Reply to RC2

In the following, the referee’s comments are reproduced (black) along with our replies (blue) and changes made to the text (red) in the revised manuscript.

General statement:

This paper (Shipborne measurements of ClNO2 in the Mediterranean Sea and around the Arabian Peninsula during summer) reports observations of ClNO2, NO3/N2O5, HCl, particle composition and other parameters made during a cruise in the Mediterranean Sea, Red Sea and Persian Gulf. This is a severely understudied region in terms of atmospheric chemistry and, as such, the dataset presented here fills a significant gap. The paper is well laid out, the figures and tables clear, and the analysis of the data is interesting and thorough. I only have a few minor observations, but other than that, I recommend publications on ACP. We thank the referee for the positive evaluation of our manuscript and the useful comments and suggestions. We modified the manuscript according to the comments listed below.

General comments:

I find the analysis in Section 3.4 a bit confused. First of all, a little introduction explaining how the factors influencing ClNO2 production efficiency are going to be evaluated in this section would be useful in order to follow the discussion. 

We added an introductive sentence to the section:

“In the following we calculate $f$ and $\gamma$ from our measurements, compare the values with the literature and quantify the contributions of $k_{\text{het}}$ and $k_{\text{dir}}$ to the overall NO$_3$ loss rate.”

Second, the values of $f$ calculated with Eq 9 and with Eq 10 are significantly different, but this discrepancy is not really explained or discussed.

With Eq. 10 we calculated median values of $f$ for each region, based on all available data, and listed them in Table 2 (here we added a note: “a Calculated from Eq. (10)”). In contrast, Eq. 9 could only be applied to four specific time periods listed in the text, when we sampled a homogeneous air mass. There is no reason to expect a perfect agreement as these four values calculated with Eq. 9 are only snapshots within different regions.

It is also not clear if the value for the Gulf of Oman is 0.6 (page 11, line 29) or 0.84 (page 12, line 3).

These are two values for two different time periods, both in the Gulf of Oman (first one shown in Fig. S14 (formerly Fig. 7), second one not shown). We added a date to the first event to make this clear.
“[…] as illustrated in Fig. S14 for data obtained in the Gulf of Oman (25–26 July 2017) for which \( f = 0.60 \pm 0.04. \)”

When it comes to \( f \), the main issue is the availability of particulate chloride. In general, it seems (page 12, lines 20-25) that the authors are focusing on fine particles, while I would expect sea salt to be a dominant source of chloride in the open sea. It may be true that the surface area of sea salt is smaller but the ClNO\(_2\) yield is higher, as the authors themselves acknowledge on page 13. Therefore neglecting sea salt in the calculation of \( f \) may not be appropriate and could possibly lead to a bias in the results of the analysis.

We agree that sea salt may contribute to ClNO\(_2\) formation (due to an \( f \) close to 1). However, the average contribution from the coarse mode during the campaign was only 14 % (as stated in the text) and \( f \) is between 0.5 and 1 for fine mode particles as well, so the fractional contribution of coarse mode sea salt to ClNO\(_2\) formation is generally low (as most of the coarse mode particles were dust). This is discussed in detail towards the end of Sect. 3.4.

We note that, the calculation of \( \varepsilon = \frac{[\text{ClNO}_2]}{[\text{NO}_3]_{\text{int}}} \) is in any case independent of \( k_{\text{het}} \) (and thus independent of the contributions of the coarse/fine mode).

Finally the statement on page 13 line 30 about the importance of \( k_{\text{dir}} \), i.e. the direct NO\(_3\) loss, seems to be in contrast with the last lines of the section. I am afraid it is not enough to refer to a future publication, given that a significant part of the analysis stands on the assumption that the direct losses of NO\(_3\) dominate over the indirect losses. At least a summary of the steady state analysis mentioned here should be given to support the statements about \( k_{\text{dir}} \).

The last lines of the section state that much of the reactivity could neither be attributed to \( k_{\text{het}} \) nor to measured VOCs but to unidentified compounds (also contributing to \( k_{\text{dir}} \)), so they are not in contrast with the statement that \( k_{\text{dir}} \) is more important than \( k_{\text{het}} \).

The result that \( k_{\text{dir}} \gg k_{\text{het}} \) is also derived from measurement data via \( \varepsilon = f \left( \frac{k_{\text{het}}}{k_{\text{het}} + k_{\text{dir}}} \right) \).

To make this clear, we modified the text:

“However, for a large fraction of each night NO\(_3\) was below the detection limit (ca. 5 pptv) despite a high production rate (large mixing ratios of NO\(_2\) and O\(_3\)). A steady-state analysis of NO\(_3\) production and loss indicated a high total reactivity which could not be attributed to measured trace gases (\( k_{\text{dir}} \)) or heterogeneous losses of N\(_2\)O\(_5\) (\( k_{\text{het}} \)). A detailed analysis of the NO\(_3\) lifetime and the role of VOCs is beyond the scope of the present manuscript and will be described in detail in a separate publication.”
Specific comments:

page 1, line 30: capitalize "Earth"

Done.

“As the Arabian Gulf already suffers from some of the most polluted air on Earth […]”

page 5, line 2: I am not sure I follow the ion chemistry from HCl to I(CN)Cl\(^{-}\). Where is the CN group coming from? Please provide more information or add the relevant reference.

Detection of HCl involves I(CN)\(_2\)^{-} primary ions. A reference (Eger et al., 2019) was added.

“HCl was observed as I(CN)Cl\(^{-}\) (\(m/z\) 188 and 190) (Eger et al., 2019) with a sensitivity of 0.17 Hz pptv\(^{-1}\) per 10\(^6\) Hz of I\(^{-}\) at \(m/z\) 188 (and 0.05 Hz pptv\(^{-1}\) at \(m/z\) 190), a detection limit of 98 pptv and a total measurement uncertainty of 20 % ± 72 pptv.”

page 5, line 7 and 12: can you provide more information on the purpose of the IMR bypass?

The bypass in front of the IMR (1 slm) was used in order to improve the transmission of CH\(_3\)C(O)O\(_2\) radicals from the thermal decomposition of PAN in the heated inlet (Eger et al. (2019). As this is not relevant for ClNO\(_2\), HCl or SO\(_2\) detection, we removed the sentence.

And it is not clear to me how 50 cm of a 1/8 inch tube reduces the pressure in a 3 m long inlet. The pressure is both reduced by a bypass flow (5 slm) and by the mentioned (coiled) piece of 1/8 inch tube (which is reducing the pressure in the inlet line via energy dissipation to the walls). We added the missing information to the text (and changed units from inch to mm):

“To avoid condensation of water in the inlet lines in the containers, the pressure in the sampling line was reduced to \(\approx\) 700–800 mbar with a bypass flow of \(\approx\) 5 slm and by including an additional \(\approx\) 50 cm long (coiled) piece of 3.18 mm (OD) PFA tubing.”

page 6, line 10: do you mean NO3?

NO\(_2\) is correct.

page 10: can you specify which of the methods explained in the supplement is being used as default in the paper discussion and in Figure 6? I am guessing method B but it should be stated.

Method C is used as default as stated in the supplement. We wanted to avoid confusion by referring to a method that is only mentioned in the supplement, since the data reduction is also (briefly) outlined in the manuscript itself. Nevertheless, we added a note with a reference to the supplement to Sect. 3.2.

“The data reduction is described in more detail in the supplement (all the data shown in the manuscript corresponds to the application of method C), where the sensitivity of \(\epsilon\) to these limitations and additional constraints is discussed.”
equation 8: I think you need to explain the $\text{keq}[\text{NO}_2]$ part of the equation and how it is related to $[\text{N}_2\text{O}_5]$. We added a definition to the text:

“[…] where $A$ is the particle surface area concentration, $\bar{c}$ is the mean molecular velocity of $\text{N}_2\text{O}_5$ ((24,400 ± 160) cm s$^{-1}$ during AQABA) and $K_{eq} = \frac{[\text{N}_2\text{O}_5]}{[\text{NO}_2][\text{NO}_3]} = 2.8 \times 10^{-27} \ (T/300)^{-0.6} \exp(11000/T) \text{cm}^3 \text{molecule}^{-1}$ (IUPAC, 2019) is the temperature-dependent equilibrium constant (Reactions R4 and R5).”

At several points in the paper the notation ICINO2- (or similar) is used for the masses measured by CIMS. But ICINO2 is a cluster not a molecule, so it should be more correctly indicated as I.CINO2-. The same for other ions mentioned throughout the paper. This was corrected throughout the manuscript. We now write I·CINO2- and I·HNO3-.