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Full length article

Characterising the ground level concentrations of harmful organic and inorganic substances released during major industrial fires, and implications for human health

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ABSTRACT

We report on the concentration ranges and combustion source-related emission profiles of organic and inorganic species released during 34 major industrial fires in the UK. These episodic events tend to be acute in nature and demand a rapid public health risk assessment to indicate the likely impact on exposed populations. The objective of this paper is to improve our understanding of the nature, composition and potential health impacts of emissions from major incident fires and so support the risk assessment process. Real world monitoring data was obtained from portable Fourier Transform Infrared (FTIR) monitoring (Gasmeter DX-4030/40) carried out as part of the UK's Air Quality in Major Incidents service. The measured substances include carbon monoxide, sulphur dioxide, nitrogen dioxide, ammonia, hydrogen chloride, hydrogen bromide, hydrogen fluoride, hydrogen cyanide, formaldehyde, 1,3-butadiene, benzene, toluene, xylenes, ethyl benzene, acrolein, phosgene, arsine, phosphine and methyl isocyanate. We evaluate the reported concentrations against Acute Exposure Guideline Values (AEGVs) and Emergency Response Planning Guidelines (ERPGs), as well as against UK, EU and WHO short-term ambient guideline values. Most exceedances of AEGL or ERPG guideline values were at levels likely only to cause discomfort to exposed populations (hydrogen cyanide, hydrogen chloride, hydrogen fluoride and formaldehyde), though for several substances the exceedances could have potentially given rise to more serious health effects (acrolein, phosphine, phosgene and methyl isocyanate). In the latter cases, the observed high concentrations are likely to be due to cross-interference from other substances that absorb in the mid-range of the infrared spectrum, particularly when the ground level plume is very concentrated.

1. Introduction

An uncontrolled open burn, such as a major industrial fire, is the unenclosed thermal decomposition of materials in the ambient environment (Lemieux et al., 2004). This generally takes place under less-than-ideal conditions whereby the inefficient mixing of fuels, limited oxygen availability, inadequate residency time, and reduced temperature for gaseous phase combustion (Lemieux et al., 2004; Zhang et al., 2015; Stec, 2017; Purser et al., 2016) leads to incomplete combustion, giving rise to higher concentrations of particulate matter ($\leq 10 \mu\text{m}$, PM_{10} ; $\leq 2.5 \mu\text{m}$, $\text{PM}_{2.5}$ and $\leq 1.0 \mu\text{m}$, PM_1), carbon monoxide (CO), methane (CH_4), and VOCs (e.g. benzene, toluene, ethylbenzene, xylenes, styrene and acrolein) compared to ideal conditions (Lemieux et al.,

2004; Shakya et al., 2008; Zhang et al., 2015). Additionally, there is concern about the concentrations of persistent organic substances that might be released during suboptimal conditions, including polycyclic aromatic hydrocarbons (PAHs), chlorinated and brominated PAHs, polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), which are often associated with the particulate phase and where, dependent on the size of the particulate fraction, could penetrate deep into the lung (Nishimura et al., 2017; Estrellan and Iino, 2010; Lemieux et al., 2004). Uncontrolled open fires also exhibit an increased ratio of mass of pollutant emitted per mass of fuel burned compared to controlled combustion processes (Persson and Simonson, 1998; Stec, 2017; Lemieux et al., 2004). Moreover, when these events occur near a human population, and the release is close to the ground

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(Lemieux et al., 2004), there is a greater potential for exposure, leading to an increased threat to physical and mental health (Baxter et al., 1995; WHO, 2002, 2009). These episodic events, tend to be acute in nature and demand a rapid public health risk assessment to determine how the elevated concentrations of PM and gaseous chemical species could impact on human health (Duarte-Davidson et al., 2018).

In this paper, we explore the range and mix of organic and inorganic species that were monitored during 34 separate major industrial fires in the UK. The data was obtained from portable (Gasmeter DX-4030 or DX4040) Fourier Transform Infrared (FTIR) monitoring carried out as part of the UK's Air Quality in Major Incident service (AQinMI). The AQinMI commenced in 2009, largely as a response to the acknowledged lack of ground level plume monitoring data available during the Buncefield (Hertfordshire, UK) oil depot explosion and sustained fire in December 2005 (Barker, 2010; Buncefield Major Incident Investigation Board, 2007; Environment Agency, 2016; Griffiths et al., 2018). The AQinMI service coordinates the submission of ground level plume monitoring data to an Air Quality Cell (AQC), which is a multi-agency response service that provides public health protection advice to responders and health services during major incident fires, which are those that are likely to "pose a significant risk to public health, or cause a significant number or type of casualties, such that special arrangements are needed to manage them" (Griffiths et al., 2018). As an operational guideline, major incident fires are those that are likely to have a duration of >6 h (Barker, 2010; Griffiths et al., 2018). The decision to institute an AQC is jointly made between the national environmental regulator (English Environment Agency, EA; Scottish Environmental Protection Agency, SEPA; or Natural Resources Wales, NRW) and the public health services, based on the scale of the incident. In making a decision, they will consider the extent of population exposure, the type of materials on fire and the likely duration before the fire is brought under control. Even where agreed to be established, an AQinMI AQC has three tiers of response ranging from tier-1 which is a smaller scale event where advice agreed between the services is all that is necessary to manage the threat to public health and the environment; tier-2, which has an AQC established with teleconferences used to develop advice whilst the event unfolds; and, tier-3, which extends tier-2 with the deployment of monitoring teams to the scene of the incident. We have previously detailed the role of the AQinMI service and AQCs in Griffiths et al. (2018).

The Gasmeter FTIR instrument allows near real-time monitoring of a customisable suite of organic and inorganic substances. For the AQinMI service, the suite comprised carbon monoxide (CO), nitrous oxide (N₂O), sulphur dioxide (SO₂), nitrogen dioxide (NO₂), ammonia (NH₃), hydrogen chloride (HCl), hydrogen bromide (HBr), hydrogen fluoride (HF), hydrogen cyanide (HCN), formaldehyde, 1,3-butadiene, benzene, toluene, ethyl benzene, m-xylene, o-xylene, p-xylene, acrolein, phosgene (COCl₂), arsine (AsH₃), phosphine (PH₃) and methyl isocyanate. In this paper, we retrospectively analyse concentration profiles of these substances, measured during the acute phase of the major industrial fire incidents. The profiles are analysed according to the composition of the source material and are also compared to relevant publicly available acute toxicological and ambient air quality standards to indicate the potential threat to public health.

As far as we are aware, taken together with our previously reported AQinMI particulate matter monitoring data (Griffiths et al., 2018), this is the most comprehensive study yet on emissions of harmful substances during major fire incidents from a range of industrial sources. There are literature reports on the monitoring of individual fires, such as the mobile tracking of HCl and chlorine release from a factory fire in Ontario Canada (Karellas et al., 2003), and several studies that have measured concentrations of toxic substances to which firefighters are exposed (Alharbi et al., 2021; Fabian et al., 2014; Burgess and Crutchfield, 1995). In addition, some studies have simulated the likely ground level concentrations at locations adjacent to an industrial waste fire (Rasmussen et al., 1998) or to bush fires (De Vos et al., 2009). Our study differs in

that we report the measured concentrations for a wide range of toxic substances from real-world industrial fires at locations and distances where local populations might be exposed. Our aim in carrying out this work is to increase the understanding of atmospheric emissions from major incident fires, thus supporting the process of public health risk assessment and response during such events (WHO, 2009; WHO, 2012; Brunt and Russell, 2012; Stewart-Evans et al., 2016; Griffiths et al., 2018; Deary and Griffiths, 2021). Two of the authors were involved in the AQinMI service, as lead for the North of England monitoring Team, and in overall incident management.

2. Methodology

2.1. Sampling and analysis

2.1.1. Source of monitoring data

Gasmeter and other monitoring data from field measurements taken during major incident fires was obtained from the respective environment agencies of the UK (with the exception on Northern Ireland, which does not have an AQinMI service). In Scotland the AQinMI service is called the Airborne Hazard Emergency Response (AHER) Service (SEPA, nd) although, for the purpose of this paper, we refer to AQinMI as including AHER. The data obtained from the UK environment agencies covered the following periods: for England, data was available for the EA from April 2009 to March 2016 (of which England and Wales data was combined for the period 2009 to 2013); for Wales, NRW disclosed data for April 2013 to March 2018; and for Scotland, the SEPA disclosure was for April 2009 to January 2018.

Details of the 76 AQC events disclosed by the respective UK regulatory authorities, covering England, Scotland and Wales, are summarised in Table S1 (EA), Table S2 (NRW), and Table S3 (SEPA), and comprised 31 AQCs for England over the period April 2009 to March 2016, 5 AQC events for Wales over the period April 2013 to March 2018 and 40 AQC events for Scotland over the period April 2009 to January 2018. However, the process of evaluating consistency for what each agency labelled an AQC event demonstrated differences in the recording of events within the disclosures. 25 SEPA events were found to be inconsistent with the standard AQC model (see Table S4). This left 15 equivalent SEPA AQC events, reducing the overall number of AQC events to 51 across the three countries, though only 34 of these contributed Gasmeter monitoring data.

2.1.2. Selection of monitoring locations for AQinMI deployment

Under the AQinMI service, monitoring locations are chosen to establish whether day-to-day functions of the population can continue without changes in public behaviour (McParland and Paranthaman, 2012). Decisions on the specific deployment locations of the field monitoring teams (generally two per incident) (Environment Agency, 2019) were dynamic, allowing the multi-agency AQC latitude to respond to changes in modelled plume behaviour such as a change in wind direction (Meteorological Office, 2017), as well as taking into account the location of vulnerable receptors, for example, primary schools, hospitals and care homes. Additional deployment considerations include the availability of an electrical supply for the monitoring equipment because whilst the Gasmeter and Osiris (for PM measurements) instruments can operate with their own batteries for several hours, other monitoring equipment, such as the high volume samplers used to collect particulate samples for organic/inorganic speciation, required an independent electrical supply, as did the recharging of batteries (Izon-Cooper, 2010). Deployment also needs to consider how the occupational health and safety of the monitoring team will be protected (Environment Agency, 2018). The teams had access to face masks for temporary protection but could not be deployed to locations where Workplace Exposure Levels were likely to be breached (Environment Agency, 2016; Lemieux et al., 2004). Furthermore, at all times during the incident the monitoring teams were required to conduct regular dynamic risk assessments to

ensure that their safety was not compromised in any way.

Figures S1 to S23 in the [Supplementary material](#) show maps of the vicinity of the major incident fires, including locations of the source of the fire and the points at which the mobile monitoring teams were deployed. Also shown, to give context on the likely exposure of local populations and vulnerable receptors, is the use category of buildings in the vicinity, i.e. residential, health, recreational, retail and industrial etc. Maps are only shown for England and Wales, as we did not have details of the precise sampling locations for the SEPA incidents.

2.1.3. Principle and operation of the Gaset instruments

The Gaset instrument (DX 4030 or DX 4040) is an indicative monitor capable of detecting a range of organic and inorganic chemical species common to open incineration or loss of containment chemical events. It is also a pragmatic choice given it can be rapidly deployed ([Environment Agency, 2016; Griffiths et al., 2018](#)) and so supports the prompt risk assessment needs of an acute public health event ([Duarte-Davidson et al., 2018](#)). Gaset instruments have been routinely deployed in a varied range of settings, such as fluidised-bed combustion ([Atimtay et al., 2017](#)), sludge drying ([Chen et al., 2014](#)), PCDD/Fs suppression ([Fu et al., 2015](#)), methane emissions from dairy cows ([Haque et al., 2014](#)), pyrolysis ([Lupa et al., 2012](#)), coffee roasting and blending ([McCoy et al., 2017](#)), bush fires in Eastern Australia ([Rea et al., 2016](#)) and fires at recycling facilities in the UK ([Gaset, 2021](#)).

The Gaset instrument was calibrated by the manufacturer with 24 pre-set substances, as listed in [Table 1](#), which also shows the respective detection limits and identifies the relevant ambient and emergency air quality guidelines available for comparison to measured levels. These substances were chosen by the AQinMI service as those likely to be released during major fire incidents and which also present a risk to public health.

When the Gaset is in operation, air is continuously drawn through a non-condensing probe at a rate of 2 L min⁻¹ with the analyser collecting 10 complete infrared spectra per second for a total measurement period of 60 s. The effective pathlength of the instrument is 9.8 m ([Quantitech Limited, nd](#)). The complex mixture of gases is resolved through a least squares algorithm that utilises the entire collected spectrum in the mid-range infrared region (2 µm to 12 µm) ([Gaset Technologies, 2016](#)).

2.1.4. Instrument quality control procedures

All instruments used in the AQinMI service were checked on a weekly basis to ensure that they were operating within the manufacturer's specification. These tests were repeated during set-up at major incident deployments. For the Gaset check, the instrument was allowed to warm-up for 30 min before flushing the measurement cell with N₂ at a flow rate of 1.5 L min⁻¹. Then, through the Calcmet Lite operating software, the hardware status of the instrument was recorded, including path length, cell temperature and pressure compared to

Table 1

Summary of species that are included in the AQinMI Gaset analysis suite, along with the corresponding limit of detection. Indicated by a tick-mark, are acute toxicological and ambient standards available for comparison in this study. Species are grouped by category of health effect. Note that carbon dioxide and methane are not species that are included in AQC reporting, though they are part of the monitoring suite ([Environment Agency, 2019](#)).

Species	Limit of detection/ppm (manufacturers information)	Emergency guidelines available		Short-term ambient air pollution standards available		
		AEGL (US EPA, 2018)	ERPG (American Industrial Hygiene Association, 2019)	European Union (2008)	Primary standards (US EPA, 2016b)	WHO (2021) WHO (2006)
Asphyxiant gases						
Carbon dioxide (CO ₂)	10	No appropriate environmental exposure standard available				
Carbon monoxide (CO)	0.25	✓	✓		✓	
Hydrogen cyanide (HCN)	0.35	✓	✓			
Methane (CH ₄)	0.11	No appropriate environmental exposure standard available				
Inorganic irritant gases						
Ammonia (NH ₃)	0.13	✓	✓			
Hydrogen bromide (HBr)	3.0	✓				
Hydrogen chloride (HCl)	0.20	✓	✓			
Hydrogen fluoride (HF)	0.20	✓	✓			
Nitrous oxide (N ₂ O)	0.02					
Nitrogen dioxide (NO ₂)	0.37	✓	✓	✓	✓	✓
Phosgene (COCl ₂)	0.20	✓	✓			
Sulphur dioxide (SO ₂)	0.30	✓	✓	✓	✓	✓
Organic irritants						
Acrolein (C ₃ H ₄ O)	0.25	✓	✓			
Benzene	0.13	✓	✓			
1,3-Butadiene	0.20	✓	✓			
Ethyl benzene	0.08	✓				
Formaldehyde (CH ₂ O)	0.09	✓	✓			
Methyl isocyanate (C ₂ H ₃ NO)	0.25	✓	✓			
m-Xylene	0.12	✓				
o-Xylene	0.12	✓				
p-Xylene	0.12	✓				
Toluene	0.13	✓	✓			
Other toxic effects e.g., including tissue oedema, central nervous system effects, haemolysis						
Arsine (AsH ₃)	0.02	✓	✓			
Phosphine (PH ₃)	0.20	✓	✓			

ambient, percentage source intensity, interference centre, electronics temperature and detector temperature. The final test step was to perform a zero calibration, with the resulting spectrum being visually compared to a sample spectrum, as well as with a range of spectrum QC parameters (Environment Agency, 2013).

2.2. Statistical analysis of the data

2.2.1. Descriptive statistics

Gasmet monitoring data was received as Excel spreadsheets. The data was checked to remove overlapping temporal data-points where multiple sheets were submitted for a single event. Excel was used to generate a range of descriptive statistics, including mean, median, quartile-1 and quartile-3 values, maximum value, and Robust Highest Concentration (RHC). The latter parameter calculates a representative estimate of peak concentrations that can reduce the influence of outliers (Cox and Tikvart, 1990; Deary and Uaipatanakul, 2014). RHC values have been calculated from a tail exponential fit of the highest observed values as shown in Equation (1) (Cox and Tikvart, 1990; Frost, 2014), where X_n is the n^{th} highest concentration and \bar{X}_{n-1} is the average of the $n-1$ highest concentrations.

$$RHC = X_n + (\bar{X}_{n-1} - X_n) \ln\left(\frac{3n-1}{2}\right) \quad (1)$$

The number of values used in the tail fit is 'arbitrary' (Cox and Tikvart, 1990) but 26 is well established for cases where $n > 100$ (Cox and Tikvart, 1990; O'Shaughnessy and Altmaier, 2011; Deary and Uaipatanakul, 2014). Where the total number of data-points is ≤ 100 the number of points used for the tail fit will be one quarter n (a range of between 10 and 25 points in our case). For our data, no RHC value was calculated when the number of data-points was ≤ 39 .

2.2.2. Utilisation of calculated RHC values to identify instrumental errors

Outlier RHC values (those exceeding 1.5 times the interquartile range (Tukey, 1977)) were identified and investigated as possible indicators of instrumental error. The approach assumes an equal distribution of data but episodic monitoring results are routinely skewed meaning that apparent outliers may not necessarily be such (Hubert and Vandervieren, 2008). Where an RHC value was indicated as an outlier, the original monitoring data was examined to identify possible reasons for this indication and to confirm that it was not simply a consequence of a skew in the monitoring results. Two instrument function parameters were found to regularly coincide with exceptionally high species concentrations and so enabled the identification of outliers for removal, these being: (1) a sharp increase or decrease in interferometer temperature readings ($\pm 109^\circ\text{C}$ where the median was 22.2°C) that affected EA20 (3.67% observations removed) and EA25 (3.18% observations removed); and (2) the cell temperature reducing from $c. 25^\circ\text{C}$ to $c. 15^\circ\text{C}$ affecting NRW5 (3.72% observations removed). Unrealistically high SO_2 concentrations in EA28 were also excluded (0.06% observations removed).

2.3. Profiling of emissions

2.3.1. Categorisation of events by 'primary material'

A range of secondary sources including the UK Standard Industrial Classification of Economic Activities (SIC code) (Office of National Statistics, 2007), Companies House listings (UK Government, 2021), company websites, media reports of incidents and fire service response records, were used to confirm the 'primary material' contributing to the combustion source in each of the events. The resultant categories were: waste electrical and electronic equipment (WEEE), mixed recyclables, timber and wood products, tyre and tyre crumb, residual mixed waste and other/undisclosed. One event, EA9, occurred at chemical manufacturing plant, and has been included as a separate category. We were then able to analyse Gasmet concentration data according to

primary combustion material, allowing an emission profile to be developed for each of these categories.

2.3.2. Relative emission factors for different primary source categories

Emission profiles, according to primary material type, were based on the mean concentrations measured during events. One significant problem in deriving such profiles is the wide range of variable factors that contribute to the ground level concentrations at a specific monitoring location, for example: distance from source, burn rate, volume of material, firefighting methods, wind direction and other meteorological variables. Therefore, for each incident, we normalised the concentrations to 100%, based on the respective contributions of each of the gases listed in Table 1, except for CO_2 and CH_4 . An average 'normalised emissions profile' (NEP) was calculated for each species and for (a) all events and (b) for each different source category.

For relative emission factors (REF) we have taken as a baseline the NEP for all events combined. Compared to this baseline, we identified the relative level of emission for each species. So, for example, if NH_3 contributed 3.48% of the total concentration of species emitted during tyre fires but 1.59% for all fires, this indicates that NH_3 is found at greater relative levels during tyre fires, and corresponds to a REF value of 2.17. Thus, REFs > 1 indicate that emissions of a particular substance are over-represented for a specific source material category compared to all events. The results of this analysis are displayed as polar plots.

2.4. Retrospective toxicological appraisal

The standards selected for the evaluation of possible toxicological effects correspond to short duration exposures, and are therefore appropriate to the acute, episodic nature of the events listed in Table 1. They include emergency standards, i.e. AEGL (US EPA, 2016a), and ERPG (American Industrial Hygiene Association, 2019), as well as ambient standards that have an appropriate short averaging period (≤ 8 -hr). Rolling average periods were used to calculate exceedances. Equation (2) (Boguski, 2006) was used to convert ambient standards expressed in $\mu\text{g m}^{-3}$ to ppm, where MW is the molecular mass of the substance and 24.45 is a constant (the number of litres occupied by 1 mol of an ideal gas at 25°C).

$$\text{Value of standard (ppm)} = \frac{24.45}{MW} \times \frac{\text{Value of standard } (\mu\text{g m}^{-3})}{1000} \quad (2)$$

3. Results and discussion

3.1. AQinMI event characteristics

Details of the 76 AQC events disclosed by the respective UK regulatory authorities, covering England, Scotland and Wales, are summarised in Table S1 (EA), Table S2 (NRW), and Table S3 (SEPA). Open uncontrolled burns comprised all EA and NRW events ($n = 36$), and 80% ($n = 12$) of SEPA events. Loss of containment contributed the remaining SEPA events (20%, $n = 3$). Tables S1 to S3 also detail the monitoring and sampling that was carried out during the incident. Gasmet monitoring was carried out at only 34 of these events.

Fires at waste management facilities were the cause of 87.1% incidents, with the relative percentages for Wales and Scotland being 100% and 60% respectively. Arguably, fires at waste management facilities are an unintended consequence of the policy and practice of sustainable resource management as defined by the Waste Hierarchy (DEFRA, 2011; US EPA, 2017). Fires at waste sites are recognised as a problem in other countries, for example in Sweden where the public health consequences and propensity to initiate secondary wildfires has been investigated (Ibrahim, 2020) and in China, where the open burning of municipal solid waste is a recognised source of hazardous anthropogenic air pollutants (Cheng et al., 2020).

Table 2 groups the 34 incidents for which there is Gasmet monitoring

Table 2

Summary of incidents that have available Gasmeter data. The events are grouped according to the primary material indicated as being present during events. Events are defined in Tables S1, S2 and S3, and the associated descriptive statistics are provided in Tables S8 to S13.

Material involved	AQInMI/AHER event
Tyres including crumb	EA 4, 8, 12, 17, 29; SEPA 5
Mixed recyclates includes paper, cardboard, plastics, and metals (WRAP, 2018)	EA 6, 14, 19, 21, 22, 23, 25, 30; NRW 1, 2, 3, 4; SEPA 11
Timber and wood products	EA 24, 28; NRW 5
Waste Electrical and Electronic Equipment (WEEE)	SEPA 20
Residual mixed wastes or similar	EA 20, 26, 27; SEPA 12, 40
Chemical manufacture	EA9
Unknown or other	SEPA 1, 2, 6, 11, 13

data available into the six categories (excluding ‘unknown/other’) of primary material used in this study (Tables S5, S6 and S7, identify the additional secondary data sources used to provide confirmatory and explanatory variables that allow categorisation of incidents by primary material). It should be noted that two categories, WEEE and chemical manufacture, have only one event each. Furthermore, the mixed recycling monitoring for NRW1 had missing species data (Table S9), and the WEEE fire, SEPA 20, had a total of only 100 min of monitoring (table S11), so was not further analysed.

3.2. Descriptive statistical analysis of emissions according to source material categorisation

Figs. 1 to 5 show box and whisker plots for ground level concentrations of 22 chemical substances measured during major fire incidents. The data, based on 1-minute measuring periods, has been analysed according to source material, as per the categories listed in Table 2

(excluding WEEE due to missing data for some species). The plot for the unknown/other category is shown for information in Figure S24, but analysis of this category is of limited value due to the uncertainties in composition. Descriptive statistics for the different categories, including the RHC values for each substance, are shown in Tables S8 to S13. In later sections we look at the REFs for different source materials and evaluate the potential health implications of the measured concentrations. For comparison, we have added the corresponding PM₁₀, PM_{2.5} and PM₁ concentrations for the fires, calculated according to source material category, using EA, NRW and SEPA particulate monitoring data (obtained using an OSIRIS instrument (Griffiths et al., 2018)).

Given a measurement resolution of 1-minute, it is expected that there will be a considerable amount of variability in the concentrations, especially the number of outliers, reflecting short-term meteorological changeability and local sources of turbulence (Karellas et al., 2003). A significant influence on variability of concentrations will be the location of the measuring instrument with respect to the source of the fire and the prevailing wind direction. However, the variability also appears to be source dependent, with tyre waste fires (Fig. 1) showing the lowest amount of variability and outliers, whilst mixed recyclables (Fig. 2), timber (Fig. 3) and residual waste (Fig. 4) show the greatest variability, including some outliers in the hundreds of ppm (the fire at the chemical plant also showed low variability, but comprised only one incident). Nevertheless, the median concentrations for all substances and all source materials are at sub-ppm levels, often near the limit of detection, whilst maximum concentrations (excluding outliers) range from sub-ppm to low single ppm concentrations. Monitoring carried out during the Buncefield event reported ambient ground level concentrations around the site (SUMMA canister grab samples, followed by GC-MS analysis) of up to 0.23 ppm for m- and p-xylenes (our average for all incidents, was 0.19 ppm), 0.14 ppm o-xylene (our average, 0.03 ppm), 0.16 ppm toluene (our average 0.31), 0.017 ppm benzene (our average, 0.19 ppm) and 0.082 ethyl benzene (our average, 0.09 ppm) (Targa

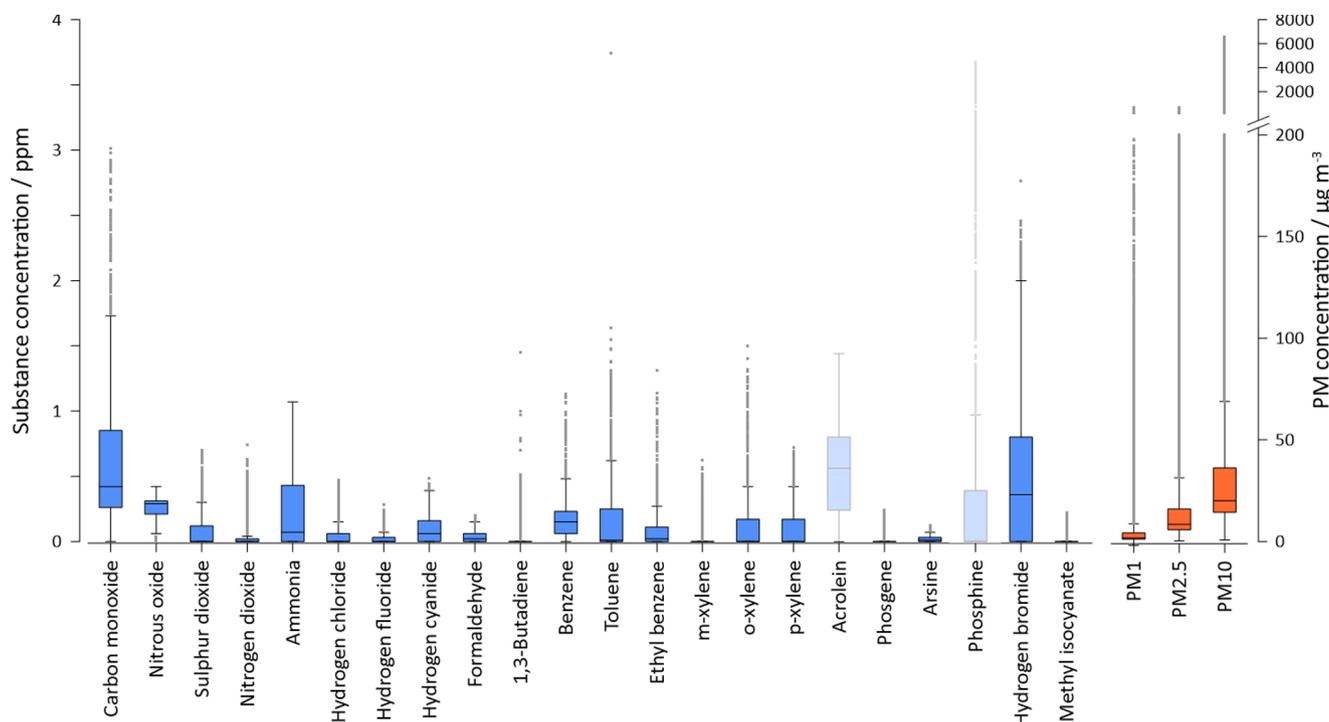


Fig. 1. Box and whisker plot for 22 substances measured using the Gasmeter DX-4030 or 4040 for incidents involving tyres and tyre crumb as the source material. The analysis was carried out on 1-minute measurements ($n = 3,605$) from six separate incidents (see Table 2 for identification). Also included are plots for 1-minute measurements for PM₁₀ and PM_{2.5} ($n = 53,673$) using an Osiris instrument (for the EA incidents only). Shown are the range (excluding outliers), the 25th to 75th percentile range (blue box) and the median. Statistical outliers are shown as dots and are determined as those measurements exceeding 1.5 times the upper quartile value. ‘Ghosted’ boxes indicate substances where significant cross-interference from other substances is likely, and so should be considered as less reliable. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

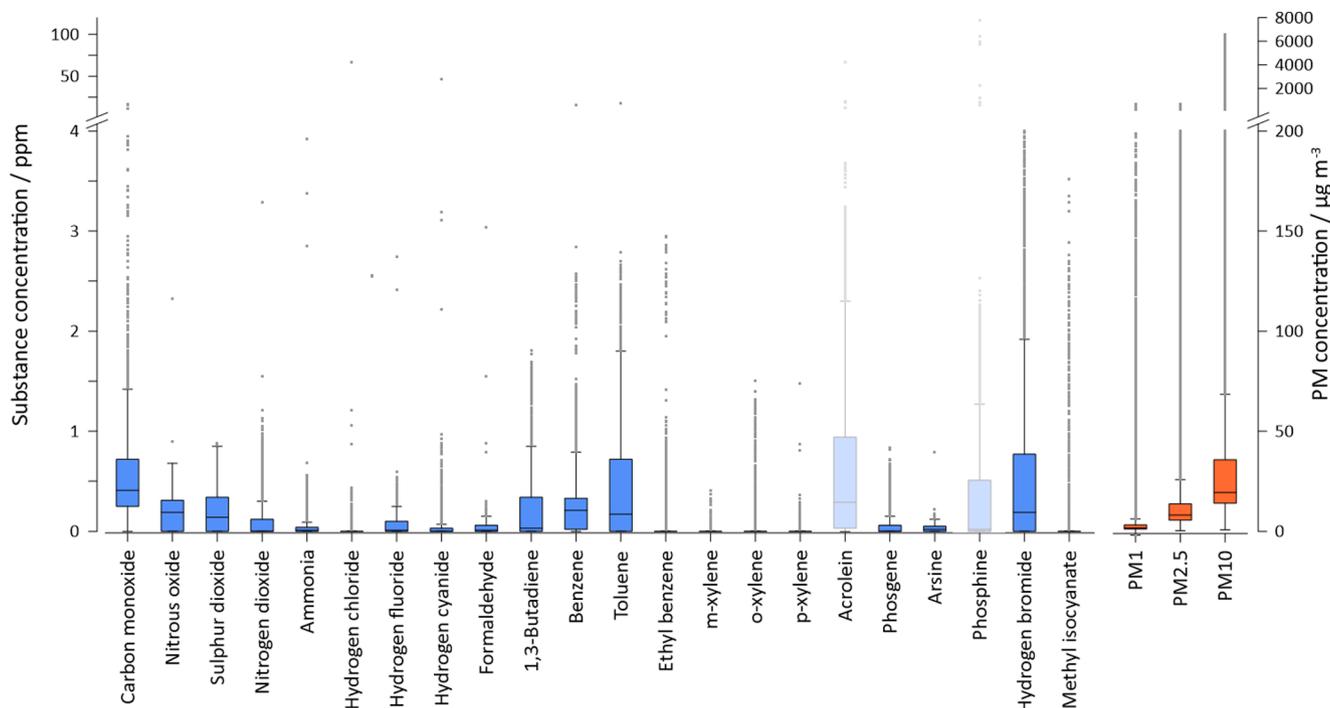


Fig. 2. Box and whisker plot for 22 substances measured using the Gasetm DX-4030 or 4040 for incidents involving mixed recycled materials as the source material. The analysis was carried out on 1-minute measurements ($n = 4,935$) from 13 separate incidents (see Table 2 for identification). Also included are plots for 1-minute measurements for PM_{10} and $PM_{2.5}$ ($n = 57,314$) using an Osiris instrument (for the EA incidents only). Shown are the range (excluding outliers), the 25th to 75th percentile range (blue box) and the median. Statistical outliers are shown as dots and are determined as those measurements exceeding 1.5 times the upper quartile value. 'Ghosted' boxes indicate substances where significant cross-interference from other substances is likely, and so should be considered as less reliable. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

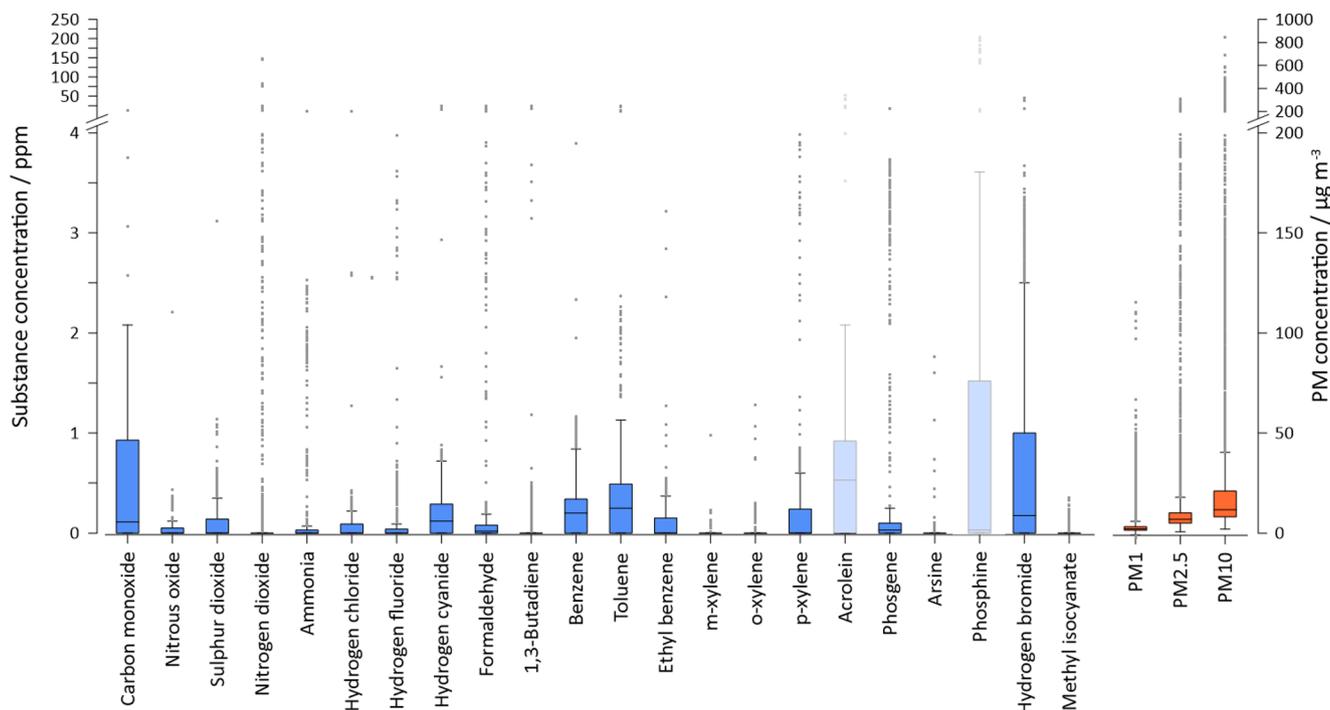


Fig. 3. Box and whisker plot for 22 substances measured using the Gasetm DX-4030 or 4040 for incidents involving timber and wood products as the source material. The analysis was carried out on 1-minute measurements ($n = 2,034$) from three separate incidents (see Table 2 for identification). Also included are plots for 1-minute measurements for PM_{10} and $PM_{2.5}$ ($n = 7,731$) using an Osiris instrument (for the EA incidents only). Shown are the range (excluding outliers), the 25th to 75th percentile range (blue box) and the median. Statistical outliers are shown as dots and are determined as those measurements exceeding 1.5 times the upper quartile value. 'Ghosted' boxes indicate substances where significant cross-interference from other substances is likely, and so should be considered as less reliable. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

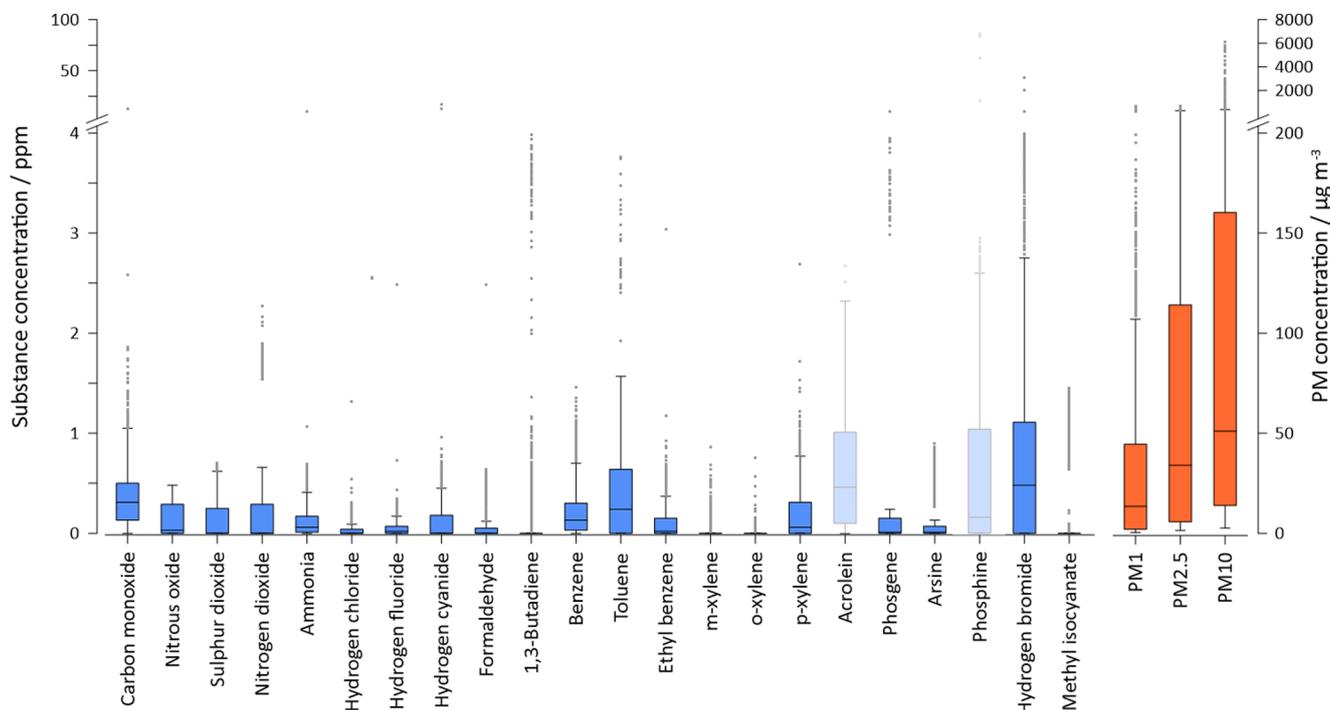


Fig. 4. Box and whisker plot for 22 substances measured using the Gasmeter DX-4030 or 4040 for incidents involving residual mixed wastes as the source material. The analysis was carried out on 1-minute measurements ($n = 1,912$) from five separate incidents (see Table 2 for identification). Also included are plots for 1-minute measurements for PM_{10} and $PM_{2.5}$ ($n = 3,778$) using an Osiris instrument (for the EA incidents only). Shown are the range (excluding outliers), the 25th to 75th percentile range (blue box) and the median. Statistical outliers are shown as dots and are determined as those measurements exceeding 1.5 times the upper quartile value. ‘Ghosted’ boxes indicate substances where significant cross-interference from other substances is likely, and so should be considered as less reliable. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

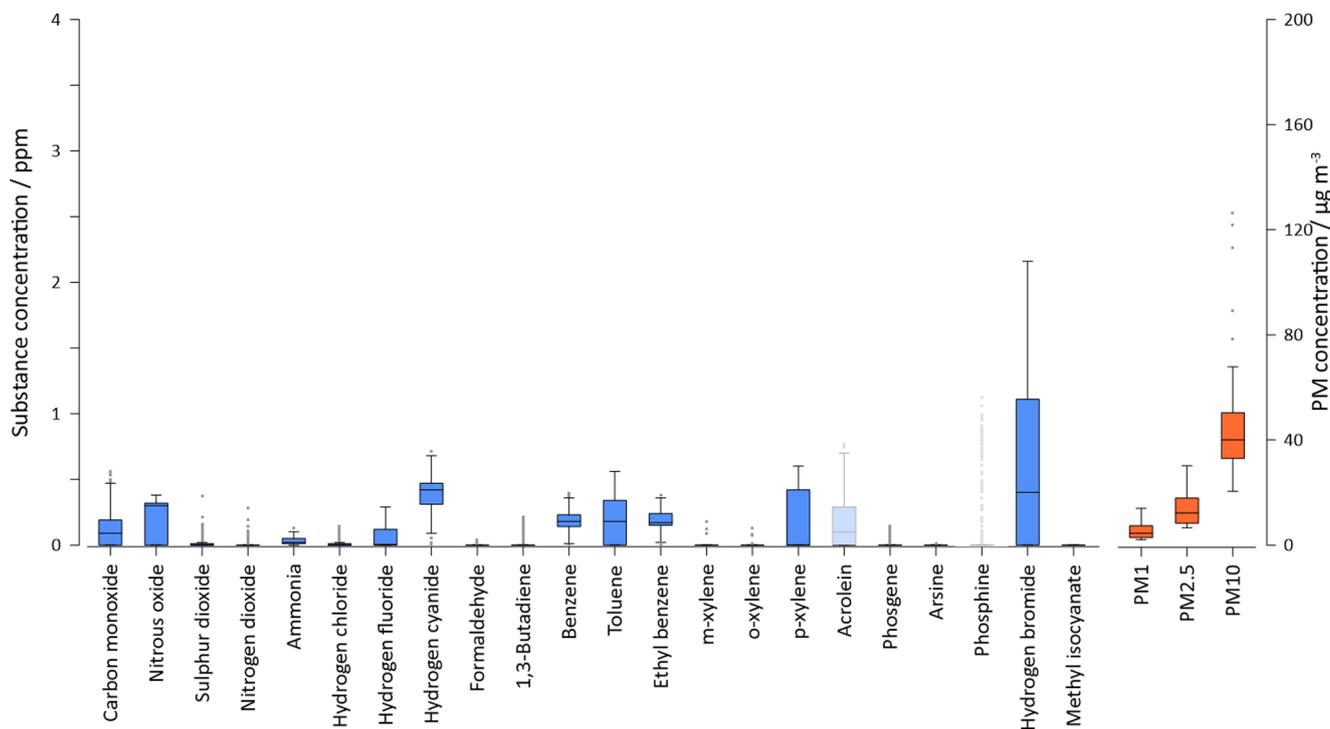


Fig. 5. Box and whisker plot for 22 substances measured using the Gasmeter DX-4030 or 4040 for EA9, a fire at a chemical plant manufacturing pesticides. The analysis was carried out on 1-minute measurements ($n = 282$) from one incident (see Table 2 for identification). Also included are plots for 1-minute measurements for PM_{10} and $PM_{2.5}$ ($n = 113$) using an Osiris instrument (for the EA incidents only). Shown are the range (excluding outliers), the 25th to 75th percentile range (blue box) and the median. Statistical outliers are shown as dots and are determined as those measurements exceeding 1.5 times the upper quartile value. ‘Ghosted’ boxes indicate substances where significant cross-interference from other substances is likely, and so should be considered as less reliable. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

et al., 2006). In addition, PM₁₀ concentrations of up to 1000 µg m⁻³ (Targa et al., 2006) were observed, which is consistent with some of the outlier PM concentrations that we have observed. In another ambient monitoring study carried out around a factory fire, Karellas et al. (2003) determined mean HCl concentrations of 0.058 ppm, similar to the mean of 0.05 ppm that we observed for all incidents.

Of the firefighter exposure studies that have been carried out (Burgess and Crutchfield, 1995; Fabian et al., 2014; Alharbi et al., 2021), the measured concentrations are much higher than the concentrations reported in our study, as is to be expected given the close proximity of the sampling/measurements to the fire. The study by Fabian et al. (2014) reported a PM_{3.5} concentration of 13,500 µg m⁻³ and the following concentrations of inorganic gases (direct reading electrochemical sensors): CO, 774 ppm; HCN, 7 ppm; NH₃, 1.8 ppm, SO₂, 31 ppm; and NO₂, 0.7 ppm. Alharbi et al. (2021) reported concentrations of CO, 174.7 ppm; HCN, 13.37 ppm; NH₃, 1.58 ppm, SO₂, 13.32 ppm; HCl, 21.5 ppm (all direct reading electrochemical cells) and BTEX, 0.017 ppm (SUMMA grab sample and GC-MS analysis) for firefighter exposure during industrial fires.

The concentrations of most of the substances in Figs. 1 to 5 appear consistent with the source material of the fires (Estrellan and Iino, 2010; Lemieux et al., 2004; Wakefield, 2010) and also with the results of other ambient studies conducted around industrial fires (Targa et al., 2006; Karellas et al., 2003). However, we find it difficult to account for the large C₃H₄O (acrolein) and PH₃ (phosphine) concentrations that are recorded by the Gasmeter instrument during many of the incidents. The mean C₃H₄O concentration across all events is 0.63 ppm, with an RHC of 21.2 ppm. Moreover, excluding outliers, the concentration ranges for C₃H₄O exceed 1 ppm for all categories of source material. Such C₃H₄O concentrations would be expected to have significant health effects: short-term irritation of the mucous membrane is expected to occur at concentrations above 0.17 ppm, whilst pulmonary damage may occur at concentrations exceeding 0.43 ppm (Burgess and Crutchfield, 1995). Short term (60-minute) US AEGL exposure standards of 0.03 ppm, 0.10 ppm and 1.4 ppm apply for AEGL-1 (discomfort), AEGL-2 (long-lasting effects) and AEGL-3 (life threatening health effects) respectively (US EPA, 2018). There is no evidence of any of these symptoms being reported from members of the public in areas exposed to the plume. We must assume that the Gasmeter-measured C₃H₄O concentrations are being overestimated during the processing of the infrared spectra obtained from the sampling. Mass spectrometry results have shown that there are over 180 individual VOCs released during biomass fires (Koss et al., 2018; Brilli et al., 2014) and it is likely that there will be similar, if not more species released during the industrial fires on which we report. The Gasmeter processing software (Calcmeter-Lite) resolves the spectra across the medium-range of the infrared region (wavelength: 2 µm to 12 µm; wavenumber: 900 cm⁻¹ to 4200 cm⁻¹); however the main C₃H₄O absorption peaks are in a spectrally congested region (Scharko et al., 2019), meaning that the many unknown substances could interfere with the quantification. Literature reported C₃H₄O concentrations during fires are: 0.25 ppm for a smoke chamber simulation of Australian wild fires (De Vos et al., 2009), 1.9 ppm for a study of occupational exposure of Tuscon firefighters (with respirators) and 0.1 ppm to 10 ppm near to the source of forest fires (Ward, 1997). Thus, even in a situation where combustion product concentrations are expected to be much higher than for our ambient monitoring, similar acrolein concentrations were reported to ours.

We are similarly concerned by the Gasmeter-measured PH₃ concentrations, which sometimes exceeded 100 ppm (e.g., for timber product fires and residual mixed waste). PH₃ is itself highly flammable and might be expected to oxidise in a fire, but there are very few potential sources, the most notable being aluminium phosphide (O'Malley et al., 2013) that is used in pest fumigation or zinc phosphide that is used as a rodenticide. Both of these will release PH₃ when wet, aluminium phosphide more readily, possibly leading to spontaneous combustion (O'Malley et al., 2013). The elevated PH₃ concentrations occurred in

only one incident for each of the two source types for which elevated concentrations were recorded, and at only one contiguous time sequence within each incident. The elevated concentrations were associated with coincident elevated concentrations of acrolein, p-xylene, toluene, benzene, hydrogen cyanide, hydrogen fluoride and ammonia. There is nothing in the nature of the incidents to suggest that PH₃ producing substances could be present (EA26, timber and wood recycling; and EA28 mixed recyclables), and so it is possible that cross-interference with other IR absorption bands is again the explanation for the elevated concentrations. The performance of Gasmeter technology for PH₃ measurement has been independently investigated by the US military and excellent agreement found over a calibration range of 1 ppm to 24.9 ppm, though this was for single gas components (similarly good agreement was also observed for NH₃, AsH₃, CO, HCN, COCl₂ and SO₂) (Austin and Hoang, 2009).

3.3. Relative emission factors

Fig. 6 presents the results of the REF analysis as polar plots, allowing an intuitive visualisation of the 'fingerprint' of emissions from each type of fire. For tyre waste, there are large (relative) signals for the xylenes (particularly o- and m-), together with NH₃, HCl, and to a lesser extent HCN and CO. Lemieux et al. (2004) has compiled a table of VOC and SVOC emission factors (mg kg⁻¹ material burned) from ambient monitoring studies conducted in the vicinity of tyre fires, which confirm our findings of significant xylene and ethyl benzene emissions but also toluene and benzene, which we found to be less significant components. Lönnnermark and Blomqvist (2005) observed xylenes in the water effluent from the extinguishing of the fire in tyre burning experiments, highlighting not only their presence in the plume but also another aspect of the environmental impact of industrial fires. In a wider study looking at emissions from automobile fires, Lönnnermark and Blomqvist (2006) reported that SO₂ should also be a significant component of tyre fires, though we found the REF value to be less than 1. The same study also showed that CO and NH₃ are emitted in significant amounts during tyre pyrolysis as we have observed, though HCN is more associated with the combustion of other car components, such as floor coverings and dashboards; nevertheless, it is possible that such materials were stored on the same sites. The form and nature of the tyre material may also affect emissions, for example tyre crumb has a different emission profile to the burning of complete tyres (US EPA, 1997), though we do not have this level of detail for the fires analysed in this paper.

Dry mixed recyclables collected in the UK include paper, cardboard, plastics, and metals (WRAP, 2018). There can be some variation to this because each local authority, acting as a Waste Collection Authority, may have different rules on curb-side collections. Because of the wide range of waste materials stored at these sites, it is not surprising that there is a wider range of species contributing to the overall relative emissions compared to tyre fires. VOC emissions are dominated by ethyl benzene, benzene, toluene, and 1,3-butadiene, as might be expected from the open burning of plastic materials, which have been shown to have some of the highest VOC emission factors (Lemieux et al., 2004; Zhang et al., 2015). Inorganic species include CO, NO₂, SO₂, HF and HBr, with these species also likely to originate from plastics, for example HBr from brominated flame retardant additives (Wakefield, 2010). HF may originate from fluorine containing polymers, for example polytetrafluoroethylene (PTFE) (Wakefield, 2010) or from incorrectly disposed lithium-ion batteries (Larsson et al., 2017).

For timber waste, Fig. 6 shows a dominance of formaldehyde, together with nitrogen-derived volatiles such as HCN and NO₂. Lemieux et al. (2004) lists formaldehyde as having the second highest emission factor (after methanol) for wood burning. In studies analysing the open burning of biomass, it was found that lower concentrations of volatile species are emitted compared to the decomposition of anthropogenic fuels (Lemieux et al., 2004) but the plumes can include organic irritants such as C₃H₄O, in addition to NO₂ (Wakefield, 2010; De Vos et al.,

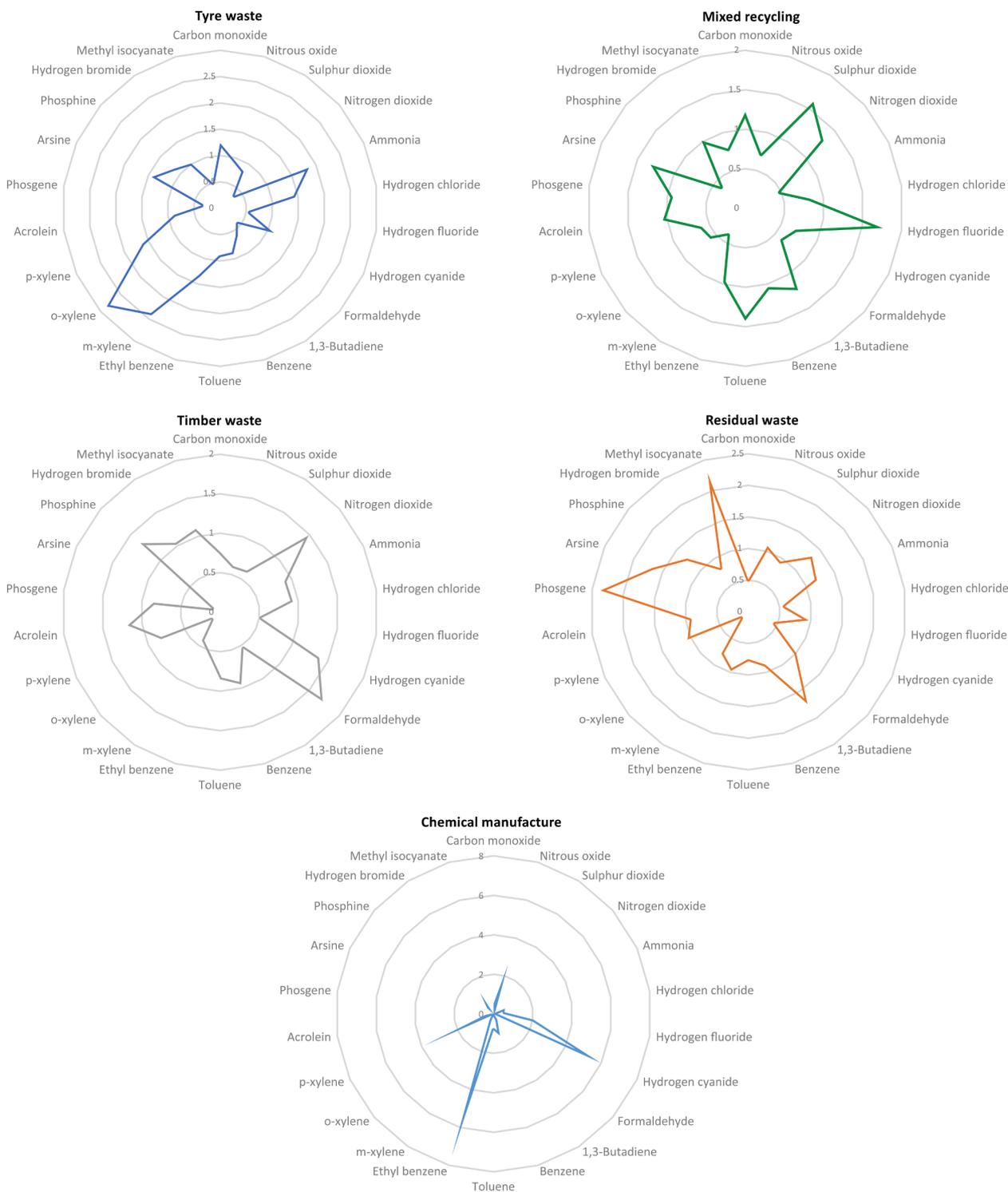


Fig. 6. Polar plot showing relative emission factors for each measured volatile gaseous substance.

2009).

For residual mixed waste, which should primarily comprise a variety of non-recyclable wastes, most likely destined for landfill or thermal recovery, Fig. 6 shows that there is a fairly even distribution of contributing components, with the exception of elevated levels of COCl_2 and $\text{C}_2\text{H}_3\text{NO}$, and to a lesser extent N_2O . COCl_2 can originate from chlorinated solvents, but can also be released during the combustion of plastics, such as PVC (Wakefield, 2010), though we might also have expected an elevated relative emission of HCl. Isocyanates, including $\text{C}_2\text{H}_3\text{NO}$, are likely to come from the thermal decomposition of

polyurethane foam that is present in many discarded furnishing items, such as mattresses, sofas and carpet underlay, and which are likely components of residual mixed waste (Wakefield, 2010).

Finally for the single incident comprising the chemical manufacturing category, the elevated REFs are limited to only a few substances (ethyl benzene, p-xylene, HCN and N_2O), likely reflecting a much narrower range of source materials.

3.4. Retrospective comparison with relevant exposure standards and guideline values

As part of the AQC management of a major incident fire, each of the events will have been evaluated for possible public health impact at the time, allowing decisions to be made about the communication of safety advice to affected populations. As these evaluations are not publicly available, we have retrospectively applied the same approach to compare the measured concentrations against appropriate toxicological and ambient standards for relevant averaging periods. In doing so, we have compiled the first reported overview of the potential public health risk presented by major industrial fires.

3.4.1. Toxicological considerations

There are multiple factors that determine a toxic effect from chemical exposures: (1) the mode of exposure e.g. inhalation, ingestion, dermal, or ocular contact; (2) the type of chemical substance or mixture of substances; (3) the concentration and duration of exposure; and (4) the susceptibility of sub-populations e.g. children, the elderly, and those with pre-existing conditions (DuTeaux, 2014; Purser et al., 2016). In responding to an episodic event, duration of exposure can be affected by the decisions of responders, including the timeliness of advice given to the public, such as to shelter indoors (Stage, 2004; HPA, 2012; Wyke and Duarte-Davidson, 2019). Rapid decisions mean that populations can evacuate an area, or shelter inside and so reduce exposure duration and/or concentrations and reduce negative health outcomes (Rusch, 2016; HPA, 2012). Thus, a timely response relies on appropriate standards being available, for example emergency (or acute) exposure standards that are designed to protect the public from progressively adverse health effects due to continued exposure to gaseous substances (DuTeaux, 2014; Öberg et al., 2010; WHO, 2009).

Two emergency exposure standards have been used for the comparison in this paper: Acute Exposure Guideline Values (AEGs) (US EPA, 2018) and Emergency Response Planning Guidelines (ERPGs) (American Industrial Hygiene Association, 2019; American Industrial Hygiene Association, 2006). Both emergency response standards use three levels of impact. For the AEGs, these are: AEG-1 (a temporary non-disabling effects threshold), AEG-2 (a disabling, escape impairment threshold) and AEG-3 (life threatening health effects threshold) (US EPA, 2018; Stewart-Evans et al., 2016). For the ERPGs, the levels are broadly similar and specifically concern the maximum concentrations below which nearly all individuals could be exposed for a 1-hour period before experiencing the effects specified as follows: ERPG-1 (mild, transient effects), ERPG-2 (irreversible or other serious effects that might hinder the ability to take protective action) and ERPG-3 (life threatening effects) (American Industrial Hygiene Association, 2019; American Industrial Hygiene Association, 2006).

AEGs provide limit values for each level at a range of averaging periods: 10-min, 30-min, 1-hour, 4-hour and 8-hour. ERPGs offer a single standard for 1-hour (Craig et al., 2000; Blakey et al., 2013; Rusch, 2016). However as emergency standards, AEGs and ERPGs do not provide an equivalent indication of impact on health, this being due to differences in how each has weighted the epidemiological evidence on which the standards are based (Cavender et al., 2008; Öberg et al., 2010; Johansson et al., 2016). AEG and ERPG values for the substances highlighted in Table 1 are available in US EPA (2018) and American Industrial Hygiene Association (2019) respectively. In addition to these toxicological standards, we have also compared monitored concentrations with the ambient short-term exposure guidelines that are available for CO, NO₂ and SO₂ (European Union, 2008; US EPA, 2016b, WHO, 2000).

3.4.2. Comparison against toxicological standards

Summarised in Table 3 are the species that have exceeded one or more AEG and ERPG standards. It should be noted that for several of the standards/averaging periods, the value of the standard was below

Table 3 Number of incidents with Gasmet FTIR monitoring results that show exceedances of AEG (US EPA, 2018) and/or ERPG (American Industrial Hygiene Association, 2019) standards. Substance entries shown in italics are those that are likely to be affected by cross-interference in the IR region of the spectrum by other substances.

Event	10 min			30 min			60 min			4 h			8 h			1 h		
	AEG-1	AEG-2	AEG-3	AEG-1	AEG-2	AEG-3	AEG-1	AEG-2	AEG-3	AEG-1	AEG-2	AEG-3	AEG-1	AEG-2	AEG-3	ERPG-1	ERPG-2	ERPG-3
Asphyxiants																		
HCN	2	0	0	1	0	0	0	0	0	0	0	0	0	0	0	N/A [√]	0	0
Inorganic Irritant Gases																		
HBr	<LD [†]	0	0	<LD	0	0	0	0	0	<LD	0	0	<LD	0	0	No standard available	0	0
HCl	1	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
HF	1	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NO ₂	<LD	1	1	<LD	0	0	<LD	0	0	<LD	0	0	<LD	0	0	<LD	0	0
COCl ₂	NR [‡]	3	2	NR	3	2	NR	4	2	NR	<LD	<LD	NR	<LD	<LD	N/A	3	2
SO ₂	<LD	2	0	<LD	2	0	<LD	1	0	<LD	1	0	<LD	0	0	<LD	0	0
Organic irritants																		
C ₂ H ₄ O	<LD	28	2	<LD	<LD	4	<LD	<LD	6	<LD	<LD	10	<LD	<LD	8	<LD	<LD	6
CH ₂ O	1	0	0	1	0	0	1	0	0	1	0	0	1	0	0	1	0	0
C ₂ H ₃ NO	NR	2	2	NR	<LD	1	NR	<LD	<LD	NR	5	3	NR	5	3	<LD	<LD	0
Other toxic effects e.g., including tissue oedema, central nervous system effects, haemolysis																		
AsH ₃	NR	4	1	NR	2	0	NR	0	0	NR	6	6	NR	0	0	N/A	0	0
PH ₃	0	6	5	0	3	1	0	5	1	0	8	6	0	8	5	N/A	18	1

[√] Not applicable for this substance.

[†] Value of standard is below the Gasmet limit of detection for this substance.

[‡] Not recommended due to insufficient data (US EPA, 2018).

that of the stated limit of detection for the Gaset instrument and so these standards are not used in the evaluation. Additionally, with only 5 data points, EA14 is excluded from this analysis.

Table 3 shows that for several incidents, there are exceedances of a range of the toxicological standards, including AEGL-3 and ERPG-3 (L-3) standards that might indicate life threatening situations. Whilst many of the exceedances are associated with C_3H_4O and PH_3 , which we have previously discussed as being unreliable because of likelihood of cross-interference from other substances in the FTIR analysis, there are also L-3 exceedances for NO_2 , $COCl_2$, and C_2H_3NO for a small number of incidents. For NO_2 (an irritant), one single event, EA28 (timber and wood products) is responsible for the L-3 exceedances, whereas for $COCl_2$ (an irritant) there are two events (EA21 and EA23, both of which are mixed recycling) and for C_2H_3NO (an irritant), three events (EA4, tyre and tyre crumb; EA23, mixed recycling; and EA26, residual mixed waste).

In corroborating the indicated magnitude of prospective health risks from the concentrations in the ground level plume, regard has been given to PM concentrations that were simultaneously measured during these events. So, for incidents that account for the C_2H_3NO and $COCl_2$ exceedances, the corresponding PM_{10} RHCs for EA4, EA23 and EA26 exceeded $6,000 \mu g m^{-3}$, whilst for EA 21 the RHC was $1925 \mu g m^{-3}$, and so confirms the presence of significant ground level concentrations of combustion products at the incidents registering L-3 exceedances. Therefore, whilst the exceedances for C_2H_3NO and $COCl_2$ may be genuine, the high ground level concentrations of combustion-related substances may have caused cross-interference between the specific species measured by the Gaset, as we have discussed for C_3H_4O and PH_3 . Such cross-interferences are likely to give rise to false positive readings and over-reporting of the concentrations for certain substances. Consequently, we recommend that collocation studies are carried using a Gaset and a mass spectral detection method (Koss et al., 2018; Brill et al., 2014) during a range of industrial fires, to evaluate the reliability of FTIR-identified substances during periods of significant combustion product concentrations. Gas detector tubes and electrochemical cell devices could also be used for corroboration of high concentrations, subject to suitable detection limits being available for these techniques.

For the NO_2 L-3 exceedances, the RHC for PM_{10} was much lower than the conditions discussed for $COCl_2$ and C_2H_3NO , with an RHC of $622 \mu g m^{-3}$ and a mean concentration of $24.5 \mu g m^{-3}$. We would expect significant NO_2 emissions from wood waste (Wakefield, 2010) and for this incident, only the AEGL-3 for a 10-minute averaging period was breached, implying a short-term peak. A closer look at the data for this incident shows that the exceedance was explained by two consecutive elevated 1-minute NO_2 readings of 81.7 and $146 \mu g m^{-3}$, perhaps occurring due to a combination of meteorological and local turbulent conditions (Karellas et al., 2003) or an anomaly of the instrument.

For the other substances in Table 3, SO_2 exceeded the AEGL-2 standard for averaging periods of 10 min, 30 min, 60 min and 4 h, while HCN, HBr, HCl, HF and CH_2O exceeded L-1 standards only.

3.4.3. Comparison with short-term ambient guidelines

The 1-hour ambient exposure guideline for NO_2 (0.11 ppm) (WHO, 2006; European Union, 2008; DEFRA, nd; WHO, 2021) was exceeded in 14 of the incidents, whilst the 1-hour guideline for SO_2 (0.13 ppm) (European Union, 2008; DEFRA, nd) was exceeded in 15 of the incidents. Additionally, the WHO 10-minute guideline value of 0.19 ppm for SO_2 (WHO, 2006; WHO, 2021) was exceeded in 21 of the incidents and the UK 15-minute guideline of 0.10 ppm (DEFRA, nd) was exceeded in 30 of the incidents. None of the short-term ambient guideline values for CO were exceeded.

3.4.4. Monitoring of persistent organic pollutants

Tables S1 to S3 indicate that sampling was carried out for dioxins/furans during three of the incidents (EA 17, EA27 and EA30). Sampling for these compounds is carried out using a polyurethane foam (PUF)

plug that is located downstream of a quartz filter in a Tecora High volume ($200 L min^{-1}$) sampling system (Griffiths et al., 2018). The quartz filters are used to collect particulates (either PM_{10} or $PM_{2.5}$, depending on the size selective sampling head used), which are analysed for a range of metal(oids), PAHs and PCBs (Griffiths et al., 2018). Unfortunately, we were unable to obtain the results for these analyses as part of the disclosure from the EA. There are likely to be significant amounts of these substances released during uncontrolled combustion processes (Estrellan and Iino, 2010; Lemieux et al., 2004).

3.4.5. Future work: Plume modelling

It should be emphasised that the sampling locations are chosen to be indicative of population exposure during an incident but, whilst 1-min measuring durations offer high resolution temporal snapshots of the ground level plume concentrations, even with two sampling teams attending any incident, there is limited spatial coverage. Furthermore, with monitoring location decisions being driven not only by prevailing meteorology and ground level plume spread but by other considerations such as access to electrical power and the need to protect the monitoring teams' occupational health and safety, the locations chosen may not have been optimal to record the greatest concentrations within the plume. Our future research in this area will focus on using dispersion modelling to back-calculate the likely emission rates from a major incident fire and to then model the resulting plume, allowing a better retrospective estimation of total population exposure. A sensitivity analysis approach will be adopted to identify the most influential model variables (Tagliaferri et al., 2022). In addition, we will analyse population exposure according to socioeconomic status, gender, age, ethnicity, and other population variables.

4. Conclusions

Using the AQINMI Gaset FTIR monitoring data, we have demonstrated that plumes arising from open fires involving different source materials, such as tyres, timber, mixed recycling and residual mixed waste, can be profiled for their chemical composition. This information will be of use in performing public health risk assessments during major incident fires, with the profiles indicating the likely species that a local population might be exposed to.

From making comparisons with literature-reported concentrations and with various toxicological standards, the concentrations of several substances appear to be unrealistically high, notably for PH_3 and C_3H_4O , but also possibly $COCl_2$ and C_2H_3NO for some of the incidents. These unrealistically high concentrations are likely to be due to cross-interference from other substances in the mid-range of the IR spectrum, particularly when the ground level plume is very concentrated (as corroborated by contemporaneously measured PM concentrations). We recommend that collocation studies with mass spectral detection instruments are carried out during a range of major incident fires in order to better evaluate those substances prone to interference when using portable FTIR instruments. In addition, some corroboration of the presence of high concentrations of substances such as PH_3 could be obtained from gas detector tubes or electrochemical cells.

Nevertheless, the concentrations of many of the substances included in the Gaset analysis suite are similar to those reported in the limited number of other studies that have monitored episodic pollution events. We have evaluated the reported concentrations against a range of toxicological and ambient standards. For most of the substances for which there were exceedances of AEGL or ERPG standards, these were mainly at level 1 (discomfort), though several exceedances occurred at L2 (long lasting effects) and L3 (potentially life threatening). It is our view that the exceedances of L-3 standards are due to cross-interference, as the exceedances correspond to exceptionally high PM concentrations, indicating a very concentrated ground level plume. In other cases, e.g., NO_2 , the exceedances were due to a short-duration (minutes) spike in concentration. It could be argued that the over-reporting of some

substances presents a worst-case scenario and is preferable to under-reporting.

Recognising that the AQinMI monitoring is limited in spatial coverage, our future work will undertake back-trajectory modelling of several incidents to determine emission rates of PM and other substances, which will allow a full plume modelling study to be carried out. This will allow a wider comparison to be made between modelled concentrations and toxicological standards. It will also allow a socio-economic and demographic analysis to be carried out for the exposed populations, thus relating these incidents to issues such as environmental justice.

CRedit authorship contribution statement

Simon D. Griffiths: Conceptualization, Methodology, Data curation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing. **Jane A. Entwistle:** Writing – review & editing, Supervision. **Frank J. Kelly:** Writing – review & editing, Supervision. **Michael E. Deary:** Conceptualization, Methodology, Visualization, Writing – original draft, Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envint.2022.107152>.

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