Response to Referee #1
Our responses to the referee's comments are in blue.

Specific Comments:
Page 8116, line 14. It would be helpful to specify a range or median rather than an upper limit for CH4 destruction.

We meant this to be a best estimate for a particular atmospheric condition. We have rephrased as follows: "Data-constrained model simulations indicate that Cl atoms account for approximately 15% of methane destruction on days when aged polluted air arrives at the site."

Page 8116, lines 21-22. While reactive Cl chemistry will catalytically destroy O3, available evidence suggests that this is a relatively minor sink for O3 in the troposphere under most conditions. I encourage the authors to either qualify or drop this statement.

Added clause 'though it is probably only a minor O_3 sink under most conditions."

Page 8116, lines 22-25. Relative reaction rates of Cl and OH with NMHCs vary greatly. In addition, it is potentially misleading to lump CH4 and NMHCs together in terms of their climate relevance. I suggest that the authors consider clarifying this section accordingly.

Good point. Changed to:
"Cl has a roughly 14-fold faster reaction rate constant than OH for reaction with methane and therefore potentially plays a role in controlling the lifetime of this important greenhouse gas. Cl also has faster rate constants than OH for reactions with non-methane hydrocarbons (NMHCs). NMHCs play an role in the production of tropospheric ozone, which is also a greenhouse gas.

Page 8117, line 1. The authors may wish to add BrCl to the list since model calculations based on MECCA suggest that it is an important and sometimes dominant Cl-atom precursor over the open ocean.

Good point, added.

Page 8117, lines 8-10. The cited studies evaluate the production of Cl-atom precursors initiated by N2O5 reaction with particulate Cl-. However, they did not explicitly address the importance of these activation pathways relative to others. In addition, the text should clarify that the pathways leading to ClNO2 and Cl2 involve reaction with particulate Cl as opposed to generic "aerosols". N2O5 also reacts with aerosol via hydrolysis to produce HNO3.

Replaced generic 'aerosols' with 'aerosol chloride.' Removed 'primarily' to indicate that other mechanisms may be important.

Page 8118, lines 10-12. I understand what the authors mean but the terminology here is a little unclear. Relative to what would O3 "increase cycling." I think the authors mean to say that reaction with O3 sustains the cycle by converting Cl to ClO whereas most reactions of Cl with NMHCs produce relatively unreactive HCl, which slows radical recycling.

The reviewer's wording is much clearer and has been adopted, as:
"Higher O_3 levels tend to sustain the cycling of reactive Clx by increasing the fraction of Cl atoms that are converted to ClO. By contrast, most reactions of Cl with NMHC's produce relatively unreactive HCl, which slows Clx cycling."

Page 8118, lines 19-20. To provide additional context, it would be helpful to include the detection limits for BrCl during these studies. Were detection limits sufficiently low to rule out BrCl as an important radical precursor?

Added "The BrCl detection limits during these studies were estimated at 2 ppt, which is lower than the nighttime levels predicted by models."

This detection limit does not preclude a significant daytime BrCl-based Cl atom source. However, if BrCl is

produced by reactions of HOBr in aerosols as models predict, BrCl should be produced as long as HOBr is present, both day and night. We will make the scale of the issue more apparent in the modeling section by adding the italicized phrase to the text:
“BrCl is the dominant source of Cl atom in the model, contributing to HOCl formation and reaching 24 ppt in the base case run. As noted above, BrCl has not been observed in marine air at levels *above the 2 ppt detection limit of our instrument. If the model overpredicts daytime BrCl production, the underprediction of HOCl in the model is an even larger problem than it first appears.*”

Page 8119, line 8. Remove redundant “remote”.

Done.

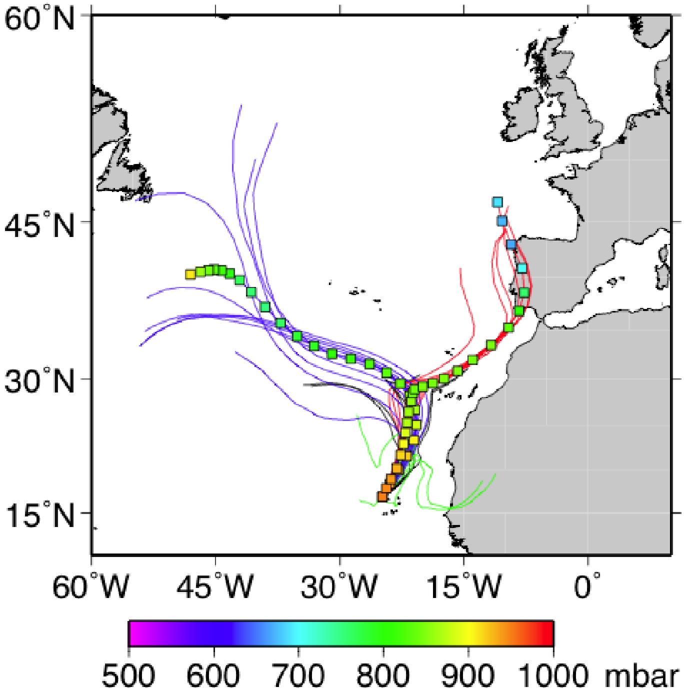
Page 8119, line 20. Suggest replacing “slightly higher” with a more quantitative descriptor.

Added “about 1 m/s higher”

Page 8119, line 22. Suggest adding additional details and/or a citation explaining the approach that was used to calculate the trajectories. In Fig. 1 and/or in the text, it would also be helpful to provide additional information regarding the altitude of transport.

Added this sentence:
“The back trajectories were calculated with the British Atmospheric Data Centre model for air reaching the field site coordinates at 950 mbar.”

We added transport altitudes to Fig. 1 for the two main transport regimes (below).



Page 8120, first two paragraphs. The manuscript indicates that ionic constituents of aerosols were measured and used to parameterize the model. A brief summary of what was measured, how it was measured, sampling frequency, and the relevant concentration ranges should be included here.

“PM10 aerosols were collected on filters on a 24-hour cycle by a high volume sampler at a height of 30 m. Particulate Na+ was determined by ion chromatography and ranged from 3.2-5.2 ug/m3 during this study.”

We do not go into greater detail because the aerosol data are going to be published in the future by the team that collected them.

Page 8120, line 4. Suggest replacing “major contribution” with the range in actual contributions of particulate NO3to NOy. Was particulate NO3sampled quantitatively by the NOy instrument? If not, NOy measurements should be described as lower limits.

Changed to “On average, particulate NO_3 contributed 56% of the total NOy observed. The total NOy measurements may not include all aerosol size ranges and are therefore lower limits.”

Page 8120, line 5. NOy includes species other than NO2, NO, HNO3, and NO3 so I don’t understand the logic here. For example, model calculations and measurements suggest that BrNO3, ClNO3, and HNO3 may be present in marine air at roughly comparable mixing ratios [e.g., Keene et al., 2009].

Removed this statement.

Page 8120, line 18. It would be helpful to briefly describe how detection limits were estimated.

Added this text to the last paragraph of section 3:

“The instrument blank was assumed to vary linearly between measured blanks. Each interpolated blank was assigned a standard error equal to the sum in quadrature of the standard errors of the two blank measurements on which it was based. Detectability was assessed by using one-sided t-tests (p=0.05) to test whether the averaged sample points were greater than the averaged interpolated blank points.

Page 8120, lines 21-22. It would be helpful to report the passing efficiency of the inlet.

Added:
“The inlet passing efficiency was not assessed during this study, but a comparable inlet previously showed a passing efficiency of 85% for Cl2 (Finley and Saltzman, 1996).”

Page 8121, lines 20-24. As described in the cited literature, the performance of Cl2 permeation tubes (both permeation rates and specificity) can vary over time and, thus, gravimetric loss may not be a reliable indicator of Cl2 permeation rates. The manufacturer of the tubes used for this study is aware of the problem and, upon request, will provide a procedure to restore specificity (but not necessarily permeation rate) after performance degrades. Consequently, the performance of one tube is not necessary indicative of the performance of another, particularly one that has been subject to different treatment (i.e., transported to and from a remote field site during which a power outage occurred). If performance of the tube used for calibration during this study was not verified via independent (i.e., iodometric) calibration or direct intercomparison with a traceable standard, it would be helpful to do so and to report the results in the revised version of the paper.

The R&D department of the perm tube manufacturer (VICI Metronics) states that a lack of specificity is rarely a problem for high vapor pressure compounds such as Cl2. The most likely contaminant is water. If water were present at significant levels in the perm tube, some Cl2 would hydrolyze to form HOCl. We performed an iodometric calibration at the reviewer’s request. The mass record to accompany it is unfortunately very brief (about a month), but the two tests match within error bars.

We replaced the statement relating to the performance of a comparable perm tube with this:
“There is no evidence that the perm tube mass loss was due to anything other than Cl2 loss. An iodometric calibration of the permeation tube performed in May 2011 matched the inferred Cl2 loss from a concurrent month-long mass record to within experimental error. The permeation tube has never released HOCl at measurable levels.”

How much did sensitivity vary over the course of the study? How was “uncertainty in the instrument sensitivity” estimated and incorporated in the standard error calculation?

Added this text:
“For each HOCl calibration, the uncertainty in sensitivity was calculated as the standard error in averaged

HOCl standard signal, divided by the mixing ratio of HOCl added. The sensitivity standard errors were linearly interpolated between calibrations. The standard error of the calculated mixing ratios was calculated with Gaussian error propagation, incorporating both the standard error in ambient averaged samples and the standard error in interpolated calibration standard error."

The terminology is confusing. In this section, it appears that sensitivity refers to precision (i.e., random variability of replicate measurements). However, elsewhere the authors refer to directional changes in sensitivity between calibrations, which implies changes in instrumental response to a given signal strength. The text should be clarified in this regard.

By sensitivity, we mean instrument response (signal per ppt). We used the words 'sensitivity' and 'response' interchangeably, and perhaps that led to the confusion. We now use 'sensitivity' exclusively.

Page 8122, lines 14 to 15. What does "roughly linear" mean? Suggest replacing with a quantitative descriptor such as the range in correlation coefficient for linear or quadratic calibration regressions.

Added "A 3-point (0, 100, and 200 ppt) calibration conducted on June 1 (day of year 152) yielded a linear fit with r2 = 0.93. A 3-point (0, 37, and 74 ppt) calibration conducted on June 3 (day of year 154) yielded a linear fit with r2= 0.97."

Page 8122, line 18. What does "varied by less than 90%" mean? Relative to what did sensitivity vary? Do the authors mean that instrument response varied by something approaching a factor of two between daily calibrations? In light of this relatively large degree of variability, did the authors test the reliability of the assumption that response varied linearly between the daily calibrations? For example did pressure in the ionization region (to which response is highly sensitive) vary linearly over time? If not, what are the implications for data quality?

For clarification, we now say it "varied by less than a factor of 2" and we have included a time series of instrument sensitivity to HOCl and Cl_2 throughout the measurement period. The source pressure was not continuously logged so we do not know that variations in sensitivity were linear between calibrations.

We added this text:
"This pressure was not dynamically controlled and tended to decrease over time. Both before and after readjusting the pressure, an HOCl calibration was taken."

Page 8124, lines 22-24, and Table 2. To facilitate comparison with published measurements, it would be helpful to add temperature, relative humidity, and the air concentrations of a sea-salt tracer and of non-sea-salt SO42- to Table 2. Presumably particulate ions were allowed to vary. The rationale for initializing species that were not measured should also be explained.

The following were added to Table 2: Cl-: 22.5 ug/m3, T= 296 K, RH= 0.8. nss-SO4: 0.12 ug/m3.

Added this text to the model desription:
"The initial HCHO mixing ratio (300 ppt) is within the range of values found by Still et al. (0.13-1.15, 2006) in the MBL. The DMS flux maintains a 13-35 ppt DMS diurnal cycle, and the NH3 flux maintains NH3 levels of about 130 ppt, within the wide range of values in the MBL (Quinn et al., 1987)."

How did the authors account for the turnover of species that were allowed to vary? For example, volatile inorganic Br in marine air is typically greater than the corresponding deficit relative to sea salt because it has a longer atmospheric lifetime against deposition than does the parent aerosol. Realizing this aspect of "steady state" in the simulations would require that aerosols turnover in the model. Did they and if so at what rate? If not, the text should so indicate and briefly discuss the implications of ignoring the deposition and emission of reactive species.

Added "The turnover times for coarse and fine aerosol were 2 days and 7 days, respectively."

Page 8125, lines 20-21 and onward. An additional source is only one of several possible explanations for the discrepancy between simulated and measured HOCl. These results suggest that HOCl vapor is produced more rapidly and/or lost more slowly in ambient air relative to the model. This could be explained by the same sources and sinks but with different rate constants in air relative to the model. Indeed, slower uptake of HOCl by aerosols is considered as a possible explanation later in the manuscript. Alternatively, as the authors suggest, an additional source or sources not considered in the model could be involved.

We agree that this statement may be too narrow. Changed it to:
"The base case simulation does not demonstrate good agreement with the HOCl and Cl2 observations, even with major perturbations aimed at improving agreement."

Pages 8127-8128, Section 5.3. Based on similar pathways in chlorinated water supplies, it seems reasonable to speculate that some HOCl reacts with organics associated with marine aerosol to form organochlorine products. However, the almost completely unconstrained nature of the model parameterization renders simulated results little more than a wild guess. In the absence of additional evidence, I suggest that authors consider dropping this section although the speculation may warrant a sentence or two that could be consolidated in the preceding section.

We feel that the model simulation has value even though it is unconstrained. The model result shows that a large supply of highly Clx-reactive organics are required to significantly slow the HOCl recycling rates in aerosols. That result might be useful in providing guidance for future attempts to detect the presence of such compounds in aerosols.

Page 8129, line 20. Relative to HNO3, SO2 and other acids including HCl, HCOOH, and CH3COOH are typically present at much higher mixing ratios in this region [e.g., Lee et al., 2010, ACP]. Consequently, most alkalinity associated with fresh marine aerosols will be titrated by acids other than HNO3. SO2 uptake and oxidation via O3 slows greatly after all alkalinity has been titrated but HNO3 continues to accumulate towards thermodynamic equilibrium, which would displace the less soluble acids (HCl and carboxylics) that would have been scavenged by freshly produced, alkaline aerosol. In addition, Chameides and Stelson [1992] investigated the potential role of S(IV) in acidifying sea salt. HNO3 was not evaluated explicitly. Erickson et al. [1999] (cited elsewhere in the manuscript) modeled the roles of HNO3, SO2, and HCl in the initial chemical evolution of fresh marine aerosol.

The Erickson reference has been added and the text was changed to:
"Seasalt aerosols originate at pH ~ 8 but rapidly acidify due to uptake of gas phase acids and aqueous oxidation of S(IV)."

Page 8130, lines 16-19. This interpretation is potentially misleading. As mentioned at the end of this section, the production and processing of halogen nitrates significantly accelerates oxidation of NOx to HNO3. In the absence of halogen chemistry, NOx mixing ratios would be substantially higher, which would in turn sustain higher OH and O3 mixing ratios. However, in the simulations, NOx was held constant and consequently the overall impact of halogens on oxidation processes is not realized in the simulations. This important point should be mentioned. The indirect effects of halogen chemistry on oxidation processes via accelerated NOx destruction are of comparable magnitude to the direct influences via halogen-atom reactions.

Added:
"This approach allows the comparison of two situations with otherwise equivalent chemistry but where one excludes halogen chemistry. This is useful for directly comparing certain impacts of halogens, but it is not useful for understanding the net oxidative impacts of halogens in the MBL. For example, the presence of halogens draws down NOx levels, which would in turn result in lower O_3 levels. Fixing NOx and O_3 prevents this effect from being realized in the model runs."

Pages 8133, lines 1-5. I'm a bit confused by this interpretation. Model calculations cited in the manuscript suggest that, under the moderately polluted conditions considered by the authors, fresh marine aerosol would be rapidly acidified in a matter of seconds to a few minutes, which implies that conversion of Cl2 to HOCl would be relatively unimportant. Acidic aerosol should be a net source not sink for Cl2. In contrast, some evidence cited in the manuscript indicates that uptake of HOCl by marine aerosol may be overestimated in the model. This latter explanation for the discrepancy between modeled versus measure ratios of Cl2 to HOCl seems equally (if not more) plausible than that based on significant conversion of Cl2 to HOCl in fresh aerosol.

We agree. The paragraph has been modified to end as follows:

"The modeling results presented here do not definitively confirm or refute any of these possibilities. They may all be involved in controlling Clx cycling in marine air."

If an organic film slows HOCl uptake by aerosols, presumably, it would also slow HOBr uptake, which could help explain a long-standing puzzle. MECCA consistently overestimates rates of Br cycling through the aerosol relative to expectations based on observations (i.e., Br deficits relative to sea salt in simulations based on the MECCA scheme are consistently greater than those measured [e.g., Sander et al., 2003, ACP; Keene et al., 2009, ACP; among others]). Slower uptake of HOBr would slow rates of Br activation via BrCl and Br2 production, which presumably would result in higher, more representative steady-state concentrations of particulate Br in the aerosol.

Good point. Added this at the end of Section 5.4:
"In particular, model overestimation of aerosol HOBr uptake could at least partially explain why models tend to overestimate Brx cycling in aerosols (Sander et al., 2003, Keene et al., 2009)."

A related issue that the authors may wish to address involves the potential implications for simulated Cl chemistry associated with the unreasonably rapid Br cycling in the model. For example, lower particulate Br concentrations in modeled versus ambient aerosols implies more efficient production of BrCl relative to Br2 in the model (R11 and R12, respectively, on page 8118) compared to ambient air [Fickert et al., 1999, JGR]. Relative to a model that reliably simulates Br cycling, the greater simulated production of atomic Cl by the photolysis of the 'extra' BrCl would yield additional HOCl (via R8 and R9 on page 8118) but no Cl2. In other words, relative to the MECCA scheme as currently configured, slower, more realistic Br chemistry in a model should yield relatively lower simulated ratios of HOCl to Cl2, which would exacerbate the discrepancy between the measured and modeled results.

Another good point. We added this text to the modeling section (already noted above):
"As noted above, BrCl has not been observed in marine air at levels above the 2 ppt detection limit of our instrument. If the model overpredicts daytime BrCl production, the underprediction of HOCl in the model is an even larger problem than it first appears."