Improvements to CAMx snow cover treatments and Carbon Bond chemical mechanism for winter ozone

Background

Snow Cover

Winter ozone formation events occur under cold conditions that differ substantially from traditional summer ozone events. Snow cover influences wintertime ozone formation by several mechanisms: (1) Increasing surface albedo and thus the amount of total ultraviolet (UV) irradiance for photolysis; (2) Promoting formation of shallow, stable atmospheric layers near the ground; (3) Inhibiting removal of emissions and secondary products via surface deposition, and; (4) Potentially introducing surface heterogeneous formation of HONO from deposited NO_2 and/or HNO_3.

The CAMx photochemical model addresses each of these effects from snow cover. Currently, snow cover input fields are developed from the meteorological model that supplies meteorological input fields to CAMx (typically the Weather Research and Forecasting Model, or WRF). The fields are characterized by 0 (no snow) or 1 (snow cover) and can vary spatially cell-by-cell and in time according to the meteorological simulation.

Photolysis rates are developed using an external radiative transfer model (TUV; NCAR, 2011), which builds a multi-dimensional lookup table for CAMx that includes clear-sky rates by photolytic reaction, solar angle, altitude, total column ozone, and surface albedo. Photolysis rates are adjusted within CAMx for non-clear skies, i.e. for cloud cover and aerosols. The surface albedo dimension of the photolysis lookup table has five bins, two for the snow-free range (0.04 and 0.08) and three that represent snow cover (0.2, 0.5 and 0.8). For snow-covered grid cells, the current implementation sets the surface albedo to the middle snow value (0.5) to represent an average condition according to a previous literature review (Herman and Celarier, 1997). Three snow cover albedos are present to allow for future refinement such as influence of snow depth, age or fractional coverage, or land-cover type (forests, shrubland, etc.). NOAA has recently measured albedo values in the Uinta Basin as high as 0.95, so the maximum value of 0.8 should be increased.

CAMx offers two dry deposition options for gasses, one based on Wesely (1989), and the other based on Zhang et al. (2003). In both cases, deposition is treated as a first-order flux driven by a deposition velocity that is in turn defined by a series of season and land-cover dependent surface resistances. The Wesely option relies on a set of surface resistances defined for five seasons (the four standard seasons, including winter with no snow and a fifth representing winter with snow). The Zhang option includes one set of baseline resistances that are weighted by monthly leaf area index (LAI) to account for seasonal variability. When snow cover is present, certain resistances are scaled up, decreasing deposition velocity. The Zhang scheme explicitly assumes 80% snow cover on ground and vegetative surfaces when snow is present.

CAMx v6.1 has recently been released with a new surface chemistry model that calculates user-defined heterogeneous and photolysis reactions for selected compounds deposited on vegetative and bare ground surfaces, and allows volatile products to be re-emitted from the surface to the atmosphere (ENVIRON, 2014). Surface areas for vegetation and bare ground are set internally according the land cover type. Reaction rates on surfaces must be specified by the user separately for these two surface types. The model was recently tested for an application in Houston, Texas to simulate surface HONO production from surface reactions of NO_2 and HNO_3 (Lefer et al., 2014). Currently, the surface model is tied to the Wesely deposition option with its specific definition of 11 land cover classes, and it does not include any specific treatment for snow covered surfaces. However, extension to the Zhang deposition option would be straightforward.

Carbon Bond Chemistry

Winter ozone events are being simulated using the CAMx and CMAQ photochemical grid models that use Carbon Bond (CB) chemical mechanisms – version CB05-TU in CMAQ (Whitten et al., 2010) and version CB6r2 in CAMx (Hildebrandt Ruiz and Yarwood, 2013). The SAPRC chemical mechanism has been used to simulate winter ozone formation with a box model. Do these chemical mechanisms require modifications to be suitable for simulating winter ozone formation?

The inorganic chemical reactions (i.e., describing NOx, HOx, O_3, CO, nitric acid) included in CB and SAPRC mechanisms are based on data that have been peer reviewed for applicability to the global troposphere (Atkinson et al., 2004 – current version here: http://iupac.pole-ether.fr/index.html) and thus are suitable for modeling winter ozone.

For reactions of simple organics (i.e., methane, ethane, formaldehyde, acetaldehyde) the state of knowledge is comparable to that for inorganic reactions discussed above.

For larger organic molecules (i.e., propane and larger) the temperature dependencies of reaction rate constants are generally known for tropospheric conditions. However, any temperature dependencies of the products formed by organic reactions are poorly known for tropospheric conditions. Carter and Seinfeld considered how the SAPRC chemical mechanism should be modified for winter ozone and made a special version of the mechanism that is better suited for winter conditions (at the expense of suitability for summer conditions).

Winter ozone events have occurred to date where oil and gas exploration and production activities emit ozone precursors and the most abundant organic compounds present in the atmosphere are alkanes. Two temperature dependencies that affect the products formed from alkanes are:

1. Competition between alkoxy radical (RO) thermal decomposition (RO -> products) and reaction with oxygen (RO + O_2 -> different products). Thermal decomposition is favored by

warm temperatures. CB mechanisms (CB6, CB05, CB4) explicitly account for this temperature dependency.

2. Competition between formation of NO_2 and organic nitrates ($R\text{-}ONO_2$) when alkyl peroxy radicals (RO_2) react with NO. Organic nitrate formation is favored by cold temperatures. CB mechanisms do not account for this effect but the temperature dependency has been studied (Arey et al., 2001) and could be added to CB mechanisms.

Increasing the yields of organic nitrates will favor ozone formation when NOx is abundant by removing NOx from the atmosphere and lessening the inhibition of ozone formation caused by abundant NOx.

References

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Scope of Work

Snow Cover Updates

1. ENVIRON will expand the treatment of surface albedo in CAMx to allow for more dynamic interactions with snow cover fields available from WRF. Specifically, albedo will be adjusted by snow depth (and possibly snow age) and by land cover type, and incoming photolysis rates will be interpolated within the range of three albedos in the photolysis rates file.
2. ENVIRON will expand the treatment of snow in the Zhang deposition algorithm to tie into the snow depth updates in (1) and allow for a range of snow cover as a function of the 26 Zhang land cover categories.
3. ENVIRON will extend the surface model to work with the Zhang dry deposition option and to add capability to handle snow-covered surfaces for both Wesely and Zhang options. It is anticipated that a third category of surface reactions would be implemented for snow (in addition to vegetation and bare ground).
4. ENVIRON will advise Utah Division of Air Quality on how to perform a series of model simulations that test and evaluate the improved snow treatments in CAMx.
5. ENVIRON will work with Utah Division of Air Quality to interpret the results of ozone simulations using the improved snow treatments in CAMx.

Carbon Bond Updates

1. ENVIRON will make the yields of organic nitrate temperature-dependent in the CB05-TU and CB6 chemical mechanisms.
2. ENVIRON will implement the CB6 chemical mechanism with temperature dependent organic nitrate yields into the latest version of the CAMx model (currently version 6.1) and provide the CAMx source code to Utah Division of Air Quality.
3. ENVIRON will work with the CMAQ model developer (EPA) to implement the CB05-TU chemical mechanism with temperature dependent organic nitrate yields and provide the CMAQ source code to Utah Division of Air Quality.
4. ENVIRON will advise Utah Division of Air Quality on how to perform model simulations using the improved chemical mechanisms in CAMx and CMAQ.
5. ENVIRON will work with Utah Division of Air Quality to interpret the results of ozone simulations using the improved chemical mechanisms in CAMx and CMAQ.

6. ENVIRON will prepare a final report describing chemical mechanism improvements and discussing results of ozone simulations (performed by Utah Division of Air Quality) using the improved chemical mechanisms

Schedule and Cost

The proposed schedule is 6 months at a cost of $110,000

Deliverables

1. CAMx source code with updates to snow interactions for photolysis, deposition and the surface model, and to CB6 for temperature dependent organic nitrate yields;
2. CMAQ source code with updates to CB05-TU for temperature dependent organic nitrate yields (this deliverable depends upon collaboration with the CMAQ developer);
3. Report describing model improvements and discussing results of ozone simulations (performed by Utah Division of Air Quality)

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