NOAA FIREX experiment

Identification of issue:
A combination of a warmer, drier climate with fire-control practices over the last century have produced a situation in which we can expect more frequent fires and fires of larger magnitude in the Western U.S. and Canada.

FIREX: Comprehensive Field Experiment from CIRES/NOAA ESRL Chemical Sciences Division

Contacts:
Carsten Warneke, James Roberts, Joshua Schwarz
Outline

1) Planned FIREX activities and timing
2) Platforms and sites
3) JFSP FASMEE, NASA FIRE-Chem and WE-CAN
4) First results of FIREX:

Missoula Fire Lab: Oct 1- Nov 15 2016

NOAA Chemical Sciences Division: Who we are and what do we do

Provide the needed scientific understanding and information about our atmosphere to make optimal decisions in the interests of the well being of current and future generations.

Over 100 scientists working on: Air Quality, Climate Change, Ozone Hole with modeling, laboratory and small and large scale field work

Recent field work: Oil&Gas, urban air quality, anthropogenic/biogenic emissions and trends
Main FIREX Science Questions in 5 Categories

1) What are the emissions of gases, aerosols, aerosol precursors, air toxics and greenhouse gases from North American fires?
   What is the composition and volatility of the previously unidentified fraction of the emissions?

2) What is the chemical transformation of those emissions?
   What are the formation mechanisms for secondary species (ozone, SOA and sulfate)?

3) What is the local air quality and visibility impact of North American fires?
   How important is nighttime smoke for populated areas?
   How well do local air quality forecast models work?

4) What are the regional and long-term impacts of North American fires on climate?

5) What are the climate-relevant properties of BB aerosols?
   What role does brown carbon and coatings on black carbon particles play in the optical properties?
   What is the composition of PM2.5?
Main FIREX Science Questions in 5 Categories

1) What are the emissions of gases, aerosols, aerosol precursors, air toxics and greenhouse gases from North American fires?
   What is the contribution and variability of the regional/£identifiable fraction of the emissions?

Detailed Science Questions in White Paper

available at: http://esrl.noaa.gov/csd/projects/firex/

Additions from FIRE-Chem, WE-CAN and FASMEE!!!

4) What are the regional and long-term impacts of North American fires?

5) What are the climate-relevant properties of BB aerosols?
   What role does brown carbon and coatings on black carbon particles play in the optical properties?
   What is the composition of PM2.5?
New science of FIREX

1. **New instrumentation** and satellites
2. **Comprehensive effort** with large science community using ground, mobile, laboratory and aircraft and modeling/forecasting
3. **Simultaneously deployments** of platforms
4. **Nighttime** fires and smoke
5. Years **building knowledge before** large field experiment
6. **Transfer new knowledge** to partners outside US

**Collaborations of FIREX**

Aircraft:
- NASA DC 8: FIRE-Chem
- NASA B200: FIRE-Chem
- NCAR/NSF C130: WE-CAN

Mobile Labs:
- NOAA CSD
- Aerodyne

Joint Fire Science Program: FASMEE project
several controlled burns in 2018-2021
Ground and Lab (TBD/potentially)

IBBI/IGAC
FIREX workflow chart

2015
Instrument Development

2016
Laboratory Studies

2016
Emissions: Fire Lab Study

2016
Chemistry: Simulation Chambers

2017-18
Ground, Mobil WE-CAN

2019
Large field mission with P3 aircraft and other platforms

Modeling and Satellite

Air Quality Forecasting

Fire Ecology and Forest Management

Public Health Information and Outreach

Long Range Transport Studies
NASA DC 8 FASMEE
2019 Large field mission with P3 aircraft and other platforms

International community: IBBI
NOAA CSD FIREX Management

Points of Contact:
Carsten Warneke, James Roberts, Joshua Schwarz

Carsten Warneke\textsuperscript{1,2} NOAA WP-3D gas phase measurements
James M. Roberts\textsuperscript{1} Fire Lab study, field observations with mobile labs
Joshua P. Schwarz\textsuperscript{1} NOAA WP-3D aerosol measurements
Robert J. Yokelson\textsuperscript{3} Fire Lab study, field observations
R. Bradley Pierce\textsuperscript{4} Modeling, data assimilation, and satellites
Barry Lefer\textsuperscript{5} FIREChem coordination
James H. Crawford\textsuperscript{6} FIREChem coordination
Kirk R. Baker\textsuperscript{7} EPA and FASMEE coordination
Amy P. Sullivan\textsuperscript{8} NSF/NCAR C130 coordination

NOAA ESRL Chemical Sciences Division, Boulder, CO
Cooperative Institute for Research in the Environmental Sciences (CIRES), University of Colorado, and NOAA, Boulder, CO
Department of Chemistry, University of Montana, Missoula, MT
NOAA NESDIS Center for Satellite Applications and Research (STAR), Cooperative Institute for Meteorological Satellite Studies, Madison, WI
NASA Earth Science Division, Tropospheric Composition Program, Washington, DC
NASA Science Directorate, Chemistry and Dynamics Branch, Langley Research Center, Hampton, VA
U.S. Environmental Protection Agency, Research Triangle Park, NC
Department of Atmospheric Science, Colorado State University, Fort Collins, CO

NOAA AC4 support of FIREX for several research groups and coordination with other funding agencies
There have always been fires in the NW U.S. in range of the NOAA WP-3 aircraft in summer.

Highly instrumented aircraft used by NOAA CSD since 25 years often used for hurricane research
NOAA WP-3 aircraft in fire season 2019

P3 aircraft max range for single flight example flight

Fires August 2013
NOAA WP-3 aircraft in fire season 2019

P3 aircraft max range for single flight example flight

NASA DC8 range

Fires August 2013
NOAA WP-3 aircraft in fire season 2019

Fire emissions (inventory validation)
Chemistry and transport (model validation)

P3 aircraft max range for single flight example flight

Fires August 2013
Operator seats:
NO\textsubscript{y}O\textsubscript{3}: C3X
Fli Sci: Sta 2
AMS-AOP: Sta. 3
CIMS: Galley
rotating: Galley
<table>
<thead>
<tr>
<th>Instrument Abbreviation</th>
<th>Full Instrument Name</th>
<th>Description</th>
<th>Principal Investigator</th>
<th>Funding Agency</th>
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<td>Column NOₓ, HONO, HCHO, O₃, SO₂</td>
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<td>CRD-AES</td>
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<td>Nick Wagner</td>
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<td>PSAP</td>
<td>Particle Soot Absorption Photometer</td>
<td>total aerosol light absorption by filter darkening; samples from LTI</td>
<td>Nick Wagner</td>
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<td>PAS</td>
<td>Photoacoustic Absorption Spectrometer</td>
<td>total aerosol light absorption by photoacoustics; samples from LTI</td>
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<td>UHSAS</td>
<td>Ultrahigh Sensitivity Aerosol size Spectrometer</td>
<td>counts and sizes 0.07-1.0 μm aerosol particles; samples from LTI</td>
<td>Chuck Brock</td>
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<tr>
<td>HR-AMS</td>
<td>High resolution Aerosol Mass Spectrometer</td>
<td>size resolved chemical composition of aerosol particles</td>
<td>Ann Middlebrook, Katherine Hayden</td>
<td>Environ. Canada</td>
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<tr>
<td>NO/NOₓ/NO₂/O₃</td>
<td>Nitrogen oxides and ozone</td>
<td>chemiluminescence detection with photolytic or catalytic conversion</td>
<td>Chelsea Thompson, Tom Ryerson</td>
<td>NOAA/ESRL</td>
</tr>
<tr>
<td>SP2</td>
<td>Single-Particle Soot Photometer</td>
<td>soot particles number, size, and coating</td>
<td>Joshua Schwarz</td>
<td>NOAA/ESRL</td>
</tr>
<tr>
<td>BrC-Pils</td>
<td>BrownCarbon-Particle into liquid sampler</td>
<td>absorption and concentration of water-soluble organic carbon</td>
<td>Rebecca Washenfelder</td>
<td>NOAA/ESRL</td>
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<tr>
<td>Filter samples</td>
<td>Filter samples for I/SVOCs</td>
<td>GCxGC/TOF-MS (EI) and LC/MS</td>
<td>Kelley Barsanti, Lindsay Hatch</td>
<td>UC Riverside</td>
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<td>j-values</td>
<td>Filter Radiometers</td>
<td>jNOₓ and jH₂O using filter radiometers</td>
<td>Chelsea Thompson</td>
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<td>ISAF HCHO</td>
<td>In-situ airborne formaldehyde</td>
<td>formaldehyde (HCHO) using laser-induced fluorescence</td>
<td>Glenn Wolfe,</td>
<td>NASA GSFC, Thomas Hanisco</td>
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<td>CH₄, CO₂</td>
<td>Picarro CH₄, CO₂</td>
<td>CO₂ and methane with IR laser absorption in a high-finesse cavity</td>
<td>Jeff Peischl, Tom Ryerson</td>
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<td>SO₂</td>
<td>Sulfur dioxide</td>
<td>SO₂ using laser-induced fluorescence</td>
<td>Andrew Rollins</td>
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<td>PAN CIMS</td>
<td>PeroxyAcyl Nitrate CIMS</td>
<td>PANs using chemical ionization mass spectrometry with I as reagent ion</td>
<td>Patrick Veres</td>
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<td>NH₃</td>
<td>QC-TILDAS ammonia</td>
<td>ammonia using Quantum Cascade Tunable Infrared Laser Differential Absorption Spectroscopy</td>
<td>Jennifer Murphy</td>
<td>University of Toronto</td>
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<tr>
<td>ACES</td>
<td>Airborne Cavity Enhanced Spectrometer</td>
<td>Glyoxal using Cavity Enhanced Absorption Spectroscopy</td>
<td>Kyle Zarzana, Steve Brown</td>
<td>NOAA/ESRL</td>
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<td>CO₂, H₂O</td>
<td>Los Gatos CO</td>
<td>cavity enhanced absorption technique in high-finesse</td>
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# Tentative Instrument List NOAA P3 2019

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Detailed instrument list/information available at: [http://esrl.noaa.gov/csd/projects/firex/](http://esrl.noaa.gov/csd/projects/firex/)
Phase 1 of FIREX
Missoula USFS Fire Science Lab
Oct 1- Nov 15 2016

Detailed smoke emission characterization in a controlled environment

First Results
Over 60 people from 20 institutions in Missoula! 9 NOAA funded projects

Wind Tunnel:
- Mini Chamber:
  - HR-AMS
  - SP-HR-AMS
  - CAPS, PASS
  - CRD-PAS, SP2
  - CO, CO2, O3
  - SP2, CLAP, POPS
  - PAX, SMPS
  - WSOC-PILS

Mixing Drum for BC and BrC:

Control Room:
- H3O+CIMS
- I-CIMS
- PAM
- GC-MS

Viewing Room:
- PILS-ESI
- Ny, NO, sampler

Samplers:
- Gas: GCxGC-ToF-MS (EI)
- Particle: GCxGC-ToF-MS (VUV)
- DI-MS, PILS

Room Burns:
- BrC-PiLS
- BBCEAS
- CRDPAS
- NEPH

Aerodyne Lab:
- LToF-AMS
- PTR-MS
- ECHAMP
- PAM
- CO, CO2, NOx, HCHO, CH4, C2H6, C3H8, ..

AMS
- ACES
- FTIR, PAX

I-CIMS
- NO3-CIMS
- Samplers
Fuels:  
- Ponderosa Pine and Lodgepole Pine
- Subalpine Fir and Douglas Fir
- Engelmann Spruce
- Chaparral: Manzanita and Chamise
- FASMEE: Subalpine Fir, Ft Stuart
- additional fuels from SE US, peat, dung, sage, excelsior

Conditions:  
- realistic with duff, litter, logs and canopy of NW US fuels
- separated burns for duff, litter, logs and canopy
- N-content and BC/BrC ratio variation

Stack burns for emissions
Room burns for detailed smoke characterization
Smoke aging in simulation chambers

Example: Volatile Organic Compounds (VOCs) with H3O+CIMS
- Different fire stages
- Different fuels
Example: Volatile Organic Compounds (VOCs) with H3O+ CIMS

- Instrument detects VOCs by proton-transfer with H$_3$O$^+$
- >500 compounds detected

Positive Matrix Factorization statistical method determining contributions of compounds to the fire stages

Different compounds are emitted at different temps.
In order to study the yield and composition of the products, the pyrolysis of biomass constituents has been studied at the bed scale in various types of reactor (fixed bed, fluid bed, ablative, rotating cone, auger, vacuum) at laboratory- and pilot-scale [46–48]. The choice of the technology which depends on the application influences many parameters such as the particle size of the feedstock, the heat transfer rate, the residence time of the solid and volatiles. The advantages of each technology and the influence on pyrolysis yields are discussed in several reviews [46–48]. The composition of the gaseous fraction (CO$_2$, CO, CH$_4$, H$_2$) is analyzed by GC [10,13,30,49]. Concerning the pyrolysis oil, its water content is generally determined by Karl–Fischer titration [10,30,50] and the composition of the main organic compounds can be analyzed by GC/MS [13,14,16,17,30]. Given the complexity and the relatively high MW of the derived-oligomers present in the oil, these compounds cannot be analyzed by GC and gel permeation chromatography is sometimes used to determine the MW distribution [16]. These analytical results give information about the reactions occurring for temperature less than or equal to the one of the reactor. In fact it is not really possible to determine precisely the temperature of the formation of the different products, as most of the volatile compounds are released before the temperature of the sample reaches the temperature of the reactor. Study of conversions realized at the bed scale with high heating rates also give information about the influence of secondary reactions on volatile composition. In this work we study the reactions occurring for pyrolysis temperature below 800°C therefore the secondary reactions will essentially be cracking reactions.

More precise information about conversion mechanisms is provided by coupling TG analysis and an on-line analyzer of the evolved products such as MS [25,51,52] or FTIR [13,49,53]. With this approach, it is possible to study the composition of the evolved products throughout the temperature rise of the sample. Given that structures of the depolymerization products are very close to the one of the units within the residue, these couplings help to understand the evolution of the composition of the sample. Besides, the study of the evolved compounds provides information about the temperature of reactions of fragmentation of unstable functions at the beginning of the conversion and of rearrangement during the charring process. Moreover, additional information can be provided by analyses by FTIR, XRD or NMR of the chemical changes occurring in the solid residue prepared by pyrolysis performed with different temperatures [32,47,54,55].

Based on a review of the experiments of individual pyrolysis of the main biomass constituents, we explicit thereafter the mechanisms involved during the main steps of the conversion of each constituent and describe the composition of the products obtained by each mechanism. Discussed mechanisms occur between 150°C and 800°C, after the evolution of the moisture. It is worth noting that by thermochemical conversion, some steps are sometimes described by ionic reactions [14,55,56], but in many cases, especially for the conversion of lignin, the authors generally propose radical reactions to explain the different evolutions [19,27,57,58].
Products from Lignin Pyrolysis

3.1. Lignin conversion
3.1.1. Description of lignin structure
Lignin is a complex three-dimensional amorphous polymer composed of three phenylpropane units: p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S). The proportions of the monomer units are highly variable and mainly depend on the lignocellulosic biomass.

Reactions of the evolved products

- Conversion of the alkyl side chains
- Conversion of short substituents of the benzene rings
- Hydrogen transfer
- Rupture of the aromatic structure
- Rupture of the aliphatic structure

Aromatic rings (within residue or evolved products)

- Conversion of aromatic rings
- Conversion of aliphatic rings

Normalized fraction of factor

<table>
<thead>
<tr>
<th>Compound</th>
<th>Naphthalene</th>
<th>Benzene</th>
<th>Phenol</th>
<th>Furfural</th>
<th>Furan</th>
<th>Guaiacol</th>
<th>Syringol</th>
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<tr>
<td>N.H.</td>
<td>0.8</td>
<td>0.6</td>
<td>0.6</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
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</tr>
<tr>
<td>N.H.</td>
<td>0.2</td>
<td>0.4</td>
<td>0.4</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
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High temp. (~ 850 °C) vs. Low temp. (~ 200 °C)

Biomass pyrolysis products
Ponderosa Pine versus Manzanita

Different fuels emit similar compounds at similar temperatures.
Over 60 people from 20 institutions in Missoula!

Special thanks to NOAA AC4 for funding!
More FIREX details and list of partners

available at: http://esrl.noaa.gov/csd/projects/firex/

Please contact me for any FIREX related questions

and potential collaborations!!!

Special thanks to NOAA AC4 for funding!
Many important VOCs we observe in fires reflect the polymer components of biomass.

- **Cellulose**

- **Hemicellulose**

- **Lignin**