

## Quantity of hydrophobic functional CH-groups – decisive for soil water repellency caused by digestate amendment

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**A b s t r a c t.** Anaerobic digestates are used as organic fertilizers; however, they are suspected to interfere negatively with soils. To investigate the relevance of the anaerobic digestates composition on potential wettability and contact angle of the soil, we mixed in a laboratory experiment 30 m<sup>3</sup> ha<sup>-1</sup> of anaerobic digestates derived from mechanically pre-treated substrates from maize and sugar beet with a homogenized Cambic Luvisol. Fourier transform infrared-spectra and diffuse reflectance infrared Fourier transform-spectra of particle intact and finely ground soil-anaerobic digestates-mixtures were analyzed to determine the quantities of hydrophobic functional groups in the soil-anaerobic digestates-mixtures that are used here as an indicator for the potential hydrophobicity. The anaerobic digestates application increased the amount of hydrophobic functional groups of the mixtures and reduced the wettability of the soil. However, for intact particle samples an up to threefold higher amount of hydrophobic groups was found as compared to the finely ground ones, indicating a dilution effect of mechanical grinding on the effectivity of the organic matter that is presumably located as a coating on mineral soil particles. For the particle intact samples, the intensity of hydrophobic functional groups bands denoting hydrophobic brickstones in organic matter is indicative for the actual wettability of the soil-anaerobic digestates-mixtures.

**K e y w o r d s:** anaerobic digestates, organic matter composition, Fourier transform infrared spectroscopy, diffuse reflectance infrared Fourier transform spectroscopy

### INTRODUCTION

Responding to the financial compensation for generating renewable energy, the installation of biogas plants on arable land increased in recent years. Anaerobic digestates (AD) are a by-product of biogas generation by anaerobic fermentation. Application of AD on agricultural soils will

influence the intrinsic soil organic matter pools, due to their organic carbon contents (Boyd *et al.*, 1980). Additionally, it will enhance the fertility of soils (Réveillé *et al.*, 2003) due to their vast amounts of plant nutrients (Albuquerque *et al.*, 2012) like plant available ammonium, potassium, and phosphorus (Sørensen and Møller, 2009). Besides these positive properties, digestates are suspected to have negative impacts on soils since they transfer recalcitrant amphiphilic substances (*eg* humic, fulvic, and fatty acids) into the soil matrix. Such amphiphilic substances cover soil particle surfaces, resulting in modification of the physicochemical properties of soils (Hurraß and Schaumann, 2006). The term amphiphilic substances describes molecules formed by both, hydrophobic and hydrophilic functional groups (Morrison and Boyd, 1983), which altogether may affect the actual wettability of soils (Franco *et al.*, 2000). Soil organic matter (OM) consists of amphiphilic components; therefore, Negre *et al.* (2002) linked the ability of water to spread on a soil surface to the macromolecular composition of OM. In consequence, the wetting behaviour of soils may change with the content and composition of OM coatings on mineral particle surfaces (Leue *et al.*, 2010) as well as the spatial arrangement of OM compounds at the molecular scale (Morrison and Boyd, 1983). Spectroscopic techniques like Fourier transmission infrared (FTIR) and diffuse reflection infrared Fourier transform (DRIFT) spectroscopy have been widely used to characterize the composition of functional groups in soil organic matter (SOM) (Capriel *et al.*, 1995; Gerzabek *et al.*, 1997; Tatzber *et al.*, 2007) and at intact aggregate surfaces (Leue *et al.*, 2010) in order to determine the potential wettability of OM.

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The hydrophobic functional groups of OM are represented by methylene and methyl groups (CH), whereas carboxyl- and hydroxyl (C=O) groups reflect the hydrophilic ones. Characteristic absorption bands in FTIR and DRIFT spectra allow analysis of the contents of hydrophobic CH- (Capriel, 1992) and hydrophilic C=O-groups (Celi *et al.*, 1997). Thus, such spectroscopy techniques (FTIR Demyan *et al.*, 2012; DRIFT *eg* Reeves *et al.*, 2001) have been widely applied to characterize the OM composition. Celi *et al.* (1997) stated the CH/C=O ratio should be appropriate to deduce the potential hydrophobic properties of the OM (Morrison and Boyd, 1983), while Ellerbrock *et al.* (2005) could not detect reduced wettability with an increasing A/B ratio. They justified these findings with the low effectiveness of the hydrophobic CH-bands to cause wettability. These results however also prove that the effectiveness of the quantity of CH-bands within OM originating from AD on the hydrophobicity in soils is still unknown. Since soil hydrophobicity results in severe ecological problems such as soil erosion, especially in sloped areas, it would be necessary to investigate the causes of this process.

Therefore, the aim of the study was to evaluate the consequences of the application of AD different in OM composition on the wettability of soil mineral surfaces. We assume that even a small amount of wetting-restraining CH-groups will be sufficient to reduce the sample wettability and that, in this case, the effect of the CH-groups dominates the effect of the hydrophilic C=O-groups. We hypothesize that the ratio between hydrophobic and hydrophilic groups is less effective in estimation of the impact of the AD application on the wetting behaviour of soils as compared to the intensity of CH absorption bands.

#### MATERIALS AND METHODS

For the laboratory measurements, disturbed soil material was sampled in June 2013 from the first 10 cm of the A-horizon of an arable Cambic Luvisol (derived from Weichselian glacial till, FAO, 1998) at the research farm Hohenschulen of the University of Kiel, Germany. The chemical parameters of the soil was analyzed using standard procedures according to Schlichting *et al.* (1995).

The soil sample (n=1) from Hohenschulen contained 166, 272, 1.2, and 7 g kg<sup>-1</sup> clay, silt, organic carbon, and nitrogen, respectively was classified as a sandy loam (FAO, 1998). The soil pH of 6.6 exhibited slightly acidic conditions and was classified as Cambic Luvisol (KA5, 2006).

Liquid digestates were produced at the Institute for Agricultural Engineering (University of Kiel) in batch-fermentation processes. Input substrates (IS) from maize (*Zea mays* L.) and sugar beet (*Beta vulgaris* L.) were mechanically pre-treated by grinding (gr) or chopping (ch) and digested in monofermentation (one IS) and cofermentation (two IS in different ratios) (Table 1).

**Table 1.** Summary of the mechanical pre-treatment (chopped, gr-ground) and the ratio of the used input substrate (IS)

Amendment	Pre-treatment	Input substrate	Ratio (%)
gr-M100	ground	maize	100
ch-M100	chopped		100
gr-SB100	ground	sugar beet	100
ch-SB100	chopped		100
gr-SB80M20	ground	sugar beet/ maize	80 / 20
ch-SB80M20	chopped		80 / 20
gr-M80SB20	ground	maize/ sugar beet	80 / 20
ch-M80SB20	chopped	maize/ sugar beet	80 / 20

The disturbed soil material from the top layer of the ploughed soil surface was air-dried and sieved to  $\leq 2$  mm. Assuming an average soil depth of 30 cm in accordance with the common agricultural practice, 480 g of the air-dried soil were mixed with 30 ml of anaerobic digestates (AD) (equivalent to 30 m<sup>3</sup> ha<sup>-1</sup>) by stirring. Additionally, a control treatment (C) was prepared using the same amount of demineralized water instead of the digestates. Two mixtures (repetitions) of each treatment were prepared. The soil remained in contact with the AD for 10 days at 10°C until a biological equilibrium was reached. Then, the mixtures were again air-dried and homogenized. From each mixture, six subsamples were taken for determining the contact angle (CA), two for transmission FTIR and four for DRIFT measurements.

To determine the wetting behaviour, the CA of the air-dried soil samples ( $\leq 2$  mm) was measured using the Wilhelmy-Plate-method (WPM) with a microtensiometer (Krüss, Hamburg, Germany) (Hartmann, 2008). The advancing and receding CA between 0 and 180° was measured by immersing a glass plate covered with a one-grain layer of soil particles into distilled water with known surface tension. The CA ( $\cos \theta$ ) was calculated from the force  $F$  (N) acting on the plate using Eq. (1):

$$\cos \theta = F / (\rho \sigma_{LV}), \quad (1)$$

where:  $\sigma_{LV}$  (mN m<sup>-1</sup>) denotes the surface tension of the liquid and  $\rho$  indicates the liquid density (g cm<sup>-3</sup>). A CA between 0° and 90° characterises hydrophilic conditions, whereas values  $\geq 90^\circ$  describe hydrophobic conditions (Bachmann *et al.*, 2003). The measurement of the CA was conducted in six replicates per sample.

The composition of the OM was characterized using transmission FTIR and DRIFT technique (Tremblay and Gagné, 2002). The functional groups of finely ground samples can be analyzed with both Fourier Transform Infrared spectroscopy (FTIR) (Haberhauer and Gerzabek, 1999) and the DRIFT technique. The DRIFT method has also been applied to detect the OM functional groups at the surface of intact soil particles (Leue *et al.*, 2010):

- FTIR spectroscopy of ground samples (G) mixed with potassium bromide (KBr),
- DRIFT spectroscopy of ground samples (G),
- DRIFT spectroscopy of particle intact samples (PI).

For the FTIR measurements, air-dried samples from the soil-AD-mixtures ( $\leq 2$  mm) and freeze-dried AD samples were finely ground in an agate mortar. For spectral analysis in the transmission technique FTIR, the KBr technique was used according to Capriel *et al.* (1992): one milligram of the ground samples was mixed with 80 mg KBr. The mixture was dried over silica gel in an exsiccator for 12 h to standardize the water content of the samples, ground again in an agate mortar, and formed into a pellet using a hydraulic press (9 t). The pellet was positioned into a sample holder.

For DRIFT measurements, the samples were either finely ground in an agate mortar (G) or left particle intact (PI) (particles of  $\leq 2$  mm diameter) to analyze the effect of particle size distribution on the DRIFT signal intensities (Ellerbrock *et al.*, 2009). One mg of the finely ground soil-digestate-mixture was filled into cylindrical cups of 8 mm diameter and a height of 2 mm. The PI samples from the soil-AD-mixtures were filled into a tinfoil box with 5 cm length and 1 cm width. The cups and box were placed on an aluminium plate, which was positioned on an XY-positioning table of the spectrometer (Leue *et al.*, 2010). 32 internal scans with four replicates of the subsamples were recorded with a DRIFT device of the BioRad FTS 135 (BioRad Corp, Hercules, CA) in a range of wavenumber from 4 000 to 400  $\text{cm}^{-1}$  each spectra and corrected against ambient air as background (McDowell *et al.*, 2012). The DRIFT spectra were recorded with a resolution of 4  $\text{cm}^{-1}$  and 16 scans (16 repetitions of single spectra) (Ellerbrock and Kaiser, 2005). The spectra were smoothed with a box-car function, which is unity within the interval and zero outside it and baseline-corrected using the software Win-IR Pro 3.4 (Digilab, Holliston, MA). Finally, the reflectance data were converted to Kubelka-Munk units using the standard KM transformation in the software to compare the adsorption intensity. The Kubelka-Munk equation relates the intensity of the reflected radiation to the concentration that can be used for quantitative evaluation. The Kubelka-Munk function produces a transmission spectrum, which demonstrates a linear relationship between band intensity and the sample preparation. The Kubelka-Munk units are dimensionless.

The spectral interpretation focusses on absorption bands at 2 920  $\text{cm}^{-1}$  (asymmetric stretch) and 2 860  $\text{cm}^{-1}$  (symmetric stretch) caused by CH-stretching vibrations of methyl and methylene groups (absorption band A) (Capriel *et al.*, 1995). These groups represent the hydrophobic functional OM groups. The absorption bands characteristic for hydrophilic carboxylic C=O-groups (*ie* brickstones of ketones, carboxylic acids, or amides) occurred at 1 701 to 1 698  $\text{cm}^{-1}$  (Günzler and Böck, 1990) (absorption band B). The cumulative heights of hydrophobic CH-absorption bands were related to that of the hydrophilic C=O-bands (A/B ratio) in order to reflect the hydrophobic character of the OM (Ellerbrock *et al.*, 2005) and to determine the potential wettability of the soil-AD-mixtures.

Statistical significance of the data was analyzed using the statistical software R (version 2.15.3). Based on the graphical residual analysis, the values were assumed to be normally distributed and heteroscedastic. Analysis of variance (ANOVA) was used to assess the statistical significance between the amendments and the control.

## RESULTS

Both types of AD (mono and co-fermentation) as well as the AD obtained from monofermentation of ground input substrates (gr-M100 and gr-SB100) showed a pH  $>8$  (Table 2). For the gr-M100 digestate, the highest ammonium content was found, while the digestates from monofermentation (ch-M100 and ch-SB100) and from cofermentation (gr-SB80M20 and gr-M80SB20) contained the highest amount of sodium ions compared to the other digestates.

The FTIR spectra indicated higher contents of hydrophobic CH-groups for the AD derived from ground IS as compared to those of the chopped IS, but the A/B ratio did not reflect such differences (Table 3). The DRIFT spectra of the AD samples showed strong signals due to light scattering caused by fibre particles contained in the AD. The signals resulting from direct scattering impeded the interpretation of the absorption bands of the CH- and C=O-groups in OM.

The transmission FTIR and the DRIFT (Fig. 1a, b) spectra of the soil-AD-mixtures showed a similar peak pattern for AD from ground and chopped (graphic not shown) IS. The FTIR spectrum of the soil (control, C) sample indicated a maximum at 1 100  $\text{cm}^{-1}$  for the absorption band C, while the soil-AD-mixtures exhibited a maximum at 1 050  $\text{cm}^{-1}$ , indicating a change in the composition of polysaccharides that caused this absorption band. Such differentiation was not found in the DRIFT spectra of the corresponding samples. After application of digestates derived from ground IS, the amount of functional groups was significantly ( $p < 0.05$ ) higher compared to the control.

All spectra exhibited absorption bands at 2 920 to 2 860  $\text{cm}^{-1}$  due to CH vibrations of aliphatic methyl and methylene groups (band A) and at 1 740 to 1 698  $\text{cm}^{-1}$  due

**Table 2.** Properties of the digestates obtained for ground (gr) and chopped (ch) input substrates (n=1). Data expressed in % of the original substance (OS)

Amendment	EC ( $\mu\text{S cm}^{-1}$ )	pH	Acetic acid ( $\text{g kg}^{-1}$ OS)	Dry solids	$\text{NH}_4\text{-N}$	Total N	P	K	Mg	Ca	Na ( $\text{mg kg}^{-1}$ OS)
gr-M100	81	8.25	<0.05	2.8	0.21	0.24	0.23	0.03	0.02	0.02	139
ch-M100	83	7.93	<0.05	3.0	0.14	0.24	0.27	0.04	0.03	0.03	179
gr-SB100	84	8.21	<0.05	2.6	0.15	0.26	0.22	0.03	0.02	0.02	138
ch-SB100	82	7.85	<0.05	2.8	0.13	0.23	0.25	0.03	0.03	0.02	167
gr-SB80M20	91	7.74	0.083	2.8	0.14	0.17	0.28	0.05	0.04	0.02	159
ch-SB80M20	85	7.82	<0.05	2.9	0.14	0.26	0.23	0.03	0.02	0.02	140
gr-M80SB20	90	7.75	<0.05	2.8	0.14	0.18	0.29	0.04	0.04	0.02	159
ch-M80SB20	87	7.85	<0.05	3.2	0.15	0.25	0.24	0.04	0.02	0.02	145

< Below the detection limit.

**Table 3.** Intensity of CH (band A) and C=O (band B) in FTIR spectra (n=4) of freeze-dried digestates derived from ground (gr) and chopped (ch) input substrate (IS)

Amendment	A	B	A/B
gr-M100	0.108	0.505	0.215
gr-SB100	0.097	0.426	0.227
gr-SB80M20	0.091	0.426	0.214
gr-M80SB20	0.093	0.426	0.219
ch-M100	0.076	0.350	0.216
ch-SB100	0.098	0.482	0.204
ch-SB80M20	0.062	0.252	0.244

to C=O vibrations of carboxylic groups (band B). However, the FTIR and DRIFT spectra differed in the intensity of the absorption bands A and B (Fig. 1). The intensity of the CH- and C=O-bands was significantly ( $p<0.05$ ) higher in the DRIFT spectra than in the transmission FTIR spectra. In comparison to the transmission FTIR spectra, the DRIFT spectra did not show the Si-O-Si band at a wavenumber of around  $1\,000\text{ cm}^{-1}$  (band C).

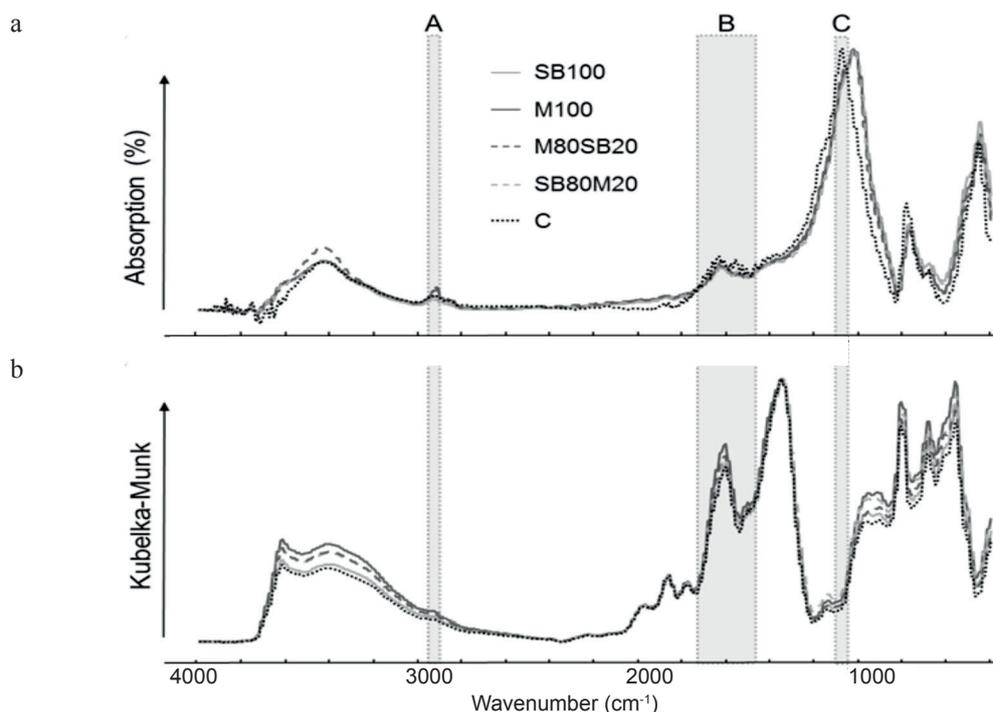
The DRIFT spectra of the soil-AD-mixtures showed significantly higher absorption intensities of the CH-band (band A) as compared to the one of the unamended control C. This was not found for the FTIR spectra. The comparison between the spectra showed higher absorption intensity at B and A bands as well as an increasing CH/C=O-ratio (A/B) of the soil-AD-mixtures from ground as compared to that from chopped IS.

The DRIFT spectra of the particle intact (PI) soil-digestate-mixture samples are similar to those from ground and chopped IS (graphic not shown). The intensity of the CH-absorption band (B) was higher for the soil-AD-mixtures compared to the one of the unamended control soil C.

The intensity of the A and B bands of the DRIFT (G) spectra was statistically higher ( $p<0.05$ ) compared to the absorption intensity of the CH- and C=O-bands of the FTIR (G) spectra (Table 4). In contrast to these former findings offered the absorption intensity of the A- and B-bands of the PI intact samples up to threefold higher absorption intensities of A- and B-bands compared to the spectra of the (G) samples, which was not least represented by the A/B ratio of the samples. However, in the FTIR (G) spectra, the gr-M80SB20 sample exhibited the highest intensity of the CH-band while in the DRIFT (G and PI) spectra gr-M100 showed the highest intensity of the CH-band (Table 4).

The control soil possessed a CA  $< 90^\circ$  and hence it could be classified as hydrophilic (Table 4). The soil-AD-mixtures showed higher CA values whereby the CA values were slightly higher for the mixtures with AD from ground (88.9 to 91.5) as compared to those from chopped IS (81.1 to 91.0) (Table 4), except for gr-SB100, which exhibited similar CA values for the mixtures from AD with chopped and ground IS.

The CA values were positively correlated (but not significantly) with the intensity of the absorption band A and with the A/B ratio of the ground and particle intact samples, respectively (Fig. 2). The A/B ratio determined from the FTIR and DRIFT spectra of the ground mixtures showed a better correlation with the CA compared to the A-band (Fig. 2a, b, d, e). The correlation between both, the A-band and the A/B ratio was higher in the DRIFT spectra of the



**Fig. 1.** FTIR (a) and DRIFT (b) spectra (ground samples) of digestate-soil mixtures (SB100: 100% of sugar beet; M100: 100% of maize; SB80M20: 80% of sugar beet and 20% of maize; M80SB20: 80% of maize and 20% of sugar beet) derived from ground input substrates.

**Table 4.** Intensity of CH and C=O band in FTIR and DRIFT spectra of ground (G) and particle intact (PI) samples (n=4) as well as the contact angle (CA) [°] of soil-AD-mixtures (n=6) and untreated soil (C)

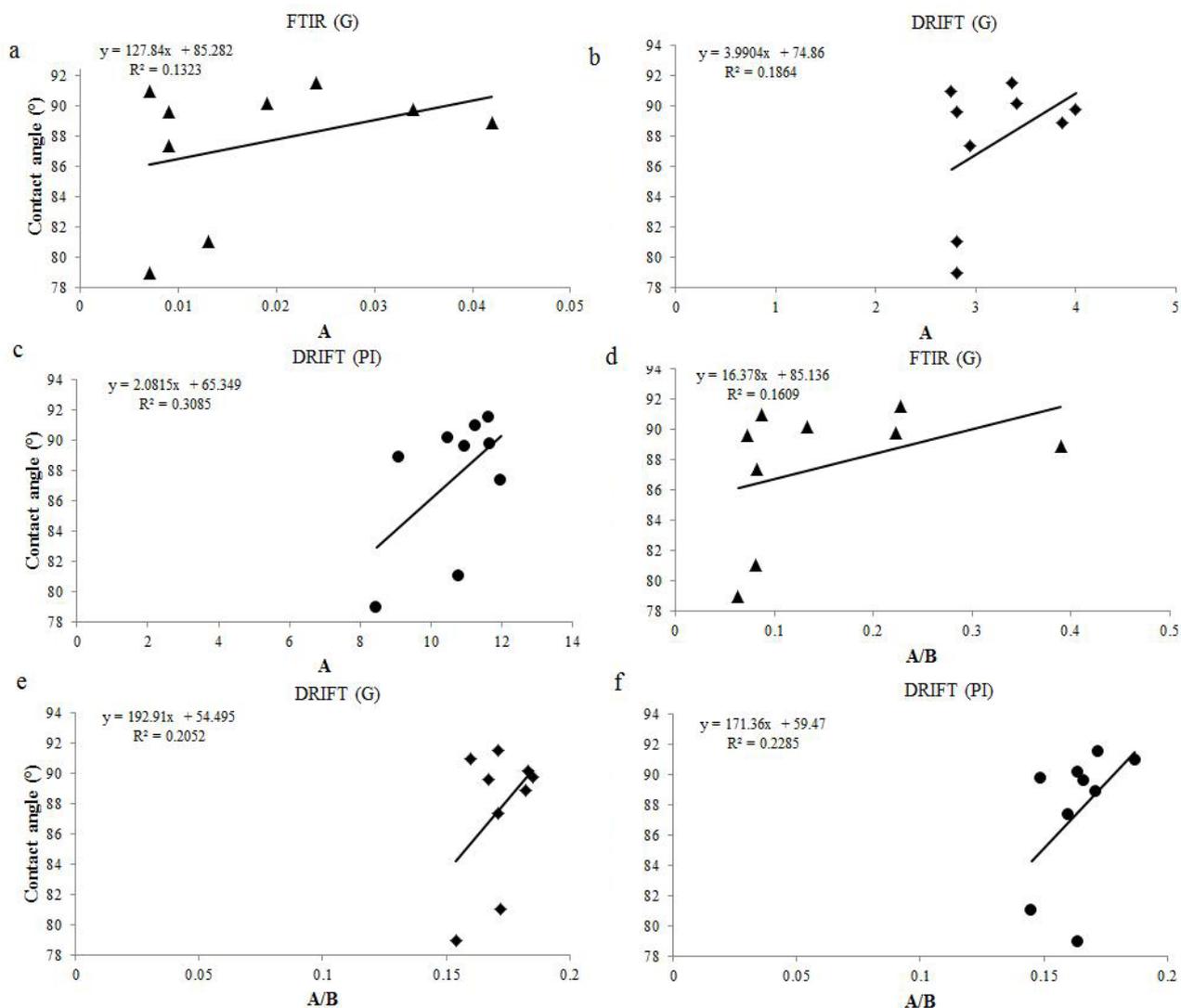
Amendment	FTIR (G)			DRIFT (G)			DRIFT (PI)			CA
	CH	C=O	CH/ C=O	CH	C=O	CH/ C=O	CH	C=O	CH/ C=O	
gr-M100	0.034b	0.152b	0.223b	4.003b	21.589a	0.185a	11.647a	78.255b	0.149a	89.8a
gr-SB100	0.024b	0.107b	0.228b	3.362b	19.612a	0.171a	11.621a	67.596a	0.172a	91.5a
gr-SB80M20	0.019a	0.146b	0.133b	3.409b	18.670a	0.183a	10.474a	64.005a	0.164a	90.2a
gr-M80SB20	0.042b	0.107b	0.390b	3.862b	21.221a	0.182a	9.087a	53.034a	0.171a	88.9a
ch-M100	0.013a	0.164b	0.081a	2.807a	16.360a	0.172a	10.792a	74.370b	0.145a	81.1a
ch-SB100	0.007a	0.082a	0.087a	2.755a	17.207a	0.160a	11.242a	59.999a	0.187a	91.0a
ch-SB80M20	0.009a	0.115b	0.082a	2.942a	17.202a	0.171a	11.977a	74.723b	0.160a	87.4a
ch-M80SB20	0.009a	0.118b	0.073a	2.811a	16.813a	0.167a	10.957a	66.127a	0.166a	89.6a
C	0.007a	0.063a	0.063a	2.808a	18.194a	0.154a	8.460a	51.548a	0.164a	79.0a

Different letters (ab) indicate statistically significant differences ( $p < 0.05$ ) of the functional groups of digestates in comparison to the control.

ground samples compared to the transmission FTIR spectra. The correlation of the intensity of the A-band as well as the A/B ratio was best using intact particle samples (Fig. 2c and f). The spectra of the PI exhibited a higher correlation between CA and the intensity of the A-band compared to the A/B-ratio.

## DISCUSSION

Soil organic matter is characterized by the amount of particulate organic matter, organo-mineral complexes (Leue *et al.*, 2013), humic acids, the content of functional groups (CH and C=O) and their spatial conformation of organic molecules on the microscale (Morrison and Boyd, 1983).



**Fig. 2.** CA (°) vs. intensity of absorption band A determined from: a – FTIR, b – DRIFT of ground (G) and c – DRIFT spectra of particle intact samples and CA (°) vs. A/B ratio determined from d – FTIR, e – DRIFT of ground (G) and f – DRIFT spectra of particle intact samples.

The organic material of anaerobic digestates contains great amounts of amphiphilic components like long-chained fatty acids, which are transferred to the soil matrix after application (Täumer *et al.*, 2005); it can flow into pore spaces or may surround mineral particles. The effect of this coating on the soil is mainly determined by the ratio of hydrophobic CH-bands to hydrophilic C=O-bands, which in term has major implications for the wetting behaviour of mineral particles (Ellerbrock and Gerke, 2004). The FTIR and DRIFT spectra of the soil-AD-mixtures indicate a change in the composition of SOM after digestate amendment: the amount of hydrophobic CH-groups is higher as compared to the unamended soil reflected by a more pronounced peak at a wavenumber of 2920 and 2860  $\text{cm}^{-1}$ . This may

be explained by a supply of hydrophobic functional groups contained in the ADs. This is in accordance with Capriel *et al.* (1997), who assessed a close relationship between CH content and soil hydrophobicity. With an increasing amount of CH-groups determined by FTIR and DRIFT the wettability of the soil-AD-mixtures decreases.

The CH/C=O ratio, which is also assumed to reflect the potential wettability of soil samples (Ellerbrock *et al.*, 2005), can just be partly related to the wettability of soil-AD-mixtures investigated here. Ellerbrock *et al.* (2009) used FTIR spectroscopy to investigate the ratio of hydrophobic CH-bands (A) to hydrophilic C=O-bands (B) in the SOM and found that the lower values of the A/B ratio indicate more hydrophilic conditions of the OM, while the

hydrophobicity increases. They concluded that the hydrophobic functional CH-groups seemed to be less effective in reducing soil wettability. These findings are consistent for the soil-AD-mixtures from the finely ground samples investigated with FTIR and DRIFT spectroscopy. The highest wettability of the soil-AD-mixture ch-M100 from the ground samples does not show the lowest A/B ratio and, at the same time, the lowest wettability of the ground samples from the soil-AD-mixtures (gr-SB100 and ch-SB100) does not exhibit the highest proportion from hydrophobic CH-bands to hydrophilic C=O-bands. However, the PI samples show compliance of the wettability and the A/B ratio of the soil-AD-mixtures. Based on these results, the composition of the functional groups of the organic matter cannot be considered as the only factor to derive the actual hydrophobicity of the soil after AD amendment.

Besides the qualitative composition of the OM, another explanation for variances in soil wettability may be the quantity of organic compounds and their spatial arrangement in the pore space, which cannot be detected with the FTIR or DRIFT spectra. Depending on the soil water content, the organic compounds – consisting of a hydrophobic carbon backbone and a hydrophilic functional group – may change their orientation in the pore space when the water content falls below critical water content (González-Peñaloza *et al.*, 2013). In a dry surrounding, the hydrophilic groups are attracted and the hydrophobic backbones are arranged around the hydrophilic centre, which results in more hydrophobic conditions. However, although the soil-AD-mixture samples are air-dried, such reorientation of the organic molecules is not reflected in a noticeably increasing contact angle. The extent of the hydrophobic effect is further dependent on the soil texture since the loamy sand contains great amounts of clay particles, which exhibit a considerable greater specific surface area with reactive binding places (Caravaca *et al.*, 2001). The additional supply of functional groups with the ADs seems to be sufficient to cover the multitude of binding places on the clay particle surfaces, as a result the impact of the functional groups on hydrophobization is less intensive. Gerin *et al.* (2003) found that for fine-textured soils, a dilution effect of the SOM might occur due to the relatively large surface areas of the soil particles, which results in a thin and less effective coating of organic compounds on the particle surface.

The FTIR and DRIFT spectra can be only detected from air-dried soil-AD-mixtures and freeze-dried ADs. As a result, the findings from this study can be transferred to field conditions in the case of a dry period but are not transferable to moist soil conditions after rainfall. For the used methods (spectroscopic technique as well as the measurement of the contact angle), homogenized soil was required. Thus, after occurrence of wetting and drying cycles in the field and subsequent soil structure formation, the results may not be transferable to field conditions any more.

Thus, we can conclude that the situation observed in the laboratory cannot be projected to field conditions one to one. Nevertheless, the measurements are a first attempt to estimate the impact of ADs on soil wetting properties on the microscale.

The analysis of the organic functional groups using FTIR and DRIFT spectroscopy shows only very small differences, but the pre-treatment of the samples seems to be the decisive factor. The PI samples exhibit the best correlation between the A/B ratio as well as the height of the A-band compared to the finely ground samples. Nevertheless, the content of hydrophobic CH bands of the PI samples reflects better the actual hydrophobicity of the soil compared to the A/B ratio. Reeves *et al.* (2005) assumed that grinding of the particles might influence the spectra of the intensity of the adsorption bands. Amelung *et al.* (2002) suggested that grinding of the particles destroyed the mineral particles as well as the organic coating. These offers further mineral surfaces without any organic compounds. Consequently, the organic compounds are diluted due to the crushing process and the spectra represent more the mineral nuclei than the organic compounds of the coating. This is confirmed by the missing Si-O-Si-band (band C) in the DRIFT spectra of the PI samples compared to the FTIR spectra. Since the ground soil-AD-mixtures exhibit low values for the A- and B-bands, the absorption intensity of the CH- and C=O bands of the PI samples are substantially higher. This indicates that mainly the organic coating of the PI particles was recorded, while the proportion of the silicate particle exceeds the quantity of the organic compounds. The ground samples from FTIR reflect both the surface consisting of organic compounds and the quartz core (Leue *et al.*, 2010), while the PI samples from DRIFT represent proportionately the coating surrounding the mineral core. Previous studies from Ellerbrock and Gerke (2004) confirmed already that the KBr-technique of FTIR spectroscopy was not suitable to determine primarily the outer surface of soil particles.

## CONCLUSIONS

1. The determination of hydrophobic and hydrophilic functional groups of organic matter contained in the anaerobic digestates using Fourier transform infrared and diffuse reflectance infrared Fourier transform is suitable to obtain information about the potential wettability of the organic compounds but is not transferable to actual wettability of soil in any case.

2. The applicability of Fourier transform infrared and diffuse reflectance infrared Fourier transform spectroscopy of differently mechanically pre-treated samples were tested in this study to explain the change of the contact angle of the samples after anaerobic digestates application. Differences in the composition of the organic matter could be detected for the soil-anaerobic digestates-mixtures compared to the unamended control for the ground and particle intact samples.

3. For the particle intact samples, the ratio of potentially hydrophobic groups and potentially hydrophilic and the quantity of potentially hydrophobic CH-bands are found to correlate best with the actual wettability of the soil, whereas the utility of the A-bands is more suitable to evaluate the anaerobic digestates induced reduced soil wettability.

4. The ground samples do not reflect the actual wettability in all cases due to a high dilution effect of the organic functional groups with the silicate core.

5. It can be summarized that the composition of anaerobic digestates organic matter will be best achieved by evaluating particle intact samples using the diffuse reflectance infrared Fourier transform technique. However, the microtopography of the particle intact samples remains unconsidered applying diffuse reflectance infrared Fourier transform spectroscopy and has to be taken into account in further investigations. At present, it is not possible to determine only the hydrophilic functional groups by considering the hydrophilic bands, but also further organic components which cannot be separated from the hydrophilic bands. This could therefore be a solution to evaluate the potential wettability of the organic matter based on the ratio of the hydrophobic bands and the silicium band according to the approach of Bernier *et al.* (2013).

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