

# Climate/chemistry feedbacks and biogenic emissions

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The oxidizing capacity of the atmosphere is affected by anthropogenic emissions and is projected to change in the future. Model calculations indicate that the change in surface ozone at some locations could be large and have significant implications for human health. The calculations depend on the precise scenarios used for the anthropogenic emissions and on the details of the feedback processes included in the model. One important factor is how natural biogenic emissions will change in the future. We carry out a sensitivity calculation to address the possible increase in isoprene emissions consequent on increased surface temperature in a future climate. The changes in ozone are significant but depend crucially on the background chemical regime. In these calculations, we find that increased isoprene will increase ozone in the Northern Hemisphere but decrease ozone in the tropics. We also consider the role of bromine compounds in tropospheric chemistry and consider cases where, in a future climate, the impact of bromine could change.

**Keywords:** tropospheric ozone; climate change; biogenic emissions; isoprene; tropospheric bromine

## 1. Introduction

Atmospheric oxidizing capacity controls the removal of many tropospheric pollutants and reactive greenhouse gases. Therefore, future changes in oxidizing capacity could have a significant role in future changes of both climate and air quality. The major oxidant in the atmosphere is OH, whose concentration depends on the ozone concentration. Ozone itself is an oxidant whose tropospheric distribution depends on chemical processes involving the nitrogen oxides, NO<sub>x</sub>, and volatile organic compounds, VOCs. Emissions of these have certainly increased during the past century, and there is clear evidence that surface ozone concentrations have also increased (Voltz & Kley 1988; Vingarzan 2004). Future emission projections suggest that the increases will continue during this century, with consequences for oxidizing capacity (Prather *et al.* 2003; Zeng & Pyle 2003).

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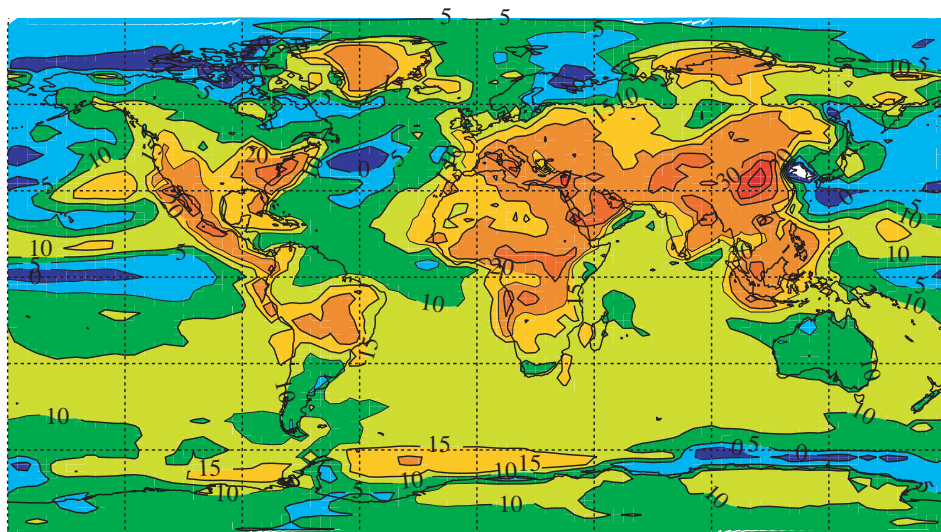


Figure 1. The difference in July mean surface ozone concentrations (ppbv) between runs C and A.

While a range of VOCs is emitted in the industrial and transport sectors, the magnitude of natural VOC emissions is greater (Guenther *et al.* 1995, 2006). Isoprene is one of the most important biogenic VOCs. Approximately 500 Tg(C) is emitted annually from the biosphere, mainly from forests, an emission comparable to that of methane. Unlike methane, isoprene is very reactive with an atmospheric lifetime on the order of hours. It is an important ‘fuel’ for VOC–NO<sub>x</sub> cycles which produce ozone; it reacts directly with ozone; its degradation leads to the formation of peroxyacetyl nitrate (PAN) which is an important reservoir species, allowing long-range transport of NO<sub>x</sub>. Isoprene nitrates might also be important sinks for NO<sub>x</sub> through wet or dry deposition, although their chemistry and eventual fate are somewhat uncertain (e.g. Grossenbacher *et al.* 2001; von Kuhlmann *et al.* 2004). Crucially, the emission of isoprene from vegetation is dependent on a number of climate-related factors. Biogenic emissions obviously depend on the biomass available, which will depend on factors controlling primary production. Isoprene emissions are known to depend strongly on plant species, temperature and light as well as on factors like season and leaf age (Guenther *et al.* 2006 and references therein). Recent work (Rosenstiel *et al.* 2003) suggests that the ambient CO<sub>2</sub> concentration can also directly affect isoprene emissions. Thus, under climate change, we can expect the emissions of isoprene to change, which could impact ozone and oxidizing capacity.

The importance of other biogenic emissions could also change in the future. For example, Yang *et al.* (2005) have shown that contemporary emissions of bromine compounds (mainly from marine halocarbons and from sea salt) could be playing a large role in the tropospheric ozone budget. In their model study, they show that including these sources can change the ozone concentration by as much as 30% in southern high latitudes (close to the large wind-driven southern ocean source of sea salt) and by several per cent globally. Again, we can speculate that changes in climate, such as sea surface temperature (SST) or wind-stress at the ocean surface, could lead to changed emission rates which could influence future oxidizing capacity.

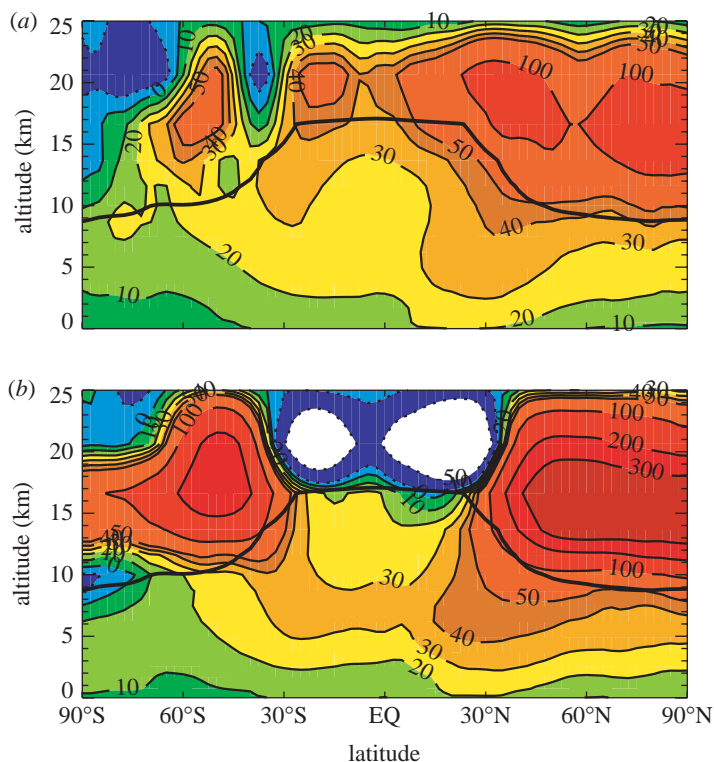


Figure 2. Cross-section of the difference in ozone (ppbv) (a) between runs B and A and (b) between runs C and A. Based on fig. 1 of Zeng & Pyle (2003).

Hence, while anthropogenic forcing of global change is a major factor, the role of feedbacks involving the biosphere and the oceans is also very important and must be considered. In this paper, we explore some of these feedback processes using a chemistry–climate model described briefly in §2. Section 3 describes a study of how tropospheric ozone could change during this century, given a particular anthropogenic emission scenario. Section 4 contrasts anthropogenic change with climate-driven changes in biogenic emissions; we concentrate on isoprene for this sensitivity study. Section 5 looks at the possible future role of halogens.

## 2. The models

We have used a 19 level version of the Met Office climate model, at UM version 4.5 (Senior & Mitchell 2000). The model employs a hybrid sigma-pressure vertical coordinate, and the model domain extends from the surface up to 4.6 hPa. The horizontal resolution is  $3.75^\circ \times 2.5^\circ$ . This version of the model is atmosphere-only and is forced using prescribed SSTs. Details of our implementation are given in Zeng & Pyle (2003).

The tropospheric chemical mechanism includes CO, methane and NMVOC oxidation as previously used in the off-line transport model TOMCAT (Law *et al.* 1998) and earlier versions of the UM+chemistry model (Zeng & Pyle 2003,

2005). An isoprene oxidation scheme adopted from Pöschl *et al.* (2000) was recently added into the model. Reaction rates are taken from the recent IUPAC (Atkinson *et al.* 2000) and JPL (DeMore *et al.* 1997) evaluations. Chemical integrations are performed using an implicit time integration scheme, IMPACT (Carver & Stott 2000), with a 15 min time-step. The model includes 60 species and 174 chemical reactions.

Instead of explicit stratospheric chemistry in the model, daily concentrations of O<sub>3</sub>, NO<sub>y</sub> and CH<sub>4</sub> are prescribed at the top three model layers (29.6, 14.8 and 4.6 hPa) using output from the Cambridge two-dimensional model, to produce a realistic annual cycle of these species in the stratosphere. Note that stratospheric NO<sub>x</sub>/HO<sub>x</sub> chemistry applies in the lowermost stratosphere (i.e. below 30 hPa) but that no halogen chemistry is included.

*p*-TOMCAT is a new parallelized version of the TOMCAT chemistry transport model, which is able to run on multiple processors. It has been used extensively for tropospheric studies and is employed here for the studies discussed in §5. The horizontal transport and vertical mixing of tracers is based on 6-hourly meteorological fields, including winds and temperature, derived from the European Centre for Medium-Range Weather Forecasts (ECMWF) operational analysis. Details of the model dynamical and chemical processes and its validation against data can be found in Stockwell *et al.* (1998), Wang *et al.* (1999), O'Connor *et al.* (2004, 2005), Savage *et al.* (2004), Yang *et al.* (2005) and Warwick *et al.* (2006*a,b*).

### 3. Anthropogenic perturbation to oxidizing capacity

The model discussed by Zeng & Pyle (2003), which excludes isoprene chemistry, has been used to consider projections of changes in tropospheric composition by the end of this century. A base run (A) representative of the year 2000 was carried out along with two 2100 runs (B and C). B included only changes in anthropogenic emissions of ozone precursors (NO<sub>x</sub> and VOCs) based on the SRES A2 scenario (Nakicenovic *et al.* 2000, and see also Prather *et al.* 2001; Gauss *et al.* 2003). This is a relatively high-emission scenario, which projects large population growth and relatively slow technological change. We do not suggest that this is a most probable scenario; it is simply used to explore possible feedbacks. Run B used the climate of 2000. Run C had identical anthropogenic emissions to B, but the background climate was with doubled CO<sub>2</sub>.

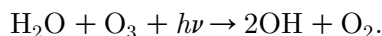
Figure 1 shows the change in monthly mean surface ozone concentrations for July between runs C and A. There is a large increase in ozone over some of the continental regions, most pronounced over Asia, approaching 40 ppbv, where the emission increases in this scenario are largest. The increase is driven by the classic ozone production cycles where increases in NO<sub>x</sub> and VOCs both enhance the rate of ozone production, following the HO<sub>2</sub>(RO<sub>2</sub>) + NO reaction.

The increase in ozone shown in figure 1 represents a significant deterioration in local air quality at some locations. Health-related targets for surface ozone are usually set at approximately 50–60 ppbv over, say, an 8 h period (WHO 2004). Within this context, it is clear that the *monthly mean increases* calculated here with the A2 scenario represent a very significant perturbation with, for example, potentially serious consequences for human health.

Table 1. Ozone budgets (in Tg yr<sup>-1</sup>) and tropospheric ozone burdens (in Tg) calculated for runs A, B and C. The chemical tendency column shows the net tendency and, in brackets and bold, the separate chemical production and destruction terms. Based on Zeng & Pyle (2003).

	STE (Tg yr <sup>-1</sup> )	chemical tendencies (Tg yr <sup>-1</sup> )	depn (Tg yr <sup>-1</sup> )	tropospheric O <sub>3</sub> burden (Tg)
run A	465	800 ( <b>4102,3302</b> )	-1265	<b>317</b>
run B	470	1486 ( <b>7405,5919</b> )	-1956	<b>489</b>
run C	838	1090 ( <b>8236,7146</b> )	-1928	<b>505</b>

Note that in some locations surface ozone decreases in run C. This is due to higher humidity in a warmer climate, which leads to increased ozone destruction, via



The effect of this reaction is most pronounced in the marine boundary layer, away from local pollution sources.

It has been argued (Johnson *et al.* 1999) that the impact of enhanced water vapour would be to reduce the anthropogenically driven increase in ozone throughout the troposphere. Clearly, the impact of this feedback is to reduce any ozone increase. However, we find that a further climate feedback, the change in stratosphere-to-troposphere transport, also needs to be considered. Figure 2, based on the Zeng & Pyle (2003) study, shows the calculated increase in zonally averaged ozone as a latitude-height cross-section between the present day, run A and runs B and C. Note the larger increase in run C, which uses the 2100 climate. Part of the increase in the subtropical upper troposphere can be attributed to increased stratosphere-to-troposphere transport (but part is also due to transport out of the tropical upper troposphere).

Table 1 presents the modelled budgets for the three runs. Note the large increase in the net chemical tendencies (and large increases in both chemical production and chemical destruction, shown in bold) in runs B and C, due to the increased anthropogenic contribution to the fuelling of ozone production. The net stratosphere/troposphere exchange (STE) flux is much higher in run C, the climate change run and, unlike in the study of Johnson *et al.* (1999), this run has a higher tropospheric burden than in run B. In our calculation, the increased STE more than compensates for the increased ozone loss in the wetter troposphere. For a range of studies we have performed, we find that the degree of compensation is quite model-dependent; the main point to emphasize is that climate-related changes in STE are large and significant when considering the future tropospheric ozone budget. Note that Collins *et al.* (2003) have also argued that net STE will increase in a future climate and Butchart & Scaife (2001) have shown that this is, in part, due to a strengthened Brewer–Dobson circulation in the future.

Detection and attribution of the kind of anthropogenic change shown in figures 1 and 2 is a challenging issue. In particular, how could atmospheric models help in determining fingerprints for detecting chemistry/climate interactions? We have considered patterns of change by looking at regional ozone probability distribution functions. Some examples, from Europe, East Asia and the North Pacific averaged over April–June, are shown in figure 3. In all cases, the

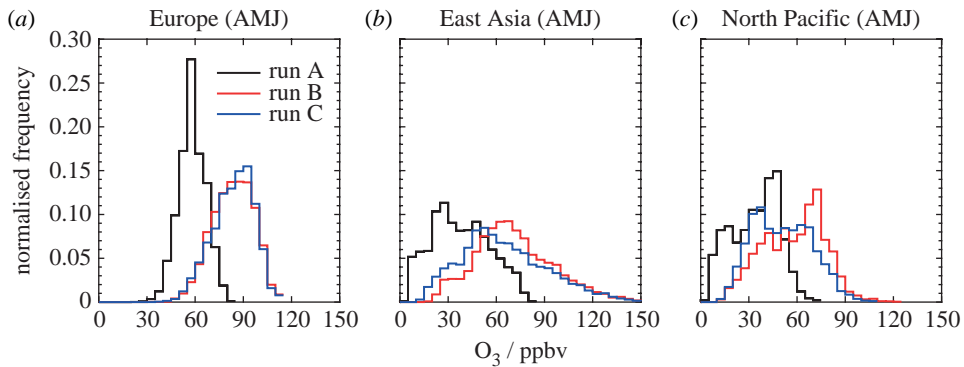


Figure 3. Probability distributions for ozone (integrated through the troposphere) for three different locations: (a) Europe (AMJ), (b) East Asia (AMJ) and (c) North Pacific (AMJ) for run A (black), run B (red) and run C (blue).

distributions in runs B and C are pushed to higher ozone values. Over Europe there is no discernable difference between runs B and C, but over East Asia the climate run, run C, has slightly less ozone than in run B, although differences are small. However, over the North Pacific all three distributions are quite different and, in particular, the impact of the increased humidity over the ocean is clearly marked by much lower ozone in run C than run B. Furthermore, for the North Pacific the shapes of the distributions in all three cases are quite different. A detailed statistical study might suggest ways in which this kind of model information could be used for detecting chemistry–climate interactions.

#### 4. Biogenic emissions and oxidizing capacity

The calculations described in §3 only considered possible future *anthropogenic* perturbations to tropospheric oxidizing capacity. However, as discussed in §1, biogenic emissions dominate global carbon emissions with, for example, current emissions of isoprene being comparable to those of methane. Isoprene makes an important contribution to tropospheric chemistry (Wang & Shallcross 2000) and in this section, we describe our modelling studies to consider the sensitivity of future ozone to changes in the isoprene emissions.

We have included an isoprene scheme into the model, based on the reduced mechanism described by Pöschl *et al.* (2000). For the present-day atmosphere, we have an isoprene source of 512 Tg(C) per year, 80% of which occurs in the tropics although the Southeastern US is one of the more important extratropical sources. The emissions vary with a number of environmental factors, such as temperature. According to the emissions model of Guenther *et al.* (1995), this dependence on temperature is characterized with an Arrhenius-type equation, giving an exponential emission increase up to an optimum temperature where the isoprene synthase enzyme starts to denature. Using this temperature dependence in conjunction with surface temperatures typical of a doubled-CO<sub>2</sub> atmosphere suggests that isoprene emissions could approximately double. As a sensitivity experiment, we have simply looked at the impact of doubling the isoprene emissions, in model runs using a 2100 climate. Note that, we have kept the distribution of emissions the same

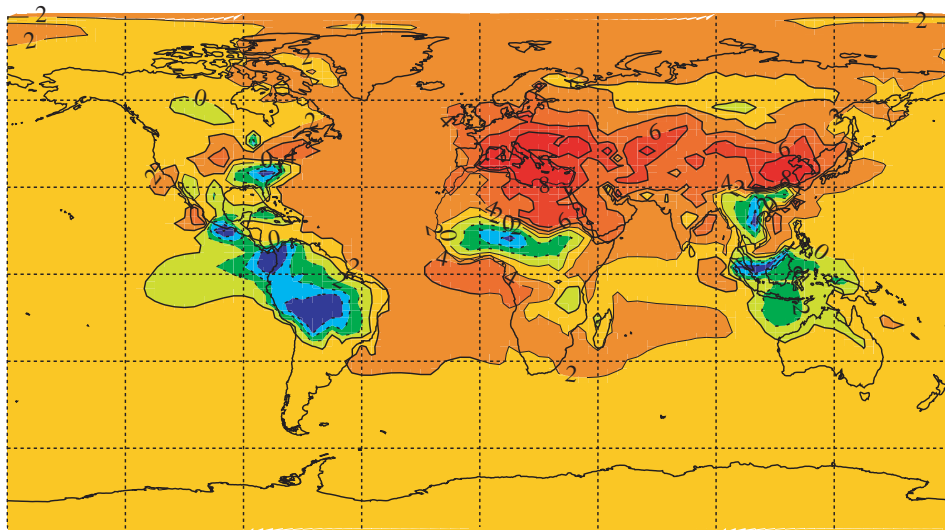


Figure 4. The change in surface ozone (ppbv) calculated between run E and run D. Both model calculations use a 2100 climate and anthropogenic emissions. Run D uses 2000 emissions of isoprene; in run E these emissions are doubled.

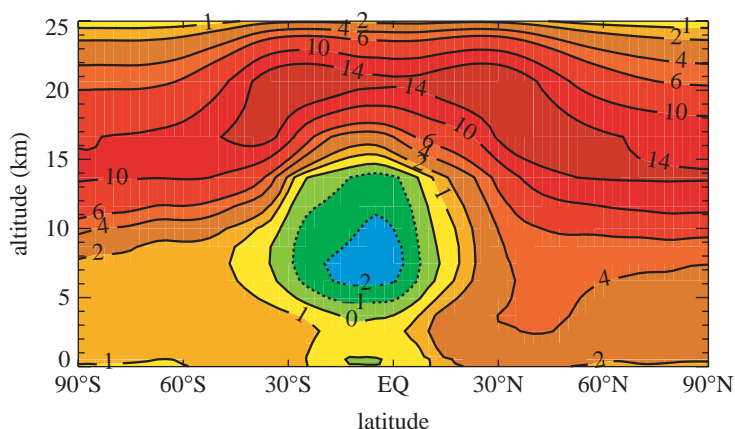


Figure 5. Latitude-height cross-section of the difference in ozone between runs D and E.

(i.e. we assume that the distribution of vegetation is unchanged) and that the possible change in other factors which could affect the emissions (the ambient  $\text{CO}_2$  and ozone concentrations, photosynthetically active radiation, water stress, etc.) has been ignored. Thus, our two runs are run D, with a 2100 climate, anthropogenic emissions from SRES A2 and the isoprene emissions at 512 Tg(C) per annum, and run E, in which we double the isoprene emissions.

Figure 4 shows the change in surface ozone between runs D and E. The response is complex, varying strongly with latitude. In the tropics, the main effect of the increased isoprene emissions is to decrease ozone locally. Thus, ozone decreases over the continental emission regions by up to approximately 8 ppbv. The chemistry in these regions is ‘ $\text{NO}_x$ -limited’ and one important effect of the extra

isoprene in run E is to tie up  $\text{NO}_y$  as PAN close to the emission regions. The PAN is then released away from the emission regions and explains, for example, part of the small increase in ozone seen over the Atlantic off the western coast of Africa. In contrast, there are ozone increases over large regions of the Northern Hemisphere with peak increase over Europe and Asia also reaching approximately 8 ppbv. Here, the chemistry is 'VOC-limited' and the oxidation of the additional isoprene in a  $\text{NO}_x$ -rich atmosphere leads to ozone production. This contrast in chemical regimes between the extratropical Northern Hemisphere and the rest of the atmosphere is seen clearly in figure 5 which shows a zonal mean cross-section of ozone change between runs D and E. Increases in ozone occur at all altitudes throughout most of the Northern Hemisphere but there are decreases in the tropics, especially in the tropical mid- and upper-troposphere.

While isoprene is the dominant emission from the biosphere, other atmospherically important compounds such as monoterpenes and methanol also have a biogenic source. The magnitude of these other emissions is linked to similar environmental factors as for isoprene and vegetation models have been used to estimate potential changes in their source strength (Lathière *et al.* 2005). Furthermore, some biogenic compounds have the potential to generate secondary organic aerosols, which extends their impact on the climate (Kanakidou *et al.* 2005). Our model calculations only consider the impact of changes in isoprene emissions on gas-phase chemistry.

## 5. Possible roles for halogen compounds

Yang *et al.* (2005) have recently discussed the possible role of brominated compounds in the troposphere. That bromine compounds are central in causing rapid spring-time depletion of ozone in the polar boundary layer has been highlighted in recent years (e.g. Barrie *et al.* 1988; Tuckerman *et al.* 1997) and several studies have since argued that the role of bromine in the troposphere may be ubiquitous. In a tropospheric study using the *p*-TOMCAT chemical transport model, Yang *et al.* (2005) considered two sources of bromine compounds. Firstly, their study included biogenic halocarbons with a source strength for short-lived biogenic halocarbons ( $\text{CHBr}_3$ ,  $\text{CH}_2\text{Br}_2$ ,  $\text{CH}_2\text{BrCl}$ ,  $\text{CHBr}_2\text{Cl}$  and  $\text{CHBrCl}_2$ ) of 690 Gg per year, primarily in the tropics, from the oceans, vegetation and biomass burning (Warwick *et al.* 2006*a,b*). Secondly, they included the potentially important inorganic source from sea salt. Sea salt aerosol is depleted in bromine relative to the ocean. The mechanism for depletion, and release into the atmosphere, is thought to follow the uptake of gaseous HOBr onto the sea salt, followed by reaction with  $\text{Br}^-$  (Fan & Jacob 1992):



In their study Yang *et al.* (2005) included a sea salt bromine source which depended on a number of factors, including a sea salt aerosol production rate,  $P$ , and the effective bromine release from the aerosol. Yang *et al.* (2005) used two different expressions for  $P$ , based on Smith *et al.* (1993), hereafter SMI, and Monahan *et al.* (1986), hereafter MON.  $P$  is a complex function of the surface wind speed over the ocean. For example, in the MON formula,  $P$  depends on the 10 m wind speed raised to the power 3.41.



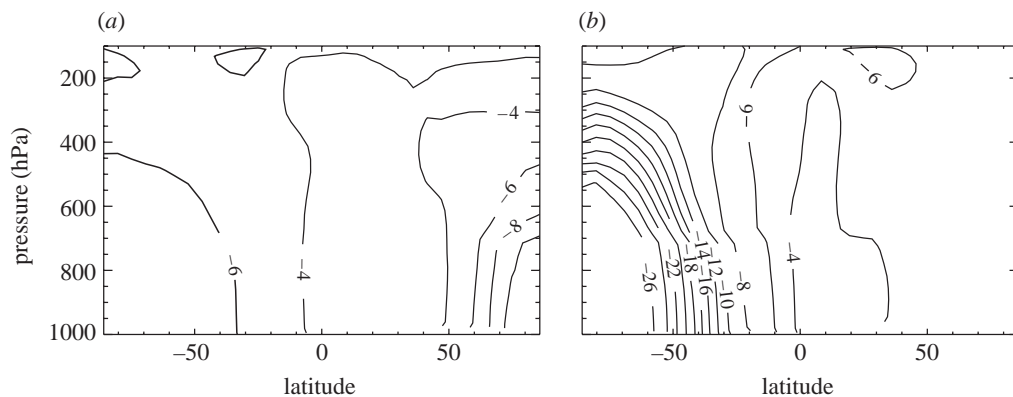


Figure 6. Monthly zonal mean of the percentage ozone reduction due to the addition of bromine chemistry for (a) June and (b) December. Based on fig. 9 of Yang *et al.* (2005), whence further details can be found.

Figure 6 is taken from Yang *et al.* (2005) and shows the change in zonal mean ozone calculated for the contemporary atmosphere when the bromine source is included into an otherwise detailed tropospheric chemistry mechanism. The changes are significant, being several per cent throughout the Northern Hemisphere free troposphere, peaking at close to 30% in the high latitude southern summer, south of the major sea salt aerosol source above the roaring forties. The sea salt aerosol dominates the bromine budget in the lower troposphere with the biogenic source being most important at higher altitudes.

The suggestion that bromine is important in the contemporary free troposphere raises questions about how that importance could change in the future. A positive correlation was observed between SSTs and bromoform fluxes by Butler *et al.* (2007) suggesting a potential link between global biogenic halocarbon emissions and climate change. Will emissions of biogenic halocarbons increase in the future, perhaps in response to increased SSTs or increased ocean productivity? Will the production of sea salt aerosol, which depends strongly on surface wind stress, increase in a future, windier climate? Will the transport of these relatively short-lived bromine sources change with changed circulation in a future climate and will this affect chemistry, perhaps following changed STE? We have addressed the latter two questions by sensitivity studies reported next.

#### (a) Wind stress-driven change in sea salt aerosol production

The study reported by Yang *et al.* (2005) was carried out using the *p*-TOMCAT chemical transport model forced by meteorological analyses for 1998 from ECMWF. We have repeated the calculation, considering only the sea salt emissions, to study the possible impact of changed sea salt emissions in 2100. (Note that the biogenic emissions do not change in this calculation.) Our methodology is simple. We have used runs A and C of the Met Office climate model, discussed in §3, to determine the difference in the monthly mean surface wind speed between 2100 and 2000 (based on a five-year average for the two periods). The ECMWF surface winds speeds in *p*-TOMCAT were then modified

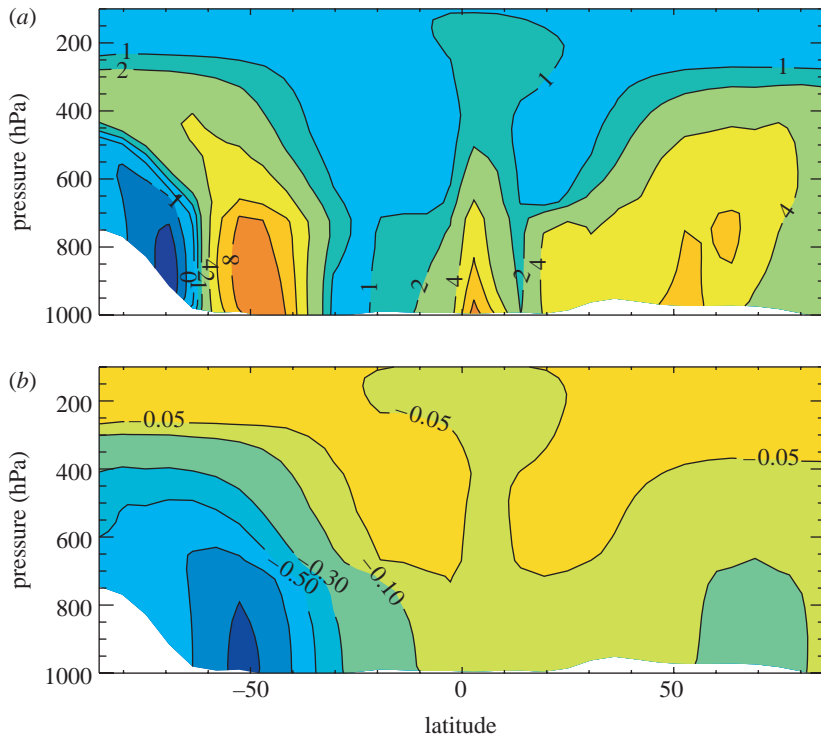


Figure 7. Percentage change in (a)  $\text{Br}_x$  and (b) ozone between 2100 and 2000. The only difference between the two model runs arises from the change in wind-driven surface emissions of sea salt.

for 2100 conditions by adding this difference to the 1998 analyses used by Yang *et al.* (2005). Figure 7a shows the change in total reactive bromine between models forced with the ‘2000’ and ‘2100’ surface wind speeds. Largest changes in bromine, approaching 10%, occur in the middle latitude Southern Hemisphere where present day emissions also peak. However, these have only a modest impact on free tropospheric ozone (figure 7b). In the Northern Hemisphere, changes (reductions) are less than 0.1%, approaching a maximum of approximately 1% in the Southern Hemisphere where the reactive bromine changes are largest. Wind-driven change in halogen abundance from sea salt appears to be a very weak climate feedback (although the nonlinearity in the emissions will be explored by considering shorter averaging periods for the surface wind change).

The sea salt production depends significantly on surface wind speed. Estimates of the source strength are quite uncertain (Gong *et al.* 2002). For example, based on the ECMWF reanalysis wind speed for 1998, we find that the sea salt production (for dry particle radii between 0.1 and 10  $\mu\text{m}$ ) ranges from 1150  $\text{Tg NaCl yr}^{-1}$  for the SMI formulation to 2060  $\text{Tg NaCl yr}^{-1}$  from the MON formulation. When the MON production is used (giving approx. two times the total flux obtained with SMI)  $\text{Br}_x$  concentrations in the Southern Hemisphere increase by a factor of up to 50% in December, corresponding to a maximum ozone reduction of 36% compared with 26% for SMI (Yang *et al.* 2005).

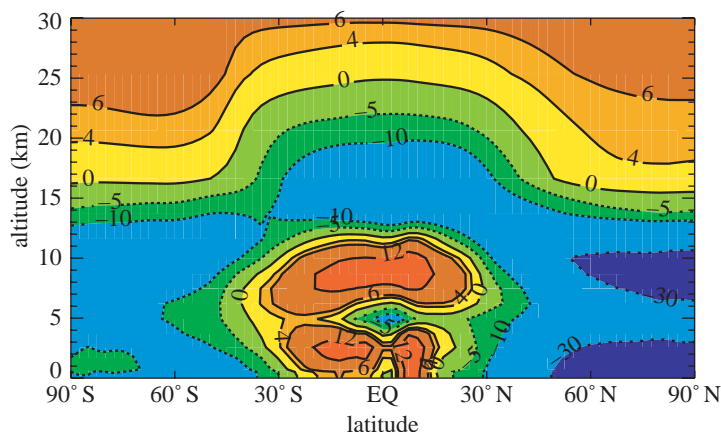


Figure 8. Percentage change in  $\text{Br}_x$  arising from the degradation of biogenic halocarbons between model calculations for 2100 and 2000. The halocarbons emissions are those described in Yang *et al.* (2005); changes in  $\text{Br}_x$  are driven solely by difference in the calculated circulation.

### (b) Circulation changes

In §3, we discussed a strengthened Brewer–Dobson circulation and increased STE in the context of a future climate. Here, we look at how changed circulation in both the stratosphere and the troposphere might change the distribution of the products of degradation of the biogenic bromine compounds. Hence, a 2100 calculation was carried out in the UM model to give a new circulation for the end of this century. This calculation included the same biogenic emissions as described by Yang *et al.* (2005). Primary oxidation of the emitted species was modelled using prescribed OH and photolysis fields. The degradation products ( $\text{Br}_x$ , the reactive inorganic bromine compounds) were calculated but played no further role in the chemical calculations. Figure 8 shows the calculated percentage change in  $\text{Br}_x$  between 2000 and 2100. There are quite large changes in the tropical troposphere, due to strengthening of convection in the 2100 simulation. Throughout the rest of the troposphere changes are small and seem unlikely to be important for the oxidizing capacity. In the lower stratosphere  $\text{Br}_x$  has increased by a few per cent. Here, bromine can play a role in the destruction of ozone with bromine being approximately 50 times more efficient in destroying ozone than chlorine on a per atom basis. It seems possible that the changes in the lower stratosphere will be more important than those in the troposphere but this remains to be assessed in a future calculation.

## 6. Conclusions

Model calculations which include projected changes in the emissions of  $\text{NO}_x$  and VOCs indicate that tropospheric ozone concentrations are likely to increase significantly in a future atmosphere. The calculated increases in surface ozone represent a serious deterioration in air quality with implications for human health; there are also important implications for the calculated change in oxidizing capacity. Under climate change several factors in addition to the

anthropogenic NO<sub>x</sub> and VOC emissions could influence the calculated ozone change. Tropospheric water vapour concentrations will increase in a warmer climate and this tends to reduce the calculated ozone increase; the reaction between O(<sup>1</sup>D) and water vapour is an important sink for ozone. Another factor is the change in the net influx of ozone from the stratosphere (STE), a crucial term in the ozone budget. Our calculations indicate that this will nearly double during this century, consistent with other calculations indicating that the Brewer–Dobson circulation will increase (Butchart & Scaife 2001). Here, we find that the increased STE more than compensates the increased water vapour driven loss. The important point is that the change in STE is large and needs to be considered.

One further important factor in determining how oxidizing capacity will change during this century is how natural, biogenic emissions will change in the future. These emissions are larger than anthropogenic emissions in the present day atmosphere so that any changes could be very significant. Future emissions will depend on how the biosphere and, in particular, primary productivity changes. The changes are expected to depend critically on climate. We have carried out a sensitivity calculation to address the possible increase in isoprene emissions consequent on increased surface temperature in a future climate. The changes in ozone are significant but depend crucially on the background chemical regime. We find that increased isoprene increases ozone in these calculations by up to 8 ppbv in the Northern Hemisphere (where the chemistry is ‘VOC-limited’) but decreases ozone by up to 8 ppbv in the tropics over the continental emission regions.

Emissions of natural bromine compounds into the troposphere are now thought to be an important player in the contemporary ozone budget. In two preliminary studies, we have looked at the possible climate sensitivity to this contribution. We find that wind-driven changes in emissions of bromine from sea salt aerosol do not make a significant contribution to future ozone change. We do, however, find that the transport of short-lived biogenic halogen species from a tropical surface source could be different in the future. It seems possible, for example, that consequent changes in lower stratospheric bromine could be more important than those in the troposphere but this remains to be assessed in a future calculation.

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