We thank all three reviewers for the time they have taken to produce thoughtful and constructive reviews which will greatly improve this paper. Our responses are given in *blue italics.*

RC1

Hopkins et al. present the production of VOCs from the ozonolysis of natural seawater via controlled laboratory experiments. The study found that VOC production ratios exhibit strong seasonal patterns linked to phytoplankton dynamics, identified fatty acids and algal-derived dissolved organic matter (DOM) as potential key precursors, and provided a preliminary scaling of the process to estimate its global significance. The manuscript is generally well-structured, the methodology is clearly described, and the research addresses an important gap in understanding marine VOC sources. However, I have several concerns on the manuscript that need to be addressed before considering for publication.

Line 14: In the phrase "representativeness of such experiments to the chemically complex", it is better to revise the word "to" to "for".

Corrected.

Line 66: Typo for "quiestcent".

Corrected.

Line 74: Please delete or revise the word "roughly" as it induces high uncertainties or a weak result.

Deleted "roughly".

Line 82-83: It is not clear how the percentage in "(59 % within 3 h, 94 % within 24 h)" represent the samples used in the experiments.

For clarity, sentence has been changed to: "Experiments were carried out between 3 h and 24 h after sample collection to minimize biological or chemical transformation of DOM".

Line 113: In the O_3 generation methodology, it was mentioned that the O_3 levels were set at 7.7 ± 0.7, 1.7 ± 0.7, and 2.1 ± 1.1 ppmv for spring, summer and winter experiments. These levels are substantially higher than ambient marine O_3 levels. In other words, do the experiments have environmental implications and what are the basis for choosing high O_3 levels for the ozonolysis experiments.

We already acknowledge at L114 – 116 that the ozone concentrations are substantially higher than typical ambient marine air, but were used to obtain strong VOC production, and high signal:noise ratio for the ozone measurement under the experimental constraints.

More details are given at L117 – 120, where we state that the relationship between VOC production vs ozone input was experimentally determined to be linear at ozone input <4ppm. We have added a figure to the SI (Figure S2) which demonstrates the relationship between VOC production and ozone input, which we refer the reader to at L 125: L180 – 185 we describe how the VOC production is normalized to account for the ozone concentrations used.

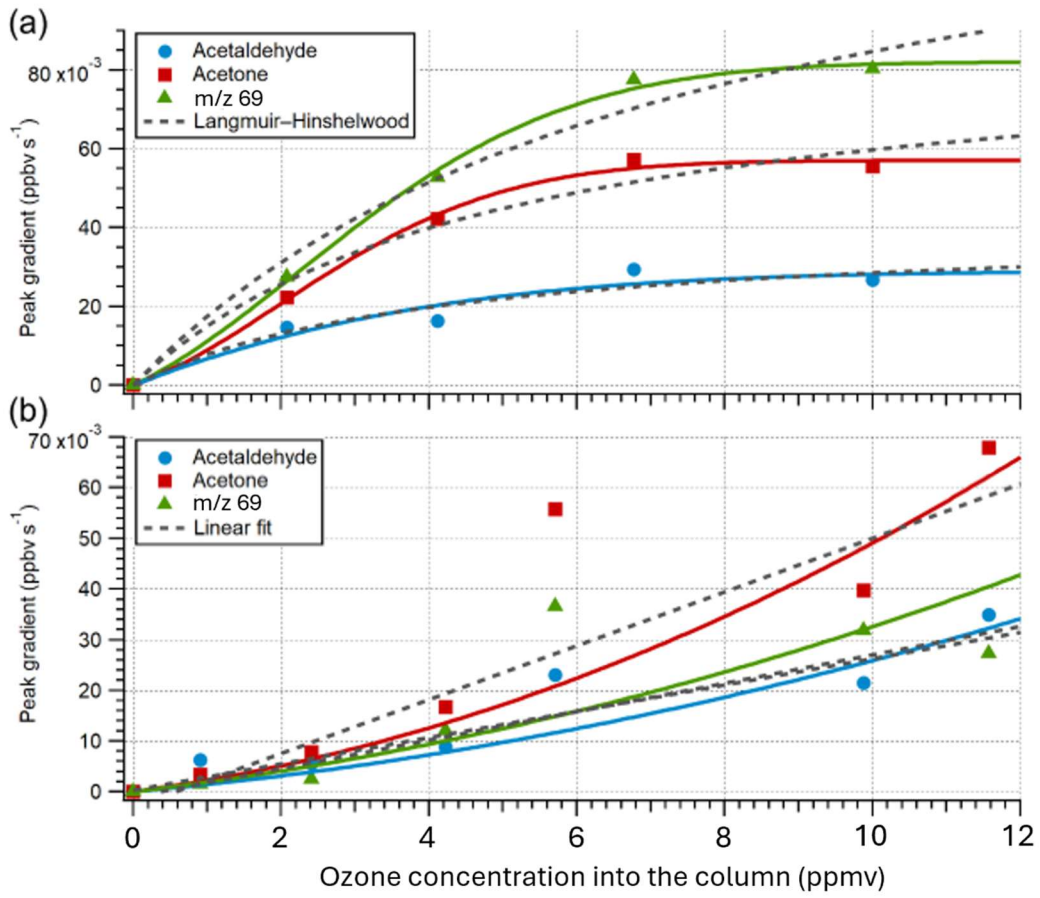

Figure S2. The effect of increasing ozone concentration with surface seawater collected from station L4 (Western Channel Observatory) using ozone heterogeneous oxidation on (a) the rate of VOC production from April 2017, and (b) the rate of VOC production from October 2020. In (b) the 5.7 ppmv measurement was omitted in regression analysis for all VOCs.

Line 134, Section 2.3: Using the bubble-column system with natural sea water, a significant number of sea-salt particles can be produced. These particles may provide a large surface area for heterogeneous reactions, and may produce VOCs in certain cases. How can the authors assure that the particles will not affect the results of the study? The authors need to clarify and exclude these influences.

Although it is possible that heterogenous reactions between aerosols and ozone could also result in VOC production as shown by Figure 1, there is a time delay between ozone input and the observed peak of VOCs, and measured ozone only starts to increase after the peaks of VOCs. This suggests that essentially all the ozone injected into the system is initially reacted with iodide and organics, and thus there's little ozone in the head space to react with sea spray.

We have added a sentence to section 3.3 at L299, wherein we outline some of the limitations and unknowns of our experimental set up:

"Furthermore, it is possible that heterogeneous reactions between ozone and sea-spray aerosols generated in these experiments may contribute to the emission of VOCs. However, the strength of this source is considered negligible because the measured ozone only starts to increase after the VOCs peaks (Figure 1), implying that essentially all the ozone injected in rapidly reacted with iodide and organics, with little remaining in the head space to react with sea spray.".

Line 169, Section 3.1: In this work, high concentration of O_3 were used in the experiments. The high concentration of O_3 can react with these VOCs, generating SOA and its intermediate precursors, may also affect the results that the VOCs are from the emission of sea water. How can the authors make sure that the measured VOCs are not secondary produced in the experimental system?

It is not possible to quantity the production of VOCs secondarily via reactions with ozone-generated SOA with this experimental setup, although we assume this is a negligible source of VOCs – see response to comment above and text that has been added at L299.

Line 285, Figure 5: Error bars should be added to the graph.

We have added the following to the legend for Figure 5:

"The uncertainty on peak heights are approximately 0.07, 0.06 and 0.09 ppb for m/z 59, m/z 69 and m/z 45, respectively".

Line 290, Section 3.3: The laboratory used high concentrations of O_3 (1.7-9 ppmv), while the real environmental concentration was three orders of magnitude lower. This means that if the rate of O_3 dry deposition on the ocean and VOCs emission rate remain unchanged, the amount of VOCs may be significantly reduced at the ambient O_3 levels. I think extrapolating the experimental results to the global ocean is not accurate enough. Furthermore, if the DOM is the key precursor, the uneven distribution of DOM in the global ocean may also affect the VOCs emissions. Therefore, I think this section is unnecessary in the text. Instead, the authors can discuss more on the potential implications of the ozonolysis.

Thank you for this important feedback. Our estimate of global VOC emission (via the production ratio) accounts for the difference in ozone input between ambient conditions and our bubble-column setup. However, on reflection we agree that this attempt at global upscaling is problematic and likely a stretch too far – so we are happy to omit this section. Instead we have added additional discussion focusing on comparing our production ratios with another study (Kilgour et al., 2024), comparing and contrasting the different experiment approaches – see response to RC2 point 9 below.

SI, Table S4: What is the limit of detection (LOD) for these VOCs measurements?

The following text has now been added to the SI at L110: "The limits of detection (LOD) were defined as 3σ following Wohl et al (2019). Using seawater-equivalent LODs reported for the PTR-MS system (0.51 nmol L^{-1} for acetaldehyde, 1.32nmol L^{-1} for acetone and 1.74 pmol L^{-1} for m/z 69), the corresponding equilibrium gas-phase concentrations are estimated to be 0.03, 0.04 and 0.08 ppbv, respectively. These values are substantially lower than the VOC enhancements observed during the ozonolysis experiments".

SI, Line 17: Please explain why the VOC peak height was used here is a more appropriate method than the peak area technique?

VOC production was quantified using the maximum PTR-MS signal increase ("peak height") following ozone addition to the bubble column because it provides a robust measure of VOC production that is less sensitive to variations in system flushing and response time than integrated signal. We have added the underlined text to the SI at L123 :

"The area under the peak corresponds to the total VOC produced from the available DOM; however, full consumption typically required ***>1.5 h****, so peak area was seldom integrated to maintain O_3-input stability. Instead, VOC production was quantified using the maximum PTR-MS signal increase (peak height) following ozone addition to the bubble column as this provided a robust measure of VOC production that is less sensitive to variations in system flushing and response time that integration of the peak".*

RC2

Summary

Hopkins et al. present new measurements of the production of volatile organic compounds from in the ozonolysis of seawater. This paper sits at the intersection of two poorly constrained areas: that of global ozone deposition to the ocean, a process governed by its reactions at the sea surface with iodide and dissolved organic matter, and the emission of volatile organic compounds produced via ozonolysis. Both processes are challenging to parameterize in chemical transport models, with significant knowledge gaps, including

what specific processes regulate the pool of ozone-reactive DOM. A prior, recent publication by this group demonstrated the significant and highly variable contribution organics to total observed ozone deposition to seawater, highlighting that VOC production from that reaction could be of importance. Hopkins et al. build from this, focusing on monitoring the seasonal trends of a few major ozonolysis VOC products and determining their production ratios. These targeted VOCs were tracked in seawater sourced from a single location in the English Channel over the course of 9 non-consecutive months. In the experiment, ozone is bubbled through a whole seawater sample containing an unknown natural mix of DOM. While the bubble column experiment does not perfectly reflect natural ocean turbulence or air-sea interactions, it provides an upper limit similar to that of a highly-aerated white cap regime.

Overall, the paper presents valuable information to the field. However, several points need to be addressed prior to publication.

General Comments:

1) The dataset focuses entirely on VOC production, however a similar experimental setup was used to measure O_3 reactivity by this same group. Does this experiment yield direct measurements of O_3 reactivity that could be interpreted alongside the VOC production term? Or does the system operate in an ozone–reactant-limited regime, where ozone is consistently fully consumed, thereby preventing meaningful comparison of ozone loss between samples? Along these lines, if VOC production is only a small fraction of O_3 loss, where does all of the O_3 go? I appreciate that some fraction will react with iodide. Is the rest forming non-volatile VOC? This is an enormous percentage!

Yes these experiments were done in an ozone-limited regime – at the time of peak VOC production, the measured ozone concentration is ~0, indicative of full consumption, such that a direct measurement of ozone loss corresponding to VOC production was not possible with this system. We expand upon this in our response to point 5 below.

2) On line 180-196 the calculation for VOC production is outlined. This is difficult to follow. In part, because it looks like there is a typo in the ozone deposition flux (equation 3). Is that term missing "D"?

Correct – there was an inconsistency between the equations and all have now been corrected. Ozone input (deposition) is now given as D_{O_3} in all equations, and $F_{(air)}$ is used for the gas flow rate.

3) Ozonolysis of organic material is extremely well studied in organic chemistry. Unfortunately, there is little to no discussion in the paper about chemical mechanisms that

link O_3 reactions to the select VOC that are suggested as products. Most notable, isoprene. It is nearly impossible to design a reaction mechanism for the production of isoprene from an ozonolysis reaction. This is most likely due to the fact that C5H9+ as measured by the PTR-MS is not isoprene. It has been well established that C5H9+ is formed in PTR through the dehydration of aldehydes (which are dominant ozonolysis products). This was discussed at length in Kilgour et al. 2024, where C5H9+ signal was dominated by the fragmentation of larger aldehydes (not from monoterpenes/sesquiterpenes as Hopkins et al., misreports). This was confirmed by GC-PTR-MS. It would be best if the authors refrained from assigning a molecular structure to the ion. I appreciate the effort to reconstruct "isoprene" from smaller fragments, but those fragments are common to aldehydes as well. Collectively, it seems most likely that the signals measured at C5H9+ are from larger aldehydes and not isoprene. I think the paper still has valuable insight on the production of VOCs, but should be careful in drawing a link between measured ion composition and molecular structure.

We accept and agree – all reference to isoprene has been removed from the manuscript and we simply refer to the C5H9+ fragment in all discussion of the data relating to m/z 69. Please also see our response to CC1 Eva Y. Pfannerstill below.

It would also be of importance to provide some literature evidence for acetone and acetaldehyde production from ozonolysis.

We have added reference to Schneider et al. (2024) and Wang et al. (2023) to the manuscript at L272, providing literature evidence of the formation of acetaldehyde and acetone/propanal from the ozonolysis of seawater:

"The suite of VOC products observed in the present experiments is generally consistent with compounds previously reported during ozonolysis of seawater and sea-surface microlayer samples. Wang et al. (2023) also observed the formation of acetaldehyde (m/z 45) and acetone/propanal (m/z 59), as well as hexanal, heptanal, octanal and nonanal during ozone-driven reactions with sea-surface microlayer samples collected from the South China Sea, while Schneider et al. (2024) reported acetaldehyde (m/z 45) and acetone/propanal (m/z 59) production from the oxidation of Arctic seawater and sea-surface microlayer samples. Kilgour et al. (2024) focused primarily on total VOC production and did not identify acetaldehyde or acetone/propanal as major products in experiments with coastal seawater. These studies did not consider the role of seasonality in influencing the influence of ozonolysis on VOC production".

4) On line 119-120, the authors note that: "The VOC production vs. ozone input relationship was experimentally determined to be linear at ozone input mixing ratio below ~4 ppmv." I think the authors need to show this in the SI. This is not intuitive as higher O_3 concentrations can lead to a divergent chemical mechanism where radical chemistry is

non-linear. If the authors want to extend the results of this study to lower O_3 concentrations, this link is essential and should be included in the analysis.

We have added the below figure (Figure S2) to the SI to demonstrate the relationship between VOC production and ozone input, which we refer the reader to at L125:

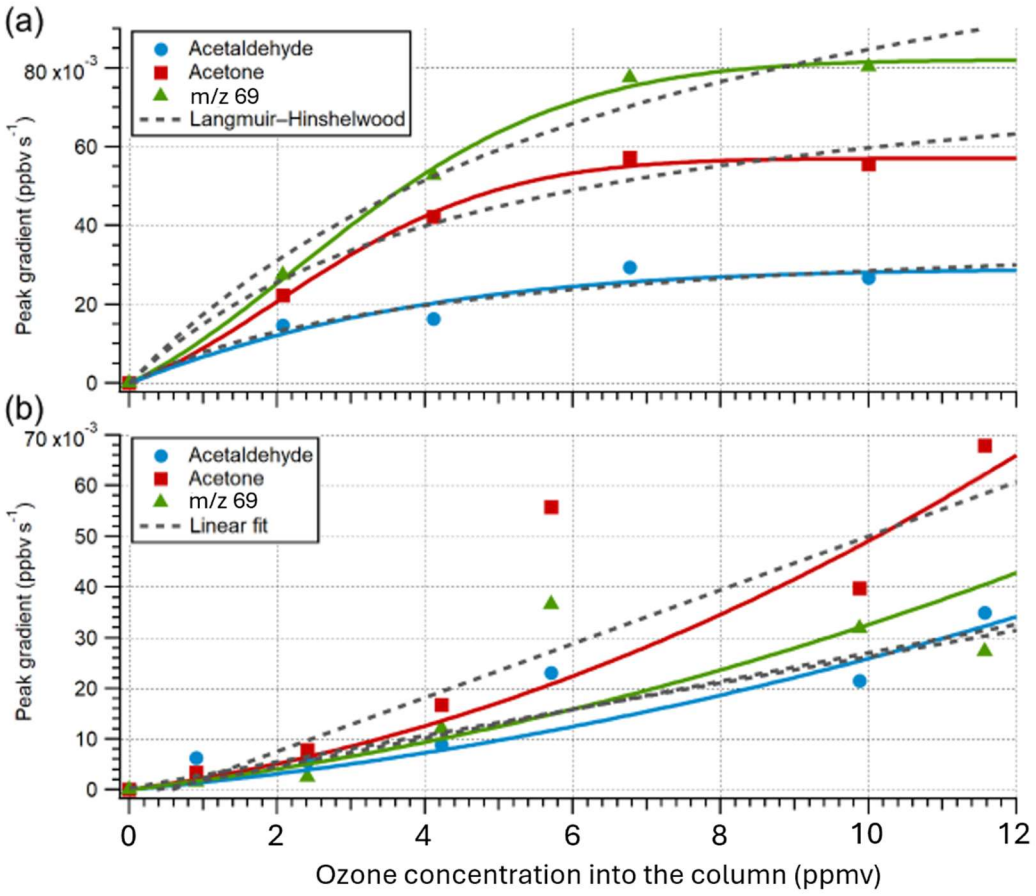

Figure S2. The effect of increasing ozone concentration with surface seawater collected from station L4 (Western Channel Observatory) using ozone heterogeneous oxidation on (a) the rate of VOC production from April 2017, and (b) the rate of VOC production from October 2020. In (b) the 5.7 ppmv measurement was omitted in regression analysis for all VOCs.

5) It seems that variability in the VOC production ratio is also sensitive to variability in ozone reactions beyond those that make VOC. As stated in the manuscript, ozone loss is not just due to reactions with DOM, as it also reacts with species such as DMS and iodide, present in unknown concentrations in seawater. These reactions also are changing in time, potentially at different rates than those of the DOM. How do you extract the other sources

of ozone loss, or is the assumption that ozone loss to other species constant? Would it impact the production ratio if ozone loss to a species like iodide is changing over the course of the experiment? Some fraction of ozone loss term is not due to DOM, and it varies in time. How do you account for the non-DOM reactive component in the fraction of ozone dependent term, FO_3? Or is this somehow accounted for in the limits of high O_2?

We agree that not all ozone contributes directly to VOC production. Ozone also reacts with iodide and other dissolved constituents such as DMS. We have clarified in the manuscript that the reported VOC:ozone ratios are normalized to total ozone rather than exclusively to ozone reacting with DOM. New text at L248:

"The VOC production ratios presented here are normalised to total ozone input and therefore implicitly include ozone consumption by competing seawater reactants. Recent observations from a trans-Atlantic study indicate that iodide contributes, on average, approximately half of ozone reactivity in temperate waters (Yang et al. 2025). Consequently, the reported production ratios should be interpreted as an effective VOC production efficiency per mole of ozone lost from the system, rather than yields based solely on the fraction of ozone reacting with DOM. To demonstrate this, we performed experiments with the same bubble-column system (see SI, Figure S3) showing that increasing iodide concentration reduced m/z 45 (acetaldehyde) and m/z 59 (acetone) production ratios, consistent with competition between iodide and DOM for available ozone".

We have added an additional figure and some text to the SI:

"The impact of iodide (I^-) on VOC production was tested by adding increasing concentrations of I^- to natural seawater (Figure S3). A slight reduction in acetaldehyde and acetone peak height and production ratios (Figure S3) with increasing I^- concentration demonstrates the competition between I^- and VOC-producing DOM for available ozone. The production of m/z 69 was unchanged, which could imply that m/z 69 production occurs at the interface, while acetone and acetaldehyde production occurs in bulk water where there is more competition with iodide".

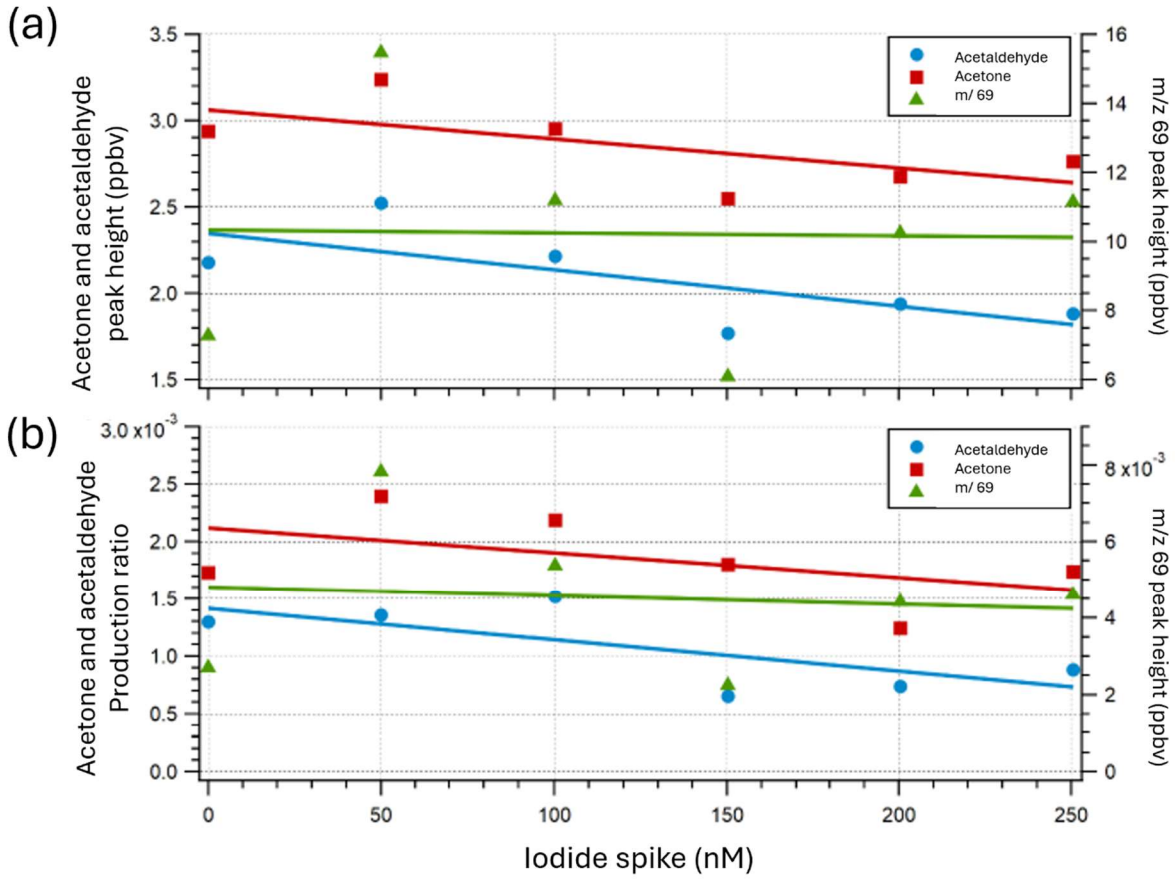

Figure S3. Influence of additional iodide on VOC production from natural seawater (a) VOC peak heights and (c) VOC production ratios.

We have also added some further text in section 3.3 at L311 – 314:

"The production ratios used in the following calculations are based on total ozone uptake and therefore include ozone loss to non-VOC-producing pathways such as reactions with iodide. As a result, they should be considered apparent production efficiencies rather than true yields relative to ozone reacting solely with DOM".

6) Mechanistically, the fatty acid experiment is confusing and the induced confusion does not help to support the goals / aims of the paper. It is already well established that you can make aldehydes from the ozonolysis of unsaturated fatty acids (O_3 + oleic acid is one of the most overstudied reactions). More specifically, I don't understand how a saturated fatty acid reacts with ozone. This gives me a lot of pause. Either the saturated fatty acid is impure or the ozone source is generating other radicals (OH?). In either case, this section is challenging to interpret and does not seem additive to the paper.

Considering the reviewer's comment, we agree that the fatty acid addition experiments do not add any useful information to the manuscript and in fact create some confusion. Therefore, we have decided to remove these experiments from the paper. All description and discussion of the fatty acid addition experiments have been deleted.

7) After reading the paper, the title is a bit misleading "Uncovering precursors for VOC production from ozonolysis of seawater" The title suggests that the paper will be a chemical investigation into the DOM pool composition or what drives it. This paper focuses mostly on the biological levers that regulate the pool as a whole, and then various targeted "checks" to explore if the three key selected VOCs can be produced by different model seawater DOM proxies. The paper also does not complete a statistical analysis of how the precursors relate to VOC production (as discussed in the next comment). It seems like the real advance of the paper is in the long-term measurements and the seasonal trends. Perhaps: "Uncovering the seasonal trends of VOC production from the ozonolysis of seawater" would be a more reflective title.

Agreed and title changed as suggested.

8) There is no analysis of the Statistical relationship between VOC product yields and chlorophyll or microbial abundance. Figure 2 paints the variability of the biological cycles over the course of seasons, but there is no attempt to directly relate the variables tracked (chlorophyll-a or the microbial abundance) to the VOC production rates. Including additional statistics or figures (such as a regression of Chl-a and VOC production) would be highly beneficial to support the paper's claims.

Although the broad trends are similar, regression analysis was performed on all of the data and no significant relationships were found. Thus, the chl-a and microbial abundance data are presented to provide biogeochemical context for the VOC data, despite a lack of direct relationships. Lack of a strong linear relationship between VOC production and simple biological proxies is also not surprising, given that although plankton and microbial activity undoubtedly influence the supply of organic precursors, the VOC production yield is more dependent on the concentration, composition and chemical reactivity of DOM.

We have added the following to the text at L240:

"Despite broadly similar temporal trends, no significant relationships were detected between VOC production ratios and concurrent chlorophyll-a or microbial abundance (r^2 <0.3), indicating that precursor composition rather than bulk biological abundance is a key control on VOC production.".

9) It would be helpful to have a bit more of a direct discussion (absolute values) between the VOC production ratios measured here (which are pretty small) to those that have been

reported in the literature. The flow reactor approach clearly has a bias toward reactions occurring in the SSML under quiescent periods as noted by Kilgour et al. 2024, which makes it not as representative of open ocean conditions. The bubble column reactor avoids those complications but requires high O_3 concentrations. It would be of interest to the reader to help connect these two approaches and the limitations of each.

We thank the reviewer for this comment. We agree that a more direct comparison with previous studies would help place the measured production rates in context and we have now expanded the discussion to compare with other key studies.

The compounds identified here (acetaldehyde and acetone/propanal) are consistent with those reported from seawater ozonolysis experiments by Wang et al. (2023) ACS Earth Space Chem. 7, 1306−1313) and Schneider et al. (2024) https://doi.org/10.1021/acsearthspacechem.4c00163). Kilgour et al. (2024) (Atmos. Chem. Phys., 24, 3729–3742), present total VOC production ratios.

However, direct comparison of production efficiencies is complicated because different reactor designs probe distinct regions of the air-sea interface and because some studies (e.g. Kilgour et al. 2024) report total VOC production rather than the production of individual compounds.

Nevertheless, we now show that the ozone-driven VOC production ratios reported here, which ranged from 0.026 -0.102 for acetaldehyde, 0.023 – 0.124 for acetone/propanal and 0.08 – 0.095 for m/z 69 (see Table 1) for summary), are lower than the total VOC yields reported by Kilgour et al. (2024) from laboratory flow-reactor experiments (0.43 – 0.62) but are comparable in magnitude to their field-derived estimates based on eddy covariance observations (0.04 -0.06).

The difference in yield between our bubble column and the flow reactor of Kilgour et al. (2024) may be due to the contrasting experimental setups which probe fundamentally different environments and reaction regimes.

Flow-reactor studies, such as Kilgour et al. (2024) and Schneider et al. (2024), are designed to maximise interactions between ozone and material concentrated at the sea-air interface and are therefore particularly sensitive to the compositions of the sea surface microlayer. In contrast, our bubble-column system generates a continuously renewed air-water interface and is intended to represent heterogeneous ozone chemistry over a larger water volume without requiring the formation of a stable surface film.

We agree that both approaches have strengths and limitations. Surface-film and flow-reactor systems provide valuable insight into the chemistry occurring within the sea-surface microlayer, where organic matter is enriched and VOC production may be

enhanced under quiescent conditions. Conversely, our bubble-column approach avoids the need to maintain an artificial or static surface film and may better represent environments where turbulence continuously renews the air-water interface, for example under high wind, wave breaking conditions. We have added discussion to the manuscript to highlight these differences and caution against direct quantitative comparison between production ratios obtained using the two methodologies.

We have added the following paragraph at L272 in Section 3.1:

"The suite of VOC products observed in the present experiments is generally consistent with compounds previously reported during ozonolysis of seawater and sea-surface microlayer samples. Wang et al. (2023) also observed the formation of acetaldehyde (m/z 45) and acetone/propanal (m/z 59), as well as hexanal, heptanal, octanal and nonanal during ozone-driven reactions with sea-surface microlayer samples collected from the South China Sea, while Schneider et al. (2024) reported acetaldehyde (m/z 45) and acetone/propanal (m/z 59) production from the oxidation of Arctic seawater and sea-surface microlayer samples. Kilgour et al. (2024) focused primarily on total VOC production and did not identify acetaldehyde or acetone/propanal as major products in experiments with coastal seawater. These studies did not consider the role of seasonality in influencing the influence of ozonolysis on VOC production.

Quantitative comparison between studies is complicated by substantial methodological differences. The flow-reactor studies employed by Wang et al. (2023), Schneider et al. (2024) and Kilgour et al. (2024) preferentially isolate chemistry occurring within a stable surface film, the bubble-column approach generates a continuously renewed gas-water interface through bubble entrainment. The production ratios measured in the present study (acetaldehyde: 0.026 – 0.102; acetone/propanal: 0.023 – 0.124; 0.08 – 0.0095 for m/z 69 (see Table 1) for summary) are lower than the laboratory total VOC yields reported by Kilgour et al. (2024) (0.43 – 0.62) but overlap with their field-derived estimates (0.04 – 0.06). This closer agreement with the field-derived estimates of Kilgour et al. (2024) may indicate that bubble-column approach better captures VOC production under naturally turbulent ocean conditions. In addition, the production ratios reported here are normalised to total ozone uptake and therefore include ozone consumption by competing pathways that do not generate the VOCs measured in this study".

We have also edited Table 1 to make the production ratios more directly comparable to Kilgour et al. (2024). They were originally shown as e.g. 2.6 x 10-², which is now presented as e.g. 0.026.

Specific Comments:

- Line 53: The SML is not always highly enriched in organic matter and surfactants - consider adjusting the language accordingly.

  Text altered to: "…can become enriched in organic matter and surfactants…"

- Section 3.2 uses "VOC-free, aged seawater" (Line 73) as the matrix for all DOM spiking experiments. Did the seawater still contain DOC that was reactive to ozone? Was the same seawater sample used for all VOC precursor experiments, or how was the baseline reactivity subtracted to compare results across samples?

  The intent was to use seawater that had substantially reduced reactive organic matter – aging for 1 month would reduce many VOCs, but likely not remove all VOCs completely. The experiments used different batches of seawater that had been treated in the same way.

  Text altered to: "organics-depleted seawater"

- Line 82: Did you evaluate if there was a significant change in VOC measurements depending on how long after sample collection the experiment was run?

No significant relationships were observed for the duration between seawater sampling and VOC production measurements. 59 % of experiments were run within ~3 h of sampling and 94% were within 24 h, thus DOM loss due to biology in the sample was expected to be minimal.

We have added a sentence at L84: "No significant relationships were observed for the duration between seawater sampling and VOC production measurements".

- Line 85-87: This sentence is a bit confusing, particularly due to the placement of "by flow cytometry" in the sentence. Additionally, what technique was used to analyze chlorophyll a? There seems to be a disconnect between the information presented in the methods section and the data shown in Figure 3. Additional context would be useful to know where the different pieces of information in Figure 3c-e come from.

  For clarity, the sentence now reads: "Chlorophyll a concentrations measured by fluorometry (Figure 3 c), and cell counts for total eukaryotes (Figure 3 d) and

heterotrophic nanoflagellates and bacteria (Figure 3 e) measured by flow cytometry were sampled, processed and analysed according to the Standard Operating Procedures of the Western Channel Observatory (https://www.westernchannelobservatory.org.uk/data.php)".

- SI Line 22-23: "Dilutions targeted final cell abundances within ambient seawater ranges (assuming no algal cells in the aged seawater)." What were the concentrations of cell abundances were used in experiments? This seems important to know, should experiments be replicated in the future.

  The senescent E. huxleyi culture used in the experiments was added at 5–20 mL to a 1.2 L aged seawater matrix, resulting in substantial dilution. Assuming typical laboratory culture abundances of order 10^5–10^6 cells mL $^{-1}$, the resulting cell concentrations in the bubble column would have been approximately 10^2–10^4 cells mL $^{-1}$, within the range of typical natural E. huxleyi abundances observed during blooms in shelf sea waters (e.g. Poulton et al. (2014) NW European shelf coccolithophore abundances ranged from <1 – 898 cells mL$^{-1,}$ Biogeosciences 11, 3919-3940).

  Text in SI now reads: "Dilutions targeted final cell abundances within ambient seawater ranges (10^2 – 10^4 cells mL^{-1}) (assuming no algal cells in the aged seawater)".

- SI Lines 11-14: DMS purge and oxidation losses. This section is not referenced in the main document. How does this relate to the relevant experiments in the paper?

  This does not relate to the relevant experiments in the paper and has now been removed.

Minor Points:

• Line 20: "dominant product" should be plural.

Corrected.

• Line 65: "influences these production of VOCs" should be "influences the production of VOCs"
Corrected.

• Lines 56 and 59: Misspelling of artificial as "artifical"

Corrected.

• Line 56: Misspelling of reactions as “reations”

Corrected.

• Line 66: Misspelling of “quiescent” as “quiestcent”

Corrected.

• Line 240: Misspelling of heterogeneous as “heterogenous”
Corrected.

• Hyphenation: Line 25 “ozone driven,” Line 159 “gas tight,” Line 29 “flow through,” Line18 “near surface water”
Corrected.

• Line 59: comma issue? “The majority of these studies used quiescent, artifical or natural seawater with the use of additives to explore potential VOC precursor compounds”
Corrected.
• Line 66-67: oddly phrased with grammatical issues. Consider removing, as the topic is discussed later in the manuscript.
Deleted.

• Line 84: the L in late should be lowercase.
Corrected.

• Line 167: “DOC” is not defined
Now reads: “dissolved organic carbon (DOC) concentration”

• Line 106 and SI lines 7-12: inconsistent formatting in equation variables (V compared to Vbub).

Removed from SI to avoid duplication (and inconsistent formatting).

• Line 276: the “3” in the unsaturated oleic acid formula should be in the subscript.
Corrected.

• SI Lines 12-13: several instances where something seems to be intended as a subscript: $C_{(}VOC_{)}$, $F_{(}air_{)}$, etc. Would be good to double check formatting.

All subscripts now correct.

CC1: Eva Y. Pfannerstill

Thank you for this interesting study on PTR-MS measurements of VOC emissions from seawater ozonolysis. I would like to offer some comments on the interpretation of the m/z 69 signal, which I believe warrants further discussion in light of recent literature.

The authors correctly acknowledge that m/z 69 is a composite signal, and I appreciate this caution. However, I think the interpretation of this signal could be brought more fully in line with recent findings.

Thank you Eve for taking your time to assess our manuscript and for your expert insight into PTR-MS measurements and the interpretation of ion fragmentation – all truly appreciated. *Please see our responses below.*

On the contribution of long-chain aldehydes

The authors cite Kilgour et al. (2024), but I think a key finding of that study deserves more emphasis: Kilgour et al. demonstrated, using GC-coupled PTR-TOF-MS, that none of the C5H9+ signal in their seawater ozonolysis experiments originated from isoprene (citation from Kilgour et al.: “Importantly, this study reveals that the RT-Vocus C5H9+ signal from ozonolysis of coastal seawater has no contribution from isoprene but rather is a fragment of larger oxygenated VOCs.”) . This is a strong result obtained with a highly reliable method, and it has direct relevance to the present study's experimental setup.

In this context, I was surprised not to find any discussion of long-chain aldehydes as contributors to m/z 69. This seems like an important omission, particularly given that:

- Schneider et al. (2024) report nonanal emissions from ozone-oxidized seawater, and it is well established in the PTR-MS literature that nonanal fragments predominantly onto m/z 69 (e.g., Pagonis et al., 2019).

- Coggon et al. (2024), also using GC-coupled PTR, confirmed that long-chain aldehydes fragment onto m/z 69 and described a correction approach for this contribution.

- The authors themselves used oleic acid as a precursor and observed m/z 69 as a dominant product. This result is entirely consistent with the established pathway:

"Nonanal is the expected product arising from the reaction of ozone with a free- or triglyceride-containing 18:1ω9 fatty acid (i.e., oleic acid)" (Schneider et al., 2024). Nonanal then fragments onto m/z 69 in PTR-MS. I would encourage the authors to discuss this result explicitly in this context.

By contrast, the suggestion that "oxygenated terpenoids" could contribute to m/z 69 is presented without comparable mechanistic support. Long-chain aldehydes are oxidation products of fatty acids, not of terpenoids, and given the experimental conditions, they seem a more likely explanation.

Thank you for the useful suggestions regarding the importance of long-chain aldehydes as contributors to the m/z 69 signal.

Text at L128 – 131 has been altered and now reads: "Though m/z 69 is often attributed to isoprene, many larger biogenic VOCs—particularly larger oxygenated VOCs and long-chain aldehydes—can undergo extensive fragmentation in PTR-MS and produce $C_5H_9^+$ ions (Kilgour et al. 2024)".

On the fragmentation correction

The authors state (l. 128) that they account for fragmentation at m/z 69 by following Wohl et al. (2019). However, as far as I can tell, Wohl et al. characterize the fragmentation of m/z 69 onto smaller product ions, not the fragmentation of larger precursor molecules onto m/z 69. If isoprene is calibrated with a gas standard, correcting for its downward fragmentation is generally unnecessary (unless those smaller masses are themselves of analytical interest). More critically, this approach does not — and cannot — correct for the upward contribution of long-chain aldehydes to m/z 69. The Coggon et al. (2024) correction method addresses this, but it requires measurement of the relevant higher-mass ions, which do not appear to have been measured in the present study. I therefore think the claim of having "accounted for" this contribution needs to be revisited.

Thank you for this useful comment. We have now omitted all references to isoprene in the manuscript and no longer include the description of the correction of the fragmentation in the context of isoprene.

On consistency of interpretation throughout the manuscript

I appreciate that the authors are careful in the early sections of the manuscript to refer to the signal as "m/z 69" rather than "isoprene." However, this caution appears to diminish in later sections — for example, in Table 1 and in the conclusions, where the signal is interpreted more directly as isoprene. Given the uncertainties discussed above, I would encourage the authors to maintain consistent caution throughout, and to consider

explicitly acknowledging that, under their experimental conditions, m/z 69 most likely reflects fragments of fatty acid ozonolysis products, i.e. long-chain aldehydes, rather than isoprene.

I raise these points in a constructive spirit and hope they are useful for revising the manuscript. I think a more nuanced interpretation of the m/z 69 signal would strengthen this valuable paper considerably.

Again many thanks for your constructive comments – we have now removed all references to isoprene throughout the manuscript, and simply refer to m/z 69, which we discuss in the context of fragmentation of larger oxygenated VOCs and long-chain aldehydes.

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