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Analysis of toxic effluents released from PVC carpet under different fire conditions

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Highlights

- PVC carpet releases CO, HCl, PAHs, and PCDD/F on burning.
- The greatest acute hazard comes from CO and HCl in under-ventilated fire conditions.
- The greatest chronic hazard arises from PCDFs and PAHs in under-ventilated conditions.
- The distribution between gas and particle phase shows most PAHs are in gas phase.
- The peak particles size ranges (<1 μm) are those causing greatest respirable hazards.

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Abstract

A large number of investigations have been reported on minimising the PAH and PCDD/F yields during controlled combustion, such as incineration. This study is an attempt to quantify acute and chronic toxicants including PAH and PCDD/F in conditions relating to unwanted fires.

This paper investigates distribution patterns of fire effluents between gas and aerosol phase, and the different particle size-ranges produced under different fire conditions. PVC carpet was selected as the fuel as a precursor for both PAH and PCDD/F. In order to generate fire effluents under controlled fire conditions, the steady-state tube furnace, was chosen as the physical fire model. Fire scenarios included oxidative pyrolysis, well-ventilated and under-ventilated fires. Fire effluent measurements included: carbon monoxide, carbon dioxide, hydrogen chloride, polycyclic aromatic hydrocarbons, chlorinated dibenzo-p-dioxins and furans and soot. The distribution patterns between gas and particle phase, and the size-ranges of the particles produced in these fires together with their chemical composition is also reported.

Significant quantities of respirable submicron particles were detected, together with a range of PAHs. Lower levels of halogenated dioxins were detected in the fire residue compared with those found in other studies. Nevertheless, the findings do have implications for the health and safety of fire and rescue personnel, fire investigators, and other individuals exposed to the residue from unwanted fires.

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1. Introduction

In fires, deaths may be caused directly by asphyxiant gases (carbon monoxide, hydrogen cyanide), or indirectly by irritant gases which impair vision and breathing and prevent escape (hydrogen chloride, organo-irritants, etc.), or by aerosols which not only impair escape ability by visible obscuration, but also pose a respiratory hazard.

HCl presents two significant hazards in fires, by causing incapacitation through sensory irritancy (leading to painful breathing, swelling of the airways, and ultimately death), and by inhibiting the conversion of CO to CO₂. HCl toxicity has been the subject of much debate with some toxicologists arguing that 100 ppm is intolerable while the other studies have shown that baboons could have survive much higher concentration at least long enough to escape (Hull et al., 2008).

At sufficiently high concentrations, or when attached to submicron particles such as soot, irritants can also penetrate deeper into the lungs (Pope et al., 1992). It has been shown that the smallest particles (<0.5 μm) are particularly dangerous, causing pulmonary irritation also known as Severe Acute Respiratory Syndrome (SARS) leading to post-exposure respiratory distress and death due to pulmonary oedema, generally occurring from a few hours to several
days after exposure (Stec and Hull, 2010). In addition the particulates can act as vehicles for transport of noxious molecules deep into the lungs. There are few fire studies investigating irritants, and organo-irritants which have sub-lethal health effects. Little has been done to investigate fire generated particles, their morphology, size distribution and chemical composition as the particle size distribution is dependent not only on the material, but also on the temperature and fire conditions (such as residence time in the flame).

Polycyclic aromatic hydrocarbons (PAHs), associated with respirable particles, can be also transported into the lungs where there are opportunities for effective absorption into the body. The phase distribution of individual PAHs is important as they have different transport and rates of chemical reactions between the gas and particle phases. The low molecular weight PAHs indicate a different transport and rates of chemical reactions between the gas and respirable particles, can be also transported into the lungs where nature and fire conditions (such as residence time in the flame).

An excess of oxygen is used. When the combustion is less efficient, toxicant yields, the ratio of PCDD/F formation in the gas phase depends strongly on a number of variables, such as the combustion conditions (variations in temperature, ventilation, residence time in flame, and oxygen environments), as well as varying concentrations of precursors and chlorine in the product gases (Ruokojärvi et al., 2000). In terms of PCDDs and PCDFs relevance to health, numerous studies using animals have confirmed that some dioxin isomers are carcinogenic and produce mutagenic effects in certain species (Van den Berg et al., 2006).

This paper present results from samples of polyvinyl chloride (PVC) based carpet. A full description of the project can be found elsewhere (Blomqvist et al., 2010). The major fire species found and investigated, under different fire conditions, were carbon monoxide (CO), carbon dioxide (CO2), hydrogen chloride (HCl), PAHs, and PCDDs/PCDFs from residue samples. The distribution patterns between gas and particle phase, and different size-ranges of particles produced in fires, together with their chemical composition, were also examined.

2. Experimental methodology

A PVC carpet, containing polyurethane components as a lacquer, commonly found in domestic buildings, was selected and used for this study. The PVC carpet had a thickness of 2.0 mm and density of 1360 kg m⁻³, and was specified as 53% polyvinyl chloride, 18% diisononyl phthalate, 24% mineral fillers, and 2% titanium dioxide, by the manufacturers. Elemental composition was determined as 38.6% carbon, 4.96% hydrogen, and 29.1% chlorine.

2.1. Fire effluents generation and fire conditions

The experimental work was conducted using the steady-state tube furnace (ISO TS 19700), the bench-scale test method, Fig. A.1, because of its proven ability to replicate different fire conditions (Stec et al., 2008a,b). A known amount of fuel is gradually fed into the furnace over about 20 min together with a specified flow of air at a present temperature. The fire effluents from the furnace are diluted in a mixing chamber prior to sampling.

The chemistry of a fire is controlled by the nature and amount of fuel, oxygen availability, and the temperature. Combustion is usually efficient and replicates a well-ventilated fire scenario if an excess of oxygen is used. When the combustion is less efficient, and there is less than the stoichiometric requirement of oxygen the conditions become under-ventilated. To achieve different fire stages, a loading of 25 mg mm⁻¹ combustible material in the sample boat, and different air flows were used. Primary air flow rates: 2 L min⁻¹ for oxidative pyrolysis (350 °C furnace temp), 10 L min⁻¹ for well-ventilated flaming (650 °C furnace temp), and 2.1 L min⁻¹ for under-ventilated flaming (825 °C furnace temp) were selected.

2.2. Fire gases and soot determination and their analytical measurements

2.2.1. Fire gases measurements

Smoke gases were continuously drawn from the mixing chamber to the gas-cell of the BOMEM MB 100 FTIR spectrometer. The spectrometer was equipped with a heated up to 150 °C gas cell (volume of 0.92 L, and 4.8 m path-length) and a DTGS detector. Sampling rate of 4 L min⁻¹, a spectral resolution of 4 cm⁻¹, and 4 averaged spectra recorded per minute were selected. Quantitative analysis was undertaken for a number of gas species, comprising CO, CO₂, HCl, etc.

2.2.2. Characterisation of soot and particles

A conventional filter method was used for determination of the total amount of the soot and particles, determined gravimetrically using a sampling flow of 1 L min⁻¹ during a steady state period of the steady state tube furnace test. Additionally, a multistage cascade impactor, Marple Series 290 Personal Cascade Impactor with 8 stages was used for particle size distribution, where particles were separated according to their decreasing aerodynamic size from d₅₀% = 21.3 μm (according the manufacturer’s calibration). The cascade impactor was chosen as the only device providing a mass based particle size distribution, which can be directly linked to toxicological outcomes. Particles were sampled at a flow rate of 2.1 L min⁻¹ for a period of 4 min for PVC carpet sample. The cascade impactor tests were carried out in triplicate.

2.2.3. Chlorine content

Elemental analysis of the soot from the filters from the gravimetric and the cascade impactor tests was carried out by a Portable X-ray Fluorescence Spectrometer (XRF). The spectrometer was a Bruker Tracer III-SD handheld XRF equipped with an Rh target X-ray tube and a 10 mm² X-flash detector. For both analysis of the residues and chlorine calibration, a tube voltage of 40 kV and a current of 3.3 μA, together with a data collection time of 200 s were used. The matrix used was cornflour so an inert organic starch would not interfere with the elements of interest. As it is a handheld energy dispersive device there were no monochromator crystals, and all experiments were run in air using the same voltage, current and filter settings.

2.2.4. PAH analysis

Analysis of the gas and particle phase of PAHs was carried out by using filter/adsorbent method. For PAHs analysis, smoke gases were sampled using a commercial PAH-sampler on which associated particles (condensed) and gaseous phase PAHs were separated. The effluent was sampled with a flow rate of 1 L min⁻¹ during a sampling period of 3 min. The samples were subsequently extracted with toluene and analysed separately, based on the 16 EPA priority pollutant PAH-compounds, using GC–MS. Quantification was made using Selected Ion Monitoring mode. Analysis details and GC–MS setting parameters are summarised below (Blomqvist et al., 2010).

- GC column: BPX5 non-polar capillary column from SGE, 25 m, 0.22 mm ID, 0.25 μm film thickness, the carrier gas helium at a rate of 1 mL min⁻¹
- Injection volume: 2 μL.
- Inlet temperature: 300 °C.
- MS transfer line: 280 °C.
- Temperature programme: 100 °C for 2 min, 8 °C min⁻¹ to 210 °C, and then 2 °C min⁻¹ to 280 °C, 280 °C for 3 min.

### 2.2.5. PCDD/F analysis

PCDD/F analysis is based on extensive extraction, sample clean-up, concentration steps and analysis by gas chromatography/mass spectrometry, as described in EPA method 1613. Homogenised residue samples were weighed (approximately 1 g), and internal standards for the quantification of PCDD and PCDF were added. Extraction with 200 mL toluene was carried out for 12 h and the solvent concentrated by a rotary evaporator, which was then extracted with sulphuric acid. Sample extracts were processed through a set of columns consisting of a carbon, multi-layer silica gel and alumina. Purified extracts were then concentrated to approximately 20 μL by micro extraction, prior to injection and analysis by gas chromatography/high resolution mass spectrometry (GC–MS/MS) (Chen et al., 2011). GC–MS/MS setting parameters are summarised below:

- GC column: VF-5MS capillary column with helium as the carrier gas at a rate of 1 mL min⁻¹.
- Injection volume: 1 μL.
- Inlet temperature: 280 °C.
- MS transfer line: 270 °C.
- Temperature programme: 160 °C for 1 min, then 27.5 °C min⁻¹ to 225 °C, 225 °C for 8 min, 5 °C min⁻¹ to 310 °C, 310 °C for 6 min.
- Saturn 2000 (Varian) ion trap mass spectrometer was used. The ion trap and manifold temperature were kept at 200 °C and 80 °C, respectively.

### 3. Results

All results are presented as the average of two or three independent tests. For oxidative pyrolysis, PVC carpet had mass loss of 45.9% and well-ventilated had mass loss of 76.9%, while under-ventilated had mass loss of 66.4%. Combustion in the well-ventilated tests is complete, as PVC carpet contain about 24 wt.% inorganic residue. In the pyrolysis tests about 30%, and in under-ventilated tests about 10% of combustible material remained.

The major combustion products CO, CO₂, and HCl are presented in Fig. 1A. The CO₂/CO ratio in the under-ventilated tests shows a lower ratio, compared to well-ventilated tests, and thus less complete combustion. This was supported by the unquantified observation of the presence of methane and other hydrocarbons in the FTIR spectra. From the elemental analysis, the maximum possible yield for HCl is 0.3 g g⁻¹ and for CO₂ is 1.42 g g⁻¹. This means that the recovery of chlorine as HCl was around 95% in these tests. The high yield (i.e. greater than theoretically possible) of HCl in the pyrolysis experiments can be explained by the fact that chlorine is degraded and emitted as HCl at a lower temperature compared to the thermal degradation of the hydrocarbon backbone of the PVC material (Stec and Hull, 2010). In the oxidative pyrolysis tests, where material is degraded without flames, lower yields for all fire gases are found.

Total soot, based on the gravimetric analysis, is shown in Fig. 1B. The absolute total production of particles, on a mass basis, was about the same for the oxidative pyrolysis and well-ventilated fire scenario and around 10 times lower for the large under-ventilated scenario.

#### 3.1. Soot size distribution

Fig. 2A shows the average of particle size distributions, taken from three tests for each fire scenarios, expressed as relative mass for each size fraction. Results are presented in terms of the aerodynamic diameter using a log scale on the X-axis.

For tests under oxidative pyrolysis, the greatest amount of soot is produced within the size range 0.52–0.93 μm and there is no trend of increasing amounts of particles for the smallest particle sizes seen for all other fire scenarios. For well-ventilated tests, the distribution shows a peak at 3.50 μm diameter (representing particles of aerodynamic diameter between 3.5 and 6.0 μm) and lower peaks at diameters of 0.52 μm and 14.80 μm. For the under-ventilated fire conditions, the main peak in the size distribution curve is centred at a diameter of 0.93 μm. An increase of mass of the particles smaller than 0.52 μm is seen for flaming combustion.

#### 3.2. Distribution of chlorine

Additional to soot size distribution, cascade impactor plates were analysed for chlorine content (Fig. 2B). For all three combustion conditions studied, the maximum chlorine content is found in the soot from the impactor plate that captured the highest amounts of particles. There is no significant difference between the well-ventilated and the under-ventilated tests. The chlorine content found in the pyrolysis test is, however, generally somewhat lower.

Fig. 3 presents a comparison of the chlorine content found on the soot samples from the cascade impactor plates (filters 1–8) and from the filter (based on gravimetric measurements). Differences, especially for oxidative pyrolysis, could be explained by limitations in the analysis methods where XRF results are influenced by the thickness of the soot layer or by a variation of the chlorine concentration across the filter surface and the choice of specific measurement point. However, the XRF was calibrated and triplicate analysis was made at different locations of the filter for each sample analysed.
Fig. 4 shows how the chlorine content in the residues varies with position along the boat for all reaction conditions. This equates to the time the sample was exposed to radiant heat in the furnace. Thus at 10 cm sample length, for the under-ventilated fire scenario, had been subjected to $825^\circ C$ for at least 10 min, while the 65 cm sample length would probably not have reached $650^\circ C$. Chlorine measurements were taken every 10 cm and compared for different fire scenarios. Results show that for oxidative pyrolysis there is found much higher chlorine content ($\approx 18–20$ wt.%) than in flaming conditions ($\approx 10$ wt.%).

3.3. Polychlorinated dibenzo-p-dioxins and dibenzofurans

PCDD/F analysis was carried out only for the residue of the samples remaining after the experiments. No analysis of PCDD/F content of soot samples was carried out. Fig. 5 compares concentrations of all toxic congeners, expressed per g of ash (residue remaining after the test). These are averages based on three repeated experiments for each set of conditions as described in Table A.1.

PCDD/F toxicity can be expressed by a single number as the International Toxic Equivalent (I-TEQ). It is based on a Toxic Equivalent Factor (TEF) method which indicates the degree of the less toxic dioxins and furans as fractions of the toxicity of the most toxic 2,3,7,8-TCDD which is given as a reference value of 1 (Van den Berg et al., 2006). I-TEQ concentrations of PCDD/F in PVC carpet residue correspond to 21 ± 5, 18 ± 6 and 174 ± 192 pg I-TEQ/g of burned material for oxidative pyrolysis, well-ventilated and under-ventilated conditions, respectively. The errors denote one standard deviation. There are noticeable variations among repeated experiments, especially for under-ventilated conditions (respectively, 95, 394 and 35 ng I-TEQ/g burned material). This variation may be explained by different heating histories experienced by segments of the sample. Only about half of each sample reached the target temperature, with the temperature experienced by the end of the sample being approximately 200–300 °C lower. Random segments of the residue were used for the analysis.

There are similar concentration of PCDD/F congeners observed for oxidative pyrolysis and well-ventilated fire scenarios. It seems that the PCDD/F toxicity of PVC residues do not depend strongly on fire condition, provided that temperature does not exceed $650^\circ C$. For the under-ventilated high-temperature fire scenario, PCDD/F concentrations are significantly higher, especially for toxic
congeners of PCDF. As the temperature increased, PCDFs start to dominate over PCDD. As the temperature in the quartz tube is changed from 350 to 650 and 825 °C, the average ratio of PCDF/PCDD (based on mono- to octa-chlorinated homologous groups) increased from 1.5, to 9.9 and 184 respectively.

PCDD are less stable at higher temperatures than PCDF which may explain the decreasing amount of PCDD shown in Fig. 5 (Fiedler, 1998). PCDD also tend to convert to PCDF under reducing conditions (Altarawneh et al., 2007). The results indicate that 1,2,3,4,6,7,8-HpCDD dominates the toxic fingerprint for the oxidative pyrolysis experiments, whereas 1,2,3,4,6,7,8-HpCDF for high-temperature under-ventilated combustion. The pattern of toxic PCDD/F at 825 °C is reminiscent of fingerprints observed for the gaseous emissions from combustion of PVC (Font et al., 2010).

3.4. Polycyclic aromatic hydrocarbons

PAHs yields, based on a mass-loss basis, in the gaseous phase and also adsorbed onto particles were investigated. For all fire scenarios, the volatile part (gaseous phase) has higher yields than the associated particle part (condensed phase). The highest yields of total PAHs are produced for under-ventilated conditions and are two orders of magnitude higher (1.781 g g⁻¹ for the condensed and 7.858 g g⁻¹ for the gaseous phase) than those from the well-ventilated tests (0.025 g g⁻¹ for the condensed and 0.097 g g⁻¹ for the gaseous phase) (Blomqvist et al., 2010). For the oxidative pyrolysis tests the PAHs yields are 0.007 g g⁻¹ for the condensed phase and 0.164 g g⁻¹ for the gaseous phase.

A general trend of PAHs presence in the gas and condensed phase for different fire scenarios is presented in Fig. 6. The data is taken as the average of two rather consistent and repeatable tests. The yields for individual PAHs have been normalised to the cancer and mutagen potency equivalent factor of benzo(a)pyrene which has a reference value of TEF = 1 (Van den Berg et al.). Data is presented as carcinogenic equivalents BaP-TEQ.

For oxidative pyrolysis, it is observed that there is much higher release of PAHs with a higher molecular weight (up to four rings) in the gaseous phase than in the condensed. There is no decreasing or increasing trend observed, and only volatile or semi-volatile PAHs are produced. Similar trends for flaming tests are observed. Both well-ventilated and under-ventilated combustion produces the complete range of PAHs. For the gas phase, individual PAH yields decrease with an increase of molecular weight for both well-ventilated and under-ventilated fire scenarios. For under-ventilated tests there are much higher PAHs yields (50 times higher) in the gas phase, than for well-ventilated tests. Additionally, there are PAHs with three and four rings observed for the under-ventilated scenario, whereas PAHs with mainly up to three rings are observed for the well-ventilated scenario. For the particle phase, similar to the gas phase, there are much higher quantities for large
under-ventilated than for well-ventilated fires, and PAHs with up to four or more aromatic rings are found.

4. Discussion and conclusions

Carbon monoxide and hydrogen chloride are the principle acute toxicants from burning PVC carpet.

It was found that most of the HCl present in the carpet was released into the gas phase. Analysis of combustion gases from PVC carpet showed that the yield of gas phase HCl is high for all types of combustion. The HCl yields found from well-ventilated and under-ventilated combustion were close to the theoretical maximum mass-loss yield. This supports an earlier study which showed that the HCl yields from PVC materials are independent of fire stages and temperature (Hull et al., 2008). In addition, it can be concluded that in the presence of HCl, CO yields are largely independent of ventilation conditions as well as at temperatures 650 °C and 825 °C (Stec et al., 2008a,b). CO may result from gas phase inhibition of flaming combustion or it is also possible that CO originated directly from the char by surface oxidation.

Surprisingly, most of the HCl was in the gas phase not associated with the soot. During the well-ventilated tests, the gas phase HCl concentration was about 4000 ppm in the gas phase what corresponds to 5.7 mg L⁻¹ HCl in gas phase, compared to approximately 1.5 mg L⁻¹ in airborne soot.

Although most chlorine appeared as HCl, other chlorine containing gas or vapour species will be produced while some chlorine may remain in the char. A number of chlorine containing species have been identified from large-scale fires burning a high proportion of PVC, including mono- and dichlorobenzenes and other chloro-aromatic and chloro-aliphatic hydrocarbons (Paul, 1989). It has been reported that, depending on the fire condition, as much as 20% of the chlorine may exist in an organic form (Lebek et al., 2005). The HCl concentration found in the well-ventilated tests corresponds to a mass-loss yield of HCl of about 0.3 g g⁻¹. Comparing the total soot yield found in these tests, about 0.05 g m⁻³, with the amount of HCl “remaining” for possible association with the soot gives similar quantities of each.

The chlorine content found on the soot and cascade impactor plates was between 0.5 and 2.5 wt.%. Similar to HCl and CO yields, there was no significant difference between the well-ventilated and the under-ventilated tests. The chlorine content found in the pyrolysis test is, however, generally somewhat lower. In addition, chlorine was also found in sample residues. As expected, for non-flaming fire conditions, a much higher chlorine content around 18–20 wt.% is found than for flaming conditions 10% wt.%.

In well-ventilated and under-ventilated tests on PVC carpet both large and small particles are generated (in the order of 1–4 μm) whereas in oxidative pyrolysis only a narrow distribution of large particle sizes were found. Compared to the well-ventilated tests, higher quantities of particles with smaller aerodynamic diameter were found for the under-ventilated fire scenario. However, the difference in combustion efficiency is not that significant between the two flaming combustion conditions, as the chlorine in PVC disrupts the combustion reactions in the gas phase and significantly reduces the combustion efficiency.

An increasing amount of particles smaller than 0.52 μm were observed for flaming conditions. From the literature, these results are supported, and mass median aerodynamic diameters in the range of 0.4–3 μm, have been found from fires with PVC (Butler and Mulholland, 2004). Some other studies, for example for cone calorimeter which replicates well-ventilated fire conditions, showed a mass-peak at a particle size around 0.35 μm (Hertzberg et al., 2003). As small particles have a higher proportion of surface area per mass than larger particles, gas phase toxicants are likely to show preferential absorption on the smaller particles.

Regarding the occurrence of individual PAHs, a general trend towards decreasing yields with increasing molecular mass was seen for all combustion conditions studied. It is interesting to note that both well-ventilated and under-ventilated combustion of the PVC carpet produced the complete range of PAHs. In the pyrolysis tests, however, only volatile and semi-volatile PAHs were produced. Presumably the greater heat of flaming combustion was required to make the larger PAHs airborne.

When the toxicity of the individual species is taken into account, the relative importance of volatile and associated particle PAHs changed. For both well-ventilated and under-ventilated conditions, the toxicity weighted yields for the associated particle PAHs increased and generally dominated over the volatile species. The toxicity weighted yields for the under-ventilated tests were orders of magnitude higher than to the yields from the well-ventilated tests, whereas for oxidative pyrolysis conditions it is observed that the volatile part dominated the toxicity.

Total amounts of PCDD/F in the residue from PVC carpet ranges from 11 to 394 pg I-TEQ/g of burned material, corresponding to 41–1170 pg I-TEQ/g residue. These measurements can be compared to the results summarised by Carroll (1996) for PVC fires from a number of literature sources, which indicate variation of between 5 and 28300 pg I-TEQ/g residue, variation of nearly four orders of magnitude. Our measurements seem to cover the lower range of the literature values. A more detailed analysis of the literature values reveals that four data sets cover a range of 5–521, and three 3600–28300 pg I-TEQ/g residue. The latter come from measurements on ash from three large-scale PVC fires, two in Germany (Lingen and Lengerich) and one in Canada (Boisbriand, Quebec). It is possible that the ashes from these three fires were contaminated with soot prior to sampling, resulting in significantly higher values of PCDD/F than reported in the present contribution. The PCDD/F load in soot from PVC fires ranges between 35000 and 539000 pg I-TEQ/g soot (Carroll, 1996). Thus a small amount of soot deposited on the ash could elevate PCDD/F concentrations in the residue from high pg level to low ng level, leading to a large variation in literature values.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2012.07.037.

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