

PARAMETERIZATION OF EPISODICAL CLOUD AND RAINOUT EVENTS IN LARGE-SCALE ATMOSPHERIC CHEMISTRY MODELS

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Abstract—A parameterization scheme taking into account the episodic nature of rainout and incloud chemical transformation has been tested in a 2-D channel model. In the liquid phase many soluble gases are observed in concentrations never experienced in the gas phase. The effects on the trace gases SO_2 and hydrogen peroxide, when they are modified by clouds and precipitation, are studied. When incloud interaction of SO_2 and hydrogen peroxide is taken into consideration, calculated hydrogen peroxide profiles are brought closer to observed distributions. The effect of varying the time periods between cloud and rain events is tested. The impact on the formation and destruction of tropospheric ozone is also discussed.

Key word index Rainout, cloud chemistry, SO_2 oxidation, parameterization

INTRODUCTION

Removal of soluble species in precipitating and non-precipitating clouds is characterized by rapid changes in time and space. A common approach in photochemical models has been to assume a first-order dependence proportional to the concentration of the compound removed. However, when the removal is faster than the gas can be replenished by physical processes from the environment, such an approach could lead to severe overestimations of the removal by cloud processes.

Thompson and Cicerone (1982) found that a reasonable removal rate for soluble species was the inverse of the time between the events. Georgi and Chameides (1985) derived a similar rate of removal by rainout. To obtain removal rates when aqueous-phase chemistry is involved is more complicated. One simple approach that has been widely used, i.e. Isaksen and Rodhe (1978), is to regard the removal by aqueous-phase transformation as a function of cloud amount and the concentration of the compound in question.

The liquid-phase reaction of sulphur with H_2O_2 , converting S(IV) to S(VI) is a fast, virtually pH-independent reaction. The reaction has been studied by a number of groups, i.e. Penkett *et al.* (1979). The lifetime against chemical removal is of the order of minutes only, resulting in an almost total depletion of the least abundant of the two species. The removal of the most abundant species stops as the other disappears. This has been confirmed by measurements (Romer *et al.*, 1982). Both SO_2 and H_2O_2 are found in cloud water, however not simultaneously. Measurements of hydrogen peroxide have been made in both rain and cloudwater samples (Kelly *et al.*, 1985, and references therein). The highest concentrations are

found in summer, whereas in winter concentrations are low. Kelly *et al.* (1985) found good agreements between measurements in rain and cloud water samples. Observations of hydrogen peroxides in air show large variations. Heikes *et al.* (1987) measured hydrogen peroxide in August over the eastern United States. Concentrations ranged from around the detection limit (0.2 ppbv) to 4.1 ppbv.

We have developed a procedure for calculating removal by chemical transformation in the aqueous phase. The method is conceptually similar to the parameterization described by Georgi and Chameides (1985) for rainout. Rainout is calculated accordingly. The method is tested out on the SO_2 - H_2O_2 liquid-phase chemistry, but may easily be extended to other species. The study is performed using a 2-D channel model describing transport and chemical transformation in the northern mid latitudes, 30–60°N. The model has been previously described by Solberg *et al.* (1989) and Isaksen *et al.* (1989). In this latitudinal belt there are strong east-west gradients in the emissions of pollutants, and thus in the atmospheric distribution of short-lived species. Considerable longitudinal variations in the liquid-phase SO_2 - H_2O_2 interaction is therefore expected, depending on the amount of SO_2 and H_2O_2 present. Comparisons are made with model estimates where first-order removal rates are adopted. We have further studied the impact of liquid-phase SO_2 - H_2O_2 chemistry on the gas-phase chemistry, and also estimated how efficiently SO_2 is removed in the liquid phase compared to gas-phase removal by reaction with OH and ground deposition. Finally we also discuss the ability of the model to predict tropospheric ozone concentrations. At low levels net ozone production is in particular shown to take place downwind from polluted conti-

nents, whereas net chemical destruction is confined to remote areas where NO_x levels are low

MATHEMATICAL FORMULATION

Removal processes of gases by clouds may be in the form of rainout or aqueous-phase transformation. Rainout describes the process where soluble gas-phase constituents are removed by precipitation. As the droplets evaporate parts of the same constituents may re-enter the gas phase. Aqueous transformation describes the loss of material through chemical reactions in the liquid phase. When referring to a species C below, C_{aq} is the aqueous-phase concentration in mole ℓ^{-1} , and C_t the total, gas and liquid, concentration in molecules cm^{-3} for a complete grid volume where both cloud and cloud-free environments are included.

Rainout

The procedure applied in this model follows the one described by Georgi and Chameides (1985). The removal W_c in molecules $\text{cm}^{-3} \text{s}^{-1}$ of a species C is given by the expression

$$W_c = \frac{C_{\text{aq}}}{55} W_{\text{H}_2\text{O}} \quad (1)$$

$W_{\text{H}_2\text{O}}$ is the removal rate of water vapour in molecules $\text{cm}^{-3} \text{s}^{-1}$, whereas the number 55 converts mol H_2O to $\ell \text{H}_2\text{O}$. The aqueous-phase concentration of C may be expressed as a function of liquid water content and solubility

$$C_{\text{aq}} = \frac{C_t^*}{L + (H_c^* RT)^{-1}}, \quad (2)$$

where C_t^* is the total gas and liquid concentration of C in mol ℓ_{air}^{-1} in a cloud environment (the volume occupied by the droplets is ignored), L is the volume ratio for liquid water, whereas H_c^* is the effective Henry's constant for C , R and T are the gas constant and the temperature, respectively. The overall loss rate, including both dry and wet periods then becomes

$$Q_c = \frac{1}{L + (H_c^* RT)^{-1}} \frac{W_{\text{H}_2\text{O}} \times 10^3}{55 A_0} \quad (3)$$

and

$$W_c = C_t Q_c,$$

where A_0 is Avogadro's number. In Equation (3) it is assumed that the concentration C_t is constant throughout the grid volume even though part of the volume will experience precipitation. This is only a good approximation for species that are washed out slowly. If the washout is faster than the species can be replenished, this assumption will result in overpredictions of the loss rate. Assuming an exponential decay for C in precipitation, Georgi and Chameides (1985)

define the following expression for the loss rate

$$Q_c^* = \frac{1}{T_s N_c} [1 - \exp(-Q_c T_s)], \quad (4)$$

where

$$N_c = 1 - f + \frac{f}{T_s Q_c} [1 - \exp(-Q_c T_s)],$$

and $T_s = T_d + T_w$ is a characteristic time period starting from the end of a precipitation event and ending at the end of the next one, T_d and T_w are the characteristic times for dry and wet periods, respectively, and $f = T_w/T_s$ is the fraction of the time that water vapour is removed by rainout as shown in Fig 1. Provided we have a large grid area $\bar{C}_t \approx C_t$ where \bar{C}_t represents the time-averaged concentration over a full cycle T_s , and C_t is the spatially averaged concentration. The removal of C_t is given by \bar{W}_c in Equation (5)

$$\bar{W}_c = C_t Q_c^* \quad (5)$$

This assumption may have to be more thoroughly verified. In Fig 2 the loss of water vapour, Q_w , the rainout of H_2O_2 , $Q_{\text{H}_2\text{O}_2}$, calculated from Equation (3) and finally, $Q_{\text{H}_2\text{O}_2}^*$, the rainout calculated from Equation (4), are depicted as functions of altitude. For comparison, the removal rate from Isaksen and Rodhe (1978), Q_{ref} , is also shown. Applying the mean concentration for rainout without taking into account the fact that concentrations may be depleted in precipitation, results in large overpredictions for a highly soluble species, such as H_2O_2 .

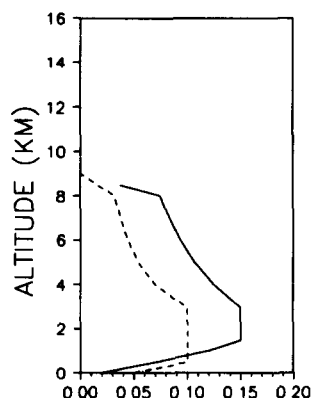


Fig 1 The full line shows the fractional time at each height the air parcel is estimated to spend within clouds (f), whereas the broken line shows the fractional time an air parcel encounters precipitation (g). The value f is calculated assuming a characteristic residence time in precipitation T_w of 24 h, corresponding to storm cycle 2 in Georgi and Chameides (1985), g is calculated assuming a characteristic residence time in clouds T_c of 4 h resembling values found by Leheveld *et al* (1989) at 40–50°N

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