

Paper entitled “Challenges associated with the sampling and analysis of organosulfur compounds in air using real-time PTR-TOF-MS and off-line GC-FID”

Response to Referee #2

Please find below our point-to-point responses to the referee’s minor comments and technical corrections as follows: Referee’s comments are presented in blue and our corresponding responses follow in black.

The authors describe a detailed study on organosulfur-compound measurements using PTR-ToF-MS and GC-FID. The application of both techniques is demonstrated by laboratory measurements of standards and ambient measurements from complex, high emission sources. Overall, the study is carefully designed, addressing the uncertainties and pitfalls of the two methods. Thus, the manuscript is appropriate for publication within the scope of AMT.

The presentation of the results is well structured and understandable. The authors provide a comprehensive overview on work that has been undertaken in this field and the language is fluent and precise.

I recommend publication in AMT, after addressing the following minor comments:

Abstract

p. 13158, l. 6: The ordering of visibility, climate and human health seems unusual. Aerosol effects on climate are rather considered as beneficial, not as “negative”, as they are counteracting greenhouse gas forcing.

=> We understand the confusion. We modified the text to read: *“Their oxidation to methanesulfonic and sulfuric acids leads to the formation and growth of atmospheric particles, which are known to influence clouds, climate and atmospheric chemical processes. In addition, particles in air have been linked to negatively affect visibility and human health.”*

l. 7: I doubt that it will be possible to “predict particle formation” events, even if one knows OSC emissions in detail. Still, improving emission inventories (which include OSC emissions) might help to reduce uncertainties in sulfuric acid production, which is linked to new particle formation.

=> We thank the reviewer for this comment, and we have modified the text to read: *“Their oxidation to methanesulfonic and sulfuric acid leads to the formation and growth of atmospheric particles, which are known to influence clouds, climate and atmospheric chemical processes. In addition, particles in air have been linked to negatively affect*

visibility and human health. Accurate measurements of the OSC precursors are thus essential to reduce uncertainties in their sources and contributions to particle formation in air.

Introduction

The unexperienced reader would appreciate if reported ranges of mixing ratios were included for pristine marine environments and being contrasted to other natural sources (e.g. wetlands) and anthropogenic sources.

=> We have included ranges of concentration measured in air in the introduction. The text now reads: *“Organosulfur compound emissions have also been reported from terrestrial biogenic sources including wetlands, soils, vegetation and biomass burning (Goldan et al., 1987; Bates et al., 1992; Kesselmeier et al., 1993; Crutzen et al., 2000; Watts, 2000; Meinardi et al., 2003; Geng and Mu, 2006; Yi et al., 2008). In addition to these biogenic sources, several recent studies report organosulfur compound emissions from anthropogenic agricultural and composting activities, and from animal waste (Burnett, 1969; Williams et al., 1999; Filipy et al., 2006; Kim et al., 2007; Shaw et al., 2007; Trabue et al., 2008; Feilberg et al., 2010; Papurello et al., 2012; Meinardi et al., 2013; Zhang et al., 2013). Atmospheric mixing ratios of OSCs range from a few ppt to hundreds of ppbs. Typically, ppt levels in pristine marine environments and the free troposphere (Nquyen et al., 1983; Andreae, 1990; Crutzen et al., 2000; Watts, 2000; de Bruyn et al., 2002), with ppb concentrations in coastal ecosystems and wetlands (Watts, 2000). Concentrations of tens to hundred of ppt have been reported above vegetation, soil and rice paddies (Crutzen et al., 2000; Geng and Mu, 2006; Yi et al., 2008; Jardine et al., 2015) with some measurements above the canopy reaching a few ppb for DMS in some cases (Kesselmeier et al., 1993). Finally, much higher concentrations have been reported from local anthropogenic sources as livestock and animal and domestic wastes, with levels reaching a few ppb to hundreds of ppb (Williams et al., 1999; Watts, 2000; Filipy et al., 2006; Kim et al., 2007; Feilberg et al., 2010; Papurello et al., 2012).”*

p. 13160, l. 19: Is the probability of fragmentation in PTR-MS only a matter of size of the molecules? What is about fragmentation probability considering different functionalities of small (<200 amu) molecules?

=> We agree that the fragmentation in the PTR-MS is not only a matter of molecular size, but also certain functional groups are more subject to fragmentation than others. Alcohols and aldehydes are, for example, often observed to lose water (-H₂O), while ketones show nearly no fragmentation (see the nice analysis by Burh et al. (2002)). We modified the text to read: *“This technique provides fast response, high sensitivity and, depending on the molecule and the instrumental conditions, relatively low fragmentation. It has been increasingly applied to the measurement of volatile organic compounds; however, it is sensitive only to molecules that have a proton affinity higher than that of water, and several classes of compounds are subject to fragmentation, which complicates attributions of peaks in complex mixtures (Buhr et al., 2002; Tani et*

al., 2003; Maleknia et al., 2007; Kim et al., 2009; Brown et al., 2010; Gueneron et al., 2015).”

Materials and methods

p. 13161, l. 18-21: Please provide a reference for that?

=> We have added a reference as follows: *“However, many reactive compounds fragment, and all fragments must be taken into account to estimate the mixing ratios of the targeted species if they are derived from PTR-ToF-MS parameters rather than calibration with standards (Kim et al., 2009).”*

p. 13162, l. 13: replace “two standard deviations” with 2σ .

=> We modified the text accordingly.

p. 13162, l. 26-28: How sure is it that the modified Gaussian function fit from another instrument applies to the used instrument? Are peak shapes changing with time, depending e.g. on ambient temperature? How does the applied modified function fit match with your reagent ion signal (which can be used to determine an instrument specific peak shape function)?

=> We applied our own custom modified Gaussian function fits defined in PTR-MS viewer software for each pure standard peak, and then the fits were applied to the atmospheric samples. We agree that peak shapes may change with time, depending on the calibration and optimization of the instrument. We understand that having the reference at the end of the sentence was misleading and removed it.

p. 13162, l. 29: resolution of 5000 at which m/z?

=> The resolution of ~ 5000 is a specification of the instrument given by the manufacturer, Ionicon Analytik. Experimentally, we defined the resolution using the TO-14 mixture (mixture of 14 aromatic compounds in nitrogen) and the values were higher than 4000 for mass-to-charge ratios m/z 79 to m/z 181. We added a statement in the experimental section as follow: *“The PTR-ToF-MS is equipped with a time-of-flight mass filter with a manufacturer-stated resolution of ~ 5000 , which allows for accurate mass determination. The resolution of the instrument for the full mass range of interest was verified using a mixture of 14 aromatic compounds in nitrogen (mixing ratios of ~ 100 ppb, TO-14, Linde) and gave resolution higher than 4000 for mass-to-charge ratios ranging from m/z 79 to m/z 181, which is sufficient to resolve the peaks of interest in this study.”*

p. 13165, l. 5: Out of curiosity: Can the higher emission rate of MTO vs H₂S be explained, although the H₂S vapour pressure is ten times higher than that of MTO?

=> Custom permeation tubes were purchased from VICI. While methanethiol (MTO) was enclosed in a typical tubular device (i.e. a sealed permeable tube), hydrogen sulfide (H₂S) was enclosed in a stainless steel wafer device. In the latter case, permeation only occurs through the polymeric wafer located at the bottom of the device. The permeation rate can be adjusted by varying the wafer material, the thickness of the wafer and the diameter of the permeation hole. Wafer devices are specifically designed for gases that have a high vapor pressure at normal permeation temperatures and that cannot be contained in a tubular device. We added a description to the experimental section as follows: *“Lastly, for a separate series of experiments, generation of gas phase DMTS, MTO and hydrogen sulfide (H₂S) standards was performed using commercially available permeation devices (VICI), which were each enclosed individually in a U-shaped glass tube and maintained at 50°C using a thermostated water bath (LAUDA, model M20). While an individual sealed permeable tube (or tubular device) was used for MTO and DMTS, the H₂S liquid standard was enclosed in a stainless steel wafer device (wafer device type 30F3, VICI), which only permeates through a small opening in a tetrafluoroethylene membrane located at the bottom of the device to allow a slow permeation rate to be obtained. A flow of 200 cm³ min⁻¹ dry, filtered air purified by passing through an FTIR purge gas generator (Parker Balston Model 75-62), carbon/alumina media (Perma Pure, LLC) and an inline 0.1 μm filter (DIF-N70; Headline Filters) served as the carrier gas and diluent through the permeation tube.”*

p. 13165, l. 15: Consider renaming into: Sampling from a complex, high emission source.

=> We thank the reviewer for the suggestion. We modified the text accordingly.

p. 13165, l. 28: Replace “inlet of the container” with “sampling line of the bin” in order to be consistent with the paragraph

=> We thank the reviewer for the suggestion. We modified the text accordingly.

Results and discussion

p. 13167, l. 25: Does the mass defect of the unidentified signal suggest it contains sulfur? Does the signal height of the isotopic signal at m/z 98 tells how much sulfur one would expect?

=> The identity of the fragment observed at m/z 96 is still very uncertain. While this fragment is clearly not S₃⁺, as shown in figure S4, it is difficult to get a definite identification. The isotopic peak ratio between m/z 96 and m/z 98 is about 5%, suggesting that this fragment might have 1 sulfur atom (ratio ³⁴S/³²S is 4.4%); however, no clear identification could be made at this time. As seen in the table below, none of the possible elemental composition formulae for unit mass m/z 96 accurately represent

the peak observed in the mass spectra within the recommended ± 3 mDa and the appropriate isotopic ratio pattern.

Elemental composition	Exact mass in Da (%)	Absolute mass difference (mDa)	Isotopic peak due to ^{34}S (%)	Absolute mass difference (mDa)
unknown peak	96.0110 (100)	-	98.0100 (5.5)	-
Possible identification for m/z 96:				
S_3^+	95.9162 (100)	-95	97.9120 (13.3)	-98
SO_4^+	95.9517 (100)	-59	97.9475 (4.4)	-62
$\text{C}_2\text{H}_8\text{S}_2^+$	96.0067 (100)	-4.3	98.0025 (8.9)	-7.5
$\text{C}_2\text{H}_8\text{SO}_2^+$	96.0245 (100)	+13	98.0203 (4.4)	+10

p. 13169, l. 17: Can one still apply the per-carbon-response-factor, if the analytes contain different numbers of heteroatoms? See also: Holm, T., J. Chromatogr. A 782 (1997), 81-86.

=> In this work, the FID response factor for each OSC was actually corrected for the presence of heteroatoms in the molecules based on an earlier work from Hermann Möckel (1976). This specific procedure was omitted in the original text, but we added the following statement and reference: *“The responses obtained from the FID were converted from area units into mixing ratios based on a per-carbon-response-factor (PCRF) as described previously (Simpson et al., 2001). Because the three sulfides contain two methyl carbons, and are thus likely to have the same FID response, we assigned a single PCRF to these compounds based on the PCRF for ethane, with the addition of a correction factor for the presence of sulfur atoms (Mockel, 1976). It is important to note that Mockel (Mockel, 1976) reported that the number of sulfur atoms does not alter the FID response and thus a single factor was used for DMS, DMDS and DMTS.”*

p. 13170, l. 5-7: Were the canisters filled simultaneously?

=> The canisters were filled successively. The experimental set up did not allow to have the canisters filled simultaneously.

p. 13170, l. 13: As cyclohexane (CH) has a different retention time than the analytes, do you still expect that FID detector saturation can be an issue? In Fig. 2, the CH signal is clearly separated from the OSC signals.

=> We agree with the reviewer’s comment, and we removed the reference to the saturation of the detector for cyclohexane.

p. 13170, l. 19: P’T’R-ToF-MS

=> We thank the reviewer for catching this; the typo was corrected.

p. 13171, l. 20: If by “stainless steel pre-concentration system” the stainless steel canister is meant, then please be consistent with the terminology.

=> What we mean by ‘stainless steel pre-concentration system’ does not include the canisters, but rather the 10-mL loop and transfer tubing surrounding the loop from the canister inlet on one side, to the GC column on the other side. We modified the text to read: *"Because no conversion of MTO to DMDS in the glass bulb was observed using PTR-ToF-MS, it is likely that the short time (< 1 min) the sample stays in the stainless steel pre-concentration system (loop and transfer tubing) was enough to allow chemistry to convert some of the MTO into DMDS."*

p. 13172, l. 3: Consider renaming into: Application to a complex, high emission source. General comment on section 3.4: Is it possible to identify OSC compounds in PTR ToF MS spectra, other than DMS, DMDS, DMTS and MTO? Can you show mass spectra of the waste bin measurements to indicate the relative intensities of OSC versus VOCs or OVOCs?

=> Figure S7, in the supplement, represents a typical mass spectrum of one of the waste bin samples. As can be seen from Fig. S7, MTO is clearly a major compound emitted from the bin sample. In the supplementary information, we have added a table that gives the elemental formulae for all the peaks in Fig. S7. No other OSC than H₂S, MTO, DMS and DMDS were observed.

Tables and Figures

Table 1: Do accurate mass measurements with R=5000 provide four decimal places?

=> Four decimal places are typical for exact mass measurements. According to Greaves and Roboz (2014), a resolution of 5000 is sufficient for low molecular masses ($m/z < 200$ amu) to give four decimal places.

Figure 1: What is the origin of the high background signals in (c) and (d)?

=> The high background observed in (d) is actually cyclohexane, as it was used as the solvent. In spectra (b) and (c), the background lines in grey should correspond to a clean Teflon chamber. We went back to the raw data and it appears that the background spectra in the original Fig 1b,c included some room air scans taken between those from the blank Teflon chamber and the sample. We have re-analyzed those data using the Teflon chamber only background and have replaced Fig 1b,c with the appropriate spectra. We have also modified Fig. 1 caption to read: *"Figure 1. Individual PTR-ToF-MS mass spectra from each organosulfur compound: (a) methanethiol (MTO) from the laboratory generated gas phase standard, (b) dimethyl sulfide (DMS) and (c) dimethyl disulfide (DMDS) from injection of the individual pure liquid standards into air in a 100 L Teflon chamber, and (d) dimethyl trisulfide (DMTS) from the dynamic injection system."*

In (b) and (c), the grey peaks correspond to ion fragments resulting from the ionization of background species in the Teflon chamber; in (d), the grey peaks correspond to ion fragments resulting from the ionization of cyclohexane which was used here as the solvent."

Short summary: "Gas phase organosulfur compounds in air serve 'as' precursors of particles [. . .]"

=> We modified the text accordingly.

References

Greaves, J. L., and Roboz, J. (2013), *Mass Spectrometry for Novices*, Taylor and Francis.

Buhr, K., van Ruth, S., and Delahunty, C.: Analysis of volatile flavour compounds by proton-transfer reaction mass spectrometry: Fragmentation patterns and discrimination between isobaric and isomeric compounds, *Int. J. Mass Spectrom.*, 221, 1-7, 2002.

New Figure S7. Representative PTR-MS mass spectrum from a bin sample. The red signal in (a) corresponds to the MS spectra with intensities multiplied by 2; the grey signal corresponds to a background MS spectrum. In (b) and (c), the signal intensity for DMDS (red trace) was overlaid on a bin sample.

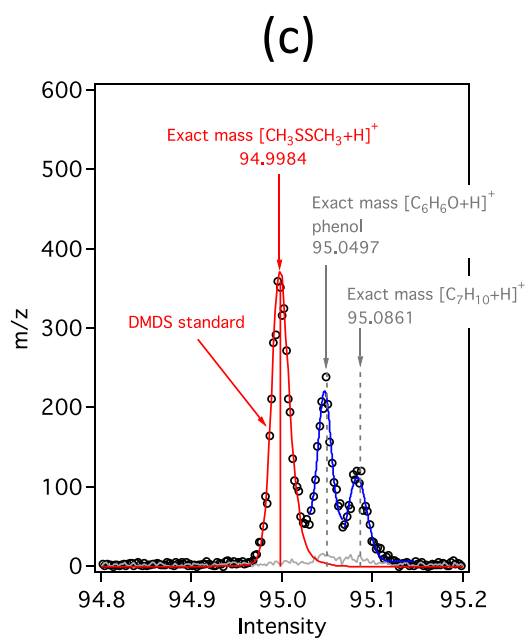
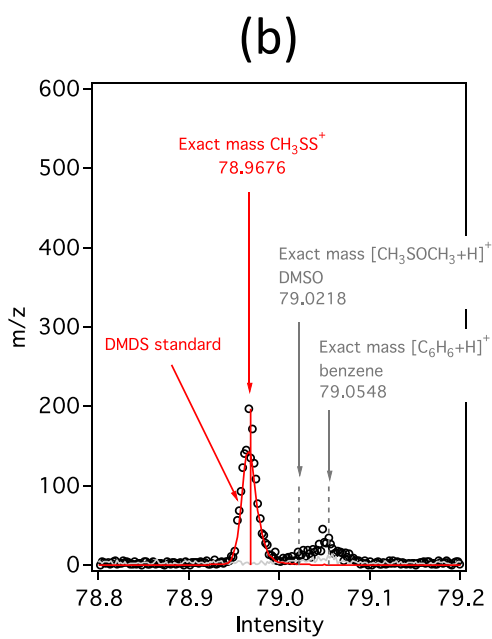
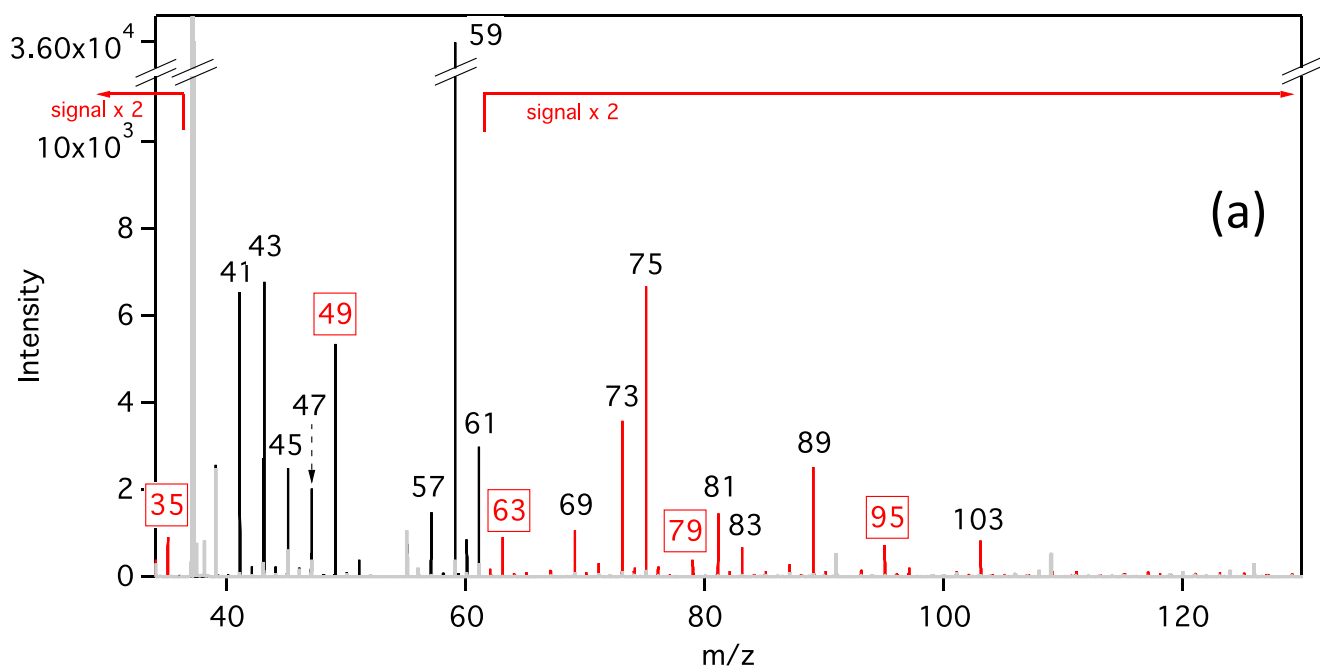


Table xx. Elemental composition of the major fragments observed for a typical bin sample

m/z	Elemental composition	Exact mass (Da)	Absolute mass diff. (mDa)	Tentative identification	Ref.
OSC compounds					
34.9949	[H ₂ S + H] ⁺	34.9955	-0.6	hydrogen sulfide	<i>(this work)</i>
49.0106	[CH ₃ SH + H] ⁺	49.0112	-0.6	MTO	<i>(this work)</i>
63.0255	[CH ₃ SCH ₃ + H] ⁺	63.0268	-1.3	DMS	<i>(this work)</i>
94.9983	[CH ₃ SSCH ₃ + H] ⁺	94.9989	-0.6	DMDS	<i>(this work)</i>
78.9668	CH ₃ SS ⁺	78.9676	-0.8	DMDS fragment	<i>(this work)</i>
Other VOCs					
41.0381	C ₃ H ₅ ⁺	41.0391	-1.0	common ethyl- fragment	<i>(a)</i>
43.0175	C ₂ H ₃ O ⁺	43.0184	-0.9	common acetyl- fragment	<i>(a)</i>
43.0537	C ₃ H ₇ ⁺	43.0548	-1.1	common propyl- fragment	<i>(a)</i>
45.0328	C ₂ H ₅ O ⁺	45.0340	-1.2	acetaldehyde [M+H] ⁺	<i>(b)</i>
47.0485	C ₂ H ₇ O ⁺	47.0497	-1.2	ethanol [M+H] ⁺	<i>(a)(b)</i>
57.0329	C ₃ H ₅ O ⁺	57.0340	-1.1	common propionyl- fragment	<i>(a)</i>
57.0691	C ₄ H ₉ ⁺	57.0704	-1.3	common butyl- fragment	<i>(a)</i>
59.0498	C ₃ H ₇ O ⁺	59.0497	+0.1	acetone [M+H] ⁺	<i>(b)</i>
				or propanal [M+H] ⁺	<i>(b)</i>
61.0276	C ₂ H ₅ O ₂ ⁺	61.0289	-1.3	common fragments from acids/formates/acetates/ hydroxyketones/hydroxyaldehydes (C _n H _{2n} O ₂ +H ⁺)	<i>(c)</i>
				ex: acetic acid [M+H] ⁺	<i>(b)</i>
				or methyl formate [M+H] ⁺	<i>(b)</i>
69.0688	C ₅ H ₉ ⁺	69.0704	-1.6	isoprene [M+H] ^{+(a)}	<i>(b)</i>
				or [pentanal – H ₂ O] ⁺	<i>(b)</i>
				or cyclopentene [M+H] ⁺	<i>(b)</i>
				or [2-methyl-3-buten-1-ol – H ₂ O] ⁺	<i>(b)</i>

73.0637	C ₄ H ₉ O ⁺	73.0653	-1.6	butanone [M+H] ⁺ or butanal [M+H] ⁺	(b)(f) (b)(f)
75.0430	C ₃ H ₇ O ₂ ⁺	75.0446	-1.6	common fragments from acids/formates/acetates/ hydroxyketones/hydroxyaldehydes (C _n H _{2n} O ₂ +H ⁺) ex: hydroxyacetone [M+H] ⁺ or propionic acid [M+H] ⁺	(c) (b) (b)
81.0693	C ₆ H ₉ ⁺	81.0704	-1.1	common fragment observed for monoterpenes	(d)
83.0843	C ₆ H ₁₁ ⁺	83.0861	-1.8	[3-hexen-1-ol – H ₂ O] ⁺ or hexadiene [M+H] ⁺ or cyclohexene [M+H] ⁺ or 2,4 dimethyl-buta-1,3 diene [M+H] ⁺	(b) (b) (b) (b)
89.0589	C ₄ H ₉ O ₂ ⁺	89.0603	-1.4	common fragments from acids/formates/acetates/ hydroxyketones/hydroxyaldehydes (C _n H _{2n} O ₂ +H ⁺) ex: butanoic acid [M+H] ⁺	(c) (f)
95.0470	C ₆ H ₇ O ⁺	95.0497	-2.7	phenol [M+H] ⁺	(b)
95.0832	C ₇ H ₁₁ ⁺	95.0861	-2.9	norbornene [M+H] ⁺ or heptanediol [M+H] ⁺	(b) (e)
103.0740	C ₅ H ₁₁ O ₂ ⁺	103.0759	-1.9	common fragments from acids/formates/acetates/ hydroxyketones/hydroxyaldehydes (C _n H _{2n} O ₂ +H ⁺) ex: methyl butyrate [M+H] ⁺ or ethyl propionate [M+H] ⁺ or ethyl pentanoate fragment or 3-methyl butanoic acid [M+H] ⁺ or pentanoic acid [M+H] ⁺	(c) (a) (a) (a) (f) (f)

(a) from (Buhr *et al.*, 2002)

(b) Source: (Williams *et al.*, 2001)

(c) from (Inomata *et al.*, 2010)

(d) from (Maleknia *et al.*, 2007) and (Tani *et al.*, 2003)

(e) from (Morisco *et al.*, 2013)

(f) from (Feilberg *et al.*, 2010)

