NO_x Source Apportionment and Oxidation Chemistry in a Coastal Urban Airshed Using Stable Isotope Techniques: An Approach to Intermittent Sources

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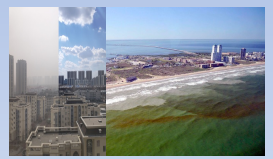
Introduction

NO_x ($NO + NO_2$) emissions decrease urban air quality and its subsequent deposition can be a significant source of excess nitrogen loading to coastal waters. **Here we use stable isotope techniques to quantify primary NO_x emission sources and NO oxidation chemistry in a coastal urban air shed.**



O_3 $PM_{2.5}$ HABs

Methods

Study Site, Corpus Christi, TX, US

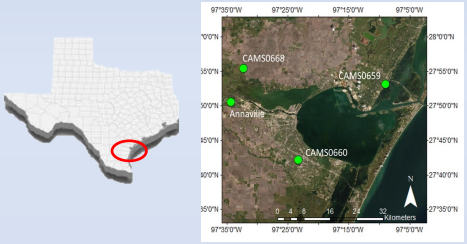


Figure 1: Map of sampling location

NO_x collection

- Ogawa passive air samplers *(Dahal, 2016)*
- Coated filter pads convert NO_x and NO_2 to NO_2^-
- Elute filter pads in 5 mL milli-Q water

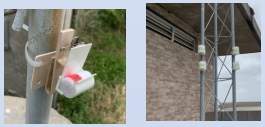


Figure 2: OGAWA passive air filters

NO_2^- concentration

Figure 3: SEAL AQ300 Discrete nutrient analyzer (left and Thermo Dionex Ion chromatography (right)

Methods cont.

Ancillary Data

- Continuous NO_x, O_3, RH, T, wind speed and direction

Figure 4: Teledyne N500 NO_x analyzer (top) T400 Ozone analyzer (bottom) and HOBO RX300 Meteorological station (right)

NO_2^- isotope analysis ($\delta^{15}N$, $\delta^{18}O$)

- Bacteria denitrifier method to convert NO_2^- to N_2O *(Sigman, 2001)*
- CF-IRMS to measure N_2O
- δ Value (‰ units)

$$\delta = \left(\frac{Rx}{R_{std}} - 1\right) * 1000$$

- $\delta^{18}O$-NO_2 must be corrected by 25%
  - Interference of water in elution
  - Loss of O atoms when converting NO_2^- to N_2O *(Dahal, 2016)*

Isotope Mixing Model

$$\delta_{mix} = \sum[(f_{endmember}) * (\delta_{endmember})]$$

$\delta_{endmember}$ = delta value of a source

$f_{endmember}$ = fraction of source contributing to the mixture

δ_{mix} = delta value of the mixture

- Use SIMMR (Stable Isotope Mixing Model in R) to calculate apportionments *(Parnell, 2013)*

Intermittent Sources (lightning and biomass burning)

- Remote sensing to determine when significant *(Qiu, in review)*
- HYSPLIT 24-hr airmass back trajectory
- GEOS-16
  - HMS for Biomass Burning
  - GLM for Lightning
- Deemed significant when estimated same order of magnitude as vehicle NEI emissions

Figure 5: Example of HYSPLIT airmass back trajectory (green dots) and fire events (purple dots)

Isotope Source Signatures

Source	$\delta^{15}N$-NO_x	$\delta^{18}O$-NO_2
Vehicle	-2±4‰ *(Walters, 2015)*	
Industrial	-16.5±10‰ *(Walters, 2015)*	
Biogenic	-35±1.7‰ *(Yu, 2017)*	
Lightning	0.5‰ *(Hoering, 1957)*	
Biomass Burning	1±4‰ *(Elliot, 2019)*	
RO_2/HO_2		~23.5‰ *(Kroopnick, 1972)*
O_3		115±5‰ *(Michalski, 2014)*

Table 1: NO_x emission sources and their $\delta^{15}N$-NO_x and NO_2 oxidation pathways and their $\delta^{18}O$-NO_2

Results

NO_x Source Apportionment

- April 2022 – February 2023
  - Overall average $\delta^{15}N$-NO_x across all sites: 0.41 ± 27.3‰
- $\delta^{15}N$-NO_x ranging from -23‰ to 11‰

Site	Average $\delta^{15}N$-NO_x (‰)	$\delta^{15}N$-NO_x Range (‰)	Ambient NO_x (ppb)
CAMS 0660	1.1 ± 3.4	-3.5 to 7.8	6.2 ± 4.8
Annaville	-1.3 ± 7.5	-9.6 to 3.8	6.4 ± 4.6
CAMS 0668	-1.5 ± 3.0	-23.9 to 6.3	9.9 ± 3.7
CAMS 0659	3.4 ± 2.8	-1.3 to 11.5	4.7 ± 3.9

Table 2: Average and range of $\delta^{15}N$-NO_x and ambient NO_x concentration in ppb observed at each sampling location

- Lightning included in apportionment model 91% of sampling period
  - Not included in May and October
- Biomass Burning included in apportionment model 62% of sampling period
  - Included December – June
    Burning season February – May

$$\delta^{15}N\text{-}NO_{x(sample)} = -35*(f_{biogenic}) + -16.5*(f_{industrial}) + -3*(f_{vehicular}) + 0.5*(f_{lightning}) + 1*(f_{biomass\ burning})$$

when significant

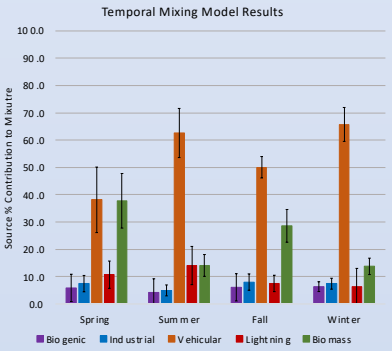


Figure 6: Mixing model results for total sampling period, averaged across each sampling location

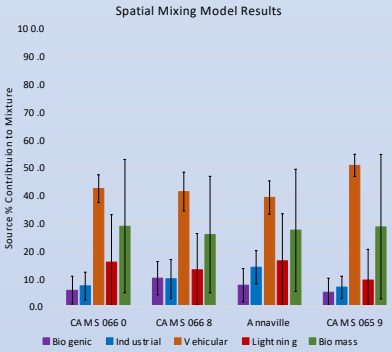


Figure 7: Mixing model results for all sampling locations, averaged across each season

Results cont.

NO_2 Oxidation Chemistry

- April 2022 – February 2023
  - Overall average $\delta^{18}O$-NO_2 across all sites: 55 ± 20‰
- $\delta^{18}O$-NO_2 ranging from 39‰ to 88‰
- Spatial variation not statistically significant (P-value = 0.3)
- Temporal changes in $\delta^{18}O$-NO_2 due to ambient O_3 concentration

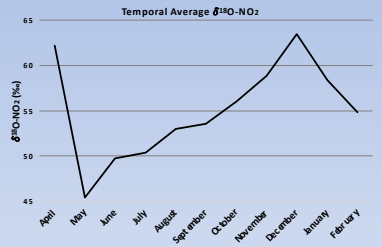


Figure 8: Observed $\delta^{18}O$-NO_2 across the sampling period, averaged across all sampling locations

$$\delta^{18}O\text{-}NO_{2(sample)} = 23.5*(f_{RO2/HO2pathway}) + 117*(f_{O3\ pathway})$$

- Majority oxidation via NO + RO_2/HO_2 -> O_3
- O_3 Oxidation significantly correlated with ambient O_3 concentration

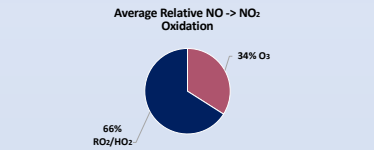


Figure 9: Average oxidation mixing model results across all sites and sampling time

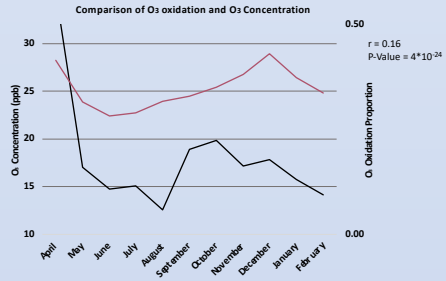


Figure 10: Plot of ambient ozone concentrations (in ppb) compared to proportion of NO oxidized to NO_2 via the ozone pathway

Conclusions

- NO_x emission contribution is primarily vehicle with competing biomass in spring due to increased biomass burning from Mexico
  - Could be over-estimation with the model as source signatures of biomass and vehicles are within standard deviations of each other
  - To further constrain biomass endmember add other biomass indicators, like potassium, to determine when to include it into the apportionment model
- Decrease in $\delta^{15}N$-NO_x over sampling time
  - Oxidation via RO_2/HO_2 pathway will increase the $\delta^{15}N$-NO_x
  - Changes in emission inputs to atmosphere
- Minimal spatial variation of $\delta^{18}O$-NO_2
  - Homogenized airmass across the entire airshed
- Increase in $\delta^{18}O$-NO_2 over sampling period
  - Due to ambient O_3 concentrations
- Majority of NO is oxidized to NO_2 via the RO_2/HO_2 pathway
  - At study site, NO_x limited regime due to low ambient NO_x and surrounding petrochemical facilities
- Knowing NO_x sources can help effectively mitigate NO_x
  - Biomass burning could be an underestimated source in this study region and potentially nationally with increased wildfires over the past decade
  - Study region could introduce things like emission checks to decrease vehicular emissions