CHEMICAL ENGINEERING TRANSACTIONS
VOL. 54, 2016

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Selena Sironi, Laura Capelli

ISBN 978-88-95608-45-7; **ISSN** 2283-9216

DOI: 10.3303/CET1654026

Air Emissions from a Sludge Thickener: Dynamic Data for Air Quality Models

Fabio Carrera-Chapela*[ab], Andrés Donoso-Bravo[c], José A. González[a], Gonzalo Ruiz-Filippi[b]

[a]Departamento de Ingeniería Química, Universidad de Santiago de Compostela. Rúa Lope Gómez de Marzoa s/n, 15782 Santiago de Compostela. Spain.
[b]Escuela de Ingeniería Bioquímica, Pontificia Universidad Católica de Valparaíso. General Cruz 34, Valparaíso, Chile.
[c]INRIA-Chile. Avenida Apoquindo 2827, Piso 12, Las Condes, Santiago, Chile

fabio.carrera@usc.es

Odor emissions from wastewater treatment facilities have paid attention during the last decade. These emissions usually are treated as stationary emissions or variable based on emission factors. This general approach does not include biological activity to explain the influence of process variations such as organic load or inorganic hydrogen sulfide promoters with odorants emissions. The present research presents a mechanistic model which includes biology influence on hydrogen sulfide air release.

1. Introduction

Regulations on odor emissions from different industrial activities have been taken attention during the past years due to numerous citizen's complaints, establishing preventive actions and thresholds limits (Capelli et al., 2014). On this framework, the daily dynamic behavior of the odor emissions from several industrial facilities, e.g. livestock farming, were outlined pointing the necessity of include them on dispersion models to carry out accurate odor impact studies (Schauberger et al., 2013). However, the dynamic on the odor emissions from wastewater treatment plants (WWTP) have been barely considered due to the lack of mathematical models focus on the emissions of odor precursors (Giuliani et al., 2014).
United States Environmental Protection Agency (USEPA) recommends the use of WATER9 software for regulatory propose to estimate air emissions of individual constituents during the collection, storage, treatment and disposal (Meri et al., 2012). Despite the fact that, there are several different air emission models focus on WWTP, Toxchem+, Baste and Cinci, none of them consider the dynamic evolution of the odorant compounds, because the model is based on algebraic equations instead of ordinary differential equations (ODE) (Carrera-Chapela et al., 2014).
Information about the emissions characteristics is crucial because they are used as key inputs for air quality models, which need reliable data in order to obtain accurate predictions. The major nuisance odor emissions sources on WWTP facilities are located on the sludge treatment process, being composed by dozens of different substances, such as VOCs, VOCSs, VFA, H_2S, NH_3, etc. (Capelli et al., 2011). From this set of typical odorants present on WWTP emissions, hydrogen sulfide is the dominant compound when the source has anoxic/anaerobic conditions. Therefore, this compound has been used as odor trace marker because of its good correlation between dynamic olfactometry and chemical analysis on these sources (Wang et al., 2014). The release of these volatile compounds to the atmosphere takes usually place on quiescent surface process, such as settling-thickening units, because the liquid-gas mass transfer is promoted on these units in agreement with its high surface area and turbulence gas phase by wind action since they are usually open (Capelli et al., 2014). These odorant substances are contained in the water phase but their formation and/or consumption could also be affected by the microorganisms contained into the biological sludge blanket (Li et al., 2014). The impact of the biological activity on the odorant formation has not been studied.

Please cite this article as: Carrera-Chapela F., Donoso-Bravo A., González J.A., Ruiz-Filippi G., 2016, Air emissions from a sludge thickener: dynamic data for air quality models, Chemical Engineering Transactions, 54, 151-156 DOI: 10.3303/CET1654026

In the literature, there is a variety of odor impact studies applied to WWTP, where lower quality emissions data has been used, which demonstrates the lack of concern on this topic (Gostelow et al., 2004). This paper aims to present a dynamic emission model focus on hydrogen sulfide formation and its gas release in a sludge thickener. The final goal is to count with an objective tool to estimate the odorant emissions that takes into account the variations of operational conditions, biological activity and mass transfer release.

2. Methodology

2.1 Mathematical model

The developed model is based on the following assumptions: (1) Horizontal homogeneity (2) The molecular diffusion on vertical axis is neglected (3) The gas bubbles achieves immediately the liquid surface (4) No biomass decay (5) Atmospheric partial pressure of released gases neglected (6) Gas solubilized in the influent (7) Hydrogen sulfide is the only odorant (indicator) on the emission (8) Sinusoidal ambient daily temperature oscillation.

The model structure is based on the formulation developed by Takacs et al. (1991) to represent the sludge gradient over the vertical axis with a discretization of the individual mass balance Eq. (1) by "n tank series" approximation, neglecting the term of diffusion ($D_C \nabla^2 C$), but in our research in order to consider the biological activity the reaction term (S_c) is included.

$$\frac{\partial C}{\partial t} + \vec{u}\nabla C = D_c \nabla^2 C + S_c \tag{1}$$

Inside the thickener, particulate matter, soluble matter and gas compounds coexist. Particulate matter consists on organic compounds, such as complex substrates and biomass, and also an inorganic fraction which contains recalcitrant compounds and other inert. The relationship between the concentration of solids and the settling velocity responds to an empirical double hyperbolic function on the first quadrant, which represents the variation of the settling velocity due to high solids concentration (Takacs et al., 1991).

$$V_s = V_o\left(e^{-r_h(X_i - X_{min})} - e^{-r_p(X_i - X_{min})}\right) \tag{2}$$

where, V_s is the settling velocity, V_o is the maximum settling velocity, r_h and r_p parameter characteristic of solids settling behavior, X_{min} is the minimum feasible solids concentration that permits settling and X_i solids concentration. The function of the settling velocity allows to define the settling down-flux between layers ($J_{s,i}$), which only applies to particulate-solid compounds. Thus, the mass balance for each layer will be,

- Surface layer (i=1):

$$h \cdot \frac{d{X_1}^j}{dt} = q_{ov} \cdot X_2^j - q_{ov} \cdot X_1^j - J_{s,1} + S_j\left(\overrightarrow{X_i}\right) \cdot h$$

- Layer up-flow zone (2 ≤ i ≤ m-1):

$$h \cdot \frac{d{X_i}^j}{dt} = q_{ov} \cdot X_{i+1}^j - q_{ov} \cdot X_i^j + J_{s,i-1} - J_{s,i} + S_j\left(\overrightarrow{X_i}\right) \cdot h$$

- Feed layer (i=m):

$$h \cdot \frac{d{X_m}^j}{dt} = \frac{Q_f}{A} X_f^j - q_{ov} \cdot X_m^j - q_{un} \cdot X_m^j + J_{s,m-1} - J_{s,m} + S_j\left(\overrightarrow{X_m}\right) \cdot h$$

- Layer down-flow zone (m+1≤ i ≤ n-1):

$$h \cdot \frac{d{X_i}^j}{dt} = q_{un} \cdot X_{i-1}^j - q_{un} \cdot X_i^j + J_{s,i-1} - J_{s,i} + S_j\left(\overrightarrow{X_i}\right) \cdot h$$

- Bottom layer (i=n):

$$h \cdot \frac{d{X_n}^j}{dt} = q_{un} \cdot X_{n-1}^j - q_{un} \cdot X_n^j + J_{s,n-1} + S_j\left(\overrightarrow{X_i}\right) \cdot h$$

Where h is the layer height, X^j_f feed concentration for variable j, A layer area, q_{ov} up-flow volumetric flux, q_{un} down-flow volumetric flux and $J_{s,i}$ settling flux on layer i and $S_j\left(\overrightarrow{X_i}\right)$ the reaction term for the biomass set $\overrightarrow{X_i}$ (Takacs et al., 1991). Similar mass balances for the soluble compounds can be obtained neglecting the settling flux terms.

2.2 Anaerobic biological model

The applied anaerobic digestion model is an extension of the AM2 model developed by Bernard et al. (2001) including the hydrolysis and sulfate reducing stages, in order to predict hydrogen sulfide formation and gas release (Carrera-Chapela et al., 2016). Ambient daily temperature (*T(t)*) usually changes following a bounded sinusoidal function between a maximum (T_{max}) and minimum (T_{min}) as in Eq. (3), where the oscillation period (*P*) trends to increase seasonally from winter to summer because of more sun hours in middle latitudes.

$$T(t) = A \cdot cos(P \cdot t) + D \tag{3}$$

$$A = \frac{T_{max} - T_{min}}{2} \tag{4}$$

$$D = T_{min} + A \tag{5}$$

Ambient temperature variation could affect the reaction kinetics since the microorganisms increase their specific growth rate. In order to evaluate the effect between the specific growth rate and system temperature, CTM1 model for the specific growth rate for each species was included (Donoso-Bravo et al., 2009).

The liquid-gas transfer flux (*J*) can be expressed by the two film layer theory, where the global mass transfer (*K*) coefficient depends on individual liquid (k_l) and gas (k_g) coefficients Eq. (8) (Meri et al., 2012).

$$J = k_l \cdot (C_l - C_l^*) = k_g \cdot (C_g - C_g^*) \tag{6}$$

$$J = K \cdot (C_l - \frac{C_g RT}{H}) \tag{7}$$

$$\frac{1}{K} = \frac{1}{k_l} + \frac{RT}{Hk_g} \tag{8}$$

where, C_l and C_g are the concentrations of the component in liquid and gas phase, C_l^* and C_g^* are the concentrations of the component in liquid and gas phase in the equilibrium, and *H* is the Henry's Law constant. Individual mass coefficient was estimated through empirical expressions as regulatory steady-state emission models include (USEPA, 1997). The empirical expressions used by WATER9 are based on previous research proposed by Springer (1984). Even these expressions trend to overestimate the emission rate, they are more accurate than other used by different steady-state models, as TOXCHEM (Meri et al., 2012).

2.3 Optimization of model parameters

Prior the parameter identification a global sensitivity analysis (GSA) was carried out in order to rank model settling parameters that are practical identifiable with the experimental data obtained. This variance-based sensitivity analysis was conducted throw SALib module in Python programming language (Herman, 2016).

Model calibration was carried out using real data obtained from an urban wastewater treatment plant. More details about the model development, sensitivity analysis and parameter identification can be found in Carrera-Chapela et al. (2016). The optimization procedure started with the calibration of the settling parameters from Takacs et al. (1991) as a reference model to describe solids profiles over time using least squares cost function. The settling parameters are included in the dynamic biological model and then the calibration was focused on hydrogen sulfide stoichiometry biological parameters.

2.4 On-site sampling and analytical methodology

The samples were collected with a graduated stick from the primary settler of a wastewater treatment plant at 10 different equally spaced depths. Sampling time was spaced on five different field campaigns, representing the dynamic operational behavior along 43 days. Hydrogen sulfide and pH were analyzed on-field with a portable electrode, while total and soluble COD, sulfate and alkalinity were measured according to standard methods for wastewater treatment samples (Eaton et al., 1998).

3. Results

3.1 Sensitivity Analysis and parameter estimation

Takacs et al. (1991) model presents five parameters which are related with the settling velocity; however, only the minimum concentration that allows particle to achieve enough weight to settle (X_{min}) is practical identifiable. This unique parameter requires 80% of the total model output variance, thus, the other parameters were fixed according to the values presented in Takacs et al. (1991).

The optimal value obtained for X_{min} with its 95% confidence interval is $(1.094 \pm 235) g \cdot m^{-3}$. The confidence interval was obtained through Jacobian finite difference approximation under the optimum following the Eq. (9):

$$se = \frac{sd}{\sqrt{N}} = \frac{diag(J)\cdot diag(J)^T}{N} \quad ; \quad ci_{95\%}: (m \pm 1.96 \cdot se) \tag{9}$$

Where *sd* is the standard deviation of the true population, *J* is the Jacobian matrix of the cost function evaluated at the optimum, *m* is the sample mean population value obtained during the optimization, *se* is the standard error of the sample population, *N* is the total measured experimental data and $ci_{95\%}$ is the 95% confidence interval. The solids profiles presented in Figure 1 are in agree with previous Takacs model using the same settling velocity parameters, although a deviation on the feed layer is observed where the biological model slightly underestimates the concentration.

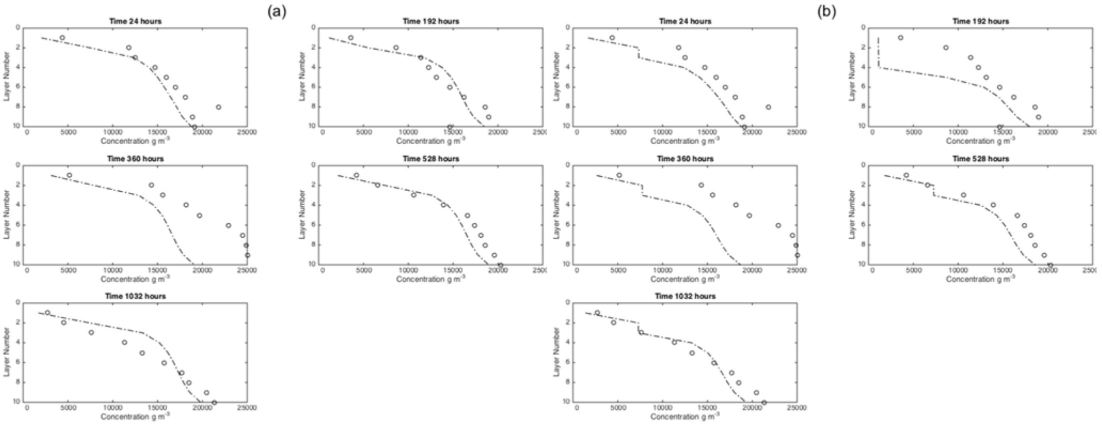

Figure 1: Solids profile concentration (g·m^{-3}) over time for the primary settler using: (a) Takacs et al. (1991) and (b) biological model. Dashed line (-·-) corresponds to model simulation and white circles (o) experimental data at 10 different depth points.

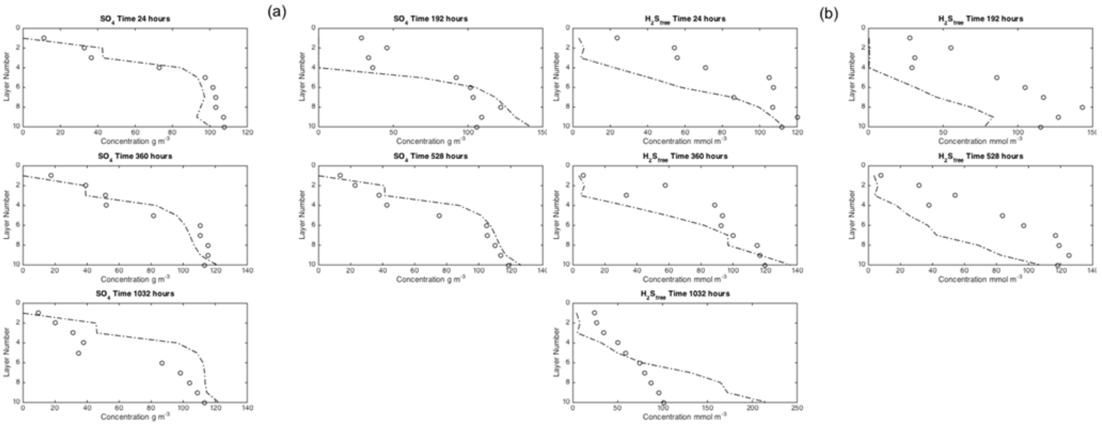

Figure 2: Sulfate (a) and hydrogen sulfide (b) water phase profiles concentration over time for the primary settler. Continuous line (-) corresponds to model simulation and white circles (o) experimental data at 10 different depth points.

3.2 Importance of biology on thickener behavior and odorant emissions

Biological activity plays an important role during organic overloads and when occurs an increase of the sludge blanket as a consequence of low storage capacity after settling units. This situation is not a rare episode on industrial facilities, because if any biosolids centrifuge fails, there will be a demand on sludge storage and usually settling tanks deals with this issue.

The model performance was compared against water phase measurements and the gas release (Figure 3) was estimated through global mass coefficient from reported USEPA algorithm application to sludge settling units. Before that, visual inspection suggests that sulfate concentration profiles (Figure 2a) are better described than sulfide profiles (Figure 2b), but a deeper statistical analysis based on the residual error reflects that both variables follow a quasi-normal density distribution. In the case of sulfate with a mean bias $ci_{95\%}$ of 23 ± 16 g·m^{-3}, meaning that experimental data are contained with a 95% of confidence inside the interval. On the other hand, hydrogen sulfide error density distribution presents a mean bias $ci_{95\%}$ of 23 ± 32 g·m^{-3} showing also a small average overestimation, but visual inspection reveals that the model tends to overestimate hydrogen sulfide at the bottom, while in the other layers underestimation is observed.

3.3 Emission comparison using conventional approach and simulation scenarios

The gas emissions of hydrogen sulfide were compared to the application of published emissions factors (EF) obtained from measurements on primary settling tank (Jeon et al., 2009). Figure 3a shows an agreement between the dynamics emissions and the values estimated by using EF. The benefit of using dynamic modeling is observed when dynamic evolution on substrate concentrations appears (Figure 2a), which reflects the dynamics on the hydrogen sulfide emissions (Figure 3a) whereas when using EF; however, this does not affect to hydrogen sulfide emissions.

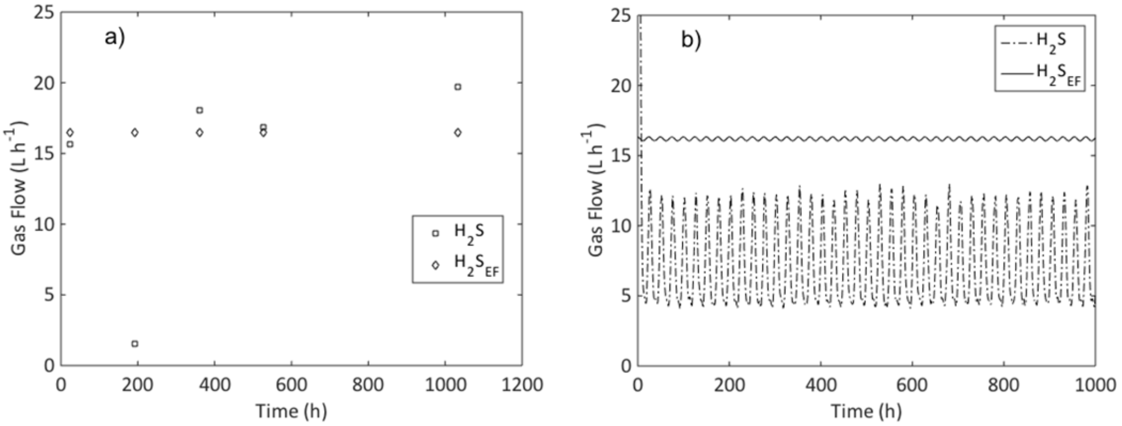

Figure 3: (a) Hydrogen sulfide air emissions flow rate from proposed dynamic model (□) and EF-based model (◊). (b) Simulation of the emission flow rates using white noise on model input variables compared proposed dynamic model (-.-) and EF-based model (-).

Based on the on field mean and variance measurements it was defined as white nose each model input and run a 1,000 hours simulation in order to rank those process variables which affect more on hydrogen sulfide emissions (Figure 3b). In this case, the temperature reflects more influence on the hydrogen sulfide air emission dynamic behavior as the sinusoidal function corresponds to daily temperature oscillations between 15-10 ºC. This performance is also present on EF but the wave amplitude is considerably lower than the proposed dynamic model, leading to overestimation depending on water temperature.

4. Conclusions

This paper describes a mechanistic biological model to reflect dynamic hydrogen sulfide air emissions changes due to variations in process environment. Dynamic model results were compared against both water phase measurements and EF-based air emissions estimations. As the major conclusion, this research aims to highlight the need of applying a dynamic mechanistic model to reflect operational changes influence on air emissions which later on are used as inputs on air dispersion modelling and air quality regulations.

Acknowledgments

This paper/work was partially supported by CONICYT PAI/ Concurso Nacional Tesis de Doctorado en la Empresa, convocatoria 2014, 781413011 and CIRIC - INRIA-Chile (EP BIONATURE) through Innova Chile Project Code: 10CE11-9157.

References

Bernard O., Hadj-Sadok Z., Dochain D., Genovesi A., Steyer J.P., 2001. Dynamical model development and parameter identification for an anaerobic wastewater treatment process. Biotechnology and Bioengineering, 75, 424–438.

Capelli L., Sironi S., Del Rosso R., Céntola P., Rossi A., Austeri C. 2011. Odour impact assessment in urban areas: case study of the city of Terni. Procedia Environmental Sciences, 4, 151–157.

Capelli L., Sironi S., Del Rosso R., 2014, Odour Emission Factors: Fundamental Tools for Air Quality Management. Chemical Engineering Transactions 40, 193–198.

Carrera-Chapela F., Donoso-Bravo A., Souto JA., Ruiz-Filippi G. 2014. Modeling the Odor Generation in WWTP: An Integrated Approach Review. Water, Air and Soil Pollution, 225(6), 1932-1946.

Carrera-Chapela F., Donoso-Bravo A., Jeison D., Díaz I., González JA., Ruiz-Filippi G. 2016. Development, identification and validation of a mathematical model of anaerobic digestion of sewage sludge focusing on H_2S formation and transfer. Biochemical Engineering Journal,112, 13-19.

Donoso-Bravo A., Retamal C., Carballa M., Ruiz-Filippi G., Chamy R., 2009, Influence of temperature on the hydrolysis, acidogenesis and methanogenesis in mesophilic anaerobic digestion: parameter identification and modeling application. Water Science and Technology, 60, 9–17.

Eaton A., Clesceri L., Greenberg A., Franson M., American Public Health Association., American Water Works Association., Water Environment Federation. 1998. Standard methods for the examination of water and wastewater. Washington, DC: American Public Health Association.

Giuliani S., Zarra T., Naddeo V., Belgiorno, V., 2014. A novel tool for odor emission assessment in wastewater treatment plant. Desalination and Water Treatment, 1–6.

Gostelow P., Parsons S., Lovell, M., 2004. Integrated odour modelling for sewage treatment works. Water Science and Technology, 50(4), 169–176.

Herman, J.D. Available online: https://github.com/jdherman/SALib accessed 17 March 2016.

Li B., Stenstrom, M., 2014. Dynamic one-dimensional modeling of secondary settling tanks and design impacts of sizing decisions. Water Research, 50, 160–170.

Meri J., Kreim V., Guillot J., Costa N., Melo, L., John, N. 2012. An experimental determination of the H_2S overall mass transfer coefficient from quiescent surfaces at wastewater treatment plants. Atmospheric Environment, 60, 18–24.

Jeon E., Son H., Sa, J., 2009. Emission characteristics and factors of selected odorous compounds at a wastewater treatment plant. Sensors, 9, 311–326.

Schauberger G., Piringer M., Petz E., 2000, Diurnal and annual variation of the sensation distance of odour emitted by livestock buildings calculated by the Austrian odour dispersion model (AODM). Atmospheric Environment, 34, 4839–4851.

Springer C., Lunney P., Valsaraj K., 1984, Emission of hazardous chemicals from surface and near surface impoundments to air. US EPA, Solid and Hazardous Waste Research Division, Cincinnati, Ohio. Project Number 808161e02.

Takacs I., Patryioand G., Nolasco D., 1991, A dynamic model of the clarification-thickening process. Water Research, 25, 1263–1271.

USEPA, 1997. Preferred and alternative methods for estimating air emissions from wastewater collection and treatment. Technical report.

Wang B., Sivret E., Parcsi G., Wang X., Le N., Kenny S., Stuetz R., 2014. Is H_2S a suitable process indicator for odour abatement performance of sewer odours? Water Science and Technology, 69(1), 92–98.