



Assessing the bias of molybdenum catalytic conversion in the measurement of NO₂ in rural air quality networks

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HIGHLIGHTS

- There is a strong artefact in molybdenum catalyst chemiluminescent instruments.
- Unselective catalysis of airborne NO_y compounds causes an overestimate of NO₂.
- The majority of global NO₂ monitoring networks will have a measurement artefact.
- Molecule specific NO₂ analysers do not suffer from this artefact.

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ABSTRACT

The measurement method of NO₂ with continuous analysers is specified for EU Ambient Air Quality Directive compliance reporting, which provides a consistent methodology and concurrent NO measurements (85/203/EEC-NO₂). While the established method of measurement of NO₂, following conversion of NO₂ to NO using a molybdenum-conversion process, has known interference uncertainties (due to conversion of other oxidised nitrogen (NO_y) chemicals, the consistency and traceability of compliance measurement is important. This study compared three continuous NO₂ analyser instruments: a Thermo-NO_x molybdenum convertor chemiluminescence analyser (Model 42C, ThermoFisher Scientific Inc., MA, USA), a photolytic chemiluminescence analyser (T200UP, Teledyne Technologies Inc., San Diego, USA) and a Cavity Attenuated Phase Shift (CAPS) analyser (T500U, Teledyne Technologies Inc., CA, USA). The instruments were run for over a year at the Auchencorth Moss long-term peatland monitoring site (Southeast Scotland) which is a low NO_x atmosphere away from sources. NO_y and NH_x chemicals were also measured concurrently. This study concludes that there is a strong artefact in molybdenum catalyst chemiluminescent instruments as a result of unselective catalysis of airborne NO_y compounds that causes an overestimate of NO₂ measured in the atmosphere. The observed artefact in concentration measurements is likely to be observed at the entire UK scale as almost the entirety of the rural air network relies on molybdenum catalyst instruments. We therefore recommend that molybdenum catalyst instruments should be phased out and replaced in air quality monitoring networks with molecule specific (spectroscopy) instrumentation (equivalent in cost, such as those described in this study) that do not suffer from the same measurement artefacts.

1. Introduction

Nitrogen dioxide (NO₂) is a short-lived reactive gas that is produced primarily by anthropogenic activities such as fossil fuel combustion and industrial processes via reaction of NO with ozone (O₃). Due to the

detrimental impact that long-term elevated concentrations of NO₂ has on human health, such as respiratory and cardiovascular mortality (Faustini et al., 2014; Héroux et al., 2015), attempts have been made to monitor, mitigate and reduce NO₂ emissions in recent years. NO₂ emissions from road traffic (fuel combustion and catalytic conversion)

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accounted for an estimated 45% of UK NO₂ emitted in 2018, with a further contribution of approximately 14% produced by other forms of traffic, such as trains, shipping and aviation (Defra, 2020). UK NO₂ emissions have fallen sharply over the past 30 years due to targeted emission reduction efforts (3068 kt in 1990 to 702 kt in 2020); however, due to continuing high levels of traffic activity, there are still many locations across the UK that surpass the NO₂ concentration limits deemed safe for long-term human exposure (Defra, 2020).

As NO₂ is short-lived and readily reactive in the atmosphere, it has a high spatial variability dependent on proximity to sources such as traffic density. Concentrations vary by several orders of magnitude over short distances, and over relatively short periods of time (Hagenbjörk et al., 2017; Kendrick et al., 2015). The measurement method of NO₂ with continuous analysers is specified for EU Ambient Air Quality Directive compliance reporting (continued in the UK under the Air Quality Standards (Amendment) Regulations 2016) which provides a consistent methodology and concurrent NO measurements (85/203/EEC-NO2). The established method of NO₂ measurement specified in the Directive uses conversion of NO₂ to NO using a molybdenum-conversion process. The consistency and traceability of compliance measurement is important to assess UK ambient concentrations at representative locations (roadside, urban and rural background for example) and underpin research (e.g. Krecl et al., 2021; Malley et al., 2018). The UK has over 160 long-term automatic monitoring sites in the automatic urban and rural network (AURN), as well as thousands of Palmes-type passive diffusion tubes (PDTs) deployed both in the national and local authority networks (Defra, 2020). PDTs are typically used with indicative uncertainty ($\pm 25\%$) and provide cost effective spatial monitoring (Cape, 2009; Palmes et al., 1976).

Chemiluminescence (CL) analyser methodology is long standing and has been used for decades to measure NO₂ (Kley and McFarland, 1980). These analysers function on the principle of the measurement of light ($h\nu$) emitted from the reaction of NO with O₃ within a reaction chamber (Equation (1)), typically using a photomultiplier tube or solid-state device. By separately measuring the NO present in an atmospheric sample (NO_{atm} , Equation (1)), and also using a heated catalyst (typically made of molybdenum (Mo), situated within the instrument) to convert NO₂ into NO and measuring the total NO in the air separately (NO_{tot}), the concentration of NO₂ ($h\nu NO_2$) can be established via Equations (1)–(3), where NO_{tot} is the sum of NO_{atm} and NO_{cat} , and $h\nu NO_2$ is the difference between $h\nu_{tot}$ and $h\nu_{atm}$.



Although better performing in terms of accuracy and precision when compared to PDTs (e.g. Boleij et al., 1986; Jiménez et al., 2011; Var-doulakis et al., 2009), NO₂ measurement using chemiluminescence method also has biases and some unquantified uncertainties, due to interference of other atmospheric chemical compounds (Alam et al., 2020; Steinbacher et al., 2007; Villena et al., 2012). Reactions within the heated Mo convertor are not chemically specific to the NO₂ molecule and hence there are artefacts in reported NO₂. For example, the catalytic reaction of NO₂ species (compounds such as nitric acid (HNO₃), nitrous acid (HONO), organic nitrates and particulate nitrates), or the reaction of ammonia (NH₃) with oxygen (O₂), may produce some additional NO inside the converter.

Due to the health and ecosystem impacts, as well as the legal ramifications of aiming to achieve good air quality standards, NO₂ measurements should be as accurate as possible. Over or underestimation of NO₂ at monitoring sites may result in unfair penalties, or unrecognised threats to health. With the number of NO₂ analysers on the market increasing rapidly over the last decade, it is possible to both improve the

understanding of NO₂ and NO_y impacts, as well as future evidence.

The commercial availability of new instrument types is now at the stage where the cost is similar to the Mo-CL instruments (the analysers used in this study are all of equivalent cost). One example is Blue Light (photolytic) convertor (BL) instruments, in which the conversion from NO₂ to NO is done photochemically using a wavelength within the blue region of visible light (Fuchs et al., 2009; Pollack et al., 2010; Ryerson et al., 2000). Although still a chemiluminescence instrument, this alternative conversion method is more molecule selective than the heated molybdenum method. However, photochemical converters can still suffer from artefacts caused by conversion of non-NO₂ molecules to NO in the conversion process (Jordan et al., 2020; Reed et al., 2016). Other instruments measure NO₂ directly including quantum cascade lasers (QCLs) (Yu et al., 2017) and Cavity Attenuated Phase Shift (CAPS) instruments (Kebabian et al., 2005, 2008). Both the QCL and the CAPS use absorption spectroscopy, where NO₂ concentrations are calculated using Beer-Lamberts law. QCLs and CAPS do not have a conversion step in the process, which in theory should make them more accurate than CL analysers; however, until recently most instruments lacked the ability to measure NO as well, which is a requirement for compliance monitoring but not necessary for some other applications.

This study compared three continuous NO₂ analyser instruments: a Thermo-NO_x molybdenum convertor chemiluminescence analyser (Model 42C, ThermoFisher Scientific Inc., MA, USA), a photolytic chemiluminescence analyser (T200UP, Teledyne Technologies Inc., San Diego, USA) and a Cavity Attenuated Phase Shift (CAPS) analyser (T500U, Teledyne Technologies Inc., CA, USA). The instruments were run for over a year at the Auchencorth Moss long-term peatland monitoring site (southeast Scotland) which is a low NO_x atmosphere away from sources. A Monitor for Aerosols and Gases in ambient Air (MARGA, Metrohm, Schiedam, NL) was also situated at the site, which was able to provide atmospheric concentrations of a variety of oxidised nitrogen species ($NO_z = NO_3^- + HNO_3 + HONO$), reduced nitrogen species ($NH_y = NH_4^+ + NH_3$) and other chemical species (Na⁺, Cl⁻, K⁺, Ca²⁺, Mg²⁺, HCl and SO₂) on an hourly basis. The study aims to identify and quantify uncertainty and biases across the three instrument types over multiple seasons with the NO_y and NH_x influence assessed.

2. Methods

2.1. Field site

Measurements taken in this study were carried out between January 2019 and June 2020 at the long-term monitoring site, Auchencorth Moss, in South-East Scotland (55.792160, -3.242900) which lies ~ 18 km south of Edinburgh. The site is an ombrotrophic mire (rainfed bog) at 270 m elevated above sea level. It is grazed by sheep with approximately <0.6 sheep ha⁻¹. Auchencorth Moss belongs to a number of national and international networks and is a supersite (level II/III) within the European Monitoring and Evaluation Programme (EMEP, Tørresth et al., 2012). Due to an extensive number of networks operating at the site, it is approximated that >300 parameters of the physical state and chemical composition of the atmosphere are reported on a routine basis. The site is classified under the European Environment Agency classification scheme as a rural background site and has been described by Malley et al. (2014) to be a remote site within the context of monthly O₃ concentrations across 100 European monitoring sites.

2.2. Measurement data

All instruments used in the study were in an air-conditioned cabin (Table S1). The NO_x and O₃ instrumentation sample air at an inlet height of 3.6 m via a common inlet made of polyvinyl chloride (PVC) (Fig. 1), which uses a fan at its base to draw down air. A sub-sample of air from the common inlet is drawn down a 4 m ¼" perfluoroalkoxy alkane (PFA) tubing connected to a polytetrafluorethylene (PTFE) 6-port manifold

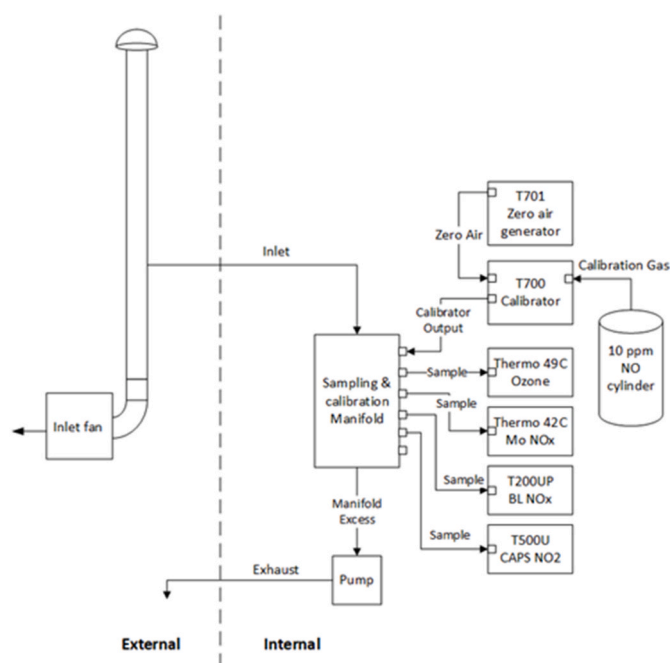


Fig. 1. Schematic of NO_x instrument and calibrator set-up during the intercomparison.

operating with a pump at $\sim 5 \text{ l min}^{-1}$. The 3 instruments then sample from the 6-port manifold, again using $\frac{1}{4}$ " PFA tubing. Each instrument specific set-up is detailed in Table S1. Also connected to the 6-port manifold is the calibration system consisting of a T700 Teledyne gas diluter, T701 Teledyne zero air generator and a 10 ppm NO gas standard (Refer to Fig. 1).

The Molybdenum convertor with chemiluminescence (MoNO_x) analyser used was a Model 42c, ThermoFisher Scientific Inc. The sample is drawn through a 47 mm ID 5 μm PTFE filter prior to the air entering the instrument to remove particulate matter, replaced monthly. The molybdenum convertor is heated to 325 $^\circ\text{C}$ to convert the NO_2 into NO. The sample is then reacted with O_3 in the reaction chamber (O_3 generated by instrument using zero air generator input as described above). The chemiluminescence of this reaction is then measured with a photomultiplier tube (PMT). The analyser reports the NO and NO_x concentrations and calculates the NO_2 concentration as the difference between these.

The Blue Light with chemiluminescence (BLNO_x) analyser used was a T200UP, Teledyne Technologies Inc., San Diego, USA. As with the MoNO_x instrument, a 47 mm ID 5 μm PTFE filter was placed in front of the inlet to limit particulate matter entering the system and is replaced monthly. It operates by the same principle as MoNO_x instrument with the exception that it converts the NO_2 to NO using an array of molecule specific blue light emitting diodes (LEDs) at 350–420 nm.

The Cavity Attenuated Shift Phase Shift (CAPS) spectrometer instrument used was a T500U, Teledyne Technologies, Inc. San Diego, USA. This measures NO_2 directly using optical absorption. It does so by using an ultraviolet (UV) LED that is centred on 450 nm into a long path length measurement cell that has high reflectivity mirrors and a vacuum photodiode detector. The concentration of the sample is determined by the phase shift comparing the change in light intensity when a sample is present and when a sample is not, due to the change of the path length as the presence of NO_2 reduces the distance that the light travels.

The ozone analyser used was a Model 49C, ThermoFisher Scientific Inc., USA. It uses the absorption of UV light at 254 nm by the ozone molecules to calculate the O_3 concentration.

2.3. Calibration of the NO_x and O_3 analysers

The calibration system (as shown in Fig. 1) is used to calibrate all the instruments measuring NO, NO_2 and O_3 . The system consists of a T700 dilution system (Teledyne Technologies, USA) which uses mass flow controllers and has an internal UV O_3 generator, which enables the generation of NO_2 . This is used in conjunction with the zero-air generator (T701, Teledyne Technologies, USA) and a certified 10 ppm NO gas cylinder (BOC Ltd, Guildford, UK). The complete system is able to produce both multipoint span and zero calibrations for NO, NO_2 and O_3 . Daily at 01:00 (GMT) the system is setup to carry out the following procedure: i) Purge with zero air (5 min), ii) Zero air (20 min), iii) 180 ppb NO (30 min), iv) Purge with zero air (5 min), v) 100 ppm O_3 (25 min), vi) Purge with zero air (5 min).

The daily zero air and span checks are used to check for instrument drift both for the NO_x and O_3 instruments. If there is a $>10\%$ deviation in the daily reported concentrations by any instrument, then a manual calibration is performed. Approximately every 90 days the system automatically carries out a linearity check of the NO_x instruments for a range of NO concentrations (0, 20, 40, 60, 90 and 130 ppb) for a period of 30 min at each dilution to ensure there is sufficient time for the concentrations to stabilise. In addition, zero and span checks are done monthly for NO in all instruments, as well as the convertor efficiencies for the MoNO_x and the BLNO_x . For quality assurance processing, no correction was applied to the reported NO and NO_2 to account for potential conversion of NO to NO_2 by O_3 in the inlet as outlined in the ACTRIS protocol ([https://www.actris.eu/sites/default/files/Document s/ACTRIS-2/Deliverables/WP3_D3.17_M42.pdf](https://www.actris.eu/sites/default/files/Document%20s/ACTRIS-2/Deliverables/WP3_D3.17_M42.pdf)), as the current EN 14211:2012 "Ambient air quality - Standard method for the measurement of the concentration of nitrogen dioxide and nitrogen monoxide" which is used as the reference method for compliance monitoring currently does not require correction for the inlet but requires a residence time to 6 s or less (inlet + instrument) to minimise the potential conversion by O_3 . The set-up presented meets the standard (Refer to Table S1 for instrument set-up details). As a common manifold was used and a minimal inlet between the manifold and analyser, it is assumed instruments should have received the same concentrations as any conversion between the manifold and instrument should have been negligible.

2.4. Monitor for AeRosols and Gases in Ambient air (MARGA)

The Monitor for AeRosols and Gases for Ambient air (MARGA, Metrohm, NL) is a wet chemistry system which monitors the water-soluble aerosols for both $\text{PM}_{2.5}$ and PM_{10} (NH_4^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , NO_3^- and SO_4^{2-}) and counter-part gases (NH_3 , HCl, HNO_3 , HNO_2 , SO_2) at hourly resolution. The MARGA system draws air through a Teflon coated PM_{10} head (URG Corp, USA) at a height of 3.55 m down an inlet of 0.89 m polyethylene inlet. The line then splits into two and the first line of 0.4 m PE tubing goes directly into a sample box, whereas the second line goes through a $\text{PM}_{2.5}$ cyclone before entering the 2nd sample box. Air on entering the sample boxes goes through a wet rotating denuder (WRD), which is a continuously rotating and has a 10 ppm solution of H_2O_2 continually pumped through, creating a liquid film on the walls of the denuders. Water-soluble gases travel through the WRD and diffuse into the liquid film, whereas water soluble aerosols do not diffuse due to their lower diffusion velocities but instead continue in the air stream where they enter a steam jet aerosol collector (SJAC) that facilitates rapid growth in a steam chamber. The aerosols are then mechanically separated out using a cyclone and along with the liquid in the WRD, continually drawn-out using syringes. The samples in the syringes are then sequentially mixed with an internal standard of 353 mg L^{-1} of LiBr prior to analysis using anion and cation chromatography. Due to the low concentrations at Auchencorth both the anion and cation are loaded onto pre-concentration columns prior to analysis by chromatography. The concentration of the sample is calculated using the specific

conductivities of each species relative to Li^+ and Br^+ internal standard. Samples which demonstrate $>20\%$ than the expected concentration of the internal standard are automatically rejected. A more detailed description of the MARGA instrument at Auchencorth Moss and the data handling can be found in [Twigg et al. \(2015\)](#). Provisional MARGA data is available at quarterly intervals and ratified data is provided annually to the UK-Air quality database (uk-air.defra.gov.uk).

Using the MARGA to further understand direct potential artefacts from gas phase nitrogen pollutants has the caveat that the MARGA itself is not an artefact free measurement for gas phase pollutants and the potential artefacts are not fully characterised. For example, it is known that dinitrogen pentoxide (N_2O_5) will be reported as HNO_3 at night ([Phillips et al., 2013](#)) but at Auchencorth Moss, it is expected that this interference will not be large due to the low NO_x environment; however, it is likely the MARGA will have suffered losses of HNO_3 to the inlet. Another challenge is that as the instrument uses an inlet and heterogeneous chemistry is likely to occur on the surface of the inlet tubing, potentially leading to formation of HONO. In a recent study by [Ramsay et al. \(2018\)](#), it was found for a similar instrument with a shorter inlet that it overestimated HONO by 6% when compared to an artefact free method (LOPAP). This however, is not likely to be significant to the overall contribution to any artefacts at this field site.

Concentrations of compounds in the MARGA system are measured in $\mu\text{g m}^{-3}$, though for the purpose of this study we report values in ppb (nmol per mol air). We use ppb to allow for the comparison of an accumulation of separate compounds in regard to their nitrogen content, as mass per volume units of separate compounds do not allow for this. As each of the nitrogen containing species only contains one nitrogen atom, the species are equivalent in molar (ppb) units.

2.5. Meteorological data

Wind speed and direction at the site was measured by a WindSonic 2-Axis Ultrasonic Anemometer (Gill Instruments, Lymington, UK), which was mounted at a height of 10 m. Temperature and relative humidity (RH) was measured using a Vaisala HMP60 humidity and temperature probe (Vaisala, Vantaa, Finland), which was housed within a radiation shield (Vaisala, DTR504A). Rainfall was measured by a tipping bucket (RM Young, Michigan, USA) and solar radiation was measured using a Skye SP1110 pyranometer (Skye Instruments, Isle of Skye, UK). Meteorological data for the site is available on the CEDA online archive (<http://www.ceda.ac.uk/>).

2.6. Statistical Analysis

Data in this study was analysed using the freely available statistical software 'R' ([R Core Team, 2021](#)), and presented using the 'ggplot2' package ([Wickham, 2016](#)). Where 95% confidence intervals (95% C.I.s) are presented, these are estimated by taking the standard error of a sample population and multiplying by 1.96, assuming a gaussian 'normal' statistical distribution of data. The "leaps" package for R was used to perform step-wise regression to find the best-fitting model, based on the Akaike information criterion (AIC) ([Lumley, 2015](#)). AIC is a measure of model goodness-of-fit derived from information theory, widely used in model selection ([Burnham and Anderson, 2004](#)). For a set of candidate models, the model with the lowest AIC value represents the best choice, given the trade-off between model likelihood and complexity.

3. Results

3.1. Overview of meteorology

Air temperature at the site ([Fig. S1a](#)) during the period studied was typical for this location and climate, with a minimum daily mean of -4.95°C (late January), and a maximum of 21.6°C in late July. Annual

rainfall at the site ([Fig. S1b](#)) was 996 mm, which is comparable with the 1995–2016 annual average of 975 mm ([Coyle et al. 2018](#)). The predominant wind direction at the site is south-westerly (225°), although the predominance switches between south-westerly, easterly (90°) and north easterly (45°) wind directions throughout the year ([Fig. S1c](#)). The annual average O_3 concentration at the site was 28.9 ppb with a daily mean 95% quantile range from 16.8 to 42.8 ppb ([Fig. S1d](#)). The minimum and maximum observed daily means of O_3 were 7.5 and 65.3 ppb on the 1st November 2019 and 22nd of April 2020, respectively.

3.2. Comparison of NO_2 and NO measured by different instruments

Half-hourly mean concentrations of NO_2 measured by all three instruments (MoNO_x , CAPS and BLNO_x) are similar magnitude and follow a gamma distribution, where 75th and 95th percentiles of all measurements were 1.38 and 3.45 ppb, respectively ([Fig. S2](#)). Monthly mean concentrations measured by the analysers were close in magnitude ([Table 1, Fig. 1](#)) in absolute terms, with the annual average of all NO_2 of 1.30 ± 0.02 , 1.30 ± 0.02 and 0.93 ± 0.02 ppb for MoNO_x , CAPS and BLNO_x instruments, respectively. However, as these concentrations were relatively low for the majority of the time (<2 ppb), relative differences between the analysers can be large (at times $>100\%$, [Table 1](#)). The BLNO_x annual average was influenced by lower data capture as the instrument was not operational during January and most of February 2019. Comparisons in the analyses presented here are made only during periods when all three instruments are in operation (full measurement period over 18 months) which show that NO_2 measured by the BLNO_x instrument were still typically lower than the other two instruments, with average of 1.20 ± 0.02 , 1.29 ± 0.02 and 0.92 ± 0.02 ppb for the MoNO_x , CAPS and BLNO_x , respectively (see [Table 1](#)).

NO measurements also followed a gamma distribution, with 75th and 95th percentiles of all data of 0.11 and 0.35 ppb, respectively. Concentrations measured by both instruments were similar over extended periods of time ([Fig. S3](#)); however, the MoNO_x instrument typically reports higher than the BLNO_x , with a mean of all points of 0.090 ± 0.003 and 0.080 ± 0.003 for the MoNO_x and BLNO_x instruments, respectively. ([Table 1](#)).

Direct comparisons of the instruments highlight discrepancies in the measurements ([Fig. 2](#)). Concentrations of NO_2 measured by the CAPS instrument are often higher than the other two analysers by a fraction of a ppb, though it varies from month to month ([Fig. 2](#)). Although approximately linear in nature ([Table 2](#)), occasionally, NO_2 concentrations measured by the MoNO_x instrument deviate significantly from those observed by both the CAPS and BLNO_x instrument ([Fig. 2a](#) and [b](#)). These large deviations are not seen in the direct comparison of the CAPS and BLNO_x instruments ([Fig. 2c](#)), suggesting that the issue is MoNO_x specific. However, concentrations of NO measured by the MoNO_x correlate well with the BLNO_x instrument with no large deviations across the comparison period ([Fig. 2d](#)). While the MoNO_x deviates towards higher NO_2 than the other instruments, the BLNO_x appears to report fractionally higher values than the MoNO_x when reporting concentrations of NO (above 4 ppb).

3.3. Aerosols and gases in ambient air

The concentrations of the compounds measured by the MARGA instrument varied largely throughout the measurement period ([Table S3, Fig. 3](#)). Large and sustained peaks in NO_z ([Fig. 3a](#) and [b](#)) and NH_y ([Fig. 3c](#)) compounds were observed in February and April (2019), with smaller peaks recorded throughout. There is a correlation between total concentrations of NO_z and NH_y compounds ($R^2 = 0.64$), and both follow the similar temporal pattern in time. This is not surprising since ammonium nitrate (NH_4NO_3) is a dominant secondary inorganic aerosol at this site ([Twigg et al., 2015](#)). The sum of all NO_z compounds was typically low at the site throughout the measurement period (18 months), with a median hourly concentration of 0.37 ppb. Hourly

Table 1

Monthly mean values for the period January 2019 to July 2020 are presented for meteorology, O₃ concentration and NO₂ and NO concentrations measured by MoNO_x, CAPS and BLNO_x instruments. The percentage of data cover for each instrument is the ratio of half hourly datapoints that were collected for each month compared to the maximum possible.

Month	Rain	Mean Temp.	Wind Direction	Ozone	MoNO _x Cover	CAPS Cover	BLNO _x Cover	NO ₂ MoNO _x	NO ₂ CAPS	NO ₂ BLNO _x	NO MoNO _x	NO BLNO _x	NO ₂ Ratio MoNO _x /CAPS	NO ₂ Ratio MoNO _x /BLNO _x	NO Ratio MoNO _x /BLNO _x
	(mm)	(°C)		(ppb)	(%)	(%)	(%)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)			
Jan 19	21.1	2.4	SW	28.4	92	92	0	2.23	1.64	NA	0.30	NA	1.4		
Feb 19	35.8	5.5	SW	31.0	94	94	5	2.26	1.06	1.33	0.21	0.18	2.1	1.7	1.2
Mar 19	108.9	4.9	SW	34.1	96	96	96	0.51	0.94	0.72	0.14	0.14	0.5	0.7	1.0
Apr 19	50.3	6.9	SE	41.1	74	74	74	2.03	1.55	1.21	0.19	0.19	1.3	1.7	1.0
May 19	78.8	8.4	SW	32.4	92	92	92	1.56	1.37	1.08	0.10	0.06	1.1	1.4	1.7
Jun 19	95.7	11.5	SE	29.9	94	94	94	1.20	1.09	0.78	0.07	0.05	1.1	1.5	1.4
Jul 19	82.8	15.0	SW	24.9	96	96	96	1.10	1.09	0.72	0.16	0.10	1.0	1.5	1.6
Aug 19	102.8	14.0	SW	27.8	95	95	95	0.76	0.94	0.50	0.11	0.06	0.8	1.5	1.8
Sep 19	99.8	11.2	SW	23.2	94	94	94	1.12	1.45	0.94	0.15	0.10	0.8	1.2	1.5
Oct 19	103.0	6.8	SW	25.5	59	91	91	1.13	1.47	1.13	0.07	0.07	0.8	1.0	1.0
Nov 19	120.4	3.5	E	22.0	91	91	91	2.75	2.99	2.48	0.15	0.16	0.9	1.1	0.9
Dec 19	96.6	4.0	SW	29.3	73	73	73	1.20	1.25	0.89	0.03	0.02	1.0	1.3	1.5
Jan 20	102.0	4.6	SW	32.1	91	91	91	0.82	0.99	0.64	0.04	0.02	0.8	1.3	2.0
Feb 20	189.3	2.9	SW	34.2	88	88	88	0.97	1.15	0.85	0.06	0.04	0.8	1.1	1.5
Mar 20	90.5	4.0	SW	33.4	91	91	91	1.21	1.33	0.92	0.08	0.06	0.9	1.3	1.3
Apr 20	9.1	7.0	SE	36.0	93	93	93	1.23	1.04	0.70	0.09	0.08	1.2	1.8	1.1
May 20	50.1	10.1	SW	34.4	90	90	90	0.64	0.76	0.46	0.03	0.03	0.8	1.4	1.0
Jun 20	90.3	12.1	SE	32.1	89	89	89	1.14	1.49	0.93	0.11	0.10	0.8	1.2	1.1

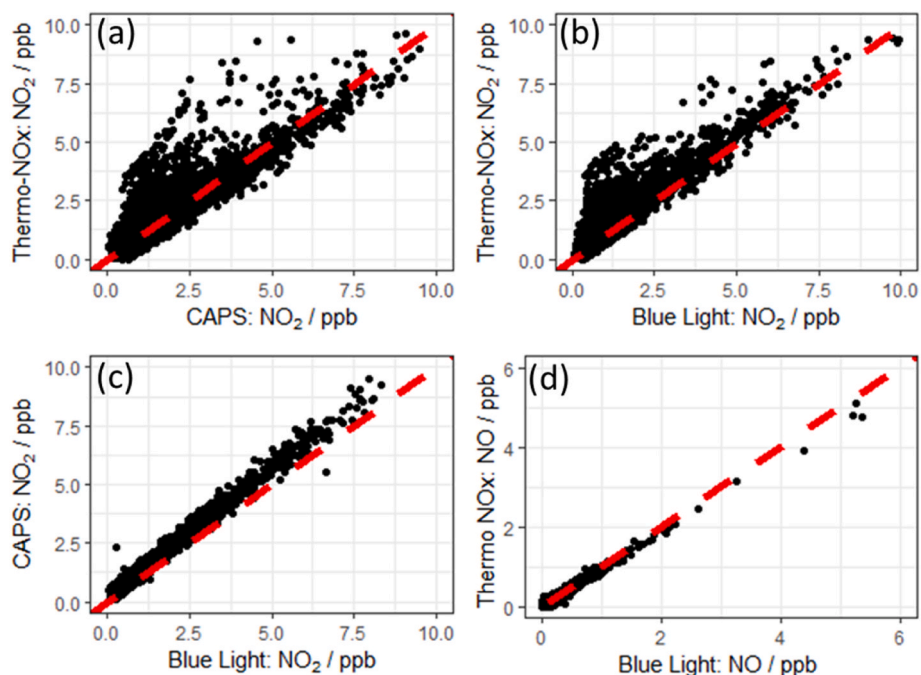


Fig. 2. (a,b,c) Direct comparisons of NO₂ concentrations (half hourly means) for the MoNO_x, CAPS and BLNO_x between January 2019 and July 2020. (d) Direct comparisons of NO concentrations (half hourly means) are made for the MoNO_x and BLNO_x for the measurement period. Linear regression statistics are displayed in the plot in the format $y = mx + c$, where m is the gradient between y and x , and c is the y intercept of the regression fitting. A 1:1 ratio line is added to ease comparison (red).

concentrations of NO₂ reached a maximum peak of 11.6 ppb on the 27th of February (2019), dominated by NO₃⁻. A second peak in NO₂ compounds of 11.2 ppb was observed on the 6th of April (2019). The sum of all NH_y was also typically low for the duration of measurements with a median hourly value of the sum of all NH_y compounds of 2.25 ppb. A

maximum peak in hourly NH_y concentration of 29.14 ppb was observed on the 25th of August (2019), with peaks of 23.09 and 22.12 ppb on the 26th of February and 19th of April (2019), respectively. Measurements of Na_{PM10}, Cl_{PM10} and HCl were also made at the site (Fig. 3d).

Table 2

Fit parameters of linear relationships between NO₂ and NO concentrations (half hourly means) for the MoNO_x, CAPS and BLNO_x between January 2019 and July 2020 as shown in Fig. 2. Standard error (SE) of the fit coefficients are provided as well as Pearson correlation factor (Pr).

Instrument (Y Axis)	Instrument (X Axis)	Gas	Slope	Slope (SE)	Intercept	Intercept (SE)	R ²	Pr
Thermo-NOx	CAPS	NO ₂	0.98	0.006	0.10	0.01	0.79	<0.0001
Thermo-NOx	Blue Light	NO ₂	1.04	0.005	0.26	0.01	0.86	<0.0001
CAPS	Blue Light	NO ₂	1.08	0.002	0.28	0.002	0.99	<0.0001
Thermo-NOx	Blue Light	NO	0.92	0.003	0.03	0.001	0.95	<0.0001

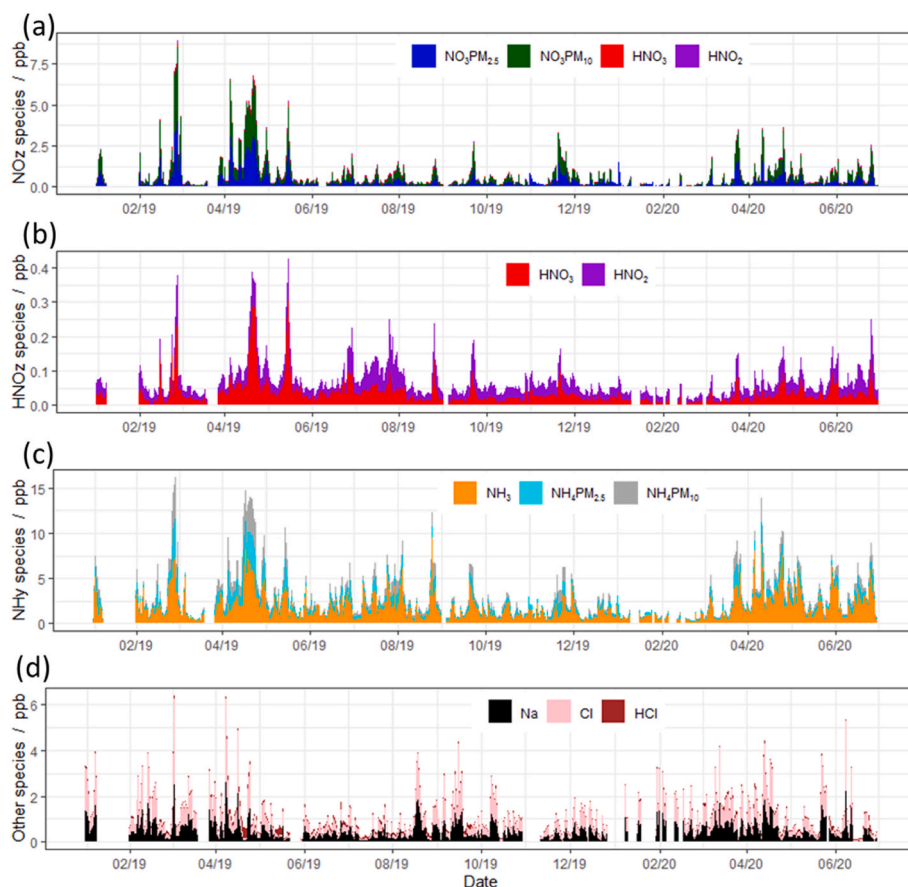


Fig. 3. Mean daily concentrations of (a) all NO_x, (b) HNO_x, (c) NH_y and (d) other species, measured using a MARGA instrument at the Auchencorth field site in 2019.

3.4. Deviations in measured NO₂ between instruments

During peaks of high NO₂ and NH_y concentrations in both February and April in 2019 (Fig. 4a and b), it can be seen that NO₂ concentrations measured by the instruments deviate significantly (Fig. 4c and d). The MoNO_x instrument appears to be the most susceptible to this effect, although the BLNO_x instrument was not operational for most of February for comparison. Deviations of up to 2.5 ppb (110 % higher) are observed for the MoNO_x instrument compared to the average of the other NO₂ instruments during periods when N species are high in concentration in the atmosphere (Fig. 4d). This behaviour is not observed between the CAPS and BLNO_x instrument, which tend to measure similar values throughout the period.

Concentrations of reactive nitrogen correlated with the deviation observed between the MoNO_x and the other instruments (Fig. S4) with adjusted R² values of approximately 0.54 for all combined forms of NO₂. An AIC linear regression analysis was carried out, only during periods when all three instruments were operational. Multiple species measured by the MARGA, ozone, and meteorological variables averaged over various lengths of time (1h, 3h, 6h, 12h, 24h, 48h) were applied, then

removed where no significant correlation was found (Fig. S4). The AIC fitting show that approximately 62 % of the variation in the deviation observed between the NO₂ instruments can be described by measured variables on an hourly basis. Using only NO₂ concentrations and air temperature (6 h mean), 59 % of the variation in the deviation observed can be described. The prediction of the 5 variable (NO₂ concentration (hourly), air temperature (6h average), O₃ concentration (hourly), solar radiation (6h average) and NH_y concentration (hourly)) multiple linear regression model (R² = 0.62) is compared with the measured data in Fig. 5 (Equation coefficients detailed in Table S3).

4. Discussion

Measurements of NO₂ measured by the MoNO_x, CAPS and BLNO_x instruments were close in magnitude for much of the measurement period and followed very similar temporal patterns. This was also true for concentrations of NO measured by the MoNO_x and BLNO_x instruments, which were highly linear in nature (see Fig. 2d). There were inconsistent differences between the analysers throughout the measurement period, and no analyser consistently reported always higher or

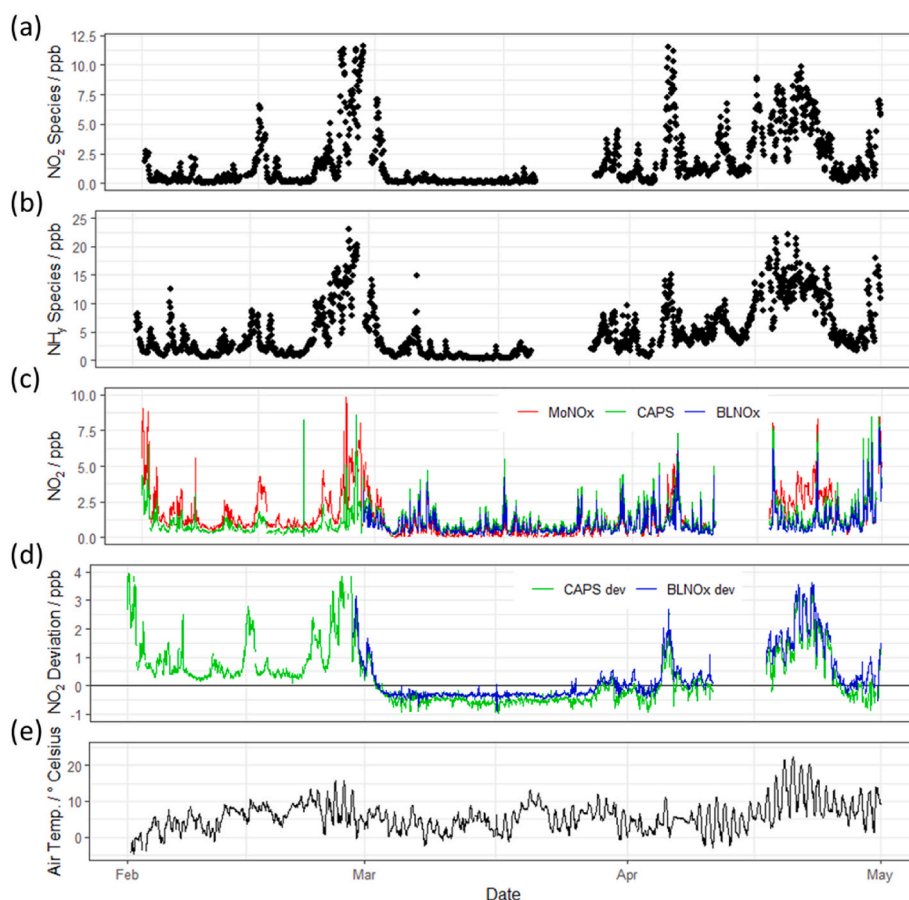


Fig. 4. Data for the period February to May 2019 are shown to highlight differences in NO_2 measured between the MoNO_x, CAPS and BLNO_x instruments during periods of high concentrations of N species in the atmosphere. Concentrations of (a) the sum of all NO_z species, (b) the sum of all NH_y species and (c) NO_2 are shown in ppb. (d) The deviation (dev) in NO_2 concentration measured by the MoNO_x instrument in comparison to the other instruments (e) Air temperature is shown to represent the diurnal cycle.

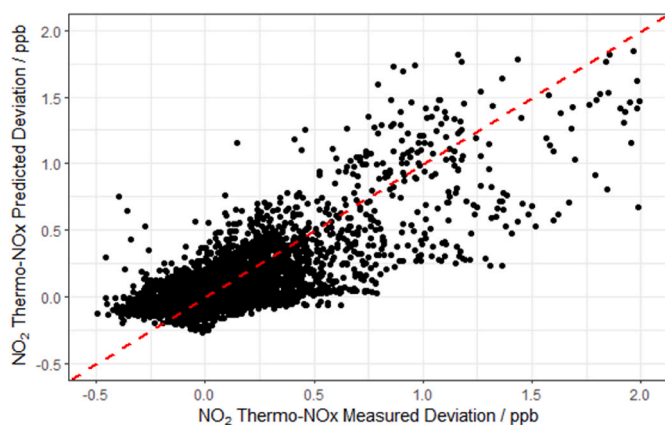


Fig. 5. The deviation predicted by linear regression model and parameters identified in the AIC model ($R^2 = 0.62$) is plotted against the actual observed measured deviation between the MoNO_x and other NO_2 instruments (the difference between the MoNO_x and the mean of both the CAPS and BLNO_x combined). A 1:1 ratio line is added to ease comparison (red).

lower than the others across the whole period. The measurements from the CAPS instruments were more often slightly higher than the other instruments during periods of low NO_2 . These differences were consistently sub-ppb and could be the result of the limitations of calibrating, aligning and performing spectral fitting in the instruments themselves (i. e. the human component or instrumental detection limits) rather than

any particular artefact caused by instrumentation. The largest difference in the NO_x species measurements was the comparisons of NO_2 measured by the MoNO_x to the CAPS and BLNO_x during periods of high atmospheric concentrations of reactive N compounds (i.e. NO_z and NH_y). During periods of elevated concentrations of reactive N species, the MoNO_x instrument reported NO_2 concentrations of up to 4 ppb higher than the CAPS or BLNO_x, in some cases reporting more than double the observed NO_2 by the more molecule specific measurements. The over-estimation is greater than reported by Jung et al. (2017) who evaluated the interference between a MoNO_x and BLNO_x, they quantified that there was a 20 % overestimation between the two instruments however the study was conducted in a higher NO_x urban environment. Jung et al. (2017) attributed the interference to total $\text{PM}_{2.5}$ rather than individual species. They proposed a correction factor for NO_2 (in ppb) of approximately 0.1 multiplied by the concentration of $\text{PM}_{2.5}$ ($\mu\text{g m}^{-3}$) for the data based on their relationship between the delta NO_2 and the $\text{PM}_{2.5}$. If we apply the same ratio used in Jung et al. (2017) (0.1 multiplied by all $\text{PM}_{2.5}$ species measured) we find that there is a significant statistical relationship between the deviation in NO_2 concentrations observed by the MoNO_x instrument and $\text{PM}_{2.5}$, but that the R^2 of this relationship (0.39) is weaker than that of NO_2 compounds alone (0.54). The reason for this is likely because NO_3^- aerosol in its $\text{PM}_{2.5}$ fraction is the most influential compound in contributing to the artefact in the MoNO_x instrument, and the fraction of NO_3^- in the total mass of $\text{PM}_{2.5}$ is location specific (i.e. urban vs rural).

There has been evidence in the literature for some time that the non-discriminating catalysis reaction stage in chemiluminescence instruments may result in an over estimation of NO_2 measured by the

instruments (e.g. Dunlea et al., 2007; Reed et al., 2016; Alam et al., 2020). While it has been known for some time that artefacts were present in molybdenum catalyst analysers, these instruments have always been relatively low cost compared to alternatives, thus widescale monitoring has favoured them. However, the analysers used in this study were all of comparable cost (£20-30k), thus this aspect is no longer of concern. The molybdenum catalyst in the MoNO_x instrument reported in this study appears to be performing a conversion from atmospheric NO_z compounds into NO (approximately 33 % conversion rate), as well as the desired NO₂ to NO conversion required for chemiluminescent analysis, thus overestimating NO₂ concentrations. The bias of NO₂ overestimation follows a first-order linear relationship, which would be expected from a direct fractional conversion during the catalysis stage. This is not the first time that NO_z compounds have been attributed to this artefact however this was attributed to HNO₃ and alkyl and multifunctional alkyl nitrates in the urban environment (Dunlea et al., 2007). Reed et al. (2016) also reported that approximately 5 % of peroxyacetyl nitrate (PAN) was also converted and measured as NO₂ by photo-chemiluminescent analysers. It is assumed this interference at Auchencorth Moss will be minimal assuming 5% conversion as a previous study demonstrated in spring 2014, that concentrations of PAN were relatively low with an average of 0.46 ppb (Malley et al., 2016). To better understand how individual species impact the conversion stage, controlled lab studies would need to be carried out to determine specific correction factors for reactive nitrogen species. It could be argued that better filtration and regular changes of filters would reduce the potential interference from NO₃⁻, however the air sampling and manifold set up and maintenance schedules are more stringent than those used in compliance monitoring networks (filters changed monthly, and PM levels very low). As discussed above, the predominant PM chemical salt is ammonium nitrate which is semi-volatile so would not be “captured” on an inline filter permanently unless it chemically captured the salt components.

This study highlights that a periodic over-reporting bias of molybdenum catalyst chemiluminescent analysers (such as the MoNO_x) is likely to be largest in areas where nitrogen pollution events occur (specifically NO_z compounds) and are likely to make a greater contribution in a low NO_x environments such as Auchencorth Moss. In our study we see peaks of reactive N during spring, around the time that agricultural activity is high due to fertiliser applications in the local area and frequency of long-range transport events of NH₄NO₃ tends to peak at Auchencorth Moss (Twigg et al., 2015; Vieno et al., 2016). In this regard we are likely to observe a greater influence of atmospheric NO₃⁻ contamination in the NO₂ analysers at rural sites where NO_x concentrations are lower compared to urban roadside settings where NO_x concentrations are larger. It is noted that in addition to this, Alam et al., (2020) has reported negative interferences in NO₂ measurements from volatile organic compounds (VOCs) when measured with molybdenum catalysts and therefore makes interpretation of the data challenging.

Away from NO_x sources, the impact of the potential overestimation of NO₂ measured by molybdenum catalyst chemiluminescent instruments could be significant, especially due to the prevalence of their use in air quality monitoring networks around the UK and abroad. In some countries, where NO₂ and NH₃ concentrations are higher it will be challenging to disentangle from immediate sources of NO_x when operated. Currently all EU and UK Air Quality Directive and Regulations-driven NO₂ monitoring sites use the MoNO_x approach as it is specified in the methodology. Globally, concern is growing around this as it leads to on-going inaccuracies in the reported NO₂ concentrations and a more limited understanding of atmospheric chemistry and pollution impacts due to the lack of specificity of the measurement technique (e.g. in the UK all NO₂ concentrations reported as part of compliance are reported by instrumentation using molybdenum catalyst conversion (Li et al., 2023)). This and other research clearly shows positive and negative artefacts in the MoNO_x method (Dunlea et al., 2007; Alam et al., 2020). The positive artefact observed at Auchencorth does not affect the

compliance reporting as concentrations are already below thresholds set in legislation (e.g. annual mean concentration of NO₂ must not exceed 40 µg m⁻³ and that there should be no more than 18 exceedances of the hourly mean limit value (concentrations above 200 µg m⁻³) in a single year). But it is relevant for scientists and policy makers to have the best available estimates of the pollutant concentrations and the understanding of why changes occur in the air pollution and what they are due to – for example fully understanding air quality during PM events.

5. Conclusions

This study concludes that there is a clear artefact in molybdenum catalyst chemiluminescent instruments as a result of unselective catalysis of airborne NO_y compounds, particularly that of particulate NO₃⁻ in PM_{2.5}. This influence causes an overestimate of NO₂ measured in the atmosphere by molybdenum catalyst chemiluminescent instruments. While it is likely that instrumental setup, environmental conditions (temperature and humidity) and filtration methods will result in a different magnitude of impact for each measurement site, this study estimates that approximately 33 % of NO_y compounds sampled in the air being analysed for NO₂ were converted to NO₂ by the molybdenum catalyst chemiluminescent instrument. As a result of this artefact, it is highly likely that many air quality measurement sites (particularly those with high atmospheric particulate nitrate concentrations) are over reporting NO₂ concentrations. As it is likely that future atmospheric chemistry will be in a low NO_x world, if policy interventions are successful, accurate low-concentration NO₂ measurements will be needed for future air pollution models. We recommend based on the findings of this study (and other previous studies where artefacts have been identified) that molybdenum catalyst instruments (which make up the vast majority of currently used NO₂ measurement instrumentation at the global scale) should be phased out and replaced in air quality monitoring networks with molecule specific (spectroscopy) instrumentation that do not suffer from the same problems with artefacts. We also recommend that further instrumental intercomparison and testing is considered to avoid further artefacts in measurement networks in future efforts.

CRedit authorship contribution statement

Nicholas Cowan: Data curation, Formal analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Marsailidh M. Twigg:** Conceptualization, Data curation, Formal analysis, Methodology, Validation, Visualization, Writing – original draft, Writing – review & editing. **Sarah R. Leeson:** Data curation, Formal analysis, Investigation, Methodology, Writing – review & editing. **Matthew R. Jones:** Funding acquisition, Project administration, Resources, Supervision, Writing – review & editing. **Duncan Harvey:** Data curation, Formal analysis, Investigation, Writing – review & editing. **Ivan Simmons:** Data curation, Formal analysis, Investigation, Methodology, Writing – review & editing. **Mhairi Coyle:** Data curation, Formal analysis, Investigation, Methodology, Writing – review & editing. **John Kentisbeer:** Formal analysis, Methodology, Writing – review & editing. **Hannah Walker:** Investigation, Methodology. **Christine F. Braban:** Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Validation, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.atmosenv.2024.120375>.

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