



## Estimating Hydrogen Sulphide Emissions from an Anaerobic Lagoon

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Hydrogen sulphide (H<sub>2</sub>S) is a toxic malodorous gas emitted by wastewater treatment plants (WWTP). In this study, two approaches to estimate H<sub>2</sub>S emissions from an anaerobic WWTP lagoon were employed: a mathematical model based on the WATER9 equations and a direct measurement by dynamic flux chamber. H<sub>2</sub>S emissions measured with the flux chamber presented correlation with some lagoon parameters depending on where the flux chamber was placed. At the lagoon inlet, only the dissolved H<sub>2</sub>S concentration influences the H<sub>2</sub>S emissions, in the middle and at the outlet of the lagoon, biogas bubbles presence prevent from finding such correlation. However, at the lagoon outlet, the liquid temperature had more influence on H<sub>2</sub>S emissions. Emission fluxes obtained by the mathematical model are overestimated by a factor of seven in relation to the flux chamber measurements. Both methods have limitations regarding the wind speed. It was found that the mathematical model overestimated the gas-liquid interface frictions, leading to the overestimation of the calculated H<sub>2</sub>S emissions and the dynamic flux chamber underestimates the same frictions, leading to the underestimation of the measured H<sub>2</sub>S emissions. Moreover, even when the wind speed was set equal to 1 m s<sup>-1</sup> for the mathematical model, obtained emissions are overestimated in relation to the dynamic flux chamber emissions measurements by a factor of three. This means that the dynamic flux chamber reduces H<sub>2</sub>S molecular diffusion of the volatilization process.

### 1. Introduction

Odour is an increasingly sensitive issue and complaints of odour nuisance are frequent (Latos et al., 2011). Many of these complaints are related to odours emitted by wastewater treatment plants (WWTP). About 80 % to 90 % of odours in WWTP are due to the presence of sulphur compounds such as hydrogen sulphide, methyl mercaptan, ethyl mercaptan, dimethyl sulphide, dimethyl disulphide (Debrieu, 2004). Hydrogen sulphide is very toxic and also highly corrosive, for that reason, its uncontrolled release can cause problems to equipment units at treatment facilities. Sulphide can be removed from the liquid phase by several mechanisms such as volatilization, stripping, biodegradation (hydrolysis), absorption and adsorption, although only the first two mechanisms contribute to atmospheric emissions. Quiescent surfaces, such as presented by anaerobic lagoons, are frequent in Brazilian WWTP (Von Sperling and Oliveira, 2009), which provide larger emitting surface area. Various mathematical models have been developed to estimate hydrogen sulphide emissions, such as

TOXCHEM+ (Enviromega, 1995), US EPA WATER9 (US EPA, 1994), among others. According to Oskouie et al.(2008), the US EPA WATER9 is among the most comprehensive models.

Santos et al. (2012) investigated volatilization rates of hydrogen sulphide from quiescent liquid surfaces under simulated laboratory conditions. The experimental values for overall mass transfer coefficient,  $K_L$ , for  $H_2S$  were compared with predicted  $K_L$  values obtained from three different emission models widely used to determine volatilization rates from the quiescent surfaces of wastewater treatment unit processes (TOXCHEM+, WATER9 and Gostelow et al., 2001). US EPA WATER9 showed the best agreement with experimental data although it was found to overestimate the overall mass transfer coefficient by a factor of up to 4.0.

Another approach to assess  $H_2S$  volatilization from quiescent surfaces in area sources is the direct measurement, called hood method. It consists in isolating a part of the emitting surface with a chamber and measuring the gas concentration of interest inside the chamber. Three devices have been frequently described in the literature to obtain a direct emission flux: static flux chamber, dynamic flux chamber and wind tunnel (Gostelow et al., 2003). The main difference between each device is the airflow in the chamber. The dynamic flux chambers are swept by airflow to maintain constant the gas concentration inside the chamber. The emission flux (EF, in  $\mu g\ m^{-2}\ min^{-1}$ ) is calculated as the product of the gas concentration ( $C_i$ ) measured at the flux chamber outlet and the airflow rate (Q) divided by the surface enclosed (A) by the flux chamber (Eklund, 1992). Different shapes of dynamic flux chambers were described in the literature to assess odorous emission fluxes (Rumsey et al., 2012; Lim et al., 2003). In order to standardize a chamber, the US EPA validated a device which has the advantage of being cost effective, easy to use and to transport (Kienbusch, 1986). The third hood method is a portable wind tunnel which is a dynamic flux chamber in which the air flow is blown longitudinally in order to reproduce the velocity profile. Airflow rates in wind tunnel are higher than in basic dynamic flux chamber and can be modified to study the influence of wind velocity on emission rate. The emission rate is calculated the same way as for dynamic chamber except that the sweep airflow rate is replaced by the product of the tunnel section ( $A_t$ ) and wind velocity ( $V_t$ , in  $m\ s^{-1}$ ). A comparison of two hood devices was carried out by Hudson et al. (2009). Authors observed that the difference between measured emission fluxes by both hoods increases as the Henry law constant of the compounds decreases (Hudson et al., 2009).

Since differences of designs between dynamic flux chambers also influence emission fluxes measured (Eckley et al, 2010), in this study the standard US EPA designed dynamic flux chamber was used.

The aim of this study is to assess  $H_2S$  emissions from an anaerobic lagoon using two approaches: an experimental approach using an US EPA designed dynamic flux chamber and a mathematical approach using the equations proposed by Mackay & Yeun (1983), Springer et al. (1984) and Mackay and Matsugu (1973) used by the WATER9 model.

## 2. Methods and Materials

The anaerobic lagoon of the chosen WWTP has a 27 m length, 27 m width and a 2 m average depth. The quiescent area, air-liquid interface, is 729 m<sup>2</sup>. The reactor was fed with raw sewage with average domestic characteristics from a residential urban area of Vitoria, ES, Brazil. The hydraulic retention time is about 6 days.

The flux chamber was built according to US EPA standard (Kienbusch, 1986). It is a dome of 0.407 m diameter made of glass fiber, the area enclosed is 0.130 m<sup>2</sup> and the enclosed volume above water surface is about 25 L. The flux chamber consists of: 3 flow meters (Dwyer Instruments, Michigan, USA) to measure airflow rate at the inlet and outlet (model VFA-24-SSV) and the sample flow (model VFA-22-SSV) collected to analyze  $H_2S$  concentration; a thermometer (Wika, Germany) and a differential pressure gauge (model Magnehelic 2000-50MM, Dwyer). A 5 L min<sup>-1</sup> clean airflow enters the chamber. A small fan was used to homogenize the air into the chamber. The gas sampling is carried out with a drilled pipe placed at the center of the flux chamber. The  $H_2S$  electrochemical detector pumps the inner gas at 1 L min<sup>-1</sup> through this pipe (4170-19.99 model, Interscan, Chatsworth, CA, USA). Prior to start measuring  $H_2S$  emissions, the dynamic flux chamber was left to stabilize 4 to 6 residence times. During the experiments, temperature of the liquid surface, pH and electrical conductivity were monitored with a

Combo Tester Model HI 98129 (Hanna Instruments, Sao Paulo, Brazil). Concentration of dissolved H<sub>2</sub>S in the wastewater was determined by the iodometric method according to the 4500-F standard and the 4500-H method (APHA, 1995). Samples of wastewater were collected from the lagoon at the liquid surface on the exact local where the flux chamber was placed. The ambient temperature and wind speed at 10 m height were monitored by a meteorological station located at 12 km from the WWTP. The solar radiation was measured 8 km south from the WWTP by another weather station. In the mathematical model, the lagoon emission flux is obtained calculating ( $\mu\text{g min}^{-1} \text{m}^{-2}$ ):

$$EF = 60.10^6 K_L C_L \quad (1)$$

Where C<sub>L</sub> is the dissolved H<sub>2</sub>S concentration, and K<sub>L</sub> is the global mass transfer. The global coefficient of mass transfer, K<sub>L</sub> is calculated according to:

$$\frac{1}{K_L} = \frac{1}{k_l} + \frac{1}{Hc k_G} \quad (2)$$

where Hc is the Henry law constant at the given temperature.

The H<sub>2</sub>S emissions estimations were carried out using Equation 2 and the mass transfer coefficients were calculated by the equations given by Springer et al. (1984), Mackay and Matsugu (1973) and Mackay and Yeun (1983).

The equations used depend on the wind velocity at 10m (U<sub>10</sub>) on the lagoon length and depth rate (F/D). The lagoon length was taken in the main wind direction at measurement time. Then, F is equal to 27 or 38 m depending on the wind direction. F/D ratio can be either 13.5 or 19, which determines the equation model used to calculate the coefficient of mass transfer in the liquid phase, k<sub>L</sub>.

### 3. Results and discussion

#### 3.1 Influences of parameters on measured H<sub>2</sub>S emissions fluxes

The wind speed did not directly influence the H<sub>2</sub>S emissions fluxes, Table 1. Indeed, the dynamic flux chamber by itself is not affected by the wind velocity since the flux chamber encloses an area and sweeps it at a constant and given airflow. Moreover, the wind speed was measured at 10 m height and the lagoon studied is directly surrounded by 5 m trees which can explain these results. These trees were planted in order to decrease the interface of wind flow on emission.

Table 1: Pearson's correlation coefficients between lagoon parameters and H<sub>2</sub>S emissions measured

	Whole lagoon <i>n</i> =34	Lagoon inlet <i>n</i> =15	Middle <i>n</i> =6	Lagoon outlet <i>n</i> =13
Ambient temperature (°C)	0.28	0.16	-0.03	0.34
Relative humidity (%)	-0.23	-0.15	0.38	-0.25
Inner chamber gas temperature (°C)	0.31	-0.08	0.20	0.38
Wind speed at 10 m height (m s <sup>-1</sup> )	0.24	0.33	0.14	0.19
Solar radiation (W m <sup>-2</sup> )	0.17	0.11	0.26	0.53
Electrical conductivity (μS cm <sup>-1</sup> )	0.05	-0.35	0.63	0.02
pH	0.14	0.12	0.23	0.10
Lagoon liquid temperature (°C)	0.54	0.33	0.21	0.86
Dissolved H <sub>2</sub> S concentration (mg L <sup>-1</sup> )	0.73	0.91	-0.02	0.53

\**n* is the number of measurements

Only two parameters seemed to have a significant impact on H<sub>2</sub>S emissions measured by the flux chamber when considering all the measurements made in the lagoon.

A gradient of dissolved H<sub>2</sub>S concentration was observed in the lagoon. The dissolved H<sub>2</sub>S concentration values at the lagoon inlet were lower (in average) increasing towards the lagoon outlet. In the middle of the lagoon were observed the highest dissolved H<sub>2</sub>S concentrations as well as the highest H<sub>2</sub>S emissions, in average.

At the lagoon inlet, only the concentration of dissolved H<sub>2</sub>S presented a significant linear correlation with H<sub>2</sub>S emissions measured by the flux chamber, Table 1. In the middle of the lagoon, due to a difficult access, only six measurements were carried out, too few to manage reliable linear correlations of variables. However, if relevance is given to these data, they show that H<sub>2</sub>S emissions do not linearly evolve with dissolved H<sub>2</sub>S concentrations. It is likely to be explained by the biogas bubbles observed at the lagoon surface, which gives an extra source of H<sub>2</sub>S since the biogas bubbles come from deeper in the lagoon.

Lagoon liquid temperature is the most important parameter influencing H<sub>2</sub>S emissions at the lagoon outlet where the solar radiation also presented a significant correlation with H<sub>2</sub>S emission fluxes, Table 1. At the lagoon outlet, no correlation was found between the dissolved H<sub>2</sub>S concentrations and the H<sub>2</sub>S emission fluxes. The observation of frequent gas bubbles at the lagoon surface can explain that.

### 3.2 Comparison between the H<sub>2</sub>S emissions measured with the dynamic flux chamber and the H<sub>2</sub>S emissions calculated with the mathematical model

As shown previously, the H<sub>2</sub>S emission fluxes measured at the lagoon inlet were highly influenced by dissolved H<sub>2</sub>S concentration, then it is logical to observe that the emission fluxes calculated at the lagoon inlet showed better correlations with the measured emission fluxes, Equation 1, Table 2.

Poor linear correlations have been found between the emissions measured and the ones estimated in the middle and near the outlet of the lagoon. Near the lagoon outlet, the parameter having more influences on the flux chamber H<sub>2</sub>S emission measurements was the liquid temperature which is of a weak importance in the mathematical model, influencing lightly the value of the Henry law constant and H<sub>2</sub>S diffusion coefficient in the liquid phase used in the model equations. Therefore, the comparison between the H<sub>2</sub>S fluxes measured and H<sub>2</sub>S fluxes calculated showed important disparity, Figure 1. The mathematical model overestimated all the flux chamber measurements. In average, the calculated emissions are 7.5 times higher than the measured emissions. Only four variables were implemented in the model equations: liquid and ambient temperature, wind speed and dissolved H<sub>2</sub>S concentration. Dissolved H<sub>2</sub>S concentrations measured could present dissimilarities with the real ones due to human manipulation mistakes during the analysis (e.g. volatilization of H<sub>2</sub>S between the sample collect and the sample analysis).

Table 2: Correlation between H<sub>2</sub>S emissions calculated and measured

Conditions	Whole lagoon <i>n</i> =34	Lagoon Inlet <i>n</i> =15	Middle <i>n</i> =6	Lagoon Outlet <i>n</i> =13
Measured conditions	0.45	0.65	0.17	0.26
Wind speed fixed at 1 m s <sup>-1</sup>	0.73	0.91	-0.01	0.53

*n* is the number of measurements

These errors of manipulations would not affect the final concentration obtained to such extent. Contrary to the wind speed, the difference between the wind speed measured at the weather station and the real friction velocity sweeping the lagoon area could induce important errors in the calculated H<sub>2</sub>S emission fluxes. The 12 points for which the mathematical model calculated emission values above 2000 µg m<sup>-2</sup> min<sup>-1</sup> represented measurements carried out when the wind speed (measured at 10 m) was superior to 5.7 m s<sup>-1</sup>. Since the wind is an important parameter in model equations when wind speed larger than 3.25 m s<sup>-1</sup> and since this lagoon due to its configuration, is not exposed to winds, it can explain such high discrepancy between the H<sub>2</sub>S emission fluxes measured by the flux chamber and the ones calculated by the equations. Moreover, the flux chamber by itself, is not influenced by the wind speed. The equations proposed by Springer et al. (1984) were artificially implemented with very low wind speed, equivalent to 1 m s<sup>-1</sup> wind speed at 10 m, Figure 2. Even in such low wind speed condition, the

calculated emissions overestimate the ones measured by the flux chamber by a factor of three. Nonetheless, the correlation significantly improved, Table 2, and are exactly the same as the ones found between the dissolved  $H_2S$  concentration and the  $H_2S$  emission fluxes, Table 1. Indeed, the ambient and liquid temperatures only affect the Schmidt numbers for water and air, thus, only the dissolved  $H_2S$  concentration will linearly affect the  $H_2S$  emissions calculated. The fact that the mathematical model still overestimates the flux chamber measurements even in this artificial condition means that the flux chamber, due to its inner gas circulation, prevents the molecular diffusion described by the equation model from occurring properly.

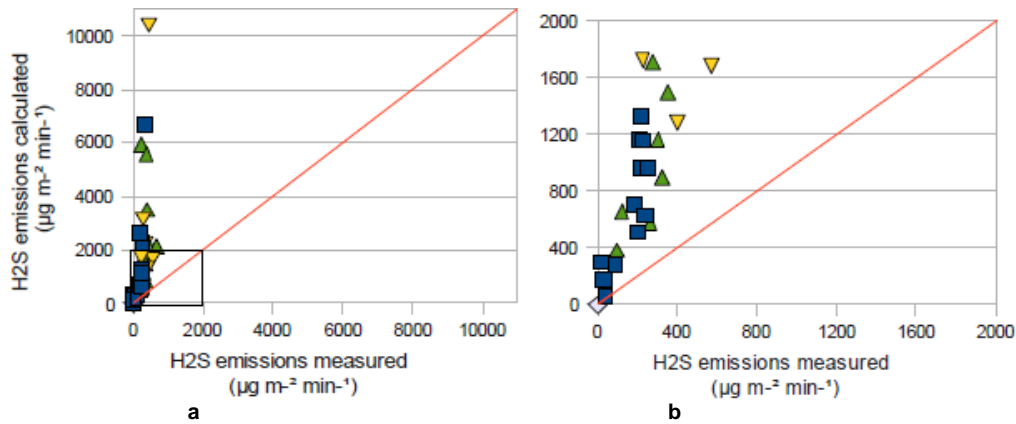


Figure 1 : Comparison between  $H_2S$  emissions measured and  $H_2S$  emissions calculated. (a) All emissions (b) Emissions lower than  $2000 \mu\text{g m}^{-2} \text{min}^{-1}$  ■ Lagoon inlet ▼ Lagoon middle ▲ Lagoon outlet.

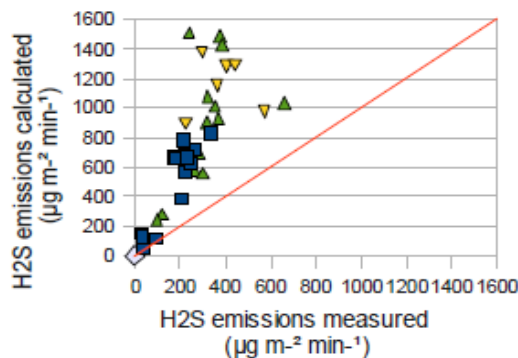


Figure 2: Comparison between  $H_2S$  emissions calculated with wind speed set equal to  $1 \text{ m s}^{-1}$  and  $H_2S$  emissions measured ■ Lagoon inlet ▼ Lagoon middle ▲ Lagoon outlet.

#### 4. Conclusion

Hydrogen sulphide emissions from an anaerobic lagoon were estimated by two approaches: a mathematical modeling and a dynamic flux chamber measurements. Different emission behaviors were found to drive  $H_2S$  emissions depending on the flux chamber position on the lagoon. At the lagoon inlet, only the dissolved  $H_2S$  concentration influences the  $H_2S$  emissions. In the middle and at the outlet of the lagoon, biogas bubbles presence prevent from finding such correlation. At the lagoon outlet, the liquid temperature was found to have more influence on  $H_2S$  emissions. Both methods have their own limitations in representing the real emissions. The mathematic model using a wind speed value measured at 10 m, increases the probability of overestimating the gas-liquid interface frictions, neglecting the lagoon vicinity. Thus, the mathematic model overestimates the lagoon  $H_2S$  emissions. On the contrary, the dynamic flux chamber measured emissions are not influenced by the wind flow,

underestimating H<sub>2</sub>S real emissions. In both methods, the wind is the parameter not adequately represented. In addition, in this study it was shown that the dynamic flux chamber affects H<sub>2</sub>S volatilization, underestimating real H<sub>2</sub>S emissions even in very low wind speed conditions.

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### References

- American Public Health Association- APHA, 2005. Standard Methods for the Examination of Water and Wastewater. 21th ed. Washington, DC: APHA.
- Debrieu C., 2004. Fight against sanitation odours (in French). Document Technique, FNDAE, n 13, Ministère de l'agriculture, de l'alimentation, de la Pêche et des Affaires Rurales.
- Eckley C.S., Gustin M., Lin C-J., Li X., Miller M.B., 2010. The influence of dynamic chamber design and operating parameters on calculated surface-to-air mercury fluxes. *Atm. Env.*, 44, 194–203.
- Enviroomega, 1995. Toxic Chemical Modeling Program for Water Pollution Control Plants, Users Manual TOXCHEM+ Model. Enviroomega, Campbellville, Ontario, Canada.
- Eklund B., 1992. Practical Guidance for Flux Chamber Measurements of Fugitive Volatile Organic Emission Rates. *Journal of the Air & Waste Management Association* 42, 1583-1591.
- Gostelow P., Longhurst P., Parsons S. A., Stuetz R. M., 2003. Sampling for the measurement of Odours. London, UK, IWA publishing.
- Gostelow P., Parsons S. A., Cobb J., 2001. Development of an Odorant Emission Model for Sewage Treatment Works. *Water Science & Technology* 44, 181-188.
- Hudson N., Ayoko G. A., Dunlop M., Duperouzel D., Burrell D., Bell K., Gallagher E., Nicholas P., Heinrich N., 2009. Comparison of odour emission rates measured from various sources using two sampling devices. *Bioresource Technology* 100, 118-124.
- Kienbusch M., 1986. Measurement of gaseous emission rates from land surfaces using an emission isolation flux chamber. EPA/600/8-86/008, US EPA, Environmental Monitoring Systems Laboratory, Las Vegas, Nevada.
- Latos M., Karageorgos P., Kalogerakis N., Lazaridis M., 2011. Dispersion of odorous gaseous compounds emitted from wastewater treatment plants. *Water, Air, & Soil Pollution* 215, 667–677.
- Lim T. T., Heber A. J., Ni J. Q., Sutton A. L., Shao P. 2003. Odor and gas release from anaerobic treatment lagoons for swine manure. *Journal of Environmental Quality* 32, 406-416.
- Mackay D., Matsugu R. S., 1973. Evaporation rates of liquid hydrocarbons spills on land and water. *Canadian Journal of chemical Engineering* 51, 434.
- Mackay D., Yeun A.T.K., 1983. Mass transfer coefficient correlations for volatilization of organic solutes from water. *Environmental Science & Technology* 17, 211-217.
- Oskouie A.K., Lordi D.T., Granato T.C., Kollias L., 2008. Plant-specific correlations to predict the total VOC emissions from wastewater treatment plants. *Atmospheric Environment* 42, 4530–4539.
- Rumsey I.C., Aneja V.P., Lonneman W.A., 2012. Characterizing non-methane volatile organic compounds emissions from a swine concentrated animal feeding operation. *Atmospheric Environment* 47, 348–357.
- Santos J.M., Kreim V., Guillot J.M., Reis Junior N.C., Sá L.M., Horan N.J., Accepted for publication. Hydrogen sulphide volatilization from quiescent surfaces at wastewater treatment plants. *Atmospheric Environment*.
- Springer C., Weijma J., Abusam A., 1984. Emissions of Hazardous Chemicals from surface and near surface impoundments to air. U.S. Environmental Protection Agency, Solid and Hazardous Waste Research Division. Cincinnati, Ohio. Project number 808161-02.
- US EPA, 1994. Air emission models for waste and wastewater. EPA-453/R-94-080A. North Carolina Research Triangle Park. <http://www.epa.gov/ttn/chief/software/water/>
- Von Sperling M., Oliveira S. C., 2009. Comparative performance evaluation of full-scale anaerobic and aerobic wastewater treatment processes in Brazil. *Water Science & Technology* 59, 15-22.