Environmental Research 239 (2023) 117378



Contents lists available at ScienceDirect

Environmental Research

journal homepage: www.elsevier.com/locate/envres





Persistence of 2,4,6-triamino-1,3,5-trinitrobenzene in the environment

Olivia Christian, Michael Spencer, Melissa Ladyman, Federica Persico *, Encina Gutierrez-Carazo, Evie Kadansky, Tracey Temple

Cranfield University, Centre for Defence Chemistry, Defence Academy of the United Kingdom, Shrivenham, SN6 8LA, UK

ARTICLE INFO

Keywords:
TATB
Insensitive high explosive
Open burning
Soil columns
Disposal methods

ABSTRACT

2,4,6-triamino-1,3,5-trinitrobenzene (TATB) is an Insensitive High Explosive (IHE) that is increasingly being used as a safer alternative to traditional energetic materials. However, the high thermal stability of TATB poses challenges for its disposal, particularly through existing open burning methods and its ability to remain in the environment for long period of time. Therefore, this study investigated the persistence of TATB in the environment by conducting small-scale experiments which were designed to examine the resistance of TATB to open burning and to assess unburnt residues. To evaluate the fate and transport of the unburnt materials in soil, laboratory-scale soil column transport studies were conducted to gauge the movement of TATB through soil. The results indicate that TATB exhibits a high resistance to burning, leaving unburnt materials that can persist in soil. The study emphasizes the importance of efficient disposal methods for explosives and highlights the need for further research to understand the environmental impact and toxicity of TATB.

1. Introduction

2,4,6-Triamino-1,3,5-trinitrobenzene (TATB), is an insensitive high explosive (IHE) with an explosive hazard division of 1.5 making it a suitable filling for insensitive munitions (IM) (Boddu et al., 2010) as it reduces the intrinsic hazards and risks associated with accidental and combat stimuli (NATO, 2018). TATB is being brought into service to replace sensitive energetic materials such as 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), without sacrificing performance. One of the main risks associated with IHE use is the potential for contamination of drinking water and further consequences on the terrestrial environment (Persico et al., 2022). Protecting the soil environment has become one of the biggest concerns of the last two decades, with increasing research and legislation around the world to ensure security of soils and decrease soil degradation (DEFRA, 2018; European Commission, 2021; Ministry of Defence, 2021; UNCCD, 2017). Moreover, hundreds of thousands of dollars have been invested to remediate contaminated environments following migration of explosive compounds in the groundwater system (Bortone et al., 2019).

TATB is a nitroaromatic explosive with high thermal stability, with thermal decomposition at greater than 250 °C and an autoignition temperature of 358 °C (Dobraz, 1995; Watt et al., 2006; Yan et al., 2020). The three amino groups have six two-sided C–H bonds, which exhibit a self-inhibitory effect arising from the strong intra and inter molecular hydrogen bonds between the amino hydrogen atoms and neighbouring oxygen atoms. Therefore, TATB arranges into a graphite-like structure, which may contribute to its insensitivity to shock, thermal or impact stimuli (Fig. 1) (Manaa et al., 2009). These factors contribute to the difficulty of disposing of TATB by open burning as complete combustion of TATB is not achievable even at high temperatures.

The thermal properties impart a resistance to burning, resulting in unburnt solid pieces of TATB in the environment after open burning which could make their way into soil and water. TATB has strong π-π stacks between the adjacent benzene rings (C. Zhang et al., 2008), which will readily interact with humic material which is in the soil organic matter. Zhang et al. (2009) suggest that non-hydrophobic sorption of nitroaromatics to soil is due to the π-π interactions (Arthur et al., 2017; D. Zhang et al., 2009). Unburned explosive may also be transported to waste disposal facilities not equipped to manage explosive waste causing a compliance and explosive risk.

TATB has a toxicity category of 3, which means it is mildly toxic and irritating, and does not directly cause health issues to environmental receptors (Jorgenson et al., 1976). However, it is bright yellow in colour and remains so after burning, and when exposed to ultraviolet light takes on a green colour (Williams et al., 2003). Although, colour changes of TATB have been attributed to various factors, such as humidity and

* Corresponding author.
E-mail address: federica.persico@cranfield.ac.uk (F. Persico).

https://doi.org/10.1016/j.envres.2023.117378
Received 23 August 2023; Received in revised form 29 September 2023; Accepted 10 October 2023
Available online 11 October 2023
0013-9351/© 2023 The Authors. Published by Elsevier Inc. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

temperature as well as light, which can change the chemical structure and physical crystallisation of the explosive which leads to colour changes that can vary from green to brown (Manaa et al., 2002; Tian et al., 2017; Williams et al., 2003; Xiong et al., 2014). As the potential toxicity associated with green/brown/yellow TATB remains unexplored, the presence of a pigmented contaminant on the soil surface possesses the capacity to generate adverse public perception (Ladyman et al., 2019), particularly given that these incidents may occur within areas that are easily accessible by the public where disposal may happen on training ranges, which are often also designated Sites of Special Scientific Interest. Moreover, TATB it is likely to be used in conjunction with fluorinated polymers such as per- and polyfluoroalkyl substances as binders. (Yeager et al., 2010). There is evidence that PFAS is a major contaminant and is currently used regularly in military applications worldwide (Field et al., 2017; Hu et al., 2016). Therefore, it is essential to understand if these combinations leave behind residues to have the potential to contaminate the environment.

Traditionally explosives are disposed of by open burning as this is a quick, safe, efficient, and cost-effective method but due to the high thermal stability of TATB these methods used for burning can be ineffective. This can occur if the temperature of the open-burn is not high enough nor a consistent temperature, e.g. if the centre of the flame is 400 °C and the outer area is only 200 °C, or cools down throughout the burn. Complete thermal decomposition of TATB may not be possible at typical open-burn temperatures resulting in unburned residue as the ignition temperature of TATB is above 230 °C (Glascoe et al., 2010). It is common to add other waste materials such as contaminated paper and cardboard, and chemical accelerants or waste solvents to increase the burn temperature and longevity of a burn. Even optimising the structure of the material to be burned to increase oxygen flow is rarely sufficient to produce a high enough temperature to ignite TATB (Glascoe et al., 2010). Manufacturers may resort to disposing of large stockpiles of TATB in combination with other High Explosives, such as HMX, to generate higher temperatures; the issue with this is the amount of TATB that can be disposed of at one time is limited by the availability of HMX and safe quantities for disposal, resulting in the accumulation of TATB in local stores waiting for disposal increasing risk to safe storage. Moreover, there is an increased hazard during open burning at higher temperatures as TATB is proven to burn significantly faster and more erratically if external conditions are not controlled (e.g. ambient temperature burns) (Glascoe et al., 2010). To ensure efficient disposal of explosives by open burning it is essential to generate a sufficiently high temperature through optimisation of the composition and geometry of the burn. Thus far, no research has shown the efficiency of disposal *via* open burning of TATB, which can lead to improper burning rendering TATB a potential threat for the soil environment.

Moreover, current, and potential future applications suggest that TATB could be used more frequently as it is safer to handle and transport, therefore it will see an increase of use at larger scale manufacturing plants and training and testing ranges (Prakash Agrawal and Dodke, 2021). However, like other energetic materials, the activities involving TATB can lead to contamination of the environment as improper use and disposal of hazardous materials can have severe consequences for ecosystems potentially disrupting organisms (Persico et al., 2023). Unfortunately, the toxicity of TATB is not fully understood and there is no sufficient experimental data openly available to indicate the toxicity of exposure to this explosive. However, TATB can be classed as a nitro-aromatic compound which have been shown to be toxic, such 1,3,5-tri-nitro-benzene (TNB) and 1,3-di-nitro-benzene (DNB) which have an oral LD50 in rats of 275 mg/kg and 59 mg/kg, respectively (Dorsey and Llados, 1995). There is well documented evidence related to the toxicity of different explosive compounds (Clausen et al., 2004; Jenkins et al., 2006; Walsh et al., 2005), and case studies show that the extensive use of explosives for military training and testing have been found in drinking water, demonstrating the importance of understanding the fate and environmental impact of explosives (Walsh et al., 2013). In addition, there is very limited information from open publications on the effects that TATB has on soils where it could have a long-term irreversible impact on the environment, which has been previously proven for Insensitive High Explosive compositions (Persico et al., 2023; Temple, T., Ladyman et al., 2018).

The favoured properties of TATB that impart high stability and insensitivity profile, also make it very difficult to efficiently dispose using typical open burning methods. However, due to the limited research into the environmental impacts of TATB, open burning likely remains the preferred option for disposal due to its simplicity and cost-effectiveness. Therefore, this research investigated the persistence of TATB in the environment by confirming the resistance to burning by various methods, and studied the consequences of unburnt materials remaining in and on soil surfaces. For this work a series of current burning methods were reproduced at small scale and the remaining unburnt TATB materials were examined for their persistence in soil. This was achieved by setting up laboratory scale soil columns with reproducible weather conditions and controlled TATB contamination. The main purpose was to evaluate if and how the TATB moves through the environment.

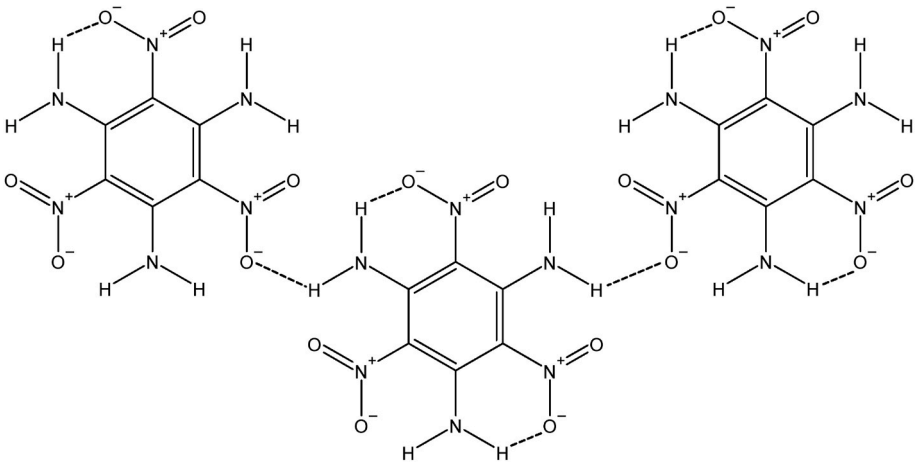


Fig. 1. Inter- and intramolecular bonding in TATB forming the graphite-like structure contributing to increasing its insensitivity to shock, thermal and impact stimuli.

2. Materials and methods

2.1. Simulated small-scale open-burning

Open burning was simulated by using steel burn trays (50 cm × 50 cm x 3 cm) laid directly on the ground in a confined hardened chamber to simulate burning in sunken burn pits. The confinement chamber has two access points, ensuring continual air flow, large enough for there to be a consistent excess of oxygen while minimising the loss of residues from inclement weather. The open burning, 10 in total (ID B1 to B10) to ensure reliability and differentiation of results, was simulated by stacking varying quantities of common waste materials (Table 1) used in manufacturing and processing of TATB. Materials such as blue roll (highly absorbent paper towel), cardboard and shredded paper, to simulate laboratory and packaging waste, were placed in the centre of the tray in either a flat or 'stacked' configuration. In the flat configuration the waste was thoroughly mixed and spread across the tray with solid pristine powder TATB (3.5 g) (acquired from an industrial partner) spread evenly across the top. In the 'stacked' configuration the waste was arranged to increase oxygen ingress by piling the shredded paper and blue roll loosely at the bottom, with the card stacked in a pyramid and TATB placed into the cone. The 'stacked' configuration was also repeated spreading the TATB evenly on the waste. For some burnings, kerosene was used as an accelerant by spreading evenly around the burn pile. The waste was ignited with a safety gas lighter and allowed to burn until completion and then left until cool.

Once cooled, the ash was collected with a sampling scoop, using filter paper to collect as much residue as possible by sweeping into the scoop and transferring to amber jars. Any large pieces of unburned or charred wood were collected separately in sterile bags. The trays were swabbed with dry cotton wool by sweeping the cotton pad over the entire plate. If excess powder remained an additional swab was used. Finally, the steel tray was swabbed with a damp cotton pad to remove any sticky explosive residue.

2.2. Open burning sample extraction

The dry cotton wool samples and the ashes collected were extracted using 50 mL of dimethyl sulfoxide (DMSO). The samples were sonicated at 70 °C for 30 min. After sonication, the mixtures were left to settle, and the supernatant was filtered using a 2 μm nylon-filter and stored at 4 °C before analysis.

2.3. Transport studies

Following transport assessment methodologies from previous studies (Persico et al., 2023; Temple, T., Ladyman et al., 2018) Clear Perspex® columns (10 cm diameter x 40 cm length) with polyvinyl chloride (PVC) (Figs. 2–3) collection funnels were fitted with stainless steel wire meshes and then placed into collection containers in triplicate. Play sand (300 g), gravel (150 g) and DI water (40 mL) were mixed and added to the bottom of the column above the meshes to minimise the loss of fine particulate sand when filling the columns. Sand was added to the column in increments of 200 g and compacted using a tamping rod (1.2 kg) until a height of 20 cm was achieved (Oliviera et al., 1996), this was to ensure a homogenous mixed column. Commercial play sand was chosen due to it being clean with low organic content. The sand (Figs. 2–4) was air-dried for 1 week and passed through a 2 mm sieve prior to use. The sand particle size was determined by passing 1 kg of sand through seven sieve sizes from 2 mm to 63 μm. The average particle size was 300 p.m., classifying the soil as sand (Warrick, 2003) and the packing density has been calculated (1457.86 ± 45 kg/m^3). Columns were saturated by adding of distilled water (800 mL) and the quantity of water that leached through was immediately recorded. The columns were left to settle for a week. Solid pristine powder TATB (0.5 g) (acquired from an industrial partner) was added to the surface of each column. Incident water was calculated to be an equivalent volume to the average yearly rainfall in South-West England and Wales from 1995 to 2015 (1160 mm) (Temple, T., Ladyman et al., 2018). Water was delivered over a 4-week period

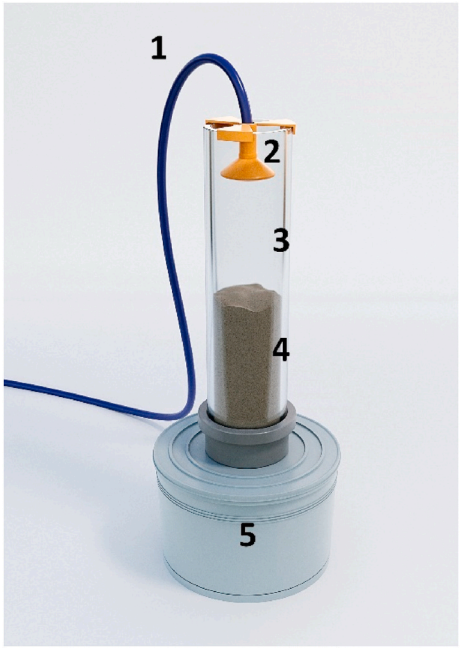


Fig. 2. Image of soil column Set-up. PVC columns (3) were set up in triplicate and filled with sand (4) covered watering can roses (2) attached to a dosing pump (1) to ensure even distribution of water. Water leachate was collected in enclosed buckets (5).

Table 1
Configuration of burning regime, common wastes used to accelerate the burns.

ID	TATB: Fuel Ratio	Configuration of burning regime	Common waste materials				
			Paper (g)	Cardboard (g)	Blue Roll (g)	Wood (g)	Kerosene (ml)
B1	1:70	TATB and materials completely mixed over entire area of tray.	65	140	40	N/A	N/A
B2	1:20	Stacked in centre using carboard to create space for oxygen ingress. TATB spread through depth.	30	35	7	N/A	N/A
B3	1:70	As B1, with kerosene added to surface as accelerant.	65	140	40	N/A	6
B4	1:20	As B2, with kerosene added to surface as accelerant.	30	35	7	N/A	6
B5	1:116	Wood added to fuel to increase duration of burn.	20	20	N/A	367	6
B6	1:44	As B5 using lower density wood.	10	10	N/A	134	6
B7	1:80	As B6.	15	15	N/A	245	6
B8	1:70	As B6. Wood as only fuel.	N/A	N/A	N/A	252	9
B9	1:45	As B1.	47	88	23.5	N/A	N/A
B10	1:45	As B2.	47	88	23.5	N/A	6

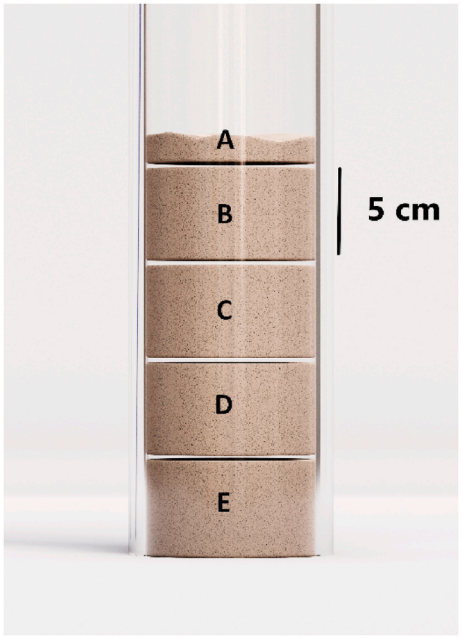


Fig. 3. Image of 5 cm column increments labelled A-E.

(352 mL every day/hour at 40 mL min^{-1}, 9.11 L) (Kramoer Dosing Pump. China). The water passed through a watering can rose (HAWS. UK) to achieve an even water distribution over the surface area of the soil column. To prevent light on the TATB, the columns were covered in silver foil.

2.4. Sample collection

At the end of the 4-week watering regime the columns were broken down into 5 increments shown in Fig. 3, with their increments labelled A-E. Each increment was removed from the column and placed on trays for 6 days to air dry in dark conditions. Column increments B-E were then extracted by taking sub-samples (10 g) in triplicate (Thermo Fisher Scientific UK), using the sonication method at 70 °C for 30 min in DMSO (20 mL). Water leachate was collected weekly and both water and soil samples were extracted using DMSO to detect the amount of TATB. All the samples were filtered using a 2 μm nylon-filter and prepared for HPLC analysis (extraction efficiency 93%). Extraction efficiency was tested by extracting a known mass of TATB from damped play sand (10 g) in DMSO (50 mL) and sonicated at 70 °C for 30 min. After sonication, the mixtures were left to settle, and the supernatant decanted into vials for storage before analysis. Increment A had a large quantity of TATB still on the surface, such that it was not feasible to extract due to the large quantities of solvent DMSO it would require. Therefore, to quantify the TATB on the surface a separation method was used. The equivalent volume of DI water to the weight of each increment was added in a separation funnel to allow the TATB to float on the water surface. The sand and the water with TATB were separated. The water was filtered, and the filtered solids were dried and weighed.

2.5. Sample analyses

Samples were analysed by HPLC (Waters-Alliance 2696, USA) using a photodiode array detector (Waters, 996, USA). The mobile phase was 45% acetonitrile (ACN), 55% water/0.1% formic acid with a flow rate of 0.4 mL min-1. The stationary phase was a reversed phase Kinetex 2.6 μm Phenyl-Hexyl 100 Å column (100 mm × 4.6 mm) L11 column. The column temperature was 30 °C. The injection volume was 10 μL. Peak identification was performed by comparing the retention time and UV profile of the compounds to TATB standards. For the standards TATB (5.3 mg) in DMSO (20 mL) stock was diluted to six concentrations between 53 mg/L and 0.6 mg/L. The output signals were monitored at a 354 nm wavelength. The HPLC run time was 2 min and TATB peaks appeared after 1.6 min (LOD: 0.219; LOQ:0.665).

3. Results and discussion

3.1. Detection of TATB from open burning

Open burns simulated at small scale using steel burn trays were first visually inspected for unburnt materials followed by HPLC analysis. Due to the low solubility of TATB in DMSO (50 mL required to solubilise 3.5 g) and the high background interference using HPLC coupled UV/VIS, it

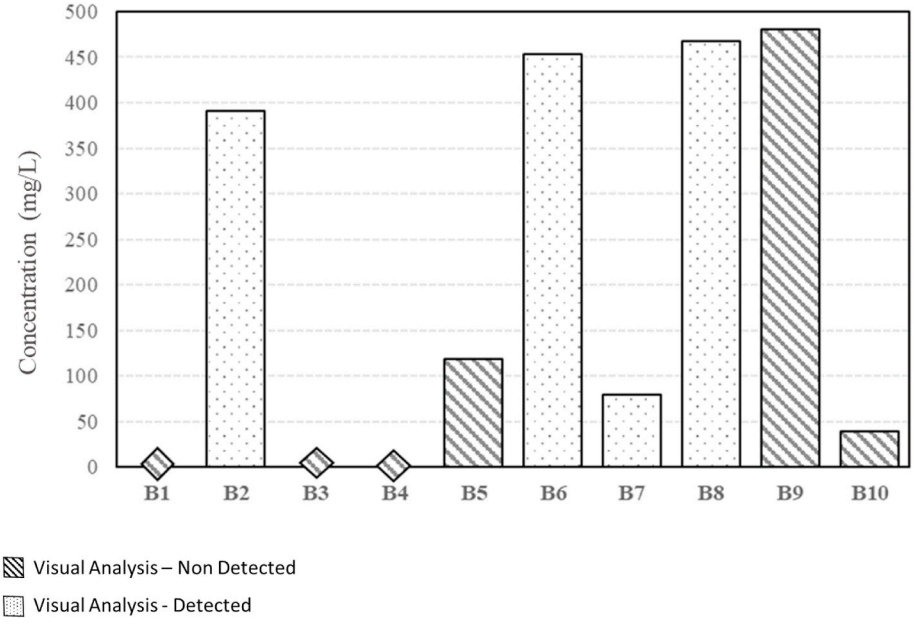


Fig. 4. Concentrations of TATB calculated using HPLC detection from the open burning and final concentrations detected. B1, B3 and B4 were detected by HPLC but not quantifiable.

was not possible to quantify the remaining TATB in all the burnings. Therefore, the 'observe or detect' approach was coupled with HPLC analysis to determine that even when there are no visible TATB residues remaining, significant quantities could be detected (Fig. 4).

The results obtained from the burning experiments revealed varying levels of detectability and quantifiability of the explosive materials (Fig. 4). As the explosive residues were difficult to identify in the ashes collected due to the amount of burn materials which interfered with the results, residues collected are linked to the number of explosive residues that were left on the witness plates recovered using cotton buds.

B2, B6, B8 and B9 had the largest quantities of explosives recovered after the burning, where explosive residues were quantified at high levels and ranged from 390.87 to 480.25 mg/L, and therefore were the most inefficient open burning configurations to dispose of TATB. B2 had a stacked configuration to increase temperature and oxygen ingress, which was expected to increase the efficiency of the burning. High quantities of TATB recovered showed that oxygen intake did not play a role in the thermal degradation of TATB. Although, the same stacked configuration was used for B4, where kerosene was added as an accelerant. In that case, TATB was detectable by HPLC although, concentration was very low compared to the initial quantity, suggesting the accelerant provided a more efficient burning method by increasing the rate of combustion and the speed at which the fire spreads. B6 and B8, showed high quantities of TATB after visual inspection, TATB presence was confirmed by HPLC analysis which found concentrations of respectively 453.29 and 467.52 mg/L. In both cases wood was used as fuel (B6:134 and B8:258 gr) which appeared to slow the combustion process likely due to it being a denser material compared to cardboard and paper. These last two materials were used in low quantities in B6 to try and increase the ignition velocity, although it did not improve combustion of TATB and left the tray with high TATB concentrations.

B9 was the least efficient, even though TATB was not observed after the burning, the highest TATB concentration was recovered (480.25 mg/L). During B9 only cardboard, paper and blue roll were utilised to open burn the TATB, therefore it was assumed that the lightweight material alone did not maintain temperature for long enough to enable full TATB combustion as the flame is likely to extinguish before ignition temperature is achieved.

B5, B7 and B10 were more efficient compared to B2, B6, B8 and B9. As these burnings shared the same configurations, the only difference was the addition of the accelerant kerosene. B10 was the most efficient of the three burnings, which did not use wood as fuel unlike B5 and B7, confirming that denser material can slow down the combustion process by not reaching high enough temperatures to ignite TATB. Even though B5 and B10 had varied amounts of TATB recovered, during visual inspection TATB was not observed confirming that a visual observation cannot confirm whether the explosive is completely destroyed after an open-burning.

B1, B3 and B4 were the most efficient burns, where TATB was not visually observed during inspection but was recovered in low quantities under the limit of quantification for the HPLC; this suggests that even though explosive materials left after these burns were not visually apparent, small concentrations of the explosives were recovered. B1 and B3 used a high mass of cardboard fuel and TATB was evenly mixed in with the materials. Carboard typically contains paper fibre and different additives such as inks and glues which can affect the burning rate of the materials, although, cardboard tends to burn faster compared to wood and slower compared to paper, which can affect the efficiency of the burning. B3 and B4 had the accelerant, which increased the efficiency of disposal although did not completely burn the TATB. While the quantified HPLC results cannot be used to determine a mass balance, it was noted that for the two burns with a higher TATB to fuel ratio (B1 and B3), the mass of TATB could not be quantified compared to B9 and B10 where a concentration of 4.8 mg/L was detected.

Results showed that the burnings in which the explosive was thoroughly mixed with the materials and the accelerants was added were the most efficient in disposing of TATB materials which may be due to kerosene decreasing the time taken for the fire to ignite. Although, it is worth noting that because of the way in which the explosives residue was collected results might underestimate the concentration of TATB that were found as more possibly was held in the left-over ashes depending on how the TATB was placed within the materials during the open burnings. These results also suggest that visual inspection alone cannot be used as the sole source for confirming explosive residues being left after a burning where more analyses are needed to confirm the traces left over which can harm the environment.

It is clear from the results that none of the methods used were able to ensure complete disposal of TATB with TATB detected by HPLC in all burnings. These results demonstrate that current methods used to dispose of TATB are not fit for purpose as they are leaving insensitive explosive residues on soil.

3.2. Persistence of TATB in the environment

Following the results from the open-burning, soil columns were contaminated with pristine explosive to investigate the persistence of TATB (Fig. 5) following residues remaining on the soil surface following current open-burning practices. Play sand was used to determine explosives transport in the column due to water infiltration, as it has a very low organic content and thus has low humic content to minimise likelihood of degradation and sorption to the soil matrix (Doyle and Kitchens, 1993). Moreover, to ensure that photodegradation did not occur all the columns were covered in aluminium foil.

Following contamination of the soil columns samples were extracted by dividing the contaminated sand in increments. Samples from column increments B-E were extracted and analysed by HPLC. Section A of each soil column was not extracted due to the high amount of TATB left on the surface and the low dissolution rates in the DMSO. The largest concentration of TATB is seen to be in increment B for all columns (Fig. 5), however there is a large discrepancy in concentration between column 3, and columns 1 and 2. The large concentration of TATB in increment B is due to TATB infiltrating the top of the soil matrix over the course of the yearly rainfall due to its low solubility in water. The concentration of TATB dramatically reduces in increments C, D and E with a very small concentration detected in increment E, 0.06, 0.19 and 0.02 mg/kg respectively in columns 1, 2 and 3. The very small concentration of TATB in increment E indicates that there should have been some TATB detected in the water leachate samples, which was not detected.

On average 2.8% of TATB was recovered across the three columns from increment B to E, with the highest recovery in column 1 (18 mg in

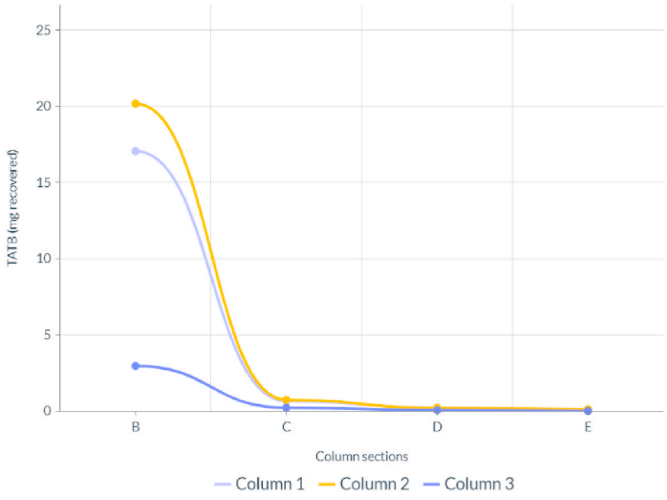


Fig. 5. TATB Concentration in each Column Increment (excluding A) for the three Soil Columns.

total) and the lowest recovery in column 3 (3.28 mg in total). This discrepancy was related to the highest TATB weight recovered in increment A in column 3 (92–99%), where TATB remained on the surface highlighting again its low transport rate. On average more than 80% was recovered in increment A, with a TATB mass that showed a low transport from increment B (where from 20.18 mg in column 2–2.98 mg in column 3 was recovered) to increment E (0.13 mg in column 2 to 0.01 mg in column 3). The presence of TATB left on the surface is a cause for concern, as previous research has shown that insoluble TATB can be degraded by sunlight, resulting in the formation of photodegraded and more soluble components (Halasz et al., 2021). The environmental risks associated with these components have not yet been considered.

Results from the soil column studies proved that TATB remains on the soil surface and only a small percentage (<4%) moved through the top-soil layers, suggesting that the rate of transport to groundwater would be so low as to be insignificant over time. This is due to the hydrophobic nature of TATB, (Yuan et al., 2020) also influenced by the non-polar bonding within the molecule making it less likely to dissolve. The chemical structure of TATB allows the molecule to be more attracted by the soil matrix than water allowing the explosive to be retained on the top-surface layer of the soil.

TATB in its original form has the potential to have minimal effect on aquatic life if it were to leach in water (Boddu et al., 2010). However, due to the limited literature and need to comply with environmental legislation contamination should be managed until further research confirms the toxicological profile of this compound and its degradation products. Moreover, the matrix used for this experiment contained a low amount of organic matter (0.15%) which decreased the opportunities for degradation to occur. Therefore, TATB's behaviour may vary as the organic matter, pH and the microbial communities of the soil matrix changes and may be subject to degradation and different transport profiles; more studies are needed to confirm the behaviour on TATB in various soils.

TATB is bright yellow in colour thus easily identified if any contamination has occurred on the soil surface and can be removed by taking away the top layer of soil. Removing the contamination is straight forward, however remediating to comply with environmental legislation and prevent further movement of TATB in the environment is still an area of concern and requires further research. The most viable and current option is to remove the contaminated soil and securely store until a remediation method is available or efficient final disposal solutions are identified.

It is worth highlighting that the removal of any TATB-contaminated soil should be undertaken as early as possible as TATB is subject to colour (from yellow to green) and chemical changes (variation of solubility) when subjected to light exposure (Halasz et al., 2021).

4. Conclusions

TATB is recognised as a moderately powerful insensitive high explosive (IHE) with exceptional thermal stability making it a suitable choice for filling insensitive munitions that meet stringent safety requirements. However, the disposal of this material poses significant challenges. Initial research indicated that TATB does not readily burn, even when combined with other accelerants or waste materials, or when arranged in different configurations. Subsequent experiments conducted as part of this study confirmed these findings.

Nevertheless, it is crucial for those involved in TATB disposal to understand effective burning methods or optimal management strategies, as leaving the material unburnt in the environment is unacceptable from both an environmental compliance standpoint and due to potential risks to environmental receptors. Moreover, this research also explored the persistence of TATB in soil environments, revealing that it remains primarily at the soil surface and is transported at a slow rate. This does facilitate straightforward removal, however, there will be concerns from the bright yellow colour of TATB, which has been observed to change to different colours when exposed to light. These colour variations and associated changes are classified as pollutants, potentially indicating the presence of more toxic by-products that could have implications for both the environment and environmental receptors in terms of toxicity.

To advance this project further, future work should focus on investigating suitable and efficient disposal options or convenient solutions to prevent the accumulation of TATB in the environment, also looking into contamination when TATB is combined with fluorinated polymers. Additionally, it is important to study the transport mechanisms of TATB in soil columns that closely resemble real soil environments, rather than just laboratory conditions. Utilising a soil type with high organic content, as suggested by Doyle and Kitchens (1993) would be beneficial to examine TATB degradation and adsorption in a soil-compost mixture, or the effect of different conditions such as pH. Furthermore, conducting toxicity studies on prolonged exposure may confirm the non-toxic nature of TATB and provide valuable insights into its environmental impact. Further research could also encompass analyses on photodegraded TATB, as our results indicate that a significant amount of unburnt materials can persist indefinitely in soils, raising concerns when the explosive undergoes photodegradation.

CRediT authorship contribution statement

Olivia Christian: Data curation, Formal analysis, Investigation, Methodology, Writing – original draft. **Michael Spencer:** Data curation, Formal analysis, Investigation, Methodology, Writing – original draft. **Melissa Ladyman:** Supervision, Writing – review & editing. **Federica Persico:** Data curation, Formal analysis, Supervision, Validation, Visualization, Writing – review & editing. **Encina Gutierrez Carazo:** Investigation, Methodology. **Evie Kadansky:** Writing – review & editing. **Tracey Temple:** Conceptualization, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data supporting this study are openly available from CORD at DOI: 10.17862/cranfield.rd.23904519

Acknowledgement

The authors would like to thank Eng. Ernesto De Gregorio for developing the images included in this paper.

References

Arthur, J.D., Mark, N.W., Taylor, S., Šimunek, J., Brusseau, M.L., Dontsova, K.M., 2017. Batch soil adsorption and column transport studies of 2,4-dinitroanisole (DNAN) in soils. J. Contam. Hydrol. 199, 14–23. https://doi.org/10.1016/J.JCONHYD.2017.02.004.

Boddu, V.M., Viswanath, D.S., Ghosh, T.K., Damavarapu, R., 2010. 2,4,6-Triamino-1,3,5-trinitrobenzene (TATB) and TATB-based formulations—a review. J. Hazard Mater. 181 (1–3), 1–8. https://doi.org/10.1016/J.JHAZMAT.2010.04.120.

Bortone, I., Coulon, F., Fawcett-Hirst, W., Ladyman, M., Temple, T., 2019. Scientific principles of environmental management. In: Global Approaches to Environmental Management on Military Training Ranges. IOP Publishing. https://doi.org/10.1088/978-0-7503-1605-7ch1.

Clausen, J., Robb, J., Curry, D., Korte, N., 2004. A case study of contaminants on military ranges: camp Edwards, Massachusetts, USA. Environ. Pollut. 129 (1), 13–21. https://doi.org/10.1016/j.envpol.2003.10.002.

DEFRA, 2018. A Green Future: Our 25 Year Plan to Improve the Environment. https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/693158/25-year-environment-plan.pdf.

Dobraz, B.M., 1995. The Insensitive High Explosives (TATB): Development and Characterization - 1888 to 1994.

Dorsey, A., Llados, F., 1995. TOXICOLOGICAL PROFILE FOR 1,3-DINITROBENZENE AND 1 (3), 5. TRINITROBENZENE.
Doyle, R.C., Kitchens, J.F., 1993. Composting of Soils/sediments and Sludges Containing High Energy Explosives. https://www.osti.gov/servlets/purl/10108235.
European Commission, 2021. A Soil Deal for Europe.
Field, J., Higgins, C., Deeb, R., Conder, J., 2017. FAQs Regarding PFASs Associated with AFFF Use at U.S. Military Sites Developed for the Environmental Security Technology Certification Program (ESTCP).
Glascoe, E.A., Maienschein, J.L., Lorenz, K.T., Tan, N., Koerner, J.G., 2010. Deflagration Rate Measurements of Three Insensitive High Explosives: LLM-105, TATB, and DAAF. *14th International Detonation Symposium*.
Halasz, A., Hawari, J., Perreault, N.N., 2021. Photolysis of the insensitive explosive 1,3,5-Triamino-2,4,6-trinitrobenzene (TATB). Molecules 27 (1), 214. https://doi.org/10.3390/MOLECULES27010214.
Hu, X.C., Andrews, D.Q., Lindstrom, A.B., Bruton, T.A., Schaider, L.A., Grandjean, P., Lohmann, R., Carignan, C.C., Blum, A., Balan, S.A., Higgins, C.P., Sunderland, E.M., 2016. Detection of poly- and perfluoroalkyl substances (PFASs) in U.S. Drinking water linked to industrial Sites, military fire training areas, and wastewater treatment plants. Environ. Sci. Technol. Lett. 3 (10), 344–350. https://doi.org/10.1021/ACS.ESTLETT.6B00260.
Jenkins, T.F., Hewitt, A.D., Grant, C.L., Thiboutot, S., Ampleman, G., Walsh, M.E., Ranney, T.A., Ramsey, C.A., Palazzo, A.J., Pennington, J.C., 2006. Identity and distribution of residues of energetic compounds at army live-fire training ranges. Chemosphere 63 (8), 1280–1290. https://doi.org/10.1016/j.chemosphere.2005.09.066.
Jorgenson, T.A., Simmon, V.F., Dilley, J.V., 1976. Preliminary Toxicological Studies of TATB, TCB, and TCTNB. https://www.osti.gov/servlets/purl/7114247.
Ladyman, M.K., Temple, T.J., Piperakis, M.M., Fawcett-Hirst, W., Gutierrez-Carazo, E., Coulon, F., 2019. Decision Framework for the environmental management of explosive contaminated land. Sci. Total Environ. 690, 730–738. https://doi.org/10.1016/j.scitotenv.2019.06.360.
Manaa, M.R., Reed, E.J., Fried, L.E., Goldman, N., 2009. Nitrogen-rich heterocycles as reactivity retardants in shocked insensitive explosives. J. Am. Chem. Soc. 131 (15), 5483–5487. https://doi.org/10.1021/JA808196E/ASSET/IMAGES/MEDIUM/JA-2008-08196E_0007.
Manaa, M.R., Schmidt, R.D., Overturf, G.E., Watkins, B.E., Fried, L.E., Kolb, J.R., 2002. Towards unraveling the photochemistry of TATB. Thermochim. Acta 384 (1–2), 85–90. https://doi.org/10.1016/S0040-6031(01)00779-1.
Ministry of Defence, 2021. Climate Change and Sustainability Strategic Approach Climate Change and Sustainability-Strategic Approach 3. https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/973707/20210326_Climate_Change_Sust_Strategy_v1.pdf.
NATO, 2018. NATO STANDARD AOP-39 POLICY FOR INTRODUCTION AND ASSESSMENT OF INSENSITIVE MUNITIONS. IM).
Oliviera, I.B., Demond, A.H., Salehzadeh, A., 1996. Packing of sands for the production of homogeneous porous media. Soil Sci. Soc. Am. J. 60 (1), 49–53. https://doi.org/10.2136/SSSAJ1996.03615995006000010010X.
Persico, F., Coulon, F., Ladyman, M., López, C.F., Temple, T., 2023. Evaluating the effect of insensitive high explosive residues on soil using an environmental quality index (EQI) approach. Sci. Total Environ. 869 https://doi.org/10.1016/J.SCITOTENV.2023.161797.
Persico, F., Temple, T., Ladyman, M., Gilroy-Hirst, W., Guiterrez-Carazo, E., Coulon, F., 2022. Quantitative environmental assessment of explosive residues from the detonation of insensitive high explosive filled 155 mm artillery shell. Propellants, Explos. Pyrotech. 47 (3) https://doi.org/10.1002/prep.202100220.
Prakash Agrawal, J., Dodke, V.S., 2021. Some Novel High Energy Materials for Improved Performance**. https://doi.org/10.1002/zaac.202100144.
Temple, M., Ladyman, T., Mai, N., Galante, E., Ricamora, M., Shirazi, R., Coulon, F., 2018. Investigation into the environmental fate of the combined Insensitive High Explosive constituents 2,4-dinitroanisole (DNAN), 1-nitroguanidine (NQ) and nitrotriazolone (NTO) in soil. Sci. Total Environ. 625, 1264–1271. https://doi.org/10.1016/j.scitotenv.2017.12.264.
Tian, X., Wang, X., Yu, K., Sun, J., Xiao, D., 2017. A new insight to the color change phenomenon of TATB: structural color. Propellants, Explos. Pyrotech. 42 (11), 1247–1251. https://doi.org/10.1002/prep.201700128.
UNCCD, 2017. Land Degradation Neutrality | UNCCD. https://www.unccd.int/land-and-life/land-degradation-neutrality/overview.
Walsh, M.R., Taylor, S., Walsh, M.E., Bigl, S., Bjella, K., Douglas, T., Gelvin, A., Lambert, D., Perron, N., Saari, S., 2005. Residues from Live Fire Detonations of 155-mm Howitzer Rounds.
Walsh, M.R., Walsh, M.E., Ramsey, C.A., Brochu, S., Thiboutot, S., Ampleman, G., 2013. Perchlorate contamination from the detonation of insensitive high-explosive rounds. J. Hazard Mater. 262, 228–233. https://doi.org/10.1016/J.JHAZMAT.2013.08.045.
Warrick, A.W., 2003. The soil system. In: Soil Water Dynamics. Oxford University Press Inc.
Watt, D., Deschambault, E., Touze, P., 2006. Insensitive munitions (IM): a key aspect of improved munitions safety. Han Neng Cai Liao 14 (5), 323–329.
Williams, D.L., Timmons, J.C., Woodyard, J.D., Rainwater, K.A., Lightfoot, J.M., Richardson, B.R., Burgess, C.E., Heh, J.L., 2003. UV-induced degradation rates of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). J. Phys. Chem. A 107 (44), 9491–9494. https://doi.org/10.1021/JP027263V.
Xiong, Y., Liu, J., Zhong, F., Xu, T., Cheng, K., 2014. Identification of the free radical produced in the photolysis of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). J. Phys. Chem. A 118 (34), 6858–6863. https://doi.org/10.1021/JP5029867/ASSET/IMAGES/MEDIUM/JP-2014-029867_0010.
Yan, T., Yang, H., Yang, C., Yi, Z., Zhu, S., Cheng, G., 2020. An Advanced and Applicable Heat-Resistant Explosive through Controllable Regiochemical Modulation † https://doi.org/10.1039/d0ta09158h.
Yeager, J.D., Dattelbaum, A.M., Orler, E.B., Bahr, D.F., Dattelbaum, D.M., 2010. Adhesive properties of some fluoropolymer binders with the insensitive explosive 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). J. Colloid Interface Sci. 352 (2), 535–541. https://doi.org/10.1016/j.jcis.2010.08.063.
Yuan, W.-L., Tao, G.-H., Zhang, L., Zhang, Z., Xue, Y., He, L., Huang, J., Yu, W., 2020. Super impact stable TATB explosives recrystallized by bicarbonate ionic liquids with a record solubility. Sci. Rep. 10 (1), 4477. https://doi.org/10.1038/s41598-020-61470-9.
Zhang, C., Wang, X., Huang, H., 2008. π-stacked interactions in explosive crystals: buffers against external mechanical stimuli. J. Am. Chem. Soc. 130 (26), 8359–8365. https://doi.org/10.1021/JA800712E/SUPPL_FILE/JA800712E-FILE001.PDF.
Zhang, D., Zhu, D., Chen, W., 2009. Sorption of nitroaromatics to soils: comparison of the importance of soil organic matter versus clay. Environ. Toxicol. Chem. 28 (7), 1447–1454. https://doi.org/10.1897/08-406.1.



https://dspace.org/

Persistence of 2,4,6-triamino-1,3,5-trinitrobenzene in the environment

Christian, Olivia; Spencer, Michael; Ladyman, Melissa K.; Persico, Federica; Gutierrez-Carazo, Encina ...

2023-12-15
Elsevier
https://doi.org/10.1016/j.envres.2023.117378
Christian O, Spencer M, Ladyman M, et al., (2023) Persistence of 2,4,6-triamino-1,3,5-trinitrobenzene in the environment. Environmental Research, Volume 239, Part 1, December 2023, Article number 117378

Downloaded from a DSpace repository. https://dspace.org/