














Effects of halogens on European air-quality†

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Halogens (Cl, Br) have a profound influence on stratospheric ozone (O₃). They (Cl, Br and I) have recently also been shown to impact the troposphere, notably by reducing the mixing ratios of O₃ and OH. Their potential for impacting regional air-quality is less well understood. We explore the impact of halogens on regional pollutants (focussing on O₃) with the European grid of the GEOS-Chem model (0.25° × 0.3125°). It has recently been updated to include a representation of halogen chemistry. We focus on the summer of 2015 during the ICOZA campaign at the Weybourne Atmospheric Observatory on the North Sea coast of the UK. Comparisons between these observations together with those from the UK air-quality network show that the model has some skill in representing the mixing ratios/concentration of pollutants during this period. Although the model has some success in simulating the Weybourne ClNO₂ observations, it significantly underestimates ClNO₂ observations reported at inland locations. It also underestimates mixing ratios of IO, OIO, I₂ and BrO, but this may reflect the coastal nature of these observations. Model simulations, with and without halogens, highlight the processes by which halogens can impact O₃. Throughout the domain O₃ mixing ratios are reduced by halogens. In northern Europe this is due to a change in the background O₃ advected into the region, whereas in southern Europe this is due to local chemistry driven by Mediterranean emissions. The proportion of hourly O₃ above 50 nmol mol⁻¹ in Europe is reduced from 46% to 18% by halogens. ClNO₂ from N₂O₅ uptake onto sea-salt leads to increases in O₃ mixing ratio, but these are smaller than the decreases caused by the bromine and iodine. 12% of ethane and 16% of acetone within the boundary layer is oxidised by Cl. Aerosol response to

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halogens is complex with small (~10%) reductions in PM_{2.5} in most locations. A lack of observational constraints coupled to large uncertainties in emissions and chemical processing of halogens make these conclusions tentative at best. However, the results here point to the potential for halogen chemistry to influence air quality policy in Europe and other parts of the world.

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.¹ Different studies have emphasised either the regional impact of these species,^{2–5} or their global impact.^{6–13} They have also tended to focus on the chemistry of chlorine,^{3,14} iodine^{10,15} or bromine,^{6,8,11} with few studies investigating the coupled chemistry of all three.^{7,12}

The tropospheric chemistry of halogens is complex (see the recent review by Simpson *et al.*¹ and references within) with significant uncertainties remaining, particularly in some aspects of the gas-phase chemistry of iodine and in the heterogenous processing of all halogens. Interactions between the halogens and HO_x, NO_x, and volatile organic compounds (VOC) species leads to halogens having a pervasive influence throughout the tropospheric chemistry system.^{11,12} The chemistry of Br and I is thought to lead to reductions in O₃ and OH mixing ratios globally^{8,10–12} whereas the chemistry of Cl is thought to lead to both increases in O₃ due to more rapid oxidation of VOCs^{2,16} and decreases due to halogen nitrate hydrolysis reducing O₃ production (*via* decreasing NO_x).¹¹ 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.¹ 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.^{17–23} For iodine, chemistry involving atmospheric ozone and ocean iodide within the surface micro-layer of the ocean leads to the emission of inorganic species (HOI, I₂).^{24,25} Other sources of halogens into the troposphere can also occur, such as direct emissions (*e.g.* HCl/Cl₂ (ref. 26 and 27)) or transport from the stratosphere.

The largest emission of bromine and chlorine into the atmosphere comes from sea-salt aerosol. However this aerosol phase chloride 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.* HNO₃); uptake of N₂O₅ to sea-salt to liberate ClNO₂;²⁸ and uptake of other halogen species (HOBr, HOI, BrNO₃, HOBr, *etc.*) to liberate di-halogen species (ICl, IBr, Br₂, BrCl, Cl₂).^{1,29,30}

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. The highest mixing ratios of these species have been found



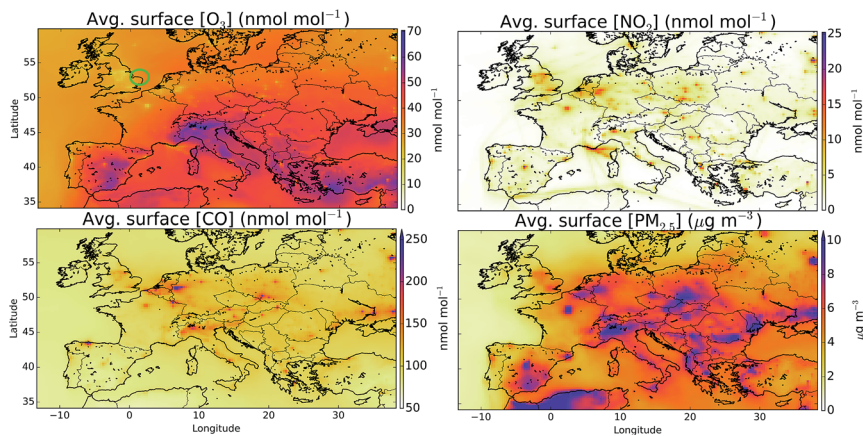


Fig. 1 Mean modelled surface O_3 , NO_2 , CO , and $PM_{2.5}$ mixing ratios/concentrations for the observational period (29th June to 1st August 2015). The green circle on the first plot gives the location of the Weybourne Atmospheric Observatory. Maximum values in plots of CO and $PM_{2.5}$ are $431 \text{ nmol mol}^{-1}$ and $35 \text{ } \mu\text{g m}^{-3}$, respectively.

ratios are evident in southern Europe and over the Mediterranean, with evidence for a reduction in O_3 mixing ratios over the northern cities compared to the rural values due to reaction of O_3 with NO . NO_2 mixing ratios are spatially variable reflecting its short lifetime, with cities and ship tracks evident. CO mixing ratios are similar to those from NO_2 but are more diffusive and don't show the ship tracks. The distribution of $PM_{2.5}$ shows similarities to the CO and NO_2 , reflecting common sources.

There are fewer studies assessing the performance of the European grid version of the GEOS-Chem model against observations⁴³ than for the model's other regional variants (*e.g.* North America,^{41,42} China^{39,40}). Future studies are required to evaluate the model against observations more comprehensively. The AirBase dataset⁷² 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 subset 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 (O_3 , CO , NO_x and NO_y) made as part of the ICOZA campaign and the model ("HAL") are shown as a time-series in Fig. 2 and as an average diel cycle in Fig. 3. The model captures much of the observed synoptic timescale variability in these species. Notable exceptions include the failure to simulate the very high O_3 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



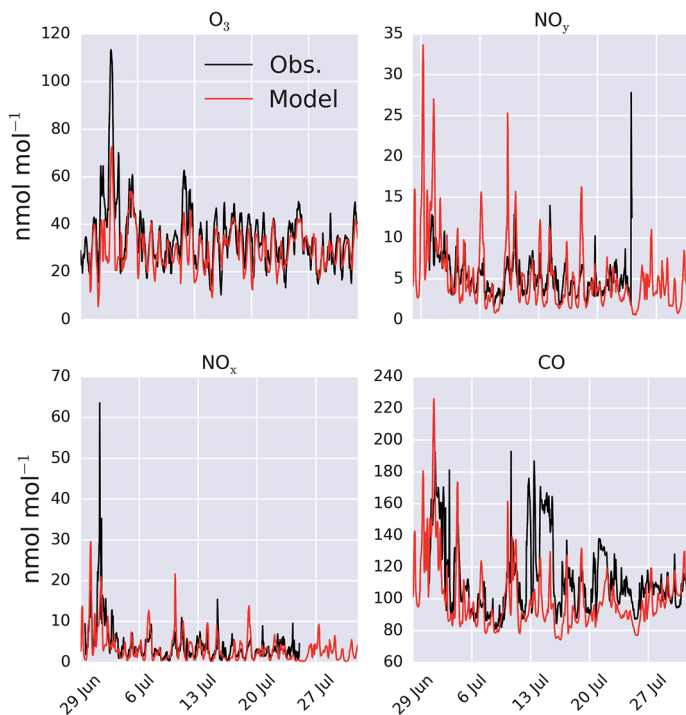


Fig. 2 Modelled (“HAL”) and observed mixing ratio at Weybourne of O_3 , NO_y , NO_x and CO during the observational period.

compounds other than for CO where the model shows a significantly larger cycle than is observed. The model has an average low bias ($(\text{“HAL”}-\text{Obs.})/\text{Obs.}$) of 9.2, 0.7, 2.5, and 11%, for O_3 , NO_x , NO_y and CO respectively.

To give a wider geographical comparison, the model (“HAL”) was compared against hourly O_3 , $PM_{2.5}$, and NO_2 observations from the UK AURN air quality network.⁵⁴ 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 O_3 is given in the ESI Fig. S13.† The model fails to capture peak O_3 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 O_3 mixing ratios between observation and the “HAL” simulation shown in Fig. 3.

The probability distribution of the O_3 observations, and the model simulation for the AURN sites for the “HAL”, “NOHAL”, “HAL-LOCAL” simulations are shown in Fig. 4 (with equivalent log plots shown for $PM_{2.5}$ and NO_2 in ESI Fig. S14 and S15†). The model without halogen chemistry in either the boundary conditions or in the region (“NOHAL”) shows substantially higher mixing ratios of O_3 (mean of $34.5 \text{ nmol mol}^{-1}$, 25th percentile = $28.5 \text{ nmol mol}^{-1}$ and 75th percentile = $41.1 \text{ nmol mol}^{-1}$) than observed (mean = $27.0 \text{ nmol mol}^{-1}$, 25th percentile = 19.0



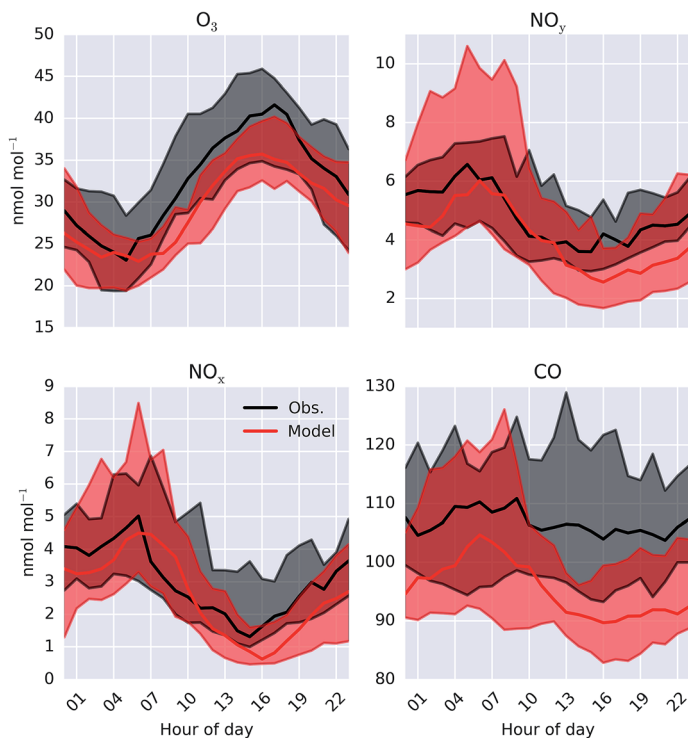


Fig. 3 Modelled ("HAL") and observed median diel mixing ratio at Weybourne of O_3 , NO_y , NO_x and CO during the observational period. Shaded regions give 25th and 75th percentiles.

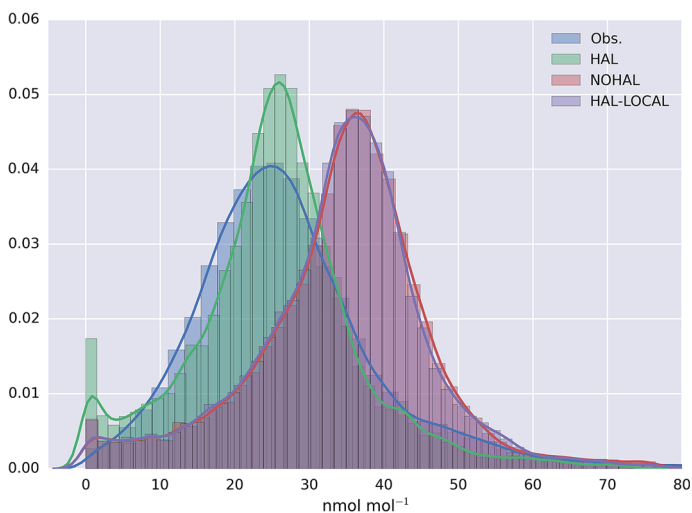


Fig. 4 Probability distribution function of observed and modelled O_3 mixing ratios at selected UK AURN background sites ($N = 63$) for the observation period (29th June to 1st August 2015). Modelled values are shown for the simulation with halogens ("HAL"), without halogens ("NOHAL"), and with halogens only within the European domain ("HAL-LOCAL").



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 PM_{2.5} (ESI plots SI7 and SI8†). 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 and 75th percentile = 10.4) nmol mol⁻¹. For PM_{2.5} the modelled “HAL” mixing ratio was 8.2 (25th percentile = 4.2 and 75th percentile = 9.7) μg m⁻³ with a “NOHAL” mean of 8.6 (25th percentile = 4.3 and 75th percentile = 10.0) and an observed concentration of 8.0 (25th percentile = 4.6 and 75th percentile = 10.0) μg m⁻³.

We now turn our attention to the model’s ability to simulate inorganic halogen compounds over Europe.

3.2 Model simulations of reactive halogens in Europe

The simulation of halogens in the global version of GEOS-Chem and its comparison with observations has been discussed previously.^{11,12} This provided a first broad-brush assessment of the mixing ratio of halogens (mainly IO and BrO). It concluded that the model appears to have some skill in simulating IO and BrO mixing ratios, but appears to underestimate Cl species.

Mean surface mixing ratios of key reactive halogens (BrO, IO and Cl) over Europe are shown in Fig. 5 with mixing ratios of total inorganic halogens (X_y, X = Cl, Br, I) given in the ESI (SI1†). We model the highest halogen mixing ratios over the Mediterranean where emissions are greatest. These emissions are notably high for iodine species where the elevated O₃ together with high sea-surface temperature (which determines the ocean iodide mixing ratio in our simulations^{24,25}) leads to a large inorganic iodine flux. A notable difference exists for Cl_y (Fig. SI1†) where a peak can be also be seen in the North Sea/English channel where high mixing ratios of sea-salt and NO_x lead to high ClNO₂ production.

Observations of bromine and iodine inorganic species have previously been reported for a few boundary layer locations in Europe, for example Ireland,^{17,18} France,^{19–22,73} and Spain.²³ We now compare values reported in the literature to the values calculated in our model for the period of the simulation (for 29th June to 1st August 2015). There are undoubtedly, large seasonal and inter-annual variability in these observations, but this comparison allows a rough assessment of the order of magnitude performance of the model.

A number of field campaigns have occurred over or near tidal coastal zones. IO has been observed at coastal Ireland (Mace Head, 53.3°N, -9.9°E) with peak mixing ratios of between 4 and 50 pmol mol⁻¹.^{74,75} The model predicts a maximum mixing ratio of 0.6 pmol mol⁻¹ here, substantially lower than the observations. IO has also been reported for Brittany (France, 48.7°N, -4.0°E) of between 7.7 (±0.5)⁷⁶ and 30 (±7)⁷³ pmol mol⁻¹ and we again calculate lower values



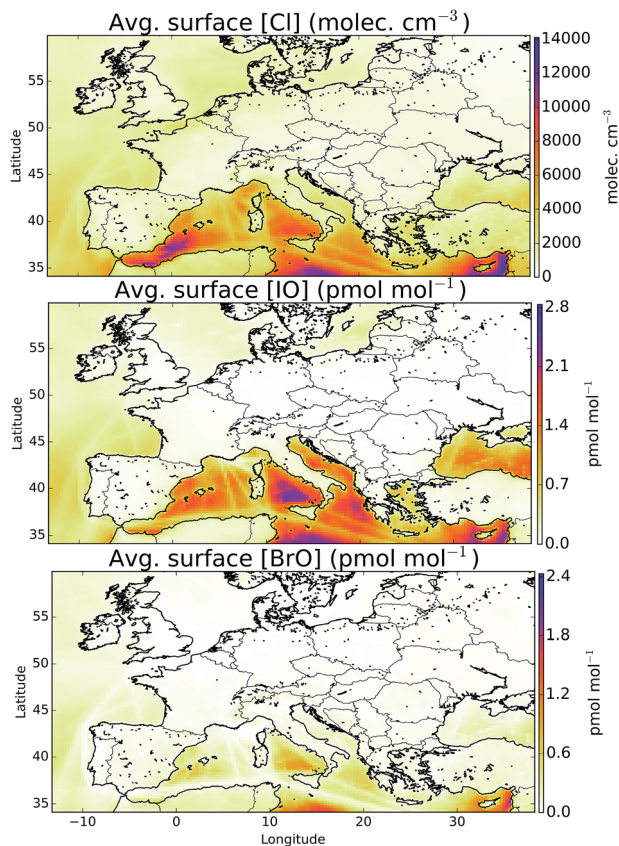


Fig. 5 Mean modelled surface mixing ratios of Cl, IO, and BrO during the observational period.

with a maximum of $0.07 \text{ pmol mol}^{-1}$. Observations 3.5 km inland in Greece (Heraklion, 35.3°N , 25.1°E) report values less than $1.9 (\pm 0.8) \text{ pmol mol}^{-1}$.⁷⁷ The model predicts a maximum mixing ratio of $1.8 \text{ pmol mol}^{-1}$ with an average below the stated limit of detection of the observations ($1.3 \text{ pmol mol}^{-1}$). Peters *et al.*¹⁸ report peak IO observations in Germany (Dagebüll, 54.7°N , 8.7°E) of $2.0 (\pm 0.7) \text{ pmol mol}^{-1}$ and Oetjen⁷⁷ for nearby Sylt reports a maximum of $1.4 \text{ pmol mol}^{-1}$. For Sylt and Dagebüll we model peak mixing ratios of 1.8 and $0.7 \text{ pmol mol}^{-1}$, respectively.

Mixing ratios of IO have been measured by a ship cruise in the marine boundary layer of between 0.4 and 1 pmol mol^{-1} (30% uncertainty).³¹ This cruise did not extend into the Mediterranean region (where we predict highest IO mixing ratios see Fig. 5), but it did finish in the Mediterranean at Cartagena (Spain) in July 2011 with the last daytime average value reported of $\sim 0.5 \text{ pmol mol}^{-1}$ (35°N , -8.4°E). For the same location we calculate an average daytime mixing ratio of $0.7 \text{ pmol mol}^{-1}$.

Observations of iodine dioxide (OIO) have also been reported. At Mace Head, peak OIO mixing ratios have been reported (at night) of between $3.0 (\pm 0.4)$ ⁷⁸ and $13 (\pm 4) \text{ pmol mol}^{-1}$.⁷⁶ The model predicts substantially lower peak values of 0.09



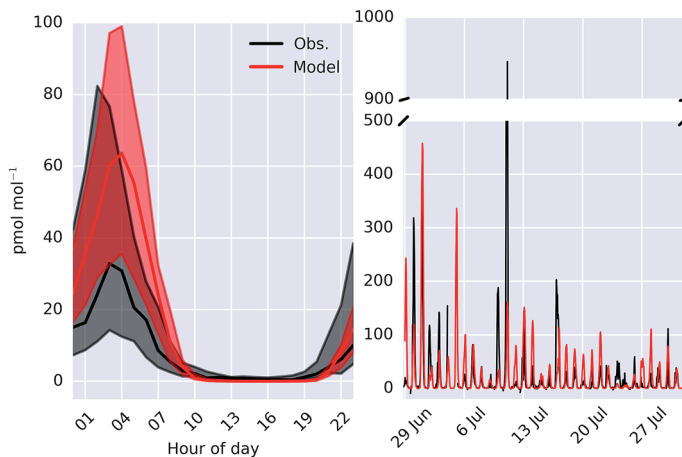


Fig. 6 Comparison of observed and modelled (“HAL”) ClNO_2 as a median diel cycle (left) and timeseries (right) measured at Weybourne. Shaded regions on the diel plot give 25th and 75th percentiles.

The published continental HCl observations show mixing ratios in the range of tens of pmol mol^{-1} to a few nmol mol^{-1} in Italy,⁸⁴ Netherlands,^{85,86} France,⁸⁷ Germany,⁸⁸ England,^{89–91} and Switzerland.⁹² The modelled mixing ratios peak at 12 pmol mol^{-1} . The model therefore significantly underestimates the HCl mixing ratios. Some of this bias is likely due to a lack of chlorine sources from anthropogenic activities, both organic and inorganic and from aerosol processing of chloride. However, it may also reflect excessive loss processes for HCl.

In summary the observational constraints on the modelled halogen concentrations are weak. Much of the observational activity has focussed on process level understanding of halogens at coastal hot spots. For these locations the model appears to systematically underestimate IO, OIO, I_2 and BrO mixing ratios. ClNO_2 mixing ratios inland appear to be underestimated. The model identifies the region with the most significant halogen chemistry as the Mediterranean, a region with a very low number of observations.

4 European ozone (O_3)

Fig. 7 shows the difference in the mean surface O_3 mixing ratio between simulations with halogens (“HAL”) and without (“NOHAL”). Fig. 8 (top) shows this in percentage terms. O_3 reduces in all locations, and in some locations by a significant fraction (45% or $28.9 \text{ nmol mol}^{-1}$). On average the surface O_3 within the domain drops by $13.5 \text{ nmol mol}^{-1}$ (25%), consistent with previous studies.^{5,12,15,93}

To assess changes to O_3 within the domain’s boundary layer further, we consider the budget of the rapidly interchanging odd oxygen species (O_x , defined previously¹²). Table 2 gives an O_x budget for the boundary layer over Europe for the period of the observations (June 29th to August 1st 2015) for the simulations with (“HAL”) and without halogens (“NOHAL”). Inclusion of halogens leads to a slight decrease in the magnitude of the O_x sources of 4%. This is predominantly due to a reduction in the mixing ratio of NO_x due to the hydrolysis of halogen



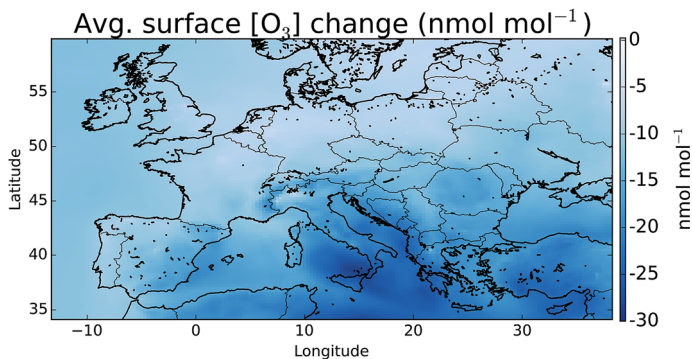


Fig. 7 Difference in surface mean O_3 mixing ratio between “HAL” and “NOHAL” in nmol mol^{-1} over the simulation period. Changes in percentage terms are shown in Fig. 8.

nitrates ($\text{XNO}_3 \rightarrow \text{aq.HOX} + \text{HNO}_3$, $\text{X} = \text{Cl, Br}$) as discussed on a global scale.^{11,12} The O_x sink term also decreases (7%) reflecting lower O_3 concentrations in the domain. The O_x chemical lifetime decreases from 8 days without halogens to 6.5 days with, a 20% reduction.

This reduction in the surface O_3 burden consists of two components: a reduction in the background O_3 entering the domain, predominantly from the West (the boundary conditions), and a change to the chemistry occurring within the domain. By running a simulation with the boundary conditions from the global simulation without halogen chemistry, but with halogen chemistry occurring inside the domain (“HAL-LOCAL”) we can separate these two factors. Fig. 8 (top) shows the percentage decrease in the O_3 mixing ratio on inclusion of halogens ($(\text{“HAL”} - \text{“NOHAL”})/\text{“NOHAL”}$). The middle panel then shows the decrease which is attributable to the local chemistry ($(\text{“HAL-LOCAL”} - \text{“NOHAL”})/\text{“NOHAL”}$), with the bottom panel showing the difference between the two panels which we attribute to the global role of halogens in determining the boundary conditions.

Over the northern and western part of the domain, the influence of halogens on the global mixing ratios (as manifested in the boundary conditions) dominates (Fig. 8 (bottom)). Mace Head (53.3°N , -9.9°E) on the west coast of Ireland is often used as the default background air quality site for North West Europe. O_3 at Mace Head drops by an average of 12 nmol mol^{-1} (31%) on the inclusion of halogen chemistry in both the boundary conditions and in the regional model (“HAL”), consistent with previous global studies.^{11,12,31} However, this reduction is only $0.51 \text{ nmol mol}^{-1}$ (1.3%) in the simulation where the boundary condition doesn’t reflect global halogen chemistry (“HAL-LOCAL”). This influence of the reduced O_3 due to the a reduction in the global background, extends over the European Atlantic regions and into the North Sea. However, its magnitude decreases over continental regions especially in the south of the domain. This is due to the local production of O_3 in these regions and the shorter lifetime of O_3 in continental regions reducing the influence of boundary conditions compared to marine regions.

Over the southern and eastern part of the domain the global background influence of halogens plays a less significant role and it is local halogen chemistry



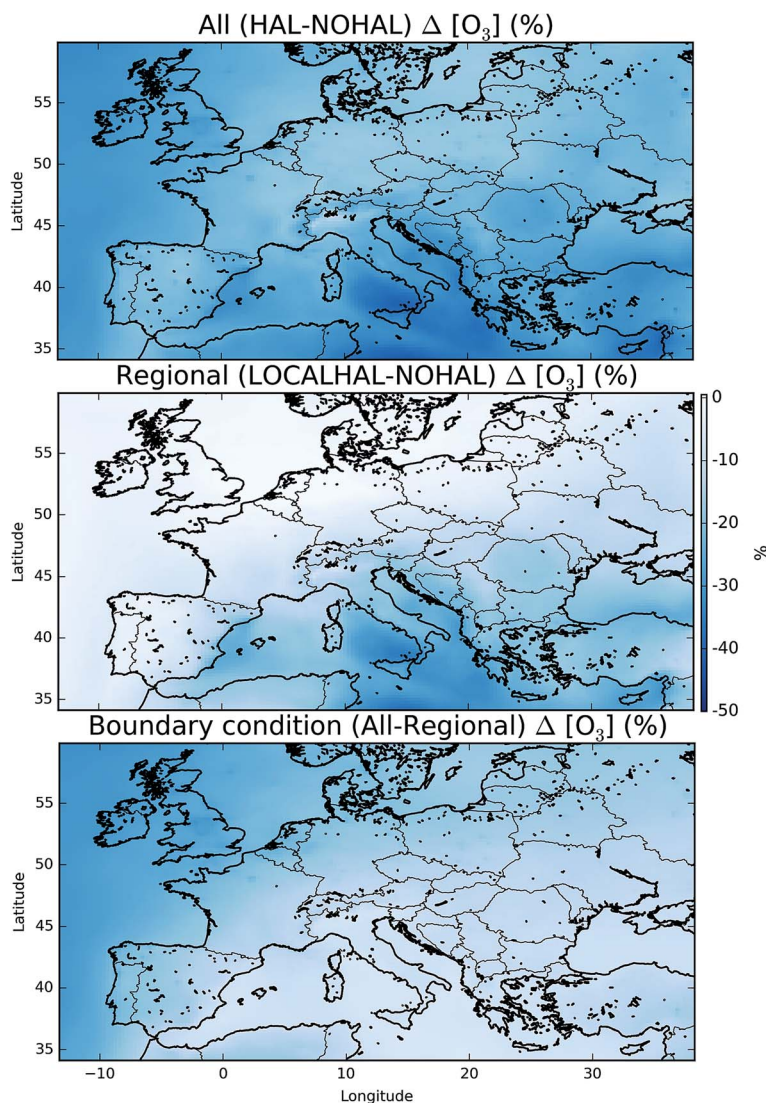


Fig. 8 Mean percentage difference in surface O_3 mixing ratio when halogens are included in all domains ("HAL" vs. "NOHAL", top), just within the European domain ("HAL-LOCAL" vs. "NOHAL", middle), and the global contribution from the difference between these two (top – middle, at the bottom) plots.

that dominates the reduction simulated in O_3 . For example over Sicily ($18.6^\circ N$, $14.2^\circ E$), O_3 mixing ratios are reduced $28.4 \text{ nmol mol}^{-1}$ (41%) on the inclusion of halogen chemistry in both the boundary conditions and in the regional model ("HAL") and by $24.3 \text{ nmol mol}^{-1}$ (35%) in the simulation with only halogen chemistry occurring within the domain ("HAL-LOCAL"). Thus in this location the impact of halogens on the global background is much less important than the local halogen chemistry. Fig. 5 shows much higher mixing ratios of halogens over the Mediterranean than any other region of the domain, however, there are no



Table 2 Modelled odd oxygen (O_x^{12}) budget within the European boundary layer (>900 hPa). Major losses and production routes are shown in units of Tg (O_x) per year scaled from the 34 days of simulation performed here. Values are rounded to one decimal place

	“Cl + Br + I”	“NOHAL”
O_3 burden (Tg)	0.9	1.2
NO + HO_2	69.3	73.6
NO + RO_2	40.8	41.3
Total chemical O_x sources	110.1	114.9
O_3 + H_2O + $h\nu$	20.4	25.0
O_3 + HO_2	10.2	13.3
O_3 + OH + O_2	6.2	9.3
Bromine O_x sinks	1.1	0.0
Iodine O_x sinks	8.0	0.0
Chlorine O_x sinks	0.3	0.0
Total chemical O_x sinks	50.6	54.4
O_3 dry deposition	69	90

obvious observational constraints for halogen species here and so their regional influence is un-assessed.

The cumulative distribution functions of surface hourly O_3 mixing ratios over Europe for the differing simulations are shown in Fig. 9. The inclusion of halogens reduces the probability of high O_3 occurring in the model but the difference between the north (>47°N) and the south (<47°N) of Europe is evident. For the north of Europe, only small changes are seen between simulations with only local halogens (“HAL-LOCAL”) compared to no halogens at all (“NOHAL”). The median O_3 mixing ratios in the north of Europe (>47°N) are 31.1, 40.0, and 40.5 nmol mol⁻¹ for the “HAL”, “HAL-LOCAL”, and “NOHAL” simulations, respectively. Local chemistry thus plays little role in determining the median concentrations. However the role of local chemistry becomes more pronounced at the upper end of the O_3 distribution, with the 95th percentile mixing ratios for these simulations being 54.0, 59.4, and 65.6 nmol mol⁻¹.

For the south of Europe (<47°N) a larger proportion of change between the simulation with halogens (“HAL”) and without (“NOHAL”) can be explained by local chemistry (“HAL-LOCAL”) and this influence is felt throughout the O_3 distribution. Fig. 9 shows a reduction in the median O_3 mixing ratio from “HAL” to “HAL-LOCAL” to “NOHAL” of 44.9, 51.1, and 61.0 nmol mol⁻¹, respectively. Similar reductions can be seen in the 95th percentile mixing ratios with values of 62.4, 70.7, and 88.1 nmol mol⁻¹.

The upper end of the O_3 distribution is most important from an air quality perspective. The model shows a decrease in average surface maximum mixing ratios of 19.9 nmol mol⁻¹ on inclusion of halogens. This is greater than the decrease seen in average surface mean mixing ratios (13.5 nmol mol⁻¹). For UK legislation, 50 nmol mol⁻¹ (100 $\mu\text{g m}^{-3}$) is important for human health reasons as above this value exceedances are considered. 45.7% of modelled surface O_3 values are above this value when halogens are not included (“NOHAL”), 34.1% when halogens are just considered locally (“HAL-LOCAL”) and 18.9% when halogens are considered in all domains (“HAL”). The O_3 mixing ratio of 40 nmol mol⁻¹ is considered an important threshold for ecosystems.⁹⁴ We see a decrease in the



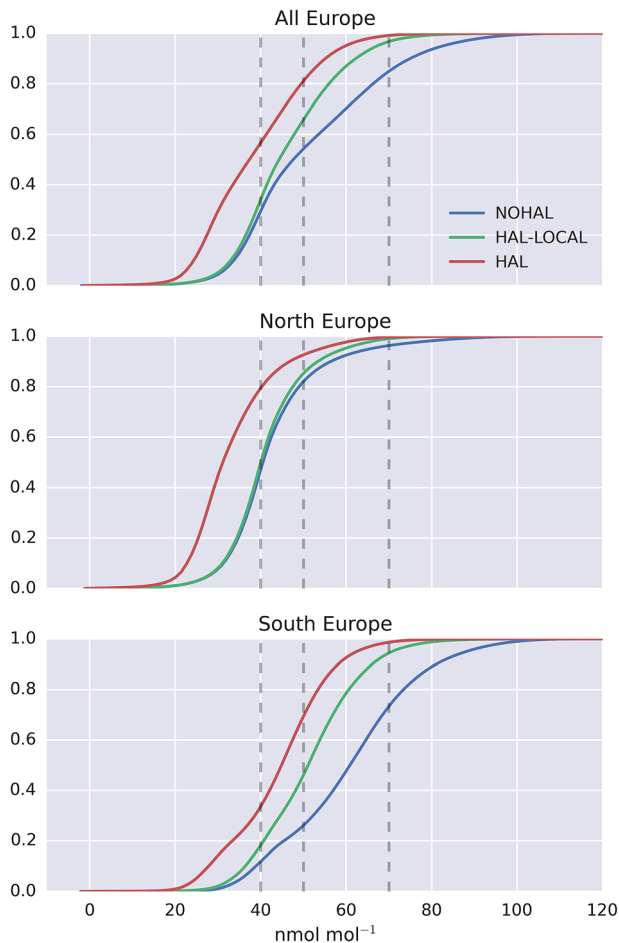


Fig. 9 Cumulative probability distribution plot of surface modelled O₃ for the observation period, for the entire domain (top), northern Europe (>47°N, middle), and southern Europe (<47°N, bottom). Modelled values are shown for the simulation with halogens ("HAL"), without halogens ("NOHAL"), and with halogens only with the European domain ("HAL-LOCAL"). Vertical dashed black lines give 40, 50 and 70 nmol mol⁻¹. The x axis is limited to 120 nmol mol⁻¹.

percentage of hourly surface values above 40 nmol mol⁻¹ from 70.5% in "NOHAL" and 65.9% in "HAL-LOCAL", to 43.3% in "HAL". Halogens reduce the percent of modelled values above 70 nmol mol⁻¹ too, with the values dropping from 15.1% in "NOHAL" to 3.2% in "HAL-LOCAL" and 0.9% in "HAL".

Within our model, with our current representation of halogen chemistry, and for the period we have investigated, halogens have a significant impact on the mixing ratio of modelled O₃. There are significant reductions in the mixing ratio of O₃ both in the north and south of Europe but for differing reasons (global background *versus* local chemistry) with influences both for the median and higher percentiles of the distribution. There is a need for significant and further evaluation of the model against an increased observation dataset to



the ESI .† These changes equate to a domain average decrease of 1.7 and 4.3%, for $\text{PM}_{2.5}$ and $\text{SO}_4^{2-} + \text{NH}_4^+ + \text{NO}_3^-$, respectively. NO_3^- shows the largest changes in topographically elevated regions, highlighting the large decreases in NO_x seen at these altitudes on inclusion of halogens.^{11,12} Small changes are seen in the concentration of SO_4^{2-} reflecting the changes in the oxidants discussed in Section 5. However, halogens may be able to directly impact the production of SO_4^{2-} through the oxidation on aerosol of SO_2 by hypohalous acids (HOX) on aerosol as has been discussed,⁹⁷ which may lead to increased SO_4^{2-} production.

8 Conclusions and discussion

We have investigated the impact of Cl, Br and I chemistry on the mixing ratio of O_3 and other pollutants over Europe in the summer of 2015 using the GEOS-Chem model in its European configuration. An initial assessment of the model against observations made at the Weybourne Atmospheric Observatory and from the UK air quality network shows some skill in capturing mean mixing ratios and diel cycle of O_3 , NO_2 , NO_y , and $\text{PM}_{2.5}$ concentrations, however a more extensive assessment of the model in this configuration is needed. Comparisons between observations of ClNO_2 made at Weybourne show a model overestimate on average. However, the model significantly underestimates ClNO_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 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 small regional increases in O_3 but this is overwhelmed by the decreases caused by other halogens. We find that mean surface O_3 mixing ratios significantly reduced by an average of $13.5 \text{ nmol mol}^{-1}$ (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 from being NO_x 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 simulations¹² 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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