**Atmospheric
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Linkages between ozone depleting substances, tropospheric oxidation and aerosols

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Abstract

Coupling between the stratosphere and the troposphere allows changes in stratospheric ozone abundances to affect tropospheric chemistry. Large-scale effects from such changes on chemically produced tropospheric aerosols have not been systematically examined in past studies. We use a composition-climate model to investigate potential past and future impacts of changes in stratospheric Ozone Depleting Substances (ODS) on tropospheric oxidants and sulfate aerosols. In most experiments, we find significant responses in tropospheric photolysis and oxidants, with small but significant effects on methane radiative forcing. The response of sulfate aerosols is sizeable when examining the effect of increasing future nitrous oxide (N_2O) emissions. We also find that without the regulation of chlorofluorocarbons (CFCs) through the Montreal Protocol, sulfate aerosols could have increased by 2050 by a comparable amount to the decreases predicted due to relatively stringent sulfur emissions controls. The historical radiative forcing of CFCs through their indirect effects on methane ($-22.6\,\mathrm{mW\,m^{-2}}$) and sulfate aerosols ($-3.0\,\mathrm{mW\,m^{-2}}$) discussed here is non-negligible when compared to known historical CFC forcing. Our results stress the importance of accounting for stratosphere-troposphere, gas-aerosol and composition-climate interactions when investigating the effects of changing emissions on atmospheric composition and climate.

1 Introduction

Stratospheric ozone (O_3) changes have been large over the past few decades mainly due to anthropogenic emissions of Ozone Depleting Substances (ODS), and are expected to be large in the future due to the phase-out of ODS emissions and to climate change (e.g. Austin et al., 2010; Eyring et al., 2010). Stratospheric ozone exerts direct radiative forcing on the Earth system (Forster et al., 2007), while it also indirectly affects other climate aspects such as tropospheric circulation and precipitation (Son et al., 2008; Kang et al., 2011). Furthermore, its changes can impact other radiatively

important species, especially by affecting the tropospheric oxidizing capacity. The latter is largely determined by the abundances of hydroxyl radicals (OH), which depend on tropospheric ozone and nitrogen oxides (NO_x), humidity, abundances of species that consume OH (Carbon Monoxide (CO), methane and Non-Methane Volatile Organic Compounds (NMVOCs)), and Ultra-Violet (UV) radiation (e.g. Thompson, 1992; Lelieveld et al., 2002; Voulgarakis et al., 2012).

Changes in stratospheric ozone can affect tropospheric oxidants via stratosphere-troposphere exchange (STE) (Collins et al., 2003; Hegglin and Shepherd, 2009; Prather and Hsu, 2010; Zeng et al., 2010; Voulgarakis et al., 2011), which enriches the troposphere with ozone, and by driving changes in the photolysis of tropospheric species (Madronich and Granier, 1992; Bekki et al., 1994; Fuglestved et al., 1994; Krol and van Weele, 1997; Isaksen et al., 2005; Lamarque et al., 2010b; Tang et al., 2011), which depends on UV radiation and, thus, the amount of overhead ozone. Photolysis has a central role in driving the formation of OH (Madronich and Granier, 1992; Fuglestved et al., 1994; Thompson, 1992; Rohrer and Berresheim, 2006; Voulgarakis et al., 2009), since it leads to the breakdown of ozone,

$$O_3 + h\nu \rightarrow O_2 + O(^1D)(\lambda < 320\,nm) \tag{R1}$$

and the excited oxygen atoms produced react with water vapor to produce OH:

$$O(^1D) + H_2O \rightarrow OH + OH \tag{R2}$$

Apart from cleansing the atmosphere from pollutants such as CO and NMVOCs, oxidation by OH also affects methane and sulfate aerosols, being the major sink of the former (Madronich and Granier, 1992; Voulgarakis et al., 2012) and a major chemical source of the latter via gaseous oxidation of sulfur dioxide (SO_2) (Unger et al., 2006; Shindell et al., 2009). Thus, OH plays a significant indirect role in determining the radiative balance of the troposphere. Sulfate aerosols are also produced through SO_2 aqueous oxidation by hydrogen peroxide (H_2O_2) (Koch et al., 2006; Unger et al., 2006), and the production/loss of the latter also heavily depends on photolysis (e.g. Lelieveld et al., 2002). Sulfate aqueous-phase production is globally more efficient than the gas-phase

process (via OH), but the former produces aerosols with shorter lifetime, due to the usual simultaneous presence of clouds.

Although effects of stratospheric ozone changes on tropospheric oxidants have been studied in the past (see above), their possible indirect link with tropospheric aerosols and their radiative forcing has not been examined. Here, we systematically explore these links in a number of model experiments, considering both past and future ODS changes. We further investigate such stratosphere-troposphere interactions in a hypothetical future scenario where ODS have not been regulated by the Montreal Protocol. Past studies examining this topic did not investigate tropospheric effects (Morgenstern et al., 2008; Newman et al., 2009). In Sect. 2, we outline the main characteristics of the model used, and describe the model experiments performed. Section 3 presents and discusses the results of the experiments, while Sect. 4 outlines the conclusions of this study.

2 Model description and experimental set-up

2.1 Model description

We used a version of the GISS composition-climate model (Shindell et al., 2006; Shindell et al., 2012), which is very similar to the ModelE2 version developed for use in simulations in support of the Intergovernmental Panel on Climate Change (IPCC) Fifth Assessment Report (AR5). The model has a 2° latitude by 2.5° longitude horizontal resolution and 40 vertical layers from the surface to 0.1 hPa. Tropospheric/stratospheric chemistry includes 156 chemical reactions among 51 gas species. Photolysis rates are simulated using the Fast-J2 scheme (Wild et al., 2000; Bian and Prather, 2002), which accounts for the effects of modelled overhead ozone, clouds, aerosols and surface reflections. The model's sulfate aerosol scheme includes prognostic simulations of the mass distributions of DiMethyl Sulfide (DMS), MethaneSulfonic Acid (MSA), SO_2, and sulfate (Koch et al., 2006).

The model's skill in capturing tropospheric oxidants and sulfate has been evaluated in past studies and shown to be realistic (Koch et al., 2006; Shindell et al., 2006). A recent model evaluation, in which a very similar version of the model was used (Shindell et al., 2012), showed that the model has improved significantly compared to its previous version (Shindell et al., 2006), especially when it comes to ozone seasonality in the stratosphere. However, the Antarctic ozone hole extends more equatorward than seen in the observations, and it lasts somewhat too long. Still, the biases in middle and low latitudes, which are of particular interest in this study (due to the abundance of oxidants and aerosols in these regions), are small, and typically less than 5 %.

The global tropospheric mean mass-weighted OH concentration is 9.9×10^{-5} mol cm^{-3}, which is in good agreement with past estimates (Lawrence et al., 2001). Furthermore, it has been shown (Voulgarakis et al., 2012) that the model's tropospheric chemical methane lifetime agrees very well with a recent observationally-constrained estimate (Prather et al., 2012). The above indicate that tropospheric oxidising capacity is simulated reasonably in the model. The model's sulfate used has been found to be more sensitive to OH changes than several other models (Fry et al., 2012), though these other models did not include liquid tracer budgets, which may mean that they are missing some of the physics that are included in the GISS simulations, though differences in sulfate chemistry could be important as well.

2.2 Experimental set-up

In the experiments presented here, present-day anthropogenic and biomass burning emissions of NO$_x$, CO, NMVOCs and aerosols follow Lamarque et al. (2010a), which were created in support of the Coupled Model Intercomparison Project Phase 5 (CMIP5). Lightning NO$_x$ emissions depend on the model's convection (Price et al., 1997), while isoprene emissions respond to temperature and solar radiation based on the algorithm of Guenther et al. (2006). Natural emissions of NO$_x$ from soils are prescribed at fixed values (2.7 Tg N yr^{-1}), as are biogenic emissions of alkenes

(16 Tg C yr^{-1}), paraffins (14 Tg C yr^{-1}), and terpenes (192 Tg yr^{-1}). The concentrations of long-lived gases, such as CO_2, methane, N_2O and CFCs, are prescribed at the surface to observed present-day values. When perturbed in our experiments (CFCs, N_2O; see next paragraph), they either follow past observations, or future projections according to the Representative Concentration Pathway (RCP; van Vuuren et al., 2011). The RCP projections for N_2O and CFC concentrations are based on calculations with the reduced-complexity coupled carbon cycle climate model MAGICC 6.3 to estimate mixing ratios that would result from the RCP emissions (Meinshausen et al., 2011).

We performed six simulations (see Table 1): (a) BASE, which represents non-perturbed present-day (2000) conditions; (b) 1960 CFCs, in which CFCs are set to 1960 levels; (c) 2100 CFCs, in which CFCs are set to 2100 levels following the RCP8.5 scenario; (d) WACFCs, in which CFCs are set to 2050 levels following a "world avoided" scenario, where CFCs are not regulated by the Montreal Protocol (Newman et al., 2009); (e) 1850 N_2O, in which N_2O is set to 1850 levels; and (f) 2100 N_2O, in which N_2O is set to 2100 levels (following RCP8.5). Non-ODS emissions/concentrations and sea-surface temperatures are representative of present-day in all experiments in order to isolate the ODS effects alone. In each experiment, we ran the model using the same conditions for 7 yr and then averaged in order to increase the signal-to-noise ratio. Two years of spin-up were performed in advance.

3 Results and discussion

Figure 1 shows the annual zonal mean photolysis rate of ozone to yield a singlet oxygen atom (J(O^{1}D); see Reaction R1), as well as its changes in the various sensitivity experiments. J(O^{1}D) is largest in the tropics, where solar zenith angles and overhead ozone columns are smallest. We find that all the perturbations applied to ODS have sizeable effects on tropospheric photolysis (Fig. 1). The changes in J(O^{1}D) are largest over polar regions, where stratospheric processes depleting ozone are more effective, and thus UV changes affecting tropospheric photolysis are also large. However, even in

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non-polar regions, such as northern midlatitudes, there are sizeable changes (mostly larger than 5 %), which can have significant impacts on tropospheric chemistry. The effects are dramatic in the WACFCs experiment, where midlatitude $J(O^1D)$ increases by more than 120 %.

Figure 2 shows differences in total ozone column, surface $J(O^1D)$, surface OH and surface sulfate concentrations, between the WACFCs and the BASE simulation, for the northern extratropics, the region where sulfate is most important for climate and air quality. Total ozone for 2050 is lower by 50–60 % due to the lack of regulation in CFCs in this scenario, in fairly good agreement with previous work (Newman et al., 2009). This leads to ubiquitous surface $J(O^1D)$ increases of more than 150 % in the northern extratropics, which, in turn leads to OH increases of 40–80 %. The highest OH increases are located in the regions with the largest total ozone and $J(O^1D)$ changes combined with high OH recycling efficiencies (Eastern US, Western Europe, East Asia) (Lelieveld et al., 2002).

We find subsequent large increases of sulfate aerosol concentrations throughout the northern extratropics (Fig. 2d). Differences range from 20 to 50 % in highly populated midlatitude regions where aerosols cause serious human health damage. The increases are around 30–35 % over the northernmost states of the US, over 40 % over the British Isles, and 15–30 % over East Asia. Increases in sulfate aerosols are correlated in several cases to the enhancement of the tropospheric oxidizing capacity, as reflected by OH, which leads to more SO_2 oxidised to sulfate. Figure 3 shows the zonal mean differences in concentration and chemical gas-phase production rate of sulfate, between WACFCs and BASE. It is clear that areas with large chemical production changes are also areas with high concentration changes, the "hot-spot" being the northern midlatitudes at low altitudes. This finding is in qualitative agreement with an earlier study on a related topic (Toumi et al., 1994).

Note that changes in H_2O_2 and aqueous-phase production of sulfate are also detectable in our perturbation experiments, especially in WACFCs, where global mean H_2O_2 changes by around 38 %, while global mean sulfate aerosol production via H_2O_2

changes by 11 %, relative to BASE. However, as mentioned earlier, the gas-phase production changes (via OH) are expected to be more important due to the longer lifetime of the sulfate produced through via gaseous processes.

Table 2 summarizes the effects of the perturbations applied in the different experiments on tropospheric OH and surface sulfate concentration, as well as on radiative forcing by methane and sulfate. We focus on global effects, and on effects in northern midlatitudes, where sulfate is important, both for air quality and climate. The OH differences are significant in all the experiments, with the WACFCs scenario showing clearly the largest effects, consistent with photolysis changes (Fig. 1). Global methane radiative forcing strongly decreases in WACFCs (by $\sim 0.5\,\mathrm{W\,m^{-2}}$), while there are also significant changes in the other experiments ($6\text{--}23\,\mathrm{mW\,m^{-2}}$).

For sulfate, in terms of both concentration and forcing, the two cases for which we find the most sizeable relative changes are WACFCs and 2100 N_2O. In the former, the differences range from around 12 to 20 %, while in the latter, they are around 1.7–2.5 %. Regionally, concentration differences can be as large as 50 % in WACFCs and 15 % in 2100 N_2O, and forcing differences reach 35 % in WACFCs and 13 % in 2100 N_2O (see Fig. 2d and Fig. 4). Areas affected heavily include East Asia, parts of Europe and parts of Northeastern America and the North Atlantic. In an additional experiment where sulfur emissions were set to 2050 values following the RCP4.5 scenario (in which SO_2 emissions decrease by more than 50 %), we found global surface sulfate aerosol concentration reductions of 24 %. This indicates that the indirect effect of ODS on aerosols discussed here (17 % globally) could have cancelled out part of the benefit gained from aerosol emissions reductions, had the Montreal Protocol not been implemented. Note that total sulfate burden changes depend on the current relative amount of SO_2 removed by deposition versus conversion to sulfate, thus it would be useful to test the variation of this balance across different models in future work.

The indirect radiative forcing of ODSs through the processes presented here has not been discussed in previous studies (Forster et al., 2007). We compared these effects to the magnitude of previously estimated direct historical ODS forcing, as well as to

indirect forcing through other processes. Our calculated global methane radiative forcing due to past CFC changes is equal to about 7 % of the direct preindustrial (PI) to present-day (PD) forcing from CFCs, and to more than half their indirect effect through stratospheric ozone radiative forcing, based on Forster et al. (2007). For sulfate radiative forcing, the effects are smaller (1 % of the direct forcing and 8 % through of the indirect stratospheric ozone effect). Similarly, the historical indirect effects of N_2O on radiative forcing through methane and sulfate (roughly equal) are equal to around 5 % of its direct PI-PD forcing and to 70 % of its indirect effects through stratospheric ozone. The effects of future N_2O changes on radiative forcing in our experiments are 2–3 times larger than the historical effects, while the future effects of CFCs are also equal or larger to the historical.

Changes in stratospheric ozone can impact tropospheric oxidation via STE, and this effect is expected to be opposite of the photolysis effect. Less ozone in the stratosphere can lead to less ozone transported to the troposphere and, thus, less OH produced by ozone photolysis. However, the effect of UV changes on photolysis appears to be dominating the OH responses that we find in the troposphere. There is even one case (WACFCs, Southern Hemisphere) in which ozone depletion in the stratosphere is followed by ozone increases in the troposphere. However, this is driven by transport modifications affecting the NO_x budget in the troposphere and, thus, tropospheric ozone production. We find that tropospheric temperature and humidity changes are very minimal (< 1 %) in all the experiments, so we rule out the possibility that climate changes induced by differences in CFCs and stratospheric ozone drive any of the changes simulated.

Our experiments presented here are idealised, since a scenario in which only ODS will change, while other aspects of the climate system remain constant is not realistic. Nevertheless, by isolating the ODS effect, we provide insight into particular processes which can be important. For the two scenarios in which we found the most sizeable differences (WACFCs and 2100 N_2O), changing future emissions and climate change would be expected to add to the effects of ODS on aerosols. In particular, studies

have found that continental regions, where sulfate aerosols are of high importance, will likely experience increases in OH abundances due to increases in NO_x emissions, while the global temperature and humidity increases expected due to global warming may lead to generally more OH production in the troposphere (Wild and Palmer, 2008). This, in addition to the oxidant increases due to ODS effects found here, could lead to even larger sulfate responses in WACFCs and 2100 N_2O. Note though, that when more optimistic scenarios are used for future NO_x emissions, there is a mixture of positive and negative OH responses over industrialised regions, with large inter-model variability (Voulgarakis et al., 2012).

Projected increases in tropical upwelling could lead to further lower stratospheric ozone decreases at low latitudes (Eyring et al., 2010), which would, again, add to the UV, oxidant and sulfate aerosol responses. Also, projected changes in atmospheric circulation may drive increased transport of ozone from the stratosphere to the troposphere (Collins et al., 2003; Shindell et al., 2006), increasing tropospheric OH production. However, in a scenario like 2100 N_2O, if we account for the simultaneous decline in CFCs, part of the tropospheric effects will be cancelled out. Finally, note that in the calculations of OH and sulfate responses, feedbacks on OH through changes in methane have not been taken into account, since methane concentrations were kept constant. Had these feedbacks been included, all responses presented here would have been stronger.

4   Conclusions

We performed model experiments to investigate the role of ozone depleting substances in driving changes in tropospheric oxidants, aerosols and radiative forcing. These links have not been examined in previous studies investigating the effects of ODS or the evolution of tropospheric aerosols. Our results indicate that changes in ODS and stratospheric ozone can induce large-scale changes in tropospheric composition, with a non-negligible effect on radiative forcing. Indirect historical forcings of CFCs and N_2O

through their effects on tropospheric methane and sulfate range from 8 % to 70 % (depending on the species) of the known corresponding indirect forcings through stratospheric ozone depletion. Special attention is needed regarding N_2O effects beyond 2100, since its emissions are expected to be the dominant driver of future stratospheric
5   ozone depletion (Ravishankara et al., 2009).

Our analysis also suggests that CFCs emissions reductions resulting from the Montreal Protocol may be translating to tropospheric composition and climate changes that have not been discussed in assessments exploring the "side-effects" of the agreement (Velders et al., 2007). We suggest that the Montreal Protocol may have been a factor
10   mediating future sulfate aerosol concentrations in the 21th century. Finally, our results imply that taking into account stratosphere-troposphere, gas-aerosol and composition-climate interactions is important when assessing the impact of regulations in emissions. Earth system models, which are designed to include all the above-mentioned interactions, are expected to facilitate such efforts in the future.

References

20   Austin, J., Scinocca, J., Plummer, D., Oman, L., Waugh, D., Akiyoshi, H., Bekki, S., Braesicke, P., Butchart, N., Chipperfield, M., Cugnet, D., Dameris, M., Dhomse, S., Eyring, V., Frith, S., Garcia, R. R., Garny, H., Gettelman, A., Hardiman, S. C., Kinnison, D., Lamarque, J. F., Mancini, E., Marchand, M., Michou, M., Morgenstern, O., Nakamura, T., Pawson, S., Pitari, G., Pyle, J., Rozanov, E., Shepherd, T. G., Shibata, K., Teyssedre, H.,
25   Wilson, R. J., and Yamashita, Y.: Decline and recovery of total column ozone using a multimodel time series analysis, J. Geophys. Res., 115, D00M10, doi:10.1029/2010JD013857, 2010.

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Bekki, S., Law, K. S., and Pyle, J. A.: Effect of ozone depletion on atmospheric CH_4 and CO concentrations, Nature, 371, 595–597, 1994.

Bian, H. and Prather, M.: Fast-J2: accurate simulations of photolysis in global climate models, J. Atmos. Chem., 41, 281–296, 2002.

5 Collins, W. J., Derwent, R. G., Garnier, B., Johnson, C. E., Sanderson, M. G., and Stevenson, D. S.: Effect of stratosphere-troposphere exchange on the future tropospheric ozone trend, J. Geophys. Res., 108, 8528, doi:10.1029/2002JD002617, 2003.

Ehhalt, D., Prather, M., Dentener, F., Derwent, R., Dlugokencky, E., Holland, E., Isaksen, I., Katima, J., Kirchhoff, V., Matson, P., Midgley, P., and Wang, M.: Atmospheric chemistry and
10 greenhouse gases, in: Climate Change 2001: The Scientific Basis, Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change, edited by: Houghton, J. T., Ding, Y., Griggs, D. J., Noguer, M., van der Linden, P. J., Dai, X., Maskell, K., and Johnson, C. A., Cambridge University Press, Cambridge, UK, 2001.

Eyring, V., Cionni, I., Bodeker, G. E., Charlton-Perez, A. J., Kinnison, D. E., Scinocca, J. F.,
15 Waugh, D. W., Akiyoshi, H., Bekki, S., Chipperfield, M. P., Dameris, M., Dhomse, S., Frith, S. M., Garny, H., Gettelman, A., Kubin, A., Langematz, U., Mancini, E., Marchand, M., Nakamura, T., Oman, L. D., Pawson, S., Pitari, G., Plummer, D. A., Rozanov, E., Shepherd, T. G., Shibata, K., Tian, W., Braesicke, P., Hardiman, S. C., Lamarque, J. F., Morgenstern, O., Pyle, J. A., Smale, D., and Yamashita, Y.: Multi-model assessment of strato-
20 spheric ozone return dates and ozone recovery in CCMVal-2 models, Atmos. Chem. Phys., 10, 9451–9472, doi:10.5194/acp-10-9451-2010, 2010.

Forster, P., Ramaswamy, V., Artaxo, P., Berntsen, T., Betts, R., Fahey, D. W., Haywood, J., Lean, J., Lowe, D. C., Myhre, G., Nganga, J., Prinn, R., Raga, G., Schulz, M., and Van Dorland, R.: Changes in atmospheric constituents and in radiative forcing, in: Climate Change 2007: The
25 Physical Science Basis, Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, edited by: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., and Miller, H. L., Cambridge Univ. Press, Cambridge, UK, 2007.

Fry, M. M., Naik, V., West, J. J., Schwarzkopf, M. D., Fiore, A. M., Collins, W. J., Dentener, F. J.,
30 Shindell, D. T., Atherton, C., Bergmann, D., Duncan, B. N., Hess, P., MacKenzie, I. A., Marmer, E., Schultz, M. G., Szopa, S., Wild, O., Zeng, G.: The influence of ozone precursor emissions from four world regions on tropospheric composition and radiative climate forcing J. Geophys. Res., 117, D07306, doi:10.1029/2011JD017134, 2012.

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Fuglestved, J. S., Jonson, J. E., and Isaksen, I. S. A.: Effects of reductions in stratospheric ozone on tropospheric chemistry through changes in photolysis rates, Tellus B, 46, 172–192, 1994.

Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I., and Geron, C.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), Atmos. Chem. Phys., 6, 3181–3210, doi:10.5194/acp-6-3181-2006, 2006.

Hegglin, M. I. and Shepherd, T. G.: Large climate-induced changes in ultraviolet index and stratosphere-to-troposphere ozone flux, Nature Geosci., 2, 687–691, 2009.

Isaksen, I. S. A., Zerefos, C., Kourtidis, K., Meleti, C., Dalsoren, S. B., Sundet, J. K., Grini, A., Zanis, P., and Balis, D.: Tropospheric ozone changes at unpolluted and semipolluted regions induced by stratospheric ozone changes, J. Geophys. Res., 110, 02302, doi:10.1029/2004JD004618, 2005.

Kang, S. M., Polvani, L. M., Fyfe, J. C., and Sigmond, M.: Impact of polar ozone depletion on subtropical precipitation, Science, 332, 951–954, 2011.

Koch, D., Schmidt, G. A., and Field, C. V.: Sulfur, sea salt and radionuclide aerosols in GISS ModelE, J. Geophys. Res., 111, 06206, doi:10.1029/2004JD005550, 2006.

Krol, M. C. and van Weele, M.: Implications of variations in photodissociation rates for global tropospheric chemistry, Atmos. Environ., 31, 1257–1273, 1997.

Lamarque, J.-F., Bond, T. C., Eyring, V., Granier, C., Heil, A., Klimont, Z., Lee, D., Liousse, C., Mieville, A., Owen, B., Schultz, M. G., Shindell, D., Smith, S. J., Stehfest, E., Van Aardenne, J., Cooper, O. R., Kainuma, M., Mahowald, N., McConnell, J. R., Naik, V., Riahi, K., and van Vuuren, D. P.: Historical (1850–2000) gridded anthropogenic and biomass burning emissions of reactive gases and aerosols: methodology and application, Atmos. Chem. Phys., 10, 7017–7039, doi:10.5194/acp-10-7017-2010, 2010a.

Lamarque, J.-F., McConnell, J. R., Shindell, D. T., Orlando, J. J., and Tyndall, G. S.: Understanding the drivers for the 20th century change of hydrogen peroxide in Antarctic ice-cores, Geophys. Res. Lett., 38, 04810, doi:10.1029/2010GL045992, 2010b.

Lawrence, M. G., Jöckel, P., and von Kuhlmann, R.: What does the global mean OH concentration tell us?, Atmos. Chem. Phys., 1, 37–49, doi:10.5194/acp-1-37-2001, 2001.

Lelieveld, J., Peters, W., Dentener, F. J., and Krol, M. C.: Stability of tropospheric hydroxyl chemistry, J. Geophys. Res., 107, 4715, doi:10.1029/2002JD002272, 2002.

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Madronich, S. and Granie, C.: Impact of recent total ozone changes on tropospheric ozone photodissociation, hydroxyl radicals, and methane trends, Geophys. Res. Lett., 19, 465–467, 1992.

Meinshausen, M., Smith, S. J., Calvin, K., Daniel, J. S., Kainuma, M. L. T., Lamarque, J.-F., Matsumoto, K., Montzka, S., Raper, S., Riahi, K., Thomson, A., Velders, G. J. M., and van Vuuren, D. P.: The RCP greenhouse gas concentrations and their extensions from 1765 to 2300, Climatic Change, 109, 213–241, doi:10.1007/s10584-011-0156-z, 2011.

Morgenstern, O., Braesicke, P., Hurwitz, M. M., O'Connor, F. M., Bushell, A. C., Johnson, C. E., and Pyle, J. A.: The world avoided by the Montreal Protocol, Geophys. Res. Lett., 35, 16811, doi:10.1029/2008GL034590, 2008.

Newman, P. A., Oman, L. D., Douglass, A. R., Fleming, E. L., Frith, S. M., Hurwitz, M. M., Kawa, S. R., Jackman, C. H., Krotkov, N. A., Nash, E. R., Nielsen, J. E., Pawson, S., Stolarski, R. S., and Velders, G. J. M.: What would have happened to the ozone layer if chlorofluorocarbons (CFCs) had not been regulated?, Atmos. Chem. Phys., 9, 2113–2128, doi:10.5194/acp-9-2113-2009, 2009.

Prather, M. J. and Hsu, J.: Coupling of nitrous oxide and methane by global atmospheric chemistry, Science, 330, 952, doi:10.1126/science.1196285, 2010.

Prather, M. J., Holmes, C. D., and Hsu, J.: Reactive greenhouse gas scenarios: systematic exploration of uncertainties and the role of atmospheric chemistry, Geophys. Res. Lett., 39, 09803, doi:10.1029/2012GL051440, 2012.

Price, C., Penner, J., and Prather, M.: NO_x from lightning, 1, Global distribution based on lightning physics, J. Geophys. Res., 102, 5929–5941, 1997.

Ravishankara, A. R., Daniel, J. S., and Portmann, R. W.: Nitrous oxide (N_2O): the dominant ozone-depleting substance emitted in the 21st century, Science, 326, 123, doi:10.1126/science.1176985, 2009.

Rohrer, F. and Berresheim, H.: Strong correlation between levels of tropospheric hydroxyl radicals and solar ultraviolet radiation, Nature, 442, 184–187, 2006.

Shindell, D. T., Faluvegi, G., Unger, N., Aguilar, E., Schmidt, G. A., Koch, D. M., Bauer, S. E., and Miller, R. L.: Simulations of preindustrial, present-day, and 2100 conditions in the NASA GISS composition and climate model G-PUCCINI, Atmos. Chem. Phys., 6, 4427–4459, doi:10.5194/acp-6-4427-2006, 2006.

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Shindell, D. T., Faluvegi, G., Koch, D. M., Schmidt, G. A., Unger, N., and Bauer, S. E.: Improved attribution of climate forcing to emissions, Science, 326, 716, doi:10.1126/science.1174760, 2009.

Shindell, D. T., Pechony, O., Voulgarakis, A., Faluvegi, G., Nazarenko, L., Lamarque, J.-F., Bowman, K., Milly, G., Kovari, B., Ruedy, R., and Schmidt, G.: Interactive ozone and methane chemistry in GISS-E2 historical and future climate simulations, Atmos. Chem. Phys. Discuss., 12, 23513–23602, doi:10.5194/acpd-12-23513-2012, 2012.

Son, S.-W., Polvani, L. M., Waugh, D. W., Akiyoshi, H., Garcia, R., Kinnison, D., Pawson, S., Rozanov, E., Shepherd, T. G., and Shibata, K.: The impact of stratospheric ozone recovery on the Southern Hemisphere westerly jet, Science, 320, 1486–1489, 2008.

Tang, X., Wilson, S. R., Solomon, K. R., Shao, M., and Madronich, S.: Changes in air quality and tropospheric composition due to depletion of stratospheric ozone and interactions with climate, Photochem. Photobiol. Sci., 10, 280–291, 2011.

Thompson, A. M.: The oxidizing capacity of the earth's atmosphere: probable past and future changes, Science, 256, 1157–1165, 1992.

Toumi, R., Bekki, S., and Law, K. S.: Indirect influence of ozone depletion on climate forcing by clouds, Nature, 372, 348–351, 1994.

Unger, N., Shindell, D. T., Koch, D. M., and Streets, D. G.: Cross influences of ozone and sulfate precursor emissions changes on air quality and climate, Proc. Natl. Acad. Sci., 103, 4377–4380, 2006.

Velders, G. J. M., Andersen, S. O., Daniel, J. S., Fahey, D. W., and McFarland, M.: The importance of the Montreal Protocol in protecting climate, Proc. Natl. Acad. Sci., 104, 4814–4819, 2007.

Voulgarakis, A., Wild, O., Savage, N. H., Carver, G. D., and Pyle, J. A.: Clouds, photolysis and regional tropospheric ozone budgets, Atmos. Chem. Phys., 9, 8235–8246, doi:10.5194/acp-9-8235-2009, 2009.

Voulgarakis, A., Hadjinicolaou, P., and Pyle, J. A.: Increases in global tropospheric ozone following an El Niño event: examining stratospheric ozone variability as a potential driver, Atmos. Sci. Lett., 12, 228–232, 2011

Voulgarakis, A., Naik, V., Lamarque, J. F., Shindell, D. T., Young, P. J., Prather, M. J., Wild, O., Field, R. D., Bergmann, D., Cameron-Smith, P., Cionni, I., Collins, W. J., Dalsoren, S. B., Doherty, R. M., Eyring, V., Faluvegi, G., Folberth, G. A., Horowitz, L. W., Josse, B., McKenzie, I. A., Nagashima, T., Plummer, D. A., Righi, M., Rumbold, S. T., Skeie, R.,

Stevenson, D. S., Strode, S. A., Sudo, K., Szopa, S., and Zeng, G: Simulations of present-day and future OH and methane lifetime in the ACCMIP project, Atmos. Chem. Phys. Discuss., in preparation, 2012.

Wild, O. and Palmer, P. I.: How sensitive is tropospheric oxidation to anthropogenic emissions?, Geophys. Res. Lett., 35, 22802, doi:10.1029/2008GL035718, 2008.

Wild, O., Zhu, X., and Prather, M. J.: Fast-J: accurate simulation of in- and below-cloud photolysis in global chemical models, J. Atmos. Chem., 37, 245–282, doi:10.1023/A:1006415919030, 2000.

Zeng, G., Morgenstern, O., Braesicke, P., and Pyle, J. A.: Impact of stratospheric ozone recovery on tropospheric ozone and its budget, Geophys. Res. Lett., 37, 09805, doi:10.1029/2010GL042812, 2010.

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Table 1. Specifications of the various model sensitivity experiments performed. The year indicated reflects the period to which the levels of each variable correspond. "SST/SI" refers to sea surface temperatures and sea-ice conditions used to drive the experiments. "Emissions" refers to anthropogenic and biomass burning ozone precursor (NO_x, CO, NMVOC) and aerosol emissions.

	CFCs	N_2O	CH_4	SSTs/SI/CO_2	Emissions
BASE	2000	2000	2000	2000	2000
1960 CFCs	1960	2000	2000	2000	2000
2100 CFCs	2100	2000	2000	2000	2000
WACFCs	WA	2000	2000	2000	2000
1850 N_2O	2000	1850	2000	2000	2000
2100 N_2O	2000	2100	2000	2000	2000

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Table 2. Differences in annual mean tropospheric OH concentration, surface sulfate aerosol concentration, methane and sulfate aerosol Top-Of-the-Atmosphere (TOA) shortwave Radiative Forcing (RF), between the sensitivity experiments and the BASE run[a].
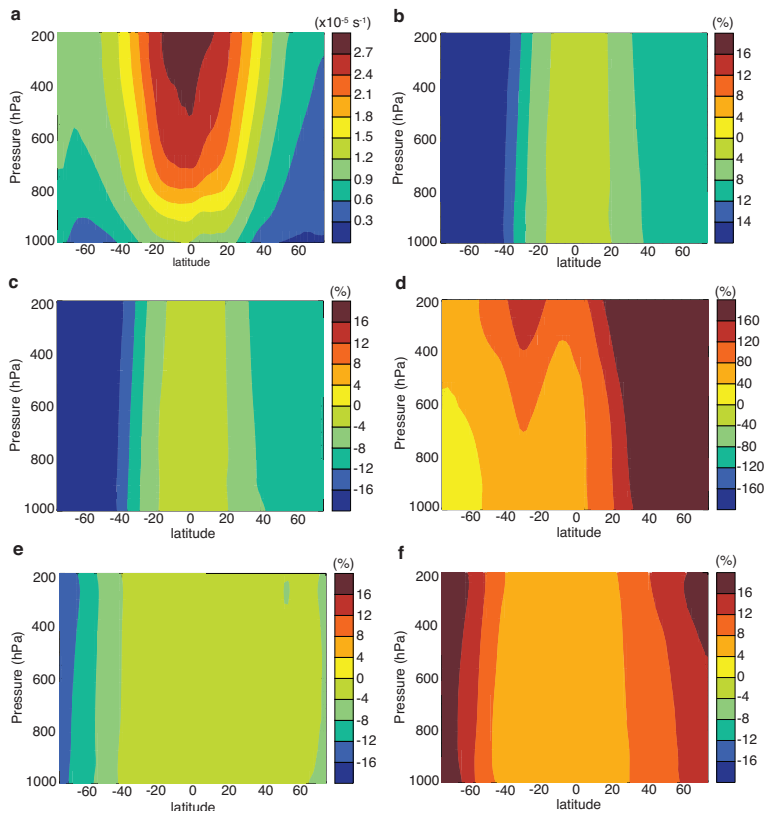
	1960 CFCs	2100 CFCs	WACFCs	1850 N$_2$O	2100 N$_2$O
GL[b] trop. OH conc.[c] (%)	−3.0 ± 0.2	−2.7 ± 0.2	+30.9 ± 0.8	−0.9 ± 0.2	+2.2 ± 0.2
GL CH$_4$ RF[d] (mW m^{-2})	+22.6 ± 1.0	+20.4 ± 1.5	−515.1 ± 1.4	+6.7 ± 1.1	−16.2 ± 1.0
NM[b] trop. OH conc. (%)	−2.1 ± 0.1	−1.8 ± 0.2	+80.5 ± 1.0	−1.0 ± 0.2	+2.7 ± 0.2
GL surf. Sulfate conc.[c] (%)	−0.3 ± 0.3	−0.8 ± 0.3	+17.5 ± 0.3	+0.5 ± 0.4	+1.7 ± 0.4
NM surf. Sulfate conc.(%)	+0.4 ± 0.4	−0.5 ± 0.3	+19.9 ± 0.4	+1.1 ± 0.5	+2.4 ± 0.6
GL Sulfate RF[c] (mW m^{-2})	+3.0 ± 1.6	+6.0 ± 2.2	−83.9 ± 1.7	−6.5 ± 1.6	−12.1 ± 2.6
NM Sulfate RF (mW m^{-2})	−3.7 ± 2.8	+2.6 ± 6.5	−157.2 ± 4.1	−17.4 ± 6.0	−18.3 ± 7.3

[a] Seven years from each simulation where averaged in order to increase the signal-to-noise ratio. The uncertainties are ±1σ standard deviations of the mean, based on the fluctuations among the different years in each simulation.
[b] GL = global; NM = northern midlatitudes (20–60° N).
[c] Mean tropospheric OH concentrations used for calculating the differences are mass-weighted, while mean surface sulfate concentrations and mean sulfate radiative forcings are area-weighted.
[d] We infer approximate global methane changes offline to calculate methane radiative forcing changes presented in Table 2. Global methane is calculated from global OH changes assuming a liner relationship between OH and methane chemical loss, and an additional chemical feedback (Prather et al., 2001). Methane radiative forcing was calculated following the standard formulations used in the IPCC Third Assessment Report (TAR).

Fig. 1. Photolysis rate changes in the sensitivity experiments. Annual zonal mean J(O^{1}D) in the BASE simulation **(a)**, and difference of annual zonal mean J(O^{1}D) in the 1960 CFCs **(b)**, the 2100 CFCs **(c)**, the WACFCs **(d)**, the 1850 N$_2$O **(e)** and the 2100 N$_2$O **(f)** simulations, from the BASE run. Note the difference in the colour scale in **(d)**.

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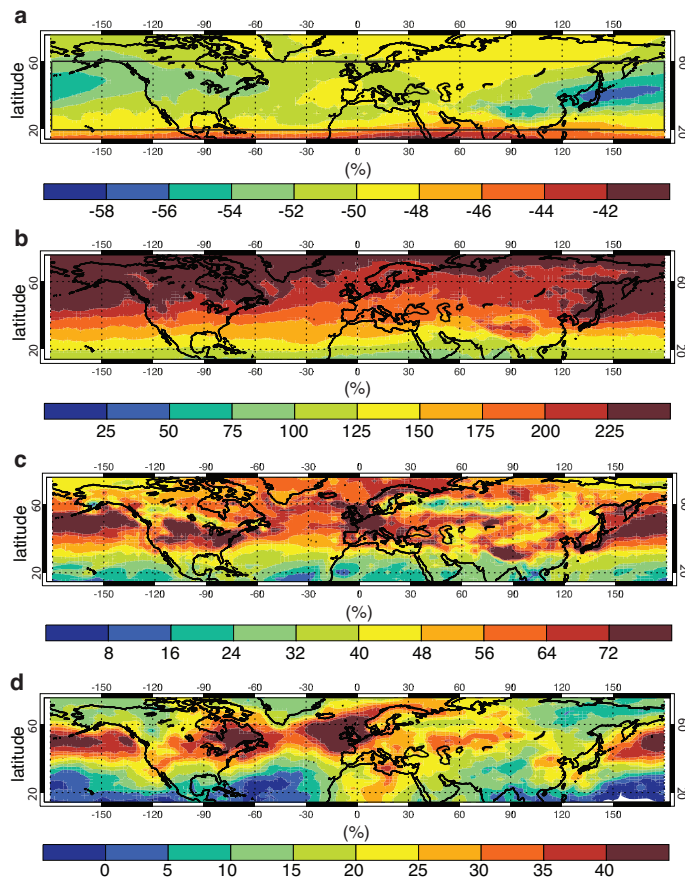
Fig. 2. Differences in annual mean total ozone column **(a)**, $J(O^1D)$ **(b)**, OH **(c)** and sulfate concentration **(d)**, between WACFCs and BASE. All differences are in percent (%), and for $J(O^1D)$, OH and sulfate they refer to the surface. Solid lines in panel **(a)** denote the midlatitude region (20–60° N) analysed in Table 2.

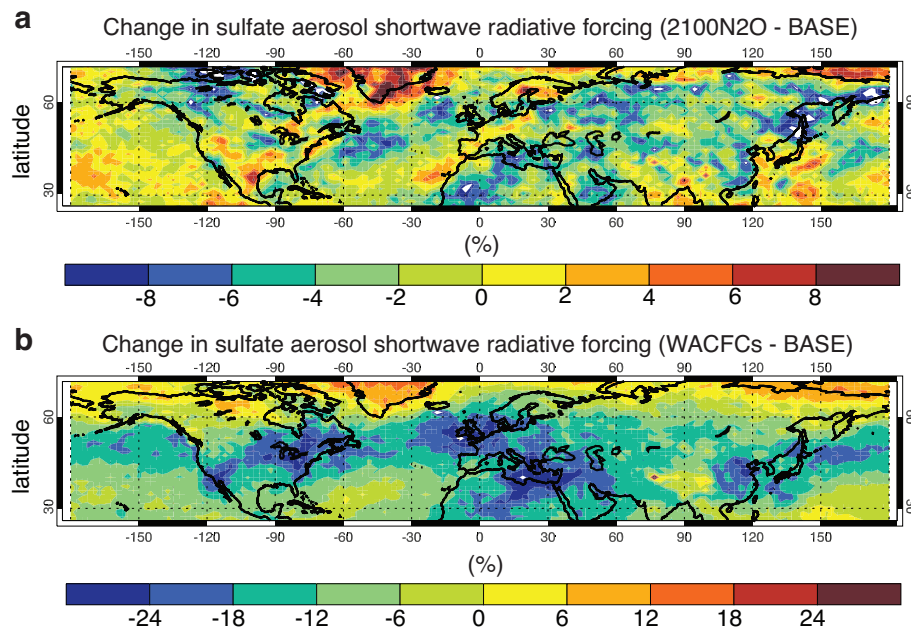**Ozone depletion and aerosols**

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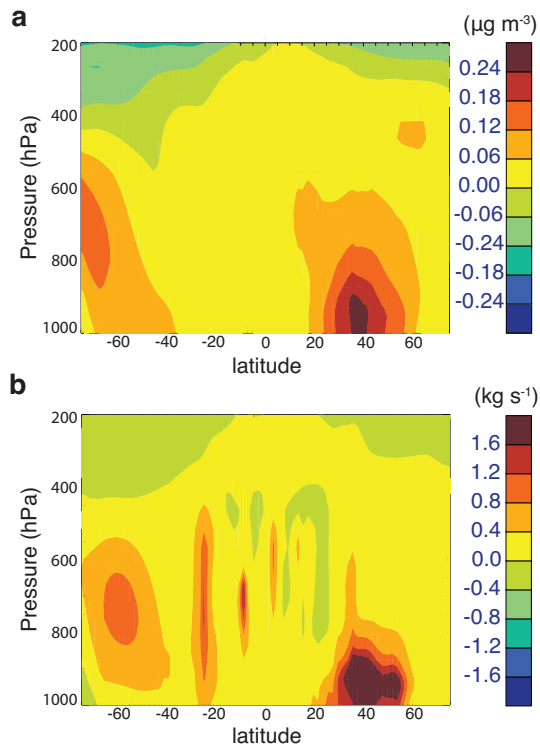
Fig. 3. Annual zonal mean differences in sulfate concentration **(a)** and gas-phase production (via OH) **(b)**, between WACFCs and BASE.

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a Change in sulfate aerosol shortwave radiative forcing (2100N2O - BASE)

b Change in sulfate aerosol shortwave radiative forcing (WACFCs - BASE)

Fig. 4. Changes in sulfate radiative forcing. Annual mean difference of midlatitude sulfate aerosol radiative forcing (shortwave, top-of-the-atmosphere) in the 2100 N_2O **(a)** and the WACFCs **(b)** simulations, from the BASE run.