CO₂ & CH₄ Emission Verification by High Frequency Mesoscale Atmospheric Observations

San Juan Power Plant

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Outline: Tackle the Emission Verification Challenge

- Can we verify CO$_2$ emissions for trading or a treaty?
  - Four Corners power plant emission attribution & verification.
- Can we quantify CH$_4$ leaks from fossil fuel infrastructure
- Fugitive CH$_4$ leaks from hydraulic fracturing are a hot issue.

Current Measurement Challenges
- Large Meteorological variability (in situ)
- Low frequency sampling (satellite)

Solar absorption spectroscopy (e.g. TCCON, Pandora)
- Mean Mesoscale ($\gamma$) 10km Column CO$_2$, CH$_4$ & NO$_2$ Observations

Model and Empirical Analysis
- High Resolution Forward Modeling with inventory (CEMS, EDGAR)
- Empirical tracer-trace relations for emission factor verification
Atmospheric CO$_2$ Paleo-climatic Variations and Rapid Growth in The Anthropocene

Ice core data from analysis of trapped bubbles

- CO$_2$ concentration, ppmv
- Antarctic temperature, °C

Real time *in situ* data from global networks

- CO$_2$ > 400ppm, 43% increase since 1750, highest in 0.8 million years
- Greenhouse gas that traps terrestrial IR to warm the earth
- Acidifies oceans and suppresses calcite precipitation (coral growth)
Global CO$_2$ Cycle: Currently ~55% of human emissions soaked up by the biosphere & oceans

**CO$_2$ Emissions = Atmospheric rise + land uptake + oceanic sink**

- **Emissions**
  - Fossil fuels and cement
  - Land-use change

**Sinks**
- Land
- Atmosphere
- Oceans

*Since 1870: 41% atmosphere, 31% land, 28% ocean

**CO$_2$ flux (GtC/yr)**

- **8.6 ± 0.4 GtC/yr**
  - 92%
- **2.6 ± 0.8 GtC/yr**
  - 27%
- **4.3 ± 0.1 GtC/yr**
  - 45%
- **8.8 ± 0.5 GtC/yr**
  - 8%

Will nature’s CO$_2$ buffering as climate change intensifies?

- Forest dieback!
- Release from thawing tundra!
- Ocean outgassing!
- Slow calcification!
Atmospheric CH$_4$: Rising again

- 150% increase since 1750
- Greenhouse gas
- Source of stratospheric H$_2$O
- Produces tropospheric O$_3$

Ice core data from analysis of trapped bubbles

Real time in situ data from global networks

Graph showing CH$_4$ concentration over time:
- Updated to 2012
- 1804 ppb
- 722 ppb
- Slowdown of rise
- Increase resumes
Methane: lifetime ~ 10 yrs, Complex source mix

Methane Sources:
A. Mining and natural gas leaks
B. Agriculture: ruminants
C. Landfills
D. Agriculture: rice paddies
E. Natural wetlands
F. Hydrates

Lifetime 12.6 years

Nature

Hydraulic Fracturing?
The need for a climate treaty or trading:

Observed emissions at high end headed to 3-5°C

Emissions on high end of past projections and are on track for 3.2–5.4°C “likely” increase in temperature above pre-industrial

Large and sustained mitigation is required to keep below 2°C

![Graph showing CO₂ emissions from fossil fuels and cement over time, with lines for different RCP scenarios: RCP2.6 (0.9-2.3°C), RCP4.5 (1.7-3.2°C), RCP6 (2.0-3.7°C), RCP8.5 (3.2-5.4°C).]
Changed Emission Patterns: Need to update treaty framework (verify both sinks to sources)

- Kyoto targeted forestation
- Copenhagen grappled with verification, unsuccessfully
- Paris needs to develop an effective framework
The need for verification: China’s CO$_2$ Provincial & National Inventories Diverge by 1.4Gt

Guan et al Nature CC June 2012
The US Verification Science Challenge: Need and Opportunity

Detect and infer emissions from small human CO$_2$ signal (<1ppm) over large and variable natural background (390 ppm) in complex flows from afar without spatio-temporally resolved inventories.

National Academies Report
March 19, 2010

Global Greenhouse Gas Information System, 2010

JAPAN’s GOSAT & NASA’s OCO2 satellites

VERIFYING GREENHOUSE GAS EMISSIONS: METHODS TO SUPPORT INTERNATIONAL CLIMATE AGREEMENTS

MULTILAB NNSA-JPL STUDY
January 2012

OCO-2 launched July 2nd 2014

LANL (DOE-OBER) sole validation target from ground in Amazon (<0.3ppm)
TCCON Science Objectives

• Constrain global fluxes of carbon and improve our understanding of the carbon cycle
• Provide the primary validation (ground-truth) dataset for satellite instruments
  – GOSAT
  – OCO-2
  – SCIAMACHY
  – ASCENDS
  – AIRS
  – TES
  – CARBONSAT
• Provide a transfer standard between the satellite measurements and the ground-based *in situ* network
TCCON Instruments

- Ground-based Fourier transform spectrometers
- Remote sensing of total columns of CO$_2$, CH$_4$, N$_2$O, CO, H$_2$O, HDO, O$_2$ via solar absorption
- Divide trace gas columns by O$_2$ column to get dry-air mole fractions: $X_{CO_2}$, $X_{CH_4}$, $X_{N_2O}$, $X_{CO}$, $X_{H_2O}$, $X_{HDO}$

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Precision</th>
<th>Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>~0.8 ppm</td>
<td>~0.8 ppm</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>~5 ppb</td>
<td>~7 ppb</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>~1.5 ppb</td>
<td>~3 ppb</td>
</tr>
<tr>
<td>CO</td>
<td>~0.5 ppb</td>
<td>~4 ppb</td>
</tr>
</tbody>
</table>
TCCON Measurements
4-Corners Site: In between San Juan & 4Corners Power Plants E/SE of Coal, Gas & Oil Mining Region

Regional (~10km) Scale Solar Fourier Transform Spectrometer Observations of Column Concentrations of Trace Gases

CO₂, CH₄, CO, N₂O, H₂O every 2 minutes during day
Four Corners GHG and Pollution Monitoring

Picarros
- CO₂, CO, CH₄
- ¹³CO₂, ¹³CH₄
- H₂O/HOD

Brewer
- O₃

Pandora
- NO₂, O₃

TCCON
- CO₂, CO, CH₄
- N₂O, H₂O/HOD

EPA
- NOₓ, SO₂
- O₃, CO

Met.
Nested WRF Chem Model of 4 Corners (NCEP) with real time CEMS power plant emissions + NEI urban inventory
WRF Chem Plume Simulation (200m res.)

16 UTC 03/15/2011: XCO2 (Max=2540.8 ppmv)

16 UTC 03/15/2011: XNO2 (Max=105.6 ppbv)
Power Plant Plume Composition

Traced in exquisite detail at multiple scales by remote (column) and \textit{in situ} (point) surface sensors.

Forward WRF-Chem simulations with CEMS reproduce the column CO$_2$ and NO$_2$ plume signals.

\textit{Lindenmaier et al PNAS 2014}
Source Attribution with *in situ* $^{13}$C Keeling Plot

$Lindenmaier et al PNAS 2014$

\[
\delta^{13}\text{CO}_2 = bx + a
\]

\[
\begin{align*}
a &= -26.0 \pm 0.5 \\
b &= 6900 \pm 200 \\
r &= 0.95
\end{align*}
\]

$\delta^{13}\text{CO}_2^{\text{Source}} = -26$ per mil

$\delta^{13}\text{C Coal} = -26.5$ per mil
75% of atmosphere sampled by FTS is polluted
Discriminate Sources

Lindenmaier et al PNAS 2014
WRF columns vs. FTS columns March 15 2011

CEMS verified to 4% accuracy by FTS column data in SJPP plume
DOE-OBER GoAmazon Manaus, Brazil 2014 (TES, ARM)

Carbon Cycle - improve Community Earth System Model (CESM) for land-atmosphere processes in the Amazon Basin, including aerosol-cloud-precipitation connections

- Objective - Reduce uncertainties in our knowledge of feedbacks between vegetation-hydrology that underlie the Amazon forest dieback hypothesis. The uncertain range of feedbacks at present leads to large differences in ESM predictions.

- Objective - Response of photosynthesis and transpiration, including BVOC emissions to changes in the direct and diffuse components of incoming solar radiation, i.e., in the context of current and future scenarios of aerosols and clouds in the Amazon Basin.
Natural Gas Opportunities & Challenges for Climate

Moniz Report

Growing Methane Supply from Hydraulic Fracturing

EPA & DOE should review & update CH₄ emissions from gas production and distribution. CH₄ leaks at the levels indicated by the new EPA estimates, could prompt efforts to capture them for environmental & business...

Need to baseline leaks from conventional mining as we quantify those from unconventional methods.
Shale Gas is Clean and Abundant Domestic Fuel that is being Mined Profitably by Hydraulic Fracturing to Supplant Coal and Oil to help US achieve Energy Independence

- **Clean Air**: No particulates or SOx and less NOx making a desirable transportation and energy fuel*
- **Climate Friendlier**: CH$_4$ produces half as much CO$_2$ per unit energy produced as coal?
- **Fugitive CH$_4$ leaks highly uncertain and a sensitive issue!**
- **CH$_4$ 25 times more potent a GHG than CO$_2$ (100yr)***
- **CH$_4$ leaks < 3% needed for smaller climate impact than coal?**
- **HC leaks and Rig & Infrastructure emissions pollute local air***
- **6-11% leaks from top-down data > x 3 EPA inventories**
- **Moniz Study**: “the environmental impacts of shale development are challenging but manageable”
Inventories & emissions factors (bottom up) underestimate actual measured CH\(_4\) emissions (top down) across scales.

Ensure CH\(_4\) leaks <3% keep it climate friendlier than coal & make it a bridge to carbon neutrality. Area of national need that DOE has prioritized & LANL is harnessing its SoS capability to assess.

*Brandt, Science 2014*
Figure 1: Average methane anomaly as seen by SCIAMACHY from 2003-2009. The four-corners region exhibits the largest regional enhancement in the conterminous US.
4-Corners: What is going on?

Also a gas hub!

Largest Coalbed methane production area in the US
Production of 1.32 trillion cubic feet per year in 2007 corresponds to about 27 Tg/yr
What part of the emissions is related to production vs. natural seepage? Hard to say...
Satellite see CH$_4$ hot spot at 4-Corners: Edgar inventory has sources at right locale.

Figure 1: Column methane anomalies and emissions over the conterminous US
High regional CH$_4$ plumes observed routinely with when winds are low and from SE

Total measurement days 2011+2012 =392

$X_{\text{CH}_4} \geq 1.85$ ppm

78 days (19.89%) $X_{\text{CH}_4} \geq 1.85$ ppm means that at least one value that day reached 1.85 ppm

198 days (50.51%) $X_{\text{CH}_4} \geq 1.82$ ppm

($X_{\text{CH}_4} \geq 1.85$ ppm means that at least one value that day reached 1.85 ppm)
Edgar emissions have to be scaled by x 3 in WRF model to match 4-Corners FTS data

Kort et al in review Nature Geosciences 2014
Satellite data confirm 4-Corners “missing” emission in inventory is double of value in current Edgar inventory.

Consistent with US wide study *Miller PNAS '13. But had* no data for 4Corners and showed Edgar emissions were too high. Turner et al 2015 inversions correct for this with our data.

Figure 2: Methane enhancement for Four Corners region & US EPA inventory estimates.

Missing 4C flux ~0.6 Tg/year, 10% of US gas sources.

% Leak CBM ~ 0.59/27 = 2.2%
Attribution of Fugitive Sources: Regional solar FTS (Mid-IR, InSb) retrievals of column C$_2$H$_6$ & CH$_4$

\[
C_2H_6/CH_4 = 1.5\%
\]

Day 66
\[
s=14.66e-3 \\
r=0.65 \\
n=230
\]

8 AM – 1 PM

3 PM – 6 PM
Inventories & emissions factors (bottom up) underestimate actual measured CH$_4$ emissions (top down) across scales.

*4Corners Attributed to conventional coal bed methane production (pre hydraulic fracturing)

Brandt, Science 2014

*4Corners
Portable mini-mobile FTS compared with TCCON at 4-Corners, Los Alamos, Armstrong & Caltech

Developing a **portable** and **robust** instrument **Without** compromising **Accuracy** and **long term** stability! EM27/SUN validated with TCCON: Promising results.

- Pendulum FTIR
- Resolution: 0.5 cm⁻¹
- 470 x 630 x 350 cm
- ~25 kg incl. tracker
TCCON-EM27SUN Comparisons

\[ y = a + b \times x \]
\[ a = 74 \pm 9 \]
\[ b = 0.81 \pm 0.02 \]
\[ r = 0.73 \]

\[ y = a + b \times x \]
\[ a = -0.24 \pm 0.03 \]
\[ b = 1.14 \pm 0.02 \]
\[ r = 0.91 \]
Low CO$_2$ Bias at High Solar Zenith

Being fixed empirically (GGG) and apriori (PROFFIT)
Mesoscale Atmospheric Emission Verification

- Remote \( \text{NO}_2 \) and \( \text{CO}_2 \) verification of power plant emissions.
- WRF simulations with CEMS agree well with FTS column, with less scatter from met. variability than in situ network (McKain 12).
- Satellite \( \text{CH}_4 \) hot spots at 4-Corners attributed to coal bed \( \text{CH}_4 \).
- Modeling of data shows current \( \text{CH}_4 \) inventory low by factor of 3.
- Remote \( \text{C}_2\text{H}_6 \) signatures used to attribute \( \text{CH}_4 \) sources.
- Compact mobile FTS expands observational opportunities.
- Amazon rainforest monitoring in Brazil with OCO2 validation.
- Mini FTS-TCCON comparisons are promising.