Bushfire smoke plume composition and toxicological assessment from the 2019–2020 Australian Black Summer

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Received: 14 February 2022 / Accepted: 12 August 2022 / Published online: 8 September 2022 © The Author(s) 2022

Abstract

Many of the population centres in southeast Australia were swathed in bushfire smoke during the 2019–2020 austral summer. Bushfires burning during what is now known as the Black Summer was historically large and severe, and the fire season historically long. The chemical composition in the gas and aerosol phase of aged plumes measured near Wollongong, NSW in early 2020 is reported in this work. Enhancement ratios to carbon monoxide are presented for thirteen species (acetaldehyde, acetone, acetonitrile, black carbon aerosol, benzene, methane, methacrolein + methyl vinyl ketone, methyl ethyl ketone, methanol, ammonium ion PM1 fraction, nitrate ion PM1 fraction, organic PM1 fraction and PM2.5). Observed plume composition is comparable to that measured in fresh smoke from Australian fires reported in the literature. Enhancements of biogenic volatile organic compounds such as isoprene (smoke-effected period mean 1 ppb, maximum 6 ppb) were observed along with elevated concentrations of particulate variables. Enhancement ratios reported here can be used in plume modelling of landscape-scale fires and assist in concentration estimates of infrequently measured atmospheric pollutants. The relative toxicological contribution of species present in the plumes was determined for plume exposure at the measurement site and for concentrated plumes at a population centre case study. Similar results were apparent at both locations. Contributions to the toxicological loading were dominated by respirable particles (~52–63% total contribution), formaldehyde (~30–39% total contribution) and acrolein. This is a reminder to consider the toxicological contributions in the gas phase when considering health impacts of population exposure to bushfire smoke.

Keywords Wildfire smoke · Air quality · Atmospheric aerosol · Australian bushfires

Introduction

Biomass burning is the largest contributor to fine carbonaceous aerosol globally and the second largest emission source of atmospheric trace gases (Akagi et al. 2011). A significant portion of total biomass burning emissions can be attributed to emissions from wildfires, which provide a climatically relevant source of black carbon aerosol and greenhouse gases to the global atmosphere (Liu et al. 2014) and contribute to enhancements of air quality pollutants in densely populated areas (Carvalho et al. 2011). Australia is a region of global significance in the biomass burning field as fires occur frequently (van der Werf et al. 2006) and Australian emissions (expressed as TgC year\(^{-1}\)) are estimated to contribute 6–8% to the global biomass burning total (Kasischke and Penner 2004; van der Werf et al. 2006).

Biomass burning is estimated to contribute 53 ± 14% to Australia’s annual black carbon aerosol emissions (Qi and
Wang 2019). Savanna fires are the dominant contributor (83%) to biomass burning carbon dioxide (CO₂) emissions in Australia (Shi et al. 2015). Forest fires along the east coast of the Australian continent also contribute to biomass burning in Australia, responsible for 13% of biomass burning CO₂ emissions annually (Shi et al. 2015). These fires are more episodic in nature, with area burned varying significantly from year to year (Australian Government Department of Industry Science Energy and Resources 2020). The variability of fire weather is influenced by a number of inter-annual climatological processes, most notably the El Niño Southern Oscillation (ENSO) (Dowdy 2018; Harris and Lucas 2019).

The atmospheric impact of forest fire smoke along the east coast of Australia is reasonably well documented. Smoke from large fires in 2013 in the Blue Mountains region of New South Wales (NSW) was demonstrated to have had detrimental impacts on air quality as far away as Brisbane, Queensland as well as in closer population centres such as Sydney and Wollongong, NSW. (Duc et al. 2018). Emission factors (EFs) for CO₂, carbon monoxide (CO), nitrous oxide (N₂O) and methane (CH₄) were calculated for these fires using in situ Fourier transform infrared spectrometer (FTIR) measurements from Wollongong, NSW (Rea et al. 2016). Fresh smoke from the firegrounds of a series of prescribed burns throughout NSW and Victoria from 2010–2015 were measured by open path FTIR (Paton-Walsh et al. 2014). Modified Combustion Efficiency (MCE: \( \text{CO}_2/(\text{CO} + \text{CO}_2) \)) was observed for some species (Guérette et al. 2018). Filter measurements of particulate matter less than 2.5-µm diameter (PM₂.₅) and grab samples (Guérette et al. 2018). Emission factors were calculated for greenhouse gases and a large range of volatile organic compounds (VOCs) from these fires (Guérette et al. 2018; Paton-Walsh et al. 2014), and a dependence on Modified Combustion Efficiency (MCE: \( \text{CO}_2/(\text{CO} + \text{CO}_2) \)) was observed for some species (Guérette et al. 2018). Filter measurements of particulate matter less than 2.5-µm diameter (PM₂.₅) from the fireground of four prescribed burns in temperate eucalypt forest in Victoria, southern Australia have been used to produce emission factors for this air quality pollutant (Reisen et al. 2018). Measurements of trace species emitted by forest fire in south-eastern Australia have also been taken from satellite (Young and Paton-Walsh 2011; Paton-Walsh et al. 2008) and aircraft platforms (Hurst et al. 1996).

The negative health implications of exposure to smoke components are well known, e.g. (Lelieveld et al. 2015; Naeher et al. 2007; Pope III et al. 2002), specifically in the Australian context (Walter et al. 2020). Positive relationships between population exposure to forest fire smoke plumes and health metrics including adult asthma and chronic obstructive pulmonary disease hospital admissions (Morgan et al. 2010), non-accidental mortality (Johnston et al. 2011) and emergency ambulance dispatches (Salimi et al. 2017) have been observed in eastern Australian cities. Each of these studies uses particulate matter with diameter less than 10-µm (PM₁₀) measurements to define plume exposure. The majority of the negative health effect of exposure to bushfire smoke is attributable to the fine particulate pollution present in smoke (Johnston et al. 2012). Nevertheless, a recent study estimated the contribution of gas phase toxics to smoke toxicity and demonstrated that considering exposure to a range of air toxics is critical to determining health impacts of bushfire smoke in Australia (MacSween et al. 2020). Historically, particulate and CO pollution experienced in eastern Australia’s population centres is attributable to smoke events (Duc et al. 2018; Paton-Walsh et al. 2019; Keywood et al. 2015), with air quality outside of these events normally relatively good. However, the episodic influence of smoke is becoming more frequent, and more sustained air quality impacts have been observed recently (Di Virgilio et al. 2021; Ryan et al. 2021).

The 2019–2020 Australian bushfire season—known colloquially as the ‘Black Summer’—was amongst the most significant in Australia’s recent history, driven by historical dryness across the landscape coupled with meteorological conditions promoting wildfire (Nolan et al. 2020). It is estimated that 7.4 million hectares of temperate forest was burnt from October 2019 to February 2020 (Australian Government Department of Industry Science Energy and Resources 2020). Fires were widespread, stretching from near the NSW-Queensland border to the Gippsland region of Victoria, a distance of over 1000 km. The fires were featured prominently in global news reports, e.g. (BBC News 2020; Cave 2020). Smoke caused exceedances of air quality monitoring criteria pollutants on an unprecedented scale at sites across Australia’s east coast from Brisbane, Queensland (Queensland Government 2020) to Melbourne, Victoria (Environment Protection Authority Victoria 2020). During the fire season (October 2019–February 2020), PM₂.₅ concentrations exceeding the 95th percentile of historical daily mean values were observed by at least one monitoring station in Australia’s eastern states on 94% of days (Borchers Arriagada et al. 2020). A total of 417 (95% CI, 153–680) excess deaths have been attributed to exposure to smoke from the 2019–2020 bushfire season along with thousands of hospital admissions (Borchers Arriagada et al. 2020). These statistics demonstrate the 2019–2020 Black Summer bushfires in the temperate forests of southeast Australia were of unique magnitude, duration and severity.

Fire seasons similar to the 2019–2020 austral summer may become more frequent in the future. The frequency of fire weather in southeast Australia has increased in the past four decades likely due to the influence of anthropogenic climate change (Harris and Lucas 2019). A trend is also observed in the onset of fire weather, with dangerous conditions occurring earlier in the year (Dawdy 2018) lengthening the so-called ‘fire season’. Forest fire frequency and intensity in the Australian southeast are predicted to increase into the future in a
changing climate (Keywood et al. 2013). It is therefore critical to understand the chemical composition of smoke plumes impacting population centres and assess whether current exposure limits and public health messaging are appropriate.

The Characterizing Organics and Aerosol Loading over Australia (COALA-2020) campaign was a comprehensive atmospheric measurement campaign which occurred from January to March 2020 at Cataract Scout Park, close to Wollongong, NSW (Paton-Walsh et al. 2022). Whilst the primary objective of the campaign was to explore the relationship between biogenic VOC emissions and organic aerosol, the first 3 weeks of measurements were significantly impacted by bushfire smoke. The measured plumes were complex and contained smoke of various ages generated by multiple fires burning across the southeast Australian landscape (Mouat et al. 2021b).

This paper presents detailed measurements of bushfire smoke from the 2019–2020 fire season in the aerosol and gas phases. This dataset is the most comprehensive measurement of bushfire smoke from the historical 2019/2020 Australian bushfire season. This paper seeks to answer two scientific questions using these measurements:

1) Firstly, what was the chemical composition of aged smoke plumes from the Black Summer fires, such as those that impacted major population centres, and how does the composition compare to previously observed plumes in the region?

2) Secondly, what is the relative toxicological impact of each chemical species present in these plumes?

In this paper, we present enhancement ratios to the commonly measured atmospheric pollutant carbon monoxide (CO) for several trace gas and aerosol-phase chemical species. These enhancement ratios can be used to estimate the pollution levels of relevant pollutants throughout the air quality monitoring networks in eastern Australia wherever CO is measured and used in epidemiological studies quantifying the health impacts of the 2019/2020 bushfire season. Assessment of the relative toxicological contribution of chemical species observed in smoke plumes that impacted Australia’s major cities is also made using current exposure limit concentrations. The methodology and results of composition determination will be presented first, followed by the methodology and results of toxicological impact determination and finally the application of this preceding work to a case study in Canberra, Australia.

**Determining smoke composition**

Cataract Scout Park (34°14′44″S, 150°49′26″ E), at which the COALA campaign took place, is located 20 km north-northwest of Wollongong on the east coast of NSW, Australia. The site is marked on the map presented in Fig. 1. The areas surrounding the site are heavily forested. Eucalypt species dominate the canopy. There are numerous longwall (underground) coal mine heads close to the measurement site. The Appin Colliery is approximately 1.5 km to the north-northeast, and the West Cliff Colliery approximately 2.5 km to the north. This site was selected for the COALA campaign as the primary objective of the campaign was to learn more about biogenic VOC emissions and secondary organic aerosol (SOA) formation from southeast Australian eucalypt forest.

The COALA campaign was conducted from January 17th till March 23rd, 2020, covering the second half of the Australian summer and the start of Autumn. Measurements presented in this study span from the beginning of the campaign until February 5th, a period of 20 days. This period will hence be referred to as the ‘smoky period’. A widespread significant rain event occurred in NSW beginning on February 7th, “cleaning” the local atmosphere of smoke and extinguishing most fires in the state (Bureau of Meteorology 2020). All dates and times are reported in local (Australian Eastern Daylight) time.

**Instrumentation**

Detailed descriptions of all instruments used in COALA are provided in an overview publication (Paton-Walsh et al. in prep.). This publication focuses on particle-phase and VOC measurements of bushfire smoke. Instruments used heavily in the present analysis are described below. All measurements were averaged to 1-min time resolution for analysis.

A Spectronus Fourier Transform Infrared Spectrometer (FTIR) (Griffith et al. 2012) was used to make continuous, high-precision measurements of CO₂, CO, CH₄, N₂O, δ¹³C in CO₂ and δ¹⁸O in CO₂ (Griffith et al. 2021). This instrument measures each trace gas simultaneously at 2-min resolution. It functioned near-contiguously for the measurement period. Ambient air was drawn through approximately 7 m of ¼” Dekabon tubing from an inlet 4.7 m above ground level, before being dried by Nafion dryer and magnesium perchlorate before passing into the instrument. The instrument was calibrated before and after the campaign, and a reference cylinder was measured each day to account for any drift in the calibration. The instrument ran for the majority of the campaign, excepting during a power failure that occurred on February 7th.

A TSI 3776 Ultrafine Condensation Particle Counter (UCPC) was used to measure condensation nuclei number concentration greater than 3 nm (CN₃) (TSI Incorporated, Shoreview, MI, USA) (Keywood et al. 2020). The instrument was operated at a sample flow rate of 300 mL min⁻¹. Sample air was drawn from a common aerosol bypass inlet.
The inlet was located 5 m above ground level. Measurements were recorded at 1-Hz temporal resolution.

A Scanning Mobility Particle Sizer (SMPS) was used during COALA to measure aerosol size distribution between 14 and 670-nm mobility diameter (Humphries et al. 2021). Full scans of this size range were recorded every 5 min. The system consisted of an X-ray aerosol neutralizer and 3071 Long Electrostatic Classifier (TSI Incorporated, Shoreview, MI, USA) coupled to a 3772 CPC (TSI Incorporated, Shoreview, MI, USA). Sample was drawn from the same inlet as used by the UCPC.

The 5012 Multi-Angle Absorption Photometer (MAAP; Thermo-Fisher Scientific, Waltham, MA, USA) is used to measure the concentration of black carbon (BC) aerosol (Keywood et al. 2021). Sample was drawn down a ½" inlet at 1000 L min⁻¹. Measurements of black carbon aerosol concentration were recorded at 1-Hz resolution. The inlet was located 4.8 m above ground level, within 1 m of the aerosol inlet, and equipped with a PM₁₀ inlet cap.

An air quality monitoring station (AQMS) owned and operated by the NSW Government Department of Planning, Industry and Environment was installed at Cataract Scout Park for the COALA campaign (Gunahanhar et al. 2021). This station included measurements of temperature, wind speed, wind direction, PM₁₀, PM₂.₅, ozone (O₃), sulphur dioxide (SO₂), oxides of nitrogen (NOₓ), CO and visibility. NSW air quality stations are accredited by the National Association of Testing Authorities and use Standards Australia methods for ambient air quality measurements where possible (Department of Planning Industry and the Environment 2020). Further details of specific measurement techniques are available on the Department’s website (Department of Planning Industry and the Environment 2020). Inlet heights for the station were as follows (metres above ground...
level): temperature: 4.5 m, wind: 5.6 m, PM$_{10}$: 4.9 m, PM$_{2.5}$: 4.9 m, gases: 4.7 m.

A Proton Transfer Reaction Time-of-Flight Mass Spectrometer (PTR-ToF–MS) (Ionicon 4000; Ionicon Analytik Ges.m.b.H., Eduard-Bodem-Gasse 3, 6020 Innsbruck, Austria) was used to retrieve concentrations of VOCs during COALA (Mouat et al. 2021a). Sample air was drawn from an inlet on a 10-m mast, down a 20-m PTFE inlet line using a bypass flow of 1.5–3 L min$^{-1}$. Calibration occurred in situ using standard cylinders and is reported with an uncertainty of ±20%. Further details of instrumental parameters and calibration processing can be found in Mouat et al. (2021b). Deployment of this instrument was delayed due to airfreight cancellations following a volcanic eruption near Manila in the Philippines, and measurements began on February 2nd. As a result of this delay, there are only 2 days of VOC measurements when significant smoke impacted the measurement site.

Measurements of particulate matter with diameter smaller than 1 µm (PM$_{1}$) aerosol composition were taken using a Time-of-Flight Aerosol Chemical Speciation Monitor (ACSM; Aerodyne Research Inc., Billerica, MA, USA). Mass concentrations of Organics (Org), sulphate (SO$_{4}^{2-}$), nitrate (NO$_{3}^{-}$), ammonium (NH$_{4}^{+}$) and chloride (Cl$^{-}$) in the aerosol fraction 40–1000-nm vacuum aerodynamic diameter range, referred to as PM$_{4}$, are reported. Measurements were taken at 10-min resolution and down sampled to 1-min resolution using cubic spline interpolation. Sample was drawn from the aerosol inlet common to the CPC and SMPS and dried using a Nafion dryer to <40% RH before sampling.

Further instrumental and sampling information are available in the metadata associated with the published data archive for each measurement set. Please see the Data Availability Statement for details.

**Determination of enhancement ratios and emission factors**

An enhancement ratio describes the way the concentration of a selected pollutant scales with the concentration of another reference pollutant during a period in which both pollutants are enhanced above the local background concentrations. Enhancement ratios provide a useful way of characterizing the composition of a plume without having to deploy specialised and expensive instrumentation, e.g. (Lonsdale et al. 2020; Decker et al. 2021). In the present analysis, the trace gas CO was selected as the reference pollutant. This is a very common choice, e.g. (Rea et al. 2016; Keywood et al. 2015) as CO concentrations are often measured at air quality monitoring stations globally. Although the largest Australian source is secondary chemistry production (Fisher et al. 2017), CO has a large biomass burning source in Australia. Enhancement ratios were calculated by fitting a linear regression to a correlation plot between the mole fraction of the pollutant of interest $x$ and the mole fraction of CO. The enhancement ratio of $x$ to CO can be taken as the gradient of the line of best fit. Although an orthogonal regression as used in previous studies (Guérette et al. 2018), weighting the regression for uncertainties in $x$ and $y$ may be most appropriate for this kind of analysis, estimates of precision for each individual species (as required for orthogonal regression) were not readily available in the present study. The high precision of the CO measurement and the location of this measurement of the $x$-axis also increase the suitability of simple linear regression for this study as this regression minimises residuals in $y$. Uncertainties quoted are total uncertainties.

The type of regression used has been shown to have limited influence on the value of the slope of the line of best fit (Wu and Yu 2018) where strong correlations are observed. As enhancement ratios were determined only for periods of strong correlation ($R^2 > 0.7$), in this analysis a simple linear regression was used. Further to this, the extremely tight correlations between CO and other atmospheric species as presented in Fig. 2 and very precise measurements captured by the FTIR (Griffith et al. 2012) mean that the expected real variability in enhancement ratios is much greater than the measurement uncertainty for this analysis. This method of determining enhancement ratios is only reliable when correlation between the species of interest and the reference species is high, as this implies limited influence from other atmospheric sources on the species in question. Previous studies have applied this method of enhancement ratio calculation only in cases where $R^2 > 0.5$ (Sinha et al. 2003; Desservettaz et al. 2017). Given the complexity of the smoke plumes observed during the present study, a stricter limit of $R^2 > 0.7$ has been applied. An advantage of calculating enhancement ratios from the slope of correlation plots is that no assumptions with respect to the site background must be made (Desservettaz et al. 2017), which is important at the Cataract site as many proximal sources of measured species were present which made determining an atmospheric background concentration difficult. Following the exclusion of relationships without strong $X$:CO correlation, some events were excluded manually after examination of the correlation plots.

Enhancement ratios were calculated event-wise. Events were identified as periods of strong correlation between known smoke tracers (e.g. CO, black carbon aerosol, acetonitrile) using a series of iterative plots. Correlation plots showing strong relationships between CO and other atmospheric species are presented for the example event Smoke 1 in Fig. 2. Similar plots for other events are presented in the supplement as Figure S1. Details of the timing of each smoke event, along with summary tables of enhancement ratio values, are presented in supplementary Tables S1 and S2 respectively. Sixteen events were identified and assigned
alphabetical names. A ‘dilute smoke’ characterization was assigned to periods between identified events. This category is distinct from the true background air of the region as CO, and black carbon aerosol remained present at concentrations significantly above measurements taken following the heavy rain which occurred February 7–9th. Identified events along with the ‘dilute smoke’ periods (grey) are plotted in Fig. 3. The PTR-ToF–MS began sampling on February 2nd, capturing events Smoke I and later.

The final enhancement ratio reported for each species is the mean slope for all events for which the relationship between $x$ and CO was sufficiently strong to meet the criteria for inclusion. The standard deviation, range and number of events included in this calculation are also presented. These values are reported in Table 1.

Emission factors for some species were also calculated. Emission factors for CO, CO$_2$ and CH$_4$ were determined for the only period where correlations between all three

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**Fig. 2** Correlation plots to CO for well-correlated measured species during the Smoke I event (February 4th, 2020, 03:11–05:12 AEDT). Slope and $R^2$ values are presented in supplementary Table S2. The aerosol:CO relationships are less strong than VOC:CO relationships, indicating variability in observed aerosol concentrations. For included species, the linear fit has been determined to be sufficient to capture the aerosol:CO enhancement ratio.
species were very strong ($R^2_{\text{CO,CO}_2} = 0.90$, $R^2_{\text{CO,CH}_4} = 0.98$, $R^2_{\text{CO}_2,\text{CH}_4} = 0.90$), overnight on February 5th. The dilute nature of the sampled plumes, coupled with the surrounding biogenic sink for CO$_2$, led to a decoupling of the expected relationship between CO$_2$ and CO in sampled smoke. The approach taken by Mouat et al. (Mouat et al. 2021b) was used to calculate emission factors for CO, CO$_2$ and CH$_4$, where the enhancement ratio of the focus species is ratioed to the sum of the enhancement ratios of CO, CO$_2$ and CH$_4$. This result is then multiplied by a fuel carbon content and the ratio of the focus species molecular mass to the molecular mass of carbon. Calculated emission factors for CO (99 g kg$^{-1}$ fuel), CO$_2$ (1665 g kg$^{-1}$ fuel) and CH$_4$ (4 g kg$^{-1}$ fuel) are comparable to mean values reported by Paton-Walsh et al. (2014) for a series of hazard reduction burns in similar forest types. This adds confidence to the use of a single period for the calculation of emission factors for these species. Emission factors for black carbon aerosol, PM$_{2.5}$ and selected PM$_1$ fractions were determined by multiplying observed enhancement ratios to CO by the emission factor to CO determined from the measurements. To compensate for the lack of variability in CO emission factors calculated in this study, the relative error for the CO emission factor is taken from Paton-Walsh et al. (2014) and added in quadrature to the variance in focus species enhancement ratio to provide uncertainty in reported emission factors as presented in Table 2. Emission factors for long lived VOC species determined from PTR-ToF–MS measurements taken during COALA-2020 are published in Mouat et al. (2021b).

![Fig. 3 Timeseries of CO concentrations from the smoky period of COALA-2020 (January 17th–February 5th, 2020). Highlighted sections of the trace correspond to identified smoke events where strong relationships exist between species emitted by biomass burning (e.g. CO, black carbon aerosol and acetonitrile)](image)

Table 1 Mean enhancement ratios of measured atmospheric species to CO, reported with the standard deviation, range and comparable literature value. The number of events included in analysis is dependent on the existence of a strong ($R^2 > 0.7$) relationship between the species and CO during a smoke event.

| Species | Mean enhancement ratio (units/ppb) | Standard dev. (units/ppb) | Range (units/ppb) | Number of events | Lit. value (units/ppb) | Source of lit. value |
|---------|-----------------------------------|---------------------------|-------------------|----------------|-----------------------|---------------------|
| Acetaldehyde | 3.2E–03                         | 1.3E–03                   | 3.3E–03          | 7              | 7.0E–03               | Guérette et al. (2018) |
| Acetone    | 2.9E–03                         | 1.1E–03                   | 2.3E–03          | 5              | 3.4E–03               | Guérette et al. (2018) |
| Acetonitrile | 9.6E–04                        | 2.5E–04                   | 6.6E–04          | 6              | 5.0E–04               | Paton-Walsh et al. (2014) |
| Black carbon aerosol | 4.0E–03                   | 1.5E–03                   | 4.3E–03          | 13             | 4.5E–03               | Surawski et al. (2016) |
| Benzene    | 8.9E–04                         | 1.8E–04                   | 5.00E–04         | 8              | 7.8E–04               | Guérette et al. (2018) |
| Methane    | 7.9E–02                         | 3.4E–02                   | 1.1E–01          | 8              | 5.0E–02               | Paton-Walsh et al. (2014) |
| Methacrolein + methyl vinyl ketone | 7.0E–04           | 1.4E–04                   | 3.4E–04          | 5              | 3.5E–03               | Guérette et al. (2018) |
| Methyl ethyl ketone | 5.5E–04                  | 2.0E–04                   | 5.0E–04          | 6              | 5.0E–04               | Guérette (2016) |
| Methanol   | 1.4E–02                         | 4.4E–03                   | 1.1E–02          | 7              | 1.7E–02               | Paton-Walsh et al. (2014) |
| Ammonium ion (NH$_4^+$) PM$_1$ fraction | 6.7E–03                  | 1.9E–03                   | 5.0E–03          | 5              | -                     | -                   |
| Nitrate ion (NO$_3^-$) PM$_1$ fraction | 5.3E–03                  | 1.7E–03                   | 6.7E–03          | 12             | -                     | -                   |
| Organic PM$_1$ fraction | 1.8E–01               | 5.4E–02                   | 1.9E–01          | 14             | -                     | -                   |
| PM$_{2.5}$ | 9.0E–02                         | 2.6E–02                   | 7.8E–02          | 7              | 3.0E–02               | Desservettaz et al. (2019) |
Meteorology and general atmospheric composition during the smoky period

Wind directions observed throughout the smoke-influenced period of COALA-2020 were variable. Winds from all directions were observed with some periods of sustained easterly and southerly airflow. The influence of anthropogenic emissions from nearby sources such as the cities of Sydney and Wollongong cannot be discounted. However, fires can be assumed to be the dominant source of most pollutants during this time, given the widespread, persistent nature of the smoke plume covering the measurement site for much of this period (e.g. Fig. 1). Local wind speeds were generally low, with a mean wind speed of 1.52 m s⁻¹ observed. The average daily maximum ambient temperature was above 29 °C. The average overnight low was 19 °C. Three days with a maximum temperature > 35 °C were observed, with the maximum recorded temperature 44 °C. Limited precipitation was observed during the smoky period.

Considering the highly vegetated setting of the measurement site, it is unsurprising that a diurnal cycle in concentration was observed during the smoky period. The average overnight low was 19 °C. Three days with a maximum temperature > 35 °C were observed, with the maximum recorded temperature 44 °C. Limited precipitation was observed during the smoky period.

Relatively low concentrations of the anthropogenic VOCs benzene, toluene and xylene were observed in the smoky period. The mean concentration of both these species was < 0.5 ppb during the smoky period with no significant enhancements observed. This implies limited influence on the measurement site during the smoky period from nearby roads (Ramirez-Gamboa et al. 2021). Significant concentrations of ozone were observed, closely correlated with temperature. The 4 days on which the highest ozone concentrations were observed were the 4 days on which temperatures were observed above 35 °C. The maximum

| Species                       | Mean emission factor (g kg⁻¹ fuel) | Error (g kg⁻¹ fuel) | Standard dev. (g kg⁻¹ fuel) | Range (g kg⁻¹ fuel) | Number of events | Lit. value (g kg⁻¹ fuel) |
|-------------------------------|-----------------------------------|--------------------|-----------------------------|---------------------|------------------|-------------------------|
| Black carbon aerosol          | 3.4E-01                           | 1.5E-01            | 1.4E-01                     | 4.0E-01             | 13               | 5.5E-01 (Surawski et al. 2016) |
| PM₂.₅                         | 7.7E+00                           | 2.5E-01            | 2.2E+00                     | 6.2E+00             | 7                | 1.3E+01 (Akagi et al. 2011) |
| Ammonium ion (NH₄⁺) PM₁ fraction | 5.7E-01                           | 1.9E-01            | 1.7E-01                     | 0.4E-01             | 5                | 1.0E-01 (Reisen et al. 2018) |
| Nitrate ion (NO₃⁻) PM₁ fraction | 4.5E-01                           | 1.6E-01            | 1.4E-01                     | 0.8E-01             | 12               | 1.0E-02 (Reisen et al. 2018) |
| Organic PM₁ fraction          | 1.6E+01                           | 5.4E+00            | 4.7E+00                     | 1.5E+01             | 14               | 5.7E+00 (Desservettaz et al. 2017) |
recorded concentration was 106 ppb, observed on the hottest day when the temperature reached 44 °C. The presence of biogenic and biomass burning VOCs in the local atmosphere (Granier et al. 2000), combined with high temperatures, provided conditions favourable for ozone formation (Utembe et al. 2018). The mean ozone concentration during the smoky period was 33 ppb. NOx concentrations were low with a mean concentration of 3.6 ppb. The two largest enhancements in NOx, in which concentrations > 20 ppb were observed occurred during periods of strong westerly winds at night. Some simultaneous enhancement is visible in SO2. A possible source for these enhancements is a national highway (Pettit et al. 2021), the Hume Motorway, which is located 15 km west of the site.

Carbon monoxide concentrations throughout the smoky period were elevated significantly above the expected background for the measurement site. For example, the clean air mean CO concentration at nearby Wollongong was 63 ppb between 2011 and 2014 (Buchholz et al. 2016). The mean CO concentration during the smoky period of 181 ppb is greater than twice the mean for the COALA campaign after the smoky period (78 ppb). The scale and extent of bushfires burning prior to and during the smoky period gave an obvious dominant source for elevated CO during this period. Other pollutants closely associated with wildfire smoke (e.g. acrolein, black carbon aerosol, PM2.5 and organic aerosol fraction) were also enhanced during the smoke period. Enhancements vary in magnitude as plumes containing varying concentrations of pollutants passed over the measurement site. These enhancements are discussed further in the following analysis.

Source of biomass burning influence

The Black Summer fires burning during COALA-2020 were numerous and occurred over a very large geographical area. Extensive fires were burning along the southern coast of NSW, in eastern Victoria and in the alpine regions during the campaign. The campaign began months after the start of the fire season. By mid-January thousands of hectares of forest had already burned (Australian Government Department of Agriculture 2021), creating a significant atmospheric smoke burden in the measurement region. These dilute plumes had continued influence on the local atmosphere for the entire summer, influenced by local meteorology such as sea breeze recirculation (Ryan et al. 2021). The numerous fire sources and complex meteorology of the region made it impossible to link any observed smoke plumes directly to a specific fire emission source. Back trajectories produced using the HYSPLIT model were used to assist in this process. Trajectory information for most plumes was difficult to interpret, as trajectories often passed near multiple burning areas in the hours and days before air mass measurement and did not capture well the local meteorology which may have influenced smoke recirculation over the measurement site.

We can deduce, however, that smoke sampled during COALA-2020 had aged significantly before measurement. There is evidence for this in both the particle and gas phases. In the particle phase, ageing of the aerosols present can be approximated using observations from the ToF-ACSM, where the fraction of organic PM1 with the mass-to-charge ratio of 44 (f44) serves as a marker for photochemically aged organic aerosols (Aiken et al. 2008; Ng et al. 2010). During this period of abundant smoke, f44 consistently ranged between 0.20 and 0.30, presented in Fig. 4, with nearly 60% of data points being over 0.25. In contrast, observations of f44 in other studies of biomass burning-affected environments show that f44 rarely exceeded 0.25 (Carbone et al. 2013; Bougiatioti et al. 2014; Zhang et al. 2015; Milic et al. 2017). The high concentrations of the aged aerosol marker f44 observed suggest dominant contributions of aged smoke to the particle phase during the campaign.

Fresh smoke VOC tracers were also present in low concentrations in the present measurements. Using the same measurements discussed here, Mouat et al. (2021b) observe oxidative products of the short-lived smoke tracer furan at concentrations indicating smoke ageing. The authors also estimate smoke transport time as ~ 8 h for the overnight period on February 3, the youngest plume sampled with PTR-ToF–MS, using HYSPLIT trajectories. The locations of active fires during the campaign lead us to suggest smoke sampled during the discussed measurements is at least 8 h old.

Comparison of enhancement ratios to literature values

Enhancement ratios to CO were determined for 13 measured variables using the methodology outlined in Sect. 2.2, as reported in Table 1. Enhancement ratios determined for measured particle-phase variables will be presented first, followed by enhancement ratios determined for gas-phase species. A plot of all enhancement ratio to CO values for each species is presented in Fig. 5. Emission factors for select particle species are presented in Table 2.

Particle-phase variables

Periods of strong correlation were observed between CO and several particle-phase variables, notably black carbon aerosol, organic fraction of PM1 and PM2.5. However, not all aerosol variables displayed periods of good correlation to CO. Aitken and accumulation mode aerosol (as measured by SMPS), CN3 and PM10 were not observed to have a strong relationship with CO during any of the selected events. A lack of correlation to CO for periods dominated by biomass
burning influence suggests either the influence of a separate source on the measured airmass, or extensive chemistry occurring since emission changing the concentration of the variable in the plume. Elevated concentrations of Aitken mode (10–100-nm diameter) particles, accumulation mode (100–1000-nm diameter) particles and CN are often associated with secondary aerosol formation (Dominick et al. 2019) as they are aerosol count measurements and therefore are heavily influenced by small, freshly nucleated particles. The measurement site, as described in Sect. 2, is surrounded by native SE Australian forest dominated by Eucalypt species. This forest type is known to be a significant source of biogenic VOC species (Ramirez-Gamboa et al. 2021; Emmerson et al. 2018) which are associated with the formation of secondary organic aerosol (Cope et al. 2014; Dominick et al. 2019). Therefore, it is suggested that particle formation originating from biogenic precursors may disrupt the relationship between biomass burning tracers such as CO and measurements of ultrafine aerosol variables. The condensation of biogenic VOCs onto existing smoke particles may also have influenced observed ultrafine particle variables during COALA-2020. Another potential disruption in the relationship between biomass burning tracers such as CO and ultrafine aerosol relates to plume ageing. It is well-known that the size and composition of aerosols emitted from wildfire change as the plume ages, e.g. (Hodshire et al. 2019; May et al. 2015; Sillanpää et al. 2005). Although the organic aerosol production has been found to be negligible in photochemically aged plumes (May et al. 2015; Zhou et al. 2017), the opposing processes of VOC condensation into the aerosol phase driven by atmospheric oxidation and VOC evaporation as the plume dilutes lead to complex changes in aerosol size distribution and composition (Garofalo et al. 2019). It is suggested these processes, along with the influence of locally emitted biogenic VOCs, possible biogenic SOA formation or condensation of these species onto existing smoke particles disrupted the relationship between CO and ultrafine aerosol variables during COALA. PM10 is not an ultrafine aerosol measure and did not display strong relationship to CO. A possible confounding source of PM10 is present during COALA-2020 is lofted mineral dust. Widespread landscape dryness (Nolan et al. 2020) and high wind speeds (Deb et al. 2020) present in the region during the fire period provided conditions conducive to the formation and transport of dust plumes from inland regions of southeast Australia.

The concentration of black carbon aerosol was strongly correlated to CO concentration for thirteen selected events. In most cases, the correlation was very strong (Fig. 2, supplementary Table S1). Calculated enhancement ratios to CO ranged between $2.1 \times 10^{-3} \text{ and } 6.3 \times 10^{-3} \mu g m^{-3} \text{ ppb}^{-1} CO$. The enhancement ratio to CO from the Kilmore East fire, a large 2009 fire in central Victoria which consumed largely similar fuel to the Black Summer fires, was calculated as $4.5 \times 10^{-3} \mu g m^{-3} \text{ ppb}^{-1}$ from the emission factor published by Surawski et al. (2016). The mean enhancement ratio from the present values is similar, $4.0 \pm 1.5 \times 10^{-3} \mu g m^{-3} \text{ ppb}$, and the value derived from literature agrees within one standard deviation. The similarity of these values suggests that the ageing process occurring in the plumes measured during COALA-2020 did not significantly change the concentration of black carbon aerosol. Atmospheric ageing of smoke from fires in the USA has been observed to have limited impact on black carbon concentration up to 5 h after emission (May et al. 2015). The plumes sampled during COALA-2020 are likely older than this. However, the relative chemical inactivity of this species and atmospheric lifetime of 4–12 days under typical oxidative conditions (Cape et al. 2012) provides an explanation for an aged smoke enhancement ratio value similar to the emission ratio calculated from a southeast Australian forest fire.

![Fig. 4 Timeseries plot of mass 44 (aged smoke tracer) from ACSM measurements during the smokey period of COALA-2020 showing relatively high concentrations, coloured by smoke event](image-url)
PM$_{2.5}$ was well-correlated with CO for seven of the identified smoke periods. The calculated enhancement ratio to CO ranged from $4.4 \times 10^{-2}$ to $1.2 \times 10^{-1}$ µgm$^{-3}$ ppb, with the mean reported value $8.6 \pm 0.2$ µgm$^{-3}$ ppb. This value is a factor of three higher than that reported from measurements of aged, diluted smoke in Sydney (Desservettaz et al. 2019). Interestingly, however, the mean PM$_{2.5}$ enhancement ratio to CO for more than 300 North American wildfire measurements is three times greater than the value observed during COALA-2020 (Prichard et al. 2020). An enhancement key is provided in Fig. 3. The red diamond marks the mean of all values. The small black diamond marks a literature value as cited in Table 1.
ratio to CO of approximately 2.6e–01 μg m⁻³ ppb⁻¹ can be calculated from emission factors reported for PM₂.₅ and CO for both flaming and smouldering fires from prescribed burn measurements in southeast Australian eucalypt forests (Reisen et al. 2018). This suggests relative concentrations of PM₂.₅ decreased between emission and sampling in the plumes measured during COALA-2020. As discussed above, there are multiple complex physical, chemical and dilution factors that change the physical and chemical characteristics of smoke plume aerosol populations after emission. The variability in reported enhancement ratios of PM₂.₅ to CO demonstrates this complexity. We suggest that coagulation to larger particle sizes and removal via dry deposition contribute to the lower relative concentration of PM₂.₅ observed during COALA-2020 compared to freshly emitted wildfire plumes. Further, plumes originating from the uncontrolled high-intensity wildfire as occurred during the Black Summer may have significant contributions from flaming combustion which is associated with lower particulate emission (Reisen et al. 2018).

Organic aerosol was the dominant fraction in speciated PM₁ measured by ACSM during COALA-2020. Organic aerosol was well-correlated with CO for all selected smoke events (correlation coefficients between 0.86 and 0.99). Of fractions reported here, organic aerosol contributed ~90% to the PM₁ loading. This value is similar to those observed in measurements from multiple smoke plumes of varying ages in the western USA (Garofalo et al. 2019). This factor is expected to be independent of smoke age as the oxidation of primary organic aerosol is balanced by the formation of SOA, giving a net maintenance of total organic aerosol loading (Enders et al. 2021). The nitrate (NO₃⁻) aerosol fraction was also frequently well-correlated to CO. Ammonium (NH₄⁺) aerosol fractions were occasionally well-correlated, with sulphate (SO₄²⁻) and chloride (Cl⁻) aerosol not well-correlated. All fractions displayed similar levels of variability to other pollutants, with the enhancement ratio to CO range of similar magnitude to the mean value (that is, the range is approximately 100% of the reported value). It is possible that sulphate and chloride aerosol may have been influenced by local marine emissions with a source in the Tasman Sea, lying 20 km to the east of the measurement site as marine aerosol is a source of both of these ions (Xiao et al. 2018). It is also possible that all three of these fractions may display large influence from nearby anthropogenic sources, particularly those involving fossil fuel combustion as this process emits sulphate (Lighty et al. 2000) and chloride (Luo et al. 2019).

Emission factors calculated in the current study (Table 2) are also compared to published values. The emission factor for black carbon aerosol, reported as 0.34 g kg⁻¹ fuel is similar to the adjusted value used by Surawski et al. (2016) for a landscape-scale fire in temperate Australian forests, 0.55 g kg⁻¹. The emission factor for PM₂.₅ calculated in the present study as 7.7 g kg⁻¹ is lower than the globally reported value for temperate forests, 13 g kg⁻¹ fuel (Akagi et al. 2011), and a factor of two lower than the factor calculated from flaming combustion during controlled burns in temperate Australian forests (Reisen et al. 2018). Speciated PM₁ fraction emission factors have been calculated from fresh smoke measurements from flaming and smouldering combustion during Australian prescribed burns (Reisen et al. 2018). Ammonium and nitrate PM₁ fraction emission factors calculated during COALA were higher than observed in fresh smoke. This may indicate different combustion processes during wildfires or ammonium and oxidative nitrate particle formation during smoke transport. The organic PM₁ fraction emission factor was higher during COALA than from a Northern Australian savannah fire counterpart value (Desservettaz et al. 2017); however, the differing fuel and fire types make this comparison difficult to draw conclusions from.

**Gas-phase variables**

Ambient concentrations of a range of VOC species were determined from PTR-ToF–MS measurements. Details of the instrumental techniques and spectrum analysis used in retrieval are presented in Mouat et al. (2021b). Many VOC species were well-correlated to CO during selected smoke events. For example, acetaldehyde, benzene, methane, methyl ethyl ketone and methanol demonstrated strong relationships with CO for six or more of a possible eight events. As with particle phase variables, the enhancement ratios to CO determined from the COALA-2020 measurements are similar to those found in the literature. Acetaldehyde was determined to have a mean enhancement ratio to CO of 3.2e–03 ± 1.3e–03 ppb ppb⁻¹ from seven smoke events. The range of measurements is of similar magnitude to the measurement. This value is smaller than the enhancement ratio to CO calculated from fresh smoke emissions during a series of laboratory burns of southeast Australian fuels by Guérette et al. (2018) of 7.0e–03 ppb ppb⁻¹. The short atmospheric lifetime of acetaldehyde may contribute to this observation; however, formation of this species through oxidation of other VOCs present in the plume would also be expected. Acetone and benzene enhancement ratios to CO calculated from COALA-2020 were similar to those determined by Guérette et al. (2018) with similar relative ranges. These values are reported in Table 1. Robust relationships were determined periodically also between CO and m/z 71 (reported as the sum of methacrolein and methyl vinyl ketone). The enhancement ratio for the sum of methacrolein and methyl vinyl ketone to CO observed
during COALA-2020 is five times less than the value reported by Guérette et al. (2018). The hours-long atmospheric lifetime for these species may partially explain this difference between fresh and aged smoke; however, more continuous measurements of ageing plumes are required to properly understand plume chemistry. No field measurements containing an enhancement ratio for methyl ethyl ketone to CO was found in the literature; however, a value from laboratory burns of Australian fuels produced a value similar to that observed in the present study (Guérette 2016). The reported enhancement ratio to CO for methane is $7.9 \pm 3.4e - 02\text{ ppb ppb}^{-1}$ from eight smoke events. This value is consistent with that calculated by Paton-Walsh et al. (2014) from open path FTIR measurements on the firegrounds of hazard reduction burns in SE Australian temperate forests. The same is true when comparing the enhancement ratio to CO determined in this study for methanol to that calculated from the results of Paton-Walsh et al. (2014). It is interesting to note that the enhancement ratio to CO values calculated from aged smoke during COALA-2020 are for many species close to those reported in the literature from fresh smoke measured on the fire ground. This suggests that dilution and chemistry effects are not significantly altering the relative amounts of these VOCs in the plume during transport from the emission site to the measurement site.

The only reported species for which the enhancement ratios to CO are significantly higher to those found in the literature is acetonitrile. Acetonitrile was calculated to have an enhancement ratio to CO of $5.0e - 04\text{ ppb ppb}^{-1}$ using the results of Paton-Walsh et al. (2014). During COALA-2020, the mean reported enhancement ratio to CO is approximately twice this value at $9.6 \pm 2.5e - 04\text{ ppb ppb}^{-1}$. This may suggest a higher emission factor of this species from the Black Summer fires, or the formation of acetonitrile in the plume during transport to the measurement site. Higher enhancement ratios of acetonitrile have been observed outside the Australian context, with a review of field measurements reporting a mean value of $2.0e - 03$, twice as large as the COALA value (Huangfu et al. 2021).

The determination of these enhancement ratios reveals that plumes measured at Cataract during the Black Summer bushfires had chemical composition similar to fresh plumes previously observed in southeast Australian temperate forest fires. This is an interesting result considering that sampled smoke had been significantly aged before reaching the measurement site. This finding provides an indication that enhancement ratios determined from firegrounds in temperate Australia may be appropriate for use in estimating population exposure at distant receptor sites in some cases. Determining the composition of these plumes is crucial in assessing the health impacts of exposure to this smoke. The relative toxicological contribution of different atmospheric species as measured during the Black Summer to the health burden of smoke exposure will now be investigated.

### Relative toxicological impacts

#### Determination of relative toxicological impact

Measurements from COALA-2020 can be related to exposure limit concentrations in order to estimate the potential toxicological contribution for each measured variable. Chemical species included in this analysis are those shown to have a >1% contribution to the toxicological impact of wildfire smoke exposure in Australia (MacSween et al. 2020) and in the western USA (O’Dell et al. 2020). The enhancement ratios to CO used from sources other than the current COALA-2020 study are presented in Table 3. The sources for these enhancement ratios (MacSween et al. 2020; Guérette et al. 2018) were selected as they are recent values measured in smoke from fires burning in similar forests to those consumed during the Black Summer fires.

Measured concentrations were compared to the Safe Work Australia (SWA) time weighted average exposure limits (Safe Work Australia 2019) for atmospheric pollutants. These limits provide a mean concentration that should not be exceeded over the course of an 8-h working day. No specific limit concentration exists for smoke particles of indeterminate composition, though limits for other types of respirable particles (e.g. wood dust, coal dust, graphite dust) are published between 1 and 5 mg m$^{-3}$. A value of 3 mg m$^{-3}$ is used here for respirable smoke particles given this is the limit specified for other carbon-dominated dusts like coal and graphite dust (Reisen and Brown 2009). This value has also been used in other publications in Australia and overseas (e.g. (Reisen and Brown 2009; MacSween et al. 2020; Miranda et al. 2010)). National Environmental Protection (Ambient Air Quality) Measure (NEPM) (National Environmental Council 1998) limit concentrations are also discussed.

| Variable (units) | Enhancement ratio to CO (unit x ppb$^{-1}$) |
|-----------------|------------------------------------------|
| Formaldehyde (ppb) | 0.0183 Guérette et al. (2018) |
| Hydrogen cyanide (ppb) | 0.0063 Guérette et al. (2018) |
| Acetic acid (ppb) | 0.015 Paton-Walsh et al. (2014) |
Measured concentrations of atmospheric variables were temporally averaged to the resolution specified by the exposure limit for comparison. Limit concentrations included in this analysis are presented in Table 4.

A series of mean concentrations were calculated from the smoke-influenced measurements of COALA-2020. An overall mean concentration was calculated for smoke events with sufficient duration for comparison to an 8-h limit concentration. Smoke H (duration 7 h) and the immediately consecutive events Smoke I-L (combined duration 9 h) were selected, as were the mean concentrations determined for the entire smoke-influenced period. For species listed in Table 3, which were not directly measured, the cited enhancement ratio to CO was used to calculate an assumed concentration. Mean concentrations were divided by exposure limit concentrations listed in Table 4 to obtain a percentage of exposure for each species. Following the methodology MacSween et al. (2020), atmospheric pollutants were grouped into toxicological classes with similar physiological effects from the MIXIE web tool (Vyskocil et al. 2007). A tabulation of these classes, the regions of the body they impact and the atmospheric pollutants that fall into each class is available in MacSween et al. (2020). Finally, the percentage exposure for each species in each toxicological class was summed together to provide a cumulative exposure estimate for each class. The physiological effect of each class is summarised in Table 5. Vyskocil et al. (2007) provide a more thorough description of these classes.

Relative contribution of atmospheric variables to toxicological load

The exposure limits selected for comparison in this study are time-weighted average workplace exposure limits set by SWA (Safe Work Australia 2019), the national government agency responsible for work health and safety. These are limits that must not be exceeded in the workplace over an 8-h working day, assuming a standard 5-day week. This limit is therefore not designed to be a measure for continuous exposure, nor the limit of exposure to air pollutants for vulnerable members of the population such as elderly people or those with respiratory illness. The concentration limits set by SWA are higher than those reported in the national measure for ambient air quality—the NEPM (National Environmental Council 1998). For example, the 8-h CO NEPM standard is 9 ppm, compared to a SWA limit of 30 ppm averaged over the time period. The SWA limit for respirable particles (classified as PM$_3$) is 1–5 mg m$^{-3}$, compared to the NEPM daily value of 0.025 mg m$^{-3}$. The NEPM ambient exposure limits for SO$_2$ and NO$_2$ are also much lower than their SWA equivalents. The NEPM framework is more suitable for contextualizing the health risk of exposure to air pollutants in the ambient setting but does not contain limits for VOC species. This must be kept in mind when assessing long-term population exposure to wildfire plumes such as those produced during the Black Summer. This gives rise to near-continuous exposure to pollutants for large populations, including vulnerable populations, for a period far extending the 8-h TWA averaging time. Results from smoke events H and I-L are presented in Fig. 6 and discussed, along with the mean results for all events.

The breakdown of species contribution to the cumulative toxicological load of exposure to Black Summer plumes is consistent between events as presented in Fig. 6. This suggests that any differences in composition observed within the plumes sampled during COALA-2020 have limited effect on the toxicological impact of exposure. The percentage of the SWA limit observed in the dilute smoke sampled at Cataract is relatively low even during smoke events (~2%) whilst averaged over the entire smoky period of measurements the

| Variable                      | Exposure limit (ppm) |
|-------------------------------|----------------------|
| Acetaldehyde                  | 20                   |
| Acetic acid                   | 10                   |
| Acrolein                      | 0.1                  |
| Benzene                       | 1                    |
| Carbon dioxide                | 5000                 |
| Carbon monoxide               | 30                   |
| Formaldehyde                  | 1                    |
| Hydrogen cyanide              | 10*                  |
| Nitrogen dioxide              | 3                    |
| Respirable particles (as PM$_3$) | 3 (mg m$^{-3}$) |
| Sulphur dioxide               | 2                    |

| Class | Description                  |
|-------|------------------------------|
| 1     | Eye disorder                 |
| 2     | Upper respiratory tract irritation |
| 3     | Lower respiratory tract disorder |
| 4     | Disruption of oxygen transport |
| 9     | Antithyroid effect           |
| 11    | Liver disorder               |
| 13    | Kidney disorder              |
| 19    | Central nervous system disorder |
| 27    | Skin disorder                |
| 30    | Embryonic or foetal disorder |
| 32    | Cancer                       |

Vyskocil et al. (2007) provide a more thorough description of these classes.
concentration limits are closer to ~1% of the SWA limit. It must be noted here that these percentage-of-limit exposure values are calculated from workplace exposure limits. The measurement site was also distant from smoke sources, and therefore plumes impacting the site were significantly diluted compared to plumes impacting population centres closer to active fires. It must also be noted that observations from COALA-2020 were taken weeks after the peak fire activity. The cumulative week-to-month long exposure and exposure of vulnerable populations to plume from the Black Summer had serious health impacts (Ryan et al. 2021; Walter et al. 2020) despite low reported exposure percentages from the COALA-2020 measurement site.

The relative contribution of particulate and gaseous species is important in the cumulative toxicological burden of exposure to plumes measured during COALA-2020. Respirable particles as PM$_3$ (measured as PM$_{2.5}$ during this study) contribute significantly to the cumulative exposure burden for each class they are included in: Classes 1, 2, 3, 27 and 32. In each of these classes for all analysed periods, the contribution from respirable particles is more than 50%. Formaldehyde also contributes significantly to each of these classes (30–39% for all analysed periods) Acrolein also contributes to Classes 1, 2, 3, 27 and 32 with contributions between 15 and 24%. Carbon monoxide has the dominant (>95%) contribution to Class 4. Overall, respirable particles contributed 52–53% to the total exposure loading during Smoke H and during the entire smoky period. During smoke events I-L, the particulate contribution was 63%.

These results are very similar to those found in MacSween et al. (2020) who used enhancement ratios derived from fresh smoke across a number of fires to find respiratory particulates, formaldehyde, acrolein and CO were the major contributors to cumulative exposure estimates. Formaldehyde and acrolein were also found to dominate the acute health risk hazard index calculated by O’Dell et al. (2020), who also reported significant contribution from benzene from VOC measurements in western US wildfire plumes. Interestingly, O’Dell et al. report the acute risk from acrolein in smoke decreases as smoke ages. The similar contribution of acrolein to the exposure contributions in Fig. 6 provides another piece of evidence that mostly aged plumes measured during COALA did not vary significantly (i.e. by days) in age. It must also be noted here that the enhancement ratio...
to CO used to calculate formaldehyde concentrations was sourced from measurements of fresh smoke. Formaldehyde is known to be a product of smoke plume chemistry in southeastern Australian bushfire plumes (Young and Paton-Walsh 2011), and as such concentrations of this compound can increase after emission. The real concentrations, and hence contribution of formaldehyde to the percentage cumulative exposure, could be higher than reported.

Smoke measured during COALA-2020 was aged and diluted. Although the maximum measured CO concentration (> 1 ppm) during the campaign is many times greater than the background expected for the site, much higher pollutant concentrations associated with smoke plumes form the Black Summer were observed in other regions of Australia (Health Protection Service 2021). For example, CO concentrations greater than 20 ppm and PM$_{2.5}$ concentrations greater than 1000 µg m$^{-3}$ in early January (Health Protection Service 2021) in Canberra, 200 km from the measurement site. The relatively homogeneous chemical composition of distinct smoke plumes observed during COALA-2020 allows the estimation of plume composition in sites closer to active fires impacted more heavily by Black Summer plumes. To assess the relative toxicological impact of atmospheric species on exposure to smoke plumes from the Black Summer, a case study site impacted heavily by undiluted plumes has been performed.

A Canberra case study

Application to a case study site: Canberra, Australia

A case study of population exposure in an urban centre heavily impacted by undiluted plumes from the Black Summer fires was also completed. The city of Canberra (Fig. 1) was selected as the smoke impacts were particularly severe during the Black Summer. Canberra is an Australian city located approximately 200 km southwest of Cataract (Fig. 1). The air quality measurements from each of Canberra’s three AQMSs were downloaded from the public data repository (Health Protection Service 2021). The AQMS at Monash was selected for analysis, as this suburb has the largest population of the three AQMS sites in Canberra. The PM$_{2.5}$ concentrations were assessed for other sites (Civic and Florey) and found to be of similar magnitude to those observed at Monash. The CO record at Florey was also similar to that recorded at Monash. There is no Civic CO record for the analysed period. It is therefore assumed that the Monash concentrations are regionally representative of Canberra’s air quality for the measured period, especially considering the spatially large pollutant source and proximity of the three AQMSs.

Toxicological contributions in Canberra

Figure 7 plots hourly CO and PM$_{2.5}$ measurements from an air quality monitoring station (AQMS) in Monash, Canberra during the period affected by smoke from the Black Summer fires. The 8-h NEPM standard for CO was exceeded for 2 days, January 01 and January 02. The maximum 8-h mean CO concentration recorded at the Monash AQMS was 15.9 ppm. This is 176% of the NEPM limit concentration for this pollutant. The maximum 24-h mean PM$_{2.5}$ concentration observed at Monash was 968 µg m$^{-3}$. This is 38 times the NEPM daily limit concentration of 25 µg m$^{-3}$. As evident in Fig. 7, the hourly mean PM$_{2.5}$ concentration was greater than the NEPM daily limit for the majority of the smoke-affected period from early December 2019 and early February 2020. Forty-nine of 64 days between December 07, 2019, and February 08, 2020, had daily mean PM$_{2.5}$ concentrations greater than 25 µg m$^{-3}$. The above statistics demonstrate that air quality was poor in Canberra during the Black Summer, and especially bad on January 01, 2020, and the following week.

Considering this, the health effects of exposure to this smoke was calculated for three selected periods: the median 8-h rolling mean CO and PM$_{2.5}$ concentrations from the entire smoke affected period (December 08–February 08), the median 8-h rolling mean CO and PM$_{2.5}$ concentrations from the worst-affected week (December 31–January 06) and the maximum 8-h rolling mean CO and PM$_{2.5}$ concentrations (January 01). Rolling mean 8-h CO concentrations were calculated for each of these periods, and a bootstrap median 8-h mean CO concentration retrieved. From these median 8-h concentrations, cumulative exposure estimates and the relative toxicological contributions of each of the species listed in Table 2 were calculated using the method described above. The results of this analysis are presented in Fig. 8. A limited number of species dominate the toxicological contributions. Respirable particles (as PM$_{2.5}$) are again the dominant contributor to toxicological classes 1,2,3, 27 and 32. For the entire smoke-affected period and for the worst week of air quality particulate contributions in classes 1, 2, 3, 27 and 32 were 54–71%. During the worst day of air quality, particulate contributions were lower (39–52%), suggesting higher relative contributions of CO. Formaldehyde and acrolein also significantly contribute to classes 1,2,3, 27 and 32. For the entire smoke-affected period and for the worst week of air quality particulate contributions in classes 1, 2, 3, 27 and 32 were 54–71%. During the worst day of air quality, particulate contributions were lower (39–52%), suggesting higher relative contributions of CO. Formaldehyde and acrolein also significantly contribute to classes 1,2,3, 27 and 32, with formaldehyde also prominent in classes 27 and 30, similar to the results from Cataract. The overall particulate contribution was 51% when considering the entire smoke period, 56% when considering the worst week of air quality and 36% when considering the worst day of air quality. The identity and magnitude of chemical species contribution are similar when comparing calculated concentrations in Canberra to (largely) measured concentrations at Cataract. This similarity suggests the enhancement ratios determined from
**Fig. 7** Hourly mean PM2.5 and CO concentrations from Monash, Canberra, ACT during the Black Summer from December 2019 until February 2020. Horizontal lines indicate NEPM limit concentrations.

**Fig. 8** Calculated contributions of atmospheric species to the cumulative toxicological burden of smoke plumes in Canberra, Australia, compared against Safe Work Australia Time-Weighted Average exposure limit concentrations plotted for periods during the Black Summer. The ‘Other’ category contains acetaldehyde, carbon dioxide, hydrogen cyanide and nitrogen dioxide.
measurements and selected from literature are appropriate for use in this context.

Workplace exposure limits are designed for workers who may be exposed for eight hours of a 24-h cycle. However, concentrations of CO, PM$_{2.5}$ and other atmospheric pollutants were elevated consistently on a timescale of weeks to months in many Australian cities during the Black Summer. Daily workplace toxicological loads were multiplied by three for the worst day of air quality observed in Canberra. This is an attempt to scale an exposure limit for 8 h out of a 24-h cycle to continuous 24-h exposure. When this scaling is applied, five toxicological classes exceed 200% of the adjusted exposure limit (Classes 1, 2, 3, 27, 32). One other class (4) exceeds 100% of the adjusted exposure limit. A similar experiment was performed on the weekly values calculated above. Weekly values were scaled by a factor of 40/((24*7), representing the proportion of a 40-h working week specified in the SWA exposure limits of the total hours in a week. This scaling results in exposure limit exceedances for two classes (Classes 1 and 2), and exposures > 80% of the limit for three further classes (3, 27, 32).

Implications

Enhancement ratios to CO from aged smoke measured during the historic Black Summer Australian bushfires have been determined in this analysis. For many gas-phase and particle species, the values determined from the present experiment are not significantly different to those found in literature calculated from fresh smoke measurements in similar forest types. The determination of these values from aged smoke is significant as it provides a starting point for future detailed epidemiological study of the health effects of smoke exposure in receptor regions distant from the fire source. This type of exposure is common in the Australian context. With the frequency and magnitude of fire events in southeast Australia predicted to increase in the future (Keywood et al. 2013), along with the population of the Australian eastern seaboard, it is critical to have an understanding of the composition of aged smoke plumes from landscape scale fire events. The publication of enhancement ratios for harmful atmospheric species will allow for the modelling of population exposure to diverse chemical species at receptor sites using a CO tracer. However, it must be noted that not all species of concern were measured during COALA-2020. Of particular note is formaldehyde, as it contributes significantly to the exposure health burden (MacSween et al. 2020; O’Dell et al. 2020) and has a known source in the Australian bushfire smoke. Furthermore, fine particle variables were not observed to correlate strongly with CO during the present measurements. Therefore, more research is required to better understand the physics and chemistry that drives variability in these species, which are of particular concern from a health perspective given their ability to penetrate deeply into the respiratory system. It must also be noted that spatio-temporal heterogeneity of smoke plume composition is being assumed in the reporting of these values. It is understood that combustion type, fuel type and meteorological conditions all influence the emissions from wildfire, and therefore this assumption is not ideal. The variability in calculated enhancement ratio to CO values presented in Fig. 4 illustrates this. A recent study has also demonstrated that despite the landscape-scale pollutant source, spatio-temporal patterns in pollutant concentrations have been observed in the Sydney region. This reinforces the need to use locally measured CO tracer values for calculation of exposure risk when possible (Di Virgilio et al. 2021).

The calculated toxicological contributions of select atmospheric species also appears similar to analyses performed on fresh smoke (MacSween et al. 2020). The importance of considering the additive effects of species impacting the same part of the body is becoming increasingly recognised. The relatively low percentage of Safe Work Australia exposure limits reached during measurements of COALA-2020 highlights the inadequacy of using ‘workplace’ exposure limits for assessing ambient exposure. An ambient exposure limit for chemical species beyond those covered in the NEPM is recommended. The United States Environmental Protection agency provides a relevant document for assessing the risk of ambient exposure to identified Hazardous Air Pollutants (US EPA 2020).

The relative toxicological contribution of measured chemical species from COALA-2020 also provide some necessary insight. The importance of particulate species to the health burden of smoke exposure is highlighted, with respirable particles contributing > 50% to cumulative exposure values for most averaging periods in Canberra and Cataract. However, the contribution of infrequently measured gases such as formaldehyde and acrolein cannot be discounted. As these gases are not included in the NEPM or widely measured, their contribution to the toxicological load from smoke plumes may be being neglected. It should also be noted that the air quality impacts of the Black Summer fires demonstrate that traditional public health measures to lessen exposure risk must be adapted to account for events on the scale of the Black Summer. Near-continuous PM$_{2.5}$ concentrations observed in Canberra $> 25$ µg m$^{-3}$ over an 8-week period (Fig. 6) invalidates the traditional advice for at-risk populations to limit time spent outside during smoke-affected periods. The contribution of gaseous species to the toxicological loading in plumes measured during the Black Summer also highlights the need to develop health advice beyond the use of personal face masks. Masks can be effective at particulate removal but have little impact on the amounts of gaseous pollutants inhaled.
Conclusions

The Black Summer bushfires which burnt across Australia’s east coast during 2019–2020 were historically large and persistent. The smoke from these fires smothered Australia’s population centres near continuously on a timescale of weeks to months. This study presents likely the most detailed measurements of atmospheric species from this event. Enhancement ratios to a commonly measured tracer species, CO, provide a means by which the concentrations of less frequently measured atmospheric pollutants can be estimated in aged, landscape-scale biomass burning plumes like those which were observed during the Black Summer. These enhancement ratios will allow for better modelling of bushfire smoke plumes and therefore better quantification of the health impacts of population exposure to these plumes. It is suggested that detailed chemico-physical study of plume ageing in the particle and gas phase should be a research priority to better understand particularly the behaviour of ultrafine particles in large smoke plumes. As so-called ‘megafires’ become a more frequent threat along the east coast of Australia into the future, population exposure to these damaging particles will increase. Given the existing knowledge of the negative impact of airborne particles on cardiovascular and respiratory health, targeted measurements of both particles in smoke plumes and specific health impacts relating to particle size and particle composition are critical. The class-based toxicological contributions of atmospheric species to the exposure burden were calculated, with significant contributions from particle and gas-phase species observed, especially respirable particles, acrolein and formaldehyde. The lack of Australian guidelines for population exposure to ambient atmospheric pollutants is highlighted, along with the need to adapt public health messaging and guidelines to account for severe and extended air quality events such as those experienced during the Black Summer. As Australia’s climate changes and its population grows, so too will population exposure to biomass burning plumes and the harmful chemicals within. It is hoped that the devastating effects of the Black Summer will prompt greater understanding and recognition of the health risks posed by population exposure to bushfire smoke in the Australian context.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s11869-022-01237-5.

Acknowledgements The authors would like to acknowledge the work of all those who assisted with the COALA-2020 field campaign especially Dr. Alan Griffiths from the Australian Nuclear Science and Technology Organisation, Alex Carter, Quang Dang and Graham Kettlewell from the University of Wollongong and staff from the New South Wales Department of Planning, Industry and Environment. We acknowledge the use of imagery from the NASA Worldview application (https://visual.earthdata.nasa.gov/), part of the NASA Earth Observing System Data and Information System (EOSDIS).

Author contribution Conceptualization, CPW, JS; methodology, CPW, JS; software, JS; formal analysis, JS, AS; investigation, CPW, TN, RH, MK, AM; resources, CPW, DG, RH, MK, JK; data curation, JS, AS, RH, MK, DG, TN; writing—original draft preparation, JS, AS; writing—review and editing, CPW, DG, JK, AM, TN, JRG; visualisation, JS, AS; supervision, CPW, JK, MK; project administration, CPW; funding acquisition, CPW, JK. All authors have read and agreed to the published version of the manuscript.

Funding Open Access funding enabled and organized by CAUL and its Member Institutions The PTR-ToF–MS measurements used in this analysis were supported by the National Science Foundation, award number 2016646.

Data availability The data presented in this study are openly available in the PANGAEA repository at the following locations: [10.1594/PANGAEA.928929, 10.1594/PANGAEA.927544, 10.1594/PANGAEA.927313, 10.1594/PANGAEA.927277, 10.1594/PANGAEA.925555, 10.1594/PANGAEA.928853, 10.1594/PANGAEA.929001]. Datasets are referenced in text, with DOI links included in the bibliography.

Declarations

Ethics approval and consent to participate This declaration is not applicable to this study.

Consent for publication This declaration is not applicable to this study.

Competing interests The authors declare no competing interests.

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References

Aiken AC, DeCarlo PF, Kroll JH, Worsnop DR, Huffman JA, Docherty KS, Ulbrich IM, Mohr C, Kimmel JR, Sueper D, Sun Y, Zhang Q, Trimborn A, Northway M, Ziemann PJ, Canagaratna MR, Onasch TB, Alfarra MR, Prevot AS, Dommen J, Duplissy J, Metzger A, Baltensperger U, Jimenez JL (2008) O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high-resolution time-of-flight aerosol mass spectrometry. Environ Sci Technol 42(12):4478–4485. https://doi.org/10.1021/es703099q

Akagi SK, Yokelson RJ, Wiedinmyer C, Alvarado MJ, Reid JS, Karl T, Crounse JD, Wennberg PO (2011) Emission factors for open and domestic biomass burning for use in atmospheric models. Atmos Chem Phys 11(9):4039–4072. https://doi.org/10.5194/acp-11-4039-2011

Australian Government Department of Agriculture WatE (2021) National Indicative Aggregated Fire Extent Datasets. http://
www.environment.gov.au/fed/catalog/search/resource/details. page?uid=57B9ACDCB09-0364-4FEB-9459-2A56C792C743%7D. Accessed 25 May 2020

Australian Government Department of Industry Science Energy and Resources (2020) Estimating greenhouse gas emissions from bushfires in Australia’s temperate forests: focus on 2019–20. Commonwealth of Australia, Canberra, ACT

BBC News (2020) Australia fires: a visual guide to the bushfire crisis. BBC. https://www.bbc.com/news/world-australia-50951043. Accessed 19 May 2020

Benjamin MT, Sudol M, Bloch L, Winer AM (1996) Low-emitting Bougiatioti A, Stavroulas I, Kostenidou E, Zarmpas P, Theodosi Borchers Arriagada N, Palmer AJ, Bowman DM, Morgan GG, Jala-Cape JN, Coyle M, Dumitrean P (2012) The atmospheric lifetime of Bureau of Meteorology (2020) New South Wales in February 2020: a Carvalho A, Monteiro A, Flannigan M, Solman S, Miranda AI, Bor-Deb P, Moradkhani H, Abbaszadeh P, Kiem AS, Engsthröm J, Kel-ney MD, Vederschoot MV, Ward J, Mallet MD, Milic A, Miljevic B, Ristovski ZD, Howard D, Edwards GC, Atkinson B (2017) Emission factors of trace gases and particles from tropical savanna fires in Australia. J Geophys Res: Atmospheres 122(11):6059–6074. https://doi.org/10.1002/2016JD025925

Des serrvetz m, Paton-Walsh C, Griffith DWT, Kettlewell G, Key-wood MD, Vanderschoot MV, Ward J, Mallet MD, Milic A, Miljevic B, Ristovski ZD, Howard D, Edwards GC, Atkinson B (2017) Emission factors of trace gases and particles from tropical savanna fires in Australia. J Geophys Res: Atmospheres 122(11):6059–6074. https://doi.org/10.1002/2016JD025925

Des serrvetz m, Phillips F, Naylor T, Price O, Samson S, Kirkwood J, Paton-Walsh C (2019) Air quality impacts of smoke from hazard reduction burns and domestic wood heating in Western Sydney. Atmosphere 10(9):557. https://doi.org/10.3390/atmos10090557

Di Virgilio G, Hart MA, Maharaj AM, Jiang N (2021) Air quality impacts of the 2019–2020 Black Summer wildfires on Australian schools. Atmospheric Environment. Atmospheric Environment 261. https://doi.org/10.1016/j.atmosenv.2021.118450

Dominick D, Wilson SR, Paton-Walsh C, Humphries R, Guertette É-A, Keywood M, Selleck P, Kubitun D, Marwick B (2019) Particle Formation in a Complex Environment. Atmosphere 10(5).

Dowdy AJ (2018) Climatological variability of fire weather in Aus-tralia. J Appl Meteorol Climatol 57(2):221–234. https://doi.org/10.1175/jamc-d-17-0167.1

Duc NH, Chang LT-C, Azzi M, Jiang N (2018) Smoke aerosols disper-sion and transport from the 2013 New South Wales (Australia) bushfires. Environ Monit Assess 190(7):428. https://doi.org/10.1007/s10661-018-6810-4

 Emmerson KM, Cope ME, Galbally IE, Lee S, Nelson PF (2018) Isoprene and monoterpenes emissions in south-east Australia: comparison of a multi-layer canopy model with MEGAN and with atmospheric observations. Atmos Chem Phys 18(10):7539–7556. https://doi.org/10.5194/acp-18-7539-2018

 Emmerson KM, Possell M, Aspinwall MJ, Pfauscht S, Tjelker MG (2020) Temperature response measurements from eucalypts give insight into the Australian impact of isoprene emissions from eucalypt. Atmos Chem Phys 20(10):6193–6206. https://doi.org/10.5194/acp-20-6193-2020

Enders JJ, Rhoad TW, Phan JA, Zoerberg M (2021) Impacts of 2018 California wildfires on organic aerosol composition and air quality under low smoke conditions. ACS Earth and Space Chemistry 5(2):163–169. https://doi.org/10.1021/acsearthspacechem.0c00202

Environment Protection Authority Victoria (2020) EPA airwatch. Environ ment Protection Authority Victoria. https://www.epa.vic.gov.au/EPAAirWatch. Accessed 19 May 2020

Fisher JA, Murray LT, Jones DBA, Deutscher NM (2017) Improved method for linear carbon monoxide simulation and source attribution in atmospheric chemistry models illustrated using GEOS-Chem v9. Geosci Model Dev 10(11):4129–4144. https://doi.org/10.5194/gmd-10-4129-2017

Garofalo LA, Pothier MA, Levin EJT, Campos T, Kreidenweis SM, Farmer DK (2019) Emission and evolution of submicron organic aerosol in smoke from wildfires in the western United States.
Granner C, Müller J-F, Brasseur G (2000) The impact of biomass burning on the global budget of ozone and ozone precursors. In: Innes JL, Beniston M, Verstraete MM (eds) Biomass burning and its inter-relationships with the climate system. Springer, Dordrecht, Dordrecht, NL, pp 69–85.

Griffith DWT, Deutscher NM, Caldow C, Kettlewell G, Riggenbach M, Hammer S (2012) A Fourier transform infrared trace gas and isotope analyser for atmospheric applications. Atmos Meas Tech 5(10):2481–2498. https://doi.org/10.5194/amt-5-2481-2012.

Griffith DWT, Paton-Walshe C, Naylor TA, Kettlewell G, Ramirez-Gamboa J, Simmons JB, Carter A, Dang QP, Webb A (2021) Greenhouse gases measurements at Cataract Scout Park, Australia, taken during the COALA-2020 campaign. PANGAEA. https://doi.org/10.1594/PANGAEA.927313.

Güerette É-A (2016) Measurements of volatile organic compound sources and ambient concentrations in south-east Australia. University of Wollongong, Thesis.

Güerette E-A, Paton-Walsch C, Desservetaz M, Smith TE, Volkova L, Weston C, Meyer CP (2018) Emissions of trace gases from Australian temperate forest fires: emission factors and dependence on modified combustion efficiency.

Gunashanhar G, Kirkwood J, Salter D, White B, Paton-Walsh C (2021) Secondary organic aerosols over oceans via oxidation of isoprene and monoterpenes from Arctic to Antarctic. Sci Rep 3(1):1–7. https://doi.org/10.1038/srep02280.

Harris S, Lucas C (2019) Understanding the variability of Australian fire weather between 1973 and 2017. PLOS One 14(9). https://doi.org/10.1371/journal.pone.0222328.

Health Protection Service (2021) Monash air quality station. ACT Government. https://www.data.act.gov.au/Environment/Monash-Air-Quality-Station/kjyg-eang. Accessed 10 August 2020.

Hodshire AL, Akherati A, Alvarado MJ, Brown-Steiner B, Jathar SH, Johnston FH, Henderson SB, Chen Y, Randerson JT, Marlier M, Defries RS, Kinney P, Bowman DM, Brauer M (2012) Estimated global mortality attributable to smoke from landscape fires. Environ Health Perspect 120(5):695–701. https://doi.org/10.1289/ehp.1104422.

Kasischke ES, Penner JE (2004) Improving global estimates of atmospheric emissions from biomass burning. Journal of Geophysical Research: Atmospheres 109(D14). https://doi.org/10.1029/2004jd004972.

Kay D, Barbato J, Brassington G, de Somer B (2006) Impacts of long-wall mining to rivers and cliffs in the southern coalfield. Paper presented at the Coal 2006: Coal Operators’ Conference, University of Wollongong.

Kesselmeier J, Staudt M (1999) Biogenic volatile organic compounds (VOC): an overview on emission, physiology and ecology. J Atmos Chem 33(1):23–38. https://doi.org/10.1023/A:10061127516791.

Keywood M, Cope M, Meyer CPM, Inuuma Y, Emmerson K (2015) When smoke comes to town: the impact of biomass burning smoke on air quality. Atmos Environ 121:13–21. https://doi.org/10.1016/j.atmosenv.2015.03.050.

Keywood M, Kanakidou M, Stohl A, Dentener F, Grassi G, Meyer CP, Torseth K, Edwards D, Thompson AM, Lohmann U, Burrows J (2013) Fire in the air: biomass burning impacts in a changing climate. Crit Rev Environ Sci Technol 43(1):40–83. https://doi.org/10.1080/10643938.2011.604248.

Keywood MD, Humphries R. S., Paton-Walsch C, Naylor TA, Gamboa JR, Simmons JB, Carter A, Dang QP, Webb A (2021) Black carbon aerosol measurements at Cataract Scout Park, Australia, taken during the COALA-2020 campaign. PANGAEA. https://doi.org/10.1594/PANGAEA.927544.

Keywood MD, Humphries RS, Paton-Walsch C, Naylor TA, Ramirez-Gamboa J, Simmons JB, Carter A, Dang QP, Webb A (2020) Condensation nuclei >3 nm (CN3) measurements at Cataract Scout Park, Australia, taken during the COALA-2020 campaign. PANGAEA. https://doi.org/10.1594/PANGAEA.925555.

Lelieveld J, Evans JS, Finais M, Giannadaki D, Pozzer A (2015) The contribution of outdoor air pollution sources to premature mortality on a global scale. Nature 525(7569):367–371. https://doi.org/10.1038/nature15171.

Lighty JS, Veranith JM, Sarofim AF (2000) Combustion aerosols: factors governing their size and composition and implications to human health. J Air Waste Manag Assoc 50(9):1565–1618. https://doi.org/10.1080/10473299.2000.10464197.

Liu Y, Goodrick S, Heilman W (2014) Wildland fire emissions, carbon, and climate: wildfire-climate interactions. For Ecol Manage 317:80–96. https://doi.org/10.1016/j.foreco.2013.02.020.

Lonsdale CR, Alvarado MJ, Hodshire AL, Rammarine E, Pierce JR (2020) Simulating the forest fire plume dispersion, chemistry, and aerosol formation using SAM-ASP version 1.0. Geosci Model Dev 13(9):4579–4593. https://doi.org/10.5194/gmd-13-4579-2020.

Luo L, Zhang Y-Y, Xiao H-Y, Xiao H-W, Zheng N-J, Zhang Z-Y, Xie Y-J, Liu C (2019) Spatial distributions and sources of inorganic chlorine in PM2.5 across China in winter. Atmosphere 10(9):505. https://doi.org/10.3390/atmos10090505.

MacSween K, Paton-Walsch C, Roulston C, Güerette E-A, Edwards G, Reisen F, Desservetaz M, Cameron M, Young E, Kubistin D (2020) Cumulative firefighter exposure to multiple toxins emitted during prescribed burns in Australia. Exposure and Health 12(4):721–733. https://doi.org/10.1017/s1224031900332-w.

May AA, Lee T, McMeeking GR, Akagi S, Sullivan AP, Urbanski S, Yokelson RJ, Kreidenweis SM (2015) Observations and analysis of organic aerosol evolution in some prescribed fire smoke plumes. Atmos Chem Phys 15(11):6323–6335. https://doi.org/10.5194/acp-15-6323-2015.

McFiggans G, Mentel TF, Wildt J, Pullinen I, Kang S, Kleist E, Schmitt S, Springer M, Tillmann R, Wu C (2019) Secondary organic
National Environmental Council (1998) National Environment Protection Act 1999. Commonwealth of Australia, Canberra.

Ng NL, Canagaratna MR, Zhang Q, Jimenez JL, Tian J, Ulbrich IM, Kroll JH, Docherty KS, Chhabra PS, Bahreini R, Murphy SM, Seinfeld JH, Hildebrandt L, Donahue NM, DeCarlo PF, Lanz VA, Prévôt ASH, Dinar E, Rudich Y, Worsnop DR (2010) Organic aerosol components observed in Northern Hemispheric datasets from Aerosol Mass Spectrometry. Atmos Chem Phys 10(10):4625–4641. https://doi.org/10.5194/acp-10-4625-2010

Nolan RH, Boer MM, Collins L, Resco de Dios M, Hidalgo A, Clarke H, Jenkins M, Kenny B, Bradstock RA (2020) Causes and consequences of bushfire seasons in eastern Australia’s 2019–2020 season of mega-fires. Glob Change Biol 26(3):1039–1041. https://doi.org/10.1111/gcb.14987

NSW Department of Planning (2008) Impacts of underground coal mining on natural features in the Southern Coalfield: strategic review. State of New South Wales, Sydney, Australia.

O’Dell K, Hornbrook RS, Permarr W, Levin EJF, Garofalo LA, Apel EC, Blake NJ, Jarnot A, Pothier MA, Farmer DK, Hu L, Campos T, Ford B, Pierce JR, Fischer EV (2020) Hazardous air pollutants in fresh and aged western US wildfire smoke and implications for long-term exposure. Environ Sci Technol 54(19):11838–11847. https://doi.org/10.1021/acs.est.0c04497

Paton-Walsh C, Griffiths DWT, Humphries R, Keywood M, Naylor T, Simmons J, Ramírez-Gamboa J (2022) COALA overview paper. Paton-Walsh C, Baynfield JS, Fiddes SL, Schofield R, Bridgeham H, Beaupark S, Broome R, Chambers SD, Chang LT-C, Cope M, Cowie CT, Desservetta M, Dominick D, Emmerson K, Forehead H, Gallabey IE, Griffiths A, Guérette É-A, Haynes A, Heyworth J, Jalaludin B, Kan R, Keywood M, Monk K, Morgan GG, Nguyen Duc H, Phillips F, Popek R, Scorgie Y, Silver JD, Utens EM, Wadlow I, Wilson SR, Zhang Y (2019) A clean air plan for Sydney: an overview of the special issue on air quality in New South Wales. Atmosphere 10(12):774. https://doi.org/10.3390/atmos10120774

Paton-Walsh C, Smith T, Young E, Griffith DW, Guérette É-A (2014) New emission factors for Australian vegetation fires measured using open-path Fourier transform infrared spectroscopy—Part 1: methods and Australian temperate forest fires. Atmos Chem Phys 14:11313–11333. https://doi.org/10.5194/acp-14-11313-2014

Paton-Walsh C, Wilson SR, Jones NB, Griffith DWT (2008) Measurement of methanol emissions from Australian wildfires by ground-based solar Fourier transform spectroscopy. Geophysical Research Letters 35(8). https://doi.org/10.1029/2007GL032951

Pettitt T, Torpy FR, Surawski N, Fleck R, Irga PJ (2021) Effective reduction of roadside air pollution with botanical biofiltration. Journal of Hazardous Materials 414. https://doi.org/10.1016/j.jhazmat.2021.125566

Pope CA III, Burnett RT, Thun MJ, Calle EE, Krewski D, Ito K, Thurston GD (2002) Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution. J Am Med Assoc 287(9):1132–1141. https://doi.org/10.1001/jama.287.9.1132

Prichard SJ, O’Neill SM, Eagle P, Andreu AG, Drye B, Dubowy J, Urbanski S, Strand TM (2020) Wildland fire emission factors in North America: synthesis of existing data, measurement needs and management applications. Int J Wildland Fire 29(2):132–147. https://doi.org/10.1071/WF19066

Qi L, Wang S (2019) Fossil fuel combustion and biomass burning sources of global black carbon from GEOS-Chem simulation and carbon isotope measurements. Atmos Chem Phys 19(17):11545–11557. https://doi.org/10.5194/acp-19-11545-2019

Queensland Government (2020) Download air data. Queensland Government. https://apps.des.qld.gov.au/air-quality/download/. Accessed 19 May 2020

Ramirez-Gamboa J, Paton-Walsh C, Galbally I, Simmons J, Guerette E-A, Griffith AD, Chambers SD, Williams AG (2021) Seasonal variation of biogenic and anthropogenic VOCs in a semi-urban area near Sydney. Australia Atmosphere 12(1):47. https://doi.org/10.3390/atmos12010047

Rea G, Paton-Walsh C, Turquety S, Cope M, Griffith D (2016) Impact of the New South Wales fires during October 2013 on regional air quality in eastern Australia. Atmos Environ 131:150–163. https://doi.org/10.1016/j.atmosenv.2016.01.034

Reisen F, Brown SK (2009) Australian firefighters’ exposure to air toxics during bushfire burns of autumn 2005 and 2006. Environ Int 35(2):342–352. https://doi.org/10.1016/j.envint.2008.08.011

Reisen F, Meyer CP, Westphal CJ, Volkova L (2018) Ground-based field measurements of PM2.5 emission factors from flaming and smoldering combustion in eucalypt forests. J Geophys Res: Atmospheres 123(15):8301–8314. https://doi.org/10.1029/2018jd028488

Roldin P, Liao L, Mogensen D, Dal Maso M, Rusanen A, Kerminen VM, Mentel TF, Wildt J, Kleist E, Kiendler-Scharr A, Tillmann R, Ehn M, Kulmala M, Boy M (2015) Modelling the contribution of biogenic volatile organic compounds to new particle formation in the Jülich plant atmosphere chamber. Atmos Chem Phys 15(8):10777–10798. https://doi.org/10.5194/acp-15-10777-2015

Ryan RG, Silver JD, Schofield R (2021) Air quality and health impact of 2019–20 Black Summer megafires and COVID-19 lockdown in Melbourne and Sydney. Australia Environmental Pollution 274:116498. https://doi.org/10.1016/j.envpol.2021.116498

Safe Work Australia (2019) Workplace exposure standards for airborne contaminants. Safe Work Australia Canberra, AUS.

Salimi F, Henderson SB, Morgan GG, Jalaludin B, Johnston FH (2017) Ambient particulate matter, landscape fire smoke, and emergency ambulance dispatches in Sydney, Australia. Environ Int 99:208–212. https://doi.org/10.1016/j.envint.2016.11.018

Shi Y, Matsunaga T, Saito M, Yamaguchi Y, Chen X (2015) Composites reduced by mixture of atmospheric vapours. Nature 526(7574):587–593. https://doi.org/10.1038/nature15861-018-0871-y

Milet A, Mallett MD, Crivagian LT, Alroe J, Ristovski ZD, Selleck P, Lawson SJ, Ward J, Desservetvart MJ, Paton-Walsh C, Williams LR, Keywood MD, Miljevic B (2017) Biomass burning and biogenic aerosols in northern Australia during the SAFIRE campaign. Atmos Chem Phys 17(6):3945–3961. https://doi.org/10.5194/acp-17-3945-2017

Miranda AI, Martins V, Cascão P, Amorim JH, Valente J, Tavares R, Borrego C, Tchepef O, Ferreira AJ, Cordeiro CR, Viegas DG, Ribeiro LM, Pita LP (2010) Monitoring of firefighters exposure to smoke during fire experiments in Portugal. Environ Int 36(7):736–745. https://doi.org/10.1016/j.envint.2010.05.009

Morgan G, Shepperd V, Khalaj B, Ayyar A, Lincoln D, Jalaludin B, Beard J, Corbett S, Kumley T (2010) Effects of bushfire smoke on daily mortality and hospital admissions in Sydney. Australia Epidemiology 21(1):47–55. https://doi.org/10.1097/EDE.0b013e3181c5d5a

Mouat AP, Kaiser J, Paton-Walsh C, Gamboa JR, Naylor TA, Simmons JB (2021a) Volatile organic compound measurements at Cataract Scout Park, Australia, taken during the COALA-2020 campaign. PANGAEA. https://doi.org/10.1594/PANGAEA.927277

Mouat AP, Paton-Walsh C, Simmons JB, Ramírez-Gamboa J, Griffith DWT, Kaiser J (2021) Emission factors of long-lived volatile organic compounds from the 2019–2020 Australian wildfires during the COALA campaign. Atmos Chem Phys Discuss 2021:1–13. https://doi.org/10.5194/acp-2021-742

Nacher LP, Brauer M, Lipsitt M, Zeilikoff JT, Simpson CD, Koenig JQ, Smith KR (2007) Woodsmoke health effects: a review. Inhalation Toxicol 19(1):67–106. https://doi.org/10.1080/08958370600985875

National Environmental Council (1998) National Environment Protection (Ambient Air Quality) Measure. Commonwealth of Australia, Canberra.
burning during 2002–2011 derived from multiple satellite products. Environ Pollut 206:479–487. https://doi.org/10.1016/j.envpol.2015.08.009

Sillanpää M, Saarikoski S, Hiltamo R, Pennanen A, Makkonen U, Spolnik Z, Van Grieken R, Koskentalo T, Salonen RO (2005) Chemical composition, mass size distribution and source analysis of long-range transported wildfire smokes in Helsinki. Sci Total Environ 350(1):119–135. https://doi.org/10.1016/j.scitotenv.2005.01.024

Sinha P, Hobbs PV, Yokelson RJ, Bertschi IT, Blake DR, Simpson IJ, Gao S, Kirchstetter TW, Novakov T (2003) Emissions of trace gases and particles from savanna fires in southern Africa. Journal of Geophysical Research: Atmospheres 108(D13). https://doi.org/10.1029/2002JD002325

Surawski NC, Sullivan AL, Roxburgh SH, Polglase PJ (2016) Estimates of greenhouse gas and black carbon emissions from a major Australian wildfire with high spatiotemporal resolution. J Geophys Res: Atmospheres 121(16):9892–9907. https://doi.org/10.1002/2016JD025087

US EPA (2020) Dose-response assessment for assessing health risks associated with exposure to hazardous air pollutants. https://www.epa.gov/fera/dose-response-assessment-assessing-health-risks-associated-exposure-hazardous-air-pollutants. Accessed September 13 2021

Utembe SR, Rayner PJ, Silver JD, Guérette E-A, Fisher JA, Emmerson KM, Cope M, Paton-Walsh C, Griffiths AD, Duc H, Monk K, Scorgie Y (2018) Hot summers: effect of extreme temperatures on ozone in Sydney, Australia. Atmosphere 9(12):466. https://doi.org/10.3390/atmos9120466

van der Werf GR, Randerson JT, Giglio L, Collatz GJ, Kasibhatla PS, Arellano AF Jr (2006) Interannual variability in global biomass burning emissions from 1997 to 2004. Atmos Chem Phys 6(11):3423–3441. https://doi.org/10.5194/acp-6-3423-2006

Vyskocil A, Drolet D, Vian C, Lemay F, Lapointe G, Tardif R, Truchon G, Baril M, Gagnon N, Gagnon F, Bégin D, Gérin M (2007) A Web Tool for the identification of potential interactive effects of chemical mixtures. J Occup Environ Hyg 4(4):281–287. https://doi.org/10.1080/15459620701225103

Walter CM, Schneider-Futschik EK, Knibbs LD, Irving LB (2020) Health impacts of bushfire smoke exposure in Australia. Respirology 25(5):495–501. https://doi.org/10.1111/resp.13798

Wayne RP (1991) Chemistry of atmospheres: an introduction to the chemistry of the atmospheres of earth, the planets, and their satellites. Oxford University Press, Oxford, UK

Wu C, Yu JZ (2018) Evaluation of linear regression techniques for atmospheric applications: the importance of appropriate weighting. Atmos Meas Tech 11(2):1233–1250. https://doi.org/10.5194/amt-11-1233-2018

Xiao H-W, Xiao H-Y, Shen C-Y, Zhang Z-Y, Long A-M (2018) Chemical composition and sources of marine aerosol over the western north Pacific ocean in winter. Atmosphere 9(8):298. https://doi.org/10.3390/atmos9080298

Young E, Paton-Walsh C (2011) Emission ratios of the tropospheric ozone precursors nitrogen dioxide and formaldehyde from Australia’s black Saturday fires. Atmosphere 2(4):617–632. https://doi.org/10.3390/atmos2040617

Yu H, Ortega J, Smith JN, Guenther AB, Kanawade VP, You Y, Liu Y, Hosman K, Karl T, Seco R, Geron C, Pallardy SG, Gu L, Mikliä J, Lee SH (2014) New particle formation and growth in an isoprene-dominated ozark forest: from sub-5 nm to CCN-active sizes. Aerosol Sci Technol 48(12):1285–1298. https://doi.org/10.1080/02786866.2014.984801

Zhang YJ, Tang LL, Wang Z, Yu HX, Sun YL, Liu D, Qin W, Cano-naco F, Prévôt ASH, Zhang HL, Zhou HC (2015) Insights into characteristics, sources, and evolution of submicron aerosols during harvest seasons in the Yangtze River delta region. China Atmos Chem Phys 15(3):1331–1349. https://doi.org/10.5194/acp-15-1331-2015

Zhou S, Collier S, Jaffe DA, Briggs NL, Hee J, Sedlacek AJ III, Kleinman L, Onasch TB, Zhang Q (2017) Regional influence of wildfires on aerosol chemistry in the western US and insights into atmospheric aging of biomass burning organic aerosol. Atmos Chem Phys 17(3):2477–2493. https://doi.org/10.5194/acp-17-2477-2017

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