Hydrogen sulphide concentrations in manure pits of dairy barns

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Abstract: The release of toxic manure gases during mixing of manure are harmful for livestock and humans and are deadly at high concentrations. As far is known long-term measurements into the concentration of toxic manure gases from manure storages in dairy barns never took place. The goal of study was to get insight in the long-term course of the hydrogen sulphide (H_2S) concentrations in the manure pit of a commercial dairy barn as an indicator for the occurrence of (potentially) dangerous situations in dairy barns by toxic manure gases. Also a short review of the literature was made. During manure mixing the H_2S-concentration rises very quickly after the start and leads (very) rapidly to a peak value. Reported peak concentrations of more than 150 ppm H_2S occurred frequently. The elevated H_2S concentrations remained frequently for longer periods of time (15 minutes). The H_2S-concentrations can vary strongly even during periods in which operational circumstances and actions were equal. During pumping of manure the H_2S concentrations could also rise, but not as much as during manure mixing. At other times the H_2S concentrations can be sometimes slightly elevated. The results from the literature review and measurements at the commercial dairy barn show that mixing of manure leads to such a quick release of H_2S that health hazards due the inhalation of toxic manure gases is greatly increased. Taking appropriate safety measures before and during mixing of manure is therefore an absolute necessity for a safe and healthy working environment.

Keywords: H_2S, Manure Gases, Mixing, Toxic.

1 Introduction

Safe working and healthy living conditions are necessary prerequisites for practising a dairy farm. The release of toxic manure gases during mixing of manure don't contribute to these conditions. The toxic manure gases are harmful for livestock and humans and are deadly at high concentrations. The danger of toxic manure gases is still being underestimated, because on a regular basis accidents still happen with manure gases in which cattle are killed and sometimes also human lives are lost [1-11]. The installation of low-emission floor types increases the safety risks of manure gases on dairy farms [12]. Also the risks are being increased by the longer required storage time of manure during the fall and winter months and the increase in amount of manure that is being stored. At the start of the manure spreading season it frequently happens that the manure reaches the concrete slats and forces the manure gases out of the manure pit.

As far is known long-term measurements into the concentration of toxic manure gases from manure storages in dairy barns never took place. Therefore it is unknown whether the danger of toxic manure gases only occur during manure mixing or if it is dormant danger which also occurs during the storage of manure. The goal of study was to get insight in the long-term course of the hydrogen sulphide (H_2S) concentrations in the manure pit of a dairy barn as an indicator for the occurrence of (potentially) dangerous situations in dairy barns by toxic manure gases. Also a short review of the literature was part of study.

2 Materials and methods

The research was carried out in the dairy barn of a commercial dairy farm. The dairy barn could house 110 milking cows and had two milking robots. The cleaning and milk residues of the milking robots were discharged into the public sewage system. The cows were permanent

housed in the barn and had no access to a pasture. The manure of the milking cows were received in three manure pits which were not connected to each other. No additives were used for the manure in the manure storage. In one of the three manure pits a prototype of a H_2S safety system was installed. This manure pit had a depth of 2 m and a volume of 396 m^3.This safety system provided the possibility to do year-round measurements of the H_2S concentration at different locations in manure pit.

The safety system consisted of an exhaust fan connected to the manure pit, operating system, four measuring points, warning lights and flash light. Measuring points were made in the mixing pit, in the tube of the exhaust fan, in the front and in the back of the manure pit. At each measuring point a H_2S-sensor was mounted with a measuring range of 0 to 100 ppm. During the research period also two extra measuring points were made at the feed fence at a height of 1 m. The H_2S-sensors were connected to the gas controller unit (Hanwei KB2160) of the safety system, which would turn on the exhaust fan, two red lights and a flashing light when a threshold of 10 ppm was exceeded and would give an alarm sound when a threshold of 15 ppm was exceeded.

The manure height in the manure storage was weekly measured and noted in a logbook. If the manure was being mixed, spread, transferred by pump or transported off the farm the data was noted in the logbook. Also a short statement about the weather during the event was noted in the logbook. Peculiarities were also noted in the logbook. The data acquisition system of the operating system had not function as was intended by the supplier. The data acquisition system had not stored the maximum value of the measured H_2S concentrations, since it only had stored one value during a period of elevated H_2S concentrations. But the measured maximum H_2S concentration was in most cases of mixing and pumping also written down in the logbook. And on some occasions there was also a movie and photos taken of the measuring display. At different times when manure was transported off the farm a manure sample was taken and analysed at the Environmental Laboratory of Wageningen UR Livestock Research on the following parameters: dry matter, total-nitrogen, ammonium-nitrogen, phosphate, potassium and sulphur. The preliminary results of measured H_2S concentration at a Dutch dairy barn were collected during the period from 13th June 2015 till 21st April 2016. The research continued after this period.

Furthermore a short review of the literature was performed into research results of measured concentrations of H_2S in manure pits of dairy barns.

3 Results and discussion

3.1 Measurements results from literature

Hydrogen sulphide has a low odour detection value of 0.005 to 0.13 ppm and has a characteristic smell of rotting eggs. However at concentrations above 100 ppm the nasal organ paralyses and the odour is no longer detectable any more for humans by which the danger can no longer be smelled. The Dutch legal limit for hydrogen sulphide is 1.6 ppm, which means that only at lower concentrations a person can work a full day without negative health consequences [1]. Table 1 gives the possible effects on the human body of exposure to hydrogen sulphide at different H_2S concentrations.

Table 1 Effects of hydrogen sulphide (H_2S) on the human body [13]

H_2S concentration (ppm)	Effect
0.005 – 0.13	– Odour threshold
1.6	– Dutch legal limit
10	– Eye irritation – After 4 – 8 hours of exposure headache and nausea
100 – 150	– Cough – Strong eye irritation – After 2 – 15 minutes paralyses of the nasal organ
150 - 250	– Headache – Dizziness – Nausea – Imbalance – Pulmonary oedema
250 - 700	– Severe irritation of the respiratory organs – Possible loss of consciousness – Chance of death between 15 minutes and 4 hours
700 - 1000	– Quick loss of consciousness – Standstill of breathing and death within 15 minutes – Chance of permanent damage
1000 - 2000	– At first breath paralysing of the midriff – Direct loss of consciousness – Death within minutes, even when the victim is being brought into fresh air (sudden knock-out, sudden death)

3.2 Literature review on measurements of hydrogen sulphide on cattle farms

Measurements were made on 22 Dutch cattle farms into the release of hydrogen sulphide (H_2S) and other gases (NH_3, O_2, CH_4 and HCN) during manure mixing. Hydrogen sulphide showed peak concentrations of up to 1000 ppm. More than 30% of the measurements were higher than 450 ppm and half were above 300 ppm which poses a direct risk for people and animals. Also the measured concentrations over a period of 15 minutes were alarming high. At a height of 1,5 metres above the slats the concentrations were more than halved [14].

Research was performed on four cattle farms into the course of the H_2S-concentation during the mixing of manure [15]:

1) At location 1, the manure of 200 milking cows was weekly flushed out of the barn into a underground tank of 57 m^3. The mixing of this underground tank led one minute after start to the highest measured value of 103 ppm after which the concentration slowly dropped. After mixing and transferring by pump to the end storage tank a concentration of 13 ppm was measured at the manure surface level and at a height of 1.2 metres above the manure surface a concentration of 6 ppm was measured.
2) At location 2, the manure of 160 dairy cows was scraped into an underground pit of 36 m^3, which was emptied weekly. Five loads of slurry were removed from the underground pit, with mixing taking place before the first and third loads. At the start of both mixing periods a rapid rise in hydrogen sulphide concentration occurred: the first time up to 140 ppm and the second time up to 40 ppm, after which the concentration slowly dropped. Also during the removal of the slurry elevated concentrations of up to 20 ppm were measured.
3) At location 3 cattle was housed in a barn with two slatted slurry channels, each about 2 m wide and 1.7 m deep, which ran the length of the building at the front of the pens adjoining the central walkway. The mixing of one manure pit took place by mixing for 5 minutes at eight different spots over the length of the manure pit. At most mixing points a considerable

increase in H_2S-concentration was measured after start of mixing. At the fifth point the highest peak concentration in direction of 300 ppm, followed by the second mixing point with a peak concentration of 200 ppm.

4) At location 4, beef cattle was housed in a barn with a central feeding passage which had on both sides a slurry channel running the length of the building. In the morning the left slurry channel was subsequently mixed at different spots and in the afternoon the right slurry channel was subsequently mixed at different spots. After the start of the mixing a rapid rise of the H_2S-concentration was measured. The measured concentration repeatedly rose above the 10-minute threshold value of 15 ppm. In the afternoon much higher concentrations were measured, because the doors of the barn had been shut due a rainstorm. Peak concentrations of 541 ppm were measured at slat level and 180 ppm at head height.

Measurements were made at different spot in a dairy cattle and a heifer barn on different days. The measurement were made at slat level before, during and after mixing of the slurry. The results showed that the H_2S-concentrations varied strongly even when operational conditions and procedures were similar. There was not a great difference between the summer and winter period. There was a tendency to lower H_2S-concentrations in the heifer barn. The 15-minute threshold values of 15 ppm were frequently exceeded. Table 2 gives the results of the measurements [16].

Table 2 Measured hydrogen sulphide concentrations in dairy-cattle barns [16]

Description and Location	Milking-cow barn		Heifer barn
	Summer	Winter	Winter
At sluice gate end			
No. of measurements	9	10	6
Peak concentration (ppm)	15 - 62	11 – 63	5 - 41
Peak 15-min avg. conc. (ppm)	6 - 31	1 - 42	2 - 30
Midway between sluice gate and nozzle			
No. of measurements	9	11	4
Peak concentration (ppm)	6 - 55	2 – 56	4 - 22
Peak 15-min avg. conc. (ppm)	6 - 31	2 – 44	3 - 11
At the nozzle end			
No. of measurements	10	11	4
Peak concentration (ppm)	3 – 42	4 - 70	4 – 23
Peak 15-min avg. conc. (ppm)	2 - 33	3 - 55	2 - 10

The composition of the air inside four manure storage tanks before and after mixing of the manure were measured. One tank contained only pig manure, while the three others contained mainly cattle manure and less than 20% pig manure. The results showed that before mixing no dangerous amounts of H_2S were measured. The maximum measured value was 2 ppm. After mixing, in some cases deadly concentrations of more than 1000 ppm were measured. The highest measured value was 4100 ppm [17].

In the winter time the H_2S-concentration in the manure pits of a beef cattle barn were measured during 99 days. In half of the manure pits the manure was mixed daily with air bubbles (Aeromix system) and in the other half the manure was mixed only once with a traditional mixer. At the non-aerated manure pits no H_2S was measured directly under the slats, while the aerated manure pits incidental H_2S was measured with maximum value of 7 ppm. During the mixing of the non-aerated manure high values of H_2S were measured with a peak value of 275 ppm directly under the slats. Direct after the start of the mixing of the non-aerated manure high

values were measured. During the transferring by pump of the aerated manure H_2S-concentrations up to 107 ppm were measured, while during the transferring by pump of the non-aerated manure H_2S-concentration of less than 10 ppm were measured. Also measurement were made in the period April-May at three commercial dairy farms which mixed the manure daily with air bubbles (Aeromix system). The results showed that the production of H_2S occurred only during the periods of mixing with the air bubbles. The highest measured value directly beneath the slats was 119 ppm, while the highest measured 5-minute value was 74 ppm. Peaks up to 30 ppm were common during the aeration [18].

3.3 Influencing factors

During their research into the release of toxic gases during manure mixing on Dutch cattle farms the researchers also looked into a number of factors which influenced the height of the concentration of the toxic gases [14].

- Manure
  On the basis of the results it was established that thick, stiff manure released less gases. No relation could be established between gas concentrations and manure temperature. Also the average storage time of the manure did not show a quantifiable influence on the gas concentrations.
- Manure storage
  No relation could be established between the depth of the storage tank or the amount of stored manure on the gas concentrations. In one case of an extended dairy barn, at the crossing of the old manure pit to the newer deeper manure pit emission of gases occurred. When manure is also stored beneath the cubicles and feeding alley the crossing of the closed manure pits under the cubicles to the open manure pits under the slats can have a strong increased effect on the gas concentrations.
- Manure treatment
  No difference was found between pumping and mixing. The rpm of the tractor showed to be of importance. At 300 to 350 rpm the gas concentrations were considerably lower. When the mixer is shut down a quick levelling out of manure levels takes place which can cause the release of a concentrated amount of a mixture of gasses into the barn.
- Ventilation
  Although no direct relation between the various factors and the released gas concentrations it became clear that also high wind speeds gave no guarantee of prevention of high gas concentrations in the barn. The wind direction is also of importance. In situations where the manure pits were located at the lee side of the barn, the problematic areas relocated to the opening of the mixer outside of the barn which sometimes led to life-threatening situations. The under pressure at the lee side apparently caused bleeding of the manure pits.

Research was done into the effect of diet and storage time on the sulphide content in dairy cattle slurry. The researched four diets consisted of silage and concentrates were formulated for a comparable milk production (20 kg/day), but differed in their protein content. The four diets had two levels of protein content (17 and 34%) and two levels of digestibility of the silage (low and high). Table 3 shows the results of the research. The diets with the high protein content showed to have a significantly higher sulphide content in the slurry. The highest sulphide content in the manure was measured at the diet with the high protein content and the highest amount of concentrates. The highest amount of sulphide was measured at the beginning of the storage time. The sulphide content decreases when sulphide is metabolised into gasses. The emission of hydrogen sulphide is depended on the pH of the manure. Also the total sulphur content of the manure decreased during the storage time with an average of 19%, from 478 mg/kg to 385 mg/kg [19].

Table 3 Fed diets, average sulphur and nitrogen content of the diet and the average sulphur and sulphide content in the dairy cattle slurry [19]

Daily animal intake and diet description	Average sulphur content of diet (g S/kg)	Average nitrogen content of diet (g N/kg)	Mean sulphur content in manure (g S/kg)	Mean sulphide content in manure (mg S/litre)
2.6 kg conc. 34% protein 9.7 kg silage: high dig.	2.36	34.6	0.45	50
4.1 kg conc. 34% protein 9.1 kg silage: low dig.	2.11	31.3	0.51	56
4.2 kg conc. 17% protein 8.3 kg silage: high dig.	1.81	28.0	0.50	42
6.9 kg conc. 17% protein 8.1 kg silage: low dig.	1.63	23.0	0.45	35

Research was performed into the effects of total solids (3, 5, 7, 9 and 11%), mixing speed (100, 200, 300 and 400 rpm), duration (5, 15, 30 and 60 minutes) and frequency (1, 2, 3 or 4 times per day) on the H_2S emission of dairy manure. The manure originated from two different dairy farms. One dairy farm fed the cows were with concentrate-based diet and the other dairy farm fed their cows with forage-based diet. The results showed that the concentrated-based diet had the highest H_2S emission from the manure. The H_2S concentration increased with the total solids content up to a maximum of 1133 ppm at a total solids content of 9%, after which it decreased at higher total solids. The H_2S-emission increased at higher mixing speeds and gave a peak concentration of 3996 ppm at 400 rpm. A similar trend occurred with an increase in mix duration where the H_2S emission increased at longer mixing durations. Al low mixing speeds (200 rpm) and short mixing duration (<15 min) the lowest H_2S emissions were measured. No significant differences were found between different mixing frequencies, but in general the H_2S emissions were higher when the manure was once a day mixed compared to more times mixing per day. The authors state that frequent mixing at low mixing speeds for a short period of time will result in lower H_2S emissions. The results also showed that H_2S is strongly depended on pH and temperature. A strong decrease from 3500 to 306 ppm was observed when de manure temperature was dropped from 24^{o}C to 10^{o}C. This effect can be explained by that sulphate reducing bacteria are sensitive to fluctuations in temperature. In addition to this the temperature is of influence on the transformation of water-soluble H_2S to gaseous H_2S. The results clearly showed that the activity of sulphate reducing bacteria exponentially increased at a temperature of 18^{o}C. Furthermore, a decrease in pH from 7.32 to 6.63 led to an increase of 285% in H_2S concentration. An increase of pH from 6.79 to 9.05 led to a decrease in H_2S concentration from 4000 to 20 ppm [20].

3.4 Preliminary results of measured H_2S concentration at a Dutch dairy barn

Mixing of the manure took place on seven days during the reported period. The rise in H_2S concentrations appeared to be depended on whether the manure good be properly mixed or not. At three occasions when a crust had formed which stayed in its place during mixing the H2S concentrations did not rise as high as during periods when no crust had been formed or when the crust was properly mixed through the manure. During 3 of the 4 occasion when the manure could be properly mixed the H_2S concentrations rose very quickly above 95 ppm at most of the measuring points.

Pumping of manure into a slurry tanker to be spread or to be transported to another farm was performed in total 15 times during the reported period. During eight times the alarm went off because of elevated H_2S-concentrations (>10 ppm), during the other 7 times no H_2S was

measured. In 7 of the 8 times the H_2S concentration was elevated at the mixer opening, and sometimes also at other measuring locations. The most problematic area during pumping of the manure therefore seems to at location where the manure is being sucked out of the manure pit.

During the period that no manure was being mixed or pumped, the alarm went off in total 10 times because of elevated H_2S-concentrations (>10 ppm). Only in two cases the H_2S concentration was elevated at the mixer opening. In 9 of the 10 times it was at the same measuring location. In 6 cases it was in a period from 18 to 26 July 2015, while manure height was low (<50 cm), see figure 1. During this period there was no hot weather with maximum temperatures between 19 and 23°C. But in the beginning of July there was hot weather with temperatures above 30°C [21]. So it could be that manure temperature was elevated because of the previous hot weather, but since the temperature of the manure has not been measured the cause of the elevations remains unclear. Also two other occasions the H_2S concentrations was elevated during a period where the wind had a specific direction on the dairy barn.

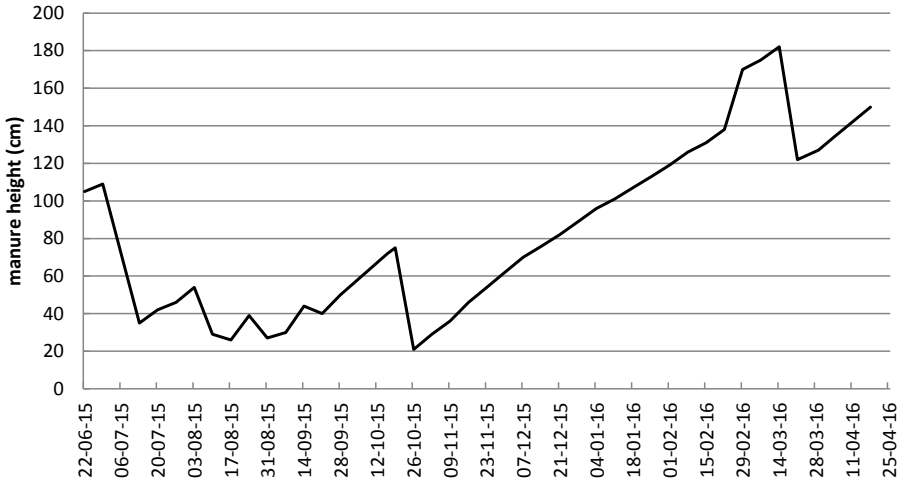

Fig. 1 Manure height in the manure pit where the H_2S concentration was being measured during the reported period.

Table 4 gives an overview of the composition of the manure in the manure pit of the dairy barn during the reported period. It appears that de nitrogen content of the manure has increased due to an increase in ammonia-nitrogen. Also the potassium showed a slight increase in value. The sulphur content of the manure varied around 0.50 g/kg.

Table 4 Manure composition in the manure pit at different times during the reported period

Date	Dry Matter (g/kg)	N-total (g/kg)	Ammonia-N (g/kg)	P_2O_5 (g/kg)	K-total (g/kg)	S (g/kg)
17-10-2015	77.6	3.79	1.68	1.12	5.31	0.56
12-03-2016	64.4	3.88	2.08	1.04	5.59	0.42
21-04-2016	74.3	4.34	2.31	1.18	5.89	0.49

4 Conclusion

The results of the short literature review were showing:

- Peak concentrations of more than 150 ppm H_2S occurred frequently. At a level of 150 ppm health effects such as headaches, dizziness, nausea and imbalance start occurring. The highest reported measured value was 4100 ppm H_2S which leads to direct loss of consciousness and death within minutes.

- The H_2S-concentration rises very quickly after the start of mixing and leads (very) rapidly to a peak value.
- The measured H_2S-concentrations vary strongly even during periods in which operational circumstances and actions were equal.
- Elevated H_2S-concentrations above 10 ppm during longer periods of time (15 minutes) were frequently reported.
- On the basis of a couple research papers it appears that feed concentrate-based rations leads to higher H_2S-concentrations.
- On the basis of a couple research papers it appears that lower mixing speeds leads to lower H_2S-concentrations.

The preliminary results of the measurements of the H_2S concentrations in a manure pit of a Dairy barn are showing that mixing of manure leads to such a release of H_2S that health hazards due the inhalation of toxic manure gases is greatly increased. Taking appropriate safety measures during mixing of manure is therefore an absolute necessity for a safe and healthy working environment. The safety measures have to be fully implemented before the start of mixing, since the H_2S-contrations rises very quickly after the start of mixing. Since H_2S-concentrations vary greatly even at similar circumstances one cannot trust the working environment is safe if nothing happened before. During the periods of pumping the H_2S concentrations could also be elevated, but not as much as during mixing of the manure. During periods when no manure was mixed or being pumped in total 10 of 313 days the H_2S concentrated was slightly elevated.

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References

1. Hietkamp D. Als vogels het loodje leggen - Gevaarlijke gassen op boerderij. Plattelands Post, 2010, 40: 6-8.
2. Meesters T. Fatale afloop mest mixen – Vergiftiging pinken door gassen uit mestkelder. Veeteelt, 2012, 29: 2:27.
3. OVV. Dodelijk ongeval in mestsilo te Makkinga. Onderzoeksraad voor Veiligheid, February 2014. Den Haag, The Netherlands.
4. Anonymous. Koeien dood bij mixen mest. Leeuwarder Courant, 9 April, 2015.
5. Anonymous. Kalfjes dood mixen van mest. Leeuwarder Courant, 16 April, 2015.
6. Anonymous. Brandweer redt man die onwel raakte bij werk aan mestopslag. Leeuwarder Courant, 17 April 2015.
7. Middelkoop J. Recente mestongevallen. Available online at http://www.hazmatcat.nl/html/mestgassen.html (accessed the 24th February, 2016)
8. Morse DL, Woodbury MA, Rentmeester K. Farmer D. Death caused by fermenting manure. Journal of the American Medical Association, 1981, 245, 1: 63-64.
9. Donham KJ. Acute toxic exposure to gases from liquid manure. Journal of Occupational medicine, 1982, 24, 2: 142-145.
10. Hallam DM, Liao J, Choi K. Manure pit injuries: rare, deadly, and preventable. Journal of Emergencies, Trauma, and Shock, 2012, 5, 3: 253-256.
11. Andriamanohiarisoamanana FJ. Sakamoto Y. Yamashiro T. Yasui S. Iwasaki M. Ihara I. Tsuji O. Umetsum K. Effects of handling parameters on hydrogen sulfide emission from stored dairy manure. Journal of Environmental Management, 2015, 154: 110-116.
12. Anoniem. Onder emissiearme vloeren zit H2S. Agrabeton, 2014. http://www.cementenbeton.nl/publicaties/agrabeton/dossiers/vloeren-en-verhardingen/vloeren/onder-emissiearme-vloeren-zit-h2s.

13. Middelkoop J. Kiek uut met stront – Leidraad veilig werken in mestopslagen. December, 2013. Soest, The Netherlands.
14. Counotte GHM. Van Keulen B. Lieben GW. Mulder E. Van der Veen LT. Verbiesen D. Zandstra P. Gevaren bij het mixen van mengmest in ligboxenstallen: het vrijkomen van zwavelwaterstof en blauwzuurgas. Gezondheidsdienst voor Dieren, January, 1988. Deventer, The Netherlands.
15. Groves JA. Ellwood PA. 1991. Gases in agricultural slurry stores. Annals of Occupational Hygiene, 1991, 35, 2: 139-151.
16. Patni NK. Clarke SP. Transient hazardous conditions in animal buildings due to manure gas released during slurry mixing. Applied Engineering in Agriculture, 1991, 7, 4: 478-484.
17. Uenk, GH. Demmers TGM. Hissink MG. Luchtsamenstelling onder de overkapping van mestsilo's vóór en na het mixen van de mest. IMAG-DLO, May, 1993 Wageningen, The Netherlands.
18. Scully H. Frost JP. Gilkinson S. Lenehan JJ. Research into hydrogen sulfide (H2S) emissions from stored slurry which undergone low rate aeration. Teagasc Grange Beef Research Centre, March, 2007. Dunsany, Ireland.
19. Stevens RJ. Laughlin RJ. Frost JP. Effects of diet and storage time on the concentration of sulphide in dairy-cow slurry. Bioresource Technology, 1993, 45, 1: 13-16.
20. Andriamanohiarisoamanana FJ. Sakamoto Y. Yamashiro T. Yasui S. Iwasaki M. Ihara I. Tsuji O. Umetsu K. Effects of handling parameters on hydrogen sulfide emission from stored dairy manure. Journal of Environmental Management, 2015, 154: 110-116.
21. KNMI. Weather statistics Leewarden Juni-July 2015. Available online at https://weerstatistieken.nl/leeuwarden/2015/juli (accessed the 16th June, 2016).