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Release of 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) from polymer-bonded explosives (PBXN-109) into water by artificial weathering

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Abstract

Polymer-bonded explosives (PBX) fulfil the need for insensitive munitions. However, the environmental impacts of PBX are unclear, even though it is likely that PBX residues from low-order detonations and unexploded ordnance are deposited on military training ranges. The release of high explosives from the polymer matrix into the environment has not been studied in detail, although polymers degrade slowly in the environment thus, we anticipate high explosives to be released into the environment. In this study, PBXN-109 (nominally 64% RDX) samples were exposed to variable UK climatic conditions reproduced in the laboratory to determine the effects of temperature, UV irradiation and rainfall on the release of RDX from the polymer binder. The most extreme conditions for spring, summer and winter in the UK were artificially reproduced. We found that up to 0.03% of RDX was consistently released from PBXN-109. The rate of RDX release was highest in samples exposed to the summer simulation, which had the lowest rainfall, but the highest temperatures and longest UV exposure. This was confirmed by additional experiments simulating an extreme summer month with consistently high temperatures and long periods of sunlight. These results probably reflect the combination of polymer swelling and degradation when samples are exposed to higher temperatures and prolonged UV irradiation.

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Keywords: polymer-bonded explosives, PBXN-109, 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), release, artificial weathering

Graphical Abstract

Abbreviations

PBX	polymer bonded explosives
RDX	1,3,5-trinitroperhydro-1,3,5-triazine
HTPB	hydroxyl-terminated polybutadiene
DOA	di-(2-ethylhexyl)-adipate
UV	Ultraviolet
HPLC	high performance liquid chromatography
IPDI	isophorone diisocyanate

Introduction

Polymer bonded explosives (PBX) are designed to meet the need for insensitive munitions, which minimise the risk of inadvertent initiation while reliably fulfilling their intended detonation functions (Ang and Pisharath, 2012). PBX compositions typically consist of a nitramine high explosive encapsulated by a polymer binder, which confers insensitivity by protecting the explosive with a flexible and rubber-like coating (Shee et al., 2015). One of the most common nitramines in PBX is 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), accounting for up to 95% of the composition.

RDX is a common soil contaminant at manufacturing sites and on military training ranges. Low order and blow-in-place detonations of legacy compositions such as Composition B can deposit thousands of milligrams of RDX on soil surfaces (Jenkins et al., 2006). Unexploded ordnance can also cause contamination when damaged because the high explosive filling is then exposed to the climate (DuBois and Baytos, 1991).

The fate and transport of RDX is highly dependent on location due to differences in climate and soil type (Larson et al., 2008). Solid RDX particles can remain in the top layer of soil for a long time

(Sheremata et al., 2001) but are more likely to undergo slow biodegradation under anaerobic conditions, yielding other undesirable contaminants such as methanol and hydrazine. RDX does not significantly adsorb to soil (Singh et al., 1998) and dissolved RDX therefore tends to migrate (Selim et al., 1995). However, RDX has low solubility in water and is unlikely to exceed current threshold limits of 2 µg/l in groundwater (Gauthier et al., 2003; Pichtel, 2012). RDX becomes more soluble at higher temperatures, doubling with every 10°C increase, so water contamination is a more significant problem in warm, wet climates (Lynch et al., 2002). Because RDX leaches slowly in temperate regions, it accumulates on or just beneath the soil surface, presenting a risk to humans, animals and plants due to its extreme toxicity (Pennington and Brannon, 2002; Pichtel, 2012). This may be exacerbated by PBX materials because the polymer protects RDX from the climate and may prevent RDX crystal distribution, resulting in more surface contamination than non-bonded high explosive. However, many polymers swell at higher temperatures and degrade when exposed to UV light, which may release RDX into the environment (Adeniyi and Kolawole, 1984).

We investigated the environmental fate of PBXN-109, an aluminized, cast-and-cured secondary explosive containing 64% RDX and 8% polybutadiene binder. The aim was to determine the effect of a variable climate on the rate at which RDX leaches from the PBXN-109 polymer matrix under controlled laboratory conditions. Samples of PBXN-109 were exposed to predetermined doses of UV irradiation and water at controlled temperatures to simulate variable conditions, i.e. cold and wet vs. hot and dry. The release of RDX from PBXN-109 was measured by analysing the RDX content of the water run-off.

1. Materials and methods

2.1 Preparation of samples

Samples of PBX (RWM Italia SpA) were supplied as small spheres (~1.5 g each / diameter = 0.5mm) containing 64% RDX, 20% aluminium, 8% hydroxyl-terminated polybutadiene (HTPB) and 8% di-(2-ethylhexyl)-adipate (DOA). The RDX content was confirmed by acetone extraction from pristine PBXN-109 in a Soxhlet extractor. The samples were used as supplied and loaded into Buchner

funnels (4 cm diameter) fitted with a glass frit before exposure to variable climate conditions (Taylor et al., 2015, 2009).

2.2 The UK climate

Climate conditions representing South-West England were simulated in the laboratory to mimic the exposure of PBXN-109 on military ranges. Climate data from 1990–2014 were obtained from the UK Meteorological Service website (Met Office website) (**Table 1**). The highest seasonal averages for rainfall, temperature and sunlight hours were identified and used in laboratory simulations to provide representative worst-case exposure scenarios. Autumn climate conditions were not reproduced in the laboratory due to the similarity between the autumn and winter rainfall and temperature, and number of daylight hour's falls between spring and winter values therefore can be estimated to be between the two.

The volume of simulated rainfall deposited on the PBXN-109 samples for winter, spring and summer was determined by calculating the equivalent rainfall on the area of the sample within the Buchner funnel housing. The rainfall was calculated by multiplying the maximum seasonal average rainfall (mm/m^2) by the area of the sinter funnel. The average sunlight per day was determined by dividing the maximum seasonal average by 90 days (the average number of days in a season) (**Table 1**). Maximum and minimum average temperatures were also taken into consideration.

Table 1: Average climate conditions in South-West England during the period 1990–2014.

Season	**Seasonal Rainfall**		**Seasonal Temperature**		**Seasonal Sunlight Hours**	
	Season average (mm)	**Equivalent artificial rainfall (mL)**	**Max. (˚C)**	**Min. (˚C)**	**Average (h)**	**Average/ day (h)**
Winter	694	872	10±1	0±1	210	2.5
Spring	332	599	15±1	3±1	601	6.75
Summer	476	417	22±1	10±1	721	8
Autumn	624	784	9±1	5±1	360	4

2.3 Simulating the UK climate under controlled conditions

Seasonal variations were simulated in the laboratory on an accelerated timescale of 11–15 days depending on the average number of rainy days in the 3 seasons under investigation. Duplicate samples, of individual spheres of PBXN-109 were housed in self-contained temperature controlled chambers to simulate the artificial seasons. The climate chambers were designed to eliminate any non-controlled sources of light, heat or water. Samples were exposed to the seasonal maximum and minimum temperatures over alternating 24-h periods to represent natural temperature fluctuations between night and day. Rainfall was simulated using peristaltic pumps to deliver a daily dose (8 mL/hour) of ultrapure water from a MilliQ Water Purification System equivalent to the average UK seasonal rainfall on a similar area (see Supporting Information for daily volumes of applied water). The maximum volume of water delivered each day was 90 mL, resulting in a minimum dry period of 11.5 hours per day. The run-off was collected in 500-ml wide-neck amber jars. Daylight hours of intense UV during the summer were simulated using a Philips high intensity UV lamp (HPW125WTPH), and daylight hours during the winter and spring were simulated using a BTL low-intensity UV tube lamp. Duplicate samples were simultaneously exposed to temperature, rainfall and sunlight representative of UK spring, summer or winter. The artificial conditions for each sample are summarized in **Table 2**.

Table 2: Summary of the conditions used for seasonal simulations.

Experiment reference	**Sample Mass (g)**	**Temperature (˚C)**		**Average UV (h/ day)**	**Total Rainfall (mL)**	**Duration of Artificial Season (days)**
		Min (7 days)	**Max (7 days)**			
Winter 1	1.66	0	10	2.5	830	15
Winter 2	1.42				846	
Spring 1	1.60	5	15	6.75	572	11
Spring 2	1.60				451	
Summer 1	1.60	10	22	8.0	465	14
Summer 2	1.60				404	
Extreme 1	1.14	22		13	389	11
Extreme 2	1.12				329	

2.4 High performance liquid chromatography

Sample run-off was collected every 24 h and analysed by high performance liquid chromatography (HPLC) to determine the percentage loss of RDX from the PBXN-109 sample. The HPLC system consisted of a Waters Alliance 2695 equipped with a Waters 996 photodiode array detector. The chromatographic separations were performed on ACE UltraCore 2.5 SuperPhenylHexyl columns (100 x 4.6 mm internal diameter) maintained at 35°C. A mixture of acetonitrile/water (3:2) was used as the mobile phase at a flow rate of 1.5 ml/min. A linear calibration curve for RDX was obtained for the concentration range 0.1–20 µg/ml.

2. Results and discussion

The samples of PBXN-109 were formulated with 64% RDX, which gave ~1 g of RDX in each sample. The concentration of RDX found in each run-off sample was determined by HPLC and expressed as a percentage based on the quantity of RDX in the sample. The total amount of pure RDX recovered from a single sphere of PBXN-109 during a laboratory season was small (3mg), probably reflecting the inability of water to penetrate deeply into the insoluble polymer matrix. However, RDX contamination could still pose a problem when frequently using PBXN-109 filled munitions over long periods of time.

The results from the first series of experiments aiming to replicate UK spring, summer and winter seasons are shown in **Table 3**. They revealed that more RDX was lost from PBXN-109 samples exposed to summer conditions (up to 2.74 mg RDX lost by the season end). The summer samples were exposed to 50% less water than the winter samples, confirming that the polymer binder limits the migration of water to accessible RDX crystals regardless of the volume of water applied. The temperature of the applied water was identical for all samples, so the higher concentration of RDX is unlikely to reflect its greater solubility at higher water temperatures.

PBXN-109 samples under spring and winter conditions lost similar percentages of RDX even though the spring accelerated season ended four days sooner than the winter season and less water was used,

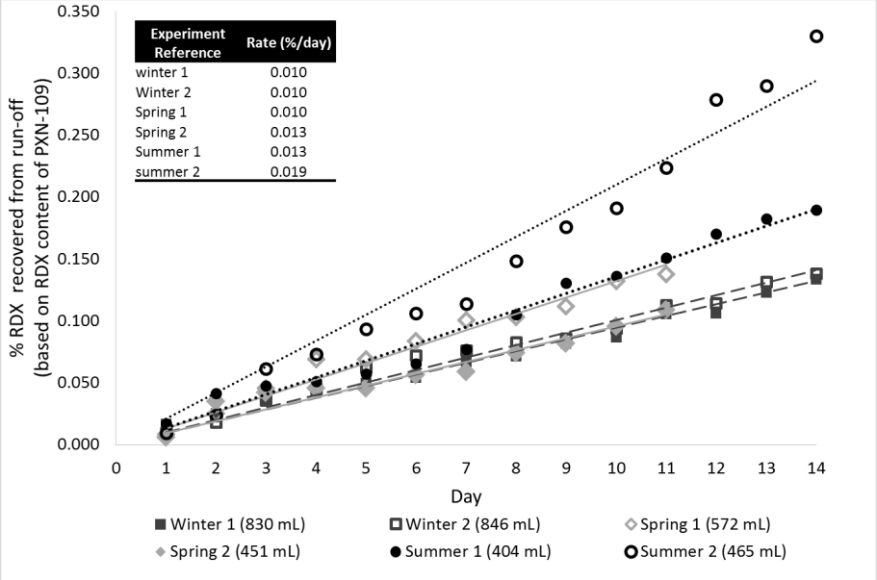
again indicating that rainfall alone is not responsible for RDX release. The percentage of RDX migrating from each replicate summer sample was noticeably different, even though the two samples received similar volumes of water at identical temperatures with the same amount of UV exposure. These differences may reflect inconsistencies between the PBXN-109 samples in terms of composition, e.g. differences in the average RDX content, the accessibility of the RDX crystals, or the micro-structure of the polymer (such as cracking).

Table 3: Summary of mass and percentage release of RDX from PBXN-109 samples at the end of the artificial seasonal.

Sample	RDX mass recovered (mg)	% Loss	Total UV Exposure	Total Rainfall (ml)	Days
Winter 1	1.56	0.11	37.5	830	15
Winter 2	1.40	0.12		846	
Spring 1	1.40	0.14	74.25	572	11
Spring 2	1.11	0.11		451	
Summer 1	1.75	0.19	112	404	14
Summer 2	2.74	0.33		465	

The rate of release indicated that RDX release was accelerated under the warmer and drier summer conditions compared to the cooler spring and winter conditions - 0.01%/ day for Winter 1 and Winter 2 samples compared to 0.013 %/day and 0.019 %/day for Summer 1 and summer 2 samples respectively (**Graph 1**). Spring sample 1 was exposed to 121 mL more water than sample 2 and lost more RDX, but this difference is more likely to reflect random differences in the distribution of RDX and the polymer structure given that the opposite effect was observed for the summer samples.

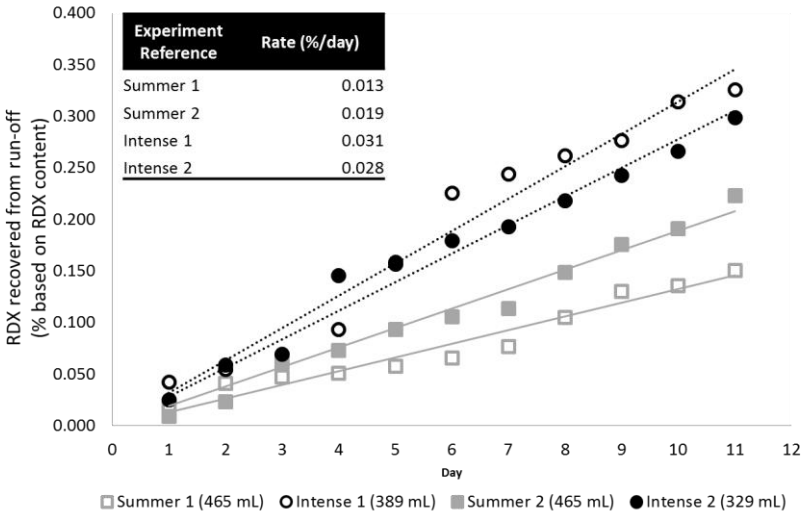
Graph 1: Rate of RDX release from PBXN-109 during artificial seasons: spring (11 days), summer (14 days), and winter (15 days).



These results suggest that the rate of RDX release from the PBXN-109 was accelerated by high temperatures and exposure to sunlight, and was not dependent on the volume of rainfall (Lynch et al., 2002). This differs from pure RDX, where the limiting factor is its solubility, which is mainly dependent on the water temperature and the volume of rainfall.

The effect of high temperatures and UV on the rate of release of RDX from PBXN-109 was investigated further by exposing two additional samples of PBXN-109 to a consistently warm climate (22°C) and 13 h UV irradiation per day, to simulate long periods of hot and bright weather (**Graph 2**). Water was applied at a volume that was representative of a dry summer (389 and 329 ml). The results confirmed that prolonged warm temperatures and intense UV exposure accelerate the release of RDX from PBXN-109 from 0.013 %/day and 0.019%/day for summer 1 and summer 2 samples compared to 0.031 %/day and 0.028 %/day for Intense 1 and Intense 2 samples. . The increase in rate of RDX release may reflect the swelling of the polymer matrix at higher temperatures, which would make it easier for water to penetrate. Furthermore, polybutadiene polymers are known to degrade under UV light, which might cause additional cracking in the matrix allowing water to penetrate deeper into the PBXN-109 and wash out the RDX.

Graph 2: RDX release from PBXN-109 at constant 22°C temperature and maximum UV exposure (13 h/day).



3. Conclusion

RDX does migrate from the polymer matrix of PBXN-109 when exposed to simulated seasonal conditions. The rate of release is low but consistent, and PBXN-109 deposits on ranges are therefore likely to result in RDX contamination in the environment by dissolution and transport in water. We also found that the rate of RDX release is accelerated in warm temperatures with intense UV exposure, probably reflecting a combination of polymer swelling and degradation allowing more access to the encapsulated RDX crystals. The results presented in this manuscript are preliminary, and long term work is currently underway to fully investigate the rate of RDX release from PBXN-109 in artificial and real environments.

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