 to 2 km thick, and then the surface boundary layer (SBL), from a few meters to a few dozen metres, in which the fluxes are conservative and stationary. The wind intensity, temperature and compound concentration profiles are logarithmic, if the conditions are homogeneous horizontally. The thickness of the SBL depends on the size of the area that can be considered homogeneous. Within the SBL, transport is convective, laminar or turbulent. The following processes then take place:

- Diffuse transport near the surface elements, where wind speed is low and air flow is laminar. This transport is caused by the difference in compound concentration in the air between the surface and the atmosphere just above this layer. Thus, it can be described by a classic diffusion equation based on the concentration gradient, the molecular diffusion coefficient of the compound in air and the thickness of this thin layer.
- Convective transport by turbulent movements from the surface above this thin laminar layer to the PBL. Convection can be either (i) free, i.e. caused by the thermal gradient between the surface and the atmosphere; (ii) forced, caused by the pressure gradient in the air mass between the high and low pressure areas (which enable wind flow); or (iii) mixed, through a combination of the two previous regimes (which is generally the case). The vertical flux of compound (F_z) can then be expressed as a function of the fluctuations w' in the vertical wind speed and the fluctuations c' of the concentration in the air of the compound with the following relationship:

$$F_z = \overline{\rho w' c'} \quad (1)$$

where ρ is air density. An analogy between turbulent motion and molecular diffusion allows the flux to be calculated as a function of the vertical concentration gradient and a vertical turbulent diffusion coefficient K_z ($\text{m}^2\cdot\text{s}^{-1}$), with or without integrating local stability/instability conditions. By analogy with electrical resistive schemes, the flux of matter at a given height can be expressed as the difference in concentrations between this height and the surface divided by the equivalent transfer resistance in each atmospheric layer below (note that sometimes the term “conductance” is used, which represents the inverse of resistance).

In the case of vegetation cover, the exchanges within the crop canopy should be considered in a mass balance equation in each layer of the canopy (Tuzet et al. 1995). In addition, in the case of a horizontal variation in surface conditions (e.g. height of cover, alternating irrigated and non-irrigated areas, succession of plots with alternating plots and livestock buildings showing differences in source level and therefore different surface concentration for a given compound), local advection may occur, i.e. horizontal transport by mean air flow. In this case, the flux is no longer conservative. Thus, within the SBL for a given study area, there are as many internal boundary layers as there are surfaces with different characteristics.

2.2 Horizontal Transfers

As previously described, the compounds in the atmosphere are diffused vertically, while being transported by the average airflow (referred to as horizontal advection) and diffused by the fluctuating movements of the air (horizontal diffusion).

Advection is the flux of matter related to the average movement of air. It is expressed as the product of the mean wind vector \vec{V} by the mean concentration of the compound and \vec{C} is therefore directed in the direction of the mean air flow: $\vec{F} = \rho \vec{V} \cdot \vec{C}$. Horizontal diffusion is related to the fluctuations of the transverse horizontal components v' and to the axis of the air velocity u' , and the diffusion flux is identical to that defined in the previous paragraph $F_{diffy} = \rho \overline{v'c'}$ and $F_{diffx} = \rho \overline{u'c'}$. Horizontal diffusion according to the wind direction (F_{diffx}) is often negligible compared to advection. It becomes important when wind speed is very low, which occurs under conditions of stable stratification, such as at night, or in polar areas (Haupt et al. 2009; Luhar and Hurley 2012). Lateral diffusion is important in all wind conditions, especially at the local level.

Horizontal transport is an essential phenomenon for understanding atmospheric transport, which occurs at two scales:

- At the regional scale, air mass movements are responsible for compound transport and are determined first and foremost by the position and intensity of anticyclones (high pressures) and depressions (low pressures), by the Coriolis force and surface roughness. At this scale, transport is therefore determined by the average wind fields. Variations in surface condition over distances of under ten kilometres do not have a significant impact on regional transport.
- At the landscape scale (< 5 km, grid scale of regional models), advection and diffusion are strongly dependent on the heterogeneity of surfaces in terms of dynamics (roughness, hedgerows, wooded or urban areas) as well as energy (colder and wetter aquatic surface, warmer and drier built areas, bare soils, forests). Indeed, these surface elements not only lead to local variations in wind fields and therefore advection, but also variations in turbulence intensities and therefore horizontal diffusion (Dupont et al. 2006). In particular, hilly areas generate significant advective fluxes and modify exchanges in the surface layer (Burns et al. 2011). Chapter “[Modelling Exchanges: From the Process Scale to the Regional Scale](#)” presents the different modelling approaches used to describe these horizontal transfers.

3 Atmospheric Chemistry

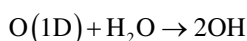
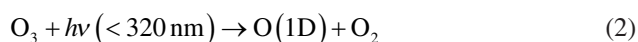
Chemical compounds released from agricultural soils or related activities are exposed during their lifetime to various atmospheric oxidants. The main processes modifying the chemical composition of the atmosphere are direct photolysis (via solar irradiation), reactions with the hydroxyl radical (OH), ozone (O₃) and the

nitrate radical (NO_3). Their importance depends mainly on solar activity and the observed oxidant concentration, but ambient temperature and the relative humidity of the atmosphere are also drivers.

Photochemical reactions caused by solar radiation play a central role in atmospheric chemistry, since they represent the main source of radicals in the troposphere and thus trigger many transformations in gaseous and particle phases. Heterogeneous and multiphase reactions are not detailed here since this would have required explanations beyond the scope of this book.

3.1 Atmospheric Oxidants

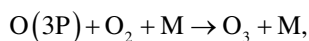
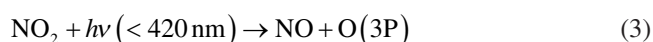
Hydroxyl radicals (OH), also known as the “detergent of the atmosphere”, is the main oxidant in the troposphere and is responsible for the degradation of most air pollutants. It comes mainly from the photolysis of ozone (Finlayson-Pitts and Pitts 1997) given by:



where $h\nu (< 320 \text{ nm})$: photolysis at wavelengths of less than 320 nm, and $\text{O}(1\text{D})$: an oxygen atom in an excited state.

Other sources of OH radicals exist, in particular photolysis of nitrous acid (HONO), hydrogen peroxide (H_2O_2) or formaldehyde (CH_2O). Oxidation of volatile organic compounds (VOC) is also likely to contribute to the formation of hydroxyl radicals (Delmas et al. 2005).

The pathway of ozone formation in the troposphere is the photolysis of nitrogen dioxide (NO_2) (Finlayson-Pitts and Pitts 1997) given by:



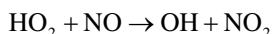
$\text{O}(3\text{P})$: an oxygen atom in its fundamental state, and M : N_2 , O_2 or any molecule capable of absorbing the excess vibrational energy and stabilizing the formed ozone molecule.

The reaction between nitric oxide and ozone subsequently regenerates NO_2 :



There is thus a photostationary equilibrium between $\text{NO}_2/\text{NO}/\text{O}_3$, governed by the Leighton relationship. Another reaction pathway, involving radicals from VOC

oxidation, such as alkoxy or peroxy radicals RO_2 and HO_2 , disrupts this cycle (Finlayson-Pitts and Pitts 1997). A sequential process follows which, depending on the concentrations of VOC and nitrogen oxides and in the presence of solar radiation, results in a net production of ozone in the troposphere:

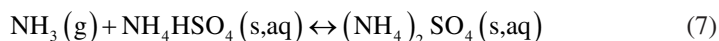


Unlike the two previous oxidants, which are mainly diurnal, the nitrate radical is present at relatively high concentrations at night. It forms during the night by the oxidation of NO_2 with O_3 , and nitrate radical photolysis is very fast during the day under the solar radiation (Atkinson and Arey 2003). These radicals are responsible for many VOC reaction pathways at night.

Understanding the reaction pathways of the various compounds in the gaseous phase with these oxidants, which produce semi-volatile compounds that can condense, is essential in figuring out the formation and evolution processes of the particulate phase. Thus, in addition to gaseous phase reactions, other reactive processes can take place, depending on the type of compound considered and the physicochemical parameters describing atmospheric conditions. Multiphase processes, which involve the gas-surface interfaces of particles or the aqueous phase, potentially represent significant sinks and/or sources of active chemical species. Heterogeneous reactivity can lead to physicochemical changes in the particulate phase. Numerous laboratory and field studies focus on the complexity of the mechanisms involved.

3.2 Atmospheric Reactivity

Once released into the atmosphere, pollutants in both gaseous and particulate phases can undergo all kinds of physicochemical processes such as oxidation or photodegradation reactions during their atmospheric transport. All these processes fall under atmospheric chemistry, a field of study that mainly seeks to establish the links between the presence and ultimate fate of these compounds in the atmosphere. Ammonia is an alkaline compound that interacts with acidic compounds in the atmosphere, such as sulphuric acid (H_2SO_4), to form two salts: ammonium bisulphate (Eq. 6) and ammonium sulphate (Eq. 7) (Seinfeld and Pandis 2016).



If the first salt remains, the aerosol is called “acid”, and the reaction with an additional ammonia molecule provides a neutralized aerosol. The excess ammonia can then react with nitric acid (HNO_3) to form ammonium nitrate (Eq. 8). These reactions therefore involve phase changes, with the formation of salts in solid form (s) or in a highly concentrated aqueous phase (aq) for relative humidity exceeding the point of deliquescence. These reactions are reversible, especially for ammonium nitrate, whose saturation pressure decreases with temperature and is therefore more stable in winter.



The fine particles thus formed contribute to particulate pollution episodes. In addition, fine particles act as condensation nuclei and thus impact cloud microphysics and the radiative balance of the atmosphere. They also affect visibility (Seinfeld and Pandis 2016).

The most abundant nitrogen oxide in the atmosphere is nitrous oxide (N_2O), but the most reactive in the troposphere are nitrogen monoxide (NO) and nitrogen dioxide (NO_2). These compounds, known together as NO_x , are produced during combustion processes as well as through biological activity in the soil (see “Emissions” section). They play an important role in the oxidation of volatile organic compounds. In France, it is now recognized that agriculture and forestry emit 50% of BVOCs. The chemical structure of VOCs in the atmosphere is the first parameter influencing their reactivity with atmospheric oxidants.

Alkanes (saturated hydrocarbons such as methane) react mainly with the OH radical. Alkenes (such as isoprene) can also react with OH, as well as with NO_3 at night. Monoterpenes, but especially sesquiterpenes and diterpenes, also react quickly with ozone. VOC oxidation leads to the formation of functionalized compounds, some of which have lower volatility and can therefore condense, resulting in the formation of secondary organic aerosols (SOAs). Particle nucleation from gaseous precursors is the main mechanism for new particle formation in the atmosphere (Kroll and Seinfeld 2008). The first step in the formation of SOAs is the gaseous phase oxidation of volatile compounds, which creates partially oxidized compounds with a high O/C ratio, sometimes as high as one or even beyond. These processes may partly explain the high rate of these oxidation reactions in the atmosphere (Atkinson and Arey 2003; Hallquist et al. 2009; Kroll and Seinfeld 2008), illustrated in Fig. 7.

As for the oxidation reactions initiated by OH and NO_3 radicals, they undergo two competing routes: (i) hydrogen atom abstraction or (ii) addition to a double bond, whereas ozone mainly initiates its reactions by addition to a double bond (Kroll and Seinfeld 2008). All radical initiation reactions lead to the formation of peroxy radicals (RO_2).

Peroxy radicals play a central role in the formation of lower volatility compounds. They mainly evolve towards the formation of alkoxy radicals (RO) by reaction with NO, NO_3 or with another RO_2 radical. The RO and RO_2 radicals evolve into low volatility oxidation products, which are partitioned between the gaseous and particulate phases and thus contribute to SOA formation and growth, such as peroxy nitrates, organic nitrates, alcohols, hydroperoxides or carbonyl compounds, with multiple functional groups such as hydroxyl and hydroperoxyl (Fig. 7).

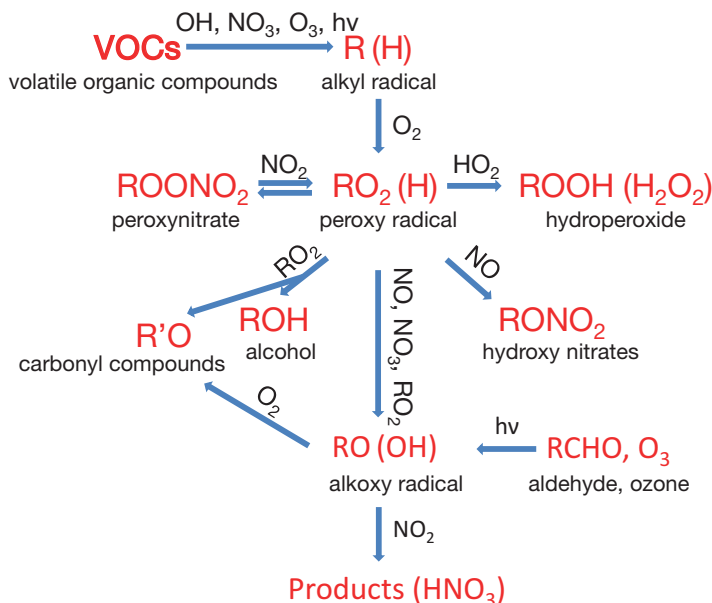


Fig. 7 Simplified mechanism for atmospheric oxidation of a VOC and formation of atmospheric radicals (from Seinfeld and Pandis 2016)

There are several possible types of evolution for alkoxy radicals (Atkinson and Arey 2003; Kroll and Seinfeld 2008). Their dissociation can lead, for example, to the formation of carbonyl compounds. The reaction of RO radicals with oxygen leads to the formation of carbonyl and hydroperoxyl radicals (Kroll and Seinfeld 2008). The structure of the initial compound in question directly influences the different pathways of the RO radical (Fig. 7) (Atkinson and Arey 2003). Dissociation leads to the formation of lower molecular weight compounds and, as a result, this reaction is considered negligible in SOA formation. In contrast, isomerization, favoured for long chain carbonaceous or cyclic compounds, leads to the formation of poly-functionalized compounds. When isomerization and dissociation processes are not possible, the reaction with oxygen is predominant and can lead to the formation of semi-volatile products.

Ozonolysis is initiated by adding an ozone molecule to a double bond to rapidly evolve into carbonyl compounds and a Criegee biradical. The latter can be stabilized by reaction with a molecule of water or other oxygenated compounds, leading to highly oxygenated organic hydroperoxides (Kroll and Seinfeld 2008). However, Criegee biradicals can decompose rapidly, producing OH radicals, especially at night (Paulson et al. 1999). These biradicals play an important role in the oxidative capacity of the atmosphere and the formation of aerosols in the troposphere. Their high reactivity to many key gaseous species (e.g. water vapour, SO₂, NO₂ and carboxylic acids) plays an even greater than expected role in atmospheric chemistry (Khan et al. 2018).

First generation oxidation products have saturation vapour pressures that can vary by several orders of magnitude and are therefore likely to be present in both gaseous and particulate phases. The most volatile oxidized organic compounds can react in turn and contribute to the formation of SOAs. Ng et al. (2006) showed that the mass of SOAs continues to increase, even when all gaseous precursors have reacted, particularly for precursors with several reactive sites, such as limonene, which has two double bonds. This observation shows that the reactivity of oxidation products also contributes to the increase in the mass of SOAs. However, it is now recognized that reactivity can be multiphase, and many other particulate phase evolution processes can occur.

The active substances of PPPs such as herbicides, fungicides, etc. are broken down through direct photolysis processes, depending on their ability to directly absorb solar radiation, and through reaction with OH, NO₃ or even O₃. These reactions can occur in all three atmospheric phases and lead to the appearance of degradation products as well as aerosol formation (Borrás et al. 2015), information that is crucial for understanding toxic effects specific to these products (Mellouki et al. 2007; Pflieger et al. 2009). It would appear that when these compounds are adsorbed or dissolved in aerosols, their degradation is altered (Socorro et al. 2016). Adsorption can slow oxidative or photochemical degradation, although it is accompanied by an increase in concentration at the interface, while ionic mechanisms such as hydrolysis on or in a droplet can lead to an acceleration in the degradation of an adsorbed molecule. The substrate on which a molecule is adsorbed represents a competitive, often reactive, pathway for the molecule in question. The physicochemical properties of the adsorbed molecule and the substrate representing the particulate phase are decisive for the fate of the molecule by controlling reactivity on aerosols (Socorro et al. 2016) (Chapter “Measuring Air Pollutant Concentrations and Fluxes”).

Aerosols generally interact with sulphur dioxide (SO₂), nitrogen oxides and ammonia during their atmospheric transport. These interactions then alter the aerosols' optical properties, modifying the hydrophilic and hydrophobic components of particles, which ultimately has a direct or indirect impact on the climate.

Many factors (such as temperature and relative humidity) can influence SOA formation by playing a role in the oxidation mechanisms of gaseous precursors or those of gas-particle transfer. Depending on their concentration, nitrogen oxides thus promote certain reactions or branching ratios (Kroll and Seinfeld 2008). Water also allows, for example, the activation of new reaction pathways such as the hydrolysis of certain functionalized compounds. Particulate acidity also plays a key role in SOA formation mechanisms, and their yields are strongly influenced in the presence of sulphuric acid (Iinuma et al. 2009; Surratt et al. 2007). Jimenez et al. (2009) showed that SOA chemical composition generally evolves according to three mechanisms: functionalization, fragmentation and oligomerization. Functionalization corresponds to the reaction of organic compounds with atmospheric oxidants. It consists of adding functional groups to the carbon skeleton of the compound and leads to the formation of lower volatility products. Fragmentation refers to the cleavage of a C-C bond, thereby forming two new organic compounds. Generally, this process creates higher volatility compounds that do not participate in the formation of SOAs or to partial re-volatilization. Finally, oligomerization processes are

non-oxidative processes that result from the addition of two compounds (Chacon-Madrid and Donahue 2011; Hallquist et al. 2009; Kroll and Seinfeld 2008). These processes very quickly lead to the formation of very high molecular weight compounds in the atmospheric aerosol.

There are still many uncertainties about the different SOA evolution paths and their occurrence under atmospheric conditions. Among the various possible reactions in condensed-phase oligomerization processes, organosulfate formation has been identified in multiple field sampling campaigns (Surratt et al. 2007).

Textbox: A Closer Look at Amines

Agricultural regions are a major source of amines* in the atmosphere. Although amine emission rates from livestock sources are two to three orders of magnitude lower than those from ammonia, particulate phase amines contribute significantly to the mass of particulate matter in plumes from livestock sources. By measuring VOCs over soils after manure application, Feilberg et al. (2015) identified emissions of amino compounds, including trimethylamine, a source of secondary organic aerosols (SOAs). Other field measurements and laboratory experiments have shown that amino compounds make up a substantial share of the aerosol mass and play a major role in new particle formation (Kürten et al. 2018; Pratt and Prather 2009). The chemical processes involved in amine particle formation depend on their class. For example, Murphy et al. (2007) showed that tertiary amines had higher aerosol yields than primary or secondary amines.

Unlike primary and secondary amines, tertiary amines form substantial amounts of SOAs. Although there has been little aerosol formation following ozonolysis of primary amines, it has been shown that high mass yields of SOA are observed from amine reactions (regardless of their class) with the nitrate radical (Silva et al. 2008) present only at night. This suggests that tertiary amine emissions could be a key nocturnal source of SOA.

Once formed, particles from all of the abovementioned processes are quickly integrated into water droplets and become a medium that facilitates condensation and thus the formation of cloud droplets. These particles are called cloud condensation nuclei (CCN). Not all atmospheric particles are likely to play the role of CCN; usually, they are limited to those between 50 and 150 nm in size. The factors that influence CCN activation are related to their size, chemical composition, solubility, hygroscopicity and ambient supersaturation. Under the most favourable conditions, the particles in question have a significant indirect effect on climate change.

* Amines are nitrogenous organic compounds derived from ammonia by replacing one, two or three hydrogen atoms with as many hydrocarbon groups. There are three classes of amines according to the degree of nitrogen substitution: primary, secondary and tertiary amines. Trimethylamine is, for example, a tertiary amine, because three methyl groups are bound to nitrogen.

4 Deposition

Although referred to as “deposition”, the processes involved are in most cases bi-directional exchanges (e.g. ammonia): the deposition surfaces can be both a source and a sink of pollutants. The exchanged flux can be expressed as the vertical flux of compound F_z between the atmosphere and surfaces:

$$F_z = w_s \Delta C \quad (9)$$

where w_s is the deposition rate of the compound ($\text{m}\cdot\text{s}^{-1}$) and the variation in vertical concentration ΔC of the pollutant between the atmosphere and surfaces (the positive or negative sign of ΔC then indicates the direction of the transfer). However, some pollutants, such as ozone, are deposited exclusively (Lamaud et al. 2009; Stella et al. 2011a, 2011b). Deposition can be dry (gas and particle transfer) or wet (wash-out of the atmosphere, rainfall, fog).

4.1 Dry Deposition (Bi-Directional Exchanges, Interface Exchanges)

Dry deposition refers to the deposition of solid particles and gases without interaction with an aqueous atmospheric phase. Deposition can occur in different ways on dry surfaces or liquids, in which, for example, acid-base balances must be considered, as in the case of ammonia (Fig. 5) (Personne et al. 2009, 2015). Deposition processes are driven by mechanisms in the atmosphere, such as turbulent and Brownian diffusion transfers and sedimentation (when heavy particles are involved), and depend on the properties of the exchange surfaces (temperature and humidity), which modify atmospheric exchanges. With regard to particles specifically, transfer processes are largely driven by aerodynamic properties, namely particle size (Fig. 8) and weight. The gas deposition is mainly dependent on air humidity, leaf surface temperature and wetness and leaf surface texture (Flechard et al. 1999; Van Hove et al. 1989; Massad et al. 2010).

4.2 Wet Deposition

The mechanisms involved in wet deposition are threefold. A first series of mechanisms is involved in the highest layers of the troposphere (Seinfeld and Pandis 2016): rainout, which refers to the scavenging of gases and particles in cloud formation processes, involving condensation on cloud nucleation nuclei in a water-saturated atmosphere. The second is washout, which refers to the scavenging of particles and the dissolution of gases when hydrometeors (raindrops, snow) fall.

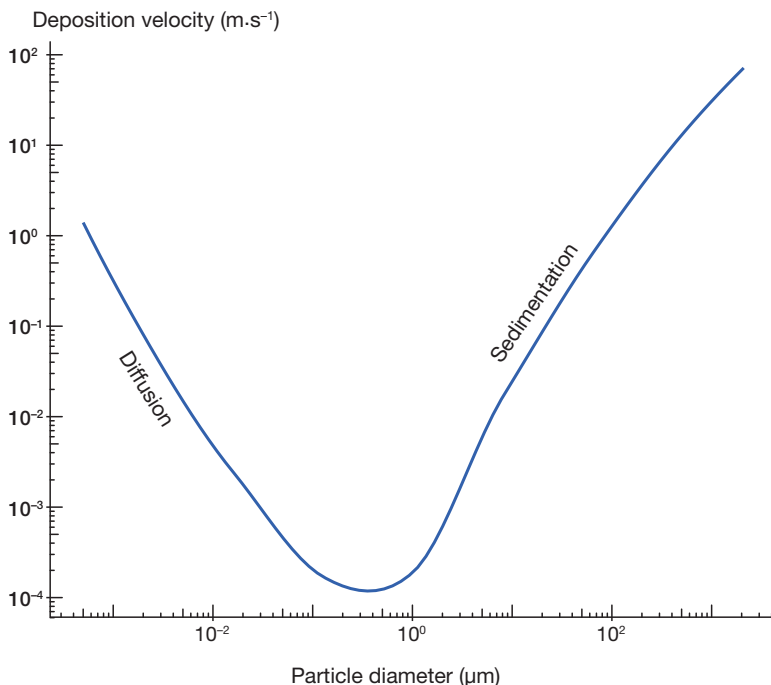


Fig. 8 Deposition rate of particulate compounds as a function of their diameter. Depending on the diameter, the mechanisms involved are different (diffusion or sedimentation) (according to Seinfeld and Pandis 2016)

The size of the raindrops is controlled by the evaporation processes for the smallest (0.2 mm) and fragmentation for the largest (5 mm), with a distribution in size ranging from 1 to 2 mm. In the lower layers of the atmosphere, rain drop deposition processes are relatively similar to those for heavy particles. Finally, the third mechanism includes the processes of occult deposition corresponding to dew and frost deposition or radiative fog formation. The strength of these processes is linked to local weather effects. Under certain conditions, the radiative energy balance is negative and favours the condensation of water vapour at the interfaces.

The dissolution and/or solvation of gas in rainwater changes its properties. For example, as in the case of acid rain, some compounds such as sulphur oxides (SO₂ or SO₃) or nitrogen oxides (NO and NO₂) form acids in the aqueous phase that reduce the pH of the water to below 5.6. Moreover, the presence of superficial water at the interfaces can change the affinity of the surface to certain compounds, and bring pollutants already dissolved in this water to the interface.

4.3 *Heterogeneous Surface Chemistry*

Once in contact with the surface, the compound can interact with it. An illustration of the surface chemistry process is the “deposition of ozone on a plant surface”. This generally occurs through two pathways: stomatal deposition and non-stomatal deposition, which includes cuticular “deposition” on the leaf surface, on the soil surface, and possibly chemical destruction in the gaseous phase in the air column above and inside the canopy (the latter two were discussed above). Stomatal deposition corresponds to the part of ozone that enters the plant via the stomata. Once in the leaf, ozone alters how the plant functions and leads to the formation of reactive oxygen species. More specifically, ozone reduces the plant’s photosynthetic capacity and leaf surface by promoting early senescence, and guides the use of assimilates to detoxification activity, changing stomatal conductance and assimilate distribution in favour of aerial parts rather than the underground parts. Soil carbon flux is also altered by changes in litter quality, in carbon rhizodeposition or in the composition of the soil microbial community (Mills et al. 2013). The stomatal deposition process allows the gaseous exchange of water, CO₂ and volatile organic compounds between the plant and the atmosphere. Ozone also reacts with chemical compounds on the plant surface. Studies on ascorbic acid degradation in the presence of ozone have shown, for example, the formation of different ozonolysis products on the surface (Enami et al. 2008; Potier et al. 2017).

Some of the ozone flux intercepted by the ground or vegetation (leaf or trunk) does not enter the leaf, but settles directly on the surfaces. This non-stomatic deposition therefore corresponds to the deposition on external plant surfaces (leaf cuticles, branches, stems, etc.) and on the ground. Ozone deposition on cuticles is estimated by measuring the ozone residue remaining after stomatal and soil deposition. Using this approach, it has been found that ozone deposition on plant cuticles is correlated with solar radiation and air temperature, and depends on soil parameters such as texture, porosity and organic matter content (Grøntoft 2004; Stella et al. 2019; Tuzet et al. 2011).

Finally, it should be noted that heterogeneous surface chemistry processes can also occur on the surface of atmospheric aerosols. Indeed, multiple molecular collisions can happen there, and each molecular shock does not necessarily lead to the incorporation of the molecule into the condensed phase. Following a collision, different processes can take place: either adsorption/desorption processes on the surface or chemical reactions with species on the surface. For more information on these particle surface processes, see Pillar-Little and Guzman (2018).

Appendix

Fundamental Aspects of Microclimate at Soil-Vegetation-Atmosphere Interfaces, Soil Conditions and Crop Physiology

For further reading, see Guyot (1998), de Parcevaux and Huber (2007), Calvet et al. (2005), Calvet (2013), Heller (2004) or Jones (2013).

Energy Balance

Emission, transport and deposition processes are highly dependent on energy transfers occurring at the soil-vegetation-atmosphere interfaces. Understanding energy transfer processes enables characterization of the carrier fluid (in this case, air) and state variables of the exchange interfaces (surface temperature, humidity, presence of superficial water), which can also be modified by the presence of pollutants (such as hygroscopic compounds, i.e. having an affinity with water). The energy transfers at the interfaces are expressed as energy flux through the interface ($\text{W}\cdot\text{m}^{-2}$). When the energy flux is positive, the interface receives energy, which generally results in an increase in temperature (de Parcevaux and Huber 2007; Guyot 1998). Conversely, when the energy flux is negative, the interface losses energy and its temperature drops. Energy exchanges are radiative (net radiation, R_n), convective (sensible heat flux, H), conductive (heat flux, G) and phase change (latent heat flux, λE), each term being expressed in $\text{W}\cdot\text{m}^{-2}$. The energy balance at the interface is expressed as:

$$R_n + H + \lambda E + G = \Delta E \quad (10)$$

where ΔE is the energy stock at the interface, often considered as null for plants and soils. The terms of the energy balance (detailed below) depend on the overall hydric and thermal states of the soil profile, the regulation processes (evapotranspiration) and the physical properties of the vegetation cover (height, leaf profile, albedo, roughness). Thus, there is constant feedback between the energy transfer and the water status of this surface. The radiative energy fluxes are sorted according to their wavelength. Short-wavelength radiation ($< 1 \mu\text{m}$) consists of direct and diffuse solar radiation in its positive components (energy input), and a proportion of the reflected solar radiation (energy loss) at the interface. The reflection coefficient of short-wave radiation is called albedo (a). In addition to short-wave radiation, there is also long-wave radiation (above $1 \mu\text{m}$) mainly in the infrared spectrum. These different types of radiations are classed by their positive component, atmospheric radiation R_a (responsible for the greenhouse effect), and their negative component, surface radiation of the interface, which is expressed as a function of its temperature. The sum of all these radiative fluxes is called net radiation, R_n . The sensitive heat flux (H) reflects the energy exchanges that modify the interface temperature controlled by

the temperature gradient. The latent heat flux λE reflects the energy exchanges that result from changes in the state of water and is driven by the gradient in water vapour concentration between the surface and the atmosphere. Finally, the heat conduction energy flux (G) reflects the heat exchange by contact and is expressed according to Fourier's law, describing the temperature gradient in the ground. These energy fluxes cause a change in the microclimate (atmospheric water content, temperature change) near the surface.

Water and Energy Transfers in the Soil

The soil moisture status is characterized by its water potential (h_w , m^{-1}); its water content (θ), which can be expressed as weight (kg water/kg soil) or volume (m^3 water/ m^3 soil); or as a proportion of the volume of pores filled by water, depending on the approach and application. It evolves in time and space due to water transfer processes (described by Darcy's law in water-saturated environments and generalized Darcy's law or the Richards equation in water-unsaturated environments) in the soil profile as well as exchanges at the surface via the surface energy balance (described above). Similarly, the soil temperature evolves according to heat transfer processes (including conduction transfers, described by Fourier's law). Since these statuses depend on the depth in the soil, it may be necessary to define layers, or soil horizons, by depth.

Depending on the weather forcing and water saturation of the soil, different hydraulic regimes exist: infiltration, hydrostatic equilibrium or capillary rise. This variability in water transfers is the largest in the thin surface layer of the soil, where the water content changes rapidly. It also implies that the ground surface can be subject to extreme local conditions, without intense meteorological forcing. In addition to local soil and climate conditions, the soil characteristics in terms of texture (sand/silt/clay distribution), density ρ_b ($kg \cdot m^{-3}$) or organic matter (OM) content must be known in order to calculate the soil transfer functions required to calculate the h_w relationships (θ) and the hydraulic conductivity K_w ($m \cdot s^{-1}$). During a rainy season, depending on the soil, slope, and the presence of crops that can intercept varying degrees of rain, surface runoff can occur and generate horizontal transfers. While water transfers determine the ability of the soil to transport the different solutes in the soil, the water status and temperature of the soil also determine the distribution of compounds between the different phases (gases dissolved in soil water or adsorbed), which in turn determine the availability of the compound for the different transfers (in aqueous or gaseous form) and their degradation.

Finally, it is important to note the high spatial heterogeneity in soil conditions, which may lead to heterogeneity in the soil structure, which can increase preferential transport and lead to rapid transfers of solutes into the deeper soil (e.g. root passage, earthworms, fissures).

Soil Biophysical and Chemical Conditions

Soil condition is characterized by its water status, chemical status and biological status. The pH of the soil solution is one of its important characteristics for physico-chemical balances and microbial functioning, as well as its cation exchange capacity (CEC). Soil organic matter is an essential component, as it conditions the chemical fertility of the soil, its structural stability and its microbial functioning. It can also influence water flows by modifying water adsorption processes. This organic matter consists of both inert and living organic matter (root, microbial biomass, meso-fauna), which impacts the physical and chemical state of the soil and the biogeochemical transformations that take place there. Many processes and interactions take place in soil, and its state varies considerably, both spatially and temporally (with highly variable scales of space and time). For further reading, see Calvet (2013).

Biological Functioning of Plants and Vegetation Cover

The presence of vegetation cover modifies ambient conditions at the ground-atmosphere interface by creating a microclimate specific to the vegetation cover. A quick review of the general functioning of plants, whether cultivated or part of a natural ecosystem, will be helpful here. Plants are autotrophic organisms. They produce their own **organic matter** from **mineral salts** extracted from the **soil** and **carbon dioxide** (CO₂) in the atmosphere, which is assimilated by the leaves by using **solar energy through the photosynthesis** mechanism. Plants need different elements to survive and grow. The first is light, which is necessary for the photosynthesis process, which then provides energy, water and soil from which nutrients are derived; the second is air, from which CO₂ is extracted. Although plants have different morphologies, they all have various organs: a stem bearing leaves and buds, and roots. These different organs are made up of tissues, organized in sets of specialized cells. The roots and the aerial part are two interdependent systems due to the conductive tissues that run through them. The xylem ensures the transport of raw sap (water and mineral salts), the phloem carries the elaborated sap (i.e. the organic and soluble compounds) from the leaves, where photosynthesis takes place, to the storage organs (tubers, roots, etc.) and fruits or grains.

The plant cells that make up these different organs are delimited by the **plasma membrane** and contain within them the vacuole (used to store water, nutrients and waste), the nucleus, and all intracellular **organelles** (namely the chloroplasts involved in the photosynthesis process). All of these elements are surrounded by a medium called cytoplasm. Plant cells are connected to each other through plasmodesms, channels that pass through the cell walls of plants to form the pathways for water, solutes, phytohormones and phytopathogenic viruses that spread through the plant. The cytoplasm of these connected cells forms one single compartment in the plant, and the intracellular continuum thus obtained constitutes the symplasm. Outside the plant cells, the extracellular continuum formed by all the interstices of

cell walls and dead **xylem** cells constitutes the apoplast. Water and solutes can use this route to infiltrate organs without entering a cell.

Roots allow the plant to be firmly and durably secured in the ground, but their main role is to draw up water and mineral salts that are essential for plant growth. This absorption is achieved through a multitude of absorbent hairs at the root tips, ensuring a very large contact surface at the root-soil interface. Water enters the roots through a hydrostatic mechanism.

The leaves are the main organs at the plant-air interface, with exchanges taking place according to two pathways: the cuticle and the stomata. The leaf generally consists of a petiole and a limb with veins (the conductive vessels) of very different shapes. A protective layer, called the epidermis, covers the plant's aerial organs. The outermost part of the epidermis that is in contact with the air is the cuticle. The cuticle's main physiological roles are related to its generally hydrophobic nature: it maintains a water-poor area on the plant surface, which protects the plant from pathogens (including germination and fungal spore development), and limits the loss of water, ions and polar solutions (sugars, organic acids, etc.) from the plant. The plant cuticle is covered by epicuticular waxes (Barthlott et al. 1998). These structures, composed of small, highly variable crystals associated with the presence of trichomes, confer roughness to the cuticle and play an important role in the wettability of leaf surfaces (Koch et al. 2008), while increasing surfaces that are potentially reactive to pollutants. Most of the leaves are green, i.e. with chlorophyll pigments. Chlorophyll is essential for photosynthesis. This biochemical mechanism allows the production of the organic compounds that make up the plant and are essential for its metabolism. It requires not only light, water and mineral salts coming through the xylem from the roots to the leaves, but also a carbon source, CO₂, which the leaf draws from the atmospheric air. CO₂, water vapour, and gaseous pollutants penetrate into the leaves through the microscopic pores of the leaves called stomata, then integrate the cells of the leaf tissues. Stomata open and close according to microclimatic conditions and plant regulation.

Plants play an important role in the surface energy balance. They are mainly made up of water, which constitutes from 80% to 95% of their total weight. They draw this water from the soil through their roots. Foliar transpiration causes sap to rise from the roots along the stems and to the leaves via the xylem using the energy provided by solar radiation. This suction phenomenon is very powerful: coupled with cohesion forces that hold the water column, it brings the water to the top of even the tallest trees. Transpiration is also a key element in regulating plant temperature. The transformation of liquid water to water vapour consumes huge amounts of energy (latent heat of vaporization) at constant temperature, which prevents the plant's temperature from rising excessively under high solar radiation. The transpired water passes through the stomata, and in the case of water stress, the stomata close, limiting water loss for the plant. Transpiration is a specific and essential manifestation of plant behaviour towards water. Its intensity is such that the quantities of water stored in a plant and those used by its metabolism are very small compared to those that pass through the plant. Evapotranspiration almost exclusively regulates a plant's water needs.

Plants growing in stands create what is called a plant canopy. Leaves are the main surfaces of exchange with the atmosphere. Their organization in space partly determines the effects of climatic factors: the penetration of wind and radiation into the different strata of the vegetation cover depends on the cumulated leaf surfaces from the top of the cover to the stratum in question. The total cumulative leaf area corresponds to the leaf area index (LAI, in m^2 of leaves per m^2 of soil). Similarly, fine roots and their absorbent hairs are the main surfaces of exchange with the soil and a total root area index (RAI, in m^2 of root surfaces per m^2 of soil) is defined.

Crop establishment for cultivated species usually begins with seeding. The different physiological stages of canopy growth and development to harvest include foliar development, flowering, fruiting and maturation. However, not all plant organs remain functional throughout the crop cycle: over time, ageing causes slow and progressive degradation of their functions and triggers a physiological process called senescence.

Effect of Agricultural Practices

In the context of agricultural fields, the implemented practices modify the state of the soil in ways that may be short or long term. For example, irrigation changes water levels and soil temperature in the short term, but it can also change albedo or surface roughness. Tillage (ploughing, stubble incorporation, seedbed preparation) causes a mixture of the different layers of soil impacted, thus drastically and instantly modifying its porosity, humidity and temperature. By incorporating any crop residues on the surface into the soil, it changes the local organic matter content and microbial activity in the soil (Boiffin et al. 2020). The energy and water balances of the surfaces may also be altered. Indeed, the energy absorbed by the surface is closely linked to the surface radiative properties (albedo, emissivity): thus, an increase in albedo (e.g. through crop establishment or crop residues) reduces the energy available at the surface and therefore the amount of heat entering the ground. The impact is generally negative on temperature, but this may depend on changes in water characteristics associated with this modification. In addition, these changes in surface properties result in a change in latent (λE) and sensitive (H) heat fluxes and consequently in the temperature of the surface and the surrounding air. In the absence of tillage, crop residues left on the soil lead to two opposite mechanisms: albedo increases while soil evaporation decreases (Ceschia et al. 2017), and surface horizons are generally acidified in relation to the accumulation of organic matter (Benoit et al. 2014). Inputs can also change the state of the environment: manure input, for example, provides a significant volume of water, alters the soil water content, temperature and surface conditions (e.g. albedo) due to the dry matter remaining on the surface. Other examples include the choice of crops, their density and the planting date, which profoundly modify the surface characteristics and temporal dynamics, as well as the energy and water transfer.

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