

**Semi-empirical
models for ClO_x and
OMD**

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Semi-empirical models for chlorine activation and ozone depletion in the Antarctic stratosphere: proof of concept

P. E. Huck¹, G. E. Bodeker¹, S. Kremser¹, A. J. McDonald², M. Rex³, and H. Struthers^{4,5}

¹Bodeker Scientific, Alexandra, New Zealand

²Department of Physics and Astronomy, University of Canterbury, Christchurch, New Zealand

³Alfred-Wegener Institut, Potsdam, Germany

⁴Department of Applied Environmental Science, Stockholm University, 10691, Stockholm, Sweden

⁵Department of Meteorology, Stockholm University, 10691, Stockholm, Sweden

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Correspondence to: P. E. Huck (petra@bodekerscientific.com)

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Abstract

Two semi-empirical models were developed for the Antarctic stratosphere to relate the shift of species within total chlorine ($Cl_y = HCl + ClONO_2 + HOCl + 2 \times Cl_2 + 2 \times Cl_2O_2 + ClO + Cl$) into the active forms (here: $ClO_x = 2 \times Cl_2O_2 + ClO$), and to relate the rate of ozone destruction to ClO_x . These two models provide a fast and computationally inexpensive way to describe the inter- and intra-annual evolution of ClO_x and ozone mass deficit (OMD) in the Antarctic spring. The models are based on the underlying physics/chemistry of the system and capture the key chemical and physical processes in the Antarctic stratosphere that determine the interaction between climate change and Antarctic ozone depletion. They were developed considering bulk effects of chemical mechanisms for the duration of the Antarctic vortex period and quantities averaged over the vortex area. The model equations were regressed against observations of daytime ClO and OMD providing a set of empirical fit coefficients. Both semi-empirical models are able to explain much of the intra- and inter-annual variability observed in daily ClO_x and OMD time series. This proof-of-concept paper outlines the semi-empirical approach to describing the evolution of Antarctic chlorine activation and ozone depletion.

1 Introduction

International best practice for projecting the evolution of the global ozone layer is to use chemistry-climate models (CCMs). However, modelling and predicting the ozone evolution with CCMs still shows large discrepancies in model-to-model and/or model-to-observation intercomparisons. Three sources of uncertainty contributing to the overall uncertainty in ozone projections were identified by Charlton-Perez et al. (2010): (1) model uncertainty due to differences in the formulation of CCMs and inaccurate representations of dynamical and/or chemical processes, (2) internal variability and (3) uncertainty in future emissions of greenhouse gases (GHGs) and ozone depleting

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substances. Charlton-Perez et al. (2010) indicate that the model uncertainty, and uncertainties arising from future emissions scenarios, are the dominant contributors to the overall uncertainty in the projections of future ozone abundances. Furthermore, one of the recommendations of SPARC CCMVal (2010) is that the simulation of the Antarctic ozone hole needs improvement in most CCMs. Many CCMs cannot represent the Antarctic ozone hole area and depth due to large ozone biases and non-representative polar vortices. Ideally, projections should be based on an ensemble of model simulations that encompass the full range of uncertainty. However, due to their complexity, CCMs are very computationally demanding and expensive to run.

In the past, alternative fast stratospheric chemistry schemes such as the Cariolle (Cariolle and Teyssèdre, 2007) and Linoz (McLinden et al., 2000; Hsu and Prather, 2009) schemes were used. However, both of these schemes are statistical rather than being based on the underlying physical processes, and are unlikely to be representative outside of the dataset on which they were trained. Therefore there is a need for an approach as a quick pathfinder for more detailed CCM studies that can be used to conduct inexpensive projections of ozone into the future.

Inter- and intra-annual variability in Antarctic ozone depletion is at root governed by meteorology and regulated by the interaction of gas-phase and heterogeneous chemistry, transport and dynamics. In this study a model with a simple realisation of the physical processes describing chlorine activation and ozone depletion over Antarctica was developed. Only bulk quantities were considered and the seasonal evolution is summarised in simplified source and sink terms. The processes considered for both semi-empirical models include: the Antarctic stratospheric polar vortex starts to spin up in April and polar stratospheric clouds (PSCs) typically form in early to mid-May. Heterogeneous reactions on PSC surfaces lead to the conversion of reservoir forms of chlorine into active forms (Solomon, 1999, and references therein). Once reactive chlorine is exposed to sunlight, chlorine-catalysed ozone destruction begins; sunlight also increases temperature, causing PSCs to sublimate, and increases chlorine deactivation rates. Furthermore, ozone production due to Chapman chemistry (Chapman,

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1930) is ongoing as long as sunlight is available (Grooß et al., 2011). The final warming event usually occurs by December and the polar vortex breaks apart (Waugh and Randel, 1999).

In addition to ozone destruction due to chlorine, bromine chemistry must be considered (WMO, 2011). On a per atom basis, bromine is much more efficient in destroying ozone than chlorine (e.g. Sinnhuber et al., 2009). However, the largest contribution to ozone depletion in the Antarctic stratosphere is due to the ClO + ClO and ClO + BrO cycles. In the absence of reactive chlorine, bromine would be inefficient in destroying ozone (Chipperfield and Pyle, 1998). Bromine reservoirs are also less stable than chlorine reservoirs and conversion of the reservoir species to reactive forms is less dependent on heterogeneous chemistry. In summary, while chlorine is the primary driver of Antarctic ozone destruction, the seasonal evolution of ClO provides a good estimate of the ozone destroying potential (WMO, 2003), and bromine can be considered as an amplifying factor (von Hobe et al., 2005).

2 Chlorine activation model

The chlorine activation model describes the conversion of stratospheric chlorine reservoir species (HCl and ClONO₂, usually the dominating Cl_y species) into active, ozone destroying forms of ClO_x and back, depending on the abundance of PSCs and sunlight. An estimate of the total inorganic stratospheric chlorine (Cl_y) was derived as described in Newman et al. (2006). The approach by Newman et al. (2006) requires knowledge of the mean age-of-air and the width of the age-of-air spectrum. In this study, Cl_y was calculated assuming a mean age-of-air of 5.5 yr and an age-of-air spectrum width of 2.75 yr which are the recommended values for the Antarctic in Newman et al. (2006).

The abundance of active, ozone destroying forms of chlorine in the stratosphere is approximated by ClO_x (here: ClO_x = ClO + 2 × Cl₂O₂). Daytime measurements of ClO are a good proxy for the active forms of chlorine since a large fraction of ClO_x resides in the form of ClO during day and as Cl₂O₂ during nighttime (Brasseur and Solomon,

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2005). The time evolution of the abundance of ClO_x can be described by integrating the terms expressing activation rates (conversion of chlorine reservoirs to active chlorine) and deactivation rates (reformation of chlorine reservoirs) over time. The time evolution of ClO_x abundances depends on the total amount of available stratospheric chlorine (Cl_y), the extent of PSCs within the polar vortex, solar illumination, and the deactivation of ClO_x due to chemical reactions forming reservoir species.

The time rate of change of the vortex average ClO_x (in parts per billion; ppb) on a given pressure surface can be described by a first order differential equation of the form:

$$\frac{d\text{ClO}_x}{dt} = \alpha \times (\text{Cl}_y - \text{ClO}_x) \times \text{FAP} \times \text{FAS} - \beta \times \text{ClO}_x (1 - \text{FAP}) \quad (1)$$

where α and β are fit coefficients derived by optimally fitting the equation to daytime ClO measurements. The $\text{Cl}_y - \text{ClO}_x$ term represents chlorine still in reservoir forms, before its conversion to active chlorine. FAP is the fractional area of the vortex covered by PSCs. FAP is calculated using NCEP/NCAR temperature fields and a PSC formation threshold temperature of 195 K. FAS is the fractional area of the vortex exposed to sunlight. When sunlight shines on the vortex it photolyzes Cl_2 , HOCl and BrCl to ClO atoms, which rapidly react with ozone to form ClO .

ClO_x becomes unavailable in the stratosphere through the following processes: (1) when ClO reacts with NO_2 to form ClONO_2 , (2) when ClO reacts with HO_2 to form HOCl and O_2 (a minor reaction in the Antarctic), (3) when Cl reacts with CH_4 to form HCl and CH_3 . The first of these reactions depends on the availability of NO_2 which is tied up in solid phase HNO_3 within the PSCs or removed permanently from the lower stratosphere through denitrification. Deactivation of ClO_x is parameterised by the second term in Eq. (1) where the decay of ClO_x is dependent on FAP (proxy for PSCs).

Equation (1) is solved using a 4th order Runge–Kutta algorithm. The equation is fitted to daytime measurements of ClO from the Microwave Limb Sounder (MLS) onboard the Upper Atmosphere Research Satellite (UARS) from 1992 to 1997 to derive a set of empirical fit coefficients. The fitting method used to find the optimal solution is a

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parameter space grid search technique. Version 5 MLS ClO measurements (Livesey et al., 2003) were averaged from 60–90° S equivalent latitude (as an approximation of vortex average ClO) and only measurements taken near midday (i.e. with local solar zenith angle smaller than 88° and local solar time between 11:00 and 14:00) were included (for details see Santee et al., 2003). The resulting fit coefficients are $\alpha = 1.21$ and $\beta = 0.76$. The fitting technique provides parameter values that best fit the data but parameter uncertainties are not estimated with this technique.

In Fig. 1 ClO observations and the semi-empirical model fit are shown. The model tracks the observations for activation and deactivation of ClO well. Because of the short data record, the ability of the model to track large inter-annual variability in chlorine activation is not immediately apparent. We are restricted to use UARS MLS ClO measurements for this study since measurements from the AURA satellite are only made in the later afternoon over Antarctica and our assumption that ClO is a good proxy for ClO_x does not apply in that case. Due to a known bias in the data (Livesey et al., 2003), the MLS ClO measurements show some deviation from zero before and after the period of chlorine activation (not shown in Fig. 1). Therefore, the fitting of the model (Eq. 1) to the observations was restricted to 20 May to 20 October.

Equation (1) describes the activation and deactivation of ClO_x on one pressure level. To derive the fit coefficients, ClO measurements at 520 K potential temperature were used for the fitting and FAP and FAS were calculated at 50 hPa which is the closest pressure level to the 520 K potential temperature surface. Using CCM output on 10 pressure levels we found that in the region of largest contribution (150–70 hPa), the fit coefficients do not vary significantly with altitude. Assuming no altitude dependence in the fit coefficients is therefore unlikely to introduce large uncertainties into our calculation of ClO_x from FAP and FAS on any pressure level. Equation (1) is applied to FAP and FAS time series from 1979 to 2010. To derive FAP and FAS only temperature and vortex edge information is needed which in this study was obtained from NCEP/NCAR reanalyses. If this is simplified further by assuming an average vortex edge at 62° S

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(Bodeker et al., 2002), then only temperature fields are required to derive ClO_x time series.

3 Ozone depletion model

The second semi-empirical model describes the time rate of change of ozone mass deficit (OMD), a measure of springtime chemical ozone loss over Antarctica (Huck et al., 2007). OMD is a bulk measure of the size and depth of the ozone hole with respect to 1980 values, and it is one of the common metrics used to describe inter- and intra-annual variations in Antarctic ozone depletion (e.g. WMO, 2007, 2011). An improved definition of OMD (Huck et al., 2007) is used in this study which is better able to capture the intra-seasonal evolution than the traditional definition (Uchino et al., 1999).

The time rate of change of OMD is described using another first order differential equation of the form:

$$\frac{d\text{OMD}}{dt} = \left[A \times \text{sMAC}^2 + B \times \text{sMAC} \right] \times (1 - S) - C \times \text{OMD} \times F_{\text{act}} - D \times \text{OMD} \times \text{WP} \times \left(1 - \frac{\kappa}{\kappa_{\text{max}}} \right) \quad (2)$$

The ozone model consists of three terms. The first term relates the time rate of change of OMD to active chlorine. The amount of ozone that can be depleted has both a linear and a quadratic dependence on the amount of activated chlorine (Jiang et al., 1996). The sunlit mass of activated chlorine (sMAC) in Eq. (2) is an estimate of the total mass of activated chlorine in the atmospheric column relative to 1980 values and multiplied by FAS. The mass of activated chlorine (MAC) in the stratosphere is calculated for each layer as:

$$\text{MAC} = (\text{ClO}_x - \text{ClO}_{x1980}) \times \frac{M_{\text{Cl}}}{M_{\text{air}}} \times A \times \Delta p \times \frac{1}{g} \quad (3)$$

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where ClO_x, obtained from Eq. (1), is the ClO_x mixing ratio between two pressure levels. ClO_{x1980} is the background ClO_x concentration corresponding to 1980 values. The time series for 1979–1981 were averaged to derive the concentration of active chlorine in 1980. The estimate for ClO_x in 1980 (ClO_{x1980}) is calculated by fitting a six-term Fourier expansion to the 1979–1981 average ClO_x time series on each pressure level. M_{Cl} is the molecular mass of chlorine (35.45 g mol⁻¹), and M_{air} is the molecular mass of dry air (~29 g mol⁻¹). A is the area of the polar vortex in m², Δp is the pressure difference for each layer in Pa, and g is the gravitational acceleration (9.81 ms⁻²). Assuming a homogeneous distribution of ClO_x over the polar vortex, MAC is multiplied by FAS to account for the fact that sunlight is needed for ozone destruction due to chlorine. Summation of MAC × FAS over all pressure levels (200, 150, 100, 70, 50, 30, and 20 hPa) results in an estimate of the sunlit mass of activated chlorine (above 20 hPa and below 200 hPa the contribution to activated chlorine is close to zero). In Fig. 2 the contribution of each layer to sMAC is shown for 2000. It can be seen that the largest contributions come from pressures between 150 and 70 hPa. To account for saturation in ozone depletion (once ozone is depleted it cannot be depleted again), S is set to OMD/OMD₁₅₀, where OMD₁₅₀ is the value OMD would have if total ozone everywhere inside the vortex was 150 DU, which is approximately the vortex average value of total column ozone when all the lower stratospheric ozone is destroyed (Bodeker et al., 2002).

The second term relates the time rate of change in OMD to in-situ production of ozone (through the Chapman cycle). This in-situ production of ozone through Chapman chemistry is approximated via a parametrisation of the the actinic flux by taking the cosine of the solar zenith angle, and the area within the polar vortex into account (Grooß et al., 2011). F_{act} is a proxy of the actinic flux available to photolyse O₂ and form O₃.

The third term accounts for dynamical entrainment of ozone-rich air from lower latitudes. This process is described by taking the wave activity and vortex strength into account. WP is the total wave power at 60° S as calculated in Huck et al. (2005). κ

is the maximum of the meridional impermeability on each day, while κ_{\max} is the maximum of the meridional impermeability for all equivalent latitudes and days in a given year (Bodeker et al., 2002). The D term therefore quantifies the exchange of ozone between the interior and exterior of the vortex which is driven by wave mixing (hence the inclusion of the WP term) but blocked by the impermeability of the vortex (hence the inclusion of the κ -based term).

A , B , C and D in Eq. (2) are fit coefficients derived by optimally fitting the equation to OMD from observations. Equation (2) is also solved using a 4th order Runge–Kutta algorithm. The equation is fitted to OMD calculated from the observational NIWA (National Institute of Water and Atmospheric research) combined total column ozone database (Bodeker et al., 2005) from 1990 to 2000. The fitting method used to find the optimal solution is the same parameter space grid search technique as used for the chlorine activation model (Eq. 1). The terms after each fit coefficient were normalised to vary between 0 and 1, to make the fit coefficients comparable to each other. They result in $A = 4.41 \times 10^{-7}$, $B = 0.67$, $C = 0.36$, and $D = 1.43 \times 10^{-2}$. Similar to the fit coefficients in the chlorine model, no uncertainties are available with this fitting technique and the parameter values give the best fit to the data. The robustness of the fitting technique was tested by fitting to different periods and different number of years. The fit coefficients A and D are small compared to B and C , which indicates that the linear dependence of ozone depletion on chlorine and the in-situ production are the critical terms when describing the inter- and intra-annual variability of OMD. When the ozone depletion model is run from 1980 to 2010, the correlation coefficient between the model and observations is $R^2 = 0.97$ over the entire period.

To test the predictive capability of the semi-empirical models, the dynamical variability term (D term) was excluded and the input parameters FAS and FAP (now the only required parameters besides Cl_y) were calculated for 2000 to 2010 assuming a constant vortex edge at 62°S (see also Huck et al., 2007). In Fig. 3 OMD observations, the full model, and the simplified model predictions are shown for 1980 to 2010. The model tracks the observations for the seasonal evolution of ozone depletion. The year-

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to-year variability of the Antarctic ozone hole is also well represented, in particular for the anomalous years 1988, 2002 and 2004. The simulation using the simplified version of the model reproduces intra- and inter-annual variability of OMD. The fact that both model versions track the observations between 2000 and 2010 (including two of the anomalous years), which were not used to derive the fit parameters, demonstrates the predictive capability of such semi-empirical models.

4 Discussion and conclusion

Fit coefficients such as those in the two semi-empirical models described above can be used to determine key sensitivities in the stratosphere. For example, the fit coefficients of the OMD model (Eq. 2) indicate a linear dependence between ozone depletion and chlorine in the Antarctic stratosphere in agreement with the findings of Harris et al. (2010).

Activation of chlorine in the polar stratosphere in the future will be linked to climate change: future increases in atmospheric concentrations of GHGs will cool the stratosphere which, together with possible increases in water vapor (WMO, 2011), will promote the formation of PSCs. In contrast, likely increases in wave activity emanating from the troposphere into the stratosphere driven by changes in surface climate will warm the stratosphere. The future interplay between these factors is unknown (WMO, 2011). Fit coefficients of semi-empirical models such as those described above can be used to investigate aspects of the interaction between climate change and Antarctic ozone depletion.

It was shown that a further simplification of the equations by excluding the dynamical variability term and by replacing the actual dynamical vortex edge with the average location of the vortex edge of 62° S provides models with the ability to project the development of Antarctic ozone into the future. As long as temperature projections and Cl_y estimates are available, these models can provide an estimate of the future evolution of Antarctic ozone. Since these models are fast and inexpensive to run, they can, for

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example, be used to produce an ensemble of ozone projections considering a range of GHG emissions scenarios.

There are limitations to these equations, which is why this study should be considered as proof-of-concept rather than a finished product. As they stand, these semi-empirical models cannot be applied outside the Antarctic vortex. Finer differentiation between physical and chemical processes might be necessary for more detailed studies of key atmospheric sensitivities of ozone depletion and climate change. These semi-empirical models which only consider bulk quantities do not appear to be very sensitive to changes in atmospheric dynamics. Due to the expected increase in the importance of dynamical processes, it might be necessary to model single levels in the atmosphere in the future.

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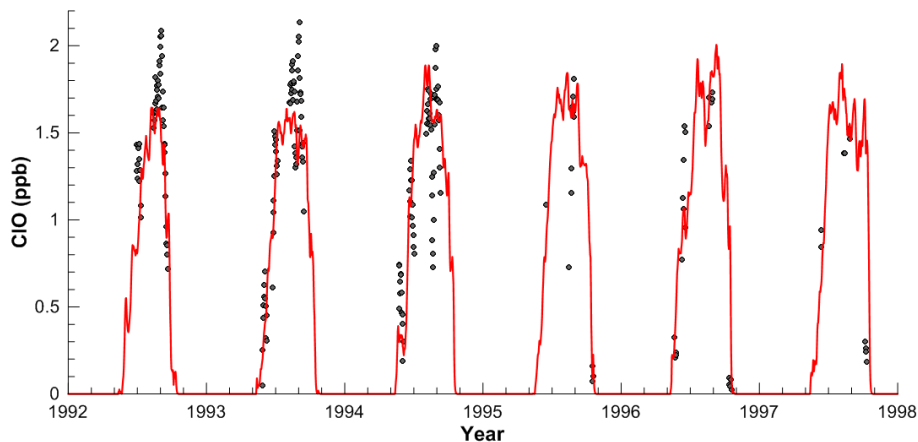


Fig. 1. UARS MLS daytime ClO measurements 20 May to 20 October (black dots) and semi-empirical model fit (red line) for 1992–1997. MLS observations are on 520 K isentropic surface and the model output is on the 50 hPa pressure level.

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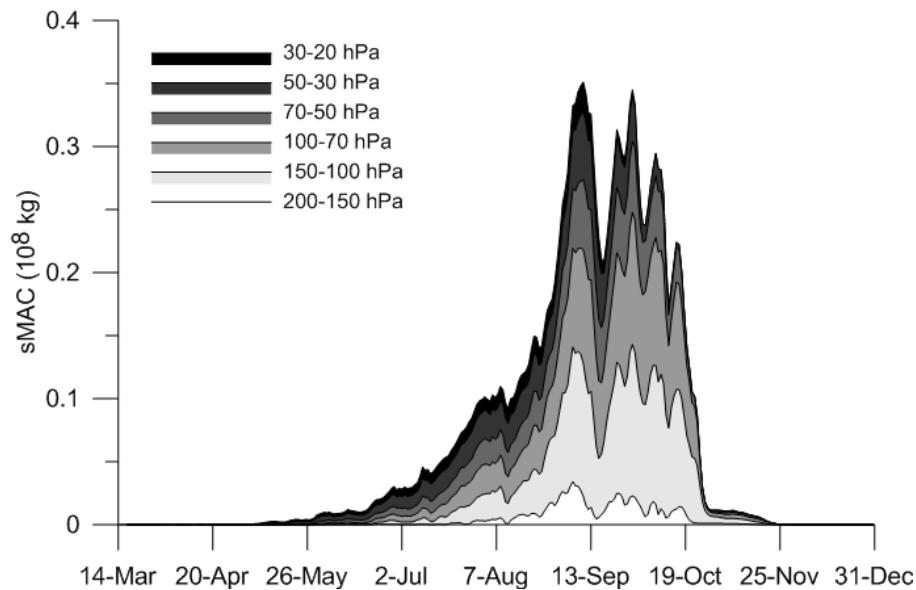


Fig. 2. Contribution from different atmospheric layers (as indicated in the legend) to the sunlit mass of activated chlorine for the year 2000. Largest contributions come from pressures between 150–70 hPa.

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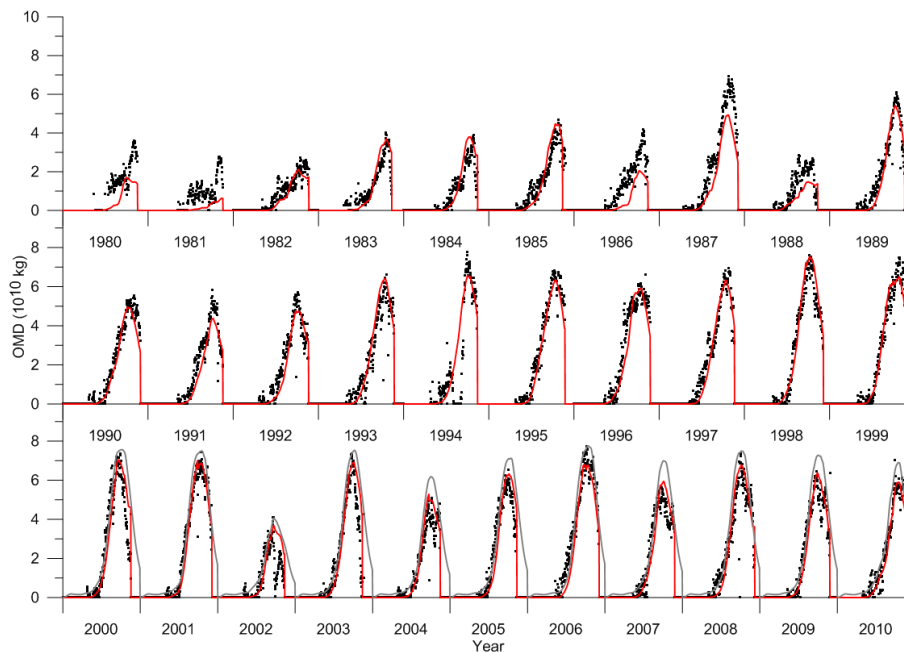


Fig. 3. OMD observations (black dots), OMD model (red line: full model, Eq. (2); grey line: simplified model). Note that the model is fitted to the OMD measurements from 1990 to 2000 and is forced to zero at the end of each season. The simplified model projections are only shown for 2000 to 2010.

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