CHEMICAL CHARACTERIZATION OF RESIDUES FROM MILITARY HC SMOKEPOTS

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Summary

HC smoke, a wide-area obscurant used in large quantity during military training, is produced by reaction of zinc oxide (46.7%), hexachloroethane (46.7%) and granular aluminum (6.6%). Previous research had identified heavy metals and organic compounds in the smoke cloud, but the compositions of residues remaining in spent canisters (13.6 kg initial charge) or deposited outside a canister during ignition were not known. Two field trials were conducted. Trial 1 examined the spatial distribution of organic and inorganic compounds in residues remaining in the canister after ignition of the munitions. Samples were taken near the edges of the canister and in the center and divided into subsections representing the bottom, middle, and top. The residue (17–23% of the original mass) was primarily Al_2O_3, elemental carbon, $ZnCl_2$, $FeCl_3$, and Fe_2O_3, with traces of Pb, Cd, and As. Lead concentrations differed across sections but not depths, while cadmium concentrations differed by section and depth. Trial 2 examined the effects of igniting smokepots singly and in pairs, in prone and upright orientations, on the compositions of canister and deposited residues. The deposited mass was 6–8 times larger from upright pots. Compositions of deposited residues, but not spent canister residues, were affected by both the number of smokepots and their orientation. Concentrations of inorganic and organic compounds were higher in residues deposited from prone smokepots.

Introduction

HC-smoke, a large-area obscurant used in military training, is produced by ignition of a heterogeneous mixture of hexachloroethane (HCE, 46.7%), zinc oxide (ZnO, 46.7%) and granular aluminum (Al, 6.6%). The HCE to ZnO ratio is generally maintained close to 1:1 while the Al content is varied slightly to regulate the burning rate. The obscurant particulates are formed by rapid
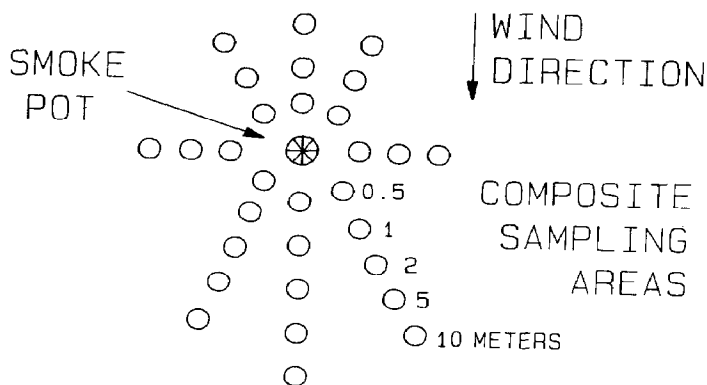
Fig. 1. Contaminated area sampling grid.

condensation of the $ZnCl_2$ vapors produced by the reaction (eqn. 1). Side reactions of the vaporized munitions canister contribute iron and other metals (as oxides and chlorides) to the aerosol. As developed in this study, residues in spent pots or deposited within a few meters are each about 20% of the 13.6 kg mass of the M-5 smokepot munitions.

$$2 Al + C_2 Cl_6 + 3 ZnO \rightarrow 3 ZnCl_2 + Al_2 O_3 + 2 C + Heat \tag{1}$$
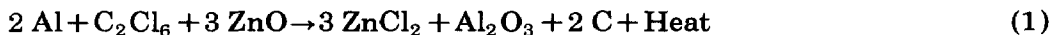
Vapors and particulate matter in HC smoke contain several toxic compounds such as phosgene, hexachloroethane, and inorganic cadmium and lead [1,2]. Humans and animals exposed to HC smoke exhibit acute toxic effects (e.g. respiratory system, eye), and humans repeatedly exposed have an increased risk of cancer [3]. The compositions of canister and deposited residues are unknown, but the chemical, health, and ecological data [4,5] for HC smoke suggested that residues may also present important human health and ecological risks. To determine the need to develop and employ measures to reduce environmental contamination and exposures to workers from spent HC munitions, this research characterized spent canister and deposited residue compositions.

Experimental

Generation of smoke and collection of residue samples

Residues from HC smokepots were collected in two trials conducted at Fort Leonard Wood, Missouri. Deposited residues were sampled using a circumferential grid with Pyrex collection plates placed at 0.5, 1.0, 1.5, 2.0, 5.0 and 10.0 m (Fig. 1). Burning time, total residue content, humidity and air temperature were monitored in each trial.

The purposes of Trial 1 (24–25 June 1985) were to confirm the sampling

C-1	B-1	A-1	B-1	C-1
C-2	B-2	A-2	B-2	C-2
C-3	B-3	A-3	B-3	C-3

Fig. 2. Canister subsampling arrangement used in Trial 1.

and analytical methods and to determine the spatial distribution of compounds in the canister residue. Five smokepots (Lot 1) were individually ignited in upright positions. The spatial distributions of compounds in the canister residue were determined by dividing the residue into three sections across the width (A, B, C) with a stainless steel sampler. Each section was divided into three subsections (top = 1, middle = 2, bottom = 3, see Fig. 2).

The second trial (16–19 December 1985) studied four ignition modes: a single smokepot fired in upright position, two smokepots stacked and fired upright, a single smokepot fired on its side (prone), and two smokepots placed back to back and fired prone. Each mode was repeated five to six times; 30 smokepots from Lot 1 and 4 from Lot 2, were used. Residues deposited within 2 m from the canister were sampled and weighed. After homogenization, residues were analyzed for metals and total carbon, and screened for major nonpolar organic moieties (tetrachloroethane, TCE; hexachloroethane, HCE; hexachlorobenzene, HCB; hexachlorobutadiene, HCBUT).

Analysis for organic constituents

The analytical scheme was optimized and validated with nonpolar model compounds consisting of polynuclear aromatic hydrocarbons, polychlorinated aliphatics and aromatics. Recoveries were maximized by varying the extraction solvents, concentration techniques and fractionation procedures. Toluene and benzene were the most efficient solvents (85–100% recoveries). Toluene was used in Trial 1. Because traces of $AlCl_3$ in the residue led to the formation of condensation products with toluene, benzene was used in Trial 1.

The validated procedure used in the analysis of Trial 2 residues consisted of an 18 h soxhlet extraction of 10–20 g residue with 300 ml glass-distilled benzene (EM Science, Cherry Hills, NJ), concentration of the extract with rotary evaporation, and screening of the concentrate by high performance liquid chromatography (HPLC). The HPLC system was a model 4 solvent delivery system with a LC75 UV-VIS detector in tandem with a model 650-10S spectrofluorometer (Perkin–Elmer Corp., Norwalk, CT). Separations were carried out with a C-18 column under a four step solvent gradient. The eluent

was 60/40 water:acetonitrile to 100% acetonitrile. Absorption, emission, and excitation wavelengths were monitored as a function of time to optimize for two through five ring polynuclear aromatics.

Residue extracts were analyzed for polyhalogenated aliphatics and aromatics using a gas chromatograph (GC) equipped with an electron capture detector (Model 560, Tracor Instruments, Austin, TX). Separation was carried out with a 30 m bonded phase fused silica capillary column (DB-5, J&W Scientific, Rancho Cordova, CA). Confirmatory analysis for extracted organic constituents was accomplished with a GC interfaced to a mass spectrometer (GC-MS) (Model OWA 30B, Finnigan Corp., Palo Alto, CA) operating at 65 eV and equipped with a 30 m bonded phase fused silica capillary column. To assure the uniformity of the extraction procedure, all residue samples were spiked with known amounts of perdeuterated naphthalene, anthracene and chrysene. Recovery was monitored by determining the areas of ions m/e 136, 188 and 240. The instrument was tuned and calibrated daily to meet US EPA decafluorotriphenyl phosphine (DFTPP) specifications [6].

Analysis for inorganic constituents

Residues were screened for 32 elements using inductively coupled plasma emission spectrophotometry (ICPES) (Model 975 Plasma Atom, Jarrell Ash, Waltham, MA). Because of high concentrations of Al_2O_3 in the samples, solution was effected by fusion 0.25 g of homogenized sample with 0.8 g of $LiBO_2$ at 1050°C. Following sample nitric acid/perchloric acid digestion, Pb, Cd and As were quantitated using atomic absorption (AA) spectroscopy (Model 3030B, Perkin Elmer, Norwalk, CT). Arsenic was determined using a hydride generation system (Model MHS-1, Perkin–Elmer) attached to a Model 603 AA spectrometer (Perkin–Elmer). Elemental carbon (EC) was determined as the difference between total carbon and total organic carbon.

Relative proportions of oxide and chloride for Zn, Fe, Pb, Cd, and As in homogenized canister residues were estimated from analytical data. Water soluble concentrations were determined using ion chromatography. Water insoluble quantities were determined as the difference from the total. The water soluble fraction was assumed to be chlorides and the water insoluble fraction was assumed to be oxides.

Results

Major inorganic constitutents

Results for the 5 smokepots used in Trial 1 are given in Tables 1 and 2 and Tables 2–4 give results for the 30 smokepots from Lot 1 used in Trial 2. Data for the 4 pots from Lot 2 (Trial 2) are given appropriately in the text. Smokepots were weighed before and after ignition; canister residues (2182–3297 g) were 16.0–24.4% of the original weight. The major inorganic constituents

TABLE 1

Composition of inorganic residue in canister subsections ($n=5$)

	Al, %	Zn, %	Fe, %	C, %	Pb, ppm	Cd, ppm	As, ppm
Section A-1							
Mean	41.16	3.24	1.00	0.96	272.00	1.61	3.84
Standard Dev.	3.43	0.72	1.01	0.25	177.25	1.23	1.45
Section A-2							
Mean	44.58	2.88	0.46	1.22	99.80	0.51	3.10
Standard Dev.	1.51	1.67	0.44	0.89	56.63	0.29	1.95
Section A-3							
Mean	39.08	6.56	0.39	2.44	93.80	0.93	4.12
Standard Dev.	3.27	5.63	0.57	1.39	45.08	0.67	1.02
Section B-1							
Mean	40.74	3.93	1.98	7.98	603.80	1.10	2.86
Standard Dev.	4.70	2.45	1.14	3.74	448.56	1.30	1.13
Section B-2							
Mean	42.17	4.35	1.18	4.62	521.00	0.84	2.85
Standard Dev.	2.04	1.85	0.74	3.14	312.82	0.75	1.03
Section B-3							
Mean	39.82	4.28	0.55	3.68	110.20	0.52	2.72
Standard Dev.	7.18	4.57	0.64	0.42	66.09	0.17	1.18
Section C-1							
Mean	29.96	11.02	1.01	2.70	928.00	7.80	2.90
Standard Dev.	4.02	5.01	0.89	4.94	296.59	2.57	1.38
Section C-2							
Mean	35.76	7.48	0.79	7.04	462.00	4.32	2.48
Standard Dev.	3.41	3.54	1.29	4.36	470.65	2.66	1.10
Section C-3							
Mean	39.58	5.18	0.72	7.16	227.00	1.24	4.30
Standard Dev.	2.91	4.10	0.93	2.26	287.98	1.07	1.66

in canister residues were Al, EC, Zn and Fe (from the canister). The predominant Al species was oxide, while Zn and Fe were present as chlorides and oxides. The concentration of Al_2O_3 in canister residues was generally highest in the upper middle section A-1 (Table 1). This was expected, as this section originally contained the highest proportion of Al (to help the initial burning process). The elemental carbon content increased towards the sides (section C). This section also had high concentrations of chloride ion.

Canister concentrations of Cd and As were generally below 1.0 ppm (Tables 1 and 3), although Cd concentrations in Lot 2 residues (not shown) reached 118 ppm. Concentrations of Pb, Cd and As in canister residues differed between lots and were most likely related to the concentration of these elements in the smokepot munitions. In contrast with unburned munitions [1], concentrations of Pb and Cd in canister residues were uncorrelated with each other.

Burning times (minutes) varied from 8.02 to 21.45 (15.67 ± 3.08 mean ± SD,

TABLE 2

Residue deposition profiles for Lot 1 smokepots, both trials

	Distance from smokepot (m)				
	0.5	1.0	1.5	2.0	5.0
Trial 1					
Mode 1	6.07 ± 1.74^a	NS^b	NS	0.862 ± 0.450	0.014 ± 0.031
Area, %[c]	2.56			0.17	0.03
n	5			5	5
Trial 2					
Mode 1	3.9 ± 3.5	6.5 ± 4.6	5.0 ± 2.4	4.4 ± 1.8	NS
Mode 2	4.1 ± 1.4	7.6 ± 2.5	8.2 ± 2.6	7.7 ± 3.1	NS
Mode 3	NS	19.0 ± 9.0	11.6 ± 6.2	8.5 ± 5.0	NS
Mode 4	NS	33.3 ± 14	18.6 ± 7.4	13.5 ± 6.2	NS
Area, %	12	6	4	3	
n	4	5	5	2	

[a]Weight (mean $\pm$ SD mg) of deposited residue.
[b]Not sampled.
[c]Percentage of deposition area sampled.

$n = 30$) for pots from Lot 1 (Table 3) and 8.78–17.12 minutes (13.38 ± 3.68, $n = 4$) for pots from Lot 2. The difference between mean burning times for the two lots was not statistically significant (t-test, $p < 0.95$). (The equivalence of the burning times for the two lots was confirmed by bootstrapping [7] the 30 Lot 1 burning times; the median burning time for 500 samples of size $n = 4$ was 15.32). The burning rate is very sensitive to small variations in the aluminum content of the mixture [1], which may explain the variability between smokepots. Thus, decreasing the aluminum content from 7.5% to 6.5% can increase the burning time 35% [1].

Major organic constituents

Total extractable organics, primarily aromatic hydrocarbons and chlorinated aliphatics, were present at concentrations below 1%. Chromatograms from the four ignition modes did not differ. The predominant nonpolar organic compounds found in Trial 1 canister residues were aromatic hydrocarbons. Using the validated analytical method in Trial 2, chlorinated aliphatics were identified as the major nonpolar organic compounds in canister residues. Aromatic hydrocarbon (alkylnaphthalenes and methylphenols) concentrations were generally 0.2–2 ppm in canister residues.

Composite samples of canister residues from Trial 1 were analyzed for polychlorinated dibenzo-p-dioxins [8]. These compounds form during incineration of chlorinated organics [9]. The reaction conditions inside the incinerator, although occurring at a lower temperature, are similar to those in the smoke-

TABLE 3

Summary statistics for canister residues from Lot 1, Trial 2

	Al	Fe	Zn	C	EXT	Pb	Cd	As	TCE	HCE	HCBUT	HCB	Time[a]
Mode 1													
No. of cases	4	4	4	4	3	4	4	4	4	4	4	4	4
Minimum	36	0.24	1.1	2.9	0.60	14	0.60	0.8	9.8	4.0	0.7	0.04	17
Maximum	43	0.57	5.6	3.7	0.70	110	0.90	1.0	32	19.8	1.3	0.09	18
Mean	40	0.32	3.3	3.1	0.63	66	0.75	0.88	16	10.0	1.0	0.06	18
Standard Dev.	3.0	0.11	2.3	0.3	0.06	40	0.11	0.1	11	6.9	0.3	0.02	0.6
Mode 2													
No. of cases	10	10	10	10	8	10	10	10	9	9	9	9	10
Minimum	38	0.14	1.2	2.6	0.34	15	0.60	0.80	6.3	0.9	0.05	0.02	12
Maximum	46	1.2	5.2	9.7	2.2	220	1.9	0.90	26	7.8	1.2	0.33	19
Mean	42	0.49	3.1	5.2	0.83	86	0.97	0.81	11	4.3	0.43	0.10	16
Standard Dev.	2.2	0.36	1.2	2.1	0.59	63	0.49	0.03	5.9	2.1	0.39	0.10	2.0
Mode 3													
No. of cases	6	6	6	6	6	6	6	6	6	6	6	6	6
Minimum	32	0.12	2.0	1.5	0.37	52	0.6	0.80	8.5	0.28	0.04	0.03	15
Maximum	44	0.36	7.6	3.7	0.81	140	0.6	0.90	33	5.8	0.85	0.35	22
Mean	38	0.26	3.9	2.9	0.63	91	0.6	0.82	16	2.6	0.43	0.10	18
Standad Dev.	4.4	0.1	2.4	0.9	0.15	31	0.0^2	0.04	8.9	2.3	0.27	0.13	2.2
Mode 4													
No. of cases	10	10	10	10	10	10	10	10	8	8	8	0	10
Minimum	38	0.18	1.4	1.2	0.33	25	0.60	0.8	0.05	0.05	0.04	0.05	8.0
Maximum	44	0.97	4.6	9.8	1.6	260	2.1	0.8	18	2.7	2.0	0.03	17
Mean	41	0.52	2.8	3.8	0.95	112	1.1	0.8	9.9	1.3	0.74	0.02	12
Standard Dev.	2.0	0.29	1.0	2.9	0.40	78	0.68	0.0^b	7.2	1.0	0.72	0.01	3.2

[a]Al, Fe, C, EXT in percent; Pb, Cd, As, TCE, HCE, HCBUT, HCB in ppm; (Burn) time in minutes. EXT = extractable organics, TCE = tetrachloroethylene, HCE = hexachloroethane, HCBUT = hexachlorobutadiene, HCB = hexachlorobenzene.
[b]Concentrations below detection limit given by the mean.

pot. For these analyses the three sections of residues at each depth for a given smokepot were combined; 15 samples were produced. If dioxins were present, concentrations were below the detection limit of 1.0 ppb.

Although the inorganic composition of canister and deposited residues were usually similar (Tables 3 and 4), the amounts of deposited residue varied with the burn mode (Table 2). However, concentrations of organic compounds in deposited residues from prone smokepots were generally higher than in residues from upright smokepots. The residues contained partially reacted compounds ejected by the force of the combustion, including as much as 15% (by weight) HCE. HCBUT and HCB were probably produced by dechlorination of HCE to perchloroethylene (PCE), dimerization of PCE to HCBUT, addition of PCE to HCBUT, and dechlorination.

Discussion

Trial 1: Range finding

Trial 1 was conducted to determine the homogeneity of inorganic and organic compound concentrations in residues remaining in the canister. The only

TABLE 4

Summary statistics for deposited residues from Lot 1 backspots, Trial 2

	Al	Fe	Zn	C	EXT	Pb	Cd	As	TCE	HCE	HCBUT	HCB[a]
Mode 1												
No. of cases	4	4	4	3	4	4	4	4	4	4	3	4
Minimum	35	0.2	8.9	0.1	0.3	31	0.6	0.8	1000	1300	6.2	13
Maximum	46	0.6	17	0.8	3.8	72	5.3	0.8	75000	2200	48.5	21
Mean	41	0.4	12	0.4	1.4	53	2.5	0.8	23500	1900	21.1	18
Standard Dev.	4.6	0.1	3.7	0.3	1.6	17	2.2	0.0[b]	35000	400	23.7	3.8
Mode												
No. of cases	5	5	5	3	5	5	5	5	5	5	3	5
Minimum	36	0.4	10	0.1	0.7	72	1.0	0.8	1000	1040	1.3	2.9
Maximum	39	0.8	16	0.9	1.9	170	3.7	0.8	60000	10600	16	26
Mean	37	0.6	13	0.5	1.2	130	2.6	0.8	29000	6200	6.3	9.1
Standard Dev.	1.3	0.1	1.9	0.4	0.5	39	1.0	0.0	21000	4300	8.6	9.4
Mode 3												
No. of cases	5	5	5	5	5	5	5	5	5	5	5	5
Minimum	22	0.3	15	0.6	2.0	24	1.0	0.8	1226	15200	8.6	21
Maximum	37	1.4	21	3.2	9.2	75	69.0	0.8	40000	144000	840	580
Mean	27	0.7	18	1.9	6.4	60	27.0	0.8	13800	54700	320	270
Standard Dev.	6.4	0.3	2.3	0.9	3.1	22	25.4	0.0[b]	15900	52600	370	220
Mode 4												
No. of cases	2	2	2	2	2	2	2	2	2	2	2	2
Minimum	24	0.5	14	3.7	1.5	61	16.0	0.8	7600	3740	68	240
Maximum	32	0.6	20	9.9	9.9	120	26.0	0.8	42000	105000	98	400
Mean	28	0.6	17	6.8	5.7	91	21.0	0.8	25000	54000	83	320
Standard Dev.	6.1	0.0	4.7	4.3	5.9	42	7.0	0.0[b]	24500	71600	21	120

[a]Al, Fe, C, EXT in percent; Pb, Cd, As, TCE, HCE, HCBUT, HCB in ppm; EXT = extractable organics, TCE = tetrachloroethylene, HCE = hexachloroethane, HCBUT = hexachlorobutadiene, HCB = hexachlorobenzene.
[b]Concentrations below detection limit given by the mean.

combustion mode considered was the upright single smokepot. The color and compactness of the residue varied with location in the canister (Fig. 2). The middle section (A) was whitish-gray in color. The shade grew darker with depth, i.e. A-1 was the lightest and A-3 the darkest. Sections B ande C were darker than A, which suggested a higher elemental carbon content. There were a few orange areas at the top and along the side of the canister, most probably from $FeCl_3$. Material from each section was separately homogenized and analyzed for major inorganic and organic constituents. The major inorganic constituents were Al, EC, Zn and Fe (Table 1). Aluminum was present mainly as oxide, while zinc and iron (from the canister) were present predominantly as chlorides and, to a lesser extent as oxides.

The stoichiometry of the smoke generation process (eqn. 1) predicts a $ZnCl_2:Al_2O_3:C$ ratio of 76.5:19.1:4.5 of the total mass of the products. Chemical data (e.g. Tables 3 and 4) suggest that $ZnCl_2$ was lost as vapor/particulate

matter from the smokepots, leaving Al_2O_3 and EC. Iron (1%), lead (50 ppm), and As and Cd (0.2–6.0 ppm) were also found. Residue concentrations of Pb, Cd and As probably reflect their concentrations in the munitions, although a direct correlation was not shown. Total ionizable chloride concentrations (determined by ion chromatography) were highest (12%) in section C (versus 4% in sections A and B) of the canister residue. The predominant species was most likely $ZnCl_2$.

The homogeneity of the distributions of inorganics in the canister residues were evaluated using a nested analysis of variance (ANOVA) design in which depths were nested within sections and canisters were replicates. The concentration of Al_2O_3 was generally highest in the upper middle section, A-1, reflecting the high Al concentrations used in this section of the smokepot to help the burning process. However, concentrations of total Al in different sections did not differ ($p < 0.95$). Appreciable quantities of zinc and chloride ion were found, especially in the outer section (C) of the canister. The chemical analyses suggested that $ZnCl_2$ was probably trapped by the high elemental carbon content of this section. However, the spatial distributions of Zn (all species), As, and Fe within a canister were homogeneous ($p < 0.95$). Analytical concentrations of EC varied significantly ($p < 0.95$) across sections and depths. Concentrations were highest at the sides and at the top (i.e. C-1), where they reached 38%. Cadmium concentrations also differed significantly across sections and depths. Concentrations of lead differed statistically across sections but not depths.

Aromatic hydrocarbons (naphthalene, methylnaphthalenes, methylphenols) were found at trace levels (2–10 ppm) in the residues in spent canisters. Since the extraction procedure was designed to maximize nonpolar species, polar species may have been present but were undetected. The analysis of composite residue samples for polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans determined their concentrations to be below the detection limit of 1 ppb. The low concentrations can be attributed to the very high temperatures (1500°C) reached during the smoke generation process [1], which lowers the chance of survival of most organics [9]. Further, the decomposition of chlorinated organics may be catalyzed by iron, zinc, and aluminum at relatively low temperatures [9]. Carbon tetrachloride yields phosgene at temperatures as low as 100°C in the presence of iron, while chloroform, dichloroethane, trichloroethylene, and tetrachloroethylene (formed by pyrolysis hexachloroethane) give detectable amounts of phosgene around 300°C [9]. Chlorinated aliphatics were not detedcted. The probable mechanism of loss was through $AlCl_3$-catalyzed Friedel–Crafts alkylation of the toluene.

The organic compounds in deposited residues differed from those identified in canister residues. The major organic compounds identified in deposited residues were HCE (100–500 ppm), HCB (5–150 ppm), HCBUT (5 ppm) and phenols. Small amounts of sample, and contamination during storage and ex-

traction with toluene, limited the characterization of aromatic hydrocarbons in deposited residues. The presence of aliphatic hydrocarbons probably reflects contamination from storage of samples in polyethylene bags and glass vials with polyethylene liners. These variations in composition might reflect differences in local temperature and oxygen concentration within an ignited pot, transport and secondary reactions of emitted compounds, inefficient trapping of trace compounds, and other factors.

Because the collection area was kept constant while the percentage of the surface area sampled increased, little or no material was found in collection plates beyond 2 m (Table 2). This is consistent with observations made during these trials that most of the deposited material was sputtered from the canister by the force of the combustion. Also, a previous field study [5] had shown that concentrations in the smoke aerosol decreased exponentially with distance to beyond 150 m. Hence, a corrected weight (cwt) was obtained by dividing the raw weight by the proportion of the area sampled. The mean corrected weights were 237 g/m^2 (0.5 m), 507 g/m^2 (2 m), 46.7 g/m^2 (5 m).

The ecological importance of deposited residues was assessed by regressing log (corrected weight + 1) (i.e. lcwt) against distance (eqn. 2). The maximum distance residue was distributed, 5.4 m, was estimated by setting lcwt to zero. An estimate of the total mass of material deposited within 5.4 m from a single upright smokepot, 2,945 g, was obtained by numerically integrating eqn. (2) between the limits 0 m and 5.4 m. The deposited material was about 22% of the initial smokepot mass.

$$\text{lcwt} = -8.010 \text{ ldist}^2 + 14.870 \text{ ldist} \quad (r^2 = 0.993, 13 \text{ df}) \tag{2}$$

In summary, Trial 1 revealed that 17–23% of the original mass remained in the canister as residue. Most of this residue was inorganic oxides and chlorides (Al_2O_3, EC, $ZnCl_2$, $FeCl_3$, Fe_2O_3). Trace amounts of Pb, Cd and As were also found. Organic compounds were a minor portion of total residue mass. The readily identified organic components were aromatic hydrocarbons. In contrast, material deposited outside the canister was characterized by unused and partially used reactants and their products, including TCE, HCE, HCB, HCBUT, and chlorophenols.

Trial 2: Characterization of residues from four burn configurations

Thirty four smokepots were ignited using four burn modes: (1) single smokepot upright, (2) double smokepot upright, (3) single smokepot on side, (4) double smokepot on side. In summary, statistical analyses [10] showed that the compositions of canister and deposited residues were related to lot. For a given lot, canister residue composition was not affected by the burn mode. The composition of the deposited residue (Table 4) depended on both the burn configuration (single or double smokepot) and the burn orientation (upright or prone). As expected, about twice as much material was deposited by a stack

(either upright or prone) of two smokepots than by a single smokepot. Concentrations of organics and metals (except for Al) were higher in deposited residues from prone, than upright, smokepots. Concentrations of Zn, EC, EXT, HCE and HCB in deposited residues decreased as the deposited Al concentration increased. Deposited concentrations of Zn, EC, HCE, HCB, and EXT were positively correlated with each other. The concentration of deposited Pb was correlated, inversely and weakly, only with deposited HCB. Doubling the number of pots apparently increased the quantity of material deposited within 7 m by 40 to 80%. Upright smokepots deposited 8 times the quantity of material deposited from a similar configuration of prone pots. The reasons for this are not known. It is likely that material deposited by a prone smokepot was either vaporized by the intense heat of the flame (which shot out at least 0.5 m) or resuspended by its force.

Environmental significance

This study has shown that a single upright M5 HC smokepot deposits several hundred grams to more than a kilogram of material within 5–7 m downwind and laterally around the smokepot. Under favorable weather conditions (i.e. low wind velocity) a single upright smokepot could deposit 3 kg, as found in Trial 1. Assume that 1 kg is deposited in a semicircular area of radius 5 m. Further assume that this material resides in the first 0.5 cm of the soil. The volume of contaminated soil is 196,350 cm^3 [that is, 3.14 (500^2) (0.5)/2]. Assuming a bulk density of 1.58 g/cm^3 for the A horizon of soil in training areas where tracked vehicles are used [11], the average concentration of residue in the soil would be 3,223 mg/kg [i.e. 10^6 mg/(196,350 g × 1.58 g cm^{-1})]. If the deposition area was 7 m, the concentration in the soil would be 1644 mg/kg [i.e. 3,223 (5/7)^2 mg/kg]. The average Pb concentration in residue deposited from a single upright canister (Table 4) is: (21 + 59 + 49 + 72)/4 = 52.75 μg Pb/g residue. Hence, a single upright canister would deposit [52.75 μg Pb/g residue (3.223 g residue/kg soil)] = 170.0 μg Pb/kg soil. Estimated soil loads (μg contaminant/kg soil) from a single upright canister for the other compounds are: Al = 1,310,000; Fe = 137,000; Zn = 371.500; EC = 16,000; EXT = 45,900; Cd = 8.3; As = 2.6; TCE = 19,665 (based on geometric mean); HCE = 6054; HCBUT = 68.0; HCB = 57.0.

Concentrations of Al, Zn, and chlorinated hydrocarbons in deposited residues exceeded 1,000 mg/kg residue. Assuming (as above) that most of the deposition was within 5 m of the smokepot, the soil concentrations of these compounds contributed by the residue from a single smokepot could exceed 3 μg/kg soil The lower levels (500 mg/kg residue) of Cd, As, Pb, and Fe in the deposited residue could increase soil concentrations by 1 μg/kg. For comparison, Illinois regulations for the application of sewage sludge to agricultural land limit the incremental amount of Cd which is added to soil. In establishing a limitation to protect soils and crops from Cd poisoning, the State assumed

that normal plowing would incorporate the sludge into the first 30 cm of soil. Assuming a training area soil density of 1.21 g cm^{-3} [11], the annual limitation is equivalent to 10 μg Cd/kg soil in the top 0.5 cm.

HC smoke and individual constituents in the combustion mix, the residue, and smoke, are of toxicological concern. Rabbits and rats, for example, exposed to single doses of HC smoke and observed for up to 14 days exhibited acute inflammation, and in some cases necrosis, of the laryngeal and tracheal mucosa. Pneumonitis and pulmonary edema were observed in decedent animals. Animals surviving to the end of the experiment showed similar but much less florid changes in the respiratory tract [12]. Most of the major compounds found in the combustion mixture or in residues are of toxicological concern. Aluminum, for example, has been implicated in senile dementias of the Alzheimer's type (SDAT) and Roberts [13; p. 175] cautions that "extra sources of entry of this metal should be eliminated insofar as is possible". On ingestion or contact, zinc chloride, the prime aerosol constituent of HC smoke, affects the lungs, skin, eyes, liver, and other organs. The general toxicology of zinc chloride has been reviewed [14]. The inhalation toxicology of zinc oxide, a HC smokepot reactant and emitted by-product, has been reported recently by Lam et al. [15]. Hexachloroethane, cadmium, and other compounds in HC smoke are carcinogenic, and since chronic exposure to HC smoke increases the excess cancer risk [3], the additional exposures from residues are of concern. Hexachloroethane, phosgene, carbon tetrachloride, and hexachlorobenzene are listed under the Resource Conservation and Recovery Act [16] as hazardous wastes.

Conclusions

Assessment of the ecological significance of deposited residues is based on both the composition of the residue and its quantity. Although this study does not provide robust estimates of quantity because samples were not taken at enough distances to properly characterize the deposition curve, the data do indicate that relatively large quantities of toxic chemicals are deposited within 5 m of the munitions. Factors such as munitions orientation during ignition, the number of munitions ignited simultaneously, lot, and probably wind speed and relative humidity, affect residue quantity and composition. This work indicates that further studies of the deposition, chemistry and toxicology of emitted and retained residues is warranted. Although canister residues are not "hazardous wastes" (as defined by the EP toxicity test [16]), exposures to canister residues and to contaminated soils should be minimized.

Acknowledgments

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