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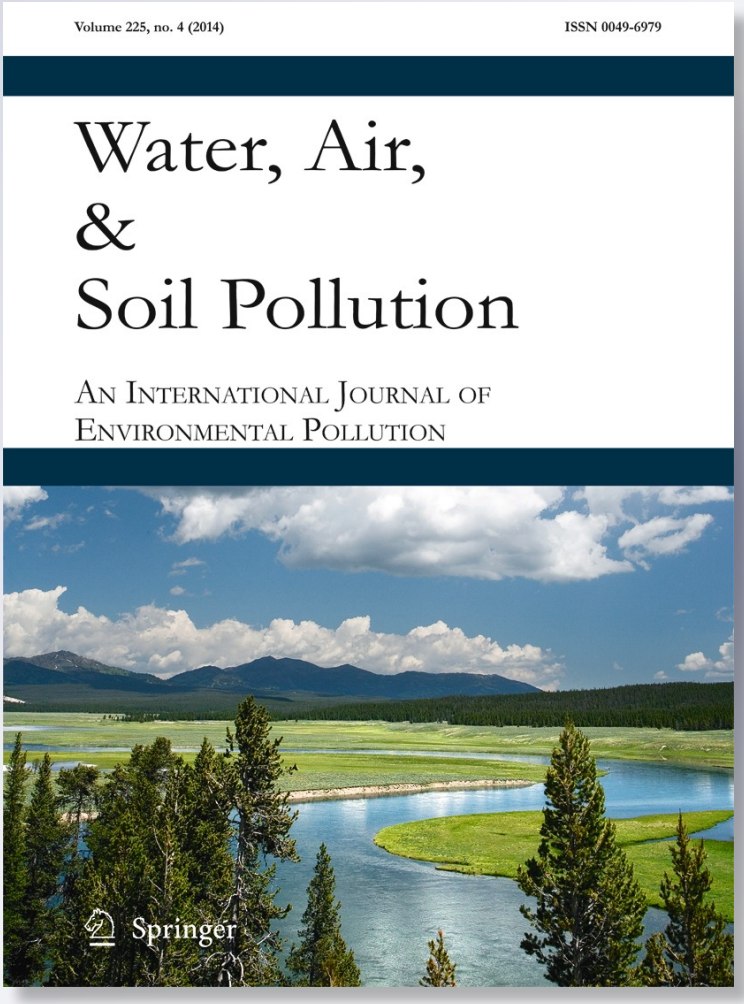

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Modeling the Odor Generation in WWTP: An Integrated Approach Review

Fabio Carrera-Chapela · Andres Donoso-Bravo · José A. Souto · Gonzalo Ruiz-Filippi

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Abstract Nuisance odors generation from waste and wastewater treatment plants are a cause of public discomfort and complaints. This situation impairs the air quality and represents a growing social and public health problem, especially in developing countries. Several modeling approaches have been developed and successfully implemented in the frame of a wastewater treatment plant for both the biological treatment and physicochemical processes. The mathematical modeling of the odor generation process is still considered a quite complex issue, mainly due to the fact that olfactory nuisance can be caused by many different chemical compounds and the perception of odors is influenced by subjective thresholds. Moreover, the impact of odor sources on air quality is highly conditioned by complex atmospheric dispersion processes. This review presents a critical state-of-art and assessment where information related to odor emissions impact studies as well as modeling applications are compiled and discussed.

Keywords Wastewater treatment plants · Odor characterization · Odor emissions · Process modeling · Air quality

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1 Introduction

Biological treatment and stabilization is widely used to reduce the organic matter and nutrient concentration of waste and wastewater, thus minimizing their environmental impact. One of the most important concerns, if not the most, about biological treatment is the generation of malodorous compounds (Liu et al. 2010). Historically, unpleasant odors have been considered as signals or warning indicators about human potential health risks, as well as a significant factor of life quality deterioration. In recent years, wastewater treatment plants odor have been the target of several community complaints, especially neighbors close to those facilities. The formation of these unpleasant odors proceeds from microbial action during the organic matter decomposition processes, i.e., food, animal scums, and organic compounds oxidation (Kalantar et al. 2002), mainly when anaerobic conditions are reached.

In regards to the chemical nature of the odors, most of unpleasant environmental odors are related

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with sulfide-derived compounds. Recently, volatile organic sulfur compounds (VOSCs) have been studied because of their different role in the global sulfur cycle and also in odor formation. The most interesting compounds in this family are methanethiol (MT) and dimethyl sulphide (DMS) (Bentley and Chasteen 2004). MT contributes to the characteristic odor of several cheeses, but in unpleasant way by the action of periodontal bacterial *Porphyromonas gingivalis*, forming halitosis and broccoli store odor. However, odors produced by short-chain dialkyl-sulfurs (methyl to propyl) are less unpleasant than the correspondents thiols, also named mercaptans (Challenger 1959). Both, DMS and MT, contribute to the characteristic sulfur odor of cooked cabbage (Kalantar et al. 2002).

Control odor strategies depend on the knowledge of the interactions between its chemical components and their dilution in the atmosphere after being emitted. Hydrogen sulfide is a common compound in the atmospheric emissions from wastewater treatment plants (WWTP) but, if other odor species (VOSCs) are also emitted, the final odor effect will be modified by the synergetic action of these organic volatile substances, changing the typical odor of rotten egg to another one more or less unpleasant (Laing et al. 1994). For this reason, it is quite complicated to predict the odor characteristics of gases mixtures even though their exact chemical composition could be determined. From the beginning of the twentieth century, plenty of research have been done in regards to the effects of several different odor constituents; however, there is little research related with mixtures odor of more than two substances (Laing et al. 1994).

Mathematical modeling aims to represent the main aspects of biological, physical, and/or chemical process that compose a specific system. Its use enables a better understanding of the process, being important for control strategies, optimization, and process monitoring (Donoso-Bravo et al. 2011). Big efforts have been lately done in the development of mathematical models of the biological processes that take place in WWTP, i.e., both the aerobic oxidation process and the anaerobic degradation of solid waste (Vollertsen et al. 2008). However, these models do not include the meteorological behavior which would be necessary in order to provide accurate information for air quality emissions studies related with odor dispersion impact in the surrenders. Considering the impact and the benefits of modeling techniques application in current industrial sectors as well as the fact that the available information to carry out an integrated study of odor impact from WWTPs is sparse in the literature, this review aims to collect, in a critical way, the information regarding the mathematical approaches used for odors generation and propagation from a WWTP.

2 WWTP Odor Generation

Nowadays, the concern about odor generation in wastewater treatment is significant. The main stages of the whole process in which the odor generation has been identified are wastewater collection, transfer, and treatment, establishing that during the wastewater transfer from the collection systems to the treatment plant, significant amount of unpleasant odor substances can be emitted from manhole, joints, and terminations, specially if anoxic conditions are developed (Gostelow and Parsons 2000; Gostelow et al. 2001; Dincer and Muezzinoglu 2007).

Among the emitted compounds, organic gases, inorganic gases, and steams can be found; many of these gases proceed from the anaerobic decomposition of organic matter with sulfur and nitrogen content. Yang and Hobson (2000) reported that hydrogen sulfide, carbon dioxide, and methane are the main atmospheric emissions from WWTP; although the precursor of the characteristic emission odor in the WWTP is the hydrogen sulfide.

Young et al. (2013) and Muezzinoglu (2003) have identified other compounds highly unpleasant in the emissions from the holes on the collection system: mercaptans, organic sulfur substances, and amines. Organic acids and ketones have been also found as a consequence of industrial discharges. An interesting classification of the emission sources from a WWTP was done by Gostelow et al. (2001), as follows:

- Sources that promote mass transfer when the odor substances have already been formed, i.e., aerated grit separator, activated sludge treatment.
- Sources where new odorants form, i.e., primary/secondary sedimentation, thickening tanks.

The main odor sources in the wastewater process may be located at the plant entrance, if the water contains septic conditions, and/or during the sludge treatment where anaerobic conditions generate

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new odorants as an inherent part of the bioprocess (Hobson 1995). Also, other process units as the primary settlers can stimulate the emission of substances previously generated in the plant entrance because of their calm flow conditions. Moreover, if the sludge purge is not enough to remove anaerobic activity, new odorants substances could be formed.

Capelli et al. (2009) reported in a research of odor emissions for 17 WWTP in Italy, that mean emission values are independent of the plant size, concluding that odor emissions is a common issue in this treatment. Their results show that the main odor source is the first treatment stage, decreasing while the process goes forward, pointing that collecting system has more influence in odor formation than treatment stages. Stuetz and Frechen (2001) carried out a quiz to the plant operators in France and Germany in order to identify the process units where more odors are generated, which is shown in Fig. 1.

These subjective results obtained by Stuetz and Frechen (2001) are in agreement with the olfatometric measures carried out by Capelli et al. (2009), who identified primary treatment and sludge treatment as the main odor sources.

Recent results obtained by Pérez et al. (2012) are also in agreement with previous research, since primary and sludge treatments are identified as the main odor sources. Nevertheless, in terms of odor flow ($OU_E\ h^{-1}$), their results show a more uniform odor distribution, including the biological aerobic reactor, which suggests that the odor emission rate in terms of mass flow is more homogeneous than the concentration of the odor source.

Smet et al. (1999) demonstrated that the WWTP odor emissions are related with VOSCs and hydrogen sulfide produced during anaerobic phases. The odor threshold values of these substances are very low, which means that low concentrations can generate highly unpleasant odor level. In this context, VOSCs precursors in WWTP along the sludge digestion process line are amino acids that conform proteins containing sulfur, as methionine ($C_5H_{11}NO_2S$) and cysteine ($C_3H_7NO_2S$). The methionine presents several degradation routes under different conditions to produce MT, DMS, or hydrogen sulfide. On the other hand, the cysteine only produces hydrogen sulfide under anaerobic conditions (Du and Parker 2012).

This complex composition of odorous emissions was confirmed by Lebrero et al. (2013) who, after an assessment of the sludge handling activities, identified not only sulphur reduced compounds but also aromatics, terpenes, aldehydes, and volatile fatty acids. According to that study, the dynamics of odorant formation are mainly governed by the sludge anaerobic fermentation and, more specifically, by hydrolysis and acidogenesis.

3 Odor Measure and Estimation

The odor response is a very subjective and difficult to predict issue since it depends on the detection response for each person. The main problem is that the odor is a result of many different odorants substances

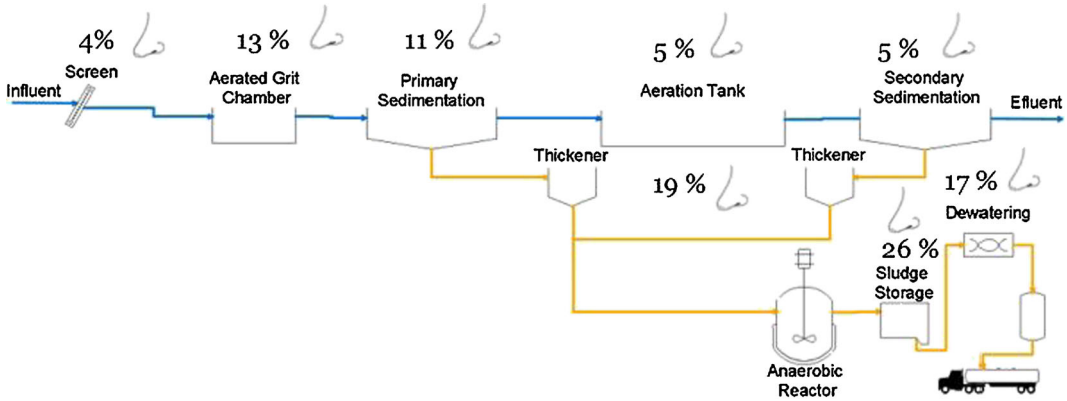

Fig. 1 Odor sources identified and contribution to odor emission in France and Germany WWTP facilities adapted from Stuetz and Frechen (2001)

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and their interaction. This odorants interaction, whose principles are still unclear, influences the odor perception (Gostelow and Parsons 2000). It is necessary, though, to distinguish between odorants and odors. The odorant is the responsible compound that actually generates an odor. On the other hand, the odor is the perceived effect when the odorant has been detected and interpreted by a sensory system. This interaction between the odorant properties and the odor generated is not very clear due to the lack of theoretical knowledge of our olfactory system (Gostelow et al. 2001).

Lebrero et al. (2011) presented an exhausted odor assessment and management review where a number of studies about of odor analysis, classified in sensory, chemical, and online analysis, are evaluated.

Many attempts have been made in order to establish a correlation between the odor concentration, expressed as odor units (OU_E m^{-3}) or odor intensity, with the actual chemical concentration for several nuisance compounds (Gostelow et al. 2001; Hobbs et al. 2002; Lacey et al. 2004; van Thriel et al. 2006; Tsai et al. 2008; Lehtinen and Veijanen 2011). Volatile organic compounds (VOCs), hydrogen sulfide, VOSCs, and ammonia have been the focus of the studies due to their known unpleasant odor and irritation character. It has been demonstrated that the relationship between odor units and chemical concentration follows an exponential function and may be expressed by the Steven's law, as follows (Ferreira 2012):

$$C_{OU,i} = k_i \cdot C_i^n \tag{1}$$

where

$C_{OU,i}$: Odor concentration of i (OU_E m^{-3}).
k_i: Proportional parameter of i (OU_E ppm^{-1}).
n: Exponential parameter for i (dimensionless).
C_i: Chemical concentration of i (ppm).

Steven's law (Eq. 1) establishes an exponential relationship between the hydrogen sulfide concentration and the odor intensity/concentration. Both the proportional and exponential parameters must be carefully calibrated in each case. This expression works well and it is meaningful for a range outside of 0.4–0.6 ratios for binary mixtures because inside this range it overestimates of the actual values (Ferreira 2012).

Steven's law has shown good results for odor estimation in sewage and wastewater treatment plants using hydrogen sulfide chemical concentration as an indicator, establishing an exponential relationship between the hydrogen sulfide concentration and the odor intense/concentration (Gostelow et al. 2001; McGinley and Sensory 2008; Lehtinen and Veijanen 2011). An important drawback of this expression is that this relationship cannot be used for other indicator compounds since the prediction accuracy decreases compared the H_2S case. For instance, ammonia does not present an apparent relation as a consequence that it preferentially occupied sensor receptor cell sites more than other odorants, producing a constant stimulus and leading to alter the olfactory acuity (Tsai et al. 2008). Furthermore, there are no conclusive results about the performance and interaction, within the emissions from WWTP facilities, for other odorant compounds such as reduced sulfur.

3.1 Automatic Odor Measurement: Electronic Nose

It is important to use accurate odor emission rate in atmospheric dispersion models and in setback distance formulas. Due to the lack of data, none of the existing models consider diurnal or seasonal variations in odor emission rates and the use of the mean value may result in great uncertainty in the assessed results (Romain et al. 2013).

Standard odor measurement methods (Committee European Normalization C 2003) are based in subjective procedures using human panels and dynamic olfactometer. Nowadays, new electronic measure devices have been developed in order to achieve better accuracy, lower detection threshold, and response to different chemical species. These sensors are mainly made of metal oxides, conducting polymers, and catalytic metals. The relative responses between the sensors can be used to produce a unique odor profile or fingerprint; then, any sample may be further analyzed against the odor fingerprint, using pattern recognition techniques and/or neural network algorithms (Stuetz et al. 1999).

The array sensor shown in Fig. 2 represents the typical behavior of an electronic nose (e-nose). The device is composed by an array of different serial transducers, each one specific to a particular organic

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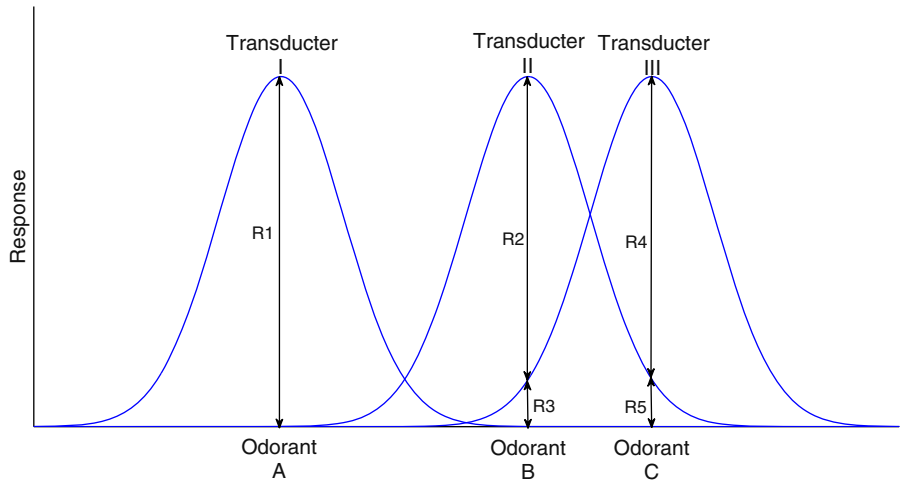

Fig. 2 Odor-intense response in an array sensor transducer (adapted from Persaud and Dodd (1982)

compound, transmitting an electrical intensity signal to the comparator window, establishing a relation between the transducers response (Ri) and odor intense/concentration. The signal response may be a combination of two or more sensor responses for the same odorant (Persaud and Dodd 1982).

Capelli et al. (2013) proves the possibility of using the electronic nose as a tool for the continuous monitoring of odors as well as to assess the odor impact in terms of relative recognition frequency of odors from the monitored plant, thereby pointing out the problem of metal oxide sensor (MOS) sensitivity to humidity.

Muñoz et al. (2010) compile several environmental applications and their results for e-noses monitoring. According to this study, the main operational and reproducibility problems are related to the unstable surrounding conditions, as temperature and humidity, which may be corrected by using inert carrier gas. Therefore, further improvements are necessary to reach the human olfactory sensitivity.

These electronic devices have been used in several environmental odor field emissions measurements and also applied in industrial facilities. For example, during the anaerobic digestion, where a common issue is the influent overloads that can lead to process destabilization, it has been demonstrated that an e-nose is capable of detecting organic load variations more efficiently than monitoring of methane content in the biogas (Adam et al. 2013). The use of e-nose on composting plants, which are treatment facilities with high number of neighbors complaints, combined with dispersion models allowed to recognize anomalous emission patterns and correct it Mantovani et al. (2010). The high selectivity of these sensors allows to recognize an odor pattern for an specific process, but can also interfere with other substances. One solution could be installing of parallel e-noses with different recognition patterns, which could transmit a better odor profile (Pinheiro et al. 2002).

Nevertheless, e-noses cannot provide high accuracy at very low concentrations as occurs with the main odorants, such as H_2S (Dentoni et al. 2012). Moreover, these devices are developed with specific sensor arrays in order to be sensitive to specific chemical compounds present in the odor pattern emitted from different industrial activities (Albert et al. 2000; Arshak et al. 2004).

3.2 Odor Estimation

The odor estimation is necessary to predict emission rate to the atmosphere of a number of odor substances by using activity parameters of the entire plant or process unit (fuel consumption, raw material rate, etc.). Several governmental guides provide procedures to estimate emission values applied to wastewater treatment plants (USEPA 1997; AUEPA 1999; NSWEPA 2001). Particularly, National Pollutant Inventory of AUEPA (1999) describes different methods, from the most to the less accurate as follows:

1. Sampling or direct measure: quantifies the associated unit emission, with high cost.
2. Mass balance: identifies the input and output amount of the odor substance referred to a control volume.
3. Fuel analysis and other engineering calculations: empirical equations based on mass transfer and

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liquid-gas equilibrium. Its complexity increases as more unit processes are involved.

4. Emissions factors (EFs): selecting the adequate EFs, emissions rates from activity process parameters are calculated. Generally, EFs are collected from a large database with similar emissions-processes.

Environmental Protection Authority of New South Wales (NSWEPA 2001) also establish that EFs should be used when either no other information is available or when it is demonstrated that the generated emissions are negligible. Therefore, although this method is the less accurate, it is the most used one in odor emissions estimation.

An emission factor is a representative value of the total emitted amount rate directly released to the atmosphere and it is related with the activity/process where it is generated. Also, it can be applied when there is no measure equipment to determine the actual emission amount (Calbó and Baldasano 1995). The EFs are used according to Eq. 2. They are a very helpful method because of its simplicity, allowing the calculation of atmospheric emissions from many different sources (point, area, or volume) as described in AP-42 document (EPA 1995),

$$E_{ij} = A_{ij} \cdot EF_{ij} \tag{2}$$

where,

A_{ij}: Activity parameter of process i which produces pollutant emission j (kg kg^{-1} of process product).

EF_{ij}: Emission factor of pollutant j for process i (kg kg^{-1} of process product).

E_{ij}: Atmospheric emission rate for pollutant j by process i (kg day^{-1}).

In many cases, EFs are obtained through measured data and assuming long operational time process representative and linear behavior between the emissions and the process activity in a normal process operation range.

During the last years, the scientific community has developed some mathematical tools to estimate the air emissions in WWTP. For instance, WATER9 model (USEPA 2001) includes a large database of physical and chemical properties for VOCs that are present in wastewater during its treatment (Maïzi et al. 2010). Likewise, TOXCHEM© includes a better user interface, following the same principles as WATER9 (Martin 2007).

Unfortunately, EFs-based methods appear to be unsuitable to evaluate WWTP control strategies for several reasons. Flores-Alsina et al. (2011) explained that these methods are based on steady-state calculations, without taking into account the wastewater treatment dynamics due to common disturbances. Therefore, it is not possible to consider how changes in the influent load (daily, weekly, and seasonal), temperature (winter/summer), and operating conditions (dissolved oxygen (DO), solids retention time (SRT), and chemical oxygen demand/nitrogen ratio (COD/N)) influence the air emissions. Furthermore, some of those estimations are focused on particular wastewater sections/ compounds/technologies, and they do not consider the whole treatment system. On the other hand, these approaches tend to overestimate the emissions rates as a consequence of the misuse of the mass transfer coefficients during regular steady-state operations and underestimate them under unsteady overload conditions. For instance, these models do not include the temperature dependence, which may be a key factor in WWTP operation.

Therefore, unsteady operation of WWTP units must be considered to obtain a realistic estimation of their odor emissions. A significant improvement of the EA use would be the application of some dynamic modeling method for each process unit.

4 Modeling of Odor-Potential Produced in WWTP Process Units

4.1 Activated Sludge Reactor

The activated sludge reactor is an aerated oxidation tank where the organic matter and nitrogen contained in the wastewater is degraded by microbial action. There are different microbial populations present in the reactor according to the different substrates utilization. The main populations are the aerobic heterotrophic bacteria (decompose organic carbon source into CO_2), anoxic heterotrophic bacteria (decompose organic carbon source into CO_2 and NH_4), and aerobic autotroph bacteria (decompose NH_4 into nitrite/nitrate using CO_2 as carbon source) (Henze et al. 1987).

The activated sludge model 1 (ASM1) was developed by Henze et al. (1987) in order to describe

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the biological behavior of activated sludge reactor and it is based in the COD mass balance for the organic matter transformation. Subsequent modifications of this model are ASM2 (Henze et al. 1999), ASM3 (Gujer et al. 1999), and modified ASM3 (Zhou et al. 2013). These models basically included hydrolysis, heterotrophic organisms (denitrification), and autotrophic organisms processes (nitrification) to the original model.

In regards to the odor generation, none of these models include individual composition of some important odorant compounds. For instance, during the particulate organic matter hydrolysis, several odor precursors like PAHs, VOCs, VOSCs, or VFA may be generated, but they are not specifically considered by ASM models; therefore, a crucial part of the odor generation is missing.

However, there are several studies where odor emission rates from the activated sludge reactor have been measured and identified (Gostelow et al. 2001; Sironi et al. 2006; Jeon et al. 2009; Zarra et al. 2009; Stellacci et al. 2010). Particularly, Stellacci et al. (2010) pointed that this process unit significantly contributes to the atmospheric odor emission, and a better understanding of odor compounds production mechanisms should be included into the process unit model. These emissions are mainly produced by the stripping action, i.e., the desorption of gas compounds from the liquid media, induced by aeration bubbles for the aerobic microorganisms.

4.2 Anaerobic Reactor Modeling

The anaerobic treatment consists in the degradation of the organic matter contained in the influent into biogas (CH_4 and CO_2) under free oxygen conditions. The whole process is commonly represented as several steps performed by different microbial population that establish a symbiosis relationship (Batstone et al. 2002). A simplified scheme of the whole process is described in Siegrist et al. (2002).

The anaerobic digestion process has been widely studied from the beginning of 70s using mathematical modeling to describe the process behavior. Donoso-Bravo et al. (2011) described the different models developed in anaerobic digestion, pointing a better understanding in the microbiology process knowledge. The anaerobic digestion model (ADM1) published by Batstone et al. (2002) is the most popular and used model so far. This general model and its modifications related to specific situations have been widely used and validated in many industrial reactors (Batstone and Keller 2003), i.e., odorants compounds generation (Parker and Wu 2006). Other applications of the ADM1 model to advanced anaerobic digestion are described in Parker (2005). Many models based on the ADM1 have been developed, adding new process to explain specific system conditions or looking for better results in certain operational variables (Batstone et al. 2006). There are also some simplified models that still keep most of the variability of the system. This is the case of the model developed by Bernard et al. (2001) which represents acidification problems in anaerobic reactors related with VFA accumulation, decreasing model complexity as well as the three-reaction model developed by Donoso-Bravo et al. (2009) for wastewater with a high fraction of particulate organic matter.

Odor formation due to hydrogen sulfide generation has caught the attention of the anaerobic digestion modelers. Hydrogen sulfide formation in sewage systems may occur in anoxic/anaerobic conditions in the reactor, piping, or pumping tanks by the action of sulfate reducing bacteria (Lomans et al. 2002; Sharma et al. 2008; Vollertsen et al. 2008). Current odorants compounds generation models explain some of the odor-promoting substances responsible for odor emissions (Parker and Wu 2006; Sharma et al. 2008). These models provide a general framework for odor abatement strategies, although they only consider chemical concentration of odor-promoting substances.

The main mechanisms of hydrogen sulfide formation correspond to two degradations routes: sulfate reducing bacteria action and amino acids transformation. Sulfate reducing bacteria use both the sulphate contained in the media and the VFA as substrates for growth. Thus, sulfate reducing bacteria can compete with methanogenic archaeas for carbon source (VFA) and electron donor, such as hydrogen sulfide, which may lead to the inhibition of the methanogenic stage (Kalyuzhnyi et al. 1998; Chen et al. 2008; Chou et al. 2008). This mechanism is important when treating salty wastewaters or with high level of soap waste. The protein degradation path is more important in the treatment of livestock wastewater (Peu et al. 2012). Methionine has been reported as the main precursor amino acid in hydrogen sulfide generation (Derbali

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et al. 1998; Du and Parker 2012). There are several kinetic expression for this process in the literature, for which some authors have used first-order rate (Du and Parker 2012) whereas others consider Monod kinetic (Mu et al. 2008; Ramirez et al. 2009).

Many authors have used hydrogen sulfide as a tracer compound to predict the odor intensity estimated from its chemical concentration, for instance using Steven's law (Gostelow et al. 2001; Stuetz and Frechen 2001; Hvitved-Jacobsen et al. 2002; Peu et al. 2012).

4.3 Settling and Thickening Tanks

Settling process allows the separation of the solids contained in the wastewater from the liquid phase. These solids are basically inorganic and organic matter, which settle in high solid content solution in both primary and secondary settlers. The solid particles fall down toward the bottom of the settler and accumulate in the lower part, developing anoxic/anaerobic conditions that promote odor formation and emission, if solids removal is not fast enough (Stellacci et al. 2010).

Sludge handling treatment has been reported as the major emission source of nuisance in WWTPs, containing tenths of different compounds, e.g., VOSCs, VOCs, VFA, H_2S, NH_3, etc. (Bonnin et al. 1990; Gostelow et al. 2001; Hvitved-Jacobsen et al. 2002; Muezzinoglu 2003; Sironi et al. 2006; Capelli et al. 2011; Jeon et al. 2009; Lebrero et al. 2013; Lebrero et al. 2011). In most cases, formation of malodor compounds can be reached by proliferation of anoxic or anaerobic conditions (Hvitved-Jacobsen et al. 2002). These conditions can be achieved during settling and/or thickening process when the SRT is not the appropriate, as a consequence of lower sludge removal rate. Under these conditions, the fermentation of the remaining organic matter produces VOCs and sulfate reducing bacteria generate sulfide compounds in the water phase, which is transferred through the interface water-air layer and then directly emitted to the atmosphere (Vollertsen et al. 2008). For this reason, the dynamics behavior modeling of these units can help to avoid anoxic/anaerobic environment.

The most widely used mathematical representation of the secondary settler, both in published studies and commercial software environments, was developed by Takács et al. (1991). The traditional "tanks-in-series" formulation amounts to a discretization of the mass balance partial differential equation (PDE) with a first-order finite volume method. The settler is spatially discretized into n layers, on which a mass balance is calculated, with the numerical concentration corresponding to the middle of each layer (David et al. 2006). In that sense, David et al. (2009) highlighted several drawbacks of this model, in particular the fact that the number of discretization layers is used as a model parameter in order to match the experimental observations. Indeed, a typical number of ten layers are used to introduce numerical diffusion and smooth off the concentration profiles. The main drawback of models based on the discretization of first-order partial PDEs is that they cannot predict continuous variation of concentration with settler/thickener depth (Hamilton et al. 1992).

An integration of the activated sludge reactor model with a PDE settling model including biological reactions was developed by Hamilton et al. (1992). It was concluded that omission of bioreactions that take place in the settler increases the nitrate-nitrogen level in the effluent by about 1 g m^{-3} instead of a lower value considering the microbial removal action. The main advantage of this dynamic model is that it allows division of the settler into a considerably larger number of layers; thereby if a sufficient number of layers are used, the model successfully predicts the blanket level of the settler.

Recent studies have focused on using PDE mass balances for the secondary settler to describe dynamic behavior of these units. David et al. (2009) concluded that PDE model is very efficiently solved and produces realistic concentration evolutions, opening a new way for further investigations in settling modeling.

5 Integrated WWTP Process Modeling

For the entire WWTP simulation, two general approaches have been used either using separated models (which were developed for the different process units) that are connected to simulate the whole plant, or using a single and general model for the whole plant.

The first approach, namely interfaces approach, is based on the use of different models to simulate different treatment units. Since the state variables of

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each model are different, the construction of artificial interfaces between the existing standard unit-process models is required. The second approach is based on the construction of the so-called general model, which includes all the state variables and transformations needed to reproduce every process that takes place in the plant. In this type of models, the same components (the state variables) and transformations are used to simulate every process unit of the WWTP; therefore, specific interfaces, which connect different unit-process models, are not required. General models consider that both anaerobic and aerobic bacteria can proliferate in all the process units (Ruano et al. 2012).

The Biological Nutrient Removal Model No. 1 (BNRM1) (Seco et al. 2004) is classified as a general model. This model has been developed as a unique model to simulate the most important physical, chemical, and biological processes taking place in a WWTP. The model is based in ASM2d model (Henze et al. 1999) for the microbial activity in the WWTP secondary biological treatment, Takac's model (Takács et al. 1991) for the settling and thickening processes, and the ADM1 model (Batstone et al. 2002) for the anaerobic sludge treatment. This model does not include odor precursors formation, as exposed before, being necessary a modification for odor management tasks.

The Combined Activated Sludge-Anaerobic Digestion Model (CASADM) was developed to explain an alternative WWTPs process where the anaerobic effluent is linked with the conventional recirculation stream from the secondary clarifier and the settling tank (Young et al. 2013). This integrated model includes the anaerobic stage during the settling of the sludge, which represents an important contribution knowing that other models usually neglect these biological reactions.

In the literature, it is possible to find models for different processes, but each one is based on particular and specific state variables. The connection between models is a useful tool to expand the system limits results and also for process optimization (Benedetti et al. 2004) because the optimal management of the individual components of the system does not necessarily yield optimal performance of the entire system (Fronteau et al. 1997).

Ad hoc solutions were typically derived to circumvent the following three problems that occur when one tries to link existing, state-of-the-art models, which were originally developed in isolation (Vanrolleghem et al. 2005),

- Some state variables used in one model do not exist in the connected model.
- The meaning of a state variable in one system may not hold for the other system (e.g., components can be considered as inert in one system but may be biodegradable in another one).
- The elemental composition of a component in one model may not be identical for the connected model and, in some instances, the elements considered are not the same (e.g., in ASM3 COD, N and charge are considered; whereas in ADM1 COD, C and N are taken into account).

A general framework using the Petersen and composition matrix was provided by Vanrolleghem et al. (2005). This methodology is friendly to the modelers because they are familiar with these matrixes.

However, if the odor formation is an important task for the plant management, these models do not provide any information about it. Due to the fact that previous models are built for other operational objectives, COD removal, biomass inhibition, oxygen consumption, biogas production, etc. Thereby, it is necessary to develop a WWTP dynamic odor model to describe and predict the odorants formation as well as their interaction in the mixed emission, including the meteorological influence on the odorants atmospheric diffusion.

6 Atmospheric and Dispersion Models

Modeling the odor dispersion from a source needs the characteristics of the emissions but also the meteorological conditions, typically wind speed and direction and atmospheric stability (De Melo Lisboa et al. 2006). Atmospheric conditions play an important role in odor dispersion as shown (Maïzi et al. 2010) with the high influence of the wind speed in the odor released from WWTP.

An atmospheric model is a mathematical representation of the dynamical processes, physical, chemical, and radiative, producing in the atmosphere. The ordinary differential equations (ODE) represent mathematically the time dependence of the processes.

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However, the partial differential equations (PDE) are used to describe time and space-dependent processes. These equations systems are usually replaced by mathematical approximations in order to solve and reduce the simulation time (Jacobson 2005).

A particular case of atmospheric model is the meteorological model, which excludes chemical transformations in the atmosphere (Souto et al. 2009). A meteorological forecast model is a model that is used to obtain weather prediction. Forecast models are usually validated with real data, observed data from meteorological stations, recording typical weather variables including wind speed, wind direction, pressure, temperature, relative humidity, and rainfall (Jacobson 2005). The main characteristics of 18 common meteorological models for numerical weather predictions used can be found in Kukkonen et al. (2012).

MM5 model is the widely used mesoscale model in forecast research topic, allowing nesting domains to achieve better resolution results. Nowadays, scientific community is moving from MM5 to weather research forecast (WRF) because of better effective resolution algorithm, less smoothing in the results reflecting better the influence of the terrain in the numerical weather results (Bowman 2009).

Commonly, the output of the forecast models are used as input by meteorological diagnostic models to achieve better grid resolution because the results for complex terrain has not enough accuracy (Hu et al. 2010). Diagnostic models do not provide any information about prognostic or future meteorological behavior, but perform a new high-resolution vector wind field that can be compared with real observation data from meteorological stations for validation. The build up of the high-resolution wind field can be done by two different approaches, interpolation by square distance of observed data or reparameterization solving again the motion equations (Wang et al. 2008).

Dispersion models describe the motion of the emitted pollutants from a specific source, being a macroscopic interpretation of the microscopic advection phenomena. Regulatory models are the most common used methodologies in order to describe and solve the dispersion equation, using algebraic equations, generally based on the Gaussian approximation for the vertical and horizontal concentration profiles.

In the literature, there are available many different dispersion models, changing their application, accuracy, model definition, resolution, etc. (Souto et al. 2001). More detailed information about these models can be found in Holmes and Morawska (2006).

Although odorant dispersion processes in the atmosphere is not different to other chemical species, some characteristics of the odorant dispersion problem drove to new and adapted odorant dispersion models. As the main characteristics,

- Processes scales are usually shorter in most of odorant dispersion problems.
- Because of that, odorant concentrations must be computed in very short periods; alternatively, peak and mean odorant concentrations are computed.
- Although chemical dispersion models usually compute pollutants concentrations, in the case of odorants, odor index is required. In fact, some odor dispersion models can compute the environmental odor based on odor emissions.

Considering these characteristics, a wide list of odor dispersion models were developed and applied. The application of odor nuisance estimation was previously discussed by Simms et al. (1999), considering ADMS model. Ormerod (2001) discussed the requirement of nonsteady conditions in odor dispersion modeling, with KSP model (Yamartino et al. 1996). Schauberger et al. (2000) presented the dynamic Gaussian Austrian Odor Dispersion Model (AODM) and its application to the microscale impact (tenths to hundred meters) of livestock emissions over residential areas. More recently, Piringer et al. (2012) analyzed the peak-to-mean relationship in odor dispersion modeling, using AODM and AUSTAL2000 models. This issue was also previously highlighted by Savunen and Rantakrans (2000) in their odor plume dispersion model.

Regulatory air pollution dispersion models provide a common and well-supported approach to simulate air pollutants dispersion. Some environmental agencies, as US EPA, try to support the availability of regulatory models, with the state-of-art and the best input datasets, in order to provide the best tools, also in odor dispersion. For instance, Sheridan (2004) and Hayes et al. (2006) applied ISCST US EPA regulatory model (USEPA 1997) to the odor impact of poultry farms emissions in Ireland.

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ISCST regulatory model was swap by AERMOD (USEPA 2001) as a regulatory Gaussian plume model. AERMOD is a steady-state plume model that incorporates air dispersion based on planetary boundary layer turbulence structure and simple/complex terrain effect. The total concentration at the receptor is calculated as the sum of the direct plume (C_d), indirect source (C_p), and the penetrate source (C_r),

$$C(x, y, z) = C_d(x, y, z) + C_p(x, y, z) + C_r(x, y, z) \quad (3)$$

However, as a steady-state model, AERMOD requires the application of approaches to estimate peak-to-mean relationship. On the other hand, the CALPUFF US EPA regulatory model (Scire et al. 1998) is a multilayer, multispecies nonsteady-state, Lagrangian, Gaussian, puff dispersion model that simulates the effects of time and space varying meteorological conditions on pollutants transport, transformation, and removal. It contains modules for complex terrain, over-water transport, and coastal influence. The total concentration at a receptor is obtained as the sum of the contributions of all nearby puffs averaged,

$$C(x, y, z, t) = \sum_{puff=1}^{totalpuffs} C_{puff}(x, y, z, t) \quad (4)$$

With environmental odorants, chemical concentrations are calculated and odor index can be derived from Stevens Law (Stevens 1960) calibrated to odor sensitivity. Also, CALPUFF is able to quantify directly odor dispersion in odor index, when just odor emissions are available, considering that odorants chemical transformation is neglected.

Generally, AERMOD tends to over predict the concentrations downwind, higher values than CALPUFF, which provides a better result for complex building/terrain. However, if the receptor is closer to the source, AERMOD do not represent properly the interaction between the plume and the complex structures dominates the plume path and its dispersion (Vieira de Melo et al. 2012). In the case of CALPUFF, as a nonsteady and three-dimensional model, it is possible to achieve better results using very high-resolution meteorological data (tenths to hundreds of meters) (Souto et al. 2014). In spite of those problems, both models were applied to odor dispersion modeling worldwide, as in Jeong (2011) and Busini et al. (2012).

7 Critical Discussion

The unpleasant odor emissions modeling from WWTPs are an important issue due to complaints of the citizens and government concern, which has led to the generation of a series of new mandatory regulations.

Regulatory approved and recommended air emission models developed for WWTPs are mainly based on steady-state operation, neglecting dynamics changes during daily, weakly, or monthly plant operation, i.e., inlet streams, maintenance activities, or environmental conditions. It is necessary to improve this topic in order to represent with better accuracy the microbial changing dynamics developed inside the processes.

The use of dynamic operational modeling allows achieving better results related with odor assessment and management, increasing the process behavior knowledge. Atmospheric dynamics is also important to be considered and even incorporated inside the air emission model to predict the emissions rates depending on changing meteorological circumstances.

Nowadays, the more innovative techniques for odor monitoring are based on linking the dynamic olfactometry with the chemical analysis using GC-MS or e-noses. The main drawback of GC-MS-O is the high price and the difficulty for obtaining real-time data. Instead, the e-noses are a promising technique to monitor online; nonetheless, but actually these devices are built ad hoc for specific industrial applications, which does not enable a global chemical-odor correlation.

Atmospheric conditions have a strong relationship with the air emission impact, being favorable decreasing the impact during periods of high atmospheric instability (high wind speed, low pressure, and absence of thermal inversion). Several meteorological models contrasted and validated are available for the international scientific community in order to provide quality weather forecast (Kukkonen et al. 2012).

Dispersion models combine meteorological conditions, terrain description, and source emissions to provide the impact of emission, also considering chemical

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and physical processes within the plume. Apart from the different dispersion models previously referred, Holmes and Morawska (2006) published a review with the dispersion models available and its application to the pollutants dispersion; they concluded the necessity of achieving more information related with the boundary surface layer behavior concerning the pollutants dispersion for nearby receptors because of the significance of surface meteorological conditions in odor dispersion.

8 Conclusions and Future Perspectives

This review presents an integral view of the odor modeling problem in WWTPs. The information regarding odor formation, sources, measure, characterization, impact assessment, process modeling, weather forecast, and dispersion modeling is rather sparse in literature.

Future improvements in terms of odor characterization from these sources are needed to develop an accurate integrated dynamic odor-processes model. Unit model processes need to incorporate new features to provide a benchmark for quality odor emissions studies in WWTPs. New innovative analytical method, as GC-MS-O, e-noses, could provide better knowledge of these complex mixtures behavior. These new linked techniques could help to establish better correlations for odor emissions from their chemical concentration, decreasing analytical costs of olfactory measures.

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