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COMBINING MEASUREMENTS AND MODELING TO QUANTIFY POWER PLANT CONTRIBUTIONS TO ATMOSPHERIC NO_2 AND CO_2

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1. INTRODUCTION

Successful adoption of international agreements to limit CO_2 emissions requires sound methods to measure and monitor anthropogenic sources of this green house gas. However, the task of verifying compliance to such agreements is very difficult. CO_2 is a naturally abundant and variable atmospheric constituent and small increases need to be measured against this high background level. Because CO_2 is a long-lived gas, background levels are also rising. Emissions inventories derived from fossil fuel consumption data are uncertain and can be subject to manipulation. To ensure fair compliance, remotely sensed measurements and an understanding of the transport of CO_2 from the sources are required.

On the other hand, a number of gasses (e.g. NO_2, SO_2, and CO) and isotopomers (e.g. $^{13}CO_2$) are co-emitted with CO_2 during energy production. These co-emitted species have relatively low background levels and energy activities produce large perturbations above background concentrations. Many of them have shorter lifetimes than CO_2 in the atmosphere and multiple species can be observed concurrently. For these reasons, the co-emitted species are more sensitive probes for attributing sources. In addition, the ratio of a co-emitted species to CO_2 depends on fuel composition and combustion process and thus varies by energy sector.

The Los Alamos National Laboratory's Remote Sensing Verification Project (RSVP) uses co-emitted species to investigate CO_2 emissions in the Four Corners region. It tests the hypotheses that 1) the ratios of co-emitted gases and isotopomers to CO_2 provide an independent method to quantify CO_2 emissions, 2) CO_2 from natural and anthropogenic sources can be distinguished and tracked by monitoring these co-emitted species, and 3) the combination of measurements and models at multiple scales will facilitate emissions estimates.

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2. THE REMOTE SENSING VERIFICATION PROJECT AT FOUR CORNERS

Establishing CO_2 ratios from multi-perspective observations requires unraveling the effects of complex chemistry and dynamics that can be very non-linear. This demands validation in real-world and well-calibrated conditions of manageable complexity. To test the hypotheses, a combination of remote sensing and in situ measurements along with model simulations are applied to the Four Corners region of Northwest New Mexico. The name Four Corners refers to the location where the corners of four states (Utah, Colorado, New Mexico, and Arizona) meet.

The region provides a well-defined environment, where population density is relatively low and the arid climate results in minimal vegetation impacts. Yet this area contains the San Juan and Four Corners power plants that together are the largest point sources of nitrogen oxides (NOx) and carbon dioxide (CO_2) in the U.S. The San Juan and Four Corners power plants are located only 12 km apart, but they have different emissions profiles because they have different scrubbers. Stack emissions are monitored by EPA Continuous Emissions Monitoring Systems (CEMS).

Furthermore, the region has significant gas, oil, and coal exploration that could leak hydrocarbons, such as methane (CH_4), into the air, plus a mid-sized urban center comprised of Farmington and Bloomfield, NM. The region's large emissions of green house gases and air pollutants provide a high signal to noise ratio that is ideal for monitoring.

Initially, we address these science questions: 1) Can we quantify CO_2 from NOx observations? 2)

Can we discriminate high NOx and low NOx CO_2 sources 12 km apart and can we distinguish them from fires? 3) Can we sense NOx trends from space?

2.1 *Satellite Measurements*

Satellite measurements of column CO_2 and NO_2 concentrations in the Four Corners region obtained from SCIAMACHY (European Space Agency) are given in Figure 1. Analysis shows some CO_2 enhancements over Denver but not over Four Corners. This illustrates the difficulty in measuring small changes to CO_2 emissions and individual sources from satellites. CO_2 is well mixed over large areas. The anthropogenic column increase in concentration is small, on the order of 1-2 %, and it has a long lifetime, on the order of hundreds of years.

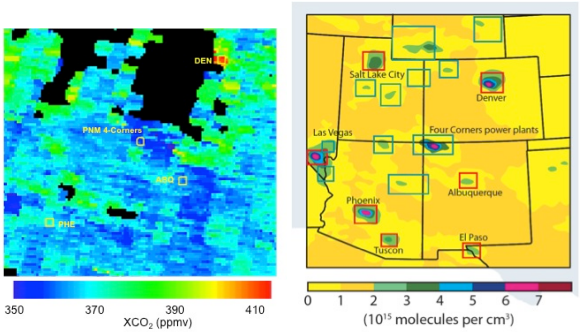

Figure 1. Column CO_2 (left adapted from Schneising et al., 2008) and Column NO_2 (right adapted from Kim et al., 2009) from SCIAMACHY.

In contrast, the NO_2 signature is evident over the cities of Denver, Albuquerque, Phoenix, and Las Vegas, as well as over the power plants. Changes in NO_2 emissions are relatively easy to measure and individual sources are readily identifiable from satellites. This is because anthropogenic column increase in concentration is large, on the order of 300% in winter, and it has a relatively short lifetime, on the order of 1-2 days.

To illustrate emissions changes in NO_2 that are detectable by satellite, December NO_2 column concentrations measured by the Ozone Monitoring Instrument (OMI) on the Aura satellite over the Four Corners region are presented in Figure 2 for 2006 and 2009. The reduction in concentrations from 2006 to 2009 is also found in the downward trend in the NO_2 concentration time series of Figure 4 (black curve). A similar trend is observed in GEOS-Chem model output analyses and bottoms-up inventory estimates from CEMS emissions at the San Juan power plant (Figure 4 blue curve). These reflect environmental upgrades to the San Juan station.

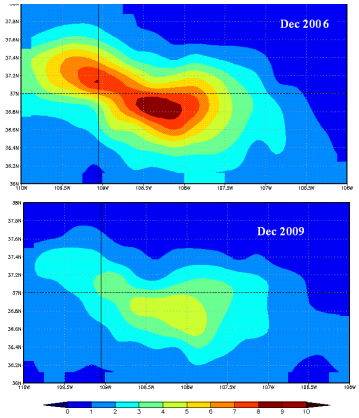

Figure 2. December OMI column NO_2 concentrations (molecules per cm^2) for 2006 (top) and 2009 (bottom).

Over the save time period, no trends are evident in the background concentrations (Figure 3 blue curve) or Four Corners power plant emissions (Figure 4 red curve).

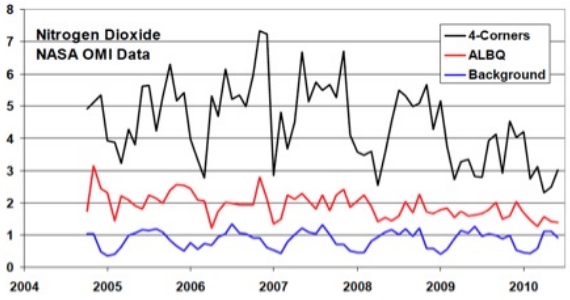

Figure 3. Time series of column NO_2 concentrations (molecules per cm^2) from OMI.

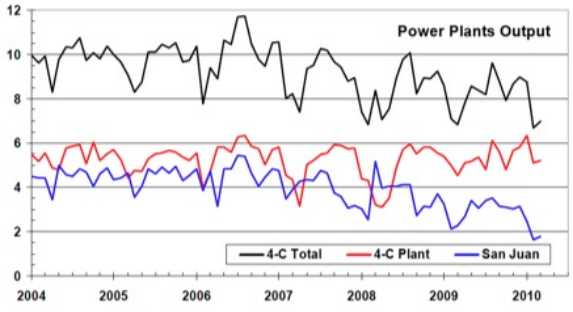

Figure 4. Time series of column NO_2 concentrations (molecules per cm^2) estimated from CEMS emissions.

2.2 *FTS Column Measurements*

A multi-scale, greenhouse gas and air-pollution, autonomous, robotic measurement system has been established in the Four Corners area of New Mexico (Figure 5). The core of the new measurement system is a robotic laboratory housing a solar tracking Fourier Transform Spectrometer (FTS, Figure 6), which measures the absorption spectra of sunlight at high resolution every few minutes. The atmospheric spectra are fitted using laboratory spectra of individual greenhouse gases (CO_2, CH_4, N_2O, and H_2O) and pollutants (CO, NO_2, and SO_2) to determine their abundances at 10-100 km scales.

Figure 5. RSVP automated solar observatory at San Juan substation, NM.

Figure 6. Bruker 125HR FTS (left) and solar tracker (right).

The international Total Column Carbon Observing Network (TCCON) has calibrated and certified the system, which will be used to validate the greenhouse gas observing satellites, such as the Japanese GOSAT and NASA's OCO-2 scheduled for launch in 2013. The system is the only one in TCCON focused on CO_2 and pollution monitoring for treaty verification. More pictures of the RSVP site can be found at the web site https://tccom-wiki.caltech.edu/Sites/Four_Corners

Calibration of the FTS was performed at the Atmospheric Radiation Measurements (ARM) facility at Pagosa Springs, CO, roughly 100 km Northeast of the Four Corners location. Figure 7 shows data collected at Pagosa Springs, where concentrations are the result of applying retrieval algorithms to the measured spectra. The instrument detected a plume at 1846 UTC with high CO concentrations (an increase of 21%), while increases in CO_2 (0.08%) and N_2O (0.25%) were small.

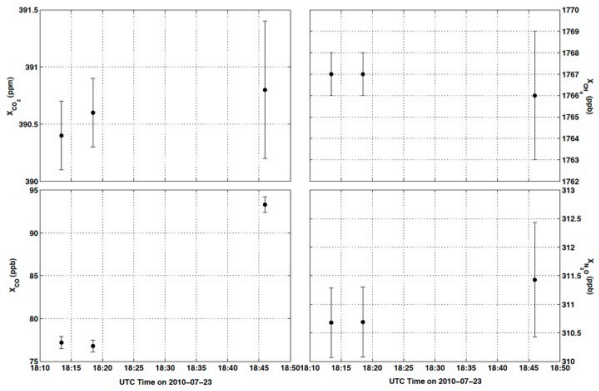

Figure 7. Column concentrations of CO_2 (upper left), CH_4 (upper right), CO (lower left), and N_2O (lower right) measured by the FTS as Pagosa Springs, 23 July 2010.

2.3 *In Situ Measurements*

A number of *in situ* instruments are also deployed with the RSVP. These include meteorological towers to measure winds and temperature, Aeronet-CIMEL to measure aerosols, and ne CO_2-Aeronet from NASA. A suite of Picarro laser-based cavity ring-down sensors provides continuous greenhouse gas and pollution monitoring. Together these instruments observe CO_2, CH_4, CO, NOx, aerosols, and $^{13/14}CO_2$.

Initial *in situ* measurements indicate enhanced levels of methane and hydrocarbons and large CO_2 enrichments from the power plants. Figure 8 depicts collected data that discriminate between methane produced from a fire at the surface and carbon dioxide from both the fire and the power plant stacks. The CO_2 concentrations are 20-100 ppm higher than the 390 ppm background concentration (the spikes in CO_2 are due to venting from the trailer when the door is opened). The CH_4 concentrations are more than 25% greater than the 1.9 ppm background concentration, even before the fire is started shortly after 1800 MST. The elevated methane levels may be due to seeps from natural gas wells in the area. Surface concentrations of CO_2 fall when the atmospheric boundary layer height is below the stack height (120 m) at about 2020 MST. With the top of boundary layer between the emissions and the sensor locations, mixing down of CO_2 from the power plant stacks to the surface is inhibited. However, CH_4 concentrations continue to increase because nighttime stable conditions

and the shallow boundary layer depth reduce dilution of the surface release from the fires. After 1000 MST the next morning, the CH_4 concentrations drop as the boundary layer grows and mixing increases.

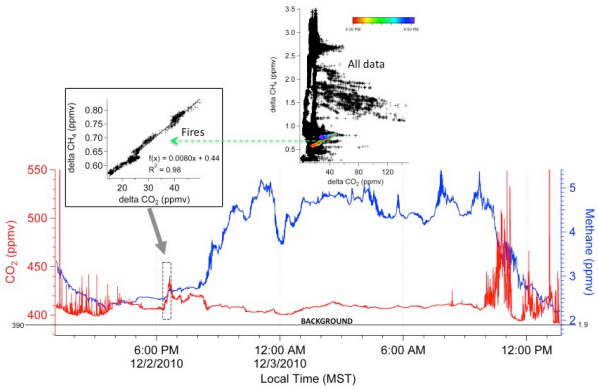

Figure 8. Time series of Picarro CO_2 (red) and CH_4 (blue) concentrations at Four Corners, 2-3 Dec 2010. Black line represents background CO_2 concentrations. Insets plot delta CH_4 vs. delta CO_2 for the fire (left) and all data (right).

Insets in Figure 8 also show that there is a linear relationship between the change in CH_4 and the change in CO_2 for the fire that is not apparent for all of the data.

2.4 *Numerical Modeling*

Two models are used to simulate the time evolution of the chemistry, CO_2, and dynamics of the power-plant plumes. LANL's high fidelity HIGRAD model incorporates a multiphase, Lagrangian, particle-based approach to track individual chemical species at ultrahigh resolution, using an adaptive mesh (Reisner, et al., 2003, Andrjchuk et al., 2008). Each particle represents the mass of various chemical species exiting each stack over a certain time period. Particles leaving the stacks exchange their temperature (330 K) and velocity (18 m/s) with the surrounding gas. Initial testing of this model is over a horizontal domain of 50x60 km employing 50 m resolution near the coal plants. Figure 9 illustrates the buoyant plumes in an idealized simulation with neutral stability and constant winds from the west.

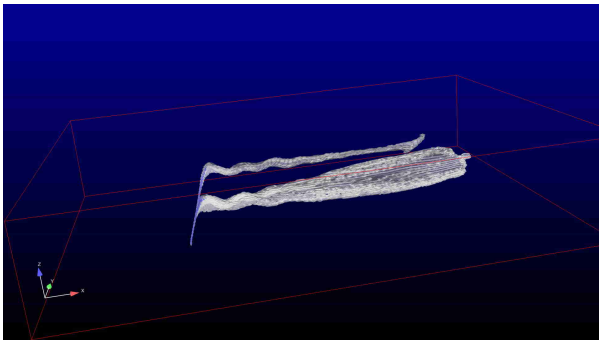

Figure 9. HIGRAD simulation of long-lived (grey) and short-lived (blue) chemical surrogates emitted from Four Corners and San Juan power plants.

The Weather Research and Forecasting model (WRF-Chem; Grell et al., 2005) simulates the regional atmospheric environment and chemical processes. WRF-Chem employs five grids, nesting to 200 m horizontal grid spacing and matching the coarsest grid spacing in HYGRAD. Although the RSVP site near the San Juan substation is quite flat, Figure 10 shows the complex topography in the region.

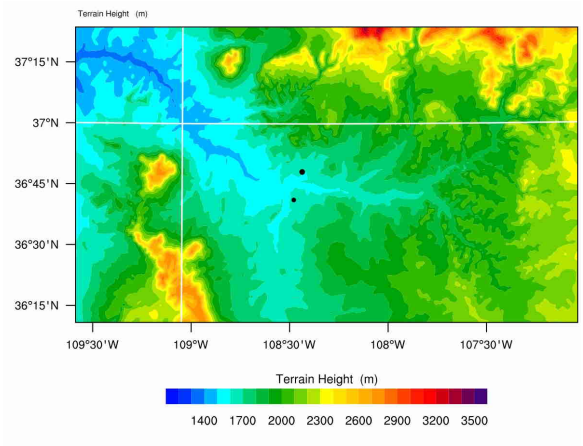

Figure 10. Topography heights (m) on WRF-Chem grid4, with 382 x 226 grid points and 600 m grid spacing. Black dots give the power plant locations.

Hourly CEMS emissions provide model CO_2 emissions input. Preliminary simulations include CO_2 as a passive tracer and assume non-buoyant emissions. During the nighttime wind transition the plume paths change direction, producing the curved plume in Figure 11. Surface concentrations are also reduced near the San Juan substation, reminiscent of the Picarro measurements in Figure 8. Column concentrations in Figure 12 still detect the San Juan plume when it is not as obvious at the surface.

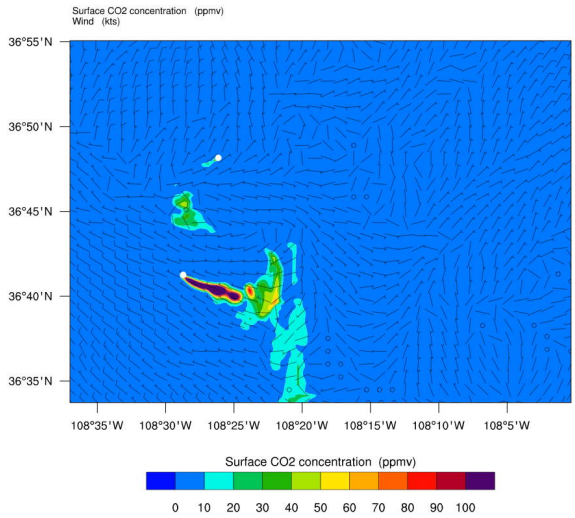

Figure 11. Surface CO_2 concentration (ppm) departures from background and wind barbs on WRF-Chem grid 5 at 0700 UTC 23 Mar 2008. White dots give the power plant locations.

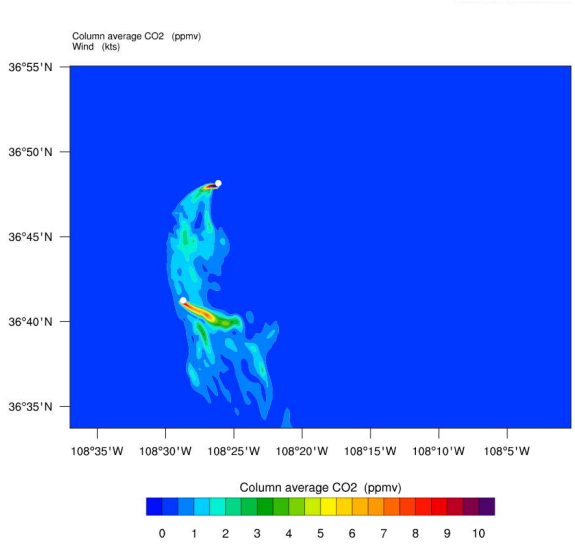

Figure 12. Column CO_2 concentration (ppm) departures from background on WRF-Chem grid 5 at 0700 UTC 23 Mar 2008. White dots give the power plant locations.

3. FUTURE WORK

Continuous greenhouse gas and pollution monitoring creates a validated science base for the attribution of greenhouse gases. This information is essential for the verification of a climate treaty. The instrumentation enables the development of next generation regional scale air quality monitoring. Therefore, our future plans include maintaining continuous, long-term monitoring with *in situ* and FTS sensors at the Four Corners site and comparing them with satellite measurements. We also plan to carry out an extensive field campaign, including aircraft measurements. The work will include analysis of signature ratios of co-emitted gases and isotopomers to CO_2 and development of intelligent satellite retrieval algorithms that focus on a few select spectral lines for increased accuracy.

We will model the chemical processes and regional and very high-resolution local transport of CO_2 and NO_2. Future HIGRAD simulations will utilize realistic topography and boundary conditions from WRF-Chem and WRF-Chem runs will include more realistic plume dynamics informed by HIGRAD results. In addition we will develop an inverse modeling method that employs an ensemble of model realizations and Kalman filtering to derive emissions estimates from downstream measurements. We will also apply uncertainty quantification to the different methods and variables relevant to our approach.

4. REFERENCES

Andrejczuk M., J.M. Reisner, B. Henson, M.K. Dubey, and C.A. Jeffery, 2008: The potential impacts of pollution on a non-drizzling stratus deck: Does aerosol number matter more than type?, VOL. 113, D19204, doi:10.1029/2007JD009445.

Grell, G.A., S.E. Peckham, R. Schmitz, S.A. McKeen, G. Frost, W.C. Skamarock and B. Eder, 2005: Fully coupled online chemistry within the WRF model. *Atmos. Environ.,* 39, 6957-6975.

Kim, S.W. et al, 2009: NO2 columns in the western United States observed from space and simulated by a regional chemistry model and their implications for NOx emissions, *J. Geophys. Res.,* 114. D11301.

Reisner, J., A. Wyszogrodzki, V. Mousseau, and D. Knoll, 2003: An efficient physics-based preconditioner of the fully implicit solution of small-scale thermally driven atmospheric flows. *J Comput. Physics.,* 189, 30-44.

Schneising, O. et al., 2008: Three years of greenhouse gas column-averaged dry air mole fractions retrieved from satellite - Part 1: Carbon dioxide *Atmos. Phys. and Chem.*, 8, 3827.

5. ACKNOWLEDGEMENTS

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