Effects on ammonia emission of dairy stables by implementing an hourly Dutch measurement and calculation method

Hans Schiricke [a,*], Lars de Reus [b]

[a] EnviVice, The Netherlands

[b] Student, The Netherlands

* Hans Schiricke. Email: hans.schiricke@envivice.nl

Abstract

The ammonia emission by dairy stables in the Netherlands is currently done on a basis of 24-hour averages. The emission calculation is based on the CO_2 mass balance and wet-chemical ammonia measurements, as described in WUR report 1032 [1]. EnviVice is investigating the effects on the ammonia emission if the 24-hour average is replaced by hourly averages. This hourly method is already proposed in the VERA protocol [2] and the CIGR calculation rules [3].

To be able to investigate the effects of the hourly method, EnviVice has performed multiple parallel measurements over the past 3 years. Implementing both the 24-hour method and the hourly method at the same time. During these measurements, EnviVice used an ammonia analyzer based on photoacoustic to determine the hourly averages. This analyzer was also compared to the wet chemical method (Standard Reference Method) in an orthogonal regression test based on WUR report 1285 [4]. Furthermore, EnviVice used a grid point approach to ensure a volume proportional sample.

The latest results show that emission values can be up to 39% higher if the hourly method is used instead of the 24-hour average. The key figure for ammonia emission for dairy cows was increased from 11 to 13 kilograms NH_3 per cow per year in 2014 (see WUR report 744 [5]). This increase was implemented on emission calculations of 24-hour averages. The hourly method estimates that this increase is insufficient and that the key figure should be raised further.

1. Introduction

EnviVice has performed ammonia emission measurements on three naturally ventilated dairy stables, both with a rubber low-emission floor. The measurement setup is based on the standard measurement setup for dairy stables in the Netherlands, see WUR 1032 [ref]. The standard measurement technique for ammonia in the Netherlands is the wet-chemical method. Due to the small ammonia concentration in dairy stables, 0.2 to 5 ppm [4], a relatively long measurement time is needed. Consequently, this means that the ammonia concentration is determined by one duplicate 24-hour measurement. The GIGR calculation rules [3] and VERA test protocol for housing [2] also describe an hourly method, in which 24 hourly ammonia concentration are measured and averaged. To investigate the difference between the standard and hourly method EnviVice executed continuous ammonia measurements using a photoacoustic laser manufactured by Synspec (LSE-monitor) parallel to the standard measurements. Furthermore, EnviVice investigated the correlation and trueness between the wet-chemical and photoacoustic laser method, to determine if the photoacoustic laser is suitable for ammonia measurements in stables. In total 15[1] measurements are performed, 6 at each of the three dairy stables. The 6 measurements are equally spaced in time over the year 2022/2023, to cohere to the standard measurement protocol [1].

The motivation for EnviVice to investigate the difference between the 24-hour and hourly method is the volumetric flow rate calculation, based on the CO_2 mass balance. The volumetric flow rate is inversely proportional to the difference of the CO_2 concentration inside the stable and outside the stable. In Figure 1, the volumetric flow rate is plotted against the difference in CO_2 concentrations using the agricultural parameters of stable 1, session 6. The figure clearly shows the steep increase in volumetric flow rate for low CO_2 differences. This low concentration behavior of the volumetric flow rate induces errors when averaging over 24 hours. For example, if during one measurement of 24 hours, 2 subsequent hours provide CO_2 differences of 80 and 150 ppm. If the CO_2 difference is first averaged before the volumetric flow rate is calculated, the calculation would return 586158 m^3/h [2]. However, if the volumetric flow rate is calculated for the individual hours and averaged afterwards, the calculation would return 645995 m^3/h, an increase of around 10%. Subsequent hours are chosen as an example to suppress the effects of animal activity, see materials and methods. The situation sketched above can occur on windy days, where strong and weak winds alternate. EnviVice also believes this phenomenon to influence the emission itself. Emission is the product of volumetric flow rate and ammonia concentration.

[1] 15 measurements are performed as one of the stables is still under investigation and only has been measured 3 times.

[2] Still using the agricultural parameters of stable 1, session 6

It is therefore not sufficient to only look at the volumetric flow rate as a function of CO_2 difference. In figure 2, the measured ammonia concentration of stables 1 and 2 is plotted against the difference in CO_2.

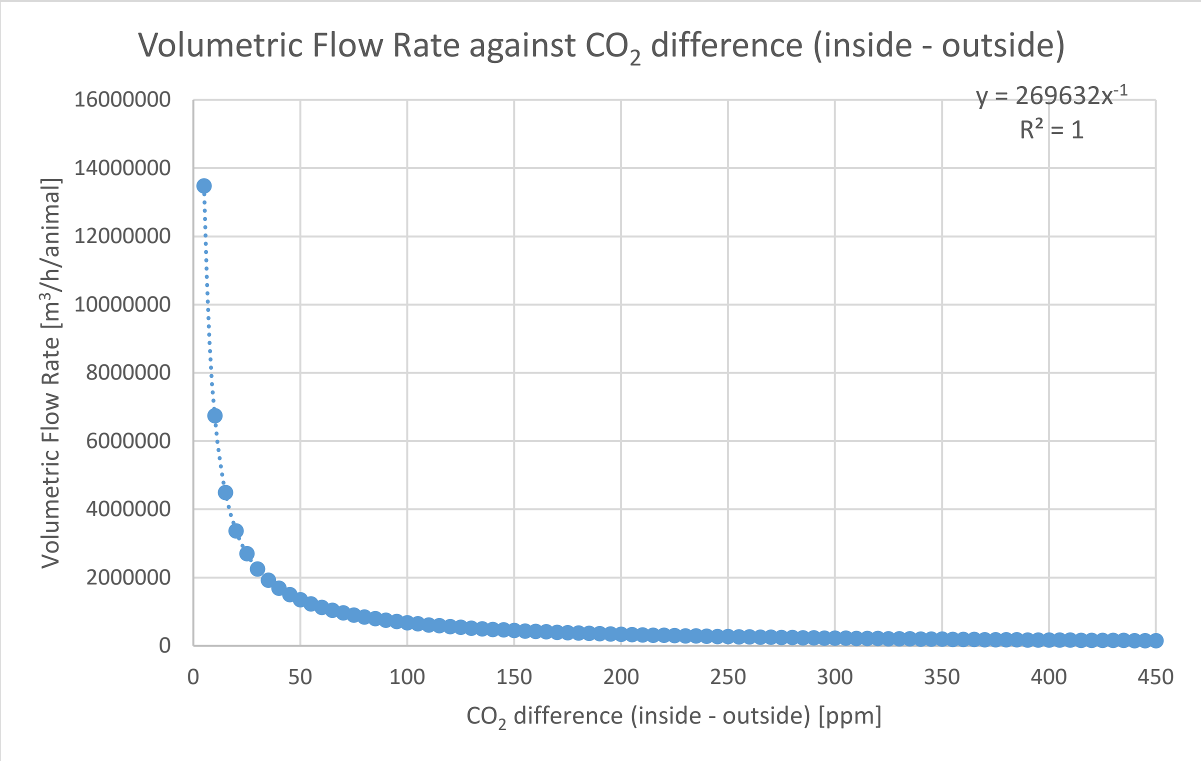

Figure 1: The volumetric flow rate against the difference in CO_2 (outside - inside) using the agricultural parameters from stable 1, session 6.

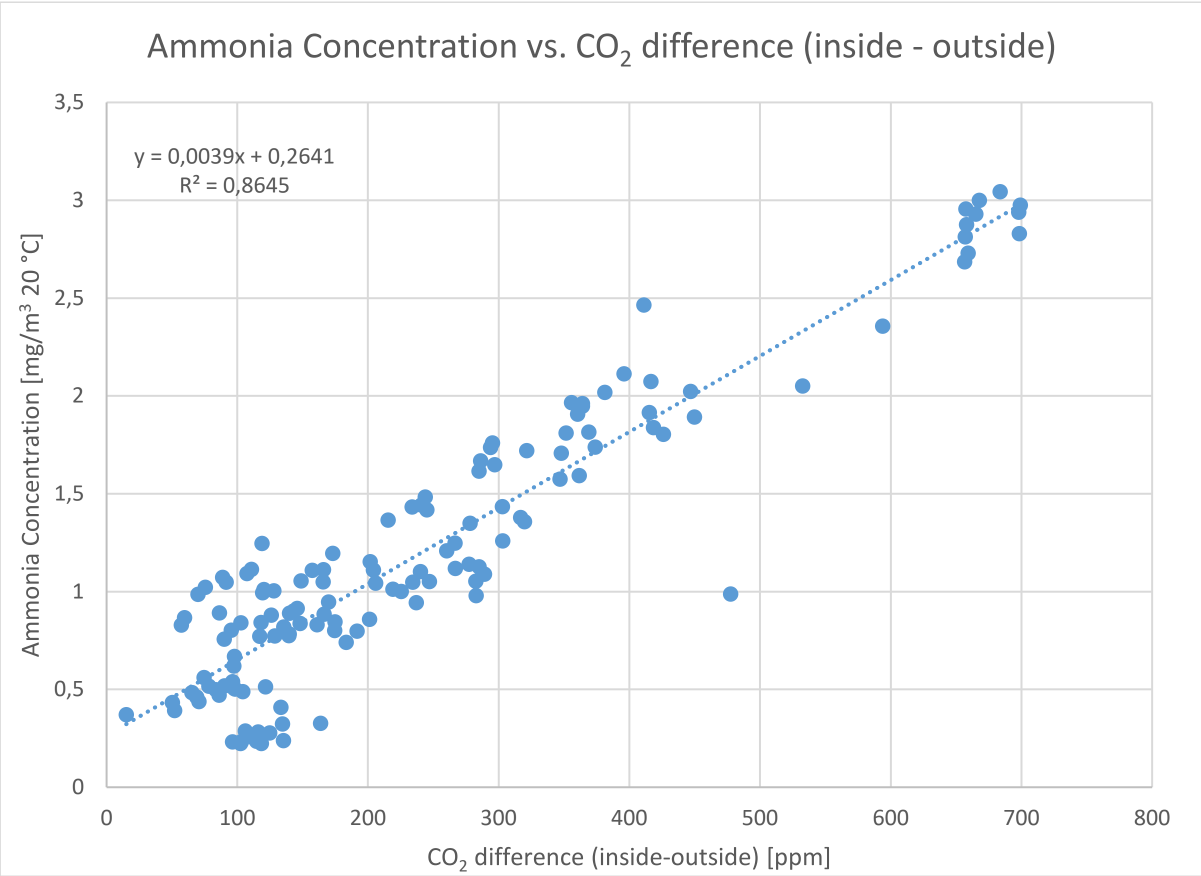

Figure 2: Measured Ammonia concentration (LSE-monitor) vs. Difference in CO_2 concentration (inside -outside). The points included are from stables 1 and 2.

Figure 2 shows that the ammonia concentration and difference in CO_2 share a linear relationship. This has the following effect on the emission factor calculation. The volumetric flow rate is equal to,

$$Q_{stable} = \frac{H * c(h)}{\Delta C_{CO_2}} \quad (1)$$

With *H*, the total heat production corrected for by temperature, see VERA calculations [2], *c(h)* a correction factor that depends on agricultural parameters and may depend on the hour of the day (only for hourly calculation) and ΔC_{CO2} the difference between the inside and outside CO_2 concentration. Figure 2 provides us with a relation between the ammonia concentration and CO_2 difference,

$$C_{NH_3} = a * \Delta C_{CO_2} + b \quad (2)$$

With *a* and *b* the slope and intersect obtained from figure 2 respectively. The emission factor can be calculated as follows,

$$E_{NH_3} = Q_{stable} * C_{NH_3} = H * c(h) * a + \frac{H * c(h) * b}{\Delta C_{CO_2}} \quad (3)$$

This shows that the emission factor is still inversely proportional to ΔC_{CO2}. It must be said that if the intersect were equal to 0 (b=0), the proportionality would not exist. This is however not the case as can be seen from figure 2. Furthermore, it must be said that equation (2) is found by analysis of data and not derived from theory. It is therefore an estimation and further research should be conducted to find evidence for the relation.

The inverse proportionality of the emission on the difference in CO_2 gives rise to an error when averaging. It is better to calculate the emission on hourly basis and then average than to average the CO_2 concentration and determine the emission one time. Again, suppose two subsequent hourly readings give CO_2 differences of 80 and 150 ppm. Using equation (2), it is possible to estimate the ammonia concentration, which would be 0,5761 and 0,8491 for 80 and 150 ppm of difference respectively. Averaging both the ammonia concentration and CO_2 difference and calculating the emission gives 14,3 kg/animal/year. Calculating the emission for the 2 hours separately and then averaging results in 14,8 kg/animal/year.[3] The error produced also becomes larger the further away the two readings are and the lower the value of the readings is, due to the inversely proportional nature of the emission curve. EnviVice performed measurements to try and uncover this effect in real stable measurements.

2. Materials and Methods

The measurement setup in both stables agrees with the setup described in the standard measurement protocol, WUR 1032 [1]. This means that the sample is collected via a measurement duct in the top of the stable. This duct is placed at least 3 meters above the ammonia producing floor and contains one critical opening (orifice) with an upstream filter per 10 meters. The last requirement ensures that a volume representative sample is taken. The measurement duct is connected to the flasks of the wet-chemical method, the photoacoustic laser (LSE-monitor) and the continuous CO_2-monitor (Siemens Ultramat23). Additionally, the CO_2 concentration outside is measured by the second channel of Ultramat23. Other parameters that are monitored are the inside (stable) and outside temperature as well as the inside and outside relative air humidity. The parameters are needed to convert the ammonia emission to a standardized ammonia emission factor, which is described in the standard measurement protocol [1]. The outside CO_2 concentration is needed to determine the volumetric flow rate via the CO_2 mass balance method, which is explained in the GIGR calculation rules [3]. It is important that this outside measurement point is chosen upwind of the stable. This is done to prevent raised CO_2-concentration from the stable to interfere with the measurement. An overview of the performed measurements with their specific instruments is given in Table 1.

The analysis and calculation of the 24-hour emission is described in WUR report 1032 and is not discussed in detail. The hourly method does require some extra steps with respect to the 24-hour method. As stated in the introduction EnviVice will check the correlation and trueness between the wet-chemical method and the LSE-monitor. This is done in the following way. Both the LSE and the wet-chemical flasks are connected to the same measurement duct, therefore both measurement instruments receive the same sample over 24 hours. The LSE-monitor provides a continuous sample (value every 60 seconds) and is therefore averaged over 24 hours. The 24-hour averages of the wet-chemical and photoacoustic method of the 12 measurements are compared to each other in a orthogonal linear regression test. This test is also described in WUR report 1285 [4]. This test provides the linear correlation between two methods. The null hypothesis in this test is that the regression line should have slope 1, intersect 0 and a correlation coefficient of 1, which would mean

[3] All these calculation are again performed using the agricultural parameters of stable 1

the methods are identical. For the calculation rules of orthogonal linear regression, refer to WUR report 1285 [4] and NEN-EN 14793.

Table 1: Measured Components/Parameters with their respective sampling and measurement methods. Also included is the norm which describes the measurement of the component/parameter.

Component/Parameter	Sampling Method	Measurement Method	norm
NH_3	Collection via measurement duct in stable	24-hour method: absorption in 0.05 M H_2SO_4 Hourly method: photoacoustic laser LSE monitor by Synspec, range: 0 – 8 ppm NH_3, detection limit 0.02 ppm NH_3	24-hour method: 24-NEN 2826 / NEN 8014 Hourly method: -
CO_2 inside	collection via measurement duct in stable.	Siemens Ultramat23 Channel 1: range 0-5000 ppm CO_2	NEN-ISO 12039
CO_2 outside	24-hour method: collection via measurement point placed upwind of the stable	Siemens Ultramat23 Channel 2: range 0-5000 ppm CO_2	NEN-ISO 12039
Temperature (inside and outside)	Measurement point in stable	thermocouple	ISO 8756
Relative air humidity (inside and outside)	Measurement point near CO_2 outside collection point	Dewpoint sensor	-
Atmospheric pressure (ambient)		barometer	NEN EN 13284-1

Another point of attention for the hourly method is the correction for relative animal activity, which influences the CO_2 production calculation in the GIGR calculation rules. Since the CO_2 production by animals linearly influences the calculated volumetric flow rate and thus ammonia emission, it is important to carry out this correction. The correct way to calculate the volumetric flow rate considering the relative animal activity can be found in the GIGR calculation rules 4th edition [3]. The rest of the emission calculation is nearly identical to the 24-method. The only difference being that this time 24 individual hourly averages are calculated, which are than averaged to obtain the final ammonia emission factor of the stable.

3. Results

First the results of the correlation test between the wet-chemical method and LSE-monitor are discussed. The graph belonging to the orthogonal linear regression test is shown in figure 3. The resulting line had a slope of 1.25, an intersect of -0.08 and a correlation coefficient (R^2) of 0.98. From the correlation coefficient and graph it can be determined that a strong correlation between the concentrations of the LSE-monitor and wet-chemical method exists. The equation relating the 24-hour concentrations of the wet-chemical and LSE-monitor is,

$$C_{LSE} = 1.25\, C_{WC} - 0.08$$

With C_{LSE} the concentration measured by the LSE-monitor and C_{WC} the concentration measured by the wet-chemical method. This relation will be used to convert LSE-monitor concentration to wet-chemical concentrations, the reason for this conversion is presented in the discussion.

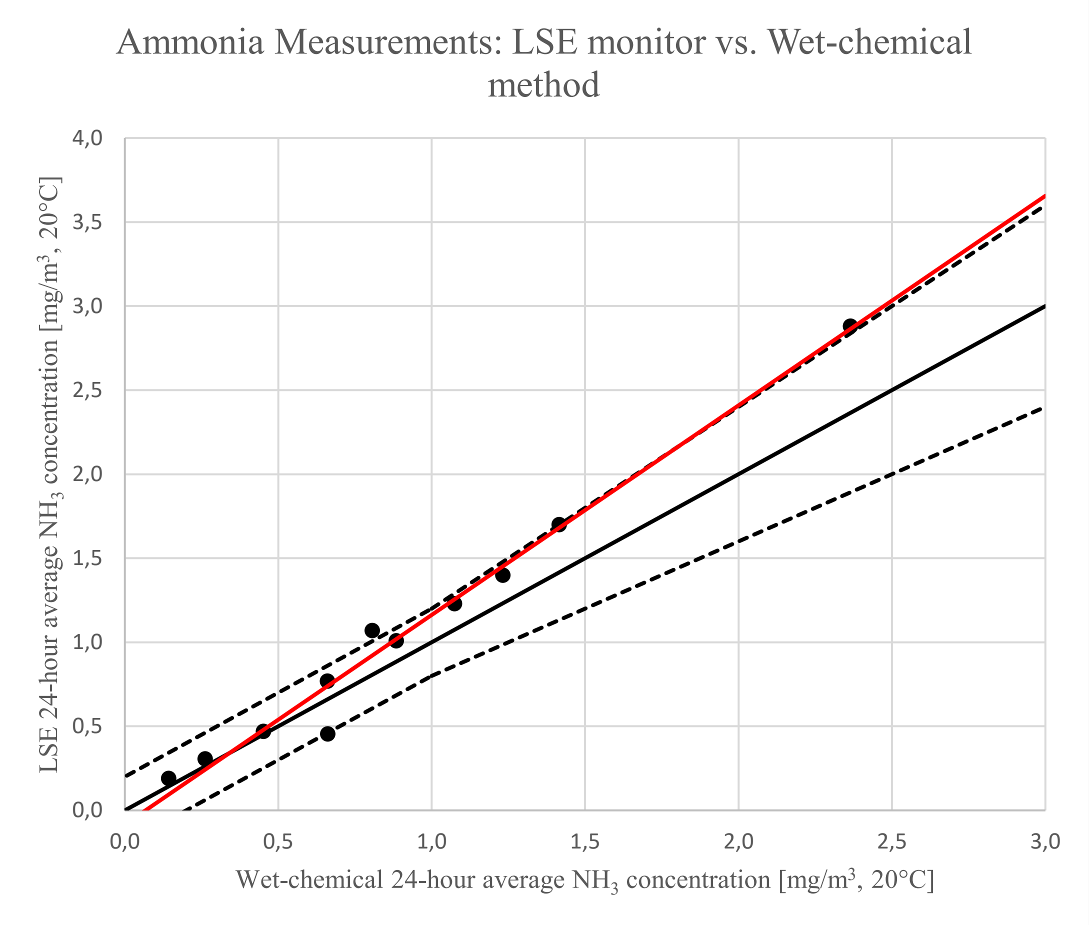

Figure 3: Orthogonal Linear Regression test using the parallel 24-hour ammonia concentrations of the LSE-monitor and wet-chemical method. The red line shows the orthogonal linear regression line, the solid black line shows the null hypothesis (y=x). The dashed black lines show a deviation of 20% from y=x, or a 0.2 deviation below a concentration of 1 mg/m^3, 20°C.

The results for the 24-hour and hourly method emissions are presented per stable in table 2 below. Not all sessions for stable 1 and 2 are usable for this project. The main reason for this is that some technical failures resulted in unusable readings of the LSE-monitor. 24-hour averages were still retrieved by the wet-chemical method, but they cannot be compared to the hourly method and are therefore not shown here. As already mentioned in the introduction stable 3 is still under investigation and therefore does not have values for sessions 4 till 6.

Stable 2 showed the smallest difference between emission calculated by the 24-hour and hourly method. With the largest deviation being 5 %. Stables 1 and 2 on the other hand both showed significant deviation, as high as 39% for session 3 of stable 3. In figure 4 the absolute difference in emission between the two methods is plotted against the average 24-hour CO_2 difference. It is observed that the spread in the absolute difference tends to become larger for a lower CO_2 difference. This is to be expected, see the introduction.

Table 2: Determined emission of stables 1,2, and 3 using both the 24-hour and hourly method.

Stable 1					
Session:	1	3	4	5	6
24-hour method NH_3 emission (kg/animal/year)	6,6	11,6	10,0	14,7	11,7
Hourly method emission (kg/animal/year)	6,5	14,2	11,0	18,3	12,3
Hourly method emission with animal activity correction (kg/animal/year)	6,5	13,3	9,9	17,0	11,5
difference in % between hourly and 24-hour method[4]	-2%	15%	-1%	16%	-1%
Stable 2					

[4] The difference is calculated between 24-hour method emission and the hourly method with animal activity correction emission.

Session:	3	4	5	6	
24-hour method emission (kg/animal/year)	10,0	10,0	11,7	19,1	
Hourly method emission (kg/animal/year)	10,4	10,1	11,8	21,0	
Hourly method emission with animal activity correction (kg/animal/year)	10,1	9,6	11,2	19,7	
difference in % between hourly and 24-hour method	1%	-4%	-5%	3%	
Stable 3					
Session:	1	2	3		
24-hour method emission (kg/animal/year)	13,1	6,0	10,4		
Hourly method emission (kg/animal/year)	14,7	7,5	13,5		
Hourly method emission with animal activity correction (kg/animal/year)	14,4	7,1	14,5		
difference in % between hourly and 24-hour method	10%	19%	39%		

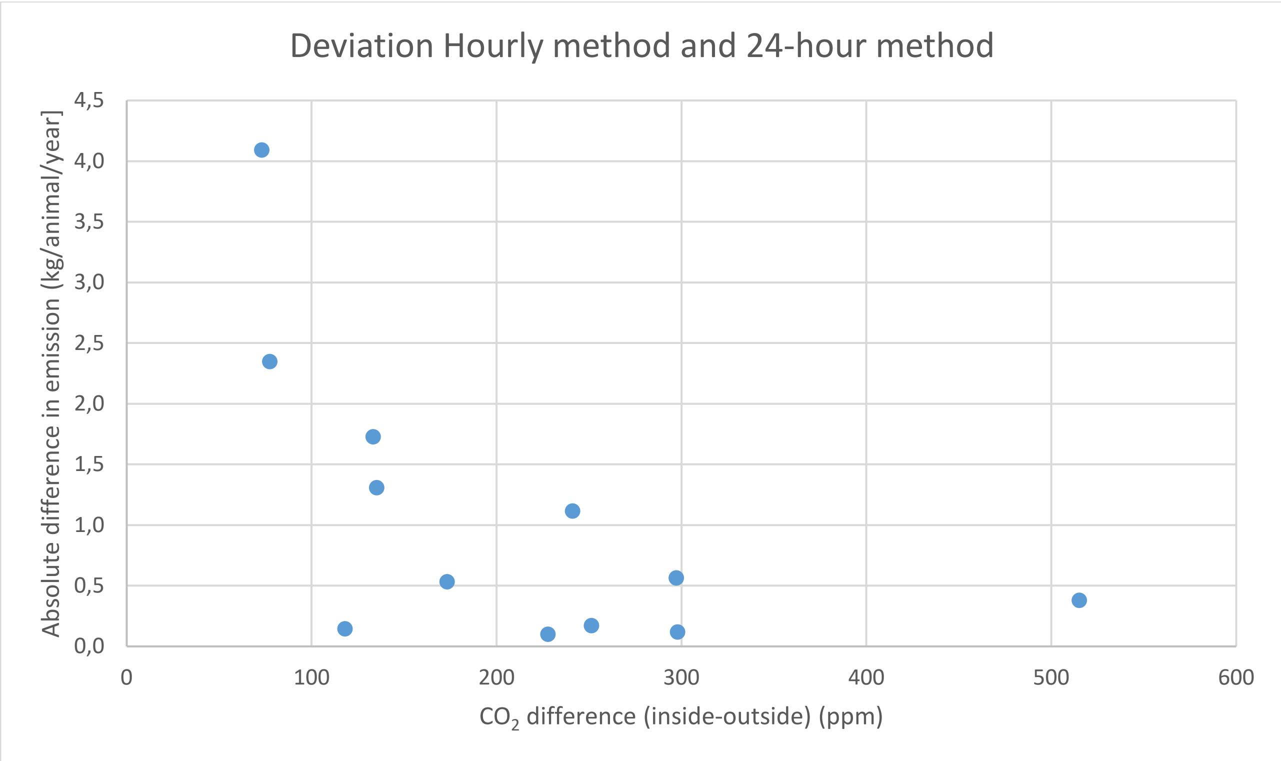

Figure 4: A plot of the absolute difference in emission againt the CO2 difference. Showing the larger spread at lower CO2 differences.

4. Discussion

During the analysis of the data the following choices were made. First the choice was made to use the relation between the NH_3 concentration of wet-chemical method and LSE-monitor. The relation was used to convert LSE-monitor concentrations to wet-chemical concentrations. This is done with the following formula,

$$C_{WC} = \frac{C_{LSE} + 0.08}{1.25}$$

The LSE-monitor concentration is converted to wet-chemical concentration as the wet-chemical method is seen as the standard in the Netherlands.

Another choice that is made, is to average hourly LSE-monitor NH_3 concentrations to retrieve the 24-hour average NH_3 concentrations. There are multiple reasons for this. First, it makes the comparison between the methods more accurate. It rules out the influence of the measurement method on the ammonia concentration determination. Furthermore, during measurements at stable 1, some hours could not be included as cows left the stable for milking sessions. This means that no CO_2 is produced in these hours, which forbids the use of the CO_2 mass balance method. With the LSE-monitor these hours can be excluded. However, this cannot be done with the wet-chemical method as this requires 24 hours of continuous measuring.

5. Conclusions

Concludingly the hourly and 24-hour method for the determination of the ammonia emission of dairy stables do not result in the same value for the ammonia emission. It is observed that the two methods can deviate as much as 39%. As expected, the spread in the deviation between the methods gets higher for decreasing CO_2 differences (inside-outside concentration). This increased spread at lower CO_2 differences is probably the result of the inverse proportionality between the volumetric flow rate and the CO_2 difference. The exact reason for the magnitude of the deviation is still unknown. However, EnviVice believes that it might be due to weather conditions. On calm days the CO_2 difference will likely be stable and will only be influenced by the animals in the stable. The animal activity correction is than sufficient to reduce the effect of variable CO_2 production. On windy days, this is not the case. It is believed that strong winds, which dilute the CO_2 concentration in the stable, can cause large differences in the CO_2 concentration over the 24-hours. The animal activity correction does not correct for this effect. Therefore, EnviVice believes that larger deviation between the methods is likely caused by strong winds and/or small CO_2 concentration in the stable.

EnviVice will further investigate the difference in results between the hourly and 24-hour method. However, at this point it can already be concluded that the hourly method is more robust than the 24-hour method. The 24-hour is prone to failure if low CO_2 differences are measured.

References

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