

FULLY COUPLED “ONLINE” CHEMISTRY WITHIN THE WRF MODEL: DESCRIPTION AND APPLICATIONS

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1. INTRODUCTION

The simulation and prediction of air quality is a complicated problem, involving both meteorological factors (such as wind speed and direction, turbulence, radiation, clouds, precipitation) and chemical processes (such as emissions, deposition, transformations). In the real atmosphere, the chemical and physical processes are coupled. The chemistry can affect the meteorology, for example, through its effect on the radiation budget, as well as the interaction of aerosols with Cloud Condensation Nuclei (CCN). Likewise, clouds and precipitation have a strong influence on chemical transformation and removal processes, and localized changes in the wind or turbulence fields affect the chemical transport on a continuous basis.

Until recently, the chemical processes in air quality modeling systems were usually treated independently of the meteorological model (as in CMAQ; Byun and Ching, 1999); (i.e., “offline”), except that the transport was driven by output from a meteorological model, typically available once or twice per hour. Due to this separation of meteorology and chemistry, there can be a loss of important information about atmospheric processes that quite often have a time scale of much less than the output time of the meteorological model, e.g., wind speed and direction, rainfall, and cloud formation. This may be especially important in air quality prediction systems, in which horizontal grid-sizes on the order of 1km may be required. In addition, the feedback from the chemistry to the meteorology – which is neglected in “offline” approaches – may be much more important than previously thought.

"The Workshop on Modeling Chemistry in Cloud and Mesoscale Models", a first step towards the implementation of chemistry into WRF, was held at NCAR on 6-8 March 2000. The goal of this workshop was to produce a community assessment of approaches and methodologies used for chemistry modeling in cloud and mesoscale models. Subsequently the WRF/Chem working group was founded that currently consists of 15 members. Over

the last few years, various chemical modules have been implemented into the WRF framework, creating an “online” WRF/chem model. Transport of species is done using the same vertical and horizontal coordinates (no horizontal or vertical interpolation), the same physics parameterization, and no interpolation in time. This WRF/Chem model is similar in its physical and chemical concepts to MM5/Chem (Grell et al. 2000). We will describe the chemical aspects of the model in section 2. This description still focuses on V1.3. Many additional modules are now available for V2. These will be described in the talk. In section 3 we will explain the setup as well as results for retrospective runs that were used for initial model evaluation.

2. Model Description

In general, most air quality modeling systems consider a variety of coupled physical and chemical processes such as transport, deposition, emission, chemical transformation, aerosol interactions, photolysis, and radiation. Details on the modules that describe these processes within WRF/chem are given below. For details describing the conservative split-explicit time integration method that is used in the mass coordinate version of the WRF model, the reader is referred to http://www.mmm.ucar.edu/individual/skamarock/wrf_equations_eulerian.pdf. The time splitting method is described in Wicker and Skamarock (2002), and an overview of the physics is given in <http://www.mmm.ucar.edu/wrf/users/wrf-doc-physics.pdf>. Here we will only discuss the aspects of the model that directly relate to the chemical part.

2.1 Transport

All transport of chemical species is done “online”. Although WRF has several choices for dynamic cores, for this paper we chose the official mass coordinate version of the model. For the mass coordinate WRF model this means the advection is fully mass and scalar conserving, fifth order in space, and third order in time. Turbulent transport is

done using a level 2.5 Mellor-Yamada closure (ETA scheme).

For the chemical mechanism used in this version of the model, 39 chemical species are fully prognostic. For the aerosol module (see description below), another 34 variables are added, including the total number of aerosol particles within each mode, as well as all primary and secondary species (organic and inorganic) for both Aitken and accumulation mode, and three species for the coarse mode (anthropogenic, marine, and soil-derived aerosols).

2.2 Dry Deposition

The flux of trace gases and particles from the atmosphere to the surface is calculated by multiplying concentrations in the lowest model layer by the spatially and temporally varying deposition velocity, which is proportional to the sum of three characteristic resistances (aerodynamic resistance, sublayer resistance, surface resistance). The surface resistance parameterization developed by Wesely (1989) is used. In this parameterization, the surface resistance is derived from the resistances of the surfaces of the soil and the plants. The properties of the plants are determined using landuse data and the season. The surface resistance also depends on the diffusion coefficient, the reactivity, and water solubility of the reactive trace gas.

The dry deposition of sulfate is described differently. In case of simulations without calculating aerosols explicitly, sulfate is assumed to be present in the form of aerosol particles, and its deposition is described according to Erisman et al. (1994).

When employing the aerosol parameterization, the deposition velocity, \widehat{v}_{dk} , for the k th moment of a polydisperse aerosol is given by

$$\widehat{v}_{dk} = (r_a + \widehat{r}_{dk} + r_a \widehat{r}_{dk} \widehat{v}_{Gk})^{-1} + \widehat{v}_{Gk}$$

where r_a is the surface resistance, \widehat{v}_{Gk} is the polydisperse settling velocity, and r_{dk} is the Brownian diffusivity (Slinn and Slinn, 1980; Pleim et al., 1984).

2.3 Gas-phase chemistry

This atmospheric chemical mechanism was originally developed by Stockwell et al. (1990) for the Regional Acid Deposition Model, version 2 (RADM2) (Chang et al., 1989). The RADM2 mechanism is a compromise between chemical detail, accurate chemical predictions, and available computer resources. It is widely used in atmospheric models to predict concentrations of oxidants and other air pollutants.

Inorganic species included in the RADM2 mechanism are 14 stable species, 4 reactive

intermediates, and 3 abundant stable species (oxygen, nitrogen and water). Atmospheric organic chemistry is represented by 26 stable species and 16 peroxy radicals. The RADM2 mechanism represents organic chemistry through a reactivity aggregated molecular approach (Middleton et al., 1990). Similar organic compounds are grouped together into a limited number of model groups through the use of reactivity weighting. The aggregation factors for the most emitted Volatile Organic Compounds (VOCs) are given in Middleton et al., (1990).

A quasi steady state approximation method with 22 diagnosed, 3 constant and 38 predicted species is used for the numerical solution. The rate equations for 38 predicted species are solved using a Backward Euler scheme.

2.4 Biogenic Emissions

WRF/chem uses a biogenic emission module based on the description of Guenther et al. (1993, 1994), Simpson et al. (1995), and Schoenemeyer et al. (1997). The module treats the emissions of isoprene, monoterpenes, Other VOC (OVOC), and nitrogen emission by the soil. For the use in the RADM2 photochemistry module, the emissions of monoterpenes and OVOC are disaggregated into the RADM2 species classes.

The emission of isoprene by forests depends on both temperature and photosynthetic active radiation. Guenther et al. (1993) have developed a parameterization formula for the isoprene emission, where the isoprene emission rate is proportional to the isoprene emission rate at a standard temperature and a standard flux of photosynthetic active radiation. A radiation flux correction term and a temperature correction term for forest isoprene emissions is applied. The isoprene emissions of agricultural and grassland areas are considered to be functions of the temperature only (Hahn et al. 1994).

The emissions of monoterpenes, OVOC, and nitrogen are also treated as functions of the temperature only. Little is known about the emission of OVOC; therefore the same temperature correction is applied for OVOC as for monoterpenes according to Simpson et al. (1995).

The emissions at the standard temperature and the standard PAR flux are given in Table 1 in Grell et al. (2000). They are taken from Guenther et al. (1994) for deciduous, coniferous and mixed forest and from Schoenemeyer et al. (1997) for agricultural and grassland. For the use with RADM2, all nitrogen emissions are treated as NO. This is a maximum estimate, because the emission of N₂O is neglected.

It must be noted that from the landuse categories used in WRF, the nature of biogenic emissions can be estimated only roughly. Segregation into tree species will be necessary.

Furthermore the fractional coverage of these species per single grid square will be required in the future.

2.5 Parameterization of Aerosols

The aerosol module is based on the Modal Aerosol Dynamics Model for Europe (MADE) (Ackermann et al., 1998) which itself is a modification of the Regional Particulate Model (Binkowski and Shankar, 1995). Secondary Organic Aerosols (SOA) have been incorporated into MADE by Schell et al., (2001), by means of the Secondary Organic Aerosol Model (SORGAM). Since the different components of the module are well documented in the above cited references, only a brief summary of the most important features shall be given here.

2.5.1 Size distributions

The size distribution of the submicrometer aerosol is represented by two overlapping intervals, called modes, assuming a log-normal distribution within each mode:

$$n(\ln d_p) = \frac{N}{\sqrt{2\pi} \ln \sigma_g} \exp \left[-\frac{1}{2} \frac{(\ln d_p - \ln d_{pg})^2}{\ln^2 \sigma_g} \right],$$

where N is the number concentration [m^{-3}], d_p the particle diameter, d_{pg} the median diameter, and σ_g the standard deviation of the distribution. The k th moment of the distribution is defined as

$$M_k = \int_{-\infty}^{\infty} d_p^k n(\ln d_p) d(\ln d_p),$$

with the solution

$$M_k = N d_{pg}^k \exp \left[\frac{k^2}{2} \ln^2 \sigma_g \right].$$

M_0 is the total number of aerosol particles within the mode suspended in a unit volume of air, M_2 is proportional to the total particulate surface area within the mode suspended in a unit volume of air, and M_3 is proportional to the total particulate volume within the mode suspended in a unit volume of air.

2.5.2 Nucleation, Condensation, and Coagulation

The most important process for the formation of secondary aerosol particles is the homogeneous nucleation in the sulfuric acid-water system. It is calculated by the method given by Kulmala *et al.* (1998).

Aerosol growth by condensation occurs in two steps: the production of condensable material (vapor) by the reaction of chemical precursors, and the condensation and evaporation of ambient volatile species on aerosols. In MADE the Kelvin effect is neglected, allowing the calculation of the time rate

of change of a moment M_k for the continuum and free-molecular regime. The mathematical expressions of the rates and their derivation are given in Binkowski and Shankar (1995).

During the process of coagulation, the distributions remain log-normal. Furthermore, only the effects caused by Brownian motion are considered for the treatment of coagulation. The mathematical formulation for the coagulation process can be found in Whitby *et al.* (1991), and Binkowski and Shankar (1995).

The change in moments due to coagulation is modified from that described by Whitby *et al.* (1991). Whereas Whitby *et al.* (1991) suggest that the collisions of particles within a mode result in the formation of a particle within that mode, MADE allows a particle resulting from two particles colliding within the Aitken mode to be assigned to the accumulation mode. For this, MADE calculates the diameter, d_{eq} , at which the two modes have equal number concentrations. Colliding particles in the Aitken mode, where at least one exceeds this diameter, are then assigned to the accumulation mode.

2.5.3 Aerosol Chemistry

The inorganic chemistry system is based on MARS (Saxena *et al.*, 1986) and its modifications by Binkowski and Shankar (1995), which calculates the chemical composition of a sulphate-nitrate-ammonium-water aerosol according to equilibrium thermodynamics. Two regimes are considered depending upon the molar ratio of ammonium and sulphate. For values less than 2, the code solves a cubic polynomial for hydrogen ion molality, and if enough ammonium and liquid water are present, it calculates the dissolved nitrate. For modal ionic strengths greater than 50, nitrate is assumed not to be present. For molar ratios of 2 or greater, all sulphate is assumed to be ammonium sulphate and a calculation is made for the presence of water. The Bromley method is used for the calculation of the activity coefficients.

The organic chemistry is based on SORGAM (Schell *et al.*, 2001). SORGAM assumes that SOA compounds interact and form a quasi-ideal solution. The gas/particle partitioning of SOA compounds are parameterized according to Odum *et al.* (1996). Due to the lack of information, all activity coefficients are assumed to be unity. SORGAM treats anthropogenic and biogenic precursors separately, and may be used with a chemical mechanism such as RACM (Stockwell *et al.* 1997) that provides the biogenic precursors. Since in WRF/chemistry we currently use the RADM2 mechanism (Stockwell *et al.*, 1990), the biogenic precursors and their resulting particle concentrations are set to zero.

2.5.4 Interaction with atmospheric radiation

The interaction of aerosols and radiation has been incorporated by means of a simplified parameterization into the short wave radiation scheme (Dudhia, 1989). This parameterization only takes into account three variables: elemental carbon, dry aerosol mass (without elemental carbon), and aerosol liquid water content. Only absorption is considered for elemental carbon, whereas for dry aerosol mass and aerosol liquid water content, only scattering is considered. This parameterization is not spectrally dependent, nor does it, at this stage, take into account the aerosol size and asymmetry dependency on radiation.

2.6 Photolysis frequencies

Photolysis frequencies for the 21 photochemical reactions of the gas phase chemistry model are calculated at each grid point according to Madronich (1987). The photolysis frequency of the gas i , J_i , is given by the integral of the product of the actinic flux $I_A(\lambda)$, the absorption cross sections $\sigma(\lambda)$, and the quantum yields $\Phi(\lambda)$ over the wavelength λ :

$$J_i = \int^{\lambda} I_A(\tau, \lambda) \sigma_i(\lambda) \Phi_i(\lambda) d\lambda$$

For the calculation of the actinic flux, a radiative transfer model by Wiscombe which is based on the delta-Eddington technique (Joseph et al., 1976), is used. This radiative transfer model accounts for absorption by O_2 and O_3 , Rayleigh scattering, and scattering and absorption by aerosol particles and clouds as described by Chang et al. (1989). The absorption cross sections and the quantum yields for the calculation of J_{gas} are given by Stockwell et al. (1990). The integral in the above equation is solved for 130 wavelengths between 186 and 730 nm.

The profiles of the actinic flux are computed at each grid point of the model domain. For the determination of the absorption- and scattering cross sections needed by the radiative transfer model, predicted values of temperature, ozone, and cloud liquid water content are used below the upper boundary of WRF. Above the upper boundary of WRF, fixed typical temperature and ozone profiles are used to determine the absorption and scattering cross sections. These ozone profiles are scaled with TOMS satellite observational data for the area and date under consideration.

The radiative transfer model permits the proper treatment of several cloud layers with height-dependent liquid water contents each. The extinction coefficient of cloud water β_c is parameterized as a function of the cloud water

computed by the 3-dimensional model based on a parameterization given by Slingo (1989). For the present study, the effective radius of the cloud droplets follows Jones et al. (1994). For aerosol particles a constant extinction profile with an optical depth of 0.2 is applied.

An online computation of the photolysis frequencies is preferred here since it has advantages over “offline” techniques and is more versatile. One advantage is that the absorption cross sections of ozone are temperature dependent. Furthermore this treatment can be used to account for the humidity dependence of the extinction by aerosol particles. As shown by Ruggaber et al. (1994), aerosol particles have a strong effect on the photolysis frequency of NO_2 . Another possible option for the model is the parameterization of cloud droplets as a function of the sulfate content according to Jones et al. (1994).

The photolysis model may be applied at any timestep. However, for numerical efficiency, the photolysis routine is called with time intervals of 30 minutes.

3. Test-bed setup and results

The modeling system was subjected to extensive evaluation. Results will be shown during the workshop.

7. References

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