COBEM 2023 27TH INTERNATIONAL CONGRESS OF MECHANICAL ENGENEERING

ABCM Brazilian Society of Mechanical Sciences and Engineering
27th ABCM International Congress of Mechanical Engineering
December 04-08, 2023, Florianópolis-SC, Brazil

COB-2023-2398
ANALYSIS OF EMISSIONS OF ODORANT COMPOUNDS WITH CHANGES TO THE INTERNAL SETUP OF THE USEPA DYNAMIC FLUX CHAMBER

Laize Nalli de Freitas
Jane Meri Santos
Bruno Furieri
Universidade Federal do Espírito Santo
laizenalli@gmail.com, jmerisantos@yahoo.com.br, furieribruno@gmail.com
Philipe Uhlig Siqueira
Pontifícia Universidade Católica do Rio de Janeiro
philipe.uhlig@gmail.com
Kamila Furtado Cupertino
Companhia Espírito-santense de Saneamento
kamilacupertino@gmail.com
Ademir Abdala Prata Jr.
Universidade Federal do Alagoas
University of New South Wales
ademir@unsw.edu.au

Abstract. *Odor compounds are air pollutants that originate from various sources, both anthropogenic and natural. Among these sources, Wastewater Treatment Plants (WWTP) are particularly notable due to their significant environmental impact on surrounding neighborhoods, causing inconvenience through the emission of pollutants. These plants also serve as significant sources of hydrogen sulfide (H_2S) and volatile organic compounds (VOCs), which are produced during the digestion of organic matter. For the measurement of such emissions, dynamic flow chambers (DFCs) are commonly used enclosed devices. Our objective was to evaluate the impact of inserting internal gas mixers in the USEPA DFC on the emission of different odorant compounds. To accomplish this, we examined three different inlet flows: 2, 5, and 10 liters per minute (LPM). For the 5 LPM flows, we introduced two fans of varying sizes, creating an ascending flow and a descending flow. The chosen odor compounds were hydrogen sulfide (with volatilization dominated by the liquid phase) and acetic acid (HAc), whose volatilization is dominated by the gas phase. Quantification of these compounds was performed through separate experiments. For H_2S, the analysis involved analyzing the liquid phase using spectrophotometry, while for HAc, the analysis focused on the gas phase using gas chromatography. The results showed that the variation in inlet flow directly influenced an increase in the emission flux ($p < 0.005$), with emissions varying proportionally to the inlet flow. Furthermore, the addition of the two internal fans also resulted in increased emissions ($p < 0.005$), ranging from 2.94E-08 to 5.23E-08 $kg.m^{-2}s^{-1}$. When comparing the emissions with the addition of fans, the impacts on the compounds differed. For H_2S, there was an increase in emission in all cases, reaching 131.23% for the Large Fan down (LFD) configuration. As for HAc, the impacts varied, with the largest increase observed for the Large Fan up configuration (20.66%), but a reduction of 9.16% in emissions for the LFD configuration. This difference is primarily due to the different volatilization behavior of the compounds and how the increase in friction velocity at the liquid-gas interface leads to an increase in the emission of only compounds dominated by the liquid phase. In conclusion, our study highlights the significance of considering the chemical characteristics of odorant compounds when measuring emissions. The results clearly demonstrate that variations in inlet flow and the introduction of internal gas mixers in the USEPA DFC directly influence the emission flux of different compounds.*

Keywords: *Fluids mechanics. Odor compound. Dynamic flux chamber. Hydrogen sulfide. Wastewater Treatment Plant.*

1. INTRODUCTION

Odorous compounds are atmospheric pollutants emitted by various natural sources, such as swampy regions, as well as anthropogenic sources like industrial processes and sewage treatment. These compounds can have a significant impact on the health and well-being of the population residing near the emission sources, causing extreme discomfort. Depending on their concentration, they can also lead to more severe symptoms, including irritation of the mucous membranes, impairment of the central nervous system, upper airway issues, and even death.

Measuring the emission sources of these compounds is essential for mitigating the impacts and gaining a better under-

standing of the underlying physical-chemical mechanisms that contribute to their volatilization. To achieve this, various methodologies are employed for emission estimation, categorized as direct and indirect methods (Andreão and de Cassia Feroni (2021); Hudson and Ayoko (2008)). Indirect methods involve the application of theoretical models and mass transfer equations to estimate emissions. On the other hand, direct methods utilize meters and devices to directly measure the concentration at the emission source, enabling the calculation of the emission flux based on the concentrations of the involved phases.

In the case of sewage treatment ponds, which are passive sources of emission, Dynamic Flow Chambers (DFCs) are commonly used for measurement. The USEPA-DFC model is widely employed for this purpose. This apparatus aims to enclose the emission from a liquid surface, and techniques such as spectrophotometry Chen *et al.* (2021), gas chromatography (Cupertino *et al.* (2020); Niu *et al.* (2019); Barczak *et al.* (2019); Prata *et al.* (2018a), or titration (Kim *et al.* (2020)) are used to determine the pollutant concentration over a specific time period. Additionally, an inlet flow is forced into the chamber, creating a friction velocity and promoting internal gas mixture. The gaseous phase is sampled through an outlet line connected to a vacuum pump. Another approach for measuring emissions is the analysis of pollutant decay in the liquid phase, where it is dissolved. Figure 1 illustrates the operating scheme of the USEPA-DFC

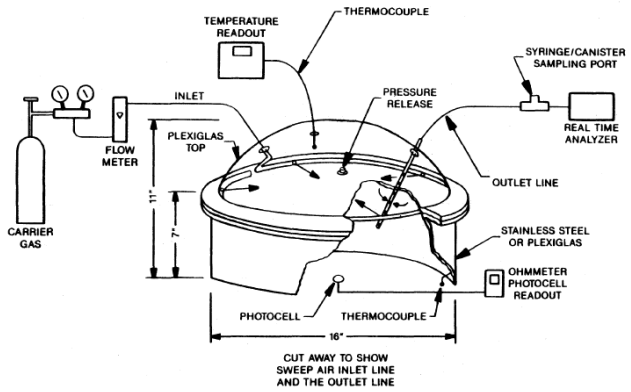

Figure 1: Schematic representation of a dynamic flux hood. Source: Kienbusch (1986)

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The literature indicates that geometry and meteorological variations have been utilized for measuring concentrations of compounds in the liquid phase. However, there is a lack of information regarding the chemical characteristics of these compounds and their impact on concentration measurements using enclosing devices. It is crucial to consider this aspect since certain compounds undergo volatilization primarily liquid, gas or both phase. For that, there's a law that describes this characteristics: Henry's Law.

Henry's Law describes the absorption of gas compounds into liquid surfaces. It states that the amount of gas dissolved in a liquid is directly proportional to its partial pressure in the gas phase at a given temperature Katyal and Morrison (2007). The proportionality factor in this relationship is known as the Henry's Law constant. This constant is important in atmospheric chemistry as it helps explain how trace species distribute between air and liquid cloud droplets or aerosol particles Sander (2015). When equilibrium is not reached, the compound can either volatilize or solubility Prata *et al.* (2018b). The Henry's Law constant (H) is derived using Equation in the liquid phase, like hydrogen sulphide (H_2S), while others do so in the gaseous phase, like acetic acid (HAc) Additionally, some compounds exhibit volatilization dominated by both phases.

In light of this context, the objective of this study was to analyze the emission of two odorant compounds: hydrogen sulfide, which is primarily volatilized in the liquid phase, and acetic acid, which is predominantly volatilized in the gas phase. Furthermore, the study aimed to investigate how changes in the USEPA-DFC setup affected the emissions of these compounds.

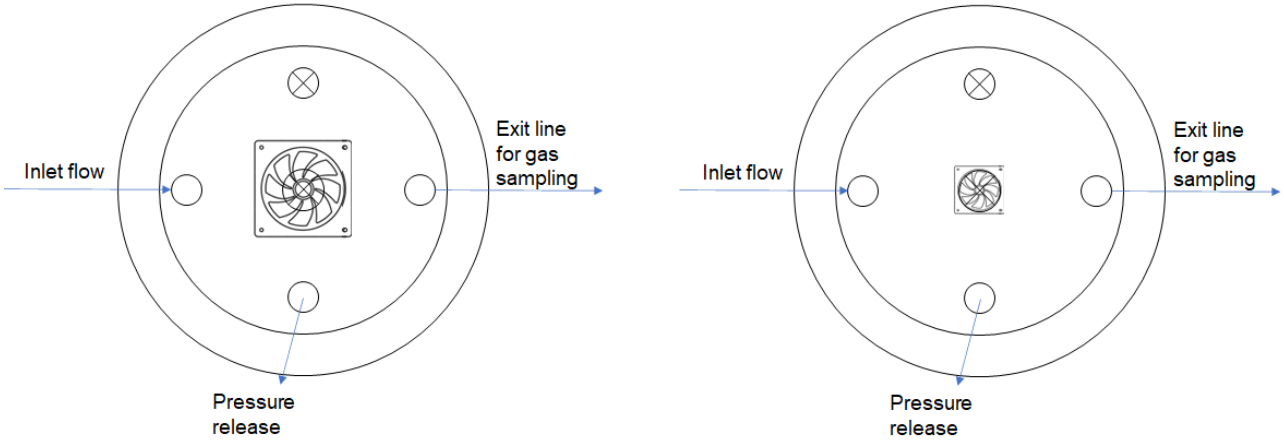
2. METHODOLOGY

In our study, we conducted separate experiments using the USEPA-DFC method to measure hydrogen sulfide and acetic acid emissions. To ensure statistical reliability and a minimum degree of freedom of 1, we performed triplicate experiments for each scenario. Our analyses were based on the data obtained from these replicates. Although we recorded temperature and humidity values during the experiments, it is important to note that they were not actively controlled. The experiments were conducted under laboratory ambient controlled conditions.

For both hydrogen sulfide and acetic acid, we conducted experiments using three different flow rates: 2, 5, and 10 liters per minute (LPM). These flow rates were chosen to investigate the impact of different airflow rates on the measurement of gas concentrations.

Specifically for the 5 LPM flow rate, we introduced fans inside the USEPA-DFC to enhance the airflow. The fans were

strategically placed to improve the distribution and mixing of the gas within the sampling system. Detailed specifications of the fans used in the experiments can be found in Table 1 and Figure 2 shows a scheme.



(a) Flux hood outline large fan, top view

(b) Flux hood outline small fan, top view

Figure 2: Flux hood with lage and small fan.

Table 1: Technical information of used fans.

Configuration	Fan dimension	Rotation per minute	Model	Manufacturer
Small fan up (SFU)	40 x 40 x 10 mm	6000 rpm	AD0412HB-G76	Berflo
Small fan down (SFD)	40 x 40 x 10 mm	6000 rpm	AD0412HB-G76	Berflo
Large fan up (LFU)	80 x 80 x 25 mm	3100 rpm	AD0812XB-A73	Berflo
Large fan down (LFD)	80 x 80 x 25 mm	3100 rpm	AD0812XB-A73	Berflo

For the preparation of the hydrogen sulfide solution, we weighed 0.704g of Sodium sulfide nonahydrate ($Na_2S.9H_2O$) and diluted this mass in 100 mL of deionized water. This step can be described by the chemical reaction below:

$$\mathrm{Na_2S.9H_2O_{(s)} \xrightarrow{H_2O} H_2S_{(aq)} + 2NaOH_{(aq)}}$$

Then, we took a volume of 10 mL of the prepared solution and transferred it to a 2L volumetric flask. To this flask, we added deionized water to reach the mark, resulting in a dilution of the solution. This step aimed to generate a 5mg/L concentration solution of hydrogen sulfide (H_2S). Next, we removed 300 mL of the diluted solution from the flask and transferred the remaining volume to a cylindrical tank with a height of 8.5 cm and a diameter of 41 cm. The purpose of this step was to transfer the solution to a larger container for further use. To acidify the solution and ensure the balance of the reaction is shifted to the right, we added 1mL of sulfuric acid (H_2SO_4). The addition of sulfuric acid promotes the generation of more hydrogen sulfide by favoring the forward reaction.Prata *et al.* (2018a); Santos *et al.* (2012). Finally, we attach the camera over the tank and turn on the system, which was powered by a nitrogen cylinder.

We performed the initial reading of the liquid phase in the spectrophotometer at a specific wavelength (e.g., 231 nm), which resulted in absorbance values. These absorbance values were previously related to known concentrations using calibration curves, allowing us to determine the initial concentration (C_0) of the solution. The experiment proceeded based on the resistance time relative to the flow rate used[1]. After the design the resistance time, triplicate samples were collected every 6 minutes. These samples were then read on the spectrophotometer to obtain their absorbance values. For each experiment, a total of five concentrations were determined by relating the absorbance values to the calibration curves. This data was used to generate decay plots, where exponential regression was applied to fit the experimental points. Based on the exponential regression analysis, we calculated the overall mass transfer coefficient. The mass transfer coefficient provides insight into the efficiency of mass transfer in the system under study. Using the calculated mass transfer coefficient (K_L), we then quantified the emission rate based on Equation 1, where J is the emission [kg/m^{2}s]; K_L is overall coefficient mass transfer [m/s]; C_L is compound liquid concentration [kg/m^3]; C_G is compound gas concentration [kg/m^3]; and K_H is Henry Constant's Law [-].

$$J = K_L \left(C_L - \frac{C_G}{K_H} \right) \tag{1}$$

[1] $\tau = \frac{30}{Q}4$, where τ is resistance time [min], Q is flow rate [L/min].

For the acetic acid analysis, 40mL of glacial acetic acid (23.53mL/L) was added to 1.7L of Milli-Q water, resulting in a concentration of 0.63g/L of acetic acid. Similar to the procedure for hydrogen sulfide, the prepared solution was transferred to the tank with dimensions of 41cm in diameter and 8.5cm in height, and the dynamic flow chamber system was activated. The analysis for acetic acid focused on the gaseous phase, utilizing the initiation system Lung System. The dilution flow rate was set at 200mL/min using a previously calibrated pump. Samples were collected and stored in a Nalophan bag to preserve their integrity. To analyze the acetic acid concentrations in the samples, manual injection into a gas chromatography (7890A, Agilent Technologies) coupled to a mass spectrometer detector (5977B, Agilent Technologies) (GC-MSD) was performed. A hermetic syringe (2.5 mL SUPLECO, USA) was used for this purpose. The samples were injected into the GC-MSD within 30 minutes of removing them from the Nalophan bag. The determination of acetic acid (HAc) concentrations in the samples was based on previously established calibration curves specific to the analysis method and instrument used. The emission J were calculate using Equation 2.

$$J = \frac{QC_m}{A} \tag{2}$$

3. RESULTS

As described in the methodology, the emission results for both analyzed compounds were obtained. The average values for the emissions are presented in Table 2.

Table 2: Average emission rate [$\mu g/m^2 s$] obtained for different configurations.

Q (LPM)	Configuration	H_2S	HAc
2	No fan	14.96	17.32
5		22.64	36.45
10		32.89	68.95
5	SFU	29.36	37.48
	SFD	30.89	34.33
	LFU	48.96	43.98
	LFD	52.35	33.11

The emissions of both compounds exhibited a progressive and direct proportionality with the flow rate in cases no fan. In other words, higher flow rates resulted in higher emissions. For hydrogen sulfide (H_2S), the emission rates were 14.96 $\mu g/m^2 s$ at 2 LPM, 22.64 $\mu g/m^2 s$ at 5 LPM, and 32.89 $\mu g/m^2 s$ at 10 LPM. Conducting a one-way analysis of variance (ANOVA) confirmed that the flow rates significantly influenced the emission ($p < 0.005$).

Similarly, for acetic acid, the emission rates increased proportionally with the flow rate. The average emissions were 17.32 $\mu g/m^2 s$ at the lower flow rate, 36.45 $\mu g/m^2 s$ at 5 LPM, and 68.95 $\mu g/m^2 s$ at 10 LPM. Statistical tests also indicated a significant impact of the flow rate on acetic acid emissions ($p < 0.05$).

It is important to note that the emissions of acetic acid were numerically higher than those of hydrogen sulfide. This can be attributed to the higher concentration of the aqueous acetic acid solution used compared to the solution of hydrogen sulfide. However, it is worth mentioning that the perception threshold for hydrogen sulfide (0.005 ppm) is significantly lower than that of acetic acid (0.21 ppm). Therefore, even with smaller emission rates, hydrogen sulfide has a much more significant environmental impact due to its lower threshold for detection. These findings demonstrate the relationship between flow rate and emissions for both compounds. Higher flow rates result in increased emissions, with the emissions of hydrogen sulfide having a more significant impact on the environment due to its lower perception threshold.

When examining the cases involving ventilators, we observe a change in the emission patterns of both compounds. Hydrogen sulfide exhibits increased emissions for all fan configurations. Conversely, in the case of acetic acid, the use of fans compromises its emission. One of the main reasons for this discrepancy between the two compounds lies in their respective physical and chemical characteristics. As previously mentioned, hydrogen sulfide's volatilization is predominantly influenced by the liquid phase, whereas acetic acid's volatilization is primarily affected by the gas phase. Consequently, the increase in friction velocities at the liquid-gas interface interferes differently with each compound.

Furthermore, the difference in emission patterns can also be attributed to the solubility and vapor pressure of the compounds. Hydrogen sulfide has higher solubility in liquids OSHA (2005), and its release from the liquid phase is facilitated by agitation caused by the fans. This leads to increased emissions when ventilators are used, as the agitation enhances the transfer of hydrogen sulfide from the liquid to the gas phase.

On the other hand, acetic acid has higher vapor pressure and lower solubility in liquids compared to hydrogen sulfide NCI (2022); NCBI (2022); USEPA (2022). When fans are introduced, the increased friction velocities at the liquid-gas interface result in higher evaporation rates for acetic acid. However, the compromised emission of acetic acid suggests that the increased turbulence caused by the fans disrupts the equilibrium between the liquid and gas phases, hindering the efficient release of acetic acid into the atmosphere. These observations highlight the significance of the physical-

chemical properties of the compounds in their behavior when exposed to ventilator-induced airflow. Understanding these characteristics is crucial for assessing and managing the emissions of different compounds in various settings, such as industrial processes or environmental monitoring. Figure 3 is a comparative graph of all situations carried out in this study for both pollutants.

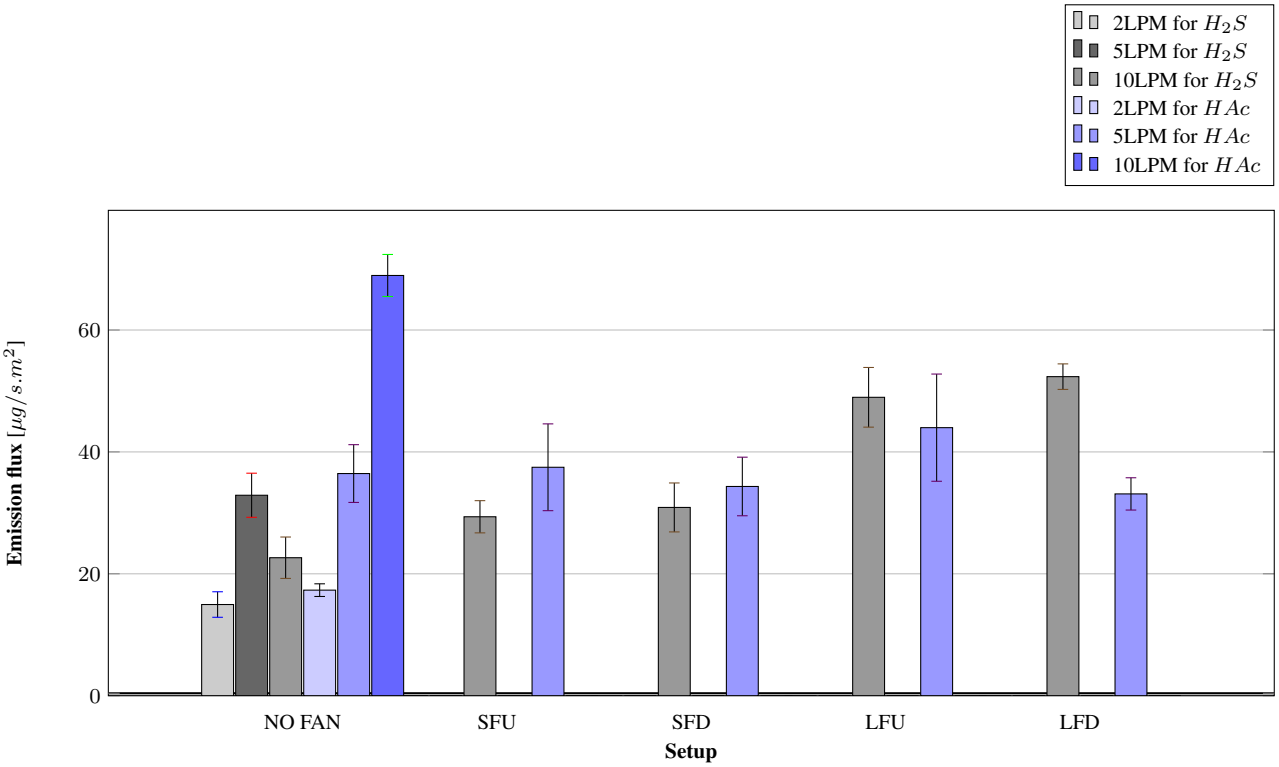


Figure 3: Comparison of emission flux (J) for all cases.

4. CONCLUSION

In conclusion, this study investigated the emission patterns of two odorant compounds, hydrogen sulfide (H2S) and acetic acid (HAc), using the USEPA-DFC method with different flow rates and fan configurations. The results showed that the emission rates of both compounds increased proportionally with the flow rate. However, when fans were introduced, the emission patterns differed between the two compounds.

For hydrogen sulfide, the use of fans enhanced the emission rates, indicating that the agitation caused by the fans facilitated the transfer of hydrogen sulfide from the liquid phase to the gas phase. On the other hand, the emission of acetic acid was compromised with the use of fans. The increased turbulence caused by the fans disrupted the equilibrium between the liquid and gas phases, hindering the efficient release of acetic acid into the atmosphere. These findings can be attributed to the physical-chemical characteristics of the compounds. Hydrogen sulfide has higher solubility in liquids and undergoes volatilization primarily in the liquid phase. Acetic acid, on the other hand, has higher vapor pressure and lower solubility, leading to volatilization primarily in the gas phase. The increase in friction velocities at the liquid-gas interface affected each compound differently due to their distinct volatilization mechanisms.

Understanding the behavior of odorant compounds under different airflow conditions is crucial for accurately measuring and mitigating their emissions. The results of this study provide insights into the impact of ventilation systems, such as fans, on emission patterns and emphasize the importance of considering the physical-chemical properties of compounds when assessing their emissions. Such knowledge can aid in developing effective strategies for managing and reducing odorous emissions from various sources, ultimately improving air quality and minimizing the associated health risks.

5. ACKNOWLEDGEMENTS

The authors acknowledge the sponsorship from Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Fundação de Amparo à Pesquisa do Espírito Santo (FAPES) and Companhia Espírito Santense de Saneamento (CESAN), Brazil.

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