Modules

# PAH_DOC_degradation

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## Summary



## 1 Introduction

This document is based on the publication K., Ouvrard, S., Houot, S., Lafolie, F., Garnier, P. (2018). Modelling the fate of PAH added with composts in amended soil according to the origin of the exogenous organic matter. Science of the Total Environment, 616-617, 658-668. , DOI : 10.1016/j.scitotenv.2017.10.269

The module simulates the degradation of a PAH molecule by cometabolism and by a specific biomass.

## 2 Assumptions

- The module assumes that only the PAH species in solution can be degraded. PAH molecules sorbed on the soil solid phase and PAH molecules bound to the organic matter are supposed to be protected from biodegradation.
- The module assumes the presence of a specific biomass able to degrade the PAH but the PAH can also be degraded by cometabolism.
- Metabolites produced can also be degraded.

The module calculates the rates of degradation, the $CO_2$ emissions by the different decomposition pathways, the formation of biologically bound residues,

the quantity of non extractible residues (NER), the size of the specific biomasses, the quantity of metabolites and the sink/source terms for the PAH in solution. The sink and source terms for PAH due to its degradation can be used in a module carrying out the balance of the PAH species in solution.

# 3 Equations

For each PAH species considered, the evolution of the specific biomass ($B_s$) obeys the following differential equation :

$$\frac{dB_s}{dt} = \left( \frac{\mu C}{K_s + C} - k_m \right) B_s \tag{1}$$

where

- $\mu$ is the growth rate for the specific biomass degrading PAH. It is the amount of carbon from PAH per unit mass of specific biomass per unit time that can be transformed into microbial specific biomass. This parameter depends on the maximum growth rate $\mu_{max}$, on the temperature and on the soil water potential. The Andren model is used to calculate the weigthing factor linked to soil water potential and the vantHoff model is used to caculate the weighting coefficient for the temperature.
- $C$ is the PAH concentration in solution expressed as kgPAH per unit mass of soil.
- $K_s$ is a Monod kinetic constant with unit of kgPAH per unit mass of soil
- $k_m$ is the mortality time constant for the biomass.

Metabolites ($M$) are produced by the decomposition of the PAH by the specific biomass and also by the biomass decomposing the organic matter (cometabolism). The metabolites are immobilized under the form of biologically bound residues. Taking into account these mechanisms, the metabolites concentration obeys the following differential equation :

$$\frac{dM}{dt} = -k_{mb} M + S \tag{2}$$

where

- $k_{mb}$ is the time constant for transformation of metabolites into residues bound to the biomass
- $S$ is the source term for the production of metabolites.

The source term $S$ is given by :

$$S = \delta\beta \left( B_{ini} + ZYB \right) C + \alpha\mu \frac{1 - Y_s}{Y_s} B_s \frac{C}{K_s + C} \tag{3}$$

where

- $\delta$ is the time constant for degradation of PAH by the cometabolism biomass

- $\beta$ is the ratio of metabolites to $CO_2$ production by the cometabolism degradation pathway (0 to 1)
- $B_{ini}$ is the initial amount of biomass for cometabolism
- $ZYB$ is the amount of newly form biomass (zymogeneous biomass). This variable is provided by a module simulating the decomposition of the organic matter by a specific biomass.
- $\alpha$ is the ratio: ( metabolites production rate ) / ( PAH degradation rate ) by the specific degradation pathway.
- $Y_s$ is the specific biomass yield for the decomposition of the PAH by a specific biomass (kg biomass/kg metabolites)

The quantity ($R$) of biologically bound residues obeys the following equation :

$$\frac{dR}{dt} = -k_{bc}R + S \tag{4}$$

where

- $k_{bc}$ is the time constant for mineralization of metabolites bound to the biomass compartment.
- $S$ is the source term for biologically bound residues.

The source term $S$ is simply given by :

$$S = k_{bm}M + +k_m B_s \tag{5}$$

The production of $CO_2$ coming from the mechanisms involved in the degradation of the PAH is the sum of the $CO_2$ produced by the specific and cometabolic pathways and of the $CO_2$ produced during the decomposition of biologically bound residues. These production rates are given by :

$$CO2_{com} = \delta(1-\beta)\left(B_{ini} + ZYB\right)C \tag{6}$$

$$CO2_{spe} = (1-\alpha)\mu\frac{1-Y_s}{Y_s}B_s\frac{C}{K_s + C} \tag{7}$$

$$CO2_{res} = k_{bc}R \tag{8}$$

# 4 Solution

The first order differential equations (eq. 1,2,4) are solved with a implicit Cranck-Nicholson method. An upper bound for the time increment is calculated from the $\mu$ and $\delta$ parameters. The bound is : $dt_{max} = 1/max(\mu, \delta)$. This upper bound is passed to the coupler. The solution was checked against a Mathlab solution.

# 5 Inputs

Some of the inputs below are *tagged* in the sense of the VSOIL platform. The *taggs* are used to identify which transported species are concerned by the input terms. Tagged variables are indicated below by the following keyword : [*tagged*].

- **soil bulk density** Bulk density of the soil $[kg.m^{-3}]$.
- **soil organic matter pools carbon mass ratio** Carbon mass ratio for the pools desccribing the organic matter $[kgC.kg_{soil}^{-1}]$.[*tagged*].
- **soil PAH strongly sorbed** Concentration of the PAH on the strong sorption sites of the soil matrix $[kg.kg^{-1}]$. [*tagged*].
- **soil solution solutes concentration** Concentrations of the species in solution $[kg.m^{-3}]$. [*tagged*].
- **soil temperature** Temperature of the soil. $[K]$
- **soil water matrix potential** Soil water matrix potential $[m]$
- **soil water volumetric content** Volumetric water content $[m^3.m^{-3}]$.

# 6 Outputs

The module provides the following variables. All the informations (localisation, type, description, unit) concerning a variable are available inside the VSOIL-MODULES application. Tagged variables are indicated by the following keyword : [*tagged*].

- **c_co2 pah production rate by cometabolism** Production rate of CO2 due to PAH decomposition by the cometabolism pathway. Expressed as C_CO2. $[kgC.kg^{-1}.s^{-1}]$
- **c_co2 pah production rate by specific biomass** Production rate of CO2 due to PAH decomposition by the specific biomass. Expressed as C_CO2. $[kg.kg^{-1}.s^{-1}]$
- **c_co2 pah metabolites production rate** Production rate of CO2 due to metabolites decomposition. Expressed as C_CO2. $[kg.kg^{-1}.s^{-1}]$
- **c_co2 pah production rate** Global production rate of CO2 due to PAH decomposition. It is the sum of the three previous variables. $[kg.kg^{-1}.s^{-1}]$
- **c_co2 pah production rate profile cumulated** Global production rate of CO2 due to PAH decomposition cumulated for the whole profile. $[kg.m^{-2}.s^{-1}]$
- **c_co2 pah production rate profile time cumulated** Global production rate of CO2 due to PAH decomposition cumulated in time and for the whole profile . $[kg.m^{-2}]$
- **soil solution solutes degradation rate** Degradation rate of molecules in liquid phase. Unit is : kg.m-3.s-1 or mol.m-3.s-1 depending on the unit used for the concentrations.. $[kg.m^{-3}.s^{-1}]$ [*tagged*]

- **soil solution solutes degradation rate profile cumulated** Degradation rate of molecules in liquid phase for the whole profile .[$kg.m^{-2}.s^{-1}$] [*tagged*]
- **soil solution solutes degradation rate profile time cumulated** Degradation rate of molecules in liquid phase for the whole profile cumulated in time [$kg.m^{-2}$] [*tagged*]
- **soil pah metabolites mass concentration** Mass concentration of the metabolites produced by the degrdation of the PAH [$kg.kg^{-1}$] **Initial values are required for all the species. At least two points are required : surface and bottom boundaries.** [*tagged*]
- **soil pah metabolites mass concentration profile cumulated** Mass concentration of the metabolites produced by the degrdation of the PAH for the whole profile [$kg.m^{-2}$] [*tagged*]
- **soil pah non extractible mass concentration** Total amount of non extractible PAH. It corresponds to the sum of the biologically bound residues and of the strongly sorbed residues.[$kg.kg^{-1}$] [*tagged*]
- **soil pah non extractible mass concentration profile cumulated** Total amount of non extractible PAH for the whole profile. [$kg.m^{-2}$] [*tagged*]
- **soil pah residues biological bound** Non extractable residues (NER) formed by microbiological processes and bound to the biomass. [$kg.kg^{-1}$] [*tagged*] **Initial values are required for all the species. At least two points are required : surface and bottom boundaries.** [*tagged*]
- **soil pah residues biological bound profile cumulated** Non extractable residues for the whole profile [$kg.m^{-2}$] [*tagged*]
- **soil specific microbial biomass mass ratio** Quantity of specific microbial and/or micorhizal biomass that contributes to the degradation. [$kg.kg^{-1}$] **Initial values are required. At least two points are required : surface and bottom boundaries.** [*tagged*]
- **soil specific microbial biomass mass ratio profile cumulated** Quantity of specific microbial and/or micorhizal biomass for the whole profile. [$kg.m^{-2}$] [*tagged*]

# 7 Parameters

The description of the parameters and their characteristics are available inside the VSOIL-MODULES application when editing the module and in the Graphic User Interface. The parameters are however decribed hereafter. Default values are available within the platform when this is possible. **These values are given to ease the use of the module but they are not waranted and probably not correct for all the situations. The user must verify the default values.**

- **deg_hap**, $[kg.kg^{-1}.s^{-1}]$, Degradation time constant for the cometabolism degradation pathway (kg C of PAH/kg soil/s). This is parameter $\delta$ in equation 3.
- **beta** $[NA]$. Ratio of metabolites to CO_2 productions for the cometabolism degradation pathway (0 to 1) This is parameter $\beta$ in equation 3.
- **k_MB** $[s^{-1}]$, Time constant for transformation of metabolites into residues bound to the biomass compartment. This is parameter $k_{mb}$ in equation 2.
- **k_BC** $[s^{-1}]$, Time constant for mineralization of metabolites bound to the biomass compartment. This is parameter $k_{bc}$ in equation 4.
- **Ks_spe** $[kg.kg^{-1}]$ ,Half saturation constant for PAH degradation by a specific biomass with a Monod equation. This is parameter $K_s$ in equation 1.
- **k_M** $[s^{-1}]$ Mortality time constant for the specific biomass degrading PAH. This is parameter $k_m$ in equation 1.
- **mu_spe_max** $[kg.kg^{-1}.s^{-1}]$ Maximum growth rate for the specific biomass degrading PAH. It is the maximum amount of carbon from PAH per unit mass of specific biomass per unit time that can be transformed into microbial specific biomass. Used to calculate the parameter $\mu$ (eq.1) using the vantHoff and Andren models for accounting for temperature and soil water potential effects on microbial activity.
- **y_spe** $[NA]$ Specific biomass yield for the decomposition of the PAH by a specific biomass (kg biomass/kg metabolite). This parameter $Y_s$ used in equations 3 and 7.
- **alpha** $[NA]$ Ratio: ( metabolites production rate ) / ( PAH degradation rate ) by the specific degradation way. This is parameter $\alpha$ in equations 3 and 7.
- **tempref** $[K]$ Reference temperature for vantHoff model.
- **qvanthoff** $[NA]$ Parameters of the vantHoff model.
- **pot_opt** $[m]$ Optimum potential for Andren model
- **pot_min** $[m]$ Minimum potential for Andren model
- **init_biomass_soil** $[kg.kg^{-1}]$ The initial cometabolism microbial biomass concentration in soil before compost application. This is parameter $B_{ini}$ in equation 3.
- **max_temperature** $[K]$ Maximum temperature that could be reached during the simulation. This parameter is used (vantHoff model) to estimate the maximum time increment acceptable by the module. It is important to give an estimation as precise as possible. When used in a model simulating batch experiments one must give the steady temperature provided by the heat transport module. For use in outdoor situations please try to give the highest temperature reached.