

Comparison of mass transfer parameters inside a USEPA flux hood for two VOCs

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ABSTRACT

Odorous emissions from area sources at wastewater treatment plants have become an environmental issue due to negative impacts on neighboring communities causing annoyance. Enclosure devices (such as dynamic flux chambers) have been used as direct methods to estimate area source emission rates from liquid–gas surfaces. Previously, model compounds have provided information about the internal mass transfer behavior of these sampling devices and the parameters estimated for certain model compounds that can be adapted for other compounds with similar liquid–gas partitioning properties. Acetic acid and butyric acid (both gas-phase-controlled compounds) were compared in order to assess the validity of adapting results from one compound to another. Mass transfer parameters for acetic acid and butyric acid were determined for a USEPA flux hood using a sweep air flow rate of 5 L/min. Mass transfer rates estimated for butyric acid, using the mass transfer parameters of acetic acid, were of the same order of magnitude as the experimental butyric acid mass transfer rates.

Key words | acetic acid, butyric acid, emission estimates, odorous emissions

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INTRODUCTION

Diffuse sources, such as industrial and domestic wastewater treatment plants (WWTPs), are associated with environmental impacts to air quality in neighborhood communities. They are important sources of odorous contaminants to the atmosphere such as nitrogen, sulfur and volatile organic compounds (VOCs). Their impacts include annoyance, which gives rise to complaints to authorities, adverse effects on human health and price depreciation of properties (Hayes *et al.* 2014, 2017; Brancher *et al.* 2017). Another potential environmental impact is related to greenhouse gas emissions generated from biological and chemical decomposition of organic matter.

Whereas point sources, such as stacks, can be easily subjected to periodic emission monitoring, this is not always the case for area sources. Nonetheless, the emission rate of odorous gaseous compounds shall be determined for the purpose of environmental impact assessments caused by such sources. The emission rate of compounds from passive liquid surfaces can be estimated by the use of one of the following methods (Gostelow *et al.* 2001; Hudson & Ayoko 2008a, 2008b; Prata *et al.* 2017): (i) predictive emission

models, (ii) reverse dispersion modelling (indirect method) and (iii) sampling with enclosure devices, such as a flux hood (dynamic flux chamber) or a wind tunnel (direct method).

Direct methods are characterized by the use of devices that enclose minimal parts of the emitting surfaces (enclosure devices) and directly sample the emissions. Flux hoods and portable wind tunnels are types of enclosure devices that are commonly used by environmental consulting firms, by wastewater treatment companies or by landfills to monitor variations in their process that can increase or decrease the emission of gases or odorants. In many instances, they are adopted by regulators as standards for the estimation of the emission rates in these enterprises.

Kienbusch (1986) presented standards and recommendations for the construction and operation of an emission insulation flux chamber (flux hood) for the assessment of gaseous emissions from contaminated soils. Later, the United States Environmental Protection Agency (USEPA) became interested in this technique for estimating emission rates from hazardous wastes and funded a series of projects

to develop and evaluate the flux chamber method (Eklund 1992). This so-called USEPA flux hood is regarded as a standardized design worldwide, and has been used as a basis for other standards, such as the Australian standard AS/NZS 4323.4:2009, which adopts the same USEPA basic design, but includes an internal fan to enhance mixing.

Although it is essential to quantitatively measure the impact of a given source through the estimation of an emission rate and to assess the dispersion, monitoring emissions of atmospheric pollutants from area sources in the field presents specific difficulties and limitations. Enclosure devices require great care in their application and thorough understanding of their internal mass transfer conditions if meaningful measurements are to be obtained.

Prata *et al.* (2018a) discussed how the uncertainty in temperature at the liquid surface and other sources of inaccuracy may affect the estimation of mass transfer parameters when using the enclosure. They also proposed that having the mass transfer coefficients for a given compound, the mass transfer coefficients for another compound inside the flux hood could be estimated using appropriate powers of their Schmidt numbers. This estimate is convenient especially when, for reasons of operational limitations, the mass transfer parameters for a compound cannot be determined.

Thus, this work aims to measure experimental mass transfer parameters for acetic acid and butyric acid volatilizing from aqueous solutions inside the USEPA flux hood and to assess the validity of adapting results from one compound to another.

MATERIALS AND METHODS

The flux hood was made of Plexiglas[®] and followed the standard design proposed by Kienbusch (1986): a cylindrical body, with diameter of 40.5 cm and height of 17.2 cm, and a dome-shaped top whose highest part (at its central point) is 26.5 cm above the bottom. Figure 1 presents a picture of the device. At the dome-shaped top there were four equidistantly positioned holes, one of which was an opening, with diameter 2.1 cm, for pressure equilibration and balance flow release. The other three had diameter 1.3 cm and were used to fit 1/4" stainless steel bulkheads with the following purposes: one connected the sweep gas feed line to the internal inlet distribution tube; another connected the internal sampling probe to the outer sampling line; and the other was kept capped during the time of the runs. The sweep gas distribution tube was made of stainless



Figure 1 | USEPA flux hood.

steel, 1/4" OD, and fixed to the cylindrical body internal wall, at the height where the dome meets the body. It contained four equidistant inlet orifices, positioned horizontally (so as to produce horizontal inlet jets), the one closest to the inlet bulkhead connection having diameter 2.0 mm, and the other three, diameter 2.4 mm. The sampling probe consisted of a 6'-long tube, capped at the tip, perforated with two rows of holes, each row containing five holes with diameter 2.4 mm. The holes were separated 1' from each other along the tube length and positioned orthogonally in the radial direction. A Teflon[®] outlet line, 1/4" OD, connected to the sampling probe via one of the bulkheads, conveyed the sampled flow to Nalophan[®] bags (for the runs with acetic acid solution), which were filled using a 'lung system' as detailed in the work of Prata *et al.* (2018a). Sorbent tubes were used for the runs with butyric acid solution. The sweep air feed line, connecting the supplying gas bottle to the inlet distribution tube, was also Teflon[®] tubing, 1/4" OD.

The basic operation of the flux hood system was conducted according to the standard sampling procedure described by Kienbusch (1986), observing the additional recommendations of Eklund (1992) concerning sampling on liquid surfaces. The sweep air feed was supplied by instrument-grade air bottles and the flow rate of 5 L min⁻¹ was adjusted by a mass flow controller (Alicat Scientific, 5 SLPM).

Volatilization of acetic acid

The flux hood was used to estimate the emission rate of acetic acid from an aqueous solution. Quantities of 1.7 L of Milli-Q[®] water and 40 mL of acetic acid glacial were mixed in an Erlenmeyer, which was sealed to avoid volatilization losses during the transport to the room where the flux hood experiments took place. The solution was

transferred to a cylindrical tank made of Plexiglas[®], with diameter 41.0 cm and height 8.5 cm; the depth of the liquid in the tank was approximately 1.3 cm. The flux hood was then placed over the tank and sweep air flow was started. The pump (Airchek Sampler) from the lung system was turned on with a pre-calibrated flow rate of approximately 200 mL min⁻¹ for Nalophan[®] bag sampling. During the experiment, the room, solution and flux hood interior temperatures were systematically measured with a thermometer, varying from 18.0 to 20.5 °C, respectively. The stabilization time was 30 min, following the recommendations of Eklund (1992). After this period, two samples were collected sequentially in Nalophan[®] bags, each being sampled for 20 min.

After removal of the Nalophan[®] bag from the lung system, a 0.5 mL sample was taken using a gas-tight syringe (2.5 mL SUPELCO, USA) and manually injected into the Gas Chromatograph coupled with a Mass Spectrometer Detector – GC (7890A, Agilent Technologies)–MSD (5977B, Agilent Technologies). Three injections were conducted for each Nalophan[®] bag sample. All samples were injected into the GC–MSD within 30 min after Nalophan[®] bag withdrawal from the lung system.

The GC–MSD was equipped with an HP-5MS 30 m × 0.25 mm × 0.25 μm column with helium as the carrier gas at a flow rate of 1.2 mL min⁻¹. The initial temperature of the GC oven was 60 °C for 0.1 min, increasing to 220 °C at 25 °C min⁻¹, and then being held for 1 min.

Calibration curves for acetic acid were established using gas samples at five known concentrations, produced by evaporating different amounts of pure standard solutions of the compounds into Nalophan[®] bags flushed with fixed volumes of sweep air as performed by Prata *et al.* (2018a).

Volatilization of butyric acid

Except for the sample collection, experiments to estimate the butyric acid emission rate followed similar procedures to those for acetic acid. The aqueous solution of butyric acid was obtained by mixing 0.5 mL of standard n-butyric acid and 1.7 L Milli-Q[®] water. The butyric acid aqueous solution was placed into the cylindrical tank, the flux hood was then placed over the tank and the sweep gas flow turned on. After the stabilization period, sampling was conducted with a sorbent tube connected directly to the exit of the sampling probe. The sampling pump was installed serially after the sorbent tube, so as to avoid contamination of the sample. A sampling flow rate of 75 mL min⁻¹ was kept by a mass flow controller (Alicat Scientific). The stabilization time was 30 min, following the recommendations of Eklund

(1992). After this period, five samples were collected sequentially in sorbent tubes, each tube having a sampling time of 5 min. Sample analysis was performed using GC (7890A, Agilent Technologies)–MSD (5975C, Agilent Technologies). A DB-VRX 30 m × 0.25 mm × 1.4 μm column was utilized for compound separation, with helium as the carrier gas at a flow rate of 1.2 mL min⁻¹. Sorbent tubes were loaded on an Ultra automatic sampler (Markes International, UK) and samples were thermally desorbed using a Unity thermal desorber (TD) (Markes International, UK). The GC column temperature was initially held at 50 °C for 2 min, then raised at a rate of 15 °C min⁻¹ to 200 °C, and then held for 5 min. The MSD data acquisition was set in full scan mode with a range from 35 to 325 m/z at a rate of four times per second.

Calibration curves for butyric acid were established using gas samples at five known volumes in duplicate, produced by evaporating different amounts of pure standard solutions of the compounds into sorbent tubes flushed with fixed volumes of sweep air. Before both sampling and calibration, the sorbent tubes were conditioned in a tube conditioner (Markes International, UK) for 30 min at a constant temperature of 50 °C so that any moisture or remaining compounds inside the tubes were evaporated.

Sorbent tubes were chosen for sampling after successive attempts to collect butyric acid gas samples using Nalophan[®] bags. GC–MSD readings showed a decay in concentrations higher than 20% for the same bag analysed, whereas this phenomenon was not observed in experiments with acetic acid in Nalophan[®] bags. Other sampling attempts were performed with Nalophan[®] bags previously conditioned with butyric acid, but the same instability was observed.

Emission rates and mass transfer coefficients from experiment results

The volatilization rate of the compounds, J (kg s⁻¹ m⁻²), inside the USEPA flux hood is calculated by Equation (1) (Kienbusch 1986). C_m is the measured gas-phase concentration (kg m⁻³), obtained directly from GC–MSD readings for acetic acid samples and calculated for butyric acid samples (mass obtained (kg) in chromatograph-reading versus sampled volume (m³)); Q is the sweep air flow rate (m³ s⁻¹) and A is the area (m²) of the surface enclosed by the hood ('footprint area'):

$$J = \frac{QC_m}{A} \quad (1)$$

The two-resistance model describes emission of compounds from the liquid phase to the gas phase inside the flux hood (see Prata *et al.* 2018a, 2018b). Based on this consideration, it is appropriate to describe the mass transfer conditions in the gas side by means of the gas-side mass transfer coefficient k_G (m s^{-1}), so that the mass flux (J_G) of a given compound through the region of major resistance in the gas phase ('gas film') can be expressed by Equation (2):

$$J_G = k_G(C_{G,i} - C_G) \quad (2)$$

where $C_{G,i}$ is the concentration of the compound immediately at the interface with the liquid phase and C_G is the concentration of the compound in the bulk gas. Analogously, the liquid-side mass transfer coefficient k_L (m s^{-1}) can be defined, and the mass flux (J_L) of a given compound through the region of major resistance in the liquid phase ('liquid film') expressed by Equation (3):

$$J_L = k_L(C_L - C_{L,i}) \quad (3)$$

where C_L is the concentration of the compound in the bulk liquid and $C_{L,i}$ is the concentration of the compound immediately at the interface with the gas phase.

Considering that the mass flux across the liquid film (J_L) is the same mass flux across the gas film (J_G), and assuming that at the interface between the liquid and gas phases the concentrations of compounds are in equilibrium and can be related by Henry's Law ($C_{G,i} = C_{L,i} K_H$, where K_H is the non-dimensional Henry's Law coefficient), Equation (4) can be obtained, in terms of the liquid-phase overall mass transfer coefficient (K_L) (see Prata *et al.* (2018b) for derivation and further comments):

$$J = K_L \left(C_L - \frac{C_G}{K_H} \right) \quad (4a)$$

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{k_G K_H} \quad (4b)$$

Assuming complete mixing in the headspace of the flux hood, the concentration of the compounds in the bulk of the gas phase C_G can be approximated by the concentration C_m sampled in the Nalophan[®] bags in the experiments with acetic acid and estimated for butyric acid (mass obtained (kg) in chromatograph-reading versus sampled volume (m^3)). The bulk liquid-phase concentration of the compounds C_L is known beforehand in the experiments, based on the amount of the pure compound used to prepare

the aqueous solutions and the dissociation equilibrium constants (only non-dissociated acid is available for volatilization). The values of the compound's K_H corrected for the experimental temperatures are taken from the literature (Sander 2015). Using these values of K_H , C_L and C_G (C_m) together with the experimental volatilization rate J (calculated via Equation (1)), Equation (4) can be solved for the experimental overall mass transfer coefficient K_L .

If an organic compound is highly volatile ($1/k_L \gg 1/(k_G K_H)$) the liquid-phase resistance controls the volatilization process, and therefore the experimental K_L will represent an approximation of its liquid-side mass transfer coefficient, that is $k_L \approx K_L$. In contrast, acetic acid and butyric acid present $1/(k_G K_H) \gg 1/k_L$, meaning that their volatilization will be gas-phase-controlled and $k_G \approx K_L/K_H$. In other words, the experiments with a highly volatile compound provide experimental values for its k_L , and the experiments with a poorly volatile compound allow its k_G to be assessed.

Having k_G for a given compound, say $k_{G,1}$, Prata *et al.* (2018a) propose that the gas-side mass transfer coefficient $k_{G,2}$ for another compound inside the flux hood can be estimated using appropriate powers of their Schmidt numbers, as in Equation (5):

$$k_{G,2} = k_{G,1} \left(\frac{Sc_{G,2}}{Sc_{G,1}} \right)^{-2/3} \quad (5)$$

where $Sc_{G,1}$ is the Schmidt number in the gas phase of the compound for which k_G is known, and $Sc_{G,2}$ is the Schmidt number in the gas phase of the compound for which k_G is unknown.

RESULTS AND DISCUSSION

Volatilization rate and mass transfer coefficients of VOCs inside the flux hood

Table 1 presents the variation of the volatilization rates J of the VOCs for the sweep air flow rate ($Q = 5 \text{ L min}^{-1}$) including average, minimum and maximum of the experimental values of the overall mass transfer coefficient K_L and the gas-side mass transfer coefficient k_G for acetic and butyric acid (gas-phase-controlled volatilization for all compounds) obtained through Equation (4a) and considering $k_G \approx K_L/K_H$.

The library search (score >80%) provided by GC-MSD identified other compounds grouped with butyric acid:

(i) butyric acid, propyl ester; (ii) butyric acid, 2-methylpropyl ester; and (iii) butyric acid, butyl ester, that were not detected in the runs for the calibration curve. The areas detected for these compounds were of the same order of magnitude as the 'pure' butyric acid compound. This loss of butyric acid concomitantly with ester formation leads to an underestimation of the emission rate calculated in Equation (1), if concentration estimates for C_m are considered only based on the 'pure' butyric acid.

Through Equation (5), the gas-side mass transfer coefficient (k_G) of butyric acid was estimated using the experimental data (k_G) of acetic acid obtained here and presented in Table 1. The estimated gas-side mass transfer coefficient for butyric acid was $3.247 \times 10^{-4} \text{ m s}^{-1}$, i.e., about 14% larger than the one obtained experimentally ($2.843 \times 10^{-4} \text{ m s}^{-1}$). If the sum of the concentrations of butyric acid and compounds grouped with butyric acid (butyric acid, propyl ester; butyric acid, 2-methylpropyl ester; and butyric acid, butyl ester) was considered for obtaining k_G , the average obtained experimentally from Equation (4a) ($3.217 \times 10^{-4} \text{ m s}^{-1}$) would be 13% larger than the average shown in Table 1 ($2.843 \times 10^{-4} \text{ m s}^{-1}$), and closer to the estimated value (1% difference).

The results discussed above indicate that some reaction with ester formation could be occurring inside the flux hood, which may impair the accuracy of the mass transfer coefficient measurement for butyric acid. A background analysis, where the sampling procedure was performed with only Milli-Q® water in the cylindrical tank and samples were collected in sorbent tubes, did not find any significant background contaminant that could be involved in the formation of the esters. Considering this, tests were performed in order to inhibit the ester formation detected in the samples collected in the flux hood experiments, described as follows.

Tests for inhibition of the formation of butyric acid ester

The proposed tests differ in some aspects from the methodology initially performed for the acetic and butyric acid experiments. The direct dumping of the aqueous solutions

into the Plexiglas® cylindrical base was avoided because it was hypothesized that ester formation would be occurring between the aqueous butyric acid solution and some contaminant or component of the Plexiglas®. Plexiglas® is a plastic material made from polymers of methyl methacrylate, an ester of methacrylic acid. To avoid hypothetical contamination, ten Petri dishes were placed inside the cylindrical base to avoid direct contact of the aqueous solution with the Plexiglas®, as shown in Figure 2. The sum of the surface area of the Petri dishes was 0.7 m^2 and was considered in the volatilization rate calculations (Equation (1)). The average ambient temperature of the six experiments was 22.3°C and the average temperature of the aqueous solution was 21.8°C . Table 2 summarizes the configurations adopted in the six experiments performed to inhibit ester formation.

In Experiment 1, the aqueous solution was placed directly into the Petri dishes and experimental settings were maintained. Experiment 2 was conducted considering the hypothesis of ester formation through the butyric acid reaction with some contaminant present in the Milli-Q® water. Thus, in this test, Milli-Q® water was replaced by tap water.

Experiment 3 was performed with Milli-Q® water, however the carrier gas used was replaced by nitrogen (instrument grade). Both pure air and nitrogen are recommended as sweep air by Eklund (1992).

In Experiment 4, air was used as carrier gas and Milli-Q® water for the butyric acid aqueous solution. In this test, the pH of the butyric acid aqueous solution was



Figure 2 | Petri dishes inside cylindrical base.

Table 1 | Emission rate and mass transfer parameters estimated for acetic acid and butyric acid through flux hood experiments

	J ($\mu\text{g s}^{-1} \text{ m}^{-2}$)			K_L (10^{-9} m s^{-1})			k_G (10^{-4} m s^{-1})		
	Average	Min	Max	Average	Min	Max	Average	Min	Max
Acetic acid	44.297	39.956	50.429	2.895	2.415	3.628	4.083	3.305	5.241
Butyric acid	0.316	0.311	0.321	1.694	1.662	1.734	2.843	2.789	2.910

Table 2 | Test configurations performed to inhibit ester formation

Experiment	Type of water		Carrier gas			Stabilization time	
	Milli-Q	Tap water	Air	Nitrogen	Addition of H ₂ SO ₄	30 min	60 min
1 Air, Milli-Q [®]	X		X			X	
2 Air, Tap water		X	X			X	
3 N ₂ , Milli-Q [®]	X			X		X	
4 Air, Milli-Q [®] , H ₂ SO ₄	X		X		X	X	
5 N ₂ , Milli-Q [®] , H ₂ SO ₄ , 30'	X			X	X	X	
6 N ₂ , Milli-Q [®] , H ₂ SO ₄ , 60'	X			X	X		X

modified by adding approximately 1 mL of sulfuric acid (H₂SO₄). After the addition of H₂SO₄, the pH of the mixture reduced on average from 3.55 to 1.85.

In Experiment 5, approximately 1 mL of H₂SO₄ was also added to the aqueous solution, prepared with Milli-Q[®] water, and nitrogen was used as the carrier gas. The liquid phase of the butyric acid aqueous solution was also sampled and analysed during this experiment to verify if ester formation was occurring in the liquid phase rather than in the gas phase. In this test, four samples of the liquid phase were collected at times 20, 50, 80 and 120 min after the initial time of the experiment; 10 mL of the liquid phase was sampled with a syringe and mixed in 100 mL of Milli-Q[®] water. Again with the use of a syringe, 15 µL of this mixture was injected into the calibration rig for sorbent tube preparation and flushed with nitrogen for 30 min. No ester was detected in the four samples from the liquid phase. The gas-phase samples were also collected, following the same methodology used in the other experiments, ester formation being observed in these samples. This is strong evidence that the esters were being formed in the gas phase.

In Experiment 6, there was a change from the methodology, with samples being collected after waiting 60 min of stabilization time, instead of the 30 min proposed by

Eklund (1992). Table 3 presents the experimental k_G results for the six tests performed inside the flux hood. The average emission rate (J) and overall mass transfer coefficient (K_L) obtained for the six experiments were $0.546 \mu\text{g s}^{-1} \text{m}^{-2}$ and 2.719m s^{-1} , respectively.

A last test was performed (Experiment 7) where the concentration of butyric acid in the solution was doubled (1 mL of pure butyric acid in 1.7 L Milli-Q[®] water, that is, 0.588mL L^{-1}). As in experiments 4, 5 and 6, about 1 mL of H₂SO₄ was added to the aqueous solution to lower the pH of the solution. With the same flow rate of 5L min^{-1} , nitrogen was used as sweep air. The prepared aqueous solution was immediately placed into the Petri dishes. The experimental average for k_G was $4.087 \times 10^{-4} \text{m s}^{-1}$, but ester compounds grouped with butyric acid were detected. These results indicate that even by doubling the initial concentration of the aqueous solution, ester formation in the gas phase was not inhibited.

CONCLUSIONS

Flux hood experiments were performed to estimate the mass transfer parameters of acetic acid and butyric acid

Table 3 | Emission rate and mass transfer parameters estimated from tests for inhibition of the formation of butyric acid esters

	$J (\mu\text{g s}^{-1} \text{m}^{-2})$			$K_L (10^{-9} \text{m s}^{-1})$			$k_G (10^{-4} \text{m s}^{-1})$		
	Average	Min	Max	Average	Min	Max	Average	Min	Max
1 Air, Milli-Q [®]	0.518	0.517	0.519	2.639	2.632	2.645	3.916	3.907	3.925
2 Air, Tap water	0.519	0.519	0.520	2.646	2.644	2.649	3.927	3.923	3.931
3 N ₂ , Milli-Q [®]	0.546	0.530	0.569	2.813	2.703	2.977	4.090	3.930	4.328
4 Air, Milli-Q [®] , H ₂ SO ₄	0.550	0.535	0.561	2.781	2.669	2.857	4.864	4.668	4.997
5 N ₂ , Milli-Q [®] , H ₂ SO ₄ , 30'	0.547	0.533	0.567	2.526	2.442	2.645	3.457	3.441	3.619
6 N ₂ , Milli-Q [®] , H ₂ SO ₄ , 60'	0.598	0.591	0.607	2.906	2.853	2.960	4.225	4.149	4.304

(both compounds having their volatilization controlled by the gas phase) from aqueous solutions inside the flux hood and to assess the validity of adapting results from one compound to another via Equation (5). Mass transfer parameters for acetic acid could be successfully measured. Mass transfer rates estimated for butyric acid, using the mass transfer parameters of acetic acid, were of the same order of magnitude as the experimental butyric acid mass transfer rates. This indicates an overall successful application of Equation (5), despite the fact that the results for butyric acid indicated the presence of esters in addition to butyric acid, which compromised the precise estimation of the mass transfer parameters for butyric acid.

Additional tests were performed to investigate the ester formation and the possibility of inhibiting it: replacement of Milli-Q[®] water with tap water; replacement of air as a carrier gas by nitrogen; and change in pH of aqueous butyric acid solution with approximately 1 mL of H₂SO₄. Although some combinations contributed to an increase in the mass transfer coefficient k_G , ester formation was still detected in all tests. Liquid-phase samples were collected during an experiment with the flux hood and no ester formation was identified in them, revealing that the ester formation was occurring in the gas phase. We recommend further research to explore this phenomenon in more detail.

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