Ozone air quality in Nigeria and isoprene organic aerosol yields and composition in the southeast US


Aura satellite
HCHO, NO₂, O₃

Aqua satellite:
CO, fires

ENVISAT satellite:
gas flares; CH₄

MetOp-A satellite:
CHOCHO

isoprene
OH
γ

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Ozone air pollution in Nigeria

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Isoprene organic aerosols in the southeast US

Non-methane volatile organic compounds in Africa

OMI Slant Column HCHO (background removed)

VOC → Oxidant → HCHO

Global tropospheric ozone burden

- Biogenic emissions
- Lightning
- Biomass burning
- Anthropogenic

[Graph showing global tropospheric ozone burden with different sources]

[Aghedo et al., 2007]

biomass burning
Nigeria: A populous country with few polluting point sources

**Population:** 170 mill. (2012); 0.5-1 billion (2100).
Megacity Lagos population: 11-20 million people.

**GDP:** 37th largest in (2012); 13th largest (2050).
Energy Mix and Dependence on Oil

**GDP:** 37\textsuperscript{th} largest in (2012); 13\textsuperscript{th} largest (2050)

**Nigerian economy and crude oil**

- **GDP per capita (USD):**
  - 300 (1960)
  - 1200 (1970)
  - 1500 (1980)
  - 1200 (1990)
  - 900 (2000)
  - 300 (2008)

- **Oil price (USD):**
  - 0 (1960)
  - 20 (1970)
  - 40 (1980)
  - 60 (1990)
  - 80 (2000)
  - 100 (2008)

[World Bank, 2009]

**Nigeria’s Energy Mix (2010)**

- **Fuelwood & waste:** 82%
- **Oil:** 13%
- **Natural gas:** 4%
- **Hydro:** 1%

[**EIA, 2012**]

**Electricity consumption (per capita):**
- 150 kWh (Nigeria)
- 13 000 kWh (USA)

**Illegal Oil Refining**

[**Elvidge et al., 2009**]
Seasonal biomass burning and Severely Restricted Ventilation

**Observed Burned Area (2001-2012)**

[Map showing burned area percentage per year]

Burned area (% yr\(^{-1}\))

[Andela et al., 2014]

**Seasonal mean GEOS-Chem \(^{222}\)Rn**

[Maps showing seasonal mean \(^{222}\)Rn concentration]

**222Rn:** Uniform source from non-frozen soils
Loss is by radioactive decay

**Interpretation:** High values indicate stagnation

**Central Nigeria is “on fire” in the dry season (December-January).**

MODIS-derived burned area product [Giglio et al., 2009]

Dry season **biomass burning** and **unpredicted stagnation** contribute to poor O\(_3\) air quality.
Observational Constraints on Local Anthropogenic Emissions

(1) Aircraft Observations

AMMA Flight tracks superimposed on MODIS EVI (June-August 2006)

Weekday CO and NMVOC concentrations over the megacity Lagos (11-20 million people)

Lagos has high VOC, low NO\textsubscript{x} emissions:

\begin{itemize}
\item 0.37 Tg VOC yr\textsuperscript{-1} (Beijing: 0.23 Tg VOC yr\textsuperscript{-1})
\item 0.03 Tg NO\textsubscript{x} yr\textsuperscript{-1} [Hopkins et al., 2009]
\end{itemize}

Gross \textbf{underestimate} in VOC emissions (RETRO inventory)
Obtain additional constraints from satellite observations of biomass burning, inefficient combustion, and extensive natural gas leakage and flaring.

**Seasonal open fires**

- AIRS CO + MODIS fires
- OMI NO₂

**Anthropogenic Volatile Organic Compounds**

- OMI HCHO
- SCIAMACHY CH₄
- GOME-2 CHOCHO

Evaluate the implications for ozone pollution using satellite observations of ozone.

**Implications for atmospheric ozone pollution (DJF in 2006)**

- TES 825 hPa O₃ retrieval
- Model sampled with TES sensitivity

[Marais et al., AE 2014]
Ozone Pollution and Human Health

Vertical distribution of MOZAIC and GEOS-Chem ozone [ppbv] in DJF

GEOS-Chem has ~10 ppbv bias at the surface.

In Nigeria DJF MDA8 O₃ is > 70 ppbv

[Marais et al., AE, 2014]
CONCLUDING REMARKS:
Ozone air quality in Nigeria: a view from space

Higher per capita anthropogenic NMVOC emissions than China

Ozone air pollution contributions includes anthropogenic inefficient combustion sources; natural gas flaring, venting, and leakage; open fires; restricted ventilation

GEOS-Chem reproduces vertical distribution of ozone, but is biased high by ~10 ppbv

According to GEOS-Chem, the EPA ozone standard of 75 ppbv would be routinely exceeded in Nigeria in DJF

Ozone air quality will worsen should Nigeria develop its energy sector to deliver cheap, affordable, and reliable electricity

ONGOING WORK:

Build a nested Africa domain (0.5°×0.667°; lat×lon) using GEOS-Chem model to interpret the impact of pollution on human health and crop yields

Develop an emission inventory for pollution sources in Africa missing from current inventories (e.g. artisanal oil refining; informal industry; gas flares)
Isoprene organic aerosol in the southeast US

Organic aerosols are ubiquitous in the atmosphere

Organic aerosols are ubiquitous in the atmosphere. Observations are limited to the northern hemisphere.

Aerosol composition measurements are now available in the tropics.

[Zhang et al., 2007]

AMAZE (2008)  
GoAmazon (2014)  
AMMA (2006)  
OP3 (2008)
Isoprene organic aerosol in the southeast US

Organic aerosol contribution is increasing where SO$_2$ emissions are declining

2010 minus 2005 SO$_2$ emissions

Global bottom-up emission inventory trends (left) corroborated by surface (below) and satellite observations

SO$_2$ emissions, and sulfate aerosol and organic aerosol mass

(Open symbols: IMPROVE; closed symbols: SEARCH)

Summertime organic aerosol fraction is increasing in the southeast US

SOAS site impacted by urban, industrial, biogenic, and agricultural emissions

[Attwood et al., 2014]
Isoprene is the dominant VOC emitted by vegetation (440-660 Tg C a⁻¹)
Isoprene emissions are several times higher than anthropogenic NMVOC emissions

MEGAN Isoprene Emissions
(µmol m⁻² h⁻¹)

[Map showing isoprene emissions for January and July]

MEGAN alpha-pinene (monoterpene) Emissions
(µmol m⁻² h⁻¹)

[Map showing alpha-pinene emissions for January and July]

[Guenther et al., 2012]
Isoprene organic aerosol is 42% of organic aerosol mass in the southeast US in Aug-Sep 2013.
Isoprene organic aerosol in the southeast US

Models underestimate summertime OA mass in the US

[Carlton et al., 2010]
Isoprene organic aerosol in the southeast US

Chamber studies that estimate total yields of isoprene OA provide limited constraints.

Chamber study mass yields of isoprene organic aerosol

- HO$_2$ dominant
- NO dominant

- Low NO$_x$/HO$_2$ dominant
- High NO$_x$/NO dominant

Yields vary from <0.1% to >10%
Isoprene organic aerosol in the southeast US

Low-NO$_x$ SOA precursor isoprene epoxide (IEPOX)

Identified as an important component of SOA in laboratory and field studies

Gas-phase IEPOX is $\sim$50% of OA mass for a lab study under HO$_2$ dominant conditions

IEPOX-SOA is 33% of OA mass in summer in downtown Atlanta
Southeast US Isoprene SOA yields

Estimate isoprene SOA yields using SEAC$^4$RS campaign measurements

SEAC$^4$RS flight tracks and MEGAN isoprene emissions (August-September 2013)

Flights were also in the western US, but isoprene emissions are low and aerosols from wildfires dominate OA mass.

Decline in isoprene emissions (temperature) and a change in oxidation regime (photolysis) in September, so use August observations only.

[Kim, P. et al., submitted]
Isoprene organic aerosol yields in the southeast US

Relationship between organic aerosol (OA) and formaldehyde (HCHO) during SEAC$^4$RS

Use GEOS-Chem to interpret the observed relationship between organic aerosol (OA) and formaldehyde (HCHO):

**Reversible partitioning**
- Semi-volatile SOA precursor
- Pre-existing aerosol

**Irreversible uptake**
- Non-volatile SOA precursor
- Pre-existing aerosol

SEAC$^4$RS-derived isoprene OA yield is 2.4% or 3.4%.

HCHO is a prompt high-yield oxidation product of isoprene

Individual points are gridded (2°×2.5°) boundary-layer (<2 km) daily means

[Marais et al., in prep]
Isoprene organic aerosol yields in the southeast US

Evaluate **OA-satellite HCHO** relationship as a constraint on isoprene OA yields

OA and HCHO measurements are not always coincident measurements, but satellites provide global coverage

**Original OMI column HCHO**

\[10^{16} \text{ molecules cm}^{-2}\]

Evaluate OA-satellite HCHO relationship as a constraint on isoprene OA yields

**Isolate biogenic HCHO** by screening for biomass burning and anthropogenic influences

**OMI biogenic HCHO** (annual mean)

[Marais et al., 2012]
Isoprene organic aerosol yields in the southeast US

Relationship between **aircraft** OA mass and **satellite** vertical column HCHO during SEAC$^4$RS

**Column HCHO** dominated by boundary-layer HCHO from isoprene

**Individual points** are gridded (2°×2.5°) daily means

The combined satellite and SEAC$^4$RS-derived isoprene OA yield is **2.8%** (aircraft-derived yield is **2.4%** and **3.4%**)

GEOS-Chem SOA parameterization:

- **Reversible partitioning**
  - Semi-volatile SOA precursor
  - Pre-existing aerosol

- **Irreversible uptake**
  - Non-volatile SOA precursor
  - Pre-existing aerosol

**Coupled satellite and SEAC$^4$RS**

- Isoprene organic aerosol yields in the southeast US
- Reversible partitioning
- Irreversible uptake
- Semi-volatile SOA precursor
- Pre-existing aerosol

[Marais et al., in prep]
Isoprene OA budget over the southeast US

Update GEOS-Chem with isoprene OA formation and uptake dynamics from laboratory studies.

Reversible partitioning of semivolatile precursors retained for ISOP+OH and removed for ISOP+NO$_3$.

Fixed $\gamma$ for carbonyls.

Gaston et al. [2014] parameterization for others.

Large uncertainty is H$_{eff}$.
Isoprene OA Mechanism Implemented in GEOS-Chem

GEOS-Chem branching ratios (Jun-Aug southeast US)

1st generation
- 2nd generation nighttime hydroxynitrates
- 1st generation nighttime alkynitrates

2nd generation
- isoprene hydroxyhydroperoxide (ISOOOH)
- C5 dihydroxyepoxide (IEPOX)

[Ng et al., 2008; Rollins et al., 2009]

[Jacobs et al., 2014]

[Aerosol precursors?]

6.6%

isoprene (ISOP)

6.3%

methyl glyoxal

87%

OH

and isomers

isoprene peroxy radical (ISOPO2)

26%

HO2

65%

NO

7%

isomerization

1st generation

[Jacobs et al., 2014]

[Jun et al., 2013; Riedel et al., 2015]

[Nguyen et al., 2013; Sumner et al., 2014]

[Liggio et al., 2005; Fu et al., 2008; Nguyen et al., 2013; Sumner et al., 2014]
IEPOX-SOA is $\sim 2 \, \mu g \, m^{-3}$ during SOAS. ISOPOOH-SOA is an order of magnitude lower.

GEOS-Chem captures temporal variability during SOAS

According to GEOS-Chem 10 mass % gas-phase IEPOX condenses to aerosols at the SOAS site.

**Timeseries of biogenic emissions, and IEPOX-SOA and ISOPOOH-SOA**

- **IEPOX SOA during SOAS**
  - $H_{ef} = 1 \times 10^7 \, M/\text{atm}$
  - AMS IEPOX-SOA
  - GEOS-Chem IEPOX-SOA

- **ISOPOOH SOA during SOAS**
  - AMS ISOPOOH-SOA
  - GEOS-Chem ISOPOOH-SOA

**Evaluate GEOS-Chem with surface and aircraft observations**
Evaluate GEOS-Chem with surface and *aircraft* observations

IEPOX-SOA vertical profile is similar to gas-phase precursor profile, but model yields decline with altitude

**Yield profile** likely driven by vertical distribution of *inorganic aerosols:*

Convex hull

**Sulfate mass during SEAC4RS**

Vertical profile of IEPOX-SOA mass and yields during SEAC4RS (August 2013)

[Kim, P. et al., *submitted*]
Isoprene OA budget over the southeast US

**GEOS-Chem branching ratios**
- 0.1% 2nd generation nighttime hydroxynitrates
- 0.22% 1st generation nighttime alkyl nitrites

**GEOS-Chem SOA mass yields**
- NO$_3$ 6.6%
- O$_3$ 6.3%
- Nitrate species from ISOP+OH << 0.01%
- Total yield is 3.2%

**NOTE:**
Yields of nitrate species from ISOP+OH is << 0.01%

**SEAC$^4$RS yield:**
2.4-3.4%

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**Isomerization**

- 87% OH
- 26% NO
- 65% HO$_2$
- 7% Aerosol precursors?

**1st generation**
- OH
- HO$_2$
- NO

**2nd generation**
- C$_5$ dihydroxyepoxide (IPOX)
- C$_4$ hydroxyepoxide (MEPOX)
- C$_5$ hydroxy carbonyl
- Methyl vinyl ketone
- Methacrolein

**Branching ratios**
- [Jacobs et al., 2014]
Isoprene OA budget over the southeast US

Contribution of sources to organic aerosol in the southeast US

Revised contribution of isoprene oxidation regimes to organic aerosol

[Original Kim et al., submitted]

Isoprene Low NO\textsubscript{x} (16%)

Isoprene High NO\textsubscript{x} (26%)

[Adapted from Kim et al., submitted]

Isoprene Low NO\textsubscript{x} (29%)

Isoprene High NO\textsubscript{x} (13%)

Isoprene OA is **70%** low NO\textsubscript{x} and **30%** high NO\textsubscript{x}

Assumes **glyoxal** is from high NO\textsubscript{x} only

\[\rightarrow\] overestimate high NO\textsubscript{x} contribution
CONCLUDING REMARKS:
Isoprene organic aerosol in the southeast US

Southeast US isoprene OA yields are 2.4-3.4% using aircraft observations or 2.8% using aircraft and satellite data.

Aerosol uptake of IEPOX is a sizable sink of IEPOX (6-10 mass % at the surface) missing from CTMs.

Close the isoprene OA budget with a few oxidation products: IEPOX-SOA (1.9% yield), glyoxal (0.94%), ISOPOOH-SOA (0.22%), night-time ISOPN-SOA (0.1%), and MACR-EPOX-SOA (0.03%).

Next Steps:
Obtain isoprene OA yields in other parts of the world with organic aerosol measurements and coincident column HCHO observations from OMI.
Isoprene OA yield in the context of chamber study yields

Chamber study, aircraft, and satellite mass yields of isoprene organic aerosol

Model gas-phase yields:

- $\text{HO}_2$ dominant
- $\text{NO}$ dominant

Current GEOS-Chem isoprene OA parameterization

- ISOP + oxidant
- $\alpha_1 P_1$
- $\alpha_2 P_2$
- $\alpha_3 P_3$
- $f(T^\circ, m_{\text{OA}})$

Favour aerosol formation where temperature is low and pre-existing aerosol mass is high