Reviewer 1

P10574 L1-3: The authors briefly list several ways in which chamber based measurements can lead to unrealistic fluxes, but provide no references and no mention of confounding mechanisms in the discussion. The authors do reference Gao et al. (1997) and Meixner et al. (1997) later in Methods, but these are very different designs than that presented here. These references list several obligatory tests that must be done before dynamic chamber results can be accepted on a scientific level. First, it must be verified that advective flux is negligible relative to diffusive flux, i.e. that the calculated sediment flux does not vary with changing airflow. Second, a 'chamber blank' must be carried out to quantify non-sediment fluxes. The latter could be substantial given that water of unknown chemistry can enter and be equilibrated with the atmosphere inside the chamber.

The main criticism of the reviewer 1 is that the description of the chamber design and the discussion of potential biases are not sufficient. In agreement with this reviewer 3 suggests a more detailed description of the chamber system. We already provided a more extensive description of the chamber system (included now in the supplements) and will discuss potential caveats more careful in the discussion section. While deposition fluxes are very sensitive towards the aerodynamic properties of the chamber, it can be assumed that the emissions of most VOCs are not sensitive against the turbulent conditions inside the chamber. The reason is that the production of most VOCs is independent of the headspace concentration (Pape et al., 2008). Further, above waterlogged sediments the surface resistance is large relative to the boundary layer resistance. As outlined in Zhang et al. (2002) this again makes the trace gas fluxes insensitive against the aerodynamic properties of the chamber. In addition to our previous reply we would like to point out that Tengberg et al. (2004) compared three different types of stirred benthic chambers and found no *significant differences between these chambers. Hence the authors concluded that benthic chambers are insensitive to the hydrodynamic conditions as long as the water is well mixed and the sediment is not re-suspended.*

As suggested by reviewer 1 we would further like to add a short section depicting the atmospheric mixing ratios of CO_2 *and* CH_4*. These data support the flux dynamics observed with our chamber.*

We would like to point out that the main focus of this manuscript are i.) to show the strong imprint of the tides on trace gas fluxes in coastal ecosystems and ii.) to highlight the importance of accurately addressing the perturbations of turbulent flows in flux chamber studies. Both points may have severe implications for our understanding of trace gas dynamics in coastal ecosystems. Regarding the magnitude of the fluxes during submersion we agree with the reviewer and have clearly stated this in the manuscript on page 10587, line 9-12: "As the strength of advection in our chamber system relative to ambient conditions is unknown we can currently not appraise the quality and reliability of the difference chamber systems ".

We do not agree with the referees' general statement that it must be verified that advective transport is negligible relative to diffusive transport. This may hold true for aerial conditions when the flux is primarily controlled by diffusion but truly not for submersed conditions. A major outcome of our study is that advective transport processes substantially affect the trace gas exchange across sediment water and leaf water interfaces during submersion. Under submersed conditions the air flow through the chamber and the position of the frits will most likely affect the advective transport processes and thus making the trace gas fluxes sensitive to the flushing flow rate through the chamber. Regarding the magnitude of the fluxes we agree with the reviewer and have clearly stated this *in the manuscript on page 10587, line 9-12: "As the strength of advection in our chamber system relative to ambient conditions is unknown we can currently not appraise the quality and reliability of the difference chamber systems. However these differences highlight the importance of accurately addressing the perturbations of turbulent flows in benthic flux chambers.*

We suppose that the reviewers statement concerning advective exchange refers to the work of Gao & Yates (1998) and hence to aerial conditions. Gao & Yates (1998) investigated the trace gas emissions above a constant soil source and pointed out that an artificial pressure deficit inside the chamber may cause an artificial advective flow. In their study they found that drawing air through the chamber is the main source for pressure deficits in the chamber headspace. In our set up the air was pumped through the chamber. The resulting pressure surplus, estimated from Poiseuilles law, is 0.8 Pa. Above impermeable waterlogged sediments this will not introduce any artificial advective flux.

Chamber blanks and losses of analytes to the chamber wall are more a problem of reactive trace gases such as NO_x*,* O_3 *or ultra-trace gases but rather a problem for* CO_2 *or methane. All materials used here have been shown to be appropriate for* CO_2 *and methane measurements and we are currently not aware of any* CO_2*-flux chamber study reporting blank problems for* CO_2 *or methane.*

The question for the exchange of water during the measurements is more serious and may become a problem under conditions of strong wave actions as we will show later. Thus metering the water exchange is clearly an improvement for future work. In our previous reply we have shown that the water exchange is not an issue for methane and the VOC's but may affect the CO_2 *fluxes.*

P10574 L8-9: The authors present no evidence for this statement. Yes, bubbling air through a small volume of water would increase turbulence, but that does not mean it is more representative of natural conditions than a static chamber, particularly when non-linear relationships are involved.

Our intention was rather to point out the main differences between our chamber system and those used in previous gas exchange studies than claiming, that our system is more representative of natural conditions than static chambers. We have clearly stated this on page 10587, line 9-12, when it comes to the discussion of the magnitude of the fluxes"As the strength of advection in our chamber system relative to ambient conditions is unknown we can currently not appraise the quality and reliability of the difference chamber systems. However these differences highlight the importance of accurately addressing the perturbations of turbulent flows in benthic flux chambers." Nevertheless there is overwhelming evidence from the literature that sufficient mixing of the water inside the chamber is a prerequisite for assessing exchange processes under submerged conditions. See for instance Tengborg et al. (2004) and references therein.

P10575 L18: Because the frits are 12 cm above the sediment surface, I expect that there would be a notable change in water turbulence and air-water-sediment transfer velocity when the water rises above or drops below 12 cm. Can the authors comment on this?

We also expected a notable change in the turbulence and corresponding change of the transfer velocity across the sediment water interface, when the water rises or drops above / below 12cm but this does not show up in our flux data. It took between 7 15 minutes to change the water level inside the chamber by 12 cm, being on the same time scale as our sampling frequency. Thus we assume that *the sampling frequency was not sufficient to monitor such an effect. In particular during rising tide this coincides with drastic changes in the* CO_2 *and methane concentrations inside the chamber superimposing changes in the transfer velocity.*

P10576 L26: The sampling regimen needs some clarification. Line 26 notes that each of three lines were sampled consecutively for 5 min, but P10578 L8 describes results on 5-10 min intervals. This gives the impression that chamber samples were collected every five minutes, with less frequent atmospheric sampling. Also, was the inlet air to the chamber pumped from the 2 m line, the 4 m line or some other intake?

The sampling lines were indeed sampled consecutively resulting in a time resolution of 15 minutes. The time interval given on page 10578 L8 is an estimate that accounts for the response time of the chamber. We will change this to < 15 min. The inlet air was taken from the 4m line.

P10577 Results: A time-series figure showing Cin and Cout would help explain some of the authors' results. Was Cin relatively constant, with most of the fluxes driven by variability in Cout? Could flux estimates have been affected by rapid changes in Cin and subsequent equilibration with the chamber water? Estimated or observed water depth would also be worth plotting here.

As shown in our previous response, the flux variability cannot be explained by variations of the inlet concentration. In particular during low wind speed the inlet concentration shows the same variability as observed in the chamber, and thus strongly supports the temporal flux pattern observed with the chamber. A section showing the atmospheric mixing ratios of CO_2 *and* CH_4 *is included in results section under point 3.4 in the revised manuscript. We prefer not adding any estimated water depth in figure 2. As this might imply a correlation* *between the fluxes and water depth that is not justified by measurements.See also the response to reviewer 3.*

P10583 L 5-8: The change described by Werner et al. (2006) was in the horizontal flow velocity and only in the top 2 cm. I expect that the horizontal flow velocity characteristics inside a chamber that is pressed 5 cm into the sediment could be very different.

This is true. Our hypothesis is based on the observation that this drop regularly occurs before the water entered or after the water left the chamber. Thus this is rather an analogy. We agree with the referee that the observed drop cannot unambiguously be attributed to changes in the horizontal flow and that the flow characteristics inside the chamber could be different to those outside.

We formulated our hypothesis more carefully and changed the sentence: "Although the chamber will certainly affect the water flow in the top sediment, this may provide a clue to explain the observed drop in the emission fluxes.".

P10583 L 18-29: Without an analysis of chamber aerodynamics, it cannot be determined whether the static air in and near the sediment was an artifact of the chamber design. Also, did the spike occur before any flood water had entered the chamber?

In our previous response we have shown that mixing of the entire chamber volume is achieved within 0.4 min preventing the buildup stagnant air layers above the sediment. Hence we can rule out a chamber artifact. The spike occurred with the flood water entering the chamber not before.

P10585 L 13-16: Can the authors suggest any reason for the disparity between their results and those of Deborde et al. (2010)?

Trace gas fluxes above natural surfaces are generally highly variable in space and time and thus may account for the disparity between our results and those of Deborde et al. (2010).The methane flux above a surface depends on the Archean community producing methane, the methanotrophic activity in the sediment and the forcing of the exchange across the sediment water interface. The difference in the methane peak between night and day in our study highlight the importance of methanotrophic acitivity at the sediment surface on the methane efflux. Finally, in the Deborde study a static chamber was used that only measured the diffusive flux as outlined there, whereas our system measures the diffusive and advective flux. This partly accounts for the differences between both studies.

P10585 L25: Refer to the comments of other G. Abril regarding CO2-based metabolism estimates.

We have done so.

P10587 L1: There are several other ways that bubbling atmospheric air through the chamber may affect fluxes. The gas concentration and temperature in the chamber water will be at near equilibrium with the air. This could introduce artificial gradients and thermal perturbations, as mentioned only briefly in the introduction. Because this is reportedly one of the first studies to measure fluxes using an aerated chamber, the authors must provide a thorough discussion of the new caveats associated with this method.

We already responded to this point in our previous reply to the reviewer. As mentioned above Tengberg et al. (2004) found benthic chambers being insensitive to the hydrodynamic conditions as long as the water is well mixed and the sediment is not re-suspended. Our system fulfills both conditions. Under *submersed conditions the temperature inside the chamber will depend on the heat conductivity of the chamber walls. With a heat capacity of 1.005 kJ* kg^{-1K-1} *for air and a mass flow of 0.28Kg h-1air the heat flow is 0.21kJ* ΔT*, where* ΔT *denotes the temperature difference between the air and the water. With a chamber volume of 8 L the resulting temperature change of the enclosed water can be approximated to 0.006* ΔT*. The heat conductivity of the chamber walls (0.005m thickness,* $0.24m^2$ *surface area) is about 0.32 kJ* ΔT*. Thus we can safely assume the chamber being in thermal equilibrium with the surrounding water.*

P10588 L25-27: I'm not sure this statement can be supported without some sort of comparative control, i.e. simultaneous measurement of fluxes using a static chamber or periodic measurement of dissolved gas concentrations outside the chamber.

The effect of mixing on exchange processes across sediment-water and plant water interfaces under submersed conditions has been shown in a variety of studies (Werner et al., 2006; Billerbeck et al., 2006; Huettel et al., 1996; Precht et al., 2004; Werner et al., 2006; Kim and Kim, 2007; Cook et al., 2007; Jansen et al., 2009; Clavier et al., 2009). We clarified this statement. It is now:" The main difference to most of the previous studies is the introduction of an turbulent flow in our flux chamber system resulting in substantially higher fluxes during immersion as previously reported for oxygen, DIC nutrients and suspended matter."

Technical corrections:

P10573 L12: References out of order.

We have changed this.

P10573 L22: Gao and Yates (1998) is not in reference section.

We suppose this refers to the citation on page 10574. We now have included the reference in the reference section.

P10573 L22-23: References out of order.

We have changed this.

P10574 L25: Change drawn to pumped.

We have changed this.

P10583 L10-11: Sentence is hard to read, it would help to reword or split into two sentences.

We have split the sentence. It is know: "Thereafter, CH_4 *fluxes dropped to increase again with tidal height. In contrast the respiratory* CO_2 *night flux showed a gradual decline."*

P10587 L10: Change difference to different.

We have changed this.

P10587 L10: Change ‘can currently not’ to ‘cannot currently’.

We have changed this.

Figure 2: It would be easier to see the CH4 fluxes if the plot were scaled such that the peaks were removed, as was done for the CO2 fluxes, with the values beyond the plot scale listed directly on the plot. There appears to be a few gaps in the CO2 flux data during the change from tidal immersion to air exposure. Can this be explained?

It should be noted whether the temperature shown in figure 2 was measured inside or outside the chamber. If both were measured, it would be a worthwhile comparison.

We rescaled the methane plot as suggested by the reviewer. The data gaps are due to maintenance work to the chamber. We forgot to remove them for CH4 and corrected this omission. We will further indicate this in the figure caption. The temperature shown in figure 2 is the air temperature 3m above the ground. As suggested by reviewer 3 we will skip the temperature data.

Reviewer 2

The paper of Bahlmann et al. presents an advanced way to directly measure fluxes from coastal sites. It was shown that the method works for several gases including CO_2, CH_4 and VOCs. The paper presents nice results over different states of tidal cover, and generally contributes to the understanding of sediment flux dynamics of different gases, especially of CO2 and CH4. This could also be a nice way to broaden our understanding of flux dynamics of further trace gases not mentioned.

However, I am a bit confused by the presentation of the VOCs. I would appreciate a small section in which it is described how the “enhancement” in fluxes was calculated. Does 1 mean that fluxes are twice as high as the mean? Which mean was used to calculate the enhancement and why this mean? Also, how could you ensure that this is really enhancement and not the drift of the measurement system if there was no standard available or was their an internal standard? I will further go into detail in the specific comments section. Nevertheless, I feel like this could also be nice for the specific compounds that could not yet be quantified once a standard for them is available. Therefore, I feel like it would be sufficient to mention that these compounds can also be measured here, but I am not sure that they need to be included to the current extent.

The calculation of the enhancement factors is explained in the figure caption of figure 4. The enhancement was calculated relative to the mean fluxes measured during air exposure. Thus, an enhancement of 2 means, that the mean flux was twice as high as the mean flux during air exposure. For the compounds present in the standard the enhancement was calculated from the absolute fluxes given in table 2.

The GC-MS was calibrated with a Scott TOC 15/17 standard containing 65 compounds at 1ppm each in nitrogen. 1ml aliquots of the standard were measured 3 to 5 times the day. These standard measurements showed no substantial drift during the day for all components in the standard. Thus we do not expect a drift for the compounds not present in the standard. Given this it is in principal possible to first calculate relative fluxes from the peak area and use these to calculate enhancement factors.

Our intention with including these compounds was to show that the flux enhancement during tidal submersion is a common feature of trace gas fluxes in tidal systems that could be observed for all compound classes. Following the reviewers suggestion we will remove DMS, COS, propane and butane because these were not quantified by a standard. But we will keep the halocarbon data and the data for CS2 and propene to show that the flux enhancement during tidal submersion is a common feature of trace gas fluxes in tidal systems that could be observed for different compound classes.

I generally would advice to check the paper for comma and apostrophe placement (e.g. VOCs is written without apostrophe). Several citations throughout the text are not in chronological order. The authors should check for this in the whole text. I would also recommend to check the text for too complicated and long sentences (especially in the discussion section). Some are difficult to follow. I have pointed some out in the specific comments below.

We have done this throughout the manuscript.

Specific comments:

P10572 L25: sulphur-bearing (or without the minus, but it needs to be persistent throughout the text)

This is now sulphur-bearing throughout the text.

P10575 L1-2: Can the authors specify in which direction fluxes were calculated? In L1, the authors measure that they calculate from the difference of the inlet to the outlet, but in the equation this is the other way around. Maybe it could also be helpful to mark the in- and the outlet in Fig. 1, then this would be clear at first glance.

We will specifiy this and rephrase the sentence in line 1 P10575 as follows:

"The fluxes were calculated from the concentration difference between the outlet and the inlet of the chamber. Hence emission fluxes are positive."

The flow direction in fig. 1 is marked by arrows. We will label the inlet and outlet in fig.1

P10577: How were the precision and the drift of the measurement systems determined / monitored? How was the working standard prepared?

The GC-MS was calibrated with a Scott TOC 15/17 standard containing 65 compounds at 1ppm each in nitrogen. 1ml aliquots the standard were measured 3 to 5 times the day. These standard measurements showed no substantial drift during the day for all components in the standard. A detailed description of the analytical procedure is given in the Supplement of an accompanied paper (Weinberg et al. 2014)

P10578 L9: "following" instead of "followed"

We have corrected this.

P10578 L21: Instead of “circadian” maybe “diurnal” (and if it’s not a clear day-night-cycle, then “diel”)

We have replaced circadian by diurnal.

P10579 L24: Here, the Scott TOC 15/17 standard is mentioned. I think some clarification regarding this standard is needed in the method section (see comment regarding P10577). Was this a liquid standard? A gaseous standard? Etc.

See previous comment.

P10580 L3: Here, clarification on how the enhancement was determined is severely needed. And why is “enhancement” discussed for the halogenated VOCs when these could actually be quantified? I understand that this is probably for comparison with the other gases, but I don’t really see the point when for example CO2 and CH4 are also given in absolute values and COS and CS2 aren’t really discussed. Either this concept needs to be better explained or I would use the total number. The concept of “enhancement” as it is used here is quite difficult to grasp.

We have added an explanation of the enhancement here. The sentence is now:" The average enhancement during tidal immersion (relative to the average fluxes during air exposure) ranged from 4 – 12 for CS_2 *the halocarbons* CH_3Br*,* CH_3I $CHCl_3$ *and* $CHBr_3$*."*

The absolute fluxes of the halogenated VOCs are discussed in detail in an accompanied paper (Weinberg et al. 2014). The main focus of this manuscript is on the tidal controls on trace gas fluxes. For this purpose we found the enhancement more illustrative because it makes the tidal effect comparable among different trace gases. This is hard to show using absolute flux values. Thus we would like to stay with the enhancements here. See also previous comment.

P10580 L16: Is it possible that there is a word missing behind "high"? E.g. "tide"?

This is true. We have inserted tide here.

P10581 L4-6: Please rephrase this sentence. Something is messed up in the word order. Maybe it would be helpful to divide the sentence. I would also recommend to break up the following sentence as it is difficult to follow as well.

We followed the reviewers recommendation: "The Ria Formosa lagoon has a negligible inflow of freshwater and a year round salinity between 35 and 36 PSU. This makes salinity driven lateral changes in methanogenesis and benthic respiration implausible."

P10582 L17-20: I would recommend breaking this sentence into two.

We have done so and further changed the order of the sentences: "In accordance Yamamoto et al. (2009, noted a concurrent increase of the redox potential of the sediment with increasing CH_4 *and* CO_2 *fluxes during tidal inundation. The* CH_4 *fluxes observed in the Ria Formosa lagoon provide a mirror image of these oxygen dynamics."*

P10582 L24: Not sure that “confounding” is the right word here. Maybe “interfering with” instead?

Following the reviewers recommendation we have replaced confounding by interfering.

P10584 L1-6: I am a bit confused by this explanation. I thought that CH4 fluxes were higher in the night (P10578 L6-7)? This doesn’t get clear here in the discussion.

Higher methane fluxes during night were only observed for the methane peak. See page 10578. However we don’t get the point here as this section does not deal with day night differences. We referred to the night time fluxes in order to compare the respiratory CO_2 *with methane.*

P10584: I would abbreviate “Methane” here as was done in the remaining text.

We have done this throughout the manuscript.

P10584: Please introduce the short explanation for DIC, some readers might not be familiar with this abbreviation.

We will do so: “(DIC =$\Sigma CO_2^{*}+HCO_3^{-}+CO_3^{2-}$)“

P10585 L13-17: Please rephrase. This sentence is too complicated to be able to follow it to the end.

We have rephrased the whole paragraph to make it more readable. It is know:” CH_4 emissions of Z. noltii community averaged 0.31 mmol m^{-2} d^{-1} with ~76% being released during tidal immersion. They are about 4 fold higher than CH_4 fluxes from the non-vegetated sediment community (0.07 mmol m^{-2} d^{-1} with

~93% being released during tidal immersion). Oremland (1975) reported CH_4 production rates raning from 0.26 to 1.80 mmol D-1 from a Thalassium testudinum bed and production rates ranging from 0.08 to 0.19 mmol d-1 from a Syringopodium sp. Community. In a study of Deborde et al (2010) the methane production rates in the surface sediments of Z.noltii sites were generally below 0.040. mmol^{-2} d^{-1} (being the detection limit of their method. Somehow in contrast to our results they observed higher production rates in unvegetated sediments ranging from 0.01 to 0.8 mmol m²d-1. However, our CH_4 fluxes from the unvegetated sediment agree well with those reported by Deborde et al. (2010) for the Arcachon lagoon (0.04 to 0,78 mmol m²d-1).

Bartlett et al. (1987) and Delaune et al. (1983) reported decreasing CH_4 fluxes with increasing salinity. CH_4 fluxes decreased from 17 to 34.2 mmol m^{-2} d^{-1} at salinities around 1 PSU to 0.17 to 0.85 mmol m^{-2} d^{-1} at salinities above 18 PSU. Though a direct comparison of these values with our data is difficult due to the differences in salinity our data fell well into the range given for higher salinities Middelburg et al. (2002) have estimated the average CH_4 flux from European estuarine waters to be 0.13 mmol m^{-2} d^{-1}, which is about twice the fluxes of the non-vegetated sediments of the Ria Formosa lagoon. Hence our data suggest that apart from body circulation (Jansen et al. 2009; Grunwald et al. 2009) skin circulation may substantially contribute to CH_4 fluxes in tidal flats."

P10585 L18-20: I wonder how variable emissions from different species of sea grass are? Is it plausible to calculate global emissions from one sampling site as the emission rates may vary significantly?

This is certainly true, but an immanent problem of upscaling trace gas fluxes is that it is simply impossible to cover all species and different biogeochemical settings. To make this clear, we used the term tentative. In the case of methane we are confident with our statement that the methane emissions from seagrass meadows will most likely not change the current view that marine ecosystems are a minor source for methane to the atmosphere. Our methane fluxes are by about one order of magnitude larger than those reported by Deborde et al.

(2010) and fivefold smaller than the largest production rates given in Oremland (1975) Including these data suggests a range from <0.01 to 2.5 Tg yr^{-1}*. This still small compared to range given for marine sources (11-18 Tgyr*$^{-1}$*). We changed the paragraph as follows:*

"A tentative upscaling using our flux data and a global seagrass coverage area of 300.000 km² (Duarte et al. 2005) reveals a global CH_4 *flux of ~ 0.5 Tg* CH_4 yr^{-1} *from seagrass meadows. Including the data from Oremland and from Deborde global emissions may range from < 0.1 Tg* CH_4 yr^{-1} *to 2.5 Tg* CH_4 yr^{-1}*. The worlds ocean including the productive coastal ecosystems are a minor source for atmospheric* CH_4 *contributing about 10% to the global emissions (Wuebbles and Hayhoe, 2002). Emissions including productive coastal areas have been estimated to be in the range of 11 to 18 Tg* yr^{-1} *(Bange et al. 1994). Despite the large uncertainty in this estimate it is reasonable to suppose seagrass meadows being a minor global source of* CH_4*. "*

P10586 L6-10: Please rephrase, this sentence is very complicated and long.

We have done so; it is now:" To the best of our knowledge, we present here the first assessment of how the respiration of a seagrass community varies over night along with the tidal cycle. Several previous studies used punctual measurements either with dark chambers or during the night to assess the community respiration Santos et al, 2004, Silva et al., 2008, Duarte et al, 2010, Clavier et al, 2011). These punctual data were upscaled to estimate daily respiration rates and to calculate daily metabolic budgets of seagrass communities. Our data show that this practice may seriously affect the estimation of the metabolic daily budgets of seagrass communities, particularly in the intertidal."

P10586 L25: Please explain the abbreviation "NCP".

NCP refers to net community production, explained now in the text.

P10587 L10: "different" instead of "difference"

We have changed this.

P10587 L17-21: To be honest, I wonder why COS, CS2 and propane are included if the discussion is beyond the scope of the paper and only enhancements of fluxes can be provided? I feel like they are actually not needed, and it would be sufficient in my opinion to mention that they can be measured. If they can't be quantified and can't really be discussed, I don't see the point to include them to this extension.

We have stated that a comprehensive discussion of their sources and sinks is beyond the scope of this paper. Nevertheless it is worth showing that the fluxes of these compounds are also affected by the tides.

P10588 L21: Please remove the "a" that is written before "very few".

We have done so.

P10588 L23: "In contrast to" instead of "contrasting to"

We have changed this.

Table 2: I find it confusing to put the compounds that can be quantified and the ones that cannot be quantified into one table. I would rather divide this table, because for me, it does not make sense to report total amounts and enhancements in one column when units are only valid for half of the entries.

We have removed the compounds that could not be quantified against a standard. See previous comment.

Figure 2: For easier understanding of Figure 1 would mark the in- and outlet.

See previous comment. The flow direction in fig. 1 is marked by arrows. We will label the inlet and outlet in fig.1

Figure 4: I don't really see the point to only show enhancements of fluxes if you can actually show real variations with total numbers. This refers to the comment that it is difficult to understand the concept of "enhancement". If this is clarified in the text, it could improve the Figure. I think I would prefer the total amounts where total amounts are possible. And I am not sure why the compounds that are not really discussed (like COS and CS2) are actually included here.

Variations of the absolute fluxes are shown in table 2. See also previous comments.

Reviewer 3

The manuscript offers new and necessary insights into the understanding of trace gas dynamics in coastal ecosystems affected by tidal cycles. The strong influence of tides on CO2 and CH4 fluxes, reported in this study, are noticeable and worth publishable, with important implications in sediment-water and water-air fluxes of green house gases.

However there are some points to consider (in order of importance) before publication in BG:

1) Some concerns arise when considering the design of the dynamic flux chambers used for the measurements. This has been a recent delicate issue that should be detailed and discuss carefully. The authors are aware of these concerns and an extended explanation of the methodology is given, but some clarifications should be added. I basically agree with the comments, regarding this issue, of Anonymous Referee #1.

We provided an extended description and discussion of the chamber design. See the response to reviewer 1.

2) Regarding the VOC results: I don't really see the point in delivering all the VOC information in the paper, unless there is a better and deeper discussion of the results. In my opinion, the results are shown in such a way that interpretation is not straight. COS, DMS, propane and butane are expressed as relative "enhancement" to the averaged flux, which makes it hard to compare with the rest. I suspect this is because they are not present in the standard used and hence no absolute magnitude can be computed. In any case, I suggest the authors keep the halocarbons data but remove the S-Compounds and Hydrocarbons data. Indeed, if they finally decide to remove also halocarbons data and just focus on CO2 and CH4 fluxes I would still suggest its publication. In that case, I definitely suggest a section in the discussion where the biogeochemical mechanisms potentially modulating these fluxes debated.

Regarding the VOC data see the response to reviewer 2. A discussion of the biogeochemical mechanisms potentially modulating the fluxes would surely help to complete the picture. However, we cannot substantiate this with additional data such as sediment oxygenation and trace gas profiles in the sediment. Thus such a discussion would remain superficially and become speculative. For these reasons we decided to discuss this not in more detail.

3) The results are discussed with detail but I miss in the discussion or conclusions an expanded view of significance and repercussion derived from the unexpected CO2 and CH4 results. There is a tentative up-scaling calculation using their CH4 flux data and a global seagrass coverage area. I don't really believe in this kind of global up-scaling estimations. Seagrasses encompasses a huge range of different ecosystem conditions that do not necessarily mirror Ria Formosa lagoon conditions. Instead of calculating global emissions, I would recommend to discuss and compare the trace gases emissions measured with those of other seagrasses worldwide. Also, how is climate change affecting Ria Formosa lagoon tidal cycles? Discuss possible effects on changes of trace gas emissions over the lagoon due to predicted tidal changes.

Though we are confident with our results we think that these unexpected flux dynamics require further substantiation. Therefore we have been careful in discussing the repercussions from these findings restricted ourselves to the statement the following statement (pp 10588-89, L. 27-4)" Hence, our results highlight the importance of accurately addressing the perturbations of turbulent flows in flux chamber studies. If the observed flux enhancements are more than just episodic events this may have fundamental implications for our understanding of the carbon and trace gas cycling in coastal environments."

With respect to the upscaling see the response to reviewer 2. A discussion of climate change is clearly beyond the scope of this paper and would be very speculative at this stage.

4) Figures and text can be improved. See specific comments below. Some sentences are too long and not easy to follow. I recommend to check on the writing (some extra commas and points would not hurt) and try to make shorter and more clear statements. Also carefully check the acronyms used. Some of them are not defined (DIC) and some are not placed properly in the sentence (NCP). Double-check also the chronological order of the references within the text.

We have carefully checked the text and the acronyms and provided definitions for all of them. See also the responses to the specific comments below and to reviewer 2.

Specific comments:

P10573, L11-12. This is a false statement. The development of benthic chambers for underwater incubations is far older than 2006, and have been used for the purpose of both trace gas and nutrient fluxes. The authors should be aware and refer to publications other than Silva et al. 2008 and Barron et al. 2006 (e.g. Nicholson et al. 1999, Larned 2003, Ferron et al. 2009). G. J. Nicholson, A. R. Longmore and W. M. Berelson. Nutrient fluxes measured by two types of benthic chamber. Marine and Freshwater Research 50(6) 567 – 572, 1999. S. T. Larned. Effects of the invasive, nonindigenous seagrass Zostera japonica on nutrient fluxes between the water column and benthos in a NE Pacific estuary. Marine Ecology Progress Series 254: 69–80, 2003. S. Ferron, S, F. Alonso-Perez, T. Ortega, J. M. Forja. Benthic respiration on the north- eastern shelf of the Gulf of Cadiz (SW Iberian Peninsula). Marine Ecology Progress Series 392: 69-80, 2009

We apologize for these omissions and include the references into the manuscript.

P10573, L16-17. Provide a reference for that statement. Suggestions: Armstrong 1979, Larkum et al. 1989. W. Armstrong. Aeration in higher plants. Adv. Botanical

Res. 7:225-332 AWD Larkum, G. Roberts, J. Kuo and S. Strother. Gaseous movement in seagrasses. In: Larkum AWD, McComb AJ and Shepherd SA (eds). Biology of Seagrasses, pp 686-722. Elsevier, Amsterdam.

We added both references.

P10573, L29-P10574, L4. References in each of the problems stated should be added.

We have added references discussing these problems in detail.

P10576, L26-27. You indicate that the lines were sampled for 5 min. Indicate also how often the sampling was performed.

The sampling lines were sampled consecutively. Thus each sampling line was sampled for 5 minutes with a sampling interval of 15 minutes.

P10577, L20. You say “High time resolution”, but how high is that. If you clarify that in the methods (see previous comment) it is not necessary to state it here again.

We think, the “high time resolution” is an important advantage of our approach and thus like to outline it here.

P10581, L1-4. Too long sentence. Please use commas, re-phrase or use two short sentences instead of a long one.

We have split the sentence. It is now:”The authors of this study did not come up with a conclusive explanation for this observation. They suggested either lateral transport in the sediment in combination with salinity gradients affecting the source strength and/or enhanced gas ebullition due to increased pressure from the water column.”

P10581, L10-12. In the sentence “Variation in the ::: ” : this statement is true only of you consider lineal variation. Add “lineal” between “ a” and “change”.

We have added linear as suggested by the reviewer.

P10581, L17-18. References should be added.

Some references are given in the following sentence. We added additional references for higher fluxes during low tide attributed to deep pore water circulation in line 21 and removed the sentence at the end of this paragraph (P.10581 L.27-29)

P10584, L3-6. It is impossible to appreciate that in the figure 2 and hence is hard to follow this sentence and some further discussion. I suggest that y-axes are re-scaled in Fig 2 accordingly.

We have rescaled the y-axis for CH4. See also the response to the reviewer’s comments to fig.2.

P10584, L8-10. Too long sentence. Add some commas (after “emission”, “methane peak”, and “pore water”), or re-phrase.

We have added commas as suggested by the reviewer.

P10584, L13. I could be wrong, but I don’t think DIC acronym has been described. If necessary please do so.

We have done so. See also the reply to reviewer 2.

P10585, L14-18. Re-phrase using shorter sentences.

We have done so and changed the order of sentences. See response to reviewer 2.

P10585, L18-24. I recommend to remove this paragraph. In my opinion is too speculative. Seagrasses encompasses a huge range of different ecosystem conditions that do not necessarily mirror Ria Formosa lagoon conditions. Instead of calculating global emissions, I would recommend to discuss and compare the trace gases emissions measured with those of other seagrasses worldwide. Also, how is climate change affecting Ria Formosa lagoon tidal cycles? Discuss possible effects on changes of trace gas emissions over the lagoon due to predicted tidal changes.

We feel confident with this statement. Even substantially higher fluxes from seagrass meadows as found here, would not change the current perception that coastal marine sources are of minor importance on a global scale. See also the response to reviewer 2. We have compared the methane and CO_2 *fluxes to with those from other seagrass studies. For methane this has been done in section 4.2. See also the respond to reviewer 2. For* CO_2 *this has been done in Section 4.3*

P10586, L26. Change the order of "(NCP)" right after its description. Place it after "production".

We have done so.

P10586, L5-10. Too long sentence. Please re-phrase with shorter statements.

We have done so.

P10588, L20. Change the word "show" for "suggest"

We have done so.

Figure 1. I recommend adding Cin and Cout for clarification

We have done so.

Figure 2. a) I recommend adding the actual tidal change, as tide changes are gradual, such as light intensity. The way it is shown now it simulates an ON/OFF

false scenario. b) I recommend to re-scale CH4 flux Y-axis to better appreciate the changes during tidal changes. c) Consider removing the Temperature. d) Add units in the legend.

a) *We would like to stay with the presentation of the tidal cycle as it is because the actual tidal height was not measured.*
b) *We will rescale the Y-Axis. See also response to reviewer 1.*
c) *We will remove the air temperature as it is not discussed.*
d) *Units were provided in the legend.*

Figure 3. I recommend adding the actual tidal change, as tide changes are gradual. The way it is shown now it simulates an ON/OFF false scenario.

See previous comment.

Table 2. and Figure 4. I suggest considering the possibility of removing S-Compound and Hydrocarbons data. See general comment above.

See response to general comments and to reviewer 2.

Tidal controls on trace gas dynamics in a seagrass meadow of the Ria Formosa lagoon (southern Portugal)

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Abstract

Coastal zones are important source regions for a variety of trace gases including halocarbons and sulphur-bearing species. While salt-marshes, macroalgae and phytoplankton communities have been intensively studied, little is known about trace gas fluxes in seagrass meadows. Here we report results of a newly developed dynamic flux chamber system that can be deployed in intertidal areas over full tidal cycles allowing for high time resolved measurements. The trace gases measured in this study included carbon dioxide (CO_2), methane (CH_4) and a variety ~~of hydrocarbons, halocarbons and sulphur-bearing~~volatile organic compounds (VOCs). The high time resolved CO_2 and CH_4 flux measurements revealed a complex dynamic mediated by tide and light. In contrast to most previous studies our data indicate significantly enhanced fluxes during tidal immersion relative to periods of air exposure. Short emission peaks ~~occured~~occurred with onset of the feeder current at the sampling site.

We suggest an overall strong effect of advective transport processes to explain the elevated fluxes during tidal immersion. Many emission estimates from tidally influenced coastal areas still rely on measurements carried out during low tide only. Hence, our results may have significant implications for budgeting trace gases in coastal areas. This dynamic flux chamber system provides intensive time series data of community respiration (at night) and net community production (during the day) of shallow coastal systems.

1 Introduction

Coastal zones are are important sites for carbon turnover and hot spots for a variety of volatile organic compounds (~~VOC's~~VOCs) including halogenated compounds (Gschwend et al., 1985; Moore et al., 1995; Baker et al., 1999; Rhew et al., 2000; Christoph et al., 2002, Manley et al., 2006; Valtanen et al., 2009~~; Moore et al., 1995~~) and sulphur-~~-~~bearing compounds (~~Leck and Rhode, 1990;~~ Dacey et al., 1987; Cooper et al., 1987a, b; De Mello et al., 1987; ~~Baker et al., 1992~~ Turner et al., 1989; Leck and Rhode, 1990; Baker et al., 1992), but a minor source for hydrocarbons such as CH_4 (Van der Nat and Middelburg, 2000; Middelburg et al., 2002). While coastal ecosystems, such as salt-marshes, macroalgae and phytoplankton communities have been intensively studied, little is known about trace gas fluxes from seagrass meadows. Seagrass meadows are amongst the most productive coastal ecosystems with an average net primary production of 817 g carbon m^{-2} yr^{-1} (Mateo et al., 2006). They cover a considerable portion of global coastal zones with estimates ranging from 300000 km^2 (Duarte et al., 2005) to 600000 km^2 Mateo et a~~.~~l., 2006. Most previous studies in seagrass meadows have focussed on carbon dynamics (e.g. Migné et al., 2004; Davoult et al., 2004; Spilmont et al., 2005, Silva et al., 2005; Hubas et al., 2006) and were often restricted to periods of air exposure. More recently, benthic chambers for underwater incubations were developed (Nicholson et al., 1999; Larned, 2003; Barron et al., 2006; Silva et al., 2008;~~ Barron et al., 2006~~Ferron et al., 2009). There is some evidence that seagrass meadows *(Zostera spec.*) are capable to form a variety of trace gases (Urhahn, 2003; Weinberg et al., 2013). ~~Furthermore, seagrass meadows may foster dimethyl sulfide (DMS) emissions (Jonkers et al., 2000; López and Duarte, 2004).~~

As other higher plants rooting in anoxic soils and sediments, seagrasses have an aerenchymatic tissue for supplying oxygen to their root system. This aerenchymatic tissue may also provide an effective transport pathway for trace gases from the sediment to the atmosphere(Armstrong, 1979; Larkum et al., 1989). The importance of this transport pathway has been shown for CH_4 emissions from a variety of vegetation types (Laanbroek, 2010). However, early incubation experiments have indicated fairly low emission rates from *Thalassia testudinum* beds (Oremland et al., 1975). More recently Deborde et al. (2010) reported CH_4 fluxes from *Z. noltii* meadows in the Arcachon lagoon (SW France) being below 1.6 µmol m^{-2}h^{-1}, which was the detection limit of the instrumentation used for the experiment.

So far, the fluxes of trace gases in coastal environments, mainly CH_4 and CO_2, have been measured in most cases using static chambers (e.g. Van der Nat and Middelburg, 2000; Delaune et al., 1983; Bartlett et al., 1987; Migne´ et al., 2002, 2004; Davoult et al., 2004; Spilmont et al., 2005, Silva et al., 2005; Hubas et al., 2006). There are several problems arising from chamber based flux measurements that require a careful testing of the chamber system. Under aerial conditions problems may arise ~~such as~~from pertubations of the turbulent fields on both air and water side, introduction of artificial gradients, pertubations of the thermal environment and the gas composition inside the chamber (Gao et al 1997; Meixner et al. 1997; Gao & Yates, 1998; Zhang et al. 2002; Pape et al, 2009). In particular deposition fluxes of reactive trace gases are very sensitive towards the aerodynamic properties of the chamber (Meixner et al. (1997; Pape et al., 2008) In contrast the emission fluxes of most VOCs are insensitive against the turbulent conditions inside the chamber. The reason is that their production is independent of the headspace concentration (Pape et al., 2008).

~~In particular~~Under submersed conditions solid static chambers will most likely introduce stagnant conditions and thus reduce the diffusive exchange and suppress advective exchange (Cook et al., 2007). This has for instance been shown for oxygen (Billerbeck et al, 2006; Werner et al, 2006; Kim & Kim, 2007; Cook et al., 2007; Jansen et al, 2009), total inorganic carbon (Cook et al., 2007), dissolved organic matter (Huettel et al., 1997)~~.~~ Tengberg et al. (2004) compared three different types of stirred benthic chambers and found no significant differences between these chambers. The authors concluded that benthic chambers are insensitive to the hydrodynamic conditions as long as the water is well mixed and the sediment is not re-suspended.

For this study we used a dynamic chamber modified to enable flux measurments over full tidal cycles. During tidal immersion the chamber is continiously purged whereby the purging introduces a~~n advective~~ a turbulent flow inside the chamber. Though artificial, this turbulent motion inside the chamber may to some extent mimic the turbulent flow outside the chamber.

The system allows continous CH_4 and CO_2 flux measurements with a time resolution of ~~10~~ 15 minutes as well as the determination of VOC fluxes by discrete sampling. Here we provide a detailed description of the flux chamber system and first results of a field study conducted in a seagrass meadow of the Ria Formosa lagoon, southern Portugal. We report tidal-cycle fluxes of CO_2, CH_4, ~~propane, butane,~~ propene, chloromethane (CH_3Cl), bromomethane (CH_3Br), iodomethane (CH_3I), chloroform ($CHCl_3$), Bromoform ($CHBr_3$) as well as~~,~~ carbondisulfide (CS_2)~~, carbonylsulfide (COS), as well as dimethyl sulfide (DMS)~~ and discuss them in terms of the factors controlling trace gas dynamics in intertidal seagrass meadows.

2 Methods

2.1 Flux chamber design

Dynamic flux chambers have been widely used in trace gas studies in terrestrial systems (Gao et al., 1997; Gao and Yates, 1998; Kim and Lindberg, 1995;~~ Pape et al., 2009;~~ Zhang et al., 2002; Pape et al., 2009). Details on the theory of dynamic flux chamber measurements are given in Gao et al. (1997) and Meixner et al. (1997). Briefly, the surface of interest is enclosed with a chamber and air is ~~drawn~~ pumped through the chamber at a predefined flow rate. Net fluxes above the covered surface are commonly calculated from the concentration difference between the ~~inlet~~ outlet and in~~out~~let of the chamber.~~:~~

$$F_{Net} = \frac{Q_N \times (C_{out} - C_{in})}{A \times V_N \times 1000} \qquad (1)$$

where F_{Net} is the net flux [mol m^{-2} h^{-1}], Q_N is the flushing flow rate through the chamber [m^3 h^{-1}, at 1013.25 mbar and 298.15 K], C_{out} and C_{in} are the air mixing ratios of target compounds [mole fractions] at the outlet and the inlet of the flux chamber, respectively, A is the bottom surface area of the flux chamber [m^2], and V_N is the molar volume [m^3] at 1013.25 mbar and 298.15 K. Note that emission fluxes are positive.

The chamber we used was made from a 10 L Duran glass bottle with the bottom cut off (fig. 1). The chamber had a volume of 8 L, a bottom surface area of 0.037 m², and a height of 0.3 m. Prior to sampling, the chamber is pressed 5 cm into the sediment resulting in a headspace volume of approximately 6 L. During tidal change water enters and leaves the chamber through a U-tube at the bottom (stainless steel tube 50 cm length, 4 mm i.d.). The tube was connected to a valve that was closed during air exposure and open during tidal immersion. During sampling, ambient air is pumped through the chamber with a membrane pump (KNF-Neuberger, Germany, mod. N86KNDC) at a flow rate between 3.0 and 3.5 L min^{-1}. The air enters the chamber through a PFA-tube at the top of the chamber and is further distributed to two metal frits (10 µm pore size). The frits are placed 12 cm above the sediment surface preventing visible dispersion of surface sediments. The outlet of the chamber is connected to an open split in 2.5 m height via a ½’ o.d. PFA-tube. The tube is inserted 30 cm into a stainless steel tube (50 cm long, ¾’ o.d.) that is open at the bottom and has two sampling ports at the top. Typically, about 0.5 L min^{-1} are directed to the CO$_2$ / ~~methane~~ CH$_4$ analyzer and 1.5 L min^{-1} are directed to the trace gas sampling system. The excess air, along with water droplets and aerosols is vented into the atmosphere via the open split. Two Teflon® membrane filters are used to further protect the sampling systems from water and aerosols. The U-tube at the bottom and the open split ensured pressure equilibrium between the chamber and the ambient water body. The performance of the chamber has been tested under aerial und submersed condition under in the laboratory. A detailed description of these tests is given in the supplementary material. Under aerial conditions the response time of the chamber is 2min. at a flushing flow rate of 3 L min^{-1}. Complete mixing of the chamber volume is achieved within 0.4 min. Hence with respect to our sampling frequency we can safely assume complete mixing of the air inside the chamber.

The physical nature of trace gas fluxes across natural interfaces is commonly described in terms of a multiresistance model (Hicks et al, 1987). This model has been applied to flux chambers Gao & Yates 1987;, Zhang et al., 2002; Pape et al. 2008:

$$F_i = \frac{c_s - c_a}{R_c + R_s} \qquad (2)$$

Where F$_i$ denotes the flux across the interface, c$_s$ is the concentration in the sediment, c$_{ag}$ is the gas concentration on the air side of the interface R$_c$ [t L^{-1}], is the overall transfer resistance of the chamber system and R$_s$ [t L^{-1}] transfer resistance of the sediment surface layer (R$_s$). While R$_c$ is dependent on the aerodynamic properties of the chamber, R$_s$ is dependent on the sediment properties. The sensitivity of the overall flux against the aerodynamic properties depends on the magnitude R$_c$ and R$_s$. When both share the same magnitude the flux across the interface depends on R$_c$ and R$_s$. On the other hand, when R$_s$ becomes large relative to R$_c$ the flux is mainly governed by R$_s$ (Zhang et al., 2002). The chamber tests revealed an upper limit of 0.162 hm^{-1} for the aerodynamic transfer resistance of the chamber. The sediment side transfer resistance has been estimated from the diffusivity of the sediment surface layer and its thickness (Gao 1986, Zhang et al. 2002). For water logged intertidal sediments with an air filled pore space from 1% to 10%, R_s ranges from 1.54 to 15.4 h m^{-1}. The transfer resistance of the seagrass leafs has been derived from the CO_2 permeability of the cuticula of submersed plants (MacFarlane (1992) and the leaf area index of Z.noltii in the Ria Formosa (Pérez-Lloréns & Niell, 1993). It has been estimated to range from 26.5 to 46 h m^{-1}. Both are one to two orders of magnitude larger than R_c. Given this it is reasonable to assume that during air exposure the gas exchange across the sediment surface and the seagrass leafs is not dependent on the aerodynamic properties of the chamber. Further our tests suggest a minor effect of the flushing flow rate on the atmospheric transfer resistance making the overall transfer resistance insensitive against the aerodynamic properties of the chamber.

During submersion the interfacial fluxes are insensitive to the hydrodynamic conditions in the chamber as long as the water inside the chamber is well mixed and the sediment is not re-suspended. Re-suspension of the sediments was avoided during the experiments and has been checked visibly. The gas flow through the chamber introduced a water flow in the order of 10 to 15 cm s^{-1} providing a corresponding boundary layer thickness in the range of 60 to 120 µm where the carbon uptake is mainly enzymatically limited. The visible inferred mixing time was in 1.1 min. Under submersed conditions the dissolved trace gases are equilibrated with ambient air. The flux and thus the response time will depend on the volatility (given by the inverse Henrys law constant) and the water air transfer resistance of the chamber system. In analogy to the air sea gas exchange the ~~flux of a trace gas~~gas air water exchange can be computed as:

$$F = k_c \times (c_w/H - c_g) = \frac{(c_w/H - c_g)}{R_c} \qquad (3)$$

where k_c is the specific gas exchange velocity [L t^{-1}] of the chamber. K_c depends on the flushing flow rate (Q) and the chamber design (in particular the chamber geometry and the gas bubble geometry) $R_c = 1/k_c$ is the corresponding transfer resistance, c_w is the water concentration [mol L^{-3}], c_g is the concentration in the gas phase inside the chamber, and H is Henry's law constant.

The response time of the chamber towards changes in the pCH_4 was 1.20± 0.20 min. The response time for DIC(dissolved inorganic carbon) depends on the carbon speciation. It ranged from 10 min to 58 min for a ΔDIC ranging from 188 to -203 µmol kg^{-1}. Reflecting the changing ratio of dissolved CO_2 to DIC. Here ΔDIC refers to the deviation of the DIC concentration from equilibrium with the inlet air. Equilibrium conditions during the tests were a DIC of 1960±15 µmol kg^{-1}, an alkalinity of 2180±15 µeg Kg^{-1} and a pCO_2 of 425±10 ppm at 296.5 K.

The U-tube at the bottom of the chamber inevitably leads to an exchange of water between the chamber and the surrounding water body that may affect the flux measurements. The water exchange was not metered onsite. From Hagen-Poiseilles law we estimated a response time towards water exchange of 2.15±0.15 h. This is substantially larger than the respective response times for the gas exchange. For CH_4 we can safely assume that the bias due to water exchange is regardless of the concentration difference between the chamber and the surrounding water less than 1%. Due to the much slower response time the bias with respect to DIC becomes larger.

For a first estimate of the bias we assumed a constant source or sink inside the chamber and an incubation time of 6h. Under these conditions the recovery for a CO_2 sink ranges from 69 to 75% and the recovery for a CO_2 source ranges from 78 to 83% with both depending on the source/sink strength. We found these recovery acceptable for a first tentative assessment of the DIC dynamics over full tidal cycles as was the primary goal of our study

2.2 Sampling site

The sampling was conducted in an intertidal seagrass meadow of *Zostera noltii* (*Hornemann)* of Ria Formosa lagoon, a mesotidal system located in southern Portugal. The lagoon has a surface area of 84 km² with about 80% of it being intertidal. It is separated from the open ocean by a system of sand barrier islands. Six inlets allow exchanges of water with the Atlantic Ocean. The tidal amplitude ranges from 3.50 m on spring tides to 1.30 m on neap tides. In each tidal cycle about 50% to 75% of the water in the lagoon is renewed. Except during sporadic periods of heavy rainfall salinity ranges from 35.5 to 36.0 PSU throughout the year; water temperature varies between 12 and 27° C in winter and summer, respectively.

Z. noltii is the most abundant seagrass species in the Ria Formosa, covering about 45% of the intertidal area (Guimarães et al., 2012). The species plays a major role in the whole ecosystem metabolism of the lagoon (Santos et al., 2004). The range of *Z. noltii* biomass variation at the sampling site is 229 - 310 g DW m^{-2} (Cabaço et al 2008).

2.3 Sampling and measurement

The CO_2 and CH_4 flux measurements were performed between 23 April and 27 April 2012. VOC fluxes were measured between April 17th and April 28th 2012. Therefore, the time base of the VOC sampling does not fully overlap the time base of the CO_2 and CH_4 sampling. The sampled seagrass patches (*Z. noltii*) were free of visible epiphytes and macroalgae. The canopy coverage was estimated to be higher than 95%.

CO_2 and CH_4 were measured on site with a Picarro 1301 cavity ring down spectrometer. A six port Valco valve was used to switch between three different sampling lines. The first sampling line was directly connected to the dynamic flux chamber and the two other sampling lines were used to sample ambient air from two different heights above the ground (2m and 4m). The sampling lines were consecutively sampled for 5 minutes and each line was connected to an additional membrane pump for continuously flushing at a flow rate of 0.5 L min^{-1} when not sampled. The sampling order was height 1, height 2, chamber. The mixing ratios from the two air sampling lines were averaged to calculate the inlet concentration of the chamber. Discrete gas samples were taken from the second sampling port of the flux chamber to determine the outlet concentration of the ~~VOC's~~VOCs. In parallel, discrete samples were taken from the feeding line to the flux chamber via a T-union to determine the inlet concentration of the ~~VOC's~~VOCs. Details of the VOC sampling system are given in Weinberg et al. (submitted). Briefly, 30±5 L of ambient air was drawn through a cryo trap at a flow rate of 1.0±0.2 L min^{-1}. The samples were thermally desorbed from the cryo trap (310°C) using a flow of helium (30 mL min^{-1} for 15 min) and recollected on peltier-cooled adsorption tubes maintained at –10°C. From the adsorption tube the samples were again desorbed into a flow of helium and refocused on a quartz capillary (0.32 mm i.d., 60 cm length) immersed in liquid nitrogen. The analytes were desorbed from the quartz capillary at ambient temperature and transferred to a GC-MS system (6890N/5975B, Agilent). ~~VOC's~~VOCs were separated on a CP-PorabondQ column (Varian, 25m, 0.25 µm i.d.) with helium as a carrier gas~~.~~. Quantification of CH_3Cl, CH_3Br, CH_3I, $CHCl_3$, $CHBr_3$, propene, and CS_2 was performed against a ~~working standard~~Scott TOC 15/17 standard containing, among others, 1ppm each in nitrogen. Typically two to four aliquots of 1ml were analyzed each day~~.~~ The overall precision of this method is better then ± 6%. ~~For COS, propane, butane, and DMS not present in the standard, relative fluxes were calculated from the measured intensities.~~

3 Results

The high time resolution of our measurements provided detailed insights into the complex dynamics of CH_4 and CO_2 fluxes of Ria Formosa intertidal. The flux patterns of CO_2 and CH_4 of both *Z. noltii* and adjacent bare sediment patches are sown in Figures 2 and 3, respectively. Table 1 provides the time-averaged fluxes for different stages of the tidal cycle. In general, much higher CO_2 and CH_4 fluxes were observed for the seagrass covered areas than for the bare sediment. The fluxes of both gases showed clear diurnal variations with similar patterns above the seagrass and the bare sediment. We observed a strong influence of the tidal cycle on fluxes of both gases with more pronounced emission fluxes generally occurring during tidal inundation. At daytime, CO_2 assimilation dominated over benthic respiration resulting in a net uptake, regardless of the tidal state. Elevated fluxes during tidal immersion were also observed for all non-CH_4 ~~VOC's~~VOCs studied here.

3.1 Methane

During air exposure at low tide CH_4 fluxes averaged 4.4 µmol m^{-2} h^{-1} at night and 6.9 µmol m^{-2} h^{-1} at day. With the flood current just arriving at the sampling site the fluxes dropped almost to zero for ~~5 to 10~~> 15 minutes. A sharp emission peak was observed for 15 minutes ~~followed~~ following this drop. Accounting for the integration time and the response time of the chamber system we deduce that these events may have actually lasted for 2 to 5 minutes. During these peak events the fluxes averaged 71 µmol m^{-2} h^{-1}. The peaks were more pronounced during the night (76 and 123 µmol m^{-2} h^{-1}) than during daytime (38 and 51 µmol m^{-2} h^{-1}). After the peak events, the fluxes rapidly decreased to values below 9±1 µmol m^{-2} h^{-1}.

During tidal immersion the CH_4 fluxes increased with rising height of the water and showed a second maximum of 30 ±1 µmol m^{-2} h^{-1} at high tide. With the ebb flow the CH_4 fluxes decreased constantly to values about 9±1 µmol m^{-2} h^{-1} at water levels below 10 cm. The change from tidal immersion to air exposure was marked by slightly elevated fluxes observed for about 15 minutes followed by a drop close to zero before the flux stabilized on the low tide level again.

The ~~circadian~~ diurnal flux cycles observed above the sediment (Fig. 3) were similar to ~~the diurnal cycles~~those above the seagrass but, with much lower values (Table 1 and Fig. 2). The CH_4 fluxes averaged 0.3 µmol m^{-2} h^{-1} during low tide, and 6 µmol m^{-2} h^{-1} (5.2 µmol m^{-2} h^{-1} at daytime and 6.6 µmol m^{-2} h^{-1} at night time) during tidal inundation.

3.2 CO_2

In contrast to CH_4, the CO_2 flux was strongly influenced by both, the time of day and the tidal cycle. Deposition fluxes were observed during the day resulting from photosynthetic carbon uptake while positive fluxes were observed during the night due to respiratory release of CO_2. During air exposure at night, the emissions were relatively constant and averaged 8.4±0.5 mmol m^{-2} h^{-1}. As observed for CH_4, the flux dropped to zero for about 10 minutes with the incoming tide and then rapidly increased to highest CO_2 emissions of up to 62 mmol m^{-2} h^{-1}. Thereafter, the CO_2 flux decreased rapidly to 38±4 mmol m^{-2} h^{-1} and then further declined slowly over the period of tidal inundation. After sunrise, roughly coinciding with high tide during our measurements, the CO_2 fluxes declined more rapidly due to the beginning of photosynthetic CO_2 assimilation. During the daylight period, CO_2 assimilation dominated over benthic CO_2 respiration resulting in a net uptake of CO_2 with average fluxes of -9.1 mmol m^{-2} h^{-1} during air exposure and of -16.4 mmol m^{-2} h^{-1} during immersion.

At night, the average sedimentary CO_2 fluxes were 1.0 mmol m^{-2} h^{-1} during air exposure and 6.4 mmol m^{-2} h^{-1} during tidal inundation. The CO_2 night time flux during inundation decreased until high tide and increased again with the onset of ebb flow indicating an inverse relation with the height of the water table. The daytime average CO_2 fluxes from sediment were -1 mmol m^{-2} h^{-1}during low tide and -2 mmol m^{-2} h^{-1} during tidal inundation.

3.3 ~~VOC's~~VOCs

Relative fluxes of~~ COS~~, CS_2, ~~DMS~~, CH_3Cl, CH_3Br, CH_3I, $CHCl_3$, $CHBr_3$, ~~propane, butane~~ and propene are shown in figure 4. ~~For those, which have been quantified against the Scott TOC 15/17 standard, ~~M~~m~~ean fluxes and ranges are provided in table 2. It has to be noted that for most of the VOC flux data the sampling time does not coincide with the sampling time for the CO_2 and CH_4 data shown above. As observed for CO_2 and CH_4, the emission rates during tidal immersion significantly exceeded those measured during air exposure. The average enhancement during tidal immersion (relative to the average fluxes during air exposure) ranged from 4 – 12 for CS_2~~, COS and propane and ~~the halocarbons CH_3Br, CH_3I $CHCl_3$ and $CHBr_3$. A higher enhancement was observed for CH_3Cl. A less pronounced enhancement ranging from 1 to 3 was observed for~~ DMS, ~~propene~~ and butane~~. Among the analysed ~~VOC's~~VOCs, only CH_3Cl fluxes increase similarly drastically as the CH_4 with the feeder current arriving at the sampling site. In this context it is important to note that the sampling time for the ~~VOC's~~VOCs was 30 minutes followed by a break of 15 minutes required to change the cryo traps. Hence, it is possible that peak flux, lasting 3 to 5 minutes for CH_4, is missed or not fully captured by our VOC sampling protocol. For ~~propane,~~ $CHBr_3$~~, and butane~~ our data also show a small enhancement when the water just starts receding from the sampling site.

The temporal flux patterns show some remarkable differences between individual VOCs during tidal immersion. Strongly enhanced fluxes during high tide were observed for ~~propane, COS and~~ CS_2, showing a similar pattern as for CH_4. The fluxes of the other monitored compounds decreased or even turned from emission to uptake during high tide and thus acted more similar as CO_2.

3.4 Atmospheric mixing ratios of CO_2 and CH_4

The atmospheric mixing ratios of CO2 and CH4 are shown in figure 5. Throughout the campaign the atmospheric mixing ratios of CO_2 (average from both heights) ranged from 395.5 to 429.7 ppm (both heights) and averaged 400.3 ppm. The atmospheric mixing ratios of CH_4 ranged from 1.831 to 1.895 ppm (both heights) and averaged 1.861 ppm. Lowest mixing ratios of 395.8±0.2 ppm for CO_2 and of 1.834±0.004 ppm for CH_4 were observed between 8:00 pm on April 25th and 4:00 am on April 26th and coincided with westerly winds from the Open Ocean and wind speeds above 4m/s. With decreasing wind speeds and during easterly winds, when the air masses passed over large parts of the lagoon the atmospheric mixing ratios of CO_2 and CH_4 increased.

The close coupling between the measured fluxes and the atmospheric mixing ratios at low wind speeds becomes in particular evident at the end of the campaign. Over the last two tidal cycles the atmospheric mixing ratios of CH_4 nicely resemble the enhanced emissions during immersion. The sharp methane emission peak observed when the water entered the chamber becomes diffuse under ambient conditions as bubble ebullition will occur throughout rising tide a the water line On April 27th this coupling is somewhat confounded because of rapidly changing wind conditions. Nevertheless, elevated CH_4 mixing ratios coincide with elevated fluxes during tidal immersion. As for CH_4 elevated mixing ratios of atmospheric CO_2 coincide with periods of strong CO_2 emissions during tidal immersion at night. Notably on April 26th at noon the atmospheric CO_2 mixing ratios show a slight drop when carbon assimilation was largest. In summary the pattern of the atmospheric mixing ratios support the flux pattern observed with the chamber.

4 Discussion

4.1 Temporal flux patterns

The most striking feature of our results is the pronounced effect of the tidal cycle on the fluxes of all trace gases, which were significantly enhanced during immersion compared to air exposure periods. Additionally, strong emission peaks of CH_4, among other VOCs, and particularly of CO_2 occurred during a short transition period from air exposure to immersion.

We are aware of only one study reporting a positive correlation of CO_2 and CH_4 fluxes with the height of the water table from a brackish coastal lagoon in Japan (Yamamoto et al., 2009). The authors of this study did not come up with a conclusive explanation for this observation. ~~but~~ They suggested either lateral transport in the sediment in combination with salinity gradients affecting the source strength and/or enhanced gas ebullition due to increased pressure from the water column. The Ria Formosa lagoon has a negligible inflow of freshwater and a year round salinity between 35 and 36 PSU. This makes salinity driven lateral changes in methanogenesis and benthic respiration implausible.~~In the case of the Ria Formosa lagoon, there is a negligible inflow of freshwater and thus significant salinity driven lateral changes in methanogenesis and benthic respiration are implausible.~~ Spatial variations in the source strength that might occur due to variations in the benthic communities and in the supply of substrate by litter production and root exudates are also not plausible as the benthic vegetation around the sampling site consisted almost exclusively of *Z. noltii* and was quite homogeneous. Variations in the above ground biomass were clearly below a factor of 2 and thus do not support a linear change in the source strength by a factor of 6 as observed for CH_4 during tidal immersion. On the other hand, a negative relation between bubble ebullition and water pressure has been reported in other studies (Baird et al., 2004; Glaser et al., 2004), including the only study we are aware of that was carried out in a tidally influenced system (Chanton et al., 1989).

Most previous studies on trace gas fluxes in tidally influenced systems have reported higher fluxes during low tide than during high tide. These higher emissions during low tide were attributed to reduced gas diffusion during inundation (Heyer and Berger, 2000; Van der Nat and Middelburg, 2000) or to deep pore water circulation in tidal flats(Barnes et al. 2006, De La Paz et al. 2008, Grunwald et al., 2009, Deborde et al, 2010). Since the pioneering work of Riedl et al. (1972) there is rising evidence that advective exchange processes at the sediment-water interface strongly affect the fluxes and concentrations of trace constituents. Billerbeck et al. (2006) proposed two different pathways for pore water circulation in intertidal sediments. The first pathway, called “body circulation”, is generated by the hydraulic gradient between sea water and pore water levels in the sediment, and leads to seepage of pore water close to the low water line at low tide. ~~Several studies have attributed elevated levels of pCO_2 (Barnes et al. 2006, De La Paz et al. 2008) and pCH_4 (Grunwald et al., 2009, Deborde et al, 2010) during low tide to this kind of deep pore water advection.~~

The second pathway, called “Skin circulation” (Billerbeck et al., 2006), refers to the advective exchange in surface sediments and is driven by bottom current induced pressure gradients at the sediment surface. Several studies have shown a prominent effect of advective transport processes on the exchange of organic matter and nutrients in tidal sand flats (Werner et al., 2006; Billerbeck et al., 2006; Huettel et al., 1996; Precht et al., 2004). Werner et al. (2006) found a more intense and deeper transport of oxygen into the sediment due to advective exchange during tidal immersion than during air exposure, when the exchange is presumably driven by gas diffusion. This is also supported by a study of Kim and Kim (2007), who reported total oxygen fluxes exceeding diffusive fluxes by a factor of 2 to 3 for intertidal sediments from Teaean Bay located in the Midwestern part of the Korean peninsula. Cook et al. (2007) reported a concurrent increase of total oxygen and TIC (total inorganic carbon) fluxes at the sediment surface by a factor of up to 2.5 under turbulent conditions relative to stagnant (diffusive) conditions. In our study the respiratory CO_2-fluxes during tidal immersion exceeded the respiratory CO_2 flux during air exposure by a a factor of 2.4 and the methane fluxes during immersion exceeded those during air exposure by a factor of 2.9.

During measurements carried out in the back barrier area of the island of Spiekeroog (Billerbeck et al., 2006, Jansen et al., 2009), the highest oxygen penetration rates were observed immediately after high tide. In accordance Yamamoto et al. (2009) noted a concurrent increase of the redox potential of the sediment with increasing CH_4 and CO_2 fluxes during tidal inundation.

The CH_4 fluxes observed in the Ria Formosa lagoon provide a mirror image of these oxygen dynamics.~~,~~ ~~in accordance with Yamamoto et al. (2009), who noted a concurrent increase of~~

~~the redox potential of the sediment with increasing CH_4 and CO_2 fluxes during tidal inundation.~~ Given this, we deduce an overall strong effect of advective solute transport at the sediment water interface on trace gas fluxes to explain the elevated fluxes during tidal immersion. Both, the observed similarities between the flux patterns among all trace gases and the relatively constant CO_2/CH_4 ratios observed at night time, when photosynthesis was not ~~confounding~~ interfering flux patterns, suggest physical forcing as the major driver of trace gas fluxes rather than the biogeochemical processes controlling their formation.

It is commonly thought that the fluxes during air exposure are most likely driven by gas evasion across the sediment-air and plant-air interface, respectively, and are hence controlled by the transfer resistance across these interfaces (Yamamoto et al., 2009 and references therein). However, this model cannot explain the observed drop to zero of CO_2 and CH_4 fluxes for about 15 minutes when the incoming tide reached the sampling site. In waterlogged sediments trace gases have to be transported to the sites of gas diffusion, such as to a water gas interface or to the root systems of higher plants. Werner et al. (2006) observed a constant flow velocity of pore water over the entire period of air exposure and noted a decreasing flow velocity in the top 2 cm shortly before the flood current reached the sampling site and flow direction reversed. Although the chamber will certainly affect the water flow in the top sediment, this may provide a clue ~~This decrease may~~to explain the observed drop in the emission fluxes.

The drop in the fluxes was followed by a dramatic peak in both, CO_2 and ~~methane~~ CH_4 emissions, when floodwater reached the chamber. Thereafter, CH_4 fluxes dropped to increase again with tidal height. In contrast t~~whereas t~~he respiratory CO_2 night flux showed a gradual decline. Similar flux peaks at incoming floodwater have been previously reported for biogenic sulphur compounds (Aneja et al., 1986; Cooper et al., 1987a, b) and ammonia (Falcão and Vale, 2003), being attributed to increased hydrodynamic pressure. In contrast to these observations, we did not observe a pronounced peak for any of the ~~VOC's~~VOCs other than CH_4. However, it is possible that the peak events were not captured due to our discrete VOC sampling method.

We speculate that the peaks are caused by the sudden release of the air trapped in the sediment pore space that becomes enriched in CH_4 and CO_2 during air exposure. The release of trapped air from the sediment may be fostered by the aforementioned reversal of flow direction in tidal surface sediments reported by Werner et al. (2006). Such an emission mechanism is further supported by the fact that a similar drop in the CH_4 emission is also observed for the change from tidal immersion to air exposure, but not followed by an emission peak, which is simply due to the lack of air bubbles in the sediment at this stage of the tidal cycle. Furthermore, the higher fluxes during tidal inundation may impede the enrichment of trace gases in the surface sediment. The short and sharp emission peak for CH_4 suggests that the CH_4 has been accumulated close to the sediment surface or close to the roots of the seagrass from where it can be readily transferred into the atmosphere. In agreement with this, our data clearly show higher CH_4 emission peaks during night time than daytime, when sediment oxygenation resulting from photosynthesis favours CH_4 oxidation.

During night time, the respiratory CO_2 flux and the CH_4 flux show a fairly constant ratio during air exposure but evolve differently during tidal immersion. In contrast to the gradual decline of CO_2 after the peak at incoming tide, CH_4 dropped sharply after this peak to increase again with tidal height. CH_4~~Methane~~ originating from deeper sediment layers has a fairly low water solubility and thus becomes strongly enriched in the entrapped gas. Hence, the transition from a bubble ebullition driven emission, as suggested for the “CH_4~~methane~~ peak”, to an advective transport of pore water, as suggested for the period of tidal immersion results in a sharp decrease of the CH_4~~methane~~ flux. The following increase in CH4 may reflect the increasing penetration depth of the advective flow with the rising water table. CO_2 is always close to equilibrium with the much larger pore water DIC pool. After the transition from bubble ebullition to advective transport the CO_2 flux is driven by the exchange of enriched pore water DIC and the observed gradual decline in the CO_2 flux reflects the dilution of the pore water with the overlying seawater.

While the seagrass incubations showed a continuous decline of the CO_2 flux during tidal immersion, the incubations at the non-vegetated sediment showed a partial recovery of the CO_2 flux after high tide and thus an inverse correlation with the height of the water table. As outlined before, this difference may result from the onset of photosynthetic CO_2 assimilation at the end of the tidal cycle at sunrise, which had a more pronounced impact within the seagrass incubations.

4.2 Magnitude of CH_4~~methane~~ fluxes

CH_4 emissions of *Z. noltii* community averaged 0.31 mmol m^{-2} d^{-1} with ~76% being released during tidal immersion. They are about 4 fold higher than CH_4 fluxes from the non-vegetated sediment community (0.07 mmol m^{-2} d^{-1} with ~93% being released during tidal immersion). Oremland (1975) reported CH$_4$ production rates raning from 0.26 to 1.80 mmol d^{-1} from a Thalassium testudinum bed and production rates ranging from 0.08 to 0.19 mmol d^{-1} from a Syringopodium sp. Community. In a study of Deborde et al (2010) the methane production rates in the surface sediments of Z.noltii sites were generally below 0.04 mmol^{-2} d^{-1} (being the detection limit of their method. Somehow in contrast to our results they observed higher production rates in unvegetated sediments ranging from <0.04 to 0,78 mmol m²d-1. The average sedimentary CH$_4$ flux of 0.07 mmol m^{-2} d^{-1} in our study is at the lower end of this range.

Bartlett et al. (1987) and Delaune et al. (1983) reported decreasing CH$_4$ fluxes with increasing salinity. CH$_4$ fluxes decreased from 17 to 34.2 mmol m^{-2} d^{-1} at salinities around 1 PSU to 0.17 to 0.85 mmol m^{-2} d^{-1} at salinities above 18 PSU. ~~Hence~~ Though a direct comparison of these values with our data is difficult due to the differences in salinity our data fell well into the range given for higher salinities~~.~~ ~~However, our CH$_4$ fluxes from the unvegetated sediment agree well with those reported by Deborde et al. (2010) for the Arcachon lagoon, which were generally below the detection limit (0.04 mmol^{-2} d^{-1}) during air exposure and ranged from below the detection limit to 0.24 mmol^{-2} d^{-1}.~~ Middelburg et al. (2002) have estimated the average CH$_4$ flux from European estuarine waters to be 0.13 mmol m^{-2} d^{-1}, which is about twice the fluxes of the non-vegetated sediments of the Ria Formosa lagoon. Hence our data suggest that apart from body circulation (Jansen et al. 2009; Grunwald et al. 2009) skin circulation may substantially contribute to CH$_4$ fluxes in tidal flats.

~~Somehow in contrast to Deborde et al. (2010), who reported substantially lower CH$_4$ production rates for sites covered by Z. noltii as compared to unvegetated sites in the Arcachon lagoon with the CH$_4$ production rates at the Z. noltii sites being mostly below the detection limits of their method, we observed 4 times higher fluxes above the seagrass site as above the bare sediment.~~

~~Anyhow, a~~A tentative upscaling using our flux data and a global seagrass coverage area of 300.000 km² (Duarte et al. 2005) reveals a global CH$_4$ flux of ~ 0.5 Tg CH$_4$ yr^{-1} from seagrass meadows. Including the data from Oremland and from Deborde global emissions may range from < 0.1 Tg CH$_4$ yr^{-1} to 2.5 Tg CH$_4$ yr^{-1}. The worlds ocean including the productive coastal ecosystems are a minor source for atmospheric CH$_4$ contributing about 10% to the global emissions (Wuebbles and Hayhoe, 2002). Emissions including productive coastal areas have been estimated to be in the range of 11 to 18 Tg yr^{-1} (Bange et al. 1994). ~~Hence we~~Despite the large uncertainty in this estimate it is reasonable to suppose seagrass meadows being a minor global source of CH_4.

4.3 Magnitude of CO_2 fluxes

As outlined in the method section our method may underestimate the CO_2-fluxes by 20±15%. In any case it is worth to compare the results from this study with those from previous studies.

During our experiment, the overall net community production (NCP) of Z. noltii ~~(NCP)~~ was 101 mmol C m^{-2} d^{-1} and that of unvegetated sediments was 50 mmol C m^{-2} d^{-1}, showing that heterotrophic metabolism was dominating in the intertidal of Ria Formosa lagoon. Santos et al. (2004) found that in July 2002, the intertidal was marginally autotrophic as the *Z. noltii* NCP was -5.5 mmol C m^{-2} d^{-1} and the unvegetated sediment NCP was -21.2 mmol C m^{-2} d^{-1}.

To the best of our knowledge, we present here the first assessment of how the respiration of a seagrass community varies over night along with the tidal cycle. Several previous studies used punctual measurements either with dark chambers or during the night to assess the community respiration Santos et al, 2004, Silva et al., 2008, Duarte et al, 2010, Clavier et al, 2011). These punctual data were upscaled to estimate daily respiration rates and to calculate~~In order to estimate the~~ daily metabolic budgets of seagrass communities~~, authors have considered that community respiration does not vary during the night, using only one point estimate, or measure it during the day using dark chambers and assume that daytime respiration rates can be applied over a 24 h period (Duarte et al. 2010).~~. Our data show that this practice may seriously affect the estimation of the metabolic daily budgets of seagrass communities, particularly in the intertidal. The average net CO_2 emissions (community respiration, CR) of *Z. noltii* during night were 10.2 mmol m^{-2} h^{-1} (air exposure), 23.2 mmol m^{-2} h^{-1} (tidal immersion) and 55.0 mmol m^{-2} h^{-1} (peak event) (Table 1). With an average daylight period of 12 h and an average period of tidal inundation of 15.30 h d^{-1}, the community respiration is estimated to 233 mmol m^{-2} during night time.

The respiratory CO_2 production peaks during incoming flood tide are immediately recycled, i.e assimilated by the seagrass community, during the day. The observed accelerated decreases in the CO_2 flux coinciding with sunrise and the much lower CO_2 peaks observed during the day at the transition from air exposure to inundation provide evidence for this.

Over the course of the experiment a net CO$_2$ assimilation occurred roughly between 9:00 am and 6:00 pm with average net assimilation rates of 9.1 mmol m^{-2} h^{-1} during air exposure and 16.4 mmol m^{-2} h^{-1} during immersion summing up to a net CO$_2$ assimilation of 125 mmol m^{-2} d^{-1}. The NCP of *Z. noltii* during air exposure estimated here compares well to the previous reported rates ranging from 10 to 15 mmol m^{-2} h^{-1} (Silva et al., 2005), whereas NCP during tidal immersion significantly exceeds previously reported rates of less than 5 mmol m^{-2} h^{-1} from the Ria Formosa (Santos et al., 2004, Silva et al., 2005, 2008). These earlier studies used static chambers prone to introduce stagnant condition. In contrast, the bubbling in our chamber introduces turbulent mixing and hence may facilitate the transport of CO$_2$ across the water leaf interface. ~~In conclusion,~~Thus, these differences can be mainly attributed to the introduction of advection in our chamber system. In accordance with our results Clavier et al, (2011) have recently reported a higher NCP during submersion than under aerial conditions from a Z. noltii bed in the Banc D'Arguin (Mauritania). In this study a benthic chamber equipped with submersible pumps was used to maintain a turbulent water flow during submersion. They found a NCP of about 3 mmol m-2 h-1 under aerial conditions and of about 20 mmolm^{-1}h^{-1} under submerged conditions with the latter being derived from DIC and oxygen measurements.. The respective gross primary production rates in the study of Clavier et al. (2011) were 6 and 42.7 mmol m^{-2} h^{-1}. From our CO$_2$-flux measurements we have estimated a net community production of 9.1 mmol m^{-2} h^{-1} under aerial conditions and of 16.4 mmol m^{-2}h^{-1} under submerged conditions. As a first rough estimate of the gross community production in our study, we can simply add the observed respiration fluxes measured during night to the net community production resulting in an estimated gross community production of 17.5 mmolm-2h-1 under aerial conditions and of 36.5 mmolm-2h-1 under submerged conditions whereas the peak occurring at the transition from air exposure to immersion has not been included. In particular under submerged conditions the net and gross community production rates from both studies agree quite well. Under aerial conditions our production rates were about three times higher than those reported in Clavier et al. (2012) When including the carbon evolution from the sediment we can estimate a gross primary production to 4.3 g C m^{-2} d^{-1} being close to that (~ 5 g C m^{-2} d^{-1}) reported by Cabaço et al. (2012) for established meadows of Z. noltii in the Ria Formosa for this time (late spring) of the year that has been computed from changes in the living biomass. In this context it should be noted that, as already outlined in Silva et al. (2005), the available data on the aerial versus submerged photosynthesis of *Z. noltii* are not consistent. While Leuschner and Rees (1993) and

Leuschner et al. (1998) measured comparable rates of CO_2 assimilation in air and water, Perez-Llorens and Niell (1994) found CO_2 uptake rates in air 10 to 20 times lower than in water. As the strength of advection in our chamber system relative to ambient conditions is unknown we cannot currently ~~not~~ appraise the quality and reliability of the different~~ce~~ chamber systems. However these differences highlight the importance of accurately addressing the perturbations of turbulent flows in benthic flux chambers.

4.4 ~~VOC's~~VOCs

The overall focus of this section is the temporal evolution of the VOC fluxes over a tidal cycle. A quantitative discussion of the VOC data and an assessment of potential intrinsic sources are beyond the scope of this paper. For the halocarbons this will be done elsewhere Weinberg et al., submitted). ~~COS,~~ CS_2~~, and propane~~ having a known sedimentary source (~~Claypool and Kvenvolden, 1983;~~ Bodenbender et al., 1999) show a similar temporal pattern as CH_4 during high tide. Thus, we conclude that the emission of ~~these compounds~~CS_2 is in analogy to CH_4 mainly controlled by advective transport across the sediment water interface.

Halocarbon production in the marine environment is generally attributed to photoautotrophic sources (Gschwend et al., 1985; Manley et al., 2006; Moore et al., 1995) though there is some evidence of a sedimentary bacterial source for iodomethane (Amachi et al., 2001). In the seagrass meadows halocarbons are presumably produced by the seagrass or by the microphytobenthos. Only in the latter case porewater flow across the sedimentary interface can directly affect the emission. However, the elevated halocarbon fluxes during tidal immersion may reflect an enhanced transport across the leaf water interface and/ or result from the enhanced net primary production during immersion. Sediments may also act as a sink for monohalomethanes (Miller et al., 2001; Bill et al., 2002) and trihalomethanes are known to be degraded by a variety of microorganisms (Alasdair and Allard, 2008). Hence, the remarkable decrease and the uptake of the halocarbons may simply reflect sedimentary degradation processes. We further noted remarkable levels of H_2S and methanethiol in our samples during high tide. In particular H_2S is a very reactive nucleophile, readily reacting with monohalomethanes (Barbash and Reinhard, 1989) and thus may additionally foster the degradation of monohalomethanes. In summary, similarly to CH_4 and CO_2, the VOC fluxes are more pronounced during tidal immersion than during air exposure but further show some differences resulting from their different sources and sinks.

5 Conclusions

We have presented flux measurements for a variety of trace gases in a tidally influenced seagrass bed (*Z. noltii*) using a newly developed flux dynamic chamber system that can be deployed over full tidal cycles. An unambiguous quantification of carbon fluxes in future studies requires additional measuressuch as pH or alkalinity to better constrain the carbonate system. Further the water exchange between the chamber and surrounding waters should be quantified. Despite this caveats our results provide new insights into the temporal flux dynamics. In particular the CO_2 and ~~CH_4~~ CH_4 -data illustrate the need for high time resolution measurements to accurately address the fluxes and dynamics of trace gases in tidally controlled systems. For CH_4 we observed short emission peaks with the flood current arriving at the sampling site. In line with previous studies that have demonstrated the importance of advective transport processes for the oxygenation of sediments, our results show a general strong control of advective transport processes on trace gas fluxes in intertidal systems during submersion. We are aware of only a very few earlier studies in intertidal systems indicating elevated fluxes during tidal immersion or periods of tidal change. Contrasting to most previous flux chamber studies, our data indicate significant enhanced fluxes during tidal immersion relative to periods of air exposure for all trace gases measured in this study~~.~~ as previously reported for oxygen, DIC nutrients and suspended matter.”~~The main difference to most of the previous studies is the introduction of an advective flow in our flux chamber system resulting in substantially higher fluxes during immersion.~~ Hence, our results highlight the importance of accurately addressing the perturbations of turbulent flows in flux chamber studies. If the observed flux enhancements are more than just episodic events this may have fundamental implications for our understanding of the carbon and trace gas cycling in coastal environments.

6 Acknowledgements

The authors thank the German Federal Ministry of Education and Research (BMBF) for funding (grants 03F0611E and 03F0662E). This work was partly supported by the EU FP7 Assemble research infrastructure initiative and the project "Whole-system metabolism and CO_2 fluxes in a coastal lagoon dominated by saltmarsh and seagrass meadows", PTDC/AAC-CLI/103348/2008. João Reis, and Bruno Fragoso (CCMAR, Universidade do Algarve) are greatly acknowledged for their extensive support during sampling site selection and sampling. Our technical staff members Sabine Beckmann and Ralf Lendt are thanked for their invaluable help.

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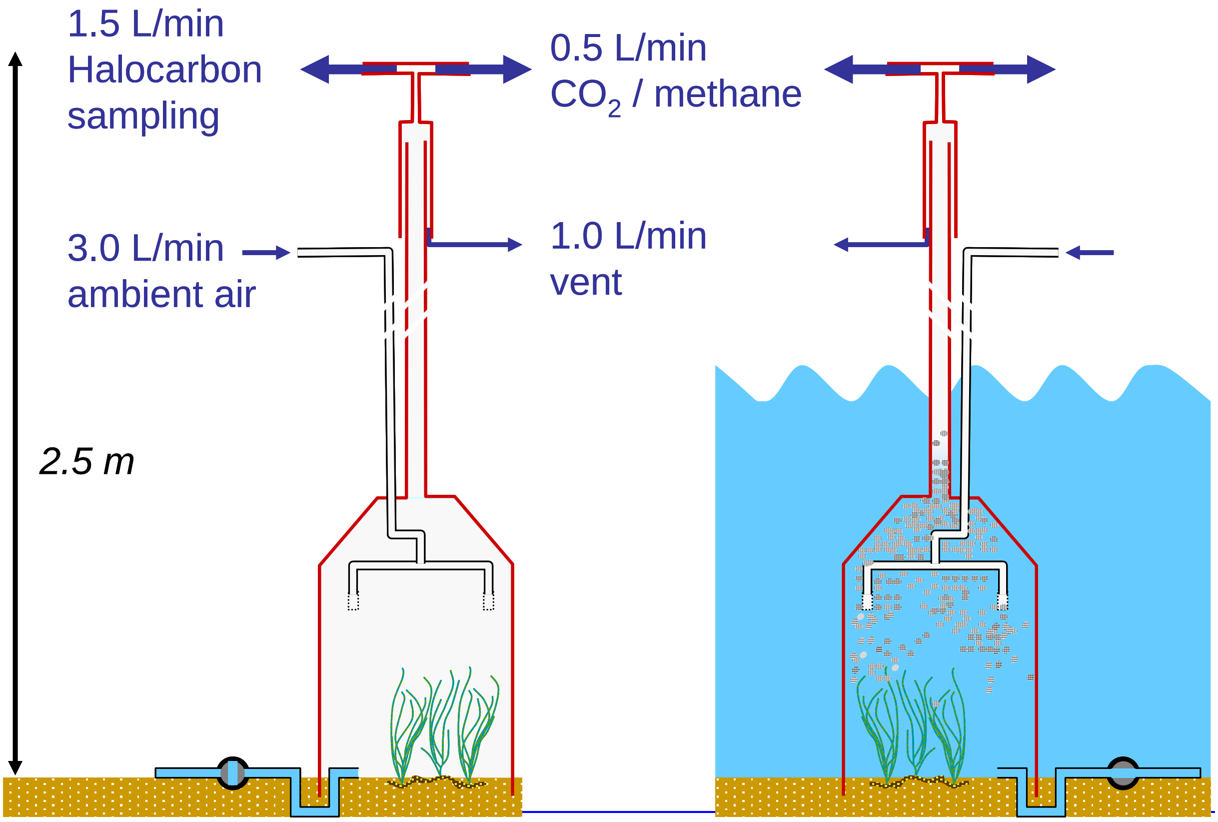
1.5 L/min
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sampling
0.5 L/min
CO_2 / methane
3.0 L/min
ambient air
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vent
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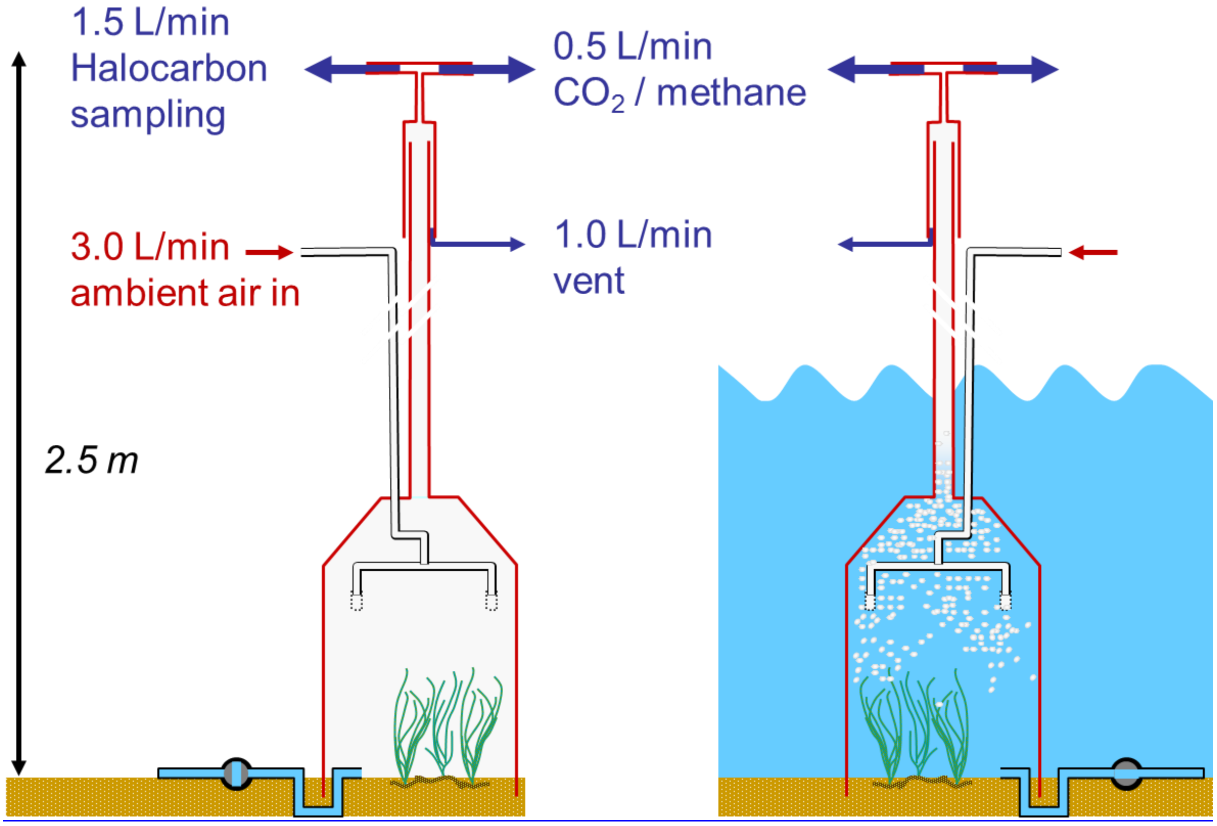
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CO_2 / methane
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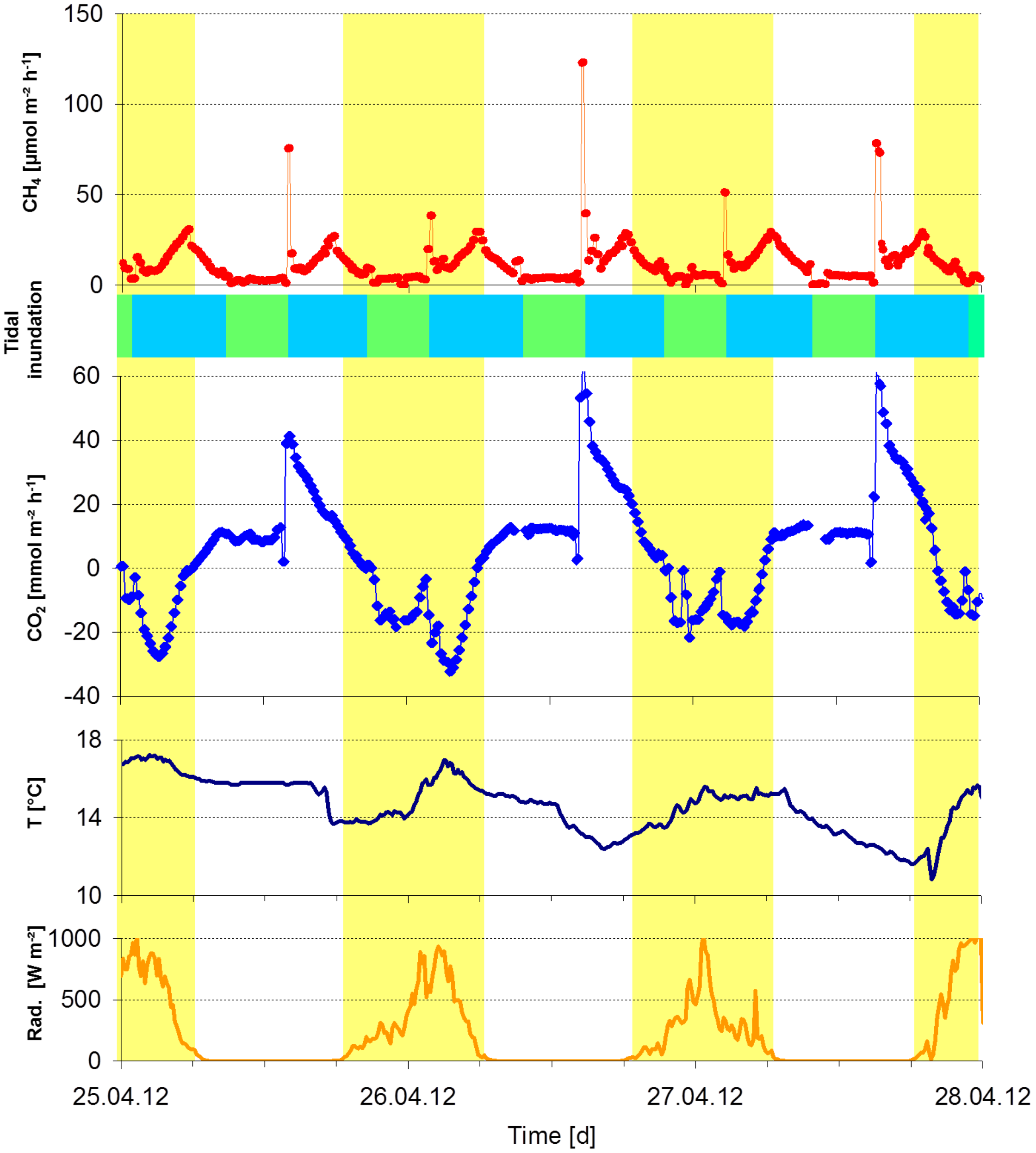
ambient air in
1.0 L/min
vent
2.5 m

Fig.1: Scheme of the dynamic flux chamber system. During air exposure the chamber acts as a conventional dynamic flux chamber. During tidal immersion the enclosed water is continuously purged with ambient air.



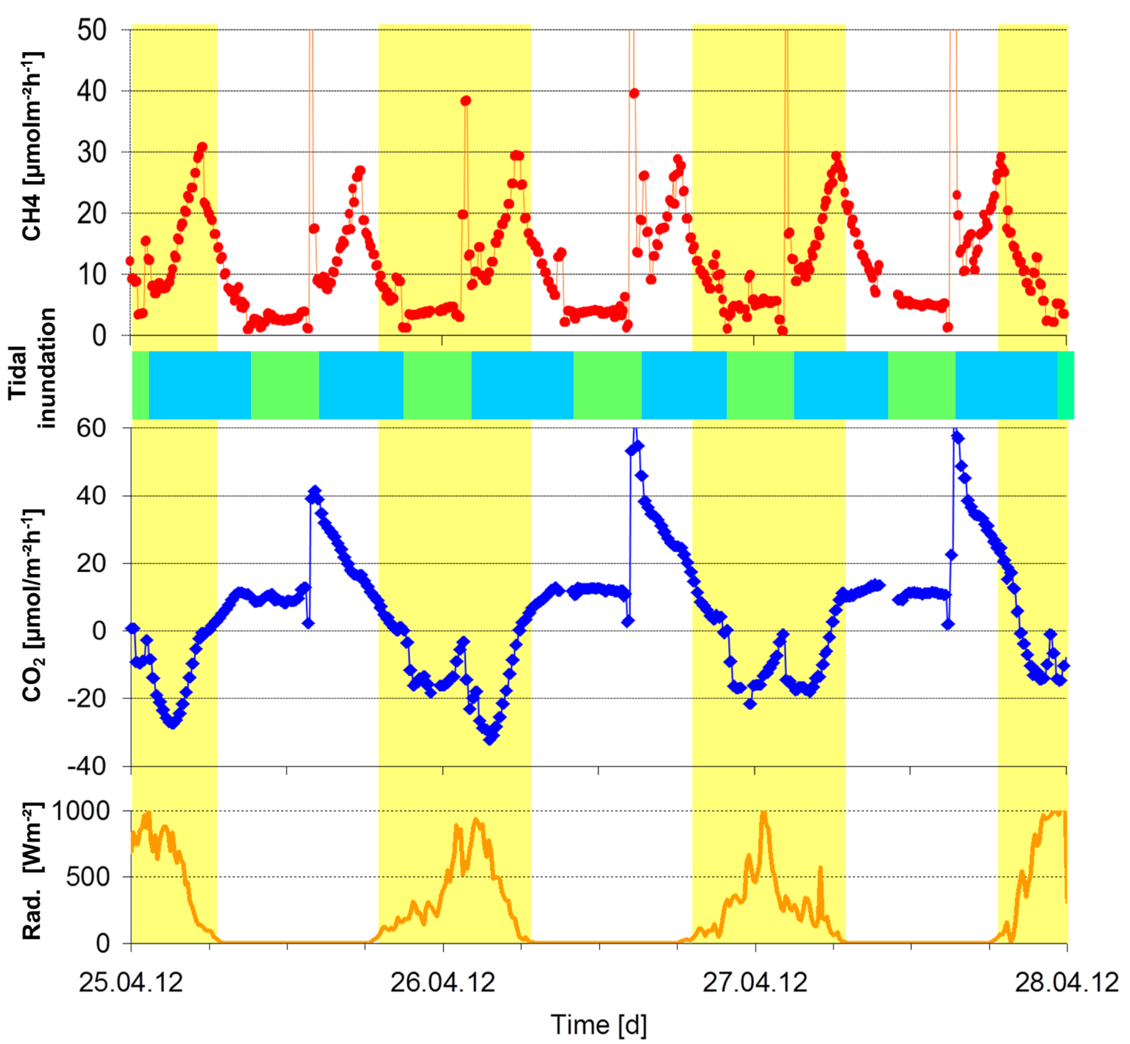


Fig. 2: ~~Circadian~~ Diurnal variations of the CH_4 and CO_2 fluxes above a meadow of the seagrass *Z. noltii*. Air temperature and light intensity are also shown. The measurements were carried out from 25 to 28 April 2012. Yellow bars indicate daylight periods, green bars indicate periods of air exposure, blue bars indicate periods of tidal immersion.

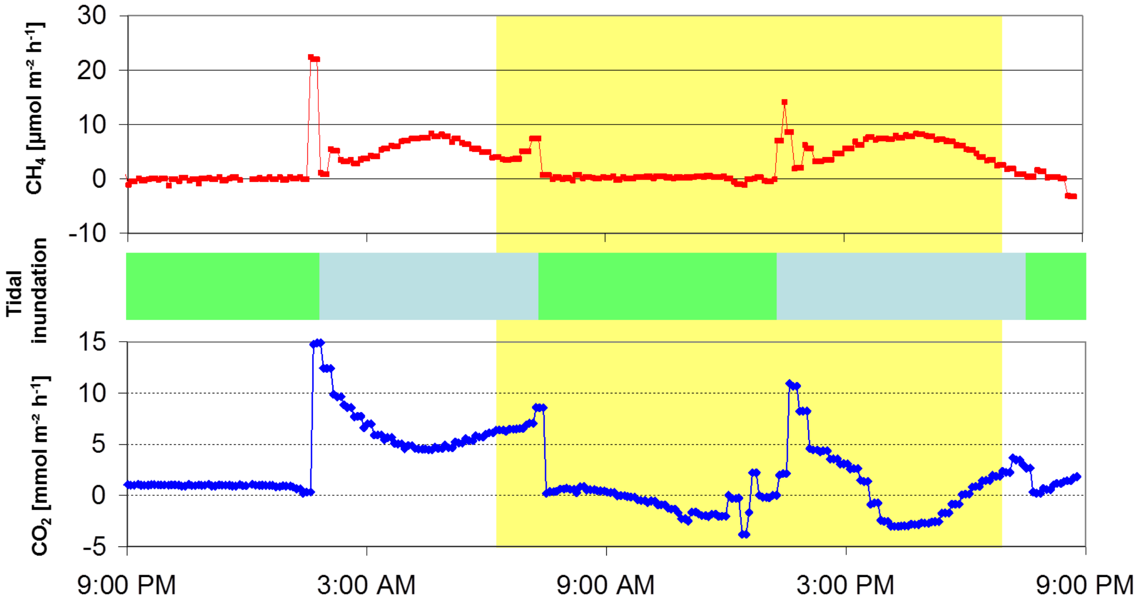
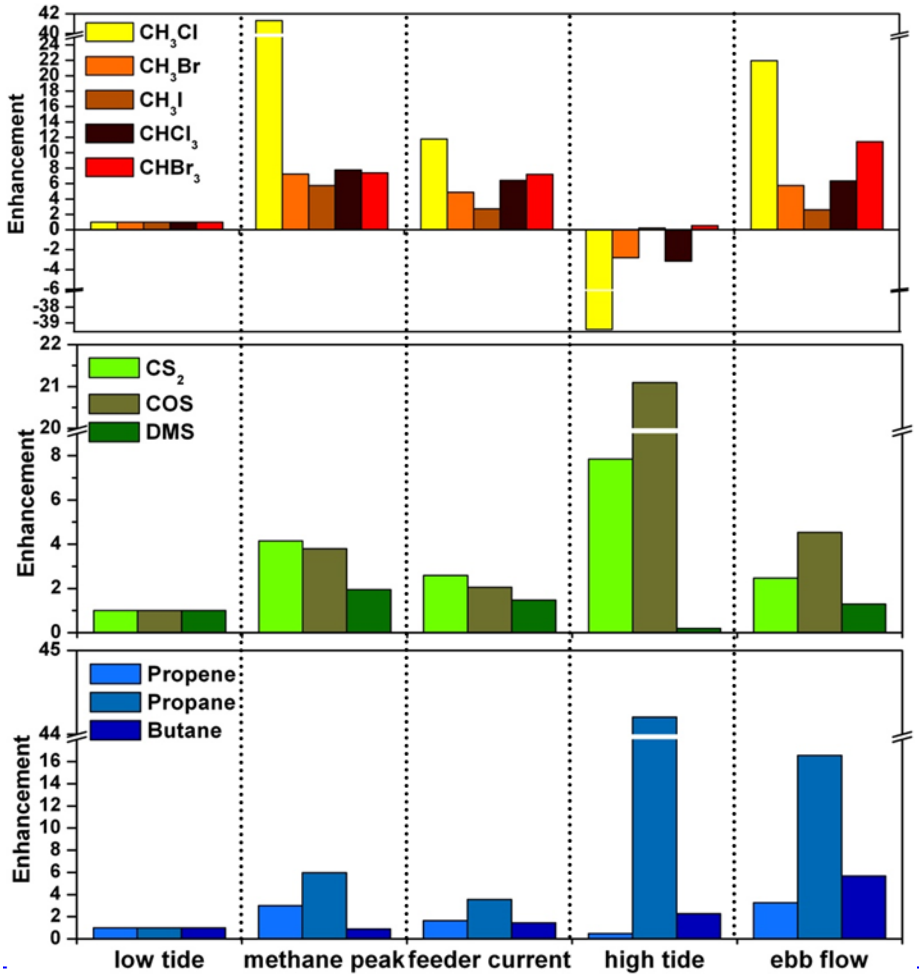


Fig. 3: CH_4 and CO_2 fluxes above a bare sediment patch recorded on April 23th. 2012. The upper graph in red shows the CH_4 fluxes in μmolm^{-2} h^{-1} and the lower graph show the CO_2 fluxes in mmol m^{-2}h^{-1}. Yellow bars indicate daylight periods, green bars indicate periods of air exposure and blue bars indicate periods of tidal immersion respectively.


Enhancement
42
40
24
22
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18
16
14
12
10
8
6
4
2
0
-2
-4
-6
-38
-39
CH$_3$Cl
CH$_3$Br
CH$_3$I
CHCl$_3$
CHBr$_3$
22
21
20
8
6
4
2
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CS$_2$
COS
DMS
45
44
16
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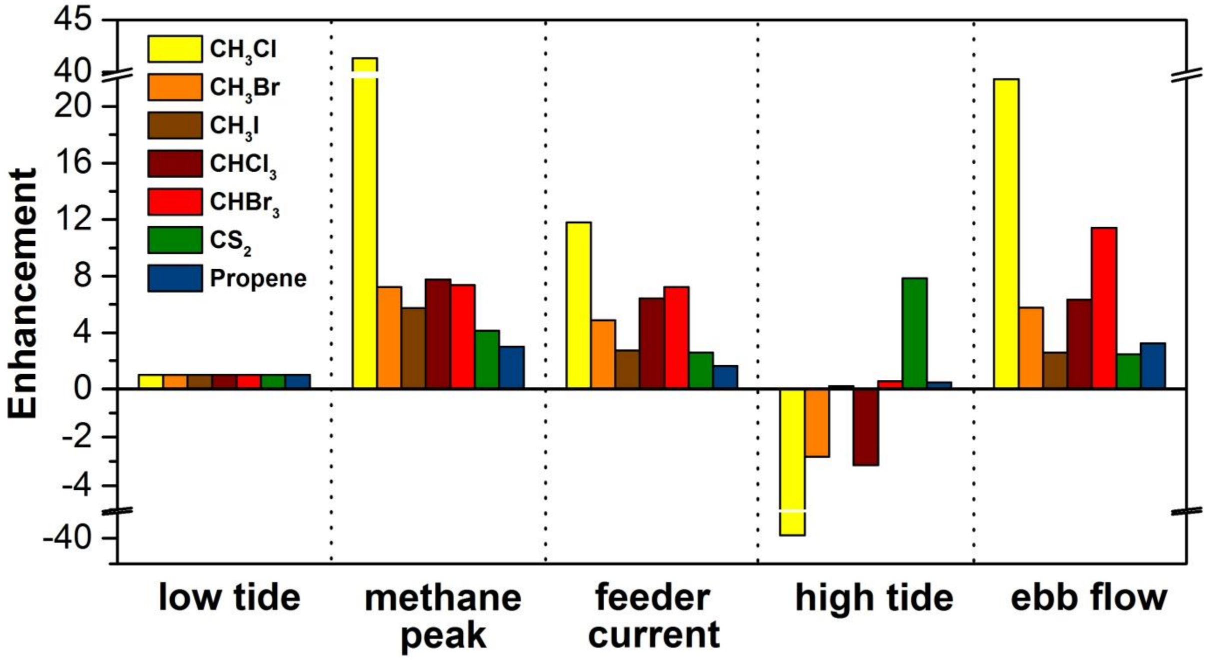
Propene
Propane
Butane
low tide
methane peak
feeder current
high tide
ebb flow


Enhancement
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CH$_3$Br
CH$_3$I
CHCl$_3$
CHBr$_3$
CS$_2$
Propene
low tide
methane peak
feeder current
high tide
ebb flow

Fig.4: Relative enhancement of selected VOC fluxes from a tidally influenced seagrass bed. All fluxes were normalized to the respective mean fluxes during low tide. Mean and ranges are provided in Table 2.

~~Fig.4: Relative enhancement of selected VOC fluxes from a tidally influenced seagrass bed. All fluxes were normalized to the respective mean fluxes during low tide. CS_2, CH_3Cl, CH_3Br, CH_3I, $CHCl_3$, $CHBr_3$, and propene were quantified against a Scott TOC 15/17 standard. Relative fluxes for COS, propane, butane and DMS were calculated from the measured intensities. For clarity the variability of the VOC fluxes is not shown. Mean and ranges are provided in Table 2.~~

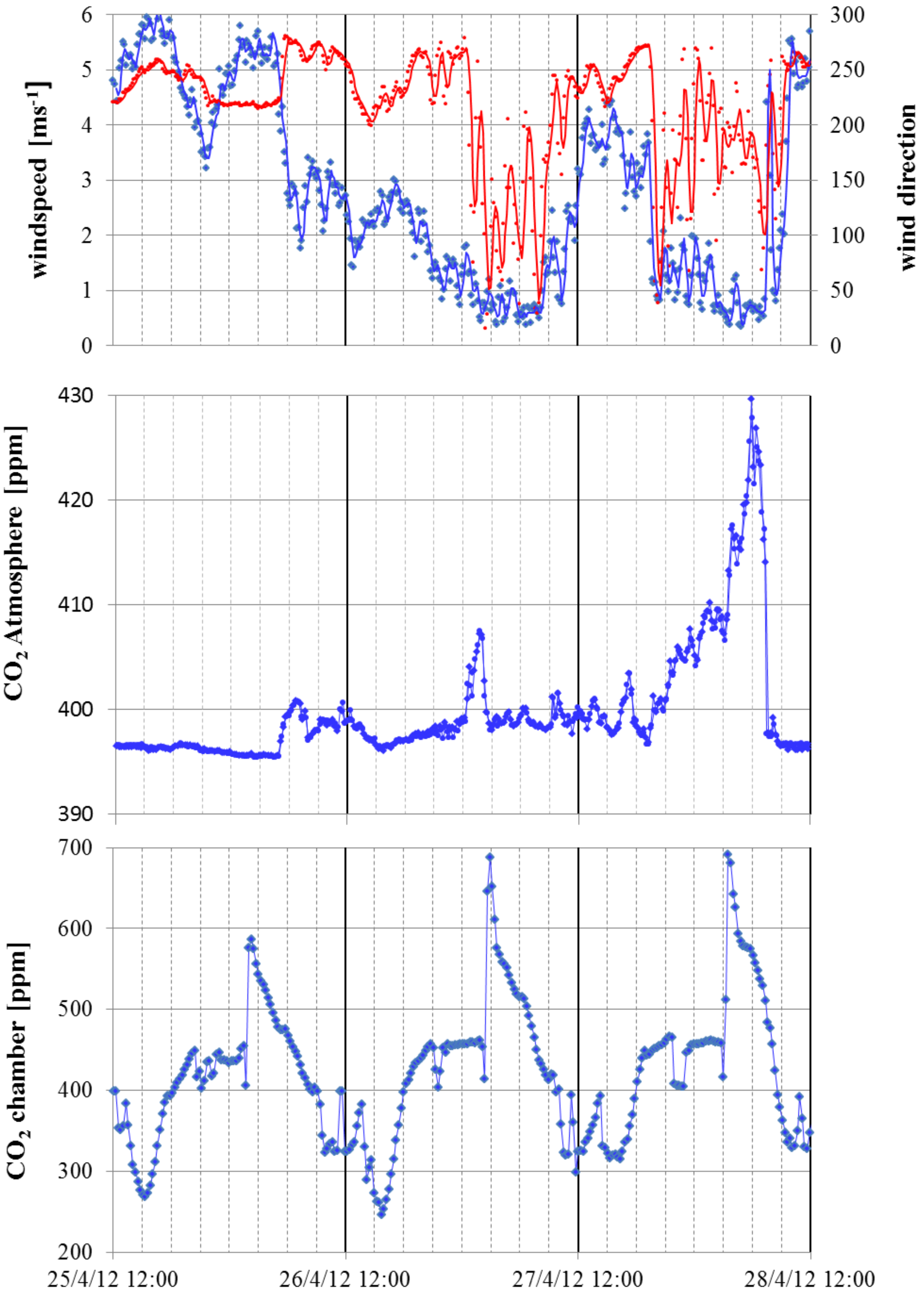

Fig. 5a Time series of CO$_2$ mixing ratios at the chamber outlet and in the atmosphere along with meteorological conditions. In the upper panel the blue diamonds indicate the windspeed.

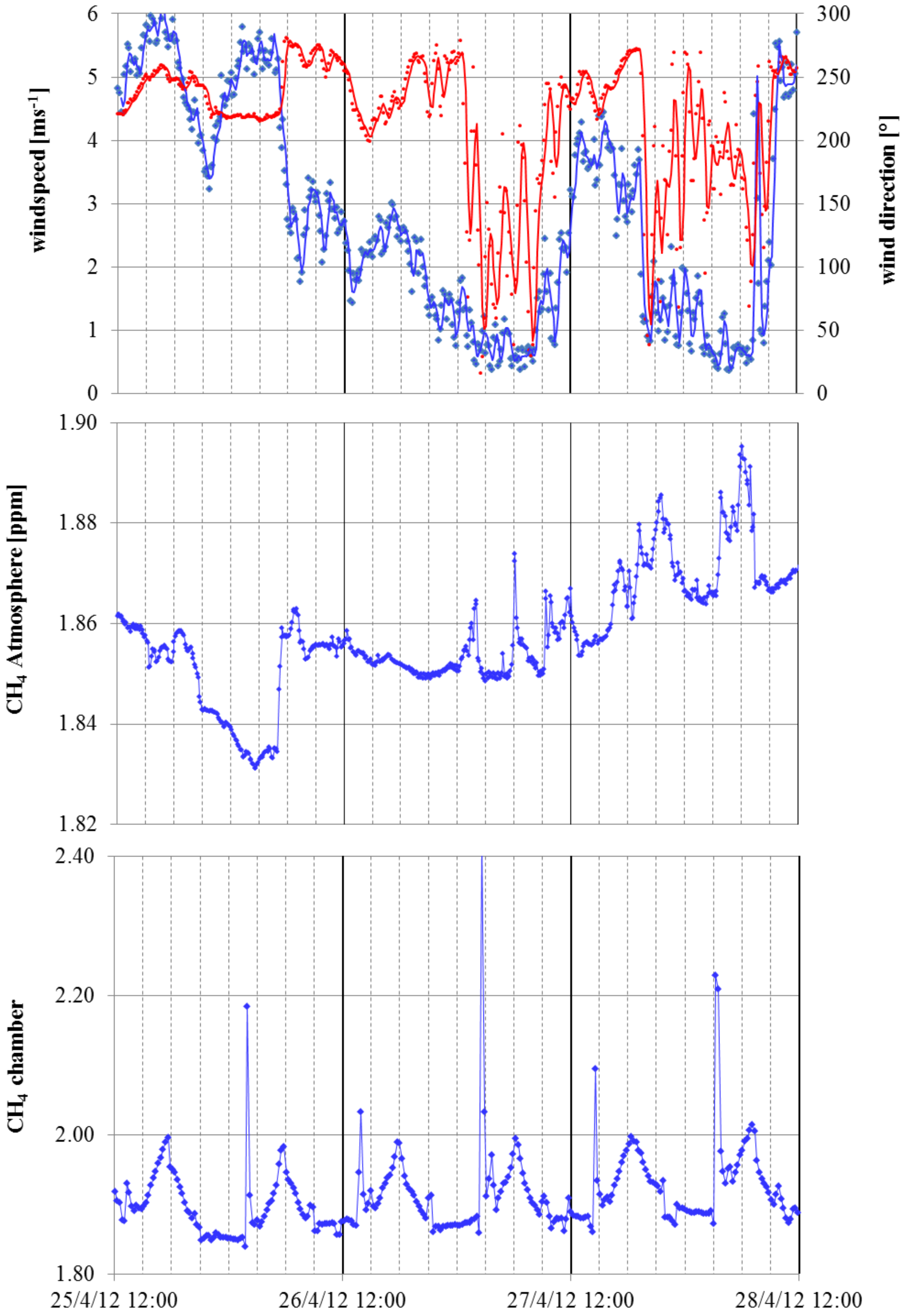
windspeed [ms^{-1}]
wind direction [°]
6
5
4
3
2
1
0
300
250
200
150
100
50
0
CH$_4$ Atmosphere [ppm]
1.90
1.88
1.86
1.84
1.82
CH$_4$ chamber
2.40
2.20
2.00
1.80
25/4/12 12:00
26/4/12 12:00
27/4/12 12:00
28/4/12 12:00

Fig. 5b Time series of CH_4 mixing ratios at the chamber outlet and in the atmosphere along with meteorological conditions. In the upper panel the blue diamonds indicate the windspeed.

Table 1: Averaged CO_2 and CH_4 fluxes above seagrass for different periods of the tidal cycle. The fluxes were calculated from the measurements of day 2 and 3. By definition emission fluxes are positive and deposition fluxes are negative.

tidal stage	**CO_2 (mmol m^{-2} h^{-1})**		**CH_4 (µmol m^{-2} h^{-1})**	
	sediment	**seagrass**	**sediment**	**seegrass**
air exposure (day)	-1.1	-9.1	0.4	6.9
air exposure (night)	1.0	8.4	0.2	4.4
tidal inundation (day)	-2.0	-16.4	6.6	14.3
tidal inundation (night)	6.4	20.1	5.2	16.6
peak (water just arriving)	14.8	55.0	10.8	71.0
mean (time averaged)	2.1	4.2	3.0	12.8

Table 2: Mean trace gas fluxes (bold) obtained from seagrass meadows along the tidal cycle. Fluxes are given in nmol m^{-2} h^{-1}. Numbers in parenthesis are the range of fluxes. Fluxes during high tide are given as single values. Further details on CH_3Cl, CH_3Br, CH_3I, and $CHBr_3$ are given in Weinberg et al. (submitted) By definition emission fluxes are positive and deposition fluxes are negative.

Compound	**low tide (n=17)** (nmol m^{-2} h^{-1})	CH_4 **peak (n=5)** (nmol m^{-2} h^{-1})	**feeder current (n=6)** (nmol m^{-2} h^{-1})	**high tide (n=2)** (nmol m^{-2} h^{-1})	**ebb flow (n=5)** (nmol m^{-2} h^{-1})
Halocarbons					
CH_3Cl	**1.0** (-29.6- 69.0)	**40.1** (-14.2- 99.7)	**11.4** (-14.7- 36.6)	**-18.1, -58.3**	**21.3** (-13.5- 46.2)
CH_3Br	**0.4** (-0.8- 3.9)	**2.7** (0.1- 8.3)	**1.8** (0.2- 3.3)	**-0.5, -1.6**	**2.1** (0.1- 4.4)
CH_3I	**0.6** (-0.6- 2.6)	**3.3** (0.1- 8.0)	**1.6** (0.1- 2.9)	**0.1, 0.1**	**1.5** (0.2- 3.0)
$CHCl_3$	**0.3** (-0.8- 2.8)	**2.4** (0.1- 6.6)	**2.0** (0.5- 3.0)	**-0.1, -2.0**	**2.0** (-0.6- 3.7)
$CHBr_3$	**0.4** (-0.5- 1.3)	**2.9** (0.2- 10.6)	**2.8** (0.2- 5.1)	**0.5, -0.1**	**4.5** (-0.4- 8.6)
~~*S-Compounds*~~					
CS_2	**52** (-34- 192)	**216** (22- 544)	**135** (-5.5- 200.0)	**420, 398**	**129** (-13.4- 230)
~~**COS**[1]~~	-	~~**3.8**~~ ~~(0.1- 7.1)~~	~~**2.1**~~ ~~(0.3- 5.1)~~	~~**22, 21**~~	~~**4.5**~~ ~~(1.0- 10.5)~~
~~**DMS**[1]~~	-	~~**2**~~ ~~(0.1- 3.0)~~	~~**1.5**~~ ~~(0.7- 1.9)~~	~~**0.2, 0.2**~~	~~**1.3**~~ ~~(0.1- 3.2)~~
~~*Hydrocarbons*~~					
propene	**56** (-26- 377)	**167** (91- 331)	**91** (-5.1- 170)	**33, 27**	**182** (3.4- 407)
~~**propane**[1]~~	-	~~**6.0**~~ ~~(-0.2- 14)~~	~~**3.6**~~ ~~(-2.7- 7.8)~~	~~**48, 44**~~	~~**16.6**~~ ~~(5.7- 37)~~
~~**butane**[1]~~	-	~~**0.9**~~ ~~(-0.5- 3.4)~~	~~**1.5**~~ ~~(-0.2- 2.8)~~	~~**3.5, 2.3**~~	~~**5.7**~~ ~~(2.6- 12)~~

[1] Fluxes are expressed as relative enhancement to the average flux during low tide experiments.