Remote sensing of volatile organic compounds release during prescribed fires in pine forests using open-path Fourier transform infra-red spectroscopy

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ABSTRACT

Background. Extreme wildfires have increased in recent decades, yet the consequences of extreme fire behaviour are not fully comprehended. The study of prescribed burning provides opportunities to advance understanding of some overlooked processes in fire behaviour, such as the role of the release of volatile organic compounds (VOC). **Aims.** The aim of this study was to assess VOC (α-pinene, β-pinene, and limonene), NH_3, CO and CO_2 emissions during prescribed fires in pine barrens vegetation at the Albany Pine Bush Preserve, USA. **Methods.** Measurements performed by open-path Fourier transform infra-red spectroscopy (OP-FTIR) quantified VOC concentrations and characterised emissions during four independent prescribed burns. **Key results.** Combustion products (e.g. CO_2, CO, CH_4) and VOC exhibited similar emission behaviour during thermal degradation, though VOC concentrations appeared to be independent of the type of biomass burned, unlike those of combustion products; *Pinus strobus* L. emitted two orders of magnitude higher than *Pinus rigida* Mill.; VOC and CO are statistically correlated ($R^2 = 0.84$). **Conclusions.** These results confirmed that OP-FTIR is a feasible approach for gathering qualitative and quantitative information regarding VOC emission during prescribed fires. **Implications.** Quantification of VOC concentrations during prescribed fires helps characterise its relationships with greenhouse gas emissions (e.g. CO_2 and CO) at different burning conditions (e.g. wind, biomass type), which could be incorporated into existing fire behaviour models to enhance their ability to better predict fire propagation.

Keywords: carbon dioxide, carbon monoxide, OP-FTIR, *Pinus rigida* Mill., *Pinus strobus* L., prescribed fires, remote sensing, volatile organic compounds.

Introduction

Extreme wildfire behaviour is related to a number of factors, including high temperature, low humidity and dry fuel accumulation, which are directly tied to climate variability and change (NOAA 2022). There has been an increase in the use of prescribed fires in different parts of the world to remove fuel at significant spatial scales (Harper *et al.* 2018). Accurate quantification of fuel loads and distribution are imperative to facilitate the management of fires to understand fire spread dynamics, and to develop efficient plans to manage forest fires (Forest Europe 2010). It is important to recognise the potential benefits of prescribed fires in supporting land and ecosystems management (e.g. new growth, greater diversity of the heather structure, recovery habitat), and increasing resilience to wildfires (Knapp *et al.* 2009). Moreover, prescribed fires have also been employed in many countries to promote more controlled production and dispersion of wildfire smoke, while simultaneously reducing accumulated hazardous fuels. Thus, prescribed fires have the potential to maintain desired conditions in various ecosystem types by promoting vegetation productivity and soil fertility, minimising the spread of pests and diseases, and acclimatising the environment for conservation of endangered native species (Akagi *et al.* 2014; Greco 2018).

The pine barrens of the Albany Pine Bush Preserve in eastern New York, US are a fire-dependent habitat type. This preserve consists of over 1300 ha of protected land registered as an official National Natural Landmark, New York State Unique Area, Heritage Site, Bird Conservation Area, and National Audubon Society Important Bird Area. This landmark is home to more than 1500 plant and animal species, including 76 wildlife species of greatest conservation need and more than 20 at-risk species. The Albany Pine Bush Commission works with local landowners and the population to lessen the impacts of development and fragmentation of the remaining pine barrens (Bried *et al.* 2015). The management program of the preserve uses prescribed fires to maintain the open ecosystem of sand dunes with *Pinus rigida* Mill., *Pinus strobus* L., and wild blue lupin (*Lupinus perennis* L.), a host of the endangered Karner blue butterfly (*Plebejus melissa samuelis* Edwards; Brickle *et al.* 2013). This fire-dependent habitat requires frequent controlled burns to maintain desired vegetation structure and composition. The main goals of the prescribed fires in the Albany Pine Bush Preserve units are: (1) to expand open patches dominated by warm-season grasses and forbs, including *L. perennis*, and reduce shrub cover; and (2) to reduced fuel loads and severe wildfire risk.

Even considering advances in fire management, extreme fire behaviour is difficult to predict, especially sudden changes in fire spread and blow-up, eruptive or flashover fires (Cramer *et al.* 2018; San-Miguel-Ayanz *et al.* 2019). Thus, it has been suggested that high concentrations of flammable volatiles released by the leaves at high temperatures may help explain erratic fire behaviour (Chetehouna *et al.* 2009; Rego *et al.* 2021). The release of large amounts of volatile organic compounds (VOC) combined with specific fuel conditions, topography, and wind can create explosive scenarios, since VOC reach critical flammability thresholds and ignite with very high intensity when provided sufficient oxygen and a potential ignition source (Chatelon *et al.* 2014). Essential oils and resins in the needles of *P. rigida* and *P. strobus* are known to contain high levels of α-pinene, β-pinene, limonene, myrcene and terpinolene (i.e. 5.8–57.8% of total VOC concentration) (Ioannou *et al.* 2014; Arango-Velez *et al.* 2018; Hwang *et al.* 2022). These low density monoterpenoids are highly flammable VOC that may accumulate at ground level (Coudour *et al.* 2019). The behaviour of flammable volatiles released by vegetation under various environmental conditions has been studied using selectively coated nanosensors, microextraction techniques and chromatographic analysis (Nunes and Pio 2001; Xiong *et al.* 2003; Winters 2010; Gonçalves 2022; Gonçalves *et al.* 2022; Magro *et al.* 2022). However, those high efficient and precise approaches for detecting trace levels of emitted organic compounds require highly specialised equipment that must be operated within controlled laboratory conditions. Development of remote sensing tools has promoted a huge advance in reliable real-time

monitoring of atmospheric gas pollutants such as ammonia (NH_3) and ethanol (CH_3CH_2OH), some VOC and greenhouse gases (GHG) such as water vapour, carbon dioxide (CO_2), carbon monoxide (CO) and methane (CH_4) (Kira *et al.* 2015; Lin *et al.* 2019). Open-path Fourier transform infrared spectroscopy (OP-FTIR) is a technique that has been used extensively over the past 50 years for analysis of these types of compounds (Wooster *et al.* 2011; Akagi *et al.* 2014; Bai *et al.* 2014, 2018; Smith *et al.* 2014; Flesch *et al.* 2016; Lin *et al.* 2019; Byrne *et al.* 2020). Due to the high temporal resolution of real time data acquisition, the OP-FTIR technique allows simultaneous monitoring of multiple molecules at ground-level, both horizontally and vertically (Flesch *et al.* 2016). In addition to the growing need to assess toxic gaseous pollutants produced during both environmental and industrial events, open-path Fourier transform infrared spectroscopy (OP-FTIR) methodologies have been used to monitor GHG, especially for ground-level smoke composition studies (Lin *et al.* 2019). For example, Wooster *et al.* (2011) used the approach to evaluate the plume released by burning biomass and determined emission ratios and factors for CO_2, CO, CH_4, formaldehyde and NH_3. Similarly, de Castro *et al.* (2007), measured concentrations of approximately 18, 35, 6 and 2 ppm m^{-1} of CO_2, CO, CH_4 and NH_3, respectively, that were emitted during burning of *Calluna vulgaris* (L.) Hull, *Chamaespartium tridentatum* (L.) P. Gibbs, *Erica umbellata* L., *Ulex europaeus* L., and *Ulex minor* Roth shrubs. Recent studies consider the applicability of other OP-FTIR approaches for the monitoring GHG emissions at farms located in Germany and Australia (Bai *et al.* 2014, 2018; Ni *et al.* 2015). Emission concentrations of different terpenoids have been commonly studied by gas chromatography and/or mass spectrometric analysis. For instance, in Scots pine (*Pinus sylvestris* L.) forests in Sweden, total terpenoid emission concentrations ranged from 3.5 to 56.0 μg m^{-3}, of which limonene, α- and β-pinene comprised 0.81 to 8.10, 1.3–13.05 and 0.45–4.5 μg m^{-3}, respectively (Janson 1992). Other studies conducted in forests, have documented even higher variation of limonene emissions, ranging from 0.9 to 12.2 g m^{-3} (Antonelli *et al.* 2020). Emission of other VOC in wildfire smoke sampled in 2016 near Fort Murray, Horse River, Alberta, Canada reached a total peak emission of 852 ng m^{-3}, which was 17-times higher than the emission detected in non-fire conditions (Wentworth *et al.* 2018). Similarly, another study of VOC in a fire plume detected concentrations ranging from 24.0 to 68.2 μg m^{-3} (Piel *et al.* 2021). Nevertheless, studies regarding the application of OP-FTIR methodologies for the assessment of other VOC emissions, such as terpenoids, have yet to be developed, especially during wildfire events.

Thus, using the Albany Pine Bush Preserve as a proof of concept, the aim of this study was evaluating the potential of OP-FTIR to measure VOC, NH_3, CO and CO_2 emissions during prescribed fires. By using prescribed fire as experimental tools, this approach will allow to better understand

how release of VOC influence fire behaviour. The measurements performed at the preserved pine forests will allow the collection of data in different fuel types, topography, and wind, providing therefore data that, to the best of our knowledge, has yet not been explored.

Materials and methods

Open-path Fourier transform infra-red spectroscopy (OP-FTIR) measurements

Spectral measurements were conducted using a RAM2000 G2 OP-FTIR system (Kassay Field Services Inc., Mohrsville, PA, USA), consisting of a FTIR, two retro-reflectors and a data processing system (Kira *et al.* 2015, 2016; You *et al.* 2021). In the most basic depiction of OP-FTIR data processing, field data spectra are collected and processed by an iterative technique that yields a reliable chemical concentration of target chemicals present in the beam path. The beam path is described by the line that the infra-red (IR) signal travels between the spectrometer (transceiver) and retro-reflectors. The IR beam from the RAM2000 G2 OP-FTIR is considered modulated since the high temperature IR source is projected into the interferometer then steered out of the instrument through the telescope mirrors. When the IR signal is returned from the retro-reflectors it goes through a second beam splitter (not the interferometer), which directs the returning IR energy to a cooled detector. In this configuration modulated energy is uniquely attributed to the original IR source propagated from the OP-FTIR. This type of configuration is referred to as 'mono static.' Mono static OP-FTIR is a preferred technique since it does not require corrections associated with other configurations (stray, passive or bi-static IR energy) emitted from far IR sources.

The data collection was performed using Remote Molecular Monitor Software, RMMSoft, approved by U.S. Environmental Protection Agency (2000) with the Environmental Technology Verification Program. During on-site measurements, the OP-FTIR spectrometer was placed on a tripod, ensuring that the line of sight was approximately 1.5 m above the ground and aligned with the retro-reflectors (Russwurm and Childers 1999; Jiao *et al.* 2019). The RMMSoft software has a series of set-up parameters that must be fulfilled to instruct the hardware. The main parameters include the number of co-adds to average together, the amplifier gain, and the path length. Once fed, the software acquisition feature can be started in order to collect the data, analyse it, present the results, and repeat the whole process. The OP-FTIR spectrometer collects an IR spectrum constrained by a user selected time interval, being that the minimum possible time is of 2 s. During this time interval, the OP-FTIR is moving mirrors and the detector, while the data acquisition system completes a cycle. The path lengths

used were specific for each case study: 58 m for the test fires and 296–340 m for prescribed fires. The IR spectra were acquired using a resolution of $0.5\ cm^{-1}$, using a detector gain of 128, which allowed the collection of average voltages of approximately 17 V for test fires and 5–7 V for prescribed fires. Collecting field data using the RAM2000 G2 OP-FTIR is made through a PC-based user interface. The number of co-adds was set to 25 to increase the signal-to-noise ratio (S/N), corresponding approximately to a 1-min acquisition interval for each individual signal (Russwurm and Childers 1999). For each measurement, the data acquisition was initiated prior the fire ignition, being held up until the plume approached and surpassed the OP-FTIR pathway to obtain the compound variation with the fire's propagation. The range of measured spectra was $700–4500\ cm^{-1}$; however, due to high water vapour interferences the analysis was restricted to the range of $850–3000\ cm^{-1}$ to increase the sensitivity. To analyse each data spectrum, on-site background spectra were recorded prior and after each field campaign using the same path as the one used to acquire the data spectrum, preserving therefore, the signal intensity (voltage) and atmospheric characteristics when applying the processing algorithms. Having the same signal intensity results in better data quality and thus lower minimum detection limits (MDL) during processing. Additionally, presenting an identical path for the background allows non-target atmospheric chemicals to be filtered out, to focus on the compound of interest. It is important to note that, since the background measurement was collected pre-burn, and the plume measurements were collected many metres down-wind (ground level) there is no need to apply temperature correction techniques. This strategy was employed to avoid measuring a high temperature plume, which would require matching high temperature reference spectra, as spectral absorption peak features changes with temperature (Smith *et al.* 2011).

The OP-FTIR data was processed using a multilevel classical least-square (CLS) method, which allows a statistical comparison of the obtained IR spectra with those included in the National Institute of Standards and Technology (NIST) reference library (U.S. Environmental Protection Agency 1999). The target chemicals monitored were α-pinene, β-pinene, limonene, NH_3, CH_4, methanol (CH_3OH), CO, CO_2, water vapour and propane (C_3H_8). The monoterpenoids (α-pinene, β-pinene and limonene) were selected as the major VOC emitted by the vegetation studied (Arango-Velez *et al.* 2018; Hwang *et al.* 2022), while propane is a surrogate for linear chain hydrocarbons that absorb in the $2800–3000\ cm^{-1}$ region of the spectrum. Additionally, NH_3 was also monitored as it is one of the main gases released to the atmosphere during wildfires, being highly related to the formation of secondary aerosols in smoke (Lindaas *et al.* 2021). Other GHG as CO, CO_2, and water vapour, which are already highly concentrated in the atmosphere, were considered as interferences during some

parts of the prescribed burns in the data processing, as well as the overlaying between terpenoids and other hydrocarbon-type molecules. Therefore, the CO and CO_2 values, determined, corresponded to the instances that the OP-FTIR signal was not saturated in the regions used to quantify those target compounds. During data collection, when the number of 25 co-adds was reached the rawest form of the data, known as interferogram, was saved, and then converted to a single-beam data spectrum by application of a Fourier transform. In simple terms, the single-beam data spectrum is divided by the background single beam to create an absorbance spectrum. It is in the absorbance spectrum mode that the CLS algorithm from the analysis method is applied. For each chemical, the analysis method identifies the spectral search region(s) to carry out the CLS statistical comparison between library reference spectrum and the data spectrum. The software also considers other chemicals absorbing within the same analysis regions as interferences within the multichemical analysis region known as matrix. For the analysis, each chemical was analysed in six independent regions, scaled by the absorbance intensity, and then presented as a concentration in $\mu g\,m^{-3}$. The analysis method was reviewed over 16-times to optimise a final method, which was used to reprocess all the final data. Each revision included analytical changes such as region end points, interferences, rejection criterion, references, and other adjustable parameters available in the RMMSoft method setup. The optimised method was able to identify the target chemicals α-pinene, β-pinene, limonene, NH_3, methanol, CH_4 and CO. When a target chemical is identified and presented by the method is due to the statistical goodness-of-fit established between the field measured data and the library reference has exceeded more than three-times the s.d. of the noise. This value is considered the MDL and can be calculated with a confidence level of 99.7%.

Field campaign at Albany Pine Bush Preserve

Test fires

Gas emissions were measured during four small test fires at the Albany Pine Bush Preserve on 19 and 20 May 2022. In each burn, fresh branches were constantly added for 15–20 min in order to have tree branches burning simultaneously; this corresponded to 5–10 kg of needle biomass with 100% moisture content. Each needle burned for about 1 min (Rothermel and Deeming 1980).

The temperature and humidity in the test burns were similar to those observed in the days of prescribed fires (maximum temperature 20–24°C; maximum humidity 40–42%). Winds speed was low but variable ($\leq 10\,km\,h^{-1}$).

Tree branches and needles of *P. rigida* and *P. strobus* emissions were compared in two assays, per species. The purpose of this assay was to optimise the measurement procedure of the VOC emitted by the selected branches and needles during combustion, as well as to identify the

specific variations of the volatile compound concentrations. The OP-FTIR equipment was placed and calibrated alongside the test-fire pathway. The data measurements and collection began prior to the beginning of each test fire and prior to the burning of the first set of tree branches. Each experiment lasted from 18 to 26 min, until branch's combustion was complete.

Prescribed fires

After the test fires, measurements were made during prescribed fires in four different management units of the Albany Pine Bush Preserve: (1) Dromedary; (2) Dorsum; (3) Cupcake; and (4) Asphalt. The placement of the OP-FTIR and the reflector in each management unit is in Fig. 1. For the open field measurements during the prescribed fires, the data acquisition with the OP-FTIR system was performed similarly as with the test fires. The total data collection time was as follows for the individual fires: 60 min for Dromedary; 90 min for Dorsum; 187 min for Cupcake; and 63 min for Asphalt.

The Dromedary and Dorsum units is characterised by dense forest of *P. rigida* trees, that was recently thinned to more closely resemble the globally rare, open pitch pine-scrub oak (*Quercus ilicifolia* Wangenh) barrens stand structure that was historically typical in the area. These units have broad sandy trails and rolling dunes. The Cupcake unit has the most diverse forest communities, with pitch pine-scrub oak barrens, native prairies on rolling sand dunes, and steep slopes and mesic conditions that support dense masses of ferns and other moisture-loving plants. *L. perennis* is evident in this area in May and June. The Asphalt unit is characterised by sandy open landscape with pitch pine, wild blue lupin, scrub oak and blueberry. A summary of each management unit topography is in Table 1. In spite of local differences all of the burn units had similar fuel load profiles, characterised by a pine litter dominated fuel model (i.e. fuel model two, Anderson 1982).

Calibration

Standards of (+)-α-pinene (α-pinene; $C_{10}H_{16}$; 98%; St. Louis, MO, USA), (−)-β-pinene (β-pinene; $C_{10}H_{16}$; 99%; St. Louis, MO, USA) and R-(+)-limonene (limonene; $C_{10}H_{16}$; 97%; Toluca, Mexico) were purchased from Sigma-Aldrich. Ultra-pure water was obtained from a Milli-Q water purification system from Merck Millipore (Burlington, MA, USA). The calibration standards were used to prepare individual standard solutions and one mixture of tree terpenoids (α-pinene, β-pinene and limonene), which were used to calibrate the OP-FTIR system in order to acquire their IR spectra and identify possible interferences. Furthermore, library references were also used on the OP-FTIR system for limonene, α- and β-pinene, obtained from the published quantitative Hanst database. To create instrument-specific gas references, an internal 10 m gas
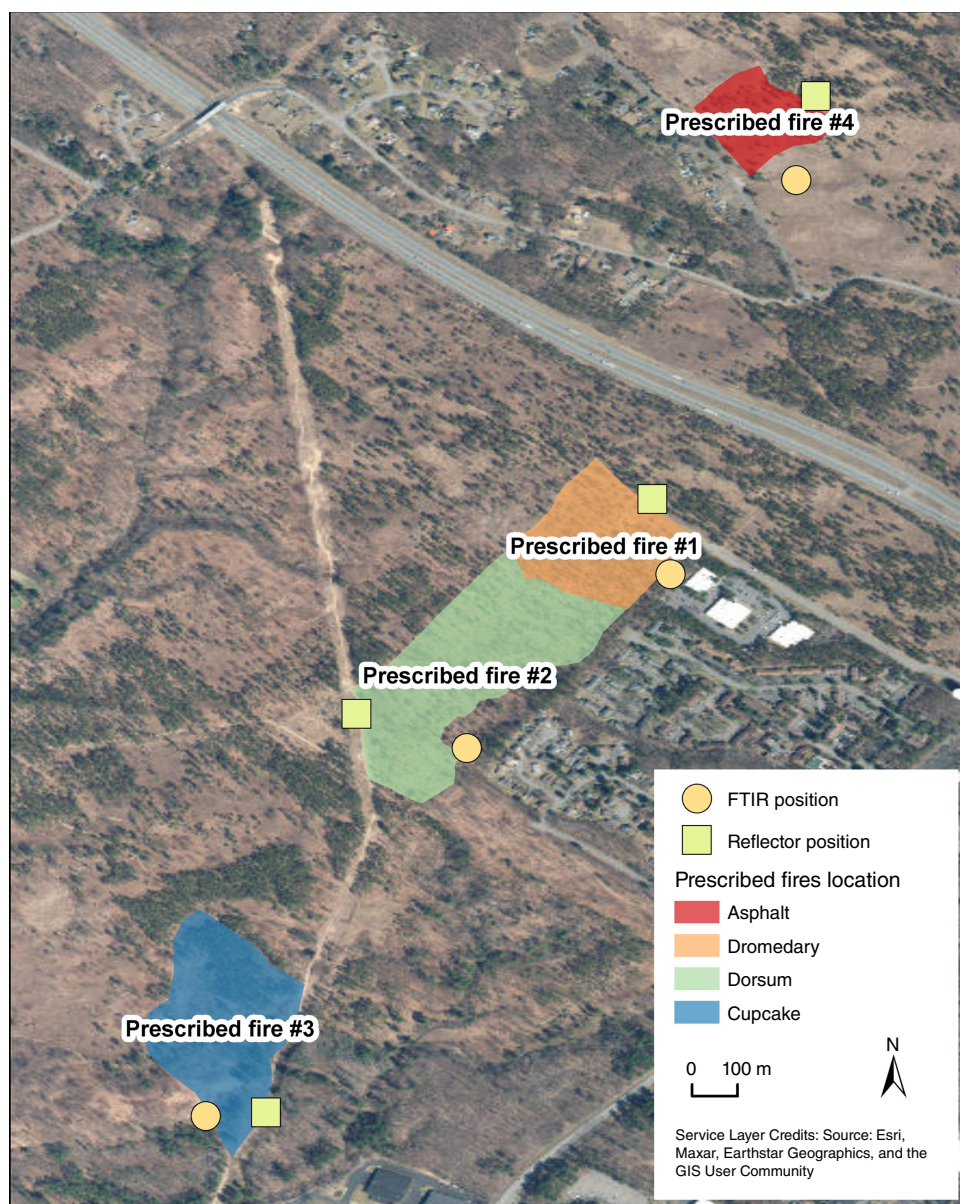
Fig. 1. Location of the prescribed fires and the position of the OP-FTIR equipment and reflector in each fire location.

cell attachment was installed into the OP-FTIR for qualitative assurance. The new references uniquely match the OP-FTIR for both the resolution, interpolation, and detector-response characteristics. The process to create the instrument-specific references was as follows: (1) pull a vacuum over the acquiesce sample to create a vapour with the target chemical; (2) extract the vapour sample into the 2-L internal gas cell installed into the OP-FTIR, the 10 m cell allows the IR beam to pass through the sample 40 times; (3) analyse the sample by comparison with the Hanst library database reference of known concentration; and (4) install the quantified sampleas a reference library to quantify other field data collected during the trial burns. This process of reference calibration through the use of an real reference standard allows a more accurate field measurement. There is a small unknown amount of quantitation uncertainty if relying exclusively on digital library references. This unknown amount of uncertainty due to the instrument specific parameters is smaller when the concentration of the target chemical measured in the field data is close to the concentration of the library reference. When the concentration of the target chemical is very low (or high) in comparison, those parameters contribute a relatively larger influence over the shape of the absorbance features, which can result in a larger error in the quantified concentration. To reduce this uncertainty, a gas-cell was used taking advantage of strong absorbance features of the library reference to quantify and assign the concentration of the newly created instrument specific reference under more ideal conditions. By flowing the known target chemical into the gas-cell in

Table 1. Characterisation of the prescribed burns conducted at the Albany Pine Bush Preserve, New York, US.

Burn name and location	Date of measurements	Weather	Maximum temperature (°C)	Maximum humidity (%)	Dewpoint (°C)	Transport winds (km h⁻¹)	Burned area (ha)	Dominant species
Dromedary; Madison Avenue Pinelands (trailhead #7)	24 May 2022	Partly sunny (45–55%)	20	42	5.5	North-east 9.7–12.9	5.3	*Pinus rigida; Quercus ilicifolia; Lupinus perennis*
Dorsum; Madison Avenue Pinelands (trailhead #7)							10.1	*Pinus rigida; Quercus ilicifolia; Lupinus perennis*
Cupcake; Great Dune (trailhead #8)	25 May 2022	Mostly sunny (40–50%)	24	40	8.3	South 4.8–8.0	4.0	*Pinus strobus; Pinus rigida; Quercus coccinea; Quercus rubra; Quercus ilicifolia; Corylus americana; Fagus grandifolia; Acer rubrum; Quercus spp. regeneration*
Asphalt; (Antelope South) Truax Trail Barrens (trailhead #12)	26 May 2022	Partly sunny (55–65%)	24	42	6.6	South 22.5–37.0	3.9	*Pinus rigida; Quercus ilicifolia; Lupinus perennis; Vaccinium corymbosum*

relatively high concentration abundance, the newly created reference will have spectral absorbance shape features, which include instrument matching parameters. Ultimately, the concentration of that newly created reference is determined by CLS method. The newly created site-specific reference is applied in the same manner as the stored digital library reference, relying on the CLS algorithm to quantify the field data. Note that the CLS technique is applied in the same manner to the newly created reference as was with the original digital reference.

Results and discussion

Assessment of OP-FTIR measurements at Albany Pine Bush Preserve

VOC emitted during the test fires

The behaviour of volatiles emitted during the combustion of *P. strobus* and *P. rigida* branches was studied through small test fires set at the Albany Pine Bush Preserve. Volatile emission patterns were unique for each test fire (Fig. 2). With the inclusion of tree branches, rapid combustion ensued, emitting the monitored volatiles, notably evident following branch placement in Fig. 2*b* and *d* (marked as 'i'). Subsequently, tree needles ignited aggressively upon being introduced to the fire, producing a surge of volatiles persisting for 1–4 min.

The target volatile compounds tended to increase and decrease in similar patterns with a major emission mid-way through each test burn and a decline towards the end. This suggests that each of the volatiles is being emitted synchronously when the tree branches and needles burn, implying that the biomass was completely burned, and that the major volatiles stored inside the tree leaves and branches were completely emitted. Similar results have been reported for the emission of CO and CO_2 during thermal degradation of *U. europaeus* leaves (de Castro *et al.* 2007), which suggest that the emission of VOC and GHG during thermal degradation is identical, regardless of vegetation type.

Overall, it is possible to observe that VOC emissions (i.e. α-pinene, β-pinene and limonene) from the *P. strobus* test burns (Fig. 2*a, b*) were more than 2-times higher than *P. rigida* (Fig. 2*c, d*). The maximum emitted concentration of VOC and CO by *P. strobus* were of 1131 and 5259 $\mu g\,m^{-3}$, respectively, compared to 638 and 2718 $\mu g\,m^{-3}$ emitted from *P. rigida*. This indicates that *P. strobus* branches and needles have higher amounts of the target VOC when compared with the *P. rigida*, and thus might release higher concentrations when ignited. Moreover, *P. strobus* emissions contained more β-pinene and limonene, while *P. rigida* pyrolysis had higher α-pinene concentrations (Fig. 2*c*). The maximum VOC emitted concentration measured are in agreement with the values reported by Antonelli *et al.* (2020) for *P. sylvestris* forests ($< 12.2\,mg\,m^{-3}$). In contrast, both species showed relatively low emissions of NH_3, CH_4,
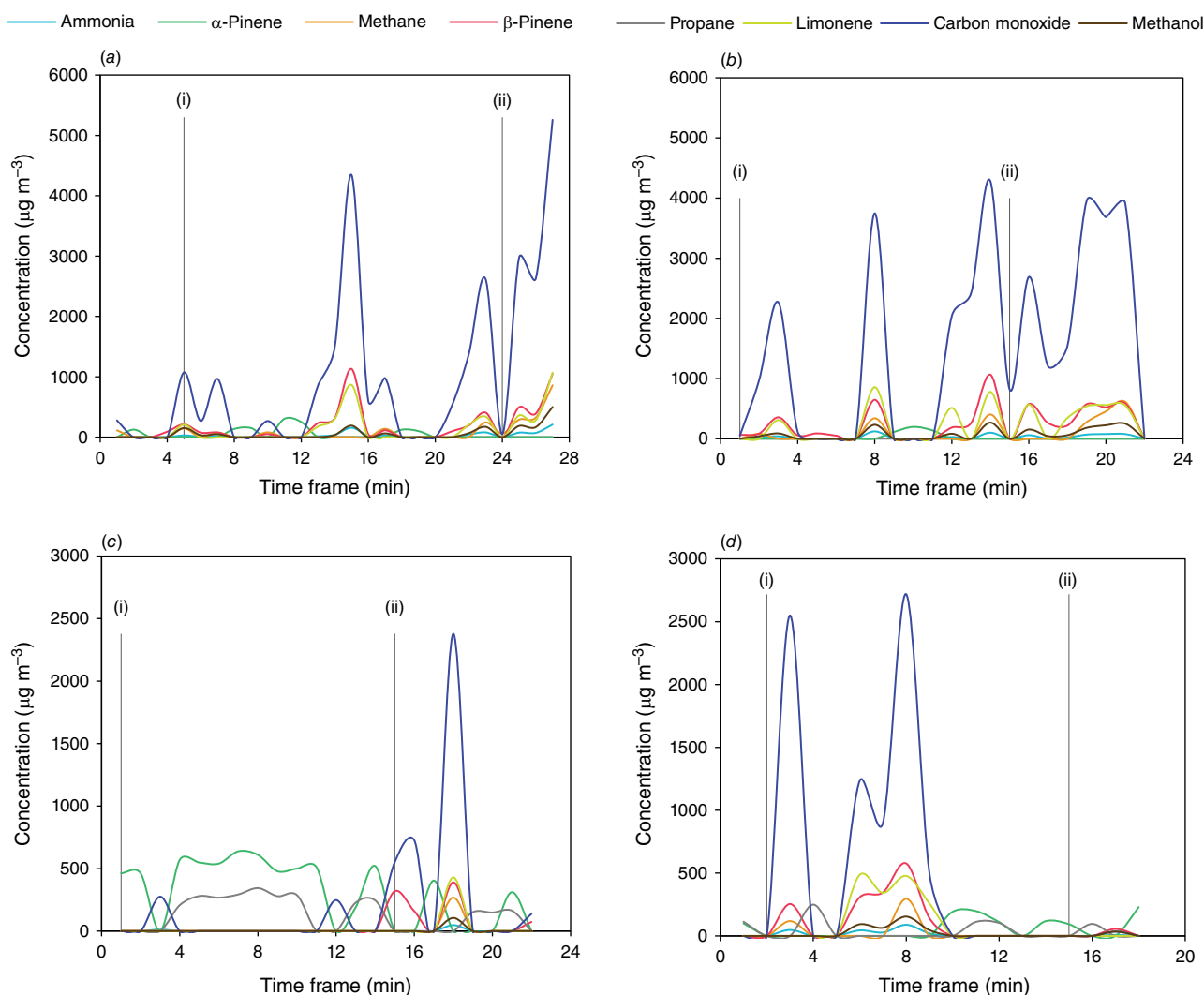
Fig. 2. Concentration of VOC and CO detected in two OP-FTIR assays of test burns conducted using branches and needles of *P. strobus* L. (*a*, *b*) and *P. rigida* Mill. (*c*, *d*). Vertical lines indicate the start (i) and end (ii) of the addition of branches.

propane and methanol (i.e. maximum values of approximately 207, 861, 350 and 500 µg m^{-3}, respectively). These concentrations are in accordance with those reported by de Castro *et al.* (2007), especially for NH$_3$. Those authors also reported an emission ratio of NH$_3$ (6%) and CH$_4$ (20%) in comparison to CO. Additionally, it was confirmed that with the exception of CO$_2$, CO was the most abundant GHG emitted during biomass pyrolysis, with an emission ratio of approximately 5:1 for CO$_2$:CO. These correlations show that, even when using different vegetation species, the OP-FTIR analytical approach is consistent with previous studies for most GHG, and is adequate for the study of the selected VOC.

VOC emitted during the prescribed fires

After evaluating OP-FTIR on test fires, measurements during prescribed fires were performed at the Albany Pine Bush Preserve in four different management units (Dromedary, Dorsum, Cupcake, Asphalt). The operations were conducted to reduce litter and duff by 10%, reduce shrub cover by 80%, reduce slash from mechanical fuel reduction treatments and expose mineral soil over 30% of the site. The measurements for CO$_2$ were compromised by its high background concentrations and reduced the sensitivity of the OP-FTIR method. Thus, the analytical thresholds (i.e. MDL) obtained for all the compounds during the prescribed fires ranged from 0.01 to 655.17 µg m^{-3} (Table 2).

The Dromedary prescribed fire was ignited at 19 min (i), when no volatile compounds emissions were detected (Fig. 3*a*, *b*). However, after the fire reached the OP-FTIR pathway (ii), VOC started to being detected and the analytical signal increased rapidly, giving a first peak of emission at minute 34 (total volatiles, 1294 µg m^{-3}). A secondary peak was then observed at 51 min (iii; total volatiles, 2713 µg m^{-3}), close to the end of the ignition. Smoke from the fire continued and recordings stopped at minute 60. To take advantage of the favourable weather conditions, the

Table 2. Analytical thresholds of the compounds measured during test and operational prescribed fires.

Compound	Limit of detection ($\mu g\,m^{-3}$)							
	Test fire 1	Test fire 2	Test fire 1	Test fire 2	Operational prescribed fires			
	P. rigida Mill.	*P. rigida* Mill.	*P. strobus* L.	*P. strobus* L.	Dromedary	Dorsum	Cupcake	Asphalt
Carbon dioxide	655.17	655.17	341.38	379.31	140.00	227.51	23.65	11.76
Ammonia	0.26	0.19	0.17	0.13	0.02	0.02	0.01	0.01
α-Pinene	0.76	0.59	0.69	0.55	0.14	0.23	0.06	0.04
Methane	2.24	2.00	1.45	1.66	0.40	0.35	0.17	0.12
β-Pinene	0.45	0.33	0.38	0.31	0.07	0.13	0.03	0.02
Propane	1.90	0.86	0.83	0.66	0.15	0.25	0.07	0.05
Limonene	0.52	0.38	0.45	0.34	0.09	0.15	0.04	0.02
Carbon monoxide	5.86	2.69	0.83	0.62	0.09	0.16	0.04	0.03
Methanol	0.55	0.38	0.38	0.33	0.04	0.05	0.04	0.02

Dorsum fire was ignited almost immediately after the Dromedary unit burn concluded. As observed in Fig. 3c, d, a major emission peak was observed at minute 15 (total volatiles, $4492\,\mu g\,m^{-3}$) suggesting that the fire approached the OP-FTIR pathway shortly after data collection started. The end of the ignitions was around Minute 20, although recordings continued until minute 90, and documented smoke from smouldering combustion. There were no high volatiles emission peaks observed prior to ignition of the Cupcake fire (I; Fig. 3e, f). As in the previous fires, a sudden increase of the volatiles was observed after the fire crossed the OP-FTIR pathway (ii), showing the higher emission peak at 99 min (total volatiles, $6187\,\mu g\,m^{-3}$). Lower amounts of VOC were released as burning abated as recorded until Minute 187. For the Asphalt unit (Fig. 3g, h), concentrations of VOC were lower than the other three units with a major emission peak near the end of the combustion, observed at Minute 41 (iii; total volatiles, $834\,\mu g\,m^{-3}$). This may have resulted from the high wind velocities ($22.5–37.0\,km\,h^{-1}$) and higher dispersal of volatiles. The fluctuating wind direction may also have contributed to the unique and variable emission pattern. The highly variable wind, fire intensity and smoke dispersal caused the cessation of burning at Minute 41 and termination of recording at Minute 63. In general, both CO and VOC had similar emission behaviour. Nevertheless, the absolute concentration of these two compounds differed between the four fires. Moreover, the VOC concentrations were higher than those previously reported for fire and non-fire conditions (Janson 1992; Wentworth *et al.* 2018; Antonelli *et al.* 2020; Piel *et al.* 2021). It is likely that patterns correspond to distinct dispersion processes where higher wind speeds correspond to higher dispersion and low CO and VOC detection.

In general, all the prescribed fires featured an initial release boost of volatiles immediately after ignition, with high concentrations occurring when smoke was within the OP-FTIR pathway. Additionally, the volatile behaviour observed during the prescribed fires included high CO emissions ($\leq 4553\,\mu g\,m^{-3}$) as well as β-pinene and limonene ($\leq 1605\,\mu g\,m^{-3}$), followed by medium methanol, NH_3, and CH_4 emissions ($\leq 698\,\mu g\,m^{-3}$) and, finally, by smaller propane and α-pinene concentrations ($\leq 311\,\mu g\,m^{-3}$). These results agree with those from test fires with pine branches and needles confirming the importance of limonene, α-pinene and β-pinene as the main VOC emitted from fire.

Relations between CO₂, CO and VOC

When fuels are completely combusted, CO_2 and water vapour are the only end products remaining. However, during most wildfires, combustion is incomplete and they generate a mixture of gases, including CO_2, CH_4, and CO. These conclusions were reported in the previous sections, where products of incomplete combustion and VOC were as detected by OP-FTIR during prescribed fires. The relationship between CO_2 and CO concentrations for the four prescribed fires (Fig. 4) was used as an index of completeness of combustion. Thus, the linear relationship derived from the four prescribed fires, make it possible to predict CO_2 concentrations from measured CO concentrations or vice versa. This relationship is estimated by Drysdale (2011) and Ward *et al.* (1996), which is based on the mole ratio of carbon released as CO_2 to the sum of the moles of carbon released as CO_2 and CO.

From the analysis of Fig. 4, it seems that CO concentrations are around 1% of CO_2 concentrations (obtained by the equation $y = 0.0109 \times$; with a $R^2 = 98\%$). This percentage indicates a very high completeness of the combustion process where oxygen from wind is not a limiting factor for fire. Wooster *et al.* (2011), described CO concentrations of around 9–12% of CO_2 concentration during open vegetation fires. The present study reported higher emission factors for CO, which indicates that the four case study burns had relatively high degree of combustion processes.

Given the main objective of the study, it was pivotal to establish correlations between CO concentrations, which are
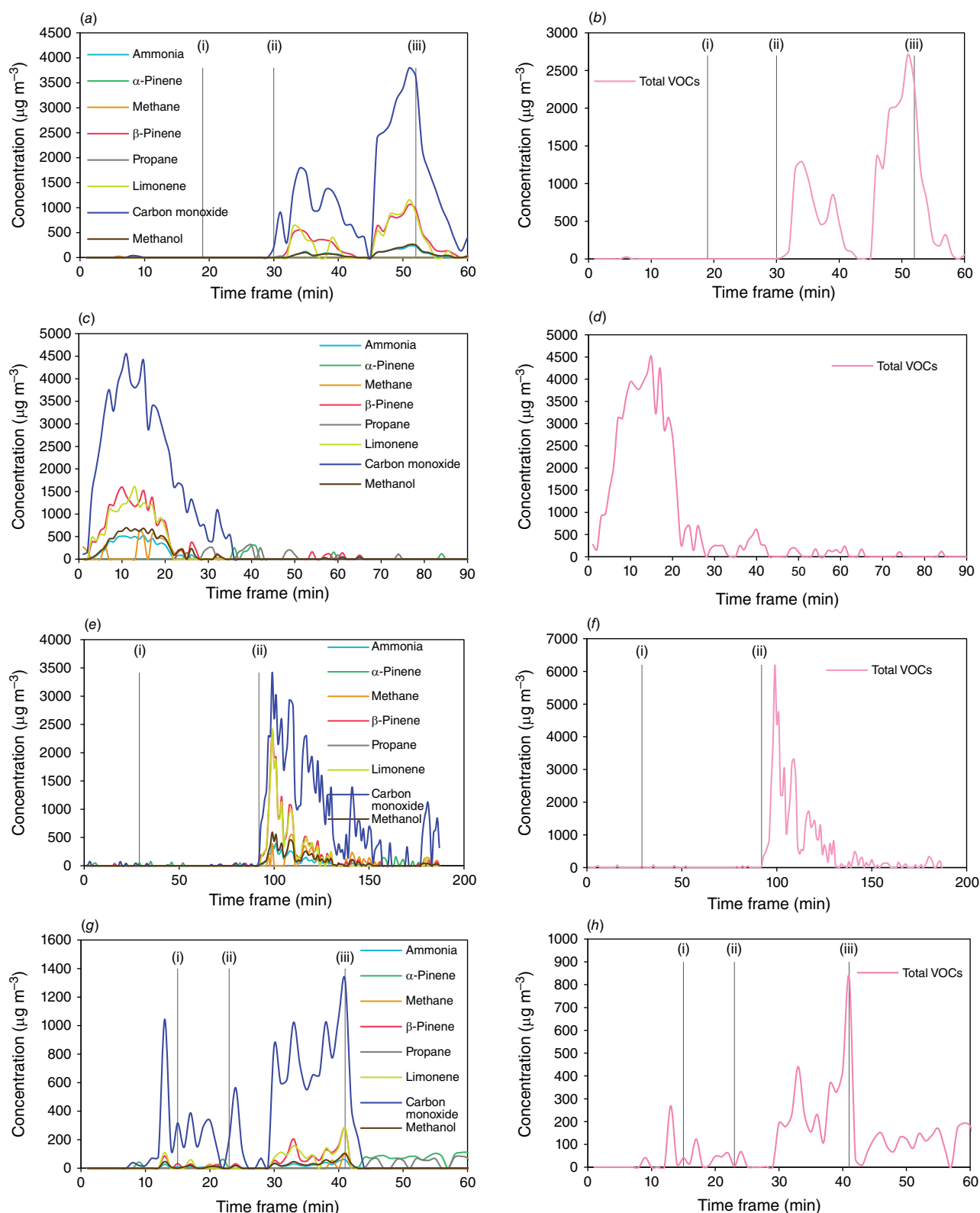
Fig. 3. Concentrations of individual and total VOC (excluding CO) emitted during the Dromedary (*a*, *b*), Dorsum (*c*, *d*), Cupcake (*e*, *f*), and Asphalt (*g*, *h*) prescribed fires. Vertical lines indicate the start of the fire (i), the instant the fire crossed the OP-FTIR pathway (ii) and the end of combustion (iii).

commonly measured in prescribed fires, and total volatile concentrations, which are not (Fig. 5). The relation between CO and VOC concentrations measured in open field conditions were well related during the four prescribed fires ($\sim R^2 > 0.8$) using a second order regression with no intercept (Fig. 5). The lower fit of the Asphalt prescribed fire may have resulted from more variable wind conditions. The capacity to estimate total volatiles from CO measurements has potential assist in modelling the possible effects of VOC release on fire behaviour.
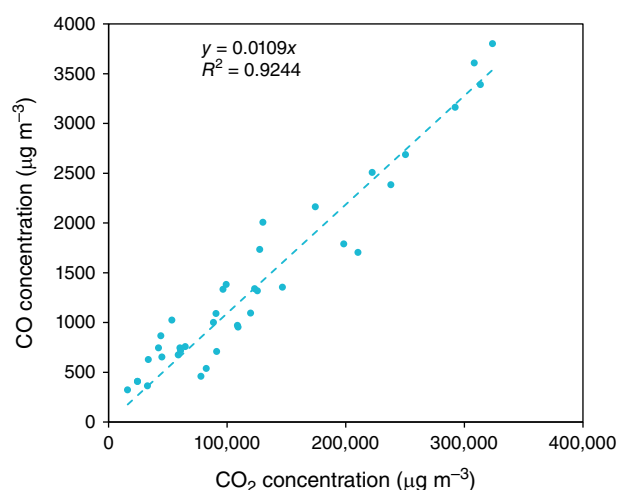
Given the high correlation with products of combustion, the VOC measurements may be included the monitoring and management risk in wildfire-prone forests. In this sense, monitoring of VOC concentrations related to vegetation temperature and its heating may improve the estimations of fire risk as well as the likelihood of wildfire occurrence.

Conclusion

This case study advances the understanding of VOC and GHG emissions during prescribed fires by using OP-FTIR advances as monitoring tool. The site and prescribed burning conditions at Albany Pine Bush Preserve, USA provided insights into how fuel types, topography, and wind influence burning in pine-dominated ecosystems.

The OP-FTIR results demonstrate the potential of the approach by providing qualitative and quantitative information. Analysing the responses of various products' concentrations (i.e. CO_2, CO, CH_4, NH_3, α-pinene, β-pinene and limonene) to different fire behaviour, site, and fuel conditions, has enabled the establishment of overarching relationships. These findings hold the potential to enhance predictive capabilities concerning extreme fire events. Specifically, the use of OP-FTIR measurements allows us to infer:

Fig. 4. Correlation between CO and CO_2 concentrations emitted during four prescribed fires.

(1) Data acquisition by OPS-FTIR (i.e. infra-red spectra and concentrations of selected VOC and GHG) is
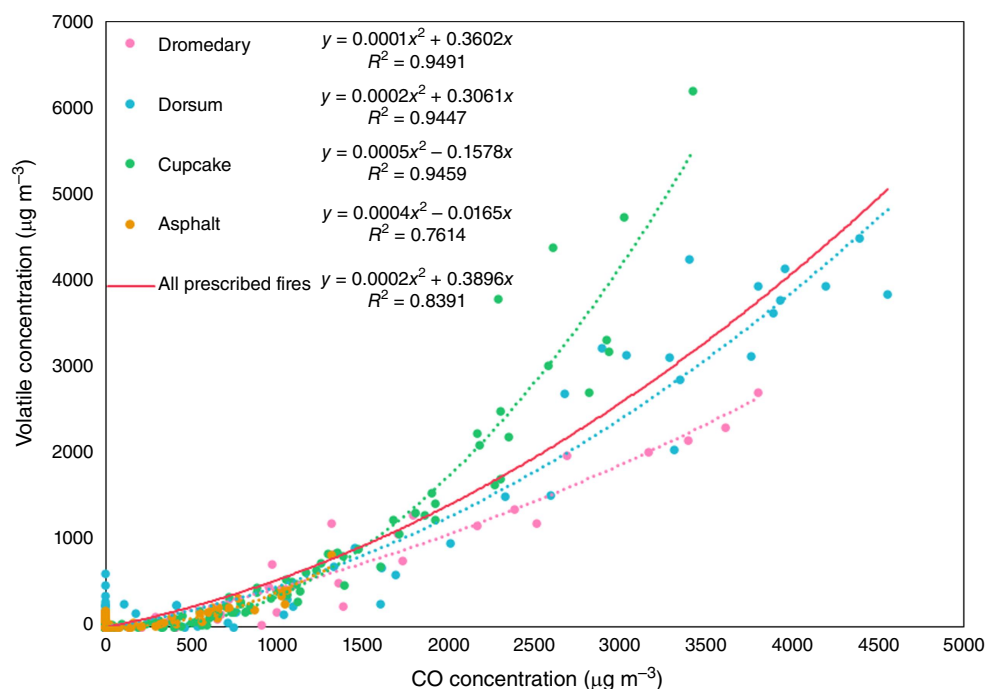

Fig. 5. Total VOC concentration (ammonia, α-pinene, methane, β-pinene, propane, limonene and methanol) in relation to CO concentrations during four prescribed fires and all fires combined. All zero values in the *y*-axis were excluded.

independent of the type fuel, but dependent on wind and distance to the detector.

(2) Combustion products and VOC display similar behaviour during thermal degradation; VOC are emitted as the tree branches and needles are burned, showing major emissions initially that decline and cease when combustion terminates.

(3) Volatile concentrations seem independent of the type of biomass burned.

(4) The VOC profile of *P. strobus* is two orders of magnitude higher than *P. rigida*, with CO, β-pinene, and limonene as the main contributors, followed by methanol, NH_3, and CH_4 emissions and, finally, by smaller propane and α-pinene concentrations.

(5) The strong non-linear correlation between VOC and CO ($R^2 = 0.84$) suggests it may be feasible to amend existing models to consider the impact of VOC on fire behaviour.

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