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# Role of ecological scenario in modelling the bioaccumulation in vegetation

Elisa Terzaghi

Supervisor: Prof. Bruno CERABOLINI

Co-supervisor: Prof. Antonio DI GUARDO

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*To my family and Stefano*

*with love*

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# 1. INTRODUCTION

## 1.1 Accumulation of organic contaminants in vegetation

Approximately 80% of the Earth land surface is covered by vegetation (Simonich and Hites, 1994), which constitutes a complex interface influencing exchange of organic chemicals between atmosphere and soil and therefore their environmental fate.

There are several pathways through which organic contaminants enter vegetation from air and soil (McLachlan, 2011). Transfer from the atmosphere to plant leaves can occur by dry gaseous deposition (absorption), dry and wet deposition of particle associated chemicals and rain dissolution. Organic chemicals can also partition from contaminated soil to plants roots and be transported through the xylem and the phloem. Vegetation plays also an important role in transferring contaminants to air by volatilization from leaves or suspension of particle associated chemicals and to soil by the processes of wash off, wax erosion and litter fall. The final concentration of an organic contaminant in plants depends on these uptake and release mechanisms but also on transformation and dilution processes such as degradation in plants (photochemical reactions and biodegradation) and growth. **Figure 1.1** shows the pathways through which organic contaminants may enter and leave vegetation.

Organic chemicals can be taken up by plant roots via the vapor or the water phase of soil (Collins et al., 2006). This happens through a passive mechanism driven by diffusion and advective processes, since there are not transporters for these compounds in plants membrane (Pilon-Smith, 2005). Subsequently, chemicals are transported to other parts of plant through xylem and phloem. However, root uptake is influenced by soil properties, such as organic carbon content (Doucette et al., 2011). Extremely hydrophobic molecules such as PCBs, PAHs and other hydrocarbons (log $K_{OW} > 3$) are tightly bound to soil organic carbon and do not dissolve in the soil pore water. This reduces chemical bioavailability, limiting their uptake by plants.

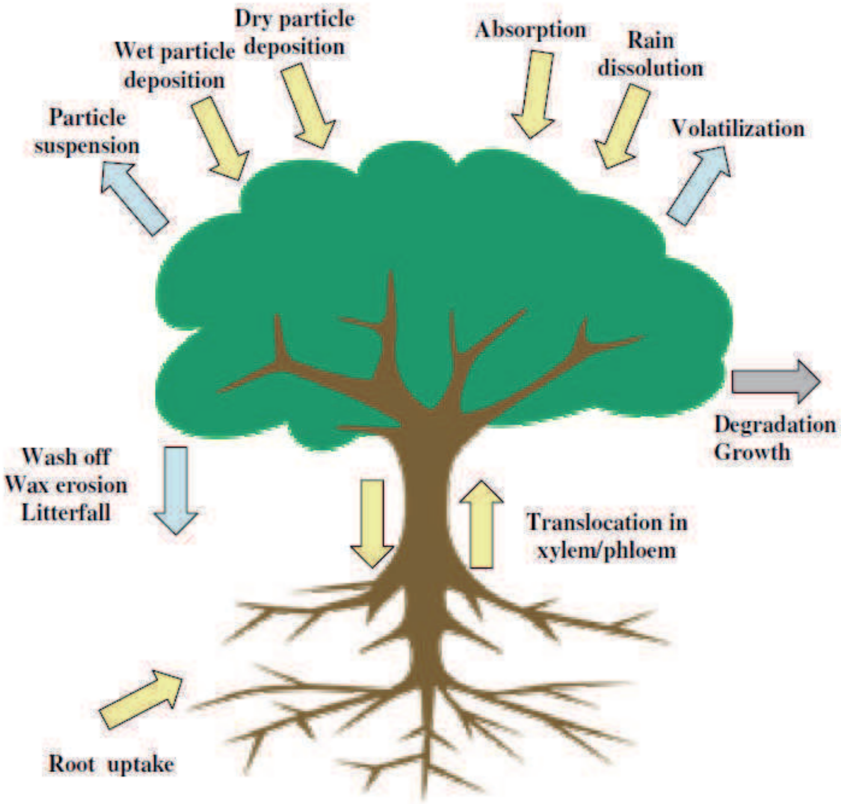

**Figure 1.1- Pathways through which organic contaminants may enter and leave vegetation**

Different studies (Brigg et al., 1982; Briggs et al., 1983; Burken and Schnoor, 1998; Dettenmaier et al., 2009) investigated the relationships between chemical lipophilicity and root uptake and translocation into stem. While the tendency to partition into roots was shown to be proportional to the hydrophobicity of the chemical, translocation into stem was maximal for compounds of intermediate polarity (Log $K_{OW}$=1.8 according to Briggs et al., 1983 and Log $K_{OW}$=2.5 according to Burken and Schnoor, 1998). Compounds that are either highly polar (Log $K_{OW} < 1$) or are highly lipophilic (log $K_{OW} > 4$) are not significantly taken up by plants, because they bound so strongly to the surface of roots and soil and they can not be easily translocated within the plant; water soluble chemicals are not sufficiently sorbed to roots nor actively transported through plant membranes. According to Dettenmaier et al., 2009 non-ionizable, polar, highly water-soluble organic compounds are most likely to be taken up by plant roots and translocated to shoot tissues. The reason is not clear, but could be due to a variety of factors including differences plant growth conditions (hydroponic vs soil), plant species, plant age, test duration, transpiration rates, losses due to metabolism and volatilization and perhaps even active compound-specific uptake mechanisms (Dettenmaire et al., 2009).

Many other more recent studies (White et al., 2005; Liu and Schnoor, 2008; Tao et al., 2009) have shown that there is almost no strong evidence of transport of hydrophobic compounds in plants to stem and leaves. However there is one interesting exception. Hulster and co- workers (1994) have shown that zucchini and pumpkin can accumulate and translocate higher concentration of PCDD/Fs from contaminated soil. This may be due to crop-specific root exudates which mobilize PCDD/Fs from the soil and make these compounds available for uptake and translocation.

Organic contaminants can reach leaf plant surfaces as vapour phase (absorption), dissolved in water droplets (rain dissolution), or associated with particles (dry and particle deposition), depending on their physical-chemical properties. Gaseous uptake is the primary pathway for chemicals with an octanol/air partition coefficient (log $K_{OA}$) less than 11, although between log $K_{OA}$ 8.5 to 11 this process is kinetically limited; the compounds with a log $K_{OA}$ higher than 11 are particle bound and deposit to plant surfaces (McLachlan, 1999).

Gaseous organic contaminants are believed to enter the plant primarily via sorption into the leaf cuticle thanks to their high lipophilicity, while transfer through stomata is generally considered negligible (Riederer, 1990).

Many authors (Bacci et al., 1990; Kömp and McLachlan, 1997; Nizzetto et al., 2008) investigated the relationships between Log $K_{OA}$ and leaf uptake and developed equations to estimate plant-air partition coefficients ($K_{PA}$) (concentration in plant (pg/g d.w.)/concentration in air (pg/m$^3$)) of gaseous phase organic compounds for different herbaceous, broadleaf and conifer species. However , although plants have been found to capture air particles with varying degrees of efficiency, depending on species-specific leaf characteristics (Neihnius and Barthlott, 1998; Burkhardt et al., 2001; Prajapati and Tripathi, 2008) such as orientation, roughness, hairiness, petiole length and rigidity, wettability and so on, these type of equations are still lacking for particle bound chemical. Furthermore there is also still a lack of knowledge concerning the transfer of chemical from particles to leaves.

Different approaches were also developed to quantitatively describe the uptake of organic pollutants to plant leaves. Leaves were treated as a single compartment system (McLachlan et al., 1995) or a two compartment system (Tolls and McLachlan, 1994; Mackay et al., 2006), consisting of a surface compartment characterized by rapid uptake and clearance kinetics and a reservoir compartment characterized by relatively slow chemical migration and accumulation with time (Simonich and Hites, 1995; Hung et al., 2001; Barber et al., 2002).

The study of the accumulation of pollutants by plants was also addressed to forest. Different studies had shown that one of the most important effects that forest has on atmospheric organic contaminants concentrations is the "forest filter effect" (McLachlan and Hortstmann, 1998; Jaward et al., 2005; Nizzetto et al., 2006). Plants in forests scavenge large quantities of organic contaminants from air, reducing atmospheric concentrations. The sequestered chemicals are subsequently deposited to the soil, increasing soil concentration below the canopy (of a factor of 2 to 3). The forest filter effect was shown to be particularly effective for compounds with $7< \text{Log } K_{OA}<11$ and $\text{Log } K_{AW}> - 6$ (McLachlan and Hortstmann, 1998). However, another important feature of vegetation is its large capacity to reversibly store organic chemicals. Plant leaves were shown to behave as a dynamic compartment (Hornbuckle and Eisenreich, 1996; Hung et al., 2001; Gouin et al., 2002; Dalla Valle et al., 2004) contributing to the diurnal variation of organic contaminant concentrations which deposit or volatilize from their surfaces in response to changes in environmental conditions, indicating that the forests play also an important role in "buffering" air concentrations.

## 1.2 Vegetation in multimedia fate models

Multimedia fate models are important tools within the Environmental Risk Assessment (ERA) procedure. They may be used, during the exposure assessment step, to integrate information about chemical properties, use and release patterns, quantities and the characteristics of the environment, in order to provide qualitative and quantitative understanding of the fate and distribution of chemicals in the various relevant environmental compartments (Cowan et al, 1995).

The most commonly used multimedia fate models are those of Mackay (2001) also known as box models. Based on the concept of fugacity, they allow to assess chemicals in "evaluative environments" split into compartments also called boxes, assumed to be internally homogeneous and well mixed. Compartments have fictitious but realistic properties such as volume, composition and temperature. The chemical in each compartment has a certain fugacity, f (Pa) i.e. a tendency to leave that compartment. Each compartment has a certain fugacity capacity, Z (mol/m$^3$Pa) i.e. an innate capacity to absorb a chemical. Transport between compartments (through advective or diffusive processes) and transformation processes in each compartment are expressed in term of D values (mol/Pa h): these parameters when multiplied by a fugacity, give rate of transport or transformation, N (mol/h).

Mackay (2001) proposed two evaluative environments (**Figure 1.2**) also called "units of world": a simple four-compartment system (air, water, soil and sediment) that illustrates the application of the general principles of environmental partitioning and a more complex, eight-compartment system (air, water, soil, sediment, aerosols, terrestrial biota, aquatic biota and suspended sediment) that better represents the real environment but at the same time it requires more data and leads to more lengthy calculation.

Initially, vegetation was not considered as possible compartment in Mackay's units of world. The reason of this was that modellers had enormous difficulty calculating the partitioning of chemicals into plants (Mackay, 2001) rather than vegetation was considered unimportant.

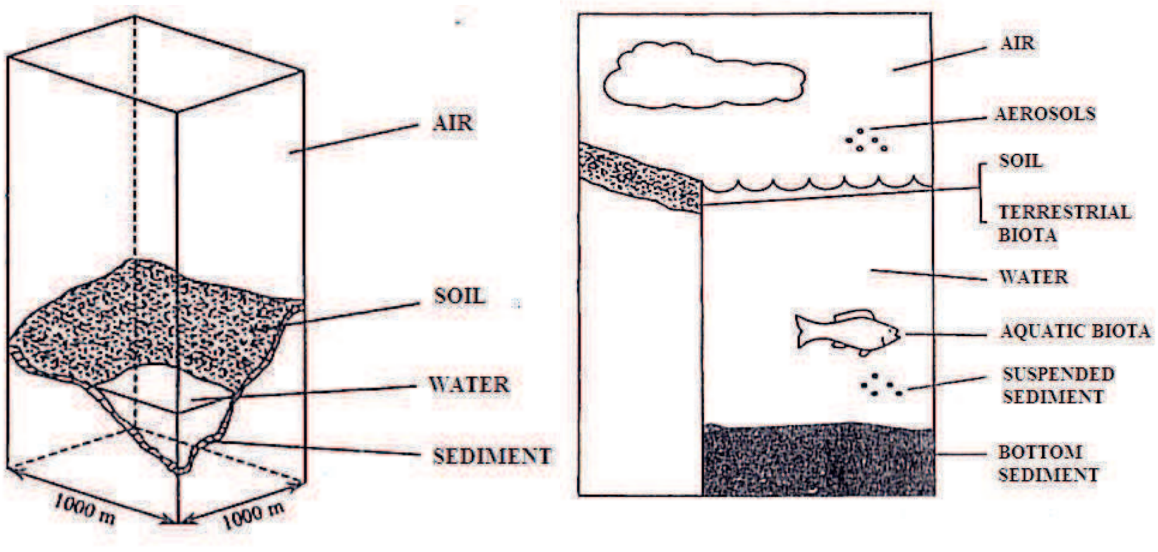

**Figure 1.2- Mackay's unit of world (redrawn from Mackay, 2001)**

The introduction of the vegetation compartment in multimedia fate models happened when: 1) vegetation appeared to be the major route for the transfer of organic chemicals along the food chain and 2) plants showed to play an important role in influencing contaminant concentrations in the surrounding compartments i.e. air and soil.

The equations to include plants in multimedia fate models were introduced in the 1980s (Briggs et al., 1982; Briggs et al., 1983; Calamari et al., 1987) and then several models, with varying degree of complexity, were developed to describe the transport, transformation and accumulation of chemicals in plants. They range from simple models that consider only a single species (Trapp et al., 1994), to more complex ones that consider mixed-forest (Wania and McLachlan, 2001); from models in which the plant compartment is split into different sub-compartments (roots, stem, leaves, fruits) (Behrendt and Brüggemann, 1993), to models that consider only foliage (Priemer and Diamond, 2002); again from equilibrium and steady state models to dynamic ones (Fantke et al., 2011). Plants were also included in the European Union System for the Evaluation of Substances (EUSES) (EC, 2004) which is a steady state model recommended in the European Union for risk assessment of organic chemicals.

## 1.3 Meteorological and ecological dynamics in vegetation models

Many plant bioaccumulation models described in the literature are steady state models (Paterson et al., 1991; Hung et al., 1997; Cousins and Mackay, 2001). These models assume that the chemical concentrations in the plant and in the surrounding media, as well as environmental and compartment parameters are constant over time.

Unlike steady state models, unsteady state ones can account for the variability of meteorological parameters, compartment features and chemical emission, predicting the concentration changes in plants and other compartments with time. However most of the existing unsteady state models consider only the variability in exposure concentrations, having the main advantage of being relatively simple and requiring less input data, but probably leading to erroneous results when comparing predictions to measured values.

Meteorological parameters play an important role in determining the variability of air and leaf concentrations. Temperature, for example, controls chemical volatilization and deposition from/to surfaces (soil and vegetation), causing increase/decrease in air concentrations (Hornbuckle et al., 1996). Moreover it is responsible of $K_{PA}$ changes (Kömp and McLachlan, 1997). Solar radiation, together with OH radicals, enhance photolytic and degradation reaction in air and on leaf surface (Calvert et al., 2002; Wang et al., 2005) during daytime hours, while wind speed influences the air-side mass transfer coefficient involved in the air-leaf exchanges (Barber et al., 2002) and the residence time of air masses. Moreover, planet boundary layer (PBL) or mixing layer height was shown to be one of the most important factors in determining the short-term variations of air concentrations (Lee et al., 1998; Gasic et al., 2009). In general, PBL exhibits a typical diel cycle characterized by low nocturnal levels and elevated day time heights, which causes an increase/dilution of air concentrations. However this pattern can be altered by the presence of a nearby point source or a local emission (Morselli et al., 2012). Finally, the dynamics of leaf biomass and of ecological parameters such as LAI (Leaf Area Index) and SLA (Specific Leaf Area) were shown to strongly affected the temporal trend of organic contaminants accumulation in plant leaves (Jaward et al., 2005; Nizzetto et al., 2007; Nizzetto et al., 2008).

Since air and leaf concentrations are controlled by a combination of factors, only a dynamic multimedia fate model that includes the variability of meteorological and ecological parameters, together with chemical emission, could assist in identifying the relative importance of each parameter and in predicting realistic environmental concentrations.

On this topic, it has recently been pointed out (Di Guardo and Hermens, 2013; EC, 2013) that the current procedure employed for environmental risk assessment lacks of ecological realism and should be improved in the coming years. Concerning the exposure assessment, this can be achieved by the development of: 1) dynamic multimedia fate models which are capable of predicting variable concentrations in time and space and 2) realistic scenario that reflect ecosystem complexity, together with the temporal and spatial variability of environmental parameters.

To account for the role played by meteorological parameters and air structure dynamics (such as those related to the PBL) in driving the fate of organic chemicals, several models were developed. For example, Morselli et al., 2011 have recently shown that air concentration diurnal trend could be predicted including a dynamic PBL in multimedia fate models. However the proposed approach does not account for vegetation as possible responsible for temporal variability. Generally, when vegetation is considered in such a type of models, it is kept constant for the whole growing season (McLeod et al., 2007) or both vegetation and PBL height are assumed not to change with time (Zhang et al., 2003; Czisar et al., 2012).

Models that include ecological parameters are scarce. Furthermore, when SLA and LAI are considered, are assumed constant over time representing the value of the leaf/canopy maturity phase (Priemer and Diamond, 2002; Wegmann et al., 2004; Bathia et al., 2008; Komprda et al., 2009; Undemann et al., 2009; Rein et al., 2011;). An attempt to coupling a multilayered ecophysiological canopy model with a fate model was also made, in order to investigate the short-term air-canopy exchanges (Nizzetto et al., 2012). However species-specific timing of bud burst and production of new leaves through the whole growing season were ignored, even if the emergence of a fresh uncontaminated lipid or wax compartment (leaf cuticle) was show to be responsible of reduction in organic chemical air concentrations (Gouin et al., 2002).

Leaves were also compared to organic films that developed on impervious surface, since both have the ability to rapidly exchange contaminants with air (Wu et al.,2008). However, models that account for a dynamic urban film compartment (Czisar et al., 2012) consider vegetation only in a static form.

Another important aspect concerns the prediction of particle-associated compounds. In general dry/wet particle deposition is modelled in a simplified way, assuming particles as a sub-compartment of the air. Only few vegetation models include a mass balance for air and canopy particles (Schaubroeck et al., 2014). However, some important processes such particle encapsulation in leaf cuticle, particle erosion and resuspension together with chemical movement from particle to leaves has not been yet considered.

A modelling approach that encompass all these features (variability of meteorological parameters and air structure, dynamic ecological parameters and canopy composition, leaf particle mass balance and so on ) does not exist yet, but in the future currently models have to be refined in order to improve the ecological realism in exposure assessment.

Some of these improvements will be the topic of the present PhD thesis which is discussed in the next section.

# 2. OBJECTIVES

The investigation of the role played by temporal dynamic of meteorological and ecological parameters in influencing chemical fate, mainly in air and plant compartments, formed the general framework of this thesis. More in details the present study focuses on the following points:

1. Investigate the role of leaves/needles of different species in capturing and releasing air particulate matter and its associate PAHs.
2. Develop a fully dynamic scenario that accounts for the variability of exposure concentrations, meteorological and ecological (SLA and LAI) compartment parameters.
3. Investigate the feasibility of employing plant leaves and organic films (which develop on window surface) to predict the short-term variability of PAH air concentrations.
4. Develop a dynamic vegetation model that accounts for the variability of meteorological and ecological parameters and integrate it in an existing air/soil model which includes a double layered air compartment (PBL and residual layer) and a multilayered litter/soil compartment.

# 3. STRUCTURE OF THE THESIS

This thesis is based on the following papers, referred to in the text by their Roman numerals:

**I.** Terzaghi E., Wild E., Zacchello G., Cerabolini B., Jones K.C. and Di Guardo A. Forest Filter Effect: Role of leaves in capturing/releasing air particulate matter and its associated PAHs. *Atmospheric Environment* (2013), 74: 378-384.

**II.** Terzaghi E., Zacchello G., Scacchi M., Raspa G., Jones K.C., Cerabolini B., Di Guardo A. Towards more ecologically realistic scenarios of plant uptake modelling for chemicals: PAHs in a small forest. *Science of the Total Environment* (2015), 505: 329-337.

**III.** Terzaghi E., Scacchi M., Cerabolini B., Jones K.C., Di Guardo A. Estimation of PAH variability in air using high volume, film and vegetation as samplers. Submitted to *Environmental Science & Technology*.

**IV.** Terzaghi E., Morselli M., Semplice M., Cerabolini B, Jones K.C., Di Guardo A. Modelling the temporal uptake of semi-volatile organic chemicals in plants using an ecologically realistic scenario. Draft to be submitted to *Environmental Science & Technology*.

# 4. SUMMARY OF RESULTS

## PAPER I

Plants play a key role in removing particulate matter and their associated Semi-volatile Organic Compounds (SVOCs) from the atmosphere. Understanding the processes involved in particle capture by vegetation is essential to understand the interactions between SVOCs, particles and plants. In the present study Two Photon Excitation Microscopy (TPEM) was used to visualise particle matter uptake and encapsulation, together with its distribution on leaf/needle surface of different broadleaf (cornel and maple) and conifer species (stone pine). Phenanthrene accumulation, the number of particles associated with this compound and its migration from particles into the leaf cuticle was also identified and quantified. Species-specific deposition velocities were estimated to model temporal $PM_{10}$ leaf/needle accumulation and to investigate the role of Planet Boundary Layer (PBL) height variation in influencing $PM_{10}$ flux to plants. Particles at the leaf/needle surface were visualised to range in size from 0.2 to 70.4 µm, but cuticular encapsulation was negligible for particles larger than 10.6 mm, which were removed by a washing procedure. Phenanthrene concentration varied between ~5 and ~10 ng/g dw according to plant species and between ~10 and ~z200 ng/g dw depending on needle age; this compound was visualized to migrate from particles into the adjacent leaf cuticle. Species-specific deposition velocity range between 0.57 and 1.28 m/h and preliminary simulations showed that the diel variability of PBL structure influenced the temporal $PM_{10}$ flux and leaf/needle concentration, e.g. during daytime hours characterized by high PBL height, $PM_{10}$ accumulated on cornel leaves was about 65% lower than the amount accumulated during night time. The capability of vegetation to capture particles from the atmosphere, retain, encapsulate them into the cuticle and release them to soil and/or lower biomass, highlighted the value of vegetation in removing pollutants from the atmosphere and influencing their environmental fate.

# PAPER II

The importance of plants in the accumulation of organic contaminants from air and soil was recognized to the point that even regulatory predictive approaches now include a vegetation compartment or sub-compartment. However, it has recently been shown that many of such approaches lack ecological realism to properly evaluate the dynamic of air/plant/soil exchange, especially when environmental conditions are subject to sudden variations of meteorological or ecological parameters. This paper focuses on the development of a fully dynamic scenario in which the variability of concentrations of selected chemicals in air and plant leaves was studied weekly and related to the corresponding meteorological and ecological parameters, to the evaluate their influence. To develop scenarios for modelling purposes, two different sampling campaigns were performed to measure temporal variability of: 1) polycyclic aromatic hydrocarbon (PAH) concentrations in air of a clearing and a forest site, as well as in leaves of two broadleaf species and 2) two important leaf and canopy traits, specific leaf area (SLA) and leaf area index (LAI). The aim was to evaluate in detail how the variability of meteorological and ecological parameters (SLA and LAI) can influence the uptake/release of organic contaminants by plants and therefore air concentrations. A principal component analysis demonstrated how both meteorological and ecological parameters jointly influence PAH air concentrations. SLA, LAI, as well as leaf density were showed to change over time and among species and to be directly proportional to leaf/canopy uptake rate.While hazelnut had the higher leaf uptake rate, maple became the most important species when considering the canopy uptake rate due to its higher LAI. Other species specific traits, such as the seasonal variation in production of new leaves and the timing of bud burst, were also shown to influence the uptake rate of PAHs by vegetation.

# PAPER III

Organic films and leaves provide a medium into which organic contaminants such as PAHs, can accumulate, resulting useful as passive air sampler. In the present work the temporal variability (weekly) in PAH concentrations and fingerprint of film developed on window surface was investigated. Moreover, film and leaves of two tree species (*Acer pseudoplatanus* and *Cornus mas*) collected simultaneously at the same time were used to derive PAH air concentration and investigate their short-term variability. In general, the most abundant chemical found in film was phenanthrene (22%) followed by pyrene (22%), perylene (21%) and fluoranthene (16%) but the fingerprint (in contrast to leaves and air) changed over time. Air concentrations estimated from leaves generally underestimated (a factor of 2 to 5) the measured one (Hi Vol sampled), while film derived air concentrations showed a large range of variability (a factor of 2 to 90 lower/higher) which could depend on rapid air concentration changes (e.g. hourly) and on uncertainties in film parameters (thickness, organic matter content and density) employed in the calculation. However, film and leaves can be usefully employed for predicting the short-term variability of low $K_{OA}$ organic contaminant air concentrations, due to their ability to rapidly equilibrate with air.

# PAPER IV

A new dynamic vegetation model was developed to simulate the fate of organic compounds in the air/plant/litter/soil system. Key features of the model are the double-layered air compartment (planet boundary layer, PBL and residual layer) interacting dynamically with vegetation and multilayered litter/soil compartments. Vegetation can represent both monospecific and multispecfic forest. Leaf biomass is dynamically calculated employing two important ecological parameters (LAI and SLA), while stem and root biomass are assumed constant over time. The model was used to investigate the air compartment structure and meteorological variability in influencing PAH air-leaf exchanges, simulating a broadleaf wood located in Northern Italy (Como). Modelled leaf concentrations showed a satisfying agreement with measured one. Leaves appeared to act as a “filter” but also as a “dispenser” of air contaminants in response to meteorological parameters and emission changes. A preliminary sensitivity analysis showed that air concentrations are most affected by emission, PBL height and wind speed, while for leaf concentrations $K_{OW}$, air temperature and SLA are also important. Illustrative simulations were then performed for PCB 52 and PCB 153 to show the influence of leaves biomass on air concentrations in realistic forest conditions in terms of air residence time, wind speed and domain size.

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