Responses to the Reviewers' Comments:

We thank the reviewers for the consideration and the constructive comments. The manuscript is revised based on the suggestions made and detailed responses to the reviewers are given in the following:

Referee #1

In this study the authors present an optimized analytical method dealing with the quantification of carbonyl compounds. The carbonyl compounds chosen for the method optimization include atmospherically relevant species from primary and secondary sources. Optimized method parameters include concentration of derivatisation reagent, derivatization time, pH during derivatization and extraction, extraction time, and extracting reagent. Thus, a comprehensive optimization of the sample preparation was carried out followed by a standard GC/MS analysis. Due to this comprehensive evaluation of parameters and the choice of relevant carbonyl compounds I think the paper is well suited for publication in AMT. However, organization and presentation of the paper should be improved prior to publication as outlined in the specific comments below.

Specific comments:

1) Apparently, the optimizations presented in this study are limited to the sample preparation part of the analytical procedure to detect and quantify atmospheric carbonyls. This should be better reflected in the title of the manuscript.

Authors' comment

The title is changed to '*Characterisation and optimisation of a sample preparation method for the detection and quantification of atmospherically relevant carbonyl compounds in aqueous medium*'

2) A clear (short) description of the overall analytical procedure is missing in the experimental section of the main text. The GC/MS analysis is only mentioned in the abstract and in the captions of Figure 2 and Table 3.

Authors' comment

A description of the GC/MS method is removed from the supplementary material and included in the experimental section of the manuscript.

3) The first two paragraphs of the results section on page 861 need to be revisited for language and clarity. The first sentence of the first paragraph is good examples for this point. In my opinion this sentence should read something like “Studies reporting optimized methods for the quantification of carbonyl compounds including a PFBHA derivatization procedure are summarized in Table 1”. The first two sentences of the second paragraph could be removed without a loss of information, if the parameters optimized in this study would be included in the next sentence.

Authors’ comment

Page 861, line 8-27: The paragraph is rewritten as follows:

‘Studies that optimised a method for the quantification of carbonyl compounds using PFBHA derivatisation are summarised in Table 1. Even that numerous studies exist optimising the derivatisation with PFBHA, only those methods are included in Table 1 which i) derivatise carbonyl compounds in aqueous phase (derivatisation on solid phase, cartridges or on a chip are not compared: Cullere et al., 2004; Nawrocki et al., 1996; Pang et al., 2013), ii) optimise one of the investigated reaction parameters that are also investigated within the present study and iii) use the same extraction techniques as in the present study (solid phase micro extraction or extraction on fibre are not included, e.g. Cancho et al., 2002). Therefore methods which do not fulfil selection criteria i-iii are not included.

Additionally, in Table S 1 (Supplement S2.1) the application of the PFBHA derivatisation method is summarised.

To improve commonly used PFBHA methods, a mixture of seven standard compounds (acrolein, methacrolein, methyl vinyl ketone, glyoxal, methyl glyoxal, benzaldehyde, 2,3-butanedione) mixed with an internal standard (cyclohexanone-2,2,6,6-d4) was used. The internal standard was used as reference for the GC/MS method or in the case of quantification to correct the peak areas for losses might occur between sampling and detection. Derivatisation parameters were optimised using a standard stock solution of 8 µmol L^{-1}.

In general, the derivatisation of a carbonyl compound leads to the formation of (E) and (Z)-isomers resulting in two peaks per compound in the chromatogram (Glaze et al., 1989).’

4) In my opinion the paper will be better perceived by the community if analytical parameters like the relative standard deviation (RSD) of repeated injections (repeatability of the measurement) would be given, e.g., in Table 3.

Authors’ comment

The relative standard deviation for the detection limits were included into the main text and additionally also summarised in Table 3.

Table 3: Detection limits of the carbonyl compounds determined in the present study with GC/MS (SIM) and in the literature.

	Detection limits [µmol L^{-1}] in the literature studies				**This work S/N ≥ 3, n = 3**	
Carbonyl compound	Glaze et al. (1989)	Seaman et al. (2006)*	Serrano et al. (2013)	EPA method 556	Detection limit ± SD [µmol L^{-1}]	RSD [%]
Acrolein	0.3	$8.6 \times 10^{-3} – 2.5 \times 10^{-2}$	-	-	0.17 ± 0.03	± 19
Methacrolein	-	$4.0 \times 10^{-2} – 1.9 \times 10^{-2}$	-	-	0.02 ± 0.003	± 16
Methyl vinyl ketone	-	$2.2 \times 10^{-2} – 2.9 \times 10^{-2}$	-	-	0.03 ± 0.003	± 10
Benzaldehyde	0.1	$7.5 \times 10^{-3} – 1.7 \times 10^{-2}$	0.1×10^{-3}	0.003	0.01 ± 0.0003	± 3
Glyoxal	0.1	$3.5 \times 10^{-2} – 1.5 \times 10^{-1}$	0.01×10^{-3}	0.01	0.01 ± 0.0006	± 5
Methyl glyoxal	0.1	$1.6 \times 10^{-2} – 2.1 \times 10^{-2}$	0.01×10^{-3}	0.01	0.01 ± 0.0004	± 4
2,3-Butanedione	-	-	-	-	0.01 ± 0.0008	± 8

The measurements were conducted with optimal parameters and repeated for three times (n = 3).

*Concentrations in the gas phase converted from µg m^{-3} to µmol L^{-1};

SD: standard deviation; RSD: relative standard deviation

Page 862 Line 20 – 25: *‘In the case of acrolein this preconcentration results in a detection limit of 0.17 µmol L^{-1} that is improved by a factor of ≈ 2 compared to Glaze et al. (1989). The detection limit of other investigated compounds showed an improvement by about a factor of 10. The detection limits were as follows: 0.01 ± 0.0003µmol L^{-1} for benzaldehyde, 0.01 ± 0.0004 µmol L^{-1} for methyl glyoxal and 0.01 ± 0.0006 µmol L^{-1} for glyoxal (for more details see S2.2 and Table 3). Based on the low standard deviations, it can be stated that the extraction with dichloromethane results in a high reproducibility.*

Due to the high reproducibility and low detection limits, dichloromethane was chosen as extraction solvent.’

Also, error bars are missing in Figure 2b.

Authors’ comment

The experiment was not repeated because it was conducted only to demonstrate the applicability of the optimised method and that the method can be easily applied to various experimental systems such as the detection of carbonyl compounds in aqueous samples.

In Figure S7 (calibration curves) it is not clear to me what is meant by the x-axis label "theoretical concentration". Were the injection volumes or the actual standard concentrations varied?

Authors' comment

The label "theoretical concentration" means the concentration that is adjusted in the stock solutions. To record the calibration curve the actual standard concentration in the sample solution was changed from 2 µmol L^{-1} to 16 µmol L^{-1}. To clarify this, the sentence is changed to *'The optimised method (dichloromethane as extraction solvent, 30 minutes extraction time, 24 h derivatisation time, 0.43 mg* mL^{-1} *PFBHA, pH = 3 for the derivatisation and pH = 1 for the extraction) was applied to a series of stock solutions. The concentrations of the seven target carbonyl compounds were varied in a range of 2 to 16 µmol* L^{-1} *(Figure S 7, supplementary material S 2.7).'*

In general, Table and Figure captions as well as subsection headings should be revised for clarity and readability.

Authors' comment

The authors agree on the reviewers comment and the following changes were made to the manuscript.

'Figure 2. Time-resolved GC/MS chromatograms obtained from the oxidation of 3-metyhlbutanone (starting time t = 0 h and reaction time t = 5 h). For comparison the GC/MS chromatogram of the authentic standard compounds of the identified products 2,3-butanedione (BuDi) and methyl glyoxal (MGly) are shown (a). Using the obtained chromatograms, the concentration of the main products BuDi and MGly was calculated (b).'

'Table 1: Studies reporting the optimisation of a PFBHA method and fulfil the selection criteria i) derivatise carbonyl compounds in the aqueous phase (derivatisation on solid phase, cartridges or on a chip are not compared: Cullere et al., 2004; Nawrocki et al., 1996; Pang et al., 2013), ii) optimise one of the reaction parameters investigated within this study and iii) use the same extraction techniques as in the present study (solid phase micro extraction or extraction on fibre are not included, e.g. Cancho et al., 2002).'

'Table S 3: Correction factors for the extraction of carbonyl compounds with hexane for an extraction time between 1 and 60 minutes in relation to an extraction time of 30 minutes with dichloromethane.'

‘Figure S 4: Dependency of the integrated peak area of investigated aldehydes (a: acrolein, black; methacrolein, red; benzaldehyde, yellow; glyoxal, blue), methyl glyoxal (a, pink) and ketones (b: methyl vinyl ketone, green; 2,3-butanedione, turquoise) as a function of PFBHA concentration in the sample solution. Please note, the internal standard is given in grey (b).’

‘Figure S 7: Calibration curve for acrolein (black, $R^2 = 0.987$), methacrolein (red, $R^2 = 0.993$), methyl vinyl ketone (green, $R^2 = 0.997$), benzaldehyde (yellow, $R^2 = 0.996$), glyoxal (blue, $R^2 = 0.995$), methyl glyoxal (pink, $R^2 = 0.984$) and 2,3-butanedione (turquoise, $R^2 = 0.984$) in the concentration range of 2 to 16 µmol L^{-1}.’

Subsection heading *‘3.4 Influence of the PFBHA concentration’*

5) The discussion on the influence of extraction time (3.2) is very interesting, as variations from the extraction times reported in other studies might lead to a decreased reproducibility of the results, if the extraction is not >99% complete after 2-3 minutes.

Authors’ comment

The authors agree with the reviewers comment.

Due to the short extraction times reported in the literature (e.g., 30 s reported by Glaze et al. 1989) the extraction cannot be complete. Consequently, lower peak intensities will be obtained. Furthermore, depending on the concentration of the target compound, the efficiency of the extraction will vary which might lead to a lower reproducibility of the extraction and thus, to a higher uncertainty of the measurement.

These facts highlight the importance of the present study. It was clearly demonstrated that extraction time of 30 min ensures a complete derivatisation. This is also reflected in the high reproducibility determined within our study as it can be seen by the small error bars illustrated in Figure S1. Furthermore on Page 863 Line 18 the sentence *‘Furthermore the incomplete extraction caused by the short extraction times might lead to a decreasing reproducibility.’* is included to answer this referee comment.

6) Personally, I would rename subsection 3.6 into “Proof of principle”. The first paragraph of this subsection could go to the experimental section and/or to supplement section 2.7.

Authors’ comment

The tile of the subsection is changed to *‘3.6 Proof of principle’* and the first paragraph is moved to the supplementary material (S 2.7).

7) Section S2.1 and Table S1: I would limit the overview of applications of PFBHA derivatization techniques used in carbonyl analysis to those relevant in the atmospheric context, but extend it to be more comprehensive. In my opinion this would be of greater interest than listing applications of methods optimized for the analysis of carbonyls in other fields.

Authors' comment

The applications of the PFBHA methods listed in Table S1 are chosen because some of them used the optimised methods shown in Table 1, which fulfil the selection criteria i-iii and are comparable to the optimised method in the present study (Derevel and Bertrand, 1993; Bao et al., 1998; Yu et al., 1998; Jang and Kamens, 1999; Cancho et al., 2002; Berànek and Kubàtovà, 2008; van Pinxteren and Herrmann, 2013).

Several methods are already included investigated the same compounds as in the present study (Bao et al., 1998; Cancho et al., 2002; van Pinxteren and Herrmann, 2003, Ortiz et al., 2006; Wardencki et al., 2001).

Furthermore Table S 1 shows the broad application area of the PFBHA derivatisation method and the possibility to detect carbonyl compounds regardless of their source or size. For example Nambara et al. (1975) analysed ketosteroids with the PFBHA derivatisation method which shows the method is suitable for high molecular weight compounds as well. Derevel and Bertrand (1993), Wardencki et al. (2003), Jelen et al. (2004) and Sowinski et al. (2005) analysed carbonyl compounds in wine, beer and spirits, which demonstrate the method is suitable in complex matrices as well.

The studies reported by Yu et al. (1995, 1997) applied the method to oxidation products obtained from the oxidation of isoprene and alkylbenzene. According to this, Fick et al., 2003 used PFBHA derivatisation to detected α-pinene oxidation products.

Another important optimised PFBHA derivatisation is the EPA method 556 which is used by numerous literature studies listed in Table S 1 (Cancho et al., 2002; Berànek and Kubàtovà, 2008; van Pinxteren and Herrmann, 2013).

Consequently, several studies are included that have a high atmospheric relevance and in addition to this, methods are presented that demonstrate the broad scope of application of PFBHA derivatisation.

The literature study by Schmarr et al. (2008) was deleted from Table S1 because this is not an application of the PFBHA derivatisation method. It is a development of a method for headspace solid-phase microextraction with on fibre derivatisation. Thus the sentence *'A headspace analysis was applied by Schmarr et al. (2008) but the derivatisation was adopted from Cancilla et al. (1992).'* is deleted from the supplement (S2.1) and the further sentence is changed to *"Yu* *et al. (1995) used the method by Cancilla et al. (1992) to quantify carbonyl compounds formed during the oxidation of isoprene.’*. The reference was deleted from the reference list in the supplement as well.

Table S 1: Analysis of carbonyl compounds involving PFBHA derivatisation methods.

Comment	Detection limits [µmol L^{-1}]	Reference	Based on
Analysis of ketosteroids Synthesis of PFBHA		Nambara et al. (1975)	-
Analysis of carbonyl compounds in wine		Derevel and Bertrand (1993)	Yamada and Somiya (1989); Glaze et al. (1989)
Analysis of isoprene oxidation products		Yu et al. (1995)	Cancilla et al. (1992)
Analysis of oxidation products from alkylbenzenes		Yu et al. (1997)	Yu et al. (1995)
SPME for extraction of carbonyl compounds	Acrolein 0.2 × 10^{-2} (LSPME), 0.2 × 10^{-2} (HSPME); Benzaldehyde 1.0 × 10^{-2} (LSPME), 0.1 × 10^{-3} (HSPME); Glyoxal 0.2 × 10^{-3} (LSPME), 0.9 × 10^{-2} (HSPME); Methyl glyoxal 0.1 × 10^{-3} (LSPME), 0.4 × 10^{-2} (HSPME)	Bao et al. (1998)	Glaze et al. (1989); Lelacheur et al. (1993)
Consecutively derivatisation with BSTFA		Yu et al. (1998)	Lelacheur et al. (1993); Yu et al. (1995)
Analysis of α-pinene oxidation products		Jang and Kamens (1999)	Lelacheur et al. (1993)
SPME for extraction of carbonyl compounds	Glyoxal 0.7 × 10^{-2} (HSPME); Methylglyoxal 0.4 × 10^{-2} (HSPME)	Cancho et al. (2002)	EPA method 556
Derivatisation in alcohols	Acrolein 3.0 × 10^{-2} (LLE), 0.2 × 10^{-2} (SPME)	Wardencki et al. (2001)	Nawrocki et al. (1996)
Analysis of α-pinene oxidation products in dependence of OH radical concentration, relative humidity and time		Fick et al. (2003)	Yu et al. (1998)
SPME for extraction of carbonyl compounds		Wardencki et al. (2003)	Wardencki et al. (2001)
SPME for extraction of C_3-C_{10} aliphatic aldehydes		Jelen et al. (2004)	Wardencki et al. (2001)
Headspace analysis Analysis in spirits and vodka		Sowinski et al. (2005)	-
Denuder-filter sampling Analysis of bifunctional carbonyl compounds Consecutively derivatisation with BSTFA		Ortiz et al. (2006)	-
Solid phase microextraction of aldehydes		Beránek and Kubátová (2008)	EPA method 556
Glyoxal and Methylglyoxal in atlantic seawater	Glyoxal 0.1 × 10^{-2} (sea water); Methyl glyoxal 0.1 × 10^{-3} (sea water)	Van Pinxteren and Herrmann (2013)	EPA method 556

SPME: solid phase micro extraction; BSTFA: N,O-Bis(trimethylsilyl)trifluoroacetamide; TMCS: trimethylchlorosilane; LLE: liquid-liquid extraction; LSPME: liquid solid phase micro extraction; HSPME: headspace solid phase micro extraction

Exemplary technical comments:

P. 858, L. 7: This sentence should be removed

Authors' comment

The sentence was removed.

P. 858, L. 8: Please clarify or remove this sentence, too

Authors' comment

The sentence is removed to Page 858 Line 14 and changed to *'With the present method quantification can be carried out for each carbonyl compound originating from fog, cloud and rain or sampled from the gas-, and particle phase in water.'*

P. 858, L. 14-16: Should be changed to "Detection limits between 0.01 and 0.17 µmol L^{-1} were achieved, depending on the carbonyl compound"

Authors' comment

The sentence is changed to *'Detection limits between 0.01 and 0.17 µmol* L^{-1} *were found, depending on carbonyl compounds.'*

P. 858, L. 16-18: This sentence reads like extraction was carried out before derivatization.

Authors' comment

The sentence is changed to *'Furthermore best results were found for the derivatisation with a PFBHA concentration of 0.43 mg* mL^{-1} *for 24 h followed by an subsequent extraction with dichloromethane for 30 minutes at pH = 1.'*

P. 858, L. 21-22: The yields reported here are not final yields but yields after 5h of reaction. This should be clarified.

Authors' comment

The sentence is changed to *'Methyl glyoxal and 2,3-butanedione were found to be oxidation products in the samples with a yield of 2% for methyl glyoxal and 14% for 2,3-butanedione after a reaction time of 5 h.'*

P. 859, L. 23: "better quantification" should be specified

Authors' comment

The sentence is changed to *'In the present study, thorough characterisation of a PFBHA-based derivatisation method was performed and an improvement was made to achieve a more efficient and optimal quantification of atmospheric relevant carbonyl compounds in aqueous samples originating from various sources (aqueous aerosol extracts, fog, cloud and rain samples).'*

P. 860, L. 18-20: This sentence needs to be clarified. What is meant by standard compound for method development – I assume the corresponding experiment was used as a proof of principle

Authors' comment

2,3-Butanedione was used as a standard compound for the method optimisation, thus the sentence is changed to *'Since 2,3-butanedione was found in the atmospheric aqueous phase it was used as a compound for the method development as well.'*

P. 861, L. 1-2: This sentence should be improved for a better readability. How much PFBHA (mL or g) was added to the sample to achieve the final concentration of 0.43 mg mL^{-1}.

Authors' comment

The sentence is changed to '*According to the optimal reaction parameters identified 5 mg PFBHA was solved in 1 mL water and 300 µL of the solution was added to the samples reaching a PFBHA concentration of 0.43 mg mL^{-1}. Afterwards the samples are allowed to rest for 24 h at room temperature.'*

Supplementary Information:

P. 1, L. 18: Heading could be "GC/MS analysis"

Authors' comment

This part is removed and included in the manuscript and the heading was changed to "GC/MS analysis".

P. 1, L. 28: Heading could be "(Exemplary) Analysis of carbonyl compounds (in an atmospheric context?) involving PFBHA derivatization methods" (see comment #7)

Authors' comment

The heading of Table S 1 is changed to '*Analysis of carbonyl compounds involving PFBHA derivatisation methods.'*