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Temperature driven variations in VOC emissions from plastic products and their fate indoors: A chamber experiment and modelling study

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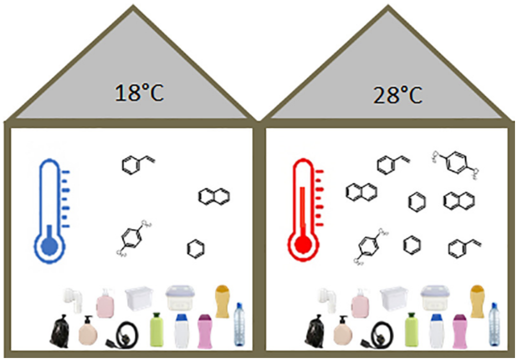
HIGHLIGHTS

- Positive associations were determined between temperature and plastic emissions.
- Emissions were attributed to the migration of impurities from within the polymers.
- Modelled emissions indicate a concurrent rise in secondary pollutants, e.g. formaldehyde.

GRAPHICAL ABSTRACT



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ABSTRACT

Plastic products are ubiquitous in our homes, but we know very little about emissions from these products and their subsequent impact on indoor air quality. This is the first study to systematically determine temperature-dependent emissions of volatile organic compounds from commonly used plastic consumer products found in the home. The plastic types included high-density polyethylene (HDPE), polypropylene (PP), polyethylene terephthalate (PET), polystyrene (PS) and polyester rubber. Plastic samples were exposed to increasing temperatures (between 18 and 28 °C) in controlled environmental chambers, connected to a proton-transfer-reaction time-of-flight mass-spectrometer (PTR-ToF-MS), where real-time emissions were detected. Average emission rates were determined and used to initialise an indoor air chemistry model (INCHEM-Py) at the highest and lowest experimental temperatures, to explore the impact these product emissions have on the indoor air chemistry. The PS tubing plastic proved to be the highest emitting polymer per surface area. Almost all selected VOC emissions were found to have a linear relationship with temperature. Upon observing the impacts of primary VOC emissions from plastics in modelled simulations, the hydroxyl radical concentration decreased by an average of 1.6 and 10 % relative to the baseline (with no plastics included) at 18 °C and 28 °C respectively. On the other hand, formaldehyde concentrations increased by 29 and 31.6 % relative to the baseline conditions at 18 °C and 28 °C respectively. The presence of plastic products indoors, therefore, has the potential to impact the indoor air quality.

1. Introduction

Populations in developed nations spend almost 90 % of their time indoors (Klepeis et al., 2001). Therefore, good indoor air quality (IAQ) is essential for an individual's health and well-being. With energy saving

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measures and enhanced insulation techniques increasingly being implemented in many UK homes (Ministry of Housing, 2019), ventilation with outdoor air can decrease (Vardoulakis et al., 2015). This reduction in airflow through a building can result in increased exposure to accumulated volatile organic compounds (VOCs) from a variety of sources indoors, such as building materials and human activities such as cooking and cleaning (Arata et al., 2021).

VOCs, such as benzene, phenol and naphthalene, as well as very volatile organic compounds (VVOCs) like formaldehyde, have been under scrutiny (Wallace, 2001) because of their association with adverse health effects (Even et al., 2019). These health effects include pulmonary effects and irritation of both the eyes and respiratory tract (Jones, 2002). Consequently, building materials, including some types of flooring (Cox et al., 2002; Afshari et al., 2004), particleboard and fiberboard (Jiang et al., 2017; Zhou et al., 2019), soft furnishings (Oz et al., 2019) and wooden furniture (Xiong et al., 2019), have been extensively evaluated for their chemical emissions and influence on IAQ (Kruza et al., 2017).

However, there is insufficient research on smaller, common household plastics for the purpose of realistic risk or exposure assessments. Polymeric materials are commonly present within the home setting and are used for a variety of purposes such as food storage, household products, personal-care products, decorative ornaments and construction materials (Haug et al., 2022). These plastic polymers, which have long been assumed to be chemically inert, can release VOCs into their surroundings (Yu and Crump, 1998). These VOCs include aromatic BTEX compounds (benzene, toluene, ethylbenzene and xylene) (Hazrati et al., 2016) as well as other smaller hydrocarbon chained compounds such as formaldehyde and acetaldehyde (Xiong et al., 2015). The accumulation of plastic surfaces in the home increases the overall surface area (SA) of polymer materials indoors. To what extent these VOC emissions from plastic surfaces contribute to indoor air quality is not fully understood.

Material emissions can be influenced by environmental parameters within a room, such as temperature. Thermal comfort has been rated as one of the most important components of IAQ for occupant satisfaction within the indoor environment, with air temperature being the main factor (Frontczak and Wargocki, 2011; Taleghani et al., 2013). Indoor air temperature is influenced by outdoor climate, season, as well as type of building. Teare et al. (2020) conducted an investigation into the correlation between indoor and outdoor temperatures in different locations across Eastern Cape Province in South Africa. Indoor temperatures were, on average, 4 °C higher compared to outdoor temperatures all year round, especially in the warmest months when the recorded outdoor temperatures were over 35 °C. Recent trends in climate change suggest we will observe more extreme weather events in the future including heatwaves (Petrou et al., 2019), such as in the UK in July 2022 when temperatures reached 40 °C (Met Office, 2022). We are also likely to observe higher indoor temperatures in the future. Indoor overheating caused by heatwave events can cause a sharp spike in recorded heat-related deaths among vulnerable groups in the population (Petrou et al., 2019; Gasparrini et al., 2022). Thus, it is vital to consider the effects that these temperatures have on IAQ.

Characterization of emissions from materials in real rooms can be difficult. Isolation of materials in chambers is a common way of determining emission concentrations (Han et al., 2010), and amplifying these chamber conditions to room size can help give a more accurate representation of materials emissions in more realistic scenarios. Emissions from materials are usually detected using headspace techniques such as solid phase microextraction (SPME) and dynamic headspace (DHS) gas chromatography mass spectrometry (GC–MS) (Abe et al., 2013; Even et al., 2019; Singh et al., 2020), despite these being highly time-consuming and also requiring significant sample preparation. In contrast, Proton Transfer Reaction Time-of-flight Mass spectrometry (PTR-ToF-MS) presents an innovative analytical technique for the detection of VOCs. This highly sensitive, easy to use instrument provides emission data in real-time, without the need of sample preparation.

The ISO (International Organisation for Standardisation) 16,000 series provides guidelines for measuring emissions of VOCs within indoor air. The focus of the standard is on emissions from building materials, but also leaves interpretation open by including “furnishings” within its scope. However, consumer products, including household plastic consumer products, are not specified within the scope of this ISO standard (ISO, 2006). The recommendation for a chamber size of up to 1000 L, is not suitable for investigations into small household consumer products, as the emissions would be too diluted in the air space and concentrations would be too low to detect. Some studies have investigated small polymer products such as children's toys and have used large volume chambers (Even et al., 2020). These large chambers can be thought of as a proxy for a child's room, though the emissions typically lead to low concentrations within such volumes and are challenging to measure. For these reasons, others have used smaller chamber sizes where the concentrations can be easier to measure, even if the conditions are less realistic (Masuck et al., 2011). Therefore, the ISO standard guidance may not be applicable to investigations of VOC emissions from household polymers, implying that smaller environmental test chambers are better suited for investigations into VOC emissions from plastics (Even et al., 2020).

This study aims to quantify VOC emissions from different household plastics over a realistic indoor temperature range. Firstly, the polymer type of each plastic sample was confirmed using Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectroscopy, the method for which is described in Section 1 of the Supplementary Information (SI). Sub-samples of the plastics were obtained and then subjected to a range of typical indoor temperatures (18–28 °C), with their VOC emissions monitored by PTR-ToF-MS and fit using the Arrhenius equation to calculate temperature dependent emission rates. The determined VOC emissions at two temperatures, 18 and 28 °C, were then used to initialise a detailed indoor chemistry model, INCHEM-Py, for realistic indoor settings. This allowed us to determine the influence of indoor temperature on primary emissions from household plastics and, consequently, the production of potentially more harmful secondary species in a typical home.

2. Methodology

2.1. Plastic polymers

The plastics used in this study are summarised in Table 1. They were all purchased from UK retailers between 2019 and 2020. The age of each plastic from their date of manufacturing, was expected to be over one year at the time of investigation. Six shampoo bottle plastics were selected, because they occur within the top 20 leading shampoo brands used in the UK. All were made with the same polymer type but are different in colour, indicating different polymer additives. The colours included black, white, red, green, orange and blue. The other plastics were a selection of two common food storage containers (one clear and the other white), one clear drinking bottle, a stripped piece of black electrical cable that is typically used to provide power to electronic items (with the internal metal wiring removed), a black bin bag liner (or a garbage bag) and a small white tubing piece used for plumbing fixtures around a kitchen sink.

The product content, if any, was discarded and the plastics were each rinsed once with acetone for a few seconds to remove any product residue and then rinsed three times with deionised water to prevent any degradation from the acetone. All plastics were stored separately in zip-lock bags, so as not to cross-contaminate, within a cold room at 4 °C in the dark prior to any testing so as to prevent exposure to any thermal- or photo-degradation. A small plastic piece was cut from each product with an approximate length and width of 10 cm by 3 cm (with varying degrees of thickness), to allow it to fit into small environmental chambers. Exact dimensions were determined prior to sampling to enable accurate calculation of the sample surface area (SA). Exact dimensions of the whole plastic products were also measured, providing the total product SA. Plastics samples were handled whilst wearing nitrile gloves, to limit contamination with skin oils.

Table 1

The plastics used in the study, a brief description of their intended use and colour along with the sample surface area (SA) and the total product SA.

Abbreviation	Material	Intended use	Colour	SA-sample (cm^2)	SA-total product (cm^2)
PE-storage-container-white	Polyethylene (PE)	Food container	White	32.3	1458
PET-bottle	Polyethylene terephthalate (PET)	Water bottle	Clear	23.9	415
Rubber-wire	Polyester rubber	Electrical wiring cover	Black	46.6	1887
PP-storage-container-clear	Polypropylene (PP)	Food container	Clear	36.3	697
HDPE-binbag	High density polyethylene (HDPE)	Bin bag	Black	65.2	6650
PS-tubing	Polystyrene (PS)	Tubing	White	21.0	156
HDPE-black	(HDPE)	Shampoo bottle	Black	31	392
HDPE-white	(HDPE)	Shampoo bottle	White	52.8	392
HDPE-red	(HDPE)	Shampoo bottle	Red	29.8	550
HDPE-blue	(HDPE)	Shampoo bottle	Blue	29.8	550
HDPE-green	(HDPE)	Shampoo bottle	Green	29.8	550
HDPE-orange	(HDPE)	Shampoo bottle	Orange	29.8	550

2.2. Instrumentation

A PTR-ToF-MS (model: QiTOF-V104-1, Ionicon Analytik GmbH, Austria) was used to measure the VOC concentrations within the chambers. This method is based on ionising trace VOC gases in continuously sampled air in proton-transfer reactions and measuring the concentrations of product ions, using hydronium ions (H_3O^+) as a chemical reagent. This soft ionisation prevents significant fragmentation of product ions (so the mass of each resulting ion equals the VOC mass plus one) (Han et al., 2010; Taiti et al., 2017). The instrument monitors the ion count per second (cps), which is proportional to the number of ions detected, allowing the volume mixing ratios of the target compounds to be calculated, see SI Section 2. PTR-ToF-MS can only determine the nominal mass-to-charge ratio of the protonated product ions, therefore not always allowing for the identification of specific VOCs (Taiti et al., 2017). However, PTR-ToF-MS technology is ideal for fingerprinting and monitoring VOC emissions from plastic polymers as it is highly sensitive, has a fast time response and does not require any pre-sample treatment (Pagonis et al., 2019). The operating conditions of the PTR-ToF-MS instrument used in this study are shown in Table 2.

The temperature of the PTR-TOF drift tube is kept at 80 °C to keep the volatile compounds in their gaseous state, preventing them from cooling and potentially condensing onto the innermost material of the instrument. The drift tube pressure and voltages (Udrift, Us, Uso and Udx) all control the ionisation conditions within this reaction chamber. The FCinlet flow determines the flow rate of the air being sampled.

Protonated water clusters, $(H_3O^+)\cdot(H_2O)n$, can form in the PTR drift tube if the collision energies are too low. The water clusters can break up when they have higher kinetic energy, resulting from acceleration in the high electric field, E, or a free path due to reduced particle density, N, or both. This process is known as collision induced dissociation (CID). The ratio E/N is used to measure the collisional energy conditions. The E/N ratio has the SI units V m^2 but this is generally given in the unit Td, Townsend, where $1\ \text{Td} = 10^{-21}\ \text{V m}^2$. Previous work conducted by Miller (2014), found that the optimum E/N ratio Td value was around 115 Td, as it enabled a good compromise between limiting water cluster formations (occurring at lower E/N ratios) and compound fragmentation (occurring at higher E/N ratios). 120 Td was selected to provide this balance and is also reported in many other PTR-TOF studies in the literature (Kajos et al., 2015; Koss et al., 2018). The description of the calibration of the PTR-ToF instrument can be found in the SI Section 3, which helped improve the measurement accuracy of the following experiments.

Table 2

Operating conditions used for the PTR-ToF-MS.

Parameter	Condition
PTR temp	80 °C
PC	325 mbar
FCinlet flow	50 sccm
E/N ratio	120Td
Drift tube pressure	3.20 mbar
Ihc	4.3 mA
Udrift	710 V
Us	150 V
Uso	80 V
Udx	45 V

2.3. Experimental

A schematic for the experimental set up can be found in SI, Fig. S2. Four 0.1 L borosilicate glass lab flasks (the sampling chambers) (Schott-Duran, Cole-Palmer, UK) were used for measurements of VOC emissions from the plastic samples. Before initial use and experimental replicates, these flasks were rinsed three times with deionised water and then baked at 100 °C for 30 min, in order to volatilise any residues. These flasks had polyether ether ketone (PEEK) lids containing integrated 1/8" I.D. inlet and outlet ports, allowing them to be connected to a stainless steel multivalve coated with sulfinert, located within the PTR-ToF-MS instrument via PEEK tubing. PEEK tubing is chemically inert and routinely used for VOC sampling. To minimise the adsorption of VOCs, all sample lines were heated to 60 °C using heating tape and insulated with foam pipe lagging. The flasks were housed within a temperature-controlled water bath (TX150, Grant, Cambridge) and covered with an opaque Perspex lid which served to maintain water temperature, block out all light and allow the suspension of the flasks within the water bath.

A zero-air generator (ZA, FID, AIR C, Swissgas), connected via a mass flow controller (EL Flow, Bronkhurst, NL) provided VOC-free air, at a rate of 0.8 L min^{-1}, divided equally across each of the four flasks (0.2 L min^{-1}). This Zero Air Generator uses a palladium catalyst, so no water vapour was removed from the filtered air. In fact, due to the combustion of VOCs within the Zero Air Generator itself, water vapour may slightly increase as the combustion mechanism of VOCs results in the formation of H_2O and CO_2. However, both the temperature and humidity of the air exiting the chambers was monitored by an EI1050 digital temperature/humidity probe (Labjack, USA). The humidity remained consistent throughout all experiments at 50 %. The PTR-ToF-MS sampled from the exhaust of each chamber at a rate of 0.1 L min^{-1} with the excess air vented. The flow rate through each chamber was measured at the start of each experimental run using a flowmeter (4100 series, TSI, UK). One of the flasks acted as a blank, containing no plastic samples throughout all experimental runs, whilst the others allowed for three replicates of each sample material.

An automation sequence, generated using the PTR software, was programmed to sample from each chamber with a 1-minute sample resolution for a total of 90 min at each set temperature, with an average concentration (in ppbv) calculated using the last 30 min. This ensured the internal environment of the flasks reached the set temperature and the VOCs achieved a steady state concentration before measurements commenced. The raw data were acquired using TofDaq software 2016 (Tofwerk AG, Switzerland) and were post processed using Tofware (version 3.2.2.1).

The first step in the analysis was to define the average peak shape and mass resolution, before applying an internal mass scale calibration based on the NO^+ peak (m/z 29.9974) and the fragment ion of the internal diiodobenzene ($C_6H_5I^+$, m/z 203.9431) standard that is continuously bled into the sample air. Next, the average mass spectrum was used to generate a peak list, whilst filtering out peaks including water clusters, and other interfering ions (e.g., oxygen, nitrogen). The peak list was then assigned chemical formulae and possible compound IDs and nine selected VOCs of interest were located via their protonated mass (Table 3), with their emission data extracted for further analysis. In the interest of specificity, the nine select VOCs of interest were chosen to be the compounds of focus throughout this study, as they were found to meet the criteria set out below:

1. The selected compound of interest has either been associated with the cause or onset of one or more adverse human health effects, such as respiratory irritations.
2. The selected compound of interest has been previously identified as plastic emissions from studies in the literature.
3. The selected compound of interest is known to substantially contribute to its given m/z signal in PTR-TOF measurements.
4. The selected compound of interest has a mass that falls within the range of the internal mass calibration of the PTR instrument (NO + with a mass of 29.9 and C6H5I + with a mass of 203.9).
5. The selected compound of interest has a degradation scheme implemented within INCHEM-Py, so that its chemical degradation indoors can be determined.

All calculations regarding conversions to emission rates are described in Section 2 of the SI. Any VOC analytes detected in the empty background chamber were accounted for when calculating the emissions from the plastic samples, as the average background concentrations were subtracted from sample averages. Temperature response coefficients, generated using the Arrhenius equation, for calculating the predicted emission rates at the selected model temperatures, including the slope, intercept, R^2 value and calculated activation energies, are displayed in Table S4 in the SI. Naphthalene could not be implemented into the model as it does not have a degradation scheme for this particular compound.

2.4. Model description

To model VOC degradation pathways, the INdoor CHEMical model in Python (INCHEM-Py v.1.1.1) was used (Shaw and Carslaw, 2021). This open-source 0D box-model has been constructed using the Master Chemical Mechanism (MCM v3.3.3), a comprehensive mechanism that treats explicitly the atmospheric degradation of VOC species (Jenkin et al., 1997, 2003; Saunders et al., 2003). The MCM has no grouping of chemical reactions or lumping of species, and contains around 15,400 reactions and 4700 species (Shaw and Carslaw, 2021). Each VOC undergoes oxidation by hydroxyl (OH) radicals, nitrate radicals (NO_3), and ozone (O_3) as well as photolytic degradation where relevant. These initial reactions form a range of radical species, such as peroxy and oxy radicals, and more stable intermediates, such as aldehydes and ketones (Carslaw and Shaw, 2019). As well as the chemical mechanism, the model contains elements to describe exchange with outdoors, deposition onto surfaces, wavelength-dependent photolysis through indoor lighting and attenuated sunlight, internal emissions, and gas-to-particle partitioning.

Table 3
Selected protonated VOCs along with their measured m/z, putative compound ID and their associated INCHEM-Py model name which can be found on the MCM website: http://mcm.york.ac.uk/roots.htt.

Protonated chemical formula	m/z measured	Compound ID	Model abbreviation
$(CH_2O)H^+$	31.018	Formaldehyde	HCHO
$(C_3H_6)H^+$	43.054	Propene	C3H6
$(C_2H_4O)H^+$	45.033	Acetaldehyde	CH3CHO
$(C_3H_4O)H^+$	57.033	Acrolein	ACR
$(C_6H_6)H^+$	79.054	Benzene	BENZENE
$(C_7H_8)H^+$	93.07	Toluene	TOLUENE
$(C_6H_6O)H^+$	95.049	Phenol	PHENOL
$(C_8H_8)H^+$	105.07	Styrene	STYRENE
$(C_{10}H_8)H^+$	129.07	Naphthalene	n/a

For this study, INCHEM-Py was initialised to represent a room with a volume of 20 m^3, with a low but realistic air exchange rate with outdoor air of 0.2/h, to minimise the influence of VOCs infiltrating from outdoors. It was assumed that there were no indoor lights, but attenuated outdoor light, with outdoor photolysis values obtained from Wang et al. (2022). We also assumed a constant relative humidity of 50 %. The model simulations were run for two days to ensure steady-state conditions and results are reported for day 2. The plastics investigated within this study act as the only indoor emission sources of the selected VOCs. Although there are clearly other sources, this paper focuses on the impact of the emissions from the plastics. The VOC emissions rates of the twelve individual plastic types, at the highest and lowest experimental temperatures (18 ˚C and 28 ˚C), were introduced into the modelled room, and scaled up to a surface area of 8.6 m^2 (explained further in Section 3.3). All other model assumptions are listed in the SI in Table S5. Particle formation was not considered in these simulations. A total of 26 model variations were simulated with the twelve plastics modelled at the highest and lowest experimental temperatures. Additionally, two background simulations, containing no plastic emissions, were also run to provide comparative baseline concentrations. Secondary pollutant concentrations were averaged between 08:00 and 18:00 h for all simulations and the relative percentage difference to background compared. The difference, either positive or negative, of pollutants caused by the introduction of the individual plastic-specific emissions provides an insight into which plastic types have the largest influence on indoor air chemistry.

3. Results and discussion

3.1. Material characterization

Average reflectance spectra were acquired for each of the plastic polymer materials investigated and were matched to similar spectra contained in a built-in library within the Agilent software. Only those with a Hit Quality (HQ) of 0.8 or higher were considered a good enough fit for identification of the polymer. Things that can potentially contribute to a lower HQ score include intentionally and non-intentionally added additives within the polymer structure. Such additives result in slight spectral differences in the sample spectra compared with the library spectra. However, good quality spectra were obtained, with a few cases where a slight band shift was observed (±10 counts) in comparison with literature values (Saviello et al., 2016). Among the twelve samples, eight were identified as high-density polyethylene (HDPE), one as polystyrene (PS) with acrylonitrile copolymer, one as polypropylene (PP), one as polyethylene terephthalate (PET) and one as polyester rubber, which was consistent with the original product labelling. The highest match fit to a library spectrum was the absorbance spectra for the polyester rubber wire, with a quality match fit of 0.92. Only the base polymer of the plastics was identified using this method, the polymer additives contained within the material were unfortunately not. A summary table (S2) containing the spectral matches for the other plastic polymers, with the average HQ values, can be found in the SI.

3.2. Plastic VOC emissions

During the experiments, the same plastic piece sample was used for the three replicate temperature runs, for consistency. Fig. S3 in the SI shows the spread of all VOC emission rates calculated from the polyester rubber wire plastic for three replicate experiments. Fig. S3 demonstrates that for the same plastic piece sample used, the VOC emissions rise with increasing temperature during each subsequent repetition, indicating that the material was not depleted throughout its multiple use. This was the same for all plastic samples used in this study.

Emission signatures were obtained at each set temperature (18, 21, 24, 28 ˚C) for the 12 plastic products tested. The PTR-ToF-MS dataset of the sampling time (minutes), normalised ion counts (ncps) which is then converted to concentration (ppb), and the ion masses (m/z). Over 400 different species of VOCs were detected as emissions from the plastic materials. For

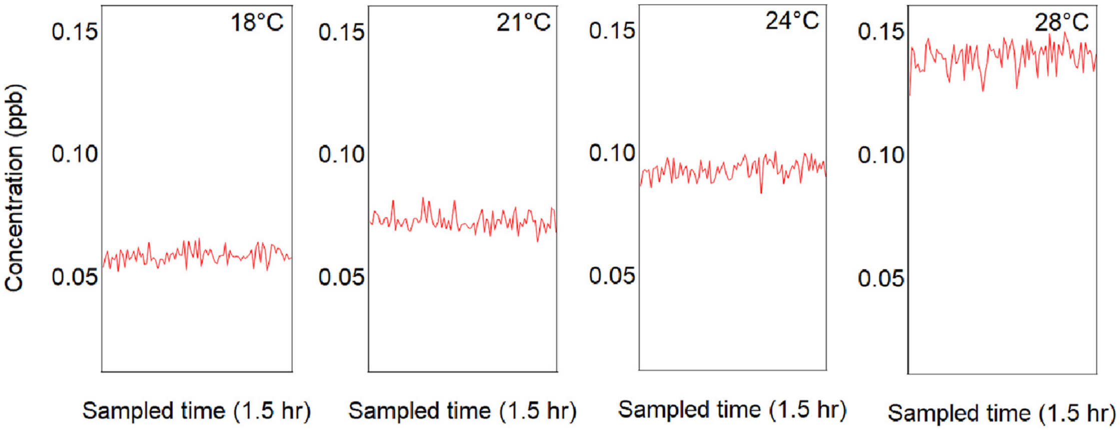


Fig. 1. Concentrations of protonated benzene ($C_6H_6H^+$) at each set temperature for the HDPE-white plastic sample.

the sake of completeness, the top 60 compounds detected for each plastic type are listed in the SI, Table S3. The nine selected VOCs of interest, which are the focus for this study, accounted for 7–8 % of the Total VOC emissions from all plastic types. As an illustration, Fig. 1 shows the average concentrations of $(C_6H_6)H^+$ (protonated benzene) emitted from the HDPE-white plastic sample, at each of the set temperatures, for one of the replicate experiments. There is an increase in the concentration of the detected ion with temperature, from 0.06 ppb at 18 °C to 0.13 ppb at 28 °C, more than a 2-fold increase. Fig. 1 also demonstrates how the VOC concentrations do not deplete during the time of the sampling experiments.

Fig. 2a shows the VOC emission rates in ng cm^{-2}/h from each plastic sample at 21 °C, whilst Fig. 2b shows the calculated total product surface area VOC emission rates per hour at the same temperature. The calculated emission rates per cm^2 have been scaled up to the total SA of the plastic product, found in Table 1.

The PS-tubing plastic proved to be the highest overall emitter of the selected VOCs when compared to the same area of the other plastic types, with $(C_8H_8)H^+$ (styrene) accounting for 60 % of the selected VOC emissions. However, when taking into account the total SA of the plastic products, the rubber-wire polymer has the highest emissions of VOCs, as shown in Fig. 2b. It has the highest emissions of $(C_6H_6O)H^+$ (phenol), $(C_2H_4O)H^+$ (acetaldehyde) and $(CH_2O)H^+$ (formaldehyde). HDPE-binbag releases the highest amount of $(C_3H_6)H^+$ (propene) and naphthalene. The clear PP-storage-container is the third highest emitter of propene, which makes up nearly 81 % of its total emissions. The PET water bottle plastic shows the overall lowest VOC emissions and did not emit any phenol or styrene.

For emissions from the total surface area of the products (Fig. 2b), it might be expected that emissions would be highest from the HDPE-binbag plastic, given it has the largest surface area (6650 cm^2). However,

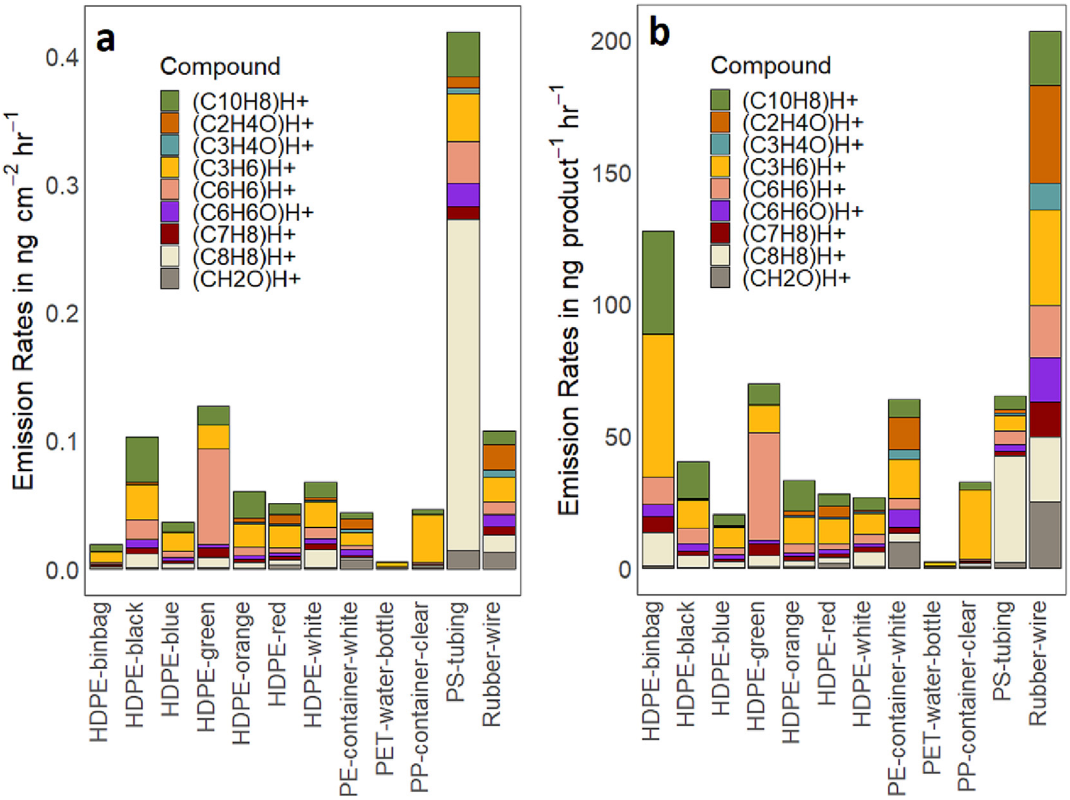


Fig. 2. Collective emission rates of all nine VOCs per (a) cm^2 and (b) total product SA.

the HDPE-green plastic, with a SA of 550 cm^2, emits a larger amount of benzene overall than the HDPE-binbag, despite having a much smaller SA. A similar comparison can be made when comparing the PET water bottle plastic (414.29 cm^2) to the PS-tubing plastic (115.5 cm^2) and the white PE-storage-container plastic (392.25 cm^2). Despite the PET plastic having a larger surface area compared to the PS-tubing and the white PE-storage-container, higher concentrations of nearly all selected VOCs were found to be emitted from the PS-tubing and the white PE-storage-container.

When observing the VOC emissions from the two storage containers, slightly higher overall emissions can be found from the clear PP-storage-container than the white PE-storage-container per cm^2, but when considering the larger SA of the white PE-storage-container (over double the size), higher VOC emissions are found from this plastic product in a typical home. Consumers should be wary of the VOC emissions from storage containers, especially when they are involved in storing foods, as many studies have found evidence of volatile compounds migrating from plastic materials upon contact with food substances (Alamri et al., 2021), in particular when they are microwaved (Nerín et al., 2002).

The emission rates determined in this study are found to be lower than many other polymer materials examined throughout the literature. This may be due to the age of the plastic in the current study being older, >1 year than most of the previous studies. Emissions of VOCs from plastic polymers can change during their lifetime, due to how they are used and what they may be exposed to. Many studies have shown that emissions from polymers are highest, following initial production, and decrease rapidly with time (Lin et al., 2009; Even et al., 2019) to reach a constant emission rate. Even et al. (2020) observed a quick decrease of aromatic VOC emissions through chamber measurements kept at a constant temperature, including o-xylene, phenol and cyclohexanone, in the first few hours or days after unpacking toy samples made from PVC and PE. Phenol emissions from one of the PVC toys dropped from 594 ng/h to 48.5 ng/h per sample piece in 5 days and then slowly decreased further, below the detection limits, after 10 days. Noguchi and Yamasaki (2020) investigated VOC emissions from polymer sheets under thermal degradation over different time lengths. They found that after 1 day of storing samples at 25, 50 and 75 °C, VOC emissions increased relative to the start of the experiment, but that emissions decreased despite being stored at these three temperatures after 30 days.

3.2.1. Temperature-dependency

The temperature dependency of the emission rates (k), in most cases, can be described using the Arrhenius equation, shown in Eq. (1).

$$k = Ae^{\frac{-Ea}{RT}} \tag{1}$$

In Eq. (1), A is the pre-exponential constant (independent of the temperature), E_a is the activation energy for emission, R is the universal gas constant, and T is the absolute temperature. The natural log (Ln) of emission rates for the nine selected VOCs for the Rubber wire polymer are plotted against the reciprocal temperature in Fig. 3. The Arrhenius plots for the other plastic types can be found in SI, Figs. S4–S14. Where a linear relationship was found the components of the Arrhenius equation could be derived. The gradient, intercept and R^2 value are displayed in Table S4, along with the derived activation energies.

Where there was a non-linear fit the VOC emission rate cannot be fully temperature dependent and the Arrhenius equation does not apply. This was found for VOC emissions from the PET water bottle plastic. This particular plastic was clear in colour indicating it contained fewer colouring additives, therefore its emissions were considerably lower when compared to the other plastic types investigated.

The increase in emission rates with temperature has been observed by many researchers (Xiong et al., 2013) for other materials commonly found indoors. Myers (1985) reported that the emission rate of formaldehyde from particleboard increased by a factor of 5.2 between 23 and 40 °C. Lin et al. (2009) showed that the initial emission rates and concentrations of toluene and xylene from flooring materials increased between factors of 7.2–17.8 and 1.3–4.0 respectively, when temperatures increased from 15 to 30 °C. Crawford and Lungu (2011) found that styrene emissions from vinyl composite materials used as building materials increased from 0.127 mg m^{-3} to 0.166 mg m^{-3} from temperatures of 23 to 40 °C within the sampling chambers, an increase of 1.3 times. In the current study, all calculated VOC emission rates increased by at least a factor between 1.1 and 2 between 18 and 28 °C. In some instances, for example acrolein emissions from the HDPE-green and blue plastic sample, emission rates increased by factors of 8.8 and 13.1 respectively, potentially owing to the additives within the polymer structure.

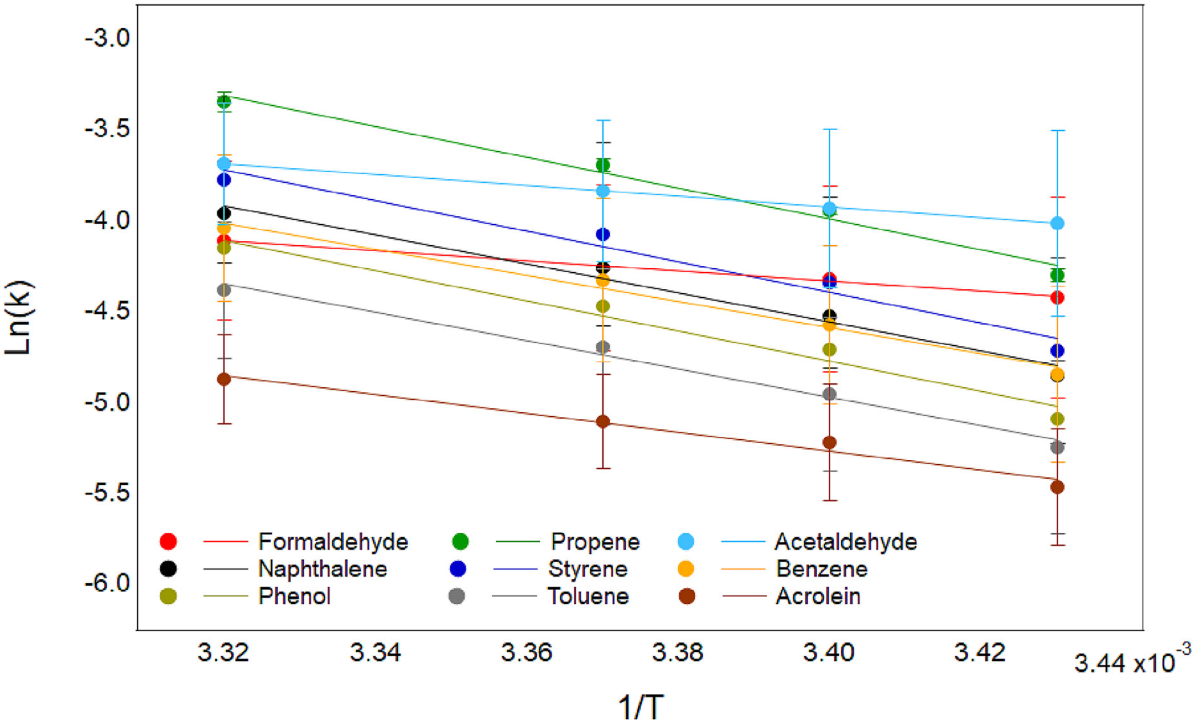


Fig. 3. Arrhenius plots for the emission rates of nine VOCs from the rubber wire plastic.

3.3. Modelling

VOC emission rates, obtained from the experiments, were input into INCHEM-Py, see Section 2 of SI. Initial concentrations of VOCs within the INCHEM-Py simulations were set to zero to match observed gradients from the experiment. A low, but realistic, air change rate with outdoor air was set to 0.2 per hour, with outdoor concentrations of the selected VOCs also set to zero. This was to ensure that the only VOC emissions into the indoor environment were from the plastics.

The World Health Organisation (WHO) determines a safe indoor air temperature to be in the range of 18–24 °C. However, maximum acceptable indoor temperatures vary across the globe, from 25 °C in the UK and the US to 32 °C for countries such as Thailand (Teare et al., 2020). The temperatures used for the modelled scenarios, 18 and 28 °C, were chosen as they cover a range of climates.

A study conducted by Manuja et al. (2019), characterised the surfaces within numerous locations and measured the total areas of different surface types, to a resolution of ~1 cm. From ten bedrooms, nine kitchens and three bathrooms, the average surface area of plastic found in these rooms came to 8.6 m^2. The highest surface area of plastic was found to be 43 m^2 in one of the office locations, accounting for almost 30 % of all surfaces measured in the room. The average value of 8.6 m^2 was selected as the total surface area of each individual plastic for the modelled simulations for this study. It is recognised by the authors that in more realistic scenarios, one would experience the collective VOC emissions from a variety of plastic types. However, the aim of this study is to determine the influence of the individual plastic VOC emission effects on the indoor air chemistry, hence why they have been used to initiate the model simulations individually.

Fig. 4 shows how the concentrations of radical species fluctuate throughout a 24-hour period, with and without the presence of a plastic surface, e.g. PS-tubing plastic. Throughout the simulated day, the diurnal variation of attenuated sunlight impacts the OH and HO_2 radical production. In the presence of PS-tubing plastic, there are lower concentrations of OH, yet higher concentrations of HO_2 compared to the case with no plastic. These differences are greater when the temperature is increased from 18 to 28 °C.

Fig. 5 shows the percentage difference in concentrations for the modelled species with and without plastic present and for all plastic types investigated. The percentage differences highlighted in green (blue) show an increase (decrease) in concentration in the presence of plastic compared to the absence of that same plastic at the same temperature. As observed in Fig. 4, as the temperature increases from 18 to 28 °C, there is a greater percentage difference, be it either positive or negative. The introduction of plastics into the modelled simulations provides more VOCs for the OH radicals to react with, in turn, lowering the OH concentrations (Figs. 4 and 5). The effect is greater for those plastics with a higher overall VOC rate, such as the PS-tubing.

Concentrations of indoor O_3 are primarily driven by exchange with outdoor ozone, which itself is controlled by outdoor nitrogen oxide concentrations. Because of the low air exchange rate of 0.2 air changes per hour, the indoor O_3 concentrations only vary slightly with temperature and plastic emissions. The concentrations of NO and HONO decrease in the presence of plastics. HONO is formed through the reaction between OH and NO in our simulations. Given that OH and NO both decrease with the addition of plastics, so does HONO. As plastics are introduced into the system and VOC concentrations increase, there are more peroxy radicals formed (see Figs. 4 and 5). These effectively titrate NO from the system, decreasing its concentration as plastics are added.

In the majority of the model simulations displayed in Fig. 5, the plastic content affects the concentrations of secondary species, such as O_3, NO_2, HONO and GLYOX by <1 %. HCHO is both emitted from the plastics and also created through secondary chemistry, which is why there is a larger deviation from the background compared to the other secondary species.

In more realistic settings, a large contribution to indoor air VOC concentrations is outdoor sources of air pollution, which infiltrate through air exchange (Carslaw and Shaw, 2019), i.e., through windows and doors. Outdoor concentrations of aromatic compounds, such as benzene, toluene, phenol and styrene, can typically be a few ppb. Depending on the outdoor concentrations of these species, ventilation may provide larger contributions to the indoor concentrations of the VOCs than emissions from plastics. Indoor activities such as cooking and cleaning will also have a larger impact than emissions from the plastics. Therefore, the impact of VOC emissions from plastics will depend on the specific conditions and activities within the building.

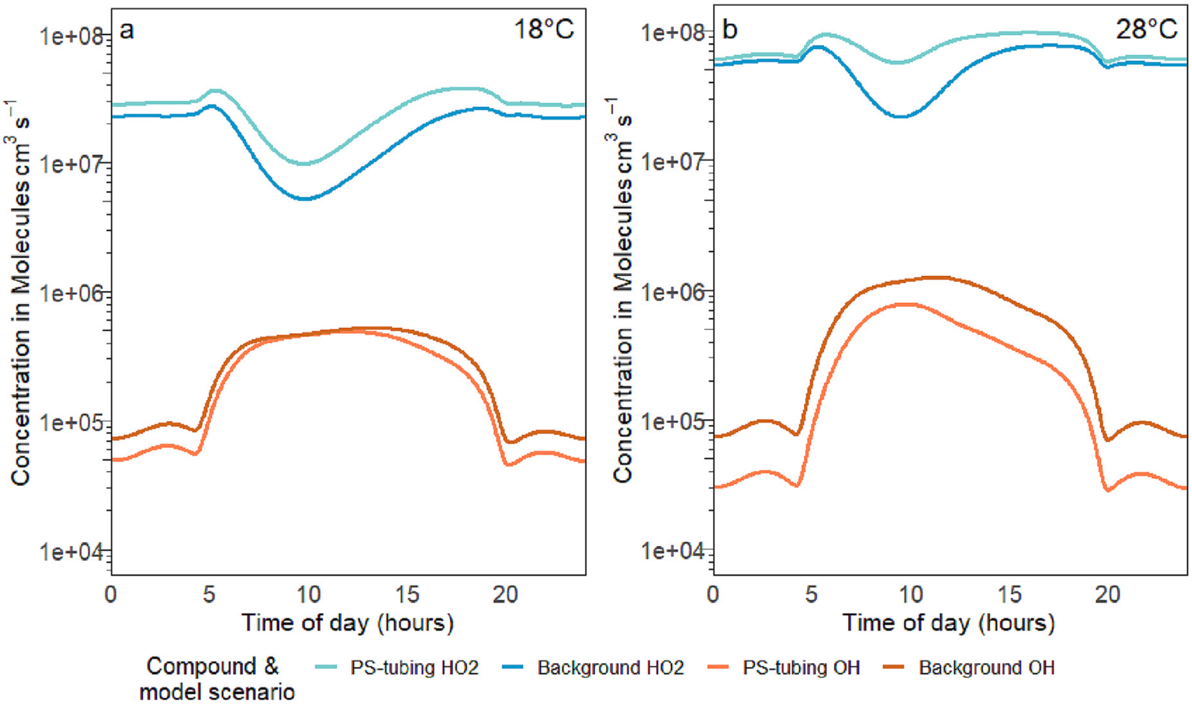
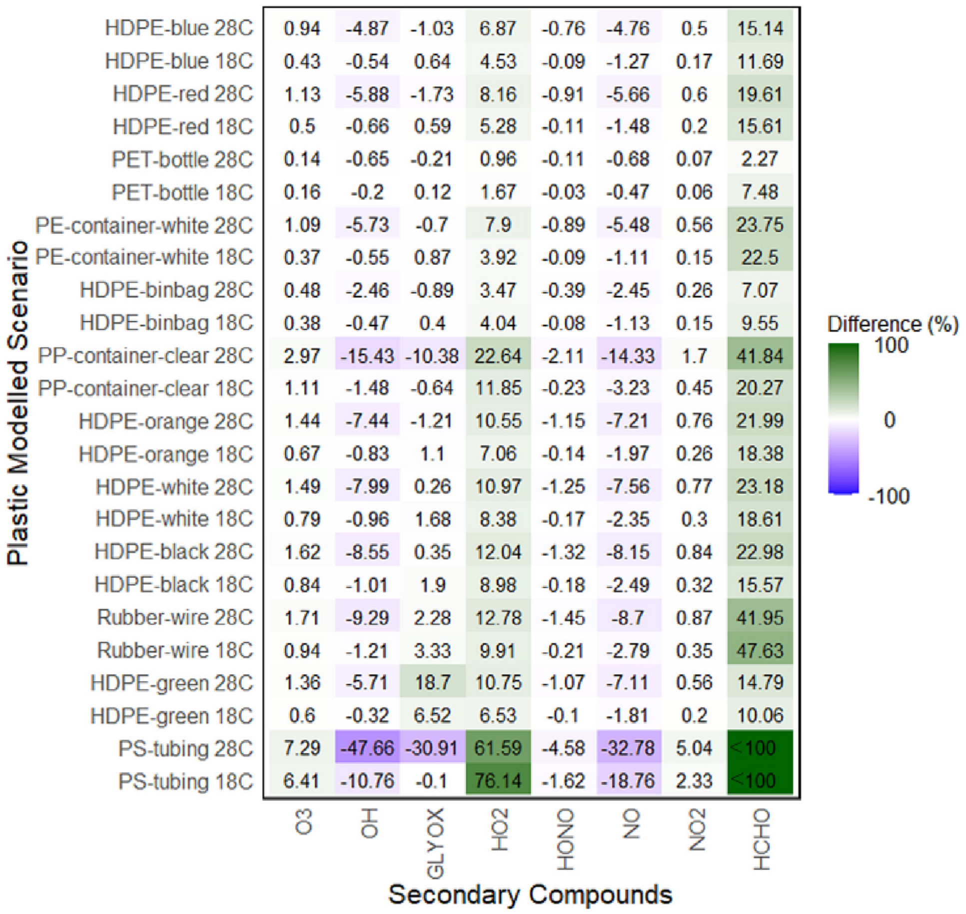


Fig. 4. Time series of radical species concentrations in the background modelled scenarios (no plastic content) compared to PS-tubing plastic modelled scenarios at both 18 °C (a) and 28 °C (b), including OH and HO_2 radicals.



	O3	OH	GLYOX	HO2	HONO	NO	NO2	HCHO
HDPE-blue 28C	0.94	-4.87	-1.03	6.87	-0.76	-4.76	0.5	15.14
HDPE-blue 18C	0.43	-0.54	0.64	4.53	-0.09	-1.27	0.17	11.69
HDPE-red 28C	1.13	-5.88	-1.73	8.16	-0.91	-5.66	0.6	19.61
HDPE-red 18C	0.5	-0.66	0.59	5.28	-0.11	-1.48	0.2	15.61
PET-bottle 28C	0.14	-0.65	-0.21	0.96	-0.11	-0.68	0.07	2.27
PET-bottle 18C	0.16	-0.2	0.12	1.67	-0.03	-0.47	0.06	7.48
PE-container-white 28C	1.09	-5.73	-0.7	7.9	-0.89	-5.48	0.56	23.75
PE-container-white 18C	0.37	-0.55	0.87	3.92	-0.09	-1.11	0.15	22.5
HDPE-binbag 28C	0.48	-2.46	-0.89	3.47	-0.39	-2.45	0.26	7.07
HDPE-binbag 18C	0.38	-0.47	0.4	4.04	-0.08	-1.13	0.15	9.55
PP-container-clear 28C	2.97	-15.43	-10.38	22.64	-2.11	-14.33	1.7	41.84
PP-container-clear 18C	1.11	-1.48	-0.64	11.85	-0.23	-3.23	0.45	20.27
HDPE-orange 28C	1.44	-7.44	-1.21	10.55	-1.15	-7.21	0.76	21.99
HDPE-orange 18C	0.67	-0.83	1.1	7.06	-0.14	-1.97	0.26	18.38
HDPE-white 28C	1.49	-7.99	0.26	10.97	-1.25	-7.56	0.77	23.18
HDPE-white 18C	0.79	-0.96	1.68	8.38	-0.17	-2.35	0.3	18.61
HDPE-black 28C	1.62	-8.55	0.35	12.04	-1.32	-8.15	0.84	22.98
HDPE-black 18C	0.84	-1.01	1.9	8.98	-0.18	-2.49	0.32	15.57
Rubber-wire 28C	1.71	-9.29	2.28	12.78	-1.45	-8.7	0.87	41.95
Rubber-wire 18C	0.94	-1.21	3.33	9.91	-0.21	-2.79	0.35	47.63
HDPE-green 28C	1.36	-5.71	18.7	10.75	-1.07	-7.11	0.56	14.79
HDPE-green 18C	0.6	-0.32	6.52	6.53	-0.1	-1.81	0.2	10.06
PS-tubing 28C	7.29	-47.66	-30.91	61.59	-4.58	-32.78	5.04	<100
PS-tubing 18C	6.41	-10.76	-0.1	76.14	-1.62	-18.76	2.33	<100

Fig. 5. Summary of percentage differences of secondary pollutant species within each plastic-specific modelled scenario from their respective temperature background simulations.

Note that the rubber wire product is associated with electronic items, which can become warm during use, causing elevated air temperatures in their immediate vicinity, which in turn can lead to increased VOC emissions. Additionally, the white PE container product and the clear PP container product are both examples of food storage containers that can be used when heating foods in the microwave. This is another example of where elevated temperatures surrounding the plastic products would cause VOC emissions to be increased (Nerín et al., 2002). The same could also be the case for any of the plastic products left on a windowsill in direct sunlight (perhaps in a bathroom), where elevated temperatures could increase VOC emissions, potentially causing hotspots of VOC concentrations.

This work has shown experimentally that VOC emissions from plastics increase with temperature, owing to the migration of chemical compounds from the bulk polymer to the surface which then diffuse into the surrounding air. This in turn impacts the secondary pollutant concentrations present in indoor air as shown through our model simulations. When comparing these experimental and modelled concentrations of VOCs to values outlined in the UK Public Health England (PHE) guidelines for indoor air quality (Public Health England, 2019), the determined concentrations did not surpass the limit values for acetaldehyde, benzene, formaldehyde, styrene and toluene. However, the guidelines are limited by the number of VOCs listed and also acknowledge the lack of consideration of the combined effect of the presence of VOCs in indoor air. As demonstrated in this work, products emit mixtures of substances, some of which currently have unknown health effects. Moreover, it should be acknowledged that consumer products only represent an additional source to other material emissions and human activities that contribute to poor IAQ.

3.4. Limitations

From the emission rates obtained in this study, it is challenging to identify the origin of the compounds being emitted, without knowing the composition and quantities of the additives within the plastic polymer itself. This information, as well as the manufacturing process for these selected plastic types, is not available, an issue for many other studies (e.g. Wiesinger et al., 2021). The variability in VOC emission rates observed in this study could therefore be due to the additives present in the plastic polymer matrix, non-intentionally added substances (ending up in the polymer mixture during the manufacturing process) or simply variability with the batch production of the individual items.

The authors recognise that the nine VOCs of interest only make up a small percentage of the overall total of compounds emitted from the plastic types, and that ~90 % of emitents are not accounted for in the model simulations. It may be possible that compounds in the remaining 90 % have an influence on the atmospheric chemistry indoors. However, their chemical degradation cannot be determined within the INCHEM-Py model, as they do not have a degradation scheme associated with them. This makes it challenging to account for the entirety of VOC emissions from plastics. A sensitivity test was carried out to attempt to account for the 90 % of VOCs that we were unable to input into the model. Alkene and aromatic species were determined as the highest contributors to the total VOCs emitted that were unaccounted for in the model, at 25 % and 30 % of the total respectively. We therefore used propene as a proxy for this additional alkene emission, and the 4 aromatic species in the model (benzene, toluene, phenol and styrene) as a proxy for the additional aromatic species. Increasing the VOC emission rates had a larger impact on the secondary chemistry as would be expected, with the major impacts on the hydroxyl radical concentration (71 % decrease compared to the case with no plastic emissions), and formaldehyde (188 % increase compared to the case with no plastic emissions). Clearly, a deeper understanding of both the identification of chemical species emitted and their subsequent degradation pathways is needed (see the additional list of compounds detected in Table S3).

The authors also recognise that the scaling of VOC emission rates into modelled rooms has its limits. The aim of the model runs was to simulate the conditions of a typical room, rather than reproduce conditions in the chamber. The results from the chamber experiments were used to calculate emission rates per cm^2 of plastic, correcting for the chamber conditions. Also, as previously mentioned, in more realistic scenarios, one would experience the cumulative effects of a variety of plastic VOC emissions indoors, however this study focuses on the individual plastic VOC effects on the indoor chemistry.

4. Conclusion

This work demonstrates a method for determining emission rates of VOCs from plastic products using a proton transfer time-of-flight mass spectrometer (PTR-ToF-MS) and flow through chambers (glass flasks). The individual emission signatures from the twelve selected plastic types showed a wide degree of variation, owing to differences in polymer type and the presence of additives in the polymer structures. Almost all selected VOC emission rates in this study increased with temperature, with the aromatic compounds (e.g., benzene and styrene) showing the strongest response. Differences in emission rates were observed between the plastic types, even between those with the same base polymer.

The modelled scenarios, using INCHEM-Py, provided an insight into the detailed indoor air chemistry as a result of introducing a variety of plastics into a room. The production of secondary pollutants such as NO_2, HO_2, O_3, HCHO and to some degree glyoxal, increased with temperature at varying rates across the different model simulations. However, for OH, NO and HONO, the opposite was found, as these species are removed from the system through oxidation reactions. Future research will focus on investigating other abiotic factors influencing VOC emissions from common household plastics, such as exposure to sunlight and indoor lighting, as well as how the age of the plastic influences VOC emissions.

CRediT authorship contribution statement

G. Beel, B. Langford: devised experimental methodology. G. Beel: collection of experimental data. G. Beel, B. Langford, N. Cowan: data analysis and visualisation. N. Carslaw, D. Shaw, modelling assistance. G. Beel: modelling of experimental data. B. Langford, N. Cowan, N. Carslaw: Supervision. G. Beel, writing of original manuscript. G. Beel, B. Langford, N. Cowan, N. Carslaw, D. Shaw: writing, reviewing and editing of revised manuscripts.

Data availability

Data will be made available on request.

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 material to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.163497.

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