Thermal Degradation and Combustion of Plant Protection Products

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ABSTRACT

In a fire, the plant protection products can produce large amounts of toxic effluents in the smoke. Since most fire deaths and injuries result from inhalation of toxic effluents, knowledge of the amount and type of generated substances is important for fire hazard assessment and investigation. In this study, thermal degradation and combustion of three plant protection products, which are based on: quinoclamine (Product 1); spiroxamine, tebuconazole and triadimenol (Product 2); and tebuconazole (Product 3) were investigated. Cone calorimeter (ISO 5660) was used to measure ignitability and heat release rate. Thermal decomposition of the materials was studied using thermal analysis coupled with the Fourier transform infrared spectroscopy. The steady-state tube furnace (ISO 19700) was used to generate gaseous combustion products. The emitted thermal degradation products were identified by gas chromatography with mass spectrometry.

Among all tested compounds, Product 2 was found to be the most flammable plant protection product. The mechanism of thermal degradation depends on the product type. In fire effluents, different kinds of chemicals were identified, including volatile and semi-volatile compounds including substituted benzenes, aldehydes, aliphatic hydrocarbons and polycyclic hydrocarbons. Most of detected substances are carcinogenic and mutagenic with biological accumulation.

KEYWORDS: Pesticide, cone calorimeter, fire toxicity, gas analysis.

INTRODUCTION

Thermal decomposition and combustion of pesticide as well as plant protection products can occur in different situations. Large amounts of these hazardous substances are handled and stored every day in chemical plants and warehouses as a consequence of their massive use in the agricultural field [1, 2]. It has been reported in the past that fire occurred in a certain number of both of these installations involving large quantities of chemicals [3]. Toxicity, thermal instability and reactivity of pesticides caused several accidents also during the production and transport of these chemicals [4-6]. Another possibility of release the toxic species is the incorrect method of disposal of agricultural waste, for example burning of empty pesticide containers in open fires [7]. Additionally even during the processing of vegetables and foods poisoned by traces of pesticides the thermal degradation products of pesticides can be released [2, 8-10].

Most fire deaths are due to toxic gases, oxygen deprivation and other effects that have been widely referred to as smoke inhalation instead of burns [11]. That's why the smoke toxicity is very important factor and has been considered in the evaluation of fire safety in new fire safety regulation. Moreover the products released during thermal degradation and combustion of pesticide and plant protection products can cause serious airborne pollution, harmful not only to firefighters but also to people living in the surrounding areas [12]. Furthermore, water used by fire fighting,

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mixed with these toxic products can contaminate the surface and ground water and cause major environmental pollution affecting the ecosystems [13].

To enable a realistic assessment of the toxicity and environmental impact of compounds, it is clearly important to understand the range and concentrations of chemical species likely to be produced in fires. Currently, the main species of interest for acute effects from exposure to fire effluents are: carbon dioxide (CO_2), carbon monoxide (CO), reduced oxygen (O_2), hydrogen chloride (HCl), hydrogen bromide (HBr), hydrogen cyanide (HCN), hydrogen fluoride (HF), nitrogen oxide (NO), nitrogen dioxide (NO_2), sulphur dioxide (SO_2), formaldehyde (HCHO) and acrolein (C_3H_4O). However this list is not exhaustive. Fire effluents also contain a number of carcinogenic and other chronic toxicants (persistent organic pollutants and polycyclic aromatic hydrocarbons) [14].

While burning behavior is dependent on physical aspects of fire scenario, such as shape and orientation of the fuel, effluent toxicity is most dependent on material composition temperature and oxygen concentration. The generalised development of the fire has been recognised, and used to classify fire growth into stages, from smoudering combustion and early well-ventilated flaming, through to fully-developed under-ventilated flaming [15].

This work presents information on the thermal degradation and combustion processes occurring upon heating of the three plant protection products under air atmosphere. Experimental work consists of thermogravimetric (TG) experiments coupled with differential scanning calorimetry (DSC). Application of the simultaneous thermal analysis (STA) coupled on-line with Fourier transform infrared spectrometry (FT-IR) allows to analyze the released gaseous products. Moreover the steady state tube furnace (Purser furnace, ISO 19700 [16]) has been used specifically to generate toxic products from real fires under different temperature conditions. The emitted species have been identified using gas chromatography with mass spectrometry (GC-MS). To achieve this goal the solid phase microextraction (SPME) was used as a technique which combines sampling and concentrating analyses as well as introducing them to the chromatographic system [17]. Moreover evaluation of flammability of the composites was performed by using the cone colorimeter [18].

MATERIALS AND METHODS

Materials

For the studies, plant protection products commonly used in Poland have been selected. The compositions of materials are shown in Table 1.

Table 1. Information on ingredients of plant protection products

Name	Active Ingredients	Composition
Product 1	Quinoclamine 25-30 %	Quartz (SiO2) 25-30 % Kaolin 10-20 %, Silica amorphous 1-2 %
Product 2	Spiroxamine 250 g/L Tebuconazole 167 g/L Triadimenol 43 g/L	N,N-Dimethyl decanamide >20 % Alkylarylpolyglycol ether >1 and < 25 % gamma-Butyrolactone >1 and< 15 %
Product 3	Tebuconazole 430 g/L	1-octyl-2-pyrrolidone 20-60 % Hydrocarbons, C10-C13, aromatics, <1% naphthalene 5-15 %

Methods

To characterize the fire behaviour, the plant protection products were investigated in the cone calorimeter (Fire Testing Technology Ltd., FTT, West Sussex), which simulated forced-flaming combustion according to ISO 5660 [18]. The specimens, 100 mm x 100 mm in size and placed in an aluminium tray, were tested at a heat flux of 35 kW/m^2. Based on gained results following parameters were estimated: Heat Release Rate – HRR (kW/m^2), peak of Heat Release Rate – pHRR (kW/m^2) time to peak of Heat Release Rate – t-pHRR (s), Maximum Average Rate of Heat Emission – MARHE, Total Heat Release – THR (MJ/m^2), Ignition Time – t_{ig} (s), Total Smoke Release – TSR (m^2), Fire Growth Rate – FIGRA ($kW/(m^2 \cdot s)$).

The Fire Growth Rate (FIGRA) is a very useful parameter that allows to evaluate reaction of tested material to the fire properties. FIGRA is defined as the p-HRR, divided by time during which the maximum value was reached according to the equation:

$$\mathrm{FIGRA} = \frac{\mathrm{pHRR}}{\mathrm{t{-}pHRR}} .$$

The thermal decomposition under air were monitored via thermogravimetric analysis and differential scanning calorimetry using a simultaneous thermal analysis (STA 449F3 Jupiter, Netzsch, Germany). The mass of the investigated materials was 10 mg. The heating rate was 10 K/min. Gas analysis was conducted by coupling the STA with a Fourier transform infrared spectroscope (FTIR Tensor 27, Bruker, Germany) via a heated transfer tube. The transfer line tube and the gas cell of FTIR were heated to 250 °C.

Because the different fire conditions can have a significant effect on the effluent produced, the Purser furnace was used to generate gaseous products from real fires. The samples of plant protection products (15 g) in special test specimen boats were delivered into the steady state tube furnace set at 350, 650 or 825 °C. The samples of effluent were taken from the mixing chamber of tube furnace by introducing the SPME device with the fiber to sampling port. The chromatographic separation was achieved with an HP-5 MS fused silica capillary column (30 m × 250 μm × 0.25 μm film thickness) from Agilent Technologies (USA). The oven temperature was initially maintained at 40 °C for 10 min, and then increased to 250 °C at a heating rate of 10 °C/min. Helium at a constant flow rate of 1 ml/min was used as the carrier gas and the split ratio was 10:1. The separated compounds were then analyzed by the mass spectrometer, which was operated in electron ionization (EI) mode at the ionization energy of 70 eV. The mass spectra were obtained from m/z 15 to 350. Chromatographic peaks were identified through comparing the mass ions of each peak with NIST MS Library. On the basis of the NIST library, the highest possibility of product identification was chosen. The chromatographic peak area of a specific compound is correlated linearly with its quantity, and its concentration can be reflected by the peak area ratio. The summed identified peak areas were normalized to 100% and the relative abundance of specific compound can be reflected by its peak area ratio.

RESULTS AND DISSCUSION

Average values of parameters characterizing the behavior of tested plant protection products under the influence of intense radiant heat gained during cone calorimeter measurements were summarized in Table 2.

Based on the date acquired from the flammability test in cone calorimeter it can be deduced that Product 2 was the most flammable plant protection product among all tested compounds. High amount of flammable solvents (~60 % wt.) such as N,N-dimethyldecanamide, gamma-butyrolactone and alkyl/aryl-glycol ethers is responsible for shot t_{ig} and in combination with active agents creates a mixture which exceeds 1000 kW/m^2 during CC test. Such high value of HRR is relatively rare even for highly flammable plastics like polyethylene or epoxy resin with similar size and mass of a sample.

Table 2. Average heat release rate (HRR) and other fire parameters results from cone calorimeter tests for tested plant protection products

Sample	*It*	F_{out}	MARHE	HRR	pHRR	t-pHRR	FIGRA	THR	TSR
	s	s	kW/m^2	kW/m^2	kW/m^2	s	kW/(m^2·s)	MJ/m^2	m^2/m^2
Product 1	43	247	56.5	44.5	126	77	1.65	8.9	312
Product 2	12	163	574	447	1019	68	14.9	66.3	769
Product 3	128	220	98.8	232	493	177	2.79	19.8	658

Presence of spiroxamine with the flashpoint ~140 °C [19], and load of 25 % wt. has also a large impact on flaming process and on the FIGRA value which is almost ten times higher than that reported for Product 1. Based on the composition of Product 1 it is reasonable to assume that all heat emitted during CC test comes from quinclamine, although some parameters like t_{ig}, FIGRA and even HRR are decreased by the overwhelming amount of non-organic compounds (over 70 %) and it's thermal capacity. On the other hand quinoclamine contains chlorine and amine groups. During fire generated ammonium acts as the oxygen diluting agent, and chlorine participates in free radical recombination process in gas phase according to presented mechanism:

- release of chlorine radicals (Cl•):

$R - Cl \rightarrow R\bullet + Cl\bullet$

- generation of hydrogen chloride (HCl):

$RH + Cl\bullet \rightarrow HCl + R\bullet$

- neutralization of energy-reach radicals:

$HCl + H\bullet \rightarrow H_2 + Cl\bullet$,

$HCl + OH\bullet \rightarrow H_2O + Cl\bullet$.

Those properties combined with a high amount of non-flammable compounds are reflected in very low HRR value, although for a mixture containing only 25 % of organic compound Product 1 shows rather high amount of released smoke, Fig. 1.

Product 3 shows the longest t_{ig} from all tested plant protection products and rather low value of HRR. Flashpoint of tebuconazole exceeds 240 °C and has great impact on flammability of tested product. Maximum value of HRR is below 500 kW/m^{2,} THR is three times lower than for Product 2 and it's important to notice that both of this pesticides burn out completely, under testing conditions, leaving no residue.

Analysis of TSR values shows that Product 2 and Product 3 produce similar amount of smoke during CC test. Lower CO production rate for Product 3 corresponds with the HRR values, yet production of CO for Product 3 clearly exceeds Product 2. Lower flame temperature and higher concentration of chloride can, possibly, be explained by these results, although it correlates with production of CO and CO_2 by Product 1.

The thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTG) of thermal degradation of the plant protection products are shown in Fig. 2.

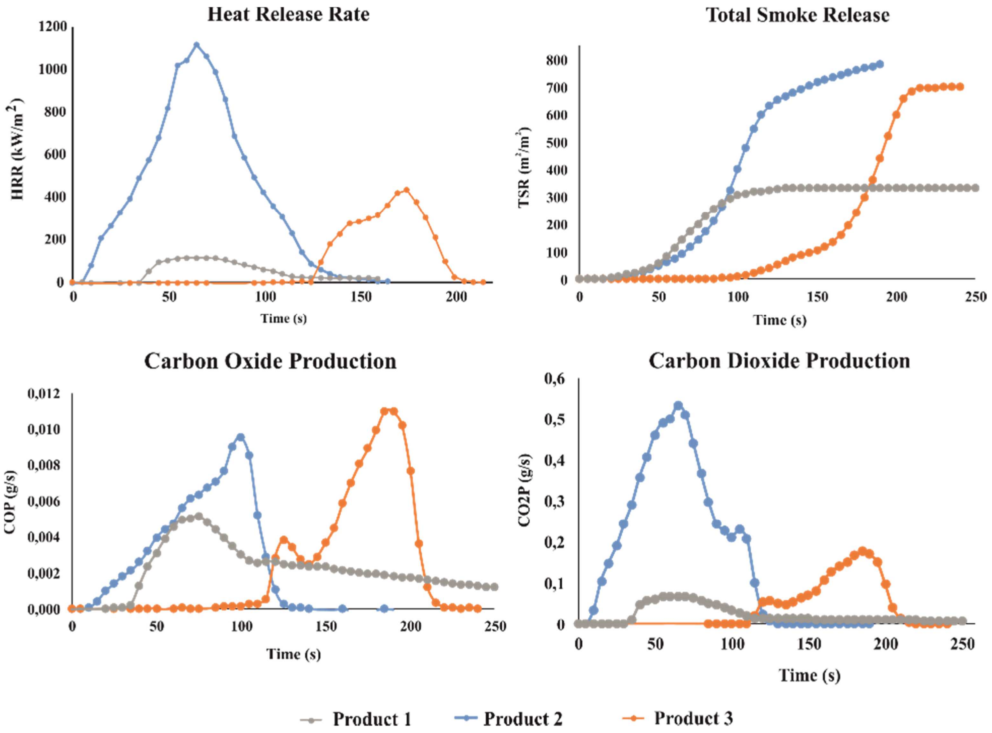

Fig. 1. Graphic representation of HRR, TSR, CO and CO_2 production for tested plant protection products.

The multi-stage degradation process was observed for all tested material. It suggests that the samples exposed to heat in air undergo both thermal degradation and oxidation. The Product 2 and Product 3 began to degrade in lower temperature then Product 1. The mass loss was about ~ 34 % for Product 1, ~47 % for Product 3 and ~ 100 % for Product 2. In case of Product 2 in the first degradation stage to the temperature about 171 °C, the substances present in the plant protection product, such as: spiroxamine, N,N-dimethyl decanamide, triadimenol and tebuconazole, were melted and evaporated. Subsequently, the individual substances were decomposed in several steps, up to the temperature of 590 °C, to form gaseous products. All tested substances were degraded to 600 °C.

Figure 2 presents also IR spectra corresponding to decomposition of the materials. The main product found during thermal degradation of Product 2 was gamma-butyrolactone. This is confirmed by the bands occurring at 1822, 1146, and 1048 cm^{-1}. The same component was also identified in the emitted products during the entire measurement. The IR spectra imply that carbon oxides also present in the volatiles evolved in thermal degradation of Product 2. The main degradation products of Product 3 and Product 1 were carbon oxides (bands at 2360 cm^{-1} associated with asymmetric tensile vibrations of the R branch). Additionally, peaks recorded at temperature 510 °C, may suggest that aliphatic compounds were also present in the gas mixture.

Based on the results obtained using Purser furnace and GC-MS, it was found that the quantity and type of products detected in the fire effluents emitted during thermal degradation and combustion of selected materials strongly depends on experiment conditions (temperature) and composition of the material, Fig. 3. The largest number of species were detected in the samples emitted in conditions representative post-flashover fire (temperature = 825 °C, primary air flow = 2 L/min) for Product 1 and in conditions representative small flaming vitiated fire (temperature = 650 °C, primary air flow = 2 L/min) for Product 2 and Product 3. Unfortunately not all detected compounds have been identified.

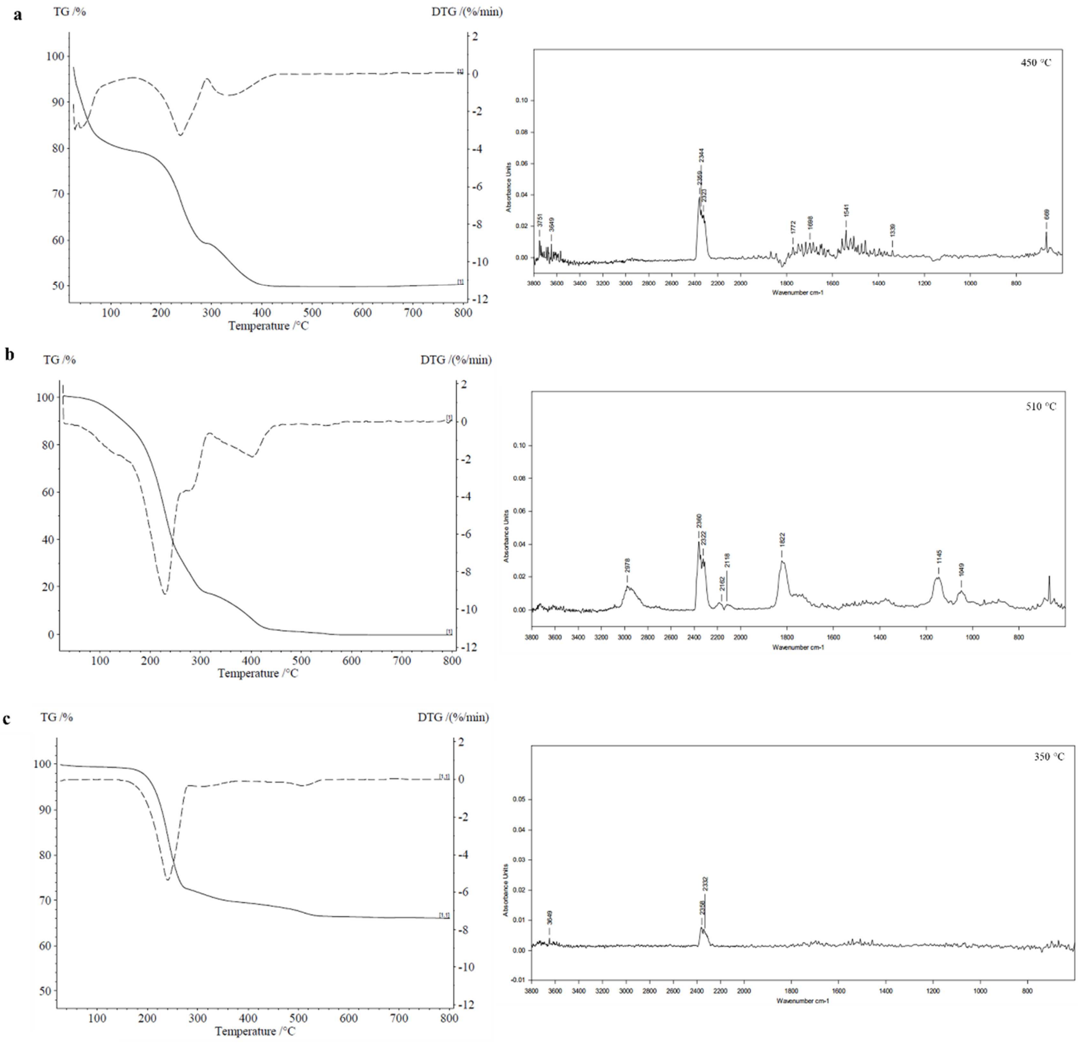

Fig. 2. TG-FTIR results: TG and DTG with corresponding IR spectra for the decomposition steps of (a) Product 3, (b) Product 2 and (c) Product 1.

When Product 1 was tested, the largest number of gaseous products was emitted when the thermal degradation occurred at 825 °C, under-ventilated flaming post flashover. In the emitted gases in the largest amount, substances such as: phthalic anhydride, 4,9-dihydro-1H-naphtho[2,3-d]triazole-4,9-dione, 6-chloro-2,3dihydrofuro-(2,3-b)-quonoline, 1H-inden-1,3(2H)-dione, benzonitrile and m-chloroamine were presented.

In contrast, in the mixture of fumes and gases emitted during decomposition of the Product 2 at 350 °C were present ingredients such as butyrolactone, N,N-dimethyldecanamide and spiroxamine.

The presence of 4-(1,1-dimethylethyl)cyclohexanone means that some of the spiroxamine has already decomposed under the test conditions. However, the main substances present in the gases samples were: 4-chlorobenzaldehyde, 1-chloro-4-ethenylbenzene, naphthalene, 1-chloronaphthalene, acenaphthylene and 2-chlorohydrocinnonitrile. When the degradation took place in 650 °C, many polycyclic aromatic hydrocarbons (naphthalene, biphenyl, acenaphthylene) and chlorine derivatives of aromatic compounds (1-chloronaphthalene, 1-(chloromethyl)-naphthalene) were identified. In gases emitted the post-flashover fire mainly polycyclic aromatic hydrocarbons were detected. However, butyrolactone and N,N-dimethyldecanamide proved to be very stable components and were still present in analyzed gases and fumes.

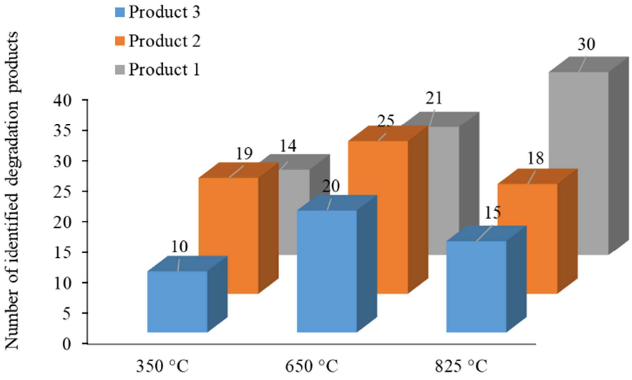

Fig. 3. The number of thermal degradation products identified in fire effluents when the decomposition occurred at 350 °C, 650 °C and 825 °C.

Decomposition of Product 3 resulted in the formation of 1-chloronaphthalene – the main thermal decomposition product of tebuconazole. In considerable amounts, 1,2-propanediol and 4-(1,1-dimethylethyl)-cyclohexanone were detected in emitted gases and smoke. In smaller amounts, substances such as 1-chloro-4-ethenylbenzene, 4-chlorobenzonitrile, naphthalene, 1-(4-chlorophenyl)-ethanone, acenaphthylene and 2-chloro-hydroxyammonitrile were present in the smoke emitted during thermal degradation of Product 3. These compounds were also detected in gas and fume samples emitted during decomposition of the active substance present in this preparation (-tebuconazole).

Based on the obtained results, it can be stated that during the combustion and thermal degradation of plant protection products, significant quantities of hazardous substances are released. At the same time in the United States, the Emergency Management Issues Special Interest Group (EMI SIG) state that "Protective Action Criteria (PACs) are the essential components for planning and response to uncontrolled releases of hazardous chemicals. These criteria, combined with estimates of exposure, provide the information necessary to evaluate chemical release events for the purpose of taking appropriate protective actions. During an emergency response, these criteria may be used to evaluate the severity of the event, to identify potential outcomes, and to decide what protective actions should be taken"[20]. PAC values are based on the following exposure limit values:

- Acute Exposure Guideline Levels (AEGL) values published by the U.S. Environmental Protection Agency (EPA),
- Emergency Response Planning Guideline (ERPG) values produced by the American Industrial Hygiene Association (AIHA),
- Temporary Emergency Exposure Limit (TEEL) values developed by SCAPA.

AEGL, ERPG and TEEL benchmark values are not available for all chemicals as the clinical effects are still an active research area. Consequently, when defining PAC values the following procedure is followed. Use AEGLs (including final or interim values) if they are available. If AEGLs are not available, use ERPGs. If neither AEGLs or ERPGs are available, use TEELs.

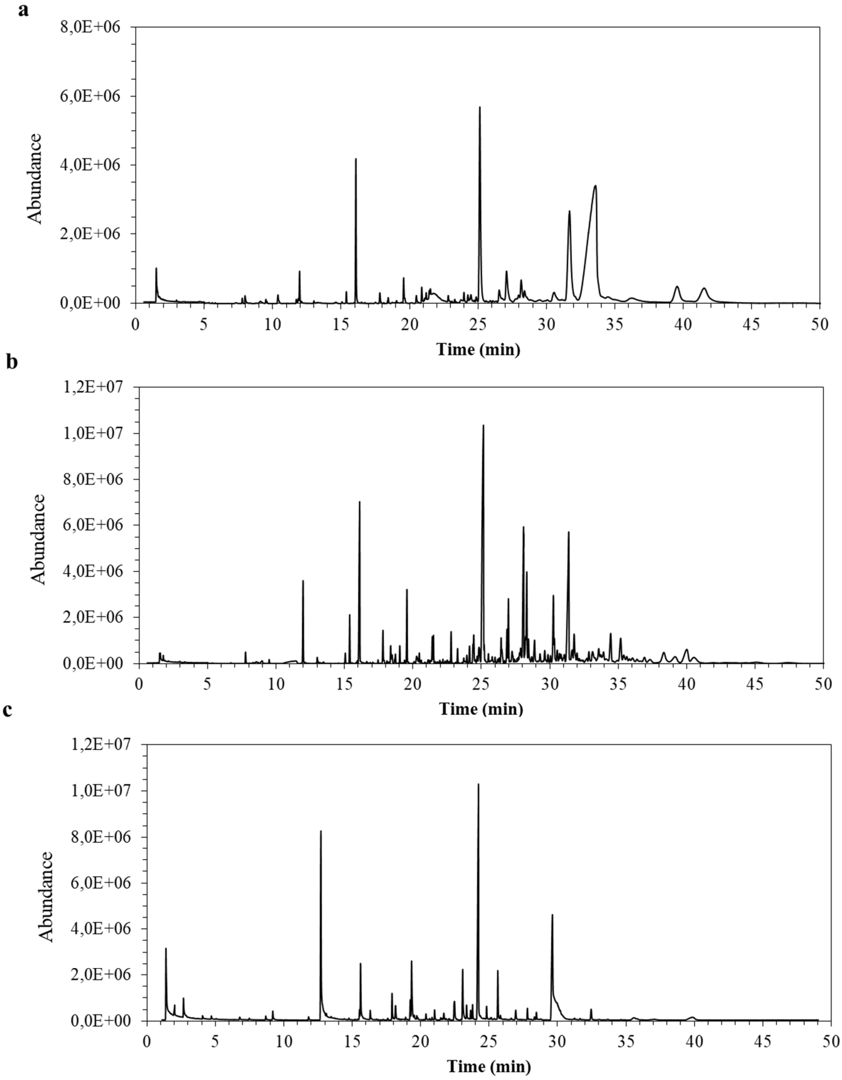

Fig. 4. Chromatograms of products emitted during thermal degradation of Product 1 (a), Product 2 (b) and Product 3 (c). The decomposition of Product 1 occurred at 850 °C, of Product 2 and Product 3 at 650 °C.

There are three levels of PAC value (1 to 3) where each successive value is associated with an increasingly severe effect from a higher level of exposure. Each level is defined as follows:

PAC-1: Mild, transient health effects.
PAC-2: Irreversible or other serious health effects that could impair the ability to take protective action.
PAC-3: Life-threatening health effects [20].

In Table 3, there are presented the value of PAC for the main organic substances that have been detected and identified in mixtures of gases and fumes emitted during the thermal decomposition and combustion of selected plant protection products. Unfortunately, the values of these parameters are not available for all detected chemicals, because clinical effects are still an active area of research.

Table 3. PAC-1, PAC-2, PAC-3 values for the main organic substances detected in mixtures of gases and fumes emitted during the thermal decomposition and combustion of plant [21]

Identificated substance	CAS	PAC-1 (mg/m^3)	PAC-2 (mg/m^3)	PAC-3 (mg/m^3)
1-chloronaphthalene	90-13-1	4,6	51	310
1,2-propanediol	57-55-6	30	1300	7900
acenaphthylene	208-96-8	10	110	660
benzonitrile	100-47-0	2.4	26_A	80_A
biphenyl	92-52-4	5.5	61_A	1900
butyrolactone	96-48-0	3.6	39	310
naphthalene	91-20-3	79	430	2600
phthalic anhydride	85-44-9	18	56	10000

PAC values marked with a subscript "A" correspond to 60-minute AEGL values.

CONCLUSIONS

It was found that Product 2 is the most flammable plant protection product. This is probably due to the presence of large amount of flammable solvents such as N,N-dimethyldecanamide, gamma-butyrolactone and alkyl/aryl-glycol ethers. All the tested plant protection products emit significant amounts of gases and fumes during combustion and thermal decomposition. Different chemicals, including volatile and semi-volatile compounds, were identified in the volatiles which appear to be very toxic and hazardous. It is worthy of note, that real fires may yield even more toxic products than the amount generated in the small-scale laboratory fire testing equipment.

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