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Field intercomparison of continuous ambient FRM and FEM NO₂ instruments in the Athabasca Oil Sands Region, Alberta, Canada and the potential impact on ambient regulatory compliance

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ABSTRACT

The Canadian Federal Government promulgated new and lower NO₂ Ambient Air Quality Standards (CAAQS) that went into effect in 2020 with additional decreases scheduled for 2025. The new hourly and annual NO_2 CAAQS are 60 and 17 ppb, respectively, and the 2025 hourly and annual CAAQS are 42 and 12 ppb, respectively. The province of Alberta has also promulgated Ambient Air Quality Objectives (AAAQO) for NO₂ currently set to 159 and 24 ppb on an hourly and annual basis, respectively. The Wood Buffalo Environmental Association (WBEA) in northeastern Alberta, Canada monitors NO2 at 21 community and industrial sites throughout the Athabasca Oil Sands Region (AOSR), for regulatory compliance using Thermo-Environmental (TEI) Model 42i Federal Reference Method (FRM) designated NO-NO₂-NOx analyzers. The 42i measures NO directly via NO-O₃ chemiluminescence, and NOx following the reduction of oxidized nitrogen to NO by a heated internal molybdenum converter. The difference between the NOx and NO channels is reported as NO₂. This study presents the results of a three-year (2018–2021) WBEA comparison of four continuous NO₂ analyzers: TEI 42i FRM; the API Model T500U cavity attenuated phase shift (CAPS) Federal Equivalent Method (FEM); a total reactive odd nitrogen analyzer (TEI Model 42i-Y); and a TEI 42i equipped with an external photolytic converter. The study showed that NO₂ data from all analyzers were highly correlated and in general agreement, with r² values (vs. the CAPS) ranging from 0.990–0.997 and slopes ranging from 0.933–0.992. Mean NO₂ concentrations over the study period ranged from 7.2–7.5 ppb. Differences between the TEI 42i, TEI 42i-Y, and PhoNO, relative to the CAPS were all positive and highly significant (p < 0.0001), based upon nonparametric tests. The potential impact from the selection of different FRM/FEM measurement methods on current and future Canadian 2025 regulatory compliance in the region is evaluated.

Implications: The study objective was to compare/evaluate different regulatory NO₂ measurement techniques from a regional monitoring authority in a routine network operational context. Relatively small NO₂ differences resulted in significant differences with respect to regulatory compliance triggers, particularly hourly standards based on daily extreme value statistics (e.g., 99th percentiles). For example, mean hourly NO₂ \triangle differences ranged from 0.02–0.26 ppb over the study period but resulted in 2–3 ppb differences in the 3-year hourly CAAQS metrics. These differences could affect regulatory CAAQS and LARP compliance (management level) at monitoring sites observed during 2019 annual and 2020 hourly LARP trigger exceedances.

Introduction

Nitrogen dioxide (NO₂) plays an important role in atmospheric chemistry. NO₂ reacts with the hydroxyl (*OH) radical to form nitric acid (HNO₃), which, in turn, deposits rapidly via wet and dry deposition, and reacts with ammonia (NH₃) to form fine particulate (PM_{2.5}) ammonium nitrate (NH₄NO₃). During the day, NO₂ participates in the photochemical production of ozone (O₃). At night, NO₂ can react with O₃ to produce nitrate (*NO₃) radical, a key nocturnal oxidant and precursor of organic nitrates and nitric anhydride (N₂O₅). These and other reactions involving NO₂ have a major impact on the global distribution of particleand gas-phase nitrogen (Finlayson-Pitts and Pitts 1999; Seinfeld and Pandis 2016).

NO₂ has been shown to have deleterious health and environmental effects and is a regulated air pollutant in Canada, the U.S., and many other countries (Health Canada 2016; EPA 2016; WHO 2006). The Canadian Federal Government recently promulgated short-term (hourly) and long-term (annual) NO₂ standards (also known as Canadian Ambient Air Quality Standards or CAAQS) that went into effect in 2020 with future reductions scheduled for 2025. The hourly and annual NO₂

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CAAQS for 2020 are 60 parts per billion (ppb) and 17 ppb, respectively, and the hourly and annual CAAQS for 2025 are 42 ppb and 12 ppb, respectively. As part of the CAAQS, there are also management levels at lower concentrations designed to maintain good air quality in clean areas and to prevent deterioration of air quality in areas somewhat below the standards. The management levels are implemented at the regional air shed and local air zone level across Canada. The management levels provide guidance to air zones on the amount of monitoring, reporting, and management actions to implement depending on the concentration of prevailing air pollutants (CCME 2019). The Athabasca Oil Sands Region (AOSR) is located in the Lower Athabasca management air zone (Alberta Government 2017). The Province also promulgated Alberta Ambient Air Quality Objectives (AAAQO) for NO2 in 1975 under Alberta Environmental Protection the and Enhancement Act (EPEA) and its most recent review was completed in 2009. The current AAAQO for NO₂ is 159 ppb and 24 ppb on an hourly and annual basis, respectively (Alberta 2019). The Province introduced the Lower Athabasca Regional Plan (LARP) in September 2012 and was the first regional plan developed under the Alberta Land-Use Framework. The LARP air quality objective is to manage releases from multiple sources so they do not collectively result in unacceptable air quality. The LARP sets out Annual Average and Annual 99th Percentile trigger levels and limits for NO_2 (AEP 2012; WBEA 2019).

The Wood Buffalo Environmental Association (WBEA) monitors continuous NO₂ at 21 community and industrial sites for regulatory purposes (e.g., protection of human health) using U.S. federal reference method (FRM) analyzers. The NO₂ FRM chemiluminescent method was developed in the early 1970s and is based upon the reaction of nitric oxide (NO) with a stoichiometric excess of O₃ to form NO₂ in a ground state and photons of light whose measured intensity is proportional to the reactant concentration of NO (Breitenbach and Shelef 1973; Stevens and Hodgeson 1973). The implementation of the NO chemiluminescent method into commercially available instruments resulted in an indirect measurement technique that calculates NO₂ by the difference between total oxides of nitrogen (NOx) and NO. The dual channel instruments contain a heated catalytic converter that, in theory, selectively converts all ambient NO₂ to NO and allows all ambient NO to pass through unchanged thereby facilitating the quantification of NOx in the converted channel, and NO in the unconverted channel. Almost immediately it was recognized that other nitrogen species such as peroxyacetyl nitrate (PAN), nitroethane, and HNO₃ could also be converted to NO to produce NO₂ measurement artifacts, but the authors pointed out "the implications of these observations are not serious for most ambient air analysis where the concentrations of the interfering nitrogenous compounds are low relative to NO₂ levels" (Winer et al. 1974). Subsequently, other researchers have reported these interferences in polluted urban environments such as Los Angles, USA (Grosjean 1983), Mexico City, MX (Dunlea et al. 2007), and Tokyo, JP (Suzuki et al. 2011) leading to significant positive NO₂ measurement artifacts. The positive NO₂ artifacts were primarily attributed to HNO₃ (Dunlea et al. 2007) and PAN (Grosjean 1983; Suzuki et al. 2011) and were observed to be as high as 65% of the reported FRM NO₂ concentrations in Los Angles (Grosjean 1983) and up to 50% in Mexico City (Dunlea et al. 2007). Since HNO_3 and PAN are formed in photochemical reactions that consume NO₂, the highest measurement artifacts were observed during daytime smog episodes and were positively correlated with O_3 . Walker et al. (2023) have estimated that NO_2 represents ~62% of annual NOy at a rural site in southwestern North Carolina, USA. Significant NO₂ artifacts are thus a possibility in both urban and rural settings, with FRM instruments effectively reporting NOz (NOy - NOx) rather than NOx and consequently inflating reported NO₂ concentrations. No such evaluations of NO₂ FRM measurements have been evaluated in remote areas with large industrial combustion emission sources, such as the AOSR.

In early 2018, WBEA initiated a field intercomparison of NO2 measurements at its community monitoring site in Fort McMurray (Athabasca Valley, ATHV). Routine FRM NO-NO₂-NOx measurements at the site were augmented by addition of three new continuous analyzers for direct or indirect measurement of NO₂: a spectroscopic method, a photolytic conversion method, and a total reactive odd nitrogen (NOy) method. The NOy method was included in the study as it was expected to show the largest positive bias, and potentially lend insights into biases of the FRM and photolytic analyzers. The three years of intercomparison field data collection was completed in June 2021. The primary objectives of this study were to (i) evaluate potential differences in the reported NO₂ measurements over the 3-year period (June 1, 2018 to June 1, 2021) and to (ii) evaluate the regulatory significance of replacing the current FRM instrument with the direct, spectroscopic approach.

Methods

Athabasca Valley monitoring site

Continuous ambient air quality and meteorological data are collected from a network of sites in the AOSR operated by WBEA. WBEA currently operates 21 continuous ambient monitoring stations (AMS), each measuring various air quality parameters (Figure 1). The Athabasca Valley (ATHV) AMS (56°44'0.21"N; 111° 23'25.80"W) is a community monitoring site located in the middle of Fort McMurray (population 111,687 according to 2019 census) in the Athabasca River Valley just south of the Clearwater River confluence (Supporting Information Figure S1). The continuously measured air quality parameters at ATHV include sulfur dioxide (SO₂), total reduced sulfur (TRS), O₃, NO, NO₂, NO_x, NO_y, carbon monoxide (CO), fine particulate matter (PM_{2.5}), total hydrocarbons (THC), methane (CH_4) , and non-methane hydrocarbons (NMHC). The site also measures ambient air temperature, wind speed, wind direction, and relative humidity (RH). For the purposes of this comparison, NO₂ was measured at ATHV using four continuous analyzers that provided 5-min time resolution (Table 1) and relatively similar technical specifications (Table 2).

Routine measurements of NO2 at ATHV and throughout the WBEA AMS network were conducted with a Thermo-Environmental (TEI; Franklin, MA, USA) Model 42i chemiluminescence NO-NO₂-NOx analyzer. The TEI 42i is a two-channel analyzer with one channel that measures NO in ambient air directly via NO-O₃ chemiluminescence, and a second channel that utilizes an internal molybdenum converter heated to ~325°C to reduce oxidized forms of nitrogen (e.g., NO₂, organonitrates) to NO, which are then analyzed along with ambient NO via chemiluminescence. A prereactor is used to continuously subtract background chemiluminescence signal from the two channels. The second channel is operationally defined as NOx and the difference between the two channels is reported as NO₂. The instrument is configured to switch between the NO and NOx channels every 10 sec with the first 3 sec after each switch designated as a flush delay. Therefore, the FRM instrument is effectively monitoring NO 35% of the time and NOx 35% of the time, with the remaining 30% of the time a nonmeasuring latency period.

A Teledyne-Advanced Pollution Instrumentation (API; San Diego, CA, USA) Model T500U cavity attenuated phase shift (CAPS) analyzer was used to spectroscopically measure NO_2 directly in ambient air. The API T500U measures optical absorption at 450 nm in a mirrored optical cell based on the phase shift of

a modulated light source. The magnitude of the phase shift is directly proportional to the concentration of NO2 in the optical cell. An API Model T200 chemiluminescence NO-NOx analyzer equipped with a Global Analyzer Systems (Calgary, AB, CA) prototype Model PhoNO external photolytic converter was used to measure NO and NOx. In this configuration the API T200 internal molybdenum converter was bypassed and the combination Global PhoNO photolytic converter plumbed into the API T200 analytical bench will hereinafter be referred to as the PhoNO-CL. Like the TEI 42i, the PhoNO-CL is a two-channel instrument and the first channel measures NO directly via NO-O3 chemiluminescence. The second channel uses a high intensity light source at ~400 nm to quantitatively photolyze NO_2 to NO, which is then quantified along with ambient NO and reported as NOx. The difference between the two channels is reported as NO₂. On March 3, 2020 the T200 coupled to the PhoNO was replaced with a TEI 42i instrument when its stability performance deteriorated. Finally, a TEI Model 42i-Y chemiluminescent analyzer was used to measure NO and NOy. This analyzer uses the same measurement approach as the TEI 42i, except the molybdenum converter is mounted outside in a weather-proof enclosure and is heated to a slightly higher temperature (~340°C vs. ~325°C). By design, the TEI 42i-Y measures all forms of reactive odd nitrogen and was included in the study not to represent NO_2 , per se, but rather the upper limit artifact in NO₂ measurements.

The TEI 42i, API T500U, and PhoNO-CL analyzers sample ambient air approximately 4 m above ground level (1 m above the shelter roof) through a high flow $(\sim 0.6 \text{ m}^3 \text{ hr}^{-1})$ glass manifold designed to limit effective air sampling void volume/air residence time (~1 sec) and minimize absorptive loss of reactive gases (Figure 2; Supporting Information Figure S2). The sample passes through a Teflon membrane filter (5 µm pressure drop equivalent) to remove aerosols and then to each instrument (Supporting Information Figure S3), the inlet filter is replaced monthly. The TEI Model 42i-Y is an exception as it has an external inlet system that is mounted on the safety railing on the roof of the ATHV monitoring shelter (Figure 2) and a heated umbilical sampling line into the instrument. The TEI 42i-Y inlet system does not filter the air sample stream prior to being pulled through the heated molybdenum catalyst housed in the inlet box. As deployed, the TEI 42i-Y measures both gas and particle phase oxidized odd nitrogen.

All four analyzers were subjected to monthly manual multipoint calibrations. Multipoint calibrations were conducted according to guidance and performance



Figure 1. Map of all WBEA AMS sites and relative location of ATHV site.

Table 1. Summary of continuous NO₂ instruments.

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Instrument	Converter Type (Temp)	Target Analytes	Analytical Method
TEI 42i	Internal Molybdenum (324°C)	NO, NO ₂ , NOx	Chemiluminescence (NO ₂ by Difference)
TEI 42i-Y	External Molybdenum (339°C)	NO, NO ₂ , NOy	Chemiluminescence (NO ₂ by Difference)
PhoNO-T200*	Global PhoNO Photolytic	NO, NO ₂ , NOx	Chemiluminescence (NO ₂ by Difference)
PhoNO-42i*	Global PhoNO Photolytic	NO, NO ₂ , NOx	Chemiluminescence (NO ₂ by Difference)
API T500u	N/A	NO ₂	Cavity Attenuated Phase Shift (CAPS)

*PhoNO-CL was used in conjunction with an API T200 from June 1, 2018 to March 3, 2020, and with an TEI 42i from March 4, 2020 to June 30, 2021. The T200 was swapped with a 42i due to observed instability.

Tabl	e 2. Summar	y of continuous	NO_2	instrument s	pecifications.
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Instrument	LDL	Response Time	Precision	Linearity	Span Drift
TEI 42i	<0.05 ppb*	60/90 sec [‡]	±0.4 ppb	±1% full scale	±1% of reading/24 hr
TEI 42i-Y	<0.05 ppb*	60 sec [†]	±0.4 ppb	±1% full scale	±1% of reading/24 hr
API T200	<0.20 ppb	<80 sec to 95%	<0.5% above 50 ppb	1% full scale	<0.5% of reading/24 hr
API T500u	<0.04 ppb	<40 sec to 95%	<0.5% above 5 ppb	1% full scale	<0.5% of reading/24 hr

*Based on 120 sec averaging time. [‡]Based on 10/60 sec averaging times. [†]Based on 10 sec averaging time.



Figure 2. Photograph of the ATHV site shelter showing the TEI Model 42i-Y inlet system mounted on the roof safety railing.

requirements outlined in the Alberta Environment and Protected Areas (AEPA) Air Monitoring Directive (AMD; Alberta, 2016) including linearity, correction factors, percent changes, slope, and intercept. AMD verification check and calibration acceptance criteria for regulatory NO-NO₂-NOx instruments are summarized in Supporting Information Table S1. All four analyzers were also subjected to automated nightly zero/ span checks. The automated zero and span (precision and accuracy checks) are intended as a quick and convenient check for possible analyzer malfunction or zero/ span calibration drift. Zero checks are compared to the most recent reference response to determine if a change has occurred. Span checks of gas concentrations are generated between 40% and 80% of the analyzer's full range and is measured for a minimum of 10 min to ensure a stable response. When deviations of more than 10% from the expected span target corrective actions are triggered. Whenever a zero or span check indicates a possible analyzer response problem, a multipoint calibration is completed prior to any corrective action. During monthly multipoint calibrations and nightly zero/span checks the WBEA data acquisition system collects 1 min data averages and the data points are automatically flagged. WBEA data flags are used to mark data when calibrations or zero/span checks are found to be outside acceptable limits per AEPA monitoring directives.

Zero air was produced on-site using two API Model T701H zero air generators and calibration gas mixtures were produced with certified API Model T700U dilution calibration systems with photometers. United States National Institute of Standards and Technology (NIST) or Dutch Metrology Institute (VSL) traceable protocol NO (c. 50 ppm) in balance nitrogen compressed gas cylinders (NIST 2020; VSL 2020) were diluted with on-site generated zero air to achieve a calibration range of 0-800 ppb. Gas phase titration with O3 from the calibration system was used to generate NO₂ in the same concentration range. The TEI 42i, API T500U, and PhoNO-CL were calibrated and zero/span checked by introducing gas at the back of each analyzer, while the TEI 42i-Y was calibrated and zero/span checked through the external inlet box. From June 2018 to May 2019, the TEI 42i was manually calibrated using a dedicated NIST-traceable/EPA protocol NO cylinder and calibration system; thereafter, all four analyzers used the same NO cylinder and calibration system. All changes made to each instrument are recorded on the WBEA online documentation system and a diagnostic data system. Instrument events recorded by the site operators into the online systems include: calibration adjustments (zero or span points), changes in instrument settings, daily system checks, observed data abnormalities, and maintenance activities.

External performance audits were also conducted by AEPA in September 2018 and June 2019 of the regulatory TEI 42i instrument. The auditors challenged the instrument using a VSL Primary Reference Material (PRM) gas and an AEPA verified portable calibration system. Audit reports of the TEI 42i regulatory analyzer show average precision of $\pm 1\%$ between the audit system and the TEI 42i concentrations across the full dynamic range.

Concentration data from the continuous analyzers was collected on two Campbell Scientific data acquisition systems (DAS). Routine monitoring and calibration data were stored on the DAS as 5-min and 1-min averages, respectively, and telemetered to the WBEA data management center. In the data management center, ambient data and calibrations were reviewed and flagged, as appropriate, and zero corrections were applied to NO and NOx data, if needed. Final 1-hr NO₂ concentrations for the TEI 42i and PhoNO-CL were then reported as the difference between the zero-corrected NOx and NO channels (NOy and NO channels for the TEI 42i-Y).

Monitoring data

WBEA real-time reported raw ambient air quality concentrations are qualified as Level 1 data. WBEA monitoring data are qualified as Level 2 after final routine quality assurance review (including baseline corrections) is completed, and project specific Level 3 review was completed after independent external review. NO₂ concentrations from all instruments calculating this value based on the difference between the total NOx/ NOy and NO channels (PhoNO-CL, TEI 42i, TEI 41i-Y) were recalculated for this study based on the difference in these values for each of the WBEA Level 3 5-min integrated values. This alleviated small differences in concentration based on rounding errors from the higher time resolution data. Summary univariate statistics for all valid 5-min Level 3 ATHV measurements utilized in this study are presented in Supporting Information Table S2 (June 1, 2018–June 30, 2021). Hourly Level 3 concentrations were then calculated based on the valid Level 3 5-min data. An hourly observation was considered valid if ≥75% of the 5-min measurements were valid.

Statistical analysis

Data processing and all statistical analyses were performed using SAS version 9.4 (SAS Institute, Cary, NC, USA). Parametric statistics used in this analysis include linear least squared regression analysis. The assumptions of the parametric procedures were examined using residual plots, skewness and kurtosis coefficients, ShapiroWilk test, and the Brown-Forsythe test. Nonparametric statistics used in this analysis include the sign and Wilcoxon signed-rank tests. A level of significance of $\alpha = 0.05$ was used for all statistical procedures unless otherwise stated. The SAS UNIVARIATE, REG, and GLM procedures were used for testing data distributions for normality and hypothesis testing $Mu^0 = 0$ (population mean is not significantly different from 0), least square general linear model regressions, and MLR analysis, respectively. Figures were produced using SigmaPlot version 14.5 (Systat Software, Inc., San Jose, CA, USA).

Results and discussion

NO₂ data analysis

A summary of all the valid 1-hr integrated ATHV study data are presented in Supporting Information Table S3. The reported Level 3 data completeness of each NOx instrument was TEI 42i (99.6%), TEI 42i-Y (98.6%), API T500U (98.1%), and PhoNO-CL (97.3%). The API

T500U and the PhoNO-CL instruments had slightly lower levels of completeness relative to the TEI instruments primarily due to some initial DAS integration issues early in the study period and instrument instability/changeout, respectively. There were data points observed in the TEI 42i and TEI 42i-Y data where the NO₂ values were negative. Since the goal of this study was to evaluate the relative performance of these instruments, these data points were not invalidated. Small negative NO₂ concentrations occurred during low concentration periods, presumably due to zero drift, and during periods of rapidly changing concentrations due to instruments switching between analytical channels and the temporal offsets between NOx/NOy and NO measurements used to calculate reported NO₂ concentrations.

While the potential impact of NOz on reported FRM NO₂ concentrations is well known, the impact of channel switching (dual channel instrument) and the resulting temporal offset between NOx/NOy and NO measurements has received little attention. Time series 5-min data from a more or less typical monitoring day (March 23, 2021) are plotted in Figure 3a to illustrate this effect for the TEI 42i, TEI 42i-Y, and PhoNO-CL dual channel instruments compared to the single-channel T500U. The black arrows in Figure 3a indicate evening and midday periods when stable concentrations lead to reasonable agreement across instruments. However, when local emissions drive rapid concentration changes in the late morning and early afternoon, the dual channel instruments report relatively large positive and negative measurement artifacts observed in the data traces and summarized in the text box insets. For hourly NO₂ concentrations, (Figure 3b) the large obvious artifacts tend to average out, but smaller biases may remain as a function of channel switching during periods of rapidly changing ambient NO-NOx.

Calibration data review

As described previously, the four nitrogen instruments were subjected to monthly manual multipoint calibrations performed by an on-site technician. Calibration criteria, per the AMD (Alberta 2016), require the linear regression calibration curve slope to be between 0.9 and 1.1 (\pm 10% from unity) and the coefficient of determination must be \geq 0.995, in addition each zero and span point must be \pm 5% of its target value (Supporting Information Table S1). For the TEI 42i, TEI 42i-Y, and PhoNO-CL, multipoint converter efficiency tests were also performed to track conversion of NO₂ to NO. In general, monthly calibration zeros were most stable for the API T500u and the TEI 42i, and least stable for the TEI 42i-Y and the PhoNO-CL. Mean zeroes for the API T500 and PhoNO-CL were 0.0 ± 0.1 ppb and -0.1 ± 0.4 ppb, respectively. These results suggest that, on average, zero drift of the analyzers and subsequent data adjustment play a minor role in the overall data comparison.

Correction factors (CF) (i.e., the multiplier needed to bring an instrument span into 1:1 agreement with the calibration gas) were calculated at the start of each monthly calibration. Results for "as found" span CFs show that the response of the instruments were relatively stable over the course of the study. In general, CFs for all analyzers, except the PhoNO-CL, were within $\pm 3\%$ for virtually all calibrations. The study mean span CFs for the API T500u, TEI 42i, and TEI 42i-Y were 0.998 ± 0.019, 0.994 ± 0.026, and 0.998 ± 0.017, respectively. In contrast with the other analyzers, the PhoNO-CL with the API T200 analyzer span CF exhibited significant month to month downward drift for the first part of the study. The overall mean span CF for the PhoNO-CL was 1.066 ± 0.034 from June 2018 to February 2020, CFs stabilized significantly after the PhoNO-CL was configured with the TEI 42i analyzer (March 2020 to June 2021) and averaged 1.006 ± 0.013 .

Converter efficiency checks show that conversion of NO₂ to NO was almost always 98–100% for the TEI 42i and TEI 42i-Y analyzers (98.9 \pm 0.5% and 99.3 \pm 1.1%, respectively). Conversion efficiency for the PhoNO-CL with the API T200 analyzer was, with one exception, always >100% (102.0 \pm 1.0%). The disparity in conversion efficiencies is relatively constant from June 2018 through June 2019, but somewhat less clear cut thereafter. Given that conversion efficiency should be no more than 100%, and that the analyzer was adjusted beforehand, this suggests that the PhoNO-CL with the T200 analyzer adjustments may have over-compensated in some fashion for analyzer drift since the previous calibration. In the PhoNO-CL with the TEI 42i analyzer configuration, the conversion efficiency was more in line with the TEI 42i and the TEI 42iY (99.3 \pm 1.6%).

In general, calibration results show that the analyzers were in reasonably good control for the study period and easily exceeded AMD requirements for regulatory monitoring purposes. Month to month and analyzer to analyzer variability in calibration responses suggest that span and zero drift exert subtle effects on analyzer performance.

Instrument comparisons

The API T500U CAPS was considered the reference instrument for comparison to the other difference method analyzers as it was the only instrument that spectroscopically measures "true NO_2 " 100% of the



Figure 3. Time series of T500U true NO₂ versus (a) 5-min and (b) 1-hr 42i, 42i-Y, and PhoNO-CL NO₂.

time, whereas the difference analyzers must share analytical time between the NO and NOx/NOy channels. A dataset containing only hourly observations where all four nitrogen instruments reported valid concentrations was created (n = 21,045) for additional analysis so results would be broadly comparable between instruments. The univariate statistics for these data distributions are summarized in Table 3. The mean ± standard deviation for each instrument were API T500U ($6.92 \pm$ 6.60 ppb) < TEI 42i-Y (6.94 ± 6.61 ppb) < TEI 42i (7.18 ± 6.81 ppb) = PhoNO-CL (7.18 ± 7.01 ppb). The difference between the API T500U reference analyzer and the chemiluminescent NOx/NOy - NO difference NO₂ analyzers (Δ) were calculated for each 1-hr observation in the "complete data" population with Δ_{42i-Y} (0.02 ± 0.62) < Δ_{42i} (0.26 ± 0.46) = $\Delta_{\text{PhoNO-CL}}$ (0.26 ± 0.68).

Analysis of NO₂ data distributions found them all to be significantly different from normal (Shapiro–Wilk), therefore paired nonparametric tests were used to test differences in population means (Mu₀). The difference between the API T500U reference analyzer and the other analyzers (Δ) were calculated (Supporting Information Tables S2 and S3; Table 3) for each 5-min and 1-hr observation, and the population of $\Delta_{PhoNO-CL}$, Δ_{42i} , and Δ_{42i-Y} were tested against the null hypotheses that the difference in population means was zero (Mu₀ = 0; Table 4). Results of the two-sided hypothesis tests indicate that all the difference method instruments report NO₂ concentrations that are significantly higher than the API T500U (p < 0.0001) for both the 5-min (Supporting Information Tables S2) and 1-hr (Table 3) data.

Linear regression analysis was then conducted to evaluate data relationships between the API T500U and the NO₂ difference methods (Figure 4a–c). The coefficient of determination (r^2) was >0.99 for all NO₂ difference method instruments relative to the API T500U. Regression slopes indicate the TEI 42i was on average 3.3% higher (Figure 4a), the TEI 42i-Y was 0.7% higher (Figure 4b), and the PhoNO-CL was 6.1% higher (Figure 4c) than the API T500U, and regression intercepts were all ±0.2 ppb. Taken together with calibration statistics, these results show that the suite of instruments easily met the ±10% accuracy requirement for regulatory NO₂ measurements.

We also analyzed NO data to investigate if differences in measured NO₂ concentrations would also be observed in the NO measurements. If so, this could suggest small calibration (zero and/or span) or channel switching offsets as the reason for the differences in addition to positive measurement artifacts from NOz. Results of the regression analysis show the NO measurements are highly correlated ($r^2 \sim 0.99$), but two-sided hypothesis tests (Table 5) indicate that all the instruments reported NO concentrations that are significantly different from one another (p < 0.0001). On average the TEI 42i was 3.4% higher than the TEI 42i-Y (Figure 5a), the TEI 42i was 3.0% higher than the PhoNO-CL

Table 3. ATHV site 1-hr complete data matrix NOx (ppb) data statistical summary.

Pollutant	п	$Mean \pm Std \; Dev$	Min	25th	Median	75th	99th	Max
NO - 42i	21,045	2.883 ± 5.893	-0.091	0.297	0.890	2.698	30.329	109.046
NO ₂ - 42i*	21,045	7.183 ± 6.811	0.033	2.211	4.931	9.936	30.516	51.775
NOx - 42i	21,045	10.066 ± 11.516	0.111	2.806	6.189	12.883	56.639	152.524
$NO_2 - CAPS$	21,045	6.919 ± 6.596	-0.104	2.073	4.778	9.646	29.286	51.293
NO-PhoNO	21,045	2.745 ± 5.707	-0.695	0.316	0.824	2.478	30.153	108.063
NO ₂ -PhoNO*	21,045	7.181 ± 7.005	-0.128	2.070	4.821	9.998	31.091	54.262
NOx-PhoNO	21,045	9.926 ± 11.565	-0.010	2.623	5.976	12.834	56.643	153.845
NO-42i-Y	21,045	2.724 ± 5.675	-0.093	0.233	0.790	2.570	28.863	103.006
NO ₂ -42i-Y*	21,045	6.939 ± 6.614	-0.016	2.164	4.769	9.570	29.976	49.575
NOy-42i-Y	21,045	9.663 ± 11.123	-0.009	2.673	5.915	12.431	54.876	144.224
APhoNO #	21,045	0.262 ± 0.677	-3.636	-0.104	0.124	0.488	2.745	5.873
Δ.4.2i	21,045	0.263 ± 0.464	-3.098	0.029	0.218	0.460	1.738	5.581
Δ _{42i-Y} [‡]	21,045	0.020 ± 0.615	-6.386	-0.221	0.028	0.262	1.815	10.265

*Recalculated based on reported NOx/NOy – reported NO concentrations.

[‡]Δ values calculated as comparison instrument – T500U true NO₂ reference instrument.

	Table 4. Non-parametric hy	pothesis test summary	comparing	CAPS true NO	versus NO	2 difference method instrument
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		Δ_{CAPS}	Sign Test		Wilcoxon Signe	d-rank Test
Instrument	Resolution	Mean (ppb)	Statistic [M]	p Value	Statistic [S]	p Value
TEI 42i*	5-min	0.260	73940	<0.0001	1.256 × 10 ¹⁰	< 0.0001
	1-hr	0.263	5901	< 0.0001	7.405×10^{7}	< 0.0001
TEI 42i-Y*	5-min	0.013	14565	< 0.0001	1.827×10^{9}	< 0.0001
	1-hr	0.020	715	< 0.0001	7.519×10^{6}	< 0.0001
PhoNO-CL*	5-min	0.261	30073	< 0.0001	6.006×10^{9}	< 0.0001
	1-hr	0.262	2904	< 0.0001	4.592×10^{7}	< 0.0001

*Recalculated based on reported NOx/NOy - reported NO concentrations.



Figure 4. Linear regression analysis of hourly T500U true NO₂ versus (a) 42i, (b) 42i-Y, and (c) PhoNO-CL.

Table 5. Nonparametric hypothesis test summary comparing NO instruments.

	ΔΜυο	Sign T	est	Wilcoxon Signe	d-rank Test
Instruments	Mean (ppb)	Statistic [M]	p Value	Statistic [S]	p Value
TEI 42i – TEI 42i-Y	0.160	6159	<0.0001	7.399×10^{7}	<0.0001
TEI 42i – PhoNO-CL	0.138	3240	< 0.0001	4.738×10^{7}	< 0.0001
TEI 42i-Y – PhoNO-CL	-0.021	-921	<0.0001	-6.191×10^{6}	< 0.0001



Figure 5. Regression analysis of NO (a) 42i versus 42i-Y, (b) 42i versus PhoNO-CL, and (c) PhoNO-CL versus 42i-Y.



Figure 6. Combined regression analysis of NO & NO₂ (a) 42i versus 42i-Y and (b) 42i versus PhoNO-CL.

(Figure 5b), and the PhoNO-CL was 0.0% different than the TEI 42i-Y (Figure 5c). When the NO₂ and NO comparisons are combined we observe that the average difference in NO₂ between the TEI 42i and TEI 42i-Y can be almost completely explained by the difference in NO as presented in Figure 6a suggesting a generalized calibration offset. In contrast, the difference between the TEI 42i and the PhoNO-CL NO₂ and NO trends in opposite directions (Figure 6b) suggest a converter efficiency offset. This is consistent with converter test results, which suggested the PhoNO-CL NO₂ should be roughly 3% higher than the TEI41i and TEI 42iY.

Time series analysis of instrument NO₂

Monthly mean and $\pm 1 \sigma$ error bars of Δ_{42i-Y} , Δ_{42i} and $\Delta_{PhoNO-CL}$ are plotted in Figure 7. Mean Δ values show a number of features that are common across analyzers and some features that are unique to certain analyzers. Deltas for all three analyzers were between -0.25 and 1.0 ppb for a large majority of months. Interestingly, there was a clear seasonal pattern in which Δ values were smaller in the summer and near 0, but higher in the winter, averaging ~0.5 ppb. If positive artifacts from NOz were a dominant contributor to Δ values, then we might expect positive Δ values in the summer that are positively correlated to O₃ (Grosjean 1983; Suzuki et al. 2011). Instead, we see higher Δ values in the winter and

significant (p < 0.0001) negative Spearman's rank correlations with O₃ and temperature for the TEI 42i and PhoNO-CL instruments. Given that all three difference analyzers vary systematically from summer to winter, we cannot rule out seasonality in the T500u response as the driver. Conversely, mean NO₂ concentrations were 3-4 times higher in winter months than summer months. This raises the possibility that the pattern is caused by small positives biases from channel switching.

Regulatory implications of instrument selection

The CAAQS are part of a collaborative national Air Quality Management System (AQMS), to protect human health and the environment. In October, 2012, the Canadian Council of Ministers of the Environment (CCME) promulgated new CAAQS for PM_{2.5} and O₃. Subsequently, new staggered CAAQS for SO₂ and NO₂ were developed with new standards becoming effective in 2020 and lower standards following on in 2025. The current and future 2025 1-hr and annual CAAQS for NO_2 are summarized in Table 6. Regulatory compliance with (i) the 1-hr standards values are calculated as the 3-yr average of the annual 98th percentile of the daily maximum 1-hr average ambient concentrations, and (ii) the annual standard is calculated as the average over a single calendar year of all 1-hr average concentrations (CCME 2020).



Figure 7. Time series analysis of monthly Δ_{CAPS} values (ppb) over the study period.

Management Level	NO ₂ 1-H	our (ppb)	NO ₂ Anr	iual (ppb)
	2020	2025	2020	2025
Red (CAAQS)	> 60 > 42		> 17	> 12
Orange	32 - 60 32 - 42		7.1 - 17.0	7.1 – 12.0
Yellow	21 -	- 31	2.1	-7.0
Green	\leq	20	≤	2.0

Table 6. Summary of present and future 1-hr Canadian ambient air quality standard NO₂ management levels.

The Lower Athabasca Regional Plan (LARP) for 2012-2022 was approved on August 22, 2012 and became effective September 1, 2012. The LARP is a comprehensive, multipollutant, legally binding framework to increase conserved land, and protect air and surface water quality. The LARP considers cumulative effects of all activities on air, water, and biodiversity. The implementation of the LARP establishes ambient NO_2 trigger levels based on (i) an annual mean ambient concentration, and (ii) the 99th percentile concentration of annual hourly average concentrations that are summarized in Table 7. If monitoring determines that an NO₂ LARP trigger (Levels 2-4) or a limit has been exceeded, then a coordinated regional management response is initiated. Management actions may include preparation of pollutant specific management plans, additional monitoring/modeling, development and application of new performance standards, and the use of best management practices (AEP 2012).

As part of the Canadian Air Quality Management System (AQMS), Alberta was divided into six air zones, with the Athabasca Oil Sands Region (AOSR) falling into the Lower Athabasca Air Zone. The ambient monitoring data for each air zone is assessed annually to evaluate compliance with management levels. The management levels are represented by the colors green, yellow, orange, and red; and each has an associated air quality objective and concentration limit:

- Green: To maintain good air quality through proactive air management measures to keep clean areas clean.
- Yellow: To improve air quality using early and ongoing actions for continuous improvement.
- Orange: To improve air quality through active air management and prevent exceedance of the CAAQS.
- Red (CAAQS): To reduce pollutant levels below the CAAQS through advanced air management actions.

Study period calculated hourly and annual CAAQS/ LARP compliance metrics are presented in Table 8. It should be noted that only two full calendar years (2019 and 2020) were included in the study period data so the 1-hr CAAQS standard values were based on a 3-yr overall period (July 1, 2018 to June 30, 2021) from the "complete" data set rather than a three calendar-year period. No exceedances of the 1-hr (60 ppb) or annual (17 ppb) CAAQS for NO₂ was reported by the TEI 42i regulatory monitoring instrument or any of the candidate instruments. The API T500U "true NO₂" instrument reported the lowest CAAQS hourly (37 ppb), LARP hourly (28.3 ppb), and CAAQS/LARP annual

Table 7. Summary of Lower Athabasca Regional Plan (LARP) air quality management framework ambient NO₂ concentration limits and trigger levels.

Description	NO ₂ Annual Mean Trigger (ppb)	NO ₂ Annual Hourly 99th Percentile Trigger (ppb)
Level 2	8	30
Level 3	16	62
Level 4	—	92
Limit [†]	24	—

[†]Annual air quality limit is based upon AAAQO.

Table 8. Athabasca \	Valley site	regulatory	review	of NO ₂ k	oy instrument	(Com	plete dat	aset)

Standard	Program	API T500u	TEI 42i	TEI 42i-Y	PhoNO-CL
NO ₂ Hourly (Study Period) [†]	CAAQS	37	39	39	40
NO_2 Annual (2019) [‡]	CAAQS/LARP	7.4	7.7	7.5	7.7
NO_2 Annual (2020) [‡]	CAAQS/LARP	6.5	6.7	6.5	6.6
NO ₂ Hourly 99th Percentile (2019) [§]	LARP	31.6	32.9	32.6	33.3
NO ₂ Hourly 99th Percentile (2020) [§]	LARP	28.3	29.4	28.7	30.2

[†]Mean of three-yearly 98th percentile daily 1-hr maximum concentrations (July 1, 2018 to June 30, 2019; July 1, 2019 to June 30, 2020; July 1, 2020 to June 30, 2021).

^{*}Mean of all valid 1-hr concentrations.

[§]Based on distribution of all valid 1-hr concentrations.

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(6.5 ppb) regulatory compliance values. All instruments reported hourly and annual values that met the current 2020 and future 2025 CAAQS limit values and would put the site into the Orange Management Plan designation. For the 2019 calendar year, only the API T500U fell below the LARP Level 2 NO₂ annual trigger level (8 ppb) after rounding up to whole numbers (e.g., to 1 ppb) as mandated (Alberta Government 2012). The TEI 42i, TEI 42i-Y, and PhoNO-CL exceeded the 2019 LARP Level 2 NO₂ annual trigger concentration; while all four instruments exceeded the LARP Level 2 annual (30 ppb) standard trigger level. For CY2020 all four instruments met the annual LARP Level 2 annual trigger and only the PhoNO-CL instrument exceeded the LARP Level 2 hourly trigger level. Across all regulatory metrics, the four instruments typically ranked API T500u < TEI 42iY < TEI 42i < API PhoNO-CL.

Conclusion and implications

As ambient NO₂ regulatory limits are reduced and new measurement methods become available, there is a need to evaluate instruments under long-term, routine network conditions. Results of a 3-yr field intercomparison of four NO₂ analyzers showed that all analyzers exhibited high reliability in the field, with data completeness, after allowance for routine calibrations, of >97%. This provided a very robust data set for statistical comparisons of the different candidate analyzers. The major conclusions from the study are enumerated below:

- (1) NO₂ data from all four candidate analyzers were highly correlated and in general agreement, with r^2 values (vs. reference analyzer) ranging from 0.991-0.996 and slopes ranging from 0.939-0.993.
- (2) Mean hourly NO_2 concentrations over the study ranged from 6.9 ppb (API T500U; TEI 42i-Y) to 7.2 ppb (TEI 42i; PhoNO-CL). Differences between the TEI 42i, TEI 42i-Y, and PhoNO-CL and the API T500U reference analyzer were all positive and highly significant (p < 0.0001), both for nonparametric sign tests and Wilcoxon signed-rank tests. Interestingly, the TEI 42i-Y NO-NOy analyzer exhibited the smallest difference with respect to the reference analyzer. Given that this measurement was expected to show the maximum measurement artifact, this result suggests that other factors, including separate location, unique inlet and calibration process, relative to the other instruments played a confounding role in the comparison.

- (3) Biases resulting from the difference method instruments channel switching and the temporal offset of NOx/NOy and NO concentrations appear to be more important than zero/span variability and NOz artifacts in explaining differences between instruments.
- (4) Though relatively small, differences between instruments resulted in significant differences with respect to regulatory compliance triggers, particularly those based on extreme value statistics (e.g., CAAQS 98th and LARP 99th percentiles). For example, mean hourly NO₂ Δ differences from 0.02–0.26 ppb (Table 3) result in 2–3 ppb differences in the hourly CAAQS metrics (Table 8). These differences could affect overall regulatory CAAQS and LARP compliance (management level) at some monitoring sites as observed in the 2019 annual and 2020 hourly LARP trigger exceedances.

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Author contributions

Matthew S. Landis served as principal investigator and prepared the manuscript with contributions from Eric S. Edgerton.

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Data availability statement

Data file uploaded to Researchgate (https://doi.org/10.13140/RG.2.2.18308.71044).

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