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D2.3.1 - Model evaluation of the role of halogens in ozone depletion events and implications for mercury in the Arctic

Summary

During Arctic springtime, reactive halogen species initiate the oxidation of elemental mercury to forms which are readily deposited to snow, ice and the open ocean. Simultaneously, boundary layer ozone is depleted to near zero levels due to the release of reactive bromine. Model predictions of these events remain a challenge due to the complexity of these processes and improved descriptions of Arctic bromine chemistry are needed in order to describe the fate of mercury in the Arctic atmosphere. Here, we implement descriptions of halogen chemistry on snow, ice and aerosols in the Arctic within a chemical transport model, WRF-Chem, to better simulate the regional effects of halogens on ozone. We implement two proposed halogen activation and recycling mechanisms within the model: (1) surface snow activation and recycling (Toyota et al., 2011) and (2) blowing snow sourced sea-salt aerosols (Yang et al., 2008). These two activation/recycling mechanisms can drive Arctic ozone depletion under different conditions. We have found that atmosphere-surface activation/recycling on snow (snow-ice, sea-ice and continental snow) described by Toyota et al. (2011) is the dominant mechanism whilst blowing snow (Yang et al., 2008) plays an important role at some sites. These results show that atmospheric models need to account for both mechanisms in order to accurately simulate surface ozone depletion processes and understand the effects on the atmospheric mercury cycle including deposition.

Introduction

It is well established that boundary layer ozone in the Arctic experiences rapid depletion to near zero levels during polar spring time (Oltmans et al., 1981). These ozone depletion events (ODEs) are observed every year during spring and have been attributed to the presence of enhanced concentrations of reactive bromine in the atmosphere (Barrie et al., 1988). Halogen activation occurs when reactive forms of bromine (Br_y=all reactive forms of bromine in the atmosphere) are produced via multiphase processes involving bromide containing solutions or surfaces that are often acidic. Bromide is a trace species found in seawater, which ultimately originates from oceanic sources, however the exact processes and surfaces involved in halogen activation are still subject to debate (Abbatt et al., 2012; Simpson et al., 2007, 2015). During polar sunrise, Br_2 or BrCl is released via heterogeneous chemistry on surfaces and is then photolysed to form atomic bromine (Br) that quickly reacts with ozone, resulting in ozone destruction. Similar to in the stratosphere, further reactions/recycling of bromine on surfaces contributes to "bromine explosion events" that catalytically destroy ozone and cause ozone depletion events.

The reaction of Br with ozone leads to the formation of bromine monoxide (BrO) which is the key species that is most often measured during bromine activation and ozone depletion events. Previous measurements, taken by both ground based and satellite instruments, have shown an inverse relationship which exists between periods of high BrO

concentrations and depleted O_3 levels (Barrie et al., 1988; Wang et al., 2019). Br_2 can be regenerated via the self reaction of BrO, which is the dominant recycling mechanism at high BrO concentrations. This is also accelerated by other processes such as the reaction of HOBr (formed as part of the bromine radical cycle) with bromide (Br^-) on surfaces in the presence of acid. Additionally, HOBr can also be photolysed to reform Br atoms directly. These processes are what make bromine species particularly efficient at depleting ozone to near-zero values and makes halogen chemistry incredibly important in the polar regions.

Furthermore, halogens play a vital role in atmospheric mercury oxidation globally (Holmes et al., 2006) and polar atmospheric mercury depletion events (AMDEs) and deposition (e.g. recent work from Douglas and Blum, 2019). Anthropogenic emissions of mercury (Hg^0) are transported to the Arctic and can undergo oxidative processes to produce more reactive forms (Hg^{II}) which are readily deposited onto the Arctic snowpack and ocean (Douglas et al., 2012; Steffen et al., 2008). Once on surfaces, such as snow and ice within the ocean, deposited mercury can undergo chemistry that enables it to be re-emitted to the air or be redistributed to the aquatic and terrestrial environment, where it can be transformed into more toxic forms that impact humans and ecosystems.

To date, two main modelling approaches have been proposed to simulate halogen activation and interactions with ozone cycles. Firstly, Toyota et al. (2011) describes the release of reactive bromine from a trigger reaction on snow covering first year sea-ice and recycling on all snow and aerosols. This involves a process of ozone deposition which facilitates the oxidation of bromide in snow to Br_2 under both light and dark conditions. Secondly, a mechanism of bromine release from sea-salt aerosols, formed by sublimation of lofted salty snow has been proposed by Yang et al. (2008). This mechanism requires strong winds to lift salty snow, containing chloride and bromide, from the surface to the atmosphere. In this work, we implement and test these two halogen activation and recycling mechanisms for the Arctic using a state-of-the-art, high resolution, regional chemical transport model. We develop an optimised model setup to simulate Arctic boundary layer dynamics and mixing, and, include new heterogeneous and gas-phase reactions to study the efficacy of the two aforementioned modelling approaches and their effects on Arctic springtime ozone concentrations. We compare simulated profiles of ozone at multiple Arctic stations with NOAA meteorological data and ground based measurements of BrO taken using a Multi-AXis Differential Optical Absorption Spectrometer (MAX-DOAS) at Utqiaġvik, Alaska (formerly Barrow, Alaska). These measurements are performed by the Simpson group at the University of Alaska and described in Simpson et al. (2017).

Figure 1. *WRF-Chem model domain.*

Methodology

We use a version of the Weather Research and Forecasting model coupled with Chemistry (WRF-Chem 4.1.1) optimised for the Arctic as described previously in Marelle et al. (2017). Within WRF-Chem 4.1.1, we include new model developments including: implementation of an additional 82 chlorine and bromine gas-phase reactions (including 15 photolysis reactions); inclusion of 50 gas-phase species within the Kinetic Pre-Processor (KPP) in WRF-Chem; dry deposition descriptions for 7 new halogen species; representation for 12 heterogeneous reactions in the SAPRC-99 MOSAIC-8bin scheme within WRF-Chem; and emissions of bromine from sea-ice, snow and open oceans. To evaluate these model developments, we perform simulations centered over the Arctic (domain shown in Figure 1) between the dates 1 March 2012 and 31 April 2012, with a spin-up time of 7 days (not considered in the model analysis). The horizontal resolution used is 100 km, with 72 vertical levels up to a pressure of 50 hPa. Meteorological boundary conditions are nudged towards observed meteorology using reanalysis data, from the NCEP-FNL Operational Global Analyses dataset, to simulate the most realistic boundary layer conditions. An evaluation of the modelled meteorology compared to 2-meter temperature measurements is shown in Figure 2.

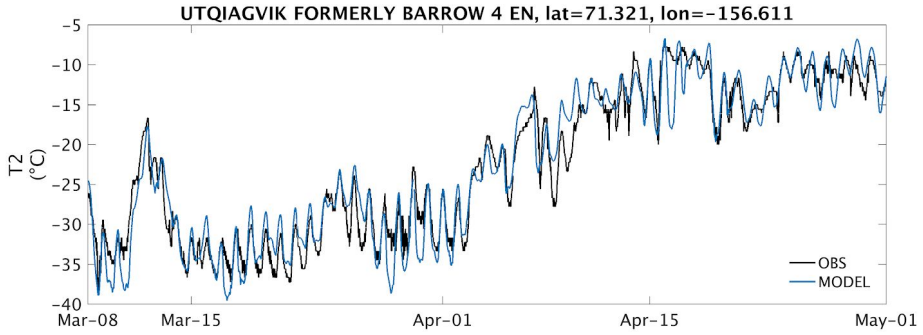

Figure 2. *Temperature predicted at 2 meters from WRF compared to measured 2-meter temperature at Utqiaġvik, AK (formerly Barrow, AK) for our model case in spring 2012.*

Within the SAPRC-99 MOSAIC-8bin scheme in WRF-Chem, we include a simple representation of halogen heterogeneous chemistry on aerosols. Heterogeneous reactions on acidic aerosols are key reactions which maintain reactive halogens in the Arctic. Additionally, gas-phase reactions involving chlorine and bromine, including photolysis reactions, have been implemented into WRF-Chem.

Results and Conclusions

Figure 3 shows the modelled concentrations of O_3 and BrO against observations at Utqiaġvik, AK (formerly Barrow, AK). With the newly implemented developments, modelled concentrations of O_3 are vastly improved and depletion events of ozone are generally well represented. The peak shapes of ozone are well captured in the model when using both mechanisms and we are able to simulate both large scale ODEs and even smaller short time depletion/regeneration events of ozone. This provides a very good representation of what is observed with respect to the timing of declining and rising ozone levels during the simulation period. It can also be observed that, at this site, surface snow activation plays a more significant role in ozone depletion than blowing snow and can be described as the main operating mechanism as it captures more of the large ODEs as well as more of the smaller peak fluctuations. We find that the blowing snow mechanism can play an important role in determining ozone concentrations at other Arctic sites (e.g. Tiksi, Russia), responsible for large amounts of ozone depletion during the middle of March (figures not shown). However, despite capturing most ozone depletion events, capturing the full nature of all events remains a challenge for future work.

Similarly, the timing and intensity of BrO concentrations are captured by the model, but the model tends to underestimate concentrations compared to the measurements. This may be due to uncertainties in BrO retrievals, incorrect activation/recycling mechanisms, poor polar boundary layer dynamics or insufficient model resolution. The modelled BrO peaks match the observational data during both periods of increasing and declining BrO

concentrations. By comparing modelled BrO and O_3, we observe that in some cases of extended periods of very low O_3 concentrations, we also find low concentrations of BrO. Under these conditions of low ozone concentrations, BrO formation is limited by the fact that there is no ozone for Br atoms to react with. In this case, other species, such as $BrNO_y$ compounds, may play a role in sustaining bromine chemistry by regenerating Br_2 (Wang et al., 2019). Similar to ozone depletion, the surface snow mechanism also plays the most important role in determining enhanced BrO concentrations.

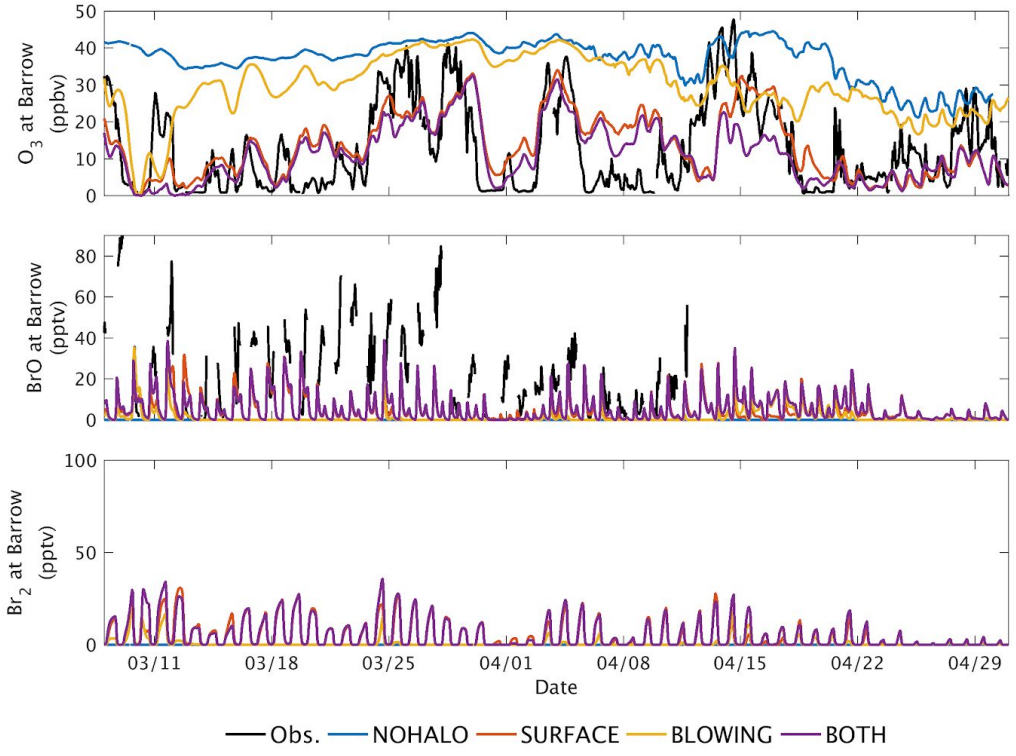

Figure 3. *Model predicted ozone, BrO, and Br_2 at Utqiaġvik, AK (formerly Barrow, AK) compared to measured surface ozone (NOAA ozonesonde) and BrO (MAX-DOAS) for our model case in spring 2012. Observations are in black (Obs.), the model run with no halogen chemistry included (NOHALO) is shown in blue. Model runs including bromine and chlorine chemistry include: a run with only the surface snow activation and recycling mechanism (SURFACE) from Toyota et al. (2011) in red, the blowing snow activation and recycling mechanism (BLOWING) from Yang et al. (2008) in orange, and both mechanisms operating at the same time (BOTH = SURFACE + BLOWING) is shown in purple.*

The independent roles of the two halogen activation mechanisms on surface ozone and BrO concentrations are illustrated in Figure 4. Here, we can distinguish more clearly the extent to which each of the mechanisms is responsible for ozone depletion over the entire model domain. It can be seen that the surface snow mechanism (left panel) is the main driver for large scale ozone depletion over most parts of the Arctic, whereas, blowing snow (right panel) is only responsible for large scale depletion in particular regions. This indicates that more reactive bromine compounds are produced via surface snow activation and this is supported by higher modelled BrO concentrations for this mechanism.

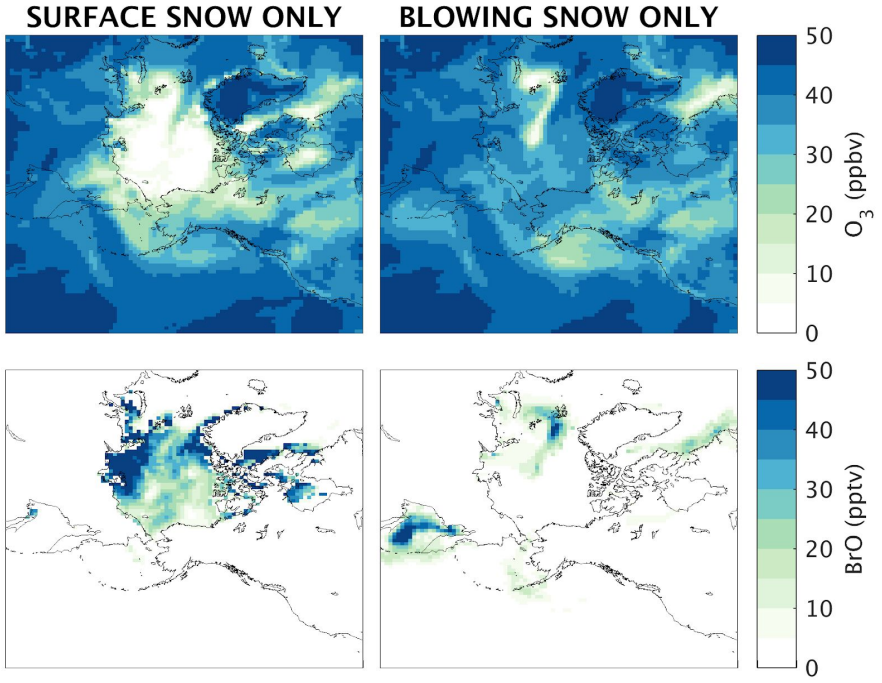

Figure 4. *Monthly averaged (1 to 30 April 2012) surface ozone and BrO predicted across the Arctic for the two different mechanisms operating: left SURFACE snow mechanism (red in Figure 3) and right BLOWING snow mechanism (orange in Figure 3).*

In this work we have implemented descriptions of halogen chemistry activation and recycling within the WRF-Chem model and shown that both mechanisms play important roles during springtime Arctic ozone depletion events. We show that surface snow activation and recycling of bromine is the key mechanism responsible for depleting ozone levels across multiple Arctic sites with blowing snow playing an important role at specific sites. These results are significant in developing model predictions of surface ozone further by improving the representation of Arctic halogen chemistry and determining the activation pathways of

reactive bromine. Improved model predictions of BrO will allow us to better understand the oxidative processes of elemental mercury and more accurately simulate AMDEs and deposition processes in a rapidly changing Arctic climate. This is extremely beneficial to support studies where there are limited observational data of Hg and Br_y species and models are required to study the cycles and processes that exist and their consequent effects including chemistry-climate interactions.

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