The effect of UV-radiation on photo-oxidants and formaldehyde in the atmosphere

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Abstract. The annual cycle of formaldehyde (HCHO) has been investigated at a remote surface-site in Antarctica. HCHO mixing-ratios during the period of stratospheric ozone depletion are significantly higher than during times of similar sunshine duration in austral autumn. This might be due to enhanced UV-B radiation.

Introduction

Solar ultraviolet radiation (UV-B, $\lambda = 280 - 315$ nm) is one of the key environmental factors controlling the chemistry of the troposphere. It causes the photolysis of several trace gases such as ozone (O_3), nitrogen dioxide (NO_2), hydrogen peroxide (H_2O_2) and formaldehyde (HCHO). The most important reaction is the photolysis of O_3 since it produces excited oxygen atoms (O^1D) that can react with water vapour to form hydroxyl radicals (OH).

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \qquad (1)$$

$$O(^1D) + H_2O \rightarrow OH + OH \qquad (2)$$

Ozone photolysis in the troposphere is strongly dependent on the available UV-B radiation, and therefore is sensitive to absorption by stratospheric ozone (Fuglestvedt et al., 1994). If stratospheric ozone is depleted, e.g. in Antarctica during spring, UV-B radiation penetrates deeper into the troposphere and increases the formation of OH radicals. Important atmospheric trace gases such as methane (CH_4) and other hydrocarbons are mainly removed by OH radicals. Therefore the lifetime of these gases is determined by OH. The photochemical degradation of CH_4 yields formaldehyde.

$$CH_4 + OH \rightarrow CH_3 + H_2O \qquad (3)$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \qquad (4)$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \qquad (5)$$

$$CH_3 + O_2 \rightarrow HCHO + HO_2 \qquad (6)$$

Since this reaction sequence is strongly dependent on OH radicals, an influence of enhanced UV-B radiation is expected. Measurements of HCHO mixing ratio during a complete year and especially during ozone depletion events were performed at the German Antarctic station Neumayer (70° 39'S/ 08° 15'W) in order to investigate this relation.

Experimental

Measurements were carried out at Neumayer station during the over wintering season 1997/98 and during a summer campaign in February 1999. The station is located on the Ekström Ice Shelf at a distance of 7 km from the coastline, 42 m above sea level. A detailed description of the location and its meteorology is given by König-Langlo et al. (1998). The analysis of atmospheric HCHO was performed with a wet chemical fluorometric technique as described by Dong and Dasgupta (1987). Formaldehyde was transferred in a Hantzsch analogues reaction to a Pyridine derivate that could be excited by a mercury vapour lamp. For details see Riedel et al. (1999). Ozone column density data were obtained by ozone sondes launched weekly at Neumayer station. Additional data from the satellite-based total ozone mapping spectrometer (TOMS) were used. UV measurements were carried out with a spectroradiometer equipped with a multichannel detector system (Groß et al., 2001).

Results and Discussion

Figure 1 shows UV-B radiation of wavelength 300 nm measured at Neumayer station between mid-September and mid-November (thin black line). Also shown are HCHO mixing ratios during the period of ozone depletion (spring, black line) and during times with similar sunshine duration in austral autumn (grey line). To achieve this plot the autumn HCHO concentrations were mirrored at the middle of the polar night (day 173 of the year) and projected on the same timescale as the spring data. This technique allows the comparison of HCHO mixing-ratios during similar sunshine durations and solar angles. It is obvious that the mixing ratios during ozone depletion are enhanced. The average HCHO mixing ratio is 409±96 pptv HCHO in spring and 276±104 pptv in autumn.

The reduction in stratospheric O_3 in austral spring causes increased penetration of UV-B radiation (Figure 1). Radical production in the atmosphere should react very sensitively to enhanced UV-B actinic fluxes. Depicted in Figure 1 is the UV radiation with a wavelength of $\lambda = 300$ nm because ozone photolysis is most sensitive to this wavelength. Due to higher photolysis frequencies of tropospheric O_3, significantly higher OH mixing ratios are expected. Model calculations from Granier et al. (1999) with a three-dimensional model (IMAGES) actually predict an increase of OH surface mixing ratios by up to 12 %. Biggest changes are calculated for high latitudes and remote areas. In response to enhanced OH mixing-ratios the degradation of methane should also be enhanced. Observations of the global CH_4 distribution have revealed a decline in the growth rate during recent decades (Dlugokencky et al., 1998). Though there is no consensus on the causes of the long-term decline in the annual growth rate enhanced OH mixing ratios might be an explanation. Since HCHO is the main product of photochemical methane oxidation higher HCHO mixing ratios can be expected. Neumayer station is a remote polar site where OH changes are predicted to be largest.

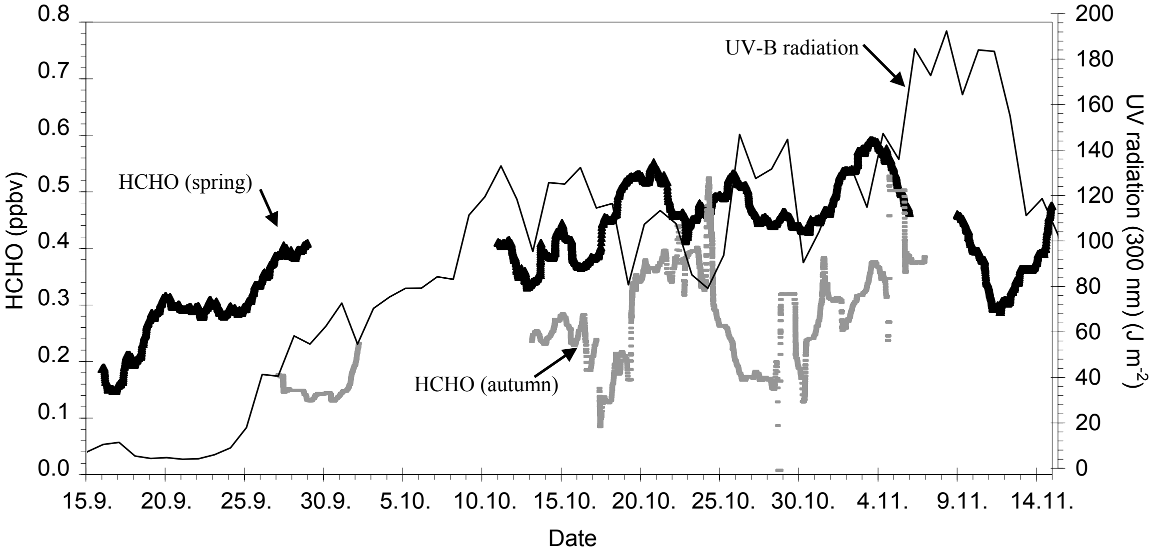

Figure 1. UV-B radiation ($\lambda = 300$ nm) and HCHO mixing-ratios, the latter shown by the heavy black line during Antarctic ozone depletion and the heavy grey line during austral autumn, mirrored on the middle of the polar night (day 173).

Photooxidation of CH_4 is the only known source for HCHO production at Neumayer Station. Therefore any observed higher HCHO mixing ratios during ozone depletion events (Figure 1) may point towards effects of increased OH levels and enhanced photochemical activity. Comparing spring (black line) and autumn (grey line) when the sunshine duration is similar, observed HCHO mixing ratios are twice as high in spring.

However, not only the photolysis of ozone is influenced by an increase of UV-B radiation. The photolysis of formaldehyde is also sensitive to a change in actinic fluxes. To quantify the response to stratospheric ozone changes Madronich and Granier (1994) defined the sensitivity factor S_i for the photolysis of different species

$$S_i = \ln(J_i * / J_i) / \ln(O_3 / O_3 *)$$

where J_i* and J_i are the photodissociation rate coefficients of a specific photolysis reaction corresponding to ozone column amount O_3* and O_3.

This factor gives the percentage increase in J_i from a 1% reduction of stratospheric ozone. Both photolysis branches of HCHO are affected by an increase of UV radiation. Sensitivity factors of 0.5 and 0.2 (Krol and van Weele, 1997) show that enhanced HCHO destruction through photolysis takes place.

$$HCHO + h\nu \rightarrow H + CHO \qquad S = 0.5 \qquad (7)$$

$$HCHO + h\nu \rightarrow H_2 + CO \qquad S = 0.2 \qquad (8)$$

Despite an increased loss of HCHO due to photolysis Figure 1 shows that HCHO mixing ratios during Antarctic spring are twice as high as in autumn. This suggests that the degradation must be counteracted by an enhanced photochemical production of HCHO due to increased ozone photolysis rates.

Conclusions and Outlook

During ozone depletion we observed much higher HCHO levels at Neumayer Station. This might be due to higher UV-B actinic fluxes and increased OH mixing-ratios. However, for a more detailed interpretation and a meaningful analysis of the processes determining the HCHO mixing-ratios, photochemical model calculations paying attention to special Antarctic conditions are indispensable and will be the topic of further investigations. Nevertheless the observations might reveal a connection between stratospheric ozone depletion and the greenhouse effect. Reduced ozone columns let more UV-B radiation penetrate deeper into the troposphere. The resulting increased OH production could lead to a slightly faster degradation of greenhouse gases, since their lifetime in the troposphere is mainly determined by the abundance of OH radicals. Possibly this effect could act as a regulating mechanism in global warming.

Acknowledgements

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