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Paper No. 05-072

## **Passive Flux Sampler for Measuring Nitrous Oxide and Methane Emissions from Agricultural Sources**

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**Written for presentation at the  
CSAE/SCGR 2005 Meeting  
Winnipeg, Manitoba  
June 26 - 29, 2005**

### **Abstract**

Increasing concerns with greenhouse gas emissions has propelled research in greenhouse gas emissions, their quantities and methods of abatement. Nitrous oxide and methane are two greenhouse gases that have large impacts. This research is the development of a new passive flux sampler, based on previous work, capable of sampling both methane and nitrous oxide simultaneously. The new sampler is 175 mm long and has a projected width of 50 mm constructed completely out of stainless steel. It contains zeolite which is capable of adsorbing both methane and nitrous oxide. In a series of tests the adsorbent was found to be 91%  $\pm$ 11% efficient at adsorbing nitrous oxide and 9%  $\pm$ 6% efficient at adsorbing methane. The adsorbent was found to be inadequate at adsorbing methane therefore further testing was done for nitrous oxide only. In another series of tests the overall sampler efficiency was found to be 99%  $\pm$ 17% efficient in wind speed up to 5 m/s and decrease with faster winds. This sampler is a cheap and effective method of sampling nitrous oxide emissions in air velocities up to 5 m/s.

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# 1. Introduction

The climate is governed by the sun, and the energy that it provides the earth. The energy provided by the sun is trapped in the earth's atmosphere by greenhouse gases. This layer of greenhouse gases is very important in keeping the earth at a temperature that sustains life. Without these greenhouse gases the earth would be 33 degrees cooler making earth uninhabitable (AAFC, 1999). The major greenhouse gases are; carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), nitrous oxide (N<sub>2</sub>O), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs) and sulfur hexafluoride (SF<sub>6</sub>) (UNFCCC, 2003, Grubb *et al.* 1999).

Increasing the amount of greenhouse gases in the atmosphere has the effect of increasing the average global temperature of the earth. The present increase in greenhouse gases has had a number of effects such as increasing the average temperature of the earth by 0.6°C, decreasing snow and ice cover and increasing sea levels (IPCC, 2001). In order to reverse or stop global warming the Kyoto Protocol was drafted in 1997 (UNFCC, 2003). The Kyoto protocol outlined legally binding commitments to reduce greenhouse gases to levels relative to 1990 levels by 2008-2012 (AAFC, 2000). In Canada approximately 9.5% of the greenhouse gases that are emitted come from agricultural production activities (AAFC 2000). The relative contributions of the main GHGs in agriculture are approximately 61% N<sub>2</sub>O, 38% CH<sub>4</sub>, and 1% CO<sub>2</sub> (AAFC 2000). In the evaluation of CO<sub>2</sub> emissions from agriculture, the emissions that originate from the burning of fossil fuels to manufacture fertilizers, and the transportation of agricultural products outside of the farm is not considered (AAFC 2000). These emissions are considered in the transportation sector and the industrial production sector. It is also estimated that 42% of the agricultural GHG emissions originate from livestock operations and that one third of these are associated with manure management (AAFC 2000). There is a high potential for the agricultural sector to be able to reduce GHG emissions.

In order to be able to manage greenhouse gases there is a need for accurate and affordable measuring techniques. There are a number of methods that are presently being used for measuring these gas emissions but most of these can be costly and labour intensive. These methods include micrometeorological methods (Delany, 1993), tracer flux method (Smith and Bogner, 1997), and the chamber methods (Yamulki *et al.*, 1995). A cheap and effect method of measuring ammonia emissions is done by using the passive flux method (Ferm, 1986; Schjoerring *et al.*, 1992). The objective of the work that was conducted was to develop, or improve upon, a passive flux sampler that is capable of measuring both methane and nitrous oxide emissions.

## 2. Passive Flux Sampling

There are two different types of passive flux samplers, indirect and direct reading samplers. The indirect samplers are typically clear plastic tube open at one end and closed at the other. The pollutants pass through a well defined diffusion barrier or permeates through a membrane (Gorecki *et al.*, 2002) where the pollutant is adsorbent onto a chemical or granular adsorbent. Another type of indirect samplers is flow through samplers, where air containing the pollutant passes through the sampler where pollutants are adsorbent by and adsorbent. After indirect samplers are exposed to pollutant for a set amount of time they are sent to laboratory for analysis. Direct reading passive flux sampler or a colorimetry detector tubes are able to measure airborne pollutants quantitatively by the coloration of an indicator layer. The length of discoloration determines the amount of pollutant present.

Passive flux samplers are generally cumulative in nature. They do not give a measure of concentration but a mass of gas that was emitted over a certain period of time. They determine an average emission over a certain period of time. Since it is not a concentration that is being measured there is no need to measure wind speed or any other meteorological measurements. Typically air is not actively passed through the sampler eliminating the need for a power source making them good for sampling in remote sites or where power is not available. Relatively little labour is needed which further decreases the cost when using passive samplers.

There are three key features that make a passive flux samplers (Scholtens *et al.*, 2003). The first is when a passive flux sampler is placed in an air stream, air must be able to pass through the sampler without being forced. The second; the air velocity through the sampler must be proportional to the air velocity that is passing around the sampler. The proportionality constant is called the sampler constant or K factor. The last is an adsorbent. The sampler must contain an adsorbent capable of adsorbing the desired gas and the adsorbent must also be able to release the gas at a future time to determine how much was captured. An example of the this type of sampler that has been widely used in ammonia sampling is the Ferm tube (Ferm, 1986; Schjoerring *et al.*, 1992).

There have been very few passive flux samplers developed for measuring nitrous oxide and methane emissions. In 1998, Mahlcke developed a sampler for measuring nitrous oxide emissions. This sampler consisted of push fit PVC fittings which held three layers of different adsorbents. The first sieve was to remove water vapour from the air being sampled, the second was to remove carbon dioxide from the air being sampled, and the last was to trap nitrous oxide. With the carbon dioxide and water removed the full capacity of the last sieve could be used for nitrous oxide. For methane, Mahlcke (1998) suggested using a separate sampler using charcoal cloths as the adsorbent but no test were performed. Mahlcke (1998) also commented that the prototype was probably too large for measuring gas emissions conveniently.

Another sampler that was developed was the stainless steel sampler developed by Godbout *et al.* (2005a, 2005b, and 2005c). The research started in 2003 at the Silsoe Research Institute with finding an adsorbent that would be capable of adsorbing both methane and nitrous oxide (Godbout *et al.*, 2005a). Three adsorbents were tested, two carboxens, the 1018 and the 1021, and a Zeolite 5A. Godbout *et al.* (2005a) found that the adsorbent that was capable adsorbing both methane and nitrous oxide was the Zeolite 5A. Zeolite is an aluminosilicate of alkali or alkali earth elements such as sodium, potassium, and calcium (Yang, 2003). Dehydrated zeolite is a structure of aluminum and silicon which has a regular structure of cages and windows (Yang, 2003). In place of water the cages are able to trap large amount of guest molecules (Yang, 2003). The adsorbents were tested by passing gas, of known methane and nitrous oxide concentrations through the adsorbents that was placed in a standard stainless steel sampling tube (Markes International). After further testing, it was found that gases could not passively pass through the stainless steel tube when they were filled with adsorbent (Godbout *et al.*, 2005c). The thickness of the adsorbent needed to be reduced, but at the same the sampling capacity needed to be maintained. A new sampler was developed where the adsorbent was held in a circular cross section 2 mm thick. The inlet and outlet of the sampler were still made from the standard stainless tubes but the inlet expanded from 5 mm diameter to a 25 mm diameter to the adsorbent surface and then reduced back down to 5 mm to the exit (Godbout *et al.*, 2005c). With a surface 25 mm in diameter and 2 mm thick it was found that air could still pass through the sampler without being forced through which is key for a passive flux sampler. This sampler with a Zeolite 5A adsorbent was found to be 72% and 39% efficient at adsorbing nitrous oxide and methane respectively. One of the major problems that was found with this sampler was that there was the development of a “hotspot” at the center of adsorbent (Godbout *et al.*, 2005c). This “hotspot would represent an area of saturation. Once the adsorbent is saturated the adsorbent no longer has the ability to adsorb any more of the contaminant. This sampler can be seen in Figure 2.1 and Figure 2.2



**Figure 2.1: Schematic of original sampler**



**Figure 2.2: Photos of the sampler; Left: Complete sampler; Right: Opened sampler and zeolite molecular sieve 5A**

### 3. Sampler Development

The sampler developed by Godbout *et al* (2005c) had a number of weaknesses. The following areas could be improved upon:

- A “hot spot,” a point of saturation, at the center of the cross section of the adsorbent bed. This would mean that all of the air is passing through the central area of the cross section of adsorbents. This was possibly due to the very quick expansion of the air flow from 5 mm to 25mm. The present angle of expansion is 90 degrees (two times the angle measured from the central axis). A less extreme angle would facilitate the expansion of the air flow so that the whole surface of the adsorbent can be used.
- In the previous work, there was a concern with the molecular sieve being saturated too quickly forcing the sampling periods to be quite short, less than one hour. A way will have to be found to increase the maximum sampling time of the sampler.
- There was also a problem with the lack of linearity of the K factor at low air velocities. At low speed the relationship was quadratic; therefore when a linear relationship was used there was an overestimation of the amount of the amount air that actually passed through the sampler. In order to increase the accuracy of the sampler at low speeds the linearity will have to be improved.
- The sampler developed by Godbout *et al.* (2005c) did not allow for the adsorbent to be easily placed into the sampler. A different method of putting the adsorbent into the sampler that is convenient and easily done would have to be found.

In order to determine whether the point of saturation was due to the expansion angle being too high, FLUENT was used. FLUENT is a computational fluid dynamics software for modeling fluid flow. After modeling in FLUENT it was found that the angle of expansion, 90 degrees, was in fact too high and most of the air was passing through the center. According to Ower and Prankhurst (1977) the ideal expansion angle for a uniform expansion is between 6 and 7 degrees. This angle was modeled in FLUENT and it was found that a 6 to 7 degree expansion angle does facilitate a better expansion of the fluid flow. A sampler that would have an inlet expansion angle of 6° and an exit that would remain at 90° would make a sampler that would be 260 mm long. Due to restrictions imposed by the size of the ovens that will be used for the experiments the sampler must be of similar in length to the one developed by Godbout *et al* (2005c). This sampler was 170 mm in length. In order to minimize the inlet expansion angle as well as keeping a sampler length close to 170 mm the inlet and outlet pipes were shortened as much as possible and instead of making a bidirectional sampler the exit of the sampler remained at 90°. By leaving the exit at 90° allowed for a minimum expansion angle of 14.6° which keep the sampler in the optimum length range.

As mentioned earlier, in order for a passive sampler to work properly there needs to be linear relationship between the air velocity inside the sampler and outside the sampler. After further investigations of the data collected by Gobout et al. (2005c) it was found that the sampler did not have a linear K factor. To correct the non-linearity an orifice will be added to the new sampler. The idea of adding an orifice comes from the passive flux sampler for ammonia, the Ferm tube (Ferm, 1986). The theory behind adding an orifice can be found in the work by Scholtens et al. (2003). Passive flux samplers are based on two basic principles, the pressure on the downwind side of the sampler, and the air flow through an orifice depends on the pressure drop across an orifice. For a sampler containing an orifice these two principles can be added to express the air velocity inside the sampler as being proportional to the air velocity around the sampler. This expression can be seen in the equation 3.1 and 3.2.

$$v_o = \sqrt{\frac{C_D}{C_o}} v_m = K_s v_m \quad (3.1)$$

where:

$K_s$  : Sampler constant.

Since the constants  $C_o$  and  $C_D$  are a function of the air velocities inside and outside of the sampler can be written as:

$$K_s = \frac{V_o}{V_s \sqrt{\cos \alpha}} \quad (3.2)$$

where:

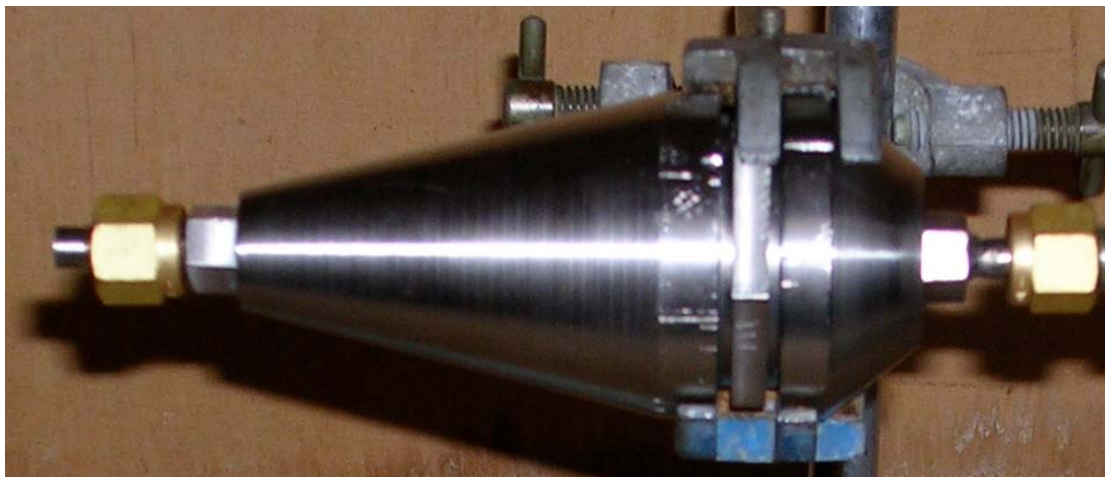
$K_s$  : Sampler constant;  
 $V_o$  : Air velocity inside the sampler;  
 $V_s$  : Air velocity outside the sampler;  
 $\alpha$  : The angle between the sampler axis and wind direction.

By adding an orifice at the exit of the sampler this will make the sampler constant more linear. The orifice will also reduce the amount of air that can pass through the sampler. If less air is allowed to pass through the sampler, the amount of time that the sampler can be exposed to an emission before it becomes saturated will increase.

In order to facilitate the loading of the adsorbent a cartridge was developed. If a cartridge were used then only the cartridge containing the adsorbent would have to be brought to the lab for analysis. If multiple measurements were needed then the sampler could be set out for a measurement and for the second measurement simply the cartridge could be replaced for a new sample to be taken. The exposed cartridges could be sealed in a container and sent to a laboratory for analysis. This would remove the need to have more samplers than is needed for 1 series of samples as a second series could be collected using the same samplers by simply replacing the cartridge. This could save time and money. The sampler that was designed and along with the cartridge can be seen in figures 3.1 and 3.2.



**Figure 3.1: Assembled cartridge; Left - inlet of cartridge; Right - outlet of cartridge**



**Figure 3.2: Assembled sampler**

#### **4. Method and Materials**

There are 4 procedures that were followed to determine the new sampler's performance. The first test is to determine the sampler's K factor. The K factor is the relationship between the air velocity passing around the sampler and the air velocity inside the sampler. This relationship was determined by placing the sampler inside a wind tunnel, and measuring the air speed around the sampler as well as inside the sampler at different wind speeds. The wind tunnel used was manufactured by Air Flow Development Co.. The sampler was placed a set distance away from the exit of the wind tunnel and the air velocity was increased from 0 m/s to 10 m/s in 10 incremental steps. At each velocity, the air velocity was measured in front of the sampler with a vane anemometer (Testo Type 452), which represented the air velocity around the sampler. The air velocity was also measured at the exit of the sampler with a hot wire anemometer (Hastings air-meter, Hastings-Raydist, Inc. Hampton, Virginia, USA), which represents the air velocity inside the sampler. This data was then graphed. The slope of this relationship was the sampler K factor. This is the same procedure that was used by Godbout *et al.* (2005a, 2005c, and 2005c), Mahlcke (1998), Fritz and Pisano (2002) Welch *et al.* (2005a) and Schjoerring *et al.* (1992).

The second step is the conditioning of the adsorbent. Conditioning is done in order to activate and clean the adsorbent. The procedure that was followed was similar to the one used by Godbout *et al.* ( 2005a, 2005b, and 2005c). The procedure involves heating the sampler containing the adsorbent and purging the sampler with pure ECD grade nitrogen gas. The sampler was attached to stainless steel tubing that delivers nitrogen gas and they are placed in an oven capable of reaching 350°C. The temperature of the oven is raised to 350°C at a rate of 15.5°C/min. Once the temperature was reached a flow of 600 ml/min of pure nitrogen gas was passed through the sampler for 150 min. Once 150 minutes has passed the sampler were taken out of the oven and the sampler was immediately sealed with stainless steel caps. Once the sampler has cooled it will be ready to be used. The oven that were used for the experiments was a Townson and Mercer, Model 8-2. Figure 4.1 shows the samplers connected to the stainless steel piping and placed in the conditioning oven.

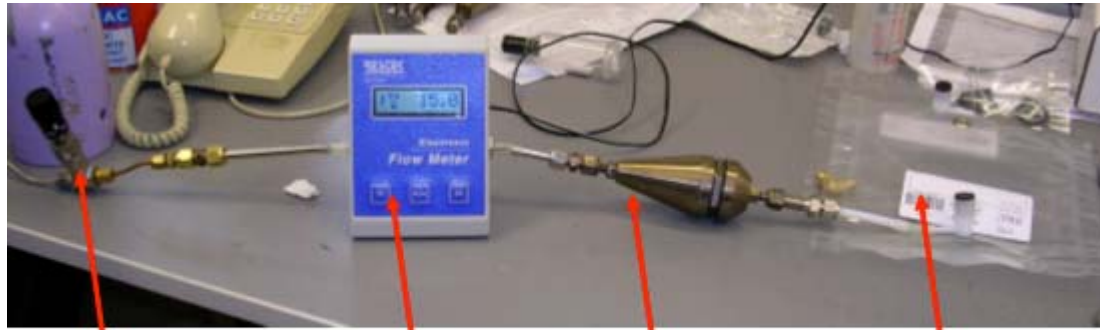


**Figure4.1: Left; Sampler connected to piping to deliver N<sub>2</sub> to sampler during conditioning. Right; Samplers and piping placed in the oven**

The next step is adsorption. In order to determine how well the sampler performs the adsorption efficiency of the adsorbent and the sampling efficiency of the sampler must be determined. This is done using two different adsorbing procedures, in-line tests and wind tunnel tests. The in-line tests are to determine the adsorption efficiency of the adsorbent, which will also determine if the rate that the gas is passed through the sampler affects that adsorption efficiency of the adsorbent. The wind tunnel test are to determine the overall sampler efficiency and will also determine if the wind speed that the sampler is placing in or if the emission rate or both will have an affect on the sampler efficiency.

The in-line test involved passing a known amount of gas through the sampler at a controlled rate. Knowing the amount and the concentration of the gases that were passed through the sampler the mass of gases that potentially could have been trapped by the adsorbent is also known. By analyzing the gases that were passed through the adsorbent, the mass of gas that was not adsorbed by the adsorbent can be determined. From these two masses the adsorption efficiency was determined. The concentrations of the gasses in the mixture that was used was 0.967 ppm nitrous oxide, 10.1 ppm methane and the balance was pure nitrogen. This gas was passed through the sampler at 4 different rates 5, 10, 15 and 20 ml/min. All of the trials were repeated four times. The mixed gas cylinder was connected to a mass flow controller through a needle valve. From the mass flow meter the gases continues on to the sampler and then from the exit of the sampler the gases were collected in Tedlar bags, Figure 4.2. Before the sampler was connected to the mass flow meter, the flow is set to 5, 10, 15 or 20 ml/min. The flow had been set the sampler was attached and the gases passes through the sampler for 68, 34, 23, or 17 minutes respectively. These times represents 40% of the maximum amount of time the samplers can be exposed to the gas before the adsorbent in the sampler becomes saturated. Once the time elapsed the flow was stopped and the bag containing the gases that passed through the sampler was closed and the sampler was sealed to be later desorption. Desorption will be discussed later on. This process was repeated for all the flow rates and repeated 4 times. The adsorption efficiency of the adsorbent in the sampler can be calculated using equation 4.1. The experimental up can be seen in figure 4.2.





Pipe supplying  
gas mixture from  
gas cylinder

Flow meter

Sampler

Gas collection  
bag

**Figure 4.2: Complete assembly for inline tests**

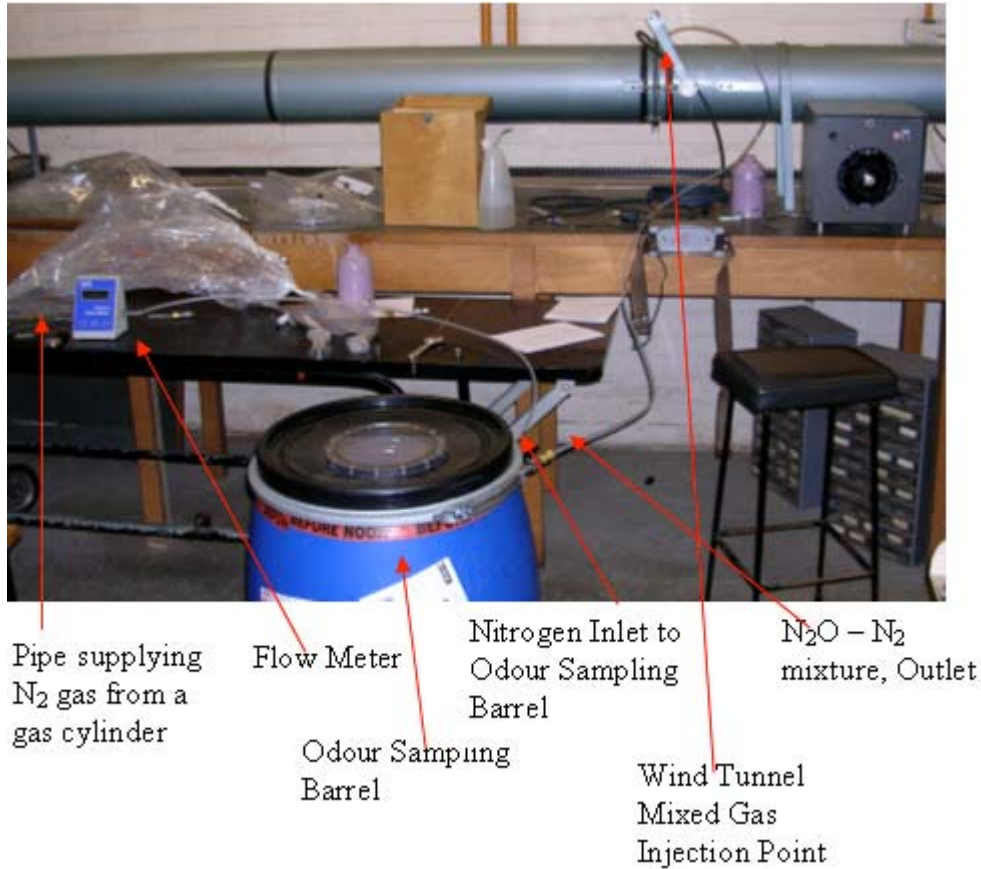
$$\eta_{ads} = \left( \frac{m_{ads} [mg]}{m_{in} [mg]} \right) * 100\% \quad (4.1)$$

Where:

$\eta_{ads}$ :	Adsorption efficiency;
$m_{ads} [mg]$ :	Mass of gas adsorbed (mg);
$m_{in} [mg]$ :	Mass of gas passed thought the sampler.

The wind tunnel test involving placing the sampler in a wind tunnel where a wind speed and an emission were simulated. In these test only a nitrous oxide emission was simulated, as it was determined from the in-line tests that the adsorbent was not effective as adsorbing methane. The sampler was subjected to 4 different wind speeds and 2 different N<sub>2</sub>O emission rates. The four different wind speeds were (V 1-4) 1, 3, 5, and 7 m/s and the two N<sub>2</sub>O emission rates which were (R 1-2) 4.5 mg/min and 9.0 mg/min. At these rates and time the adsorbent in the sampler will not saturate. The first step was to make an N<sub>2</sub>O-N<sub>2</sub> mixtures. This mixture was made in a 20 litre Nalophan bag. The mixture that was made was a mixture of 25 000 ppm N<sub>2</sub>O. In a 20 liter Nalophan bag, 14.625 liters of pure nitrogen gas was mixed with 375 ml of pure N<sub>2</sub>O. Once the mix was made the wind tunnel was then set to the desired wind velocity (1, 3, 5 and 7 m/s). A bag containing 25,000 ppm N<sub>2</sub>O (N<sub>2</sub>O and N<sub>2</sub>) was then placed in an odour-sampling barrel. The exit of the barrel was connected to the wind tunnel injection point. The injection point was immediately after the orifice plate of the wind tunnel. By using nitrogen gas metered using a needle valve and a mass flow meter 100 or 200 ml/min of nitrogen was pushing into the barrel, which pushed out the equivalent amount of mixed gas. See Figure 4.1 to view gas injection assembly





**Figure 4.1: N<sub>2</sub>O gas injection assembly**

Once the wind speed and nitrous oxide emission rate was set, one of the conditioned samplers with an orifice fastened to the exit was placed in the wind tunnel air stream. The sampler was placed the same distance away from the exit of the wind tunnel as when the test for the determination of the K factor was performed. The sampler was left in the air stream for 60 min. The actual concentration N<sub>2</sub>O in the wind tunnel was determined by analyzing an air sample from the air stream. Once the 60 minutes lapsed, the sampler was removed from the air stream, the orifice removed and the sampler was sealed. Knowing the sampler K factor, the wind speed, the adsorption efficiency of the adsorbent and the concentration of gas in the air stream the theoretical amount of gas that should have been captured can be determined. By dividing the amount of gas that was desorbed (the desorption procedure will be discussed next) by the theoretical amount of gas that could have been captured by the adsorbent an overall sampler efficiency can be determined (see equation 4.2).

$$\eta_{sampler} = \frac{m_{des} [mg]}{m_{thr} [mg]} * 100\% \quad (4.2)$$

Where:

$\eta_{sampler}$ : Sampler efficiency;

$m_{des} [mg]$ : The total mass of gas that was desorbed from the adsorbent.

$m_{thr} [mg]$ : The theoretical mass of gas that was passed through the adsorbent.

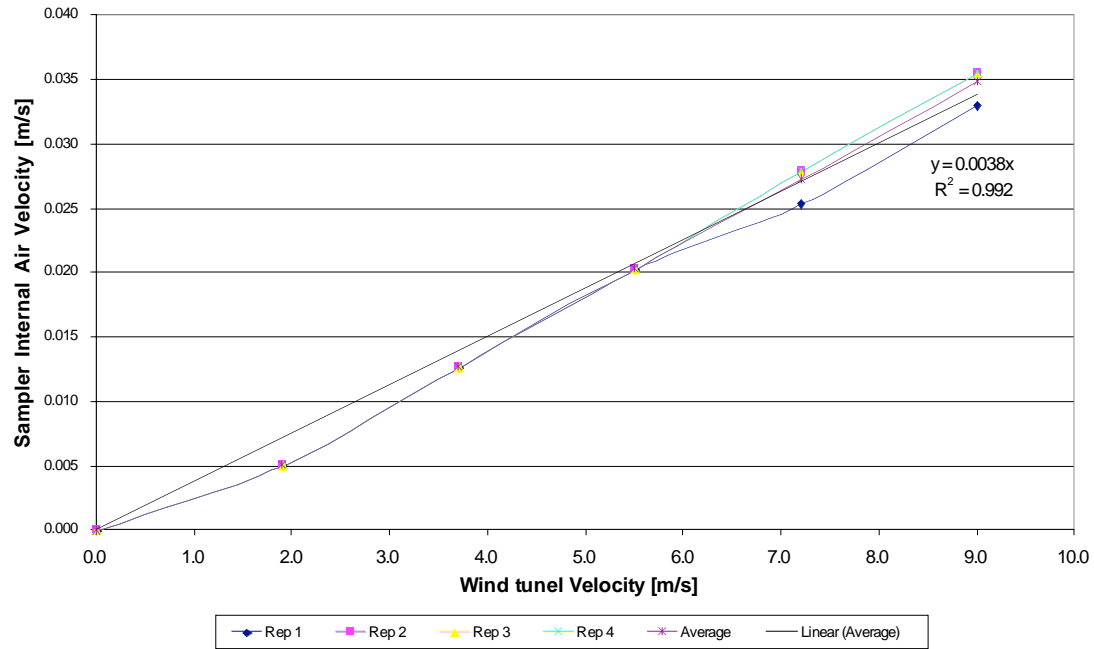
The last step is desorption. Desorption is the procedure where the gases that were trapped in the adsorbent are released. A two stage desorption procedure developed by Godbout *et al.* (2005c) was used. The sampler was placed in an oven and the inlet of the sampler was connected to a stainless steel pipe that delivered pure ECD grade nitrogen. The exit of the sampler was also connected to stainless steel pipe that was connected to a Tedlar bags that collected the gases that passed through the sampler. The oven was then heated to 100°C at a rate of 12°C/min. Once the temperature was attained, pure ECD grade nitrogen gas was passed through the samplers at a rate of 21 ml/min for 40 minutes. The exhaust gases were collected in 1 litre Tedlar bags. At the end of the 40 minutes the bags were closed and replaced with 3 litre Tedlar bags. The temperature was then raised to 250°C at a rate of 12°C/min. Once this temperature was reached pure ECD grade nitrogen was again passed through the sampler at a rate of 45 ml/min for 40 minutes. The exhaust gases for this stage were collected in a 3 litre Tedlar bag. After the 40 minutes, the bag were closed and removed from the stainless steel piping. The bags were then taken to a GC for the analysis of nitrous oxide and methane content (nitrous oxide for the wind tunnel tests). From the concentration a mass was calculated. By adding the mass from stage one and two the total mass that was desorbed is determined. For the in-line tests the desorption efficiency was calculated by dividing the mass that was desorbed by the mass of gas that was passed through the sampler (See equation 4.3). For the wind tunnel tests the sampler efficiency was be calculated dividing the mass desorbed by the theoretical mass of gas that was passed through the sampler (See equation 4.3)

$$\text{Desorption efficiency (\%)} = \left( \frac{M_{des}}{M_{ads}} \right) \times 100\% \quad (4.3)$$

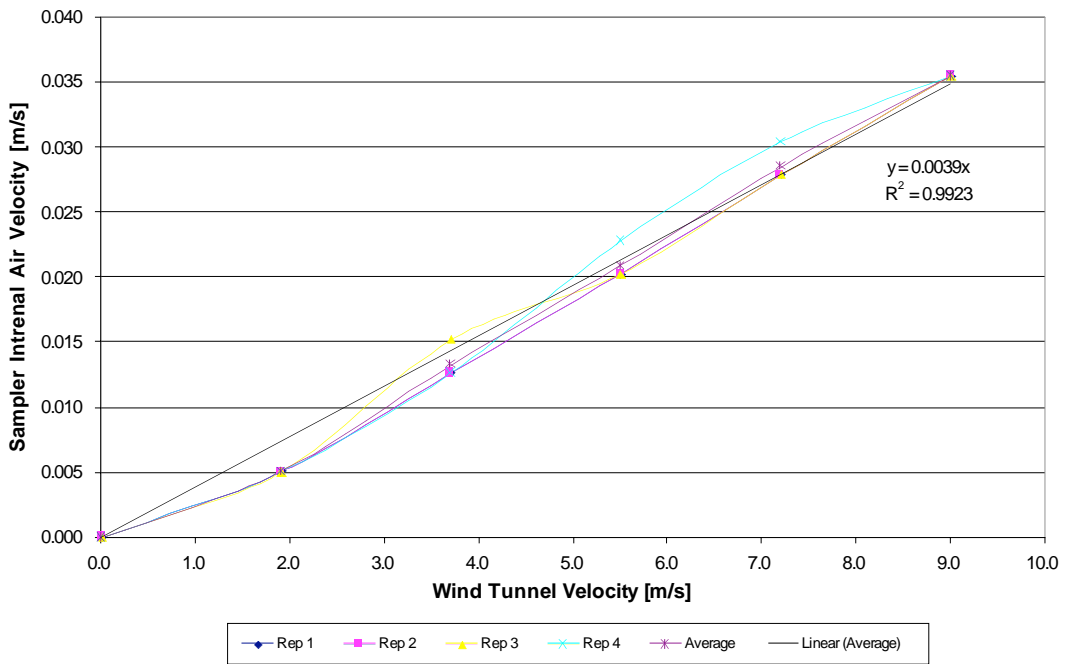
## 5. Results and Discussion

### 5.1 Sampler K Factor

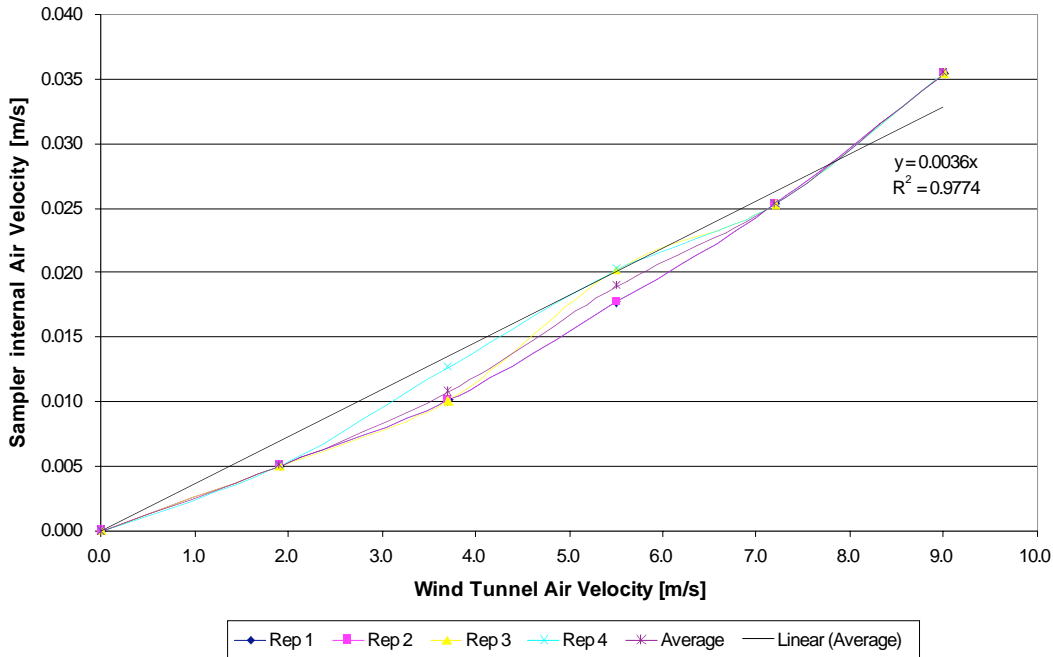
In order to be able to determine the amount of gas that was emitted using a flow through passive flux sampler, the sampler K factor needed to be determined. To determine the K factor, a regression analysis was performed to determine the relationship between the air velocity around the sampler and inside the sampler. This regression was forced through the origin as when there is no air going around the sampler there is no air going through the sampler. The slope of the linear regression is the K factor. Figure 5.1 to Figure 5.4 shows the relationship of the 4 samplers that were built. All four samplers produced nearly identical K factors. This regression is the application of equation 3.2 where the angle between the sampler axis and wind direction is zero.



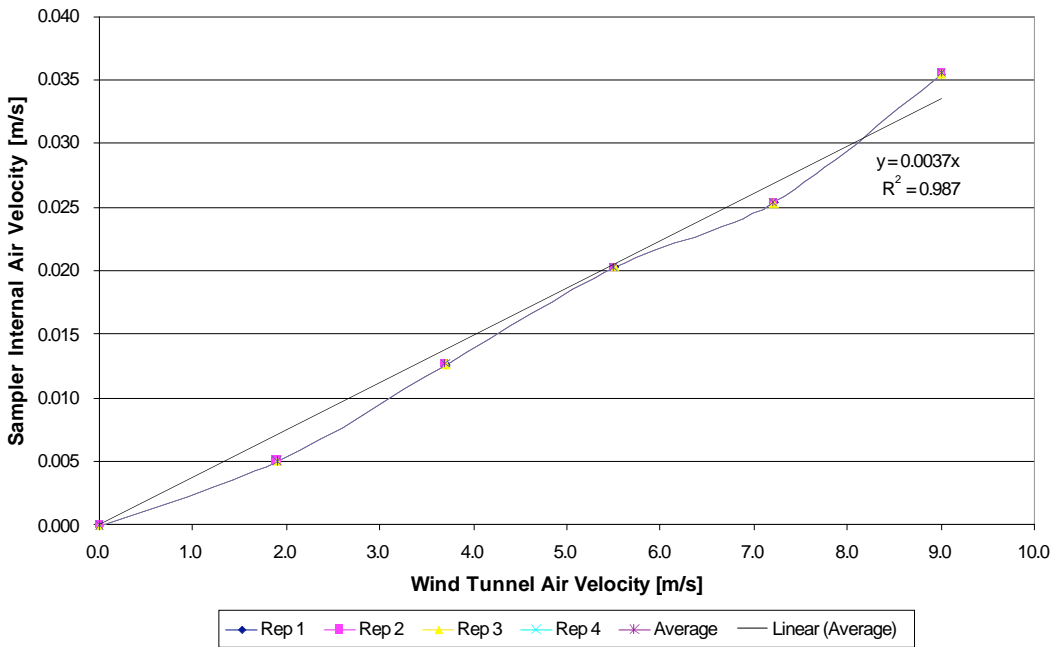
**Figure 5.1: Relationship between air speed inside the sampler to the air speed outside sampler 1**



**Figure 5.2: Relationship between air speed inside the sampler to the air speed outside sampler 2**



**Figure 5.3: Relationship between air speed inside the sampler to the air speed outside sampler 3**



**Figure 5.4: Relationship between air speed inside the sampler to the air speed outside sampler 4**

Table 5.1 summarizes the K factors and the  $R^2$  values of the regressions that were done for the four samplers. By adding the orifice at the exit of the sampler the linearity at low air speeds increase compared to the sampler developed by Godbout *et al.* (2005c) and reduced the over estimation of the amount of gas that passed through the

sampler at low speeds. By reducing the K factor it also allowed less air to pass through the sampler and therefore allows for a longer sampling period as it will take longer for the adsorbent to saturate. This resolves the problem of having a short sampling period, which was encountered with the sampler developed by Godbout *et al.* (2005c).

**Table 5.1 Summary of K factors and wind speeds**

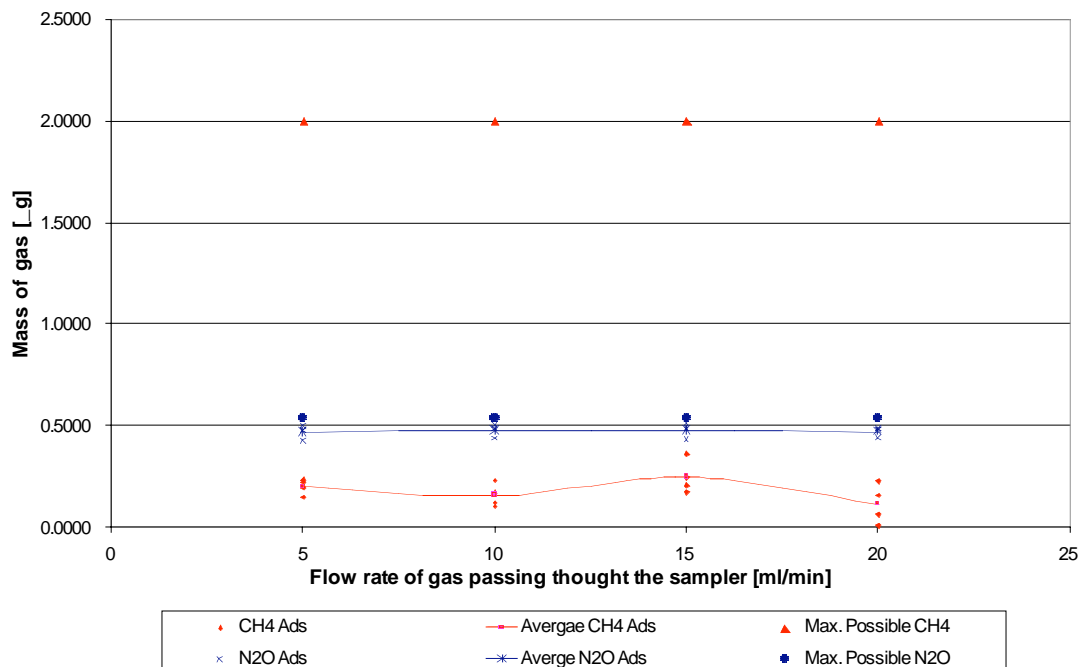
Sampler	K Factors		Outside v	Inside v
	K	R <sup>2</sup>	m/s	
1	0.0038	0.99	0-9.0	0 - 0.025
2	0.0039	0.99	0-9.0	0 - 0.035
3	0.0036	0.98	0-9.0	0 - 0.032
4	0.0037	0.99	0-9.0	0 - 0.033

## 5.2 In-Line Test

The in-line adsorption tests were determined how well the adsorbent in the sampler was able to adsorb methane and nitrous oxide. A mixture of methane (10.1 ppm), nitrous oxide (0.967 ppm), and nitrogen gas (balance) was passed through the sampler at four different flow rates. These experiments also determine if the rate at which the gases were passed through the sampler affected the adsorption efficiency. All of the trials were done in a completely random design.

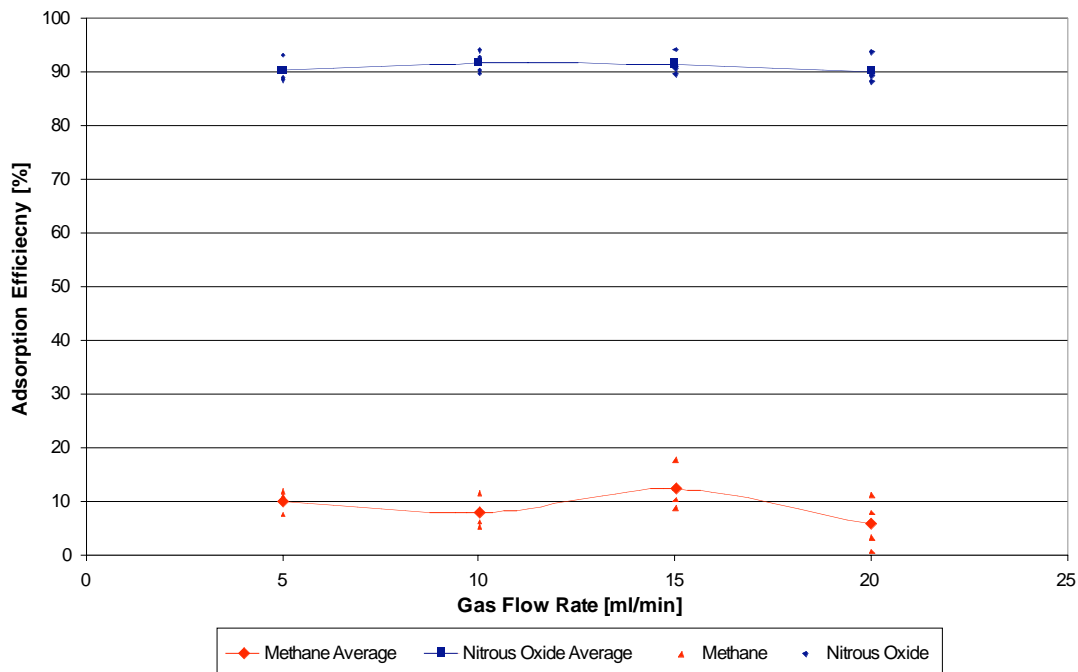
### 5.2.1 Adsorption

To determine the adsorption efficiency of the adsorbent, 2.0 µg of methane and 0.54 µg of nitrous oxide was passed through the adsorbent present in the sampler. On average, for all of the experiments there was 0.18 µg of methane and 0.48 µg of nitrous oxide that was adsorbed onto the adsorbent (see Figure 5.5).



**Figure 5.5: Mass of gas adsorbed relative to the maximum that could be adsorbed**

Statistical comparisons were done to determine if the adsorption efficiencies were affected by the rate the gas was passed through the sampler. The statistical hypothesis was that the adsorption efficiencies would not be affected by the rate. The analysis revealed that the adsorption efficiency was not affected by the rate that the gases were passed through the sampler. There were no significant differences ( $\alpha=0.05$ ) between the adsorption efficiencies for the different flow rates. The average adsorption efficiency was found to be 91% with a pooled standard deviation of 2.11 for nitrous oxide and 9.2% with a pooled standard deviation of 3.49 for methane. Figure 5.6 shows the adsorption efficiencies of methane and nitrous oxide for the different flow rates of gas through the sampler.

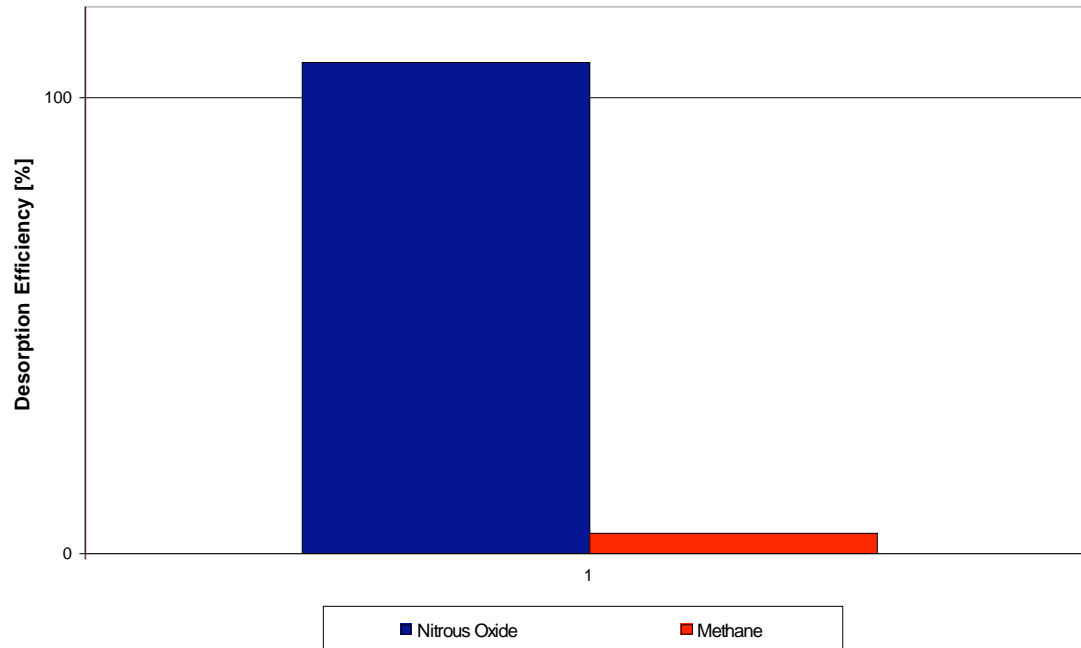


**Figure 5.6: Adsorption efficiency of CH<sub>4</sub> and N<sub>2</sub>O onto zeolite**

The 91% adsorption efficiency that was obtained for nitrous oxide is an improvement of 20% from the sampler developed by Godbout *et al.* (2005c). The 9% adsorption efficiency that was obtained for methane was a significant reduction compared to the 41% that was obtained by Godbout *et al.* (2005c).

### 5.2.2 Desorption

Before the desorption procedure the samplers contained on average 0.18  $\mu\text{g}$  of methane and 0.48  $\mu\text{g}$  of nitrous oxide. The desorption procedure released on average 0.0079  $\mu\text{g}$  of methane and 0.52  $\mu\text{g}$  of nitrous oxide. The average desorption efficiency of N<sub>2</sub>O was found to be 108% with a relatively low standard deviation of 15.4. The average desorption efficiency of the CH<sub>4</sub> was found to be 4% with a relatively high standard deviation of 7.4. Figure 5.7 summarizes the desorption efficiencies for the in-line tests. The nitrous oxide desorption stayed steady while the methane desorption varied.



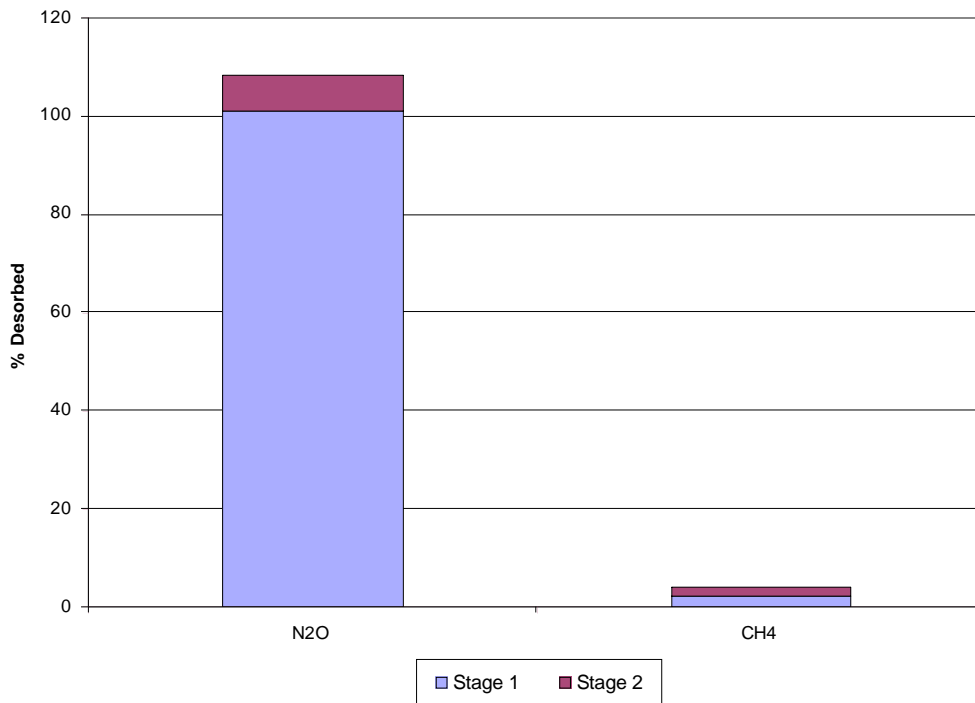
**Figure 5.7: Desorption efficiency of CH<sub>4</sub> and N<sub>2</sub>O onto zeolite**

For the in-line tests methane had very low adsorption efficiencies. This might be due to the pore size in the zeolite. The pore openings of zeolite 5A are 4.3 Å (Yang, 2003) and the molecular size of methane is 4.0 Å (L'Air Liquide, 1976). Zeolite can also act as a sieve allowing some molecules in and other out. Perhaps the size of methane molecule was too close to the size of the pore opening of the zeolite and the methane was not able to enter the zeolite cages. This can also explain why desorption was also very low. If the methane had trouble entering it could also have had trouble exiting, once trapped in the zeolite. This finding also confirms the finding by Godbout *et al.* (2005c) that zeolite 5A was not ideal for adsorbing methane.

### 5.2.3 Two Stage Desorption

The procedure that was used to desorb the gases occurred in two stages. This was the same procedure that was developed by Godbout *et al.* (2005b). The first stage was to desorb the nitrous oxide at 100 degrees Celsius and the second stage was to desorb the methane at 250 degrees Celsius. Previous work by Godbout *et al.* (2005c) found that stage 1 was on average 98% efficient at removing nitrous oxide from the adsorbent and stage 2 was 37% efficient at desorbing methane. Figure 5.8 shows the amount of methane and nitrous oxide that was desorbed from stage 1 and 2. The first stage was found to be 2% efficient at desorbing methane and 101% at desorbing nitrous oxide. The second stage was found to desorb an additional 2% of the methane and 7% of the remaining nitrous oxide. These results confirm that nitrous oxide can be desorbed at low temperatures as most of the nitrous oxide was removed from the adsorbent during stage 1 of desorbing.





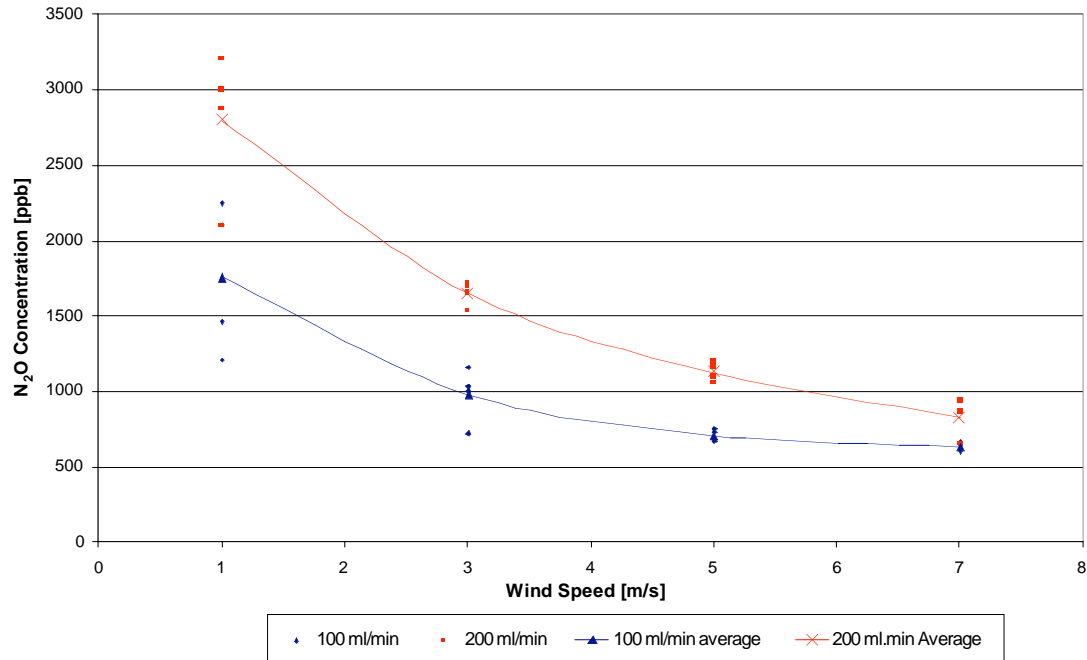
**Figure 5.8: Percentage of gas that was desorbed in stage 1 and 2 of the 2 stage desorption procedure**

### 5.3 Wind Tunnel Adsorption

#### 5.3.1 Sampler Efficiency

After analysis of the in-line test it was found that adsorption efficiency for methane was much lower than expected and at those low efficiencies it would not be practical to use the sampler for methane. Therefore, only nitrous oxide was measured in the wind tunnel.

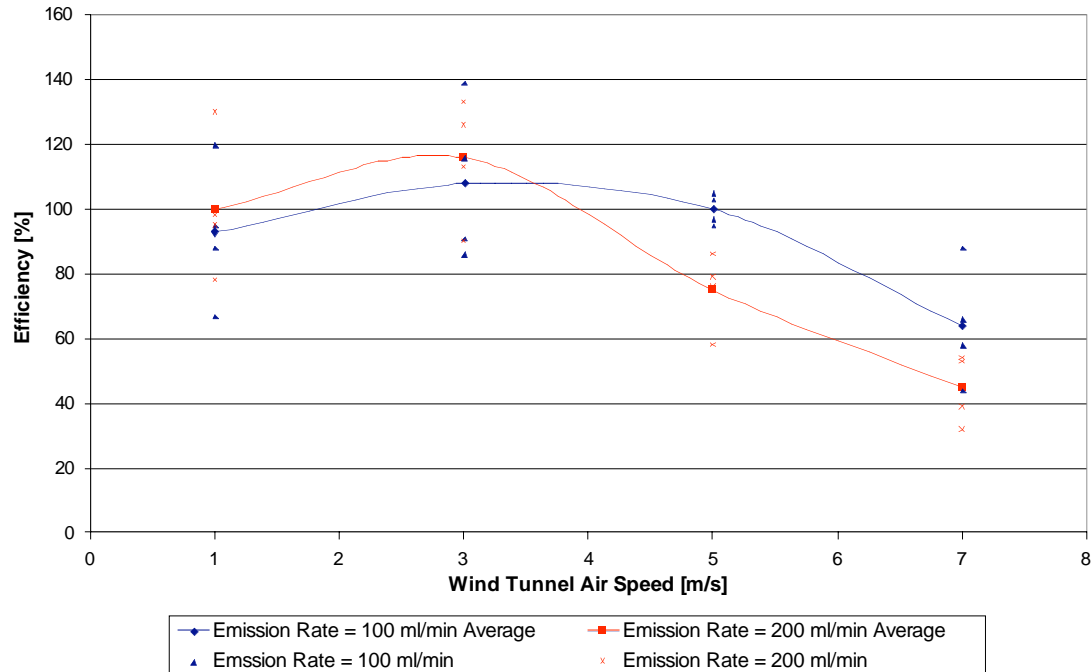
The wind tunnel adsorption tests were done in order to determine whether wind speed or emission rate or both had an effect on the sampler efficiency. The emission rates that were simulated in the wind tunnel were 4.7 and 9.4 mg N<sub>2</sub>O per minute. By adding this amount of gas to the ambient concentration of N<sub>2</sub>O that was present and applying different wind speeds, 1-7 m/s, gave varying N<sub>2</sub>O concentration between 2800 and 600 ppb. Figure 5.9 shows how the concentration of N<sub>2</sub>O changed in the wind tunnel for the two different emission rates and four different wind speeds. These concentrations are the actual concentrations that were measured during the experiments. The ambient concentration of N<sub>2</sub>O varied significantly as the room in which the wind tunnel was located was not ventilated therefore the N<sub>2</sub>O concentrations were higher than normal. Precautions were taken in order to minimize this increase in concentration.



**Figure 5.9: N<sub>2</sub>O Concentration in the wind tunnel for different air speeds and emission rates**

Figure 5.10 summarizes the results. As the air speed increased the sampler efficiency decreased. For the emission rate of 100 ml/min the sampler efficiency does not start to decrease until speeds of 5 m/s are reached. For an emission rate of 200 ml/min the efficiency starts to decrease at air speeds of 3 m/s. A statistical 2X4 factorial analysis was done to determine if there was a wind speed or emission rate effects.

It was found that there was no emission rate - wind speed interaction and that the emission rate does not have a significant effect ( $\alpha=0.05$ ) on the efficiency but the emission rate did. Further statistical analysis was performed to determine at which wind speed the efficiency starts to significantly decrease. The analysis revealed that the sampler efficiency is only significantly lower once the wind speed exceeded 5 m/s. The sampler is therefore, on average 99% efficient and could be used for measuring nitrous oxide emissions up to 5 m/s. Beyond 5 m/s the sampler efficiency drops to as low as 45% and is not longer suitable for measuring gas emissions.



**Figure 5.10: Sampler efficiency when measuring N<sub>2</sub>O**

No definite conclusions can be drawn for wind speeds beyond 5 m/s. In the in-line test the adsorbent was found to be 91% efficient at adsorbing nitrous oxide for flow rates up to 20 ml/min. This flow rate in the sampler, when taking the sampler constant into consideration, corresponds to an approximate external wind speed of 5.0 m/s. As the wind tunnel tests were done in wind speed up to 7 m/s, it is not known whether the adsorption efficiency stayed constant at higher flow rates. An in-line test where the gas was passed through the sampler at 30 ml/min would have corresponded to a wind speed of 7 m/s. Since the sampler efficiency falls after 5 m/s it is assumed that the adsorption efficiency falls below 91%. If it does fall below 91% then the present calculation will over estimate the amount of nitrous oxide trapped in the adsorbent causing the overall sampler efficiency to drop since the amount of gas trapped is less than what is calculated. It can still be said that the sampler is 99% efficient at sampling nitrous oxide emissions in wind speeds of up to 5 m/s.

## 6 . Conclusion

1. Nitrous oxide emissions can be measured using the passive flux method which supports the hypotheses stated in the objectives. Methane emissions can not be measured using the passive method which does not support the hypotheses stated in the objectives.
2. By changing the physical configuration of the sampler the following was achieved:
  - a. A more uniform expansion of the air flow entering the sampler which was achieved reducing the angle of entry and by placing a diffuser at the center to assist the expansion.
  - b. The utilization of the complete surface area of the adsorbent.
  - c. The cartridge facilitates the loading of the zeolite into the sampler.
3. By placing an orifice at the exit of the sampler the following was achieved:

- a. Nearly perfectly linear K factor of 0.0038, 0.0039, 0.0036, and 0.0037 with R<sup>2</sup> values of 0.99, 0.99, 0.98 and 0.99 respectively.
  - b. The small K factor means that less air passes through the sampler which means that the maximum time that the sampler can be exposed to an emission increases.
4. Zeolite can easily adsorb and desorb nitrous oxide. In the tests that were performed zeolite was able to adsorb 91% ±11% of the nitrous oxide that was passed through the sampler for flow rate up to 20 ml/min. The flow rate corresponds to a wind speed of up to 5 m/s depending on the sampler constant. The desorption procedure was able to remove 108% ± 15%. The overall efficiency of the sampler when tested in a wind tunnel was found to be 99% ±17 for wind speeds up to 5 m/s. In the wind tunnel tests that were performed in wind speed higher than 5 m/s the sampler efficiency decreased. Nothing can be concluded for wind speeds over 5 m/s as the adsorption efficiency of the adsorbent was just determined for situations where the wind speed would be up to 5 m/s. It can be deduced that the adsorption efficiency of the zeolite decrease when gases pass through the sampler at a greater flow than 20 ml/min.
  5. Zeolite does not easily adsorb and desorb methane. On average only 9% ±6% of the methane that passed through the sampler was adsorbed and only 4% ±3% was desorbed. The overall sampler efficiency was not determined as the zeolite was not found to be very effective at adsorbing methane. A new adsorbent would have to be found for sampling methane.
  6. The first stage of the desorption procedure was effective at removing 98% of the of the nitrous oxide present in the adsorbent. This confirms that nitrous oxide can be desorbed effectively at low temperatures.

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