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ARTICLE

Evaluating Health Risks of Volatile Organic Compounds in Various UK Environments: Insights from Health Indices

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ABSTRACT

The health risks of twelve volatile organic compounds (VOCs) across three sites in the UK were analysed across an 11-year period (2013–2023) using US EPA proposed health indices; Inhalation Unit Risk (IUR) and Reference Concentration (RfC) for carcinogenic and non-carcinogenic risk, respectively. Significant decreases in carcinogenic risk were observed over the study period for 1, 3-butadiene, with reductions of 63%, 36%, and 45% at urban traffic, suburban background and rural background sites, respectively. Similar decreases in the carcinogenic risk associated with benzene (52%, 28% and 27%) and toluene (50%, 38% and 51%) are found for the three site types, respectively. However, the carcinogenic risk of these three pollutants still exceeds the acceptable threshold of 1×10^{-6} at the urban traffic and suburban background sites, necessitating further emission control strategies. Conversely, the carcinogenic risk associated with isoprene has increased at the urban traffic site over the study period. The study revealed a decrease of 51%, 39% and 37% of the total non-carcinogenic risk at all three sites over the study period. The seasonal variations in carcinogenic and non-carcinogenic health risks of pollutants with anthropogenic origin exhibit winter maxima and summer minima. Moreover, diurnal variations of pollutants with anthropogenic origin demonstrate a bimodal distribution reflecting that of traffic flow, e.g., peaks around 08:00 LT and 18:00 LT, corresponding with rush hours. This trend demonstrates the influence of traffic sources supported by the characteristic species ratio whereby Toluene/Benzene (T/B) ratios were less than two (0.72, and 0.42 at suburban and rural background sites, respectively), illustrating the influence of vehicular emissions. Despite following the same bimodal trend suggesting the dominance of vehicular emission sources, mean T/B ratios at urban traffic sites were consistently above 2 for all years considered (average 2.76) suggesting other VOC sources are becoming more dominant at this site.

Keywords: Volatile organic compound; Health indices; Carcinogenic risk; Non-carcinogenic risk; Urban traffic site; Diurnal variation

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1. Introduction

There is a growing concern over public health problems related to volatile organic compound (VOC) exposure. The physical and chemical properties of VOCs, combined with relatively long atmospheric lifetimes, allow their transport from the emission source to the human body before their degradation [1]. VOCs can enter the body through dermal contact, ingestion, and inhalation [2,3]. Due to the high vapour pressure of VOCs, the inhalation pathway is dominant, and the effects of dermal contact and ingestion are near-negligible [4].

Once inside the body, the lipophilicity of VOCs allows them to cross biological membranes, e.g., through the mucous epithelia of the respiratory tract [1]. The VOC's biotransformation determines the health hazard; toxicity, irritation, teratogenicity, or carcinogenicity. The variation in the VOC's structure and reactivity induces the diversity in the magnitude and class of these health hazards. Although we cannot deny the association between ambient VOC exposure and adverse health effects, researchers have yet to establish many specific toxicity mechanisms, resulting in the lack of predetermined health indices for many VOCs.

Many studies have shown that long- and short-term exposure to VOCs negatively affects human health, leading to acute symptoms such as throat and eye irritations, headaches, nausea, dizziness, and allergic skin reactions [5,6]. Additionally, long-term VOC exposure is consistently associated with increased mortality and morbidity from chronic health risks, including damage to the immune system, liver, and kidneys and a decline in pulmonary function [5–8]. Many studies have also demonstrated that VOC exposure can exacerbate pre-existing respiratory conditions like asthma, emphysema, and chronic bronchitis [9].

Additionally, the US Environmental Protection Agency (US EPA) has identified a multitude of VOCs as carcinogenic, which the International Agency for Research for Cancer (IARC) has classified into five groups (**Table 1**) [10]. The carcinogenicity of VOCs arguably poses the most severe health risk.

Table 1. The possible classifications of compounds by the International Agency for Research on Cancer (IARC) along with their corresponding description and an example.

Group	Definition	Example
1	Classified as carcinogenic	Benzene
2a	Probably carcinogenic	Ethylene, Aldehyde
2b	Possibly carcinogenic	Isoprene
3	Not classifiable based on carcinogenicity	1, 2, 3-trichloroethane
4	Probably not carcinogenic	N/A

This study investigates the health risks of VOC air pollution in various environment types across the UK, including urban traffic, suburban background, and rural background sites. The US EPA has identified numerous VOCs as hazardous air pollutants, with several classified as known or suspected carcinogens. Other VOCs have non-carcinogenic health effects such as liver and kidney damage and adverse impacts on the neurological, immune, and respiratory systems. Given the significant contribution of VOCs to air pollution and the wide range of health implications, it is crucial to investigate their health risks in the UK. Such research is paramount for policymakers to make informed decisions about strategies for improving air quality in the UK and mitigating the associated disease burden.

2. Materials and methods

2.1 Site selection

Three different sites in the UK were chosen to investigate the health risks of VOCs. The locations used in this project represent various environments in the UK, including an urban traffic site (London Marylebone Road; LMR), a suburban site (London Eltham; LE), and a rural background site (Auchencorth Moss; AM) (**Table 2**).

The LMR monitoring station is approximately 1 m from the highly congested six-lane A501 road. DEFRA categorises LMR as an urban traffic site meaning its pollution is determined predominantly by the emissions from nearby traffic [11]. Moreover, the surrounding area is a street canyon comprising

education buildings, tourist attractions, shops, and housing. LMR is also bordered to the north by Regent's Park and to the south by Hyde Park, two of London's larger public parks. This monitoring site provides a reliable indication of hourly VOC concentration emitted from mobile sources in London's urban traffic area. As well as some of the heaviest traffic in London, various constructions and businesses surround Marylebone Road; therefore, it can illustrate an extreme example of the UK emission character.

Table 2. Names, site types and coordinates of each measurement site from which data was extracted.

Site name	Environment Type	Site Coordinates
London Marylebone Road (LMR)	Urban traffic	51.522530, –0.154611
London Eltham (LE)	Suburban background	51.452580, 0.070766
Auchencorth Moss (AM)	Rural background	55.792160, –3.242900

The LE monitoring station is situated in the London Borough of Greenwich approximately 25 m south of the A210 and surrounded by a mixture of environments, including trees, parks, a golf course, and housing, giving LE its characterisation as a 'suburban background' site [12]. Background stations describe monitoring sites where the pollution level is not influenced significantly by any single source/street but rather by the integrated sources upwind of the station. This monitoring site provides a more reliable and consistent indication of hourly VOC concentrations than many UK suburban background sites.

The AM monitoring site is in a transitional lowland raised bog, approximately 1.5 km Northwest of the A701 at Leadburn and 18 km South of Edinburgh city centre, over 300 miles from the other monitoring sites considered in this study [13]. Hence, it is defined as a 'rural background' monitoring site, meaning it is not influenced significantly by any singular source/street but rather by the integrated contribution of all sources upwind of the station. The site monitors the concentration of a range of VOCs hourly and with reasonable consistency.

2.2 Data collection

The VOC measurement data from January 1st, 2013, to December 31st, 2023, were obtained from the Department for Environmental Food and Rural Affairs website (DEFRA, https://uk-air.defra.gov.uk/). The hourly data was taken from the Automatic Hydrocarbon Network, which used an automatic PerkinElmer gas chromatograph to monitor the 29 VOCs, with an associated measurement uncertainty of 15% [14].

Of the 29 VOCs reported by DEFRA, the 12 with reported US EPA indices have been selected and listed below (**Table 3**). Additionally, VOCs with less than 50% coverage for a given site are excluded from the analysis to ensure the data is representative of an annual average.

Table 3. The 12 VOCs were analysed with associated RfC and IUR values, taken from the US EPA, where available.

VOC	RfC ($\mu g/m^3$)	IUR $(\mu g/m^3)^{-1}$
n-pentane	1000	-
1,3-butadiene	2	3.6×10^{-5}
Isoprene	2	3.6×10^{-5}
n-hexane	700	-
n-heptane	400	-
Benzene	3.00×10^{-2}	7.8×10^{-6}
Toluene	4000	3.2×10^{-6}
Ethylbenzene	70	-
M,p-xylene	100	-
o-xylene	100	-
1,2,4-trimethylbenzene	60	-
1,3,5-trimethylbenzene	60	-

Indices proposed by the US EPA were deployed in this study to measure the non-carcinogenic and carcinogenic risks associated with inhaling toxic chemicals across the three sites. The Reference Concentration (RfC) and Inhalation Unit Risk (IUR) quantitatively describe the non-carcinogenic and carcinogenic risks, respectively [15].

The US EPA developed these indices using a comprehensive and recently updated approach [15]. The development of both indices relied upon the US EPA's inhalation dosimetry methodology for extrapolating

experimental conditions to equivalent human concentration. Pharmacokinetic (PBPK) models determine the amount of a chemical that reaches the animal's target organ under various exposure scenarios. Subsequently, these models can estimate the corresponding level of human exposure that would result in a similar level of damage [15]. PBPK is the preferred methodology for calculating health indices, yet; scientists rarely use this approach as extensive chemical-specific data is required; hence IUR and RfC are available for a relatively small proportion of VOCs.

The inhalation exposure concentration (EC_i) was assessed in line with US EPA recommendations [15]. As exposure considered is to ambient air, exposure concentration is equivalent to the measured concentration.

The US EPA has also devised equations using the RfC and IUR indices to calculate HQ (hazard quotient for non-carcinogenic), HI (hazard index for non-carcinogenic risk), and RISK (carcinogenic risk) used in this study's health risk evaluation method.

The hazard quotient was applied to assess the non-carcinogenic risk for a single species, using RfC values. The US EPA suggests that an HQ value of 1.0 or less indicates adverse health effects are unlikely due to environmental exposure to that substance. As the HQ increases above 1.0, the probability of adverse health effects also increases. Calculating the HQ is possible according to the dose-response relationship as shown in equation (1).

$$HQ_i = \frac{EC_i}{RfC_i \times 1000} \quad (1)$$

Where EC_i is the exposure concentration and RfC_i is the associated RfC for a given VOC. The total hazard index (HI) is a sum of the HQs from multiple VOC species used to assess the overall non-carcinogenic health risk in each environment as shown in equation (2).

$$HI = \sum_{i=1}^{i=n} HQi \quad (2)$$

The following equation (3), which uses the IUR, can calculate a single species lifetime carcinogenic risk (RISK). The US EPA suggests the acceptable RISK level is 1×10^{-6}; when the RISK level exceeds this value, the species may contribute potential carcinogenic risk to residents in the given environment [15].

$$RISK_i = IUR_i \times EC_i \quad (3)$$

Moving forward, characteristic species ratios based on the average VOC concentration at each site have been used to deploy source apportionment to assess the origin of VOC emissions. The characteristic species ratio method uses the ratio of two VOC species to qualitatively infer the impact of some specific emission source [16]. One can deploy it to identify the major sources of ambient VOCs based on the correlation between individual species with low or similar reactivity.

Benzene, toluene, ethylbenzene and m,p-xylene (BTEX) can be used in preliminary investigations to identify the source of VOC emissions [16]. By comparing the toluene to benzene (T/B) ratio, it can be inferred whether the emissions are likely to have a traffic origin (**Table 4**). A low T/B ratio (< 2) indicates strong influences from vehicle emissions or biomass burning, whereas high T/B (> 2) ratios are suggestive of non-vehicle emissions, e.g., solvent usage [16].

Additionally, the ratios of m,p-xylene to ethylbenzene (X/E) and benzene (X/B) have emerged as indicators of photochemical ages of air mass (**Table 4**) [16]. Since m,p-xylene has a shorter lifetime than ethylbenzene and benzene, air masses that have travelled further from the source and are thus aged are expected to exhibit low X/E and X/B ratios. In contrast, fresh air and local emissions would yield higher ratios.

Table 4. Commonly utilised VOC ratios and implied sources.

VOC ratio	Value	Implied source
m/p-xylene: ethylbenzene	High	Fresh Air Mass
	Low	Aged Air Mass
m/p-xylene: benzene	High	Fresh Air Mass
	Low	Aged Air Mass
Toluene: Benzene	< 2	Traffic/Biomass Burning
	> 2	Non-traffic, e.g., solvent usage

Undoubtedly, the RfC and IUR indices have sig-

nificant uncertainty associated with them. The formulation of IUR and RfC values relies upon animal models to assess human risks, and the relevance of this approach must be considered in any analysis [17]. In some cases, animal data may overestimate or underestimate the risk, necessitating further research to compare toxicity mechanisms in animals and humans [17]. Furthermore, the US EPA defines these variables by American standards and environments, which may differ significantly from those in the UK due to meteorological and social factors, such as weather patterns and lifestyle choices, respectively.

Moreover, there is wide variation in how people respond to pollutants. The biological bases for this variation response include the importance of inherited genes that may predispose individuals to disease [18]. Variability also exists in exposure concentration within a population due to differences in lifestyle choices. Some individuals are likely to spend more time outdoors, commuting to work by cycling/walking or working outdoors. Therefore, generalising the population may cause over- or under-representation of health risks for many people.

Additionally, not all VOCs measured by the UK monitoring effort have a defined IUR and RfC value, as proposed by the US EPA. Thus, this study may be significantly underrepresenting the overall health threats. Similarly, the UK monitoring effort does not measure all VOCs with IUR and RfC values. Despite the uncertainties, the indices remain critical to risk assessment and are essential in setting standards/guidelines for exposure to hazardous substances (including VOCs) in the atmosphere. Therefore, such indices are necessary to inform decision-making related to protecting public health.

3. Results and discussion

The total mean VOC burden, obtained by summing the yearly mean concentrations of the 12 VOCs (**Figure 1**), was higher at LMR than at LE. The total VOC concentration was significantly lower at AM than at the urban and suburban sites. A heightened level of VOC pollution at LMR is due to dense traffic and pollution from local sources such as construction sites. The 'background' nature of sites AM and LE rationalises their lower concentrations. The monitoring stations are suitably far away from dense pollution, so they are not affected by a single source but by the collective influence of sources upwind from the monitoring sites [19]. VOCs may degrade during transport before they reach the AM and LE monitoring stations, thus reducing the total VOC concentration.

Differences in the distribution of the 12 analysed VOCs across the three sites also arise (**Figure 2**). The dominant VOCs at LMR were toluene, m,p-xylene and n-pentane (2.54, 1.70, and 1.20 μg m^{-3}, respectively). The dominant VOCs at LE were toluene, n-pentane and m,p-xylene (0.85, 0.64 and 0.52 μg m^{-3}, respectively), while at AM benzene, n-pentane and toluene (0.20, 0.16, and 0.13 μg m^{-3}, respectively) dominated. The differences regarding the concentration and variation of VOCs between sites reflect the influence of local sources.

Benzene, toluene, ethylbenzene, m-xylene, p-xylene, and o-xylene (BTEX) represent a class of common urban pollutants related to traffic emissions [20]. BTEX are of great concern because of their human health impact. They represent a significant fraction of the VOCs emitted in an urban environment by road traffic, especially unleaded petrol, which is rich in aromatic hydrocarbons [20]. Unsurprisingly, the concentration of BTEX is significantly higher at LMR (5.83 μg m^{-3}) than at LE (2.07 μg m^{-3}) and AM (0.43 μg m^{-3}). LMR is surrounded by heavily congested roads and tall buildings, leading to high BTEX concentration and poor dispersion of pollutants. Benzene and toluene concentrations are higher at all sites than the xylenes. For example, at LMR, mean benzene and toluene concentrations are 0.92 and 2.54 μg m^{-3} compared with m,p-xylene, and o-xylene of concentrations 1.70 and 0.68 μg m^{-3}, respectively. This is in agreement with other studies demonstrating lower loadings of the xylenes in vehicular emissions compared with toluene [21]. Additionally, benzene and toluene have longer lifetimes (9.4 and 1.9 days, respectively) compared with the xylenes (0.6–0.8 days) due to their higher reactivity [22]. As a result, benzene and toluene are more likely to persist in the atmosphere for sufficient time to allow measurement.

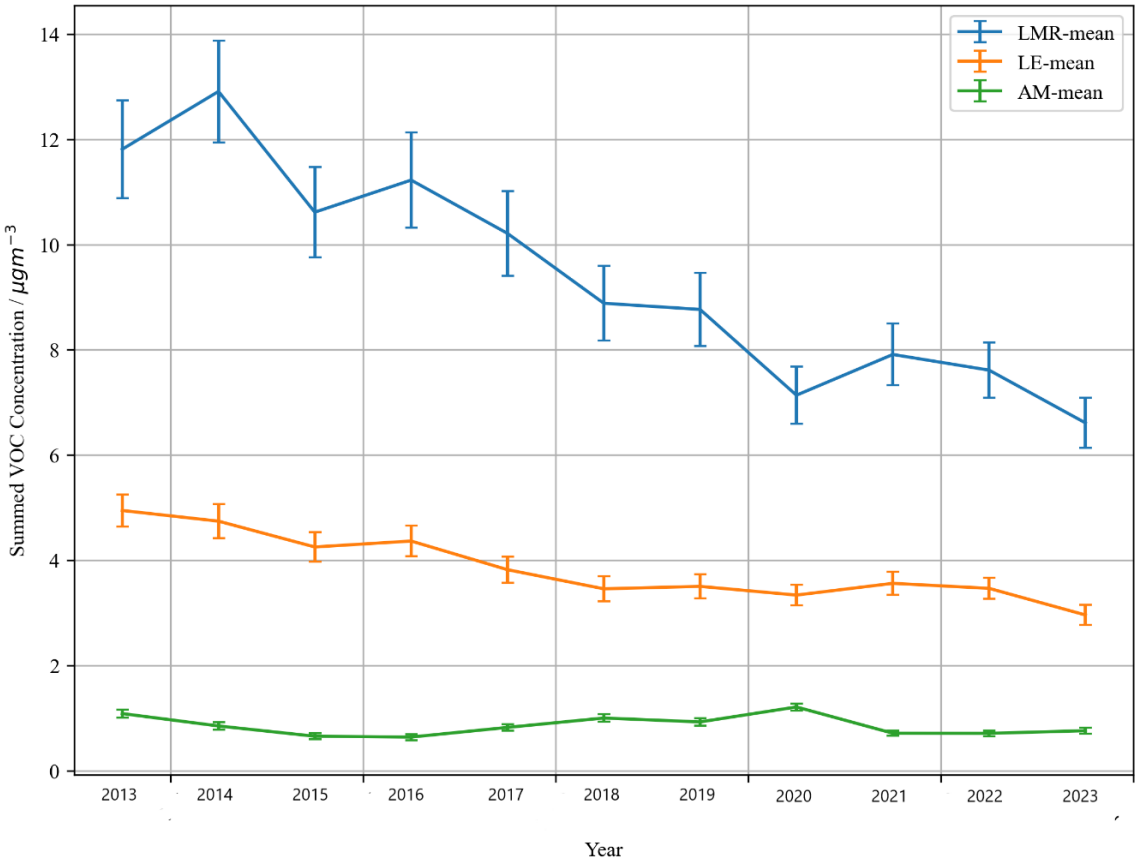

Figure 1. The annual mean of the summed concentrations of the 12 VOCs analysed at London Marylebone Road, London Eltham and Auchencorth Moss sites. Error bars represent ± 1 SD for all data in each year.

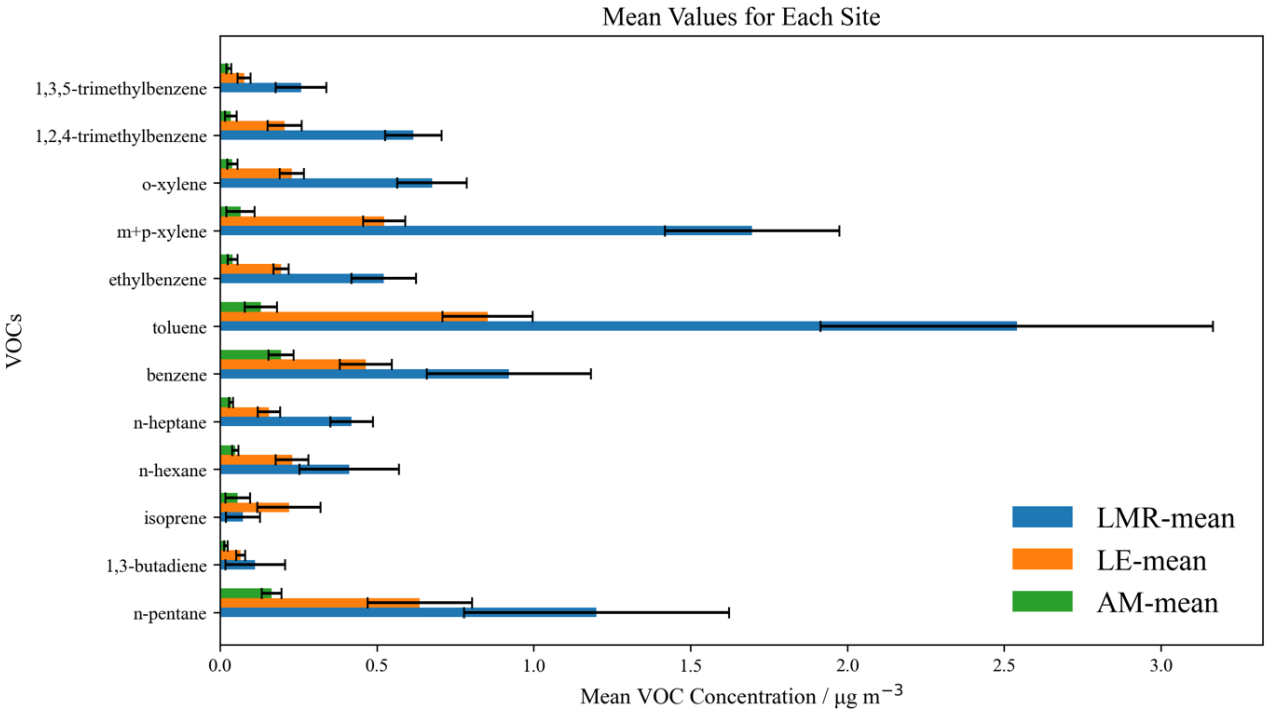

Figure 2. The overall mean concentrations (µg m^{-3}) of the 12 analysed VOCs at the three monitoring sites. The error bar represents ± 1 SD of the whole data series.

Analysis of BTEX ratios at the sites considered can be used to infer information about potential sources of pollution. The average toluene: benzene (T/B) ratio, calculated by dividing the average concentrations of toluene by the average concentrations of benzene (**Table 5**), was consistently less than two at all background sites, indicating the presence of traffic-related sources of VOC emissions [16]. However, slight differences in the ratio between sites suggest variations in source contributions, with a ratio closer to two suggesting the influence of additional sources, such as solvent evaporation. For example, as the T/B ratio decreases, from LMR (2.76) to LE (1.83) to AM (0.67), the probability of other sources contributing to VOC concentration also decreases, according to previous research [16]. Unsurprisingly, LMR has other competing sources, as urban areas often have increased solvent evaporation and industrial emissions [23]. This is supported by it having a T/B ratio >2 across the entire period considered.

Table 5. Average Toluene/Benzene (T/B), m.p-Xylene/Ethyl benzene (X/E) and Xylene/Benzene (X/B) ratios for each site.

	LMR	LE	AM
T/B	2.76	1.83	0.67
X/E	3.25	2.70	1.64
X/B	1.84	1.12	0.34

Low m,p-xylene: ethylbenzene (X/E) and m,p-xylene: benzene (X/B) ratios imply that aged air masses influence pollution, while fresh air and local emissions would yield higher ratios [16]. For example, the low X/E and X/B ratios at LE and AM imply that aged air masses dominate the pollution, which is unsurprising as these sites are considered 'background' sites and are not significantly influenced by a single source, instead by the integrated sources upwind of the station. LE has higher X/E and X/B ratios than AM which is reasonable as the LE site can be influenced by the pollution of nearby urban traffic site, LMR. LMR has significantly larger X/E and X/B ratios indicating the presence of fresh pollution. This observation is consistent with the environmental characteristics of the monitoring site, where nearby sources influence pollution at traffic sites.

While focusing on concentration alone can provide a preliminary investigation to understand how VOC emissions vary at different locations, it provides limited information on the potential consequences of the emissions on human health. VOCs can vary significantly in their toxicity even at similar concentrations, so relying solely on concentration levels may not accurately reflect the health risks associated with VOC exposure. Therefore, adopting health indices can provide a more holistic understanding of the potential health risks associated with VOC exposure.

Toluene, benzene, 1,3-butadiene, and isoprene are unsaturated VOCs ubiquitous in the troposphere. The US EPA classifies them as air toxins for their detrimental effects on human health and potential carcinogenic nature using their carcinogenic risk (RISK) [24]. The former three VOCs are considered primarily anthropogenic in origin, e.g. from combustion, fuel evaporation, solvent usage, and industrial processes, whereas isoprene is predominantly biogenic [25, 26].

Additionally, twelve VOCs with an associated RfC value, including the four that also have a RISK value, were analysed to infer non-carcinogenic risk. Of the twelve VOCs, toluene had the most significant non-carcinogenic risk value, exceeding the acceptable threshold of 1.0×10^{-6} in both the urban and suburban sites. n-pentane followed, with a non-carcinogenic risk value approaching the threshold for all sites and significantly exceeding the threshold at the LMR monitoring site. The 10 remaining VOCs were suitably below the threshold, so they will not be discussed individually. Instead, the HI (total non-carcinogenic risk) will be discussed.

3.1 Annual trends

For most of the 21st century, the UK government has employed many emission reduction initiatives related to road transport [27]. Hence, it is unsurprising that LMR, a site heavily influenced by traffic emissions and changes in them, demonstrates the most significant decrease in anthropogenic VOC health risks since 2013 (**Figure 3**) [28].

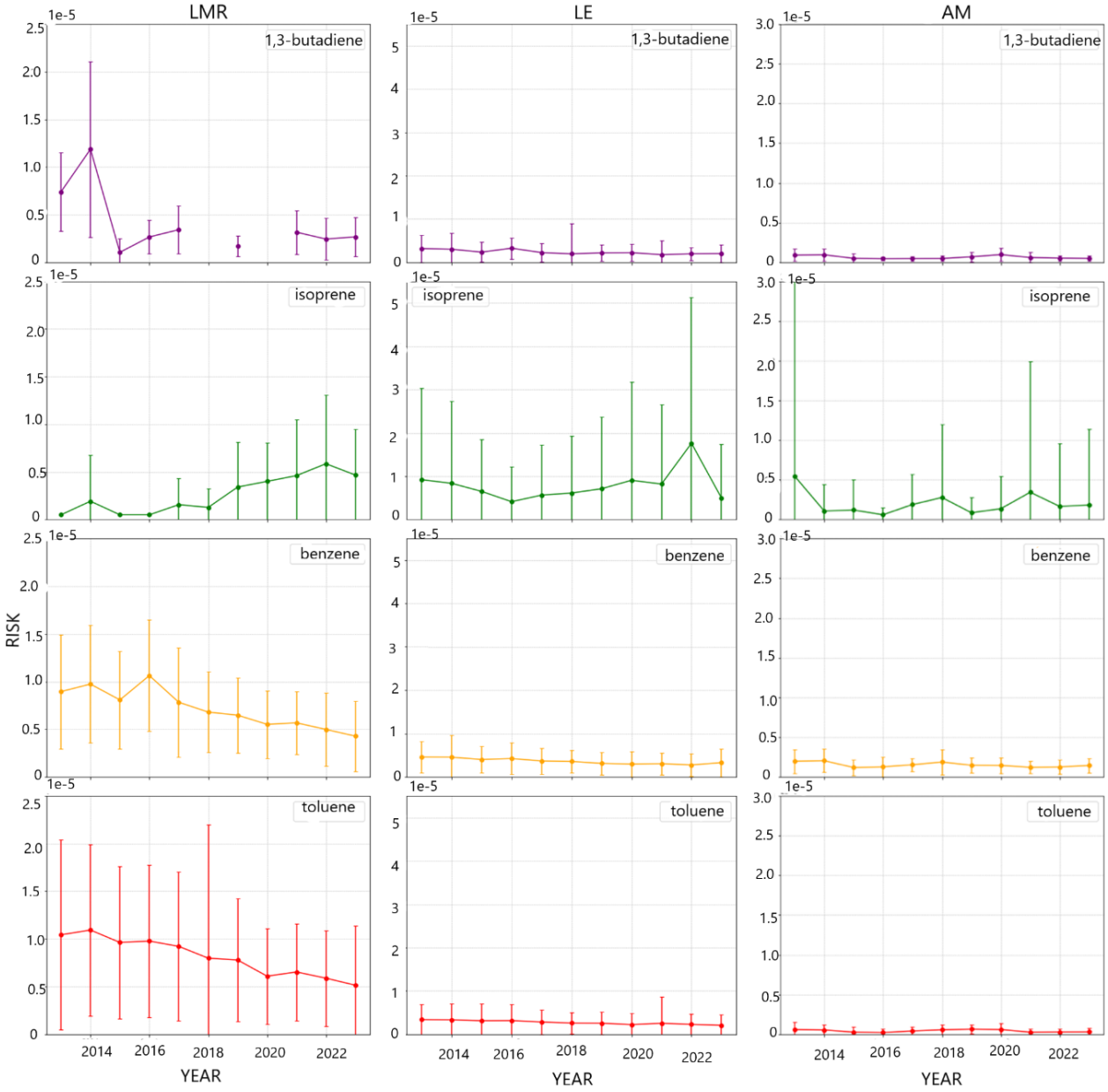

Figure 3. Line graphs depicting the annual variation in carcinogenic risk of 1,3-butadiene, isoprene, benzene and toluene for (from left to right) LMR, LE and AM. Error bars represent ± 1 SD for all data in each year.

Moreover, emission control strategies in London work to reduce emissions from the oldest, most polluting vehicles and reduce traffic congestion, respectively. Moreover, 12 million tons of oil equivalent (Mtoe) petrol has been replaced with diesel from 1990 to 2017 [29]. Since diesel contains fewer hydrocarbons than petrol, this switch likely brought on the steady decline of anthropogenic VOCs in LMR and LE and a reduction in their corresponding carcinogenic risk values (**Figure 3**) [30]. Despite diesel mitigating some hydrocarbon pollution, the emissions from this fuel type may cause increased NO_2 and $PM_{2.5}$ pollution issues [31]. The clear emphasis on and relative effectiveness of traffic-related mitigation strategies is corroborated by the minimal decrease in RISK value observed at the non-traffic sites, where these measures exert less influence than the traffic sites.

On the other hand, the carcinogenic risk associated with isoprene has increased at LMR since 2013 (**Figure 3**). A possible reason behind this is the cor-

relation between rising temperatures and increased isoprene emissions from biogenic sources. The highest decadal global land and ocean surface temperature was recorded from 2010–2020, with a global surface temperature of + 0.82 °C above the 20th century average [32]. The increased warming, which stimulates plant metabolic activity, may be responsible for the observed increase in isoprene emissions from vegetation as plants produce isoprene as a protective response to environmental stresses such as high temperatures [33]. The overall carcinogenic risk of isoprene has decreased at LE and AM, but, **Figure 3** shows the notable fluctuations in the yearly average isoprene RISK value. This suggests that factors such as temperature, sunlight, and environmental stressors like drought, which can significantly influence the rate of isoprene emissions, substantially impact isoprene emissions and the associated carcinogenic risk value. Since AM is a rural site with a strong biogenic influence, the yearly changes in these factors likely contribute to the observed fluctuations, and no clear overall trend is apparent. These findings highlight the synergic effect between climate change and air pollution, emphasizing the need to mitigate global warming.

It is crucial to highlight that isoprene emissions arise from both biogenic and anthropogenic sources. Biogenic emissions have traditionally been considered the dominant source of isoprene. However, anthropogenic activities, such as vehicular exhaust and human exhalation, also contribute to isoprene emissions, albeit estimated to account for only ~ 15% of the global isoprene flux [34]. Nevertheless, anthropogenic isoprene emissions may have an impact on air quality in urban areas where vehicular emissions can accumulate, leading to an increased isoprene concentration and associated carcinogenic risk.

Fortunately, due to the implementation of stricter traffic-related regulations, anthropogenic isoprene emissions have decreased in recent years. Research by Khan et al. and Von Schneidemesser have shown that biogenic emissions have become relatively more important in urban areas [34, 35].

Overall, there has been notable progress in reducing the carcinogenic risk associated with benzene, toluene, and 1,3-butadiene, likely due to strategies that reduce anthropogenic VOC emissions in urban environments [36]. Additional background sources must be addressed to further reduce the non-carcinogenic risk associated with these VOCs, e.g., industry. Moreover, progress has not necessarily been extended to sites less influenced by traffic emissions (i.e. LE and AM). There is a need for further efforts to ensure the improvement of air quality in both rural areas and urban environments.

As demonstrated by **Figure 4**, the LMR and LE monitoring sites show pronounced decreases in the total non-carcinogenic risk from 2013 to 2023. This is likely a result of emission control strategies implemented as part of the London Mayor's Air Quality Strategy, such as the London Congestion Charging Scheme and the London Low Emission Zone [37]. The findings from this study suggest that the development of such initiatives has positively affected non-carcinogenic health risks associated with VOCs from 2013 to 2023, not only as the source (LMR) but away from the source (LE).

It is important to acknowledge the impacts of the COVID-19 pandemic in the UK. The emergence of the corona-virus in Wuhan, China, in December 2019 led to a global pandemic that affected over 210 countries within five months, with devastating consequences for public health [38]. To contain the spread of the disease, the government enforced lockdown measures in March 2020, which led to a sharp decline in economic activity, bringing transport and mobility to near-negligible levels [39]. The impact of this is seen between 2019 and 2020 where a significant decrease in the mean is observed at the urban sites. However, this decrease is partially offset by a subsequent increase between 2020–2021 at both the urban and suburban sites when restrictions were lifted. Overall, a reasonably steady decrease is seen across the whole time period considered. As such, analysis moving forward will not include a discussion of this time period.

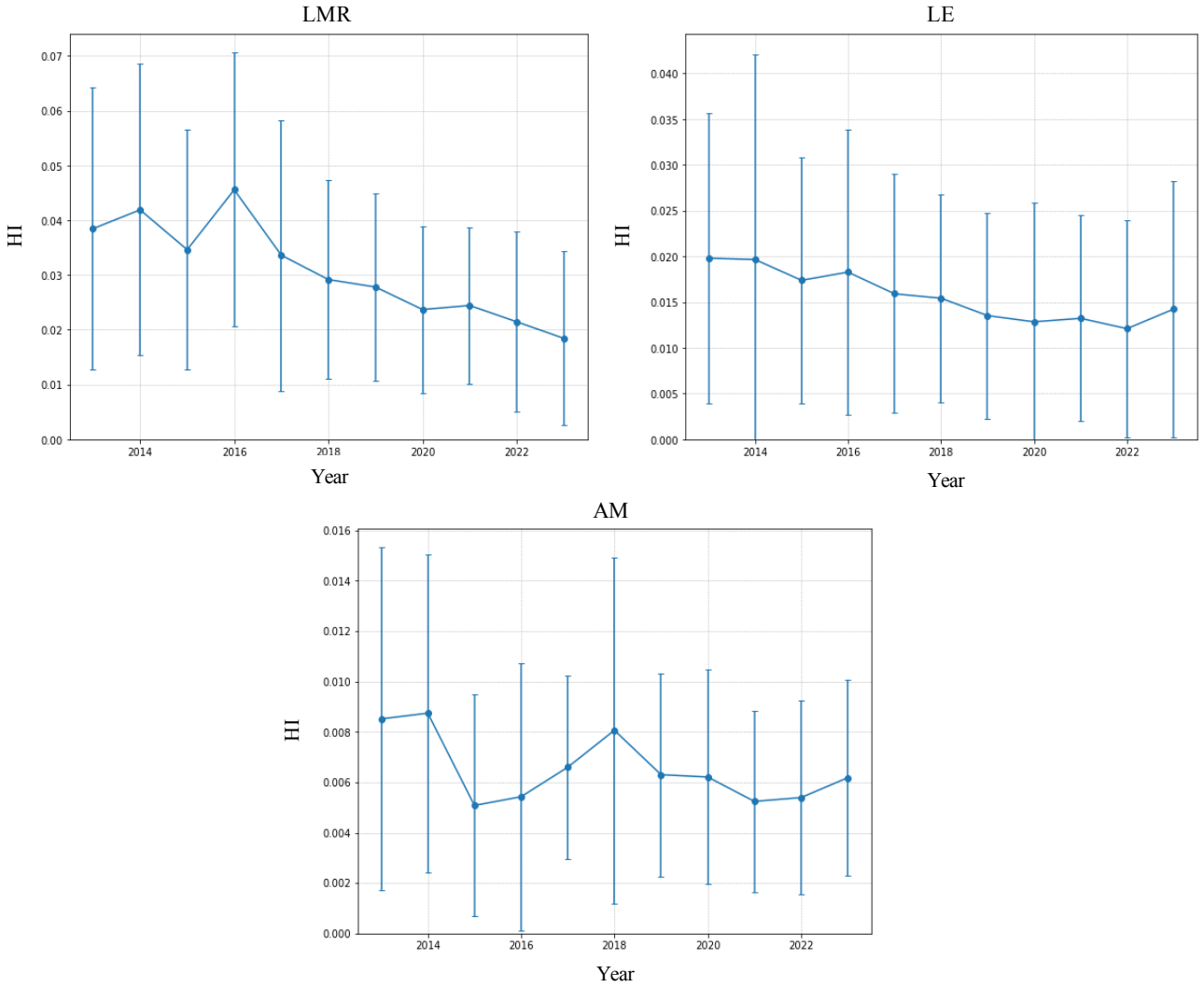

Figure 4. The annual variation of the combined non-carcinogenic risk of the 12 VOCs considered in this study at (**a**) LMR, (**b**) LE and (**c**) AM. Error bars represent ± 1 SD for all data in each year.

3.2 Seasonal variation

Figure 5 shows the monthly variation of carcinogenic risk (RISK) of 1,3-butadiene, isoprene, benzene and toluene for LMR, LE and AM sites.

The carcinogenic risk value (RISK) associated with isoprene exhibits a consistent seasonal pattern across all three locations (**Figure 5**). Peaks in variation occur during the summer (between June and September), with maximum values in July of 6.34×10^{-6}, 2.82×10^{-5}, and 1.26×10^{-5} at LMR, LE, and AM, respectively, characterising the trend. During this period, there is likely to be a rise in isoprene concentration. Since biogenic sources account for most isoprene emissions, the release rate is contingent upon factors that govern the rate of photosynthesis and enzyme action in plants, such as temperature and solar radiation, so, unsurprisingly, the emission of isoprene increases over this period [40–42]. Consequently, the carcinogenic risk associated with isoprene exceeds the acceptable threshold of 1.0×10^{-6} for all three locations between June and September.

In contrast, benzene and 1,3-butadiene exhibit high RISK values during winter, displaying similar patterns across all three sites under investigation (**Figure 5**). VOC emission rates typically rise during the winter due to increased rates of fossil fuel combustion to satisfy the greater energy demands for residential heating [43]. In addition, cars are susceptible to cold starts in the winter, contributing to increased VOC emissions [44, 45]. Benzene is above the accept-

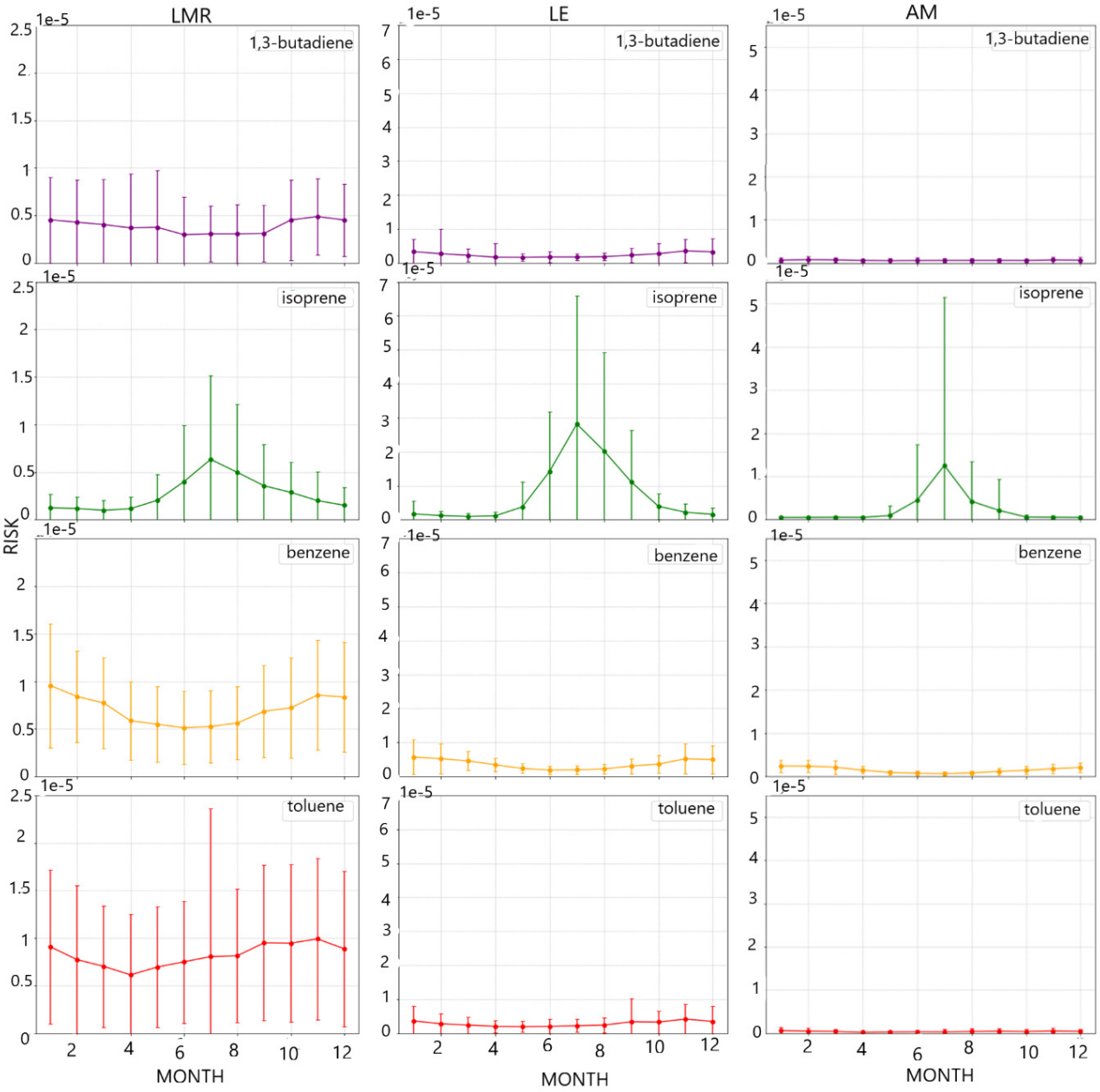

Figure 5. Line graphs depicting the monthly variation in carcinogenic risk of 1,3-butadiene, isoprene, benzene and toluene for (from left to right) LMR, LE and AM. The error bar represents ± 1 SD of the whole data series.

able threshold during winter for all three sites, and 1,3-butadiene is above the threshold of 1.0×10^{-6} during winter for both the urban and suburban sites. Benzene displays maxima in January of 9.55×10^{-6}, 5.72×10^{-6}, and 2.44×10^{-6} at LMR, LE, and AM, respectively.

Conversely, during the summer, benzene and 1,3-butadiene concentrations decline due to enhanced atmospheric removal by the OH radical, which forms through the photolysis of O_3. This degradation becomes more pronounced in summer than winter due to the increased frequency and intensity of solar radiation therefore greater OH production [46,47]. Consequently, there is a significant dip in benzene and 1,3-butadiene RISK values across all sites considered, whereby the values recorded for AM satisfy

the guidelines proposed by the US EPA. However, the RISK for these VOCs still exceeds the acceptable threshold at both LMR and LE, even during the summer, highlighting the urgent need to enhance air quality measures throughout the year as even when meteorology favours lower concentrations, the RISK value is over the 'safe limit'.

It is often assumed that benzene and toluene originate from mostly the same anthropogenic sources in urban areas and have proportional emission rates [48]. Hence, the RISK value for toluene should follow a similar seasonal trend to benzene, yet, the two VOCs demonstrate significant differences. The carcinogenic health risk of toluene at LMR was higher in June, July, and August (7.51×10^{-6}, 8.06×10^{-6}, 8.15×10^{-6}) than in March, April and May (7.02×10^{-6}, 6.14×10^{-6}, 6.96×10^{-6}). Toluene's seasonal variations opposed the seasonal variations of benzene, whose RISK value was generally higher during March, April, and May (7.72×10^{-6}, 5.86×10^{-6}, 5.49×10^{-6}) than in June, July, and August (5.13×10^{-6}, 5.25×10^{-6}, 5.62×10^{-6}).

The elevated toluene RISK value from late spring to early Autumn is most likely an increase in emission concentration due to changes in reformed gasoline hydrocarbon content to meet annual US EPA-mandated VOC requirements from the 1st of June to the 15th of September [48]. To fulfil these requirements, refineries often substitute highly volatile high-octane compounds with heavier alkenes and aromatic compounds. However, this substitution can lead to increased toluene evaporation and subsequently raise its associated carcinogenic risk value during this period. LE is a background site unaffected by singular sources, so this phenomenon does not affect the seasonal toluene carcinogenic risk change here.

Although the monthly variations in carcinogenic risks are similar across all three sites, there are significant differences in the intensity of these risks. At LMR, the carcinogenic risks of all four VOCs remain above acceptable levels throughout the year, except for isoprene in March (9.92×10^{-7}). These results indicate a high possibility of inducing cancer in humans exposed to the environments for an extended time. Conversely, at AM, the RISK value for all four VOCs remains below the threshold except for isoprene, whose RISK value exceeds the threshold from June-September, implying that the risk of humans who are exposed to the environment surrounding AM for a prolonged period is lower than its urban counterparts. This discrepancy is due to different environmental conditions across all three sites.

Given the context of LMR as a heavily polluted traffic site, concentrations of VOC emissions resulting from fossil fuels are high. In contrast, the AM monitoring station is situated in an elevated rural environment with few local influences. Therefore, different VOCs dominate the carcinogenic risk at each site. These findings underscore the importance of adapting policies to address different backgrounds to improve air quality and human health throughout the UK. By tailoring policies to specific conditions, policymakers can take more effective steps toward reducing exposure to VOCs.

Figure 6 shows the monthly variation of the combined non-carcinogenic risk of 12 VOCs for LMR, LE and AM sites. The contribution of toluene to the total non-carcinogenic risk value at LE and LMR is significant, with the Hazard Quotient (HQ) value of toluene being over ten times higher than that of n-pentane, the second most significant contributor. As a result, seasonal trends in toluene primarily influence the monthly variations in the total non-carcinogenic risk (HI). For LMR and LE sites, the variation in health effects appears to be more typical for VOCs, as these are the sites that are not significantly influenced by single sources. Hence, HI values are found to be lowest in June, July, and August and highest in November, December, and January (**Figure 6**). A similar trend of a much lower magnitude is seen at AM (**Figure 6**).

Overall, the influence of toluene on non-carcinogenic risk is evident, indicating the need for policymakers to prioritize the development of initiatives to reduce toluene emissions throughout the year. Initiatives reducing the toluene fraction in fuels and implementing measures to decrease traffic flow in highly congested areas would be conducive to enhancing air quality and improving public health.

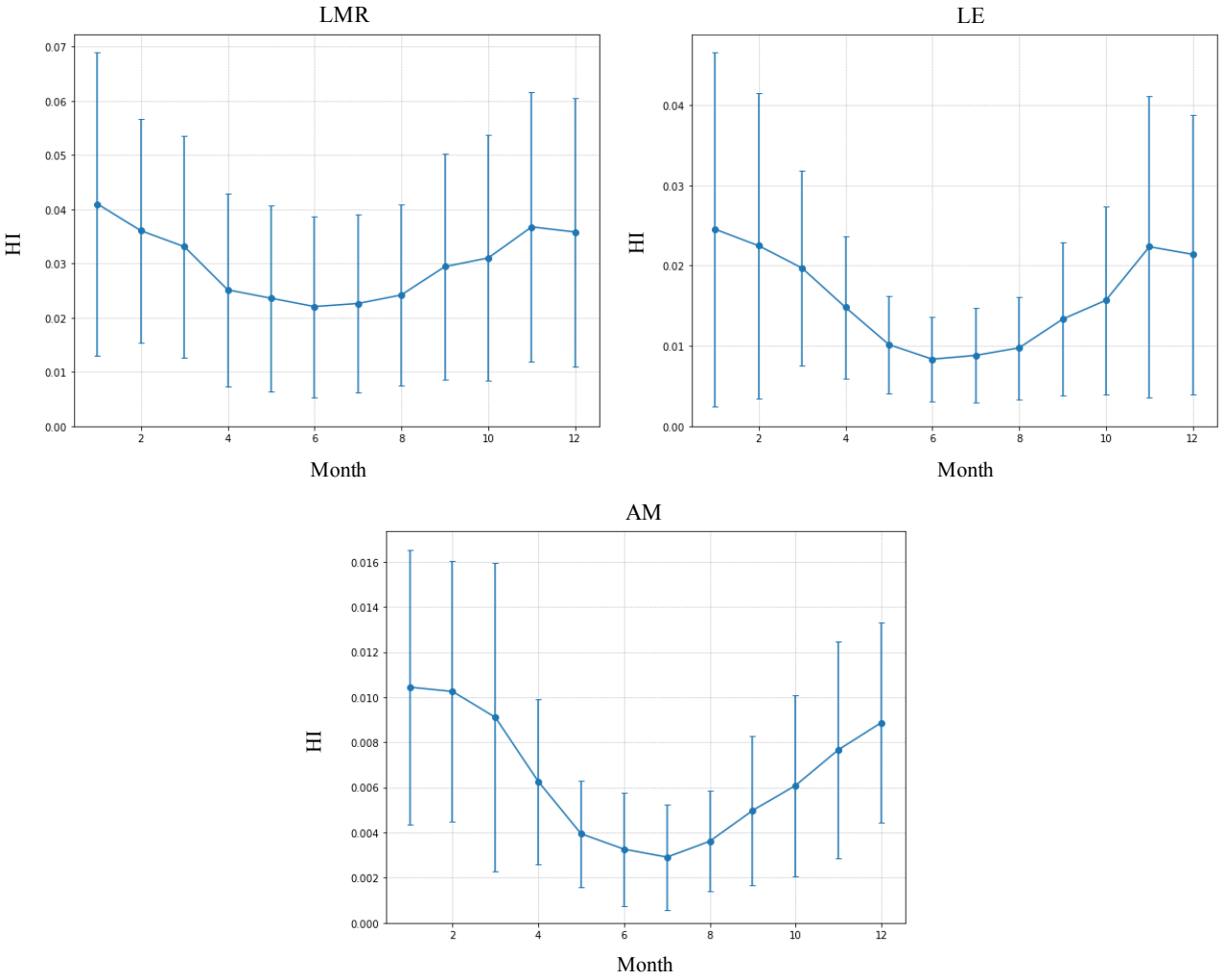

Figure 6. The monthly variation of the combined non-carcinogenic risk of the 12 VOCs considered in this study at (**a**) LMR, (**b**) LE and (**c**) AM. The error bar represents ± 1 SD of the whole data series.

3.3 Diurnal trends

Diurnal profiles of the carcinogenic risk associated with aromatic VOCs (benzene and toluene, AVOC) follow a clear bimodal distribution (**Figure 7**), paralleling the occurrence of two rush hours at LMR and LE [49]. Additional advection of traffic-related pollution, as well as planetary boundary layer effects and photochemistry cause the peaks in concentrations of these compounds [50]. The RISK value of 1,3-butadiene follows the same bimodal trend at LMR, yet, to a lesser extent. Gasoline combustion is known to contain a higher proportion of aromatic compounds than 1,3-butadiene. Moreover, the lifetime of 1,3-butadiene (6 hours) [51] is significantly shorter than that of benzene and toluene (9.4 and 1.9 days, respectively) resulting in less accumulation of 1,3-butadiene.

The rate of traffic flow is the main driver behind the trend in anthropogenic VOC concentration and the associated carcinogenic risks. Hence, the first maximum in anthropogenic VOC carcinogenic risk occurs between 05:00 LT and 09:00 LT, with toluene reaching an 08:00 maxima of 1.00×10^{-5} and 3.48×10^{-6} at LMR and LE, respectively. These values are significantly higher than the US EPA's appropriate threshold of 1.0×10^{-6}.

There is a subsequent dip in the carcinogenic risk of anthropogenic VOCs at LE and LMR from 09:00 LT until approximately 14:00 LT. This behaviour is caused not only by reduced traffic and enhanced photochemical sink but also by increasing thermal convection during the daytime hours, leading to the

dilution of atmospheric pollution with cleaner air masses from above the planetary boundary layer [52]. Moreover, increased solar radiation and temperature lead to a higher concentration of OH radicals available to remove VOCs from the atmosphere [53].

Due to the evening rush hour, there is a second significant increase in the RISK value of anthropogenic VOCs at LE and LMR. Toluene reaches 17:00 LT maxima of 1.39×10^{-5} at LMR and 20:00 LT maxima of 3.13×10^{-6} at LE. The increased traffic flow coincides with the stratification of the atmosphere, caused by the faster cooling of air near the surface compared to the warm air above, leading to a shallower planetary boundary layer [42]. As a result, the evening RISK peak is more prominent than in the morning as a lower boundary layer causes a substantial accumulation of VOCs leading to higher ambient concentrations [42].

It is worth noting that the anthropogenic VOC RISK values at the LE monitoring site peak until

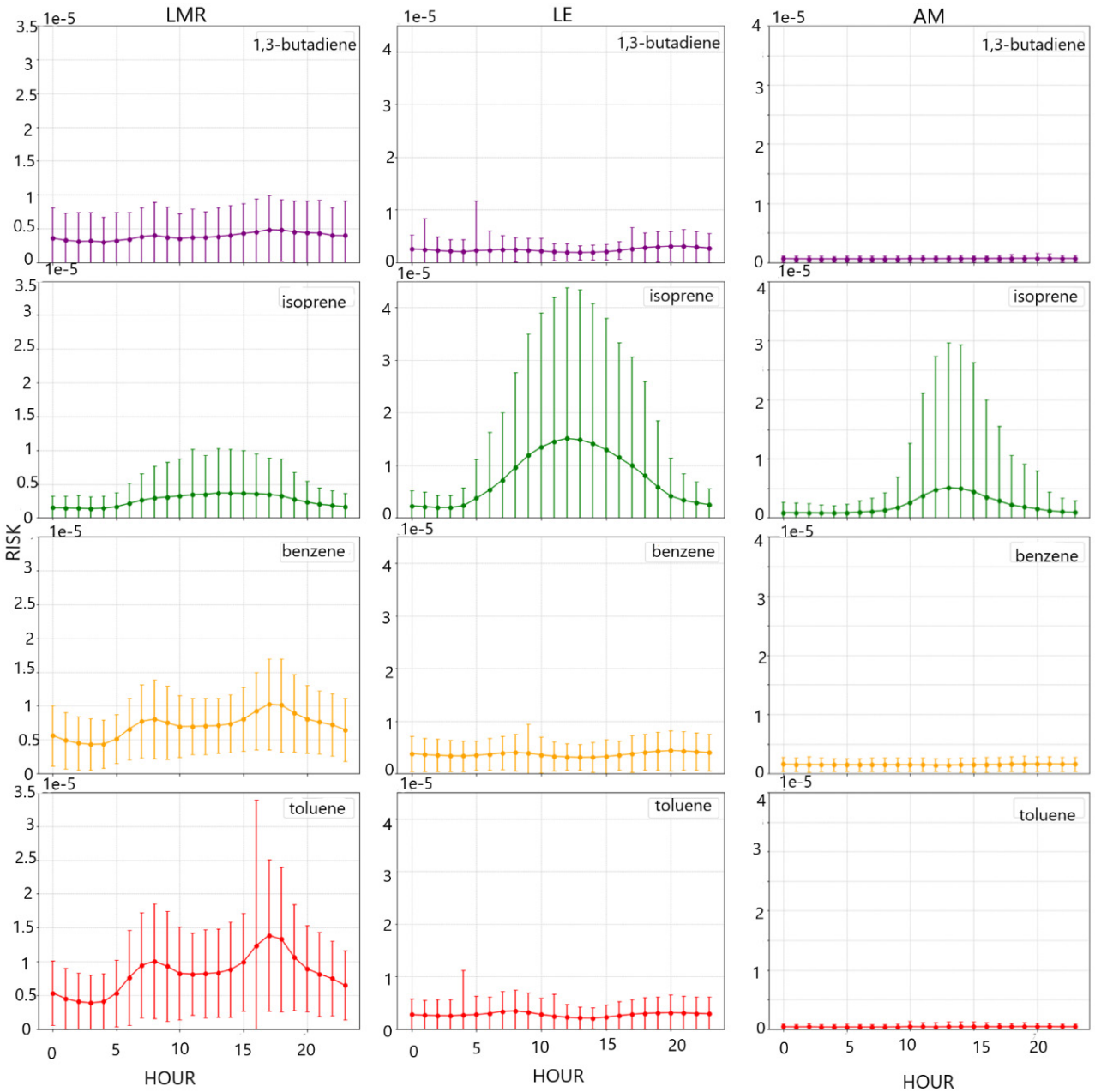

Figure 7. Line graphs depicting the diurnal variation in carcinogenic risk of 1,3-butadiene, isoprene, benzene and toluene for (from left to right) LMR, LE and AM. The error bar represents ± 1 SD of the whole data series.

22:00 LT. The transport of aged emissions upwind of the LE monitoring site may be responsible for the extended second peak in RISK compared to LMR due to the influence exerted by integrated sources upwind of the station at LE. The time taken to transport emissions from the source to the monitoring station prolongs the evening peak in RISK value. Following the second diurnal peak there is a rapid decline in the anthropogenic VOC RISK values at night, with toluene reaching a 03:00 LT minimum of 3.88×10^{-6} and 2.54×10^{-6} at LMR and LE, respectively.

The AM monitoring site is relatively stable to emissions from anthropogenic VOCs owing to its rural surroundings and isolation from any main road. Indeed, the carcinogenic risks associated with benzene and 1,3-butadiene remain generally unchanging throughout the day, emphasising the isolation of the AM monitoring site.

Conversely, isoprene exhibits a different diurnal pattern to the VOCs mentioned above due to the influence of biogenic sources on its emission. The carcinogenic risk associated with isoprene increases significantly from ~ 05:00 LT to its peak at ~ 13:00 LT, reaching a maximum of 3.70×10^{-6}, 1.51×10^{-5}, and 5.11×10^{-6} at LMR, LE and AM, respectively. Factors governing the rate of enzyme action and photosynthesis are responsible for the rate of biogenic isoprene emission [41,42]. Since plants can only photosynthesise during daylight hours, isoprene concentrations and its corresponding carcinogenic risk increase during the day [25]. Consequently, the carcinogenic risk associated with isoprene remains well above an acceptable level for all three sites during this period.

Notably, the significance of the RISK value associated with isoprene is considerably higher at LE and AM than at LMR. Considering the environments surrounding the sites can rationalise the difference in RISK value. Trees, parks and grassy areas surround the LE monitoring site, and the AM monitoring site is located amongst a traditional lowland raised bog. Thus, biogenic emissions are expected to be significant in these locations. LMR has significantly less biogenic influence as it is primarily surrounded by urban agglomerations and traffic. Nonetheless, Reagents and Hyde Park are reasonably close by, and biogenic emissions from these areas will influence the carcinogenic risk value of isoprene throughout the day [54]. Furthermore, there is evidence of notable isoprene emissions from traffic [34].

The nocturnal removal of isoprene by NO_3 leads to a notable reduction in carcinogenic risk with minimum values of 1.39×10^{-6}, 1.99×10^{-6}, and 8.35×10^{-7} for LMR, LE, and AM, respectively, between the hours of 03:00 LT and 04:00 LT. This is due to the rapid reaction between NO_3 and isoprene at night, facilitated by a high-rate coefficient, resulting in a half-life ranging from 0.9 to 1.9 hours [55]. During the day, this reaction becomes negligible as NO_3 quickly undergoes photolysis with NO. Despite the significant reduction during night-time, the associated carcinogenic risk of isoprene remains above the safe level for LMR and LE. The environment surrounding the AM monitoring site lacks tall buildings and other urban structures, likely resulting in a taller and less turbulent planetary boundary layer. In turn, a more stable atmosphere develops where the significant dissolution of pollution occurs, resulting in lower pollutant concentrations. As a result, the isoprene RISK value falls below the 'safe' threshold at night at AM.

The diurnal pattern of total non-carcinogenic risk (HI) at LMR and LE follows the same trend as (**Figure 8**) the diurnal pattern for the carcinogenic risk, as explained above. The HI at AM fluctuates minimally throughout the day with no clear trend.

4. Conclusions

The decreasing trends observed in the total non-carcinogenic health risks associated with VOCs at the urban and suburban background sites (LMR and LE, respectively) since 2013 highlight the effectiveness of emission control strategies implemented in the UK. The significant reduction in non-carcinogenic health risks can be attributed to the decline in VOC concentrations. Emission reductions are due to the reduced influence of road traffic, as indicated by characteristic species ratios. Similar decreases in the carcinogenic health risk of 1,3-butadiene, benzene, and toluene over the same period at LMR and LE emphasise the success of these government initiatives.

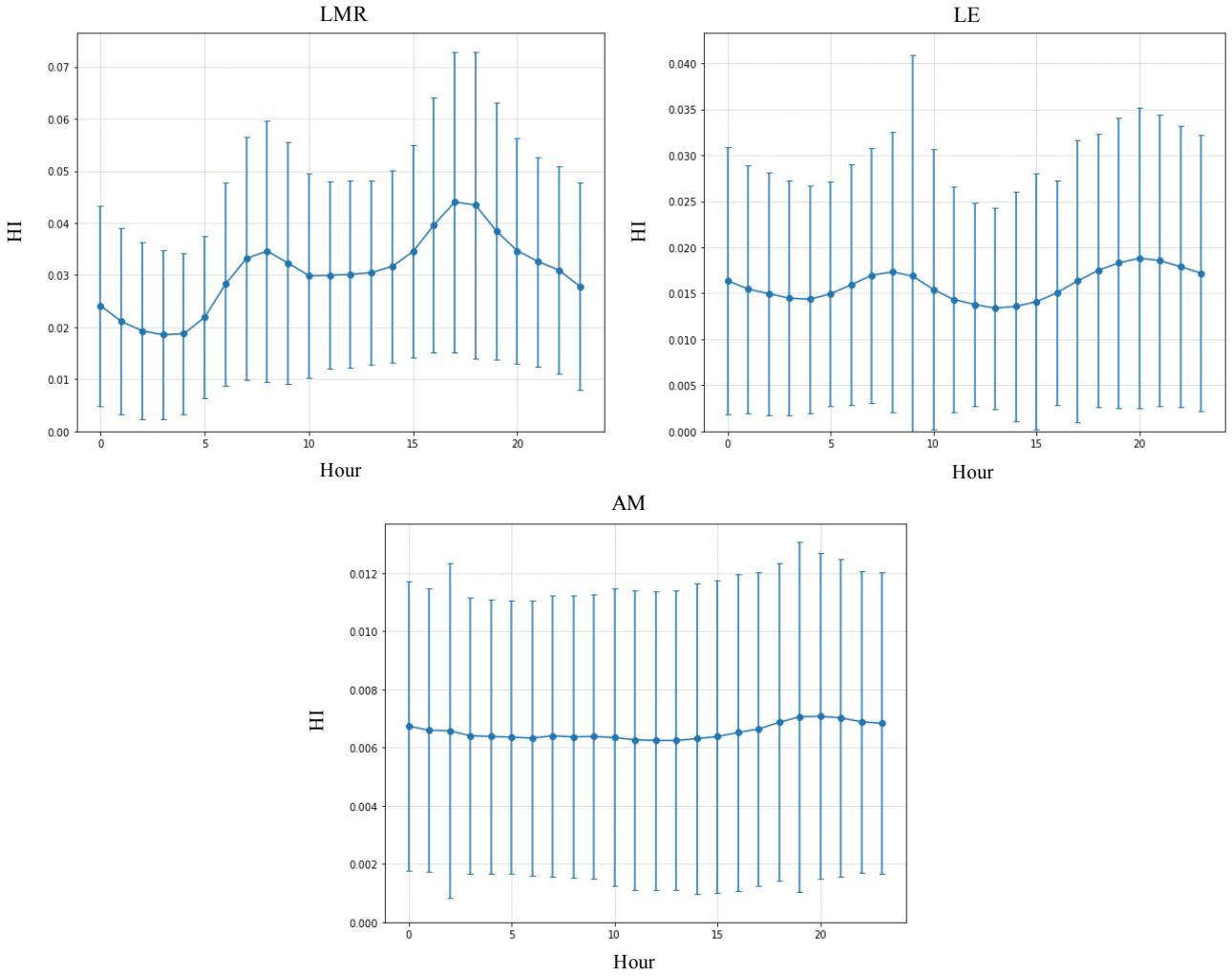

Figure 8. The diurnal variation of the combined non-carcinogenic risk of the 12 VOCs considered in this study at (**a**) LMR, (**b**) LE and (**c**) AM. The error bar represents ± 1 SD of the whole data series.

The average VOC concentration was ~ 10-fold higher at the urban site (LMR) than at the rural site (AM), paralleling with far lower carcinogenic and non-carcinogenic risk values at the rural site. These findings underscore the importance of adapting policies to address different backgrounds to improve air quality and human health throughout the UK. By tailoring policies to specific conditions, policymakers can take more effective steps toward reducing exposure to VOCs. However, it is demonstrated that the carcinogenic risk of benzene and 1,3-butadiene often exceeds the acceptable threshold of 1×10^{-6} at this rural site. Therefore, a measurable cancer impact is still likely even at this low-emission site. Additionally, despite the notable decrease in non-carcinogenic and carcinogenic risk at the urban and suburban sites (LMR and LE), the yearly carcinogenic risk for toluene, benzene, and 1,3-butadiene remains considerably above the threshold, and carcinogenic health risks are likely. Therefore, although pollution targets have successfully cut emissions, they have not yet effectively protected human health.

Moreover, the carcinogenic risks of isoprene have increased over the nine years at LMR, demonstrating the need for decreasing the factors that govern its release, e.g., solar radiation and temperature, by mitigating global warming, as well as better characterisation of the influence of traffic emissions on isoprene. Regarding the diurnal and seasonal patterns, anthropogenic VOCs health risks increase during rush hour peaks (05:00–09:00 LT and 17:00–20:00 LT) and during the winter months, whereas biogenic VOCs health

risks are increased during sunlight hours (08:00–20:00 LT) and during the summer months across all three sites. These findings underscore the need for tailoring emission control strategies temporally.

Notably, this study's carcinogenic and non-carcinogenic indices are not without uncertainty. Epidemiology and exposure relationships are complex, and the indices proposed may represent an oversimplification of the relationship and many confounding factors are not considered. However, this study reflects a preliminary investigation of the health effects of VOCs, the patterns, and how legislation intervention has impacted the health effects. As such, the analysis used in this work could be applied across a more extensive temporal and spatial range to improve health data and direct future policy development.

Author Contributions

Dudley E. Shallcross, M. Anwar H. Khan and Rayne Holland conceived and designed the study; Rayne Holland and Molly Guy analyzed the data; Rayne Holland and Molly Guy wrote the paper; Dudley E. Shallcross and M. Anwar H. Khan helped with discussion to improve the paper.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data presented in this study are available on request from the corresponding author.

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