



Full length article

Development of an environmental hazard-based rating assessment for defence-related chemical compounds in ecological soil systems

Federica Persico^a, Frederic Coulon^b, Melissa Ladyman^a, Tracey Temple^a^a Cranfield University, Centre for Defence Chemistry, Defence Academy of the United Kingdom, Shrivenham SN6 8LA, UK^b Cranfield University, School of Water, Energy and Environment, Cranfield MK43 0AL, UK

ARTICLE INFO

Handling Editor: Adrian Covaci

Keywords:

Toxicity
Ecotoxicity
Soil contamination
Hazard
Soil

ABSTRACT

Environmental hazard-based methods are commonly used to categorise the severity of chemical contamination to ecological soil systems, although a traffic-light approach (green, amber, red) has never been used to assess these consequences. A traffic light approach is an easy to interpret data as it has a clear visual display which can provide an early warning approach for stakeholders to identify areas that require further investigation. This approach should be underpinned by extensive research data and systematic methods of development. However, the extent of reliable data available for specific chemicals can be limited and therefore decision making may rely on expert judgement. Therefore, in this study, an environmental hazard-based rating methodology was developed by combining the guidelines from the European Chemical Agency (ECHA) and the USEPA for Predicted Non-effect Concentration (PNEC) and Ecological Soil Screening Levels (Eco-SSL) for defence-related chemicals (2,4,6-trinitrotoluene (TNT), 1,3,5-trinitro-1,3,5-triazinane (RDX), cypermethrin, perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS)). The developed hazard-based rating assessment was design to categorise the chemicals into low, medium and high environmental hazards priority to inform and ease the decision-making process for contaminated areas to ensure that sustainable operations are carried out.

1. Introduction

To characterise and manage the ecological hazards posed by chemicals in the soil system a variety of approaches have been developed. Rating systems have been widely utilised to simplify and better visualise consequences across a variety of disciplines (San et al., 2020; Pan et al., 2020) (e.g. low, medium and high rating systems) to enable practitioners to rapidly interpret data and implement mitigation. However, developing the different categories requires a wide and comprehensive body of data.

Risk/hazard based rating systems have been used across a variety of disciplines from financial to environmental and are usually based on a matrix that categorises the occurrence and the impact of each activity to infer the level of risk or hazard i.e. low, medium or high (Finizio and Villa, 2002; Murray et al., 2011; Pickering and Cowley, 2010). However, these processes are frequently reliant on qualitative assessment by subject matter experts and while providing a subjective assessment, cannot provide quantitative assessments (Pickering and Cowley, 2010). An alternative approach is to use a ranking evaluation, which use 'traffic light' colour coding system e.g. green, amber and red to represent low,

medium and high-hazard levels. While these systems are based on quantitative data, multiple variables are used to compile the data, and subject matter expert opinion is still required to make decisions regarding the data used and therefore the system is still heavily subjective (Kovačević et al., 2019). Therefore, an additional system is required to ensure to underpin the hazard-based rating system with a more thorough and comprehensive body of data to enable practitioners to easily define different levels of hazard.

The process of gathering a viable body of data has been presented by different nations although they have not been considered for broader applications such as informing rating systems to define different levels of ecological hazards.

The United States Environmental Protection Agency (USEPA), use a score-grading procedure of the literature data, and calculates a set of Ecological Soil Screening Levels (Eco-SSLs) based on contaminants that have been proven to be a threat for both flora and fauna (USEPA, 2005). In Europe, a step further has been made by the European Chemical Agency (ECHA) by developing Soil Screening Values (SSVs) based on reliable data in the literature and statistical analyses (Environment Agency, 2017). Unlike the Eco-SSL technique, the gathering of data

E-mail addresses: federica.persico@cranfield.ac.uk (F. Persico), f.coulon@cranfield.ac.uk (F. Coulon), m.ladyman@cranfield.ac.uk (M. Ladyman), t.temple@cranfield.ac.uk (T. Temple).

<https://doi.org/10.1016/j.envint.2022.107392>

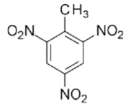
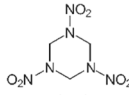
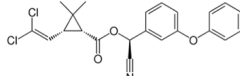
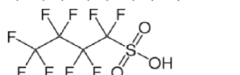
Received 5 November 2021; Received in revised form 29 June 2022; Accepted 1 July 2022

Available online 5 July 2022

0160-4120/Crown Copyright © 2022 Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

Table 1

The chemical substance name, empiric formula and structure of the five defence related chemicals used for the application phase in this paper.

Chemical name	Empiric Formula	Chemical Structure
2,4,6-Trinitrotoluene (TNT)	$C_7H_5N_3O_6$	
1,3,5-Trinitroperhydro-1,3,5-triazine (RDX)	$C_3H_6N_6O_6$	
cyano-3-phenoxybenzyl-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate (Cypermethrin)	$C_{22}H_{19}Cl_2NO_3$	
Pentadecafluorooctanoic acid (PFOA)	$C_8HF_{15}O_2$	
Heptadecafluorooctane-1-sulfonic acid (PFOS)	$C_8HF_{17}O_3S$	

occurs through the ECHA database under the Regulation (EC) No 1907/2006 introduced in Europe in 2007, Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) (Merrington et al., 2008). The data obtained from this procedure are selected and extrapolated where gaps are identified. However, due to the lack of records related to different chemicals, the researcher must rely on the expert opinion to decide whether or not the data can be used to develop SSVs.

The USEPA methodology develops Eco-SSL values based on experimental data, specifically, to concentrations that produce changes (i.e. reproduction, inhibition of growth) to 10% or 20% of the studied population (EC_{10} , EC_{20}), or the highest effective concentration at which there was not an observed toxic or adverse effect (NOAEC) and the lowest effective concentration at which there was an observed toxic or adverse effect (LOAEC).

In contrast, SSVs are derived from the calculation of the Predicted No Effect Concentration (PNEC) value which is different depending on the ecosystem. The PNEC is a regulatory concentration level under which sufficient protection for the ecosystem considered is ensured (ECHA, 2008; Environment agency, 2017). The considered ecosystems are characterised by different groups of organisms and since there is more than one set of data for each organism in different soil environments the PNEC calculation is estimated on the values that are most reliable. The reliability of the results are chosen based on the expert's opinion having discrepancies dependent on who is carrying out the procedure.

These methodologies have wide applications, particularly in the agricultural sector, although they have also been applied to other sectors (Checkai et al., 2014). This study focussed on military training ranges, which can be exposed to a range of chemical contaminants from the use of explosives, fire-fighting foams and other military equipment.

Regulating and minimising the environmental risks associated with routine operations at military training ranges (e.g. live-fire training, transportation), is necessary to maintain training and to support military capability (Bortone et al., 2020). Historically for both security and safety reasons, military training ranges are almost always situated in remote areas, so that essential training activities can be carried out without interfering with built-up areas (Havlíček et al., 2018). Despite restricted access, many rare or uncommon species of plants, insects and birds thrive in these areas which consequently become classified as Sites of Special Scientific Interest (SSSI) and/or as EU Special Areas of Conservation (SAC), as well as Special Protection Areas (SPA) for birds protected under the European Birds Directive.

Routine operations on site can also lead to contamination of military areas, with consequences to soil and groundwater (Broomandi et al., 2020; Ferreira et al., 2020). This means that the natural environment and military activities coexist, leading to the need to protect these areas

while continuing essential training activities (Bortone et al., 2020; Broomandi et al., 2020). To ensure the safe use and sound management of these military areas, Environmental Risk Assessments (ERA) are typically conducted to assess the environmental impact of defence-related chemical substances.

Chemical substances used on military training ranges (Table 1) comprise a wide range including among others, traditional explosives (e.g. 2,4,6 – trinitrotoluene (TNT), 1,3,5-hexahydro-1,3,5-trinitrotriazine (RDX)), which may be a threat to the environment including surface and groundwater, soil and biota (Clausen et al., 2004; Dodard et al., 2003; Gong et al., 2007; Kuperman et al., 2005; Lotufo, 2017; Robidoux et al., 2002; Vila et al., 2008). Aqueous Film Forming Foam (AFFF) containing per- and polyfluoroalkyl substances (PFAS) which are used for extinguishing inflammable liquid fires which may also be persistent and a threat to the environment (Filipovic et al., 2015; Place and Field, 2012; Turner et al., 2021; Zhao et al., 2011); and the use of pyrethroid insecticides such as cypermethrin and its isomers to treat military uniforms and equipment (e.g. bed nets) so that military personnel are protected from insect bites, such as mosquitos during military operations (Army, 1994; Friedl et al., 2007; Hassan et al., 2010; Khoobdel et al., 2005). During washing of the uniforms, water contaminated with the pesticide can enter soil and water courses (Hassan et al., 2010) and threat soil quality impacting agriculture (Shiping et al., 2008; Hassan et al., 2010; Khoobdel et al., 2005). Moreover, this insecticide has a high affinity to organic matter which can harm both soil invertebrates (Zhou et al., 2008, 2011; Zortéa et al., 2015) non-target organisms such as aquatic invertebrates (e.g.insects and crustaceans) (Conte et al., 2005; Environmental Agency, 2019; Birch et al., 2015; Das and Mukherjee, 2003; Shiping et al., 2008).

Using a hazard-based ranking system, based on a green, amber and red visual aid, ensures that proper decision making is carried out on training ranges considering the contamination that is already in place. This approach can be applied to varying soil types and is not limited by the activity at the site.decision

Therefore, the aim of this work was to develop an environmental hazard-based rating assessment which characterises the ecological hazards posed by chemicals (TNT, RDX, cypermethrin, PFOA and PFOS) used in defence-related activities based on a comprehensive body of data objectively selected. This was achieved by combining the USEPA ECO-SSLs and ECHA SSVs methodologies to develop a maximum contaminant concentration in soil that would not require short-term further investigation of the site (low hazard level). In contrast, contaminant concentrations in the medium and high-hazard levels would require further site investigation to ensure that sustainable operations are carried out. This method has been designed to ease the decision-making

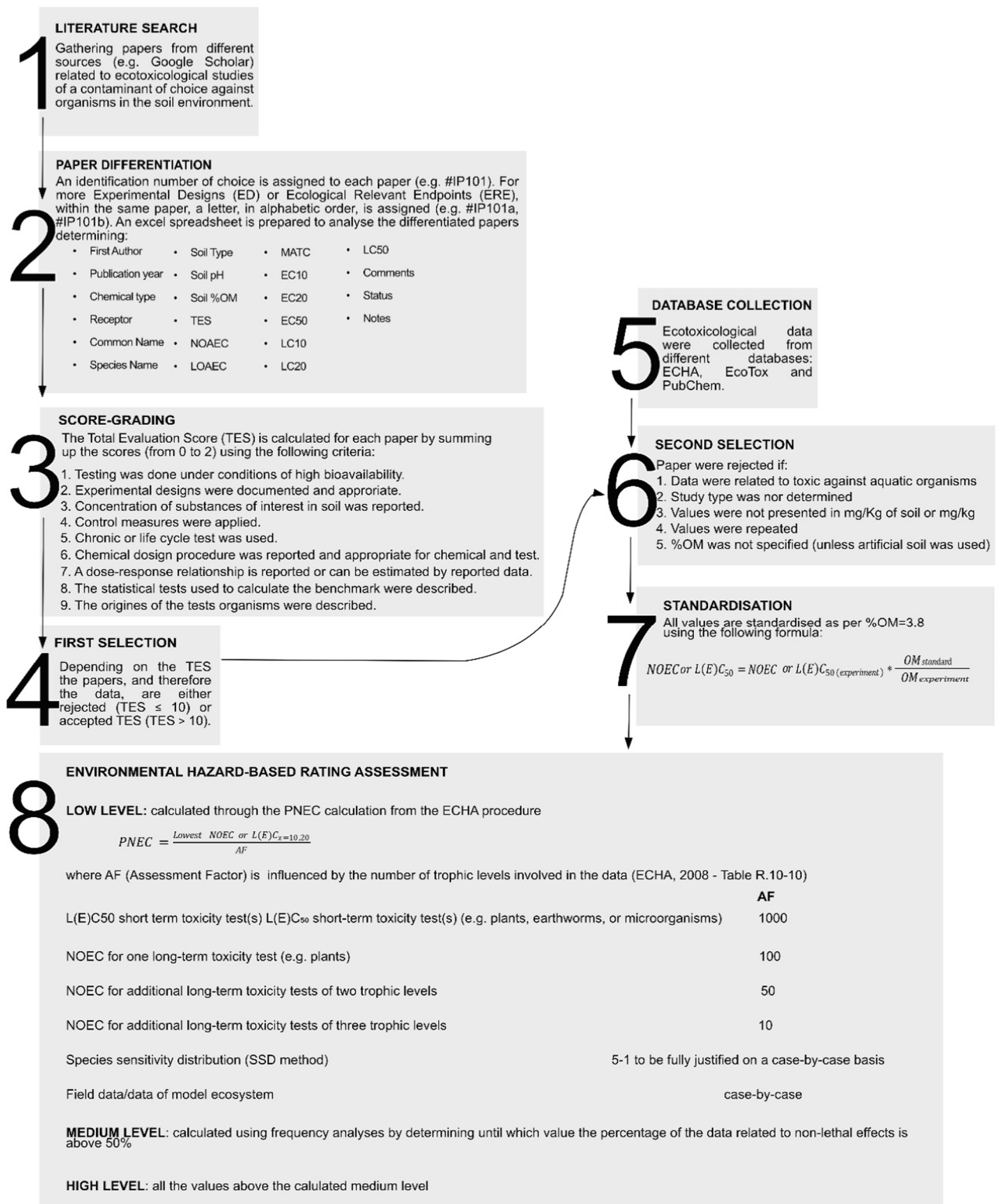


Fig. 1. The methodology for developing the toxicity scale, from the gathering of the data to the calculated values for the low, medium and high hazard levels (steps 1 to 8), to determine the possible level of hazard towards the ecological soil systems data against the biota. Differently from the USEPA procedure, in this methodology all the ERE and experimental designs were considered and all the values were part of the dataset used to develop the environmental hazard-based rating assessment.

assessment process for soil such that a threshold value could inform whether further site investigation is required.

2. Methodology

2.1. The process

The following section outlines a summary of the methodology

Table 2

Criteria evaluation for each chosen paper for the evaluation of Eco-SSL values (USEPA, 2005).

Criteria	Evaluation
1	Testing was Done Under Conditions of High Bioavailability
2	Experimental Designs were Documented and Appropriate
3	Concentration of Substance of Interest in Soil was Reported
4	Control Measures were Applied
5	Chronic or Life Cycle Test was Used
6	Chemical Dosing Procedure was Reported and Appropriate for Chemical and Test
7	A Dose-Response Relationship is Reported or can be Estimated from Reported Data
8	The Statistical Tests used to Calculate the Benchmark and the Levels of Significance were Described
9	The Origin of the Test Organisms were Described

undertaken to develop the environmental hazard-based rating assessments by combining the methodologies for soil screening levels from the ECHA and USEPA procedures (Fig. 1) to ensure an objective data collection to determine different hazard levels for the ecological soil systems.

A thorough **literature search** has been carried out (Step 1) of available toxicity data, for terrestrial organisms and plants.

The **paper differentiation** (Step 2) and **Score-grading** (Step 3) was carried out following the Standard Operating Procedure (SOP) #1 and #2, attachment 3.1 and 3.2 for invertebrates, developed by the USEPA.

A **first selection** was carried out (Step 4) and paper were either rejected or accepted depending on the Total Evaluation Score (TES) where scores ≤ 10 were accepted and >10 were rejected.

In Step 5 '**database collection**' values from different databases (e.g. PubChem, EcoTox) were collated to create a body of data, which was added to the papers that scored a TES > 10 .

The next step was the **second selection** (Step 6), where a selection of data was rejected based on the following:

- relationship to toxicity against aquatic organisms
- study type was not determined
- values were not presented in mg/kg of soil or mg/kg
- values were repeated
- %OM was not specified (unless artificial soil was used)
- the experimental design scored < 10 .

Once all data were standardised, the calculation of the PNEC or SSVs values were carried out to determine the upper boundary of the low-hazard toxicity level (Step 8) for the different contaminants.

The evaluation of the medium and high level of hazard for the soil environment in the cumulative environmental hazard-based rating assessment was then determined using frequency analysis of all the chosen data, clustering them based on the study type (e.g. reproduction, survival) (Step 8).

2.2. Research strategy

Various sources (e.g. Google Scholar, Web of Science) were utilised for the collection of secondary data through a literature search. A first screening procedure was carried out following the USEPA procedure, considering the literature related to ecotoxicological experiments involving TNT, RDX, PFOA, PFAS and Cypermethrin within the terrestrial environment. Each selected paper was differentiated based on different variables, which translated in different experimental designs (e.g. type of soil, organisms); additionally, unlike the USEPA procedure, each paper was also evaluated separately based on different Ecologically Relevant Endpoints (ERE) (e.g. reproduction, growth) and more data were included in the selection such as: EC₅₀, LC₂₀, LC₅₀ or data reported in mg/kg together with the EC₁₀, EC₂₀, NOAC and LOEC and data in mg/kg of soil considered from the USEPA procedure.

Each paper was assigned an identification number (e.g. IP#101) which differentiated not only different research articles but also different ERE and studies distinguished by use of different variables within the same paper (e.g. IP#101a, IP#101b). Each paper associated with an identification number was scored following the nine criteria from the USEPA procedure.

2.3. Data selection

In the USEPA procedure each paper is scored against nine criteria (Table 2) from 0 to 2 (with 0 being the lowest). The process is rendered unbiased by the usage of tables and specific instructions contained in the SOP #2 attachment 3.2 (USEPA, 2005). Using this method, a paper was scored more than once if more than one set of variables were investigated, thus considering them as different studies in within the same paper. For example, if two different soils were used to compare changes in the reproduction of a specific organism this was classified as two different studies. This differentiation was also applied if ERE were recorded. For example, if results from changes in reproduction and growth were presented in the same paper and the soil considered was the same, the paper was again evaluated as two different studies.

The previously presented scoring process differs from the USEPA procedure whereby the differentiation of studies within the papers was not applied when more than one consequence, or ERE, on the biota was recorded. For example, in the USEPA procedure if toxicological data on the same soil were collected and results recorded were related to reproduction and growth of the organism, the paper is considered as one study and the toxicity was selected according to a pre-settled hierarchy for the invertebrates (Reproduction $>$ Population $>$ Growth) or the most sensitive measurement of biomass production for plants.

For example, following the USEPA methodology, the first criteria analyses whether the experiments were carried out under conditions of high availability, and depending on the pH and the % organic material (OM) in the soil, a different score is selected based on the bioavailability tables given in the SOP #2 (USEPA, 2005). Although, the scoring of the papers should be completed by more than one researcher to ensure that complete unbiased decisions are achieved. All the scores for each paper were summed to determine the Total Evaluation Score (TES) of each article. Data was accepted, to develop the environmental hazard-based rating assessment, if the TES had more than 10 total points as stated in the USEPA procedure. Once all the gathered information had been organised further data was added from the ECHA database.

The non-confidential toxicity information, that has been submitted to ECHA, and are also available from other databases, such as EcoTox, PubChem, were reported and organised as follows: data related to aquatic organisms was excluded; only values presented in mg/kg of soil or mg/kg was considered; where %OM was not reported the data was not considered (except for artificial soil); data with no study type listed was also excluded from the research.

Since different studies include different soil types, a standardisation of the data to is required (ECHA, 2008; Environment Agency, 2017) and it is applied to all the gathered data using formula (1).

2.4. Data standardisation

Different soil characteristics (e.g. pH, %OM) can influence the toxicity and bioavailability of a chemical and the %OM has been defined as one the most influencing parameters, meaning that there is a need for normalisation to ensure that the toxicity of the compound are representative of the bioavailability in soil, meaning that the data needs to be standardised (Step 7) as they are presented in a standard soil (Environment Agency, 2017). For OECD guidelines, a standard soil has 3.8% of OM and all the values are standardised against this percentage to make the data comparable as follows:

Table 3

Assessment factors (reproduced from ECHA, 2008 Table R.10–10).

Information Available	Assessment Factor
L(E)C ₅₀ short-term toxicity test(s) (e.g. plants, earthworms, or microorganisms)	1000
NOEC for one long-term toxicity test (e.g. plants)	100
NOEC for additional long-term toxicity tests of two trophic levels	50
NOEC for additional long-term toxicity tests of three trophic levels	10
Species sensitivity distribution (SSD method)	5–1 to be fully justified on a case-by-case basis
Field data/data of model ecosystem	case-by-case

$$NOECorL(E)C_{50} = NOECorL(E)C_{50(inexperiment)} * \frac{OM_{standard}}{OM_{inexperiment}} \quad (1)$$

where $NOECorL(E)C_{50(inexperiment)}$ represent the values that have been found for each paper in the literature research; $OM_{standard}$ equals 0.038 and $OM_{inexperiment}$ are the OM values found in the literature for each experiment (ECHA, 2008).

2.5. Low-hazard toxicity level calculation

A low-level hazard for the ecological soil system can be defined as the concentration at which no effects were observed. This definition is also representative of the SSVs or the PNEC, meaning that the value that correspond to an SSVs or PNEC of a specific contaminant are utilised as the upper boundary of the low-hazard level.

The PNEC value was calculated using Eq. (2).

$$PNEC = \frac{LowestNOECorL(E)C_{x=10,20}}{AF} \quad (2)$$

where NOEC or L(E)CX values represent the lowest value identified from the procedure utilised and AF is the Assessment Factor.

The Assessment Factor (AF) is derived as summarised in Table 3.

Preferably the NOEC or EC₁₀ values should be used (either by calculation or from the literature) because they represent chronic

exposures which represent more appropriate and relevant measures for understanding the protection of population and communities, compared to acute toxicity tests. The presented methodology defines the most reliable results as the ones with the highest TES. If, from the most reliable data, values presented from experiments with the same settings and organisms, were less or equal to one magnitude apart, a geometric mean was calculated merging the presented data together (Environment Agency, 2017). PNEC values are considered as SSVs but only if there is enough data to support the calculations; this is usually when the assessment factor is <50 (Environment Agency, 2017), indicating that values from more than one trophic level are presented.

As the SSVs, the low-hazard level is defined as “levels of chemicals in soil below which there is unlikely to be any risk to its health and functions” (Environment Agency, 2017). Once the PNEC value has been calculated, the chemical concentration range in which no deleterious effects on the soil environment are expected can be defined.

2.6. Medium and High-hazard toxicity level calculation

Once the upper boundary of the low-hazard level has been defined, an analysis of the frequency is carried out on all the data based on the different study types (e.g. reproductivity, survival). Frequency analysis were used to determine different ranges of values, related to the analysed studies, in which lethal and non-lethal effects are evaluated. The range of concentration that determine the medium-hazard level was determined as the highest value in the set of data where 50% of the studies resulted in non-lethal effects on terrestrial organisms. All the values above the calculated boundary were considered to be related to a high-hazard level. As such, the medium-hazard level was defined as “levels of chemicals in soil in which it is likely to have deleterious effects on ecological soil functionalities” and the high-hazard level as “levels of chemicals in soil above which it is likely to have irreversible effects on ecological soil functionalities”. All the values above the most frequent values that did not cause a deleterious effect on the biota (death of the organisms) are considered a high-hazard level in, defining the range of concentration of the contaminants in which it is expected to have a lethal effect on the ecological soil system. Similarly, the most likely values

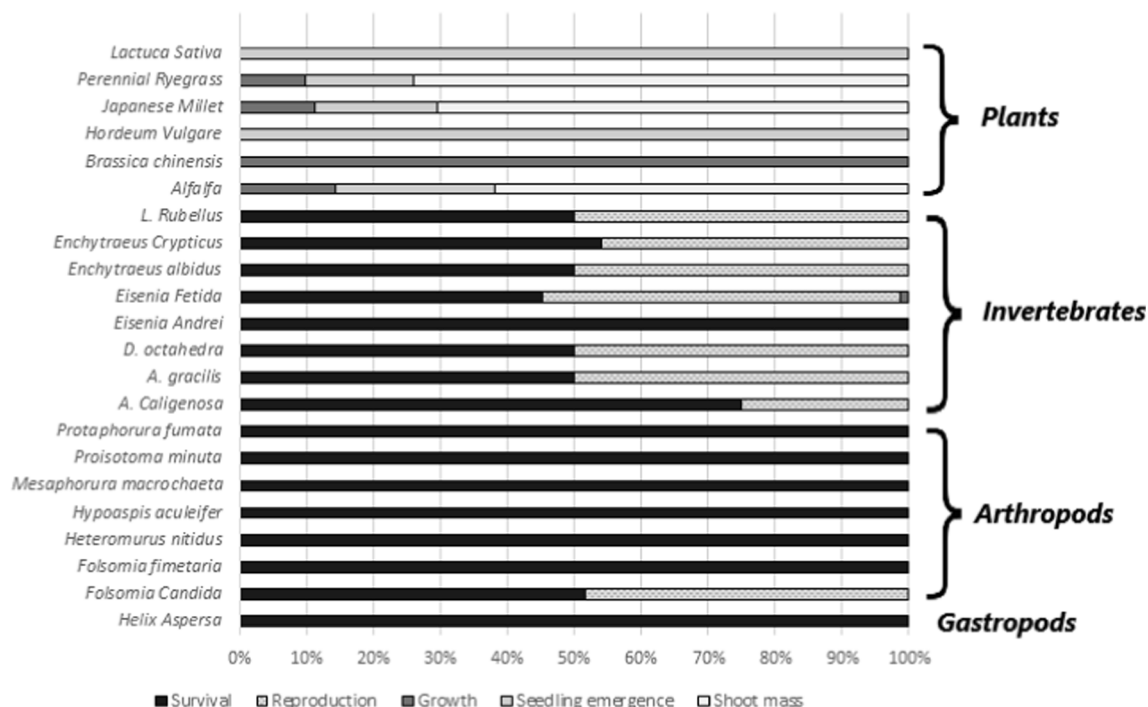


Fig. 2. Percentages of values for each organism related to different ERE found during the literature search using the USEPA procedure.

Table 4

Total numbers of values gathered from a selection of sources e.g. from the open literature (USEPA) and the following databases: ECHA, EcoTox, PubChem (ECHA). Within each study, more EREs and EDs were differentiated.

Contaminant	Number of values gathered from literature and databases					
	Total ERE and E. D.* (USEPA)	Accepted ERE (USEPA)	n. Values from accepted ERE (USEPA)	Total data from databases (ECHA)	Accepted data from databases (ECHA)	Number of values for the environmental hazard-based rating assessment
TNT	78	73	230	1976	140	370
RDX	104	104	255	821	155	410
CYPERMETHRIN	37	33	45	2251	21	66
PFOA	4	0	0	1300	131	131
PFOS	10	6	16	2860	93	109

*Experimental Designs.

Table 5

Each trophic level that was identified during the literature search and the database collection was listed and the equivalent AF factor was chosen. PNEC calculation was carried out as follows.

Contaminant	Previous values using the ECHA approach		Calculated values using new approach			
	AF	PNEC	AF	Trophic levels	Lowest NOEC or EC10	PNEC (or SSV) (MG/KG)
TNT	50	0.01	10	Plants Earthworms Arthropods	2.61	0.3
RDX	100	7.56	50	Plants Earthworms	51.3	0.1
CYPERMETHRIN	100	0.08	10	Plants Earthworms Arthropods Gastropods	0.17	0.02
PFOA	N/A	N/A	10	Plants Earthworms Arthropods	8.99	0.9
PFOS	N/A	N/A	50	Plants Earthworms	40	0.8

in which it is expected to have deleterious effects on the soil environment (because of their consequences on the biota) will represent the medium-hazard level in the environmental hazard-based rating assessment.

3. Results and discussion

3.1. Research evaluation

For the application phase of this research five different contaminants from defence related activities were selected: TNT, RDX, Cypermethrin, PFOA and PFOS (Table 1). During the first part of the literature search undertaken in accordance with the established USEPA methodology (USEPA, 2005) 30 reports and peer-reviewed papers in total, were identified as suitable for a first data analysis. The papers that were selected evaluated toxicity against a range of invertebrates and plants (Fig. 2).

From these papers 233 studies were identified, which led to the evaluation of 709 values for the environmental hazard-based rating assessment during the first part of the procedure (Supplementary data). The studies, represented by the different changes in variables, were individually scored following the 9 criteria in Table 2, and calculated TES varied from a minimum of 4 to a maximum of 18 points. Because of how the USEPA methodology is developed, PFOA and PFOS related papers have scored the lowest TES values. This is because the first scored criteria "Testing was done under conditions of High Bioavailability" is

not adequate for evaluating soil conditions with synthetic contaminants, therefore, a score of 0 has been selected for all the ERE that were PFOS or PFOA related.

In general, the experimental designs that scored ≤ 10 points were rejected and data related were not used to develop the environmental hazard-based rating assessment because they were considered unreliable. Across all the contaminants, 14 studies were rejected and 205 accepted. Each study contained 1 or more result relating to the percentage of the studied population that was affected by a certain amount of contaminant (e.g EC10, EC50), consequently the total accepted values that have been used, from the USEPA methodology, for determining the environmental hazard-based rating assessment was 546 (230 for TNT, 45 for Cypermethrin, 255 for RDX, 0 for PFOA and 16 for PFOS).

Furthermore, a total of 9208 values were collated from the ECHA, EcoTox and Pubchem databases and only 540 were used in the environmental hazard-based rating assessment (140 for TNT, 21 for Cypermethrin, 155 for RDX, 131 for PFOA and 93 for PFOS) (Supplementary data). This was due to several studies either not reporting results in mg/kg or mg/kg of soil, related to terrestrial organisms, or the study type was not specified. The final body of data that was analysed is shown in Table 4.

All data were standardised for 3.8% OM (Supplementary data).

3.2. Low-hazard level

PNEC values were determined for all the contaminants (Table 5) using Equation (1) and the AF factor was derived following the criteria listed in Table 3.

These values are representative of the upper boundary of the low-hazard level where adverse effects are unlikely to occur in the biota. Consequently, no changes in soil are expected in the defined range meaning that a concentration within the range of the low-hazard section represent momentarily a safe environment. Although, future considerations are needed as those contaminants are likely to bioaccumulate in the environment causing, potentially, different problems for people and the environment.

PNEC values have been previously defined in the literature (Table 5) for TNT, RDX and cypermethrin, as respectively 0.01 mg/kg soil dw (AF of 50), 7.56 mg/kg soil dw (AF of 100), 0.08 mg/kg (AF of 100) (ECHA database); although, PNEC values that were calculated using the presented combined methodology included a wider body of data influencing the number of values used to calculate the PNEC showing a difference between data. Data in mg/kg have been included and more trophic levels have been considered, with a recent growing body of data that included a wide range of values for the arthropods class.

The PNECTNT that has been calculated is currently higher than the literature, where an AF of 10 has been used has previously established. During the data gathering, 2 values reported ecotoxicity data against arthropods, adding a third trophic level, changing the AF to 10 which has been used for the PNECTNT calculation.

PNECRDX has been previously calculated using the ECHA procedure using an AF of 100 when only one trophic level was evaluated. Using the

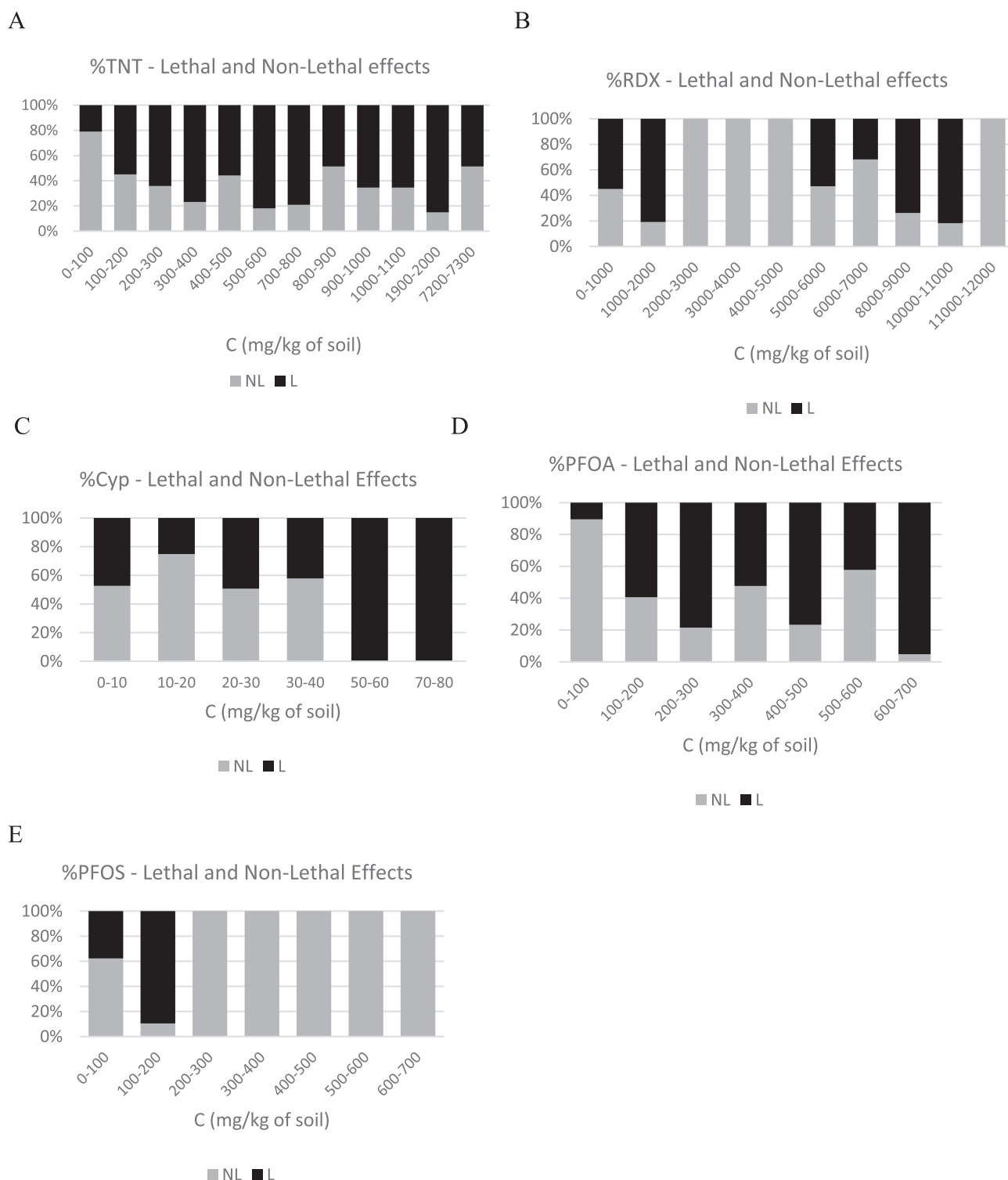


Fig. 3. Gathering of concentration (C) data in mg/kg using frequency analyses (showed in %) of the studied contaminants whose data are related to deleterious effects (e.g. reproduction, growth, dry biomass) which did not cause death in the organism (grey) and lethal effects (black).

presented combined methodology an AF of 50 has been used because, a wider body of data, included more than one trophic level. The PNECRDX calculated using the presented combined methodology, significantly lowered the previously calculated PNECRDX.

Compared to the PNECCYP calculated in the ECHA (7.56 mg/kg soil dw) the PNECCYP determined by this methodology was considerably lower because of the more inclusive body of data which incorporated Cypermethrin isomers and recently published literature. This is despite,

compared to the average of data that has been used to calculate the different environmental hazard-based rating for each contaminant (217.2), the number of values used is 70% lower (66). Furthermore, more trophic levels (plants, earthworms, arthropods, and gastropods) were included in the analysis and an AF of 10 was used unlike the ECHA where an AF of 100 was utilised meaning that the concentration that defined the value under which no changes are expected in the ecological soil system is much lower.

Table 6

Environmental hazard-based rating assessment for each contaminant resulting from the presented methodology.

Level of hazard	Value (mg/kg of soil)				
	TNT	RDX	Cypermethrin	PFOA	PFOS
Low	0–0.3	0–0.1	0–0.02	0–0.9	0–6.6
Medium	0.3–194.7	0.1–839.5	0.02–20.4	0.9–176.2	6.6–183.2
High	>194.7	>839.5	>20.4	>176.2	>183.2

PNECPFOA and PNECPFOS were calculated respectively with an AF of 10 and an AF of 50, unexpectedly the number of values collected for the PNEC calculation was more than 100 even though these contaminants are extremely new compared to the other evaluated chemicals.

3.3. Medium and high – Hazard levels

A frequency analyses of the data were done by determining the occurrences of the values respectively related to survival and different responses (e.g. reproduction, growth) which are not related to death of the organism. The data that had a toxic effect on the biota, without causing death of the organism, were considered to be representative of the medium-hazard level of the toxicity scale because these values are representative of different concentrations of the contaminants that can have a deleterious, but not lethal, effect on the soil environment. All the values above this range were considered high-hazard level.

Different ranges of values were calculated for the chosen chemical compounds. For TNT (Fig. 3a) the values ranged from 0.03 to 1906.8 mg/kg of soil. Between the range of 100 to 200 mg/kg concentration in soil lethal effects on the organisms were observed in more than 50% of the organisms. Within that range, the highest value with a non-deleterious effect was 194.7 mg/kg (Supplementary data) representing the upper boundary of the medium-hazard level. For RDX has been highlighted (Fig. 3b), in the range between 0 and 2000 mg/kg, that 56% of the data is related to lethal effects against organisms, determining upper boundary of the medium-hazard level in between 0 and 1000 mg/kg. For first instance only, 45% of the data represented non-lethal effects against organisms in that range outlining the medium hazard level as between 0.1 and 839.5 mg/kg.

The same process was followed for Cypermethrin, PFOA and PFOS where less data has been recorded compared to TNT and RDX using the combined methodology. The results obtained from the Cypermethrin data analysis showed that 50% of the data were between 20 and 30 mg/kg (Fig. 3c) and are related to lethal effects towards organisms. Using frequencies analyses the upper boundary of the medium-hazard level has been established to be 20.4 mg/kg. For PFOA and PFOS lethal effects data exceed 65% (Fig. 3d) and 89% (Fig. 3e), respectively between the range of 100–200 mg/kg, compared to data related to lethal effects, defining the upper boundaries at 176.2 mg/kg and 183.2 mg/kg.

All the values above the upper boundary of the calculated medium level of hazard must therefore belong to the high-hazard level. For each contaminant the environmental hazard-based rating assessment has been carried out, and the low, medium and high hazard levels have been evaluated (Table 6):

The advantage of this new approach is to facilitate the decision-making process with a hazard-based rating system approach. Translating effects on the biota to consequences on the soil environment has been a wide area of research, although, with the toxicity scale, future literature can focus their effort on understanding, at these different concentrations, if the predictions are adequate and the changes that are undermining the soil. Therefore, a completion of this study will evaluate, by knowing the contaminants concentration in the soil environment, the hazard associated with the chemical, decreasing further investigation costs.

4. Conclusion

Various chemicals associated with defence-related activities have the potential to impact on ecological soil systems. Therefore, ERAs are used to assess the likelihood of an activity causing harm to the environment, and to understand the consequences of these contaminants on the soil environment.

The purpose of this study was to develop an environmental hazard-based rating assessment that can be used as part of the ERA procedure. It did this by combining ecotoxicological data which have been previously used by USEPA and ECHA to evaluate the consequences of a contaminant in the soil environment. The hereby presented methodology merged these two techniques to ease and inform the decision-making process. Consequently, it was possible to develop an environmental hazard-based rating assessment for different defence-related contaminants. Although, this study is not only limited to a few representative classes of chemicals used in defence related activities and can have much broader implications evaluating only secondary data present in the literature. Moreover, a broader application can be considered for different ecosystems (e.g. aquatic environment) which can be achieved by changes in the procedure specifically to the PNEC value calculations as determined in the ECHA procedure. The understanding and calculation of different levels of hazard can determine a baseline for future human toxicity evaluations related to bioaccumulation process happening through the trophic chain.

Different hazard-levels have been calculated for TNT, RDX, Cypermethrin, PFOA and PFOS as defence-related chemicals based on ecotoxicological secondary data as representation of risks to the matrix in which the entity leaves. Future work will include validating the developed hazard levels in the environmental hazard-based rating assessment for changes in soil to pre-empt the chemical impact on the environment and to avoid severe consequences on the environment to ensure that sustainable operations are appropriately conducted on military training ranges.

Funding

This work was supported by The Natural Environment Research Council (NERC).

CRedit authorship contribution statement

Federica Persico: Conceptualization, Data curation, Formal analysis, Methodology, Writing – original draft, Writing – review & editing. **Frederic Coulon:** Conceptualization, Funding acquisition, Resources, Supervision, Writing – original draft, Writing – review & editing. **Melissa Ladyman:** Conceptualization, Resources, Funding acquisition, Supervision, Writing – original draft, Writing – review & editing. **Tracey Temple:** Conceptualization, Resources, Funding acquisition, Supervision, Writing – original draft, 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.

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envint.2022.107392>.

References

Army, I. (1994). Health Effects of Permethrin Impregnated Army Battle-Dress Uniforms.

- Birch, G.F., Drage, D.S., Thompson, K., Eaglesham, G., Mueller, J.F., 2015. Emerging contaminants (pharmaceuticals, personal care products, a food additive and pesticides) in waters of Sydney estuary, Australia. *Marine Pollut. Bull.* 97 (1–2), 56–66. <https://doi.org/10.1016/j.marpolbul.2015.06.038>.
- Bortone, I., Coulon, F., Fawcett-Hirst, W., Ladyman, M., Temple, T., 2020. Scientific Principles of environmental management. In: Temple, T., Ladyman, M. (Eds.), *Global Approaches to Environmental Management on Military Training Ranges*. IOP Publisher, Bristol.
- Broomandi, P., Guney, M., Kim, J.R., Karaca, F., 2020. Soil contamination in areas impacted by military activities: A critical review. *Sustainability* 12 (21), 9002.
- 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>.
- Checkai, R., Van Genderen, E., Sousa, J.P., Stephenson, G., Smolders, E., 2014. Deriving site-specific clean-up criteria to protect ecological receptors (plants and soil invertebrates) exposed to metal or metalloid soil contaminants via the direct contact exposure pathway. *Integr. Environ. Assess. Manage.* 10 (3), 346–357.
- Conte, P., Agretto, A., Spaccini, R., Piccolo, A., 2005. Soil remediation: humic acids as natural surfactants in the washings of highly contaminated soils. *Environ. Pollut.* 135 (3), 515–522. <https://doi.org/10.1016/j.envpol.2004.10.006>.
- Das, B.K., Mukherjee, S.C., 2003. Toxicity of cypermethrin in Labeo rohita fingerlings: biochemical, enzymatic and haematological consequences. *Comparative Biochem. Physiol. Part C: Toxicol. Pharmacol.* 134 (1), 109–121. [https://doi.org/10.1016/S1532-0456\(02\)00219-3](https://doi.org/10.1016/S1532-0456(02)00219-3).
- Dodard, S.G., Renoux, A.Y., Powlowski, J., Sunahara, G.I., 2003. Lethal and subchronic effects of 2, 4, 6-trinitrotoluene (TNT) on *Enchytraeus albidus* in spiked artificial soil. *Ecotoxicol. Environ. Saf.* 54 (2), 131–138. [https://doi.org/10.1016/S0147-6513\(02\)00046-5](https://doi.org/10.1016/S0147-6513(02)00046-5).
- EUCHA, 2008. Characterisation of dose [concentration]-response for environment. Guidance on Information Requirements and Chemical Safety Assessment. European Chemicals Agency, Helsinki, Finland.
- Environment agency (2017). Derivation and use of soil screening values for assessing ecological risks (Report SHARE id26). Retrieved from: <https://www.gov.uk/government/publications/soil-screening-values-for-assessing-ecological-risk>.
- Environment Agency (2019). Cypermethrin: Sources, pathways and environmental data. Retrieved from: https://consult.environment-agency.gov.uk/++preview++/environment-and-business/challenges-and-choices/user_uploads/cypermethrin-pressure-rbmp-2021.
- Ferreira, C., Freire, F., Riberio, J., 2020. Environmental management of military ranges with the support of a life-cycle assessment approach. In: Temple, T., Ladyman, M. (Eds.), *Global Approaches to Environmental Management on Military Training Ranges*. IOP Publisher, Bristol.
- Filipovic, M., Woldegiorgis, A., Norström, K., Bibi, M., Lindberg, M., Österås, A.H., 2015. Historical usage of aqueous film forming foam: A case study of the widespread distribution of perfluoroalkyl acids from a military airport to groundwater, lakes, soils and fish. *Chemosphere* 129, 39–45. <https://doi.org/10.1016/j.chemosphere.2014.09.005>.
- Finizio, A., Villa, S., 2002. Environmental risk assessment for pesticides: A tool for decision making. *Environ. Impact Assess. Rev.* 22 (3), 235–248. [https://doi.org/10.1016/S0195-9255\(02\)00002-1](https://doi.org/10.1016/S0195-9255(02)00002-1).
- Friedl, K.E., Grate, S.J., Proctor, S.P., Ness, J.W., Lukey, B.J., Kane, R.L., 2007. Army research needs for automated neuropsychological tests: monitoring soldier health and performance status. *Arch. Clin. Neuropsychol.* 22 (1), S7–S14. <https://doi.org/10.1016/j.acn.2006.10.002>.
- Gong, P., Guan, X., Inouye, L.S., Pirooznia, M., Indest, K.J., Athow, R.S., Deng, Y., Perkins, E.J., 2007. Toxicogenomic analysis provides new insights into molecular mechanisms of the sublethal toxicity of 2, 4, 6-trinitrotoluene in *Eisenia fetida*. *Environ. Sci. Technol.* 41 (23), 8195–8202.
- Hassan, V., Hossein, M., Mansoreh, S., Reza, A.M., Reza, Y.E.M., Ahmad, R., Mohammad, A., Fatemeh, R., Fatemeh, N., 2010. Evaluation of bioefficacy of α -cypermethrin in long lasting impregnated net (Interceptor®) using analytical method. *Asian Pacific J. Trop. Med.* 3 (8), 642–646. [https://doi.org/10.1016/S1995-7645\(10\)60155-1](https://doi.org/10.1016/S1995-7645(10)60155-1).
- Havlíček, M., Skokanová, H., Dostál, I., Vymazalová, M., Pavelková, R., Petrovič, F., 2018. The consequences of establishing military training areas for land use development—A case study of Libavá, Czech Republic. *Land Use Policy* 73, 84–94. <https://doi.org/10.1016/j.landusepol.2018.01.039>.
- Khoobdel, M., Shayeghi, M., Ladonni, H., Rassi, Y., Vatandoost, H., Alipour, H.K., 2005. The efficacy of permethrin-treated military uniforms as a personal protection against *Culex pipiens* (Diptera: Culicidae) and its environmental consequences. *Int. J. Environ. Sci. Technol.* 2 (2), 161–167.
- Kovacević, N., Stojiljković, A., Kovač, M., 2019. Application of the matrix approach in risk assessment. *Operat. Res. Eng. Sci.: Theory Appl.* 2 (3), 55–64. <https://doi.org/10.31181/oresta1903055k>.
- Kuperman, R.G., Checkai, R.T., Simini, M., Phillips, C.T., Kolakowski, J.E., Kurnas, C.W., 2005. Weathering and aging of 2, 4, 6-trinitrotoluene in soil increases toxicity to potworm *Enchytraeus crypticus*. *Environ. Toxicol. Chem.: Int. J.* 24 (10), 2509–2518. <https://doi.org/10.1897/04-513R.1>.
- Lotufo, G.R., 2017. Toxicity and bioaccumulation of munitions constituents in aquatic and terrestrial organisms. In: *Energetic Materials*. Springer, Cham, pp. 445–479.
- Merrington, G., Crane, M., Ashton, D., Benstead, R., 2008. Guidance on the use of soil screening values in ecological risk assessment. *Environ. Agency Bristol*.
- Murray, S.L., Grantham, K., Damle, S.B., 2011. Development of a generic risk matrix to manage project risks. *J. Indust. Syst. Eng.* 5 (1), 35–51.
- Place, B.J., Field, J.A., 2012. Identification of novel fluorochemicals in aqueous film-forming foams used by the US military. *Environ. Sci. Technol.* 46 (13), 7120–7127.
- Pan, Y., Qi, R., He, P., Shen, R., Jiang, J., Ni, L., Jiang, J., Wang, Q., 2020. Thermal hazard assessment and ranking for organic peroxides using quantitative structure–property relationship approaches. *J. Therm. Anal. Calorimetry* (140), 2575–2583. <https://doi.org/10.1007/s10973-019-08966-3>.
- Pickering, A., Cowley, S.P., 2010. Risk Matrices: implied accuracy and false assumptions. *J. Health Safety Res. Practice* 2 (01), 11–18.
- Robidoux, P.Y., Hawari, J., Bardai, G., Paquet, L., Ampleman, G., Thiboutot, S., Sunahara, G.I., 2002. TNT, RDX, and HMX decrease earthworm (*Eisenia andrei*) life-cycle responses in a spiked natural forest soil. *Arch. Environ. Contam. Toxicol.* 43 (4), 379–388.
- San, E.S., Topal, T., Akin, M.K., 2020. Rockfall Hazard Assessment Around Ankara Citadel (Turkey) Using Rockfall Analyses and Hazard Rating System. *Geotech. Geol. Eng.* (38) <https://doi.org/10.1007/s10706-020-01261-1>.
- Shiping, Z.H.O.U., Changqun, D.U.A.N., Xuehua, W.A.N.G., Michelle, W.H.G., Zefen, Y. U., Hui, F.U., 2008. Assessing cypermethrin-contaminated soil with three different earthworm test methods. *J. Environ. Sci.* 20 (11), 1381–1385. [https://doi.org/10.1016/S1001-0742\(08\)62236-6](https://doi.org/10.1016/S1001-0742(08)62236-6).
- Turner, L.P., Kueper, B.H., Jaansalu, K.M., Patch, D.J., Battye, N., El-Sharnouby, O., Mumford, K.G., Weber, K.P., 2021. Mechanochemical remediation of perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) amended sand and aqueous film-forming foam (AFFF) impacted soil by planetary ball milling. *Sci. Total Environ.* 765, 142722. <https://doi.org/10.1016/j.scitotenv.2020.142722>.
- Usepa, 2005. Guidance for developing ecological soil screening levels. *OSWER Directive* 9285.7-55.
- Vila, M., Lorber-Pascal, S., Laurent, F., 2008. Phytotoxicity to and uptake of TNT by rice. *Environ. Geochem. Health* 30 (2), 199–203.
- Zhao, H., Chen, C., Zhang, X., Chen, J., Quan, X., 2011. Phytotoxicity of PFOS and PFOA to *Brassica chinensis* in different Chinese soils. *Ecotoxicol. Environ. Saf.* 74 (5), 1343–1347. <https://doi.org/10.1016/j.ecoenv.2011.03.007>.
- Zhou, S., Duan, C., Wang, X., Michelle, W.H.G., Yu, Z., Fu, H., 2008. Assessing cypermethrin-contaminated soil with three different earthworm test methods. *J. Environ. Sci.* 20 (11), 1381–1385. [https://doi.org/10.1016/S1001-0742\(08\)62236-6](https://doi.org/10.1016/S1001-0742(08)62236-6).
- Zhou, S., Duan, C., Michelle, W.H.G., Yang, F., Wang, X., 2011. Individual and combined toxic effects of cypermethrin and chlorpyrifos on earthworm. *J. Environ. Sci.* 23 (4), 676–680. [https://doi.org/10.1016/S1001-0742\(10\)60462-7](https://doi.org/10.1016/S1001-0742(10)60462-7).
- Zortéa, T., Baretta, D., Maccari, A.P., Segat, J.C., Boiago, E.S., Sousa, J.P., Da Silva, A.S., 2015. Influence of cypermethrin on avoidance behavior, survival and reproduction of *Folsomia candida* in soil. *Chemosphere* 122, 94–98. <https://doi.org/10.1016/j.chemosphere.2014.11.018>.

Further reading

- Hodgson, E. (Ed.). (2004). *A Textbook of Modern Toxicology*. John Wiley & Sons.
- Simini, M., Checkai, R.T., Kuperman, R.G., Phillips, C.T., Kolakowski, J.E., Kurnas, C.W. (2013). Toxicities of TNT and RDX to the earthworm *Eisenia fetida* in five soils with contrasting characteristics. *Army Edgewood Chemical Biological Center APG MD Research and Technology Dir.*



DSPACE

<https://dspace.org/>

Development of an environmental hazard-based rating assessment for defence-related chemical compounds in ecological soil systems

Persico, Federica; Coulon, Frederic; Ladyman, Melissa K.; Temple, Tracey

2022-08

Elsevier

<https://doi.org/10.1016/j.envint.2022.107392>

Persico F, Coulon F, Ladyman M, Temple T. (2022) Development of an environmental hazard-based rating assessment for defence-related chemical compounds in ecological soil systems. Environment International, Volume 166, August 2022, Article number 107392