Quantifying use of lethal $ZnCl_2$ on Black Lives Matter demonstrators by United States Homeland Security

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Short title: US Homeland Security uses lethal gas on demonstrators

ABSTRACT

Law enforcement's use of chemical weapons is a threat to human and environmental health, exemplified during 2020 racial justice protests in Portland, OR. 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 help from the community, I combined first-hand accounts, videos and photos of munitions, primary literature, and analytical chemistry to identify the weapon as gaseous $ZnCl_2$ from Hexachloroethane (HC) "smoke" grenades. Using Bayesian methods, I estimated that DHS deployed 26 (25 – 30; 95% CI) HC grenades. Given toxicity that is enough $ZnCl_2$ to have killed over 200 people. Although no fatalities were reported, the exposed population experienced acute, delayed, and persistent health issues. DHS's wanton use of $ZnCl_2$ will have lasting impacts and was identified through a community standing up for Black Lives.

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 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; S1 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[9,10,11]. This is despite their being fundamentally indiscriminate, often deployed against specifications, and lethal[9,10,11]. 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 to demonstrators 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, at the time, 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[21,22,23]:

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

Indeed, despite being called Hexachloroethane Smoke grenades, the goal in using them is to produce gaseous $ZnCl_2$, which refracts light and thus creates a "smoke". 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)[21,22,23].

Hundreds of cases of toxicity from HC smoke have been documented across the intervening decades since its development, 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 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[27,28,29]. This is of particular note, as HC grenades were deployed in the catchment of Portland's untreated stormwater system that outfalls directly into nesting and rearing habitats of salmonids. 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 quantify use of HC by DHS to and provide a basis for estimating human and environmental impacts. To accomplish this, I combined 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. 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. 2). 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 LD50 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 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 yd (three city blocks in Portland, 183 m) from detonation has a maximum of 24 min of safety before significant acute symptoms appear[16]. An individual a 1,000 yd (0.9 km) away is still at risk and only has 2.5 h[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[37,38,39,40,41,42,43].

The impact of $ZnCl_2$'s novelty cannot be overstated, as both veteran and newer demonstrators, press, medics, and legal observers were unprepared for this weapon specifically. Virtually all existing chemical weapons seen prior to HC's use produced liquid or solid particles, despite being called "tear gas" for example, that could be filtered using particle filters such as respirators. As such, many individuals had insufficient filtration to remove gaseous $ZnCl_2$. Only those with filters designed for gases are able to prevent inhalation, as evidenced by the Zinc found on the medic filter (SI Data Set S2). Even when using a proper gas mask, however, $ZnCl_2$ is absorbed into the body via dermal uptake[16-18,24]. Further, given its capacity to bioaccumulate and cause delayed severe inflammation responses, $ZnCl_2$ exposure is measured cumulatively over 10 d[16,24], a significant departure from other presently used chemical weapons[9,10,11]. Despite these life-threatening differences with HC, the public was never informed of DHS's use of the weapon. Indeed, DHS has continued to deny using HC, in spite of the overwhelming evidence to the contrary.

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 in Portland, OR.

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):

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

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:

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

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

$$\begin{aligned} \lambda^* &\sim \mathrm{Normal}(0,1) \\ \nu^* &\sim \mathrm{Normal}(0,1) \\ \rho^* &\sim \mathrm{Normal}(0,1) \\ \sigma &\sim \mathrm{Uniform}(0,100) \end{aligned} \qquad \text{(Eq. 4).}$$

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.

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 11 environmental samples from a variety of sources around the areas of hexachloroethane deployment (Fig. 5, SI Data Set S2, SI Appendix):

[1] **Medic Filter**: filter medium from a NIOSH Organic Vapors DMA 6001 filter set worn by a medic only on 2020-07-27, 2020-07-28, 2020-07-29 in the area of SW 4th and Main. Medic only brought out mask when chemical weapons were used and always positioned themselves outside of the visible plume to treat individuals as they came out.

[2] **HC Can**: dust/particle residue from inside Defense Technology Hexachloroethane (HC) Smoke can deployed and recovered post "completion" on 2020-07-28 night into 2020-07-29 (Fig. S16).

[3] **A's Backpack**: Cut out from a black Jansport backpack that was worn by a protester the night of 2020-07-23 and prepped for sampling thereafter.

[4] **3rd and Salmon Plants**: shrub within the fence at the Federal Courthouse and Tree at the corner of Lownsdale, samples taken 2020-07-27 night after a bleach smell was noticed and 2020-07-28 during the following daytime.

[5] **Lownsdale Surface Soil SW 3rd and Salmon**: Scoop of topsoil from the NE corner of the park taken 2020-07-28 midday.

[6] **SW 3rd Street**: samples of paper and other refuse on the street in front of the Federal courthouse on 3rd near Salmon from immediately after a bleach smell was noticed 2020-07-27 into 2020-07-28.

[7] **E's Shirt**: water taken from a soak of a shirt worn by a protester on 2020-07-26 into 2020-07-27, with noticeable bleach-like smell and visible loss of coloration.

[8] **Green Smoke Can**: dust/particle residue from inside Defense Technology Green Smoke canister deployed and recovered post "completion" on 2020-07-28 into 2020-07-29.

[9] **S's Leggings**: water taken from a soak of leggings worn by protester recovering spent canisters 7-28 into 7-29.

[10] **Witches' Tent**: passive sample taken from existing cotton rounds, paper towels, etc that were present in the Witches' medical tent in Lownsdale the night of when the tent reeked of bleach 2020-07-26.

[11] **Spicy Bucket Scrape**: residue scraped from inside of a Home Depot 5 gallon bucket used to cover smoke and gas canisters during 2020-07-27 and 2020-07-28 nights.

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).

ACKNOWLEDGEMENTS

This work would not have been necessary without federal law enforcement's desire to poison a city to show how much they believe Black lives don't matter, and would not have been possible without civilians standing up despite the wanton use of chemical weapons to say that Black lives DO matter. Front-line journalists including Alissa Azar, Garrison Davis, Robert Evans, Mariah Harris, Laura Jedeed, Jacob Hanning, Melissa Lewis, Sergio Olmos, Mac Smith, Tuck Woodstock and many anonymous individuals provided invaluable documentation. Additional contributions to the dossier are cited in SI Appendix. Substantial thank you to the Don't Shoot Portland team for documenting, researching, and organizing around use of chemical weapons in Portland; Sarah Riddle for life-cycle documentation; The Recompiler Magazine for aggregated protest news; and Eric Greatwood for particularly useful standardized footage. Mason Fidino gave helpful feedback on the model and Sandy Simonis provided editing support. Black Lives Matter. Land Back.

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TABLES

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
ν^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).

FIGURES

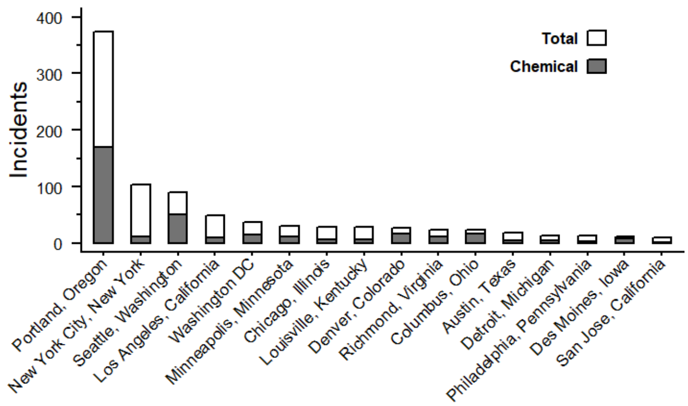

Figure 1. Total and chemical-weapons-based incidents of police brutality during the George Floyd Black Lives Matter 2020 protests through 2020-10-01 for all cities with at least 10 incidents.

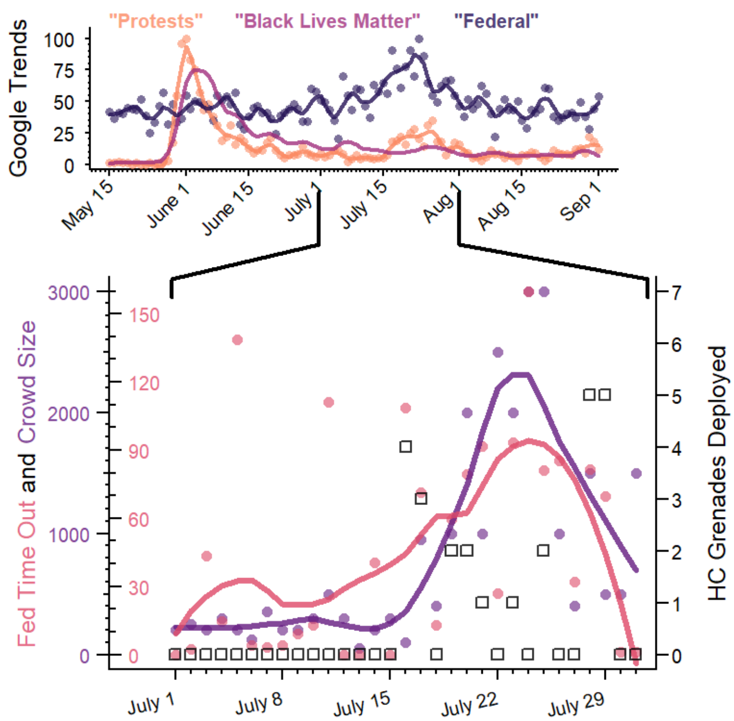

Figure 2. Top: time series of general interest (normalized Google search Trends) for the Portland Metro Area in "protests" (orange), "Black Lives Matter" (red), and "federal" (purple) during the 2020 George Floyd Black Lives Matter protest period to 1 September. Bottom: July-focused time series of crowd 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.

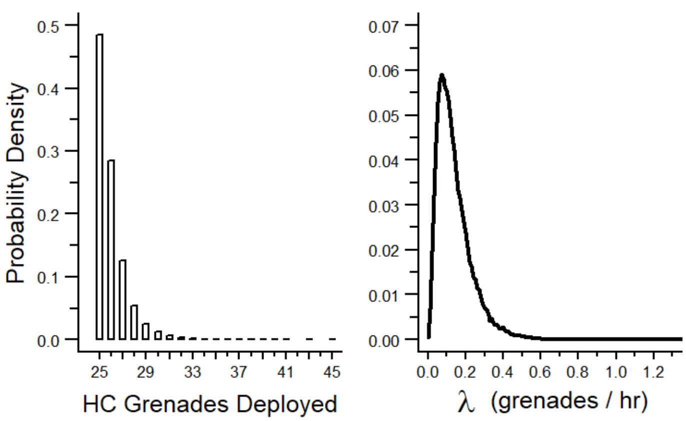

Figure 4. Posterior distributions for the number of HC grenades deployed (left) and the rate of grenade deployment (grenades per hour) (right).

Figure 5. Sample locations and pictures for the 11 environmental chemistry samples taken around the downtown area of present-day Portland, OR. (a) Medic Filter, (b) HC Can, (c) A's backpack, (d) 3rd and Salmon Plants, (e) Lowndsdale Surface Soil SW 3rd and Salmon, (f) SW 3rd Street, (g) E's Shirt, (h) Green Smoke Can, (i) S's Leggings, (j) Witches' Tent, (k) Spicy Bucket Scrape. Blue lines on the street map show the streets drained by the stormwater system that empties unfiltered into the Willamette river.