National Technical University of Athens
Chemical Engineering Department

ATHENS2017
5th International Conference on
Sustainable Solid Waste Management
21–24 June 2017
Athens, Greece

DYNAMIC MODEL OF HUMIC AND FULVIC COMPOUNDS DETERMINATION IN COMPOST

Christina Tsiodra, Anestis Vlysidis , Apostolos Vlyssides

School of Chemical Engineering

National Technical University of Athens

Aim of this work

In this work, a dynamic mathematical model for the prediction of fulvic and humic acids evolution during the humification stage of an olive mill waste residues (OMWR) composting process was developed.

The aim of this work is the application of a suitable methodology, so as to derive a dynamic mathematical model for the control of an operating industrial composting plant. The methodology chosen is the regression analysis by residuals, whose main advantages are:

- The model's construction only needs data of routine determinations usually performed in any industrial plant.
- The derived model takes into account all the particularities of the specific plant thus can successfully control plant's operation.

Composting phases

- ***Thermophilic phase or phase of stabilization*** of biodegradable organic carbon.

Actinomycetes degrade organic compounds

Increasing T > 50^{o}C

- ***Mesophilic phase or maturation phase***

Eukaryotic microbes control bioreactions

Complete nitrification

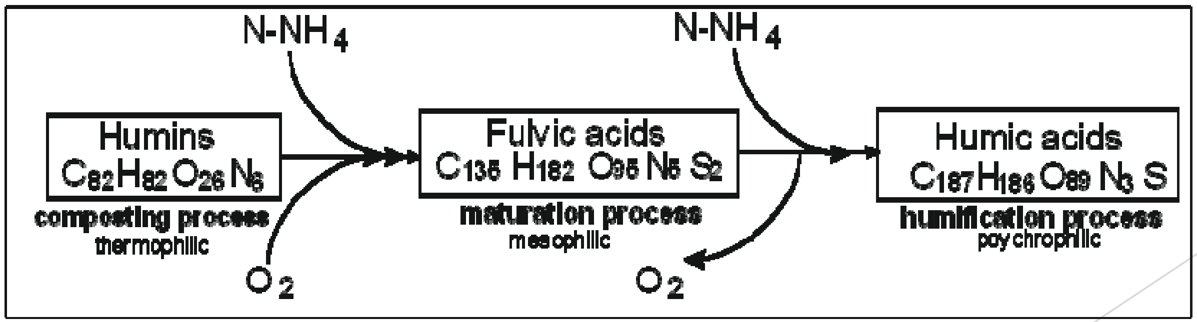
- ***Cold or phasing phase***
- Organic products Fulvic and Humic compounds

Humification

- At the beginning of the composting process the mass is at ambient temperature which starts to increase and usually slightly acidic. Microorganisms use soluble and easily degradable carbon sources, such as monosaccharides, starch and lipids, in the early stage of composting. pH value decrease due to the formation of organic acids from these compounds during degradation.
- The compost is immature and contains higher amounts of fulvic acids than humic. As the composting process is evolving microorganisms start to degrade proteins, as a result the liberation of ammonium and an increase in the pH.
- After the easily degradable carbon sources have been consumed, more resistant compounds such as cellulose, hemicellulose and lignin are degraded and partly transformed into humus

The evolution of humic substances into the composting process

Humus consist of humins, fulvic acids and humic acids.
Humins are exist in the initial substrate and during the composting period, mainly in thermophilic period, they are increased due to the adding material from the hydrolysis of dead microorganisms.
During the maturity period, the humins, partially are bio-converted into FA.
This is not a well known biological procedure but that is a synthetic procedure that needs oxygen and nitrogen.
FA are increased up to a critical concentration, a humification procedure is started when the FA transformed into HA. This transformation is a FA degradation-synthetic procedure which needs more nitrogen but less oxygen. So, during a composting process, the humic acids production passes through the production of fulvic acids uptaking ammonia nitrogen in parallel



Case study

In this study, multiple linear regression was used to develop a discrete dynamic model for an Olive Mill Waste Residues humification composting process. For the construction of the dynamic model a historical data record from ten composting reactors in which pomace from olive oil processing mills was used as biosolids organic substrate.

The pomace was collected from three olive mills located in Thraki (northern Greece) during the olive harvesting period of year 2015. The reactors, windrow open type, were of about 100 m^3 volume each with a solid's retention time (SRT) of about 100 days.

Data collected every day from 3 different point of each of 10 windrow open type.

Main initial characteristics of OMWR used for the composting procedure

Parameter	Mean value	Range
Total Nitrogen, %	0.25	+/- 0.05
Total Phosphorous,%	0.045	+/- 0.015
Potassium, %	0.15	+/- 0.05
Lipids%	6.1	+/- 2.6
Total phenolic compounds, %	0,67	+/- 0.47
Total sugars, %	11.85	+/- 10.86
Olive stone, %	30	+/- 15
Dry matter, %	45	+/- 6.5
Ash, %	2.85	+/- 1,5
Organic matter, %	**85**	**+/- 8**
Cellulose, %	20.72	+/- 1.54
Hemicellulose, %	9.46	+/- 1.54
Lignin, %	7.19	+/- 6.98

Experimental analysis

- In order to control the reactor's operation and efficacy, various parameters such as
- lipids content (FOG, %),
- moisture content (MC, %)
- temperature (T,oC),
- pH,
- oxygen uptake rate (OUR),
- water holding capacity (WHC, %),
- electrical conductivity (EC, mS/cm),
- ammonia nitrogen content (N-NH4, g/kg),
- nitrate nitrogen content (N-NO3, g/kg),
- Humic acids content (HA, g/kg),
- Fulvic Acids content (FA, g/kg),
- germination index (GI, %)

All measurements are frequently measured in the plant's laboratory. The fluctuations of FA and HA characterize the evolution of the humification stage of composting. From all above 13 independent parameters the pH, EC, WHC and N-NH4 are the most simple/easy and quick analyses.

Experimental Results

- Moisture of the composting material was maintained in the first weeks to 50-60% by adding pretreated Olive mill wastewater (OMWW) while during the final stages of the composting process the moisture was dropped to 43%.
- Water holding capacity (WHC) was reduced from 282% to 144%.
- The pH range was between 5.5 to 8.7
- Electrical conductivity was reduced from 3800 mS/cm to 1700 mS/cm.
- Phytotoxicity values showed that the composting material at the end of the process has been bio converted to a nontoxic soil conditioner.

- The rising of HA and in parallel reduction of FA was signed the beginning of the humification period The HA concentration was increased from 0 which is the initial value, to 8 g/kg during the last 50 days of composting.
- As concern the FA concentration was reduced from 3.8 to 0.8 g/kg.

Model Form

- The model form, which is linear in the coefficients, is:

$$Yt = k0 + A1Yt\text{-}1 + A2Yt\text{-}2 + \cdots + AnYn + k10X\ 1,t + \cdots + k1mX\ 1,t\text{-}m + k20X2,t + \cdots + k2nX2,t\text{-}n + \cdot\cdot\cdot$$

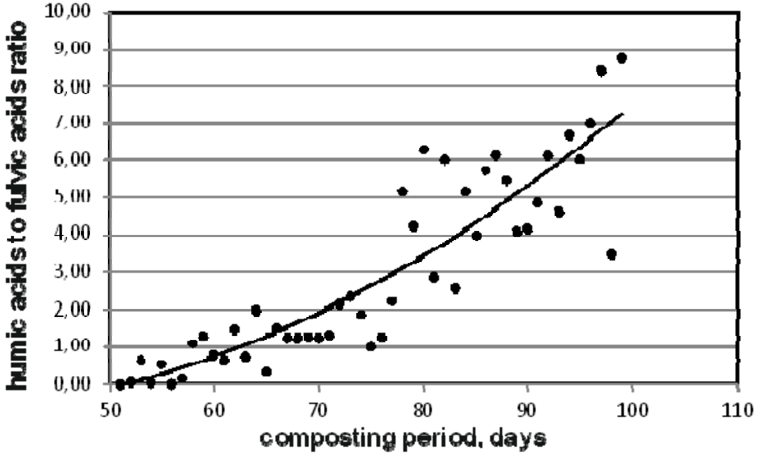
- This model is called a lagged regression model because the variables that are the ‘independent variables’ are current values or values at previous times or ‘lags’

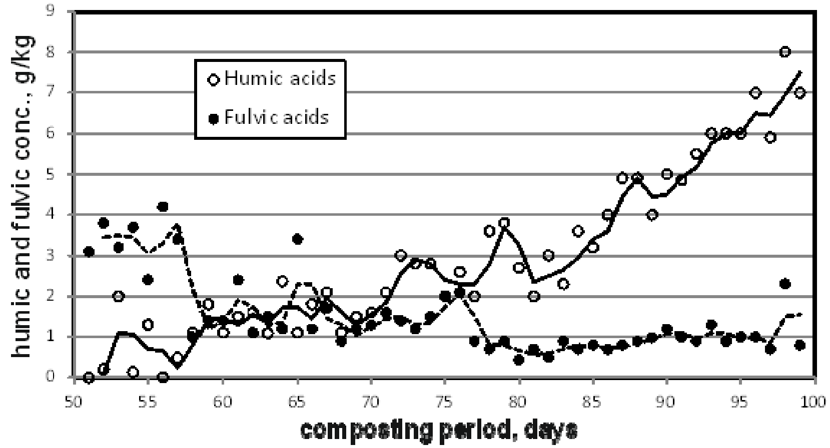
Residual analysis

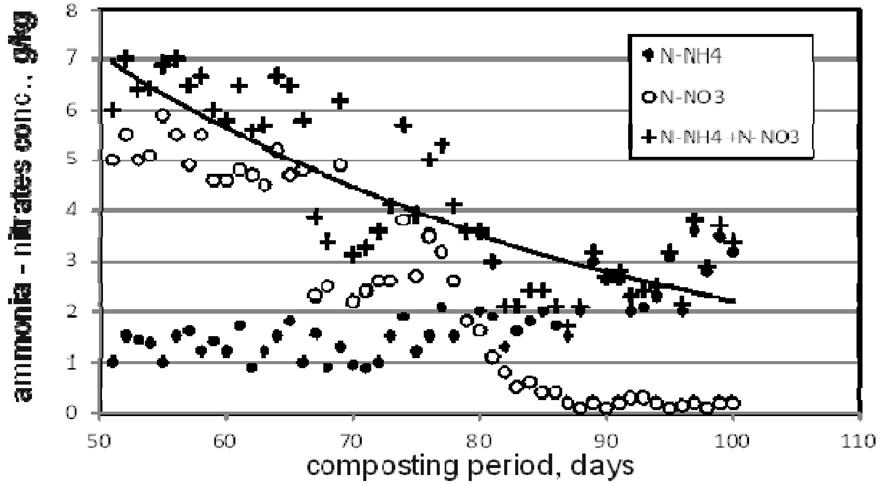
Building the regression models by residual analysis. The method consists of the following steps:

- Step 1: Choose the variable best correlated with the Y-variable, transform it as necessary to produce a straight line, and perform a least-squares regression with the dependent variable (F-variable to be predicted with a correlation coefficient Ro). The result will be an equation of the form:
  - $F = bo + bi\ f\ (X1)$
- where F is the predicted value of F-variable, b0 and b1 are constants and X1 is a variable
- Step 2: Calculate 'residuals' as follows:
  - $Zi = Fi — [bo + b1\ f\ (X\ 1,i)]$
- where Zi is the residuals, Fi the data for variable to be predicted and X1i the data for variable X1.
- Step 3: Choose the best-correlated X-variable. Transform the X-variable, if necessary, to yield a linear plot.
- Step 4: Add the new, transformed variable to the regression model, and perform a least-squares fit by computer, resulting in:
  - $F = bo + b1\ f\ (X1) + b2\ g(\ X\ 2)$
- Step 5: Calculate residuals and repeat the process until all variables have been added. Each time the correlation coefficient R of the model is:
  - $R = Ro + R1(1 — Ro) + \cdots$
- Each term of the equation expresses the participation of each variable in the final correlation coefficient.
- Step 6: Check the goodness-of-fit of the model. Moderate deviations from a straight line may not be serious (Ingels, 1980). The adequacy of a theoretical model implies the difference between the observed and the expected results. This was checked by and F2 test.

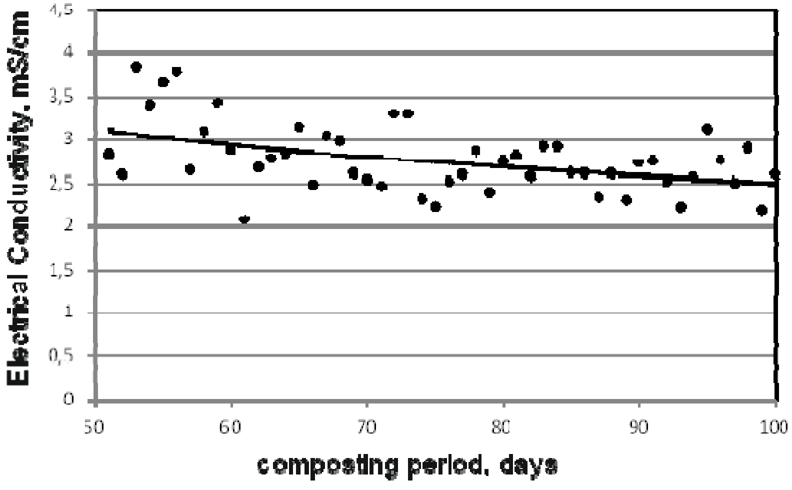
Fluctuation of characteristics during the humification period.

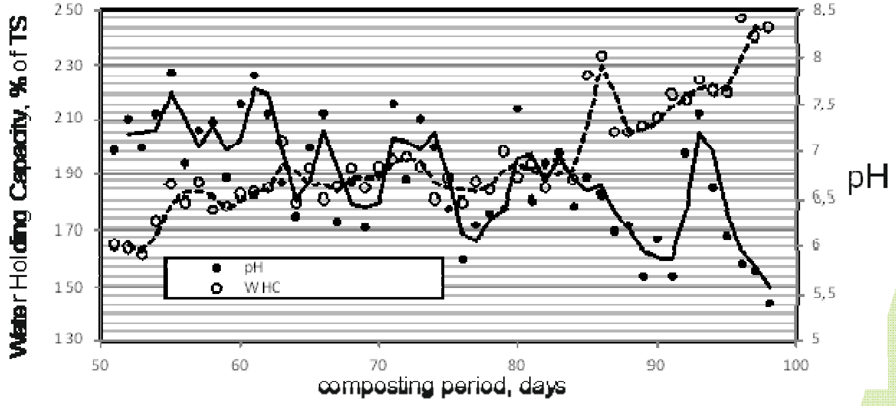






Fluctuation of characteristics during the humification period.





Goodness of fit test

- The correlation coefficient R that was calculated for the resultant models cannot give sufficient information for its adequacy. In other words, it cannot predict how the model will react in an unknown data range. In order to check the model, X2 test was conducted for a data record of another composting process at a different time period but with the same initial substrate .

Dynamic Models for HA concentration

Levels of the regression by residual analysis of the model for HA

Level	Best-fitted variable	Lag time	Variable's participation % in the final regression coefficient R^2
1st	pH	1 day	70.6%
2nd	WHC, % of TS	2 days	12.82%
3rd	$N\text{-}NH_4$, g/kg	4 days	5.57%

$$HAt = 3.15\ (pH)t\text{-}1 - 0.0185\ (WHC)t\text{-}2\ + 0.4739\ (N\text{-}NH_4)t\text{-}4 - 16.197 \quad (R^2 = 89\%)$$

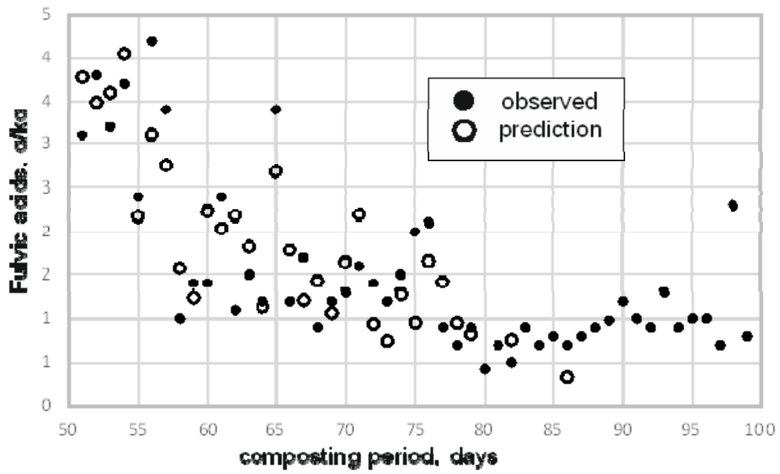
Dynamic Models for FA concentration

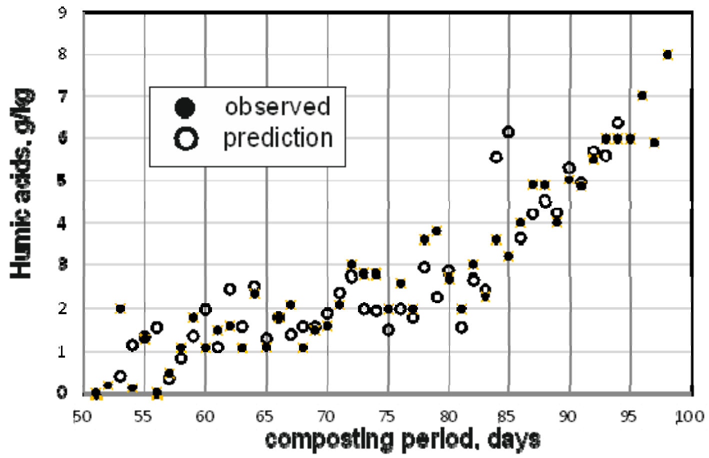
Levels of the regression by residual analysis of the model for FA

Level	Best-fitted variable	Lag time	Variable's participation % in the final regression coefficient R^2
1st	HA	today	80%
2nd	pH	today	5.6%

$$(FA)t = 53.617/(pH)t + (HA)t/(1.232(HA)t-0.447) - 7.29 \quad (R^2 = 85.4\%)$$

HA and FA concentration (g/kg), predictions and observed values for the new time period.





Other models

Other models have been developed that identify equally important factors such as

- lipids content (FOG, %),
- oxygen uptake rate (OUR),
- germination index (GI, %)
- ammonia nitrogen content (N-NH_4, g/kg),

Conclusion

- The methodology of regression analysis by residuals for the construction of a dynamic model proved to be ***quite satisfactory***.
- It is worth noticing that for this kind of model construction it is not necessary to conduct tedious factorial experiments, but routine determinations in an industrial plant are sufficient.
- The models that arise from these data can be used as powerful tools for the plant's control.

- ***Strong reverse relation*** between FA and HA as well as a clear evidence of influence of N-NH_4 to HA production.
- HA content could be characterized as ***the final product*** of the humification process, in which compounds of natural origin are partially transformed into relatively inert humic substances
- The experimental results demonstrate that the HA slightly increase during the last phase of composting period in comparison with FA which decrease.
- The dynamic model shows the strong correlation between humic acids and fulvic acids concentrations as well as the other parameters such as pH, N-NH_4, and WHC.

Acknowledgments

This work was supported by the composting industry ORGANOHUMIKI THRAKIS

ATHENS2017

5th International Conference on Sustainable Solid Waste Management
21–24 June 2017
Athens, Greece

Thank you for your attention

Any question????