



XVIIth World Congress of the International Commission of Agricultural and Biosystems Engineering (CIGR)

Hosted by the Canadian Society for Bioengineering (CSBE/SCGAB)
Québec City, Canada June 13-17, 2010



IMPROVEMENT OF A PASSIVE FLUX SAMPLER FOR THE MEASUREMENT OF NITROUS OXIDE (N₂O) EMISSIONS

J.H. PALACIOS¹, S. GODBOUT¹, R. LAGACÉ², F. PELLETIER¹, J-P. LAROUCHE¹,
L. POTVIN¹, S.P. LEMAY¹

¹ J.H. PALACIOS, Research and Development Institute for the Agri-Environment (IRDA), 2700. Einstein Street, Québec, Québec, Canada G1P-3W8, joahn.palacios@irda.qc.ca.

¹ S. GODBOUT, stephane.godbout@irda.qc.ca.

¹ F. PELLETIER, frederic.pelletier@irda.qc.ca.

¹ J-P. LAROUCHE, jean-p.larouche@irda.qc.ca.

¹ L. POTVIN, lise.potvin@irda.qc.ca.

¹ S.P. LEMAY, stephane.lemay@irda.qc.ca.

² R. LAGACÉ, Département des sols et de génie agroalimentaire, Faculté des sciences de l'agriculture et de l'alimentation, Université Laval, Sainte-Foy, Québec, Canada G1K-7P4, robert.lagace@fsaa.ulaval.ca.

CSBE1555 – Presented at Section II: Farm Buildings, Equipment, Structures and Livestock Environment Conference

ABSTRACT This paper presents the research projects performed on the development of a passive flux sampler used to measure nitrous oxide (N₂O) from agricultural sources. The main objective was to improve sampler efficiencies and analysis methods. Many aspects of the developed sampler were improved: 1) the sampler was modified to insure air tightness and to facilitate maintenance; 2) the gas adsorption capacity was increased by enlarging the thickness of the adsorbent layer; 3) a new desorption process was evaluated; 4) a more accurate K factor (relation between inside and outside air velocity of the sampler) was calculated for every adsorbent thickness tested. The adsorbent thickness was increased from 2 mm (original thickness) to 4, 6 and 8 mm, gaining adsorption capacity of 96, 187 and 275%, respectively while having a similar adsorption efficiency of 98%. The new desorption process improved desorption efficiencies for every adsorbent thickness: from 68% to 83% in 2 mm layer, from 57% to 75% in 4 mm layer, from 45% to 82% in 6mm layer and from 30% to 74% in 8 mm layer. The accuracy of the sampler was also improved to reach 77% ± 14%. The calculated K factors were between 7.9 x10⁻⁴ and 8.8 x10⁻⁴. The results confirmed that the modifications done to the sampler and analysis methods contributed to improve its performances and development.

Keywords: Passive flux sampler, Nitrous oxide emission, Molecular sieve, Zeolite.

INTRODUCTION At present, greenhouse gases (GHG) have become the center of attention of the whole world because of their contributions to global warming. The agriculture is one of the most important issues of GHG, especially nitrous oxide (N₂O). However, the agriculture sector can also play an important role to reduce the emission of this gas in the atmosphere.

To be able to know the impact of reduction technologies or techniques, it is necessary to develop quick, effective and economic methods to measure gases from agricultural sources. For sources with weak emissions (i.e. agriculture sector), the conventional approaches are often sophisticated and expensive. Nevertheless, for several years, the passive flux sampling has demonstrated to be a suitable tool to measure gas emissions and concentrations even at low intensity.

Passive samplers are usually based on the phenomenon of mass transport due to the difference between the chemical potentials of analytes in a given environmental compartment and the collection medium inside a dosimeter (Kot-Wasik et al, 2007). In this case, there is no chemical reaction during sampling; it is simply the adsorption of a gas into a medium. Then, gas emission is determined by the measurement of the mass of the gas trapped into the adsorbent by the subsequent laboratory operations (i.e. extraction, identification and determination of analytes).

Unlike active sampling, where the air is pumped during sampling, passive samplers require no electricity, pumps and flow meter, have no moving parts, and are simple to use. The equipment used in passive sampling is relatively simple and small, which is great advantage since sampling sites are often located far from the laboratory, where further handling of samples has to be performed.

The concentration of the analyte is integrated over the whole exposure time, making such a method immune to accidental or extreme variations of pollutant concentrations (Namiessnik et al., 2005). It makes it easy to determine time-weighted average (TWA) concentrations of the analytes and to obtain a long-term overview of pollutant levels in a given environmental compartment

THE PASSIVE FLUX SAMPLER DEVELOPED BY GODBOUT ET AL. (2006a, 2006b) AND GAUDET (2005) The sampler developed by Godbout et al. (2006a, 2006b) and Gaudet (2005) is based on the concept of the sampler developed by Ferm (1986) and the theoretical principles of Scholtens et al. (2003) and Schjoerring et al. (1992). This type of sampler uses the wind as the driving force to flow-through the sampler. As the air passes through the sampler, the target gases are collected by an adsorbent bed.

In order for a passive sampler to work in practice, it is important that the relationship (K factor, eq. 1) between the air velocity outside the sampler, v_o (m/s), air velocity inside the sampler, v_i (m/s) and the angle between the sampler's axis and wind direction, α , is linear for all air velocity variations. Knowing this factor removes the need to measure wind velocity in the sampling process, as the amount of gas trapped is proportional to the sampler constant.

$$K = \frac{v_o}{v_i \sqrt{\cos \alpha}} \quad (1)$$

This sampler constant is an expression of the amount of air that passes through the sampler in relation to the air that passes around the sampler (Gaudet, 2005). Thus, the emission rate, F ($\text{g m}^{-2} \text{s}^{-1}$) is determined by dividing the amount of trapped gas, m (g) by the sampler constant (K), the cross-sectional area inside the sampler where the air velocity is measured, A (m^2) and the exposure time, Δt (s):

$$F = \frac{m}{K A \Delta t} \quad (2)$$

The sampler developed by Godbout et al. (2006a, 2006b) and Gaudet (2005) is an instrument made of standard stainless steel with an aerodynamic shape (fig 1). The sampler is composed of three parts, namely, the inlet cone, the cartridge, and the exit cone (fig.1a, 1b, and 1c, respectively). A 2 mm bed of molecular sieve zeolite 5A is used as the adsorbing material which is held in the cartridge. At the outlet of the exit cone, an orifice of 0.52 mm diameter is placed (fig. 1d), which allows linearity between the external and internal air velocity and further reduces the air flow inside the sampler, thus, longer sampling times are obtained.

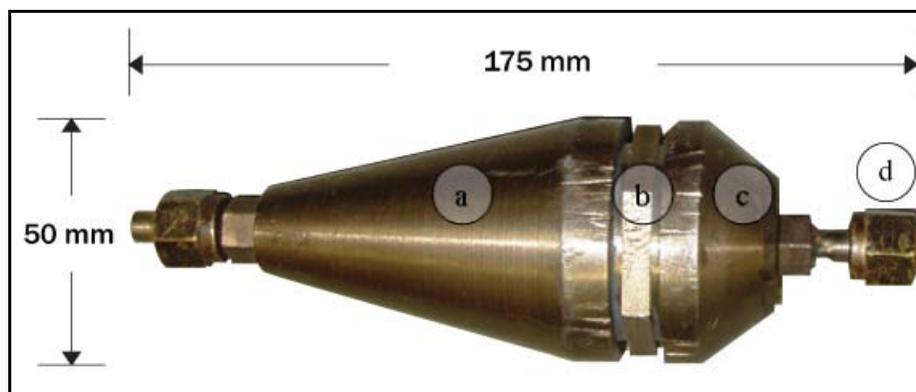


Figure 1: Flux sampler developed by Godbout et al. (2006a, 2006b) and Gaudet (2005)

Nonetheless, Gaudet (2005) reported that while the sampler is exposed to a N_2O source of 2 ppm concentration and a flux of 15 ml/min, the adsorbent was saturated in 50 min. In passive sampling, longer sampling times are considered necessary in order to obtain representative emission measurements.

There are typically four processes to follow when using passive samplers with molecular sieves. These are conditioning, adsorbing, desorbing and analysis.

Conditioning is the process where the adsorbent is cleaned and activated. It is important that the sieve is free of the molecule that is being sampled, otherwise emission measurements will present an over estimation. The conditioning of molecular sieves is generally done by heating the adsorbent in a flow of inert gas. However, the exact procedure depends on the type of molecular sieve.

Adsorption is the stage where the conditioned sampler is exposed to a source of air containing the specific gas to be determined. Then, the molecules in the sampler are concentrated in the adsorbent. This phenomenon allows the bed of molecular sieve to store, capture, or selectively separate the gases that are passing through them (Godbout et al., 2006a). Gaudet (2005) obtained an adsorption efficiency of 91 % (± 11 %) for N_2O .

Desorption and Analysis Desorption is the phase where the adsorbed gas is recovered. There are two desorption methods in passive sampling: chemical and thermal desorption. Thermal desorption is the one used in the present study. This technique involves the use of heat and a flow of inert gas through the adsorbent in order to volatilize the N_2O and

drive it towards a collection bag. The temperature and the length of time that the adsorbent is heated depend on the type of the adsorbent and the type of gas analyte. Though nitrogen is generally used as carrier gas (Gaudet, 2005; Godbout et al. 2006a and 2006b; Kumagai and Koda, 1999), helium can also be used (Henderson et al., 2003; Markes International, 2002 and Park, 1998). Tests done by Gaudet (2005) reported 134% average desorption efficiency, meaning that the mass of N₂O desorbed was greater than the gas adsorbed. The excess mass of N₂O was coming from the ambient air. Even if the author adjusted the result by subtracting the amount of N₂O in the ambient air, the desorption efficiency still came out to be 108%.

Another important stage is the calibration of the samplers that has to be done once only in the laboratory after assembling the new sampler. The calibration consists of determining the K factor. The K factor determined by Gaudet (2005) varies between 0.0036 and 0.0039 with coefficients of correlation between 0.9923 and 0.9774.

MATERIALS AND METHODS In order to improve the performance of the sampler, the study was focused basically in two aspects: sampling time and desorption efficiency.

Since the results obtained by Godbout et al. (2006a) show that the adsorption capacity for N₂O is linearly dependent on the mass of zeolite 5A molecular sieve in the sampler, a system of screens was introduced, which allowed the adsorbent bed thickness in the sampler to be enlarged. The bed thickness was increased from 2 to 4, 6, and 8 mm, thereby increasing the mass of zeolite 5A from 749 mg to 1467, 2153 and 2810 mg, respectively. Thus, the sampling time was theoretically increased to 96%, 187% and 275%, respectively. This increase prolonged the available exposure time before the zeolite got saturated.

In order to improve the desorption efficiency and to avoid excess N₂O in the adsorbent, the following measures were implemented:

- **Ensuring air tightness in the sampler.** Gas leaks in the sampler were detected. When the sampler was used in the different stages, the leaks generated irregularities in the results. Also, the leaks caused contamination in the adsorbent when the sampler was not in used (e.g during storage) due to the diffusive air flow that exists in the adsorbent and the exchange of gas particles between adsorbent and ambient air. This diffusive flow is caused by the concentration gradient in both media (adsorbent and environment air) according to Fick's law of diffusion. This contamination reduces the adsorption capacity and induces errors in the measurements. To ensure gas tightness in the sampler, Viton O rings were placed between the cartridge and the cones of the sampler. To verify the tightness of the samplers, tests at 200 kPa internal pressure were carried out. Moreover the resistance of the rings to support high temperatures (up to 310 °C) was tested.
- **Replacement of N₂ by He as carrier gas.** Because the target gas is a nitrous compound, the use of He instead of N₂ as carrier gas during the conditioning and desorption stages avoids possible reactions between N₂, N₂O and the ambient air.
- **Implementation of a conduit purging practice.** A step which involves purging out the air from the conduits of the systems was added in every stage. Purging was achieved by pumping He (during conditioning and desorption stages) or N₂O

- (during adsorption stage) before beginning the tests. Valves were installed in every pipe line to restrict the re-entrance of the ambient air.
- **Special care in system design.** During the construction of the adsorption and desorption systems, pipes were installed with minimal lengths in order to minimize the air remaining in the conduits for cases where purging is not possible. Also, leak-tight connections were installed and tested in all systems.

Following the modifications applied to the sampler and to the laboratory procedures, the adsorption efficiency, desorption efficiency, accuracy, and precision of the sampler at each bed thickness (2, 4, 6 and 8 mm) were determined. Four samplers identified as C, D, E and Y were tested. The methodology for testing followed the four procedures of passive sampling (conditioning, adsorption, desorption and analysis). The experimental plan was structured as an incomplete random block because only four trials in each session could be realized. A total of eight blocks were formed and each block had four trials resulting to a total of 32 trials.

Conditioning The samplers were put in the oven and the temperature was increased gradually from room temperature to 310 °C and was then held constant. Purging of the samplers was achieved by pumping 600 ml/min of helium through each sampler for 180 min.

Adsorption The adsorption procedure was conducted in the laboratory in order to have a total control on the nature and quantity of gas being sampled. The frontal sides of the samplers were connected directly to a source of N₂O and a flow meter. An air-tight bag was connected to the exit cone of the sampler. The assembly allows control and measurements on the flow of gas which passes through the sampler. As the gas passed through the adsorbent, the N₂O molecules were adsorbed. Then, the off gases were collected in the bags and analyzed by a gas chromatograph (GC) to determine the amount of N₂O adsorbed (eq. 3).

$$m_{ads} = m_{in} - m_{out} = (C_{in} - C_{out}) \rho_{N_2O} V_{in} \quad (3)$$

where: m_{ads} is the mass of gas adsorbed in ng; m_{in} is the mass of gas that passed through the sampler in ng; m_{out} is the mass of gas in the outlet adsorption bag in ng; C_{in} and C_{out} are the concentrations of the gas that passed through the sampler and of that collected in the outlet adsorption bag respectively, in ppm; ρ_{N_2O} is the gas density in mg/ml (1.8 mg/ml, source: Air Products and Chemicals, Inc, 2003); V_{in} is the total volume of gas that was pumped through the sampler during the adsorption period in ml.

Four flow rates (6.5, 13, 19.5 and 26 ml/min) of 2 ppm of N₂O were tested for an adsorption period of 20 min.. The total mass of N₂O injected were 0.468, 0.936, 1.404 and 1.872 µg, respectively. Each test was duplicated for every bed thickness, thus, a total of 32 experiments were carried out. The adsorption efficiency was then calculated as a function between the amount of gas adsorbed and the amount injected. The mass of gas adsorbed was calculated using eq. 3.

Desorption and analysis The exposed samplers were put in the oven and the temperature was increased gradually from room temperature to 100 °C. Then, desorption flows of 21

ml min⁻¹ sampler⁻¹ of helium were pumped in the backward direction through the sampler for 30 min. The off gases were collected in air-tight bags and subsequently analysed by GC. The mass of gas desorbed was calculated using eq. 4.

$$m_{des} = C_d V_d \rho_{N_2O} \quad (4)$$

where: m_{des} is the mass of gas desorbed in ng; C_d is the gas concentration in the outlet desorption bag in ppm; V_d is the volume of gas that was pumped through the sampler during the desorption period in ml.

Efficiency calculations The adsorption and desorption efficiencies (η_{ads} (%) and η_{des} (%), respectively) were calculated using the following equations:

$$\eta_{ads} = \left(\frac{m_{ads}}{C_{in} \rho V_{in}} \right) \times 100 \quad (5)$$

$$\eta_{des} = \left(\frac{m_{des}}{m_{ads}} \right) \times 100 \quad (6)$$

Accuracy and precision The accuracy of the sampler was determined from the total efficiency, η_{total} (%), which is defined as the ratio of the mass of N₂O desorbed (m_{des}) to the mass of N₂O that was pumped through the sampler, m_{total} , (ng).

$$\eta_{total_i} = \frac{m_{des}}{m_{total}} \times 100 \quad (7)$$

The coefficient of variation, CV (%), is the statistical parameter of dispersion used in the present study to describe the precision of the sampler measurements. Thus, from the results of the total efficiency, the coefficient of variation was calculated by the following equation:

$$CV = \frac{\sigma}{\bar{x}} \times 100 \quad (8)$$

where CV is the coefficient of variation in percentage (%); σ is the standard deviation and \bar{x} is the average of the total efficiency.

Calibration The calibration of the samplers at each bed thickness was carried out by exposing the samplers to nine air velocities (from 0.5 to 6.5 m/s) inside a wind tunnel. The wind tunnel was built according to ANSI/ASHRAE 41.2 (1992) standard. The air velocity inside the sampler was calculated from the internal air flow measurements at every wind velocity in the tunnel. The K factor was determined as the slope of the linear trend line from the graph of the wind tunnel velocity vs. the exit sampler air velocity. It is important to note that the line was forced through the origin of the axes. The structure of the experimental plan was a completely randomized design with 16 treatments and three repetitions (48 trials).

RESULTS AND DISCUSSION

Adsorption efficiency The results of the whole experiments are summarised in table 1. The four adsorbent thicknesses obtained very similar average adsorption efficiencies,

which are close to 100%, and low variation (99.4±1.5, 98.1±1.6, 97.9±2.7 and 99.3±1.7 % for 2, 4, 6 and 8 mm, respectively, fig. 2). The performance of the sampler in the adsorption stage was not affected by the increase in the amount of adsorbent and showed an independent relationship between adsorption efficiency and gas flow at each bed thickness case.

Table 1: Summary of results on the performance of passive flux sampler

Thickness (mm)	Flow (ml/min)	m _{in} (µg)	Adsorption		Desorption		η _{total} (%)
			m _{ads} (µg)	η _{ads} (%)	m _{des} (µg)	η _{des} (%)	
2	6.5	0.468	0.4680	100	0.3856	82	82
	6.5	0.468	0.4680	100	0.3289	70	70
	13	0.936	0.9360	100	0.7484	80	80
	13	0.936	0.9360	100	0.6691	71	71
	19.5	1.404	1.4040	100	0.9752	69	69
	19.5	1.404	1.4040	100	0.7144	51	51
	26	1.872	1.7878	96	1.1340	63	61
	26	1.872	1.8720	100	0.9979	53	53
		\bar{x}	99.4		67.6		67.3
		σ _g □□□□	1.6		9.1		8.8
		CV (%)	1.6		17		17
4	6.5	0.468	0.4469	96	0.2835	63	61
	6.5	0.468	0.4282	92	0.3742	87	80
	13	0.936	0.9360	100	0.3969	42	42
	13	0.936	0.9360	100	0.6010	64	64
	19.5	1.404	1.4040	100	0.5670	40	40
	26	1.872	1.8720	100	1.0093	54	54
	26	1.872	1.8720	100	0.8618	46	46
			\bar{x}	98.1		56.8	
		σ _g □□□□	1.6		13.6		12.3
		CV (%)	3.4		29		25
6	6.5	0.468	0.4680	100	0.1928	41	41
	6.5	0.468	0.4352	93	0.2268	52	48
	6.5	0.468	0.4282	92	0.1928	45	41
	13	0.936	0.9360	100	0.8051	86	86
	13	0.936	0.9360	100	0.3629	39	39
	19.5	1.404	1.4040	100	0.5216	37	37
	19.5	1.404	1.3549	97	0.2835	21	20
	26	1.872	1.8720	100	0.8618	46	46
	26	1.872	1.8720	100	0.7144	38	38
			\bar{x}	97.9		45.0	
		σ _g □□□□	3.1		16.4		16.3
		CV (%)	3.5		39		40
8	6.5	0.468	0.4423	95	0.2608	59	56
	6.5	0.468	0.4680	100	0.0907	19	19
	13	0.936	0.9360	100	0.2495	27	27
	13	0.936	0.9360	100	0.3289	35	35
	19.5	1.404	1.4040	100	0.3515	25	25

19.5	1.404	1.4040	100	0.2608	19	19
26	1.872	1.8720	100	0.6350	34	34
26	1.872	1.8720	100	0.4423	24	24
\bar{x}			99.3		30.2	29.8
σ_g 			1.9		14.9	13.9
CV (%)			2.0		43	41

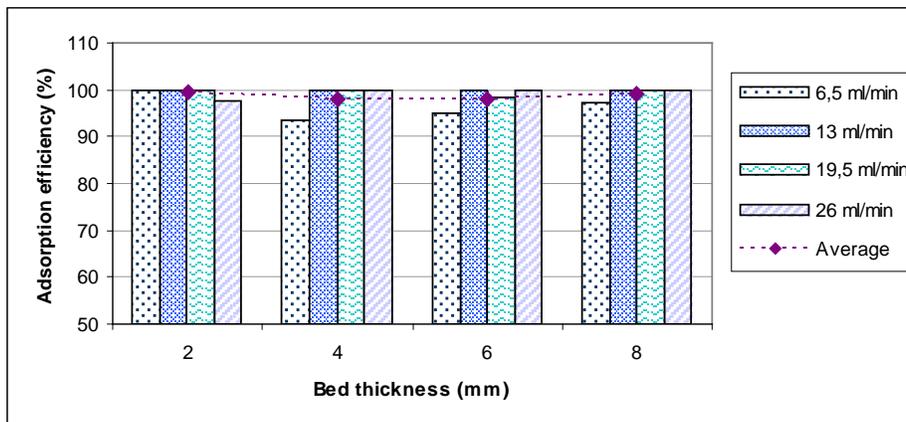


Figure 2 : Adsorption efficiency

Desorption efficiency. Figure 3 presents desorption efficiencies for every bed thickness and the respective average adsorption efficiencies. It shows that desorption efficiency decreases as the bed thickness increases. The reason for this is that greater quantity of energy is required to release the particles from the zeolite when the adsorbent bed is thicker. For example, an 8-mm bed needs more energy than a 2-mm bed to have the same temperature at the center of the bed. This hypothesis was confirmed with further tests where new desorption parameters such as an increase in the temperature (from 100 °C to 200 °C) and in the gas flow rates (from 21 to 42 ml/min). The duration of the desorption was decreased from 30 to 15 min. in order to keep the same ratio of N₂O/He in the outlet desorption bags. Figure 4 compares the desorption results from both desorption procedures. The new desorption parameters obtained an independent relationship between bed thickness and desorption efficiency. In fact, no significant differences on desorption efficiencies were found among different bed thicknesses. In addition, the new procedure increases desorption efficiencies from 68 % to 83 %, from 57 % to 75 %, from 45 % to 82 % and from 30 % to 74 %, respectively, for each bed thickness (2, 4, 6 and 8 mm).

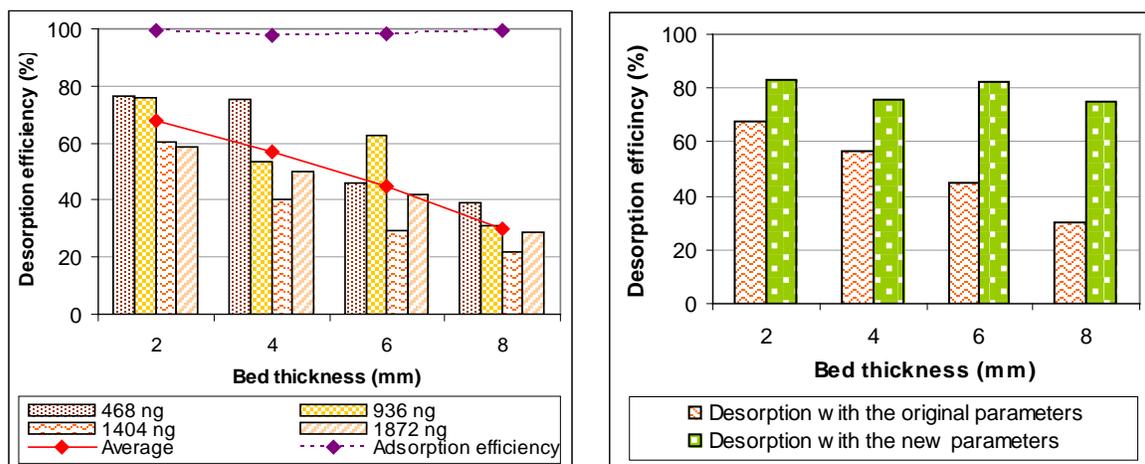


Figure 3 : Desorption efficiency

Figure 4: Desorption efficiency of two desorption procedures

Accuracy and precision The averages values of the total efficiencies in table 1 show clearly the decrease on the accuracy of the samplers when the adsorbent bed thickness was increased (67 %, 55 %, 44 % and 30 % total efficiency for 2, 4, 6 and 8 mm bed thickness, respectively). Also, CV shows that samplers presented less precision when they had a thicker bed (coefficients of variation are 17 %, 25 %, 40 % and 41 % for 2, 4, 6 and 8 mm, respectively). This effect was caused mainly by the sampler's performance during the desorption stage, since the sampler in this stage presented less efficiency and precision than in the adsorption stage.

Table 2 summarizes the accuracy and precision of the samplers when the parameters of the original desorption procedure (DP 1) and those of the new desorption procedure (DP 2) were used. Results show that samplers had higher accuracy when DP 2 procedure was used. Additionally, DP 2 reduces the variation in the measurements by approximately 50%, thus resulting to more precise measurements.

Table 2: Comparison on the accuracy and precision of samplers according to desorption procedure used.

Thickness (mm)	η_{total} (%)		CV (%)	
	DP 1	DP 2	DP 1	DP 2
2	67.3	80.3	13	7
4	55.4	74.5	22	14
6	44.1	80.8	37	18
8	29.8	73.6	47	15

Calibration Table 3 presents the results of the calibration constants of the samplers (K factor) and coefficients of determination (R^2). The constants were very similar among samplers and among adsorbent thicknesses (K ranged from 7.9×10^{-4} to 8.8×10^{-4}). Furthermore, K factor for each bed thicknesses presents good approximation to a linear behaviour (R^2 ranged from 0.93 to 0.95). However, the constants were approximately 4.5 times smaller than those determined by Gaudet (2005), which ranged from 3.6×10^{-3} to 3.9×10^{-3} . This difference could be due to the flow sensor used to measure v_i . The sensor interfered the free flow of the air, thus the resistance reduced the flow measurements.

Table 3: Calibration constants (K factor)

Thickness Sampler	2mm		4mm		6mm		8mm	
	K	R^2	K	R^2	K	R^2	K	R^2
C	8.4×10^{-4}	0.94	8.2×10^{-4}	0.94	8.3×10^{-4}	0.95	8.4×10^{-4}	0.93
D	8.5×10^{-4}	0.94	8.5×10^{-4}	0.93	8.4×10^{-4}	0.94	8.6×10^{-4}	0.94
E	7.9×10^{-4}	0.94	8.2×10^{-4}	0.94	7.9×10^{-4}	0.93	8.1×10^{-4}	0.93
Y	8.2×10^{-4}	0.93	8.8×10^{-4}	0.94	8.2×10^{-4}	0.93	8.4×10^{-4}	0.93

CONCLUSION The modifications done to the sampler and to the methods of analysis improved the adsorption capacity and adsorption efficiency. However, the desorption efficiency reduced as the adsorbent bed thickness increased. Nevertheless, the increase in the temperature and flow of the carrier gas in the desorption stage improved the desorption efficiency as well as the accuracy and precision of the sampler for each thickness layer. Linear K factors were obtained, however the technique to measure v_i has to be improved. In general, this study improved the performance of the passive flux sampler developed by Godbout et al. (2006a, 2006b) and Gaudet (2005). In this stage, the sampler is ready to be tested in farm environments.

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