Emissions of selected climatically relevant gases from sugar beet mash in open storage

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Abstract

Due to the seasonally limited availability of sugar beets in Germany different conservation and storage methods for generating biogas have been developed to ensure all-year use. The following experiment aimed at the quantitative determination of emitted nitrous oxide (N_2O), methane (CH_4) and carbon dioxide (CO_2) from sugar beet mash in practice-oriented open storage (given in lagoons) under simulated practically relevant environmental conditions on an experimental scale.

A mash of freshly harvested sugar beets was stored indoors (mean 20°C) in three differently dimensioned experimental containers (volume vs. surface) for 31 days under systematic moistening and ultraviolet-light. Gas samples were discontinuously taken by the closed chamber method. Before and after measuring wet chemical lab-examinations were made. Each of the three variants showed quantitatively different accumulated amounts (between 2.36 and 7.33 g N_2O t^{-1}) and different courses of N_2O emissions, which were always limited to the first eight days of storage. In a prior measurement (mean 5°C) an accumulated release of 21.25 g N_2O t^{-1} during 33 days of emission was found out. After the fermentation process, detected by a decrease of CO_2 emissions, the N_2O emissions stopped, not caused by the missing availability of nitrogen. A release of CH_4 was never detected.

The extent of N_2O potentially emitted in the time of fermentation suggests the urgency of an examination in practice. The applied method is able to offer reliable field work data for the consideration of an ecological aspect in the evaluation of the presented conservation and storage method.

Keywords: Fermentation, lagoon, temperature, nitrous oxide, carbon dioxide, closed chamber method.

1. Introduction

In the last years sugar beets have been used increasingly as a substrate for generating biogas. From a procedural point of view an all-year availability of sugar beets is aimed for. That is why in practice different storing methods all comprising a fermentation process have been developed. For a reliable evaluation of the different methods a comparison of procedural, economic and ecologic aspects is needed.

A procedure widely spread in Germany is the storage of mashed sugar beets in film-lined basins without any structural cover. Because of the strong tendency of freshly mashed, pulpified sugar beets to ferment within a short time a mushy, alcohol-containing paste with a pH-value between 3.3 and 3.5 develops, which can be pumped automatically into the fermenter throughout the year. During the storage, caused by weathering and substantial conversions, a crusty layer of about 15 centimeters thickness develops at the surface “protecting” the material below from substantial aerobic conversions. The occurring processes in the upper layers are involved with big losses of organic dry mass (DM) (Weissbach, 2013), which shows a reduced amount of biogas produced per unit of mass.

The experiments aimed for a quantitative determination of gaseous emissions from open-stored sugar beet mash in context with determining substantial losses. The influence of the relationship between volume and surface of the containers as well as the influence of the surrounding temperature were examined. The tests made on an experimental scale and in the main under practically oriented conditions are meant to offer improved knowledge that can be put into practice. Gas samples were taken and analyzed for nitrous oxide (N_2O), methane (CH_4), carbon dioxide (CO_2) and oxygen (O_2).

2. Materials and Methods

2.1. Sugar beets, experimental containers and environment

Within the scope of experiments there were two series of measurements. The first took place as a preliminary test in the period between 2014/15, the second in 2015/16.

Table 1. Geometric and volumetric construction of the experimental containers (mean).

variant	**161in**	**4in**	**18in**	**17out**
storage		indoor (±20°C)		outdoor (±5°C)
diameter cm (bottom)	10.3	22.0	22.0	22.0
diameter cm (top)	10.3	25.5	25.5	25.5
height cm	206.0	26.0	26.0	26.0
base cm^{-2}	83.3	380.1	380.1	380.1
fill level cm (day 1)	180.0	5.0	20.0	19.2
FM kg (day 1)	13.4	1.7	7.0	6.6
FM g cm^{-2}	**161.0**	**4.4**	**18.4**	**17.4**

The geometrical construction of the containers was determined in a way that showed the different relationships between volume and surface of the mash. The naming of the different variants followed the respective amount of mash per surface unit (g cm^{-2}) and the location of storage.

In the course of the second, essential series differently dimensioned experimental containers (161in, 4in, 18in; Table 1, Figure 1) were filled with a mash of freshly harvested sugar beets, each in a four-fold repetition and stored for 31 days. All twelve containers were permanently stored in a ventilated and heated room. According to a personal data collection on a biogas plant in November 2014 concerning a basin filled with 2500 t of sugar beet mash different temperatures in different depths (0.1-2.0 m) were measured. Following the average temperature of 17.7°C a constant room temperature of about 20.0°C was chosen. At three different places in the room and in variant 161in at a height of 90 cm loggers (Fa. Testo; 174-H, n=3; 174-T; n=3) were set in place to measure temperature and humidity. Immediately above the experimental containers ultraviolet-lamps (20 W, 350 nm, n=4) were installed and continuously running to simulate the effect of the sun's rays on the surfaces of the mash (Weissbach, 2013). To avoid a drying out of the material water was added systematically to the mash. The added amount of water was fixed according to a drawn-up, theoretical model which showed a loss of fresh mass (FM) of 0.62 % (variant 4in) or 0.49 % (variant 18in) per day of storage. For variant 161in an increase of fresh mass of 0.08 % per day was given. While storing and removing the mash wet chemical lab-examinations were carried out.

The preliminary experiment included one variant (variant 17out; Table 1, Figure 1) and four experimental containers filled with freshly mashed sugar beets stored in the inner courtyard of the institute exposed to natural climatic conditions (rainfall and sunshine) for 44 days. A logger (Fa. Testo; 174-T; n=1) recorded the surrounding temperatures. There was no wet chemical lab-examination.

2.2. Gas measurements

In order to be able to lock the experimental containers airtight if required structural coverings had been developed, each of them containing a septum. In both series of experiments the closed chamber method with evacuated vials (20 ml) and multiple sample needles (20Gx1″/0.9x25 mm) was applied (Figure 1). Immediately after covering the containers (0 min) samples from all headspaces were taken at 5-minute intervals (5, 10 and 15 min). Additionally, samples of the surrounding air were taken. During the preliminary tests samples from the headspaces were taken every 20 minutes. The measuring intervals in both series were adapted to the meanwhile worked out analysis results. They tendentially declined in number in the course of the storage (see Figure 2 and 3).

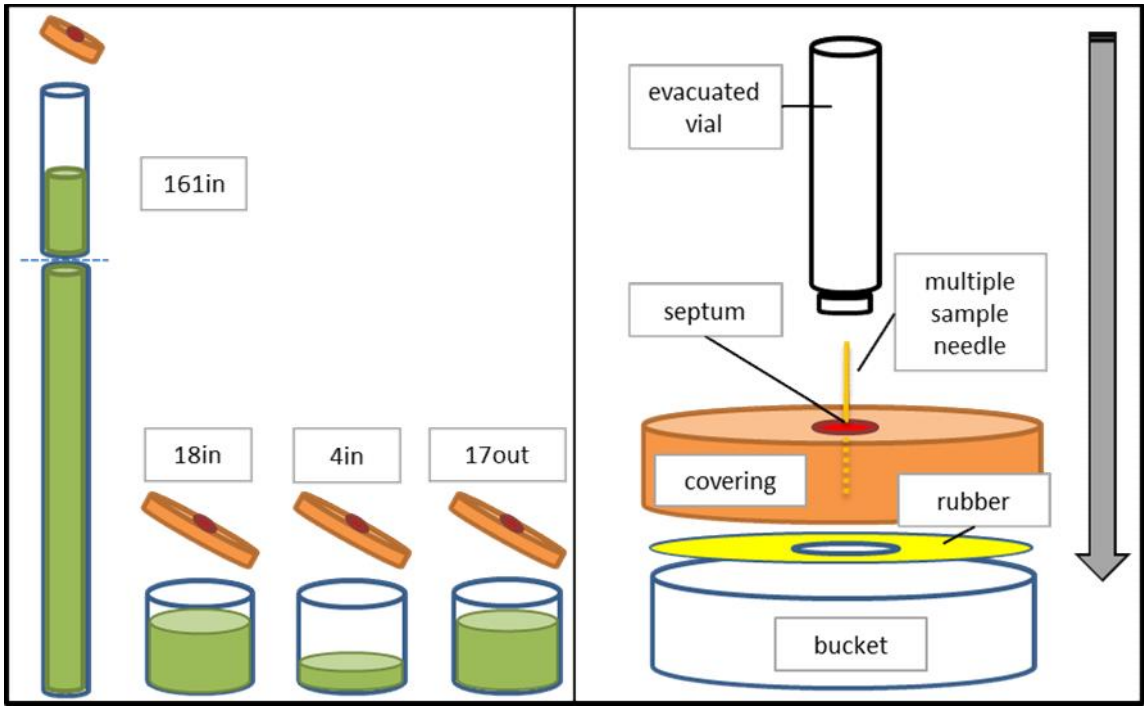

Figure 1. Scheme of experimental containers (left) and of taking gas samples (right).

2.3. Calculations of gaseous emissions

Based on the gas chromatographic analysis (8610 C, SRI instruments, Torrance, USA) of the vials' contents (Wulf et al., 2002) by an external institution it was possible to determine the increase of the gases' concentrations per unit of measurement (ppm min^{-1}) for CO_2, N_2O and CH_4 or the decrease of O_2 in the respective headspace at the moment of measuring. By including the volume of the headspace and the mass of sugar beet mash at the moment of measuring the calculation of the amount of emitted gases per unit of weight and time or per unit of surface and time was possible. The recorded results in between determined the different periods of storage in the experimental series.

3. Results and Discussion

3.1. Storage conditions and visual quality of the fermented material

During the 31 days of storage the average temperature in the room was 20.2°C (2.1), measured out of the reach of the direct radiation of the ultraviolet-light, with an average humidity of 44.9 % (3.9). The temperature of the mash was 19.77°C (3.1). During the preliminary tests the average surrounding temperature right next to the experimental containers was 5.06°C (2.9). The amount of rainfall amounted to 75.1 L m^{-2} or 2.85 L per container. The fresh mash showed an average increase of 31.1 % of mass compared to the initial filling.

On completion of the measurements the ensiled sugar beet mash showed visible differences between the different procedures and experimental series. Variant 4in showed a negatively changed, slimy consistency as well as a darker colouring and a pungent smell with a slight formation of mould. To some extent variant 18in showed a mouldy cover, too. The ensiled mash in variant 161in didn't show any visible deficiencies, nor did the mash from the preliminary tests.

3.2. Emission of gases

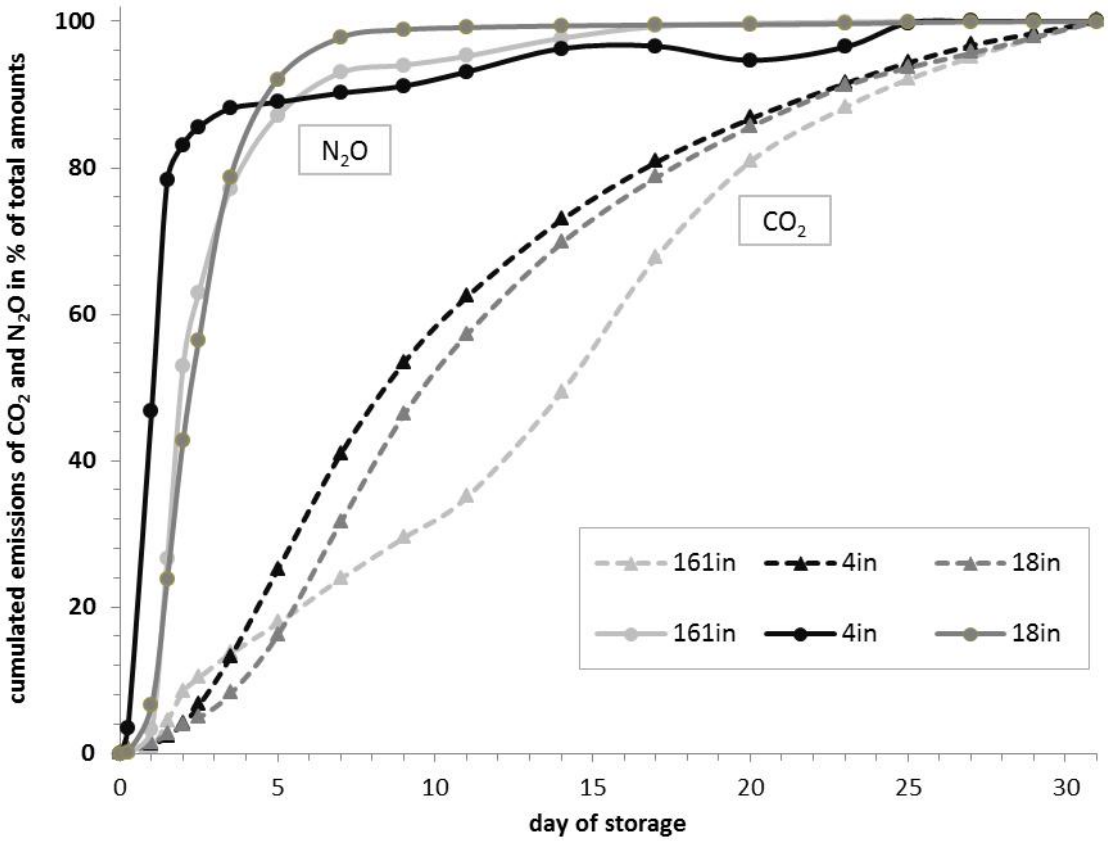

Figure 2. N_2O and CO_2 release rates (mean) for the indoor stored variants over the duration of storage.

Figure 2 shows variant 4in with a rather quick emission of N_2O starting at a high level, as well as a quicker release of CO_2. The calculations of CO_2 for 4in and 18in (not given in Figure 2) showed emission rates of 22.35 kg t^{-1} d^{-1} on day 5 or 9.78 kg t^{-1} d^{-1} on day 7. Variant 161in is characterised by a less intensive release of CO_2 in the course of the experimental period. In general, the line graph with the CO_2 emissions shows an extended continuous course while relevant N_2O emissions in the 12 containers were limited to the first eight days, especially to the first 36 hours. There was no release of CH_4 in the course of the tests.

Table 2. Cumulated emission of N_2O and CO_2 over 31 days* of sampling for all variants.

	variant	mean (n=4)	SD	spread abs.	CC (in %)
N_2O g t^{-1}	161in	6.96	0.62	1.27	8.91
	4in	2.36	0.43	0.98	18.22
	18in	7.33	1.51	3.38	20.60
	17out*	21.25	8.53	19.65	40.14
CO_2 kg t^{-1}	161in	41.23	8.66	18.70	21.00
	4in	268.29	8.75	19.86	3.26
	18in	76.30	7.96	19.29	10.43
	17out*	40.90	16.74	29.70	40.93

with SD = standard deviation and CC = correlation coefficient

* 17out = 44 days of sampling, see Figure 2

In spite of the delayed start of the emitting process (Figure 2) the accumulated amount of N_2O for 18in was by 0.37 g higher than for 161in (Table 2). However a conducted unpaired t-test showed no significant differences ($p \leq 0,05$). A conducted unpaired t-test for 18in and 17out showed significant differences ($p \leq 0,05$) for the cumulated N_2O emissions between this two variants. Compared to 18in variant 17out showed a cumulated emission of CO_2 which was by 46 % lower. Variants 161in and 17out, both characterized by an increase of fresh mass, showed an accumulated amount of CO_2

with an absolute deviation of 0.33 kg. But variant 17out, stored at about 5°C, emiout

tted the triple amount of N_2O. CO_2 emissions of 4in were 5.1-times higher than the average of the other variants. The differences in N_2O emissions from 4in are significantly different from other variants as proved by conducted t-Tests ($p \leq 0,05$).

Variant 17out showed the strongest variations of all variants concerning N_2O as well as CO_2. The CC for both gases within a variant was remarkably different, except for variant 17out.

Table 3. Mean nitrogen (N-)-content for indoor stored variants after 31 days.

variant	Total-N (Kjehldahl)	NH_4-N	NO_3-N	NO_2-N
	mg kg^{-1} FM			
161in	2035.0	83.1	11.2	< 3
4in	2452.5	48.5	7.7	< 3
18in	2312.5	36.9	3.5	< 3

As shown by the results of the wet chemical lab-analysis of the ensiled samples the stop of the release of N_2O can't be attributed to a lacking availability of nitrogen (N) (Table 3). The differences concerning the content of the different N-fractions and different ways of developing N_2O won't be discussed here.

The cumulative emission rates for 17out (Figure 3) showed a distinctive feature on day 33 of storage. There is a relevant decrease of CO_2 and N_2O release or O_2 consumption (here amount in g multiplied by *10 for a better visualization). A high amount of emitted CO_2 from stored organic material is caused by microbiological metabolism during fermentation, reheating or decomposing processes (Pahlow et al., 2003). Because of a decrease of the pH-value in the sugar beet mash through fermentation most of the lactic acid bacteria, producing CO_2 as a by-product, are inactivated. The characteristic pH-value in completely ensiled sugar beet mash is between 3.3 and 3.5. Yeasts, typically active in an anaerobic way in sugar beet mash, are less influenced in their activity. O_2-using yeasts and moulds at the surface resistant to low pH-values partly reduce the amount of generated acids (Weissbach, 2013). This way further emissions of CO_2 can be measured even after the fermentation process ended (Figure 3). As a consequence the emission of CO_2 from the material is usually strongly reduced after fermentation. There is no relationship between the consumpction of O_2 at the surface of the mash and anaerobic fermentation of the complete material. Considering the statistical results (SD and CC in Table 2) there is no direct functional connection between N_2O and CO_2 emissions.

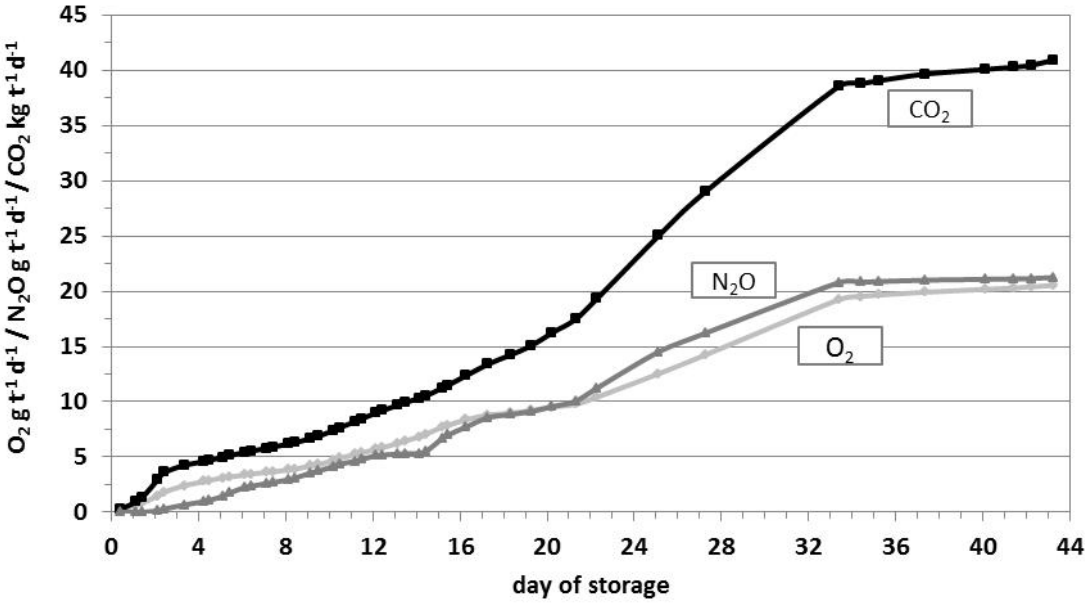

Figure 3. Cumulative N_2O and CO_2 release rates and O_2 consumption rate (amount*10) for 17out over 44 days of storage at about 5°C.

The extent of the respiration by aerobic microorganisms in fermenting material is determined by the amount of O_2 in the material, the temperature and the pH-value. An increased temperature leads to a more intensive respiration (Rooke and Hatfield, 2003) which stands for a quicker consumption of O_2 in the mash and a fermentation process starting more

quickly. As carried out in the surveys the temperature of the mash is mainly determined by the surrounding temperature. According to Gross and Riebe (1974) the optimum temperature for lactic acid bacteria is between 20 and 40°C; the critical pH-value for an activity of lactic acid bacteria is given between 3.0 und 3.6 with respect to species-specific differences. As a consequence, the temperature of about 20°C must have led to a quicker decline of the pH-value than the temperature of about 5°C.

In the following, (incomplete) denitrification is assumed to be a decisive bio-chemical releasing process because of parameters like a high available amount of nitrate and carbon compounds which can be broken down easily, in combination with the given aerobic and anaerobic conditions in freshly mashed sugar beets (Leick, 2003). Besides, as the sugar beets were not cleaned, typical microorganisms from the soil are transferred into the mashed beets and are probably subsequently responsible for most of the N_2O production. The impeding influence of temperatures below 5°C on the intensity of (de-)nitrification in soils and a shifting of the relationship between N_2O und N_2 during denitrification have been described sufficiently (Granli and Bøckmann, 1994 in Leick, 2003). The optimum pH-value for the process of denitrification in soils is between 7 and 8. In general, microbiotic metabolism is increasingly held back by falling pH-values (Ottow, 2011).

Influenced by the different storage temperatures in the experimental containers the metabolic activity of the microorganisms determines the course of the ensiling process. An inhibiting influence caused by lower temperatures results in a slowed down reduction of the pH-values (here identified by the CO_2 rates), which explains the extended duration and this way the amount of N_2O as well. This context becomes evident in variant 161in (about 20°C) and variant 17out (about 5°C), to some extent in 18in (about 20 °C). In variant 17out, showing by far the highest accumulated N_2O emissions (Table 4), an accumulation of a bigger amount of rainwater in the containers because of the relatively low depth e.g. compared to a lagoon could have resulted in a stronger formation of N_2O. According to Ottow (2011) a strong saturation of soils leads to an inhibited diffusion of O_2 and strictly anaerobic conditions supporting an intensive denitrification. The influence of the different FM-outcomes (see 4in, 18in vs. 17out) on the amount of the recorded N_2O emissions in the test series cannot be further determined in the scope of these experimental tests. Studies by Weinberg et al. (2001) prove that chopped maize stored for 63 days at temperatures between 37 and 41 °C compared to a temperature of 28°C (1.0) showed a comparatively higher pH-value with a reduced content of lactic acid and bigger mass losses with a stronger susceptibility to reheating processes under aerobic conditions at the end of storage. Storage at 20°C with a large surface exposed to O_2 could indicate a tendency to an increased reheating up to a decay of the sugar beet mash in variant 4in.

For N_2O a positively correlated relationship between the amount of emission and the amount of mash can be deduced. The quantity of released N_2O during the ensiling process (i.e. fermentation of lactic acid and anaerobic activity of yeasts) is mainly determined by the amount of sugar beet mash. Concerning the cumulated amount (6.96 g t^{-1}) the variant with the smallest surface (161in) was only slightly exceeded by variant 18in (7.33 g t^{-1}) showing a mass which was 9-times smaller per cm^{-2}. The crust, here found as a mash of about 5 cm thickness, correspondingly given in all variants, produced a relatively small part of the N_2O emissions.

3.3. Quantitative classifying of the emitted gases

According to Haenel et al. (2016) and Bouwman (1996) one hectare of sugar beet farmland fertilised with 100.0 kg N per year causes an emission of 1.0 kg N_2O-N ha^{-1} a^{-1}. Based on a yield of 80 tons of sugar beets per hectare and year Table 4 shows the emission results for the different variants founded on the mean worked out emission rates.

Table 4. Emissions of N_2O and N_2O-N in the variants related to N_2O-N per hectare sugar beet field per year.

	variant	N_2O abs.	N_2O-N abs.	% of 1 kg N_2O-N ha^{-1} a^{-1}
N_2O g 80 t^{-1}	161in	556.8	354.3	35.4
	4in	188.8	120.2	12.0
	18in	586.4	373.2	37.3
	17out	1700.0	1081.8	108.2

The results in Table 4 have to be seen as additional emissions into the atmosphere, which have to be added to the amount of gas released from a hectare of sugar beet farmland. The examination of the different emitted CO_2 amounts with regard to effects on the climate does not correspond to the production of biogas. In general the varying amounts of released CO_2 in the different variants are an indicator for losses of DM. As CH_4 was not detected and atmospheric O_2 was used by microorganisms these three gases have not been considered concerning a possible ecological evaluation.

4. Conclusions

Because of the volumetric conditions and the described storage conditions the emissions from 161in can be considered very practically oriented. Consequently, with 6000 t of stored material in a lagoon theoretically there could be emissions up to 42 kg N_2O possible. The results of the measurings at temperatures of about 5°C show even though in more theoretical way, a far bigger potential of emissions.

The conversion processes shown in the material determine the extent of emissions concerning CO_2 as well as N_2O. Under the same environmental conditions the amount of released N_2O is dependent on the mass of mashed sugar beets. The quickest possible reduction of the pH-value to lower than 3.5 has a positive effect on the end of N_2O emissions. Obviously, N_2O is produced spontaneously and throughout the whole fermenting process of freshly mashed sugar beets. In order to minimize DM losses the surface of the mash should be as small as possible. The aerobic conversions in the crust are part of the storage method.

A direct transmission of the results into practice is not practicable for the time being. Based on a compliance with strict regulations adapted to a greater number of samples and different placements of sampling points in a lagoon, the used methodology will offer data with a high precision. A possible methodological, but different sampling design is given by Amon et al. (1996) handling emission measurements concerning livestock farming.

The results prove that the recent approach offers the possibility to quantify emissions from a lagoon filled with mashed sugar beets in a reliable way. It is necessary to examine the emissions in practice as well as to carry out a validation of the methodology. Then the N_2O emissions detected in practice can be taken into consideration from an ecological point of view.

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