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Biogas crops grown in energy crop rotations: Linking chemical composition and methane production characteristics

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HIGHLIGHTS

- Methane formation characteristics from 405 silages of 43 crop species are presented.
- Silages from a wide range of crop species are well suited for biogas production.
- Besides lignin, products of silage fermentation significantly affect methane yield.
- The content of nitrogen-free extracts mainly determines methane contents.
- The fibre fraction has the largest impact on the rate of methane production.

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ABSTRACT

Methane production characteristics and chemical composition of 405 silages from 43 different crop species were examined using uniform laboratory methods, with the aim to characterise a wide range of crop feedstocks from energy crop rotations and to identify main parameters that influence biomass quality for biogas production. Methane formation was analysed from chopped and over 90 days ensiled crop biomass in batch anaerobic digestion tests without further pre-treatment. Lignin content of crop biomass was found to be the most significant explanatory variable for specific methane yields while the methane content and methane production rates were mainly affected by the content of nitrogen-free extracts and neutral detergent fibre, respectively. The accumulation of butyric acid and alcohols during the ensiling process had significant impact on specific methane yields and methane contents of crop silages. It is proposed that products of silage fermentation should be considered when evaluating crop silages for biogas production.

1. Introduction

Biogas production via anaerobic digestion has become a well-established technology for renewable energy production in Europe. Several benefits of this process such as the reduction of greenhouse gas emissions, inactivation of pathogens, recycling of nutrients and the potential for flexible, demand-driven energy supply makes it a valuable means that contributes to the renewable energy mix and facilitates regional economic structures and employment in rural areas (Fröschle et al., 2015; Molinuevo-Salces et al., 2014; Zegada-Lizarazu and Monti, 2011). The anaerobic digestion process is capable of converting complex organic feedstock into methane, including agricultural by-products, organic wastes as well as animal manure and energy crops. The use of energy crops as feedstock in agricultural biogas plants is common in several European countries, mainly due to their high specific methane yields which makes the co-digestion of low-yielding animal manure feasible, and due to limited availability of industrial organic wastes (Herrmann and Rath, 2012; Nges et al., 2012). However, the production of energy crops is debatable since it requires agricultural land and can compete with food and feed supply. Furthermore, biogas production from energy crops largely concentrates on maize and the sustainability of maize-based biogas production is in question (Herrmann, 2013).

One important measure towards a sustainable biogas crop production would be the integration of energy crops in crop rotations. Crop rotations can provide versatile benefits such as the control of diseases, reduction of agrochemical and fertiliser input, reduced soil erosion, a more effective use of water and nutrients, lower economic and climatic risks, and higher biomass yields (Zegada-Lizarazu and Monti, 2011). Owing to the flexibility of the anaerobic digestion process in terms of feedstock conversion, opportunities

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are manifold: a large variety of different crop species can serve as biogas crops, which can be integrated in conventional cropping systems or can be part of multi-purpose cropping systems. They can be integrated as main crops, secondary crops for a second harvest after the main crop in double cropping systems, catch crops or perennial crops. For the adequate planning and design of crop rotations the knowledge of characteristics of a wide range of potential biogas crops is necessary. This regards effects on soil fertility and structure, on weed and disease control, and on biomass yields, but also knowledge about digestibility and methane production characteristics within the anaerobic digestion process is crucial. High methane yield potentials are desired for an efficient biogas production.

Several studies that analyse and compare the methane production potential of different crop species already exist (e.g. Amon et al., 2007; Dandikas et al., 2014; Gissén et al., 2014; Triolo et al., 2011). However, these studies investigate a comparatively low number of different crop species (usually less than 10). Different parameters have been reported to be correlated with the methane production potential of biomasses and several models have been developed for prediction of specific methane yields from biomasses. Promising correlations have previously been found for several chemical components such as acid detergent lignin (ADL), cellulose, acid detergent fibre (ADF), hemicellulose and crude fat (Dandikas et al., 2014; Gunaseelan, 2009; Rath et al., 2013; Triolo et al., 2011). However, correlation studies are usually either based on only few datasets (Dandikas et al., 2014; Triolo et al., 2011), mainly examine waste biomasses (Gunaseelan, 2009; Kafle and Kim, 2013), or focus on differences in methane yields within one crop species (Rath et al., 2013). Crops used as feedstock for biogas production are commonly harvested seasonally as whole crops, and are preserved for year-around supply to the anaerobic digestion plant by wet anaerobic storage via ensiling. It has been shown that ensiling can preserve the methane yield of crop biomass for up to one year or longer, yet the course and products of silage fermentation can significantly influence the specific methane yields of crop biomass (Herrmann et al., 2011). Nevertheless, parameters of ensiling, such as volatile fatty acids and alcohols, have not been included in correlation analyses in literature.

The novelty of the present study lies in that it is based on a comprehensive dataset obtained by the application of consistent methods of analyses and considers the ensiling process which is the typical method used to preserve seasonally harvested crop material for the year-around supply of biomass for biogas production. Analyses include 405 biogas silages from 43 different crops species, crop mixtures or positions within crop rotations (i.e. as main or secondary crop, or catch crop). The objective of the present study is to (1) characterise the chemical composition and methane formation of a wide range of crops grown in energy crop rotations under different agro-climatic conditions in Germany and preserved by ensiling; and (2) identify main chemical parameters that affect the methane production characteristics of biogas crop silages.

2. Methods

2.1. Description of raw materials

Crop material was obtained from energy crop rotations that were cultivated in field plot experiments at 8 different sites in Germany from the year 2005 to 2012 (Gödeke et al., 2007). An overview of crop species, location of cultivation, years and dates of harvest as well as the range of stages of maturity at harvest is given in Table 1. The experimental sites are further described in detail in Table S1 of the supplementary information. Directly after harvest of whole crops, crop materials were chopped to a particle length <20–30 mm and preserved by ensiling. If the dry matter (DM) content at harvest was estimated to lie below 25%, crop materials of annual grass and legume mixtures and forage cereals (catch crops) were wilted to a target DM content of 30–35% prior to chopping and ensiling.

2.2. Silage preparation

All crop materials investigated in the present study were preserved by ensiling. Crops were ensiled in 1.5 L glass silos (J. WECK GmbH u. Co. KG, Wehr, Germany) immediately after chopping. Chopped crop materials were pressed into the glass jars with a manually operated plunger. All silos were filled completely leaving no headspace in the jars, and were subsequently sealed airtight. A glass lid, rubber ring and four metal clamps were used to close the silos in a way which prevented air from infiltrating into the silo but allowed gases formed during ensiling to escape. Silos were stored at 25 °C for a storage period of 90 days. Ensiling in this study was generally conducted without silage additives. Silages were prepared in triplicate or quadruplicate for each variant.

2.3. Chemical analyses

After taken out of the silos, ensiled crop materials were immediately frozen and stored at −18 °C before they were further processed for analyses of chemical composition and methane production. DM and organic dry matter (ODM) content were measured by oven drying at 105 °C and ashing of the dried sample at 550 °C according to standard procedures (VDLUFA, 2006). The pH-value of the silages was determined using a measuring electrode Sen Tix 41 (WTW, Weilheim, Germany). Lactic acid, volatile fatty acids and alcohols were measured in cold water extracts of the silages. A high performance liquid chromatograph (Dionex, Sunnyvale, USA) equipped with an Eurokat H column (Knauer, Berlin, Germany) and refractive index detector was applied for analyses of lactic acid. Analyses of volatile fatty acids (acetic, propionic, n-butyric, iso-butyric, n-valeric, iso-valeric and n-caproic acid) and alcohols (ethanol, propanol, 1,2-propanediol, 2,3-butanediol) were conducted using a gas chromatograph (Agilent Technologies Inc., Santa Clara, CA, USA) equipped with a PERMABOND® FFAP capillary column (Machery-Nagel GmbH & Co KG, Düren, Germany) and a flame ionisation detector. The DM content of the silages was corrected for losses of organic acids and alcohols during oven drying, as suggested by Weißbach and Kuhla (1995). All parameters that are based on DM, refer to the corrected DM content.

Crude fat, crude fibre, neutral detergent fibre (NDF), ADF and ADL were analysed as described in detail previously (Herrmann et al., 2011, 2014), using the Ankom^{XT10}-Extractor (Ankom Technology Corp., Macedon NY, USA) for crude fat and the Ankom^{2000} Fibre Analyser system and filter bag technology (Ankom Technology Corp., Macedon, NY, USA) for fibre analyses. Elemental carbon and nitrogen were detected with an elemental analyser (vario EL, Elementar Analysensysteme GmbH, Hanau, Germany), applying the DUMAS combustion method (VDLUFA, 2006). Crude protein was calculated as 6.25 times the elemental nitrogen content. The C/N ratio of silages was calculated as the elemental carbon content divided by the elemental nitrogen content. Nitrogen-free extracts were obtained by subtracting the crude protein, crude fibre, crude fat and crude ash content from $100\%_{DM}$. The cellulose content is represented by the difference between ADF and ADL, and the hemicellulose content is represented by the difference between NDF and ADF.

2.4. Batch anaerobic digestion test

Biogas production characteristics including specific methane yields of silages and the quality of the produced biogas were

Table 1
Description of raw materials.

Crop species	Taxon	Location	Stage of growth[1]	Year of harvest	Period of harvest (day/month)	No of variants
Main and secondary crops						
Sugar beet	*Beta vulgaris*	SN	91	2011, 12	18/09–20/09	2
Spring barley/Italian ryegrass/ hybrid ryegrass	*Hordeum vulgare, Lolium multi-florum, Lolium* × *hybridum Hausskn.*	MP	77–83	2010, 11	27/06–05/07	2
Maize	*Zea mays*	BB, BV, BW, LS, MP, SN, TH	79–87	2005, 06, 07, 09, 10, 11	18/08–14/10	59
Winter barley	*Hordeum vulgare*	BB, BV, BW, LS, SN, TH	63–83	2009, 10, 11	20/05–15/06	13
Winter triticale	*X Triticosecale*	BB, BW, LS, SN, TH	71–83	2006, 07, 09, 10, 11, 12	05/06–04/07	23
Marrow stem kale	*Brassica oleracea var. medullosa Thell*	BV, HS	41–50	2009	23/09–19/10	2
Spring barley	*Hordeum vulgare*	BW, LS, TH	57–85	2005, 06	30/06–13/07	5
Winter rye/winter triticale	*Secale cereale/x Triticosecale*	BB, MP	71–83	2009, 10	02/06–22/06	4
Potatoe (tuber)	*Solanum tuberosum*	SN	99	2011	06/09	1
Oat/forage pea/false flax	*Avena sativa/Pisum sativum/Camelina sativa*	BB	73–79/ 75–83/ 83–85	2005, 09, 10, 11	23/06– 12/07	5
Winter rye	*Secale cereale*	BB	71–85	2007, 09, 10, 11	20/05–16/06	8
Winter wheat	*Triticum aestivum*	BV	83–85	2010, 11, 12	07/07–12/07	3
Sudangrass hybrid	*Sorghum bicolor x. sudanense*	BB, BW, SN, TH	47–85	2005, 06, 07, 09, 10, 11, 12	11/08–19/10	40
Forage sorghum	*Sorghum bicolor x bicolor*	BB, BW, LS, TH	57–85	2005, 06, 09, 10, 11	15/09–18/10	15
Winter rye/fodder vetch	*Secale cereale, Vicia villosa*	BV	71–83	2009, 10, 12	09/06–27/06	3
Winter barley/turnip rape	*Hordeum vulgare, Brassica rapa*	BV	43–51, 61–65	2009, 10	11/05–19/05	2
Spring rye	*Secale cereale*	BB, SN	71–83	2005, 06	28/06–14/07	7
Oat	*Avena sativa*	BW, LS, SN, TH	73–83	2005, 06, 09, 10	30/06–21/07	8
Amaranth	*Amaranthus cruentus* L.	BV, HS	75–79	2009	23/09–19/10	2
Quinoa	*Chenopodium quinoa*	BV	85–93	2008, 12	18/09–24/10	4
Rapeseed	*Brassica napus*	BB, BV, BW, SN	65–83	2006, 10, 11	02/05–14/07	5
Sunflower	*Helianthus annuus*	BB, BW	73–87	2005, 06, 09, 10, 11	20/07–17/09	10
Forage pea	*Pisum sativum*	BV	76	2011	30/09	1
Buckwheat	*Fagopyrum esculentum*	BV, HS	75–93	2009, 11, 12	31/08– 24/09	6
Catch crops						
Forage triticale	*X Triticosecale*	BW	29–53	2010, 11	10/05–20/05	2
Forage barley	*Hordeum vulgare*	BW	29–57	2010, 11	10/05–20/05	3
Forage rye	*Secale cereale*	BB, BW, LS, SN, TH	45–59	2006, 07, 10, 11	24/04–18/05	15
Landsberger mixture: Fodder vetch/crimson clover/Italian ryegrass	*Vicia villosa/Trifolium incarnatum/Lolium multiflorum*	SN	61–69	2011, 12	12/05–24/05	2
Sudangrass hybrid	*Sorghum bicolor x sudanense*	BB, BV, BW, LS, TH	34–83	2009, 10	01/10–19/10	7
Forage sorghum	*Sorghum bicolor x bicolor*	BV, SN	55–59	2009, 10	24/09–18/10	3
Annual ryegrass	*Lolium multiflorum Lam. var. westerwoldicum Wittm.*	BW, BV, LS, SN, TH	51–79	2011, 12	02/08–24/09	9
Phacelia	*Phacelia tanacetifolia*	BW, BV, LS	63–71	2012	24/09–11/10	3
Fodder radish	*Raphanus sativus var. Oleiformis Pers.*	BB, BW, SN, TH	51–69	2005	22/09–08/11	5
Buckwheat/phacelia	*Fagopyrum esculentum/Phacelia tanacetifolia*	BV	71	2012	24/09	1
Annual grass and legume mixtures						
Ryegrass mixtures	*Lolium multiflorum Lam./Lolium* × *hybridum Hausskn./ Lolium perenne* L.	BB, BV, LS, MP, TH	30–81	2006, 07, 08, 09, 10, 11	26/04–10/06 (1st cut) 14/05–10/08 (2nd cut) 26/07–22/10 (3rd cut) 23/09 (4th cut)	66
Clover grass mixtures	*Lolium multiflorum Lam./Lolium* × *hybridum Hausskn./ Lolium perenne* L., *Festuca pratensis, Phleum pratense, Trifolium pratense*	HS, LS, TH	20–63	2006, 07, 08, 09	26/04–29/05 (1st cut) 10/06–16/07 (2nd cut) 19/09 (3rd cut)	17
Alfalfa grass mixtures	*Dactylis glomerata/Arrhenatherum elatius/Festuca pratensis x*	BB, BW, TH	51–60	2005, 06, 07,	11/05–05/06	5

(*continued on next page*)

Table 1 (*continued*)

Crop species	Taxon	Location	Stage of growth[1]	Year of harvest	Period of harvest (day/month)	No of variants
	Lolium multiflorum Lam./Phleum pratense L./Medicago sativa			09, 11, 12	(1st cut) 19/06–20/07 (2nd cut) 22/08–23/09 (3rd cut)	
Alfalfa clover grass mixtures	*Festuca pratensis x Lolium multiflorum Lam./Phleum pratense/Arrhenatherum elatius/Trifolium pratense/ Medicago sativa*	SN, TH	41–59	2006, 09, 12	22/05–26/05 (1st cut) 16/07 (2nd cut) 19/09 (3rd cut)	16
Perennial crops						
Tall wheatgrass	*Elymus elongatus subsp. ponticus cv. Szarvasi-1*	BV	60–69	2012	28/06 (1st cut), 24/10 (2nd cut)	2
Country mallow	*Sida cordifolia* L.	BV	50–65	2012	02/08–04/10	3
Jerusalem artichoke (haulm)	*Helianthus tuberosus*	BB, TH	39–61	2005, 06, 07, 11	29/08–09/10	8
Miscanthus	*Miscanthus × giganteus*	SN	33–77	2006, 07	24/07–22/08	4
Cup plant	*Silphium perfoliatum*	BV	77–85	2011, 12	07/09–28/09	4

[1] Growth stages are determined according to the BBCH-scale described by Meier (2001); BB: Brandenburg; BV: Bavaria; BW: Baden-Württemberg; HS: Hesse; MP: Mecklenburg-West Pomerania; LS: Lower Saxony; SN: Saxony; TH: Thuringia.

analysed in batch anaerobic digestion tests. Tests were performed in 2 L glass vessels filled with 1.5 L of inoculum and 50 g of crop feedstock. The inoculum consisted of digestate of previously completed batch digestion tests with crop materials (average chemical characteristics and standard deviation: pH 8.1 ± 0.3; DM 3.7 ± 0.8%; ODM 59.5 ± 5.3%$_{DM}$; N 2.8 ± 0.6 g kg^{-1}; NH_4–N 1.4 ± 0.3 g kg^{-1}; organic acids 1.5 ± 0.6 g kg^{-1}). A ratio of $ODM_{Substrate}$ to $ODM_{Inoculum}$ (a_i) of 0.5 ± 0.2 was met for the tests. Vessels were placed in a water bath that maintained a temperature of 35 °C and were incubated for 30 days. In order to dissolve scum layers vessels were shaken manually once a day. Biogas formed during the incubation period was collected in wet gas meters and was measured by displacement of an acidified saturated NaCl barrier solution (VDI, 2006). The volume of biogas was determined daily, corrected for the volume of biogas produced by the inoculum without substrate and normalised to standard conditions (dry gas, 0 °C, 1013 hPa). The biogas composition including the content of methane and carbon dioxide was measured with a portable gas analyser equipped with infrared sensors (GA94, Ansyco, Karlsruhe, Germany). A certain amount of biogas was required for analyses of gas composition, which allowed measurement of biogas composition on average 15 times per test. Specific methane yields are calculated as the sum of methane produced during the test period, referring to the ODM of silage added to the test. The methane content equates to the total methane volume produced during the test period divided by the total biogas volume.

2.5. Kinetic analyses

Kinetic analyses were performed in order to assess the rate of degradation of different crop silages during batch anaerobic digestion. A first order differential equation (Eq. (1)) and a modified Gompertz equation (Eq. (2)) were fitted to the cumulative methane production curves from the batch anaerobic digestion tests:

$$y(t) = y_m \cdot (1 - e^{(-k_1 t)}) \tag{1}$$

where, $y(t)$ is the cumulative specific methane yield at time t ($L_N\ kg^{-1}_{ODM}$), y_m is the maximum specific methane yield at theoretically infinite digestion time ($L_N\ kg^{-1}_{ODM}$), t is the time (days) and k is the first order decay constant (day^{-1}).

$$y(t) = y_m \cdot \exp\left\{-\exp\left[\frac{R_m \cdot e}{y_m} \cdot (\lambda - t) + 1\right]\right\} \tag{2}$$

where, $y(t)$ is the cumulative specific methane yield at time t ($L_N\ kg^{-1}_{ODM}$), y_m is the maximum specific methane yield at theoretically infinite digestion time ($L_N\ kg^{-1}_{ODM}$), R_m is the maximum specific methane production rate ($L_N\ kg^{-1}_{ODM}$ day^{-1}), t is the time (days) and λ is the lag phase (days). The half-life (t_{50}) was obtained from the fitted modified Gompertz equations as the time when 50% of the maximum specific methane yield is reached (days). The software Matlab R2009a (TheMathWorks Inc., Natick, MA, USA) was used for kinetic analyses.

2.6. Statistical analyses

Statistical analyses were conducted using the software SAS 9.3 (SAS Institute Inc., Cary, NC, USA). Pearson's correlation coefficients were calculated in order to determine the correlation between the chemical composition, parameters of silage fermentation and methane formation characteristics, and the interrelation among chemical constituents. Multiple regression analyses for the prediction of specific methane yield, methane content, decay constants and half-life were performed stepwise with up to four independent variables by applying the REG procedure and stepwise option in SAS, thereby excluding chemical constituents with strong interrelation effects from regression equations. For comparison of regression models, the coefficient of determination (R^2), the adjusted coefficient of determination (R^2 adj.), the root mean square error (RMSE) and the relative root mean square error (RRMSE) were considered.

3. Results and discussion

3.1. Silage fermentation characteristics

Silages of different crop species revealed diverse silage fermentation characteristics (Table 2). The average DM content ranged from 11.5% to 48.7% (Table 2). Low DM contents were analysed for some of the main crops, such as marrow stem kale, sugar beet, amaranth, quinoa, sunflowers or buckwheat, and for most of the catch crops which are usually harvested at an earlier stage of growth. Despite wilting of the harvested crop material, the average DM content of the annual grass and legume mixtures was partly below the target DM content of 30%. High DM contents were measured for some of the whole crop cereal silages such as winter wheat, spring rye or spring barley, harvested at the development of fruit to ripening stage of growth. As opposed to the DM content, the variation in ODM content between crop species was comparatively low (Table 2).

The DM content is one of the main parameters that influence silage fermentation. The aim of the ensiling process is to reduce the pH of the crop material below a critical value by formation of organic acids, mainly lactic acid, under anaerobic conditions which results in the inhibition of the growth of spoilage microorganism, such as clostridia or enterobacteria (McDonald et al., 1991). Clostridia are more sensitive to acidity at a decreasing water activity, thus, a low DM content necessitates a lower pH of the silage and higher lactic acid formation for inhibition of clostridia (Weißbach et al., 1974). Furthermore, DM contents below 25–30% lead to formation and release of silage effluent associated with additional mass losses (McDonald et al., 1991). High DM contents, on the other hand, can hinder sufficient compaction of the crop material within the silo and promote aerobic deterioration at feed-out (McDonald et al., 1991). A DM content of 28–40% is often stated as a rough estimate for optimal ensiling conditions. However, the critical DM content required to ensure good ensilability also depends on available water-soluble carbohydrates and on the buffering capacity of the crop material (Weißbach et al., 1974). In the present study the predominant number of silages (85%)

Table 2
Dry matter, organic dry matter and parameters of silage fermentation (mean, range of values in parenthesis).

Crop species	DM (%)	ODM ($\%_{DM}$)	pH (–)	Lactic acid ($\%_{DM}$)	Acetic acid[1] ($\%_{DM}$)	Butyric acid[2] ($\%_{DM}$)	Alcohols[3] ($\%_{DM}$)
Main and secondary crops							
Sugar beet	21.3 (18.3–24.2)	92.1 (87.7–96.6)	3.7 (3.6–3.9)	5.0 (3.8–6.1)	2.2 (1.3–3.0)	0.0 (0.0–0.0)	2.8 (1.5–4.1)
Spring barley/ryegrass	27.8 (26.0–29.6)	91.1 (89.3–92.8)	4.1 (4.0–4.1)	5.0 (4.6–5.3)	2.0 (2.0–2.0)	0.0 (0.0–0.0)	0.8 (0.6–1.1)
Maize	30.2 (15.2–42.1)	95.8 (93.7–96.9)	3.7 (3.1–4.1)	5.1 (3.5–9.5)	1.6 (0.2–3.6)	0.0 (0.0–0.3)	1.3 (0.2–4.2)
Winter barley	30.8 (24.3–36.9)	94.0 (91.6–95.4)	4.1 (3.8–4.2)	4.9 (3.4–5.7)	1.9 (0.7–3.1)	0.1 (0.0–1.1)	1.8 (0.4–4.8)
Winter triticale	35.2 (27.4–52.8)	95.1 (94.2–96.5)	4.2 (3.8–5.0)	3.5 (1.0–6.6)	1.5 (0.3–4.3)	0.3 (0.0–1.9)	1.3 (0.2–4.4)
Marrow stem kale	15.4 (14.5–16.4)	87.4 (86.3–88.5)	4.0 (4.0–4.0)	13.4 (9.9–16.8)	2.0 (1.6–2.3)	0.0 (0.0–0.0)	0.9 (0.9–1.0)
Spring barley	40.2 (31.4–58.9)	93.9 (92.3–96.7)	4.1 (3.6–5.2)	3.9 (0.5–5.4)	1.0 (0.3–1.7)	0.2 (0.0–0.7)	0.8 (0.6–1.5)
Winter rye/winter triticale	32.0 (28.8–35.8)	94.4 (93.6–95.2)	4.0 (3.9–4.1)	4.6 (3.9–6.2)	1.6 (1.3–2.0)	0.0 (0.0–0.1)	1.6 (0.5–3.1)
Potatoes	27.3 (–)	96.6 (–)	4.5 (–)	2.4 (–)	0.8 (–)	0.0 (–)	0.1 (–)
Oat/forage pea/false flax	38.9 (35.4–42.6)	93.8 (92.8–94.7)	4.5 (4.0–5.4)	4.2 (2.6–5.6)	1.3 (0.3–2.4)	0.6 (0.0–2.7)	0.8 (0.4–1.0)
Winter rye	33.1 (29.9–35.2)	94.8 (93.8–95.3)	4.0 (3.8–4.2)	5.1 (3.1–6.5)	1.6 (1.1–2.1)	0.0 (0.0–0.0)	0.7 (0.3–1.8)
Winter wheat	48.7 (40.3–57.9)	95.7 (94.9–96.1)	4.4 (4.0–4.6)	2.7 (2.0–3.9)	0.5 (0.3–0.6)	0.3 (0.0–0.8)	0.4 (0.0–0.9)
Sudangrass hybrid	25.1 (14.8–36.5)	94.3 (86.6–96.2)	3.8 (3.2–5.5)	6.7 (2.5–12.0)	1.5 (0.3–2.4)	0.0 (0.0–0.4)	1.5 (0.5–4.3)
Forage sorghum	24.3 (15.1–28.6)	94.3 (89.7–95.6)	3.7 (3.1–4.0)	6.7 (5.2–11.3)	1.5 (0.0–2.6)	0.0 (0.0–0.1)	2.0 (0.6–4.1)
Winter rye/fodder vetch	33.6 (28.8–36.9)	94.3 (93.3–95.3)	4.3 (4.0–4.8)	3.6 (1.3–5.7)	1.4 (0.4–2.2)	0.6 (0.0–1.8)	0.9 (0.7–1.2)
Winter barley/turnip rape	32.8 (18.4–47.1)	89.0 (88.3–89.8)	4.6 (4.2–5.0)	8.2 (5.5–10.9)	2.2 (1.4–3.1)	0.1 (0.0–0.1)	0.8 (0.6–1.0)
Spring rye	42.3 (33.7–57.1)	94.9 (93.2–95.7)	4.8 (4.1–5.8)	2.2 (0.1–5.1)	0.7 (0.2–1.4)	0.6 (0.0–2.6)	0.6 (0.2–1.6)
Oat	37.9 (29.8–55.3)	92.4 (90.3–94.5)	4.3 (3.7–5.6)	5.6 (1.3–10.5)	1.1 (0.3–1.8)	0.3 (0.0–1.4)	0.5 (0.3–1.3)
Amaranth	21.1 (19.4–22.7)	86.4 (85.9–86.9)	4.2 (4.1–4.2)	7.4 (5.8–9.1)	1.1 (1.1–1.1)	0.0 (0.0–0.0)	0.7 (0.4–1.0)
Quinoa	22.5 (18.6–30.1)	85.3 (83.5–89.4)	4.0 (4.0–4.2)	6.4 (4.0–7.7)	1.6 (0.9–3.0)	0.1 (0.0–0.3)	1.0 (0.2–3.1)
Rapeseed	26.8 (21.3–31.6)	91.1 (89.7–92.0)	4.2 (3.8–4.5)	6.6 (3.7–10.6)	1.7 (1.1–2.8)	0.1 (0.0–0.3)	0.4 (0.2–0.6)
Sunflower	23.0 (17.3–35.9)	87.5 (81.2–90.5)	4.2 (3.6–4.6)	7.4 (4.3–11.3)	2.0 (1.0–2.9)	0.1 (0.0–1.1)	0.8 (0.4–1.5)
Forage pea	25.3 (–)	90.3 (–)	3.9 (–)	10.1 (–)	1.4 (–)	0.0 (–)	0.2 (–)
Buckwheat	23.1 (18.3–29.3)	89.1 (85.2–92.6)	5.0 (3.9–7.2)	4.5 (1.8–8.1)	1.3 (0.9–2.1)	0.6 (0.0–1.5)	0.3 (0.1–0.3)
Catch crops							
Forage triticale	25.4 (21.4–29.5)	91.6 (89.7–93.5)	4.1 (4.0–4.1)	5.5 (3.2–7.7)	2.4 (2.3–2.4)	0.1 (0.0–0.1)	0.9 (0.4–1.4)
Forage barley	27.3 (20.6–38.6)	91.9 (90.3–94.5)	4.2 (4.1–4.3)	5.3 (0.8–7.7)	2.0 (1.9–2.1)	0.1 (0.0–0.4)	1.0 (0.7–1.4)
Forage rye	24.0 (17.0–33.1)	91.5 (84.7–95.8)	4.3 (3.8–5.2)	5.8 (0.6–11.3)	1.7 (0.8–2.9)	0.5 (0.0–2.8)	1.5 (0.2–6.5)
Landsberger mixture	20.4 (19.0–21.9)	89.7 (88.9–90.4)	4.8 (4.3–5.3)	4.7 (0.1–9.3)	2.3 (2.0–2.6)	3.6 (0.3–7.0)	0.6 (0.6–0.6)
Sudangrass hybrid	23.3 (19.0–30.3)	94.0 (92.6–95.3)	3.8 (3.7–4.1)	6.7 (5.0–7.9)	1.9 (1.4–2.8)	0.0 (0.0–0.0)	2.1 (0.7–3.2)
Forage sorghum	24.3 (23.6–25.3)	93.6 (92.7–94.2)	3.9 (3.9–3.9)	6.2 (5.3–6.7)	2.3 (1.5–2.8)	0.0 (0.0–0.1)	2.5 (0.8–4.0)
Annual ryegrass	33.1 (19.2–58.0)	89.0 (85.7–91.4)	5.0 (4.1–7.9)	4.5 (0.1–11.2)	1.4 (0.6–2.2)	1.0 (0.0–6.7)	0.5 (0.1–1.2)
Phacelia	20.2 (11.8–27.5)	85.3 (83.3–86.5)	5.2 (4.5–5.6)	2.9 (0.0–6.9)	2.2 (0.4–3.2)	2.8 (0.4–5.5)	0.7 (0.5–1.0)
Fodder radish	11.5 (9.1–15.5)	81.1 (73.3–88.2)	4.4 (3.5–5.3)	10.3 (6.6–14.5)	3.6 (2.1–4.3)	0.7 (0.0–1.8)	0.9 (0.4–1.5)
Buckwheat/phacelia	25.6 (–)	91.5 (–)	4.0 (–)	3.9 (–)	2.1 (–)	0.3 (–)	0.2 (–)
Annual grass and legume mixtures							
Ryegrass mix.	29.9 (14.9–48.0)	90.5 (85.2–93.5)	4.5 (3.5–5.9)	5.6 (0.1–13.6)	1.7 (0.3–7.4)	0.6 (0.0–3.3)	1.1 (0.1–3.9)
Clover grass mix.	25.7 (15.2–38.5)	90.4 (89.2–92.0)	4.7 (3.8–5.6)	5.3 (1.9–12.8)	2.0 (0.5–5.1)	0.9 (0.0–4.1)	2.0 (0.3–12.7)
Alfalfa clover grass mix.	25.9 (18.0–35.5)	89.3 (87.7–90.4)	5.0 (4.3–5.9)	6.8 (1.9–12.4)	2.5 (1.0–3.8)	0.4 (0.0–1.6)	1.1 (0.3–3.0)
Alfalfa grass mix.	30.1 (17.0–43.3)	89.4 (86.2–91.0)	4.4 (3.7–5.0)	6.5 (4.3–8.2)	2.2 (1.4–3.2)	0.0 (0.0–0.5)	0.5 (0.0–1.4)
Perennial crops							
Tall wheatgrass	25.6 (19.4–31.8)	90.1 (86.7–96.6)	4.8 (4.3–5.3)	4.4 (3.5–5.4)	1.2 (0.8–1.6)	1.0 (0.0–2.0)	0.4 (0.1–0.6)
Country mallow	23.5 (17.3–27.3)	88.3 (85.3–90.5)	5.0 (4.7–5.7)	6.8 (6.0–7.8)	2.0 (1.4–2.7)	0.1 (0.0–0.1)	0.3 (0.1–0.4)
Jerusalem artichoke (haulm)	28.2 (14.3–41.3)	89.7 (87.2–92.2)	3.9 (3.6–4.3)	7.2 (5.1–9.6)	1.6 (0.6–2.6)	0.0 (0.0–0.0)	0.4 (0.2–0.7)
Miscanthus	33.9 (30.2–40.2)	94.2 (92.7–95.5)	4.8 (4.5–5.1)	0.3 (0.0–1.3)	1.2 (0.4–2.1)	1.6 (0.5–2.4)	0.3 (0.2–0.4)
Cup plant	27.1 (25.4–29.1)	88.4 (87.5–89.0)	5.1 (4.3–6.2)	4.2 (0.0–8.5)	1.9 (1.2–2.8)	1.2 (0.0–4.3)	0.5 (0.0–1.1)
Mean	28.9	92.2	4.2	5.6	1.7	0.4	1.2
Median	28.5	92.7	4.1	5.5	1.6	0.0	0.9
SD	8.0	3.4	0.6	2.5	0.9	0.9	1.1
CV (%)	27.6	3.7	13.9	44.7	51.2	261.3	95.3

[1] Sum of acetic and propionic acid.
[2] Sum of i-butyric, butyric, i-valeric, valeric and caproic acid.
[3] Sum of ethanol, propanol, 1,2-butanediol, 2,3-propanediol; DM: dry matter; ODM: organic dry matter; SD: standard deviation; CV: coefficient of variation.

revealed pH values below the critical value and good to very good silage qualities according to DLG (2006), while 10% of the silages showed poor or very poor silage quality. With only few exceptions, lactic acid was the prevailing product of silage fermentation in silages with good quality. Considerable concentrations of acetic (up to 60% of the fermentation products) or butyric acid (up to 74% of the fermentation products) and elevated alcohol contents were found in silages with poor quality. The largest share of silages with poor quality was found for catch crops (phacelia, Landsberger mixture, annual ryegrass), perennial crops (miscanthus, tall wheatgrass, cup plant), and annual clover grass and alfalfa clover grass mixtures. The concentration of fermentation products was negatively correlated with the DM content of the silages ($R = 0.679$). In tendency, the content of fermentation products was at a higher level for crop species or samples ensiled at a low DM content. This is in line with findings of other studies summarised by McDonald et al. (1991) which indicate that a higher amount of moisture present in the ensiled crop stimulates the growth of bacteria leading to higher levels of lactic, acetic and butyric acid in the silage while silage fermentation is restricted when DM contents increase.

3.2. Nutrient and fibre composition of crop silages

The means and ranges of values of parameters that further describe the nutrient and fibre composition of the different crop silages are presented in Table 3. Crop silages were characterised by generally low crude fat content (on average <4%$_{DM}$), with rapeseed and sunflower silages being the only exceptions that reached crude fat concentrations up to 22%$_{DM}$. The crude protein content of the silages of different crop species ranged from on average 4.8%$_{DM}$ to 17.1%$_{DM}$ (Table 3). Early harvested main crops (marrow stem kale, winter barley-turnip rape mixture), catch crops (Landsberger mixture, annual ryegrass, fodder radish) and annual grass and legume mixtures revealed protein contents in the upper range while lowest protein concentrations were determined for miscanthus, sugar beet and potato silage. Carbohydrates generally represented the dominant constituent within the crop silages. High protein contents result in low C/N ratios within the crop biomass. For an optimal conversion of biomass to biomethane a sufficient availability of macro-nutrients is required. In general, a C/N ratio of 20/1 to 30/1 is regarded as optimal for the methanogenesis step (Drosg et al., 2013). Low C/N ratios can cause problems due to excessive ammonia production by degradation of the nitrogenous matter and ammonia inhibition of the anaerobic digestion process, while high C/N ratios can entail insufficient degradation and low methane yields (Chen et al., 2008). The crop biomasses investigated in the present study revealed C/N ratios in a wide range from on average 16–60 (Table 3). It is noteworthy that C/N ratios also differed markedly between silages of the same crop species. C/N ratios were rather low in silages of annual grass and legume mixtures and in some of the catch crops, such as the Landsberger mixture, annual ryegrass and fodder radish. Highest C/N ratios were determined in silages of sugar beet, potatoes, miscanthus and forage sorghum.

The fibre fraction within the crop biomass is another important characteristic of feedstocks for biogas production since it includes the hardly or non-digestible organic compounds of the plant cell wall (Triolo et al., 2011). The NDF content of the crop silages varied from on average 7–76%$_{DM}$ and the ADF content varied from 3%$_{DM}$ to 55%$_{DM}$. Absolute variation of ADL content was lower with on average 0.5–13%$_{DM}$ within the crop silages but relative variation was higher as compared with ADF or NDF. Highest fibre fractions were analysed for miscanthus, buckwheat, forage pea, tall wheat grass and Jerusalem artichoke while fibre fractions were lowest in sugar beet and potatoes silages.

In general, catch crops as well as annual grass and legume mixtures were characterised by rather low lignin and cellulose, higher protein contents and lower C/N ratios. Perennial crops revealed comparatively high fibre contents, while the chemical composition of main and secondary crops varied largely depending on the crop species.

3.3. Specific methane yields of crop silages

Specific methane yields of crop silages ranged from 183 to 426 L_N kg_{ODM}^{-1}. Highest average specific methane yields were measured for sugar beet, whole-crop cereals cultivated as catch crops and for ryegrass and grass-clover mixtures (Fig. 1). Lowest average methane yields were obtained for buckwheat, Jerusalem artichoke, miscanthus and cup plant.

Maize is often used as a standard substrate for comparison of specific methane yields. In the present study, 59 different maize silages were analysed and a range in specific methane yield from 312 to 408 L_N kg_{ODM}^{-1} with a mean specific methane yield of 355 L_N kg_{ODM}^{-1} was found. The average specific methane yield of maize was exceeded by sugar beet silages, forage cereals cultivated as catch crops, and silages of ryegrass mixtures. However, a large variation in methane yields was found especially for the ryegrass silages, depending on location of cultivation and management i.e. time of harvest and number of cuts. Methane yields in the order of those of maize silage or slightly lower were identified for whole-crop winter cereal silages (main crops), especially winter barley and winter triticale. Sorghum as a potential substitute for maize showed on average 11% lower methane yields than maize when cultivated as main or secondary crop and 6–7% lower methane yields when cultivated as catch crop. In tendency, specific methane yield decreased with increasing ADF or ADL concentrations within the crop biomass. Lowest specific methane yields were obtained from perennial crops which were characterised by highest fibre fractions and showed on average 22–37% lower methane yields compared with maize silage.

A similar range in specific methane yields of biogas crops as in the present study has been reported in literature. E.g. Gissén et al. (2014) found specific methane yields of 317–419 L_N kg_{ODM}^{-1} when comparing six different crop species. Specific methane yields of 41 samples of 11 different crop species ranged from 177–401 L_N kg_{ODM}^{-1} in the study of Dandikas et al. (2014). The span in methane yields of energy crops is usually found to be lower as compared with the range found for organic wastes or residues (e.g. Labatut et al., 2011), which might be due to a less diverse chemical composition of the crop material.

The methane yield of maize as the most commonly used biogas crop has been intensively analysed. However, results in literature reveal a large variation. Rath et al. (2013) analysed 96 maize samples varying in genotype and location of cultivation and reported specific methane yields of 317–476 L_N kg_{ODM}^{-1} with a mean value of 373 L kg_{ODM}^{-1}, which is in close agreement with results of the present study. A larger range (276–557 L_N kg_{ODM}^{-1}) and higher mean of the specific methane yield (419 L_N kg_{ODM}^{-1}) of 379 maize silages was found by Mayer et al. (2014). In contrast, considerably lower specific methane yields of maize silages (196–335 L_N kg_{ODM}^{-1}) are reported elsewhere (Gao et al., 2012). Besides genotype and cultivation conditions, the pre-treatment of crop samples and the experimental setup for analyses of specific methane yield in batch anaerobic digestion tests can have a significant impact on methane yield results and restrain comparability of different studies (Herrmann and Rath, 2012; Raposo et al., 2011). Crop samples investigated in literature are either analysed as fresh or ensiled samples. Ensiling can increase the measured specific methane yield to some extent. If silages are analysed, it is important to correct the DM and ODM content for losses of volatile compounds that occur

Table 3
Chemical characterisation of silages from different crop species (mean, range of values in parenthesis).

Crop species	Crude fat ($\%_{DM}$)	Crude protein ($\%_{DM}$)	NfE ($\%_{DM}$)	NDF ($\%_{DM}$)	ADF ($\%_{DM}$)	ADL ($\%_{DM}$)	C/N (–)
Main and secondary crops							
Sugar beet	0.4 (0.4–0.5)	6.7 (3.8–9.5)	79.2 (71.8–86.6)	11.1 (9.2–12.9)	7.2 (6.1–8.3)	0.6 (0.3–0.8)	47 (27–66)
Spring barley/ryegrass	2.4 (2.1–2.8)	9.2 (8.5–9.9)	54.8 (53.0–56.6)	44.2 (43.8–44.6)	28.2 (25.3–31.0)	2.7 (2.4–2.9)	30 (28–31)
Maize	2.6 (1.0–3.9)	7.8 (4.4–12.1)	64.7 (53.8–71.4)	41.2 (26.8–53.7)	24.0 (14.7–37.1)	2.9 (1.0–6.1)	37 (23–61)
Winter barley	2.3 (1.6–2.8)	9.3 (7.3–12.0)	55.0 (42.3–64.9)	50.1 (39.5–60.5)	30.5 (20.2–40.9)	3.7 (2.7–4.7)	31 (25–39)
Winter triticale	2.2 (1.5–3.1)	8.9 (6.3–12.5)	54.9 (47.0–60.8)	52.3 (45.1–60.3)	31.3 (25.3–40.7)	4.5 (3.1–6.4)	34 (24–47)
Marrow stem kale	3.5 (2.6–4.4)	14.9 (12.4–17.4)	42.9 (37.6–48.1)	37.2 (33.6–40.7)	30.5 (29.9–31.1)	4.8 (3.7–5.8)	18 (15–22)
Spring barley	3.4 (2.3–5.4)	9.9 (6.7–12.2)	56.6 (47.8–64.8)	53.1 (46.2–62.5)	28.4 (23.4–33.5)	4.7 (3.3–5.4)	31 (24–44)
Winter rye/winter triticale	1.8 (1.4–2.4)	8.7 (7.1–9.8)	49.3 (44.4–55.3)	55.3 (52.9–60.2)	37.2 (34.8–40.9)	5.1 (4.9–5.3)	34 (30–38)
Potatoes	0.2 (–)	5.4 (–)	88.4 (–)	7.2 (–)	3.2 (–)	0.5 (–)	48 (–)
Oat/forage pea/false flax	3.3 (2.5–3.7)	9.3 (8.5–10.1)	51.2 (46.7–56.6)	53.5 (45.1–60.8)	33.7 (25.3–39.2)	5.5 (2.9–7.4)	31 (27–34)
Winter rye	2.0 (1.6–2.2)	9.0 (7.3–10.1)	50.4 (45.5–57.1)	55.6 (51.2–59.3)	36.6 (30.4–41.6)	5.5 (4.2–7.7)	32 (29–40)
Winter wheat	2.2 (2.1–2.3)	7.5 (7.0–7.9)	62.5 (57.5–65.6)	47.1 (41.4–50.4)	27.1 (23.1–31.5)	4.1 (3.4–4.5)	38 (35–41)
Sudangrass hybrid	1.8 (0.5–3.2)	8.9 (5.3–17.0)	52.2 (40.8–58.4)	58.0 (48.2–69.1)	36.6 (28.5–42.7)	5.5 (2.9–7.2)	33 (15–54)
Forage sorghum	1.4 (0.3–2.4)	8.0 (5.8–11.7)	52.3 (40.7–57.5)	60.0 (48.6–67.5)	38.6 (31.2–44.6)	5.7 (3.5–6.8)	35 (22–48)
Winter rye/fodder vetch	2.2 (1.9–2.4)	6.9 (6.4–7.6)	49.3 (44.4–55.3)	62.3 (59.0–65.9)	41.1 (36.1–45.4)	7.0 (6.0–8.7)	42 (40–43)
Winter barley/turnip rape	3.0 (2.8–3.2)	13.8 (13.2–14.4)	35.9 (34.7–37.2)	52.3 (49.7–54.9)	42.4 (42.0–42.8)	5.6 (5.2–6.0)	20 (19–20)
Spring rye	2.5 (1.6–3.4)	9.5 (6.6–13.7)	49.1 (45.8–53.0)	60.3 (54.6–66.0)	37.7 (33.8–43.6)	6.9 (5.8–7.6)	33 (22–44)
Oat	3.1 (2.5–3.7)	9.2 (6.2–13.2)	51.5 (47.3–54.6)	55.1 (49.0–62.0)	34.3 (28.7–39.0)	5.5 (4.2–8.0)	32 (22–46)
Amaranth	3.5 (3.3–3.6)	9.5 (9.4–9.6)	46.7 (42.9–50.5)	40.0 (35.2–44.7)	33.9 (30.2–37.6)	5.2 (4.0–6.3)	27 (27–28)
Quinoa	3.6 (2.4–4.8)	13.4 (8.9–16.1)	45.3 (41.7–52.2)	36.2 (31.0–39.8)	26.4 (20.9–29.3)	3.8 (3.1–4.4)	21 (16–30)
Rapeseed	8.1 (3.4–17.2)	9.9 (8.9–11.3)	39.1 (34.1–46.5)	48.5 (41.2–53.4)	39.6 (34.6–51.2)	7.6 (5.7–11.4)	29 (24–31)
Sunflower	11.1 (4.1–21.6)	9.4 (6.9–11.7)	40.5 (26.5–54.6)	39.9 (30.0–50.7)	37.6 (24.5–47.3)	9.5 (6.7–12.1)	31 (24–39)
Forage pea	1.8 (–)	9.7 (–)	45.3 (–)	55.1 (–)	42.0 (–)	12.0 (–)	27 (–)
Buckwheat	1.7 (0.9–2.5)	11.4 (7.0–19.2)	44.4 (38.5–51.4)	52.2 (47.4–58.1)	42.6 (38.2–46.3)	13.4 (9.7–18.0)	26 (14–39)
Catch crops							
Forage triticale	1.7 (1.6–1.8)	7.9 (6.6–9.1)	51.9 (47.2–56.7)	55.1 (54.8–55.3)	33.1 (31.0–35.3)	2.4 (2.4–2.4)	36 (30–42)
Forage barley	1.8 (1.6–2.0)	8.7 (6.3–10.3)	50.1 (45.3–59.4)	57.9 (54.2–61.0)	34.2 (29.7–37.2)	3.3 (3.1–3.5)	34 (27–46)
Forage rye	2.6 (1.7–5.1)	11.1 (6.7–16.6)	45.5 (38.2–62.4)	55.1 (40.9–66.2)	34.6 (24.2–42.0)	3.6 (2.0–5.1)	27 (17–43)
Landsberger mixture	3.8 (3.5–4.2)	17.1 (15.8–18.5)	37.8 (34.5–41.1)	52.0 (44.6–59.4)	35.1 (30.1–40.1)	6.0 (5.0–7.1)	16 (14–17)
Sudangrass hybrid	1.8 (1.4–2.1)	7.5 (4.9–10.3)	53.5 (48.0–56.7)	58.7 (53.6–62.2)	36.6 (28.5–42.7)	4.7 (3.5–6.5)	39 (28–57)
Forage sorghum	1.5 (1.2–1.7)	6.1 (5.4–7.5)	55.3 (54.3–56.5)	59.5 (56.0–63.5)	38.6 (31.2–44.6)	4.8 (3.7–5.6)	46 (37–51)
Annual ryegrass	3.4 (1.9–5.1)	13.9 (7.9–25.5)	42.0 (30.1–49.9)	53.1 (41.9–63.5)	32.0 (26.6–38.8)	5.3 (3.4–9.2)	22 (11–33)
Phacelia	3.2 (2.8–3.6)	9.4 (7.8–11.9)	42.7 (41.7–43.8)	48.5 (43.7–56.8)	34.9 (32.5–38.7)	7.6 (5.5–9.1)	29 (22–34)
Fodder radish	2.6 (2.2–3.5)	14.9 (10.9–18.9)	42.0 (37.3–45.7)	31.0 (24.9–46.1)	34.7 (28.4–44.3)	4.3 (2.2–9.4)	17 (13–25)
Buckwheat/phacelia	2.7 (–)	9.4 (–)	52.3 (–)	42.9 (–)	32.8 (–)	8.5 (–)	29 (–)
Annual grass and legume mixtures							
Ryegrass mix	3.3 (1.8–4.9)	12.5 (7.6–20.0)	46.4 (38.1–63.0)	48.0 (31.8–59.1)	30.3 (19.8–38.9)	3.9 (1.0–8.6)	24 (14–36)
Clover grass mix	3.3 (2.2–4.2)	13.3 (7.2–19.2)	45.2 (39.2–56.1)	45.2 (37.9–54.7)	32.0 (23.9–39.5)	4.9 (1.6–9.6)	22 (14–37)
Alfalfa clover grass mix	2.9 (2.0–3.8)	14.5 (11.9–16.8)	44.0 (42.9–47.1)	47.3 (42.3–52.8)	35.4 (31.2–37.9)	6.2 (3.6–8.6)	19 (16–23)
Alfalfa grass mix	3.2 (1.8–5.2)	15.8 (8.6–19.9)	39.3 (31.1–49.2)	46.8 (39.5–52.6)	35.6 (24.3–39.5)	6.9 (2.4–10.0)	18 (14–32)
Perennial crops							
Tall wheatgrass	2.1 (1.8–2.4)	9.2 (8.8–9.5)	40.2 (39.1–41.3)	68.0 (61.8–74.2)	44.5 (40.6–48.4)	10.0 (8.4–11.7)	29 (27–32)
Country mallow	3.3 (2.9–3.9)	11.5 (9.9–13.1)	39.5 (34.9–44.0)	50.8 (47.0–53.7)	36.5 (35.0–39.1)	7.1 (6.1–8.0)	24 (21–28)
Jerusalem artichoke (haulm)	1.9 (0.9–3.3)	9.8 (4.6–15.0)	49.6 (43.6–57.2)	44.1 (37.6–49.8)	39.6 (34.7–45.8)	11.7 (8.3–17.7)	31 (18–57)
Miscanthus	1.4 (0.9–1.8)	4.8 (4.1–5.7)	40.9 (38.0–42.8)	76.2 (74.7–77.5)	55.4 (52.5–56.9)	13.3 (11.7–17.1)	60 (51–67)
Cup plant	4.0 (2.1–5.4)	11.5 (9.9–13.1)	42.5 (40.3–44.6)	52.3 (48.3–58.0)	36.5 (35.0–39.1)	7.9 (7.7–8.5)	39 (35–46)
Mean	2.9	10.2	50.9	49.8	32.7	5.1	30.4
Median	2.5	9.4	50.5	49.7	33.0	4.5	29.9
SD	2.1	3.4	9.2	9.6	7.2	2.7	9.9
CV (%)	72.6	33.4	18.0	19.4	22.0	52.7	32.5

NfE: nitrogen-free extracts; NDF: neutral detergent fibre; ADF: acid detergent fibre; ADL: acid detergent lignin; C/N: carbon to nitrogen ratio.

during DM measurement by oven drying. Lost substances include volatile organic acids and alcohols which are present in silages to larger amounts. This is not considered in many studies and leads to an overestimation of methane yields (Herrmann et al., 2011; Kreuger et al., 2011). Furthermore, digestion tests in reactors with small volumes usually require drying and milling of the samples (VDI, 2006). This can lead to losses or alteration of organic compounds, but also to an increased availability of organic compounds and an enhanced microbial conversion due to physical pre-treatment.

One advantage of the present study lies in that crop samples were analysed for methane production potentials in the same form as they would be used for large scale anaerobic digestion, i.e. chopped and ensiled without further pre-treatment. The use of identical methods in a single laboratory eliminates the effects of the measuring method and facilitates comparable estimates of specific methane yields for a wide range of crop species. Methane yields obtained in the present study showed good repeatability. The average coefficient of variation of the specific methane yield with three to four repetitions of the same feedstock was 2.3%. However, methane yields were analysed in 48 different runs of the batch anaerobic digestion system over a period of several years. Since it is not possible to standardise the inoculum over several years, an effect of the inoculum on the specific methane yield cannot be ruled out. In order to control the activity of the inoculum and possible effects on methane yield results, microcrystalline cellulose was used as constant reference material with known methane yield potential throughout the batch test runs. Presuming a complete conversion and considering biomass regeneration, a maximum methane yield of 370–375 $L_N\ kg_{ODM}^{-1}$ can be obtained from cellulose (VDI, 2006). An average methane yield of cellulose of 361 $L_N\ kg_{ODM}^{-1}$ was measured in the present study, which equates

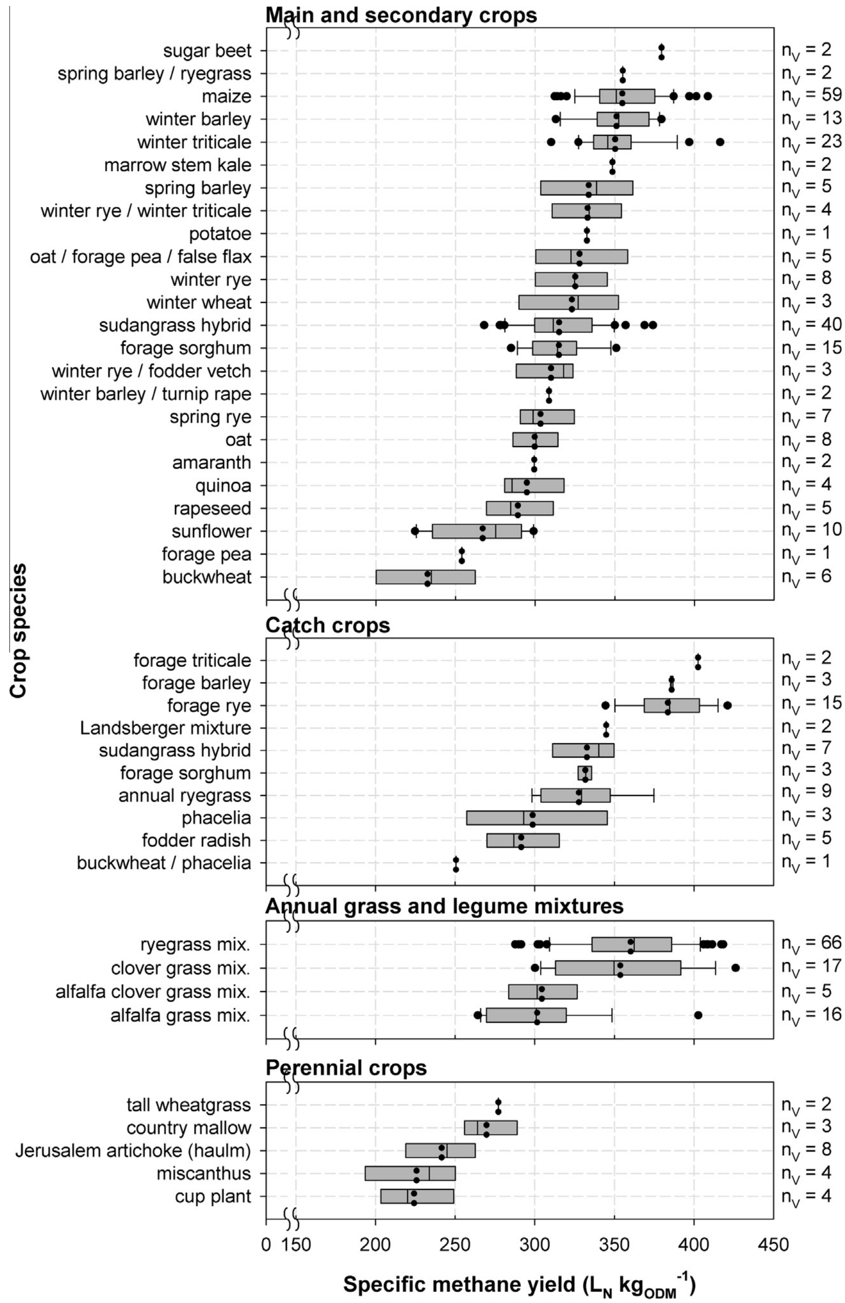

Fig. 1. Specific methane yields of silages from different crop species and position within crop rotations (n_v: number of variants).

to 96–98% of the maximum methane yield. The coefficient of variation over all test runs was 5.2% which is considerably lower than reported by others. A variation of repeated measurement of the specific methane yield of 10% was reported to be common for triplicate determination of cellulose and crop feedstocks in batch digestion tests (Heuwinkel et al., 2009).

3.4. Methane content of biogas from crop silages

Variation in the quality of the biogas obtained from different crop silages was comparatively low. The average methane content within the biogas of the investigated crop species ranged from 49% to 61% (Table 4). Lowest methane contents were found in biogas from sugar beet and potatoes silages while highest average methane contents were measured for forage pea, phacelia, alfalfa clover grass mixtures and miscanthus. For 30 out of 43 investigated crop species the average methane content laid between 54% and 57% of the produced biogas. The methane content typically shows a lower variation than the specific methane yield (Rath et al., 2013). The range of values of methane contents within the biogas produced from crop silages in this study is concordant with data from literature (Dandikas et al., 2014; Triolo et al., 2011; Rath et al., 2013).

3.5. Rate of methane production

First order decay constants, half-life and maximum methane production rates were derived from kinetic analyses of batch anaerobic digestion results in order to describe the rate of biodegradation (Table 4). Diverse pattern of methane production curves have been observed in previous batch test studies, including curves that indicate temporary product inhibition and distinct lag

Table 4
Methane production characteristics of silages from different crop species.

Crop species	Methane content (%)	k (d^{-1})	BMP_{Gomp} ($L_N\ kg^{-1}_{ODM}$)	R_m ($L_N\ kg^{-1}_{ODM}\ d^{-1}$)	t_{50} (d)
Main and secondary crops					
Sugar beet	48.5 (46.3–50.7)	0.312 (0.305–0.320)	374.9 (350.4–399.4)	296.8 (291.2–302.5)	2.33 (2.24–2.42)
Spring barley/ryegrass	54.8 (54.4–55.2)	0.176 (0.144–0.208)	328.1 (325.7–330.6)	109.8 (89.8–129.7)	4.02 (3.32–4.73)
Maize	55.0 (53.1–58.4)	0.204 (0.122–0.307)	328.2 (294.5–376.2)	135.1 (94.1–198.6)	3.47 (2.26–4.70)
Winter barley	56.0 (53.0–59.8)	0.208 (0.155–0.241)	320.1 (287.4–346.8)	125.0 (84.1–159.2)	3.41 (2.89–4.41)
Winter triticale	55.3 (52.9–57.7)	0.199 (0.120–0.300)	315.0 (275.4–365.7)	120.7 (78.9–215.6)	3.52 (2.21–5.15)
Marrow stem kale	54.8 (54.8–54.9)	0.459 (0.459)	325.4 (322.6–328.1)	298.9 (285.7–312.0)	1.53 (1.53–1.53)
Spring barley	55.1 (53.9–56.6)	0.088 (0.028–0.200)	321.2 (256.7–361.1)	140.7 (128.8–157.2)	7.21 (3.26–10.09)
Winter rye/winter triticale	56.3 (54.8–57.4)	0.186 (0.159–0.216)	300.1 (275.9–323.6)	92.0 (82.9.5–97.9)	3.80 (3.31–4.28)
Potatoes	49.4 (–)	0.189 (–)	330.6 (–)	173.3 (–)	3.66 (–)
Oat/forage pea/false flax	56.9 (55.7–58.2)	0.138 (0.058–0.204)	304.1 (271.4–333.1)	78.6 (56.1–110.3)	5.36 (3.39–8.38)
Winter rye	55.8 (53.7–57.9)	0.185 (0.158–0.244)	296.8 (262.5–327.9)	91.5 (71.0–122.4)	3.96 (2.90–4.60)
Winter wheat	54.3 (54.1–54.5)	0.129 (0.155–0.147)	300.8 (269.2–327.6)	73.7 (60.7–91.8)	5.25 (4.61–5.72)
Sudangrass hybrid	56.8 (53.6–61.1)	0.154 (0.103–0.235)	288.9 (248.4–348.5)	82.6 (53.3–175.6)	4.55 (2.98–5.73)
Forage sorghum	56.5 (53.5–58.9)	0.151 (0.118–0.199)	287.8 (263.1–327.7)	83.7 (59.4–114.9)	4.49 (3.32–5.23)
Winter rye/fodder vetch	56.7 (56.4–57.2)	0.147 (0.123–0.166)	283.8 (262.3–299.2)	68.1 (59.3–72.7)	4.78 (4.23–5.60)
Winter barley/turnip rape	58.6 (57.6–59.5)	0.199 (0.163–0.235)	284.1 (254.4–313.8)	106.9 (82.9–130.9)	3.56 (2.95–4.17)
Spring rye	55.6 (53.7–58.4)	0.097 (0.054–0.148)	281.5 (255.3–325.7)	66.7 (57.2–77.3)	6.54 (4.63–8.72)
Oat	56.0 (54.5–58.4)	0.118 (0.029–0.185)	277.0 (252.3–304.2)	79.0 (49.8–110.3)	5.71 (3.57–9.72)
Amaranth	58.8 (58.4–59.1)	0.263 (0.263)	278.4 (268.9–287.8)	117.9 (113.6–122.2)	2.71 (2.67–2.76)
Quinoa	55.1 (53.9–57.3)	0.232 (0.219–0.241)	267.3 (250.2–299.7)	116.9 (108.3–128.4)	2.97 (2.85–3.10)
Rapeseed	59.8 (57.3–62.8)	0.184 (0.144–0.265)	259.2 (244.2–276.3)	81.0 (45.1–136.7)	4.05 (2.62–5.11)
Sunflower	56.6 (50.2–62.8)	0.178 (0.145–0.243)	247.8 (210.0–286.1)	89.6 (58.7–117.2)	3.87 (2.79–4.81)
Forage pea	60.5 (–)	0.087 (–)	245.1 (–)	46.8 (–)	7.11 (–)
Buckwheat	57.4 (55.0–60.7)	0.171 (0.117–0.210)	210.4 (167.5–253.1)	55.6 (28.9–72.9)	4.63 (3.49–6.84)
Catch crops					
Forage triticale	55.7 (54.6–56.8)	0.228 (0.208–0.248)	371.0 (366.1–375.8)	170.6 (166.2–175.1)	3.06 (2.81–3.30)
Forage barley	55.3 (53.9–57.7)	0.203 (0.172–0.239)	355.4 (353.7–358.7)	140.7 (128.8–157.2)	3.44 (2.91–3.89)
Forage rye	57.7 (54.4–62.7)	0.188 (0.125–0.265)	355.9 (329.3–385.1)	141.4 (85.9–177.3)	3.68 (2.63–5.20)
Landsberger mixture	59.9 (59.8–60.0)	0.147 (0.114–0.181)	319.2 (308.0–330.5)	121.6 (99.4–143.8)	4.48 (3.67–5.28)
Sudangrass hybrid	56.9 (54.4–58.2)	0.190 (0.168–0.221)	303.4 (264.7–341.3)	105.0 (66.7–125.2)	3.66 (3.14–4.17)
Forage sorghum	56.0 (55.2–57.3)	0.170 (0.157–0.179)	305.5 (298.9–311.3)	97.5 (81.0–110.8)	4.08 (3.82–4.55)
Annual ryegrass	57.1 (54.7–62.6)	0.166 (0.109–0.224)	300.1 (261.9–345.2)	98.6 (59.8–154.3)	4.29 (3.04–6.02)
Phacelia	60.5 (58.8–63.6)	0.210 (0.146–0.256)	274.8 (235.4–319.7)	100.2 (56.2–143.8)	3.53 (2.76–4.71)
Fodder radish	55.1 (53.9–57.3)	0.234 (0.190–0.273)	291.2 (249.4–338.0)	160.0 (120.5–196.2)	3.00 (2.68–3.69)
Buckwheat/phacelia	57.6 (–)	0.153 (–)	232.9 (–)	52.1 (–)	4.78 (–)
Annual grass and legume mixtures					
Ryegrass mix.	56.9 (52.4–63.1)	0.206 (0.100–0.306)	334.0 (261.3–387.9)	144.6 (69.0–246.4)	3.43 (2.30–6.08)
Clover grass mix.	58.9 (55.0–64.0)	0.227 (0.099–0.287)	327.1 (268.7–386.1)	154.0 (66.8–240.0)	3.15 (2.40–6.10)
Alfalfa clover grass mix	60.4 (57.6–63.7)	0.216 (0.134–0.307)	288.4 (252.5–327.3)	115.8 (66.4–141.0)	3.43 (2.53–4.98)
Alfalfa grass mix	57.4 (54.2–63.4)	0.207 (0.153–0.254)	280.0 (239.6–381.0)	130.8 (87.0–206.5)	3.28 (2.29–4.19)
Perennial crops					
Tall wheatgrass	57.4 (54.6–60.2)	0.107 (0.091–0.122)	257.9 (257.2–258.7)	55.1 (50.6–59.7)	5.96 (5.63–6.29)
Country mallow	55.1 (54.3–55.9)	0.219 (0.204–0.240)	240.8 (230.9–258.8)	94.3 (85.7–100.6)	3.12 (2.86–3.32)
Jerusalem artichoke (haulm)	54.9 (51.7–57.3)	0.192 (0.092–0.303)	218.9 (198.9–236.7)	88.4 (49.9–124.9)	3.81 (2.27–6.18)
Miscanthus	61.1 (60.5–62.1)	0.066 (0.048–0.088)	217.2 (178.6–242.0)	35.1 (26.2–40.6)	8.49 (7.29–9.55)
Cup plant	56.3 (53.4–59.3)	0.169 (0.132–0.217)	203.0 (181.6–237.6)	62.7 (47.1–85.3)	4.15 (3.11–5.05)
Mean	56.5	0.187	304.8	116.3	3.92
Median	56.2	0.188	305.7	111.8	3.62
SD	2.5	0.057	42.1	45.8	1.28
CV (%)	4.4	30.4	13.8	39.3	32.7

k: first order decay constant; BMP_{Gomp}: biochemical methane potential derived from the modified Gompertz equation; R_m: maximum specific methane production rate; t_{50}: half-life.

phases (Labatut et al., 2011). However, no inhibition or temporary inhibition of methane formation was observed in the present study. The methane formation started rapidly and a lag phase of methane production curves was not detectable or insignificant for almost all samples investigated. 90% of the silages were degraded with a lag phase of less than 0.5 days and 98% of the silages exhibited a lag phase of less than 1 day (data not shown). This might be due to the use of a well-adapted inoculum with high activity and due to the lack of substrates with high lipid contents or other potentially inhibitory compounds which, for example, can be found in food processing wastes (Labatut et al., 2011). Nevertheless, the rate of methane formation was influenced by the crop species (Table 4). A range in decay constants from 0.07 to 0.46 d^{-1} was observed. A rapid degradation and highest decay constants above 0.3 d^{-1} were found for marrow stem kale and sugar beet silages. 50% of the specific methane yield was formed after less than 2.5 days, indicating that only short hydraulic retention times would be necessary for continuous anaerobic digestion of these crop species. High average decay constants above 0.2 d^{-1} were also analysed for amaranth and quinoa, winter barley and maize silages, some of the catch crops (forage triticale, forage barley, phacelia, fodder radish), for grass and legume mixtures and country mallow as a perennial crop (Table 4). In contrast, miscanthus and spring cereal silages exhibited low decay constants (<0.1 d^{-1}). Feedstocks that are characterised by rapid degradation and high maximum methane production rates can potentially play a role in demand oriented biogas production that is assisted by a demand-driven feeding management. However, since the rate of methane production also depends on harvest date and maturity, comparatively large differences in decay constants and half-life

Table 5
Pearson's correlation coefficients of chemical components and methane production characteristics of all crop silage samples (dark-grey shading: strong correlation, R = |0.7|–|1.0|; light-grey shading: moderate correlation, R = |0.4|–|0.7|; no shading: no or weak correlation, R = |0|–|0.4|.).

	ODM	CL	CP	NfE	NDF	ADF	ADL	HCEL	CEL	LA	AA	BA	ALC	C/N	a_i	SMY	MC	k	BMP_{Gomp}	R_m	t_{50}
DM	0.39	0.01	-0.18	0.18	0.17	-0.07	0.02	0.34	-0.09	-0.53	-0.41	-0.12	-0.20	0.24	0.67	-0.05	-0.34	-0.35	-0.08	-0.29	0.36
ODM		-0.33	-0.59	0.71	0.23	-0.18	-0.24	0.56	-0.12	-0.31	-0.29	-0.22	0.16	0.60	0.34	0.21	-0.37	-0.20	0.17	-0.14	0.19
CL			0.23	-0.37	-0.27	-0.06	0.12	-0.35	-0.14	0.05	-0.01	0.06	-0.10	-0.23	-0.03	-0.06	0.18	0.04	-0.07	0.01	-0.06
CP				-0.63	-0.23	-0.06	0.02	-0.28	-0.10	0.22	0.12	0.10	-0.07	-0.91	-0.22	0.08	0.26	0.17	0.11	0.27	-0.20
NfE					-0.31	-0.60	-0.46	0.21	-0.55	-0.14	-0.09	-0.25	0.14	0.58	0.20	0.29	-0.54	0.07	0.29	0.15	-0.09
NDF						0.77	0.37	0.67	0.81	-0.20	-0.16	0.12	0.01	0.23	0.15	-0.26	0.23	-0.53	-0.30	-0.62	0.55
ADF							0.72	0.03	0.94	0.01	0.01	0.12	-0.07	0.07	0.01	-0.59	0.39	-0.38	-0.61	-0.59	0.43
ADL								-0.26	-0.45	-0.08	-0.10	0.13	-0.18	-0.01	0.07	-0.78	0.27	-0.36	-0.78	-0.56	0.44
HCEL									0.17	-0.32	-0.26	0.05	0.09	0.28	0.21	0.28	-0.09	-0.39	0.24	-0.27	0.37
CEL										0.05	0.06	0.09	-0.02	0.10	-0.01	-0.39	0.37	-0.31	-0.41	-0.50	0.34
LA											0.31	-0.39	0.05	-0.28	-0.36	0.01	-0.01	0.24	0.04	0.20	-0.29
AA												-0.04	0.09	-0.16	-0.39	0.02	0.11	0.26	0.05	0.18	-0.29
BA													0.03	-0.08	-0.08	0.04	0.46	-0.04	0.04	0.04	0.09
ALC														0.03	-0.12	0.24	0.15	0.15	0.23	0.18	-0.15
C/N															0.22	-0.09	-0.26	-0.19	-0.11	-0.25	0.25
a_i																-0.11	-0.19	-0.44	-0.07	-0.25	0.53
SMY																	-0.07	0.41	0.98	0.69	-0.43
MC																		-0.00	-0.07	-0.07	0.04
k																			0.36	0.80	-0.91
BMP_{Gomp}																				0.69	-0.36
R_{max}																					-0.73

|0|-|0.4| No or weak correlation |0.4|-|0.7| Moderate correlation |0.7|-|1.0| Strong correlation

DM: dry matter; ODM: organic dry matter; CL: crude fat; CP: crude protein; NfE: nitrogen-free extracts; NDF: neutral detergent fibre; ADF: acid detergent fibre; ADL: acid detergent ligning; HCEL: hemicellulose; CEL: cellulose; LA: lactic acid; AA: acetic acid; BA: butyric acid; ALC: alcohols; C/N: carbon to nitrogen ratio; a_i: substrate to inoculum ratio; SMY: specific methane yield; MC: methane content; k: first order decay constant; BMP_{Gomp}: biochemical methane potential derived from a modified Gompertz equation; R_m: maximum methane production rate; t_{50}: half-life.

values between samples of the same crop species are apparent (Table 4).

3.6. Effects of chemical composition on methane formation

Results of the correlation analyses for chemical components and methane production characteristics are given in Table 5. The specific methane yields and biochemical methane potentials of the crop silages were negatively correlated with parameters that describe fibre fractions. The closest relationship was found between ADL content and specific methane yields (Table 5). This confirms findings of previous studies that identified lignin as the main influencing chemical component on methane yields (Dandikas et al., 2014; Triolo et al., 2011). Lignin is not degradable and thus, decreases methane production and controls the ODM degradation during the anaerobic digestion process (Triolo et al., 2011). Furthermore, lignin can be cross-linked with other cell wall components such as cellulose and hemicellulose and decrease degradability of these components when bound within the ligno-cellulosic matrix. This is also reflected in significant negative correlations between ADF, cellulose or hemicellulose and specific methane yields (Table 5), although the association with these compounds was much weaker as compared with lignin.

Multiple regression analyses were performed stepwise in order to identify further significant explanatory variables for the specific methane yield of crop silages (Table 6). Besides the lignin content, parameters of silage fermentation, namely the butyric acid and alcohol content positively contributed to methane yields (Table 6). Butyric acid, higher volatile fatty acids and alcohols are associated with high theoretical methane yields based on their elemental composition (Herrmann et al., 2011). Silages that underwent clostridial fermentation and exhibited higher butyric acid and alcohol contents have been shown to produce higher methane yields based on the ODM added to the anaerobic digestion process (Herrmann et al., 2011). Thus, a positive relation between butyric acid and the methane yield of crop silages is feasible although butyric acid fermentation is also associated with higher storage losses during ensiling (Herrmann et al., 2011). This suggests that the course of silage fermentation plays an important role and products of silage fermentation should be considered when evaluating crop silages for anaerobic digestion.

The crude protein content was identified as another parameter with positive impact on methane yields (Table 6). In general, it is known that crude protein and crude fat can contribute to higher methane yields as compared with carbohydrates (VDI, 2006). Some of the previous studies on crop feedstocks established a positive relationship between crude protein and/or crude fat content and specific methane yields (Amon et al., 2007; Rath et al., 2013). However, only crude protein was identified as a significant parameter that determines the methane yield in multiple regression analyses of the present study, possibly due to limited variation in crude fat contents of the crop silages (Table 3).

The methane content within the biogas from crop silages was mainly affected by the content of nitrogen-free extracts, the DM content and butyric acid and alcohol content as parameters of silage fermentation (Tables 5 and 6). The NfE-fraction includes rather easily degradable carbohydrates such as sugar, starch or pectins. Increasing NfE-contents decreased the methane content which may reflect the lower methane content in biogas produced from carbohydrates (~50%) as compared with biogas from lipids and proteins (up to 72%) (VDI, 2006). Similar to their effects on methane yields, accumulation of butyric acid and alcohols formed during ensiling can increase the methane content of the produced biogas. The theoretical methane content in biogas produced from these substances (63–75%) exceeds the methane content of water-soluble sugars such as glucose or fructose (50%) which serve as substrates of silage fermentation (Herrmann et al., 2011). The impact of products of silage fermentation on methane yield and methane content is reflected in results of the multiple regression analyses.

Kinetic parameters that describe the rate of methane production were predominantly influenced by the fibre fractions (Table 5). The sum of lignin, cellulose and hemicellulose, represented by the NDF content, had the largest impact on decay constants, half-life and maximum methane production rates. Since lignin can create barriers to microbial degradation and degradable compounds of

Table 6
Stepwise linear regression equations and statistical data for specific methane yields, methane content, decay constants and the half-life of methane production of all crop silage samples.

Dependent variable	Independent variables	R^2	R^2 (adj.)	RMSE	RRMSE	p	Equation
SMY	ADL	0.607	0.606	27.95	8.45	<0.001	SMY = 396.4 – 12.82 ADL
	ADL, BA	0.629	0.627	27.20	8.23	<0.001	SMY = 395.5 – 13.15 ADL + 7.44 BA
	ADL, BA, ALC	0.636	0.633	26.96	8.15	<0.001	SMY = 390.1 – 12.88 ADL + 7.20 BA + 3.52 ALC
	ADL, BA, ALC, CP	0.643	0.640	26.73	8.08	<0.001	SMY = 378.5 – 12.87 ADL + 6.76 BA + 3.78 ALC + 1.12 CP
MC	NfE	0.294	0.293	2.07	3.67	<0.001	MC = 63.94 – 0.15 NfE
	NfE, BA	0.419	0.416	1.89	3.34	<0.001	MC = 62.38 – 0.12 NfE + 1.01 BA
	NfE, BA, DM	0.470	0.466	1.80	3.19	<0.001	MC = 63.96 – 0.11 NfE + 0.95 BUA - 0.07 DM
	NfE, BA, DM, ALC	0.496	0.491	1.76	3.11	<0.001	MC = 63.63 – 0.12 NfE + 0.93 BUA – 0.06 DM + 0.37 ALC
k	NDF	0.285	0.284	0.048	25.7	<0.001	k = 0.346 – 0.0032 NDF
	NDF, a_i	0.412	0.401	0.044	23.4	<0.001	k = 0.369 – 0.0029 NDF – 0.0874 a_i
	NDF, a_i, ADL	0.440	0.436	0.043	22.6	<0.001	k = 0.369 – 0.0025 NDF – 0.0869 a_i – 0.0038 ADL
	NDF, a_i, ADL, ALC	0.445	0.441	0.043	22.7	<0.001	k = 0.363 – 0.0025 NDF – 0.0845 a_i – 0.0034 ADL + 0.0044 ALC
t_{50}	NDF	0.305	0.304	1.055	26.9	<0.001	t_{50} = 0.31 + 0.07 NDF
	NDF, a_i	0.504	0.502	0.893	22.8	<0.001	t_{50} = –0.35 + 0.06 NDF + 2.42 a_i
	NDF, a_i, ADL	0.565	0.561	0.838	21.4	<0.001	t_{50} = –0.33 + 0.05 NDF + 2.39 a_i + 0.12 ADL
	NDF, a_i, ADL, ALC	0.569	0.564	0.835	21.3	<0.001	t_{50} = –0.23 + 0.05 NDF + 2.35 a_i + 0.12 ADL – 0.07 ALC

SMY: specific methane yield; MC: methane content; k: decay constant; t_{50}: half-life; ADL: acid detergent lignin; BA: butyric acid; ALC: alcohols; CP: crude protein; NfE: nitrogen-free extracts; DM: dry matter; NDF: neutral detergent fibre; a_i: substrate to inoculum ratio.

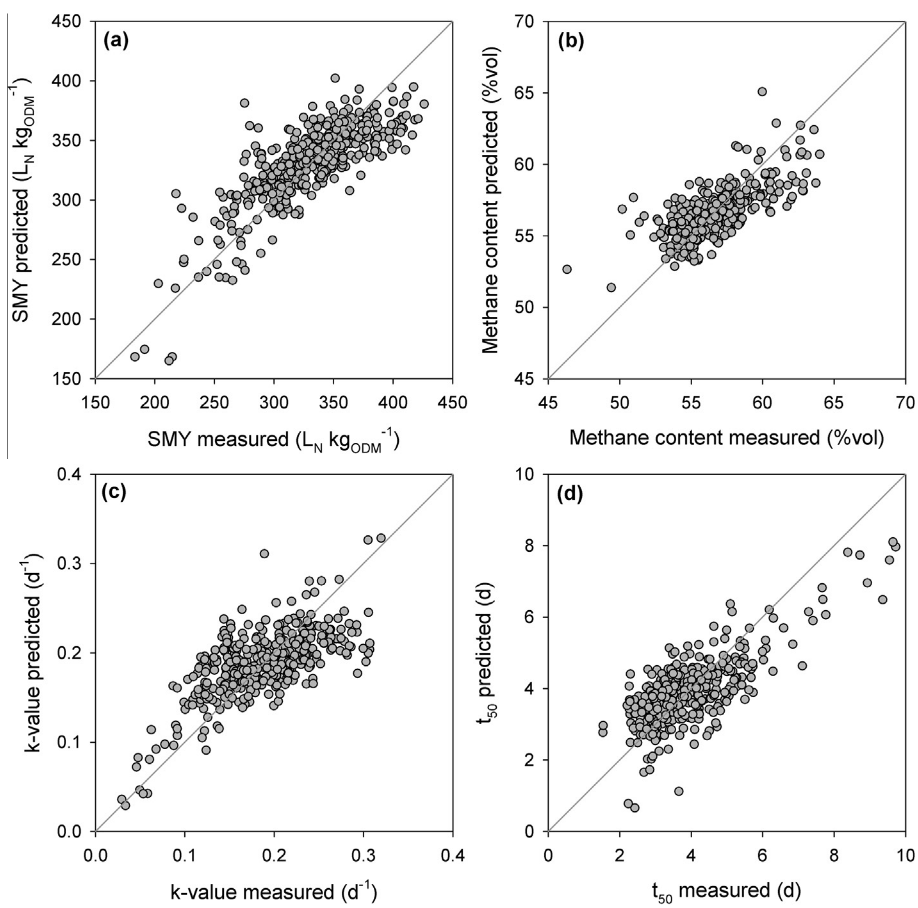

Fig. 2. Measured vs. predicted (a) specific methane yield (SMY), (b) methane content, (c) k-value and (d) half-life (t_{50}) of methane production from crop silages.

the lignocellulosic cell wall matrix are less easily available than other cell contents (Triolo et al., 2011), an increasing lignocellulosic fraction can decrease both the specific methane yield and rate of methane production. Batch anaerobic digestion tests in this study were conducted with ODM from an active inoculum present in excess of the ODM from the substrate, yet, the substrate to inoculum ratio of individual tests varied to some extent (Section 2.4). The substrate to inoculum ratio of the batch digestion tests did not significantly affect the methane yield of the silages, but was determined as a parameter that significantly influenced the rate of methane production (Tables 5 and 6). This is in agreement with findings of Raposo et al. (2011) who observed that the methane yield did not depend on the substrate to inoculum ratio but the methane production rate constant was markedly affected by an a_i between 0.3 and 1.

The coefficients of determination of regression models established in the present study were comparatively low. For example, only up to 64% of the variation in specific methane yield of crop silages could be explained (Table 6, Fig. 2), whereas coefficients of determination of 70–95% are obtained for multiple regression equations in literature (Dandikas et al., 2014; Thomsen et al., 2014; Triolo et al., 2011). However, it needs to be considered that the R^2 value depends on the total variation of the dependent variable and is remarkably less precise for small sample sizes. Thus, despite a lower R^2 value, a relative error of prediction (RRMSE = 8%) in the same range or lower than those reported in other studies (RRMSE = 6–19%) (Dandikas et al., 2014; Thomsen et al., 2014; Triolo et al., 2011) was obtained for specific methane yields, indicating adequate accuracy of the regression model.

Nevertheless, deficient coefficients of determination suggest that the chemical parameters employed in the present study are not sufficient to precisely estimate the parameters of methane formation for a wide range of biogas crop silages and cultivation conditions. The main reason for this might be the variation in the structure of the lignocellulosic matrix and in interactions between cell wall components of crop biomass which are not reflected in absolute values of the content of lignin, cellulose and hemicellulose. The structure and cross-linkage of lignin with cell wall polysaccharides varies between crop species and also changes with crop maturity (Monlau et al., 2013). Furthermore, some parameters that influence the methane production such as the particle size distribution and available surface area of the crop feedstock (Herrmann et al., 2012) were not considered. In particular, the accuracy of prediction of kinetic parameters was limited (Table 6, Fig. 2), probably due to interrelated effects of fibre components and considerable effects of particle size and the microbial population and diversity of the inoculum on the rate of methane production (Raposo et al., 2011). A low repeatability of methane production rates in batch anaerobic digestion tests was demonstrated by Raposo et al. (2011). Further research could focus on the impact of structural aspects of the lignocellulosic matrix of crop biomass on methane formation.

4. Conclusions

This study confirmed that a large range of crop species is suitable for anaerobic digestion. Lignin is the most important biomass constituent that determines specific methane yields. Methane production decreases with increasing lignin content and fibre fractions. Silage fermentation characteristics further affect methane production significantly. It is proposed that parameters of silage fermentation are considered for evaluation of methane formation from ensiled biomass. Besides methane production characteristics, biomass yields, crop rotation effects, site-specific requirements and costs and environmental effects of biomass supply further need to be taken into account for the design of sustainable crop rotations.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2016.01.058.

References

Amon, T., Amon, B., Kryvoruchko, V., Machmüller, A., Hopfner-Sixt, K., Bodiroza, V., Hrbek, R., Friedel, J., Pötsch, E., Wagentristl, H., Schreiner, M., Zollitsch, W., 2007. Methane production through anaerobic digestion of various energy crops grown in sustainable crop rotations. Bioresour. Technol. 98, 3204–3212.

Chen, Y., Cheng, J.J., Creamer, K.S., 2008. Inhibition of anaerobic digestion process: a review. Bioresour. Technol. 99, 4044–4064.

Dandikas, V., Heuwinkel, H., Lichti, F., Drewes, J.E., Koch, K., 2014. Correlation between biogas yield and chemical composition of energy crops. Bioresour. Technol. 174, 316–320.

DLG, 2006. DLG-Information 2/2006. Grobfutterbewertung. In: Teil B: DLG-Schlüssel zur Beurteilung der Gärqualität von Grünfuttersilagen auf der Basis der chemischen Untersuchung, Deutsche Landwirtschafts-Gesellschaft, DLG-Ausschuss für Futterkonservierung, DLG-Arbeitskreis Futter und Fütterung, 5 p.

Drosg, B., Braun, R., Bochmann, G., 2013. Analysis and characterisation of biogas feedstocks. In: Wellinger, A., Murphy, J.D., Baxter, D. (Eds.), The Biogas Handbook. Woodhead Publishing Limited, Cambridge, UK, pp. 52–84.

Fröschle, B., Heiermann, M., Lebuhn, M., Messelhäusser, U., Plöchl, M., 2015. Hygiene and sanitation in biogas plants. In: Guebitz, G.M., Bauer, A., Bochmann, G., Gronauer, A., Weiss, S. (Eds.), Biogas Science and Technology, 151. Springer International Publishing, pp. 63–99.

Gao, R., Yuan, X., Zhu, W., Wang, X., Chen, S., Cheng, X., Cui, Z., 2012. Methane yield through anaerobic digestion for various maize varieties in China. Bioresour. Technol. 118, 611–614.

Gissén, C., Prade, T., Kreuger, E., Nges, I.A., Rosenqvist, H., Svensson, S.-E., Lantz, M., Mattsson, J.E., Börjesson, P., Björnsson, L., 2014. Comparing energy crops for biogas production – Yields, energy input and costs in cultivation using digestate and mineral fertilisation. Biomass Bioenergy 64, 199–210.

Gödeke, K., Nehring, A., Vetter, A., 2007. Crop rotation systems for sustainable energy farming. In: Proceedings of the XVI International Plant Protection Congress, vol. 1, 15–18 October 2017, Glasgow, Scotland, UK, pp. 172–173.

Gunaseelan, V.N., 2009. Predicting ultimate methane yields of *Jatropha curcus* and *Morus indica* from their chemical composition. Bioresour. Technol. 100, 3426–3429.

Herrmann, A., 2013. Biogas production from maize: current state, challenges and prospects. 2. Agronomic and environmental aspects. Bioenergy Res. 6, 372–387.

Herrmann, A., Rath, J., 2012. Biogas production from maize: current state, challenges, and prospects. 1. Methane yield potential. Bioenerg. Res. 5, 1027–1042.

Herrmann, C., Heiermann, M., Idler, C., 2011. Effects of ensiling, silage additives and storage period on methane formation of biogas crops. Bioresour. Technol. 102, 5153–5161.

Herrmann, C., Heiermann, M., Idler, C., Prochnow, A., 2012. Particle Size reduction during harvesting of crop feedstock for biogas production. I: effects on ensiling process and methane yields. Bioenergy Res. 5, 926–936.

Herrmann, C., Prochnow, A., Heiermann, M., Idler, C., 2014. Biomass from landscape management of grassland used for biogas production: effects of harvest date and silage additives on feedstock quality and methane yield. Grass Forage Sci. 69, 549–566.

Heuwinkel, H., Aschmann, A., Gerlach, R., Gronauer, A., 2009. Die genauigkeit der messung des gasertragspotentials von substraten mit der batchmethod. In: Internationale Wissenschaftstagung Biogas Sience 2009, vol. Band 1, Bayerische Landesanstalt für Landwirtschaft. 02–04 December 2009, Erding, Germany, pp. 95–103.

Kafle, G.K., Kim, S.H., 2013. Effects of chemical compositions and ensiling on the biogas productivity and degradation rates of agricultural and food processing by-products. Bioresour. Technol. 142, 553–561.

Kreuger, E., Nges, I.A., Björnsson, L., 2011. Ensiling of crops for biogas production: effects on methane yield and total solids determination. Biotechnol. Biofuels 4, 44.

Labatut, R.A., Angenent, L.T., Scott, N.R., 2011. Biochemical methane potential and biodegradability of complex organic substrates. Bioresour. Technol. 102, 2255–2264.

Mayer, F., Gerin, P.A., Noo, A., Foucart, G., Flammang, J., Lemaigre, S., Sinnaeve, G., Dardenne, P., Delfosse, P., 2014. Assessment of factors influencing the biomethane yield of maize silages. Bioresour. Technol. 153, 260–268.
McDonald, P., Henderson, A.R., Heron, S.J.E., 1991. The Biochemistry of Silage, 2nd ed. Chalcombe Publications, Marlow, England, 341 p.
Meier, U., 2001. Growth Stages of Mono-and Dicotyledonous Plants – BBCH Monograph, 2nd ed. Federal Biological Research Centre for Agriculture and Forestry, Berlin and Braunschweig, Germany, 158 p.
Molinuevo-Salces, B., Fernández-Varela, R., Uellendahl, H., 2014. Key factors influencing the potential of catch crops for methane production. Environ. Technol. 35, 1685–1694.
Monlau, F., Barakat, A., Trably, E., Dumas, C., Steyer, J.-P., Carrère, H., 2013. lignocellulosic materials into biohydrogen and biomethane: impact of structural features and pretreatment. Crit. Rev. Environ. Sci. Technol. 43, 260–322.
Nges, I.A., Escobar, F., Fu, X., Björnsson, L., 2012. Benefits of supplementing an industrial waste anaerobic digester with energy crops for increased biogas production. Waste Manag. 32, 53–59.
Raposo, F., Fernández-Cegrí, V., De la Rubia, M.A., Borja, R., Béline, F., Cavinato, C., Demirer, G., Fernández, B., Fernández-Polanco, M., Frigon, J.C., Ganesh, R., Kaparaju, P., Koubova, J., Méndez, R., Menin, G., Peene, A., Scherer, P., Torrijos, M., Uellendahl, H., Wierinck, I., de Wilde, V., 2011. Biochemical methane potential (BMP) of solid organic substrates: evaluation of anaerobic biodegradability using data from an international interlaboratory study. J. Chem. Technol. Biotechnol. 86, 1088–1098.
Rath, J., Heuwinkel, H., Herrmann, A., 2013. Specific biogas yield of maize can be predicted by the interaction of four biochemical constituents. Bioenergy Res. 6, 939–952.
Thomsen, S.T., Spliid, H., Østergård, H., 2014. Statistical prediction of biomethane potentials based on the composition of lignocellulosic biomass. Bioresour. Technol. 154, 80–86.
Triolo, J.M., Sommer, S.G., Møller, H.B., Weisbjerg, M.R., Jiang, X.Y., 2011. A new algorithm to characterize biodegradability of biomass during anaerobic digestion: influence of lignin concentration on methane production potential. Bioresour. Technol. 102, 9395–9402.
VDI, 2006. VDI Standard Procedures 4630: Fermentation of Organic Materials. Characterisation of the Substrate, Sampling, Collection of Material Data, Fermentation Tests Verein Deutscher Ingenieure. Beuth Verlag, Berlin, 92 p.
VDLUFA, 2006. Die Chemische Untersuchung von Futtermitteln. Methodenbuch Band III. 6th Supplementary Delivery, third ed. VDLUFA-Verlag, Darmstadt, Germany.
Weißbach, F., Kuhla, S., 1995. Substance losses in determining the dry matter content of silage and green fodder: arising errors and possibilities of correction. Übersicht Tierernähr 23, 189–214.
Weißbach, F., Schmidt, L., Hein, E., 1974. Method of anticipation of the run of fermentation in silage making, based on the chemical composition of green fodder. In: Proceedings of the XII International Grassland Congress, 11–20 June 1974, Moskau, pp. 663–672.
Zegada-Lizarazu, W., Monti, A., 2011. Energy crops in rotation: a review. Biomass Bioenergy 35, 12–25.