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Federal Agents Use $ZnCl_2$ Gas Against Black Lives Matter Protesters

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Abstract

Law enforcement's use of chemical weapons is a threat to human and environmental health, exemplified during 2020 Black Lives Matter (BLM) protests in Portland, OR, where city, county, state, and federal agencies have deployed various chemicals for over 100 days. In July, US Department of Homeland Security (DHS) agents used an exceptionally toxic and unknown weapon to quell free speech in support of Black lives and against federal presence. With significant support from the community, I combined first-hand accounts, print media, videos and photos of munitions, primary literature, and analytical chemistry to identify the weapon as gaseous Zinc Chloride ($ZnCl_2$) from Hexachloroethane (HC) "smoke" grenades. I used hierarchical Bayesian methods to estimate that DHS deployed 26 (25 – 30; 95% CI) HC grenades in July, which, given the toxicity of $ZnCl_2$, was enough to kill 235 (156 – 306) people. Although no fatalities have been associated with this $ZnCl_2$ release thus far, it has led to acute, delayed, and persistent major health issues in the exposed population, including bystanders. Further, symptoms overlap with influenza/COVID-19 and Zn is not regularly assayed in patients, hampering medical diagnoses. Given alignment of novel mass symptoms with prior case histories, however, $ZnCl_2$ is certainly the causal agent and has created an ongoing human and environmental health crisis extending well beyond the protests' footprint in downtown Portland. DHS's wanton use of $ZnCl_2$ against protesters will have lasting impacts for decades and was identified through a community of civilians standing up to say Black Lives Matter.

Significance Statement

The US Army Chemical Warfare Service invented Hexachloroethane (HC) smoke screens after World War I, but by the mid-1950s armed services around the world were well-aware of HC's acute and chronic toxicity. The "smoke" produced by HC devices is gaseous Zinc Chloride ($ZnCl_2$), a known lethal compound that induces heavy metal poisoning ("metal fume fever"); chemically burns dermal, bronchial, and gastrointestinal epithelia; and bioaccumulates. Despite well-established impacts, US Department of Homeland Security (DHS) agents deployed HC in Portland Oregon to quell Black Lives Matter protests in July 2020. I use a hierarchical Bayesian model that combined multiple observation streams to compile community-collected video and photographic evidence and estimate that DHS deployed enough grenades to kill or maim hundreds of people.

Main Text

Introduction

"The use of poison in any manner, be it to poison wells, or food, or arms, is wholly excluded from modern warfare. He that uses it puts himself out of the pale of the law and usages of war."

General Orders No. 100, Article 70, signed President Abraham Lincoln 1863 (1)

Following the murder of George Floyd in Minneapolis Minnesota on May 25 2020, Black Lives Matter (BLM) protesters took to the streets around the world to demand justice (2). In present-day Portland Oregon (on traditional land of Chinook, Clackamas, Cowlitz, Kalapuya, Kathlamet, Molalla, Multnomah, Tualatin, and Wasco Tribes), BLM protests have continued for over a hundred days, only interrupted by hazardous wildfire smoke (3-4). In response to gatherings, various law enforcement agencies have deployed chemical weapons, building upon a legacy of chemical weapons usage by Portland Police Bureau (2). Indeed, since the start of the George Floyd protests and as of October 1 2020, Portland had the most total instances of police brutality among US cities (374) and more chemical attacks (169) than the next city has total attacks (103) (Fig.1; SI Appendix) (5).

Although they were outlawed for American wartime use by Abraham Lincoln via the Lieber Code in 1863 (1) and internationally in the Hague Conventions of 1899 and 1907 (6,7) as well as the Geneva Protocol of 1928 (8), chemical weapons have a long history of use by law enforcement against civilians to quell unrest (9-11). This is despite their being fundamentally indiscriminate, often deployed against specifications, and lethal (9-11). In the United States, the use of chemical weapons exacerbates systemic inequities and limits constitutionally protected expression of speech and assembly (2). In Portland Oregon, law enforcement only deploys chemical weapons to prevent free speech in support of Black lives; no such actions are taken against gatherings of recognized white supremacist hate groups (2), even when occurring on the same day (12).

During the second half of July, as interest in Portland's BLM protests was resurging and focused particularly on federal presence (Fig. 2; Data Set S1) (3), agents of the US Department of Homeland Security's (DHS) new Protecting American Cities Task Force (PACTF) (13,14) deployed deadly gaseous Zinc Chloride ($ZnCl_2$) via Hexachloroethane (HC) Smoke grenades (Figs. 3, S1-S24) during Operation Diligent Valor (15). At the time, $ZnCl_2$ was not a familiar chemical weapon nor were HC cans among any munitions recovered in the previous two months of protests (Fig. S25). Indeed, it took an incredible effort by frontline journalists, scientists, community leaders, legal observers, medics, and protesters to document the munitions so that HC use could be definitively identified, tied to DHS, and connected to production by Defense Technology, a subsidiary of The Safariland Group (SI Appendix, Fig. S26).

Hexachloroethane is a munitions "smoke" developed in the early 1930s by the US Army Chemical Warfare Service that was understood by the mid-1940s to be a poisonous chemical agent (16-18) and which has since been replaced throughout the US Armed Services (19). HC itself is listed as hazardous by the International Agency for Research on Cancer, Environmental Protection Agency, Department of Transportation, Occupational Safety and Health Administration, American Conference of Governmental Industrial Hygienists, National Institute for Occupational Safety and Health, and National Toxicology Program (20) and has significant human and environmental health consequences. A more dire result of the use of HC grenades, however, is that they produce a high volume (> 75% of all products w/w) of gaseous $ZnCl_2$, a lethal vapor during the focal reaction (21-23):

$$C_2Cl_6 + 3ZnO \rightarrow 3ZnCl_2 + Al_2O_3 + C \qquad \text{(Eq. 1).}$$

Additionally, due to the high-energy of the reaction, many noxious gaseous byproducts are created depending on temperature and humidity, most notably carbon monoxide (CO), phosgene ($COCl_2$), hexachlorobenzene (C_6Cl_6), tetrachloroethene (C_2Cl_4), carbon tetrachloride (CCl_4), hydrogen chloride (HCl), and chlorine (Cl_2) (21-23).

Indeed, hundreds of cases of toxicity from HC smoke have been documented across the intervening decades, showing a range of significant symptoms including immediate dyspnea, coughing, lacrimation, chest pain, vomiting, nausea, and mucosal irritation; delayed and prolonged inflammation of skin and internal organs as well as tachycardia; chronic genotoxicity of the bronchial epithelium; and an average fatality rate of 0.14 among case clusters (24). HC smoke has further significant effects on the environment, including defoliation and long-term reduction in tree growth (25,26) and stunted development, scale deterioration, skeletal weakness, and bioaccumulation in fish (27-29). Given the lethality of its products, the wanton use of HC by DHS in Portland is incredibly alarming and warrants significant further investigation.

The goal of this manuscript was therefore to estimate the quantity and scope of DHS's HC use by combining multiple data streams of observations (visual confirmations, recovered canisters) on HC use into a single Bayesian hierarchical model (30,31) fit using a Gibbs sampler. I then sampled the protest environment (soil, plants, clothing, canisters, ground, tent) for signatures of HC use (Zinc, Hexachloroethane, other chlorinated hydrocarbons) using standard analytical chemistry methods (SI Appendix). Such an exercise would not be necessary if DHS were to release actual chemical weapons deployment data. Given the lack of transparency regarding chemical weapons use by all law enforcement agencies in Portland, however, including retrieval of canisters to prevent identification and shooting those who touch canisters (32,33) estimation is a critical starting point on the road to understanding the scope and scale of HC's impacts.

Results

Over the course of July 2020, DHS deployed an estimated 26 (25 - 30, 95% posterior interval) grenades of hexachloroethane in the focal protest area in downtown Portland Oregon, specifically in the immediate vicinity of the Wyatt Federal Building and Hatfield Federal Courthouse (Fig. 4, Table 1). Twenty grenades were recovered (Figs. S1-24, Table S1), five more were observed being deployed by agents but not recovered (Figs. S1-S24, Table S1), and 1 (0 - 5) was estimated to be not observed or recovered. The estimated rate of HC grenade deployment (λ) by DHS during July was 0.12 grenades per hour of federal agents on the street (0.03 – 0.39, 95% posterior interval; Fig. 4, Table 1). The rate of recovery (ρ) was 0.73 (0.57 – 0.85, 95% posterior interval), notably higher than the observation rate (ν; 0.50, 0.32 – 0.68 95% posterior; Table 1).

The Gibbs sampler efficiently sampled and effectively searched the joint posterior distribution (Eq. 1). Convergence was high among the parallel chains: the potential scale reduction factors (psrf, a.k.a. Gelman-Rubin statistic; 27) being all ~1.0 (Table 1). All parameters exhibited very small MCMC autocorrelations (~0.0) and had resultingly large effective sample sizes (Table 1).

Translation of the total estimated HC deployment to $ZnCl_2$ gas produced (15,20) using published lethal doses (34) and weights (35) shows that hundreds of fatalities could have occurred (median: 235, 95% posterior interval: 156 – 306), although there was large uncertainty due to LD_{50} and weight variation among individuals. While the canisters were deployed outside, which certainly prevented many deaths, diffusion was limited by crowds of thousands of people (Fig. 2), closed tree canopies, cars, and tents (Simonis, *personal observation*). Indeed, the off-gassing $ZnCl_2$ presented significant risks to individuals in the vicinity as evidenced by high levels of zinc in environmental samples (SI Data Set 3, 36); immediate (37,38), delayed (39,40), and chronic (41,42) symptoms; and odors detectable miles away (43).

Of particular note from the environmental chemistry samples was a "spent" hexachloroethane canister (Fig. 3b,c), from which I sampled the solid residue. Ion chromatography and Gas Chromatography/Mass Spectrometry (GC-MS) identified that the residue was 27% Zinc w/w and contained hexachloroethane, identifying that the munition was not fully spent (SI Data Set S2). The grenade also contained tetrachloroethene, benzene, toluene, phthalic anhydride, Chromium, and Lead (SI Data Set S2). The spread of $ZnCl_2$ through the protest area and beyond was shown through all environmental samples having significant concentrations of Zinc (SI Data Set S2). Perhaps the most notable of which was the organic vapor filter worn by a medic outside of the plume on the far side of the protest area which contained Zinc (made gaseous as $ZnCl_2$), yet no Chromium or Lead (neither of which were made gaseous), as well as phthalic anhydride, toluene, and xylene (SI Data Set S2).

Discussion

Under ideal conditions in a wide open field at night, the concentration of $ZnCl_2$ produced by a typical HC grenade is high enough that an unmasked individual 200 yards (three city blocks in Portland) from detonation has a maximum of 24 minutes of safety before significant acute symptoms appear and an individual a full 1,000 yards away still only has 2.5 hours (16). It is unclear how $ZnCl_2$ dissipates through a densely-gassed, tree-lined urban landscape within a river valley like Portland, but reported signs and symptoms indicate that it spread widely, entered the stormwater system that flows to the Willamette River, and cut through protective equipment worn by journalists, protesters, medics, legal observers, and bystanders (37-43).

Given its bioaccumulation and the delayed severe inflammation response, $ZnCl_2$ exposure is measured cumulatively over 10 days (16,24), a departure from many presently used chemical weapons (9-11). As a highly mobile and poisonous gas that lacks an odor itself, $ZnCl_2$ poses a significant risk to humans as well as the environment (18,25). Building upon a legacy of resistance to police brutality (2), a community of protesters, activists, journalists, legal observers, and scientists standing up for Black lives documented its use and are just beginning to understand its impacts on the residents and environment of Portland. Human health and environmental impact studies are urgently needed to grasp the full impact of DHS's literal salting of the earth using Hexachloroethane smoke grenades.

Materials and Methods

Bayesian Model

Having evaluated a large volume of photographic, video, and print media, I identified deployments of hexachloroethane (HC) grenades and recovery of munitions during July 2020 (SI Appendix, Figs. S1-S24). I also estimated the time federal agents were out of their buildings and crowd size for each day from the media compilation (Fig. 2, SI Data Sets S1,S3). I combined these data with the two observation streams (visual confirmation of deployment and recovery of canister) using a hierarchical Bayesian model to infer the underlying unknown number of canisters deployed by the Department of Homeland Security (DHS) on a given day (d_i) and over all days ($D = \sum d_i$) (30,31).

The hourly rate of deployment for that day (λ_i) is a log-linear (to handle Poisson response) function of the raw intercept (λ^*) and stochastic error term (ε_i), and then is weighted by the time DHS agents were on the street/out of their buildings each night (FT_i). The number of canisters deployed each day is then a Poisson distribution with rate $\lambda_i \mathrm{FT}_i$ truncated at the minimum by the known cans deployed on that day (c_i):

$$\begin{aligned} &\varepsilon_i \sim \mathrm{Normal}(0, \sigma^2) \\ &\lambda_i = e^{\lambda^* + \varepsilon_i} \\ &d_i \sim \mathrm{Poisson}(\lambda_i \mathrm{FT}_i)_{c_i} \end{aligned} \quad \text{(Eq. 2).}$$

Deployed grenades were then subjected to each detection process via Binomial distributions: observation (regardless of recovery) is governed by rate ν to give daily observed cans o_i and by recovery (regardless of observation) by rate ρ to generate daily recovered cans r_i. The processes are joined using a third, constrained Binomial describing the number of grenades that were both observed and recovered (or_i) by applying the recovery process to observed grenades, and capping the number at the total grenades recovered. Both rates are fit on the logit scale:

$$\begin{aligned} &o_i \sim \mathrm{Binomial}(\nu, d_i) \\ &r_i \sim \mathrm{Binomial}(\rho, d_i) \\ &or_i \sim \mathrm{Binomial}(\rho, o_i)^{r_i} \\ &\nu = \mathrm{logit}^{-1}(\nu^*) \\ &\rho = \mathrm{logit}^{-1}(\rho^*) \end{aligned} \quad \text{(Eq. 3).}$$

This model therefore assumes no false positives, fair given the distinctive burn pattern and resulting canister (Figs. 2, S1-22). I used generally uninformative priors on the raw scales:

$$\begin{aligned} &\lambda^* \sim \mathrm{Normal}(0,1) \\ &\nu^* \sim \mathrm{Normal}(0,1) \end{aligned} \quad \text{(Eq. 4).}$$

$\rho^{*} \sim \text{Normal}(0,1)$
$\sigma \sim \text{Uniform}(0,100)$

I fit the model using JAGS (Just Another Gibbs Sampler, v4.2.0) (42,43) via the runjags v2.0.4-6 package (46) in R (47). I used four MCMC chains with varying starting values for parameters and ran each for 10,000 adaptation, 100,000 burn-in, and 1,000,000 final samples thinned to 10,000 per chain to total 40,000 samples across chains. I evaluated chain convergence using the autocorrelation, sample size adjusted for autocorrelation, and Gelman-Rubin statistic (30) for each parameter. All code is included within SI Data Sets S4,S5.

Potential Fatalities

I converted the estimated number of cans deployed each day to the potential number of human fatalities from $ZnCl_2$. A standard Military Style can contains 19 oz of HC mix Type C (18), there are 28.4 g in an oz, and assuming no loss of mass, 1 g of Type C mix generates 1 g products. $ZnCl_2$ constitutes 0.764 w/w of all products (23), which translates to 412.3 g $ZnCl_2$ per grenade. It is difficult to gauge specifically the lethal dose or concentration of $ZnCl_2$, given the multiple modes of uptake (inhalation, orally, dermally). Thus, for a simple approximation, I use a log-normal distribution based on nine studies included in PubChem that report LD_{50} values for mammal models (34), which has a back-transformed mean of 555 mg/kg (SI Appendix). For the distribution of human sizes, I used the most recent (2017-2018) National Health and Nutrition Examination Survey with available data (35) and combined the reported binary genders to construct a log-normal distribution with a back-transformed mean of 83 kg (SI Appendix). Thus, an average LD_{50} is ~46 g/person and an average grenade contains enough $ZnCl_2$ to kill 9.0 people. I treated the $ZnCl_2$ as a resource pool consumed by individuals up to their LD_{50} to calculate number of fatalities of each sampled MCMC iteration. All code is included within SI Data Sets S4,S5.

Chemical Analyses

I collected eleven environmental samples from a variety of sources around the areas of hexachloroethane deployment (Fig. S27, SI Data Set S2, SI Appendix). Samples were stored frozen in quart-sized mason jars until submitted to Specialty Analytical in Clackamas, Oregon for evaluation. Each sample was tested using standard EPA methods for volatile organic compounds (SW8260D and E8260D); semi-volatile organic compounds (E8270E); and Zinc, Chromium, and Lead (SW 6020B) (SI Data Set S2).

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Figures and Tables

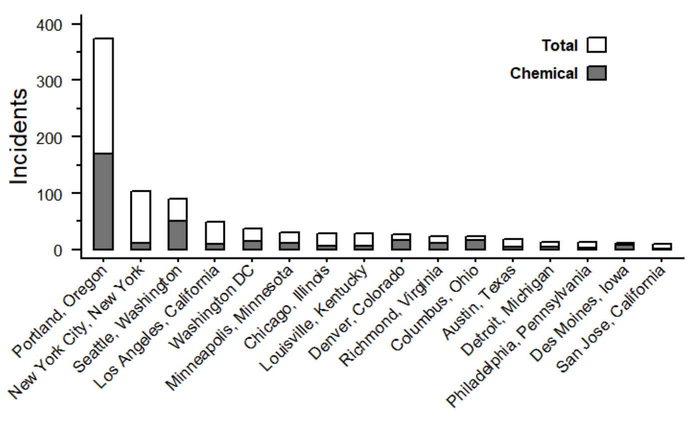

Figure 1. Total and chemical-weapons-based incidents of police brutality during the George Floyd Black Lives Matter 2020 protests through 2020-10-01 for all cities with at least 10 incidents (5).

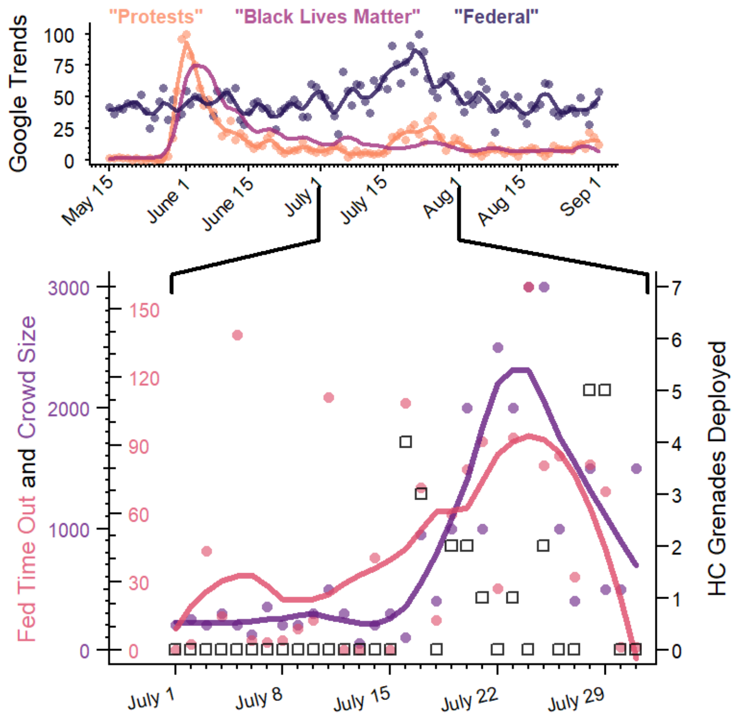

Figure 2. Top: time series of general interest (normalized Google search Trends) for the Portland Metro Area in "protests" (orange), "Black Lives Matter" (red), and "federal" (purple) during the 2020 George Floyd Black Lives Matter protest period to 1 September. Bottom: July-focused time series of crowd size (purple) and the number of minutes federal agents were out (red) each night. Box points show the number of hexachloroethane (HC) grenades used each night, based on observations and collections combined. Lines in both portions were fit using local polynomial regression (loess) (48).

Figure 3. Hexachloroethane (HC) / Zinc Oxide canisters: (a) Unexploded ordnance clearly marked as “Military Style Maximum Smoke HC” from “Defense Technology”; (b) HC ordnance off gassing Zinc Chloride mid-deployment; (c) Same canister from (b) after reaction stopped, showing charred remains of the label that matches the canister in (a); and (d) three exploded HC canisters, including the one from (b) and (c) in the middle. Photos (a) and (d) from the author, (b) and (c) from Sarah Riddle and used with permission.

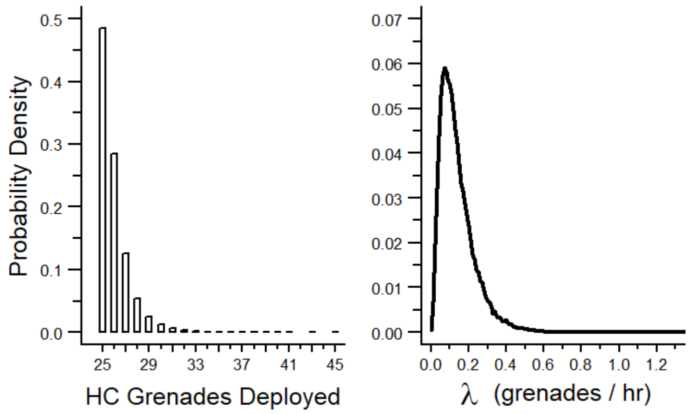

Figure 4. Posterior distributions for the number of HC grenades deployed (left) and the rate of grenade deployment (grenades per hour) (right).

Table 1. Statistical fit results and diagnostics from the Bayesian estimator of hexachloroethane grenade use.

	Lower 95	Median	Upper 95	Mean	SD	Mode	MC err	MC % of SD	SS eff	AC 1000	psrf
D	25	26	30	25.953	1.34	25					
λ^r	-3.425	-2.113	-0.859	-2.149	0.66		0.003	0.5	38820	-0.003	1.00
v^r	-0.752	0.006	0.744	0.008	0.38		0.002	0.5	39526	0.001	1.00
ρ^r	0.247	0.978	1.701	0.985	0.37		0.002	0.5	40000	0.002	1.00
σ	0.000	1.335	8.021	2.427	3.81		0.034	0.9	12730	0.013	1.00

^{r} indicates untransformed (raw) scale

MCMC diagnostics are not included for D, a state variable, just the parameters. MC err: MCMC standard error; MC % of SD: MCMC standard error as a percentage of the Standard Deviation of the posterior distribution; SS eff: Effective Sample Size; AC 1000: Autocorrelation at 1000 MCMC steps (AC 10 for the thinning interval of 100 used); and psrf: potential scale reduction factor (Gelaman-Rubin statistic; 27).