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Gas chromatographic–mass spectrometric separation and identification of combustion products of organo-phosphorus and chlorine pesticides and evaluation of their impact on the environment

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Abstract

A simple and rapid GC–MS method for separation, identification and quantitative determination of combustion products of organophosphorus and chlorine pesticides viz; monocrotophos, chloropyriphos, butachlor and benzenehexachloride has been developed. The method provides a positive means of identifying organic combustion products and enables to assess not only their toxicity to human beings but also their impact on the environment. The data is useful for emergency preparations in case of fire in chemical plants and warehouses that store pesticides in large quantities. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Chemical fires seem to be one of the most common hazards of a large number of plants and warehouses that handle and store pesticides [1,2]. Over the years a number of incidents have occurred at several pesticide plants in different parts of the world [3–5]. During a fire, pesticides and their decomposition products may cause disastrous consequences for the environment. Thus it is necessary to visualize the consequences of such releases and the

amount of damage to the surrounding areas. Generally, the physical effects resulting from the release of the hazardous substances can be assessed by means of various consequence and risk analysis models [6–8]. However, the toxicological effects of fire products are difficult to assess mainly because of a general lack of knowledge regarding the chemical nature and amount of the toxic substances that could be generated [9,10]. It is difficult to estimate the inhalation effects of a complex mixture of fire products because of the combinations of reactions of different chemicals whose nature is not known. Considering the serious effects that warehouse and chemical plant fires have on the environment, there

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is a pressing need for conservative studies of preliminary estimates of survival fractions to allow hazard assessment and emergency planning. It is therefore important to develop test methods that could be used for assessment of risk from fire in chemical installations.

Generally, micro scale experiments are used to investigate the combustion products of pesticides [11,12]. These studies involve identification and quantification of the combustion products under various conditions and provide valuable information for large-scale experiments which are very difficult and expensive to carry out [13,14]. A few studies on the decomposition kinetics of organophosphorus pesticides were reported in the literature [15]. However, the results were not conclusive enough to say whether the measured quantities of pesticides were due to combustion or losses of evaporation during boiling. Several workers have carried out experiments on combustion of 2-methyl-4-chlorophenoxy-acetic acid (MCPA) and other pesticides at different temperatures and measured the contents of organic products which are toxic to human beings [16,17].

This paper describes the results of small scale laboratory experiments on combustion of some organophosphorus and chlorine pesticides viz., monochrotophos, chloropyriphos, butachlor and bezenehexachloride and the analysis of organic combustion products by gas chromatography–mass spectrometry (GC–MS). The environmental impact and toxicity of the products of combustion have been discussed. This information is a pre requisite for emergency planning and ensuring that those exposed to fumes receive appropriate treatment both for acute and chronic symptoms.

2. Experimental

2.1. Materials

Monochrotophos (MCP), chloropyriphos (CPP), butachlor (BCH) and bezenehexachloride (BHC) of technical grade samples were obtained from M/s Vantech (Hyderabad, India) and used as received. Chloroform of A.R grade was obtained from Spectrochem (Mumbai, India), IOLAR-grade helium and nitrogen from BOL (Mumbai, India) were used.

2.2. Apparatus

The combustion and sampling apparatus was fabricated for small scale experiments as per the specifications of DIN 53436 in our laboratory and its schematic is shown in Fig. 1. It consists of a air cylinder (1) (BOL, Mumbai, India) for supply of air, monometer (2) (SAMC, Mumbai, India) to control the flow of air, dimmerstat (3) (AEPL, Mumbai, India) to regulate the flow of current and control temperature in the electrical heating system, a temperature indicator (4) (Zetatek, Hyderabad, India), quartz cuvette (5) (Srinivasa Products, Bangalore, India) for placing the sample, ring oven (6) (Tempo Ind, Mumbai, India) which moves along the cuvette and bums the test material, cold trap (7) containing chloroform for collecting organic combustion products, activated carbon (8) to collect low boiling organics, midget impinger (9) containing 0.05 N NaOH to collect NO_x , SO_2 and HCl, midget impinger (10) containing ammonium molybdate to trap PO_x and sampling pumps (11) (Hindvac, Bangalore, India). A gas-chromatograph (Shimadzu, Kyoto, Japan) equipped with a flame ionization detector (FID) and a fused-silica capillary column DB-I7HT, J&W (30 m×0.32 mm I.D., 0.1 μm film thickness) was used. Peak retention times and areas were calculated using a microprocessor connected to the instrument. A VG70-70H mass spectrometer (Micromass, Manchester, UK) coupled with a gas-chromatograph (Pye-Unicam, London, UK) was used for GC–MS studies.

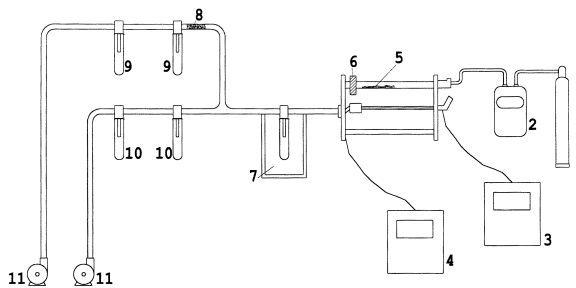


Fig. 1. A schematic diagram of the apparatus used for combustion of pesticides: (1) air cylinder; (2) manometer; (3) dimmerstat; (4) temperature indicator; (5) quartz cuvette; (6) ring oven; (7) cold trap; (8) activated carbon; (9) midget impinger for NO_x ; (10) midget impinger for PO_x ; and (11) sampling pumps.

2.3. GC–FID

The combustion products of the test samples were separated on a fused-silica capillary column DB 17 HT (30 m × 0.32 mm I.D., 0.1 μm). The carrier gas was nitrogen, constant flow 0.9 ml/min, injection temperature: T_{inj} = 320 °C, detector temperature: T_{det} = 325 °C. The temperature programme was as follows; initial period 100 °C for 1 min, then 20 °C/min to 300 °C held for 2 min.

2.4. GC–MS

Analyses were carried out on a fused-silica capillary column HP-5 (30 m × 0.32 mm I.D., 0.1 μm). The carrier gas was helium, constant flow 0.8 ml/min. Splitter (1:20) (period 1 min), 2 μl, injection temperature: T_{inj} = 300 °C, detector temperature: T_{det} = 320 °C. The temperature programme was as follows: initial period 100 °C for 1 min, then 20 °C/min to 300 °C, held for 1 min. Ionization voltage: 70 eV. Transfer line temperature was 280 °C. The selective scan range was 1–600 u.

2.5. Sample preparation

The test samples of organophosphorus and chlorine pesticides were subjected to combustion in air flow of 10 l/h inside the quartz tube. In all experiments 0.5 g of pesticide was burnt at a temperature of 300 °C for 30 min. The organic combustion products trapped in chloroform were collected and analyzed by GC–MS.

3. Results and discussion

In the present investigation micro scale experiments were carried out to characterize the combustion products of CPP, MCP, BCH and BHC using GC–MS. The first two are organo phosphorus pesticides while BCH and BHC are organochlorine in nature, among which one is a herbicide and the other is an insecticide. All the experiments were carried out using technical grade pesticides either prepared in our laboratory or obtained from industry. The chemical formulae of these pesticides is shown in Fig. 2. General information regarding the behavior of

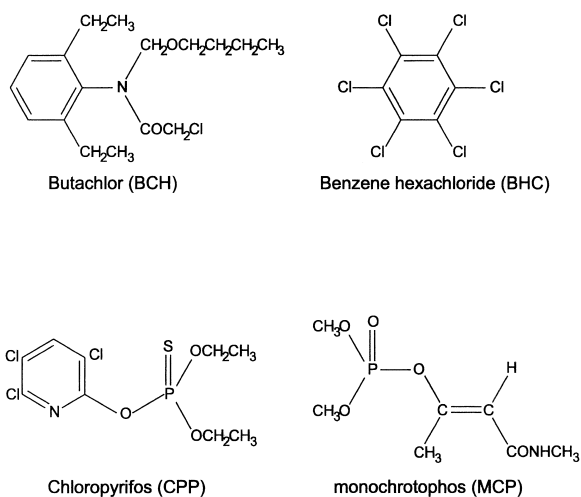


Fig. 2. Chemical formulae of the organochlorine and organophosphorus pesticides studied.

organophosphorus compounds indicates that on heating CPP and MCP may undergo decomposition, isomerization and polymerization. The molecules are generally unstabilised by an interchange of sulphur atoms with oxygen and decompose on heating before reaching their boiling points. In addition, significant differences in behavior are expected between the compounds of organophosphorus and chlorine pesticides under investigation.

3.1. Chloropyrifos

Chloropyrifos (CPP) has a melting point of 42 ± 2 °C. It was burnt down readily on heating at 300 °C for 30 min. The substance was melted before it entered the ring oven. It was ignited and converted to inorganic and organic decomposition products including elemental carbon. The combustion products were collected in respective sampling traps and analyzed separately. The distribution of combustion products is given in Table 1. It could be seen from Table 1 that the majority of combustion products are organic in nature. About 23% of inorganic products viz; SO_2 , PO_x , NO_x and HCl are formed. The organic products were collected in chloroform and analyzed by GC–MS. The total ion chromatogram showed three major distinct peaks at 14.05, 14.40 and 20.07 min separated from CPP. The molecular ions of these

Table 1
Organic and inorganic components of combustion products of CPP, MCP, BCH and BHC

Sample number	Pesticide	Amount (g)	Elemental carbon (g)±(SD) ^b	Organics (g)±(SD) ^b	Inorganics ^a (g)±(SD) ^b
1	CPP	0.536	0.132±(0.003)	0.270±(0.008)	0.134±(0.005)
2	MCP	0.579	0.105±(0.004)	0.461±(0.012)	0.013±(0.001)
3	BCH	0.528	0.016±(0.001)	0.262±(0.009)	0.250±(0.007)
4	BHC	0.524	0.011±(0.001)	0.421±(0.015)	0.092±(0.002)

^a Includes HCl, SO₂, PO_x, NO_x and NH₃.

^b Number of determinations (*n*=3).

compounds were found to be 219, 279 and 254, respectively. Their relative area percentages were 38, 22 and 30%. The GC–MS data including the molecular ions and fragmentation patterns are given in Table 2. This data has been found to be quite valuable in identification of the products of combustion of CPP. The three major components were

identified as dibenzyl phosphate, diphenyl sulphone, dibutyl phenyl phosphate. These compounds were found to be around 90% of the organic combustion products formed on heating CPP at 300 °C for 0.5 h. The toxicity data of these products indicates that these compounds may be carcinogenic to human beings.

Table 2
GC–MS data of products of combustion of CPP, MCP, BCH and BHC

Compound name	Retention time (min)	Mass fragments
MCP	5.00	181(M+), 53, 77, 94, 108, 122, 137
	7.85	247(M+), 51, 77, 112, 147, 181, 219
	9.33	219(M+), 56, 77, 109, 119, 133, 147, 162, 181
	10.40	254(M+), 50, 85, 96, 109, 121, 147, 156, 181, 219
	10.56	191(M+), 57
	11.04	318(M+), 57, 231, 247
	12.34	255(M+), 57, 71, 91, 108, 19, 132, 148, 157, 191, 207, 219, 238, 245
	14.05	247(M+), 57, 70, 91, 112, 175
	15.36	311(M+), 57, 91, 117, 132, 146, 160, 176, 188, 202, 224, 237, 276
	17.06	223(M+), 57, 87, 149
	19.07	359(M+), 57, 87
	21.38	241(M+), 57, 71, 83, 101, 112, 129, 147
	24.80	279(M+), 57, 71, 83, 113, 149, 167, 279
CPP	14.05	219(M+), 51, 61, 85, 96, 109, 121, 145, 156, 181,
	20.07	254(M+), 51, 61, 77, 85, 109, 128, 147, 158, 181, 207, 219
	14.38	279(M+), 57, 71, 83, 113, 149
BHC	14.05	219(M+), 51, 85, 96, 109, 121, 147, 156, 183
	20.07	219(M+), 57, 71, 83, 113, 149, 167, 179
	32.11	279(M+), 57, 71, 83, 113, 149, 167, 219
BCH	32.12	311(M+), 57, 77, 91, 105, 188, 146, 160, 176, 188, 207, 225, 237, 276

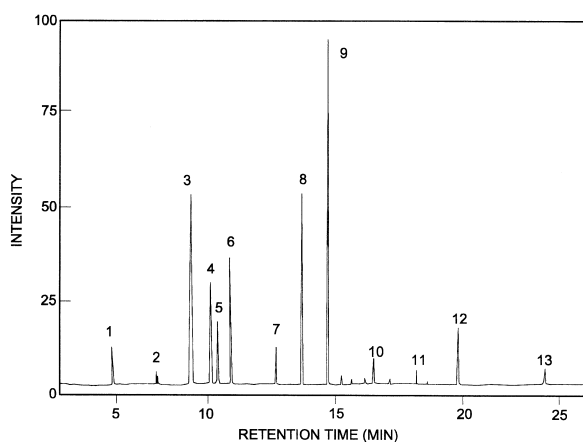


Fig. 3. Total ion GC chromatogram of 300 °C combustion products of MCP.

3.2. Monochrotophos

Monochrotophos (MCP) has a melting point of 54 °C. On heating at 300 °C for 30 min, it has yielded different types of organic and inorganic products as shown in Table 1. The inorganic products were collected and analyzed by spectrophotometric techniques while the GC chromatogram of organic products has shown 12 peaks at different retention times indicating the presence of different organic compounds evolved during the combustion of MCP. A typical total ion GC chromatogram of the combustion products of MCP is shown in Fig. 3. It could be seen from Fig. 3 that all the compounds are well separated using a fused-silica column of 30 m×0.32 I.D. and 0.1 μm thickness and the peaks are with excellent symmetry and reproducibility. The EI mass

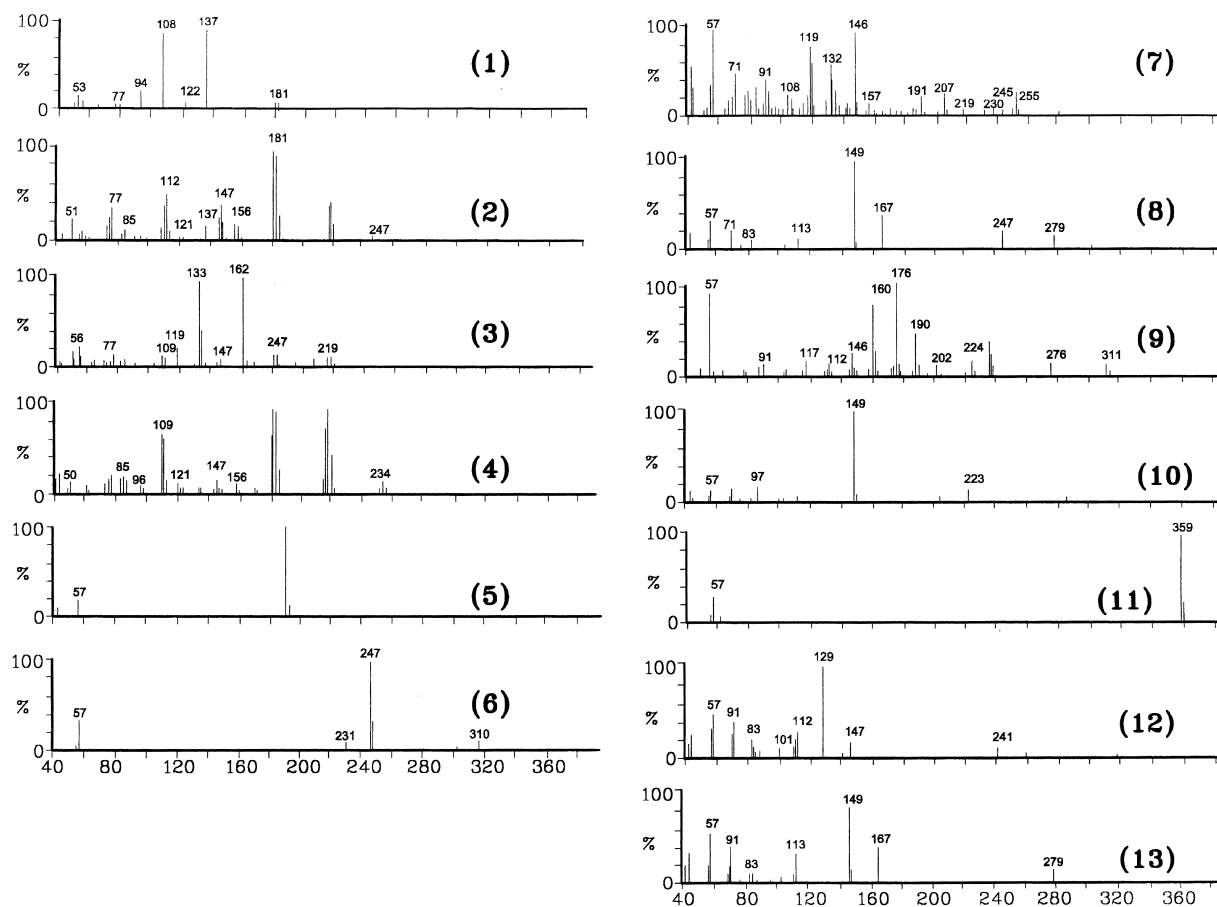


Fig. 4. EI mass spectra of the peaks 1–13 separated by GC (shown Fig. 3) of the organic combustion products of MCP.

spectra of all the major components are shown in Fig. 4. The GC–MS fragments and the molecular ions of the products obtained using MS in the electron impact mode are presented in Table 2. The fragmentation pattern was found to be quite indispensable for unambiguous identification of combustion products of MCP. From the molecular ions and fragmentation patterns, triethyl phosphate, dibutyl phosphate, dioctylamine, diethyl phosphoro acetaldehyde, diethylacetal and N-methyl dioctylamine were identified tentatively. In this case low molecular mass phosphorus bearing materials such as triethyl phosphate are formed but at lower levels. Most of these compounds have structures closely related to the parent compound and similar toxicity on weight by weight basis. These results suggest that the main toxicity risk is from the original compound. In our previous communication, we have studied the isomerization of technical MCP using reversed-phase high-performance liquid chromatography (HPLC) and observed that the *cis*–*trans* isomerization occurs probably because of the structure of MCP lends itself to a stereochemical rearrangement [18]. However, the mass spectra could not be used with certainty to discriminate between the possible structures of isomers that might be formed via this mechanism. The peak at 17.6 min is probably a mixture of two unresolved compounds. The other compounds eluted at 9.33, 11.04, 14.05 and 15.36 min are produced in large quantities relative to MCP. All these compounds were found to be highly toxic to human beings.

3.3. Butachlor

Butachlor (BCH) has a melting of 196 °C. The substance was found to be melted even before it entered the ring oven and there by decomposed rapidly. The combustion products were collected in the respective sample traps and analyzed separately. Fig. 5 shows the bar diagram of distribution of combustion products of BCH as well as CPP, MCP and BHC formed at 300 °C. It could be seen from Fig. 5, that no elemental carbon has been formed. About 80% of the oxidised products are organic in nature. The yields of different organic and inorganic products were given in Table 2. The mass spectral fragmentation pattern of BCH before and after

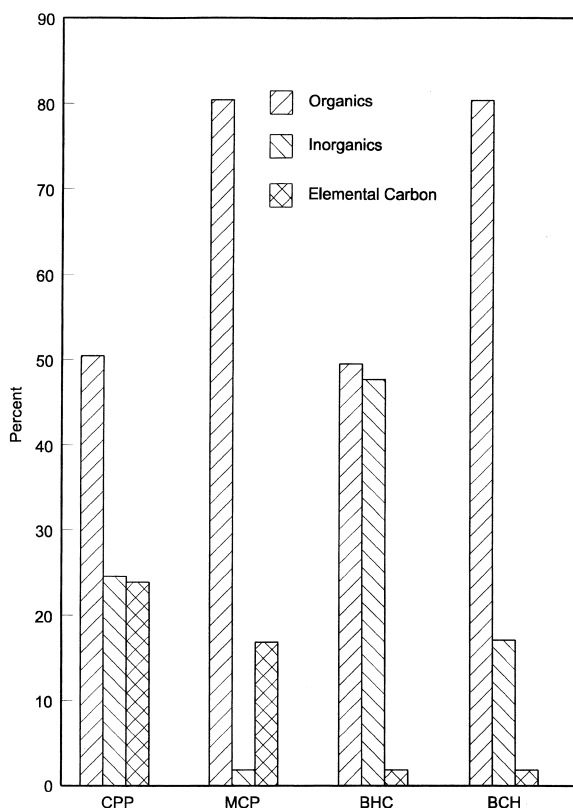


Fig. 5. Distribution of combustion products.

combustion were compared and no major differences were noticed. These results suggest that BCH is not oxidised completely at this temperature and may be higher temperatures are required for its decomposition. However, some of the important degradation products of BCH are identified and given in Fig. 6. The major component of these products has been found to be 2, chloro 2,6-diethyl acetanilide (CDA).

3.4. Benzene hexachloride

Benzene hexachloride (BHC) has a melting point of 112.5 °C. The organic compounds were analyzed by GC–MS. The presence of isotope peaks in the mass spectra suggests that these materials contains chlorine, but their structures are unknown. The chromatogram has shown three peaks at different retention times. However the concentration of the major peak was found to be 66.6% and the fragmentation pattern was found to be similar to the

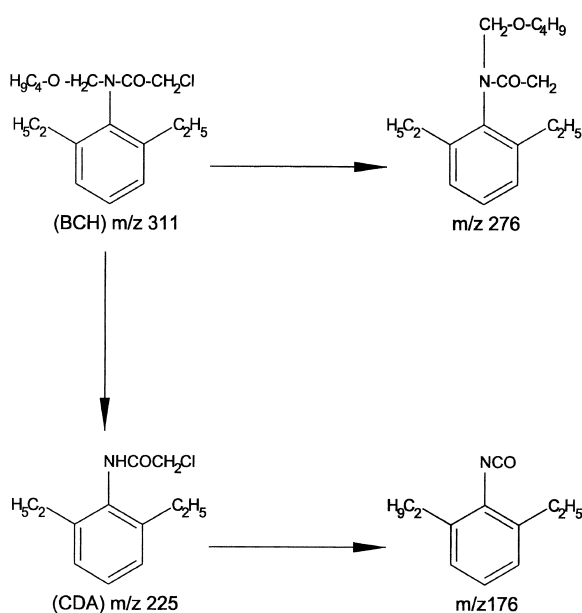


Fig. 6. Combustion products of BCH.

sample submitted before combustion. It indicates that the BHC is resistant to oxidation at 300 °C and still high temperatures may be required for its combustion. Some of the major products of combustion of BHC, BCH, MCP and CPP identified by GC–MS are recorded in Table 3.

3.5. Validation

The validity of the data generated both for organo phosphorus and chlorine pesticides was tested by carrying out the combustion of each product for three times under identical conditions. The quantities of organic and inorganic products obtained on combustion of all the four pesticides were found to be reproducible in the present investigation. The val-

Table 4

Percent of organics, inorganics and elemental carbon obtained on variation of ± 5 °C during the combustion of CPP, MCP, BCH and BHC at 300 °C

Sample number	Pesticide	Elemental carbon (%)	Organics (%)	Inorganics (%)
1	CPP	24.6 \pm 2.1	50.4 \pm 6.0	25.0 \pm 4.0
2	MCP	18.1 \pm 4.3	79.6 \pm 4.0	2.3 \pm 1.0
3	BCH	3.0 \pm 1.0	49.6 \pm 6.0	47.4 \pm 7.0
4	BHC	2.1 \pm 1.0	80.3 \pm 5.0	17.6 \pm 4.2

Number of determinations ($n=3$).

idated data including the number of experiments and the standard deviations (SD) obtained for combustion of each compound studied at 300 °C are recorded in Table 1. Further, the experimental conditions viz., temperature, air flow, and time of heating were slightly altered and the effect of each parameter was observed carefully on the quantities of the toxic products formed on combustion. It was found that there was no significant change in the quantities of the combustion products when the air flow was altered by ± 1 l/h and the time of heating by ± 5 min. However, a slight variation of temperature by ± 5 °C resulted in a maximum of 3–6% change in the quantities of organics, inorganics and elemental carbon obtained on composition of CPP, MCP, BHC and BCH. The results are recorded in Table 4.

4. Conclusions

Chemical fires are the most common risks from chemical plants where pesticides are stored in large quantities. The fire products are harmful not only to people but also the ecosystem. In the present investigation micro scale experiments were conducted

Table 3

Major organic compounds of combustion products of CPP, MCP, BCH and BHC identified by GC–MS

Pesticide	Organic products of combustion identified by GC–MS
CPP	Dibenzyl phosphate, diphenyl sulphone, dibutyl phenyl phosphate
MCP	Triethyl phosphate, dibutyl phosphate, diocylamine, diethyl phosphoro acetaldehyde, diethyl acetal and N-methyl dioctylamine
BCH	Butachlor, 2-chloro-2'-6 diethyl acetanilide
BHC	Benzene hexachloride

to characterize and quantify the combustion products of CPP, MCP, BCH and BHC using GC–MS. These studies have shown that the compounds generated in case of a fire in a chemical warehouse containing organophosphorus and chlorine pesticides are toxic to human beings. The analysis of the combustion products indicated the presence of several decomposed organic products of original pesticides in different quantities. The combined effects of the individual components of gaseous organic combustion products may prove to be quite dangerous to life or health of the fire fighters on the site and near by residents.

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