Authors' response on "Studying boundary layer methane isotopy and vertical mixing processes at a rewetted peatland site by unmanned aircraft system"

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1 Authors' response

Based on the comments of the two anonymous referees, we revised the manuscript substantially. We have the impression that the manuscript is much improved now.

Besides smaller issues, the most important changes are:

- A more precise description of the novelty of the study (combination of two established techniques, namely airborne sampling and isotopic analyses, to create a new tool for atmospheric research)
- We added three authors that performed numerical simulations of the flow around a propeller blade of the quadrocopter, which strengthens our discussion of the impact of the measurement system on sampling, with a new illustrative figure
- A clearer description of the aims of the study
- A more detailed explanation of the sampling with manual and electromagnetic valves, including a new illustration
- We corrected the methane concentration time series with an additional data set, and included the data in the time series plots of the meteorological parameters
- A more thorough discussion on precision and error bars
- A clearer discussion of the results, taking into account the aspects raised by the referees
- We improved the use of technical terms (delta values, isotopic composition)

- We replaced the figure of the quadrocopter setup with a clearer version with neutral background and more information on the valves
- We removed the figure showing methane fluxes, as suggested by a referee.
- In the figues of the time series of meteorological parameters, we included the times of the quadrocopter flights
- In the figure of the temperature and humidity profiles, we included a box showing the altitude of the inversion
- We modified the figure of the profiles of the difference in delta values obtained by parallel sampling
- In the discussion, we added two pictures visualising beginning turbulence induced by aircraft disturbance, illustrating high vertical and horizontal gradients of concentration

Unfortunately it was not possible to create the latexdiff file - during the process, one of the latex files was destroyed each time, and we did not get a pdf with track changes. Of course we can provide immediately both the original and the new latex file separately.

2 Answers to referees

The authors would like to thank the anonymous referee for the comments on the manuscript. In the following, the comments are given in *italic*. The answers are given in normal letters. The modified text in the manuscript is given in quotation marks.

3 Referee 1

The manuscript presents a quadrocopter equipped with a flask sampler in a proof of concept study looking at delta 13C in methane above a peatland on two mornings. Using unmanned aircraft for sampling in the lower atmosphere is not new. Comparable approaches are referred to in the introduction. The novelty here is perhaps the target parameter: delta 13C in methane.

We changed the beginning of the abstract to "The combination of two well-established methods, of quadrocopter-borne air sampling and of methane isotopic analyses, is applied to determine the origin of methane at different altitudes and to study mixing processes. A proof of concept study was performed to demonstrate the capabilities of quadrocopter air sampling for subsequently analysing the methane isotopic composition δ^{13}C in the laboratory. The advantage of the system compared to classical sampling at ground and at tall towers is the flexibility concerning sampling location, and in particular the flexible choice of sampling altitude, allowing to study layering and mixing of air masses with potentially different origin of methane."

Precision of the isotope measurement in the laboratory is indicated to be about 0.5 permill (page 5, line 28). Could this indication be more precise? Are the 0.5 permill one sigma for the same, repeatedly measured sample?

We changed the text to: "Precision, determined as the maximum difference of delta values during repeated analysis of ambient Bremerhaven air samples taken simultaneously and analysed consecutively many times per year, is better than 0.5 ‰. "

Considering the difference in isotopic signal between nocturnal boundary layer and the air above during the first flight of a day is only about 1 permill, the isotopic signal of the polder is barely significant.

We agree that the isotopic signature of the air surrounding the polder is similar. This can be expected as the rewetted area is larger than the polder. Further, the methane isotopic signature from ruminants is similar, as summarised by Röckmann et al. (2016). We added in the abstract: "The systematically more negative delta values occurred only as long as the nocturnal temperature inversion was present."

Its size may be limited by three factors. First, the difference may be small in isotopic signature between the polder and other, presumably also biogenic sources in the larger surroundings.

We agree with this point, and changed the text in the discussion to "The difference in delta values obtained for air samples near ground and above the temperature inversion during stable stratification is around 1.5 ‰, thus significantly higher than the uncertainties (flight 1 for each measurement day). This shows that the observed systematic differences are real measurement features, not measurement uncertainty. Other methane sources in the surroundings of the polder are presumably of biological origin as well, they may include larger areas of the rewetted peatland and ruminants, with similar isotopic composition (Röckmann et al., 2016)."

Second, the polder area may be too small to substantially alter atmospheric methane isotopic composition in the lower tens of metres, especially at wind speeds of several metres per second.

During the night, when the temperature inversion inhibits mixing and the locally emitted methane is trapped, the wind speed was below $2\,\mathrm{m\,s^{-1}}$. Therefore, the effect of a different isotopic composition below the temperature inversion can be traced back to local emissions. We changed the discussion text to: "Under stable atmospheric conditions and low wind speed smaller than $2\,\mathrm{m\,s^{-1}}$ during the night and in the early morning hours, the near-surface methane concentration is enhanced, as no vertical mixing is possible, in agreement with Emeis (2008); Brosy et al. (2017)."

A simple box model would suffice for an initial estimate.

We do not agree that a box model is helpful for this case. As underlined by the very different methane concentrations in the water, we assume local inhomogeneities of sources. On the contrary, a suitable method for qunatifying small and inhomogeneous sources is urgently needed. We changed the text in the conclusion section to: "The differences in delta values of water and air, the differences in delta values between both flight days and the development during each day emphasize the highly complex and inhomogeneous nature of methane processes on horizontal scales below 1 km in sediments, at the sediment-water and the water-atmosphere interface. Therefore, a suitable method is required for quantifying small-scale inhomogeneous methane sources."

Third, the flights were performed well after sunrise. Much of the methane trapped near the surface during the night had already been mixed to greater altitude, as can be seen in the methane concentration in Figure 9.

We agree with this point, the methane concentration was higher during the night, as indicated in Fig. 9. We changed the text in the discussion to: "Under stable atmospheric conditions and low wind speed smaller than 2 m s^{-1} during the night and in the early morning hours, the near-surface methane concentration is enhanced, as no vertical mixing is possible, in agreement with Emeis (2008); Brosy et al. (2017). This can be seen in the time series of the methane concentrations for both days as well (Figs. 9 and 10). During the flights, the methane concentration was already smaller again, which can be explained by vertical mixing up to the temperature inversion of around 100 m. This dilusion also influences the isotopic composition."

The data in Figures 9 and 10 seems to include erroneous measurements (e.g. zero methane around 18:00 on 5 September and a large number of spikes going above 0.3 mmol/m3 on both days).

Originally, we used only the data set of the LICOR 7700. Now we corrected the data with the quality controlled closed path data set of the Los Gatos sensor. We further included the time series in the figure of the diurnal cycle of the meteorological parameters.

Page 9, last paragraph: "The hypothesis ..." is not plausible at all. Horizontal gradients in air decrease with altitude because of higher windspeeds and more efficient mixing with increasing height above ground. Any remaining gradient will certainly not be large enough to cause measurable differences in samples taken simultaneously "only 13 cm apart". The sampling container is filled "within less than 2 s" (page 4, line 32). A horizontal wind speed of 2 m/s already results in a sample integrating air over a few metres in the horizontal direction.

We added in the text information about the sample integration:

"Assuming that in the worst case the sampling takes place within the downwash of the rotor blades of not more than -19 m s^{-1}, the sampling time of 1.3 s duration results in a vertical resolution of around 25 m. Sampling during descent with a speed of -2.5 m s^{-1} adds an uncertainty in the altitude of 5 m. Altogether, the sampling is influenced by air in a height interval of 30 m. This is the sufficient for the sampling intervals of around 100 m, and for determining that the sampling was done below or above the temperature inversion."

Further, we added in the discussion: "In the presented case, the parallel samples obtained at 10 m altitude seem to be mostly of the same origin with small differences in the delta value. Above, differences in the delta values are higher. A wind speed of less than 2 m s^{-1} during the sampling results in horizontal sample integration over not more than 4 m. Small-scale differences in methane isotopic composition can be introduced by mixing processes, and may be reinforced by mixing induced by the quadrocopter system. A high variability of methane sources is in agreement with the highly variable methane water concentrations measured within a radius of 100 m on 5 September 2018." A visualisation of such small-scale mixing processes is shown in Figs. 5 and 6. In this case, colour was released artificially near ground (inhomogeneous sources). The homogeneous layer building up due to stable stratification was disturbed by turbulence, in this case induced by the aircraft, and large horizontal gradients are visible as a result.

In addition, the turbulence caused by the rotors will add several metres across which the sample integrates in the vertical dimension.

We included three more co-authors who have done numerical simulations, and added a section about simulations of the flow induced by a propeller blade:

"In order to quantify the effect of the vertical flow induced by the quadrocpter, numerical simulations were performed with the software ANSYS CFX. The simulations were transient in nature using a Reynolds-Averaged Navier Stokes (RANS) approach with the Shear Stress Transport (SST) turbulence model (Menter, 1994). A simplified model of the propeller blade was used, with a multidomain approach: The blade is enclosed in a rotating domain, surrounded by a static domain. Simulations were performed for hover with a propeller rotation speed of 3167 min^{-1}, for vertical climb at a speed of 6.5 $\mathrm{m\,s}^{-1}$ with a rotation speed of 3913 $^{-1}$ and of vertical descent at a speed of -2.5 $\mathrm{m\,s}^{-1}$ with a rotation speed of 2880 min^{-1}. An ambient temperature of 0° C and pressure of 1023 hPa were considered. Contours of relative vertical velocity show a core region of positive relative velocity directly below the center of the blade, and a negative relative velocity up to 19 $\mathrm{m\,s}^{-1}$ below the blade for a distance exceeding 0.75 m (Fig. 2). Additionally, zones of recirculation can be seen around the tips of the propeller, especially for the descent case. The air sampling system is contained in the middle of the copter, and is less affected by artificial turbulence than the areas below the rotor blades.

Assuming that in the worst case the sampling takes place within the downwash of the rotor blades of not more than -19 $\mathrm{m\,s}^{-1}$, the sampling time of 1.3 s duration results in a vertical resolution of around 25 m. Sampling during descent with a speed of -2.5 $\mathrm{m\,s}^{-1}$ adds an uncertainty in the altitude of 5 m. Altogether, the sampling is influenced by air in a height interval of 30 m. This is the sufficient for the sampling intervals of around 100 m, and for determining that the sampling was done below or above the temperature inversion."

Further, we added in the discussion section: "In the presented case, the parallel samples obtained at 10 m altitude seem to be mostly of the same origin with small differences in the delta value. Above, differences in the delta values are higher. A wind speed of less than 2 $\mathrm{m\,s}^{-1}$ during the sampling results in horizontal sample integration over not more than 4 m at the sampling altitude. Small-scale differences in methane isotopic composition can be introduced by mixing processes, and may be reinforced by mixing induced by the quadrocopter system. A high variability of methane sources is in agreement with the highly variable methane water concentrations measured within a radius of 100 m on 5 September 2018."

Hence, the "difference" between samples taken in parallel is pure noise caused by differences in the tightness of the sample containers, in handling, and in the analysis in the laboratory. I wonder how this issue can have escaped a group of nine authors.

We do not agree with the referee. The tightness of each of the sample containers was controlled by a pressure sensor, and the pressure data were both provided in real-time to the operators and recorded as well. Sample containers were air tight until being filled with air. The smaller pressure due to sampling above ground level was checked before closing the manual valves. Further, it cannot be assumed that the methane concentration was homogeneous. As an illustration, Fig. 5 and 6 show artificially released colour in a stably stratified morning atmosphere. Large horizontal concentration gradients can exist, and it is particularly difficult to quantify such non-stationary cases, as described by Schaller et al. (2018).

Finally, the difference between the delta values of the samples is height dependent, with much lower differences at the lowest sampling altitude, and an apparent temporal development of the difference for the sampling at higher altitudes. Pure noise should follow a more stochastic distribution of the differences in delta values.

Abstract Line 10: isotopic signature of what? delta13C or D/H ?

We changed the text to "methane isotopic composition δ^{13}C"

Page 2, line 6: "Yet, current knowledge of CH4 sources remains inadequate." What do you mean by "inadequate"? Inadequate to justify or guide mitigation measures? I do not think so. We know very well where methane is produced and what could be done to reduce emissions.

We totally agree with the referee. The text is now changed to "Yet, current knowledge of CH_4 biogeochemical processes, transport and small-scale distribution remains inadequate."

What is the size of the sample containers (flasks)? Also, more detail about the valves and their connection with the glass flasks is necessary.

We added a figure explaining details of the valves and included in the text: "The air sampling system consists of 12 glass flasks (sample containers) of 100 ml content"

I do not understand the sentence on page 4, line 33-34 ("The most critical point were the manual plastic valves deployed routinely for the glass flasks in open position.")

We explain now more in detail and added Fig. 1. The text has been changed to: "The air sampling system consists of 12 glass flasks (sample containers) of 100 ml content, which are evacuated before take-off. They are equipped with two manual valves, one on each side, and additionally one electromagnetic valve, which is applied only during the flight (Fig. 1). Directly before the mission, each glass flask is linked with a vacuum pump RE5 of Vacuubrand, Germany. One valve is left open, and an electromagnetic valve is connected, which is normally closed. Then the flask is evacuated, and the pressure is controlled by a pressure sensor integrated in the electromagnetic valve. The flasks are opened during the flight with magnet valves, that are triggered either manually by remote control or automatically at altitudes predefined by the operator. After triggering, ambient pressure is reached within less than 2 s. The pressure sensors integrated in the valves are used to monitor air tightness. The most delicate component are the manual plastic valves, used to close the glass flasks for transport, which are designed to be air tight when closed, but not when open. They had to be treated individually and controlled to make sure that no leakage occurred during the mission. For quality control and redundance, two glass flasks were filled simultaneously, resulting in six possible sampling altitudes during one flight."

What is the vertical resolution of sampling, given the turbulence caused by four rotors keeping 19 kg of vehicle and payload afloat?

We added a figure of simulations showing the vertical velocity induced by the propeller blades (Fig. 2) and added in the text: "Assuming that in the worst case the sampling takes place within the downwash of the rotor blades of not more than -19 m s^{-1}, the sampling time of 1.3 s duration, results in a vertical resolution of around 25 m. Sampling during descent with a speed of -2.5 m s^{-1} adds an uncertainty in the altitude of 5 m. Altogether, the sampling is influenced by air in a height interval of 30 m. This is the sufficient for the sampling intervals of around 100 m, and for determining that the sampling was done below or above the temperature inversion."

Page 6, line 11: "The restoration of the peatland area towards a net sink of greenhouse gases, and in particular CH4, ..." Why should a rewetted peatland turn into a sink of methane?

This is indeed wrong. The idea was to point out that the restoration of a peatland area takes some time to act as CO_2 sink. Further, the restoration is usually accompanied by enhanced methane emissions, and it takes some years until the system is not such a strong methane source any more. We changed the text to:

"The restoration of the peatland area towards a net sink of the greenhouse gas CO_2 is a process of several years to decades. Initially, the restoration is accompanied by a strong increase in CH_4 emissions, which depend on vegetation and the water level (Couwenberg et al., 2011; Zak et al., 2015)."

What is the size of the rewetted Polder Zarnekow and other peatlands in its vicinity?

We included in the text: " The total rewetted area is 421 ha in size (Gelbrecht et al., 2008)."

The number of Figures is too large for a short article.

We removed the original Fig. 3 and Fig. 14. We further suggest to combine Fig. 4 and Fig. 13 in the final publication.

4 Referee 2

The study by Lampert et al. describes an approach by which air samples can be obtained from different altitudes reaching far into the atmospheric boundary layer (ABL) using an unmanned aerial system. Though the higher level ideas and potential benefits behind the determination of CH4 isotopic composition within the ABL are distributed throughout the manuscript, a concise summary of the higher level aims of this study in both abstract and introduction is missing.

We changed the beginning of the abstract to

"The combination of two well-established methods, of quadrocopter-borne air sampling and of methane isotopic analyses, is applied to determine the origin of methane at different altitudes and to study mixing processes. A proof of concept study was performed to demonstrate the capabilities of quadrocopter air sampling for subsequently analysing the methane isotopic composition δ^{13}C in the laboratory. The advantage of the system compared to classical sampling at ground and at tall towers is the flexibility concerning sampling location, and in particular the flexible choice of sampling altitude, allowing to study layering and mixing of air masses with potentially different origin of methane."

We added in the introduction: "The need to improve understanding of the heterogeneous methane source and the transition from the surface into the atmosphere in the Arctic motivated the development of a flexible airborne sampling system, which provides information on atmospheric stability."

In addition, there is inadequate use of terms with regard to isotopic compositions and isotope ratios, as well as imprecision in describing footprint sizes.

We checked the text for consistency in wording. Now the terms "isotopic composition" and "delta values" are used throughout the text.

Further, we now avoid the term "footprint", which is used as a specific technical term. We changed the interpretation section to:

"The isotopic composition of the two air samples taken on 5 September 2018 simultaneously but with a constant horizontal

distance of 13 cm agree within 0.1‰ at the lowest altitude of 10 m for Flight 1 to 4 (Fig. **??**). Besides this strong locally and temporally related agreement of the isotopic composition, for other altitudes and flights this difference is larger than the uncertainty, and therefore the systematic differences are treated as features. There are several striking features in the profiles of isotopic composition, from lower to higher altitudes:

- On 5 September 2018 the difference in delta values between the two simultaneous samples is systematically smaller at 10 m altitude compared to the higher altitudes, except the last profile.
- On 5 September 2018 the differences in delta values at 100 m altitude increase during the course of the day. The profiles of differences in delta values exhibit similarities for parts of the profile between subsequent flights on both days.
- The delta values are more negative in the morning before vertical mixing starts, as long as a temperature inversion is present (first flight on 23 May 2018 below 150 m, and first flight on 5 September 2018 below 70 m). This is in agreement with methane from biologic processes emitted from the surface that are not vertically mixed.

As the order of analysing the air samples was chosen randomly, the differences of the delta values exceed the uncertainty and the differences in delta values correlate in section between subsequent flights, it is assumed that the differences in delta values are physically present in the air samples. Two aspects can be highlighted:

- An ideally vertically stratified delta value would not be sampled by the present system as the very dynamic circulation process around the copter does not result in a homogenously mixed air at the sample ports. On the contrary, this circulation process can even amplify natural inhomogeneity. It is assumed that the differences in delta values indicate natural inhomogeneity, but it is not possible to prove it based on the data set.
- Beside the buoyancy vertical turbulent mixing the natural inhomogeneity of delta values is not known for the measurement site. Small-scale horizontal variability can be induced by inhomogeneous sources. Episodic CH_4 outbursts on short time scales of few min have been observed by Schaller et al. (2018). The high spatial and temporal variability of methane concentration and isotopic composition reported here is in agreement with their observations. Such variability of methane emissions at the field site as well as the potential upwind CH_4 sources cause the inhomogeneous character of the air samples.

Respecting that the air sample profiling gives a snapshot of a turbulent mixing process, a clear transition in the vertical distribution of the delta values can be seen."

After considering the below specified aspects, this publication could be reconsidered for publication in AMT.

We hope that we can answer all concerns satisfactorily.

1. At this stage, the abstract is not convincing and stops short of revealing the scientific benefit that may arise from profiles of methane isotopic composition reaching far into the atmospheric boundary layer.

We changed the beginning of the abstract to: "To determine the source of methane emissions at different altitudes and to study mixing processes, a quadrocopter air sampling system was developed. A proof of concept study was performed to demonstrate

the capabilities of quadrocopter air sampling for analysing the methane isotopic composition δ^{13}C in the laboratory. The advantage of the system compared to classical sampling at ground is the flexibility concerning sampling location, and in particular the flexible choice of sampling altitude, allowing to study layering and mixing of air masses with potentially different origin of methane."

There is a more or less recent publication by Roeckmann et al. in ACP that summarizes nicely the potential benefit of tall tower and, thus, probably also airborne measurements.

We would like to thank the referee for pointing out this interesting publication. We included the following sentence in the introduction: "Field measurements of methane isotopic composition have been performed at the Cabauw tower at a sampling altitude of 20 m, demonstrating the potential of isotopic analyses to determine contributions from isotopically different sources to the dominating source (Röckmann et al., 2016)." Further, we added "UAS can be operated in remote areas, requiring less infrastructure in comparison with permanent measurement stations, and they can be used more flexibly than manned aircraft, enabling fast reactions to environmental events like changes of emissions through rain, drought, construction, or fire."

I suggest using this overarching view to introduce the topic and made a suggestion in this direction in the abstract- section of this referee comment. Some of the ideas can also be found in the conclusions section.

We would like to thank the referee for the practical recommendation, which we took into account (see answer to comment above).

2. In the methods section, I am missing information on from where exactly air is sampled. There is quite some discussion on the adverse effect air parcel transport due to rotor downwash, so that this issue, and how it was tackled (if at all), should be mentioned already in the methods section.

We included three more co-authors who have done numerical simulations, and added a subsection about simulations with the following text: "In order to quantify the effect of the vertical flow induced by the quadrocpter, numerical simulations were performed with the software ANSYS CFX. The simulations were transient in nature using a Reynolds-Averaged Navier Stokes (RANS) approach with the SST turbulence model (Menter, 1994). A simplified model of the propeller blade was used, with a multidomain approach: The blade is enclosed in a rotating domain, surrounded by a static domain. Simulations were performed for hover with a propeller rotation speed of 3167 min^{-1}, for vertical climb at a speed of 6.5 $\mathrm{m\,s}^{-1}$ with a rotation speed of 3913 $^{-1}$ and of vertical descent at a speed of -2.5 $\mathrm{m\,s}^{-1}$ with a rotation speed of 2880 min^{-1}. An ambient temperature of 0° C and pressure of 1023 hPa was considered. Contours of relative vertical velocity show a core region of positive relative velocity directly below the center of the blade, and a negative relative velocity up to 19 $\mathrm{m\,s}^{-1}$ below the blade for a distance exceeding 0.75 m (Fig. 2). Additionally, zones of recirculation can be seen around the tips of the propeller, especially for the descent case. The air sampling system is contained in the middle of the copter, and is less affected by artificial turbulence than the areas below the rotor blades.

Assuming that in the worst case the sampling takes place within the downwash of the rotor blades of not more than -19 $\mathrm{m\,s}^{-1}$, the sampling time of 1.3 s duration results in a vertical resolution of around 25 m. Sampling during descent with a speed of -2.5 $\mathrm{m\,s}^{-1}$ adds an uncertainty in the altitude of 5 m. Altogether, the sampling is influenced by air in a height interval of 30 m. This is the sufficient for the sampling intervals of around 100 m, and for determining that the sampling was done below or

above the temperature inversion."

3. In the methods section, water samples are referred to as a proxy for spatial heterogeneity of the emitted methane isotopic composition. However, methane dissolved in water and the methane emitted to the atmosphere will have a different isotopic composition due to the fractionation effect of volatilization. I wonder why the authors have not taken air samples from a closed chamber several times and used the keeling-plot approach to determine the isotopic composition of the emitted methane? This would be a direct measurement of the isotopic composition of emitted methane.

We agree that it would be good to have closed chamber samples for comparison of the delta value. However, the aim of this study is to show the vertical distribution of the methane isotopic composition in dependence of atmospheric stability, which we interpret as related to different methane sources.

4. Possible influence from surrounding sources, i.e. surrounding land cover/land use, is not discussed at all, but is necessary in view of the highest altitudes at which measurements took place.

We agree that we cannot fully understand the processes without taking into account more information, like land cover. However, the aim of the manuscript is to show that it is possible to identify vertical layers of different isotopic composition with the experimental setup of the quadrocopter. Further, the case study shows that there is a high horizontal variability of methane sources, which requires specific tools to further understand the observations. We changed the introduction to: "The goal of the study is two-fold:

- Proof-of-concept for the experimental setup of the quadrocopter borne sampling system, and subsequent laboratory analyses, to identify vertical layers of different isotopic composition
- Identification of small-scale atmospheric methane inhomogeneities which require the development of new methods for understanding dynamic processes

In order to test the system's capabilities of providing reliable vertical profiles of the isotopic composition, measurements were performed at a rewetted peatland site, Polder Zarnekow (Zerbe et al., 2013), which is known as a source of biologically produced methane **?**. In the absence of turbulent mixing, local emissions of the wetlands produce a depleted delta value compared to the atmospheric background above the temperatue inversion. During the morning transition, when the stable stratification is gradually replaced by a convectively mixed atmospheric boundary layer, the isotopic composition should adjust to a constant delta value throughout the profile within the uncertainties of laboratory air sample isotopic analyses. To support the hypothesis of the small-scale horizontal inhomogeneity at the study site, the methane concentration of water samples from locations within a radius of 100 m was analysed."

5. When on page 4, the design point is mentioned, and the reasoning behind, the introduction makes more sense. Please underline this connection already in the introduction.

We added earlier in the introduction: "The need to improve understanding of the heterogeneous methane source and the transition from the surface into the atmosphere in the Arctic motivated the development of a flexible airborne sampling system, which provides information on atmospheric stability."

6. There is a fundamental misunderstanding of isotope ratios. The isotope ratio (not isotopy ratios) cannot be negative. After transformation of the isotope ratios to the delta scale, negative values arise if the abundance of the heavy atom is lower than that of the reference material. The use of technical terms in a scientific journal has to be right.

We apologize for the sloppy use of the terms. Now the terms "isotopic composition" and "delta values" are used in the text accordingly.

7. There seems to be quite some imprecision when the discussion addresses footprints. I suggest consulting the literature, one example is given in the detailed comments. It is unclear why footprints for a measurement taken at 100 m should be similarly small as for a measurement at 10 m, as long as stable atmospheric conditions prevail.

We admit that we used the technical term "footprint" in an imprecise way, and rephrased the sentences without using it.

8. Especially the photographs in figure 2 are at least inadequate for a journal like AMT. Both the picture detail and the background makes it practically impossible to discern anything. In addition, the font color is illegible.

We replaced the picture with Fig. 1.

9. Figure 3 is not helpful for the manuscript.

We removed the figure and the reference in the text.

10. Figure 9: showing concentration until 10:00 would be enough, source isotopic composition may be best reflected during night. What is the increased concentration at approx. 12:00?

We corrected the plots and included them in the figures of the time series of meteorological parameters.

P1L1: A higher level rationale is missing in the abstract.

We changed the beginning of the abstract to: "To determine the source of methane emissions at different altitudes and to study mixing processes, a quadrocopter air sampling system was developed. A proof of concept study was performed to demonstrate the capabilities of quadrocopter air sampling for subsequently analysing the methane isotopic composition δ^{13}C in the laboratory. The advantage of the system compared to classical sampling at ground is the flexibility concerning sampling location, and in particular the flexible choice of sampling altitude, allowing to study layering and mixing of air masses with potentially different origin of methane."

In addition, the first sentence sounds a bit like quadrocopter air sampling influences laboratory analysis. I get the drift of the authors, but suggest something like "The determination of the methane isotopic composition at a tall tower and in high temporal resolution indicated a high potential to further constrain methane budgets at regional scales. However, tall towers are rare research infrastructures that may be supported by airborne measurement approaches. In this proof of concept study, we demonstrate the feasibility of using aquadrocopter to obtain air samples at heights between 10 and 600 m above ground. The methane isotopic composition of the air samples was subsequently determined in the laboratory."

We added in the introduction: "The need to improve understanding of the heterogeneous methane source and the transition from the surface into the atmosphere in the Arctic motivated the development of a flexible airborne sampling system, which provides information on atmospheric stability. In this context, unmanned aerial systems (UAS) fill an observational gap for methane mixing processes. They are able to sample small scales with a typical horizontal distance of 1 km, if they are required to be operated in the line of sight, and they reach the top of the atmospheric boundary layer, with a maximum altitude of

typically around 1 km. UAS can be operated in remote areas, requiring less infrastructure in comparison with permanent measurement stations, and they can be used more flexibly than manned aircraft, enabling fast reactions to environmental events like changes of emissions through rain, drought, construction, or fire."

P2L1: I suggest changing to "32 times that of CO2"

We changed as suggested.

P2L6: Please elaborate on what exactly remains inadequate. The source categories are quite clear I think, but the relative contributions of the different categories need better constraints.

We totally agree with the referee. The text is now changed to "Yet, current knowledge of CH_4 biogeochemical processes remains inadequate."

P2L20: please revise typo in background

We corrected the typo.

P2L21: I suggest changing to "indicates", since isotopic compositions of biological sources and fossil / thermogenic methane may overlap in the region of -55 per mil.

We changed the text as suggested.

Figure 2: please use a monochrome background for the figure, and change to "battery" on left picture

We replaced the figure and changed as suggested (see Fig. 1)

P3L17: please decide either for methane isotopic composition or for isotope ratio. Isotopic ratio is at least uncommon.

We now use the terms "isotopic composition" and "delta value" consistently throughout the manuscript.

In addition, line 16 starts naming the aim, and in line 17, the goals are listed. Please revise the section.

We revised the section, and changed to:

"The goal of the study is two-fold:

- Proof-of-concept for the experimental setup of the quadrocopter borne sampling system, and subsequent laboratory analyses, to identify vertical layers of different isotopic composition
- Identification of small-scale atmospheric methane inhomogeneities which require the development of new methods for understanding dynamic processes

"

P3L22: I suggest sharing your hypotheses that this is due to the more pronounced influence of the wetland producing depleted CH4 compared to the atmospheric background in absence of turbulent mixing.

We changed the text to: "In the absence of turbulent mixing, local emissions of the wetlands produce a depleted delta value compared to the atmospheric background above the temperature inversion."

See comment above with regard to isotopic ratio - isotope ratio

We now use the term "isotopic composition" throughout the text.

P4L2: it sounds like the quadrocopter was not based on a commercial chassis. If this applies, please state more clearly.

We changed the text to "The quadrocopter ALICE was designed as platform to carry meteorological sensors and 12 glass bottles for air sampling. The construction of the quadrocopter was calculated for the specific tasks and payload described in the following. Therefore, all relevant load cases that were expected during the flight were applied in analytical and numerical models to optimize the structure of the quadrocopter. Modern manufacturing methods like selective laser sintering and laser cutting where used to build the structure as light-weight as possible but as stable as necessary."

P4L3: unclear why the payload should alter the dimensions of the UAV. Please provide details.

We changed the sentence to "ALICE has dimensions of 1.56 m x 1.56 m x 0.38 m, not including the scientific payload."

P4L4: I suggest: "At a tare weight of 4 kg, ALICE's maximum take-off weight is 25kg." Does the tare weight include batteries for driving the rotors, or are the LiPo batteries for both operating the scientific instrumentation and driving the rotors?

We changed the text to "At a tare weight of 4 kg, ALICE's maximum take-off weight is 25 kg. For the operations presented here, the total weight was 19 kg, which is composed of 4 kg the quadrocopter system itself, 7.2 kg of LiPo batteries with a total capacity of 21 Ah and a nominal voltage of 44.4 V for rotor power supply, and 7.8 kg payload including sensors, glass bottles, data acquisition, power supply for payload and a safety parachute of 12 m^2."

P4L27-31: I don't understand exactly, if there are both manual and magnetic valves necessary. Please explain in more detail. My first impression would be that only magnetic valves that are normally closed would suffice the purpose?

We replaced the figure of the ALICE system and included more information about the valves (see Fig. 1).

P4L34: From this sentence I guess that I am right that there are two sets of valves. However, the meaning of this sentence is unclear.

We hope that the setting of valves becomes clear with the new figure (Fig. 1).

P5L4-6: this section seems redundant to me. The electromagnetic valves were explained some lines above.

We agree that this is already mentioned before, and removed the sentence.

P5L16: I suggest starting with where the samples were analysed and that they were brought there directly after the end of the mission, and then go into detail. Otherwise the transport issue pops up out of the blue.

We changed the order of the sentences to "Following the quadrocopter mission, the sample containers (SC) were transported to the laboratory at the Alfred Wegener Institute in Bremerhaven, Germany for aanalysis of the isotopic composition. The $\delta^{13}C$ value of the air samples was analyzed using a Delta plus XP mass spectrometer combined with a combustion oven, a gas pressure interface and a pre-concentration device (PreCon) (ThermoFinnigan, Bremen, Germany)."

P6L11: I cannot follow that a restored peatland should become a net sink for methane?

This is indeed wrong. The intention was to point out that the restoration of a peatland area takes some time to act as CO_2 sink. Further, the restoration is usually accompanied by enhanced methane emissions, and it takes some years until the system is not such a strong methane source any more. We changed the text to:

"The restoration of the peatland area towards a net sink of the greenhouse gas CO_2 is a process of several years to decades. Initially, the restoration is accompanied by a strong increase in CH_4 emissions, which depend on vegetation and the water level (Couwenberg et al., 2011; Zak et al., 2015)."

P6L25: I suggest including subsection heads "site description", "water sampling" and "flight strategy"

We modified the structure as suggested.

P6L35: Please provide rationale for sampling during descent only.

We added in the text: "During ascent, the temperature profiles were studied, as a base to plan sampling altitudes for the descent."

P7L5: Please explain why the first flights were after sunrise though the aim was to investigate the transition from night time stable conditions to daytime turbulence.

We added in the text: "Flights were permitted between sunrise and sunset. As it takes some hours until the nocturnal temperature inversion is heated away, it was possible to take the air samples during the transition from nocturnal stable boundary layer to the convectively mixed boundary layer. "

P7L11/12: please change typo to evidenced, suggest to change to "indicated"

We changed to "indicated" as suggested.

P7L22: Please indicate nocturnal temperature inversion in figure.

We indicate the height interval of the temperature inversion with a horizontal box in the figures of potential temperature and water vapour mixing ratio.

P8L25: please change to stratification

We changed the text as suggested.

P9L9: -48to -49 is not an isotope ratio, but the delta value. I suggest using the term isotopic composition throughout the manuscript.

We now use the terms "isotopic composition" and "delta value" consistently throughout the text.

P9L26: This assumption is erroneous. The footprint of a measurement at a given height is larger under stable conditions, because the effect of advective transport is much more distinct compared to a situation dominated by turbulence in which vertical mixing is stronger. Please refer to several papers for example by Kljun et al., e.g., "A three-dimensional backward lagrangian footprint model for a wide range of boundary layer stratifications". In addition, the footprints of measurements at 10 m height will be much smaller than those at 100 m height.

We admit that we used the technical term "footprint" in an imprecise and misleading way, and rephrased the sentences without using it.

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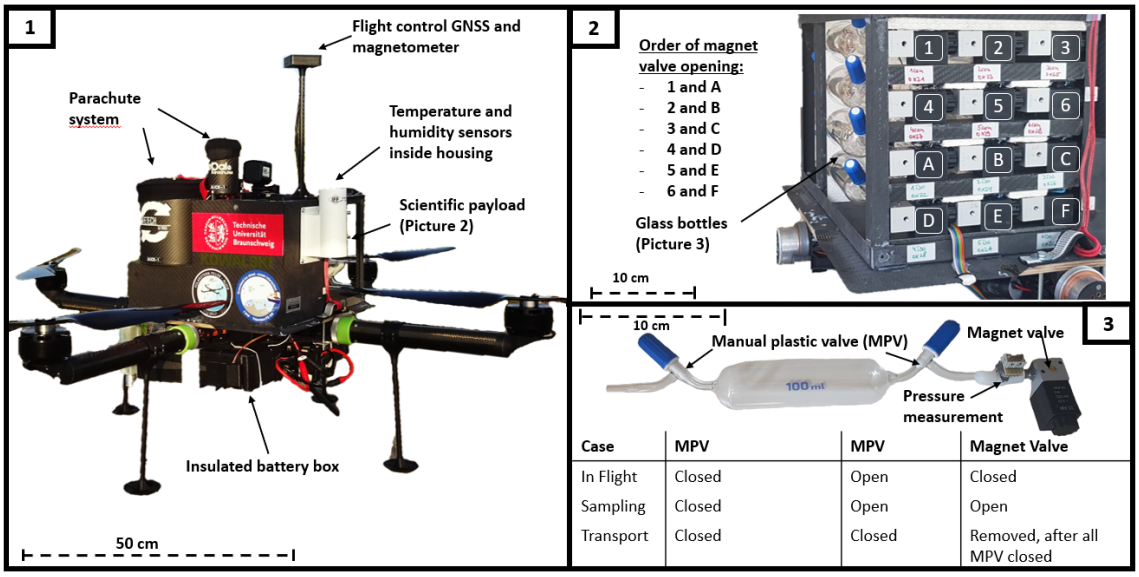

Case	MPV	MPV	Magnet Valve
In Flight	Closed	Open	Closed
Sampling	Closed	Open	Open
Transport	Closed	Closed	Removed, after all MPV closed

Figure 1. ALICE vital components.

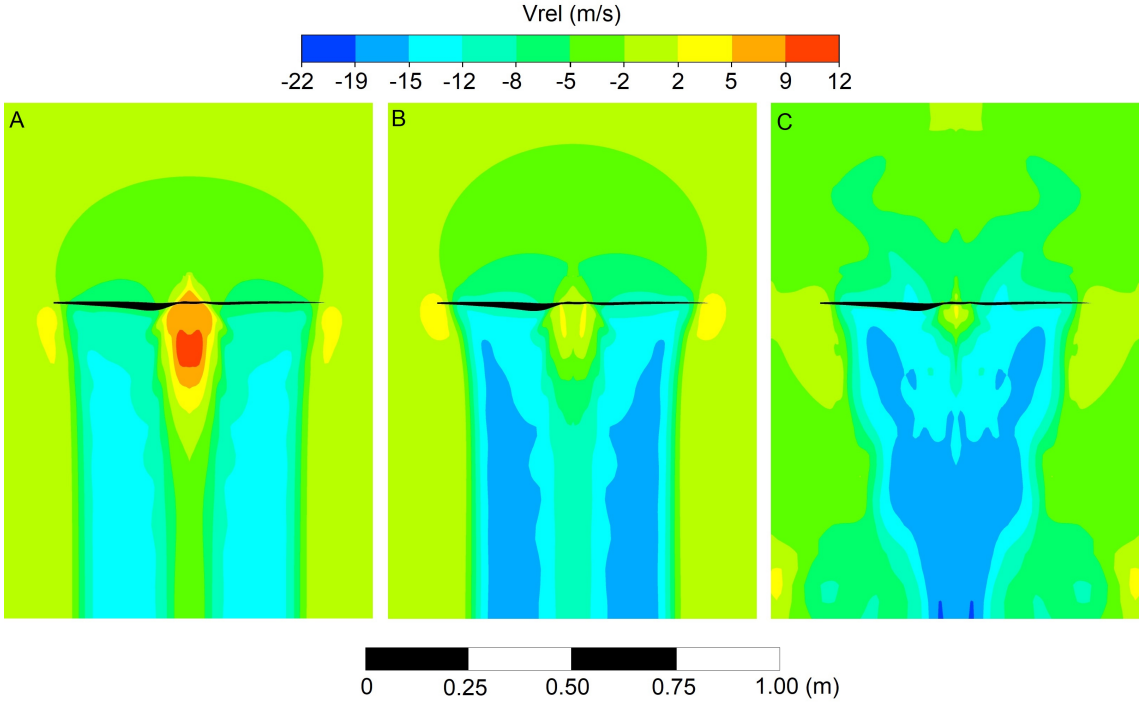

Figure 2. Simulation of the flow induced by a propeller blade during hover, climb and descent.

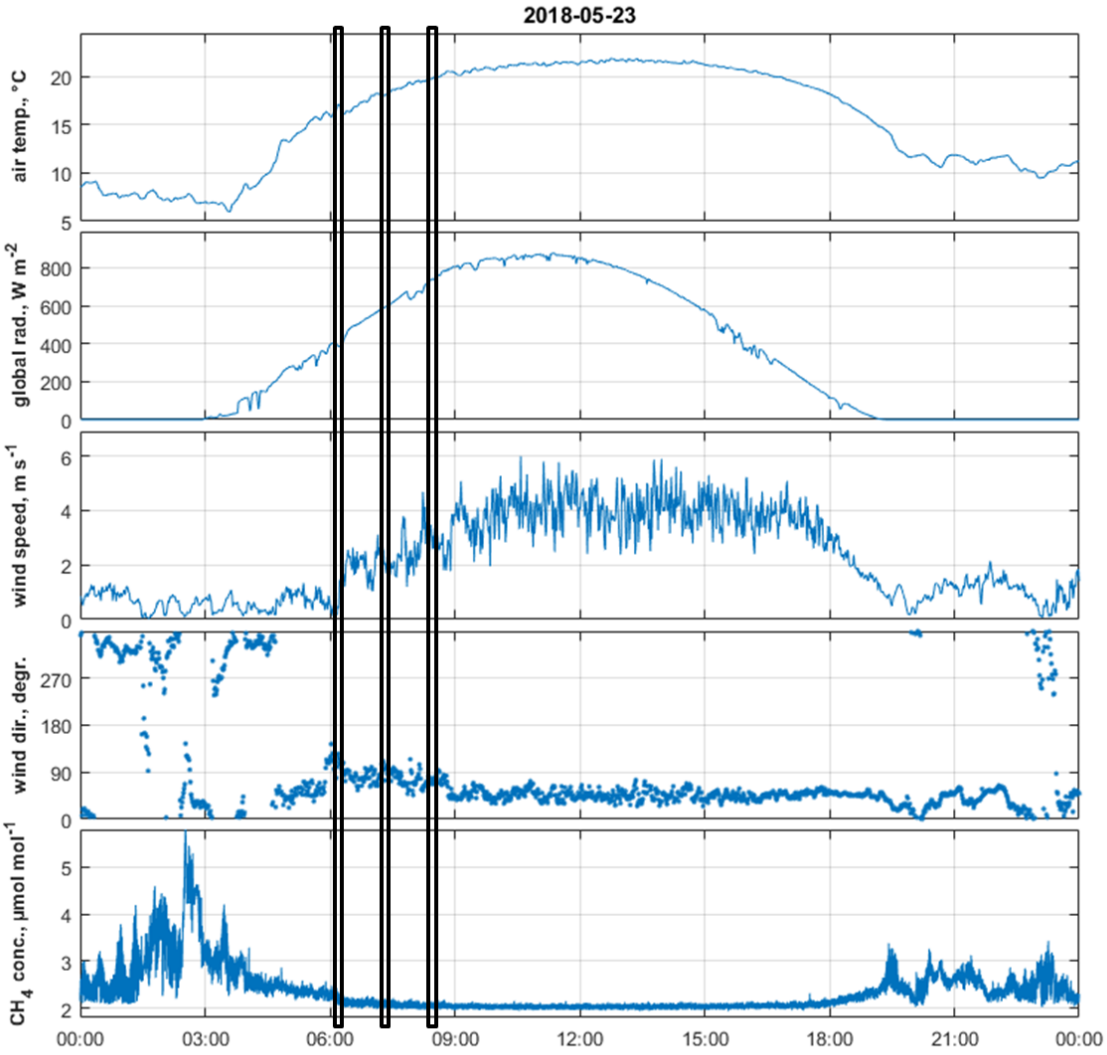

Figure 3. Diurnal course of the main meteorological parameters air temperature, global radiation, wind speed, wind direction, and methane concentration recorded at the meteorological mast at Zarnekow on 23 May 2018.

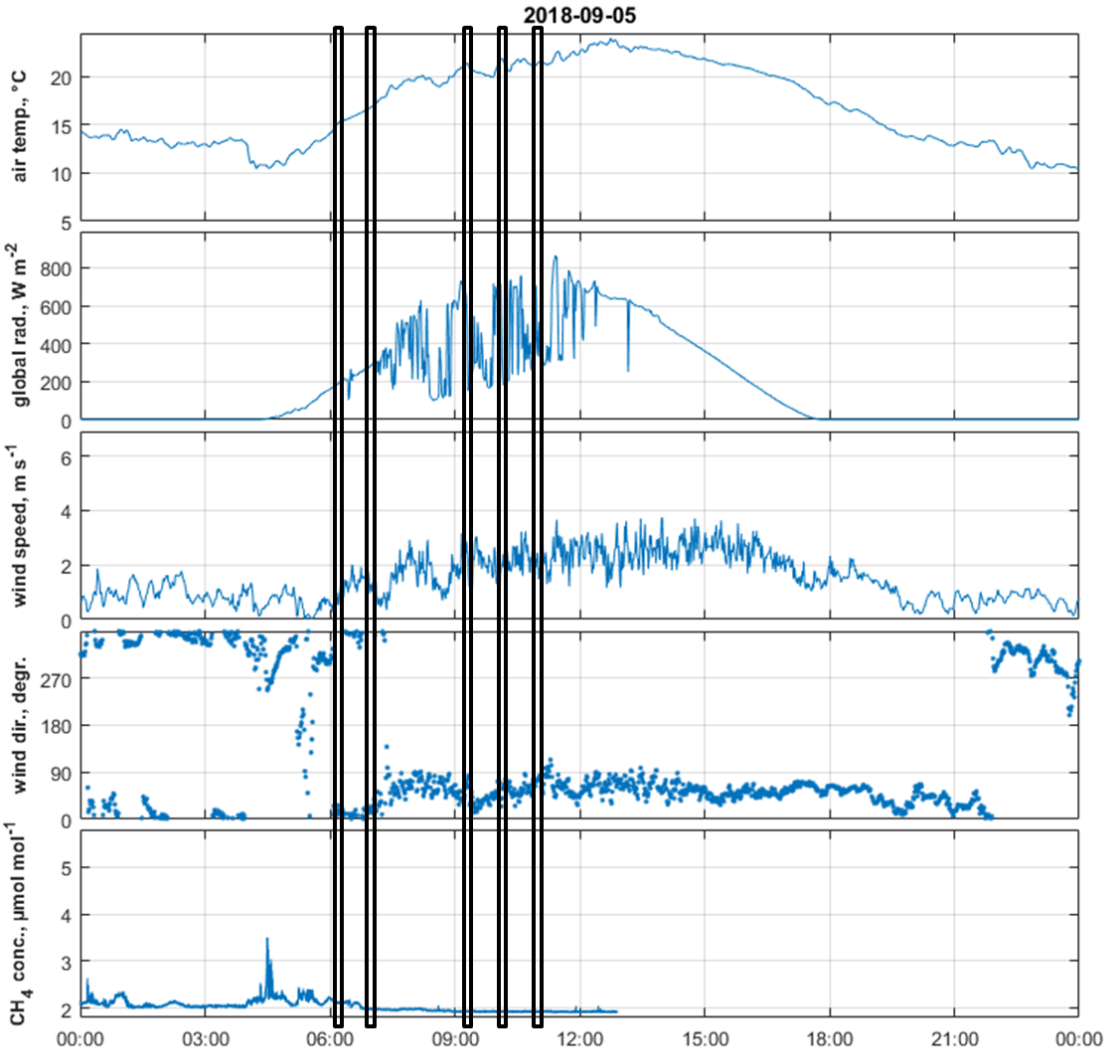

Figure 4. Diurnal course of the main meteorological parameters air temperature, global radiation, wind speed, wind direction, and methane concentration recorded at the meteorological mast at Zarnekow on 05 September 2018.

Figure 5. Illustration of concentration during stable stratification. The photo was taken at the air field Aue/Hattorf, Germany, on 2 October 2011 at 16:15 UTC, copyright Institute of Flight Guidance, TU Braunschweig

Figure 6. Illustration of small-scale concentration variability induced by aircraft. The photo was taken at the air field Aue/Hattorf, Germany, on 2 October 2011 at 16:15 UTC, copyright Institute of Flight Guidance, TU Braunschweig

Studying boundary layer methane isotopy and vertical mixing processes at a rewetted peatland site by unmanned aircraft system

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Abstract.

The combination of two well-established methods, of quadrocopter-borne air sampling and of methane isotopic analyses, is applied to determine the origin of methane at different altitudes and to study mixing processes. A proof of concept study was performed to demonstrate the capabilities of quadrocopter air sampling for subsequently analysing the methane isotopic composition $\delta^{13}C$ in the laboratory. The advantage of the system compared to classical sampling at ground and at tall towers is the flexibility concerning sampling location, and in particular the flexible choice of sampling altitude, allowing to study layering and mixing of air masses with potentially different origin of air masses and methane. Boundary layer mixing processes and the methane isotopic composition were studied ~~with a quadrocopter system~~ at Polder Zarnekow in Mecklenburg–West Pomerania in the North East of Germany, which has become a strong source of biogenically produced methane after rewetting the drained and degraded peatland. Methane fluxes are measured continuously at the site. They show high emissions from May to September, and a strong diurnal variability~~with maximum methane fluxes up to 2 μmol m^{-2} s^{-1} for summer 2018.~~ . For two case studies on 23 May 2018 and 5 September 2018, vertical profiles of temperature and humidity were recorded up to an altitude of 650 m and 1000 m, respectively, during the morning transition. Air samples were taken at different altitudes and analysed in the laboratory for methane isotopic composition. The values showed a different isotopic ~~signature~~ composition in the vertical distribution during stable conditions in the morning (delta values of -51.5 ‰ below the temperature inversion at an altitude of 150 m on 23 May 2018 and at an altitude of 50 m on 5 September 2018, delta values of -50.1 ‰ above). After the onset of turbulent mixing, the isotopic ~~signature~~ composition was the same throughout the vertical column with a mean delta value of -49.9 $\pm$ 0.45 ‰. The systematically more negative delta values occurred only as long as the nocturnal temperature inversion was present. During the September study, water samples were analysed as well for methane concentration and isotopic composition in order to provide a link between surface and atmosphere. The water samples reveal high variability on horizontal scales of few 10 m for this particular case. The airborne sampling system and consecutive analysis chain were shown to provide reliable and reproducible results for two samples obtained simultaneously. The method presents a powerful

tool for ~~constraining~~ indicating the origin of methane by analysing its isotopic ~~signature~~composition, and for measuring the vertical distribution of methane isotopic ~~signature~~composition, which is based on mixing processes of methane within the atmospheric boundary layer.

1 Introduction

Methane's (CH_4) global warming potential is 32 times ~~higher than~~ that of carbon dioxide (CO_2) on a century timescale (Etminan et al., 2016), and 72 times higher on a decadal time scale (Solomon et al., 2007) producing a near-future, greater overall impact on the atmospheric radiative balance (Solomon et al., 2007). As a result, CH_4 regulation has a far higher potential for near-term climate change mitigation than CO_2. Moreover, global warming feedbacks and rising anthropogenic emissions will likely increase CH_4 emissions (Wunch et al., 2009). Yet, current knowledge of CH_4 ~~sources~~ biogeochemical processes, transport and small-scale distribution remains inadequate. This is in part caused by the complex processes of production, transformation and transport, and in part caused by the lack of sufficiently accurate assessments of the vertical distribution of methane and the temporal and spatial behaviour of highly variable anthropogenic and natural CH_4 surface fluxes (Solomon et al., 2007). Global mean CH_4 concentration increased until the early 1990s, then mostly stabilized for about a decade (Dlugokencky et al., 2003). Since 2007, growth has resumed (Dlugokencky et al., 2013), which is visible in the remote polar areas as well (Nisbet et al., 2016). The stabilization was proposed to have been a consequence of reduction in methane emissions from Siberian gas fields and other sources inside the Soviet Union after its collapse, changes in rice agriculture, and changes in microbial emissions (Dlugokencky et al., 2009). The recent increase has been proposed to be related to enhanced emissions from tropical wetlands associated with the extremely wet season in 2009 in the Amazon region (Dlugokencky et al., 2009; Chen et al., 2010).

For separating natural and anthropogenic emission, the methane isotopic ~~signature δ^{13}C‰~~ composition is of particular interest: Transformation of the isotope ratio to the delta scale δ^{13}C‰ results in values that allow to distinguish the source. Biologically produced methane has a typical δ^{13}C ratio of -70 to -55 ‰ (France et al., 2016; Nisbet et al., 2016), methane from fossil fuels has a typical value of -55 to -25 ‰ (Kirschke et al., 2013), and methane from fires has values of -25 to -13 ‰ (Kirschke et al., 2013; Nisbet et al., 2016). Further, smaller differences in the isotopic ~~signature~~ composition are observed for different geographic regions. The ~~backgound~~ background value of air in the free troposphere currently has a value of around -47.4 ‰ at northern latitudes (Nisbet et al., 2016). The isotopic shift towards depleted (lower, more negative) δ^{13}C values ~~provides evidence of~~ indicates predominantly biogenic origin (Nisbet et al., 2016).

The origin of methane and the importance of different natural sources is under discussion for various locations worldwide. Known sources in northern latitudes are permafrost areas (Sachs et al., 2010; France et al., 2016; Sasaki et al., 2016; Kohnert et al., 2018), the Arctic ocean (Yu et al., 2015; Mau et al., 2017) and wetlands (Bellisario et al., 1999). Each source region has

a unique isotopic ~~signature~~composition, and mixing of different air masses results in a linear combination of the corresponding $\delta^{13}C$ ~~signature (France et al., 2016).~~ values (France et al., 2016). Field measurements of methane isotopic composition have been performed at the Cabauw tower at a sampling altitude of 20 m, demonstrating the potential of isotopic analyses to determine contributions from isotopically different sources to the dominating source (Röckmann et al., 2016).

In the Arctic, inter-annual shifts in the sea ice drift patterns generate an inter-annually patchy methane excess in polar surface water and methane efflux (Damm et al., 2018). The origin of this enhanced methane concentration and the exchange processes between ocean, atmosphere and sea ice are subject to current investigation (Mau et al., 2017; Uhlig and Loose, 2017; Platt et al., 2018). The exchange of gas between air and sea strongly depends on the water stratification (Andersson et al., 2017). Further, isotopic fractionation towards depletion of $\delta^{13}C$ in the range of few to several ‰ is observed at the water-air interface for diffusion processes (Happell et al., 1995)

The need to improve understanding of the heterogeneous methane sources and the transition from the surface into the atmosphere in the Arctic motivated the development of a flexible airborne sampling system, which provides information on atmospheric stability. In this context, unmanned aerial systems (UAS) fill an observational gap for methane mixing processes. They are able to sample small scales with a typical horizontal distance of 1 km, if they are required to be operated in the line of sight, and they reach the top of the atmospheric boundary layer, with a maximum altitude of typically around 1 km. UAS can be operated in remote areas, requiring less infrastructure in comparison with permanent measurement stations, and they can be used more flexibly than manned aircraft, enabling fast reactions to environmental events like changes of emissions through rain, drought, construction, or fire.

First applications of measuring the methane concentration with UAS have been demonstrated: The air sampling inlet integrated into multirotor systems is either directly connected to the ground-based methane analyser via a sampling line (Brosy et al., 2017), or the air is stored in a tubing, which is analysed after the flight with a cavity ring down spectrometer (Andersen et al., 2018). The limiting element for both techniques is the length and weight of the sampling line or tube, and sampling altitudes up to 50 m have been published (Brosy et al., 2017; Wolf et al., 2017; Andersen et al., 2018). An air sampling concept based on filling evacuated stainless steel containers by remotely opening a valve and subsequent chemical analyses of trace gases and first applications on multicopter systems have been shown (Chang et al., 2016, 2018). In-situ methane analysers small enough to be integrated on a UAS have been presented (Gurlit et al., 2005; Miftah El Khair et al., 2017; Graf et al., 2018), and first scientific articles showing field measurements of in-situ multicopter borne methane concentrations up to an altitude of 600 m have been published (Golston et al., 2017). The method of air sampling and methane isotopic analyses has been applied to (manned) airborne measurements with high payload capacity in the lower troposphere, e.g. above Siberian peatlands to distinguish emissions from fossil and biogenic emissions (Umezawa et al., 2012), up to balloon borne observations to study sink mechanisms of methane in the stratosphere (Sugawara et al., 1997).

~~To contribute to constraining the source and vertical mixing processes of methane at different locations, a quadrocopter borne sampling system has been developed. The aim is in-situ air sampling for obtaining the vertical distribution of the methane isotopic ratio in the lower troposphere (up to 1 km) for subsequent laboratory analyses.~~ The goal of the study is two-fold: ~~On~~

~~the one hand to show the reliability of the measurement chain from the airborne sampling to the laboratory methane isotopic analyses, on the other hand to provide new insights into~~

- Proof-of-concept for the experimental setup of the quadrocopter borne sampling system, and subsequent laboratory analyses, to identify vertical layers of different isotopic composition
- Identification of small-scale ~~methane dynamics at the study site.~~ atmospheric methane inhomogeneities which require the development of new methods for understanding dynamic processes

In order to test the system's capabilities of providing reliable vertical profiles of the isotopic ~~signature~~composition, measurements were performed at a rewetted peatland site, Polder Zarnekow (Zerbe et al., 2013), which is known as a source of biologically produced methane ~~. Under stable stratification, it is expected that the methane isotopic ratio is depleted for this source, whereas~~ (Franz et al., 2016). In the absence of turbulent mixing, local emissions of the wetlands produce a depleted delta value compared to the atmospheric background above the temperature inversion~~, an isotopic ratio typical of mixed air masses is expected~~. During the morning transition, when the stable stratification is gradually replaced by a convectively mixed atmospheric boundary layer, the isotopic ~~signature~~ composition should adjust to a ~~consistent~~ constant delta value throughout the profile within the uncertainties of laboratory air sample isotopic analyses. To support the hypothesis of the small-scale horizontal inhomogeneity at the study site, the methane concentration of water samples from locations within a radius of 100 m was analysed.

2 Methods

In the following, the quadrocopter ALICE (Airborne Tool for Methane Isotopic Composition and Polar Meteorological Experiments) as the carrier system, the payload consisting of the air sampling subsystem and the meteorological sensors and data acquisition are described. Further, the laboratory air analysis procedures, and the measurement site for system tests are introduced. For evaluating the whole measurement chain, a local source of methane of particular isotopic composition, and atmospheric conditions that first inhibit and then enforce vertical mixing processes (morning transition) were required. These conditions were met at Polder Zarnekow on 23 May 2018. For confirming the results, the same measurement strategy was applied to the same site on 5 September 2018.

2.1 Quadrocopter ALICE and instrumentation

The quadrocopter ALICE (Fig. 1) was designed as platform to carry meteorological sensors and 12 glass bottles for air sampling. ~~It~~ The construction of the quadrocopter was calculated for the specific tasks and the payload described in the following. Therefore, all relevant load cases that were expected during the flight were applied in analytical and numerical models to optimize the structure of the quadrocopter. Modern manufacturing methods like selective laser sintering and laser cutting where used to build the structure as light-weight as possible but as stable as necessary. ALICE has dimensions of ~~1.56~~1.82 m x ~~1.56~~1.82 m x ~~0.38~~0.78 m ~~without~~ including the scientific payload. The arms are quickly removable (rotating lock) for conve-

nient storage and transport. ~~It was developed for a~~ At a tare weight of 6.3 kg, ALICE's maximum take-off weight ~~of~~ is 25 kg. For the operations presented here, the total weight was 19 kg, ~~with 4~~which is composed of 6.3 kg the quadrocopter system itself, ~~7.2~~4.9 kg of LiPo batteries with a total capacity of 21 Ah and a nominal voltage of 44.4 V for rotor power supply, and 7.8 kg payload including sensors, glass bottles, data acquisition, power supply for payload and a safety parachute of 12 m^2. The payload is placed in the center of the system on a platform with dimensions of 370 mm x ~~210~~370 mm. The temperature and humidity sensors are located in a housing to shield against radiation and protect against impact of dust at the edge of the platform. An electronics box contains the central data acquisition.

The quadrocopter is constructed with a thrust-to-weight ratio of 2:1. Each propeller has a diameter of 330 mm. The system was designed for wind speeds up to 35 km h^{-1} during take-off and landing, and up to 70 km h^{-1} during free flight. At a wind speed of 60 km h^{-1}, a climb rate of the current system of 8 m s^{-1} was still possible. ALICE has been designed to reach altitudes up to 1 km. It is electrically powered with four motors U11 KV120 of T-Motor, China.

As the system was intended for operations in the polar regions, the design point of the system is -30 °C. All parts have been tested extensively in a climate chamber down to -30 °C, taking into account vibrations of the carrier, which were simulated with a shaker after in-flight measurements. The pre-heated batteries are insulated passively, and the temperatures of the batteries and the internal avionics are monitored.

Air temperature is recorded with various temperature sensors of different behaviour. Fast fine wire temperature sensors, manufactured at the Institute of Flight Guidance (Bärfuss et al., 2018), have the advantage of a high temporal resolution up to 100 Hz. Further, standard long-term stable sensors were used (Pt1000 "Humicap" HMP110, Vaisala, Finland, digital sensor TSYS01, Measurement Specialities, US). Relative humidity is measured with two different sensors, the Humicap HMP110 (Vaisala, Finland), and the Rapid P14 (Innovative Sensor Technology, Switzerland). Absolute pressure is recorded with AMSYS 5812-0150-B sensors, AMSYS, Germany. Two pyranometers ML-01 of EKO Instruments, Japan, with nadir and zenith viewing geometry are integrated, which allow to estimate cloudiness and surface properties at a sampling rate of 100 Hz. Further, a surface temperature sensor Melexis MLX90614, Belgium, is mounted into the airframe and fixed at the bottom of the UAS. A Global Navigation Satellite System (GNSS) receiver and an inertial measurement unit (IMU) ~~iμVRU of iMAR, Germany,~~ ADIS16488 (Analog Devices, US) are integrated. Data is recorded at a sampling frequency of 100 Hz.

The air sampling system consists of 12 glass flasks (sample containers) of 100 ml content, which are evacuated before take-off. They are equipped with two manual valves, one on each side, and additionally one electromagnetic valve, which is applied only during the flight (Fig. 2). Directly before the mission, each glass flask is linked with a vacuum pump RE5 of Vacuubrand, Germany. One valve is left open, and an electromagnetic valve is connected, which is normally closed. Then the flask is evacuated, and the pressure is controlled by a pressure sensor integrated in the electromagnetic valve. The flasks are opened during the flight with magnet valves, that are triggered either manually by remote control or automatically at altitudes predefined by the operator. After triggering, ambient pressure is reached within ~~less than 2~~approximately 1.3 s. The pressure sensors integrated in the valves are used to monitor air tightness. The most ~~critical point were~~ delicate component are the manual plastic valves~~deployed routinely for~~ , used to close the glass flasks ~~in openposition~~for transport, which are designed to be air tight when closed, but not when open. They had to be treated individually and controlled to make sure that no leakage occurred

during the mission. For quality control and redundance, two glass flasks were filled simultaneously, resulting in six possible sampling altitudes during one flight. ~~The whole quadrocopter system with technical details and instrumentation is shown in Fig. 2.~~

The ~~data are displayed at the ground station~~ onboard data are downlinked to a ground station and displayed to the operator. Depending on the atmospheric structure, the operator decides on the altitude of taking samples during the descent, e.g. above/below the temperature inversion, or within altitudes of enhanced humidity, as required for the scientific question. The ~~evacuated flasks are opened by electromagnetical valves via telemetry command at specific altitudes or by remote control. The~~ whole mission can be flown automatically by a PixHawk autopilot. It is supervised by a safety pilot and a scientific operator who is controlling the system and performance as well as the measurements. Two small cameras, one pointing downwards (GoPro HERO5 Black, 12 Megapixel), one looking to the side (GoPro HERO Session Actionkamera, 8 Megapixel), were integrated. The captured video of the downward pointing camera was transmitted to the operator with 720p resolution and 60 Hz. There are different telemetry connections: A 2.4 GHz link is used for the remote control. A 868 MHz connection serves to send commands to the autopilot, and a 868 MHz link is used for activating the safety parachute trigger. Further, a ~~5~~5.8 GHz video link is established. Scientific data are transmitted via ~~an additional 868~~a 433 MHz connection.

2.2 Quadrocopter flow simulations and impact on sampling

In order to quantify the effect of the vertical flow induced by the quadrocpter, numerical simulations were performed with the software ANSYS CFX. The simulations were transient in nature using a Reynolds-Averaged Navier Stokes (RANS) approach with the Shear Stress Transport (SST) turbulence model (Menter, 1994). A simplified model of the propeller blade was used, with a multidomain approach: The blade is enclosed in a rotating domain, surrounded by a static domain. Simulations were performed for hover with a propeller rotation speed of 3167 min^{-1}, for vertical climb at a speed of 6.5 $\mathrm{m\,s}^{-1}$ with a rotation speed of 3913 $^{-1}$ and of vertical descent at a speed of -2.5 $\mathrm{m\,s}^{-1}$ with a rotation speed of 2880 min^{-1}. An ambient temperature of 0° C and pressure of 1023 hPa were considered. Contours of relative vertical velocity show a core region of positive relative velocity directly below the center of the blade, and a negative relative velocity up to 19 $\mathrm{m\,s}^{-1}$ below the blade for a distance exceeding 0.75 m (Fig. 3). Additionally, zones of recirculation can be seen around the tips of the propeller, especially for the descent case. The air sampling system is contained in the middle of the copter, and is less affected by artificial turbulence than the areas below the rotor blades.

Assuming that in the worst case the sampling takes place within the downwash of the rotor blades of not more than -19 $\mathrm{m\,s}^{-1}$, the sampling time of of 1.3 s duration results in a vertical resolution of around 25 m. Sampling during descent with a speed of -2.5 $\mathrm{m\,s}^{-1}$ adds an uncertainty in the altitude of 5 m. Altogether, the sampling is influenced by air in a height interval of 30 m. This is the sufficient for the sampling intervals of around 100 m, and for determining that the sampling was done below or above the temperature inversion.

2.3 Laboratory isotopic analyses

Following the quadrocopter mission, the sample containers (SC) were transported to the laboratory at the Alfred Wegener Institute in Bremerhaven, Germany for analysis of the isotopic composition. The $\delta^{13}C$ ~~methane signature in~~ value of the air samples was analyzed using a Delta plus XP mass spectrometer combined with a combustion oven, a gas pressure interface and a pre-concentration device (PreCon) (ThermoFinnigan, Bremen, Germany). All valves and traps are automatically operated by the mass spectrometer software. ~~Following the quadrocopter mission, the sample containers (SC) were transported to the laboratory at the Alfred Wegener Institute in Bremerhaven, Germany.~~ Each SC was installed onto the PreCon and the connections were flushed with helium before the SC was opened. The air sample was first carried by helium carrier gas through a chemical trap and then trapped in a cool box filled with liquid nitrogen (-196°C) to remove CO_2, CO and H_2O. Afterwards the CO_2 free air was carried by helium carrier gas to the combustion oven (1000°C) for methane conversion into CO_2 which then was purged into a second cool box filled with liquid nitrogen and trapped therein. When the combustion is finished, the gas stream is purged and trapped in a third cool box filled with liquid nitrogen to pre-concentrate the sample, and carried by helium carrier gas into the isotope ratio mass spectrometer. Methane stable carbon isotope data are given in δ notation (in ‰) relative to the Pee Dee Belemnite (PDB) standard:

$$\delta^{13}C‰ = \left(\frac{\frac{^{13}C}{^{12}C}sample}{\frac{^{13}C}{^{12}C}reference} - 1\right) \cdot 1000 \quad (1)$$

Precision, determined ~~by~~ as the maximum difference of delta values during repeated analysis of ~~Bremerhaven air is about~~ ambient Bremerhaven air samples taken simultaneously and analysed consecutively many times per year, is better than 0.5 ‰. Further applications of the system have been described in Mau et al. (2013); Damm et al. (2015); Verdugo et al. (2016); Fenwick et al. (2017).

2.4 Study site~~, water sampling, and flight strategy~~

The shallow Polder Zarnekow with a water depth of less than 1 m belongs to a large area of rewetted peatlands in the Peene River valley in North-Eastern Germany (53°52.5' N 12°53.3' E, less than 0.5 m a.s.l). It formed after the dikes were opened in 2004/05 in order to restore the peatlands, taking up CO_2 to reduce ~~the sources of~~ greenhouse gases. The total rewetted area is 421 ha in size (Gelbrecht et al., 2008). The site is a Fluxnet site (DE-Zrk) and is part of the Northeast German Lowland observatory of the Terrestrial Environmental Observatories Network TERENO (Heinrich et al., 2018).

It is equipped with state of the art eddy covariance (EC) instrumentation recording the wind vector, temperature and the concentration of water vapour, CH_4 and CO_2 at a frequency of 20 Hz. The measurement height above the water surface is around 2.6 m, depending on the water level. Water vapour and CO_2 are measured with a LI-7200 sensor of LI-COR, US. Methane is measured with a LI-COR sensor LI-7700. Further, a Los Gatos Fast Greenhouse Gas Analyser (FGGA, US) records the concentration of the three greenhouse gases at a frequency of 20 Hz. Four automatic measurement chambers are installed along a transect between the EC system and the shore of the lake for spatially resolved CO_2 and CH_4 flux investigations (Hoffmann et al., 2017).

The restoration of the peatland area towards a net sink of ~~greenhouse gases, and in particular CH_4,~~ the greenhouse gas CO_2 is a process of several years to decades~~, which strongly depends~~. Initially, the restoration is accompanied by a strong increase in CH_4 emissions, which depend on vegetation and the water level (Couwenberg et al., 2011; Zak et al., 2015). The shallow eutrophic lake in particular acts as a strong source of CH_4 (Franz et al., 2016). Maximum methane emissions are typically observed in summer (Franz et al., 2016). In the diurnal cycle, the maximum CH_4 emissions were recorded during night (Franz et al., 2016). This is in agreement with stronger convective mixing of the lake induced thermally from May to October (Franz et al., 2016), which leads to diffusive CH_4 emissions (Hoffmann et al., 2017). ~~The time~~ Time series of methane fluxes of the 3-year period 2016 to 2018 ~~(Fig. ??)~~ reveal a high variability over the entire period and within time periods of few days, with noticeable fluxes during the growing season between May and September (not shown).

2.5 Water sampling

For identifying the reason for small-scale inhomogeneities of the atmospheric methane isotopic ~~ratio~~composition, the methane source located within the surface water was sampled at different locations on 5 September 2018. Six water samples were taken with Kemmerer glass bottles of 50 ml at the locations Z-1 to Z-6 indicated in Fig. 4. After filling and locking with screw cap, the water samples were stored and transported light-tight in a cool box. They were analysed in the laboratory for methane concentration and isotopic composition at the Alfred Wegener Institute in Bremerhaven on 6 and 7 September 2018, thus directly after the sampling.

2.6 Flight strategy

The aerial measurement strategy consists of an automatic climb flight up to 1 km altitude and down again with real-time data transmission of selected parameters at 1 Hz. For the missions presented here, a permission from the nature protection agency and coordination with the German Civil Aviation Agency (DFS, Deutsche Flugsicherung) were required. Flights were permitted between sunrise and sunset. As it takes some hours until the nocturnal temperature inversion is heated away, it was possible to take the air samples during the transition from nocturnal stable boundary layer to the convectively mixed boundary layer.

On 23 May 2018, three consecutive measurement flights of around 10-11 min duration were performed over a time period of 3 h in the morning, with take-off times 06:04, 07:30, and 08:29 and UTC, corresponding to a local time between 08:04 and 10:29. Sunrise was at 04:55 local time.

Each flight consisted of manual take-off and climb up to around 50 m altitude, then handing over the ~~mission~~ system to the autopilot. The flight pattern followed 3 waypoints at 50 m altitude leading to a position directly above the open water fraction of the polder. There, a vertical ascent with a mean vertical speed of 5 m s^{-1} up to a height of 650 m agl and subsequent descent with a vertical speed of -2 m s^{-1} took place. For this feasibility study, air samples were taken during descent at the approximate altitudes of 600 m, 400 m, 300 m, 200 m, 100 m and 10 m. Then the quadrocopter flew to a waypoint close to the landing point

and was landed manually. During ascent, the temperature profiles were studied, as a base to plan sampling altitudes for the descent. The air samples were analysed in the laboratory for methane isotopic composition at the Alfred Wegener Institute in Bremerhaven on 11, 12 and 13 June 2018, thus 3 weeks after the sampling.

On 5 September 2018, five consecutive measurement flights of around 12-13 min duration were performed over a time period of 5 h in the morning, with take-off times 06:04, 07:15, 09:12, 10:05 and 10:57 UTC, corresponding to a local time between 08:04 and 12:57. Sunrise was at 06:23 local time. The same flight strategy as described above was applied. ~~However, the~~ The ascents reached an altitude of 1000 m, but the sampling altitudes remained the same. The vertical ascents were done with a mean vertical speed of 6.5 m s^{-1} and the descents with a vertical speed of ~~-2~~-2.5 m s^{-1}.

3 Results

3.1 Synoptic conditions and meteorological observations

On 23 May 2018, the synoptic situation was characterized by a pronounced high-pressure system above Scandinavia and the Baltic Sea, leading to conditions of low wind speed below 5 m s^{-1}, north-easterly wind directions and a cloudless sky, as ~~evdenced~~ indicated from the smooth behaviour of global radiation (Fig. 5).

On 5 September 2018, the synoptic situation was determined by two strong high pressure systems located above the Atlantic Ocean and above Northern Russia, and a low-pressure system above Southern Europe. This resulted in low wind speed below 4 m s^{-1} of north-easterly direction at the observation site, similar to the conditions on 23 May 2018. In the morning, until 05:30 UTC, around 30 min before the first flight, fog was observed, which was denser towards the East. Starting around 09:00, before flight 3, shallow convective cumulus clouds were present. This is also evident in the high variability of the global radiation (Fig. 6).

On 23 May 2018, the near-surface temperature increased from around 13-14° C at 6 UTC to around 17° C at 08:30 UTC (Fig. 7). The profiles of potential temperature show a strongly stable stratification in the morning, with an increase of potential temperature of around 2 ° C (06:04 UTC) from the surface to 250 m. The top of the nocturnal temperature inversion was located at around 150 to 250 m altitude. At this altitude range, the water vapour mixing ratio decreased as well from around 7 g kg^{-1} in the boundary layer close to the surface to around 5 g kg^{-1} above. After 07:30 UTC, the atmosphere was less stably stratified. The water vapour mixing ratio was enhanced in the lowermost 150 m at 06:04 UTC. Above and later, the water vapour mixing ratio was almost constant with height.

On 5 September 2018 during the first flight, the profiles show a mixed-layer up to 50 m altitude and a stable stratification above (Fig. 8). The water vapour mixing ratio was lower in the mixed layer (11 g kg^{-1}) and increased above up to 14 g kg^{-1}. For the following four flights, the near surface temperature increased, and the potential temperature increased only slightly with altitude. The water vapour mixing ratio decreased with time throughout the whole profile.

3.2 Observations of methane ~~emissions~~ concentrations and isotopic ~~signature~~composition

For both observation days, the methane concentration recorded at the eddy covariance tower at 2.6 m altitude above the surface shows a high variability during the night and the morning, and a relatively constant concentration during the day. During the time period of the first flight on 23 May 2018, the methane concentration was still slightly enhanced compared to the background value during the day (Fig. ~~??~~5). The first flight on 5 September 2018 took place during the high fluctuations of the CH_4 concentration (Fig. ~~??~~6).

The isotopic ~~signature~~ composition of the air samples was different during the first flight of each day at the altitudes located within the stable stratification. On 23 May 2018, the ~~isotopic ratio~~ delta value was depleted at 10 m and 100 m altitude with a value of -51.5‰ (see Fig. 9). Above, the mean ~~isotopic ratio~~ delta was -50.1‰, almost the same as during the next flights throughout the profile, with an average value of -49.9‰. On 5 September 2018, the same systematic behaviour was observed: During the first flight, the ~~isotopic ratio~~ delta value was depleted at an altitude of 10 m, in agreement with a temperature inversion above an altitude of 50 m. Above, the ~~isotopic~~ delta value of -49.9‰ was the same as during all other flights throughout the profile (Fig. 10).

Aerial pictures obtained during the measurement flights for the two case studies show the difference in water level: On 23 May 2018, the lake was filled with water (Fig. 11). On 5 September 2018, almost the whole lake had fallen dry, with only few wet areas remaining, and the sediment still saturated with water (Fig. 4). The depth was in the range of few cm.

The water samples taken on 5 September 2018 within a radius of 100 m revealed highly different CH_4 concentrations (see Table 1). The highest CH_4 concentration of around 4770 ppm was measured from the water sample Z-4 in one of the small remaining water areas with a depth less than 5 cm within the former polder. Directly next to this, the water sample Z-3 taken at a depth of 5-10 cm had a methane concentration of 2310 ppm (see Figs. 4 for exact locations). The water sample Z-4 contained more suspended sediment load than sample Z-3. The sample sites are located within small remaining water areas, which are not connected.

4 Discussion

4.1 Plausibility of the observed isotopic ~~signature~~composition

~~The methane~~ Methane flux data indicate that the observation site was a source of methane during both measurement days, but had much higher emissions on 23 May 2018 (~~Fig. ??~~not shown). During the first flights in the early morning, under stable ~~stratifications~~stratification, an enhanced methane concentration ~~in the ABL~~ representing local emissions close to the observation site can be expected (Röckmann et al., 2016), as observed by Andersen et al. (2018) above wetlands. ~~This is the case~~ A stable stratification was present at the beginning on both measurement days with the UAS. An enhanced methane concentration and high variability was observed until around 06:30 UTC on 23 May 2018 (Fig. ~~??~~5), and even higher concentrations and stronger fluctuations were observed until 6:45 UTC on 5 September 2018 (Fig. ~~??~~6). Under stable atmospheric conditions and low wind speed smaller than 2 m s^{-1} during the night and in the early morning hours, the near-surface

methane concentration is enhanced, as no vertical mixing is possible, ~~e. g. Emeis (2008); Brosy et al. (2017)~~in agreement with Emeis (2008); Brosy et al. (2017). This can be seen in the time series of the methane concentrations for both days as well (Figs. 5 and 6). During the flights, the methane concentration was already smaller again, which can be explained by vertical mixing up to the temperature inversion. This dilusion also influences the isotopic composition. With a local methane source, the near-surface methane concentration above agricultural land therefore increases during stable atmospheric conditions (Wolf et al., 2017), as this prevents dilusion with the free troposphere. However, a high local horizontal inhomogeneity in methane concentrations resulting from mixed-use areas ~~have~~ has been reported, an effect which is visible in the lowermost 10 m above the surface, but smeared out above due to an increase in horizontal wind speed (Wolf et al., 2017). In the presented case, the parallel samples obtained at 10 m altitude seem to be mostly of the same origin with small differences in the delta value. Above, differences in the delta values are higher. A wind speed of less than 2 m s^{-1} during the sampling results in horizontal sample integration over not more than 4 m at the sampling altitude. Small-scale differences in methane isotopic composition can be introduced by mixing processes, and may be reinforced by mixing induced by the quadrocopter system. A high variability of methane sources is in agreement with the highly variable methane water concentrations measured within a radius of 100 m on 5 September 2018.

The ~~isotopic difference~~ difference in delta values obtained for air samples near ground and above the temperature inversion during stable stratification is around 1.5 ‰, thus significantly higher than the uncertainties (flight 1 for each measurement day). This shows that the observed systematic differences are real measurement features, not measurement uncertainty. Other methane sources in the surroundings of the polder are presumably of biological origin as well, they may include larger areas of the rewetted peatland and ruminants, with similar isotopic composition (Röckmann et al., 2016).

Assuming that the parts of the surface with high methane concentrations, like sample Z-3, Z-4 and Z-6, act as a methane source, with ~~an isotopic ratio~~ a delta value of around -48 to -49 ‰ (water sample Z-4 and Z-6), an isotopic fractionation of around 3 ‰ would occur across the water-air boundary. This is in the order of magnitude of carbon isotope depletion observed for emitted relative to floodwater CH_4, ranging from 1.8 to 3.4‰ (Happell et al., 1995), thus can be considered realistic.

4.2 Interpretation of isotopic ~~signature~~ composition from measurement point of view

~~Generally, the isotopic ratios~~ The isotopic composition of the two air samples taken on 5 September 2018 simultaneously but with a constant horizontal distance of 13 cm agree within 0.1‰ at the lowest altitude of 10 m ~~agree to within 0.2 ‰~~ for Flight 1 to 4 (Fig. ~~9 and Fig.~~ 10). ~~However, during flight 1 on 23 May 2018, parallel to the high variability of the methane concentration, and flight 5 on 5 September 2018, the isotopic signature of the two air samples taken simultaneously at 10 m altitude reveal a significant isotopic difference of 0.75‰. As the repeatability~~ Besides this strong locally and temporally related agreement of the isotopic ~~ratio of samples taken within identical air masses is 0.5‰,~~ composition, for other altitudes and flights this difference is larger than the uncertainty, and therefore the systematic differences are treated as features. There are several striking features in the profiles of isotopic ~~signatures~~composition, from lower to higher altitudes:

- ~~The isotopy ratio has more negative values~~ On 5 September 2018 the difference in delta values between the two simultaneous samples is systematically smaller at 10 m altitude compared to the higher altitudes, except the last profile.
- On 5 September 2018 the differences in delta values at 100 m altitude increase during the course of the day. The profiles of differences in delta values exhibit similarities for parts of the profile between subsequent flights on both days.
- The delta values are more negative in the morning before vertical mixing starts, as long as a temperature inversion is present (first flight on 23 May 2018 below 150 m, and first flight on 5 September 2018 below 70 m). This is in agreement with methane from biologic processes emitted from the surface that are not vertically mixed.
- ~~The difference in isotopic ratio between the two simultaneous samples is systematically smaller at 10 m altitude compared to the higher altitudes on 5 September 2018, except the last profile.~~
- ~~The differences in isotopic ratio at 100 m altitude increase during the course of the day on 5 September 2018.~~

~~The hypothesis is that~~ As the order of analysing the air samples was chosen randomly, as the differences of the ~~air samples obtained at 10 m altitude are influenced by air masses representative of a smaller, thus more homogeneous area. At an altitude of 100 m, air masses are influenced by a similarly small area, as long as stable stratification is present. With increasing~~ delta values exceed the uncertainty, and as the differences in delta values show a similar height profile for subsequent flights, it is assumed that the differences in delta values are physically present in the air samples. Two aspects can be highlighted:

- An ideally vertically stratified delta value would not be sampled by the present system as the very dynamic circulation process around the quadrocopter does not result in a homogenously mixed air at the sample ports on the quadrocopter. On the contrary, this circulation process can even amplify natural inhomogeneity. It is assumed that the differences in delta values indicate natural inhomogeneity, but it is not possible to prove it based on the data set.
- Besides the vertical turbulent mixing, ~~a different footprint influences the air masses, and small-scale inhomogeneities can impact measurements only 13 cm apart~~the natural spatial inhomogeneity of delta values is not known for the measurement site. Small-scale horizontal variability can be induced by inhomogeneous sources. Episodic CH_4 ~~ourbursts~~ outbursts on short time scales of few min have been observed by Schaller et al. (2018). The high spatial and temporal variability of methane ~~emissions reported here confirm~~ concentration and isotopic composition reported here is in agreement with their observations. Such variability of methane emissions at the field site as well as of the potential upwind CH_4 sources may cause the inhomogeneous character of the air samples.

Respecting that the air sample profiling gives a snapshot of a turbulent mixing process, a clear transition in the vertical distribution of the delta values can be seen.

5 Conclusions

The measurements serve both as a proof of concept for the system and show the vertical mixing of methane in the ABL by means of its isotopic ~~signature~~composition. With ALICE air samples and subsequent laboratory analyses, it is possible to

determine differences in the methane isotopic ~~signature~~ composition in agreement with atmospheric stability. ~~For the future, a combination of in-situ high resolution~~

The first application of ALICE and the analyses of the air samples show potential for improvement for future missions:

- Air sampling during descent should be compared with air sampling during climb. The higher vertical climb speed due to efficiency reasons has to be taken into account. The initial operation idea was to observe at first the atmospheric stratification in climb and determine the sampling altitudes for subsequent descent based on the altitude of the temperature inversion. However, first simulation results quantify the difference in additional vertical velocities induced by the measurement system, which are much higher during descent.

- The punctual air sampling for delta value determination should be complemented with onboard fast and accurate methane concentration measurements~~and air sampling for isotopic analyses is required for substantial progress in understanding vertical exchange and trace back methane concentrations to specific sources and sinks in the atmospheric boundary layer.~~ . Light-weight instruments with sufficient accuracy and temporal resolution might be operational in the near future.

- Double sampling is highly recommended for system assessment.

- For better understanding processes, methane concentrations should be measured simultaneously.

The differences in ~~isotopic~~ delta values of water and air, the differences in ~~isotopic~~ delta values between both flight days and the development during each day emphasize the highly complex and inhomogeneous nature of methane processes on horizontal scales below 1 km in sediments, at the sediment-water and the water-atmosphere ~~border~~interface. Therefore, ~~the representativeness of individual methane flux measurements have to be treated with care, and footprint analyses are required to extrapolate the measurements on a larger area~~a suitable method is required for quantifying small-scale inhomogeneous methane sources. Vertical layering of air masses with different methane properties strongly depends on atmospheric stability, both concerning concentration as well as the isotopic ~~ratio~~composition. A holistic approach is needed to ~~approach~~ investigate methane processes from sediments to the atmospheric boundary layer, including dedicated measurements of the isotopic fractionation. Despite some points that can be improved, the first applications of ALICE for air sampling and methane isotopic analyses show the potential to contribute substantially to investigate layering and mixing processes of atmospheric methane of different sources. The use of the multicopter represents an advantage over air sampling at tall towers, as it is much more flexible and easier to apply.

Data availability. The data of the flight is available upon request from the authors of TU Braunschweig. Biomet and flux data will be uploaded to the European Fluxes Database Cluster (http://www.europe-fluxdata.eu/) and the TERENO Data Portal (http://teodoor.icg.kfa-juelich.de/ddp/) after final processing and quality control.

Author contributions. AL wrote the paper, FP developed the quadrocopter payload, TK developed the quadrocopter, FP, TK, TR, AL and MA conducted the measurement campaigns, FP and ED performed the laboratory methane isotope analyses, CW and TS performed the methane flux measurements, LL performed the quality check of the copter measurements, DG, DSZ and SB performed the simulations. All authors contributed to and commented on the manuscript.

Competing interests. The authors declare that they have no conflict of interest.

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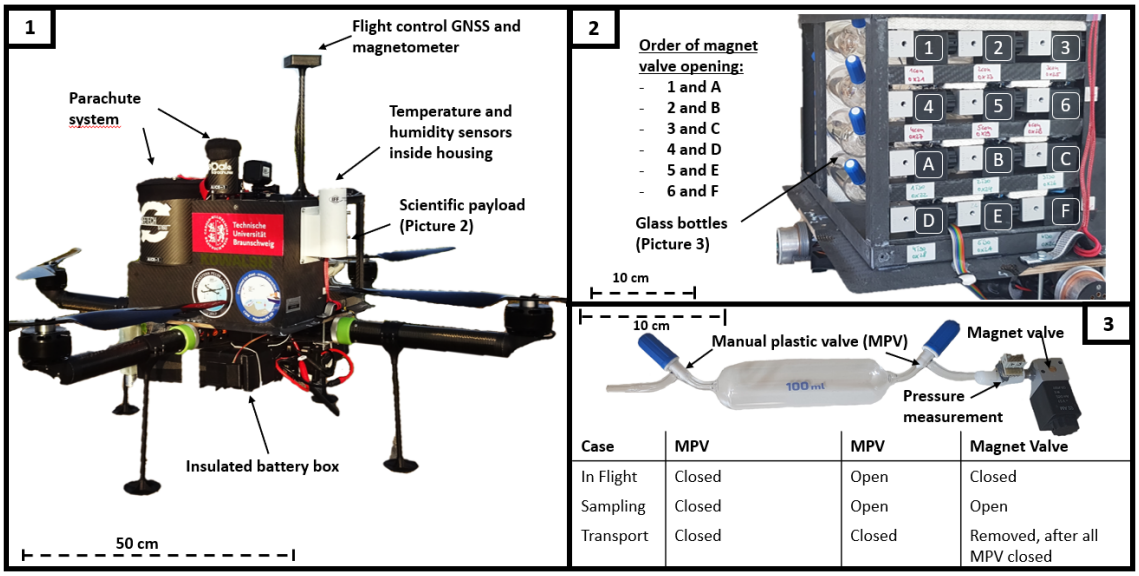
Figure 1. The quadrocopter ALICE during take-off in Zarnekow on 5 September 2018.



Case	MPV	MPV	Magnet Valve
In Flight	Closed	Open	Closed
Sampling	Closed	Open	Open
Transport	Closed	Closed	Removed, after all MPV closed

Figure 2. ALICE vital components. 1: Overall view of the system 2 : Gas sampling payload consisting of 12 evacuated glass flasks which can be filled by opening an electromagnetic valve during the flight. The positions of the two samples taken simultaneously are indicated. 3: Principle of air sampling with manual and electromagnetic valves, showing the configurations of the valves during flight, sampling and transport.

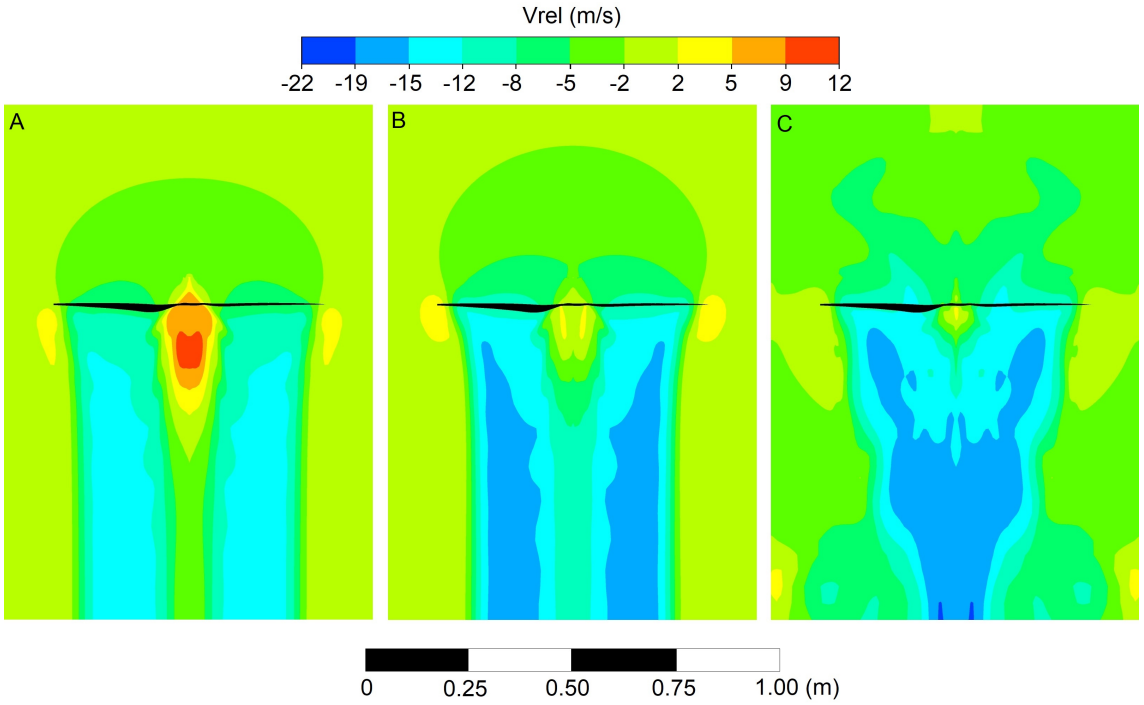


Figure 3. ~~Methane fluxes at polder Zarnekow for the years 2016-2018. Indicated as vertical lines are~~ Simulation of the ~~two measurement days~~flow induced by a propeller blade during hover, ~~23 May 2018~~ climb and ~~5 September 2018.~~descent.

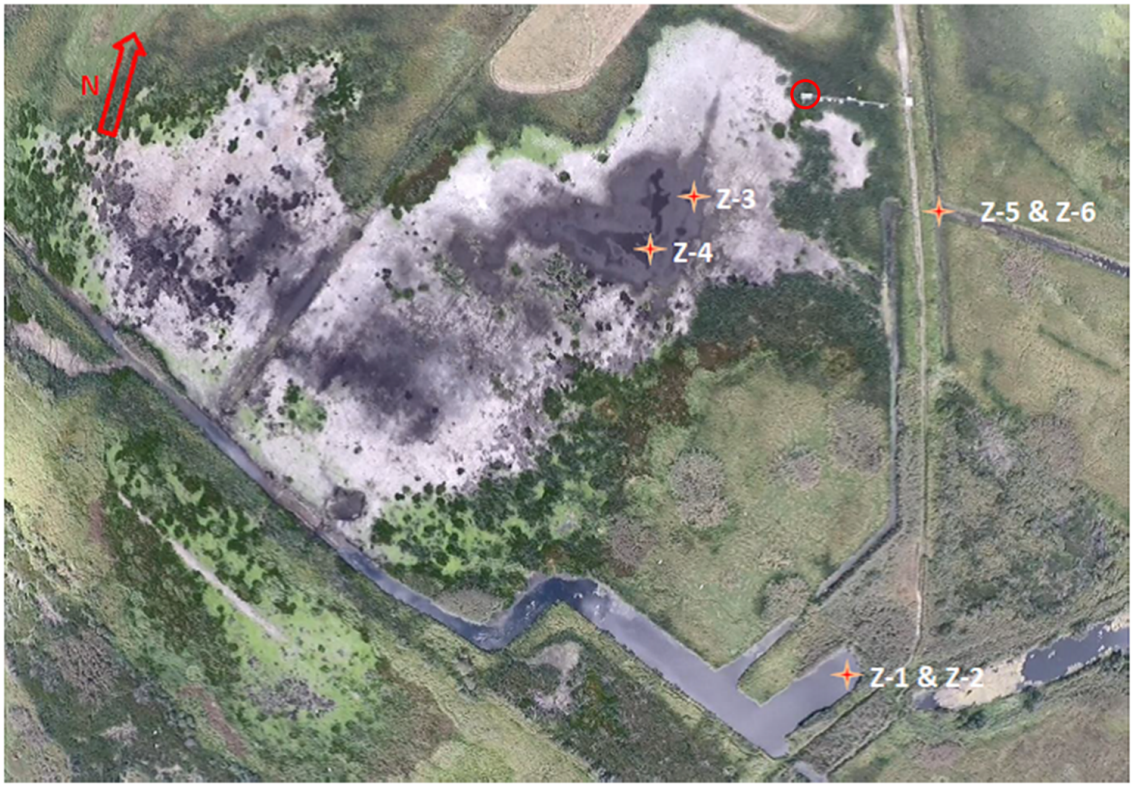


Figure 4. Aerial picture of the polder Zarnekow obtained with the quadrocopter ALICE on 5 September 2018. Almost the whole polder fell dry after the extremely warm and dry summer 2018. The sites where water samples were taken are indicated with Z1 to Z6. The location of the EC station is indicated with a red circle.

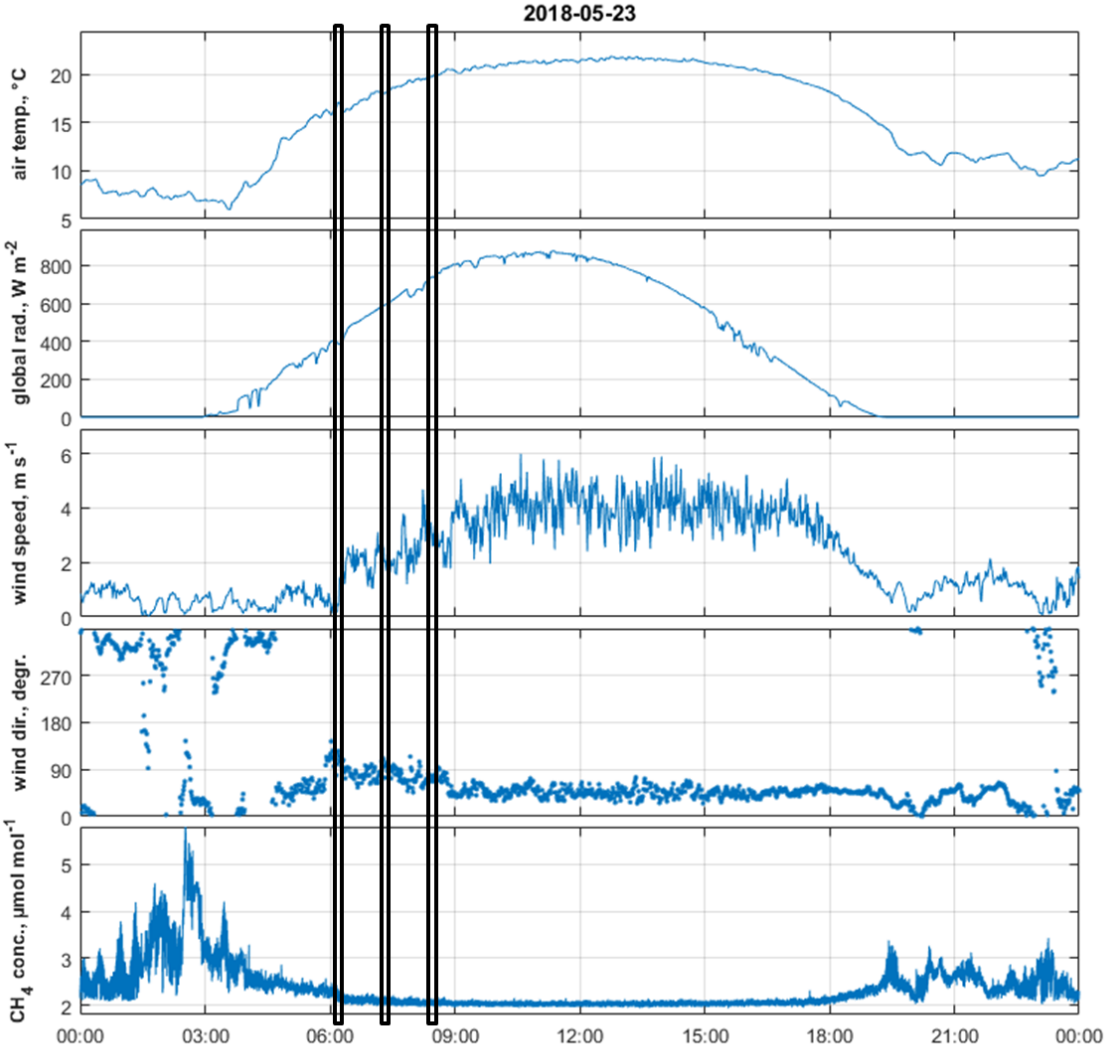


Figure 5. Diurnal course of the main meteorological parameters air temperature, global radiation, wind speed, wind direction, and methane ~~flux~~ concentration (closed-path Los Gatos sensor) recorded at the meteorological mast at Zarnekow on 23 May 2018. The times of the quadrocopter air sampling are indicated by vertical boxes.

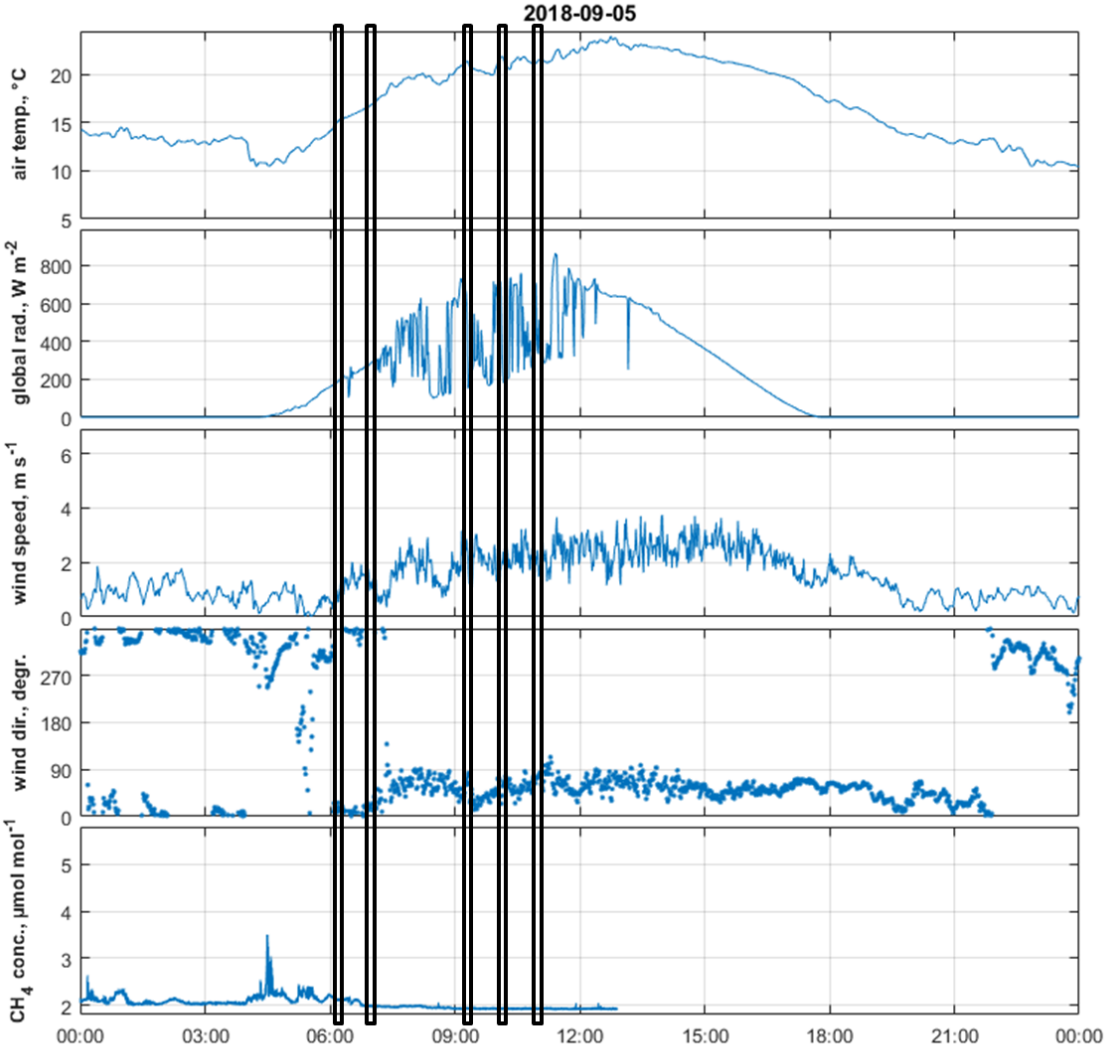


Figure 6. Diurnal course of the main meteorological parameters air temperature, global radiation, wind speed, wind direction, and methane ~~flux~~ concentration (closed-path Los Gatos sensor) recorded at the meteorological mast at Zarnekow on 05 September 2018. The times of the quadrocopter air sampling are indicated by vertical boxes.

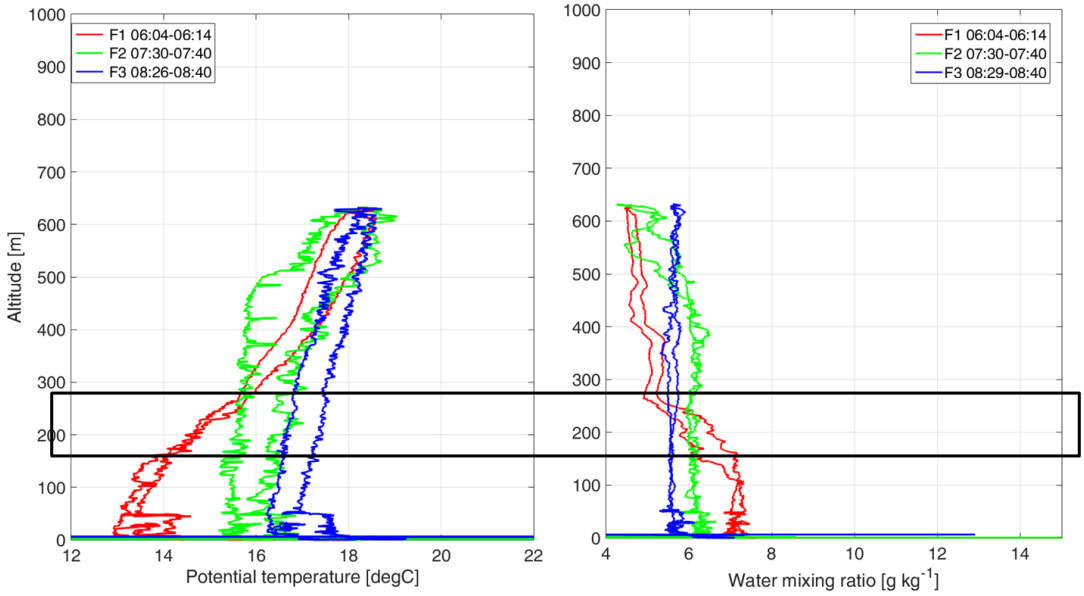


Figure 7. Profiles of potential temperature and water vapour mixing ratio obtained on 23 May 2018. The times of the five flights are given in UTC. The horizontal box represents the height interval of the temperature inversion, which is also visible in the large changes of the water vapour mxing ratio.

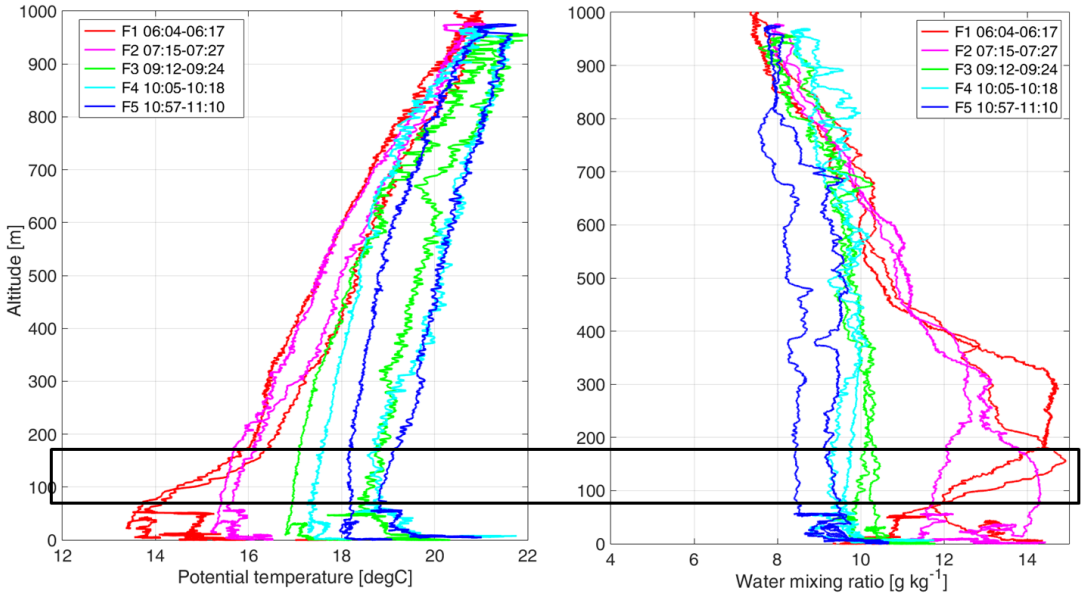


Figure 8. Profiles of potential temperature and water vapour mixing ratio obtained on 5 September 2018. The times of the three flights are given in UTC. The horizontal box represents the height interval of the temperature inversion, which is also visible in the large changes of the water vapour mxing ratio.

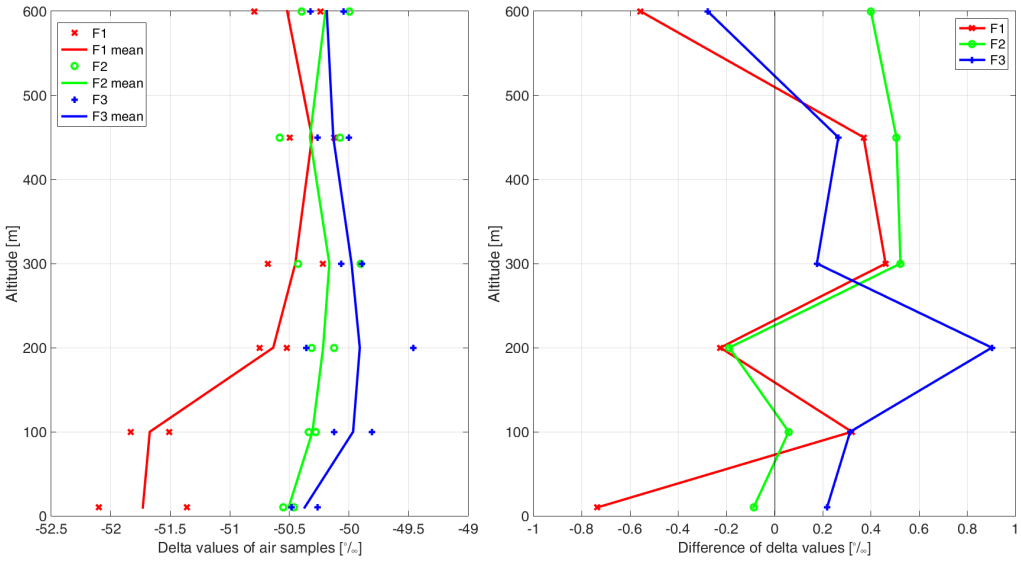


Figure 9. Profiles of a) $\delta^{13}C$ ~~isotopy ratio~~ values for all air samples during the flights on 23 May 2018, and b) ~~isotopy~~ difference of delta values between the double samples filled simultaneously at the same altitude.

~~Continuous methane concentration recorded by the LI7700 sensor of the EC flux tower on 23 May 2018. The vertical bars represent the times of the quadrocopter flights, same colours as in Fig. 7.~~

~~Continuous methane concentration recorded by the LI7700 sensor of the EC flux tower on 5 September 2018. The vertical bars represent the times of the quadrocopter flights, same colours as in Fig. 8.~~

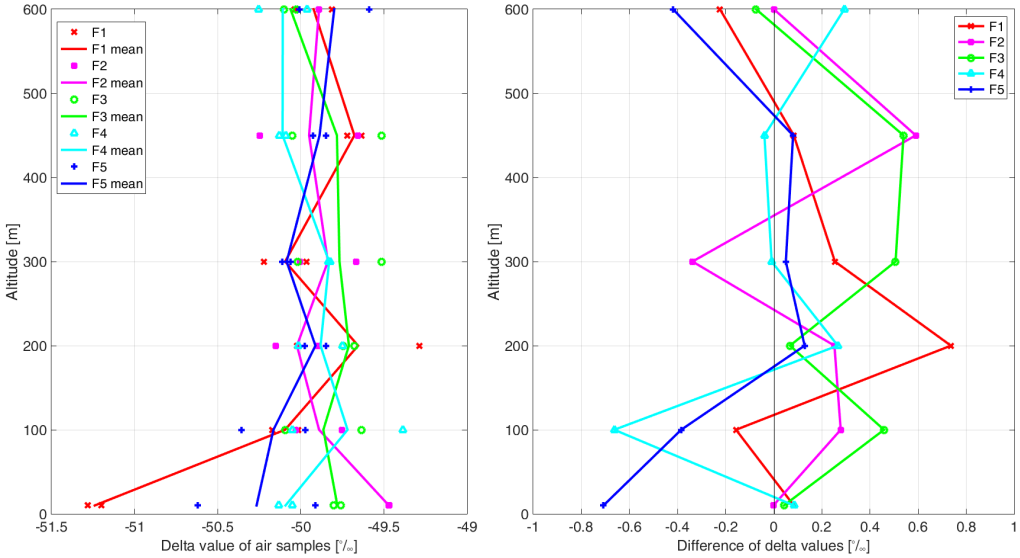


Figure 10. Profiles of a) $\delta^{13}C$ ~~isotopy ratio~~ values for all air samples during the flights on 5 September 2018, and b) ~~isotopy~~ difference of delta values between the double samples filled simultaneously at the same altitude.

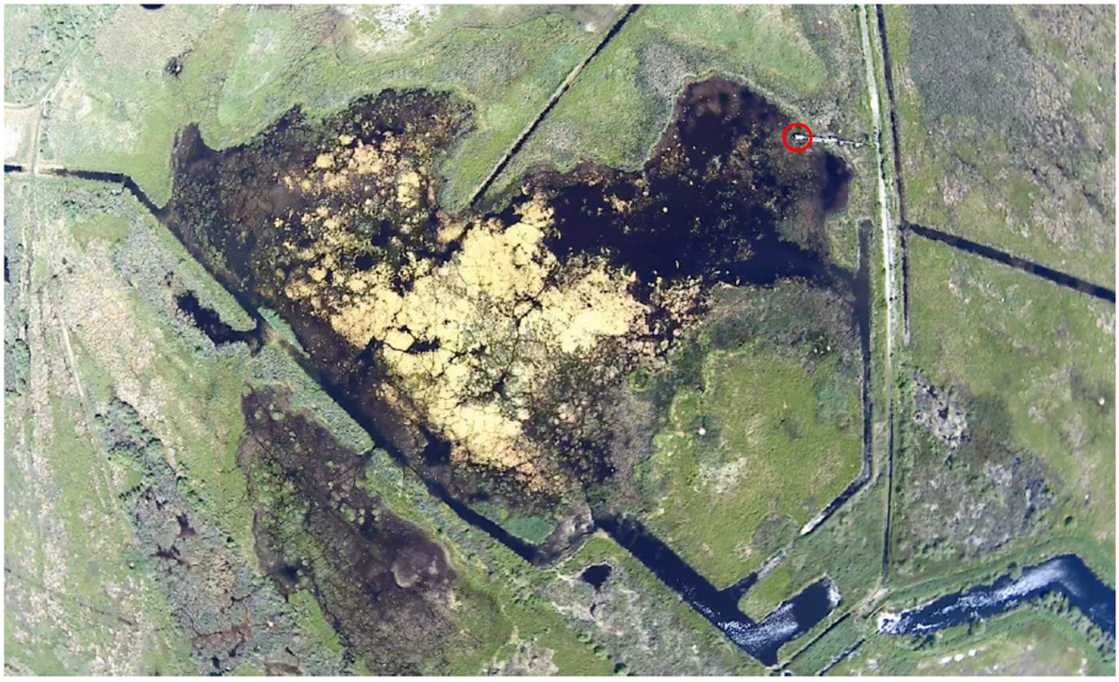


Figure 11. Aerial picture of the polder Zarnekow obtained with the quadrocopter ALICE on 23 May 2018. The location of the EC station is indicated with a red circle.

~~Methane fluxes during the two measurement days, 23 May and 5 September 2018.~~

Table 1. Water samples on 5 September 2018.

Number	location	water depth	colour	concentration [ppm]	isotopic ratio [‰]
Z-1	Peene River influx, surface water, 2 m from shore	5-10 cm	middle yellow	0.339	-30.5
Z-2	Peene River influx, deep water, 2 m from shore	40-50 cm	middle yellow	0.246	-30.1
Z-3	Polder Zarnekow, surface water, pond, 30 cm from edge	less than 5 cm	strong yellow	2312.7	-42.8
Z-4	Polder Zarnekow, surface water, pond	5-10 cm	strong yellow	4765.2	-48.2
Z-5	Trench in the East, 1 m from shore, between plants	5-10 cm	light yellow	111.38	-5.1
Z-6	Trench in the East, near shore	5-10 cm	light yellow	2397.9	-49.2