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Gaining Insights Into Positive Measurement Bias Of Nitrogen Dioxide In An Ambient

Monitoring Station In Fort Saskatchewan, Alberta

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Abstract:

This paper presents findings from the collocated deployment of two commercial Thermo Fisher Scientific Chemiluminescence NO_X (42i) Analyzers, one with the original Heated Metal Converter (HMC) and the second one equipped with a Photolytic converter (PhoNO) instead of the HMC, in an ambient monitoring station. The aim was to gain insights into known measurement bias introduced by HMCs (in this case a heated Molybdenum Catalyst) during ambient NO_X monitoring. During the first two months of the long term collocated study, results indicate that periodically, the traditional HMCs cause erroneous over-reporting of NO_2 by up to 48% at the monitoring site (Fort Saskatchewan, Alberta). This over estimation (or positive bias) becomes an obvious inflection point on a 1:1 correlation scatter plot between NO_2 reported by the PhoNO vs NO_2 reported by the HMC. This paper concludes that chemiluminescent NO_X analyzers equipped with HMCs indiscriminately convert both NO_2 and organic nitrates in ambient air but erroneously reports the sum of these values as only NO_2.

Introduction

Nitrogen Dioxide (NO_2) and Nitric Oxide (NO), which are summed and termed NO_X, are mostly co-emitted from combustion sources such as vehicles, industrial processes, etc. (*1-4*). The NO_2 emitted is extremely toxic to humans and it is known to be a precursor to the production of another equally toxic gas, O_3, ozone in the troposphere (*2, 5*). Due to its toxicity, NO_2 emission is regulated and the actual concentration must be monitored as accurately as possible and reported to promote better emission control policies and processes (*3*). Over the last two decades, precise and accurate measurement of NO_2 has been a subject of intense research. This is due to insights gained from numerous studies which showed that HMCs inside the chemiluminescence NO_X analyzers thermally dissociate NO_2 and other organic nitrates into NO and the analyzers erroneously report these values as only NO_2. As a result, new direct NO_2 measurement techniques have been introduced and approved for use (*6*). Results from deployment of these new direct monitoring methods have further provided more compelling evidence about this positive measurement bias of NO_2 using HMCs.

Despite these new direct measurement techniques, none of them attempt to address the known uncertainties within the chemiluminescence analyzers. In fact, regarding these NO-Ozone chemiluminescence analyzers, the only source of the positive bias is the HMC (*4, 6, 7*). This means that if a more selective photolytic converter replaces the HMCs, these analyzers will perform as accurately as the direct NO_2 measurement analyzers. Over the years other photolytic converters have been developed however they could not realize the high efficiency, linearity and wide dynamic NO_2 conversion range of the HMCs. More so, any replacement for the HMCs must be a

direct drop-in replacement without modifying flow schematic of the host analyzer in any functional way that may compromise the regulatory approval of the instrument (*8*).

To this end, a new patented photolytic converter (PhoNO) was introduced and tested to be a direct retrofit replacement for HMCs found inside these commercial analyzers described above (*7, 9-12*). The PhoNO has undergone numerous field trials and testing around the globe where its benefits are well documented (*13, 14*).

This white paper presents findings from the deployment of the plug and play PhoNO converter inside a Thermo Fisher Scientific 42i NO_x analyzer at an ambient monitoring site (AMS) in Central Alberta, Canada.

The Ambient Monitoring Site

The monitoring site is located in the urban city centre of Fort Saskatchewan and managed by the Fort Air Partnership (FAP). This site's coordinates are 53.698833°N -113.223194°W (Figure 1). This monitoring site is part of the National Air Pollution Surveillance (NAPS) network. The site is also approximately 80 meters west of Highway 15, a major traffic artery. The monitoring station is impacted by local air pollution and also by transported air mass to the site from ancillary industrial facilities and potentially pollution from nearby cities such as Edmonton. Some of the pollutants monitored at this site are Ammonia (NH_3), Carbon Monoxide (CO), Hydrogen Sulfide (H_2S), Methane (CH_4) and Non-Methane Hydrocarbons (NMHC), Nitrogen Oxides (NO_X), Ozone (O_3), Particulate Matter ($PM_{2.5}$), Sulphur Dioxide (SO_2), outdoor temperature, relative humidity, wind speed, wind direction, etc.
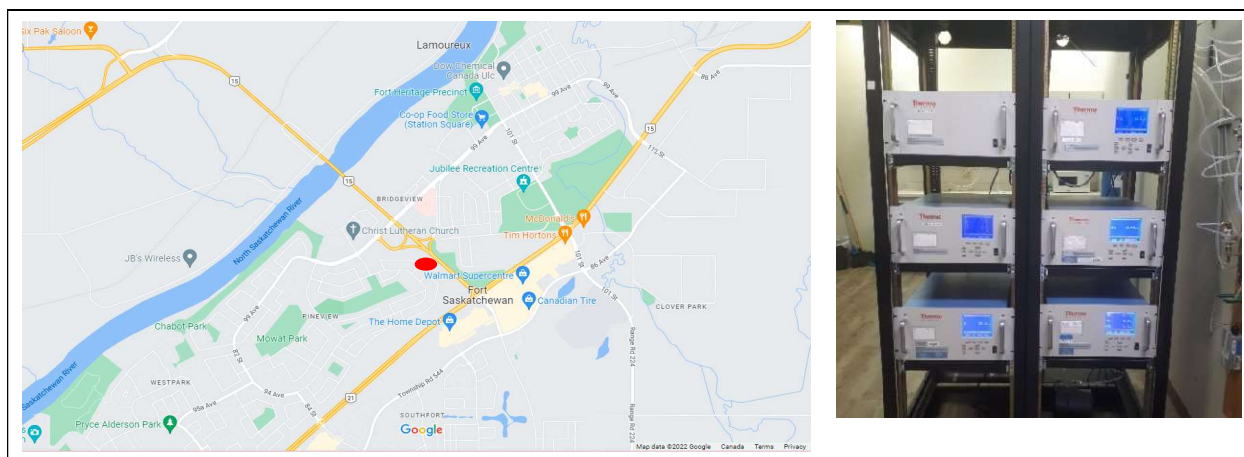
Figure 1: (Left) The location of the ambient monitoring site in Fort Saskatchewan (red dot) and (right) layout of the instruments in the monitoring station

The Collocated Set up

Historically the site has been impacted by wildfire smoke and temperature inversions. The monitoring site houses numerous ambient monitoring analyzers. One of the NO_X analyzers had its HMC replaced with a PhoNO. The PhoNO (Figure 2a) has the same footprint as the HMC making it easy to integrate effortlessly into the host analyzer (Figure 2b). The operational parameters such as reaction cell pressure (160 mmHg) and sample flow rate (0.493 lpm) remained unchanged after the converstion from the HMC to the PhoNO. The indicated converter temperature (317 °C) remained the same as well. This temperature is simulated by the PhoNO's onboard electronics to mimic the host analyzer's normal HMC temperature. This step ensures the analyzer does not enter an alarm state (due to low converter temperature) while the PhoNO is in operation. The PhoNO is actually operating at a reduced temperature (<40 °C) which further prevents the unwanted thermal decomposition of organic nitrates. The replacement of the HMC with the PhoNO also reduces the energy consumption of the analyzer.
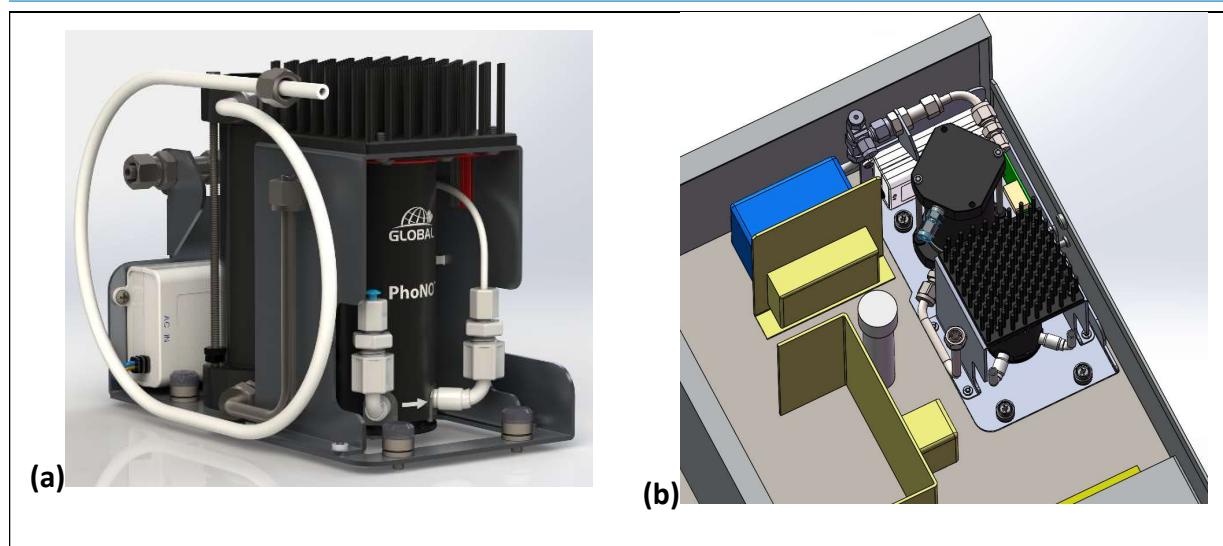
Figure 2: Rendered image of the photolytic converter installed inside a 42i NO_X analyzer replacing the molybdenum converter.

This analyzer was continuously operated within the same ambient air monitoring station and connected to the same sampling manifold as the reference NO_X analyzer. Analyzers were arranged in close proximity within the shelter (see set-up in Figure 1 (right)). The PhoNO was integrated into the 42i NO_X analyzer by reconnecting all tubing in an identical manner to the HMC Molybdenum converter setup inside the 42i (Figure 2). An ozone scrubber was included as part of the PhoNO design to remove the excess ozone prior to venting through exhaust manifold of the analyzer.

The calibration of the instruments was undertaken by the technical staff of WSP under the oversight and direction of the Fort Air Partnership (FAP). A sample of an NO_2 gas phase titration (GPT) is presented below (Figure 3). The slope of the calibration curve was 0.969918 representing a converter efficiency of 97% with regression coefficient (r^2) of 0.999998. The converter efficiency over the two months of deployment was 97% ± 0.1. The GPT was carried

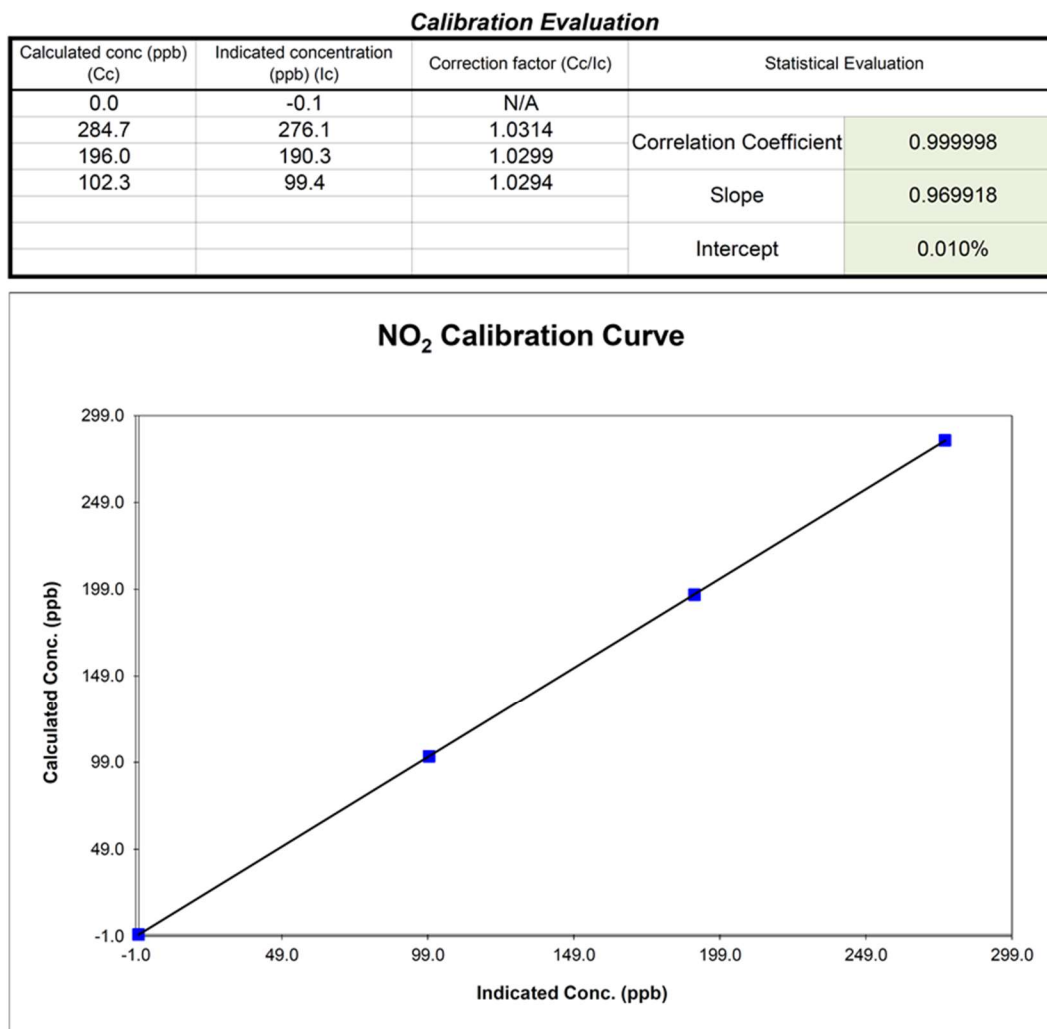out by the technical staff of WSP Canada, and the results were electronically captured and

recorded.

Calibration Evaluation

Calculated conc (ppb) (Cc)	Indicated concentration (ppb) (Ic)	Correction factor (Cc/Ic)	Statistical Evaluation	
0.0	-0.1	N/A		
284.7	276.1	1.0314	Correlation Coefficient	0.999998
196.0	190.3	1.0299		
102.3	99.4	1.0294	Slope	0.969918
			Intercept	0.010%

Figure 3: A graph showing the calibration of the PhoNO photolytic converter deployed inside a Thermo Fisher Scientific 42i NO$_x$ analyzer.

Results and Discussion

It is important to note that there are industrial facilities and vehicular traffic surrounding the monitoring site. When wind blows towards the monitoring site, emissions are measured and reported. Since this monitoring site is located at an urban setting, there is an expected background level of criteria pollutants such as ozone and nitrogen oxides present. The data over the referenced two months indicated that the site is impacted periodically by fresh air mass characterized by high NO levels which titrated the background ambient O_3 to NO_2. See periods of anti-correlation in the ambient O_3 and NO_2 concentration (Figure 4).

<u>March 2022</u>

The collocation commenced in late March, 2022. The last week of March 2022 produced a data set that revealed a divergence of the NO_2 measured by the two different converter technologies. On average, the analyzer equipped with HMC (Molybdenum) reported approximately 48% more NO_2 than the analyzer equipped with the PhoNO converter.

On days when there were fresh vehicular emissions or sources with fresh nitric oxide, both converters matched closely with less than 2% difference in NO_2 observed (for instance Figure 4, March 25th & 29th, 2022). The titration of NO-O_3 yields only NO_2 and as such both converters are expeted to report identical NO_2 levels when organic nitrates are absent as observed during these particular periods.
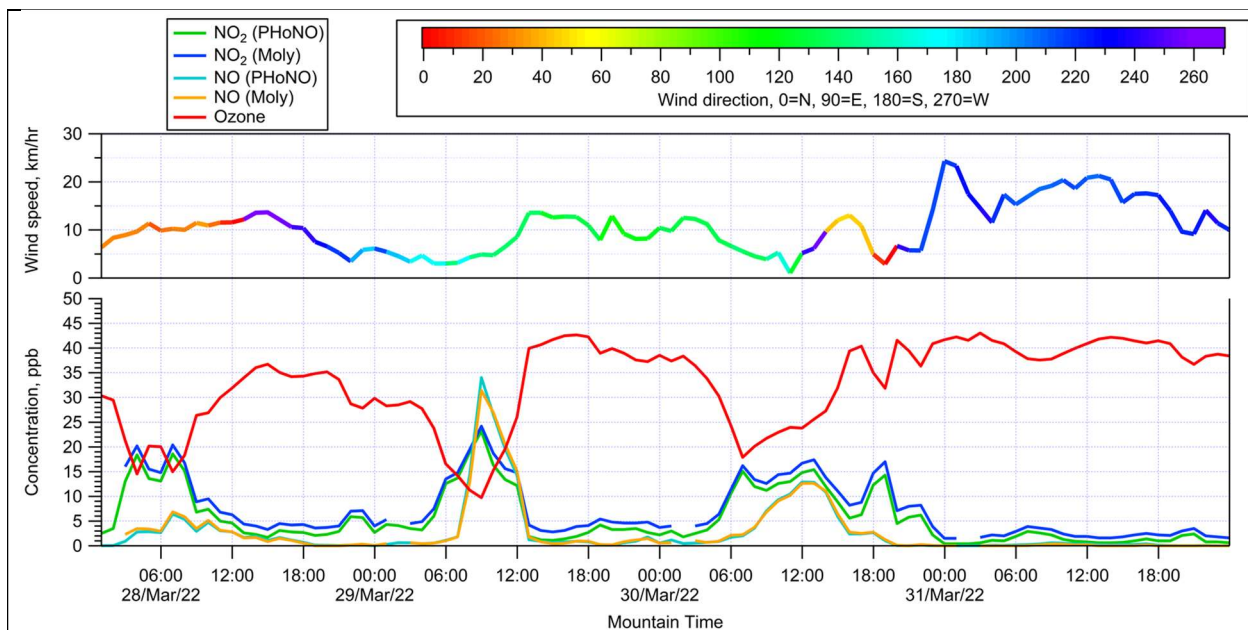
Figure 4: Daily trends of NO_X, O_3, Wind Speed and Wind Direction monitored at the site in March 2022. Sharp dips in the ozone concentration show periods of fresh emissions where both converters indicated similar levels of NO_2.

As an air mass ages, photochemistry causes the formation of organic nitrates. As can be seen in Figure 4 these organic nitrates create a positive NO_2 measurement bias on the analyzer with an HMC while the analyzer with the PhoNO is immune to this bias.

In Figure 5, during the same last week of March 2022, the wind rose plot showed that NO_2 concentrations above 25 ppb normally came from the south of the site and corresponded to the rapid titration of the ambient ozone levels to produce NO_2. The NO_2 indicated by both analyzers closely matched to within 1-2% taking into consideration instrument uncertainties.

As an additional measure to quality assure the NO_2 data, the ambient NO reported by the analyzer with the HMC and the NO reported by the analyzer with the PhoNO matched to within <1%. All the span factors were applied hence data quality assurance was guaranteed. All the data

validation was completed by Fort Air Partnership and submitted to the Government of Alberta

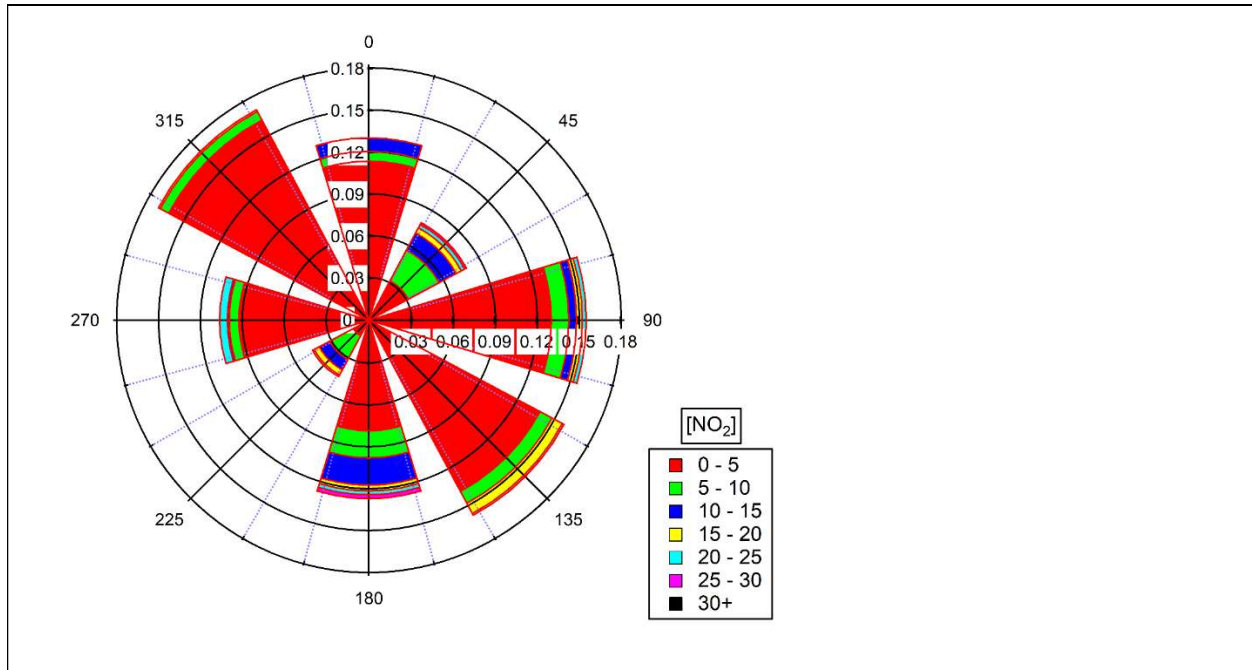Data warehouse and it is publicly available.

Figure 5: Wind rose plot of the distribution of measured NO_2 at the site. The highest NO_2 levels were measured when air impacted the site from the south during the month of March, 2022.

April 2022

During the month of April 2022, both analyzers reported NO_2 values below 10 ppb (most of the time). Even at such low levels of NO_2, there were clear differences in the NO_2 concentrations indicated by both converters: both break down NO_2 however the HMC goes beyond breaking down only NO_2 and also reduces any other oxides of nitrogen which can be thermally broken down to NO such as peroxyacyl nitrates (PANs) if any are present in the air mass.

The PhoNO selectively converted only the NO_2 present in the sampled air all the time as the time series of data indicates (Figure 6). The monthly average for reported NO_2 in April by the analyzer

with the HMC was about 22% higher than what was reported by the analyzer with the PhoNO.

Again, in April, on days where both instruments were sampling fresh plumes evidenced by the

titration of the ambient ozone concentration, both NO_2 values matched, for instance

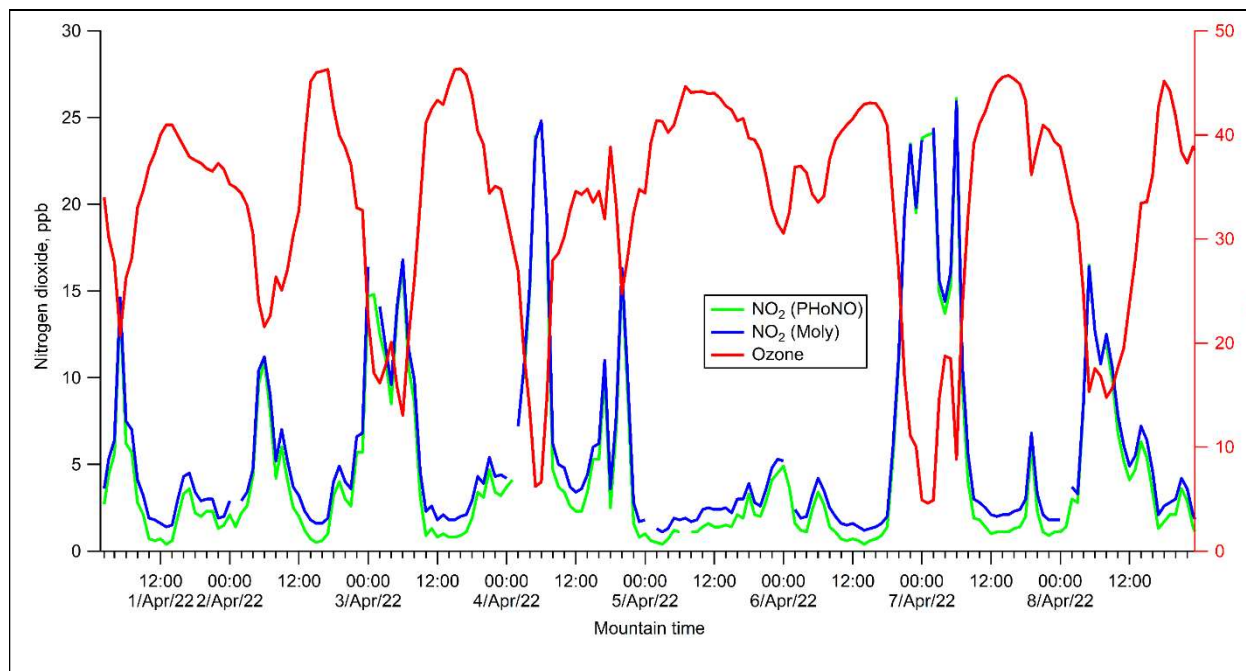observations on April 2, 4 & 7, 2022 at this site (Figure 6).

Figure 6: Daily trends of Nitrogen Dioxide by PhoNO and Heated Molybdenum converter in April 2022

Conclusion

This short paper clearly demonstrates that HMCs did convert both NO_2 and organic nitrates and

erroneously reported everything as just NO_2. The PhoNO, specifically designed to be a plug and

play replacement for HMCs inside commercial NO_X analyzers, has shown to be stable during long

term deployment. The calibration results indicate linear conversion over a wide dynamic range

(Figure 3). A commercial $NO-O_3$ chemiluminescence NO_x instrument equipped with a PhoNO will

report accurate NO_2 and contribute scientifically to a more accurate, efficient and cost-effective means of monitoring NO_2. This will help improve air quality models, emission inventories, and control measures. These policy driven analyses will lead to better outcomes since all the model input parameters are measured accurately.

Finally, the data set presented indicates that there was an excellent agreement in the NO_2 numbers by both analyzers during periods where fresh air mass plumes impacted the site. However, as soon as there are periods of very low levels of NO but elevated O_3 and NO_2, the reported NO_2 by both analyzers drifted apart. This divergence of NO_2 measurements remained so over hours (and sometimes days) until a fresh plume reached the site. A detailed modelling of the air's chemical composition in this region will be a subject of interest to further understand drivers of photochemistry in this area.

Subsequent analysis will be published from this ongoing field collaboration with Fort Air Partnership (FAP).

Acknowledgement

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