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Soil and Litter Exchange of Reactive Trace Gases

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Introduction

The soil and litter play an important role in the exchange of trace gases between terrestrial ecosystems and the atmosphere.

- The exchange of ammonia between vegetation and the atmosphere is highly influenced by soil and litter emissions especially in managed ecosystems (grasslands and croplands) mainly due to the input of mineral and organic forms

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of N, which leads to increases in available N at the soil surface. Apart from fertiliser-induced NH_3 volatilisation, significant emissions may also occur from barren soil and senescent plants and leaf litter (Massad et al. 2010; Sutton et al. 2009). Ammonia emissions from the leaf litter, even if understood in principle, remain very uncertain due to the limited number of studies.

- Soils and litter are sources of several VOCs (furfural, butanoic acid, methanol, etc.), but these sources have not yet been well quantified (Insam and Seewald 2010; Leff and Fierer 2008). Similarly composts and slurry applications may be sources of nitrogen containing VOCs. Recent research on VOC emissions from soil and decomposing litter suggest that microbes may be important sources of VOCs and that such emissions are highly variable across litter types and soils (Gray et al. 2010).
- Soil emission of NO occurs as a by-product of soil nitrification and denitrification processes. The latter are a function of temperature, moisture, and substrate availability (available N, dissolved O_2 , and soil moisture). For natural ecosystems, the substrate availability is mainly a function of productivity (input via plant residues) and wet and dry deposition, while for managed ecosystems it depends mainly on fertiliser input (Bouwman et al. 2002; Ganzeveld et al. 2010).
- Concerning NO_2 and O_3 , uptake/deposition is considered the main pathway of exchange with the soil. This deposition of O_3 and NO_2 at the soil surface is often masked in the measurements by the activity and the transfer resistance of the vegetation cover and therefore not very well quantified (Gut 2002; Pilegaard 2001).

Products of the Discussion

The discussions in the working group were structured around two main parts. During the first part we discussed the state of the art and already existing models treating soil and/or litter exchange of trace gases. The main focus was around ammonia and some models dealing with CO_2 , CH_4 and N_2O . Other trace gases such as NO, NO_x , O_3 and VOCs were addressed very briefly. The second part consisted of elaborating a theoretical scheme for an ideal soil/litter exchange model and establishing a priority list of what are the characteristics of a model that could be immediately feasible (the silver model) and a model that would be ideal but more of a long-term outcome (the golden model).

Existing Modeling Schemes

A lot of recent efforts have gone into developing soil models for greenhouse gas emissions mainly accounting for mineralization, nitrification and denitrification processes (DNDC, CERES-NC SOIL, ACASA, etc.). Those models particularly account for incorporated residues or bare soils. Few mechanistic models exist that account for emissions from soil and litter of reactive trace gases.

- **Volt'air** (Génermont and Cellier 1997) is a mechanistic model that simulates the NH_3 and pesticide volatilization from field applied slurry or pesticides. It accounts for controls by soil, meteorology and slurry/pesticide characteristics on volatilization; it simulates the transfers and equilibria in the topsoil and between the soil and the atmosphere. The model includes an energy balance and advection sub-models, which makes it suitable for field scale applications using simple meteorological data. Sensitivity analysis showed that soil pH has a large influence on volatilization. The model is also sensitive to soil adsorption capacity and some hydraulic characteristics (saturation water conductivity, water content at field capacity) (Garcia et al. 2011). Volt'air has also been extended to simulate emissions by mineral fertilizers.
- **Guano** model (Blackall et al. 2007; Riddick et al. 2012) simulates NH_3 emissions from seabird excreta (guano) on the ground of land-based colonies. The model describes four steps in the processes of NH_3 emission: (i) Excretion of nitrogen rich guano, in the form of uric acid; (ii) conversion of uric acid to total ammoniacal nitrogen (TAN), with a climate- and surface pH-dependent rate; (iii) TAN partition between NH_4^+ and NH_3 on the surface; and (iv) NH_3 volatilization to the atmosphere, controlled by meteorological conditions. Emissions from seabird colonies present similarities to emissions from field excreted dung and their study and modelling proves relevant in this context.
- **EPIC** is a semi-empirical biogeochemical process model developed by the United States Department of Agriculture (USDA) in the early 1980s to assess the effect of wind and water erosion on crop productivity (Williams et al. 1984) and expanded to include soil N and C biogeochemistry (Izaurre et al. 2006). This model was developed for managed agricultural simulations and includes parameterizations of the crop growth, fertilization management, soil hydrology, N and C biogeochemistry (mineralization, nitrification, and denitrification), and energy balance. Nitrogen losses are modelled for vegetation uptake, NO_3 infiltration and runoff and NH_3 volatilization. Field scale simulations can be made using observed meteorology or regional scale simulations can be made using the output of a regional meteorological model.
- Modeling NO emission from soils with Artificial Neural Network (**ANN**) algorithm. An emission algorithm has been developed for the calculation of NO biogenic emissions (Delon et al. 2007). NO fluxes depend on soil moisture, soil temperature at two depths, wind speed, pH, sand percentage and fertilization rate.
- Several other models were cited that do not explicitly deal with trace gas emissions but that could be useful in terms of modeling the energy and water balance of the top soil layers or of litter and mulch disposed at the surface of the soil. Among those models: (i) **PASTIS** a model that has a top layer of residues and that simulated mineralization and nitrification (Garnier et al. 2003). (ii) an energy balance model for surface mulch (Bussière and Cellier 1994).

Theoretical Ideal Model

A theoretical ideal model scheme was developed, Fig. 1. The scheme depicts the 4 different states of litter decomposition that should be accounted for, their residence time and the different gases exchanged at each state.

- State 1 is the few hours/days following the litter (leaves) detachment from the plant. This state is characterized by the litter being clearly distinguished from the soil. At this stage, NH_3 and probably CO_2 are the main gases being exchanged.
- State 2 lasts a few days to weeks it is characterized by the litter starting to decompose, the leaves are mixed with fungus material but are still clearly distinguished from the soil. At this stage, NO , NH_3 , CO_2 and probably VOCs are exchanged.
- State 3 is the litter that has fallen the past year and thus lasts from one to several months. The litter can barely be distinguished from the soil but it is still lying on top of the soil. At this stage, the primarily exchanged gases are NO , N_2O , N_2 , CH_4 and CO_2 .
- State 4 is the ultimate decomposition state of the litter. At this point it is almost incorporated with the soil and can last decades depending on soil and environmental conditions. At this stage main exchanged gases are N_2O , N_2 , CH_4 and CO_2 .

The main requirements for the ideal model were discussed and two options were set as described in Table 1 (gold medal and silver medal options). Whatever the case the model should however be able to generate a pool of $\text{N}_2\text{O}/\text{NO}/\text{NH}_3$ that is then transported (by diffusion and advection) into the system, it should have a

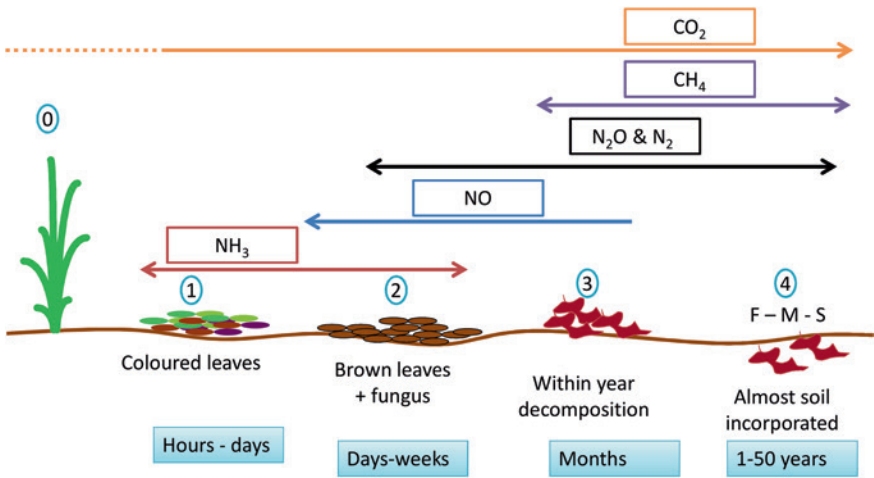


Fig. 1 An ideal soil/litter model scheme for simulating exchange of trace gases with the atmosphere

Table 1 Different variables that should be accounted for in the soil/litter ideal model, together with their purpose and their origin, whether the gold medal or silver medal option is chosen

Variables	Purpose	Gold model	Silver model
Substrate/litter moisture	Process description	Water balance model	External input
Soil moisture	Boundary conditions	Water balance model	External input
Substrate/Soil Temperature	Boundary conditions	Energy balance model	External input
Fertilisation	N condition of soil	Input/parameterisation	Input
Incorporation—discontinuity		Spatial model (horizontal transfer)	1 D spatialized model
Organic inputs (leaves—dung—external OM)		Input at stages 2 or 3	
Soil texture and porosity	Water and energy balance, infiltration	External input	External input
Substrate/soil pH	Thermodynamics, processes (biological, chemical)	Empirical parameterisation	Lookup table
Plant species and litter quality	C & N content and form	Ecosystem/soil model	Lookup tables and/or satellite data
Litter porosity/structure	Litter diffusive resistance	depends on species, management	Lookup table
Litter mass and thickness	Mass balance	Ecosystem model 1 litter layer and multiple soil layers	1 litter and soil layer

OM Organic matter; C Carbon and N Nitrogen.

litter water and energy balance as well as a litter degradation module and it could be part of a soil model. One major challenge resides in setting the boundary between the different phases of litter decomposition especially between phases 3 and 4.

The major variables that should be accounted for but at different levels of complexity according to the model option chosen (see Table 1) are: substrate moisture to allow reactions as well as determine states of aerobiosis/anaerobiosis, substrate temperature, agricultural practices (fertilization, incorporation, etc.), soil texture, substrate pH, plant species and therefore litter quality and litter structure and porosity.

Areas of Uncertainty

Processes and mechanisms concerning soil/litter NH_3 exchange are well identified and documented. However, a lot of uncertainty remains around the exchange of other trace gases mainly NO_2 , NO , O_3 and VOCs all along litter decomposition. One of the major challenges concerns the modelling of organic matter decomposition including N transformation in the litter and to measure the exchange of trace gases between the soil/litter and the atmosphere and their differentiation

between exchanges at the whole canopy. Concerning ozone for example the question remains open around what part is deposited to the litter and what part interacts with chemistry. Furthermore, does O₃ impact the litter quality and quantity (C/N ratio in fallen leaves)? Concerning VOCs, we estimate that 10 % of canopy emissions originate from soil/litter. There is a lack of observations to constrain this assumption and it is likely to vary with VOC species. For some compounds this may not be important to emissions or deposition, because uptake occurs before the VOC escapes the canopy. Still a slight shift in the uptake may lead to high emissions and elevated concentrations in the canopy, and because of this cycling, may impact the in-canopy chemistry. Measurements, most likely using cuvettes, are needed to constrain and determine the importance of these processes on net emissions and in-canopy chemistry. Additional uncertainties exist in VOC emissions from wounded plants as well as litter fungus, e.g. methanol.

One major challenge concerning soil/litter trace gases exchange for all compounds is to determine substrate pH. Accurately simulating substrate pH is still problematic while this impacts all major processes involving exchanges of NH₃, other trace gases, microbial decomposition and fermentation processes.

Conclusions

The major conclusion from this working session was that the knowledge we actually have around soil/litter exchange of trace gases is sufficient to build a mechanistic model whose purpose would be simulating exchanges with the atmosphere. The degree of complexity of the model could be determined around each case and/or gas studied. The model could be directly coupled to a soil model and/or be part of a canopy/plant model. Several initiatives are envisaged within the different groups that go in this sense. A simplified version of the Guano model applied to cattle dung is being developed. A litter layer is also being introduced in the Volt'air model to account for pesticide and NH₃ exchange. EPIC is being developed to explicitly model soil NO and N₂O emissions in addition to NH₃ emissions and is being coupled to a regional air-quality model.

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