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Methane Emissions of a Western Dairy Manure Storage Basin and Their Correlation with Hydrogen Sulfide Emissions

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Abstract: Anaerobic decomposition in manure storage contributes to hydrogen sulfide (H_2S) and methane (CH_4) emissions. Coincident emission measurements were made of these gases from a western free stall dairy manure storage basin over a two-month period (August and September) as manure filled the basin and dried to assess the similarity or differences in the emissions characteristics. Path-integrated CH_4 concentrations were measured from sampled air using photoacoustic spectrometric technology. Half-hourly emissions were determined using a backward Lagrangian Stochastic method utilizing on-site turbulence measurements. The median daily CH_4 emission for the basin was 3.5 mg CH_4 m^{-2} s^{-1} (772 g d^{-1} hd^{-1}). Aging of the manure over the 44 days of this study did not appear to influence the CH_4 emissions. A high correlation between the CH_4 and H_2S emissions during the study period suggested that the production and transport of these two gases from the basin were influenced by the same factors. Emissions did not appear to be influenced by the above-ground environmental conditions (wind speed, turbulent mixing, air temperature, change in barometric pressure, or vapor pressure deficit) but were likely more a function of the bacterial population present and/or available substrate for bacterial decomposition. Similarity in the CH_4 to H_2S emission ratio during basin manure filling and drying down to that of a slurry storage in a midwestern US dairy suggested that the bacterial species involved in the decomposition of dairy manure slurry is similar regardless of climate.

Keywords: methane; emissions; dairy; manure slurry; hydrogen sulfide; anaerobic decomposition; Lagrangian modeling; crust; micrometeorology

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1. Introduction

Manure management accounts for 9.2% of methane (CH_4) emissions in the United States of America (US) in the 2020 emission inventory [1]. Estimating CH_4 emissions requires an understanding of the influences of manure composition, type of manure storage, age of the manure, and the environment on the emissions [2]. The anaerobic environment that produces CH_4 also produces hydrogen sulfide (H_2S), a major odorant and asphyxiant associated with animal agriculture [3]. While few studies have evaluated the CH_4 emissions from dairies, fewer studies have measured both CH_4 and H_2S emissions to assess the similarities in the production and emissions of these gasses.

Dairy operations in the dry western US are typically free stall systems with exercise areas or open lots. Reported CH_4 emissions from waste storage facilities in such dairies are limited and vary widely. Emissions from the wastewater pond of one Idaho open-lot dairy during 13 d of measurements across six months ranged from 152 g d^{-1} hd^{-1} (hd = head) to 1774 g d^{-1} hd^{-1} (0.46 mg m^{-2} s^{-1} to 5.32 mg m^{-2} s^{-1}) with the highest emissions not corresponding to the warmest conditions [4]. A short-term study of CH_4 emissions from a waste pond at a dairy in Idaho ranged from 2.8 to 22.8 g d^{-1} hd^{-1} [5]. Emissions from a batch-filled shallow waste storage tank at an Ontario dairy ranged from 9 g d^{-1} hd^{-1} to 41 g d^{-1}hd^{-1} (0.011 mg m^{-2} s^{-1} to 0.153 mg m^{-2} s^{-1}) from 105 half-hourly measurements from January through mid-July [6]. A deep, long-term storage tank in Ontario had a mean

CH_4 emission based on daily sampling near noon from mid-June to mid-November of 833 g d^{-1} hd^{-1} (1.8 mg m^{-2} s^{-1}) [7]. Mean daily CH_4 emission in October and November of 295 g d^{-1} hd^{-1} (0.270 mg m^{-2} s^{-1}) and 166 g d^{-1} hd^{-1} (0.152 mg m^{-2} s^{-1}) at a Wisconsin dairy storage basin [8].

Methanogenesis within the manure is regulated by the availability of organic substrate, the temperature and pH of the substrate, and the salinity of the solution [9]. A simplified representation of the reaction associated with anaerobic heterophilic bacteria and methanogenic archaea [9,10] is:

$$VS, HCO_3^-, H_2 => CH_4 + CO_2 + \text{new cells} \quad (1)$$

with VS (volatile solids) representing the readily decomposable organic carbon substrate of the waste. The temperature sensitivity of emissions is due to the biological methanogenesis of various organic components in solid dairy waste [11,12]. The optimum temperature range for methanogenic bacteria is 35 °C to 45 °C, with a decrease in CH_4 production of approximately an order of magnitude as the temperature decreases to 15 °C [13]. The temperature sensitivity of dairy manure CH_4 emissions is evident in mixing chamber studies [14,15] and some field studies [8,16] but not in other field studies [4,7]. These conflicting results are likely related to the specific temperature measurements used in the association (air or slurry), the coupling of the air temperatures to the slurry temperatures, and the complexity of CH_4 production [17] and oxidation [18] within the manure. The aging of manure enhances the diversity of methanogenic bacteria and archaea [17].

Methane is produced throughout the vertical column of manure in a basin [19]. Since methane has a very low solubility in water (0.0014 mol kg^{-1} bar^{-1}) [20], the CH_4 produced forms bubbles [3]. Hydrogen sulfide also has low solubility in water (0.10 mol kg^{-1} bar^{-1}) [20]; however, the solubility is 100-fold greater than CH_4. Bubbles of predominantly H_2S, CH_4, or a combination of these gases will be buoyant in the liquid manure column since the densities of H_2S (0.136.3 g m^{-3}) and CH_4 (0.00066 g m^{-3}) are much less than that of pure water (1000 kg m^{-3}).

Dairy manure storage commonly crusts at the surface as a result of high total solids content and high evaporation rates. The dry climates in the western US often result in the formation of crusts on the stored manure [21–23]. The transport of the gases from the bottom of the crust to the open air above the crust depends on interstitial spaces and cracks in the crust and can occur by molecular diffusion and convection. The convective transport may be influenced by the barometric pressure, resulting in pressure pumping [24,25]. Crusts themselves can have significant methanogenic activity [19]. Gas released on bubbles bursting along the base of the crust will rise through the porous crust, interact with the microbial populations in the crust, and enter the overlying air of the manure storage area since the density of both gases is much less than that of air at ambient pressure. However, as the gas moves through the crust the presence of methane oxidizing bacteria (MOB) consuming the produced CH_4 on microsites on the fibrous crust structure [18] may result in an overall reduction in CH_4 emissions.

Hydrogen sulfide (H_2S) is also produced as a byproduct of the breakdown of animal manure [26]. In treatment lagoons, heterotrophic sulfate-reducing bacteria reduce sulfate (SO_4^{-2}) from the organic matter in the manure to produce H_2S, carbon dioxide and new cells [3] at depth in the anaerobic lagoon. In addition, purple sulfur bacteria can oxidize CH_4 in the presence of sulfate in anoxic environments as [27]:

$$CH_4 + SO_4^{-2} => HCO_3^- + HS^- + H_2O \quad (2)$$

with the HS^- in equilibrium with H_2S depending on pH of the solution: $HS^- + H^+ \Leftrightarrow H_2S$. Consequently, the production of CH_4 and H_2S may not only be both occurring in the anoxic environment of the manure sludge, but may also be inter-related stoichiometrically, with decreases in CH_4 emissions corresponding to increases in H_2S emissions. Mukhtar and Mutlu measured H_2S emissions from a lagoon manure storage system of a western US open-lot dairy during several days in winter and summer of 1 to 17 g d^{-1} hd^{-1} depending on the cell measured [28].

This study describes characteristics of CH_4 emissions from a slurry storage of a western US free-stall dairy during filling and drying of the basin and explores the similarities in the CH_4 emissions with those of H_2S at the same dairy where the mean daily H_2S emissions was greater when the slurry storage basin was filling than when drying [23]. The goals of this study were to: (1) to estimate the daily mean CH_4 emissions and explore the factors influencing the emissions and (2) to understand the similarities and differences in CH_4 and H_2S emissions associated with the storage of manure at a western free stall dairy. It was hypothesized that, since both CH_4 and H_2S are anaerobically produced and partially determined by the available organic matter substrate, biological activity, and environmental conditions, they are likely produced in the same region of the manure storage. Furthermore, since both CH_4 and H_2S are relatively insoluble in water and hence largely rise through the liquid manure column as bubbles that either break or reside at the bottom of the manure crust and transport through the porous manure crust similarly, it was hypothesized that: (1) the emissions of CH_4 and H_2S at this dairy are highly correlated given the same environmental conditions and (2) the emission of CH_4 decreases as the stored manure ages and the basin shifts from filling to drying as was indicated in a prior study of H_2S emissions at this dairy [23].

2. Methods

Emissions of CH_4 from a manure storage basin during filling and drying were monitored over 44 days (11 August–23 September) in 2008. Measurements of H_2S emissions from the same basin and time period [23] were reanalyzed and compared to the CH_4 emissions.

2.1. Farm Description and Operation

The western free stall dairy facility was located in Washington along the south side of an east–west valley [23,29]. The producer indicated an average of 4839 milking cows, 609 dry cows, and 80 beef cattle in the barns loading the basin during the study period (Table 1). Calf hutches, with an unknown inventory of calves, were located to the SE of the monitored basin (Figure 1). No mean mass for each animal type was provided by the producer. It was assumed that the animals were in the barns or on the lots (Figure 1) 14 h per day. Manure from the barns and milking parlor were automatically flushed four times daily [23]. Flushed manure was separated with the liquid fraction transferred to a lagoon (Figure 1) and the manure solids separated from the sand bedding and transferred to one of two earthen-lined settling basins 6 m above the separators (Figure 1). The monitored basin (Eastern storage basin; Figure 1) was 0.6 km SSE and 20 m upslope from the barns and had a design volume of 56,796 m^3 and surface area of 13,100 m^2. The basin inlet was at the northwest corner of the basin while a skimmer ran along the entire south end of the basin. Manure liquid from the active basin was skimmed, further separated from suspended solids to the north of the basin, and returned as flush to the barns or stored in the lagoon and applied by no-till injection to the field to the east of the storage basins (Figure 1). Manure filled the east basin in approximately 280 d, corresponding to a loading rate of 203 m^3 d^{-1} (based on assumed animal mass After filling, the west basin was filled and the east basin was allowed to air dry after which the sludge was removed by front-end loader and carried to a drying pad north of the basin and 6 m lower elevation from the basin rim. After drying, the manure solids were put in windrows to the east of the basins. Unseparated manure was occasionally applied by spreader to the field to the northeast of the storage basins. Dates of windrowing, manure spreading or liquid injection are indicated in Table 1.

Table 1. Farm activity data [1].

Start Date	End Date	Animal Inventory			Producer Manure Handling
		Milking	Dry	Beef	
8 August 2008	3 September 2008	4700	655	85	3, 4, 9, 10, 16, 17, 24 and 25 August 2008: Spread on E field 4–7, 10–14, 17–22 and 25–30 August 2008: Disc on E field 7–9, 14, 15, 23 and 31 August 2008: Windrow to E 2 and 3 September 2008: Spread on E field
3 September 2008	26 September 2008	4977	563	75	3–8, 9–14, 16–22 and 24–30 September 2008: Disc on E field 8–22 September 2008: Inject on SE field 8, 9, 16, 23 and 24 September 2008: Spread on E field

1: modified from [22].

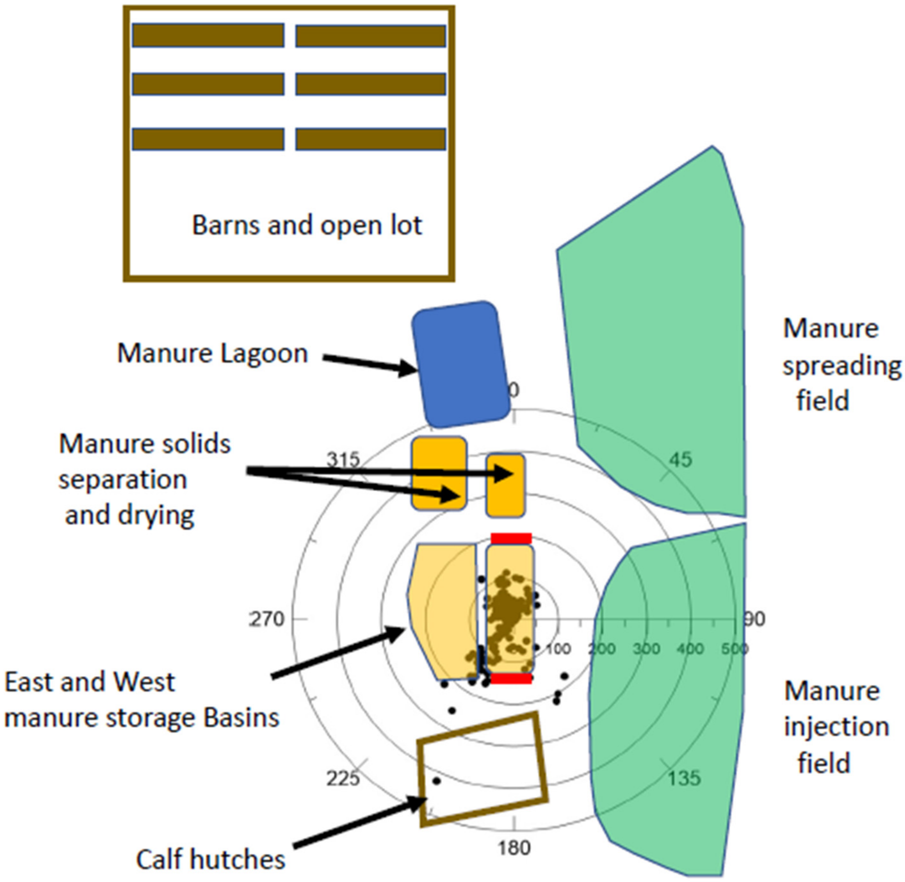

Figure 1. Configuration of dairy with CH_4 emissions superimposed. Half-hourly CH_4 emissions (g s^{-1}) are indicated (solid circles) in radius away from the measured basin based on wind direction. The monitored basin has the line-sampling systems (solid red line) to the north and south of the basin. North is at top of figure.

The activity and animal population were reported by the producer (Table 1). The appearance of the basin was recorded on almost every site visit by visual observation and photograph.

2.2. Measurements

Meteorological measurements (barometric pressure, air temperature (T_{air}), relative humidity, solar radiation, and surface wetness) were located on a 2.5 m meteorological mast and recorded as 30 min means of 5 min measurements. The meteorological mast was located 23 m north of the southwest corner of the east basin from 10 August to 3 September 2008 and then 110 m from the northwest corner from 4 to 23 September 2008 (moved to prevent line power losses associated with farm operations) (Figure 1). The vapor pressure deficit (*VPD*) was derived from the air temperature and humidity measurements.

A sonic anemometer (81,000, RM Young, Inc., Traverse City, MI, USA), used in the characterization of turbulence at the site, was located 2.5 above berm level (abl) on the meteorological mast. Measurements were recorded at 16 Hz. Turbulence statistics were calculated without rotation of the axes since the variable terrain near the sources did not assure that the flow would truly be parallel to a flat horizontal surface. Statistics were calculated at 5 min intervals and considered valid when at least 90% of the possible 16-Hz measurements were recorded and the sonic temperature variance was less than 2.5 K^2. Mean wind speed and direction as well as turbulence statistics were calculated over 30 min averaging periods when at least three of the six 5 min interval statistics contained in the 30 min period were valid. Turbulence stationarity was assessed by comparing the 5 min covariances of the perturbations of the wind vector in horizontal direction of flow (u') and in the vertical direction (w') to the 30 min averaged covariances using:

$$\sum [\![\left(\overline{u'w'}\right)_{5\text{min}} - \left(\overline{u'w'}\right)_{30\text{min}}]\!] / \left(\overline{u'w'}\right)_{30\text{min}} \tag{3}$$

Values greater than 0.30 were excluded from further analysis [30]. The homogeneity of turbulence was evaluated by comparing the theoretically derived and measured integral turbulence scales of w' as:

$$\frac{\sigma_w}{u_*} = 2.00\left(-z/L\right)^{1/6}, 2.00\left(-z/L\right)^{1/8},\ 1,\ 1.41,\ \text{and } 1.25 \tag{4}$$

where σ_w is the standard deviation of the wind vector component in the vertical direction, z is the height abl and values are for z/L values of <-1, $-1 < z/L < -0.0625$, $-0.0625 < z/L < 0$ and ≥ 0, respectively. A difference between measured and derived values of more than 30% excluded the measurements from further analysis [30].

Line-sampling of the air to the north and south of the basin (Figure 1) was made using ten flow-balanced inlets containing 1 μm Teflon® filters spaced evenly along a 50-m long 9.5-mm Teflon® line 1.5 m above berm level (abl). To account for lags in the sampling line and gas sampling system, only the last 2 1 min average concentration measurements were used for analyses from the 15 min sampling time per line sample. Both line sampling systems were sampled during a 30 min interval. Attack angle of the 1/2 h mean wind direction was determined for both line sampling systems. Air samples were considered valid when the 1/2 h mean wind direction was less than 60° off the perpendicular to the line sample.

Methane concentrations in the sampled air were measured using photoacoustic infrared absorption spectroscopy (PAS) technology (Model Innova 1412 Multigas Analyzer, Lumasense Technologies, Ballerup, Denmark). The 2σ MDL of the PAS instrument was 0.62 mL L^{-1}. Multi-point calibrations were conducted twice during the measurement period. Calibration checks at zero and 10 μL L^{-1} were conducted three times, with a mean instrument error of 11%. The CH_4 emission measurements based on the PAS analyzer were corrected for a water vapor interference [8]. All concentration measurements were normalized to 101.325 kPa and 20 °C within the instruments.

2.3. Emissions

Emissions of H_2S and CH_4 were determined using an inverse dispersion emissions model using inputs of line-sampled upwind and downwind concentrations of H_2S and CH_4, turbulence statistics, and meteorological conditions.

Emissions of CH_4 were determined at 1/2 h intervals using a backward Lagrangian Stochastic (bLS) inverse dispersion emissions model (WindTrax, Thunder Beach Scientific, Edmonton, Canada; http://thunderbeachscientific.com/windtrax.html, accessed 1 August 2019) with inputs of upwind and downwind concentrations of H_2S and CH_4 measured from the air streams coming from the two line-samples, turbulence statistics, and meteorological conditions. The model quantifies the relationship between a measured integrated line sample concentration and the average surface flux density across the source area, assuming the relationship is only a function of flow characteristics [31]. Five thousand back trajectories based on the measured turbulence statistics were used for the mean emission estimation. A background concentration (C_{BG}) for each gas is calculated in the single value decomposition of the two linear equations relating concentration to emission. Emission estimates were excluded when the friction velocity (U_*) was less than 0.15 m s^{-1}, the Monin Obukov length (L) was less than $|2\text{ m}|$, turbulence was not stationary (Equation (3)) or homogeneous (Equation (4)), the touchdown fraction was less than 0.05, the mean gas concentration measurement was invalid or missing, the minimum CH_4 concentration was within 1 ppm of the CH_4 C_{BG}, or the angle of attack of both upwind and downwind S-OPS exceeded 60°. The half-hour emission errors were determined based on the errors in the calibration gases, diluters, gas analyzers, and emissions model. Given a 30 min error of the stochastically derived emissions of 24% [32] and the error in the gas concentrations (11%), the CH_4 emissions errors were estimated to be 26%. Given the average number of half-hourly emissions averaged for a daily mean emission (11 values), the error in daily mean CH_4 emission was estimated at 17%.

Emissions reported on an animal (head; hd) basis were scaled by the mean inventory of lactating cows during the study period. Emissions reported on an animal unit (AU; 1 AU = 500 kg) basis were scaled by a mean mass of 624 kg for a lactating cow and 755 kg for a dry cow [33]. The manure production was based on the mean total farm mean population of 4398 milking cows and 682 dry cows (producer supplied) with average manure production volumes of 66 L d^{-1} hd^{-1} and 80 L d^{-1} hd^{-1}, respectively [34]. Overall basin loading rate was estimated at 214 m^3 d^{-1}. Manure was transferred to the monitored basin over the period 11 August 2008 through 3 September 2008 and then transferred to a second basin beginning 4 September 2008. Beginning 4 September, the monitored basin began to dry down. The basin had begun to be filled approximately 28 November 2007 and was 100% crusted for the entire study period.

Outlier half-hourly and daily mean emissions were determined using Tukey's criteria [35] according to:

$$\{[E(\mathrm{Q3}) + [E(\mathrm{Q3}) - E(\mathrm{Q1})] \times 1.5\} \tag{5}$$

where Q1 and Q3 refer to the first and third quartiles of the modeled emission (E) for all valid half-hourly and daily mean emissions estimates. Linear correlations of the non-outlier half-hourly and daily mean emissions estimates were made using Pearson's Linear Correlation [36]. Non-outlier daily mean emissions distributions were evaluated for normality using the Kolmogorov–Smirnov (K-S) test with $p = 0.05$ [36]. Comparisons of normally distributed emissions were tested using the Student's t-test with $p = 0.05$ [36]. Comparisons of non-normally distributed emissions were tested using the Mann–Wilcoxon sum test [37]. The K-S test and Student's t-tests were made using Microsoft Excel spreadsheets. Mann–Wilcoxon tests were conducted using an on-line calculator [38] or the Mann–Whitney U test in the Statistical Analysis System (SAS).

Potential causative relationships between atmospheric environmental conditions and non-outlier CH_4 emissions were assessed. Although the basin manure surface was almost entirely crusted at all times, the potential influence of air temperature (as a proxy of the liquid surface temperature) on the volatility of CH_4 at the liquid: air interface and, consequently, the CH_4 emissions was evaluated using the van't Hoff equation [39] for both non-outlier half-hourly and mean daily emissions. Linear correlations between barometric pressure, daily change in barometric pressure, and U_* and non-outlier CH_4 emissions were calculated to assess possible environmental influences on CH_4 half-hourly and mean daily emissions.

Although the substrate and microbial activity for H_2S production is largely different than CH_4, the anaerobic conditions conducive to CH_4 production should also promote H_2S production provided substrate and microbial populations are present. Since both CH_4 and H_2S have relatively low solubility in water, the controls on emission of these two gases from a manure basin should be similar. Half-hourly and mean daily emissions of H_2S from this basin were reported by Grant and Boehm [23]. The estimated error (including emissions model and gas concentration measurement error) of half-hourly H_2S emission was 24% while that of the daily mean emission was 7%. Comparisons of the CH_4 and H_2S emissions during the period of CH_4 measurements are made at both the half-hourly and daily time intervals.

3. Results and Discussion

The daily air temperature varied from 9.3 °C to 31.7 °C over the entire period, with a mean of 20.8 °C (SD 4.5 °C). Measurements were made for 23 days when the basin was filling and 21 days when the basin was drying down. Most meteorological conditions were similar between the manure filling and manure drying periods. The daily mean barometric pressure varied from 97.3 kPa to 98.9 kPa during manure filling and 97.6 kPa to 99.1 kPa during manure dry down. Daily mean atmospheric water vapor ranged from 0.6 to 1.7 kPa (0.6 to 1.4 kPa) during manure filling (drying). Daily mean wind speeds varied from 1.6 m s^{-1} to 6.2 m s^{-1} (1.2 m s^{-1} to 4.0 m s^{-1}) during filling (dry down). The daily mean temperatures were higher during filling (15 °C to 32 °C) than during dry down (9 °C to 22 °C).

Prevailing winds were from the north northwest. Winds were mostly associated with katabatic and anabatic slope flow with upslope anabatic winds (northerly winds) during the daytime (8 to 17 LT) and downslope katabatic winds (southerly winds) during the nighttime (20 to 6 LT) (Figure 2). Downslope katabatic winds corresponded with relatively stable air (positive z/L) (Figure 2). The most turbulent winds ($U_* > 0.4$ m s^{-1}) largely occurred during the daytime in an unstable surface boundary layer.

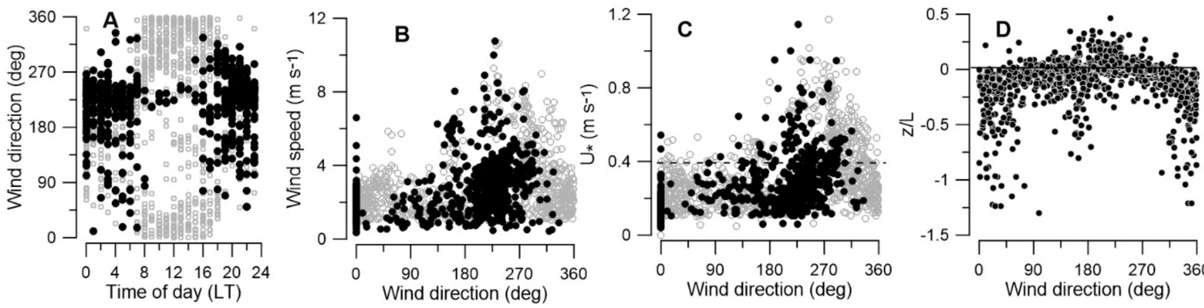

Figure 2. Variation in half-hourly air flow in the surface boundary layer over the course of a day. The diurnal variation in wind direction (panel (**A**)) and variation in wind speed and friction velocity with wind direction (panels (**B**,**C**), respectively) are shown, where filled circles indicate winds with $z/L > 0$ and grey open circles indicate winds with $z/L \leq 0$). Panel (**D**) illustrates the variation in stability (z/L) with wind direction.

Exclusion of mean half-hour measurements due to the criteria stated above reduced the 1553 half-hour measurement intervals to 528 valid half hourly mean emission measurements: 395 half hour measurements during the filling period and 133 measurements during the drying period. The mean daily emissions for both phases of manure handling were determined by averaging the 1/2 h emissions for each day regardless of the number of measurements. The error in mean emissions during the filling and dry-down phases were estimated to be 1% and 2%, respectively.

3.1. Half-Hourly Mean Emissions

The median CH_4 emissions were 34.2 g s^{-1}. The distribution of half-hourly CH_4 emissions measurements was non-normal with more than 60% of half-hourly CH_4 emissions less than 40 g s^{-1} (Figure 3). Log10 transformation of the half-hourly emissions was likewise non-normal (Kolmogorov–Smirnov D statistic of 0.17 with D_{max} of 0.03; n = 712). Outlier CH_4 emissions were half-hour mean values above 119.6 g s^{-1}. Outlier emissions occurred more often in the night time than day time; likely due to the more variable flow conditions in a stable boundary layer (positive z/L) with relatively low friction velocities. The non-outlier mean half-hourly CH_4 emissions over the study period were 45.0 g s^{-1} with a median emission of 34.0 g s^{-1}. Half-hourly CH_4 emission were highest under southerly winds (Figure 1). Since the basin inlet was on the north end of the basin, this could be due to the close upwind proximity of the inlet to the line air sampler.

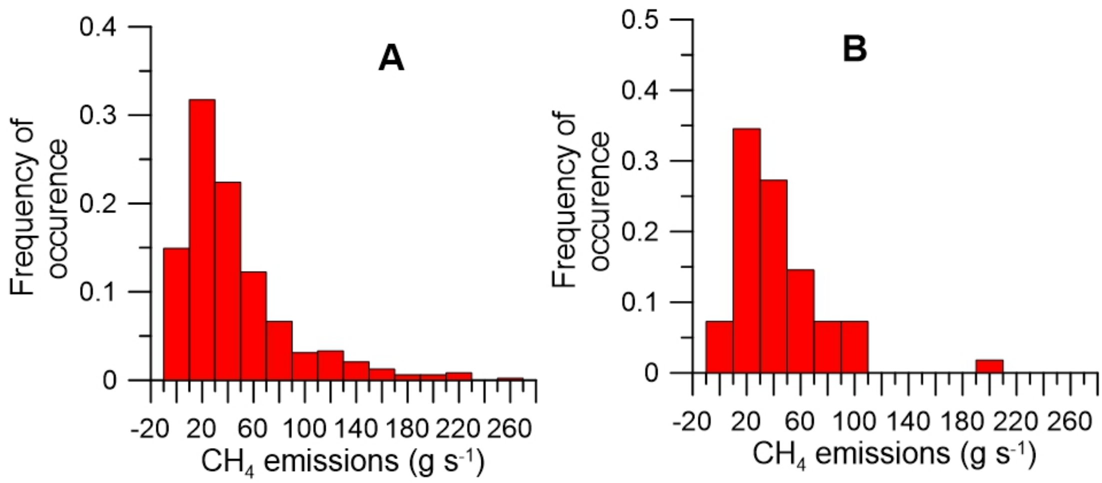

Figure 3. Frequency of occurrence of CH_4 emissions. The frequency of half-hourly CH_4 emissions (panel (**A**)), and daily mean CH_4 emissions (panel (**B**)) are indicated.

Given the nominal duration of filling of the basin, measurements were made from day 257 to day 280 of manure filling and the first 23 days of drying. On 3 September, the fresh manure was rerouted from the monitored basin to a second basin to the west and the manure in the monitored basin began to dry down.

3.2. Influence of Meteorological Conditions on Half-Hourly Mean Emissions

There was no evident influence of air temperature (used as a proxy for manure temperature) on the non-outlier emissions of CH_4. (R = 0.08; n = 459). The lack of correlation between air temperature and CH_4 emissions (R^2 for van't Hoff solubility function of 0.01 for half-hourly emissions) was probably related partly to a combination of minimal CH_4 diffusion associated with gas solubility in solution (solubility of CH_4 0.0014 mol kg^{-1} bar^{-1} [20]) resulting in most CH_4 transported through the manure as bubbles and partly to the lack of correspondence of air temperature to the manure temperature under the crust where methanogenesis occurred. Similarly, the half-hourly CH_4 emissions were not linearly correlated with the VPD (R = 0.1) and therefore unlikely to influence the drying.

There was a weak linear correlation between wind speed and non-outlier emissions of CH_4 (R = 0.31; n = 459). The corresponding measure of turbulent mixing (U_*), was however not correlated with non-outlier emissions (R = 0.03). The lack of linear correlation of CH_4 emissions with U_* was likely due to the changes in surface boundary layer stability. Wind speeds were greater when the wind was from the SSW than all other directions (Figure 2B), corresponding with a stable layer of downslope katabatic flow (Figure 2D) on the 11°

slope. In contrast, the U_* was highest during the day with winds from the west (Figure 2C). Since the catabatic nighttime winds were more stable than the anabatic upslope winds, the linear correlation between U_* or U would be expected to differ. As a result, the linear correlation between U_* or U and CH_4 emissions will be confounded by the differences in the relationship of U_* to U. This lack of linear correlation of wind speed and CH_4 emissions has also been reported for slurry stores in Idaho [4] and Ontario [6].

Methane emissions were slightly greater during the night time (mean = 60.9 g CH_4 s^{-1}, SD= 75.6 g CH_4 s^{-1}, n = 231; Figure 4) than day time (mean = 38.1 g CH_4 s^{-1}, SD = 32.6 g CH_4 s^{-1}, n = 258) during both basin filling and dry-down. Excluding outlier emissions, CH_4 emissions were not significantly different between night time (mean = 37.7 g CH_4 s^{-1}, SD = 30.3 g CH_4 s^{-1}, n = 201) and day time (mean = 33.2 g CH_4 s^{-1}, SD = 25.7 g CH_4 s^{-1}, n = 257) (Student's t = 0.01). Similarly, neither Leytem et al. [4] or Bjorneberg et al. [5] observed clear diurnal CH_4 emissions variations for dairy storage ponds in Idaho.

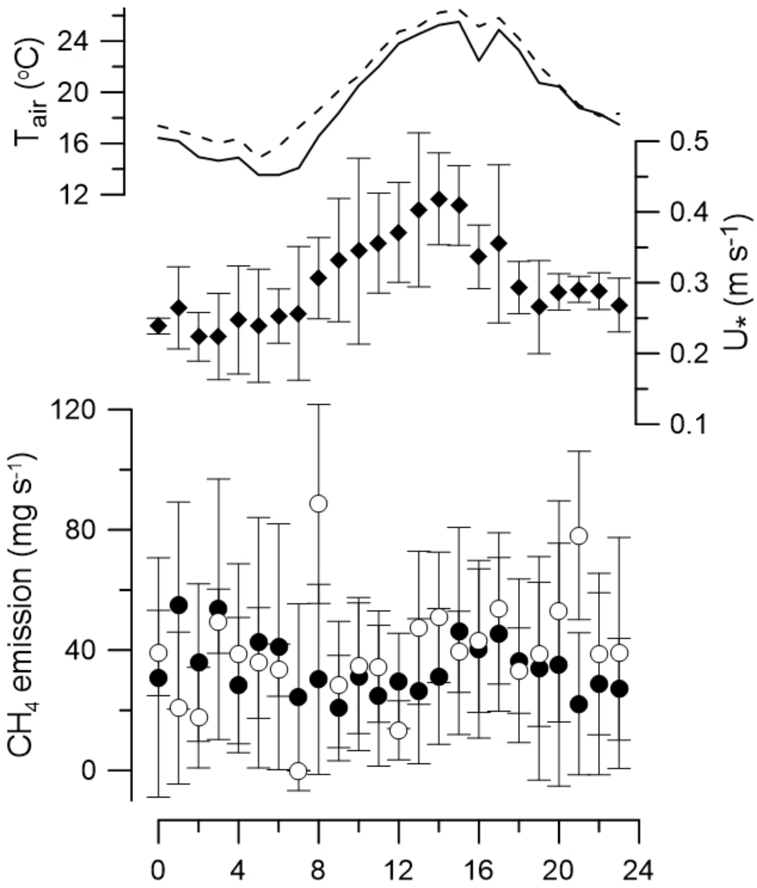

Figure 4. Diurnal variation in mean CH_4 emissions. Mean hourly emissions of CH_4, friction velocity (U_*) and air temperature are indicated over the course of a day. CH_4 emissions are segregated by emissions when filling (solid circle, solid line) and emissions when drying (open circle, dashed line).

3.3. *Influence of Producer Activity on Half-Hourly Mean Emissions*

Basin CH_4 emissions were segregated between emissions while filling and emissions while drying down. Non-outlier median CH_4 emissions were slightly higher during filling (47.1 g CH_4 s^{-1}) than during dry down (45.0 g CH_4 s^{-1}). The distributions of the CH_4 emissions during the two phases of operation were not normally distributed (filling: Kolmogorov–Smirnov D statistic of 0.06 with D_{max} of 0.05, n = 226, dry-down: Kolmogorov–Smirnov D statistic of 0.15 with D_{max} of 0.01, n = 133). The emissions during filling and dry-down were not significantly different (Mann–Wilcoxon test; Z statistic 0.41, $p < 0.68$).

Emissions during filling and to a lesser extent during drying appeared to be more consistently low during the daytime when the U_* was high (Figure 4). Emissions during drying also showed lower emissions during the daytime when the U_* was high, but less distinctly than during filling (Figure 4).

3.4. Daily Mean Emissions

There were 23 measurement days during the filling phase and 21 measurement days during the dry-down phase (Figure 5; supplementary material). Given the modeling and measurement errors, the mean emission during each phase had an error of 4%. The median CH_4 emission for the basin was 45.4 g CH_4 s^{-1} with values above 111.8 g CH_4 s^{-1} determined to be outliers. The only outlier CH_4 emissions occurred on 24 August 2008 with a daily mean methane emission of 156 g CH_4 s^{-1}. No producer activity involving dried manure piling or wet manure spreading, injecting, or discing was unique to this date [23]. The non-outlier daily mean CH_4 emissions were not normally distributed (Kolmogorov–Smirnov D statistic of 0.26 with $D_{max}(0.05)$ of 0.23).

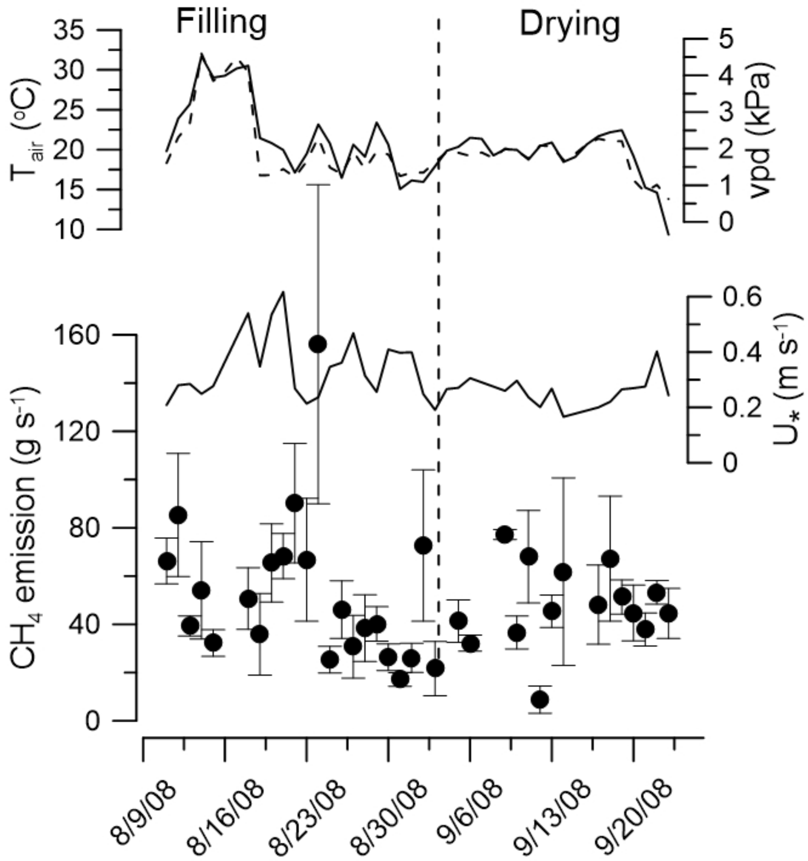

Figure 5. Daily mean basin CH_4 emission and environmental conditions. The temporal variation in daily mean air temperature (solid line), vapor pressure deficit (dashed line) and U* (solid line). The vertical dashed line separates the manure filling and drying phases of the basin. Bars represent the standard error of the mean daily emissions (solid circles).

The daily mean CH_4 emissions for the basin on an area basis were 3.9 mg CH_4 m^{-2} s^{-1}. This area-based mean emission was similar to that of one Idaho open-lot dairy (0.46 mg m^{-2} s^{-1} to 5.32 mg m^{-2} s^{-1}) [4], greater than a second Idaho dairy (0.41 to 1.1 mg m^{-2} s^{-1}) [5], and less than the 18.3 mg CH_4 m^{-2} s^{-1} mean emissions across six slurry store emission studies [40]. Emissions were greater than from an Ontario waste storage tank, where emissions ranged from 0.011 mg m^{-2} s^{-1} in January to 0.153 mg m^{-2} s^{-1} in July [6].

The daily mean CH_4 emission for the slurry basin on a per-head basis was 861 g d^{-1} hd^{-1}. This CH_4 emission was within the range of 152 g d^{-1} hd^{-1} to 1774 g d^{-1} hd^{-1} reported from the wastewater pond of one Idaho open-lot dairy [4] and greater than the per-head emissions at a second Idaho dairy (single day emissions measured in four months ranging from 2.8 g d^{-1} hd^{-1} to 22.8 g d^{-1} hd^{-1}) [5] and for a storage tank on an Ontario dairy (ranging from 9 g d^{-1} hd^{-1} to 41 g d^{-1} hd^{-1} [6]. The daily mean emissions were greater than the 276 g d^{-1} hd^{-1} mean emission across six slurry store emission studies in western Europe [40].

3.5. Influence of Meteorological Conditions on Daily Mean Emissions

Emissions from the crusted surface were expected to be related to the environmental conditions. The crust was expected to thicken (although not measured) over time as solids rise to the surface and evaporation occurs at the surface. Increased evaporation occurs when the *VPD* increases at the liquid: air interface, when the liquid: air interface is near the crust surface, and when turbulent mixing between the crust surface and the air increases. During the course of this study, the environmental T_{air}, U_*, and *VPD* all trended downwards (Figure 5).

The linear decrease in T_{air} was −0.2 °C d^{-1} (R = 0.56, n = 43). However, there was no evident influence of air temperature (commonly used as a proxy for manure temperature) on the emissions of CH_4. A linear correlation of daily mean air temperature with CH_4 emissions had an R of 0.1 (n = 43). Similarly, the R^2 for van't Hoff solubility function was less than 0.01. The lack of significant relationship between daily mean air temperature and CH_4 emissions was probably a result of the low solubility of CH_4 and the lack of correspondence between air temperature and the temperature of the manure at the biologically active surfaces. This was consistent with the lack of apparent influence of air temperature on emissions of another low-solubility but biologically produced gas, H_2S (0.10 mol kg^{-1} bar^{-1}; [41], from the same basin [23] as well as from other manure storages [4,6]. This was in contrast to Leytem et al. [16] and Grant et al. [8] who found air temperature to correlate with CH_4 emissions from smaller settling and storage basins.

The mean daily U_* decreased with time over the study period, largely a result of two days with high U_* in August (Figure 5). The correlation coefficient for a linear function between daily mean U_* and daily mean CH_4 emissions was only 0.30 (n = 38), which suggests that the transport of CH_4 was not primarily limited by the turbulent transport but must be limited by processes at or below the crust surface. The lack of linear correlation between winds and CH_4 emissions was consistent with the emissions from large manure storage basins in Idaho [4] but contrasts with correlations at another large manure storage basin in Idaho [5] and a smaller manure storage basin in Wisconsin [8].

There was a linear decline in *VPD* of 0.03 kPa (R = 0.47, n = 43) over the course of the study period, trending in the same pattern as the air temperature (Figure 5). It was expected that the drying of a moist crust would be a function of *VPD*, with the drying crust shifting the liquid air interface further into the crust and increasing the resistance to CH_4 transport. However, as was the case with U_*, the daily mean CH_4 emissions were not linearly correlated with the *VPD* (R = 0.14, n = 43). Visual assessments of the crust surface confirmed that very little of the surface was moist. Leytem and coworkers [4] suggested that crusts on the manure dry out as the air temperatures rises, resulting in increased crust porosity and decreased resistance to gas transport.

Cracks were often observed in the 100% crusted surface throughout the study period. If transport of the gasses through the was driven partly by convective pressure pumping [21,22], daily changes in barometric pressure should correlate with emissions. The lack of linear correlation between daily mean CH_4 emissions (R $\leq$ 0.01, n = 35) and changes in barometric pressure implies that the diffusion through the cracks dominated the transport to the manure surface and/or the transport was not influenced by pressure gradients and/or the variation in pressure gradients was too small to detect an influence.

3.6. Influence of Producer Activity on Daily Mean Emissions

The daily mean emissions decreased at a rate of 0.3 g s^{-1} d^{-1} throughout the study period (Figure 5). This would suggest that the daily mean emissions during the basin manure drying phase would be less than that of the filling phase- in contrast to the mean half-hourly emissions. Daily mean CH_4 emissions ranged from 17 g CH_4 s^{-1} (1.5 mg CH_4 m^{-2} s^{-1}) to 156 g CH_4 s^{-1} (11.9 mg CH_4 m^{-2} s^{-1}) during filling (n = 23) and 9 g CH_4 s^{-1} (0.7 mg CH_4 m^{-2} s^{-1}) to 77 g CH_4 s^{-1} (5.9 mg CH_4 m^{-2} s^{-1}) during dry down (n = 21). Median daily emissions over the period of basin filling were 46 g CH_4 s^{-1} (3.5 mg CH_4 m^{-2} s^{-1}; 784 g d^{-1} hd^{-1}, n = 23) while those while the basin manure was drying were 45 g CH_4 s^{-1} (3.4 mg CH_4 m^{-2} s^{-1}; 766 g d^{-1} hd^{-1}, n = 21). However, as found for the half-hourly CH_4 emissions, the daily mean emissions during the filling and drying down were not significantly different (Mann–Wilcoxon test; W statistic 187, p = 0.4). This lack of difference in CH_4 emissions as the manure ages in the basin is consistent with laboratory studies [14]. So even though the manure changes composition and presumably also increases methanogenic population diversity [17] as the manure ages in the basin from filling to drying, there was no net emissions effect.

Variation in the measured daily mean CH_4 emissions may be due in part to interference from other nearby sources. The producer spreading, discing, and injecting of manure as well as nearby windrows may potentially decrease the measured emissions by advection and deposition of CH_4 in the basin from this activity. Relatively high half-hourly mean CH_4 emissions occurred when the winds were coming from the SE (Figure 1). There were however only three days of manure handling activity when winds were from between 0° and 135°. Advection of CH_4 from field emissions was not likely on these days since the median daily C_{BG} (4.8 ppm) was within the measurement error of the instrument (11%) of the median C_{BG} for all days with valid emission estimates (4.5 ppm). The median daily CH_4 emissions when the winds were from direction of the field activity (n = 3) were 67.2 g s^{-1}, while the median daily mean CH_4 emissions for all days with wind directions between 0° and 135° was 45.4 g s^{-1} (n = 9). This difference in emission on the days of manure handling and no manure handling was however significant: the Mann–Wilcoxon test indicated a significant difference (W statistic 16, p = 0.04) and the difference was much greater than the calculated 9.8% measurement error for the mean emission for these three days. Two of the three days with winds between 0° and 135° occurred during filling. Again, since the basin inlet was on the north end of the basin, the higher emissions could also be due to the close upwind proximity of the inlet to the line air sampler and not the manure handling activity.

3.7. Relationship between Basin CH_4 and H_2S Emissions

During the period of measurement of CH_4 emission, H_2S emissions ranged from 21 mg H_2S s^{-1} to 346 mg H_2S s^{-1} during filling and from 15 mg H_2S s^{-1} to 336 mg H_2S s^{-1} during drying. The median H_2S emission was 204 mg H_2S s^{-1}. There were no days with outlier daily mean H_2S emissions: the single day of outlier CH_4 emission corresponded to the highest daily mean H_2S emission. The median H_2S emissions during filling were 204 mg H_2S s^{-1} (156 µg H_2S m^{-2} s^{-1}) while those during dry-down were 193 mg H_2S s^{-1} (147 µg H_2S m^{-2} s^{-1}).

Emissions of CH_4 were correlated with those of H_2S during both the filling and drying phases for both half-hourly mean values and daily values (Figure 6). The linear correlation between half-hourly emissions of CH_4 and H_2S were similar both during filling (n = 43) and drying (n = 75) at R = 0.69 and 0.66, respectively, with the slope of the filling period correlation within the 95% confidence interval of the drying period (Figure 6). Similarly, the linear correlation between daily mean emissions of CH_4 and H_2S were similar, but the correlation during filling (n = 12) was somewhat lower than that during drying (n = 17) at R = 0.42 and 0.66, respectively. This difference in the relationship was, however, not significant at the 95% confidence interval (Figure 6).

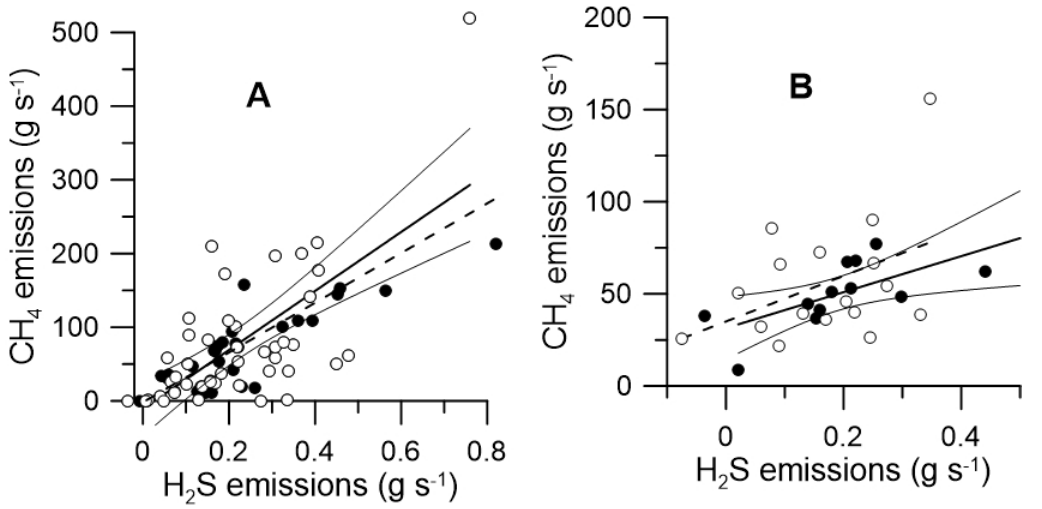

Figure 6. Relationship between H_2S and CH_4 emissions during the filling and drying of manure in the basin. All half-hourly mean emissions of H_2S and CH_4 during basin filling (open circles) and drying (closed circles) are indicated in panel (**A**). Paired mean daily emissions during filling (open circles) and drying (closed circles) are indicated in panel (**B**). Linear regressions between emissions during filling and drying are indicated by thick solid and dashed lines, respectively. The 95% confidence interval of the drying period regression slope is indicated by thin solid lines.

The high linear correlations between CH_4 and H_2S emissions for both half-hourly and daily time periods suggests that similar processes influenced their emissions as hypothesized. Since differences in the environmental conditions did not correlate with CH_4 emissions (discussed previously) or H_2S emissions [23], but do correlate with each other, we conclude that conditions for microbial activity within the manure basin were likely similar for the production of the gases and that the mechanisms of emissions of the produced gases from the basin were likely similar. Since the diversity of bacterial populations increase with age of manure [17], one might expect changes in the relationship between CH_4 and H_2S emissions. Furthermore, we conclude that significant populations of purple sulfur bacteria linking the consumption of CH_4 to the production of H_2S was unlikely since enhanced production of H_2S at the expense of CH_4 over time was not observed.

Aging of the manure appeared to reduce the emissions of both gases. The median daily CH_4 emissions were 3% higher during basin filling than during dry down, while H_2S emissions were 5% higher during drying than filling. However, as stated above, this difference in daily mean CH_4 emissions was not significantly different at $\alpha = 0.05$ (without considering the measurement error). Similarly, the daily mean H_2S emissions were lower during dry-down of the basin manure than filling but not significantly (filling $n = 12$; dry-down $n = 17$) n (Mann–Wilcoxon test; W statistic 89, $p = 0.98$).

The CH_4/H_2S emission ratio for the basin was 223 g CH_4 g H_2S^{-1} +/− 16 g CH_4 g H_2S^{-1}. Although the periods of measurement differ for emissions of CH_4 and H_2S from a slurry storage that never fully dried and was not always crusted at a Wisconsin dairy, the ratio was similar at 268 g CH_4 g H_2S^{-1} [8,42]. This suggested that the bacterial species involved in decomposition of the dairy manure slurry were similar between locations while the population present and/or available substrate for decomposition differed.

4. Conclusions

Methane emissions from the storage basin were not influenced by environmental conditions during the study period. Resistance to transport of the CH_4 from the crusted slurry surface was not limited by the winds over the surface or the drying of the surface from evaporation. Emissions were not related to the daily mean T_{air}, suggesting that T_{air} was a poor proxy for the slurry temperature. Methane emissions also did not vary as the manure aged suggesting that the biological decomposition rate remained steady under the crust for at least the 44 days of this study.

Daily mean emissions of the anaerobic decomposition gases of CH_4 and H_2S from the manure storage basin were linearly correlated, supporting the null hypothesis that emissions should be highly correlated since both gases are primarily anaerobically produced in the stored manure and both have low solubility in water. The similarity in CH_4 to H_2S emissions ratio between this western dairy and a midwestern dairy suggests that similar bacterial species may be active in dairy slurry basins in a variety of climates. While the null hypothesis supports the contention that there was similarity in biological factors influencing emissions, no measurements of bacterial species, populations or organic substrates available were made. Such information is needed from several different farm basins in diverse locations to determine the relative importance of these factors on the relationship between emissions.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/atmos14091420/s1.

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Data Availability Statement: The data presented in this study are found in the supplementary material.

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