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Effects of halogens on European air-quality
1 Introduction

Over the last decade, there has been increasing evidence, from both an observational and modelling perspective, that halogens (Cl, Br and I) play a role in determining the composition of the troposphere. Different studies have emphasised either the regional impact of these species, or, their global impact. They have also tended to focus on the chemistry of chlorine, iodine or bromine, with few studies investigating the coupled chemistry of all three.

The tropospheric chemistry of halogens is complex (see recent review by Simpson et al. and references within) with significant uncertainties remaining, particularly in some aspects of the gas-phase chemistry of iodine and in the heterogeneous processing of all halogens. Interactions between the halogens and HO\(_2\), BrNO\(_2\), and volatile organic compounds (VOC) species leads to halogens having a pervasive influence throughout the tropospheric chemistry system. The chemistry of Br and I is thought to lead to reductions in O\(_3\) and OH mixing ratios globally whereas the chemistry of Cl is thought to lead to both increases in O\(_3\) due to more rapid oxidation of VOCs and decreases due to halogen nitrate hydrolysis reducing O\(_3\) production (via decreasing NO\(_3\)). However, the calculated magnitude of these impacts will be critically dependent on the emissions and chemistry of halogens used.

Both biogenic and anthropogenic sources of gas-phase halogen precursors exist, from a mix of oceanic, terrestrial, and anthropogenic sources. The oceanic source of halocarbons can be spatially variable reflecting different ecosystems and driving processes. For example, areas of tidal sea-weed can have significant emissions of iodine precursor gases which vary with the tide state. For iodine, chemistry involving atmospheric ozone and ocean iodide within the surface micro-layer of the ocean leads to the emission of inorganic (HOI, I\(_2\)) species. Other sources of halogens into the troposphere can also occur such as direct emissions (e.g. HCl/Cl\(_2\)) or transport from the stratosphere.

The largest emission of bromine and chlorine into the atmosphere comes from sea-salt aerosol. However this aerosol phase and bromide must be liberated by heterogenous chemistry to become a gas-phase source. Different mechanisms allow for activation to the gas phase: acid displacement (e.g. HNO\(_3\)); uptake of N\(_2\)O\(_5\) to sea-salt to liberate ClNO\(_2\); uptake of other halogen species (HOBr, HOI, BrNO\(_3\), HOB, etc) to liberate dihalogen species (ICl, IBr, BrCl, Cl\(_2\)).

Measuring the concentration of reactive halogen species in the atmosphere is difficult due to their low mixing ratio and reactivity. Although there remains some debate, recent observations have demonstrated the pervasive existence of bromine and iodine species throughout the troposphere over oceanic regions by a range of techniques. Highest mixing ratios of these species have been found close to tidal sources but measurable mixing ratios have been found above the remote ocean and in the upper troposphere.

Observations of reactive chlorine species are particularly sparse. However, a relatively large dataset of ClNO\(_2\) observations have now been made which show a build up at night and then a rapid decrease (due to photolysis) at sunrise. The observations in polluted coastal regions are explicable through the uptake of N\(_2\)O\(_5\) onto sea-salt. However, high mixing ratios of ClNO\(_2\) in continental regions have proved harder to explain due to the short lifetime of sea-salt in the atmosphere. Various explanations have been postulated ranging from non-oceanic sources of both natural and anthropogenic chlorine species to the movement of chloride from sea-salt to fine mode sulfate aerosol via gas phase chemistry.

Previous model studies of Br and I chemistry have focussed predominantly on their global scale impacts. Whereas, studies of the impact of Cl have typically focussed on a smaller hemispheric or regional (air quality) scale. The combined impact of all halogens on the regional scale is less well explored. Here, we use a new version of the GEOS-Chem model, which includes a representation of halogen chemistry run in its regional grid configuration for Europe to explore the roles that halogens may play in controlling European air quality with a focus on O\(_3\). We focus on the summer of 2015 as this allows us access to an observational dataset made on the North Sea coast of the UK. We explore the model fidelity against this data and that offered from the UK air quality network. We explore the differing role of halogens in determining both O\(_3\) concentrations through changes to regional scale chemistry and the hemisphere background. We then consider impacts of halogens on oxidation and contribution of atomic chlorine. The relative contribution of the halogen families on O\(_3\) are then considered, and the impacts on aerosol concentrations. Finally we suggest future areas of research to allow better representation of the halogen chemistry of the atmosphere on a regional scale.

2 Experimental

2.1 Observations

The Integrated Chemistry of Ozone in the Atmosphere (ICOZA) campaign at the Weybourne Atmospheric Observatory (52.95°N, 1.12°E) was designed to examine the composition of the atmosphere and local chemical processes at a coastal site in the UK during the summer of 2015 (29th June-1st August). Weybourne is a World Meteorological Organisation (WMO) Global Atmospheric Watch (GAW) programme site. In addition to the standard observations (CO, and O\(_3\)), additional NO\(_x\) (NO, NO\(_2\), total reactive nitrogen (NO\(_x\)), nitryl chloride (ClNO\(_2\)) and molecular chlorine (Cl\(_2\)) measurements were made during this period.

The NO, NO\(_2\) and NO\(_x\) observations were made ~4 m above ground level. The NO and NO\(_2\) measurements were made using...
a dual channel Air Quality Design Inc. (Golden, Colorado, USA) chemiluminescent instrument equipped with a UV-LED photolytic NO\textsubscript{2} converter as described by Reed et al.\textsuperscript{44,46} NO\textsubscript{3} was measured using a Thermo Environmental 42i TL NO\textsubscript{3} analyser equipped with a molybdenum catalytic converter. A second high temperature (375°C) molybdenum converter was placed upstream directly at the gas inlet. Heated molybdenum catalysts have been shown to convert NO\textsubscript{x} species such as PAN, HNO\textsubscript{3} and particulate nitrate into NO\textsubscript{2}.\textsuperscript{47-50} Limits of detection were 1.5 pmol mol\textsuperscript{-1} and 1.9 pmol mol\textsuperscript{-1} averaged over 1 minute for NO and NO\textsubscript{2}, and 50 pmol mol\textsuperscript{-1} averaged over 1 minute for NO\textsubscript{3}.

Carbon monoxide (CO) observations are part of the National Centre for Atmospheric Sciences (NCAS) long-term measurement programme and O\textsubscript{3} observations are part of the Department for Environment, Food and Rural Affairs (DEFRA) Automatic Urban and Rural Network (AURN). It was measured by a Reduction Gas Analyser (RGA3, Trace Analytical, Inc., California, USA) to the WMO CO X2004 scale and O\textsubscript{3} was measured using UV absorption (TE49i, Thermo Fisher Scientific Inc.).

The observations of CINO\textsubscript{2} and Cl\textsubscript{2} were made with the University of Leicester Chemical Ionization Mass Spectrometer (CIMS). The instrument, manufactured by THS Instruments (Georgia, USA), is based on the CIMS technique described by Slusher et al.,\textsuperscript{51} and is similar in configuration to the instrument used by Liao et al.\textsuperscript{52} The Leicester CIMS was calibrated for Cl\textsubscript{2}, using a certified standard by BOC (5 μmol mol\textsuperscript{-1} in nitrogen), and for CINO\textsubscript{2}, using the methodology described by Thaler et al.\textsuperscript{53} The detection limit was 8.5 pmol mol\textsuperscript{-1} for Cl\textsubscript{2} and 5.1 pmol mol\textsuperscript{-1} for CINO\textsubscript{2}. The instrument and the measurements are discussed in more detail in Sommariva et al. (in prep.).

Wider UK air-quality observation data (O\textsubscript{3}, NO\textsubscript{2}, PM\textsubscript{2.5}) from the DEFRA’s AURN\textsuperscript{54} was extracted for the period of observations using the OpenAir R package.\textsuperscript{55}

2.2 Modelling

We used the GEOS-Chem model (version 10-01, http://www.geos-chem.org), which includes O\textsubscript{3}, HO\textsubscript{x}, NO\textsubscript{x}, and VOC chemistry\textsuperscript{56} and a mass based aerosol scheme.\textsuperscript{57,58} The model also has a representation of bromine and chlorine chemistry,\textsuperscript{8,59} which has updated further to include (Cl, Br, I) chemistry\textsuperscript{11,15} as described by Sherwen et al.\textsuperscript{12} The chlorine scheme is described by Schmidt et al.,\textsuperscript{11} with additions described in Sherwen et al.\textsuperscript{15} including further reactions of chlorine and bromine with organics, CINO\textsubscript{2} emission following N\textsubscript{2}O\textsubscript{5} uptake on sea-salt,\textsuperscript{60} and heterogenous iodine cycling to produce IX (X=Cl,Br).\textsuperscript{29} The model is run without sea-salt de-bromination following Schmidt et al.,\textsuperscript{11} and does not contain acid displacement of chloride or anthropogenic chloride sources. The halogen cross-sections and rates have been updated to latest NASA-JPL (15-10) recommendations.\textsuperscript{16}

The model includes biogenic emissions (MEGAN\textsuperscript{61}), biomass burning (GFED\textsuperscript{42}), biofuel emissions,\textsuperscript{63} and aerosols emissions (inc. dust,\textsuperscript{57} sea-salt,\textsuperscript{58} and black and organic carbon\textsuperscript{64}) as well as NO\textsubscript{x} from Lightning,\textsuperscript{65} soils,\textsuperscript{66} and aircraft.\textsuperscript{67} For anthropogenic emissions, the model uses the Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP) emissions (http://www.emep.int) for NO\textsubscript{x},\textsuperscript{68} SO\textsubscript{x},\textsuperscript{69} CO, and NH\textsubscript{3} for the latest available year (2013). EMEP anthropogenic VOC emissions are also used here, but for 2012. Emissions for formalddehyde and acetone were scaled from the EMEP acetaldehyde emissions, ethane emissions were scaled from the EMEP propane emission, and a scaling factor was applied to the acetaldehyde emission following the approach taken previously in Dunmore et al.,\textsuperscript{70} and described in table S11 in the supplementary information.

The halogen emissions used are as described in Sherwen et al.\textsuperscript{12} Emissions of organic iodine species are taken from the monthly values of Ordonez et al\textsuperscript{71} at 1x1°. Emissions of inorganic iodine (I\textsubscript{2}, HOI) use the parameterisation of Carpenter et al.,\textsuperscript{22} which describes a dependancy on model parameters of surface O\textsubscript{3} mixing ratio, wind speed, and ocean surface iodide concentrations. Ocean surface iodide concentrations are parameterised based on sea-surface temperatures following MacDonald et al.\textsuperscript{25} Coastal and tidal processes are not considered here, and the 1x1° resolution of the organic emissions cannot be expected to capture very localised halogen sources.

The GEOS-Chem model is run at two resolutions. A global simulation (4x5°) generates boundary conditions to allow “nesting” of a domain at a ∼25 km (0.25x0.3125°) resolution covering a domain (32.75-61.25°N, -15-40°E) over Europe. The global model is run for two years (1\textsuperscript{st} January 2004-1\textsuperscript{st} January 2006), with the first year discarded as “spin up”. Using the March 1st 2005 concentrations fields for March 1st 2015, the global model is run for three further months of “spin up” and to cover the observational period in order to generate boundary conditions. The regional model is then run from two weeks prior to the observational period (as “spin up”), before running for the campaign period (29\textsuperscript{th} June-1\textsuperscript{st} August 2015) using the boundary conditions generated by the global model.

PM\textsubscript{2.5} is calculated from the model based on the mass of sulfate, nitrate, ammonia, hydrophilic and hydrophobic carbon, sea-salt, and dust, assuming relative humidity of 50 %. Using the assumed value of 50 % relative humidity allows for comparison with DEFRA observations which follows the method prescribed by European Committee for Standardisation (EN 14907). The coarse mode sea-salt and the two largest dust size bins are ignored for the calculation. We have not used the model’s secondary organic aerosol scheme in these model simulations. A full description of the PM\textsubscript{2.5} calculation is given in supplementary information table SI2.
Model runs performed are described in Table 1. Simulations were performed with halogen chemistry switched on (“HAL”) and off (“NOHAL”) in both the global (to generate the boundary conditions) and regional model. A simulation was also performed using the boundary conditions calculated with the halogens switched off but with the halogen chemistry in the European domain switched on (“HAL-LOCAL”). A final simulation (“NOCINO2”) was performed with halogen chemistry in both the regional and local version of the model but with the uptake of N₂O₅ uptake on sea-salt aerosol leading to the production of 2HNO₃ rather than HNO₃ + ClNO₂.

### Table 1 Model runs

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Regional model chemistry</th>
<th>Boundary condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAL</td>
<td>Halogens on.</td>
<td>Halogens on.</td>
</tr>
<tr>
<td>NOHAL</td>
<td>Halogens off.</td>
<td>Halogens off.</td>
</tr>
<tr>
<td>HAL-LOCAL</td>
<td>Halogens on.</td>
<td>Halogens off.</td>
</tr>
<tr>
<td>NOCINO2</td>
<td>Halogens on. No ClNO₂ production</td>
<td>Halogens on.</td>
</tr>
</tbody>
</table>

### 3 Model performance

Figure 1 shows the averaged modelled (“HAL”) surface distribution of O₃, NO₂, CO and PM₂.₅ for the period from 29th July to 1st August 2015. Highest O₃ mixing ratios are evident in southern Europe and over the Mediterranean, with evidence for a reduction in O₃ mixing ratios over the northern cities compared to the rural values due to reaction of O₃ with NO. NO₂ mixing ratios are spatially variable reflecting its short lifetime, with cities and ship tracks evident. CO mixing ratios are similar to those from NO₂ but are more diffusive and don’t show the ship tracks. The distribution of PM₂.₅ shows similarities to the CO and NO₂ reflecting common sources.

There are fewer studies assessing the performance of the European grid version of the GEOS-Chem model against observations compared to the model’s other regional variants (e.g. North American, China). Future studies are required to evaluate the model against observations more comprehensively. The AirBase dataset is well suited for this task but this data is not currently available for 2015. Instead here we make some provisional assessment of the model against two observations datasets of standard air quality pollutants. First, against a sub-set of observations made at Weybourne as part of the Integrated Chemistry of Ozone in the Atmosphere (ICOZA) campaign and secondly against the observations made as part of the UK AURN network.

Once we have evaluated the model against these compounds we turn our attention to its simulation of halogen compounds

#### 3.1 General model performance

A comparison between a sub-set of the observations (O₃, CO, NOₓ and NO₂) made as part of the ICOZA campaign and the model (“HAL”) are shown as a time-series in Figure 2 and as an average diel cycle in Figure 3. The model captures much of the observed synoptic timescale variability in these species. Notable exception include the failure to simulate the very high O₃ mixing ratios occurring at the start of the campaign and the high CO mixing ratios in the middle of the campaign. The diel average shows a reasonable ability to reproduce the daily signal in these compounds other than for CO where the model shows a significantly larger cycle than is observed. The model has an average low bias of 9.2, 0.7, 2.5, and 11 %, for O₃, NOₓ, NO₂ and CO respectively.

To give a wider geographical comparison, the model (“HAL”) was compared against hourly O₃, PM₂.₅, and NO₂ observations from the UK AURN air quality network. Sites reporting data and classed as “rural”, “rural background” or “urban background” by DEFRA are used for the comparison. Sites influenced by localised emissions (e.g. roadside sites) are excluded as they are unlikely to provide an appropriate comparison for a model run at 0.25° resolution. A point-by-point comparison between the hourly measured and the spatially and temporally equivalent model values for O₃ is given in the supplementary figure S13. The model fails to capture peak O₃ mixing ratios, which could be expected considering the limited reactive organics present in the model and could also contribute towards the slight underestimate in average O₃ mixing ratios between observation and the “HAL” simulation shown in Figure 3.

The probability distribution of the O₃ observations, and the model simulation for the AURN sites for the “HAL”, “NOHAL”, “HAL-LOCAL” simulations are shown in Figure 4 (with equivalent log plots shown for PM₂.₅ and NO₂ in the supplementary figures S14 and S15). The model without halogen chemistry in either the boundary conditions or in the region (“NOHAL”) shows substantially higher mixing ratios of O₃ (mean of 34.5 nmol mol⁻¹, 25th percentile=28.5 nmol mol⁻¹ and 75th percentile=41.1 nmol mol⁻¹) than observed (mean=27.0 nmol mol⁻¹, 25th percentile=19.0 nmol mol⁻¹ and 75th percentile=32.8 nmol mol⁻¹). The model without the halogen chemistry in the boundary conditions (“HAL-LOCAL”) calculates similarly higher O₃ mixing ratios. However, including halogen chemistry in both the boundary conditions and in the domain leads to a substantial decrease in the modelled O₃ mixing ratios (mean reduction of 26.1 %) improving the simulation (mean=25.5 nmol mol⁻¹, 25th percentile=19.5 nmol mol⁻¹ and 75th percentile=31.1 nmol mol⁻¹).

Unlike for O₃, where large changes are seen on inclusion of halogens, modest changes are seen for NO₂ and PM₂.₅ (Supplementary plots S17 and S18). For NO₂ the mean hourly modelled mixing ratio for the “HAL” simulation is 6.7 (25th percentile=1.4 and 75th percentile=9.5) nmol mol⁻¹ whereas the mean in the “NOHAL” simulation is 7.1 nmol mol⁻¹. Both can be compared to the observational mean of 7.7 (25th percentile=2.6
A number of high-confidence aerosols have occurred over the North Pacific.

The model predicts a maximum mixing ratio of 2.0 g mol⁻¹ at 180°E and 30°N, with peak mixing ratios of 3.0 g mol⁻¹ at 130°E and 30°N. These observations, which are also consistent with the model simulations, further support the hypothesis that the model is an accurate representation of the observed mixing ratios.

3.2 Model simulations of reactive halogen in Europe

The simulation of the model is shown in Fig. 4. The model simulations are compared with observations from the Global Atmosphere Watch (GAW) network. The model results are in good agreement with the observations, particularly in the regions with high mixing ratios. The model also shows good agreement with the observations in the regions with low mixing ratios.

4 Conclusion

The model simulations of reactive halogen in Europe are in good agreement with the observations. The model is able to reproduce the observed mixing ratios and provide a comprehensive understanding of the processes involved. The model results can be used to improve our understanding of the impact of reactive halogen on the atmosphere.

Fig. 1: Mean modeled surface O₃ mixing ratios (in ng m⁻³) for the period 1 January to 31 December 2015. The mean modeled surface O₃ mixing ratios are shown for the observation period (29 January to 31 December 2015). The model simulations are compared with observations from the Global Atmosphere Watch (GAW) network. The model results are in good agreement with the observations, particularly in the regions with high mixing ratios. The model also shows good agreement with the observations in the regions with low mixing ratios.
Fig. 6 shows the observed and modelled time-series and mixing ratios of CO during the observational period. The modelled mixing ratios are in reasonable agreement with the observations, particularly for the later part of the observational period. However, the model slightly underestimates the mixing ratios in the early part of the period. The modelled mixing ratios for CO are in good agreement with the observations, particularly for the later part of the period. However, the model slightly underestimates the mixing ratios in the early part of the period.

Fig. 7 shows the observed and modelled time-series and mixing ratios of NO during the observational period. The modelled mixing ratios are in reasonable agreement with the observations, particularly for the later part of the period. However, the model slightly underestimates the mixing ratios in the early part of the period. The modelled mixing ratios for NO are in good agreement with the observations, particularly for the later part of the period. However, the model slightly underestimates the mixing ratios in the early part of the period.

In summary, the modelled mixing ratios are in reasonable agreement with the observations, particularly for the later part of the period. However, the model slightly underestimates the mixing ratios in the early part of the period.

Fig. 8 shows the observed and modelled mixing ratios of CH4 during the observational period. The modelled mixing ratios are in reasonable agreement with the observations, particularly for the later part of the period. However, the model slightly underestimates the mixing ratios in the early part of the period. The modelled mixing ratios for CH4 are in good agreement with the observations, particularly for the later part of the period. However, the model slightly underestimates the mixing ratios in the early part of the period.

In summary, the modelled mixing ratios are in reasonable agreement with the observations, particularly for the later part of the period. However, the model slightly underestimates the mixing ratios in the early part of the period.
Figure 4 shows the difference in the mean surface O$_2$ mixing ratio between simulations with hydrogen (H$_2$), nitrogen (N$_2$), and air (O$_2$). The model shows that the mean surface O$_2$ mixing ratio is higher in the model with air than in the model with hydrogen or nitrogen. This suggests that the presence of oxygen in the atmosphere is crucial for maintaining high O$_2$ mixing ratios.

Figure 5 presents the modelled surface mixing ratios of O$_2$, N$_2$, and O$_3$ over Europe. The model shows that the O$_2$ mixing ratio is highest in the model with air, while the N$_2$ mixing ratio is highest in the model with nitrogen. The O$_3$ mixing ratio is highest in the model with hydrogen, which indicates that hydrogen is more reactive with oxygen than nitrogen.

The observations of O$_3$ show good agreement with the model predictions, indicating that the model is capable of accurately simulating the chemical processes in the atmosphere.

In conclusion, the model accurately predicts the O$_2$ mixing ratio and provides insights into the impact of different atmospheric compositions on O$_2$ dynamics. The model also highlights the importance of oxygen in maintaining high O$_2$ mixing ratios, which is crucial for the health of the atmosphere.
conditioned compared to marine regions.

Table 2: Molecular oxygen and photodissociation of NO in the boundary layer of the marine environment and the continental shelf. The data are presented in the form of box plots, showing the median and interquartile range. The bottom and top of the box represent the 25th and 75th percentiles, respectively.

Table 2: Molecular oxygen and photodissociation of NO in the boundary layer of the marine environment and the continental shelf.

<table>
<thead>
<tr>
<th>Region</th>
<th>Median (ppb)</th>
<th>Interquartile Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marine</td>
<td>178</td>
<td>121-230</td>
</tr>
<tr>
<td>Continental</td>
<td>200</td>
<td>150-250</td>
</tr>
</tbody>
</table>

Figure 2: Difference in surface mean O mixing ratio between NH$_3$ and NO$_x$. Significant reduction in NH$_3$ mixing ratio observed over the continental shelf compared to the marine environment.
The European Commission (2010a, b) in the presence of NO
discussions on the European Union’s views of CO2 emissions and

European Corridors of Growth (2009). The European Commission

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8 Conclusions and discussion

Increased SO2 production (HNO3) on aerosols has been discussed, which may lead to increased NOx production. The oxidation of aerosols by hydrogen peroxide (HO2) through the oxidation of aerosols of NOx for SO2 increases the oxidation of aerosols of NOx for SO2. However, the mechanisms may be different, depending on the conditions. Figure 12 shows the change in the oxidation of aerosols of NOx for SO2. Significant increases in the oxidation of aerosols of NOx for SO2 are seen in the conditions of SO2 emissions. In the presence of NOx, the oxidation of aerosols of NOx for SO2 is enhanced. In opposition, the absence of NOx decreases the oxidation of aerosols of NOx for SO2. These suggest that the oxidation of aerosols of NOx for SO2 is enhanced in the presence of NOx, while it is decreased in the absence of NOx.

The increase in NOx emissions due to the production of NOx from photochemical reactions is significant. In the presence of NOx, the oxidation of aerosols of NOx for SO2 is enhanced. In opposition, the absence of NOx decreases the oxidation of aerosols of NOx for SO2. These suggest that the oxidation of aerosols of NOx for SO2 is enhanced in the presence of NOx, while it is decreased in the absence of NOx.

In our model, the dominant source of reactive chlorine in the boundary layer is the production of NOx from photochemistry, which is in agreement with previous studies. However, the mechanisms may be different, depending on the conditions. Figure 12 shows the change in the oxidation of aerosols of NOx for SO2. Significant increases in the oxidation of aerosols of NOx for SO2 are seen in the conditions of SO2 emissions. In the presence of NOx, the oxidation of aerosols of NOx for SO2 is enhanced. In opposition, the absence of NOx decreases the oxidation of aerosols of NOx for SO2. These suggest that the oxidation of aerosols of NOx for SO2 is enhanced in the presence of NOx, while it is decreased in the absence of NOx.

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the UK air quality network shows some skill in capturing mean mixing ratios and diel cycle of $O_3$, NO$_2$, NO$_x$, and PM$_{2.5}$ concentrations, however a more extensive assessment of the model in this configuration is needed. Comparisons between observations of CINO$_2$ made at Weybourne, show a model over estimate on average. However, the model significantly underestimates CINO$_2$ observations reported for more inland regions suggesting some missing processes. The mixing ratios of inorganic bromine and iodine species reported from European sites are significantly higher than those calculated. This likely reflects the the lack of realistic representation of coastal processes in the model.

Halogen chemistry has a significant impact on the $O_3$ mixing ratios calculated over Europe. The north of Europe is mainly sensitive to the reduction in the global $O_3$ background, whereas the south (notably the Mediterranean) is sensitive to the local halogen chemistry. Chlorine from ClNO$_2$ leads to a small regional increases in $O_3$ but this is overwhelmed by the decreases caused by the other halogens. We find that mean surface $O_3$ mixing ratios significantly reduced by an overage of 13.5 nmol mol$^{-1}$ (25 %), with the frequency of hourly mean surface $O_3$ mixing ratios above 50 nmol mol$^{-1}$ falling from 46 % to 18%. The frequency of occurrence of hourly mean surface ozone mixing ratios above 70 nmol mol$^{-1}$ falls from 15.1% to 0.9%. Halogen chemistry may therefore play an important role in determining the $O_3$ exposure over Europe. Oxidant mixing ratios are changed by halogens with OH at the surface dropping due to a reduction in primary production. Atomic Cl leads to some additional oxidation of VOCs notably for ethane, propane and acetone. Halogens appear to have little impact on aerosol mixing ratios.

Given these simulations it would appear that halogen chemistry may play a significant role in determining the $O_3$ mixing ratios found during summertime in Europe, and should be included in model analyses. Further studies are necessary to confirm these findings and to evaluate whether they have any specific relevance to European air quality policy. For example, do regions change or VOC limited on inclusion of the halogens? How does the model respond to future emissions scenarios? It would be surprising if Europe was alone in this sensitivity. Previous global model simulations$^{12}$ show other regions where halogens may play a role in determining the $O_3$ concentrations such as the west coast of the United States and Canada, western India, northern Japan, southern West Africa etc. Air quality simulations for these regions may similarly be sensitive to the inclusion and representation of halogen chemistry.

However, there is little observational constraint on these conclusions. The current set of observations of halogens in Europe are sparse and potentially biased by coastal specific processes. Future efforts to provide observations of atmospheric chlorine, bromine and iodine species in a range of environments, together with ocean iodide observations especially in the Mediterranean would provide a useful constraint here. Continued development of the laboratory measurements especially of the heterogenous phase chemistry would also help to provide a better basis for these model simulations and our understanding of the role of halogen chemistry in determining air-quality.

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