Parameters determining the use of zeolite 5A as collector medium in passive flux samplers to estimate N_2O emissions from livestock sources

Araceli D. Larios [1,2]

Satinder Kaur Brar [1,*] Phone+ 418 654 3116 Emailsatinder.brar@ete.inrs.ca

Antonio Avalos Ramírez [1,3]

Stéphane Godbout [4]

Fabiola Sandoval-Salas [1,2]

Joahnn H. Palacios [4]

Patrick Dubé [4]

Beatriz Delgado [4,5,6]

Anne Giroir-Fendler [5]

[1] Institut National de la Recherche Scientifique (INRS), Centre Eau, Terre & Environnement, 490, rue de la Couronne, Québec, QC G1K 9A9, Canada

[2] Instituto Tecnológico Superior de PeroteKm 2.5. Carretera Perote-México91270PeroteVERMexico

[3] Centre National en Électrochimie et en Technologies Environnementales (CNETE)2263, av. du CollègeShawiniganQCG9N 6V8Canada

[4] Institut de Recherche et de Développement en Agroenvironnement (IRDA)2700 rue EinsteinQuébecQCGIP 3W8Canada

[5] Université Lyon 1, CNRS, UMR 5256, Institut de recherches sur la catalyse et l'environnement de Lyon (IRCELYON)2 avenue Albert Einstein69626VilleurbanneFrance

[6] Université Laval, 2425 rue de l'agricultureQuébecQCG1V 0A6Canada

Abstract

The present study analyzes the effect of parameters that determine the use of the zeolite 5A as collector medium in passive flux samplers (PFS) developed to estimate N_2O emissions from livestock buildings. The study analyzes the mass of N_2O collected on the zeolite 5A as a function of gas flow rate (40 and 130 ml/min), inlet mass of N_2O to the PFS (from 7 to 84 µg), adsorbent mass (4 and 13.6 g), length of the adsorbent bed (1.9 and 10.9 cm), and inlet N_2O concentration (0.6 and 2 ppmv). The mass of N_2O collected on the zeolite 5A ranged from 1.24 to 6.19 µg of N_2O/~~gram~~g of adsorbent, which was mainly affected by inlet N_2O concentration and mass of adsorbent contained in the PFS. The mass of N_2O collected presented a significant relationship with the

inlet N_2O concentration and the adsorbent bed. Tests were performed using PFS in a laboratory farm under semi-real conditions. It was found that at sampling time of 1.5 h, the accuracy and precision of PFS was appropriate. Under evaluated conditions, a maximum variation between PFS and direct detection of around 12% was estimated.

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Keywords

Greenhouse gases
N_2O
Passive flux sampling
Zeolite 5A
Adsorption capacity
Breakthrough time

Introduction

The measurement of N_2O emissions from agricultural sources, such as livestock sector, faces challenges because most of the methodologies used are complex and expensive. Moreover, there are substantial spatial and temporal variations among sources, which are often not considered in the estimation of emission factors used to integrate local and global inventories (FAO 2014; Larios et al. 2016). Therefore, lack of appropriate, robust, and economic methodologies has been recently identified (Berndt and Tomkins 2013; FAO 2014).

Passive flux sampling (PFS) encompasses low operational and capital investment requirements to quantify gas emissions (Mosquera et al. 2003; Dore et al. 2004). This technique has been widely used to estimate NH_3 emissions from soil, manure management, and buildings with mechanical ventilation (Leuning et al. 1985; Mosquera 2003; Scholtens et al. 2003). However, the application of PFSpassive flux sampling to measureestimate N_2O emissions is scarce.

Frequently, PFSpassive flux samplers (PFS) are considered similar to passive samplers (PS) which are widely used for monitoring environment air quality to determinate gas concentrations (Carmichael et al. 2003). In PS, gaseous molecules cross a cylindrical tube or box by diffusion, which is mainly driven by the concentration gradient between the environmentambient and the sorbent, which should be negligible, compared to the ambient concentration

(Carmichael et al. 2003; Supelco 2016). Also in PS, other transport mechanisms than molecular diffusion or permeation must be negligible. In contrast, PFS are used to quantify the mass flow, which enables directly to estimate the emission of the gas target.

PFS are based on two principles: (1) aerodynamic behavior which requires that air velocity inside the PFS is proportional to the gas flow velocity surrounding the sampler (Scholtens et al. 2003). This behavior is mainly regulated by an orifice placed in the sampler and (2) adsorption capacity of the collector medium to capture the gas sample, which is generally dependent on the air flow rate passing through the sampler, the N_2O concentration in the inlet air, and the mass of the adsorbent used. In PFS, the mass of adsorbent must be correctly estimated to ensure the complete trapping of a gas sample during a specific sampling time. The saturation of the adsorbent used as collector medium has to be avoided for accurate measurement.

The application of passive flux sampling technique in the measurement of N_2O emissions was reported by Godbout et al. 2006. They designed passive flux sampler prototypes packed with several adsorbents to capture N_2O and CH_4 being the zeolite 5A the best adsorbent compared to activated carbon Carboxen 1018 and Carboxen 1021. According to literature, zeolite 5A shows higher adsorption capacity due to its higher affinity to adsorb N_2O at elevated partial pressures ~100 kPa (Saha et al. 2010). However, as the collection of the target gas using PFS packed with zeolite 5A must be performed under atmospheric conditions of pressure and temperature, the adsorption capacity of zeolite 5A can be significantly decreased.

The mass of N_2O collected in PFS will depend on the adsorption capacity of the adsorbent, as well as the characteristics of the adsorbent bed and the conditions under which the PFS are exposed. The objective of this work was to analyze the parameters that determine the use of zeolite 5A as collector medium in PFS under required conditions to estimate N_2O emissions from livestock sources. The mass of N_2O collected on zeolite 5A as a function of the air flow rate, the length of the adsorbent bed, and the initial N_2O concentration was evaluated at atmospheric pressure and temperature from 20 to 25 °C. The mass of N_2O collected on zeolite 5A was estimated using the breakthrough point method when the outlet N_2O concentration corresponds to 5% of inlet concentration. Afterwards, statistical analysis was performed to evaluate the relationship between the evaluated parameters and mass of N_2O collected on zeolite 5A. Also, the performance of zeolite 5A in PFS exposed to lower N_2O concentrations in a laboratory farm is presented.

Materials and methods

Passive flux sampler and adsorbent material

A prototype of passive flux sampler <mark>(PFS)</mark> constructed on PVC using 1.9-cm-diameter tubes was used to study the adsorption of N_2O on zeolite 5A (mSORB®, Delta Adsorbents Co., USA). Two configurations were evaluated in this work. The first one included an arrangement of three consecutive layers of 4 g of adsorbent. The second one included one single layer containing 13.6 g of adsorbent (Fig. 1). Configurations 1 and 2 had a bed depth of 1.95 and 10.9 cm, a bed volume of 5.52 and 22.2 cm³, and a void volume of 0.50 and 2.04 cm³, respectively.

Fig. 1

Passive flux samplers configurations
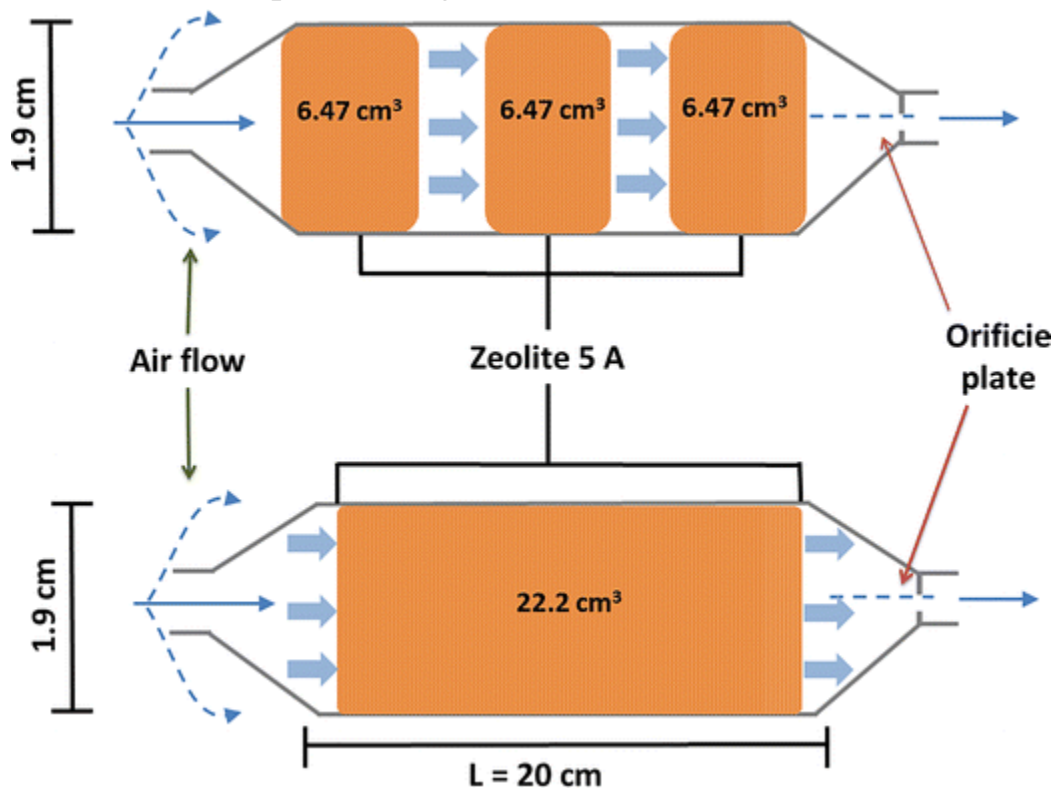
The adsorbent used was zeolite 5A in spheres with particle size distribution from 1.6 to 2.5 mm. The adsorbent proprieties such as surface area, pore volume, and pore diameter 5.2 Å were evaluated using a sorptometer (ASAP 2010, Micromeritics, Germany), with N_2 molecule as reference model at 77 K. Samples of 0.12 g were outgassed overnight before analysis at 573 K under vacuum (5E-3 Torr). The surface area and the pore volume were then

calculated by multi-point BET and Horvath-Kawazoe methods, respectively (Horváth and Kawazoe 1983; Sing 1985).

Adsorption tests

In order to activate zeolite 5A, it was conditioned by heating at 320 ± 1 °C for 4 h. Thereafter, the adsorbent was placed in a desiccator for 30 min. Hermetic glass vials of 20 ml (Chromatographic specialties Inc., USA) were prepared using 4 or 13.6 g of adsorbent. Later, vials containing the conditioned adsorbent were opened to put the adsorbent in the sampler before each corresponding adsorption test. At the end of adsorption tests, the adsorbent was placed back in the vials for N_2O desorption.

Two N_2O concentrations (0.6 and 2 ppmv) were evaluated in the adsorption tests. Certified gas at a concentration of 2 ppmv of N_2O diluted in N_2 (BOC GAZ, Canada) was used for the first set of adsorption tests. The gas was directly injected to the sampler at a flow rate of 40 and 130 ml/min corresponding to a low and a high internal flow rate that sampler prototype will have during field conditions. The outlet gas from sampler was collected each 15 or 30 min in ethyl vinyl acetate (EVA) bags of 2 l (Metrix Co., USA). The gas concentration in EVA bags was determined by using gas chromatography analysis (Clarus 680 GC coupled to Clarus SQ 8T MS, Perkin Elmer, USA). The adsorption tests were concluded in the time required to define the breakthrough point. This point was established when the concentration of the outlet gas, after passing through the adsorbent bed, was 5% of inlet concentration. In the second set of experiments, the N_2O at 2 ppmv was diluted with compressed dry air by using a dynamic dilution calibrator (Model 700E, Teledyne Instruments, USA) in order to produce a gas mixture containing N_2O at 0.6 ppmv. This concentration was selected in order to enable the detection of the N_2O in the outlet gas at $C/C_o = 0.05$ by gas chromatography and to determine the adsorption capacity of zeolite 5A at N_2O concentration close to that in a livestock building, which is reported from 0.35 to 0.6 ppmv (Rong et al. 2014; Mihina 2015). The gas was injected into the sampler at a flow rate of 130 ml/min. The outlet gas from sampler was also collected in EVA bags each 15 or 30 min to determine the gas concentration by using gas chromatography analysis as in the first set of experiments. The adsorption test was finished in the time required to define the breakthrough point. Two passive flux samplers were evaluated in each one of the tests, and the experiment was duplicated.

Estimation of the mass of N₂O collected on zeolite 5A in the breakthrough point

The breakthrough point determined in the adsorption tests was used to estimate the mass of N_2O collected on zeolite 5A. Using a plot of the relation of N_2O concentration as a function of time, the breakthrough point was identified (McClenny and Colón 1998; Salthammer and Uhde 2009; Markes-International 2014). Furthermore, the mass of N_2O collected on adsorbent bed by unitary mass of adsorbent was calculated as a function of time at the breakthrough point, air flow rate, N_2O concentration in the inlet gas, and adsorbent mass by using Eq. 1 (Chang et al. 2013). Two passive flux samplers were evaluated in each one of the tests, and the experiment was duplicated.

$$1$$

where m_c/g_{ad} is the mass of N_2O collected at the breakthrough point (microgram of N_2O adsorbed per gram of adsorbent); Q is the air flow rate (ml/min), t_b is breakthrough time (min), C_0 is the inlet concentration of N_2O (ppmv), ρ is the N_2O density at 25 °C (µg/ml), m is the mass of adsorbent (g), and 1,000,000 is the factor for converting from cubic meter to milliliter.

Performance of zeolite 5A in PFS exposed to lower N₂O concentrations in a laboratory farm

The experiments were carried out in two rooms of a laboratory farm used in lateral projects for animal growth. The dimensions of the room were 1.2 m wide × 2.4 m long × 2.4 m high. Three pigs with a weight of around 287 kg were allotted in each room. N_2O concentration was directly measured by gas chromatography by pumping the air to a mobile laboratory through Teflon™ tubing. A data logger then recorded the values measured every 180 min. The N_2O concentration was around 0.38 ppmv during all the sampling campaign. Concentration measurements were continuously taken during the entire experiment and were synchronized with the air flow rate. The air flow rate was calculated by measuring the difference in static pressure produced by a controlled 204-mm-diameter orifice damper (200 Original Iris Damper, Continental Inc., accuracy ± 5%) located in the ventilation duct. The air flow rate and N_2O concentrations were used to estimate the mass flow of N_2O from the emissions source (Godbout et al. 2012). The air flow rate was maintained from 4 to 4.5 m³/min; at ~20 °C and the moisture from 22 to 30% throughout the experimental period. In parallel, two passive flux samplers packed with adsorbent were placed facing the emission source direction in the ventilation

shafts of each room. A configuration of a PFS in three layers was used. The first layer was packed with silica gel to collect the moisture from the air flow in the inlet of the PFS. The second layer was packed with 13.6 g of zeolite 5A in order to collect N_2O. The third cartridge was left empty. The adsorbent in the samplers was replaced with respect to sampling time (from 1.5 to 3.75 h). At the end of each sampling period, the adsorbent used was placed in a glass vial hermetically closed and conserved at 4 ± 1 °C. After each sampling period, the samples were transported to the laboratory. The gas adsorbed on zeolite 5A was then desorbed and quantified by thermal desorption to estimate the mass of N_2O collected during each sampling point. N_2O adsorbed on silica gel was also measured. However, under evaluated conditions, the mass of N_2O adsorbed on silica gel was estimated as negligible in comparison with the N_2O adsorbed on zeolite 5A. The mass flow estimated by PFS was calculated using Eq. 2. This experiment comprised 16 passive flux sampling tests. In each test, two passive flux samplers were placed by room to include a replica by each test in the experiment.

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where F is the mass flow (g N_2O/h); m is the mass of the target gas collected in the PFS (g); r is the radius of the internal orifice (m); K is the Ferm constant from the calibration of the PFS; Δt is the sampling time (h); and A is the area of the ventilation shafts (Mosquera 2003).

Gas chromatography analysis

N_2O concentration was analyzed using a gas chromatograph (GC Clarus 680) coupled to a mass spectrometer (Clarus SQ 8T; Perkin Elmer, USA). The GC was calibrated at the beginning of each day with certified calibration gas mixture of N_2O at 2 ppmv (BOC GAZ, Canada) and each of the four unknown samples. The samplers were placed in the thermostated oven compartment for 2 min at 50 °C. Afterwards, the samples were pressurized for 2 min at 110.32 kPa. A gas sample volume of 100 μl was injected into an analytical column Rt-Q-bond (30 m × 0.25 mm i.d., 8-μm film, Restek, Canada) using 0.9 ml/min of He as carrier gas. The temperature in the GC injector was kept at 100 °C and the temperature in the oven was 30 °C for 4 min, then it was increased to 150 °C at 100 °C/min and kept constant for 1 min. For these conditions, the N_2O peak was observed at 3.42 min. The interface temperature between column and MS detector was 150 °C. An electron impact ionization of 70 eV and an ion source temperature of 220 °C were used. The mass spectrometer was used in SIM mode.

Statistical analyses

A Student's *t* test was applied to evaluate the difference between the mass of N_2O collected by using different adsorbent beds. Also, a multiple linear regression analysis was applied to analyze the linear relation among the evaluated parameters and the mass of N_2O collected. R statistical software version 3.1.3 for Windows was used to perform this analysis. Also, Microsoft Excel software was used to estimate the standard deviation in each serial of experiments.

Results and discussion

Characterization of zeolite 5A and mass of N_2O collected on zeolite 5A (in the breakthrough point) as a function of gas flow rate and adsorbent mass

Firstly, the characteristics of zeolite 5A were evaluated and results are presented in Table 1. Results showed similar values to those reported for zeolite 5A in the literature (Jacobs et al. 2001; Cejka et al. 2007). After that, the mass of N_2O collected on the adsorbent bed was estimated in the breakthrough point. This point was established when the N_2O concentration in the outlet gas was 5% of inlet concentration. Figure 2 shows the breakthrough curve of zeolite using a N_2O concentration of 2 ppmv on 4 g of adsorbent (1.9-cm length) at two levels of flow rate, 40 and 130 ml/min. For the air flow rate of 40 ml/min, the breakthrough point was reached in 98 min. The mass of N_2O collected in this time was 3.53 μg of N_2O/g of adsorbent. However, when the air flow rate was increased to 130 ml/min, the breakthrough point was quickly reached at 15 min. During this time, the mass of N_2O collected was 1.76 μg of N_2O/g of adsorbent. This behavior could be related to the fact that, the contact time of the gas with the adsorbent decreased, affecting the physicochemical interactions between N_2O and zeolite 5A, and hence the weak physisorption links. Similar effect of the air flow rate has been reported for studies related to removal of pollutants using adsorption columns (Kananpanah et al. 2009).

Table 1

Characterization of zeolite 5A

Surface area (m²/g)	Pore volume (cm³/g)	Pore diameter (Å)
539	0.27	5.2

Fig. 2

Breakthrough curve of zeolite 5A to collect N_2O at two gas flow rates ($[N_2O]$ at 2 ppmv, 4 g of adsorbent, and length column of 1.9 cm)

Considering the previous results, the length of the adsorbent bed was increased from 1.95 to 10.9 cm containing 13.6 g of adsorbent. The mass of N_2O collected on the adsorbent bed was also evaluated at the breakthrough point at an air flow rate of 40 and 130 ml/min. Figure 3 shows the breakthrough curves from these experiments. It can be seen that the breakthrough point was extended to 570 and 180 min, respectively. Under these conditions, 82.1 and 84.2 µg of N_2O at 2 ppmv were adsorbed on 13.6 g of zeolite 5A for the air flow rate of 40 and 130 ml/min, respectively. Thus, the adsorption capacity for the zeolite 5A in these conditions was 6.04 and 6.19 µg of N_2O/g of adsorbent for 40 and 130 ml/min, respectively. According to the results from a Student's t test, the difference between these two values was not significant at $\alpha = 0.05$. This indicates that for bed length smaller than 10.9 cm, diffusion and flow rate patterns should interfere with gas-adsorbent interactions decreasing the mass of gas that can be collected when these interferences are eliminated.

Fig. 3

Breakthrough curve of zeolite 5A to collect N_2O at two gas flow rates ($[N_2O]$ at 2 ppmv, 13.6 g of adsorbent, and length column of 10.9 cm)

Mass of N_2O collected on zeolite 5A (in the breakthrough point) as a function of concentration in the inlet gas

The effect of N_2O concentration in the inlet gas on the breakthrough time, when it changed from 2 to 0.6 ppmv was also studied for the sampler containing 13.6 g of adsorbent at an air flow rate of 130 ml/min (Fig. 4). It can be seen that in comparison with the N_2O concentration of 2 ppmv, the breakthrough time decreased from 180 to 115 min and the adsorbed mass of gas to 1.24 µg of N_2O/g of adsorbent. Since the inlet N_2O concentration changed, the driving force for the mass transfer was also affected decreasing the diffusivity of gas in the adsorbent bed. As consequence, a lower number of molecules were in contact with active sites of the adsorbent causing that a smaller amount of adsorbate mass was retained onto the adsorbent surface area. This behavior is in concordance with the behavior of gases adsorbed on zeolite 5A and other adsorbents in the region of low partial pressure. In this region, the amount of

gas adsorbed decreased lineally with respect to the partial pressure (Saha et al. 2010).

Fig. 4

Breakthrough curve of zeolite 5A to collect N_2O at two [N_2O] (130 ml min^{-1}, 13.6 g of adsorbent, and length column of 10.9 cm)

Table 2 resumes the mass of N_2O collected in the PFS for the evaluated conditions. Table 3 presents the statistical results from the multiple linear regression analysis. This analysis was applied in order to determine which operating parameter has an effect on the adsorption of N_2O on zeolite 5A. According to the values shown in Table 3, the inlet concentration was the parameter presented the highest effect on the mass of N_2O adsorbed, followed by the mass of adsorbent used. Under laboratory conditions, it is difficult to evaluate with accuracy the breakthrough point ($C/C_0 = 0.05$) at low N_2O concentrations due to the detection level of the gas chromatograph which is around 0.03 ppmv (Rapson and Dacres 2014).

Table 2
Mass of N_2O collected on zeolite 5A estimated in the breakthrough point ($C/C_0 = 0.05$)

Air flow rate (Q) (ml min^{-1})	[N_2O] in the inlet gas (C_0) (ppmv)	Adsorbent mass used (m_{ad}) (g)	Length of adsorbent bed (L) (cm)	Breakthrough time ($t_{b5\%}$) (min)	Mass of N_2O collected (m_c) (µg)	Mass of N_2O collected/adsorbent mass ($m_c\, m_{ad}^{-1}$) (µg g^{-1})
130	2	4	1.9	15	7.02	1.76
40	2	4	1.9	98	14.11	3.53
130	2	13.6	10.9	180	84.24	6.19
40	2	13.6	10.9	570	82.08	6.04
130	0.6	13.6	10.9	120	16.85	1.24

Table 3
Statistical analysis to estimate the linear relation between evaluated parameters and the mass of N_2O collected on zeolite 5A

Parameter	Estimate	Std. error	t value	Pr ($>|t|$)
Intercept	4.39	2.55	−1.723	0.335
Q (ml min^{-1})	−0.009	0.010	−0.903	0.532
C_0 (ppmv)	3.20	0.88	3.637	0.171
m_{ad} (g)	0.36	0.097	3.699	0.168
L (cm)	NS	NS	NS	NS

Table 3
Statistical analysis to estimate the linear relation between evaluated parameters and the mass of N_2O collected on zeolite 5A

Parameter	Estimate	Std. error	*t* value	Pr (>|*t*|)
NS not significant				
Residual standard error = 0.93, multiple and adjusted *R*-squared = 0.9597 and 0.8389, respectively. *F* statistic = 7.94 and *p* value = 0.254				

Performance of zeolite 5A in PFS exposed at lower N_2O concentrations in a farm laboratory

Taking into account previous results, the performance of zeolite 5A used as a collector medium in PFS was evaluated at lower N_2O concentrations (~0.38). The experiments were carried out in two rooms of a laboratory farm. Table 4 shows the mass of N_2O collected on zeolite 5A as a function of sampling time from 1.5 to 3.75 h evaluated during 4 days. During these experiments, the N_2O concentration was ~0.38 ppmv, air flow rates were from 4 to 4.5 m^3/min, at ~20 °C, and the moisture was from 22 to 30%. Table 4 shows that the mass collected on zeolite 5A increased with respect to time suggesting that zeolite was not completely saturated in this time interval. The experiment was replayed during 4 days, and similar results were found for each sampling time. It can be seen that, small variations between the two rooms were identified, which are attributed to the typical variations among rooms of a farm. Thus, an appropriate precision of PFS when zeolite 5A was used as collector medium can be observed. However, to identify the time where the breakthrough point occurs under these conditions, the mass flow of N_2O present in the rooms was estimated by direct detection in field. These results were then compared with those of PFS. Figure 5 shows the comparison between PFS and direct detection to estimate the mass flow of N_2O issued in each room. It was found that, at around 1.5 h of sampling, the mass flow estimated by using PFS was near to the confidence interval of values from direct detection. In this sampling time (1.5 h), the maximum difference between PFS and direct detection values was around 12%. Thus, the breakthrough point could occur around this sampling time where a mass of around 0.2 µg of N_2O was collected by g of zeolite 5A. In comparison with the value obtained at 0.6 ppmv under laboratory conditions, where a mass of 1.24 µg of N_2O was collected by g of zeolite 5A, the capacity of zeolite 5A to collect N_2O was decreased six times. Thus, there is a significant effect at lower N_2O concentration on the capacity of zeolite 5A to collect N_2O. Therefore, if zeolite 5A is used as a collector medium in PFS

developed to estimate N_2O emission from livestock sources where lower N_2O concentrations are expected, sampling times of 1.5 h or shorter should be considered in order to avoid underestimation. By taking into account typical conditions which can arise in livestock production systems, other parameters different than N_2O concentration may influence the collection of N_2O on zeolite 5A and should be evaluated in future studies to validate the use of zeolite 5A as a collector medium in PFS.

Table 4

Mass of N_2O collected in PFS exposed at lower N_2O concentrations in a farm laboratory

N_2O concentration ppmv	Sampling day	Sampling time (h)	Mass of N_2O collected (µg)	Mass of N_2O collected (µg)
			Room 8	Room 12
0.37–0.38	1	1.5	2.71	2.95
0.37–0.38	2	1.5	2.82	2.98
0.38–0.39	3	1.5	2.50	2.70
0.37–0.38	4	1.5	2.61	2.75
0.37–0.38	1	2.25	3.24	3.22
0.37–0.38	2	2.25	3.06	3.27
0.37–0.39	3	2.25	3.09	3.16
0.37–0.38	4	2.25	3.28	3.05
0.37–0.38	1	3	3.67	3.82
0.37–0.38	2	3	3.77	3.46
0.37–0.39	3	3	3.51	3.64
0.37–0.38	4	3	3.55	3.77
0.37–0.38	1	3.75	4.19	4.32
0.37–0.38	2	3.75	4.38	4.00
0.37–0.39	3	3.75	3.94	3.99
0.37–0.38	4	3.75	4.57	4.35

Fig. 5

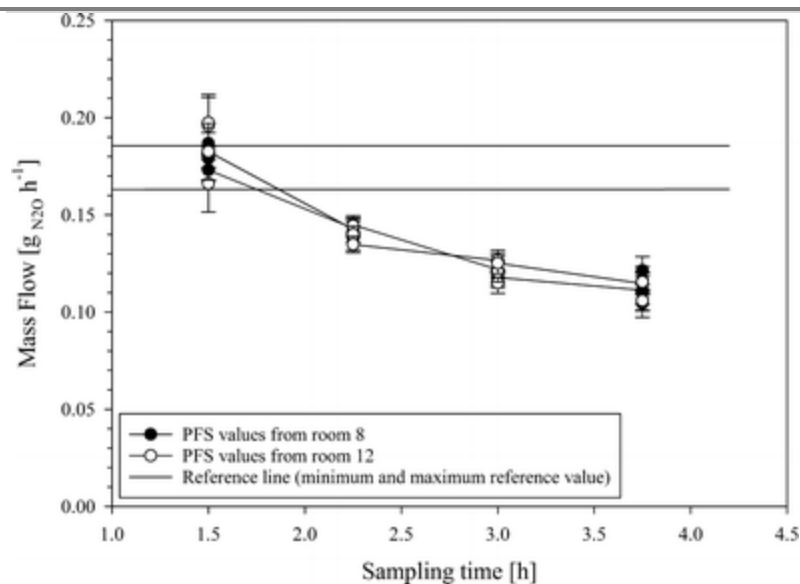Estimation of N_2O mass flow emissions by using passive flux sampling

Table 5
Parameters to consider in the collection of N_2O on zeolite 5A used as a collector medium in PFS

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Parameter	Confinement system	Mixed system
[N_2O] (ppmv)	From 0.35 to 0.60	From 0.35 to 2.50
Air velocity in the inlet gas (m s^{-1})	From 1 to 8	From 1 to 8
Temperature (°C)	15–25	<0 to >25
Moisture (%)	20–70	20–70
Length of the adsorbent bed	Maximum 30 cm	Maximum 30 cm

Conclusions

The use of a passive flux sampler to estimate N_2O emissions was proposed, and the sampler was validated. Among the main parameters to consider in the application of PFS, the mass of adsorbent presented a critical threshold to eliminate diffusion and interaction interferences to adsorb N_2O, whereas the effect of the air flow rate was negligible. The mass of N_2O adsorbed on the zeolite 5A presented a significant relationship with respect to the inlet concentration of N_2O and the mass of the adsorbent. The inlet N_2O concentration was the parameter which has the highest influence on the N_2O adsorption. In sampling times around 1.5 h, the accuracy and precision of PFS was appropriate.

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